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der Fakultät für Chemie und Pharmazie

der Ludwig-Maximilians-Universität München

Gallium(III) Complexes with Aminecarboxylato-, Amine- and Carboxylato Ligands

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Erklärung

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Eidesstaatliche Versicherung

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Sebastian Brück

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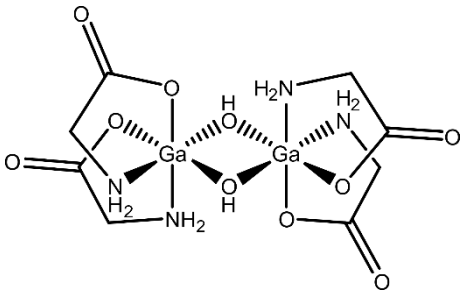
Abbreviations

AA	proteinogenic amino acid
aa	proteinogenic aminecarboxylato
ala	L-alaninato/alaninate
arg	L-argininato/argininate
asn	L-asparaginato/asparaginate
asp	L-aspartato/asparate
calcd.	calculated
CIS	coordination-induced shift
CShM	continuous shape measure
cys	L-cysteinato/cysteinate
d	doublet
edda	ethylenediamine-*N*,*N*′-diacetato
equ.	equivalents
Et	ethyl
Ac	acetyl
gln	L-glutaminato/glutaminate
glu	L-glutamato/glutamate
gly	glycinato/glycinate
his	L-histidinato/histidinate (if not specified as D-histidinato)
ida	iminodiacetato/iminodiacetate
ile	L-isoleucinato/isoleucinate
IR	infrared
leu	L-leucinato/leucinate
lys	L-lysinato/lysinate
m	multiplet
mal	L-malato
malo	malonato
Me	methyl
met	L-methioninato/methioninate
ms	multiple signals
NMR	nuclear magnetic resonance
nta	nitrilotriacetato
ox	oxalato

phe	L-phenylalaninato/phenylalaninate
ppm	parts per million
pro	L-prolinato/prolinate
q	quartet
R	residue
s	singlet
ser	L-serinato/serinate
t	triplet
thr	L-threoninato/threoninate
tren	tris(2-aminoethyl)amine
trien	triethylenetetramine
trp	l-tryptophanato/tryptophanate
UV-Vis	ultraviolet-visible
val	L-valinato/valinate

Overview of crystalline compounds

Glycinatogallium(III) complexes



[{Ga(gly)$_2$(μ-OH)}$_2$]

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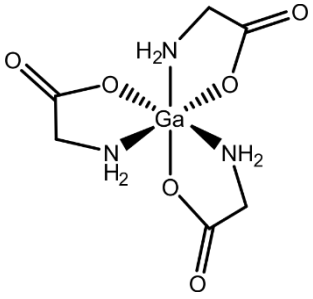
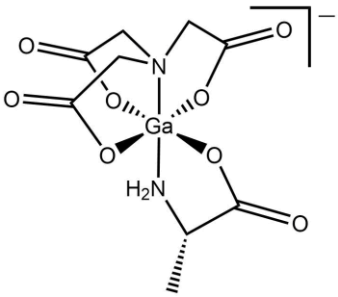


[Ga(gly)$_3$]

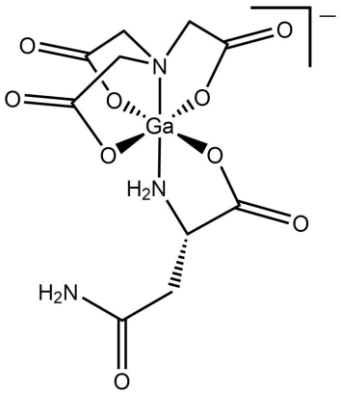
(**1b**)

Nitrilotriacetatogallate(III) complexes



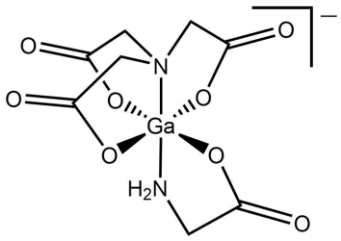
[Ga(ala)(nta)]$^-$

(**2a**)



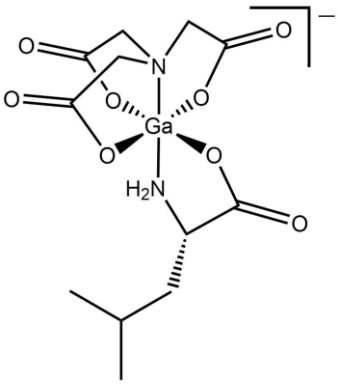
[Ga(asn)(nta)]$^-$

(**2b**)



[Ga(gly)(nta)]$^-$

(**2c**)



[Ga(leu)(nta)]$^-$

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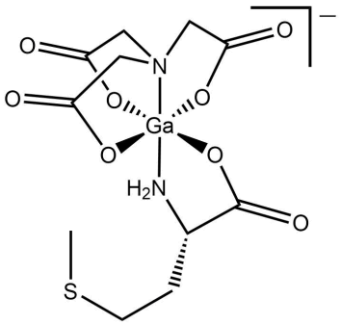
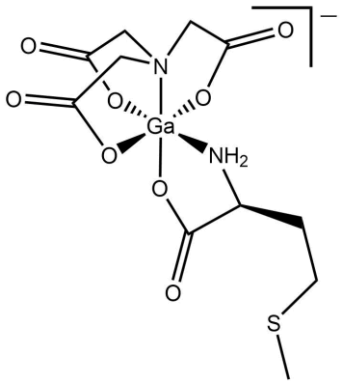


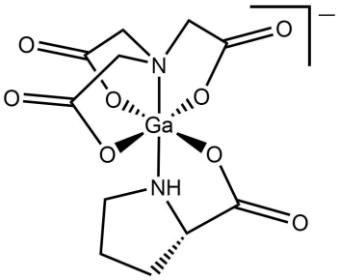
[Ga(met)(nta)]$^-$

Isomer **I** (**2e**)



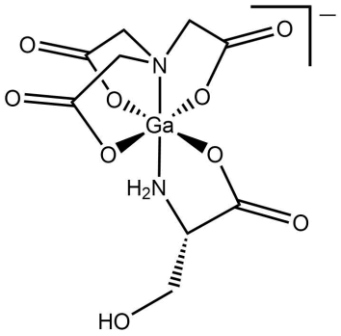
[Ga(met)(nta)]$^-$

Isomer **II** (**2f**)



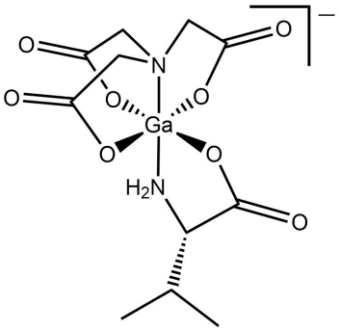
[Ga(nta)(pro)]$^-$

(**2g**)



[Ga(nta)(ser)]$^-$

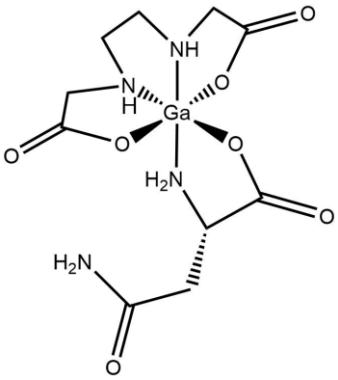
(**2h**)



[Ga(nta)(val)]$^-$

(**2i**)

Ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes



[Ga(asn)(edda)]

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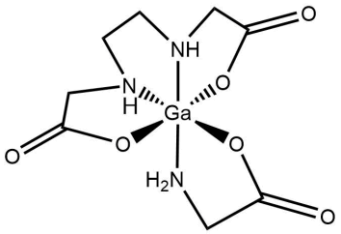
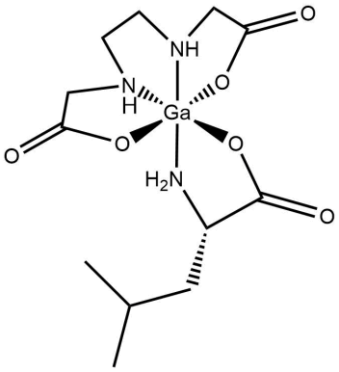


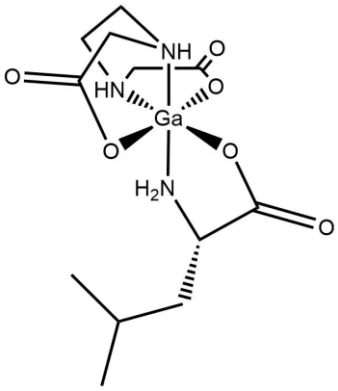
[Ga(edda)(gly)]

(**3b**)



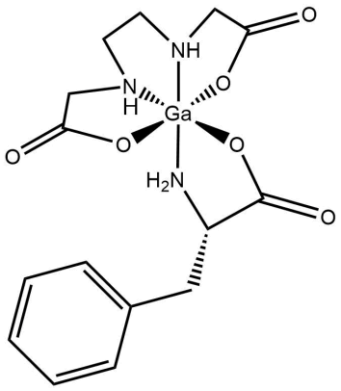
[Ga(edda)(leu)]

(**3c**)



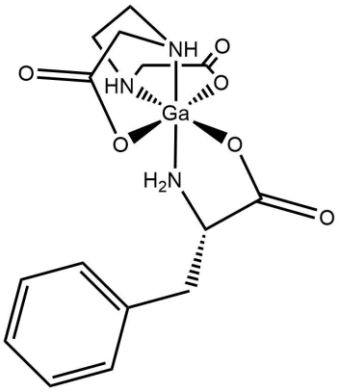
[Ga(edda)(leu)]

(**3d**)



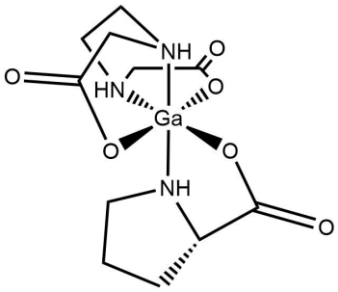
[Ga(edda)(phe)]

(**3e**)



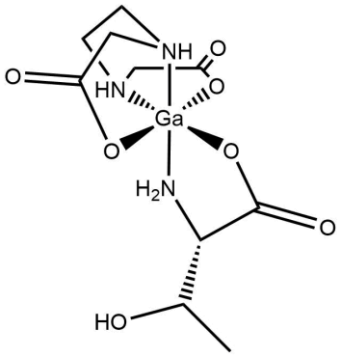
[Ga(edda)(phe)]

(**3f**)



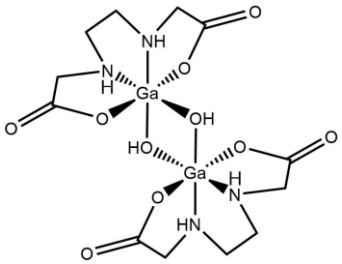
[Ga(edda)(pro)]

(**3g**)



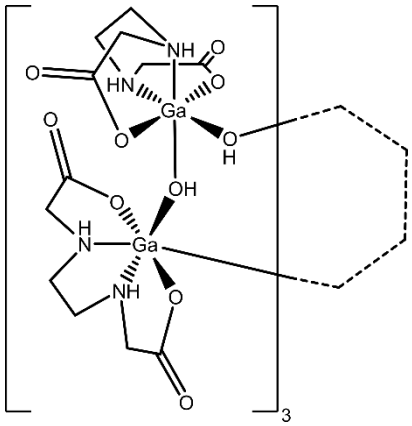
[Ga(edda)(thr)]

(**3h**)



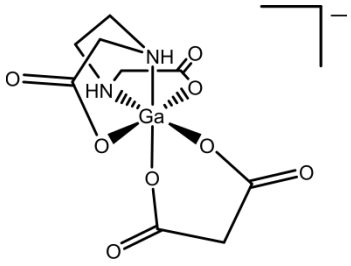
[{Ga(edda)(μ-OH)}$_2$]

(**3i**)



[{Ga(edda)(μ-OH)}$_6$]

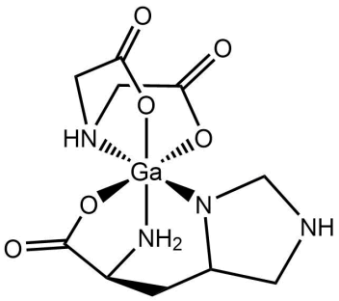
(**3j**)



[Ga(edda)(malo)]$^-$

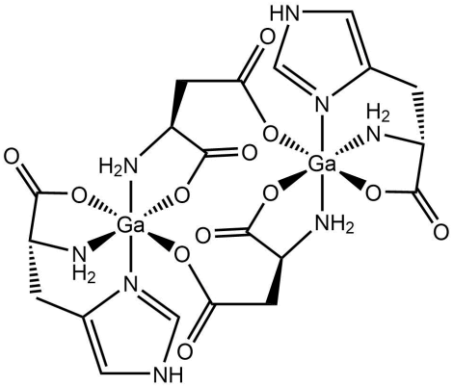
(**3k**)

Histidinatogallium(III) complexes



[Ga(his)(ida)]

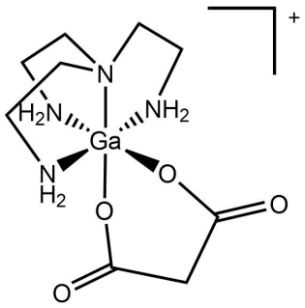
(**4a**)



[{Ga(μ-asp)(D-his)}$_2$]

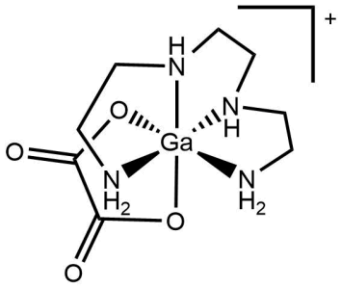
(**4b**)

Tris(2-aminoethyl)amine- and triethylenetetraminegallium(III) complexes



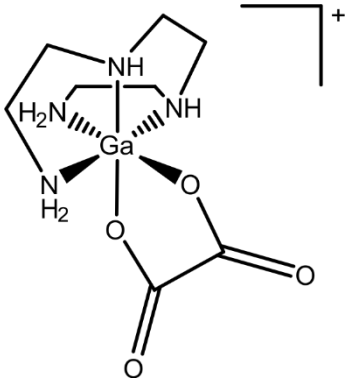
[Ga(malo)(tren)]$^{+}$

(**5a**)



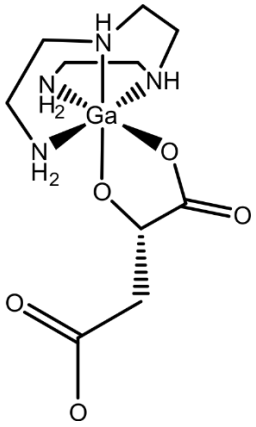
[Ga(ox)(trien)]$^{+}$

(**5b**)



[Ga(ox)(trien)]$^{+}$

(**5c**)



[Ga(mal)(trien)]

(**5d**)

1 Introduction

1.1 Gallium

Gallium's existence was first predicted in 1869 by Dmitri Mendeleev before Paul Émile Lecoq de Boisbaudran actually discovered the element in 1875.[1,2] With the atomic number 31 it is the heavier homologue of aluminium in the boron group. Gallium is a silvery white and brittle element with a melting point at 29.78 °C and a boiling point at 2403 °C. Despite its rather high electric conductivity ($5.77 \times 10^4\ \Omega^{-1}\ cm^{-1}$), gallium is still referred to as a metalloid. This is mostly due to its melting behaviour as well as characteristics found in structures of solid gallium. The melting of gallium causes a volume contraction, a property shared with elements such as silicon, germanium, antimony and bismuth. Furthermore, the metalloid has a strong tendency to supercool below its melting point enabling it to stay liquid at room temperature and below for an extended period of time.[2]

There are only two naturally occurring isotopes of gallium—^{69}Ga and ^{71}Ga. The element can be found in trace concentrations associated with aluminium, and zinc or germanium.[2] Thus there are only very few known minerals in which gallium is a major component[3-5] and it is mainly produced as a byproduct of zinc and aluminium[2]. The overall abundance of gallium in the upper continental crust is estimated to be 17–18 µg/g[6,7], therefore it can be considered a rare element[1]. According to the current state of research, gallium is not an essential element[2].

1.2 Chemistry of gallium

Gallium and aluminium share similarities concerning their chemical nature. Just as aluminium, gallium is stable in dry air and water due to the formation of a passive, protective oxide/hydroxide layer. The metalloid is soluble in non-oxidising acids (formation of Ga^{3+} salts) and bases (formation of gallates). In general, the chemistry of gallium is dominated by the stability of its oxidation states 0 and III. Even though gallium(I) compounds exist, these are considered to be highly unstable and get easily oxidised, thereby forming stable gallium(III) compounds.[2]

In acidic aqueous solution (pH < 3), gallium(III)—just like its lighter homologue aluminium(III)—forms mononuclear species like $[Ga(OH)(H_2O)_x]^{2+}$ and $[Ga(OH)_2(H2O)_x]^{+}$ aside from the hexaquagallium(III) complex.[8-10] With rising pH value of the solution, aqua ligands get deprotonated leading to the formation of hydroxido ligands which can get further deprotonated to oxido ligands. Both can function as bridging ligands to form various polynuclear species.[8,11] In weakly acidic, neutral and weakly basic aqueous solutions precipitation of hydroxidooxido species occurs. $Ga(OH)_3$ is the main component of these precipitates. It is stable across a wide range of pH values while occurring predominantly between pH 4.5 and 8.5[11] and displays a very low solubility in water ($K_s = 1.585 \times 10^{-37}$).[12] At around pH 8, tetrahydroxidogallate(III) begins to form, which is the only species in strongly basic solutions.[8,13,14] On a side note, the formation of precipitates often hinders reliable potentiometric solution studies.[10,11]

Gallium shows different coordination modes ranging from one to six ligands with the coordination numbers four and six dominating.[2] Various complexes of gallium(III) are formed with carbon-, nitrogen-, phosphorus- and oxygen-bearing ligands. A difference in the chemical behaviour between aluminium and gallium can be found in the tendency to bind oxygen ligands. The thermodynamic driving force behind much of the chemistry of aluminium is the Al–O bond formation.[1] While gallium(III) does readily form complexes with oxygen ligands, it also has a tendency to bind nitrogen ligands. Hence it follows the trend of an increased affinity to nitrogen ligands with higher period in the 13th group of the periodic table. This was demonstrated by Hegetschweiler *et al*.[15] by using 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) as a ligand for 13th group elements. The ligand is capable of forming two isoenergetic chair conformations with either three amine groups or three hydroxide groups in axial positions for facial coordination. Therefore, when two of these ligands are used for the formation of an octahedral complex with a metal centre, three different arrangements around the centre are possible: two metal centres surrounded with either all oxygen (MO_6) or nitrogen (MN_6), and one with mixed oxygen and nitrogen surrounding, MO_3N_3. Aluminium(III) does form the complex with only oxygen surrounding the metal centre, whereas the gallium(III) complex has the mixed adjacency GaO_3N_3 (Figure 1.1) and thallium(III) is surrounded only by nitrogen.[15] As indicated before, examples of gallium(III) complexes with all oxygen[1,16] and all nitrogen[1,17] ligands are existent, though mixed N/O-surroundings seem to be preferred when there is opportunity (and no hindrance) to form these as shown by Hegetschweiler *et al*.[15].

It should be noted that the $[Ga(taci)_2]^{3+}$ complex hydrolyses in aqueous solution, and the hydrolytic polymerisation reaches significant levels after a few hours.[15] Of course, in the investigation with taci as ligands no other mixed N/O surroundings of gallium(III) other than

GaO_3N_3 can potentially be formed. Hence, no assertion concerning the best ratio of oxygen-to-nitrogen ligands is possible with this ligand.

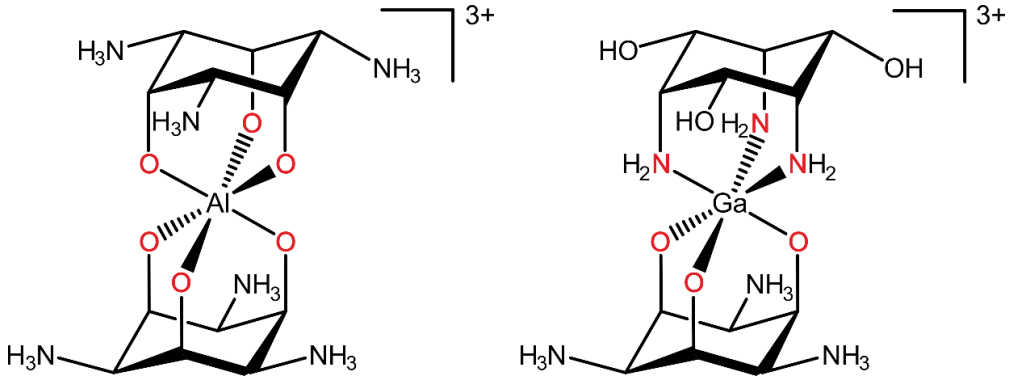


Figure 1.1: Aluminium(III) and gallium(III) complexes with chelating taci ligands.[15] Charges on ammonium functions are omitted.

1.3 Applications of gallium compounds

Gallium compounds are applied predominantly in the field of solid state chemistry, for example in semiconductors (GaAs)[18] or superconductors (V_3Ga)[19]. However, in recent years, gallium(III) compounds have raised attention to their potential pharmaceutical applications. For example, gallium(III) used in the form of gallium(III) nitrate or gallium(III) citrate displays antimicrobial activity.[20,21] ^{68}Ga radiolabelled complexes formed with chelating aminopolycarboxylic acids such as 1,4,7-triazacyclononane-1,4,7-triacetic acid (NOTA, Figure 1.2) or 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA, Figure 1.2) as well as derivatives of those compounds are used and/or tested for their applicability in PET imaging.[22,23] Furthermore, the antineoplastic activity of gallium(III) nitrate, tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III) (Figure 1.3) was studied in clinical trials.[24]

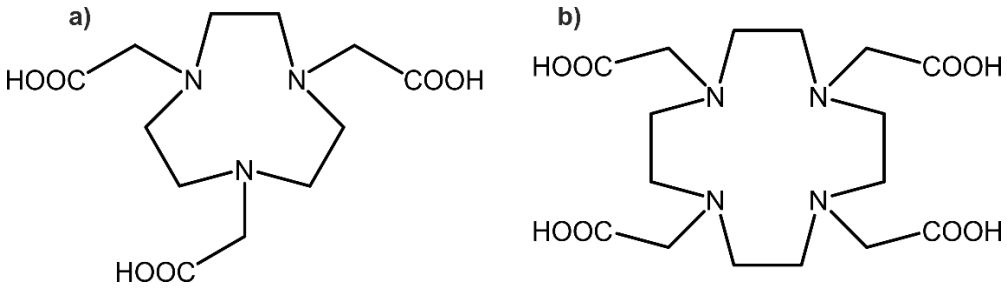


Figure 1.2: Chelating ligands NOTA (a) and DOTA (b).[22]

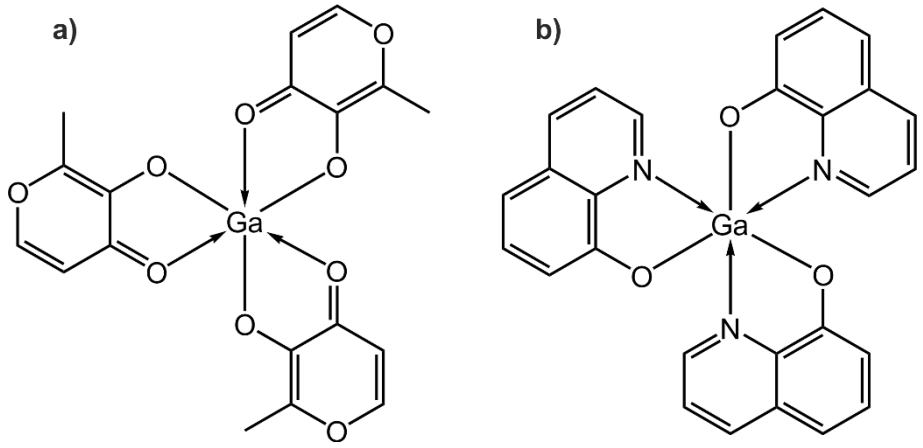


Figure 1.3: Tris(maltolato)gallium(III) (a) and tris(8-hydroxyquinolinato)gallium(III) (b).[24]

While complexes of gallium(III) need to be very stable and fast in formation for imaging applications—which is assured by the use of hexa- or octadentate chelators like NOTA and DOTA[22]—therapeutic agents are based on the release of gallium(III) in cells. The therapeutic effect seems to be due to similar chemical properties—for example the ion radius, coordination chemistry and ionisation potential—of gallium(III) and iron(III), which renders them indistinguishable for many biological systems.[20,25] The presence of gallium(III) affects cellular uptake of iron as it competes by binding to iron transport proteins like transferrin, lactoferrin and ferritin.[20,24,25] The gallium–transferrin complex inhibits the binding of the iron–transferrin complex to transferrin receptors competitively, leading to lower iron concentrations in the cells. Cellular deprivation of iron seems to play an important role in the therapeutic effect of gallium, as does the replacement of iron with gallium(III) in several enzymes.[24] Gallium(III), unlike iron(III), is not redox-active at physiological conditions, therefore gallium(III)-containing enzymes lose their activity.[20] A vulnerable target of gallium(III) might be ribonucleotide reductase, an iron(III)-containing enzyme essential for deoxyribonucleotide synthesis.[20,25] The replacement of iron(III) with gallium(III) in this enzyme impairs DNA synthesis, which causes death in rapidly proliferating cells (for example tumour cells or bacteria).[20] Another potential effect of gallium(III) on iron-containing enzymes might be located in the mitochondria, which could lead to apoptosis.[24]

As the pharmacological properties of gallium(III) compounds are different from those of other antibiotics, gallium-based therapies might be possible for antibiotic-resistant bacterial pathogens.[20] One important property of gallium-based therapeutic agents is their bioavailability, especially allowing for oral supplementation. However, this is not true for gallium(III) nitrate which shows very low bioavailability when administered orally[24] and is poorly soluble at physiological conditions due to the formation of gallium(III) hydroxide[8,21].

When compared to gallium(III) nitrate, the use of tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III) increases the bioavailability of gallium(III). This was an important advance in gallium-based therapeutics research.[24]

1.4 Aminecarboxylatogallium(III) complexes

While complexes with NOTA- and DOTA-based ligands have been studied extensively[23], ligands with lesser denticity have not raised such attention. Although proteinogenic amino acids (AAs) have been used as proteinogenic aminecarboxylato (aa) ligands for the formation of gallium(III) complexes, earlier investigations were mainly done by IR spectroscopy and products were not studied by X-ray diffraction or $^{13}C\{^{1}H\}$ NMR and ^{1}H NMR spectroscopy. These studies implied the existence of Ga(aa) complexes with aa ligands bound to gallium(III) as chelating ligands and/or with just one functional group. Among others, complexes with up to three aa ligands in an octahedral gallium(III) complex [$Ga(aa)_3$] were discussed. In this kind of complex the aa ligand binds via the amine function and the deprotonated carboxylic function in a bidentate fashion (Figure 1.4).[26-33] The formation of such complexes with the ligands L-histidinato, L-methioninato, L-prolinato and L-tryptophanato were also described in the most recent publication[34] on this topic, though still no X-ray diffraction experiments were done to confirm the structure of these complexes. As a side note, the products described in this particular work did always contain residual sodium nitrate due to the use of gallium(III) nitrate and sodium carbonate in the course of synthesis.

Among all aforementioned studies, only the AAs L-asparagine, L-arginine, L-glutamine and L-tyrosine were not used as ligands for gallium(III) complexes.[26-35] While molecular structures of gallium(III) complexes which incorporate glycinato and L-prolinato ligands as bidentate ligands in combination with methyl ligands (Figure 1.5) are known, those complexes were prepared under strictly inert conditions.[36,37]

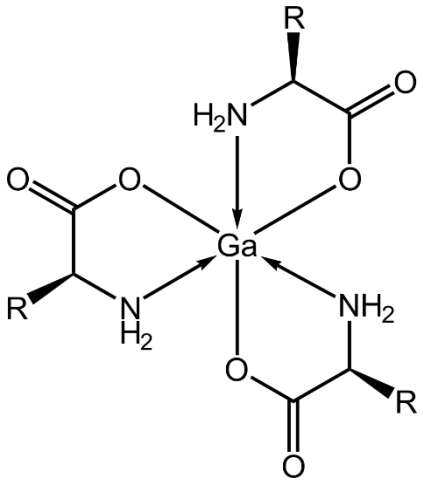


Figure 1.4: General structure of $[Ga(aa)_3]$ complexes. R is the side chain of the respective aa ligand.

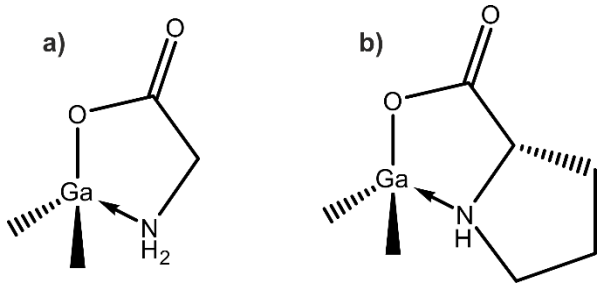


Figure 1.5: Glycinatodimethylgallium(III) (a) and dimethyl-L-prolinatogallium(III) (b).[36,37]

Complexes with the tridentate iminodiacetato (ida) ligand or the tetradentate nitrilotriacetato (nta) ligand are more thoroughly documented via crystallographic data.[38-40] For example, nta forms a dinuclear complex $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ (Figure 1.6) with two bridging hydroxido ligands and two capping nta ligands. The anionic complex was crystallised in water with sodium and caesium cations at pH 6.[39,40] Furthermore, two molecular structures of mononuclear nitrilotriacetatogallate(III) complexes, $NH_4/Cs[Ga(nta)(SCN)_2]$ and $NMe_4[Ga(nta)F_2]$ have been reported.[39,40] The synthesis and crystallisation of the monoanionic octahedral $[Ga(ida)_2]^-$ complex (Figure 1.6) was accomplished in aqueous solution at pH 3 as the respective potassium salt.[38]

Overall, it was shown that aminecarboxylato ligands are suitable ligands for gallium(III) complexes and yet structural information of those gallium(III) complexes and details of their behaviour in aqueous solution are scarce, especially when it comes to Ga(aa) complexes.

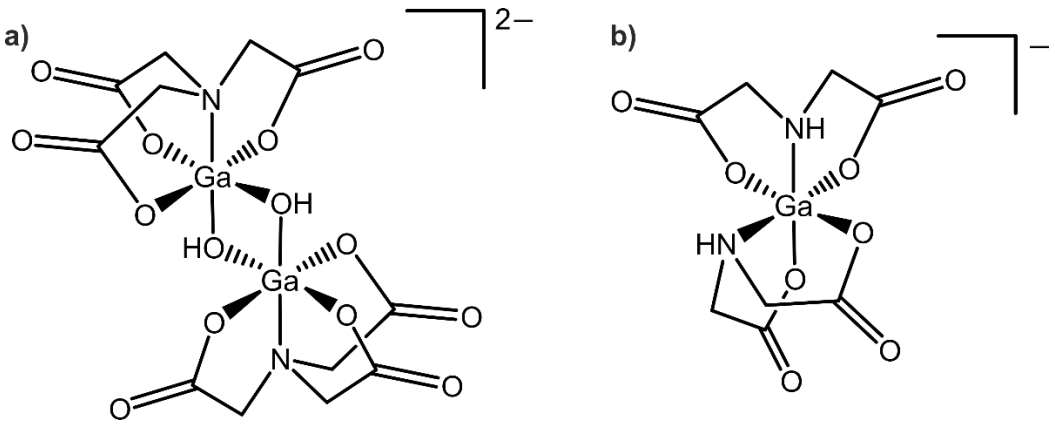


Figure 1.6: The complexes $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ (a) and $[Ga(ida)_2]^-$ (b).[38-40]

1.5 Aim of this work

The overall goal was to synthesise and characterise gallium(III) complexes suitable for pharmacological applications, specifically as antibiotic or antineoplastic agents.

As described before, gallium(III) compounds need to release gallium(III) in cells to achieve pharmacological effects (Section 1.3). Consequently, at least two properties concerning the stability of the complexes are key for their applicability as therapeutic agents. On the one hand, the complexes need to be stable enough to allow for transport to the targeted cells. Hence, the complexes should not precipitate gallium(III) hydroxide in aqueous solution at physiological pH levels. On the other hand, the complexes need to release gallium(III) in cells. Thus, the composition of the complexes must still allow for ligand exchange reactions, for which gallium(III) complexes with hexa- or octadentate ligands are not suitable.

As previous studies have shown (Section 1.3), tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III) are potential therapeutic agents. The ligands of these complexes are bidentate, just as in a further publication[34] with the subject of potential gallium-based pharmaceuticals. Among others, the formation of $[Ga(aa)_3]$ complexes with proteinogenic aminecarboxylato (aa) ligands is described in that work.

Since no structural information about these $[Ga(aa)_3]$ complexes—or overall gallium(III) complexes with aa ligands at non-inert conditions—was yet available, the synthesis and structural characterisation of such complexes was chosen as a first goal. Previous investigations have also shown that the combination of nitrogen- and oxygen-bearing ligands is favourable for the formation of gallium(III) complexes. Although some

aminecarboxylatogallium(III) complexes are known and characterised, this type of complex has not been thoroughly investigated yet, especially if the ligands are not of high denticity. Hence, the examination of further complexes with a combination of ligands that feature amine and carboxylic groups was another point of interest.

Elemental analysis was used as a first glance on the composition and the overall purity of every product. Since structural investigations of the target complexes were sought for, X-ray diffraction experiments with crystalline compounds were utilised as a major analytical method. Since the behaviour of gallium(III) compounds at physiological pH levels in aqueous solution is crucial when it comes to pharmaceutical applications and some characteristics of the examined compounds called for it, extensive studies by $^{13}C\{^{1}H\}$ NMR and ^{1}H NMR spectroscopy in combination with 2D NMR techniques were done.

2 Results

2.1 Glycinatogallium(III) complexes

As mentioned in section 1.4, several studies on the topic of gallium(III) complexes with aa ligands have been published, yet no structural investigation has confirmed the existence of such complexes. In general, past investigations stated that gallium(III) can form octahedral, mononuclear and neutral $[Ga(aa)_3]$ complexes with bidentate monoanionic aa ligands. To assess this hypothesis and obtain crystalline compounds for structural investigations, the most simple amino acid, glycine, was used to synthesise $[Ga(gly)_3]$. Glycine, unlike every other proteinogenic amino acid, is not chiral and does not feature a side chain at the C2 atom. Therefore, the crystallisation of the target complex should not be hindered by steric effects or disordered side chains of the ligand.

One issue that was encountered in the latest publication on the topic of $[Ga(aa)_3]$ complexes is the contamination of products with sodium nitrate. This was due to the use of sodium carbonate as a basic compound and gallium(III) nitrate as a starting material.[34] The solubility of sodium nitrate and the solubilities of the target complexes are too similar to allow for full separation of product and byproduct, hence the implementation of different bases in the synthesis is advised. Triethylamine (NEt_3), when used as a base in reactions with gallium(III) salts, should form the corresponding triethylammonium salts. For example, triethylammonium chloride is more soluble in organic solvents like ethanol when compared to the respective alkali salts[41] and should enable the separation of the $[Ga(aa)_3]$ complex and the byproduct.

$$GaCl_3 + 3\ Hgly + 3\ NEt_3 \xrightarrow{H_2O} [Ga(gly)_3] + 3\ HNEt_3Cl$$

Figure 2.1: Attempted synthesis of $[Ga(gly)_3]$.

The attempt to synthesise $[Ga(gly)_3]$ was done by letting gallium(III) chloride react with glycine and triethylamine in a molar ratio of 1:3:5 in water at room temperature (Figure 2.1). An excess of base was needed to yield a solution (pH 10.0) and, therefore, ensure that every reactant was available for the reaction. This was important to guarantee that no gallium(III) was withdrawn from the reaction mixture by the potential formation of gallium(III) hydroxide. After 16 hours, a slurry had formed which was treated with 2 mL of ethanol. This was done to ensure that the target complex was precipitated and

triethylammonium chloride was still kept in solution. The choice of solvents was also loosely based on the reaction conditions used by Thottathil *et al*.[34] The solid was separated by filtration, washed with ethanol, dried and first examined by elemental analysis. This was done to ensure the removal of the side product triethylammonium chloride and to get information about the obtained gallium(III) complex. Contrary to expectation, the elemental analysis did not show the formation of $[Ga(gly)_3]$. Rather, a mixture of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ and unreacted glycine seems to be present in the product. This implies that one equivalent of glycine did not bind to gallium(III) (Figure 2.2).

$$2\ GaCl_3 + 4\ Hgly + 6\ NEt_3 \xrightarrow{H_2O} [\{Ga(gly)_2(\mu\text{-}OH)\}_2] + 6\ HNEt_3Cl$$

Figure 2.2: Chemical equation for the synthesis of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$.

To confirm the result of the elemental analysis, several crystallisation experiments were done. After six weeks, a solution of the raw product in water and triethylamine (pH 10.0), which was stored over 1,4-dioxane, yielded crystals of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ (Figure 2.3).

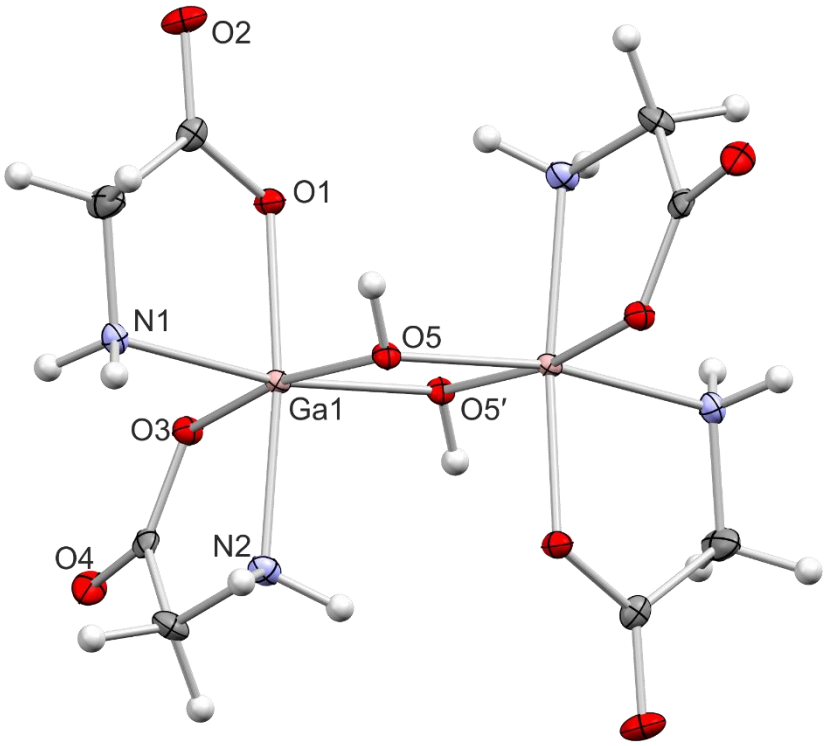


Figure 2.3: Plot of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ in crystals of **1a**. Space group: $P2_1/n$. $CShM_{OC\text{-}6}$: 0.738. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0547(15), Ga1–N2 2.0692(15), Ga1–O1 1.9898(12), Ga1–O3 1.9836(12), Ga1–O5 1.9620(12), O3–Ga1–O5 170.35(5), N1–Ga1–O5 169.75(5), N2–Ga1–O1 172.89(6), N1–Ga1–N2 93.81(6), N1–Ga1–O1 82.35(6), N1–Ga1–O3 92.77(6), N1–Ga1–O5 95.09(6), N2–Ga1–O5′ 95.77(6), O5–Ga1–O5′ 81.09(5).

The octahedral GaN_2O_4 coordination of gallium(III) is slightly distorted and was quantified with a $CShM_{OC-6}$ (continuous shape measure, as established by Alvarez *et al*.[42]) value of 0.738. The distortion is expected, as five-membered chelate rings should lead to angles of less than 90° in the complex. In addition, the Ga–N and Ga–O distances should differ and, indeed, the Ga–N distances are slightly longer than the Ga–O distances.

The molecular structure is the first structure of a glycinatogallium(III) complex that was obtained by growing crystals in aqueous solution. While this is a positive result, there were negative aspects to that outcome. Obviously, the formation of the expected $[Ga(gly)_3]$ complex was not achieved. Despite the supply of three equivalents of glycine for the reaction, only two equivalents reacted with gallium(III). The octahedral coordination of gallium(III) is completed by bridging hydroxido ligands, thereby forming a binuclear instead of the targeted mononuclear complex. Furthermore, the synthesis and the crystallisation experiments had to be done at basic conditions due to the extremely low solubility of the product at pH levels that resemble physiological conditions.

The main question is, of course, why no $[Ga(gly)_3]$ was obtained. Common reasons for the formation of one complex instead of another can be issues with its charge, coordination and thermodynamic effects. As $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ and $[Ga(gly)_3]$ are both neutral complexes, the charge of these complexes can be ruled out as a factor for the formation of one complex instead of the other. Also, the formation of $[Ga(gly)_3]$ instead of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ should be slightly favoured when it comes to entropy as two complexes are formed instead of one while the same number of ligands is contained (Figure 2.4). Entropic effects would, therefore, suggest the opposite result.

$$2\,[Ga(gly)_3] + 2\,H_2O + 2\,NEt_3 \rightleftharpoons [\{Ga(gly)_2(\mu\text{-}OH)\}_2] + 2\,gly^- + 2\,HNEt_3^+$$

Figure 2.4: Potential equilibrium reaction between $[Ga(gly)_3]$ and $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$.

One possible restriction to bonding the third glycinato ligand may be found in a heavier distortion of the octahedral coordination sphere in the complex. However, the angle between the two bridging hydroxido ligands is the smallest and, therefore, farthest away of an ideal octahedral coordination. A $[Ga(gly)_3]$ complex should therefore be more symmetrical. This assumption was confirmed later, as, in a later experiment, crystals of $[Ga(gly)_3]$ (Figure 2.5) were obtained from an unexpected source. In that experiment glycylglycylglycine and glycine were used in combination with gallium(III) chloride to form a heteroleptic, mononuclear complex. Instead, crystals of $[Ga(gly)_3]$ were obtained by

storing an aqueous solution of this reaction's product for one year. Hence, a structural investigation of [Ga(gly)$_3$] was possible, yet the reproduction of crystals was not feasible.

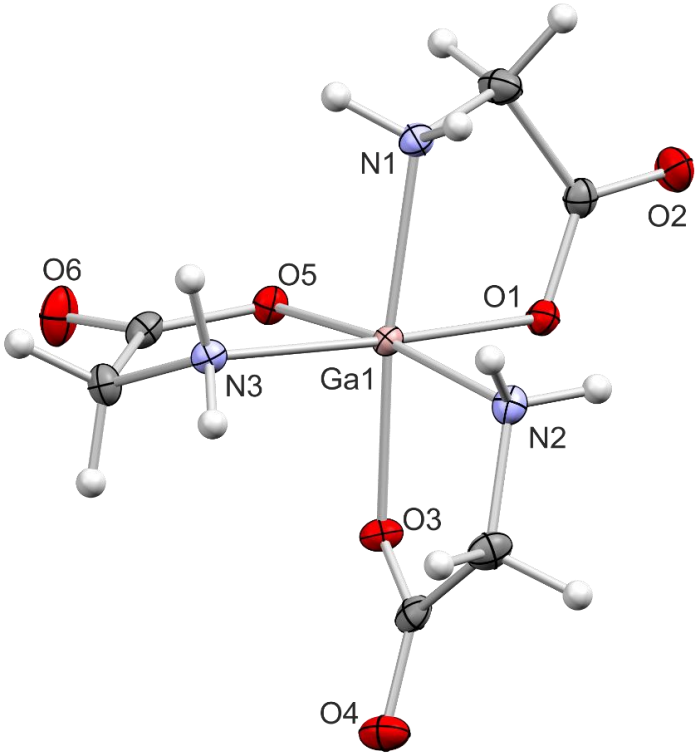


Figure 2.5: Plot of [Ga(gly)$_3$] in crystals of **1b**·H$_2$O. Space group: *P*2$_1$/*c*. CShM$_{OC-6}$: 0.642. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0498(14), Ga1–N2 2.0577(14), Ga1–N3 2.0437(14), Ga1–O1 1.9732(12), Ga1–O3 1.9823(11), Ga1–O5 1.9857(12), N1–Ga1–O3 173.35(5), N2–Ga1–O5 171.80(5), N3–Ga1–O1 170.70(5), N1–Ga1–N2 96.39(6), N1–Ga1–N3 97.21(6), N1–Ga1–O1 82.55(5), N1–Ga1–O5 91.63(5), N2–Ga1–O3 81.92(5).

Each of the glycinato ligands in [Ga(gly)$_3$] is bound in a bidentate fashion and with the oxygen atom of the carboxylato function opposing a nitrogen atom of another glycinato ligand. Therefore, the nitrogen and the oxygen atoms form a facial pattern. The interatomic distances are in the expected range, with Ga–N slightly longer than Ga–O. Also, as expected, the angles of the five-membered chelate rings are smaller than 90°. Once again, the distortion of the octahedral coordination sphere was quantified with a CShM$_{\mathbf{OC-6}}$ value of 0.642. Therefore, [Ga(gly)$_3$] features a slightly smaller deviation from the perfect octahedral shape than [{Ga(gly)$_2$(μ-OH)}$_2$].

As possible comparisons in literature are not available and both complexes were obtained—though not in the same experiment—it is difficult to explain why [{Ga(gly)$_2$(μ-OH)}$_2$] instead of [Ga(gly)$_3$] was formed despite the use of stoichiometric ratios. It may be assumed that to some extent gallium(III) has a disposition to form complexes with hydroxido ligands which would imply a thermodynamic cause for the

formation of [{Ga(gly)$_2$(μ-OH)}$_2$]. However, more experimental data is needed to reach a satisfactory level of evidence. This issue will be discussed further in section 3.3.

At this point it was obvious that the synthesis of gallium(III) complexes with aa ligands is not as straightforward as expected and several problems can be specified. The formation of two different complexes was observed, and their synthesis was not achieved by the stoichiometric use of ligands. Further problems arose when the synthesis of the complexes should have been repeated. In the case of [{Ga(gly)$_2$(μ-OH)}$_2$], uncoordinated glycine was still present in solution and, to some extent, in the raw products if three equivalents of glycine were used. Hence, the circumstances must be ideal to precipitate [{Ga(gly)$_2$(μ-OH)}$_2$] with as little contamination with uncoordinated glycine as possible. Unfortunately, the attempt to synthesise [{Ga(gly)$_2$(μ-OH)}$_2$] with stoichiometric ratios of starting materials at basic pH levels was not successful. Also, crystals of both molecular structures were obtained only once and in very small yields. When it came to [Ga(gly)$_3$], only few crystals were obtained and, as mentioned, the exact conditions were dubious. Thus, the results remain generally irreproducible.

To conclude, instead of gathering information to consolidate previous findings reported in literature, these experiments raised many questions about the chemistry of gallium(III) complexes with aa ligands in aqueous solution. As the most simple AA glycine already caused these issues, it was obvious that the use of only aa ligands in experiments was not reasonable. Therefore, to get more conclusive data and controllable experiments, the use of co-ligands in combination with aa ligands was inevitable.

2.2 Nitrilotriacetatogallium(III) complexes

A suitable co-ligand for gallium(III) complexes in combination with aa ligands had to meet a few requirements. The ligand should be tetradentate and allow the bonding of the aa ligands to gallium(III) in *cis* configuration as bidentate ligands. The resulting charge of the complex should ideally be close to neutral and last, but not least, the ligand should not allow the formation of too many different complex isomers in combination with aa ligands to keep the experiments as simple as possible.

Nitrilotriacetic acid (H_3nta) was chosen as a co-ligand since it is known to form gallium(III) complexes in the form of dinuclear $M_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ complexes with monovalent cations like Na^+ and Cs^+.[19,20] In this complex, the two binding sites of the hydroxido ligands are located in *cis* configuration to one another. Therefore, it was expected that mononuclear octahedral complexes could be formed with a combination of nta and aa ligands. At neutral or slightly basic pH levels the carboxylic functions of both ligands should be deprotonated, while the amine group of the ligand is uncharged. Hence, complexes of the composition $[Ga(aa)(nta)]^-$ should be monoanionic when polar or nonpolar proteinogenic amino acids are used as ligands. In addition, only two different isomers of this kind of complex can be formed provided the side chains of the aa ligands are not involved in the complex formation (Figure 2.6).

Due to the fact that both the synthesis of $[Ga(aa)(nta)]^-$ and $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ involve basic compounds in the reaction, it can be assumed that an optimal pH range for the formation of one or the other exists.

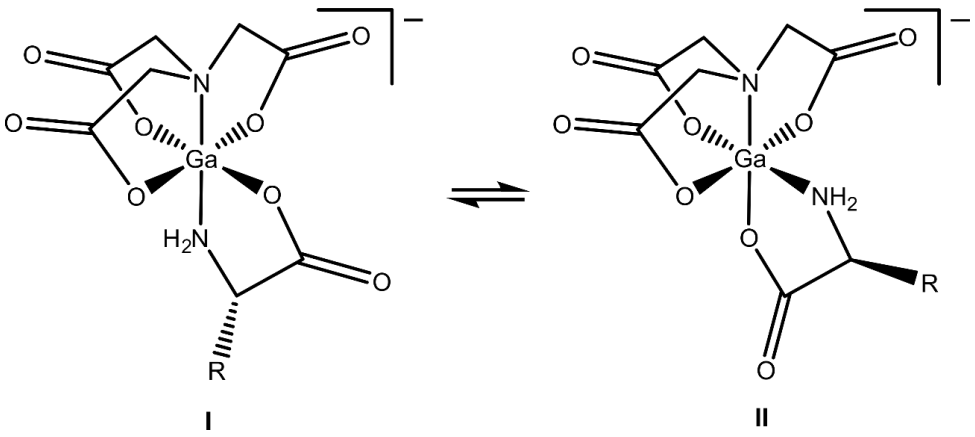


Figure 2.6: The two possible isomers of $[Ga(aa)(nta)]^-$. R is the side chain of the respective aa ligand.

2.2.1 Triethylamine and -ammonium compounds

To synthesise the target complexes, equal conditions as described for the synthesis of glycinatogallium(III) complexes (Section 2.1) were chosen. Water was used as a solvent and gallium(III) chloride, nitrilotriacetic acid and the respective proteinogenic amino acid were used as starting materials in a molar ratio of 1:1:1. The reaction would result in the formation of the complex salt and the chloride of the respective base, hence triethylamine (NEt_3) was chosen as the basic compound because triethylammonium chloride is easy to remove from the products due to its solubility in organic solvents. Triethylamine was used in excess to guarantee the full deprotonation of the AA over the length of the reaction (Figure 2.7) which led to a pH of around 8.0–8.5 in every reaction mixture. The complex salts were precipitated by the addition of organic solvents to the aqueous reaction solutions. On occasion, the removal of water before the addition of organic solvents was necessary to reach satisfying product yields.

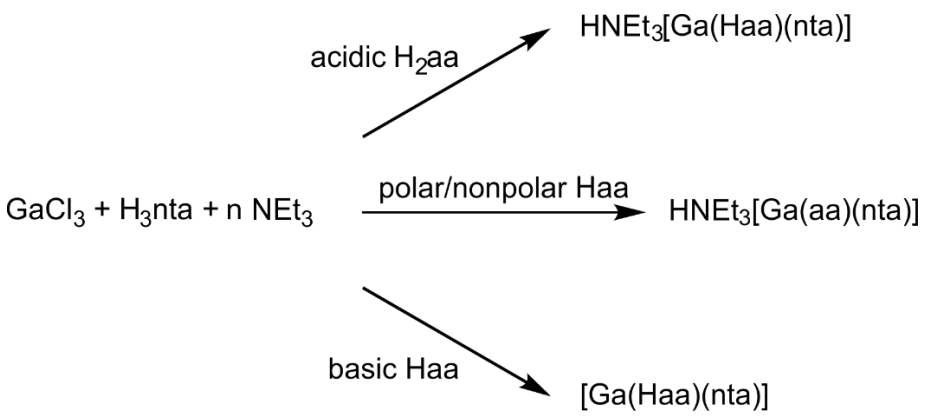


Figure 2.7: Reaction scheme for the synthesis of compounds containing Ga(nta) fragments and aa ligands by use of NEt_3 as base. Water is used as a solvent and, depending on the AA used in the reaction, n is either 4.5 or 5.5.

The abbreviations used in Figure 2.7 and throughout this work are based on the definitions of aa ligands by IUPAC. Amino functions are uncharged and carboxylato groups are negatively charged when proteinogenic amino acids are bound as ligands. Hence, polar, nonpolar and basic aa ligands are defined as monoanionic ligands, while acidic aa ligands bear a double negative charge. The zwitterionic forms of those compounds are, therefore, Haa in the case of polar, nonpolar and basic proteinogenic amino acids and H_2aa in the case of acidic proteinogenic acids.

Every product was characterised by elemental analysis. In contrast to section 2.1, the elemental analyses indicate the successful formation of the target complexes in most cases. However, the formation of well-defined target complexes is dependent on the respective amino acid in use. In particular, the main differences can be seen when products with polar and nonpolar amino acids (Table 2.2) are compared to products obtained with acidic and basic amino acids (Table 2.1). Since the basic and acidic aa ligands are potential tridentate ligands, nta is not a well-suited co-ligand in combination with those. This is clearly visible in the compositions of the raw products listed in Table 2.1 which have to be explained in detail.

Table 2.1: Interpretation of elemental analyses: nitrilotriacetatogallium(III) compounds with acidic or basic aa ligands and NEt_3. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex/complex salt	contamination	max. diff.
[Ga(Harg)(nta)]·0.10NEt_3	1.55 H_2O + 0.10 EtOH	0.07
$HNEt_3$[Ga(Hasp)(nta)]·0.30NEt_3	1.40 H_2O	0.22
$HNEt_3$[Ga(Hglu)(nta)]·0.10NEt_3	0.55 H_2O	0.05
[Ga(Hhis)(nta)]·0.30NEt_3	1.60 H_2O	0.11
[Ga(Hlys)(nta)]·0.10NEt_3	2.15 H_2O	0.20

The amount of triethylamine displayed after the complexes and complex salts might also be interpreted as a non-integer amount of triethylammonium ions present in the product. $HNEt_3$[Ga(Hasp)(nta)]·0.30NEt_3 might therefore also be described in a different way, for example, that 70% $HNEt_3$[Ga(Hasp)(nta)] and 30% $(HNEt_3)_2$[Ga(asp)(nta)] are present. The style of displaying the compositions of the crude products in Table 2.1 may seem awkward, but was chosen for two reasons. First of all it is a more concise visual display, but the more significant reason is found in the properties of the products. To explain this, $HNEt_3$[Ga(Hasp)(nta)]·0.30NEt_3 is used as an example. Regardless of the interpretation, the result of the elemental analysis of this product states that the aa ligand is protonated once to at least about 70%. This is not due to a lack of triethylamine in the reaction, as an excess of this compound was used. The synthesis was done at basic conditions which should result in full deprotonation of H_2asp if the ligand is bound to gallium(III) with the amino group and one carboxylato function. This is likely, since the same results were obtained when L-glutamato was used as a ligand instead of L-aspartato. L-glutamato should not be bound to gallium(III) with both carboxylato groups, since this requires the

formation of a seven-membered chelate ring. Hence, the acidic aa ligands should be bound to gallium(III) with the amino function and one carboxylato group.

The reaction was, therefore, not the reason for the protonated state of the aa ligand. Instead, this was caused by the instability of the complex salt. At room temperature, the solid releases triethylamine, which can be proven both by the compound's strong odour of amines and the declining amount of triethylammonium cations which was observed in subsequent analyses. Because of the instability of the complex salt, the non-integer amount of triethylammonium ions is shown in the form of a triethylamine adduct. The same reasoning is applicable for the glutamatogallium(III) complex.

A closer look at the elemental analyses of the products with basic aa ligands reveals a similar issue. The side chains of the basic aa ligands are at least partially protonated which is due to the basic function of the ligand competing with triethylamine in the reaction mixture. This led to a non-integer amount of triethylamine/triethylammonium ions in the products. In addition, the products were not entirely stable and emitted a slight odour of amines which was due to the loss of triethylamine. The instability of the product was not as significant as found for $[Ga(Haa)(nta)]^-$ compounds with acidic aa ligands, but was still recognisable. Therefore, the products are also displayed in the form of triethylamine adducts with fully protonated side chains of the aa ligands.

In general, the synthesis of the target complexes was successful with every acidic and basic amino acid, though the acidic and basic functions of the side chains did prevent the formation of stable well-defined products. These results were backed with elemental analysis as well as NMR spectroscopy.

In contrast, the products with polar and nonpolar aa ligands were better defined in general. With one exception, L-tyrosine, the synthesis of the target complexes was successful with every polar and nonpolar amino acid (Table 2.2).

L-tyrosine, which is almost insoluble in water, did not seem to react with gallium(III). Instead of the target complex, the attempt of synthesis resulted in a mixture of L-tyrosine and $(HNEt_3)_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$, according to elemental analysis. This peculiarity will be further addressed in section 3.3.1.

Two of the synthesised target complexes—$HNEt_3[Ga(cys)(nta)]$ and $HNEt_3[Ga(nta)(trp)]$—are special. $HNEt_3[Ga(cys)(nta)]$ was not obtained without free L-cysteine still present in the crude product and the elemental analysis of $HNEt_3[Ga(nta)(trp)]$ indicate that a non-integer amount of triethylammonium-cations is present. A small amount of complex salt seems to be protonated in this case, most likely due to the nitrogen atom in the side chain.

Table 2.2: Interpretation of elemental analyses: $HNEt_3[Ga(aa)(nta)]$ compounds with polar or nonpolar aa ligands. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex salt	contamination	max. diff.
$HNEt_3[Ga(ala)(nta)]$	0.60 H_2O	0.09
$HNEt_3[Ga(asn)(nta)]$	0.20 $Ga(OH)_3$ + 0.10 EtOAc	0.13
$HNEt_3[Ga(cys)(nta)]$	1.25 H_2O + 0.10 Hcys	0.05
$HNEt_3[Ga(gln)(nta)]$	0.75 H_2O	0.09
$HNEt_3[Ga(gly)(nta)]$	0.20 H_2O	0.08
$HNEt_3[Ga(ile)(nta)]$	-	0.07
$HNEt_3[Ga(leu)(nta)]$	0.05 $Ga(OH)_3$	0.14
$HNEt_3[Ga(met)(nta)]$	0.70 H_2O	0.13
$HNEt_3[Ga(nta)(phe)]$	1.10 H_2O	0.07
$HNEt_3[Ga(nta)(pro)]$	0.75 H_2O	0.13
$HNEt_3[Ga(nta)(ser)]$	0.15 $Ga(OH)_3$ + 0.10 H_2O	0.06
$HNEt_3[Ga(nta)(thr)]$	0.15 H_2O	0.08
$HNEt_3[Ga(nta)(trp)]$ + 0.10 [Ga(nta)(Htrp)]	1.65 H_2O	0.04
-	Htyr + 0.35 $(HNEt_3)_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 1.15 H_2O	0.16
$HNEt_3[Ga(nta)(val)]$	0.15 H_2O	0.06

Overall, the formation of 19 target complexes was achieved according to elemental analyses. These products were not pure, solvent residue—most often water—and sometimes gallium(III) hydroxide were found in the crude products along with the aforementioned impurities. Water was an expected contaminant as the complex salts proved to be hygroscopic. The existence of gallium(III) hydroxide might indicate that the respective ligand combination was not optimal to form the target $[Ga(aa)(nta)]^-$ complexes. However, gallium(III) hydroxide may have been present because of unfavourable reaction conditions or imprecise amounts of the starting materials. In any case, the contaminants which were present in the crude products did not interfere with any subsequent analyses or experiments and were, therefore, not regarded as problematic.

Of course, elemental analysis is only a first glance at a product composition and is not sufficient on its own. Hence, crystallisation experiments with the obtained crude products were necessary.

2.2.2 Structural investigations of $HNEt_3$[Ga(aa)(nta)] salts

The crystallisation method of choice was to slowly add anti-solvent to aqueous or methanolic solutions of the compounds by vapour diffusion. Crystallisation experiments with the crude products shown in subsection 2.2.1 were successful in a few cases. X-ray diffraction experiments with these crystals show the formation of $HNEt_3$[Ga(aa)(nta)] salts and support the results that were derived from elemental analyses. Unfortunately, only four data sets obtained by single crystal X-ray diffraction were of high enough quality to allow for presentation. The molecular structures of these complex salts—$HNEt_3$[Ga(gly)(nta)], $HNEt_3$[Ga(met)(nta)], $HNEt_3$[Ga(nta)(pro)] and $HNEt_3$[Ga(nta)(ser)]—are shown in Figure 2.8–Figure 2.11.

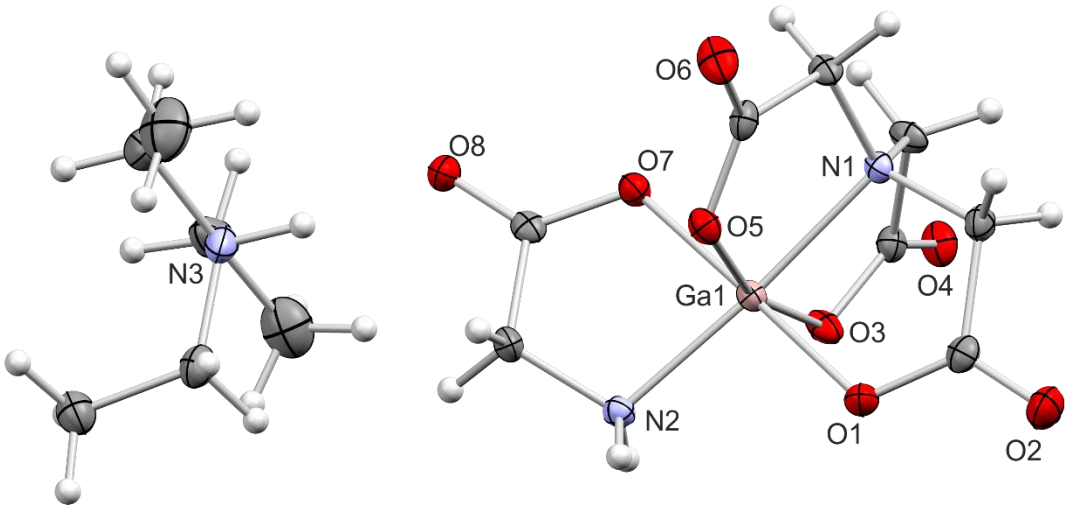


Figure 2.8: Plot of $HNEt_3$[Ga(gly)(nta)] in crystals of ($HNEt_3$)**2c**. Space group: $P2_1/c$. $CShM_{OC-6}$: 0.569. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0627(18), Ga1–N2 2.0052(18), Ga1–O1 1.9414(16), Ga1–O3 1.9571(15), Ga1–O5 1.9975(15), Ga1–O7 1.9995(16), N1–Ga1–N2 175.62(7), O1–Ga1–O7 178.23(7), O3–Ga1–O5 164.66(6), N1–Ga1–O5 81.53(7), N2–Ga1–O1 95.74(7), N2–Ga1–O3 99.97(7), N2–Ga1–O5 94.98(7), N2–Ga1–O7 83.24(7), N3–O8 2.732(3).

As illustrated, the gallium(III) ions in these complexes have a slightly distorted octahedral GaN_2O_4 coordination. The distortion of the octahedral geometry is expected due to the formation of five-membered chelate rings between the chelating ligands and the gallium(III) centre and was interpreted in greater depth with the $CShM_{OC-6}$ values. The interatomic distances and angles between gallium(III) and the nitrogen and oxygen atoms of the ligands are consistent with the observation of a distorted octahedral geometry and are in the anticipated range. As expected, the Ga–N distances are slightly longer than the Ga–O distances.

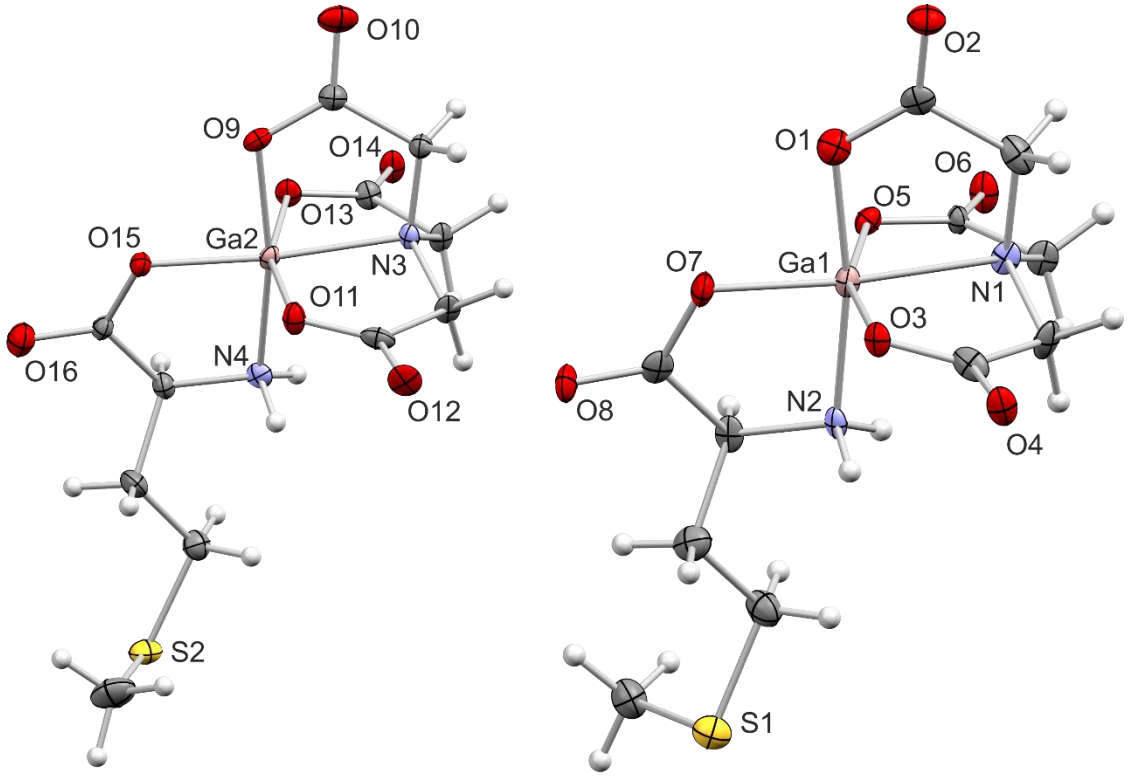


Figure 2.9: Plot of the two symmetrically independent $[Ga(met)(nta)]^-$ ions in crystals of $(HNEt_3)$**2f**. Space group: $P2_1$. $CShM_{OC-6}$: Ga1 1.322, Ga2 1.298. To avoid overlap in the picture the $HNEt_3^+$ ions are not displayed. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.099(8), Ga1–N2 2.039(8), Ga1–O1 1.943(8), Ga1–O3 1.992(5), Ga1–O5 2.010(5), Ga1–O7 1.905(6), Ga2–N3 2.098(8), Ga2–N4 2.044(8), Ga2–O9 1.963(7), Ga2–O11 1.978(6), Ga2–O13 2.025(5), Ga2–O15 1.917(6), N1–Ga1–O7 173.4(3), N2–Ga1–O1 170.5(3), O3–Ga1–O5 160.9(2), N1–Ga1–N2 102.8(3), N1–Ga1–O3 80.4(2), N2–Ga1–O3 91.6(3), N2–Ga1–O5 90.3(3), N2–Ga1–O7 83.7(3), O5–Ga1–O7 100.8(2), N3–Ga2–O15 173.3(3), N4–Ga2–O9 169.8(3), O11–Ga2–O13 161.4(3), N3–Ga2–N4 102.8(3), N3–Ga2–O13 80.1(3), N4–Ga2–O11 93.5(3), N4–Ga2–O13 88.6(3), N4–Ga2–O15 83.9(3), O11–Ga2–O15 97.8(2).

The nitrogen atoms of nta and the respective proteinogenic amino acid are – with the exception of $HNEt_3$[Ga(met)(nta)] (isomer **II**, Figure 2.6) – always coordinated *trans* to one another (isomer **I**, Figure 2.6). This observation will be discussed in greater detail in section 3.7.

$HNEt_3$[Ga(gly)(nta)] and $HNEt_3$[Ga(met)(nta)] were crystallised from aqueous solutions at neutral pH levels, while $HNEt_3$[Ga(nta)(pro)] and $HNEt_3$[Ga(nta)(ser)] were crystallised from methanolic solutions. Only $HNEt_3$[Ga(gly)(nta)] was obtained in significant amounts and reasonable time, while only a few small crystals of the other compounds were obtained. In the case of $HNEt_3$[Ga(nta)(pro)] the crystallisation did almost take one year.

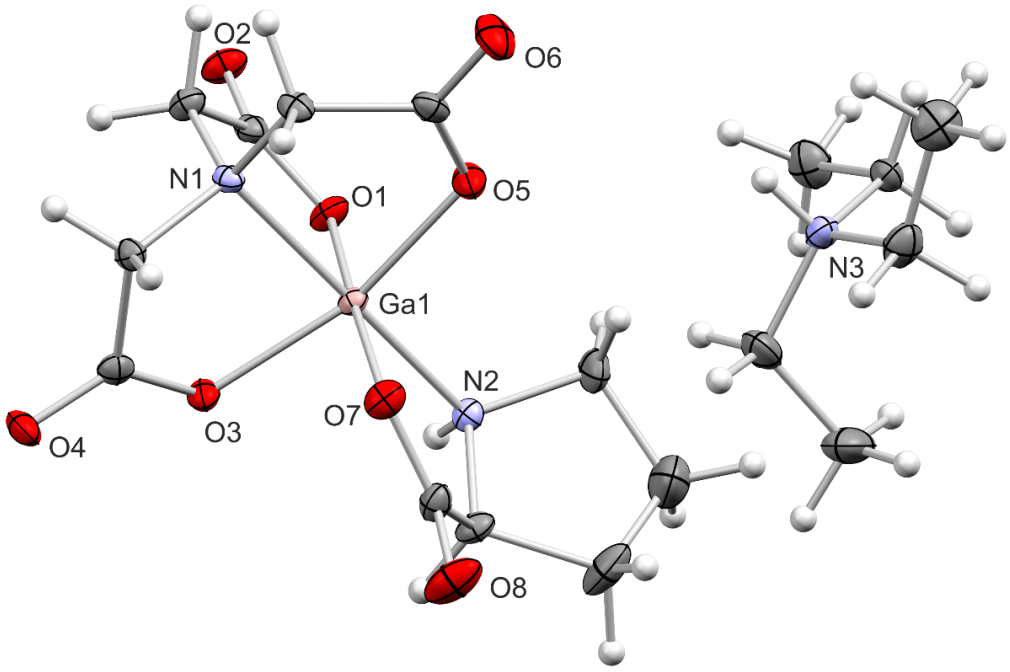


Figure 2.10: Plot of $HNEt_3$[Ga(nta)(pro)] in crystals of ($HNEt_3$)**2g**·H_2O. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.889. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.108(2), Ga1–N2 2.004(2), Ga1–O1 1.955(2), Ga1–O3 1.977(2), Ga1–O5 1.971(2), Ga1–O7 1.978(2), N1–Ga1–N2 176.92(10), O1–Ga1–O7 175.33(10), O3–Ga1–O5 162.27(9), N1–Ga1–O3 81.04(9), N2–Ga1–O1 91.22(9), N2–Ga1–O3 98.21(9), N2–Ga1–O5 99.03(9), N2–Ga1–O7 84.13(10).

The crystalline compounds resemble the target complexes, therefore the use of nta as a co-ligand proved to be successful for a controlled and straightforward synthesis of gallium(III) complexes with aa ligands. Unfortunately, in many cases the triethylammonium cation was heavily disordered in crystal structures, which prevented a reasonable structure solution of further $HNEt_3$[Ga(aa)(nta)] salts. The structure solution of $HNEt_3$[Ga(met)(nta)] already required the use of partial isotropic refinement for some atoms. As a result, the crystal structure is presentable but of mediocre quality. Therefore, better suited cations needed to be found for further structural investigations of $[Ga(aa)(nta)]^-$ complexes.

Additionally, in some crystallisation experiments crystals of the respective AA in use were obtained. At this stage of the work the cause of this was not determined and two possible explanation were considered. The complexes might either be unstable which leads to their decomposition in solution or the interpretation of the elemental analyses of the particular raw products was flawed. This issue will be further addressed in subsection 2.2.6.

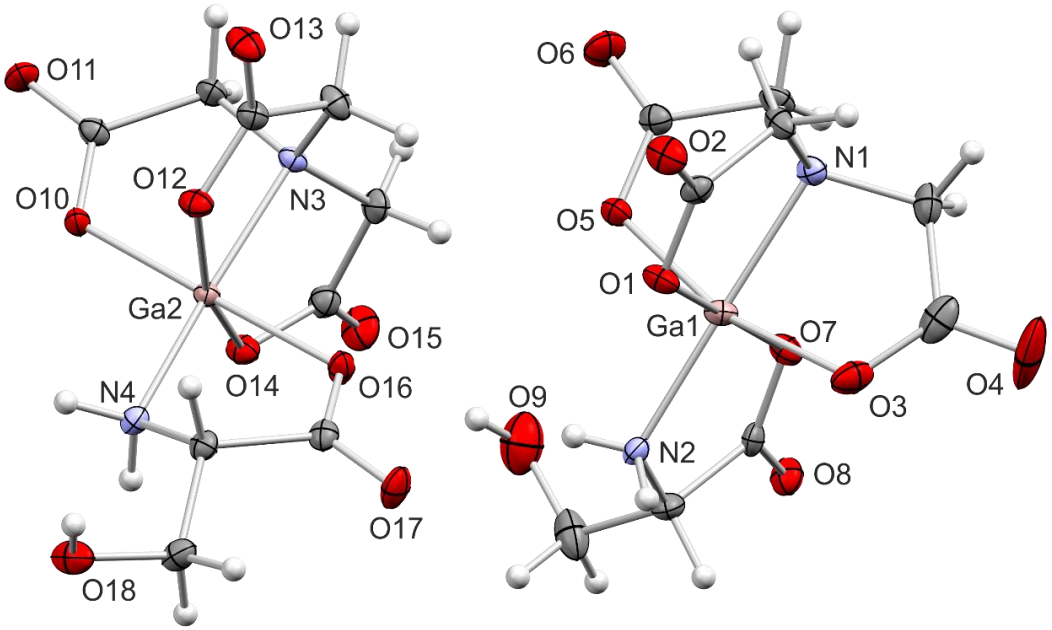


Figure 2.11: Plot of the two symmetrically independent $[Ga(nta)(ser)]^-$ ions in crystals of $(HNEt_3)$**2h**$\cdot 0.14H_2O$. Space group: *P*1. $CShM_{OC\text{-}6}$: Ga1 0.537, Ga2 0.787. To avoid overlap in the picture the $HNEt_3^+$ ions are not displayed. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.079(3), Ga1–N2 1.994(3), Ga1–O1 1.976(3), Ga1–O3 1.996(3), Ga1–O5 1.961(3), Ga1–O7 1.958(3), Ga2–N3 2.086(3), Ga2–N4 2.002(3), Ga2–O10 1.942(3), Ga2–O12 1.985(3), Ga2–O14 1.962(3), N1–Ga1–N2 178.97(15), O1–Ga1–O7 177.41(14), O3–Ga1–O5 164.01(12), N1–Ga1–O3 81.59(14), N2–Ga1–O1 94.43(13), N2–Ga1–O3 97.44(15), N2–Ga1–O5 98.53(13), N2–Ga1–O7 85.65(13), N3–Ga2–N4 171.96(13), O10–Ga2–O16 179.15(15), O12–Ga2–O14 163.44(11), N3–Ga2–O14 81.34(13), N4–Ga2–O10 98.70(12), N4–Ga2–O12 91.53(12), N4–Ga2–O14 104.84(13), N4–Ga2–O16 81.91(12).

2.2.3 *N*,*N*-diisopropylethylamine and -ammonium compounds

During the search for suitable cations to enhance the crystallisation of $[Ga(aa)(nta)]^-$ complexes, *N*,*N*-diisopropylethylamine (DIPEA) was identified as an adequate substitution for triethylamine. The same synthesis and purification procedures as described for the triethylamine and -ammonium compounds (Subsection 2.2.1) were applicable for the synthesis of HDIPEA[Ga(aa)(nta)] salts. Hence, the stoichiometric ratios were left unchanged (Figure 2.12). A welcome effect of DIPEA usage was the better separability of the targeted product and *N*,*N*-diisopropylethylammonium chloride, as the latter proved to be soluble even in ethyl acetate.

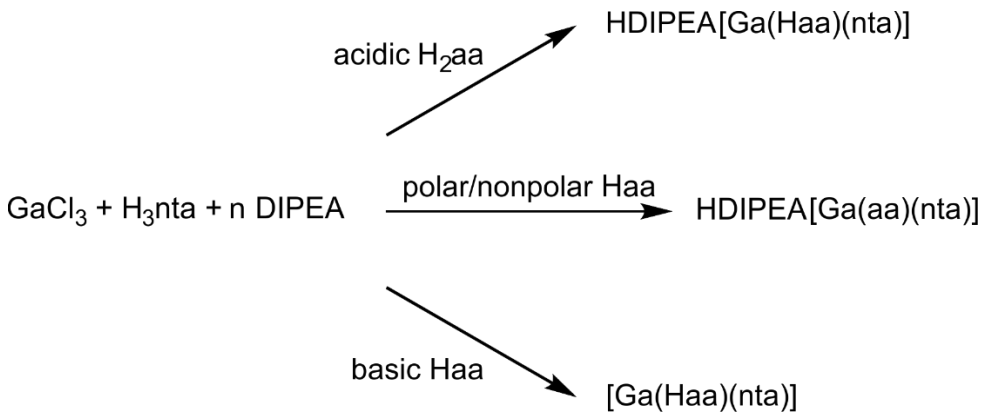


Figure 2.12: Reaction scheme for the synthesis of compounds containing Ga(nta) fragments and aa ligands by use of DIPEA as base. Water is used as a solvent and, depending on the AA used in the reaction, n is either 4.5 or 5.5.

The obtained crude products were examined by elemental analysis (Table 2.3 and Table 2.4). According to these, the synthesis of HDIPEA[Ga(aa)(nta)] salts was successful in most cases and the results were very similar to those of the $HNEt_3$[Ga(aa)(nta)] salts (Subsection 2.2.1). Due to this fact, the discussion of the product compositions is not that detailed. An elaborate description can be found in subsection 2.2.1.

As expected, the formation of the target complexes depends on the amino acid. In particular, the main differences are found when products containing polar and nonpolar amino acids (Table 2.4) are compared to products with acidic and basic amino acids (Table 2.3).

Table 2.3: Interpretation of elemental analyses: nitrilotriacetatogallium(III) compounds with acidic or basic aa ligands and DIPEA. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex/complex-salt	contamination	max. diff.
[Ga(Harg)(nta)]·0.05DIPEA	2.45 H_2O	0.10
HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA	0.10 $Ga(OH)_3$	0.22
HDIPEA[Ga(Hglu)(nta)]·0.05DIPEA	0.30 H_2O + 0.05 $Ga(OH)_3$	0.21
[Ga(Hhis)(nta)]·0.25DIPEA	2.10 H_2O + 0.05 EtOH	0.17
[Ga(Hlys)(nta)]·0.05DIPEA	2.25 H_2O + 0.15 EtOH	0.17

According to the elemental analyses, the side chains of the acidic as well as the basic aa ligands are protonated once and adducts with *N*,*N*-diisopropylethylamine are formed. Those compounds were not stable at room temperature and released *N*,*N*-diisopropylethylamine.

Table 2.4: Interpretation of elemental analyses: HDIPEA[Ga(aa)(nta)] compounds with polar or nonpolar aa ligands. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex-salt	contamination	max. diff.
HDIPEA[Ga(ala)(nta)]	0.85 H_2O	0.03
HDIPEA[Ga(asn)(nta)]	0.20 $Ga(OH)_3$ + 0.05 EtOH	0.11
HDIPEA[Ga(cys)(nta)]	0.10 $Ga(OH)_3$ + 0.10 H_2O + 0.05 EtOH	0.07
HDIPEA[Ga(gln)(nta)]	0.20 H_2O + 0.05 EtOH	0.06
HDIPEA[Ga(gly)(nta)]	0.95 H_2O	0.13
HDIPEA[Ga(ile)(nta)]	0.20 H_2O	0.07
HDIPEA[Ga(leu)(nta)]	0.15 H_2O + 0.05 EtOAc	0.04
HDIPEA[Ga(met)(nta)]	0.05 H_2O	0.11
HDIPEA[Ga(nta)(phe)]	0.90 H_2O	0.10
HDIPEA[Ga(nta)(pro)]	0.05 $Ga(OH)_3$ + 0.05 H_2O	0.09
HDIPEA[Ga(nta)(ser)]	0.80 H_2O	0.09
HDIPEA[Ga(nta)(thr)]	0.50 H_2O	0.18
HDIPEA[Ga(nta)(trp)]	0.25 H_2O + 0.20 $Ga(OH)_3$	0.02
0.05 HDIPEA[Ga(nta)(tyr)]	tyrH + 0.05 $Ga(OH)_3$	0.19
HDIPEA[Ga(nta)(val)]	0.15 H_2O	0.08

Hence, the resulting compositions are similar to those obtained with triethylamine (Subsection 2.2.1) and the synthesis of the target complexes was successful with every acidic and basic amino acid.

Consistently, products with polar and nonpolar amino acid ligands were better defined in general. The synthesis of the target complexes was successful with every polar and nonpolar amino acid. When compared to the use of triethylamine, an almost insignificant difference was found when L-tyrosine was used as a ligand. A very small amount of the actual target complex was synthesised according to elemental analysis. Still, the major component of the product is unreacted L-tyrosine, therefore the synthesis of $[Ga(nta)(tyr)]^-$ was once again not achieved. This peculiarity will be addressed further in subsection 3.3.1.

Overall, the formation of 19 target complexes was successful according to elemental analyses. The products were not pure since solvent residue and sometimes gallium(III) hydroxide were present in those. As described in subsection 2.2.1, these particular contaminations could be ignored. It should be noted, that the HDIPEA[Ga(aa)(nta)] salts were obtained in overall higher grades of purity when compared to $HNEt_3$[Ga(aa)(nta)] salts.

In general, triethylamine and *N*,*N*-diisopropylethylamine are both adequate bases for the synthesis of the target complexes. The product compositions are very similar, albeit a very impactful difference between $HNEt_3$[Ga(aa)(nta)] and HDIPEA[Ga(aa)(nta)] salts is found when the results of crystallisation experiments are compared.

2.2.4 Structural investigations of HDIPEA[Ga(aa)(nta)] salts

In some cases crystallisation experiments in methanolic and aqueous solutions or mixtures of water and methanol with the crude products of subsection 2.2.3 yielded crystals of suitable quality for X-ray diffraction experiments. The resulting molecular structures showed that the disorder of the *N*,*N*-diisopropylethylammonium cations was significantly reduced when compared to the triethylammonium cations in $HNEt_3$[Ga(aa)(nta)] salts. On average, this resulted in an improvement of crystal quality. Altogether, the molecular structures of the following seven different complex salts with two different modifications of HDIPEA[Ga(gly)(nta)] (Figure 2.13–Figure 2.20) were obtained.

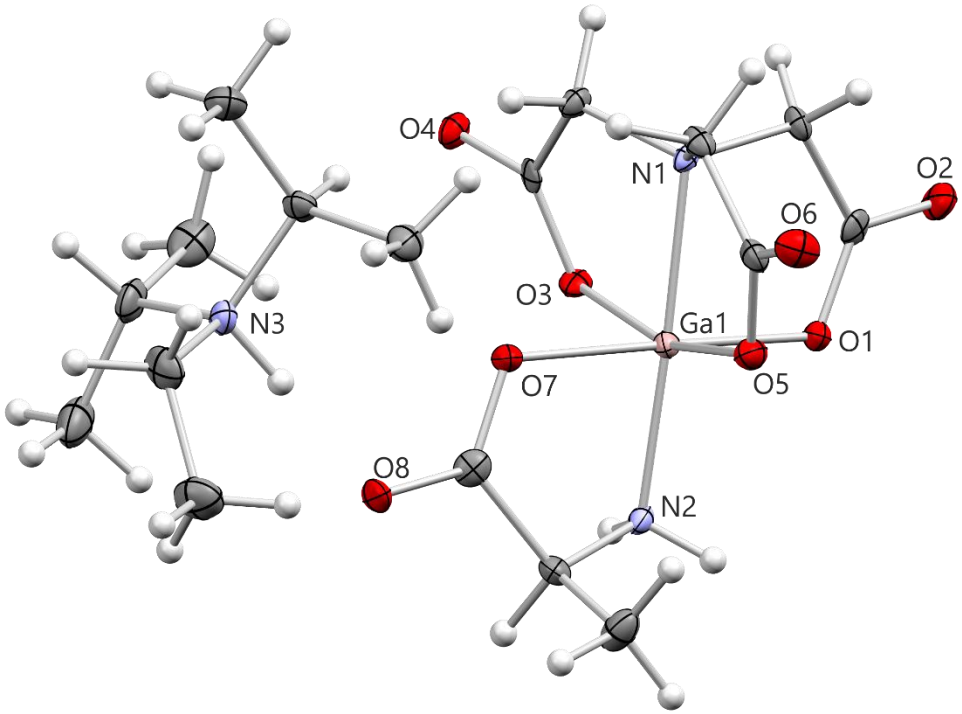


Figure 2.13: Plot of HDIPEA[Ga(ala)(nta)] in crystals of (HDIPEA)**2a**·2H_2O. Space group: *P*2_1. $CShM_{OC-6}$: 0.686. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.089(4), Ga1–N2 1.982(4), Ga1–O1 1.943(3), Ga1–O3 1.989(3), Ga1–O5 1.973(3), Ga1–O7 2.010(3), N1–Ga1–N2 177.56(16), O1–Ga1–O7 176.95(14), O3–Ga1–O5 162.71(12), N1–Ga1–O3 80.91(13), N2–Ga1–O1 94.53(14), N2–Ga1–O3 97.03(13), N2–Ga1–O5 99.58(14), N2–Ga1–O7 83.38(14), N3–O8 2.791(5).

The molecular structures of the complex salts display octahedral coordination of the gallium(III) centre with GaN_2O_4 environments. As expected, the $CShM_{OC-6}$ values illustrate slight distortions of the octahedral coordination spheres which resemble the distortions found in $HNEt_3$[Ga(aa)(nta)] salts. The interatomic distances and angles between

gallium(III) and the nitrogen and oxygen atoms are also in the expected range, with Ga–N slightly longer than Ga–O.

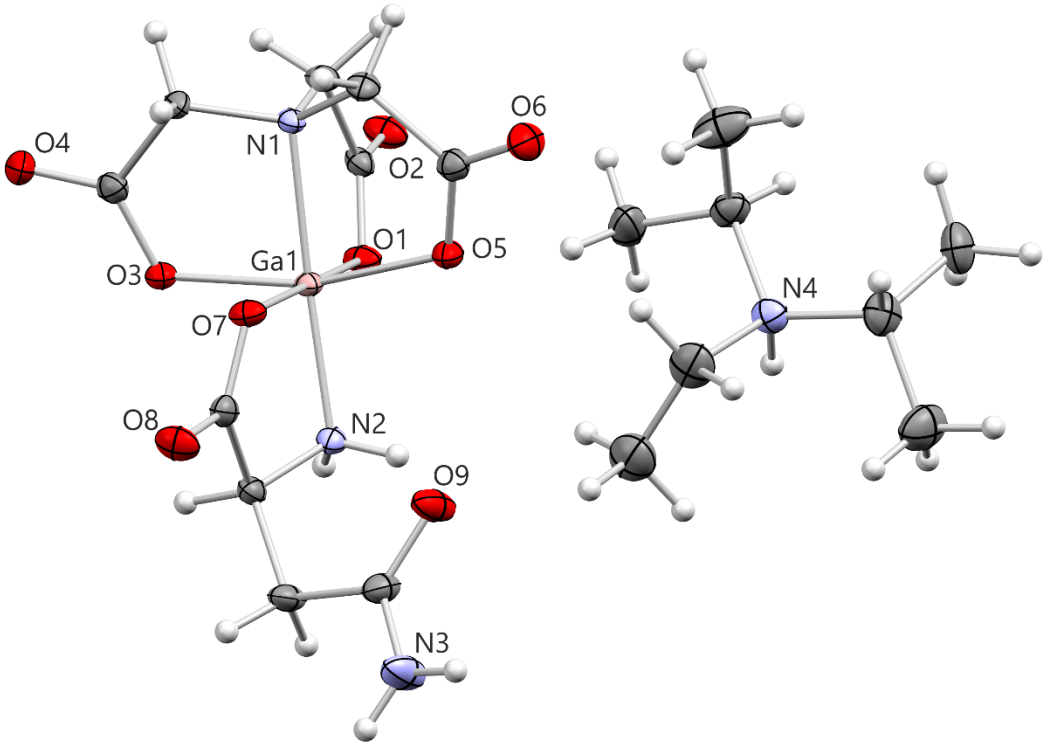


Figure 2.14: Plot of HDIPEA[Ga(asn)(nta)] in crystals of (HDIPEA)**2b**. Space group: $P2_1$. $CShM_{OC\text{-}6}$: 0.613. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.072(2), Ga1–N2 1.987(2), Ga1–O1 1.949(2), Ga1–O3 1.975(2), Ga1–O5 1.964(2), Ga1–O7 1.994(2), N1–Ga1–N2 175.70(9), O1–Ga1–O7 177.25(11), O3–Ga1–O5 164.91(8), N1–Ga1–O3 82.51(8), N2–Ga1–O1 96.14(9), N2–Ga1–O3 100.84(9), N2–Ga1–O5 93.62(9), N2–Ga1–O7 82.97(10), N4–O8 2.793(3).

In the molecular structures of HDIPEA[Ga(aa)(nta)] salts the N-atoms of nta and the respective proteinogenic amino acid are, without exception, coordinated *trans* to one another (isomer **I**, Figure 2.6).

It is odd that one isomer seems to be favoured to such an extent. To get an understanding of the preferred occurrence of isomer **I** over isomer **II** (Figure 2.6), more structural data of complexes that resemble isomer **II** would certainly be beneficial. At least, the molecular structures of the constitutional isomers **I** and **II** of the same complex anion were obtained. Isomer **I** was found in crystals of HDIPEA[Ga(met)(nta)] and isomer **II** in crystals of $HNEt_3$[Ga(met)(nta)] (Figure 2.9).

To start the comparison of the two isomers, a closer look at the $CShM_{OC\text{-}6}$ values is reasonable. The values of both complex anions show a slightly distorted octahedral coordination sphere, but, indeed, the distortion of isomer **I** ($CShM_{OC\text{-}6}$: 0.574) is not as

significant as in isomer **II** ($CShM_{OC-6}$: Ga1 1.322, Ga2 1.298, mean value 1.310). Unfortunately, due to the lack of further data, it is not possible to tell if this is always the case and, therefore, causing the preferred occurrence of isomer **I**. However, the difference between the $CShM_{OC-6}$ values in the two isomers is quite small. Hence, it is at least doubtful whether such a significantly higher prevalence of one isomer is caused by such slight differences in distortion.

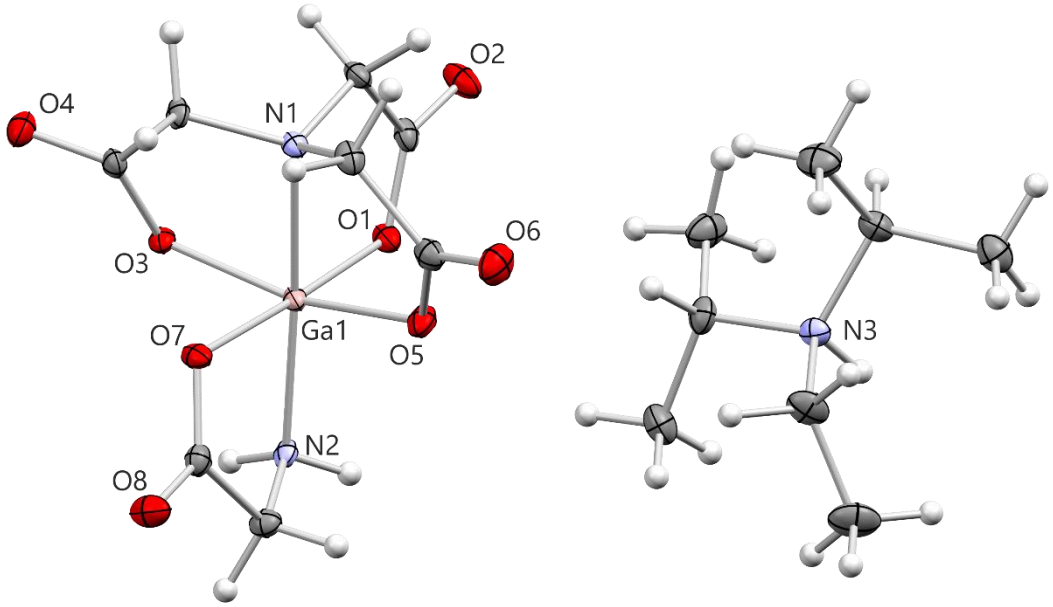


Figure 2.15: Plot of HDIPEA[Ga(gly)(nta)] in crystals of (HDIPEA)**2c**·MeOH. Space group: *Pna*2_1. $CShM_{OC-6}$: 0.536. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.074(2), Ga1–N2 1.997(2), Ga1–O1 1.947(2), Ga1–O3 1.981(2), Ga1–O5 1.962(2), Ga1–O7 2.011(2), N1–Ga1–N2 173.03(9), O1–Ga1–O7 177.73(8), O3–Ga1–O5 164.58(8), N1–Ga1–O3 81.89(8), N2–Ga1–O1 99.45(8), N2–Ga1–O3 98.93(8), N2–Ga1–O5 95.82(9), N2–Ga1–O7 82.53(8), N3–O8 2.821(3).

Another possible reason for the preferred formation of isomer **I** may be found in some kind of steric hindrance in isomer **II**. However, the molecular shape of both isomers of $[Ga(met)(nta)]^-$ does not reveal any steric hindrances of the aa ligand's side chain and the rest of the complex molecule. Hence, the reason for the preferred occurrence of isomer **I** may not be found in the molecular structures, but in the formation of the complexes in solution. If there is a mechanistic reason that leads to the prioritised formation of isomer **I**, the likelihood of crystallising isomer **II** may be drastically reduced. This will be discussed later in more detail (Section 3.7).

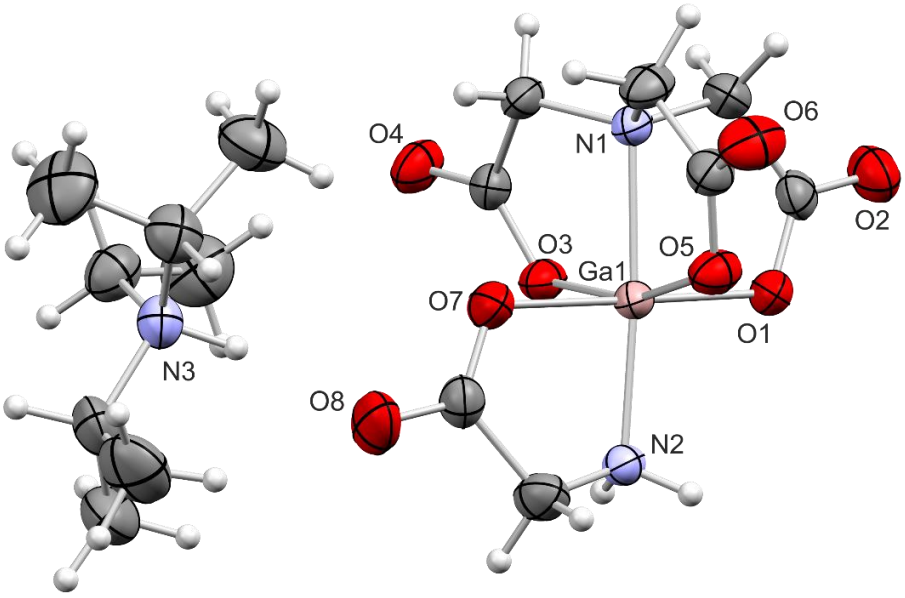


Figure 2.16: Plot of HDIPEA[Ga(gly)(nta)] in crystals of (HDIPEA)**2c**·H_2O. Space group: $P2_1/n$. $CShM_{OC-6}$: 0.574. The thermal ellipsoids are drawn at 50% probability (room temperature data collection). Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0891(13), Ga1–N2 1.9812(13), Ga1–O1 1.9386(12), Ga1–O3 1.9775(12), Ga1–O5 1.9728(12), Ga1–O7 2.0065(12), N1–Ga1–N2 175.70(5), O1–Ga1–O7 178.65(5), O3–Ga1–O5 162.91(5), N1–Ga1–O3 80.88(5), N2–Ga1–O1 96.89(5), N2–Ga1–O3 96.79(5), N2–Ga1–O5 99.48(5), N2–Ga1–O7 83.85(5), N3–O8 2.847(2).

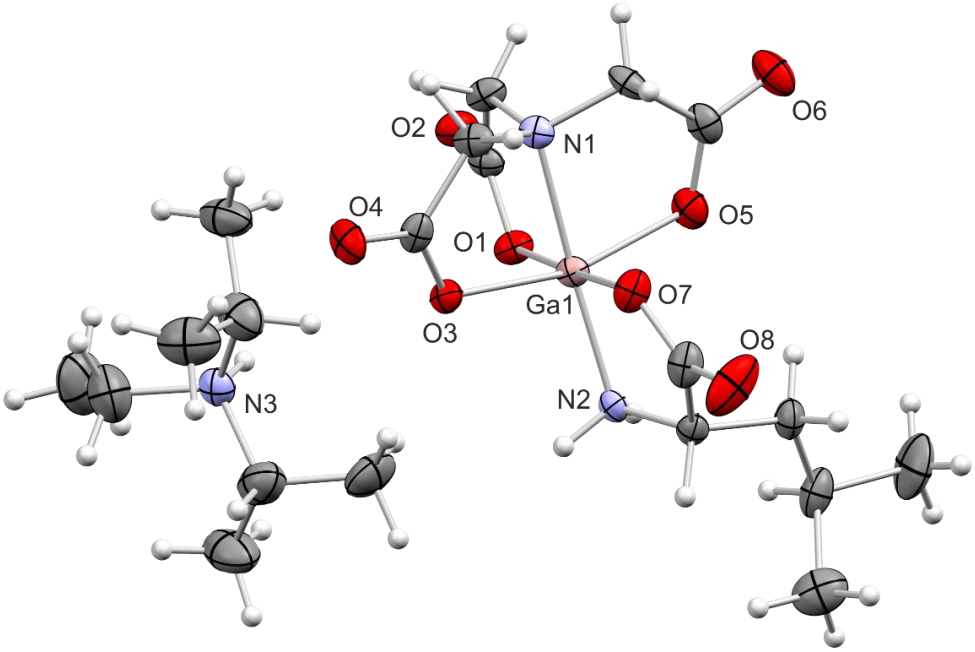


Figure 2.17: Plot of HDIPEA[Ga(leu)(nta)] in crystals of (HDIPEA)**2d**. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.585. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.086(4), Ga1–N2 2.001(4), Ga1–O1 1.959(4), Ga1–O3 1.982(4), Ga1–O5 1.989(4), Ga1–O7 1.961(4), N1–Ga1–N2 175.33(17), O1–Ga1–O7 177.80(18), O3–Ga1–O5 163.37(17), N1–Ga1–O3 81.46(18), N2–Ga1–O1 98.10(17), N2–Ga1–O3 99.02(18), N2–Ga1–O5 97.55(18), N2–Ga1–O7 83.97(17), N3–O6 2.779(6).

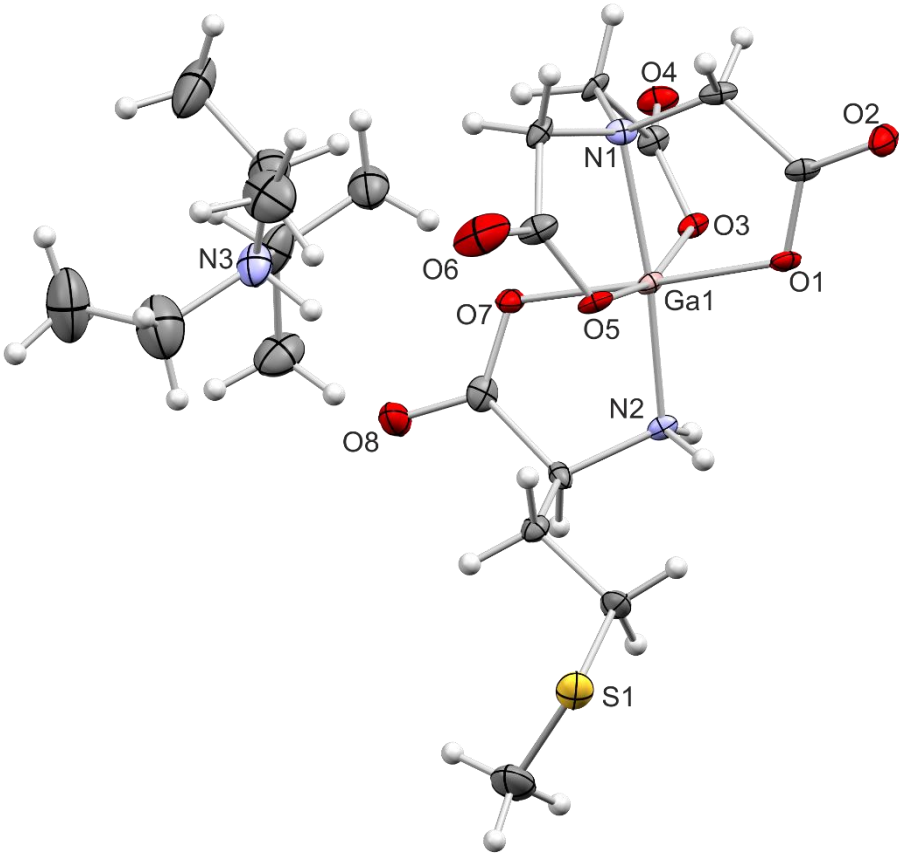


Figure 2.18: Plot of HDIPEA[Ga(met)(nta)] in crystals of (HDIPEA)**2e**. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.574. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.079(4), Ga1–N2 1.987(4), 1.987(4), Ga1–O1 1.944(4), Ga1–O3 1.990(4), Ga1–O5 1.951(4), Ga1–O7 2.012(4), N1–Ga1–N2 173.4(2), O1–Ga1–O7 177.8(2), O3–Ga1–O5 164.6(2), N1–Ga1–O3 81.3(2), N2–Ga1–O1 98.9(2), N2–Ga1–O3 97.4(2), N2–Ga1–O5 97.5(2), N2–Ga1–O7 82.5(2), N3–O8 2.859(8).

Overall, the molecular structures prove the successful synthesis of $[Ga(aa)(nta)]^-$ complexes. It was expected that crystals suitable for X-ray diffraction were not obtained of every complex salt. The molecular structures of eight different $[Ga(aa)(nta)]^-$ complexes—regardless if triethylammonium or *N*,*N*-diisopropylethylammonium salt—in combination with the elemental analyses could be seen as proof of the existence of the other eleven $[Ga(aa)(nta)]^-$ complexes, though.

Still, in some crystallisation experiments only crystals of the respective AA were obtained. This issue was encountered in crystallisation experiments with $HNEt_3[Ga(aa)(nta)]$ salts, too (Subsection 2.2.2). As the successful synthesis of 19 target complexes is reasonable to assume, this might indicate that the target complexes are not entirely stable in aqueous solution. Further information on this topic will be presented in subsections 2.2.6–2.2.9.

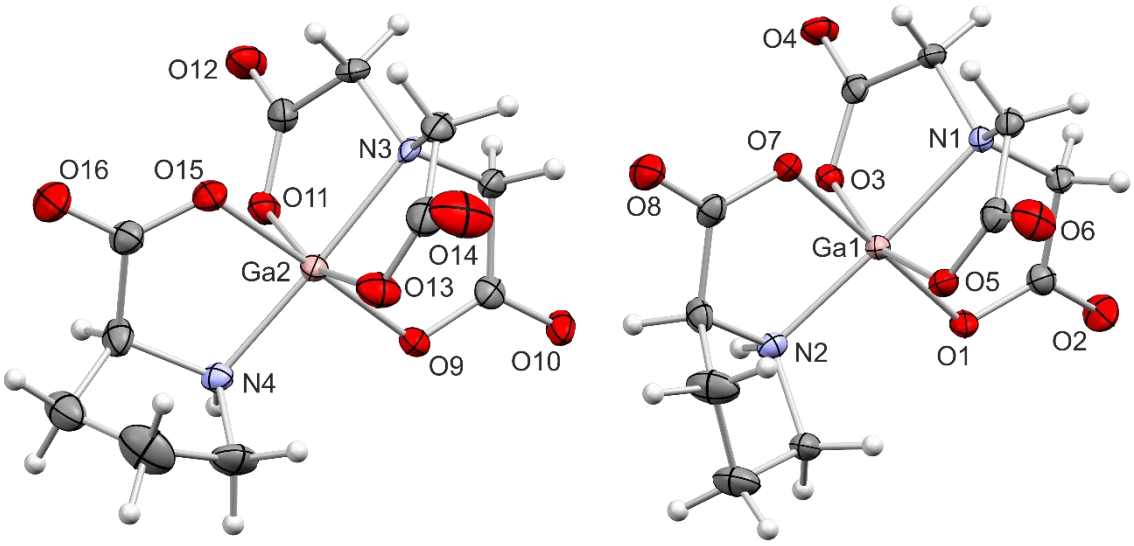


Figure 2.19: Plot of the two symmetrically independent $[Ga(nta)(pro)]^-$ ions in crystals of (HDIPEA)**2g**. Space group: $P2_1$. $CShM_{OC-6}$: Ga1 0.485, Ga2 0.634. To avoid overlap in the picture the $HDIPEA^+$ ions are not displayed. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.076(4), Ga1–N2 2.006(5), Ga1–O1 1.939(4), Ga1–O3 1.989(3), Ga1–O5 1.966(4), Ga1–O7 1.995(4), Ga2–N3 2.076(5), Ga2–N4 2.005(5), Ga2–O9 1.947(4), Ga2–O11 1.983(4), Ga2–O13 1.944(4), Ga2–O15 1.981(4), N1–Ga1–N2 176.8(2), O1–Ga1–O7 178.5(2), O3–Ga1–O5 164.6(2), N1–Ga1–O3 82.0(2), N2–Ga1–O1 95.1(2), N2–Ga1–O3 96.1(2), N2–Ga1–O5 98.3(2), N2–Ga1–O7 84.8 (2), N3–Ga2–N4 175.8(2), O9–Ga2–O15 178.2(2), O11–Ga2–O13 164.1(2), N3–Ga2–O11 81.7(2), N4–Ga2–O9 94.0(2), N4–Ga2–O11 94.1(2), N4–Ga2–O13 100.8(2), N4–Ga2–O15 84.2(2).

Up to this point, only tertiary amines were used as basic compounds to yield the respective complex salts. Unfortunately, these amines are toxic.[43,44] Hence, the substitution of the ammonium cations with nontoxic materials would be favourable if a pharmacological application of the $[Ga(aa)(nta)]^-$ complexes is intended, even though the presence of nta in such compounds would still be problematic since it is potentially carcinogenic.[45]

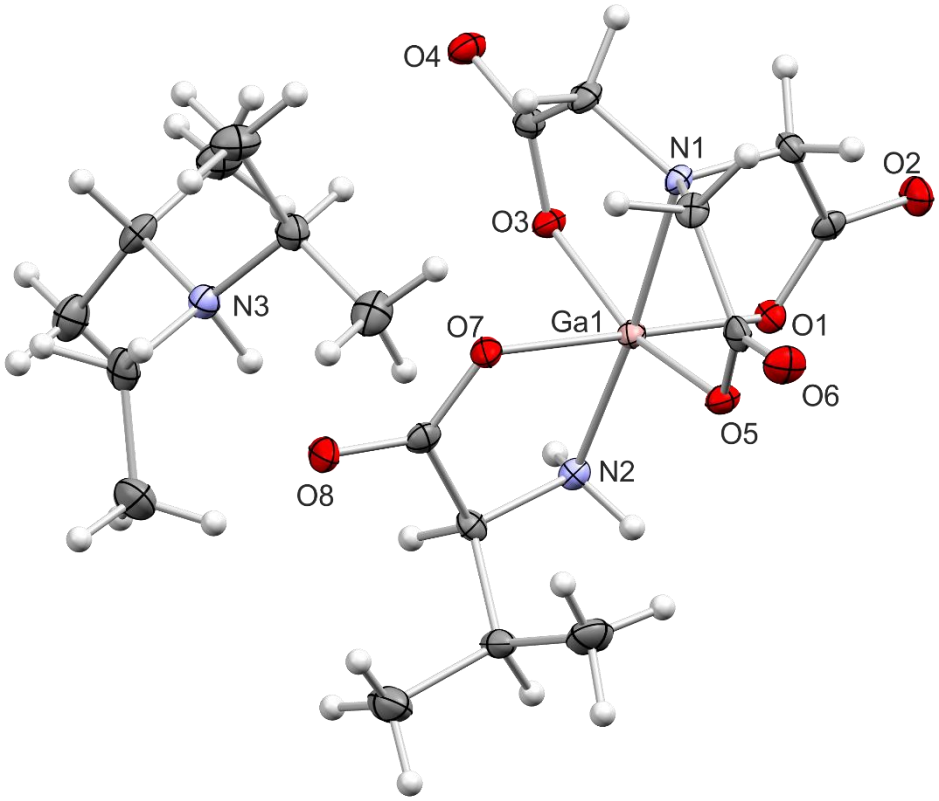


Figure 2.20: Plot of HDIPEA[Ga(nta)(val)] in crystals of (HDIPEA)**2i**·H_2O. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.737. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.095(3), Ga1–N2 1.999(3), Ga1–O1 1.944(2), Ga1–O3 1.997(2), Ga1–O5 1.967(2), Ga1–O7 1.986(2), N1–Ga1–N2 174.73(11), O1–Ga1–O7 177.80(10), O3–Ga1–O5 162.13(10), N1–Ga1–O3 80.99(10), N2–Ga1–O1 94.90(10), N2–Ga1–O3 94.10(10), N2-Ga1-O5 103.62(10), N2–Ga1–O7 83.85(10), N3–O8 2.730(4).

2.2.5 Substitution of cations

A simple way of substituting the tertiary ammonium cations is the use of alkali cations. As described before, a very advantageous characteristic of those tertiary amines is the simple separability of the target complex and the respective ammonium chloride byproduct after the reaction due to the different solubilities of those compounds in organic solvents. In contrast to the ammonium chlorides, the alkali chlorides are far less soluble in ethanol.[41] Moreover, the solubilities of most alkali chlorides are similar to the solubilities of the target compounds. As a consequence, the implementation of the procedure which was used to obtain $[Ga(aa)(nta)]^-$ salts with tertiary ammonium cations is not recommended for yielding M[Ga(aa)(nta)] salts in adequate purity. Therefore, an alternative procedure which utilises a cation exchange reaction by reacting $HNEt_3$[Ga(aa)(nta)] salts with alkali hydroxides in water was thought to be the best route to receive the respective M[Ga(aa)(nta)] salts.

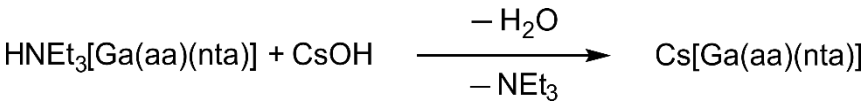


Figure 2.21: Cation exchange reaction with CsOH and $HNEt_3$[Ga(aa)(nta)] salts.

Preliminary tests indicated that CsOH is the most suitable alkali hydroxide for this purpose. The reactions were done only with the $HNEt_3$[Ga(aa)(nta)] salts of polar and nonpolar aa ligands as starting materials since those aa ligands provided the best-defined compounds. This is important, as close to equimolar amounts of alkali hydroxide and the complex salt are needed to ensure a stoichiometric reaction to the respective Cs[Ga(aa)(nta)] salts (Figure 2.21) without contamination of the product with caesium hydroxide. Therefore, only stoichiometric amounts or, sometimes, a small excess of caesium hydroxide were used in the reactions. Water was used as a solvent and the products were precipitated by the use of organic solvent. Afterwards, the crude products were examined by elemental analysis (Table 2.5).

While the target complexes were obtained according to the elemental analyses, the contaminations found in the crude products indicated an overall inferior quality when compared to the products obtained with tertiary ammonium cations. In particular, the formation of $Cs[\{Ga(nta)(\mu\text{-}OH)\}_2]$ in eleven cases indicates the decomposition of the target complexes in the reaction.

Table 2.5: Interpretation of elemental analyses: Cs[Ga(aa)(nta)] salts with polar or nonpolar aa ligands. The maximum difference (max diff.) is given between the found and calculated percentages of the listed compositions.

Complex-salt	contamination	max. diff.
Cs[Ga(ala)(nta)]	0.25 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 1.00 H_2O + 1.00 MeOH	0.03
Cs[Ga(asn)(nta)]	2.35 H_2O + 0.25 $Ga(OH)_3$	0.03
Cs[Ga(gln)(nta)]	0.25 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 2.80 H_2O	0.11
Cs[Ga(gly)(nta)]	0.35 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 5.20 H_2O	0.16
Cs[Ga(ile)(nta)]	0.65 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.15 H_2O	0.18
Cs[Ga(leu)(nta)]	3.40 H_2O + 0.25 EtOH	0.03
Cs[Ga(met)(nta)]	0.15 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.05 H_2O	0.12
Cs[Ga(nta)(phe)]	0.05 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.25 H_2O	0.22
Cs[Ga(nta)(pro)]	0.05 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 1.60 H_2O	0.11
Cs[Ga(nta)(ser)]	0.30 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.10 H_2O	0.05
Cs[Ga(nta)(thr)]	0.15 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.05 H_2O	0.07
Cs[Ga(nta)(trp)]	1.65 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 4.00 H_2O	0.24
Cs[Ga(nta)(val)]	0.35 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 3.85 H_2O	0.07

This result is surprising as the $HNEt_3$[Ga(aa)(nta)] salts which were used as starting materials were synthesised at similar reaction conditions. However, as elemental analysis is not conclusive on its own, crystallisation experiments with the raw products were done.

No crystallisation attempt of these crude products yielded crystals of Cs[Ga(aa)(nta)] salts. Instead—whenever crystals were obtained—only the respective AA and/or the already known $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ complex[40] were crystallised. The crystallisation of $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ supports the results of the elemental analyses. As further experiments with alkali cations did not point to a different outcome, alkali cations were discarded as a reasonable replacement for the tertiary ammonium ions. Hence, the presence of tertiary ammonium ions seems to be essential for the crystallisation of the target $[Ga(aa)(nta)]^-$ complexes.

These findings imply the existence of either an equilibrium between $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ and $[Ga(aa)(nta)]^-$ complexes or perhaps progressing degradation of $[Ga(aa)(nta)]^-$ complexes in aqueous solution. In order to obtain more information about this issue it was necessary to study the aqueous solutions of $[Ga(aa)(nta)]^-$ complexes.

2.2.6 Solution studies of $[Ga(aa)(nta)]^-$ salts

Established techniques like UV-Vis, IR, and potentiometric titration are not suitable for studying the composition of these gallium(III) complexes in solution. The first two techniques are not reasonable choices as the starting materials and complexes lack the disparity in colour or functional groups to allow for a differentiated analysis. As mixtures of the starting materials of $[Ga(aa)(nta)]^-$ salts did usually form suspensions over a wide pH range, already intricate potentiometric titrations were excluded as a potential approach of the issue. Hence, $^{13}C\{^1H\}$ and ^1H NMR spectroscopy in combination with 2D NMR techniques were used to examine the aqueous solutions of $[Ga(aa)(nta)]^-$ salts. However, one problem with this approach is the low coordination-induced shift (CIS) which is generated in the ligand by the coordination of gallium(III). Therefore, exact referencing of every spectrum against the signals of added methanol is key to detect these slight changes in signal shift. Unfortunately, ^{71}Ga and ^{69}Ga NMR spectroscopy was not applicable. This issue will be discussed in section 3.2.

The following experiments were conducted mainly with the HDIPEA[Ga(aa)(nta)] and $HNEt_3$[Ga(aa)(nta)] salts, as these are generally of higher quality and are better soluble in water and methanol as the corresponding Cs[Ga(aa)(nta)] salt. Since not every complex salt was crystallisable, the NMR experiments were done with the isolated crude products of the respective compounds (Table 2.1–Table 2.5). 2D NMR techniques were only utilised with HDIPEA[Ga(aa)(nta)] solutions due to the superior solubility of these compounds. Since fewer overlaps of signals were observed in ^1H NMR spectra of $HNEt_3$[Ga(aa)(nta)] solutions, the ratios of compounds in solutions (Table 2.15) were derived from those spectra.

It was only possible to combine information from the NMR spectra of $HNEt_3$[Ga(aa)(nta)] and HDIPEA[Ga(aa)(nta)] solutions with one specific aa ligand as the spectra of the triethylammonium and *N*,*N*-diisopropylethylammonium salts of one specific complex were almost perfectly identical. Hence, it was feasible to identify the compounds with 2D NMR techniques in HDIPEA[Ga(aa)(nta)] solutions and then use the information to assign signals in spectra of $HNEt_3$[Ga(aa)(nta)] solutions without difficulty. This was also possible because the pH values of the aqueous solutions were similar regardless if the respective HDIPEA[Ga(aa)(nta)] or $HNEt_3$[Ga(aa)(nta)] salt was examined (Table 2.6). In general, the solutions of $HNEt_3$[Ga(aa)(nta)] were slightly less acidic than the solutions of HDIPEA[Ga(aa)(nta)] salts since those were as concentrated as possible to allow for 2D NMR experiments. There were, however, differences regarding the pH levels

depending on the aa ligand present in the complex. To not influence the composition in solution, pH levels were not adjusted by addition of acid or base.

Table 2.6: pH values of solutions: $[Ga(aa)(nta)]^-$ complexes with polar or nonpolar aa ligands in D_2O.

aa ligand	$HDIPEA^+$	$HNEt_3^+$ (c = 0.25 mol L^{-1})
L-Alaninato	6.0	6.5–7.0
L-Asparaginato	5.5	6.5–7.0
L-Cysteinato	4.5–5.0	5.0
L-Glutaminato	6.5	6.5–7.0
Glycinato	6.0–6.5	6.5–7.0
L-Isoleucinato	6.5–7.0	6.5–7.0
L-Leucinato	6.5	6.5–7.0
L-Methioninato	6.5	7.0
L-Phenylalaninato	7.0	6.5–7.0
L-Prolinato	6.0	7.0
L-Serinato	6.0–6.5	7.0
L-Threoninato	6.5	6.5–7.0
L-Tryptophanato	4.5–5.0	5.0
L-Tyrosinato	-	-
L-Valinato	6.5–7.0	7.0

The spectra displayed differences when polar/nonpolar, basic or acidic proteinogenic aa ligands were present in the complexes and are therefore discussed separately. This was expected, as the elemental analyses already showed distinct differences in product composition depending on the functional groups of the aa ligand in use (Subsections 2.2.1 and 2.2.3).

First, the spectra of polar/nonpolar amino acids are discussed using NMR spectra of HDIPEA[Ga(ala)(nta)] as an example. As shown in Figure 2.22b, the $^{13}C\{^1H\}$ NMR spectrum of an aqueous solution of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O shows more signals than expected for the mononuclear complex. In fact, exactly two signal sets are found for each ligand, while only one signal set of the HDIPEA cation can be seen. Those assignments were proven by 2D NMR spectroscopy.

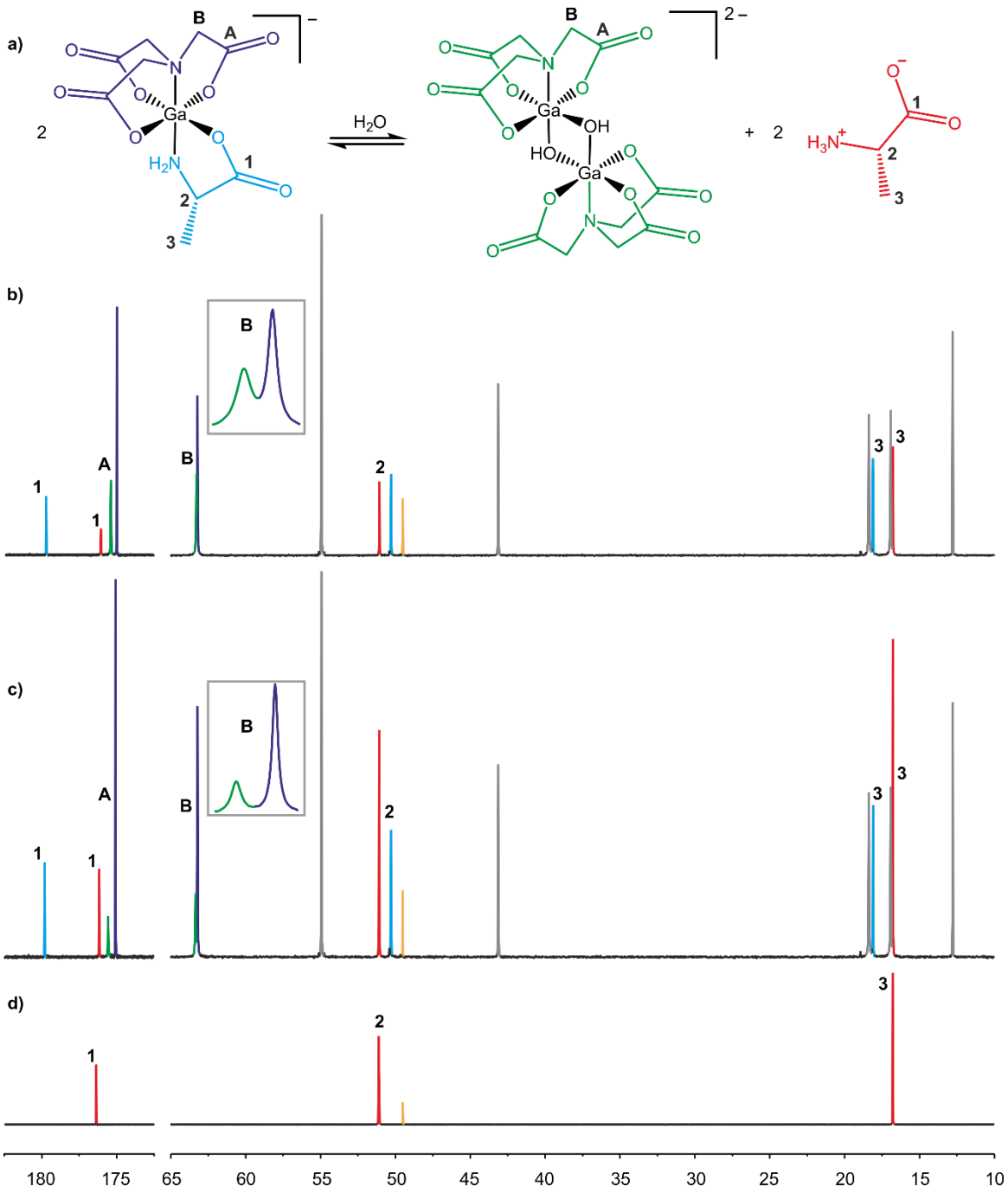


Figure 2.22: HDIPEA[Ga(ala)(nta)] + 0.85 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O with 0.5 equ. of L-alanine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-alanine in D_2O*. Red: L-alanine, cyan: L-alaninato in $[Ga(ala)(nta)]^-$, blue: nta in $[Ga(ala)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

The $^{13}C\{^1H\}$ NMR spectrum indicates the existence of at least two different complexes in solution, while the cation is unaffected. If these two complex anions are $[Ga(ala)(nta)]^-$ and $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, an equilibrium reaction as shown in Figure 2.22a should be present. In this equilibrium, free L-alanine and a coordinated L-alaninato ligand as well as two bound

nta ligands in slightly different chemical environments should exist. A comparison of the signal sets assigned to L-alanine with the signals of a solution of pure L-alanine in D_2O (Figure 2.22d) shows that one set of signals matches perfectly. The chemical shifts and the corresponding coordination-induced shifts are given in Table 2.7. It should be noted that the pH of the complex solution and the solution of free amino acid were not adjusted to the same level, hence CIS values are derived from the signals of free amino acid in the complex solution to achieve the highest possible accuracy.

Table 2.7: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-alanine and the L-alaninato ligand in $[Ga(ala)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3
$HDIPEA^+$	$[Ga(ala)(nta)]^-$	δ	179.7	50.3	18.1
	L-Alanine	δ	176.1	51.1	16.8
		$\Delta\delta$	3.6	−0.8	1.3
$HNEt_3^+$	$[Ga(ala)(nta)]^-$	δ	180.0	50.3	18.0
	L-Alanine	δ	176.3	51.1	16.8
		$\Delta\delta$	3.7	−0.8	1.2

Because of these findings it was safe to assume that the $[Ga(ala)(nta)]^-$ complex is not stable against hydrolysis in aqueous solution and releases free L-alanine by forming $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$. This was further proven by addition of 0.5 equivalents of L-alanine to the solution of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O in D_2O and re-measuring the $^{13}C\{^1H\}$ NMR spectrum (Figure 2.22c). As expected, the intensity of the signals assigned to free L-alanine are drastically increased.

The addition of L-alanine also effects the intensity of the nta-related signals. The intensity of one signal set increases significantly, while the other shows a significant decrease in intensity. This observation is also consistent with the predicted equilibrium, as the addition of free proteinogenic amino acid should shift the equilibrium from the side of the $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ complex and L-alanine to the mononuclear $[Ga(ala)(nta)]^-$ complex, therefore increasing the intensity of the signal set correlated to nta in the $[Ga(ala)(nta)]^-$ complex and decreasing the intensity of the signal set of nta in the $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ complex. To further prove the existence of $HDIPEA_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$, this compound was synthesised by the reaction of $GaCl_3$ and nta in a molar ratio of 1:1. Analytical proof of $HDIPEA_2[[\{Ga(nta)(\mu\text{-}OH)\}_2]$ was possible only by elemental analysis, as crystallisation attempts remained unsuccessful. Nevertheless, the $^{13}C\{^1H\}$ NMR spectrum of this compound displays the same signals as found in the spectrum of HDIPEA[Ga(ala)(nta)] +

0.85 H_2O. Since $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$readily crystallises with Cs^+ and Li^+ as cations, the existence of $[\{Ga(nta)(\mu\text{-}OH)\}_2]^-$ in the equilibrium can be proven by comparing the NMR spectrum of Cs[Ga(ala)(nta)] with the spectra of HDIPEA[Ga(ala)(nta)] and $HNEt_3$[Ga(ala)(nta)]. The $^{13}C\{^1H\}$ NMR spectrum of a solution of Cs[Ga(ala)(nta)] + 0.25 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 1.00 H_2O + 1.00 MeOH in D_2O (c = 0.25 mol L^{-1}, Figure 2.23) indeed shows the same signals as the $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O, therefore the equilibrium shown in Figure 2.22a also exists in the solution of the Cs[Ga(ala)(nta)] salt. The only difference can be found in the position of the equilibrium. With about 75% free L-alanine, the amount of free amino acid is roughly 15% higher than in a comparable solution of $HNEt_3$[Ga(ala)(nta)] with the same concentration (Table 2.15).

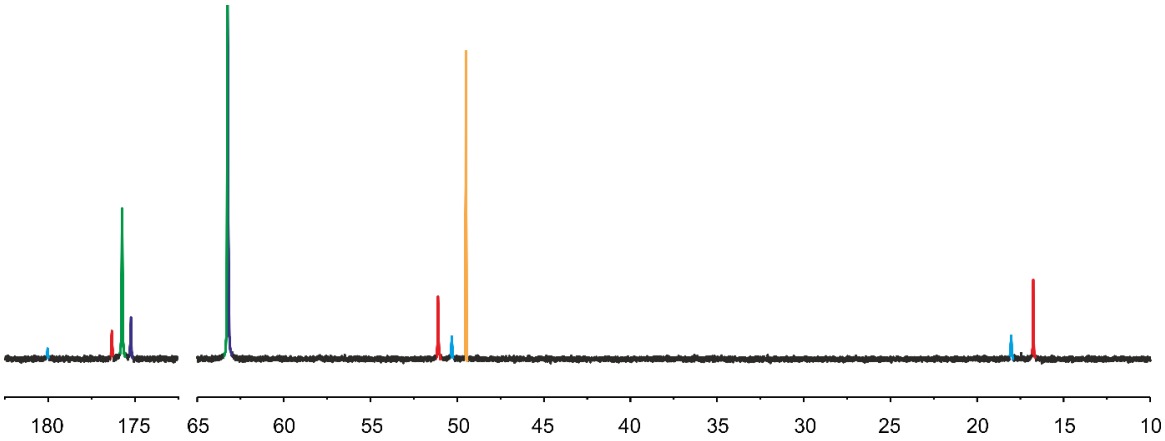


Figure 2.23: $^{13}C\{^1H\}$ NMR spectrum of Cs[Ga(ala)(nta)] + 0.25 $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ + 1.00 H_2O + 1.00 MeOH in D_2O (c = 0.25 mol L^{-1}). Red: free L-alanine, cyan: L-alaninato in $[Ga(ala)(nta)]^-$, blue: nta in $[Ga(ala)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, orange: MeOH. * One drop of MeOH was added for referencing.

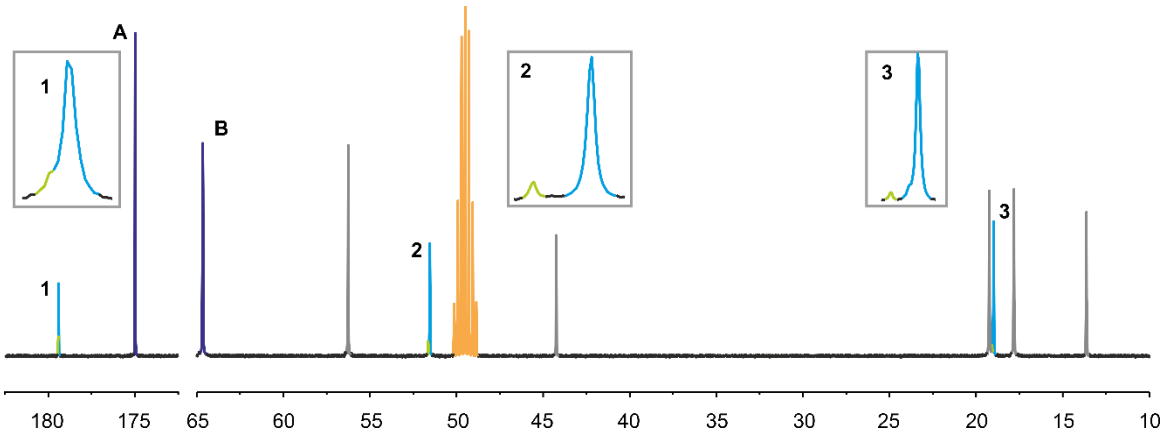


Figure 2.24: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ala)(nta)] in MeOD. Cyan and light green: L-alaninato in $[Ga(ala)(nta)]^-$, blue: nta in $[Ga(ala)(nta)]^-$, grey: $HDIPEA^+$, orange: MeOD.

The equilibrium between $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ and $[Ga(ala)(nta)]^-$ should exist only in aqueous solution since water is needed for the formation of $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$. Hence, to guarantee that the assumption is correct and the specific equilibrium is present in solution, thoroughly dried HDIPEA[Ga(ala)(nta)] was dissolved in dry MeOD. As expected, no equilibrium can be seen in this case: only one set of signals of nta ($[Ga(ala)(nta)]^-$) and no signal set of free L-alanine is present in the $^{13}C\{^1H\}$ NMR spectrum (Figure 2.24) of this solution. This confirms the conjecture and is one last proof of the equilibrium reaction in aqueous solution. In addition, it explains why some complexes were only crystallisable from methanolic solution.

However, on close inspection, two signal sets of L-alanine/L-alaninato are visible in the spectrum (Figure 2.24). One set of signals is very prominent while the other is of very low intensity. As stated, there is no second signal set of nta, therefore none of these signal sets is related to free L-alanine. Also, both signal sets are in very close proximity to one another, hence they are assigned to L-alaninato ligands. Since two different isomers of the $[Ga(ala)(nta)]^-$ complex can be formed, it is reasonable to assume that one set of signals has to be assigned to isomer **I** and one to isomer **II** (Figure 2.6). Why this preference of one isomer over the other should be so striking is not yet explained but this observation matches the aforementioned remarkable preference of isomer **I** over **II** in crystal structures of $[Ga(aa)(nta)]^-$ salts. Based on that information, it seems plausible to assign the signal set with low intensity to isomer **II**, while the signal set with high intensity is assigned to isomer **I**. These signals are potentially present in the $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ala)(nta)] + 0.85 H_2O in D_2O as well, but are lacking the intensity to be identified with confidence. Though this is true for most other $[Ga(aa)(nta)]^-$ complexes, this additional signal set of low intensity seems to be present in a few other $^{13}C\{^1H\}$ NMR spectra of aqueous $[Ga(aa)(nta)]^-$ solutions. It is certainly present in the spectra of [Ga(Harg)(nta)]·0.05DIPEA + 2.45 H_2O (Figure 2.28) and [Ga(Hlys)(nta)]·0.05DIPEA + 2.25 H_2O + 0.15 EtOH (Figure 2.29), while the spectra of HDIPEA[Ga(gly)(nta)] + 0.95 H_2O (Figure 6.4), HDIPEA[Ga(nta)(ser)] + 0.80 H_2O and HDIPEA[Ga(nta)(thr)] + 0.50 H_2O (Figure 6.10 and Figure 6.11) may feature it, although the signals are too weak to be absolutely certain and are therefore not explicitly labelled in those. The spectra of compounds containing [Ga(Harg)(nta)] and [Ga(Hlys)(nta)] are interpreted later (Subsection 2.2.8), but this particular feature is mentioned here to support the hypothesis. The two different isomers of $[Ga(aa)(nta)]^-$ and their occurrence are a relevant issue in this work. Hence, data about this topic will be summed up and further discussed in section 3.7.

The equilibrium of $[Ga(aa)(nta)]^-$ with its corresponding proteinogenic amino acid and $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ is present in every aqueous solution of HDIPEA[Ga(aa)(nta)] and

$HNEt_3$[Ga(aa)(nta)] salts with polar and nonpolar aa ligands. This was tested by addition of the free proteinogenic amino acid if the respective AA exhibits good solubility in water (glycine, L-proline, L-serine, L-threonine, L-valine). The corresponding spectra as well as the chemical shifts and the CIS values are displayed in section 6.1 while the position of the respective equilibria is shown and further discussed in subsection 2.2.10.

The only exceptions were found when the two polar amino acids L-tyrosine and L-cysteine were used as ligands. No spectra of the $[Ga(nta)(tyr)]^-$ can be shown, as L-tyrosine did not form $HNEt_3$[Ga(nta)(tyr)] at all, and HDIPEA[Ga(nta)(tyr)] was formed only as a minor side product according to elemental analysis. Instead, the main product was unreacted L-tyrosine, which was likely due to the extremely weak solubility of L-tyrosine in water even at higher pH levels. An examination of such a complex is therefore not possible. In contrast, L-cysteine formed the target complex but features a more complex equilibrium in aqueous solution which needs to be discussed in detail (Subsection 2.2.7).

2.2.7 Solution study of $[Ga(cys)(nta)]^-$

L-Cysteine—and its respective $[Ga(cys)(nta)]^-$ complex—is special in three ways. First, L-cysteine decomposed in aqueous solution. This was observed in NMR spectra as well as in crystallisation experiments, since, in one case, crystals of S_8-sulfur were obtained. Hence, no re-measurement of the $^{13}C\{^1H\}$ NMR spectrum after addition of free amino acid was possible to further investigate the equilibrium in solution. In addition, the pH value of the solution was significantly more acidic than every other solution of $[Ga(aa)(nta)]^-$ complexes with polar and nonpolar aa ligands (Table 2.6). Furthermore, as mentioned in subsection 2.2.6, the equilibrium in aqueous solution is more complex than it is in solutions of other $[Ga(aa)(nta)]^-$ complexes.

In-depth examination of the spectra and comparison with the $^{13}C\{^1H\}$ NMR and ^1H NMR spectra of other $[Ga(aa)(nta)]^-$ compounds reveals distinct deviations. According to the ^1H NMR spectra of $HNEt_3$- and HDIPEA[Ga(cys)(nta)] salts one difference is the position of the equilibrium. In contrast to the other equilibria, the ratio of bound to free L-cysteine in a solution of $HNEt_3[Ga(cys)(nta)] + 1.25\ H_2O + 0.10$ Hcys in D_2O ($c = 0.25\ mol\ L^{-1}$) is about 60 : 40 (due to overlap of signals, the amount of bound L-cysteine could be about 5% higher or lower). Hence, L-cysteine has the highest ratio of $[Ga(aa)(nta)]^-$ to free amino acid of all examined complexes in solution (Table 2.15). Another difference can be found in the $^{13}C\{^1H\}$ NMR spectra (Figure 2.25b): instead of only two signal sets for each nta and L-cysteine, a third signal set of both ligands is visible in the spectrum. These findings suggest that at least three different complexes are present in solution. Unfortunately, none of these complexes was crystallisable, therefore any assumptions about their characteristics is dependent on the information derived from NMR spectroscopy. Hence, the following conclusions are not certain, but appear to be the best explanation at the current state of research.

Since the free aa ligand can be identified, an equilibrium as described before is present and the $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ complex is one of the compounds in solution (Figure 2.25a). This is consistent with the signal shifts in the $^{13}C\{^1H\}$ NMR spectra. Two further signal sets of nta and L-cysteinato ligands indicate the presence of two different $[Ga(cys)(nta)]^-$ complexes. The signal sets are not as close in proximity as seems to be reasonable if those were to be assigned to isomers **I** and **II** of [Ga(cys-κ*O*,*N*)(nta)]$^-$ (Figure 2.6).

The obvious difference between L-cysteine and the other proteinogenic amino acids used in this work is the thiol group, which could be bound to gallium(III) by including the amine

group to form a five-membered chelate ring or the carboxylato group to form a six-membered chelate ring.

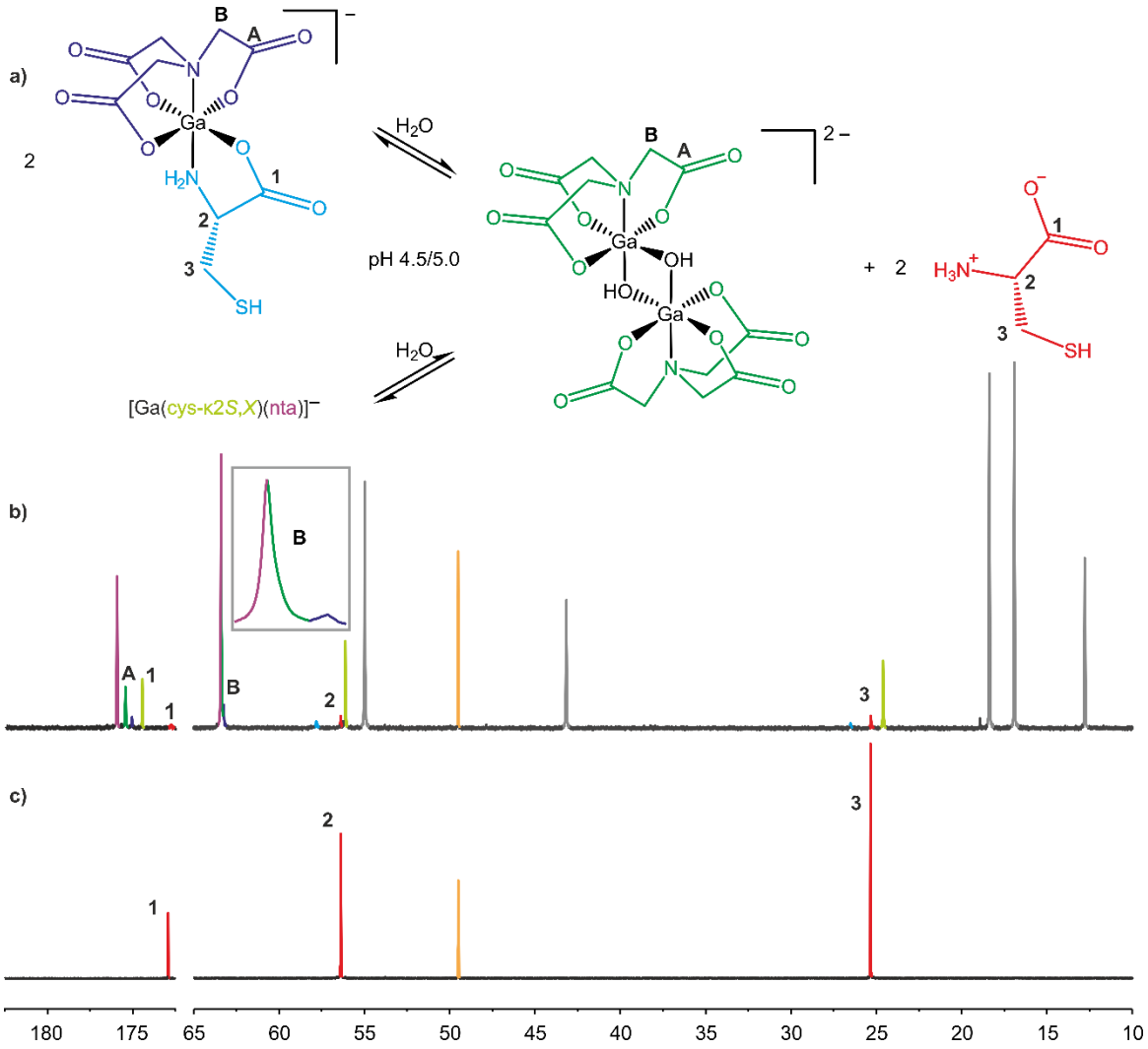


Figure 2.25: HDIPEA[Ga(cys)(nta)] + 0.10 $Ga(OH)_3$ + 0.10 H_2O + 0.05 EtOH in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(cys)(nta)] + 0.10 $Ga(OH)_3$ + 0.10 H_2O + 0.05 EtOH in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-cysteine in D_2O*. Red: free L-cysteine, cyan: L-cysteinato in [Ga(cys-κ*O*,*N*)(nta)]⁻, light green: L-cysteinato in [Ga(cys-κ^2*S*,*X*)(nta)]⁻, blue: nta in [Ga(cys-κ*O*,*N*)(nta)]⁻, purple: nta in [Ga(cys-κ^2*S*,*X*)(nta)]⁻, green: nta in [{Ga(nta)(μ-OH)}$_2$]$^{2-}$, grey: HDIPEA⁺, orange: MeOH. * One drop of MeOH was added for referencing.

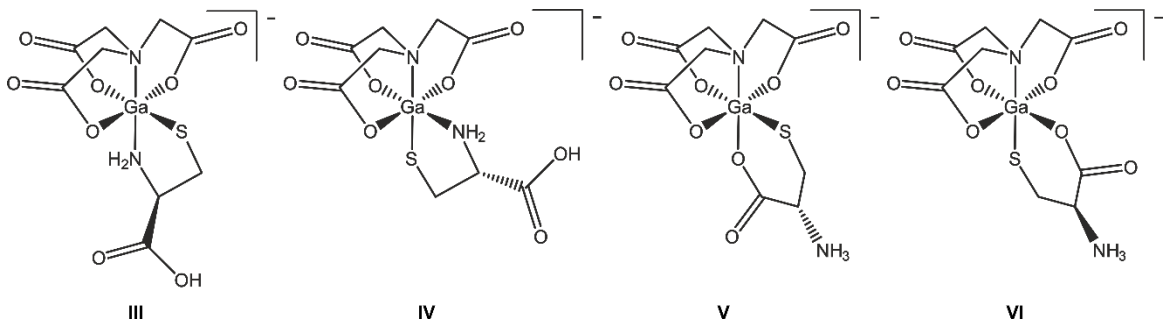


Figure 2.26: The four possible constitutional isomers of [Ga(cys-κ^2*S*,*X*)(nta)]⁻.

The four possible isomers of these complexes are shown in Figure 2.26. Two further potential isomers are not shown as reasonable options since these would have resembled the isomers **III** and **IV**, but with deprotonated carboxylic functions and protonated thiol groups. With the data at hand it is not possible to identify which isomer is formed in aqueous solution, but the sharp signal in the $^{13}C\{^1H\}$ NMR spectrum indicates that, most likely, not all of these—perhaps only one—are present in solution. Interestingly, the [Ga(cys-κ^2*S*,*X*)(nta)]$^-$ complex is not only present but seems to be the main [Ga(cys)(nta)]$^-$ complex in solution. This can be derived from the shifts of the carboxylic C-atoms assigned to nta. The well-known shifts of [{Ga(nta)(μ-OH)}$_2$]$^-$ and [Ga(cys-κ*O*,*N*)(nta)]$^-$ are present, but the most prominent signal is the new signal at 174.5 ppm (Table 2.8). Therefore, the equilibrium described in Figure 2.25a should be present in solution, while [Ga(cys-κ^2*S*,*X*)(nta)]$^-$ is the main compound.

Table 2.8: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-cysteine and the L-cysteinato ligand in [Ga(cys)(nta)]$^-$ complexes. The relative shift is given in $\Delta\delta$ (CIS).

			C1	**C2**	**C3**
HDIPEA$^+$	[Ga(cys-κ*O*,*N*)(nta)]$^-$	δ	-	57.8	26.5
	L-Cysteine	δ	172.8	56.4	25.3
		$\Delta\delta$	-	1.4	1.2
HDIPEA$^+$	[Ga(cys-κ^2*S*,*X*)(nta)]$^-$	δ	174.5	56.1	24.6
	L-Cysteine	δ	172.8	56.4	25.3
		$\Delta\delta$	1.7	−0.3	−0.7
HNEt$_3^+$	[Ga(cys-κ*O*,*N*)(nta)]$^-$	δ	-	57.8	-
	L-Cysteine	δ	172.9	56.4	25.3
		$\Delta\delta$	-	1.4	-
HNEt$_3^+$	[Ga(cys-κ^2*S*,*X*)(nta)]$^-$	δ	174.5	56.1	24.6
	L-Cysteine	δ	172.9	56.4	25.3
		$\Delta\delta$	1.6	−0.3	−0.7

Whether thiolate groups have a higher tendency to bind to gallium(III) than carboxylate groups or amine groups cannot be determined with the scarce information at hand. However, this might be an interesting topic for future investigations. At the current state of research, a comparative study concerning the preference of gallium(III) towards amine, carboxylate or thiol groups has not been done yet. However, gallium(III) complexes featuring ligands with all of these functional groups coordinated to gallium(III) are known, for example, with the ligands 2-carboxy-8-mercaptoquinoline[46] or *N*,*N*'-ethylenedi-L-

cysteine[47,48]. Those complexes are monoanionic due to the fact that both the carboxylate groups and the thiol groups are deprotonated. In the case of *N*,*N*'-ethylenedi-L-cysteine this is true despite the neutral pH level during the crystallisation from aqueous solution.[48]

Since the $[Ga(cys)(nta)]^-$ complexes were not essential for this work due to their rapid degradation in solution, a fact which does not fit the aimed-for characteristics of compounds, no further efforts to identify the specific complex isomers in solution were made.

2.2.8 Solution studies: complexes with basic aa ligands

As described in the subsections 2.2.1 and 2.2.3, the elemental analyses of the synthesised nitrilotriacetatogallium(III) complexes with basic aa ligands suggested the formation of adducts between [Ga(Haa)(nta)] complexes and the respective tertiary amine in use. This was expected, since the basic side chain of these aa ligands competes with the tertiary amine as a base in use at the pH levels of the syntheses (ca. 8.5–9.0). To some extent, the differing basicity of the side chains can be seen even in the composition of the crude products, as the compounds with L-argininato and L-lysinato ligands contained significantly lower amounts of tertiary amine than the L-histidinato compounds.

The crystallisation of nitrilotriacetatogallium(III) complexes with basic aa ligands was not successful despite several attempts. A structural characterisation of these complexes was therefore not possible. However, the conclusions drawn from the elemental analyses were backed by the $^{13}C\{^{1}H\}$ NMR and ^{1}H NMR spectra of these compounds in aqueous solution, as these showed the presence of the same amounts of tertiary amine which were indicated in the elemental analyses.

The $^{13}C\{^{1}H\}$ NMR spectrum of an aqueous solution of [Ga(Hhis)(nta)]·0.25DIPEA + 2.10 H_2O + 0.05 EtOH (Figure 2.27b) with neutral pH level (Table 2.9) shows two signal sets each for nta and the proteinogenic amino acid. Therefore it is reasonable to assume that the same equilibrium as found in solutions of $[Ga(aa)(nta)]^-$ complexes with polar and nonpolar aa ligands is also present in this solution. However, as the L-histidinato ligand is a potential tridentate ligand, there are different possibilities to form a [Ga(Hhis)(nta)] complex. The signals of nta are very similar to the signals found in the aforementioned spectra of $[Ga(aa)(nta)]^-$ complexes, therefore the tetradentate ligand seems to be unaffected and should, therefore, be bound to gallium(III) in the familiar manner.

Table 2.9: pH values of solutions: [Ga(Haa)(nta)] complexes with basic aa ligands in D_2O.

aa ligand	DIPEA	NEt_3 (c = 0.25 mol L^{-1})
L-Argininato	7.0	7.0
L-Histidinato	6.5	6.5–7.0
L-Lysinato	7.0	7.0

The L-histidinato ligand can bind to gallium(III) in three different ways: two κ*O,N*-configurations and one κ*N,N*-configuration. The κ*N,N*-pattern is unlikely to form, as a majority of the L-histidinato ligands is protonated in one position. Since the carboxylic function is deprotonated at neutral pH levels, one of the amine groups has to be protonated which prevents the coordination of gallium(III) in this manner. Therefore, only two κ*O,N*-configurations are possible. It is reasonable to assume that the formation of a seven-membered chelate ring with N^{δ} and the carboxylato function is unlikely to prevail when the formation of a five-membered chelate ring with the amine group at C2 and the carboxylato function is also possible. Therefore, either isomer **I** or **II** of [Ga(Hhis)(nta)] should be present. The NMR shifts and CIS values of the compounds in solution are listed in Table 2.10.

Table 2.10: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-histidine and the L-histidinato ligand in [Ga(Hhis)(nta)]. The relative shift is given in $\Delta\delta$ (CIS).

adduct			**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
DIPEA	[Ga(Hhis)(nta)]	δ	176.9	53.7	26.8	129.6	116.5	133.3
	L-Histidine	δ	173.5	54.4	27.7	129.6	118.2	136.2
		$\Delta\delta$	3.4	−0.7	−0.9	0.0	−1.7	−2.9
NEt_3	[Ga(Hhis)(nta)]	δ	176.9	53.7	26.9	129.0	116.5	133.2
	L-Histidine	δ	173.5	54.5	27.7	129.0	118.2	136.2
		$\Delta\delta$	3.4	−0.8	−0.8	0.0	−1.7	−3.0

A noteworthy feature of the spectrum is the broadening of aromatic signals. The cause of this may be found in the protonation of the side chain, which should be dynamic due to the reaction with the present tertiary amine. A rapidly changing chemical environment leads to broadening of signals. This is, of course, just an assumption based on the most likely isomer in solution. The cause may also be found in the existence of isomer **I** and **II**, though the non-aromatic signals do not suggest this due to the lack of a third signal set. Another issue can be found with the spectrum of the free amino acid L-histidine which was measured in D_2O for comparison (Figure 2.27c). The pH of this solution is basic, which leads to significant differences when compared to signals of L-histidine found in solutions with neutral pH levels. If pH values of solutions differ too much, the comparability of their spectra is practically non-existent. This should be kept in mind for the remainder of this work.

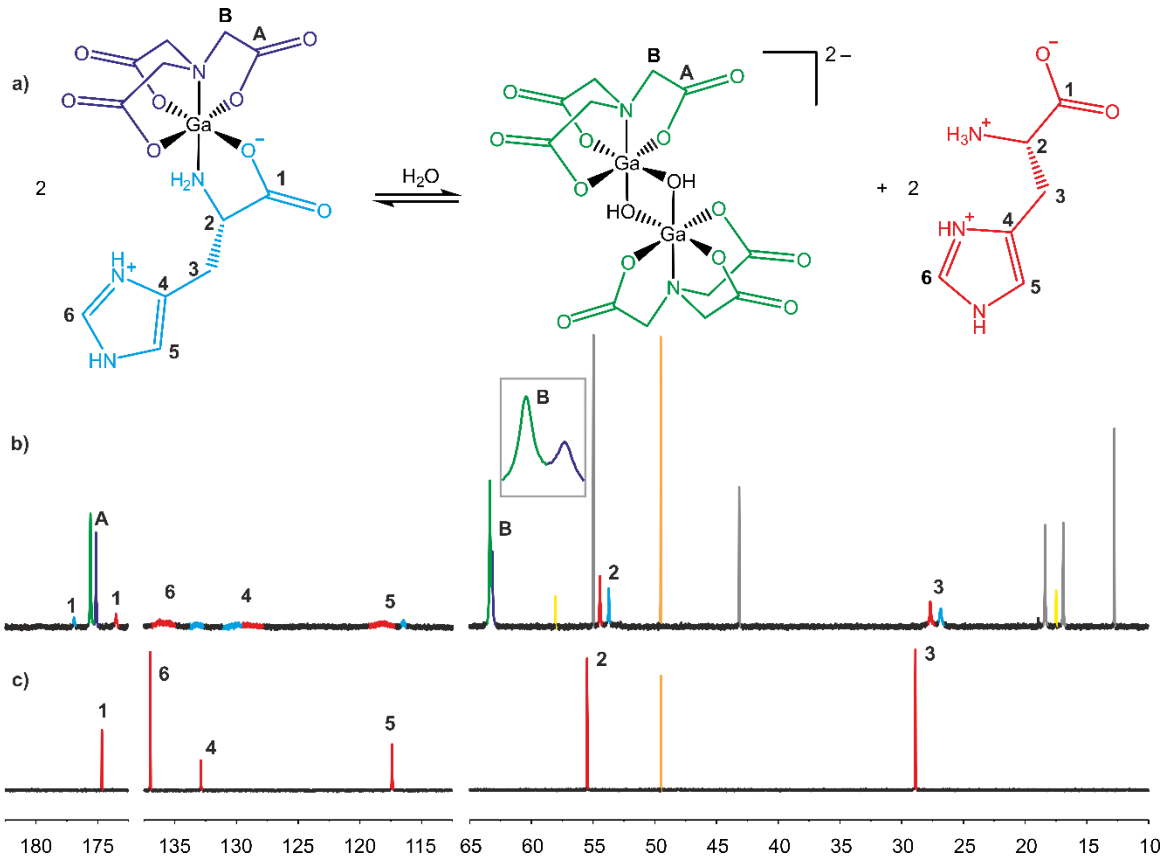


Figure 2.27: [Ga(Hhis)(nta)]·0.25DIPEA + 2.10 H_2O + 0.05 EtOH in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(Hhis)(nta)]·0.25DIPEA + 2.10 H_2O + 0.05 EtOH in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-histidine in D_2O*. Red: L-histidine, cyan: L-histidinato in [Ga(Hhis)(nta)], blue: nta in [Ga(Hhis)(nta)], green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, yellow: residual EtOH, orange: MeOH. * One drop of MeOH was added for referencing.

While the $^{13}C\{^1H\}$ NMR spectrum of [Ga(Hhis)(nta)]·0.25DIPEA + 2.10 H_2O + 0.05 EtOH features two signal sets for each ligand and, therefore, shows the equilibrium found in the aqueous solutions of most $[Ga(aa)(nta)]^-$ complexes with polar and nonpolar aa ligands, the $^{13}C\{^1H\}$ NMR spectra of [Ga(Harg)(nta)]·0.05DIPEA + 2.45 H_2O (Figure 2.28) and [Ga(Hlys)(nta)]·0.05DIPEA + 2.25 H_2O + 0.15 EtOH (Figure 2.29) in aqueous solutions contain two signal sets of nta and three signal sets of the proteinogenic amino acid. Just as in the spectrum of [Ga(Hhis)(nta)] the two signal sets of nta and two signals sets of the amino acid can be attributed to the equilibrium of $[Ga(aa)(nta)]^-$ with the the respective AA and $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$. This leaves the third set of signals which must be attributed to an aa ligand.

Partial protonation of the basic functions in the side chain of the aa ligand can be ruled out as the cause of the third signal set since the signals of the side chain's carbon atoms are almost not affected. Instead, the signal shift of the carbon atoms 1 and 2 is significant

when these signals are compared to the signals of the respective atoms in the other signal sets of aa ligands. If protonation in the side chain was the cause of the third signals set, the most significant signal shift would be expected for the carbon atom C6.

Therefore, a different mode of complexation seems to be present. Despite L-arginine and L-lysine being potential tridentate ligands, only the κ*O*,*N*-configuration involving the amino group at C2 and the carboxylato function should form since every binding pattern involving the basic side chain would lead to the formation of at least seven-membered chelate rings in case of the L-arginato ligand or eight-membered chelate rings in the case of the L-lysinato ligand.

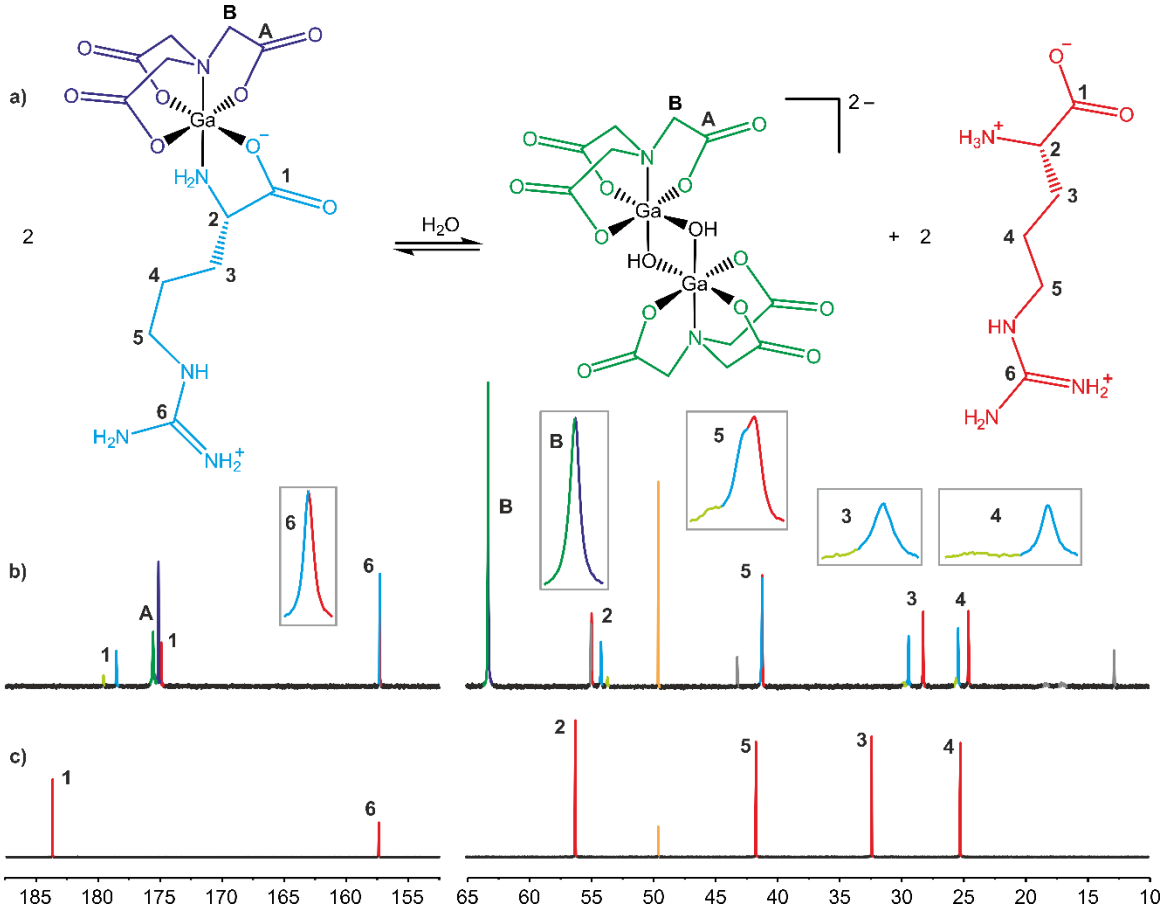


Figure 2.28: [Ga(Harg)(nta)]·0.05DIPEA + 2.45 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(Harg)(nta)]·0.05DIPEA + 2.45 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-arginine in D_2O*. Red: L-arginine, cyan: L-argininato in [Ga(Harg-κ*O*,*N*)(nta)] (**I**), light green: L-argininato in [Ga(Harg-κ*O*,*N*)(nta)] (**II**), blue: nta in [Ga(Harg-κ*O*,*N*)(nta)] (**I** and **II**), green: nta in in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

As mentioned before, the most significant signal shift is found in the atoms C1 and C2. Therefore—and due to the lack of a better explanation—the third signal set is attributed to constitutional isomers **II** (Figure 2.6). The aqueous solutions of [Ga(Harg)(nta)] and [Ga(Hlys)(nta)] should therefore be the only solutions which feature prominent signal sets

of both isomer **I** and **II**. Regrettably, it is not possible to explain why this isomerisation should be favoured when L-arginine or L-lysine are used as ligands.

In conclusion, the most likely interpretation of the two spectra seems to be that signals of both isomer **I** and **II** are visible. With regard to the other spectra of $[Ga(aa)(nta)]^-$ complexes, the signal sets with higher intensity are assigned to isomer **I** and the signal sets with lower intensity to isomer **II**. The signal shifts of the species and the CIS values of those complexes are listed in Table 2.11 and Table 2.12.

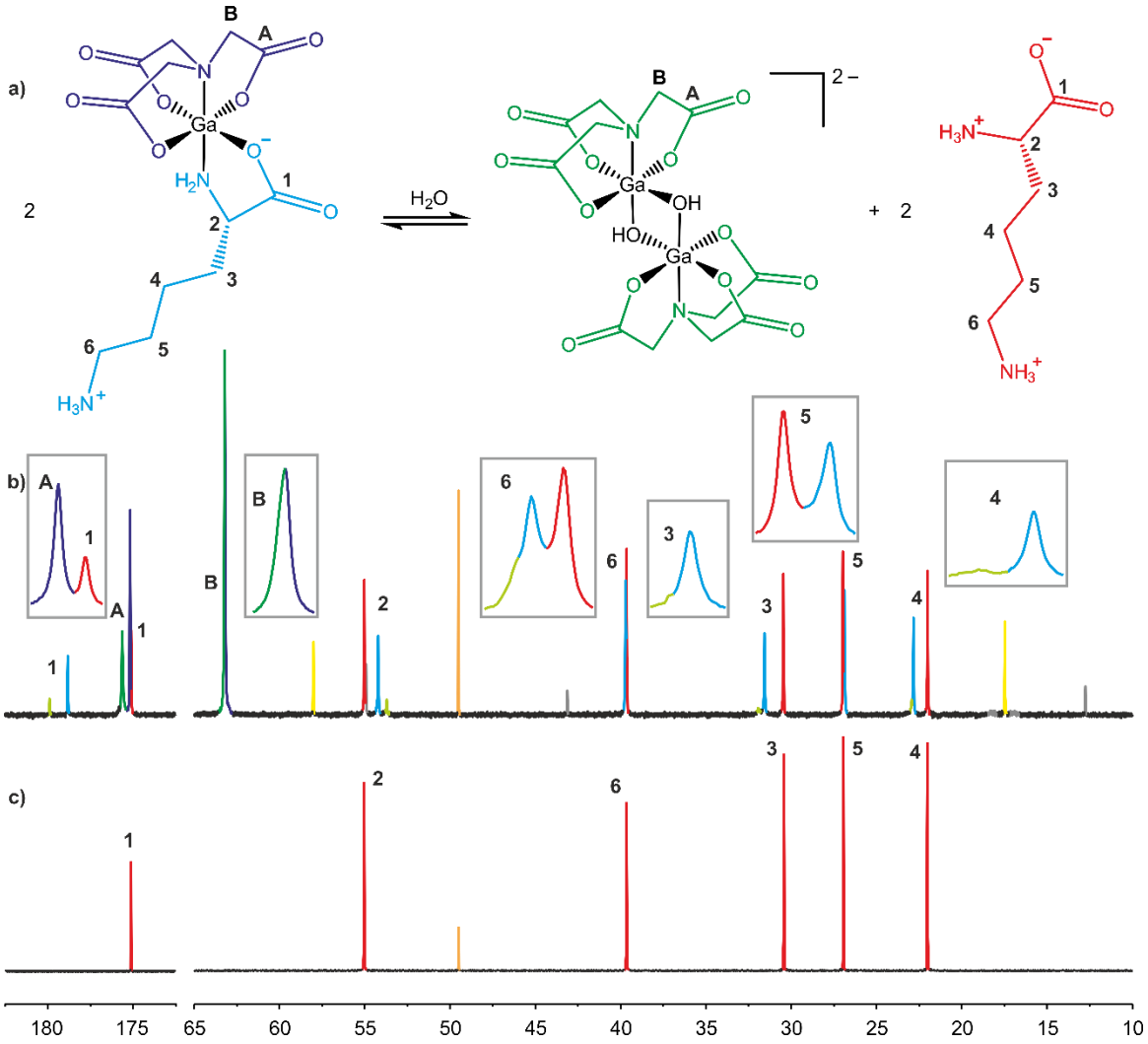


Figure 2.29: [Ga(Hlys)(nta)]·0.05DIPEA + 2.25 H_2O + 0.15 EtOH in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(Hlys)(nta)]·0.05DIPEA + 2.25 H_2O + 0.15 EtOH in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-lysine hydrochloride in D_2O*. Red: L-lysine, cyan: L-lysinato in [Ga(Hlys-κ*O,N*)(nta)] (**I**), light green: L-lysinato in [Ga(Hlys-κ*O,N*)(nta)] (**II**), blue: nta in [Ga(Hlys-κ*O,N*)(nta)] (**I** and **II**), green: nta in in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, yellow: residual EtOH, orange: MeOH. * One drop of MeOH was added for referencing.

Table 2.11: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-arginine and the L-argininato ligand in [Ga(Harg)(nta)] complexes. The relative shift is given in $\Delta\delta$ (CIS).

adduct			**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
DIPEA	[Ga(Harg-κ*O*,*N*)(nta)] (**I**)	δ	178.6	54.1	29.3	25.3	41.2	157.3
	L-Arginine	δ	174.9	54.9	28.2	24.5	41.1	157.3
		$\Delta\delta$	3.7	−0.8	1.1	0.8	0.1	0.0
DIPEA	[Ga(Harg-κ*O*,*N*)(nta)] (**II**)	δ	179.6	53.6	29.7	25.5	41.2	-
	L-Arginine	δ	174.9	54.9	28.2	24.5	41.1	157.3
		$\Delta\delta$	4.7	−1.3	1.5	1.0	0.1	-
NEt_3	[Ga(Harg-κ*O*,*N*)(nta)] (**I**)	δ	178.6	54.1	29.3	25.3	41.2	157.4
	L-Arginine	δ	174.9	54.9	28.2	24.5	41.1	157.4
		$\Delta\delta$	3.7	−0.8	1.1	0.8	0.1	0.0
NEt_3	[Ga(Harg-κ*O*,*N*)(nta)] (**II**)	δ	179.7	53.6	29.7	25.5	41.2	-
	L-Arginine	δ	174.9	54.9	28.2	24.5	41.1	157.3
		$\Delta\delta$	4.8	−1.3	1.5	1.0	0.1	-

Table 2.12: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-lysine and the L-lysinato ligand in [Ga(Hlys)(nta)] complexes. The relative shift is given in $\Delta\delta$ (CIS).

adduct			**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
DIPEA	[Ga(Hlys-κ*O*,*N*)(nta)] (**I**)	δ	178.8	54.2	31.6	22.8	26.9	39.7
	L-Lysine	δ	175.1	55.0	30.5	22.0	27.0	39.7
		$\Delta\delta$	3.7	−0.8	1.1	0.8	−0.1	0.0
DIPEA	[Ga(Hlys-κO,*N*)(nta)] (**II**)	δ	179.9	53.7	31.9	22.9	-	39.7
	L-Lysine	δ	175.1	55.0	30.5	22.0	27.0	39.7
		$\Delta\delta$	4.8	−1.3	1.4	0.9	-	0.0
NEt_3	[Ga(Hlys-κ*O*,*N*)(nta)] (**I**)	δ	178.9	54.2	31.6	22.8	26.9	39.7
	L-Lysine	δ	175.1	55.1	30.5	22.0	27.0	39.7
		$\Delta\delta$	3.8	−0.9	1.1	0.8	−0.1	0.0
NEt_3	[Ga(Hlys-κO,*N*)(nta)] (**II**)	δ	180.0	53.7	-	22.9	-	-
	L-Lysine	δ	175.1	55.1	30.5	22.0	27.0	39.7
		$\Delta\delta$	4.9	−1.4	-	0.9	-	-

2.2.9 Solution studies: complexes with acidic aa ligands

The elemental analyses of nitrilotriacetatogallium(III) complexes with acidic aa ligands suggested the formation of adducts between HDIPEA[Ga(Haa)(nta)]/$HNEt_3$[Ga(Haa)(nta)] complexes and non-integer amounts of the respective tertiary amine (Subsections 2.2.1 and 2.2.3).

As described before, the salts were not stable and the volatile tertiary amines were evolved even from the solid state which led to their description as adducts. This was accompanied by the protonation of the aa ligands' side chain and had to be considered in the analysis of NMR spectra. One direct consequence of this protonation was found in the pH level of aqueous solutions of these compounds. While almost every other aqueous $[Ga(aa)(nta)]^-$ complex solution (with exception of $[Ga(cys)(nta)]^-$ and $[Ga(trp)(nta)]^-$) was approximately neutral, solutions of $[Ga(Hasp)(nta)]^-$ and $[Ga(Hglu)(nta)]^-$ were acidic (pH 4.0, Table 2.13). In addition, or because of, the instability of the complex salts, no crystals of these compounds were obtained despite extensive efforts. Therefore, only elemental analysis and NMR spectroscopy are available for the characterisation of the complexes.

Table 2.13: pH values of solutions: $[Ga(Haa)(nta)]^-$ complexes with acidic aa ligands in D_2O.

aa ligand	$HDIPEA^+$/DIPEA	$HNEt_3^+/NEt_3$ (c = 0.25 mol L^{-1})
L-Aspartato	4.0	4.0
L-Glutamato	4.0	4.0

In the $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA + 0.10 $Ga(OH)_3$ (Figure 2.30b) two signal sets of nta and of the proteinogenic amino acid are visible. With the information gathered before, these signals and their pattern do indicate the existence of the known equilibrium reaction (Figure 2.30a) and can be assigned to $[Ga(Hasp)(nta)]^-$, $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ and aspartic acid. In the reaction scheme, isomer **I** but not isomer **II** is shown. Of course, with the data at hand, it is not possible to state if one or the other is present, it is just an assumption based on the experience with other $[Ga(aa)(nta)]^-$ complexes.

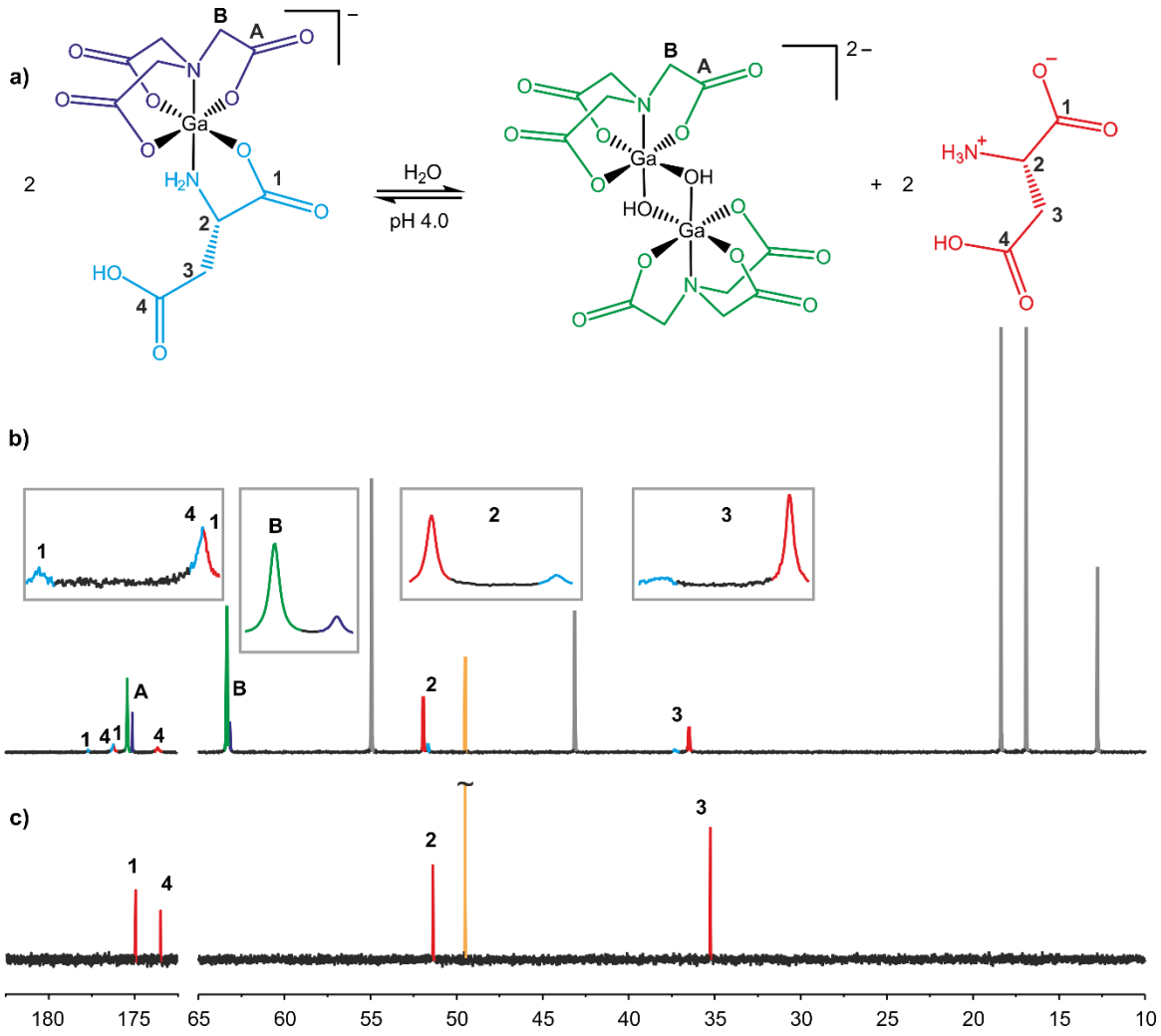


Figure 2.30: HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA + 0.10 $Ga(OH)_3$ in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA + 0.10 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-aspartic acid in D_2O*. Red: L-aspartic acid, cyan: L-aspartato in $[Ga(Hasp)(nta)]^-$, blue: nta in $[Ga(Hasp)(nta)]^-$, green: nta in in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, yellow: residual EtOH, orange: MeOH. * One drop of MeOH was added for referencing.

Table 2.14: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-aspartic acid and the L-aspartato ligand in $[Ga(Hasp)(nta)]^-$ complexes. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4
$HDIPEA^+$	$[Ga(Hasp)(nta)]^-$	δ	177.7	51.7	37.3	176.2
	L-Aspartic acid	δ	176.2	51.9	36.5	173.6
		$\Delta\delta$	1.5	-0.2	0.8	2.6
$HNEt_3^+$	$[Ga(Hasp)(nta)]^-$	δ	177.9	51.8	37.5	176.7
	L-Aspartic acid	δ	176.7	52.1	36.7	173.9
		$\Delta\delta$	1.2	-0.3	0.8	2.8

In fact, it is not even possible to rule out the existence of another [Ga(Hasp-κ*O,N*)(nta)]$^-$ complex which could be formed by creating a six-membered chelate ring with the amine function and the carboxylato function of C4. This is an issue only with the potential tridentate ligand aspartic acid, though, since glutamic acid would require the unlikely formation of a seven-membered chelate ring in such a case. The signals of the aspartato ligand are broadened, which might be due to the simultaneous presence of some or even all four potentially existent isomers of the [Ga(Hasp)(nta)]$^-$ complex, isomer **I** and **II** of both [Ga(Hasp-κ*O,N*)(nta)]$^-$ complexes. In addition, or perhaps instead of this explanation, the acidic pH of the solution could have also led to a broadening of the signals by causing fast protonation and deprotonation and/or an accelerated equilibrium reaction. To summarise, since the spectrum is not very informative, the [Ga(Hasp)(nta)]$^-$ complex or complex isomers in solution could not be characterised.

The $^{13}C\{^1H\}$ NMR spectra of HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA + 0.10 $Ga(OH)_3$ and HDIPEA[Ga(Hglu)(nta)]·0.05DIPEA + 0.30 H_2O + 0.05 $Ga(OH)_3$ (Section 6.1, Figure 6.3) are almost identical. Therefore, the same conclusions are drawn for [Ga(Hglu)(nta)]$^-$ with just one exception concerning the possible number of different complex isomers. As stated, glutamic acid should not allow for two different κ*O,N*-binding modes to gallium(III), therefore, only the isomers **I** and **II** of [Ga(Hglu)(nta)]$^-$ should potentially be formed. The signal shifts of the complexes [Ga(Hasp)(nta)]$^-$ and [Ga(Hglu)(nta)]$^-$ as well as the corresponding CIS values are displayed in Table 2.14 and in section 6.1, Table 6.3.

In conclusion, the NMR spectra of the two compounds did not allow in-depth interpretations of the composition in solution. This should be kept in mind when aspartato or glutamato ligands are present, and, in general, if aqueous solutions of different compounds are acidic. The overall behaviour of these two compounds might also suggest that a charge higher than −1 of the gallium(III) complex is avoided, if possible, for example when the charge is not directly located at a functional group bound to the metal centre. If this is true, the selection of potential ligands is limited to some extent.

2.2.10 Equilibria in solution: ratios of components

The ratios of compounds illustrated in Table 2.15 reveal some trends regarding the equilibrium reaction of different nitrilotriacetatogallium(III) complexes in aqueous solutions. Only the values of compounds containing triethylamine and/or triethylammonium ions are given, since fewer signal overlaps are present in ^{1}H NMR spectra of those when compared to ^{1}H NMR spectra of compounds containing *N*,*N*-diisopropylethylamine and/or *N*,*N*-diisopropylethyl-ammonium ions.

Table 2.15: Nitrilotriacetatogallium(III) complexes in D_2O: ratios of coordinated aa ligand and free AA in solutions (0.25 mol L^{-1}). The ratios are derived from the respective ^{1}H NMR spectra and are given in %. * Signal overlap, values may differ up to 5%, # Signal overlap, values may differ up to 10%.

	aa ligand [%]	free AA [%]
L-Alaninato/L-alanine	38	62
L-Argininato/L-arginine*	45	55
L-Asparaginato/L-asparagine	48	52
L-Aspartato/L-aspartic acid	27	73
L-Cysteinato/L-cysteine*	60	40
L-Glutaminato/L-glutamine	47	53
L-Glutamato/L-glutamic acid*	20	80
Glycinato/glycine	45	55
L-Histidinato/L-histidine#	50	50
L-Isoleucinato/L-isoleucine	44	56
L-Leucinato/L-leucine	49	51
L-Lysinato/L-lysine*	41	59
L-Methioninato/L-methionine	49	51
L-Phenylalaninato/L-phenylalanine	42	58
L-Prolinato/L-proline	46	54
L-Serinato/L-serine*	40	60
L-Threoninato/L-threonine	55	45
L-Tryptophanato/L-tryptophan*	42	58
L-Tyrosinato/L-tyrosine	0	100
L-Valinato/L-valine	44	56

While the values must be seen as not perfectly precise due to their derivation from ^{1}H NMR spectral data—the signals in ^{1}H NMR spectra are usually in very close proximity and signal-overlap is common—the overall magnitude can be used to examine some trends. Most of the solutions consisted of about 40–50 percent of $[Ga(aa)(nta)]^-$ complex, while the remaining amount of those complexes reacted with water by forming the respective free amino acid and the $[\{Ga(nta)(\mu\text{-}OH)\}_2]$ complex. Overall, the kind of aa ligand did not lead to a significant impact on the position of the equilibrium in most cases.

The most outstanding difference was found when the complex featured acidic aa ligands. As described before (Subsection 2.2.9), the amorphous solids containing those compounds were not stable and the aa ligand's side chains of these complexes were protonated once. This led to the compounds acidic reaction when solved in water (pH 4.0). A direct consequence was the substantial difference found in the position of the equilibria, with the ratio of $[Ga(Haa)(nta)]^-$ complex less than 30%. Since the deprotonation of the amino acid—especially of the ammonium group of the zwitterion—is key for the formation of $[Ga(Haa)(nta)]^-$, the overall low amount of this complex present in acidic solution was expected. In general, to support the formation of complexes with aa ligands, deprotonation of the carboxylic function and ammonium group is key.

Only two [Ga(aa)(nta)] complexes reached ratios of over 50% in 0.25 M solutions, $HNEt_3$[Ga(cys)(nta)] and $HNEt_3$[Ga(nta)(thr)]. This peculiarity was already discussed for $HNEt_3$[Ga(cys)(nta)] in subsection 2.2.7. Unfortunately, no complex of L-threonine was crystallisable, therefore potential intramolecular interactions or other stabilising characteristics of this specific complex could not be examined.

In general, the high amount of free amino acid in solution indicated that acidic proteinogenic amino acids—with the exception of L-tyrosin—were the least appropriate proteinogenic amino acids to form the target complexes. The differences between the other proteinogenic amino acids, with the exception of L-threonine and L-cysteine, were not very significant.

2.3 Ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes

The synthesis of heteroleptic gallium(III)-complexes with nta and aa ligands was successful, but did not fulfil every requirement that was set as a goal. The well-defined complexes with polar and nonpolar aa ligands are anionic, therefore cations were always present in the compounds. This led to the aforementioned problems, especially with crystallisation and, therefore, structural investigation of these complexes. Although this problem was largely prevented by the use of *N*,*N*-diisopropylethylammonium cations ($HDIPEA^+$) which did not lead to significant disorder in the crystal structures, the toxicity of *N*,*N*-diisopropylethylamine is not ideal.[43] In addition, nta is suspected to be carcinogenic.[45] None of these properties is desirable for potential pharmaceuticals if alternatives are available.

Concerning these issues, the formation of a neutral complex by replacing nta with a different, non-hazardous ligand could potentially solve both the problems with toxicity and crystallisation with just one ligand exchange. As the use of aminecarboxylato ligands was proven to be reasonable, another ligand of this type was chosen. Ethylenediamine-*N*,*N*′-diacetic acid (H_2edda), a tetradentate anionic ligand with two amine and two carboxylate functions should—in combination with polar and nonpolar proteinogenic amino acids—form neutral [Ga(aa)(edda)] complexes. In addition, edda is not classified as hazardous. Admittedly, this is due to the lack of toxicological data.

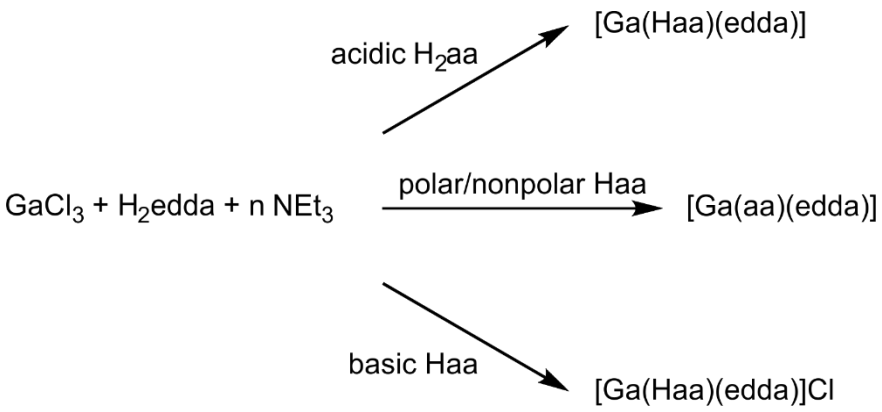


Figure 2.31: Reaction scheme for the synthesis of compounds with $Ga(edda)^+$ fragments and aa ligands. Water is used as a solvent and, depending on the AA used in the reaction, n is either 3.1, 3.5 or 4.5.

To obtain the target complexes, the procedure of synthesis for $HNEt_3$[Ga(aa)(nta)] complexes was adopted. Likewise, every AA was used as a potential ligand. This was done despite the target of forming neutral complexes for a better understanding of overall complex formation with all aa ligands. The starting materials $GaCl_3$, H_2edda and the

respective AA were used in a stoichiometric ratio of 1:1:1, while a slight excess of triethylamine was used to ensure that enough basic compound was present for the reaction (Figure 2.31). After precipitation and washing of the products with organic solvent the resulting crude products were first tested by elemental analysis.

According to the results of these analyses (Table 2.16), the target complexes were obtained with every polar and nonpolar AA except L-tyrosine. This outcome was consistent with the experiences gained with nitrilotriacetatogallium(III) complexes.

Table 2.16: Interpretation of elemental analyses: [Ga(aa)(edda)] complexes with polar or nonpolar aa ligands. The maximum difference (max. diff) is given between the found and calculated percentages of the listed compositions.

complex salt	contamination	max. diff.
[Ga(ala)(edda)]	0.20 H_2O	0.08
[Ga(asn)(edda)]	0.15 H_2O	0.16
[Ga(cys)(edda)]	1.05 H_2O + 0.10 $HNEt_3Cl$	0.11
[Ga(edda)(gln)]	0.80 H_2O + 0.05 $HNEt_3Cl$	0.19
[Ga(edda)(gly)]	1.40 H_2O + 0.10 $Ga(OH)_3$	0.02
[Ga(edda)(ile)]	0.80 H_2O + 0.05 $HNEt_3Cl$	0.10
[Ga(edda)(leu)]	1.50 H_2O	0.05
[Ga(edda)(met)]	0.55 H_2O + 0.15 $Ga(OH)_3$	0.08
[Ga(edda)(phe)]	1.05 H_2O	0.04
[Ga(edda)(pro)]	0.10 H_2O	0.11
[Ga(edda)(ser)]	1.55 H_2O + 0.10 $Ga(OH)_3$	0.05
[Ga(edda)(thr)]	1.75 H_2O	0.19
[Ga(edda)(trp)]	1.50 H_2O	0.06
-	tyrH + 0.05 H_2O	0.10
[Ga(edda)(val)]	0.50 H_2O	0.08

As expected, the main difference was found between the [Ga(aa)(edda)] complexes formed with polar and nonpolar aa ligands and the complexes formed with acidic and basic aa ligands. The elemental analyses of [Ga(Haa)(edda)] complexes (Table 2.17) with acidic aa ligands indicate the formation of triethylamine adducts. This had been the case with the respective nitrilotriacetatogallate(III) complexes as well and was therefore expected. Of course, nta is a trianionic ligand while edda is dianionic, therefore the resulting complexes are neutral.

Table 2.17: Interpretation of elemental analyses: ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes with acidic or basic aa ligands. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex salt	contamination	max. diff.
[Ga(Harg)(edda)]Cl	2.00 H_2O + 0.05 $HNEt_3Cl$	0.09
[Ga(Hasp)(edda)]·0.30NEt_3	1.30 H_2O	0.07
[Ga(edda)(Hglu)]·0.15NEt_3	1.25 H_2O	0.07
[Ga(edda)(Hhis)]Cl	0.10 H_2O + 0.05 $HNEt_3Cl$	0.13
[Ga(edda)(Hlys)]Cl	0.60 H_2O	0.10

According to experiences with nta, the basic aa ligands of edda complexes should feature protonated side chains in the isolated amorphous solids. The complexes would therefore be cationic which is, indeed, shown by the elemental analyses (Table 2.17). The [Ga(Haa)(edda)]Cl complexes feature full protonation of the basic side chain. These compounds might also be described as well-defined hydrochlorides, but, as they are stable at room temperature and do not release hydrogen chloride, it seems reasonable to not label them as hydrochloride adducts.

The obtained raw products were not pure. Water, sometimes gallium(III) hydroxide or low amounts of triethylammonium chloride were present in the crude products. The first two compounds were regularly found in raw products of nitrilotriacetato complexes as well. Water proved to be difficult to remove due to the hygroscopic nature of the compounds. The contamination of some products with $Ga(OH)_3$ may have been due to incomplete complex formation or may have originated in flawed stoichiometric amounts of starting material. In five cases—due to the similar solubilities of triethylammonium chloride and the target complexes—the complete removal of triethylammonium chloride was not possible despite several attempts. This could have been avoided by the use of *N*,*N*-diisopropylethylamine instead of triethylamine since *N*,*N*-diisopropylethylammonium chloride proved to be more soluble in organic solvents than triethylammonium chloride. However, none of the contaminants were problematic when it comes to crystallisation experiments or further analytical examinations. This statement may seem odd because triethylammonium chloride is a readily crystallising compound. Still, with such low amounts present and its good solubility in many solvents it should not crystallise before the target complex.

2.3.1 Structural investigations of [Ga(aa)(edda)] complexes

Crystallisation experiments with the raw products presented in section 2.3 yielded crystals which were suitable for X-ray diffraction experiments in a few cases. Six of the thereby obtained crystal structures displayed in Figure 2.32–Figure 2.33 and Figure 2.34—Figure 2.41 are of adequate quality and show the formation of the target complexes [Ga(aa)(edda)]. In contrast to the successful crystallisation experiments of $[Ga(aa)(nta)]^-$ salts, the crystals of [Ga(aa)(edda)] compounds were obtained only from aqueous solutions. All crystals were grown from neutral solutions, except the crystals of [Ga(edda)(phe)] which were obtained from a basic (pH 9.5) solution. Unfortunately, while further crystals of different [Ga(aa)(edda)] complexes were yielded, those did not allow for reasonable structure solutions. For example, the L-tryptophanato ligand in crystals of [Ga(trp)(edda)] was heavily disordered which prevented a structural solution of sufficient quality.

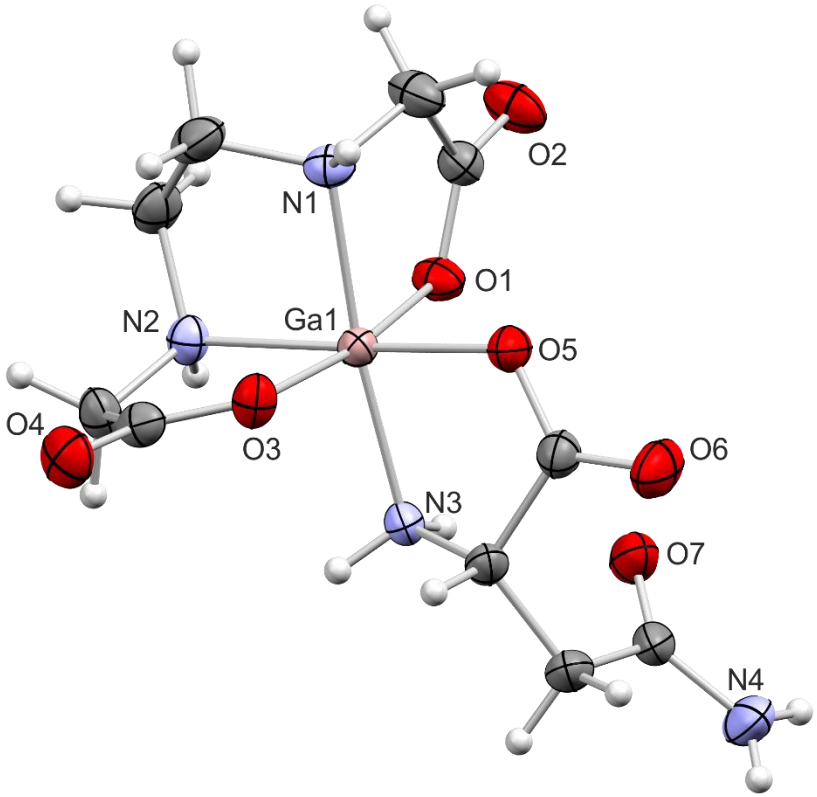


Figure 2.32: Plot of [Ga(asn)(edda)] in crystals of **3a**·2H$_2$O. Space group: $P2_1$. CShM$_{OC-6}$: 0.533. The thermal ellipsoids are drawn at 50% probability (room temperature data collection). Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.044(4), Ga1–N2 2.084(3), Ga1–N3 2.030(3), Ga1–O1 2.002(3), Ga1–O3 1.985(3), Ga1–O5 1.938(2), N1–Ga1–N3 174.16(15), N2–Ga1–O5 175.76(11), O1–Ga1–O3 171.07(13), N2–Ga1–N3 99.34(13), N2–Ga1–O3 82.03(13), N3–Ga1–O1 94.07(12), N3–Ga1–O3 91.34(16), N3–Ga1–O5 83.42(12).

As shown, the gallium(III) ion in the [Ga(asn)(edda)], [Ga(edda)(gly)], [Ga(edda)(leu)], [Ga(edda)(pro)], [Ga(edda)(phe)] and [Ga(edda)(thr)] complexes features an octahedral GaN_3O_3 environment. The octahedral coordination is slightly distorted in every case, which is illustrated by the $CShM_{OC-6}$ values and consistent with the observed interatomic distances and angles between gallium(III) and the N/O atoms of the ligands. These distortions are due to the formation of five-membered chelate rings and were, therefore, anticipated. The interatomic distances of Ga–N bonds are slightly longer as Ga–O bonds and are in the expected range.

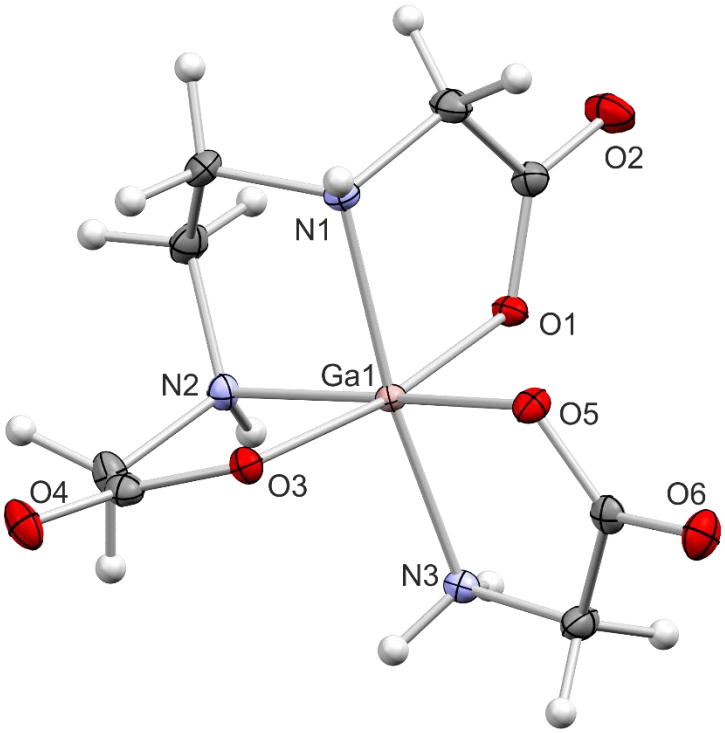


Figure 2.33: Plot of [Ga(edda)(gly)] in crystals of **3b**·2H₂O. Space group: *P*2₁/*c*. $CShM_{OC-6}$: 0.541. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0621(17), Ga1–N2 2.0854(17), Ga1–N3 2.0142(17), Ga1–O1 1.9746(14), Ga1–O3 1.9990(14), Ga1–O5 1.9548(14), N1–Ga1–N3 172.53(7), N2–Ga1–O5 173.14(6), O1–Ga1–O3 170.80(6), N2–Ga1–N3 97.28(7), N2–Ga1–O3 82.47(6), N3–Ga1–O1 90.49(6), N3–Ga1–O3 96.06(7), N3–Ga1–O5 85.01(6).

Only crystals of [Ga(aa)(edda)] complexes with polar or nonpolar aa ligands were obtained. This was also true for the $[Ga(aa)(nta)]^-$ complexes presented in this work and thus not surprising. In contrast to $[Ga(aa)(nta)]^-$ complexes, an octahedral gallium(III) complex with the tetradentate chainlike ligand edda and a bidentate aa ligand enables the formation of six different constitutional isomers of [Ga(aa)(edda)] (Figure 2.35) instead of only two isomers. Of those six possible [Ga(aa)(edda)] isomers only two (isomer **III** and **V**) feature a facial coordination of the nitrogen and oxygen atoms. Despite this variety of

possible constitutional isomers, only the isomers **I** and **VI** are found in crystal structures of the [Ga(aa)(edda)] complexes. In crystals of [Ga(asn)(edda)], [Ga(edda)(gly)] and [Ga(edda)(pro)] only isomer **I** is present, while crystals of [Ga(edda)(leu)] and [Ga(edda)(phe)] feature both isomers **I** and **VI** and crystals of [Ga(edda)(thr)] only contain isomer **VI**. These two isomers are mirror images of each other if the aa ligand is not chiral. It is reasonable to assume that their formation and crystallisation is preferred due to less strain in the molecule, as in every other isomer one nitrogen atom of edda is forced to bind with non-ideal angles to its neighbouring atoms (Figure 2.35, isomers **II**–**IV**, axial position).

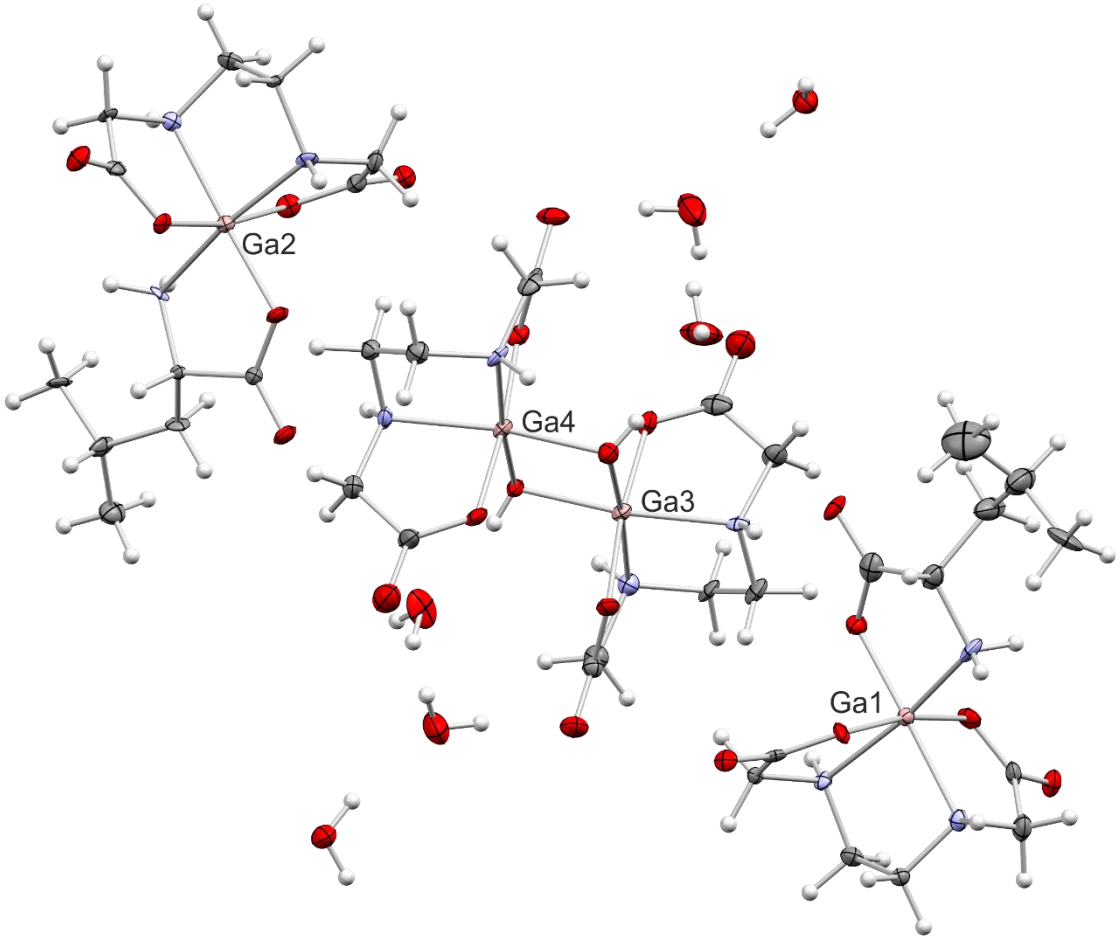


Figure 2.34: Plot of the asymmetric unit of $[Ga(edda)(leu)]_2 \cdot [\{Ga(edda)(\mu\text{-}OH)\}_2] \cdot 6H_2O$ in crystals of **3c**·**3d**·**3i**·$6H_2O$. Space group: *P*1. The thermal ellipsoids are drawn at 50% probability.

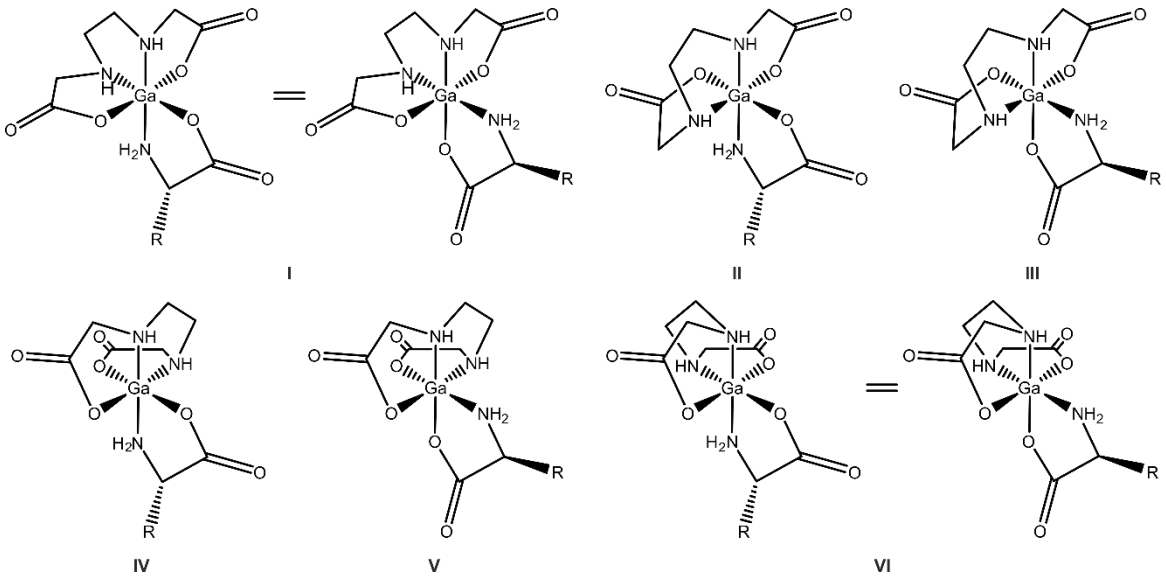


Figure 2.35: The six possible [Ga(aa)(edda)] complex isomers. R is the side chain of the respective AA used for complex formation.

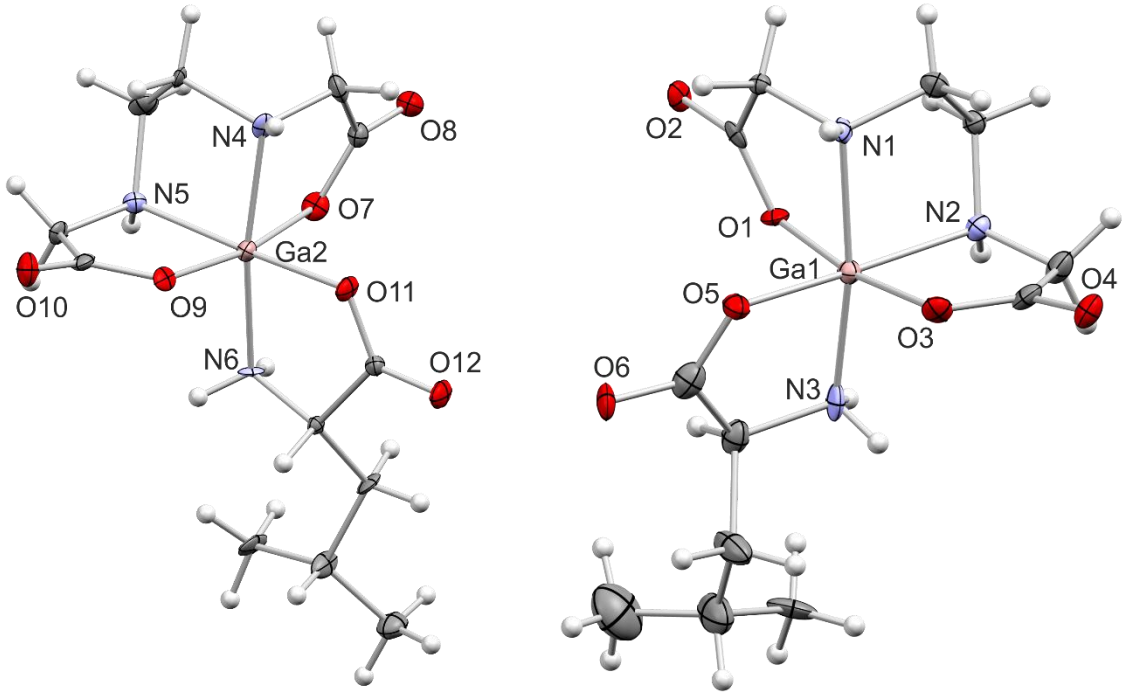


Figure 2.36: Plot of the two isomers of [Ga(edda)(leu)] in crystals of **3c**·**3d**·**3i**·6H_2O. $CShM_{OC-6}$: Ga1 0.631, Ga2 0.677. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.091(11), Ga1–N2 2.101(11), Ga1–N3 1.988(12), Ga1–O1 1.991(8), Ga1–O3 1.957(8), Ga1–O5 1.931(9), Ga2–N4 2.055(11), Ga2–N5 2.099(11), Ga2–N6 2.048(10), Ga2–O7 1.972(8), Ga2–O9 1.979(8), Ga2–O11 1.933(9), N1–Ga1–N3 170.6(4), N2–Ga1–O5 173.9(4), O1–Ga1–O3 170.8(4), N2–Ga1–N3 100.0(4), N1–Ga1–O5 91.2(4), N2–Ga1–O3 81.9(4), N3–Ga1–O1 89.3(4), N3–Ga1–O3 96.6(4), N3–Ga1–O5 84.5(4), N4–Ga2–N6 169.4(4), N5–Ga2–O11 174.7(4), O7–Ga2–O9 170.4(4), N5–Ga2–N6 99.7(4), N4–Ga2–O11 90.9(4), N4–Ga2–O7 81.7(4), N6–Ga2–O7 88.9(4), N6–Ga2–O9 97.2(4), N6–Ga2–O11 84.8(4).

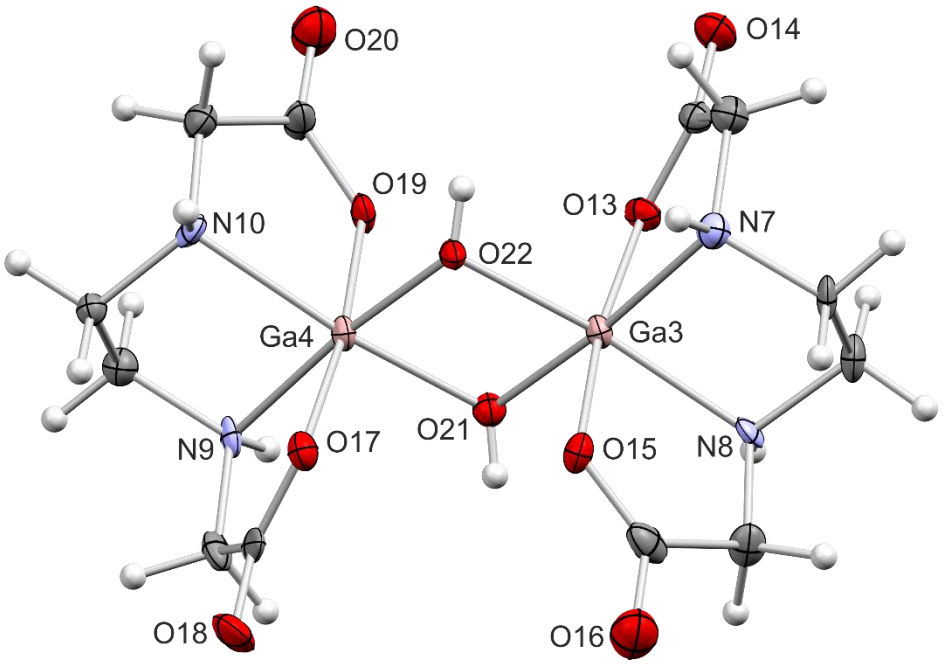


Figure 2.37: Plot of [{Ga(edda)(μ-OH)}$_2$] in crystals of **3c**·**3d**·**3i**·6H$_2$O. CShM$_{OC-6}$: Ga3 0.718, Ga4 0.737. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga3–N7 2.075(10), Ga3–N8 2.087(10), Ga3–O13 1.973(9), Ga3–O15 1.992(9), Ga3–O21 1.942(9), Ga3–O22 1.961(9), Ga4–N9 2.096(10), Ga4–N10 2.113(10), Ga4–O17 1.966(9), Ga4–O19 1.972(9), Ga4–O21 1.949(9), Ga4–O22 1.941(9), N7–Ga3–O21 173.6(4), N8–Ga3–O22 171.5(4), O13–Ga3–O15 172.2(3), N7–Ga3–N8 84.4(4), N8–Ga3–O21 98.7(4), N7–Ga3–O22 96.3(4), N7–Ga3–O33 82.3(4), N7–Ga3–O15 92.7(4), O21–Ga3–O22 81.4(3), N9–Ga4–O22 173.3(4), N10–Ga4–O21 170.9(4), O17–Ga4–O19 172.9(3), N9–Ga4–N10 85.1(4), N9–Ga4–N10 85.1(4), N9–Ga4–O21 95.4(4), N10–Ga4–O17 92.8(4), N10–Ga4–O19 81.3(4), N10–Ga4–O22 98.7(4).

The structures of [Ga(edda)(leu)]$_2$·[{Ga(edda)(μ-OH)}$_2$]·6H$_2$O and 2[Ga(edda)(phe)]·3H$_2$O are only of mediocre quality. Some of the atoms in those needed to be solved partially anisotropic. However, the molecular structures are not shown just to amass more crystal structures of edda complexes. Both feature molecular structures which are of interest due to their characteristics.

As illustrated in Figure 2.36 and Figure 2.39, the crystals of [Ga(edda)(leu)]$_2$·[{Ga(edda)(μ-OH)}$_2$]·6H$_2$O (Figure 2.34) and [Ga(edda)(phe)] each feature two isomers of the respective complex. In addition, [Ga(edda)(leu)]$_2$·[{Ga(edda)(μ-OH)}$_2$]·6H$_2$O contains a third complex, [{Ga(edda)(μ-OH)}$_2$] (Figure 2.37). This complex resembles the [{Ga(nta)(μ-OH)}$_2$]$^{2-}$ complex which is described in sections 1.4 and 2.2. It seems that gallium(III) has a tendency to form amincarboxylatogallium(III) complexes with bridging hydroxido ligands at neutral pH levels.

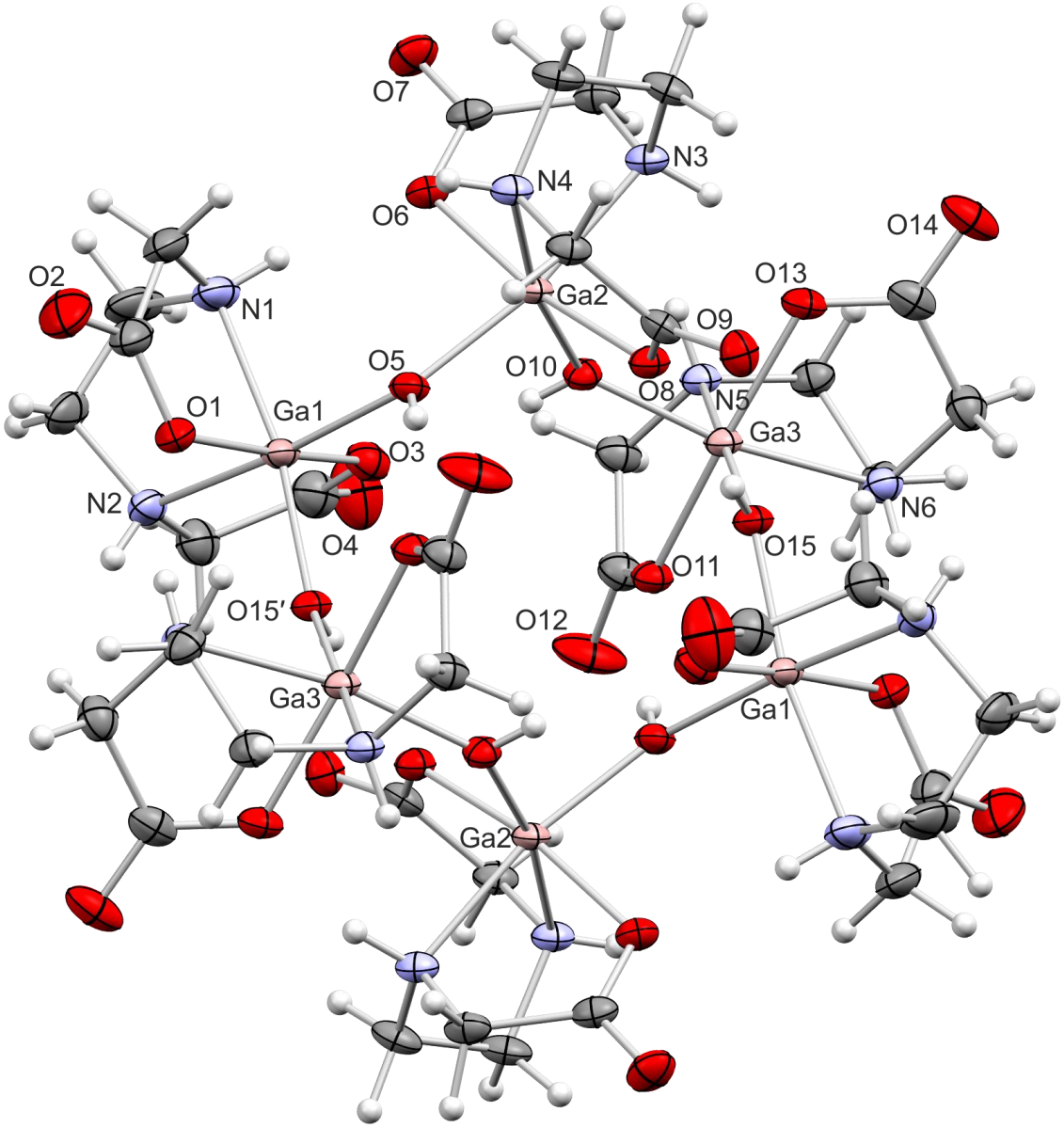


Figure 2.38: Plot of [{Ga(edda)(μ-OH)}$_6$] in crystals of **3j**·xH_2O. Space group: $I4_1/a$. $CShM_{OC-6}$: Ga1 0.443, Ga2 0.422, Ga3 0.422. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.107(3), Ga1–N2 2.118(3), Ga1–O3 1.968(3), Ga1–O5 1.946(2), Ga1–O15′ 1.927(2), Ga2–N3 2.117(3), Ga2–N4 2.115(3), Ga2–O5 1.930(2), Ga2–O6 1.987(2), Ga2–O8 1.964(2), Ga2–O10 1.945(2), Ga3–N5 2.138(3), Ga3–N6 2.102(3), Ga3–O10 1.947(2), Ga3–O11 1.973(2), Ga3–O13 1.972(2), Ga3–O15 1.936(2), N1–Ga1–O15′ 169.23(13), N2–Ga1–O5 170.35(12), O1–Ga1–O3 171.55(10), N1–Ga1–O1 81.57(13), N1–Ga1–O5 91.92(11), O1–Ga1–O5 95.04(10), O3–Ga1–O5 90.37(10), O3–Ga1–O15′ 96.29(10), O5–Ga1–O15′ 95.13(10), N3–Ga2–O5 169.35(11), N4–Ga2–O10 169.74(11), O6–Ga2–O8 170.01(9), N3–Ga2–O6 81.21(10), N3–Ga2–O10 89.28(10), O5–Ga2–O8 97.47(10), O5–Ga2–O10 96.75(10), O6–Ga2–O10 94.58(10), O8–Ga2–O10 91.67(10), N5–Ga3–O15 170.63(10), N6–Ga3–O10 169.63(11), O11–Ga3–O13 171.47(10), N5–Ga3–O11 81.84(10), N6–Ga3–O15 91.48(11), O10–Ga3–O11 95.39(10), O10–Ga3–O15 95.20(10), O11–Ga3–O15 91.69(9), O13–Ga3–O15 94.92(10).

This trend was emphasised by the crystal structure of [{Ga(edda)(μ-OH)}$_6$] (Figure 2.38). Characteristic tetragonal crystals of this complex were frequently obtained, sometimes even in combination with crystals of [Ga(aa)(edda)] complexes or free AA.

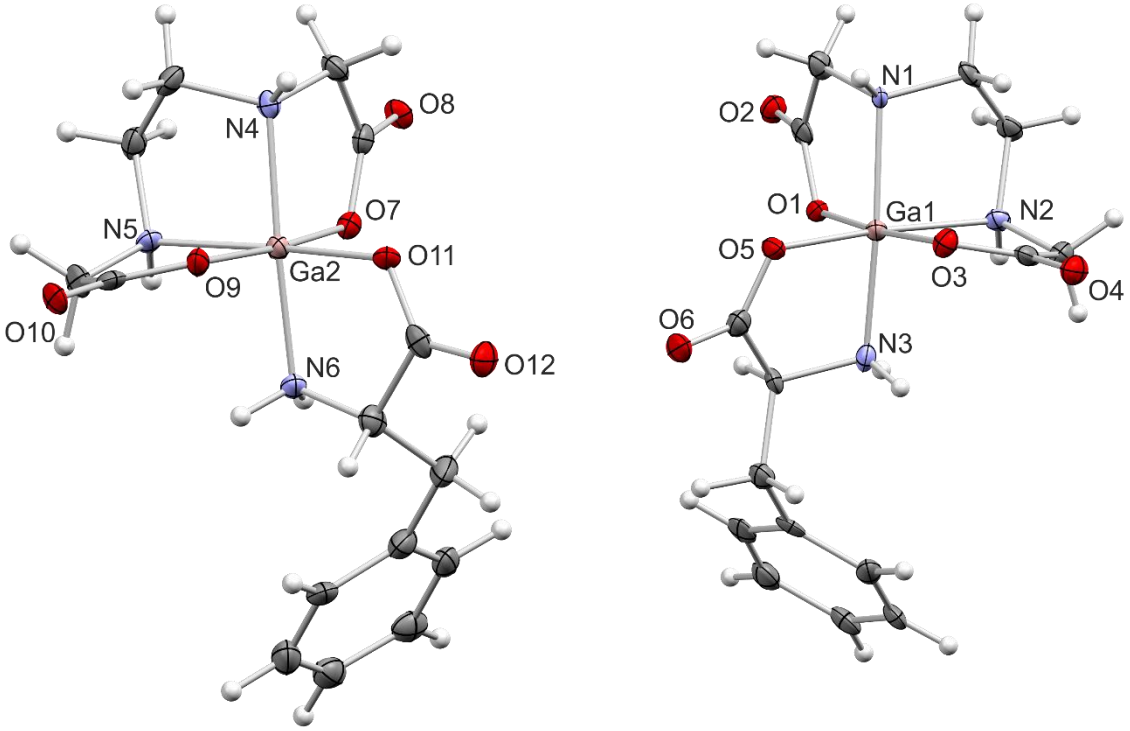


Figure 2.39: Plot of the two isomers of [Ga(edda)(phe)] in crystals of **3e**·**3f**·3H$_2$O. Space group: *P*2$_1$. CShM$_{OC-6}$: Ga1 0.708, Ga2 0.544. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.071(7), Ga1–N2 2.096(8), Ga1–N3 2.019(7), Ga1–O1 1.968(6), Ga1–O3 1.973(6), Ga1–O5 1.975(6), Ga2–N4 2.062(7), Ga2–N5 2.092(8), Ga2–N6 2.026(7), Ga2–O7 1.962(6), Ga2–O9 1.977(6), Ga2–O11 1.948(6), N1–Ga1–N3 171.4(3), N2–Ga1–O5 170.0(3), O1–Ga1–O3 173.9(3), N2–Ga1–N3 94.4(3), N1–Ga1–O5 98.3(3), N2–Ga1–O3 81.8(3), N3–Ga1–O1 87.8(3), N3–Ga1–O3 95.5(3), N3–Ga1–O5 83.8(3), N4–Ga2–N6 173.8(3), N5–Ga2–O11 171.0(3), O7–Ga2–O9 175.0(3), N5–Ga2–N6 94.8(3), N4–Ga2–O11 96.5(3), N5–Ga2–O9 81.9(3), N6–Ga2–O7 89.8(3), N6–Ga2–O9 93.5(3), N6–Ga2–O11 84.6(3).

While the molecular structure of [{Ga(edda)(μ-OH)}$_6$] is easy to determine, the full structure solution was prevented by disordered water molecules in combination with the large cell. This was the case despite several attempts and data collections. Hence, the compound is described as [{Ga(edda)(μ-OH)}$_6$]·xH_2O. Since the molecular structure of [{Ga(edda)(μ-OH)}$_6$] was resolvable, a few characteristics can still be described. The octahedral coordination spheres of the GaN_2O_4 surroundings are slightly distorted, which is illustrated by the CShM$_{OC-6}$ values and consistent with the observed interatomic distances and angles between gallium(III) and the nitrogen and oxygen atoms of the ligands. The gallium(III) centres are connected by hydroxido ligands, forming the ring-like structure. Those

hydroxido-ligands are bound to gallium(III) in neighbouring positions. Also, edda is coordinated to gallium(III) in a C_2-symmetric fashion, a characteristic found in every molecular structure of complexes featuring $Ga(edda)^+$ fragments. Also, the surrounding of gallium(III) in [{Ga(edda)(μ-OH)}$_2$] and [{Ga(edda)(μ-OH)}$_6$] is similar.

The direct synthesis of [{Ga(edda)(μ-OH)}$_6$] was possible, too. However, crystals obtained by this method were of poor quality. This complex seems to require a very slow growth rate to form well-defined crystals, which seems to be provided more easily when they are obtained as a side product. This makes sense if the compound is present only in small amounts due to an equilibrium reaction in water or if it evolves slowly over time due to degradation of other complexes in solution.

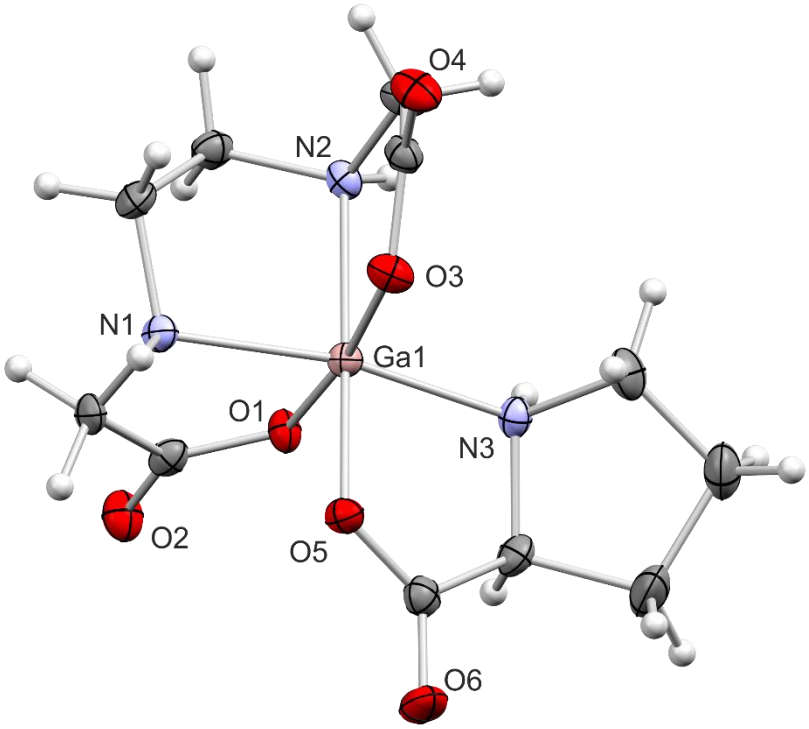


Figure 2.40: Plot of [Ga(edda)(pro)] in crystals of **3g**·3H$_2$O. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.906. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.058(2), Ga1–N2 2.101(2), Ga1–N3 2.031(2), Ga1–O1 1.988(2), Ga1–O3 1.960(2), Ga1–O5 1.956(2), N1–Ga1–N3 167.29(9), N2–Ga1–O5 171.42(8), O1–Ga1–O3 173.00(8), N2–Ga1–N3 100.72(10), N1–Ga1–O1 82.31(8), N3–Ga1–O1 86.40(9), N3–Ga1–O3 99.05(9), N3–Ga1–O5 83.13(9).

In addition, sometimes only crystals of the respective AA were obtained. Again, just as with the nitrilotriacetatogallium(III) complexes, these findings imply the presence of an equilibrium reaction between different compounds in solution. The molecular structure of [Ga(edda)(leu)]$_2$·[{Ga(edda)(μ-OH)}$_2$]·6H$_2$O even shows three complexes which might be components of such an equilibrium. Of course, the complete decomposition of

[Ga(aa)(edda)] complexes in aqueous solution could not be ruled out as a potential cause for the formation of hydroxido-bridged complexes without performing solution studies.

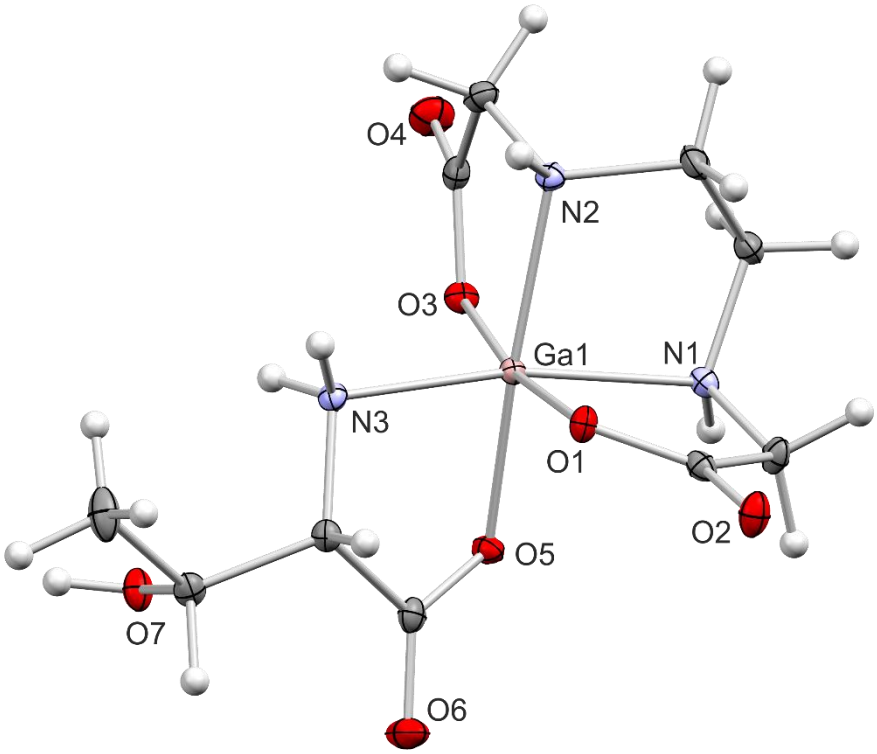


Figure 2.41: Plot of [Ga(edda)(thr)] in the crystals of **3h**·2H_2O. Space group: $P2_1$. $CShM_{OC-6}$: 0.828. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.060(2), Ga1–N2 2.096(2), Ga1–N3 2.024(2), Ga1–O1 2.006(2), Ga1–O3 1.967(2), Ga1–O5 1.950(2), N1–Ga1–N3 167.46(9), N2–Ga1–O5 173.63(7), O1–Ga1–O3 171.28(7), N2–Ga1–N3 102.66(9), N2–Ga1–O3 82.14(7), N3–Ga1–O1 88.11(7), N3–Ga1–O3 97.75(7), N3–Ga1–O5 82.61(9).

2.3.2 Solution studies of [Ga(aa)(edda)] complexes

As described in subsection 2.3.1, different complexes, complex isomers and sometimes only the respective AA were crystallised from solutions containing [Ga(aa)(edda)] complexes. Crystals of $[Ga(edda)(leu)]_2 \cdot [\{Ga(edda)(\mu\text{-}OH)\}_2] \cdot 6H_2O$ even demonstrated that two different complexes exist at the same time, potentially in an equilibrium reaction.

The sheer number of potential [Ga(aa)(edda)] complex isomers (Figure 2.35), hydroxido bridged complexes and free AA that might exist in an equilibrium should result in a large number of signals in both $^{13}C\{^1H\}$ NMR and ^1H NMR spectra. A first look at the $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(thr)] + 1.75 H_2O in D_2O (Figure 2.42b) confirms this assumption. Despite the overall chaotic appearance of the spectrum, it was possible to assign most of the signals to specific carbon atoms with the help of 2D NMR techniques and by comparison with the respective spectra of $[Ga(nta)(thr)]^-$ complex solutions. In general, the NMR-spectroscopic studies presented in subsections 2.2.6–2.2.10 were an important source of information for the interpretation of the spectra of ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes (Subsections 2.3.2–2.3.6).

First of all, the most uncommon feature of the $^{13}C\{^1H\}$ NMR spectrum (Figure 2.42b) needs to be addressed. The signals of edda resemble clusters of more or less broadened individual signals. While these signals are not assignable to a certain carbon atom, complex or complex isomer, these signal clusters indicate that the ligand is bound to gallium(III) in various ways. This supports the assumed presence of an equilibrium in aqueous solution (Figure 2.42a).

Altogether, up to five different signals sets can be assigned to L-threonine. The signal set with the highest intensity has to be assigned to free L-threonine. This can be verified by comparison with a $^{13}C\{^1H\}$ NMR spectrum of L-threonine in D_2O (Figure 2.42d) and by addition of L-threonine to a solution of [Ga(edda)(thr)] + 1.75 H_2O in D_2O which leads to a more significant increase of the intensity of this particular signal set than any other signal set (Figure 2.42c). Every other signal set not assigned at this point has to be assigned to L-threoninato ligands which indicates the existence of at least four out of six different [Ga(edda)(thr)] complex isomers (Figure 2.35) in solution. Since not every signal of the L-threoninato ligands is sharp, even more [Ga(edda)(thr)] complex isomers might exist in solution with their signal sets indistinguishable from the other signals. This is a common characteristic of the spectra of [Ga(aa)(edda)] complexes.

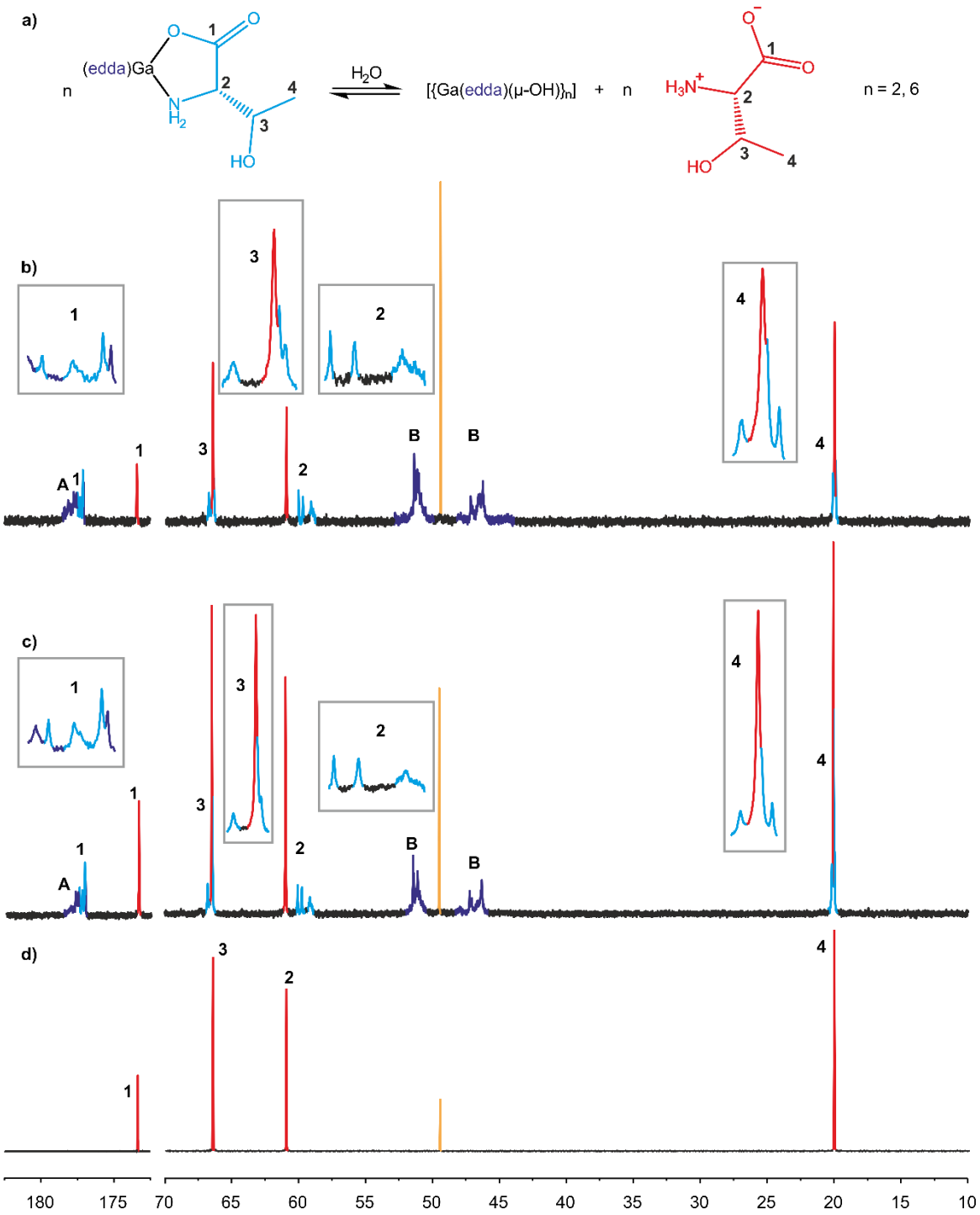


Figure 2.42: [Ga(edda)(thr)] + 1.75 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(thr)] + 1.75 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(thr)]+ 1.75 H_2O with 1.0 equ. of L-threonine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-threonine in D_2O*. Red: L-threonine, cyan: L-threoninato in [Ga(edda)(thr)], blue (**A** and **B**): edda in [Ga(edda)(thr)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

In addition, the concentration of complex isomers might just have been too low to be detected. Unfortunately, increasing the overall concentration of the solution was not feasible to deal with this issue. Although almost all [Ga(aa)(edda)] complexes are soluble in water, their solubility is generally lower when compared to the respective $[Ga(aa)(nta)]^-$ complexes. The [Ga(aa)(edda)] solutions used for the measurement of NMR spectra in this work were often already saturated. In fact, the concentration of the $HNEt_3$[Ga(aa)(nta)] solutions used for NMR spectroscopy was determined by the highest possible concentration reachable with [Ga(aa)(edda)] complexes to allow for some comparability.

The existence of the assumed equilibrium (Figure 2.42a) in solution was proven by the aforementioned addition of free L-threonine to the complex solution. This not only had an impact on the intensity of the signals of free L-threonine, but also led to an increase of the intensity of signals corresponding to L-threoninato ligands. In fact, it was possible to get the ratio of L-threoninato ligands to free L-threonine with the information derived from the ^{1}H NMR spectra. In a 0.25 M solution of [Ga(edda)(thr)] + 1.75 H_2O in D_2O 48% of L-threoninato ligands and 52% free L-threonine are present. After addition of one equivalent of free L-threonine, the ratio of bound L-threonine almost doubled. The equilibrium had shifted and about 90% of edda is now bound in [Ga(edda)(thr)] complexes and only 10% in [{Ga(edda)(μ-OH)}$_n$] complexes. The impact of L-threonine addition on the signals of edda in the ^{13}C{^{1}H} NMR spectrum is not as prominent, but the signal clusters are less broadened and in general fewer signals of edda are found. This was expected, as almost no edda should be bound in [{Ga(edda)(μ-OH)}$_n$] complexes at this point, which in turn reduces the variety of possible chemical environments of edda. When comparing the “vanished” signals of this solution with an aqueous solution of directly synthesised [{Ga(edda)(μ-OH)}$_n$] complexes it was further proven that these signals indeed belong to [{Ga(edda)(μ-OH)}$_n$] complexes. Unfortunately, the solubility of dry [Ga(aa)(edda)] complexes in dry MeOD is quite poor. Therefore it was not possible to conclusively prove this point by preventing the formation of [{Ga(edda)(μ-OH)}$_n$] complexes in methanolic solution and then assigning the missing signals to the [{Ga(edda)(μ-OH)}$_n$] complexes by NMR spectroscopy.

In general, the findings supported the assumed existence of an equilibrium reaction between the [Ga(thr)(edda)] complexes on the one side and [{Ga(edda)(μ-OH)}$_n$] complexes and free L-threonine on the other and were, therefore. consistent with the results of solution studies with $[Ga(aa)(nta)]^-$ complexes. As stated, an assignment of signals to specific complex isomers was not possible. Therefore, in contrast to the nta complexes, no CIS values are reported for edda complexes.

NMR-spectroscopic analyses of most [Ga(aa)(edda)] complexes with polar and nonpolar aa ligands showed similar results and proved the existence of the equilibrium (Figure 6.14, Figure 6.15, Figure 6.17, Figure 6.19, Figure 6.20, Figure 6.22—Figure 6.24, Figure 6.26) at neutral pH levels (Table 2.18). In two cases the equilibrium was verified by addition of free AA and re-measuring the spectra (Figure 6.17 and Figure 6.23). However, there were exceptions: the solubility of [Ga(cys)(edda)] in water is too low, hence no NMR-spectroscopic analysis was feasible. In addition, [Ga(edda)(gln)], [Ga(edda)(phe)] and [Ga(edda)(trp)] are only soluble in water at basic pH levels. This posed a problem since changes in the pH value have a significant effect on the composition of the solution. Hence, the spectra of these compounds are discussed separately (Subsection 2.3.3).

Table 2.18: pH values of solutions (c = 0.25 mol L^{-1}): [Ga(aa)(edda)] complexes with polar or nonpolar aa ligands in D_2O.

compound	pH value
[Ga(ala)(edda)]	6.0–6.5
[Ga(asn)(edda)]	7.0
[Ga(cys)(edda)]	-
[Ga(edda)(gly)]	6.0
[Ga(edda)(ile)]	6.5
[Ga(edda)(leu)]	6.0
[Ga(edda)(met)]	6.5
[Ga(edda)(pro)]	6.5
[Ga(edda)(ser)]	6.5–7.0
[Ga(edda)(thr)]	7.0
[Ga(edda)(val)]	6.0–6.5

2.3.3 Solution studies at basic pH levels

The low solubilities of [Ga(edda)(gln)], [Ga(edda)(phe)] and [Ga(edda)(trp)] did not allow NMR-spectroscopic analyses at neutral pH levels. Hence, the solution studies of these compounds were done at basic pH levels (Table 2.19) by adding the lowest possible amount of triethylamine in order to obtain solutions. [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ is soluble at pH 8.5–9.0 by addition of one equivalent of triethylamine to obtain a 0.25 M solution. The $^{13}C\{^1H\}$ NMR spectrum of such a solution is displayed in Figure 2.43b. A striking difference in comparison to every other $^{13}C\{^1H\}$ NMR spectrum of [Ga(aa)(edda)] complexes with polar and nonpolar aa ligands can be seen in the "tidiness" of this spectrum. Unlike before, no chaotic clusters of signals and only few broadened signals—those of edda—are visible. Only two sets of signals are found for L-glutamine, one of the free amino acid and one of the L-glutaminato ligand. There may be a second signal set of another L-glutaminato ligand, but only two very weak signals are visible and it is, therefore, disregarded in the subsequent analysis. The signal assignment was proven by re-measuring the $^{13}C\{^1H\}$ NMR spectrum after addition of L-glutamine (Figure 2.43c).

Table 2.19: pH values of solutions (c = 0.25 mol L^{-1}): [Ga(aa)(edda)] complexes at basic pH levels in D_2O. Triethylamine was added to solve the compounds.

compound	pH value
[Ga(edda)(gln)]	8.5–9.0
[Ga(edda)(phe)]	9.5
[Ga(edda)(trp)]	10.0

The signals in this spectrum indicate that only one out of six possible complex isomers of [Ga(edda)(gln)] is present in solution at the specific pH level. Even more exceptionally, this isomer is the main species in solution. Due to signal overlaps in the ^1H NMR spectrum, the ratios were not quantifiable with certainty, but the $^{13}C\{^1H\}$ NMR spectrum supported this assertion as well. It was also not possible to specify the complex isomer present in solution with the information at hand since no crystals of this complex were obtained.

To summarise, an equilibrium between free L-glutamine and [{Ga(edda)(μ-OH)}$_n$] on the one side and one isomer of [Ga(edda)(gln)] seems to be present in solution (Figure 2.43a) and the basic pH level seems to shift the equilibrium in favour of the [Ga(edda)(gln)] complex. In addition, the higher-than-usual pH value in solution also affects the number of different complexes isomers.

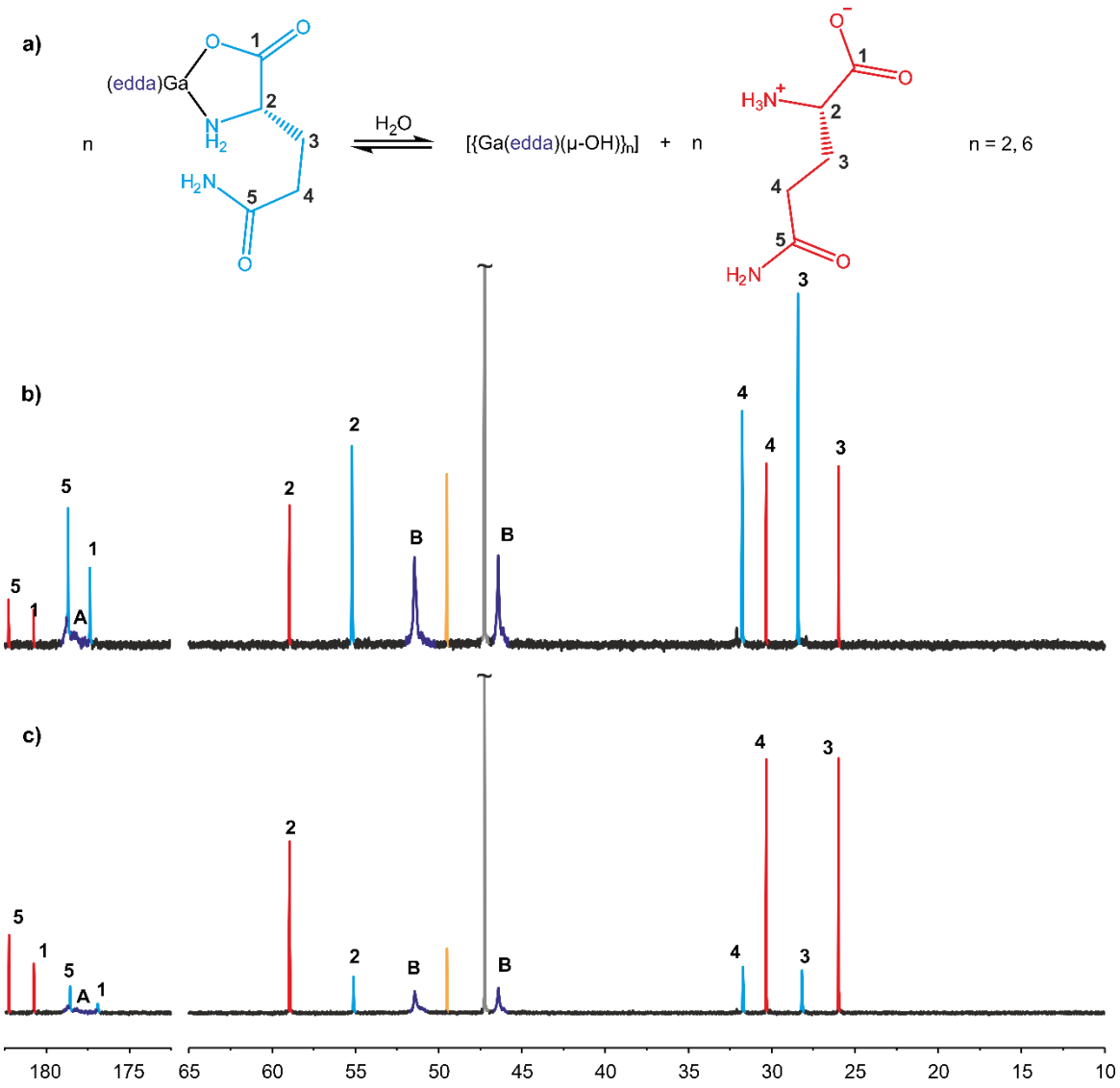


Figure 2.43: [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ in basic aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ in D_2O and triethylamine*, c: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ with 0.8 equ. of L-glutamine in D_2O and triethylamine*. Red: L-glutamine, cyan: L-glutaminato in [Ga(edda)(gln)], blue (**A** and **B**): edda in [Ga(edda)(gln)] and [{Ga(edda)(μ-OH)}$_n$] complexes, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

The $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(phe)] + 1.05 H_2O (Figure 2.44b) needs to be discussed separately. The solution of this compound had a pH of 9.5, which was significantly more basic than the solution of [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ and drastically changed the characteristics of the NMR spectra.

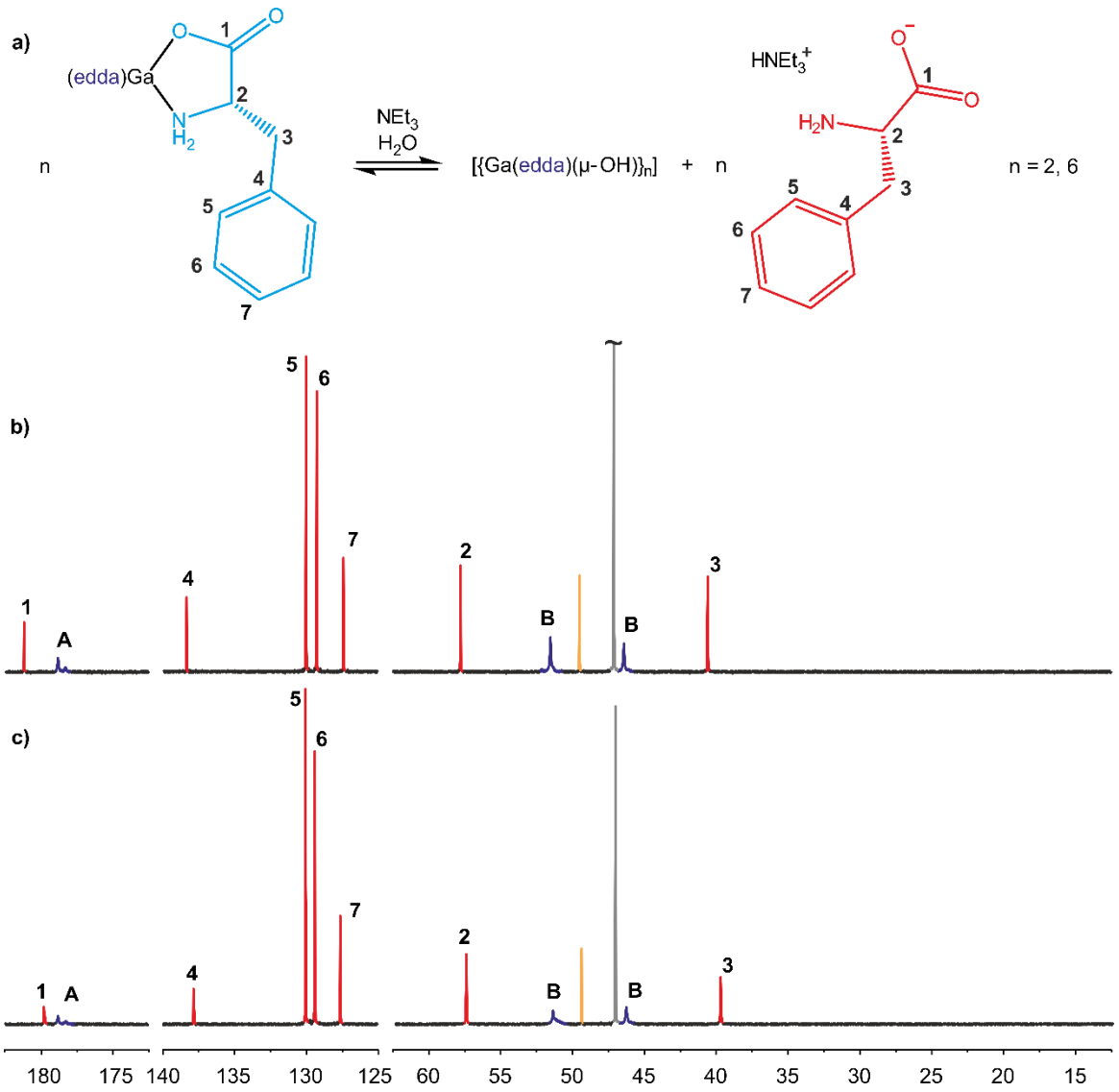


Figure 2.44: [Ga(edda)(phe)] + 1.05 H_2O in basic aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(phe)] + 1.05 H_2O in D_2O and triethylamine*, c: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(phe)] + 1.05 H_2O with 0.8 equ. of L-phenylalanine in D_2O and triethylamine*. Red: L-phenylalaninate, blue (**A** and **B**): edda in [{Ga(edda)(μ-OH)}$_n$] complexes, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

In comparison with the $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(gln)] + 0.80 H_2O + 0.05 $HNEt_3Cl$, the $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(phe)] + 1.05 H_2O features even fewer signals sets. While the signals of edda are still slightly broadened, implying that different chemical surroundings of the carbon atoms exist, only one set of well-defined signals of L-phenylalanine can be seen in the spectrum. This is curious, and a feature which was not seen in any of the $^{13}C\{^1H\}$ NMR spectra in this work before. Since crystals of [Ga(edda)(phe)] were obtained from such a solution with quite high yields, it seems obvious that the signals in this spectrum need to be assigned to the L-phenylalaninato

ligand. Therefore, the equilibrium in solution (Figure 2.44a) seems to be shifted entirely to the side of [Ga(edda)(phe)].

This subject was further investigated by re-measuring the solution after the addition of L-phenylalanine. Surprisingly, the $^{13}C\{^{1}H\}$ NMR spectrum of this solution (Figure 2.44c) featured no additional signals. Therefore, it seems that the equilibrium in solution (Figure 2.44a) is actually shifted entirely to the side of free L-phenylalanine and [{Ga(edda)(μ-OH)}$_n$]. It should be mentioned that with the amount of triethylamine in solution, any free L-phenylalanine should be fully deprotonated and, therefore, feature the same protonation state as a L-phenylalaninato ligand in the [Ga(edda)(phe)] complex. Since the coordination-induced shift caused by gallium(III) is very low, it might be possible that the signals of fully deprotonated L-phenylalanine and L-phenylalaninato are shifted by exactly the same amount, but this is highly unlikely. Hence, the signals in the spectrum are assigned to the deprotonated L-phenylalaninate and not to a L-phenylalaninato ligand.

It seems that the crystallisation of the [Ga(edda)(phe)] complex was dependent on the addition of organic solvent or the evaporation of triethylamine to shift the equilibrium in solution in its favour. An alternative explanation might be that a very small untraceable amount of the [Ga(edda)(phe)] complex still existed in solution and this compound just happened to be the first to crystallise.

The pH of the solution (Table 2.19) of [Ga(edda)(trp)] + 1.50 H_2O (Figure 6.25) is even higher than in the solution of the [Ga(edda)(phe)] complex. Consistently, the $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(edda)(trp)] is similar to the spectrum of [Ga(edda)(phe)]. The signals in this spectrum are therefore also assigned to the deprotonated L-tryptophanate and not to a L-tryptophanato ligand.

In general, the spectra of complexes in basic solutions differ from those in neutral solutions. Since it shows how significant the influence of the pH level on the equilibrium is, this issue will be discussed further in section 3.2.

2.3.4 Solution studies: complexes with basic aa ligands

The complexes formed with basic aa ligands and the Ga(edda)$^+$ fragment are different when compared to the complexes with the Ga(nta) fragment. In the isolated products, the basic side chains of the aa ligands are protonated when used in combination with nta. Consequently, neutral complexes are formed. Since adducts are formed with a non-integral amount of the respective tertiary amine in use, the compositions of the compounds are ill-defined. With edda, the resulting complex would be neutral if the side chains are not protonated. Of course, the side chains feature basic functions, therefore their protonation in the isolated product is likely. Indeed, this is the case according to elemental analysis. Therefore, a positive charge is present in the complex which is compensated with chloride as an anion in the complex salt. As a result, the products are homogeneous and easy to characterise by elemental analysis. Formally, these compounds could be described as hydrochlorides. Still, as these were stable and did not emit hydrogen chloride, in the course of this work the compounds will be referred to as the chlorides with the proton located at the aa ligand. This should emphasise the difference to the adducts formed with tertiary amines and [Ga(Haa)(nta)] complexes with basic aa ligands.

Table 2.20: pH values of solutions (c = 0.25 mol L^{-1}): [Ga(Haa)(edda)]Cl complexes with basic aa ligands in D_2O.

compound	pH value
[Ga(Harg)(edda)]Cl	7.0
[Ga(edda)(Hhis)]Cl	7.0
[Ga(edda)(Hlys)]Cl	6.5–7.0

Aqueous solutions of the [Ga(Haa)(edda)]Cl compounds are neutral (Table 2.20). Consequently, $^{13}C\{^1H\}$ and ^1H NMR spectra of aqueous solutions of those compounds were quite similar to the spectra obtained when [Ga(aa)(edda)] compounds with polar and nonpolar aa ligands are examined. For example, a $^{13}C\{^1H\}$ NMR spectrum of [Ga(Harg)(edda)]Cl + 2.00 H_2O + 0.05 $HNEt_3Cl$ (Figure 2.45b) in aqueous solution features the same signal patterns which are present in the spectrum discussed in subsection 2.3.2. The $^{13}C\{^1H\}$ NMR spectra of [Ga(Harg)(edda)]Cl + 2.00 H_2O + 0.05 $HNEt_3Cl$, [Ga(edda)(Hlys)]Cl + 0.60 H_2O (Figure 6.21) and [Ga(edda)(Hhis)]Cl + 0.10 H_2O + 0.05 $HNEt_3Cl$ (Figure 6.18) are, therefore, not discussed in detail as the same reasoning applies and the conclusions drawn are equal to those in subsection 2.3.2.

In the $^{13}C\{^{1}H\}$ NMR spectra of those three compounds, three signals sets of the respective aa ligands are found.

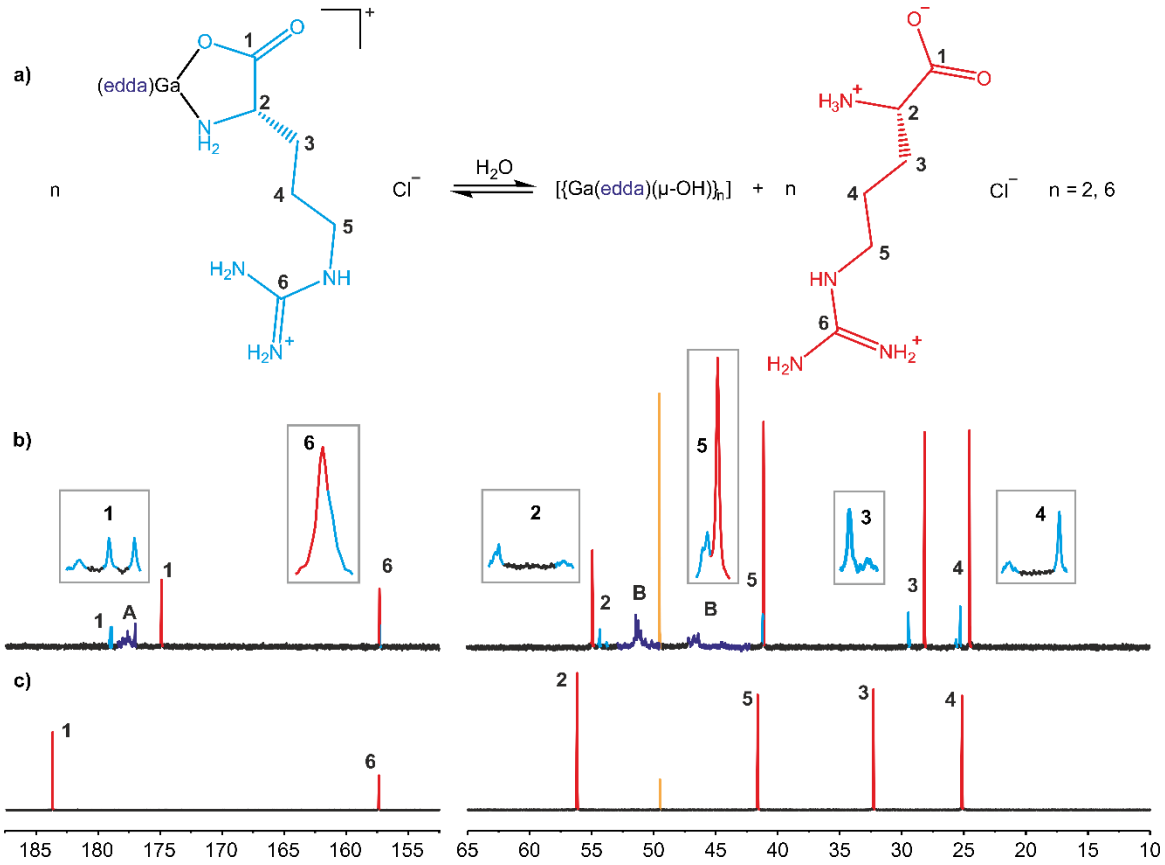


Figure 2.45: [Ga(Harg)(edda)]Cl + 2.00 H_2O + 0.05 $HNEt_3Cl$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(Harg)(edda)]Cl + 2.00 H_2O + 0.05 $HNEt_3Cl$ in D_2O*, c: $^{13}C\{^{1}H\}$ NMR spectrum of L-arginine in D_2O*. Red: L-argininate, cyan: L-argininato in $[Ga(Harg)(edda)]^+$, blue (**A** and **B**): edda in $[Ga(Harg)(edda)]^+$ and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ complexes, orange: MeOH. * One drop of MeOH was added for referencing.

In contrast to the spectra of the complexes containing the Ga(nta) fragment, the spectra of $[Ga(Harg)(edda)]^+$ and $[Ga(Hlys)(edda)]^+$ do not feature more signals than the spectra of other [Ga(aa)(edda)] complexes. This implies that the formation of different complex isomers is not that dependent on the aa ligand when edda is bound.

2.3.5 Solution studies: complexes with acidic aa ligands

As mentioned in section 2.2, nitrilotriacetatogallium(III) complexes with acidic aa ligands are special since they form unstable adducts with the tertiary amine used as base. In the isolated products, the acidic side chains of the aa ligand are not deprotonated. Aqueous solutions of these compounds are, therefore, acidic. [Ga(Haa)(edda)] complexes with acidic aa ligands showed the same characteristics (Section 2.3). Of course, this could also be seen in the $^{13}C\{^{1}H\}$ NMR spectra of those adducts. As expected, the solutions were also acidic (Table 2.21) due to the protonated acidic side chain. The similarities of the $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(Hasp)(edda)]·0.30NEt_3 + 1.30 H_2O (Figure 2.46b) with those of $[Ga(Haa)(nta)]^-$ complexes are easily spotted. The signals of the L-aspartic acid are broadened in all of these spectra, sometimes to such an extent that they are no longer visible in the spectrum.

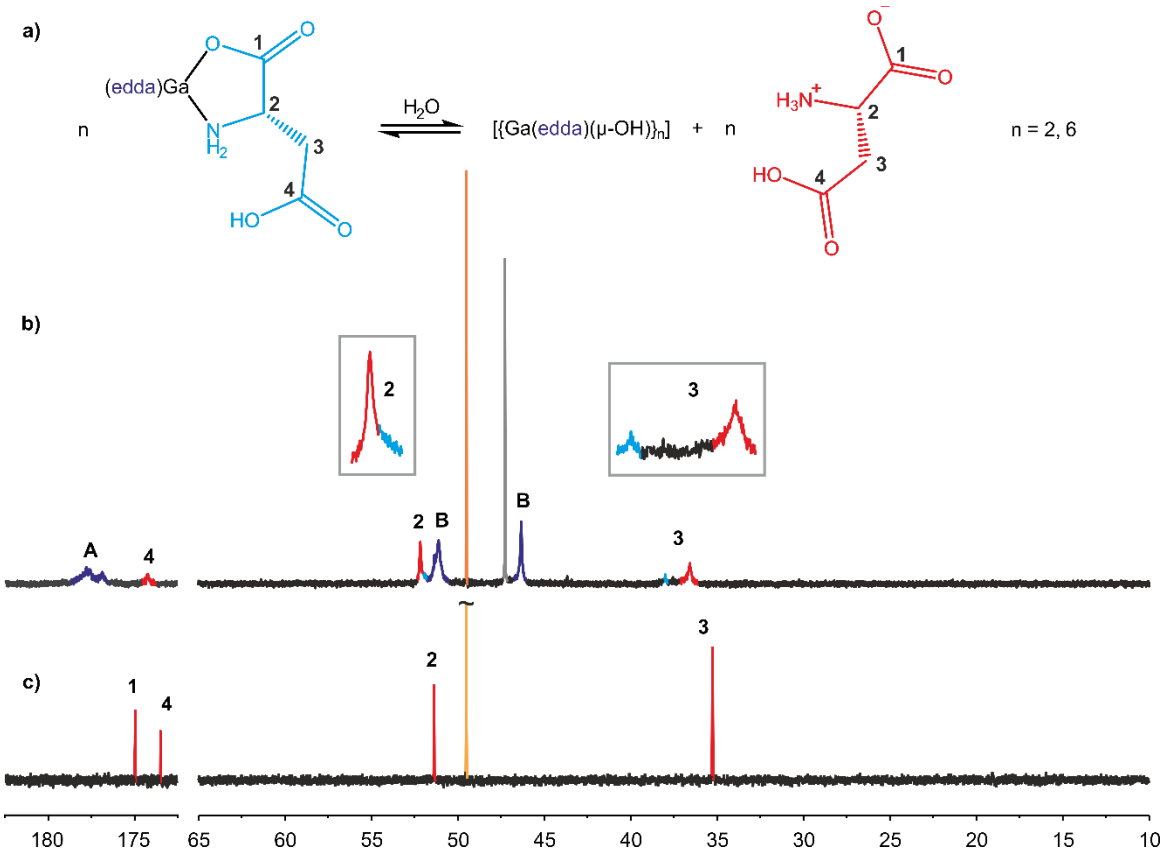


Figure 2.46: [Ga(Hasp)(edda)]·0.30NEt_3 + 1.30 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(Hasp)(edda)]·0.30NEt_3 + 1.30 H_2O in D_2O*, c: $^{13}C\{^{1}H\}$ NMR spectrum of L-aspartic acid in D_2O*. Red: L-aspartic acid, cyan: L-aspartato in [Ga(Hasp)(edda)], blue (**A** and **B**): edda in [Ga(Hasp)(edda)] and [{Ga(edda)(μ-OH)}$_n$] complexes, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 2.21: pH values of solutions (c = 0.25 mol L^{-1}): [Ga(Haa)(edda)] complexes with acidic aa ligands in D_2O.

compound	pH value
[Ga(Hasp)(edda)]	4.5
[Ga(edda)(Hglu)]	4.5

This is due to the acidic pH of the compound's solutions. Still, the signals of free amino acid in the spectra of [Ga(Hasp)(edda)] + 1.30 H_2O can be identified. The unassigned signals with very weak intensity are, therefore, assigned to the aa ligand, which means that at least a small amount of the [Ga(Haa)(edda)] complex should be present in solution. This indicates that an equilibrium (Figure 2.46a) exists in solution and it is expected to be similar to the equilibria of other [Ga(aa)(edda)] complexes. But, in contrast to the spectra of most [Ga(aa)(edda)] complexes, no signal sets of different [Ga(Haa)(edda)] complex isomers could be identified. This was a recurring problem of complexes with acidic aa ligands and a more in-depth discussion of the subject is found in subsection 2.2.9. Of course, this prevented the identification of different complex isomers and it was not even possible to state whether different complex isomers were formed.

The $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(Hglu)]·0.15NEt_3 + 1.25 H_2O (Figure 6.16) is similar to the spectrum of [Ga(Hasp)(edda)] + 1.30 H_2O and, therefore, not discussed separately. In conclusion, the spectra seem to show the existence of the equilibria (Figure 2.46a and Figure 6.16a) in solution. Other than that, the informative value of the spectra is low, which was expected since spectra of $[Ga(Haa)(nta)]^-$ complexes with acidic aa ligands are very similar in this regard. Since the pH levels of solutions had a huge impact on the equilibrium reaction and on the information that can be derived from the spectra, this subject is discussed in more detail later (Section 3.2). It would have been possible to adjust the pH levels with the addition of basic ligand. This was not done in order to show the difficulties caused by the acidic pH levels and the combination of tri- and tetradentate ligands.

2.3.6 Equilibria in solution: ratios of components

One striking feature found in all spectra of complexes with Ga(edda)$^+$ fragments and aa ligands is the dominant species of free proteinogenic amino acid. While the existence of free amino acid was expected due to the experiences with complexes containing the Ga(nta) fragment and aa ligands, the amount of uncoordinated AA was significantly higher in solutions of ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes. Unfortunately, the overlap of signals in the ^{1}H NMR spectra did not allow for the specification of ratios between free and bound ligand in most cases. The values which could be derived with some certainty are presented in Table 2.22.

Table 2.22: Ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes in D_2O: ratios of coordinated aa ligand and free AA in solutions (c = 0.25 mol L^{-1}). The ratios are derived from the respective ^{1}H NMR spectra and are given in %. *Signal overlap, values may differ up to 5%. $^{\#}$In basic solution.

	aa ligand [%]	free AA [%]
L-Argininato/L-arginine*	18	82
L-Glutaminato/L-glutamine*$^{\#}$	75	25
Glycinato/glycine*	35	65
L-Histidinato/L-histidine*	40	60
L-Isoleucinato/L-isoleucine	23	77
L-Phenylalaninato/L-phenylalanine$^{\#}$	0	100
L-Prolinato/L-proline*	10	90
L-Threoninato/L-threonine	48	52
L-Tryptophanato/L-tryptophan*$^{\#}$	0	100
L-Valinato/L-valine	20	80

The NMR spectra of basic solutions have already been discussed extensively in subsection 2.3.3. In short, if the pH is slightly higher than neutral, the equilibrium is shifted to the side of the [Ga(aa)(edda)] complex. This is illustrated by a ratio of approximately 75% of L-glutaminato bound in [Ga(edda)(gln)] in an aqueous solution with a pH of 8.5–9.0. If it gets too high—somewhere between 9.0 and 9.5—the equilibrium is drastically changed and completely shifted to the side of free AA. This was found when an aqueous solution containing [Ga(edda)(phe)] was analysed at pH 9.5.

Neutral solutions (c = 0.25 mol L^{-1}) tend to contain 60% or more free AA. Hence, less than 40% of gallium(III) is coordinated in [Ga(aa)(edda)] complexes. The rest is likely found in [{Ga(edda)(μ-OH)}$_n$] complexes, be it [{Ga(edda)(μ-OH)}$_6$] or [{Ga(edda)(μ-OH)}$_2$]—which were both found in crystals—or maybe other, unidentified complexes of this kind.

One exception is the solution of [Ga(edda)(thr)] which features a significantly higher amount of bound aa. The difference in regard to other complex solutions is prominent enough that it can be seen even in the $^{13}C\{^1H\}$ NMR spectrum of this complex. Even though a molecular structure of one [Ga(edda)(thr)] complex isomer is available for closer inspection, no obvious intramolecular interaction or other cause which would explain the higher stability of [Ga(edda)(thr)] in comparison to other ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes is apparent. However, $[Ga(nta)(thr)]^-$ was also slightly more stable than comparable complexes. Hence, gallium(III) complexes with L-threoninato ligands seem to be, generally, more stable than complexes with other aa ligands.

In conclusion, the abundancy of ethylenediamine-*N*,*N*′-diacetatogallium(III) complexes with aa ligands is significantly lower than the abundancy of the respective nitrilotriacetato complexes in solutions with the same concentration. On average, only around 30% of the proteinogenic amino acid is bound in the complexes. The formation of the respective nitrilotriacetato complexes seems to be favoured. This is most likely due to the lower steric demand of the nta ligand when compared to edda.

2.4 Gallium(III) complexes with tridentate aminecarboxylato ligands

Since the synthesis of gallium(III) complexes with combinations of tetra- and bidentate aminecarboxylato ligands was possible, a logical follow-up was to use combinations of tridentate aminecarboxylato ligands. While monovalent complex anions with tetra- and bidentate aminecarboxylato ligands were structurally characterised, the cation did effect the quality of the crystal structures obtained. In addition, experiments with edda had shown that neutral complexes can be formed and crystallised with tetra- and bidentate aminecarboxylato ligands. Last but not least, the gallium(III) compounds which were described as most promising therapeutic agents in clinical trials (Section 1.3) are neutral complexes. Therefore, it seemed appropriate to use ligand combinations which would allow the formation of neutral complexes.

2.4.1 Iminodiacetatogallium(III) complexes

As described in section 1.4, $[Ga(ida)_2]^-$ is an already characterised gallium(III) complex with a tridentate aminecarboxylato ligand. Iminodiacetic acid (H_2ida) is comparable to aspartic acid, but allows the formation of two five-membered chelate rings and is a more symmetrical ligand in addition to not being chiral. Therefore, ida is one of the most simple tridentate aminecarboxylato ligands and should be a viable starting point for the formation of heteroleptic gallium(III) complexes.

To form a neutral iminodiacetatogallium(III) complex, the second tridentate ligand should be monoanionic. Of the proteinogenic amino acids, only the basic amino acids would be fitting ligands to form [Ga(aa)(ida)] complexes while still featuring the established Ga-N/O environment with carboxylate and amine functions. Of those three—L-arginine, L-histidine and L-lysine—only L-histidine should be a suitable tridentate ligand since the two other ligands would require the unfavourable formation of seven-, eight- or even nine-membered chelate rings.

The synthesis of [Ga(his)(ida)] was done in aqueous solution and the starting materials were used in stoichiometric ratios (Figure 2.47, pH 5.5).

$$GaCl_3 + Hhis + H_2ida + 3\ NEt_3 \xrightarrow[-3\ HNEt_3Cl]{H_2O} [Ga(his)(ida)]$$

Figure 2.47: Chemical equation for the synthesis of [Ga(his)(ida)].

After the reaction the product was precipitated by addition of ethanol and examined by elemental analysis.

According to this analysis, the target complex was formed with a small amount of residual water still present in the product: [Ga(his)(ida)] + 0.40 H_2O. The maximum difference between the found and calculated percentages of this composition is 0.03. Unfortunately, the isolated compound is not soluble in water at neutral pH levels. Hence, crystallisation experiments were done with a solution of the crude product in water and triethylamine (pH 9.0). Crystals of [Ga(his)(ida)] (Figure 2.48) were obtained by storing an open vessel of this solution for one week.

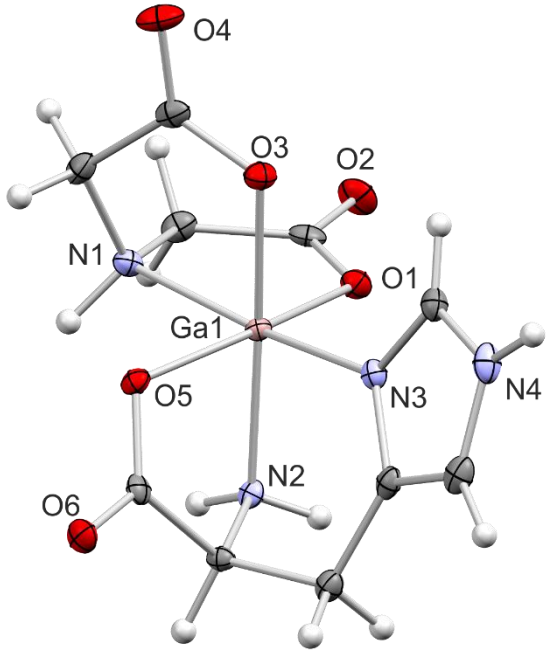


Figure 2.48: Plot of [Ga(his)(ida)] in crystals of **4a**. Space group: $P2_12_12_1$. $CShM_{OC-6}$: 0.756. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.094(2), Ga1–N2 2.039(2), Ga1–N3 2.026(2), Ga1–O1 1.946(2), Ga1–O3 1.957(2), Ga1–O5 2.010(2), N1–Ga1–N3 169.71(8), N2–Ga1–O3 174.61(8), O1–Ga1–O5 168.95(7), N1–Ga1–N2 99.52(8), N2–Ga1–N3 88.56(8), N2–Ga1–O1 94.00(8), N2–Ga1–O5 81.54(8), N3–Ga1–O1 101.17(8).

Just as expected, the complex molecule features an octahedral GaN_3O_3 coordination of gallium(III) which was interpreted in greater depth by using continuous shape measures. The $CShM_{OC-6}$ value shows a slight distortion of the octahedral coordination sphere which is in the range of the values found for the complexes with tetra- and bidentate ligands. This is true for the atomic distances and angles between gallium(III) and the N/O atoms as well.

The ligands of the crystallised isomer are coordinated facially, while the N- and O-atoms of the ligands each have a meridional arrangement. This result was repeatedly obtained,

therefore, only one of three different possible constitutional isomers was found in the crystal structure. The limited number of potential complex isomers is due to the nature of the ligands in use. L-histidinato can be a tridentate ligand only when it binds facially as the meridional arrangement is sterically not possible. A difference between this complex and every other complex presented until now is the formation of one six-membered chelate ring, proving that the formation of such a chelate ring with aa ligands is possible.

One important characteristic of the crystallisation experiments is the instability of the mother liquor over extended periods of time. This can be observed by the progressing discolouration of the solution from slightly yellow to a brownish colour. It also leads to the formation of a brownish, amorphous solid which coats the crystals if the crystallisation experiment is stored for a few weeks. Since the intention of these experiments was to obtain crystals of high quality, the process was set up to be slow. Thereby crystals of good quality were obtained, but the yield was limited to only a few crystals before contamination with the amorphous brown solid occurred. To reach higher yields of the target complex, faster crystallisation methods or just the precipitation method which is used to get the crude product should be applied.

As in previous sections of this work, the composition of an aqueous solution of [Ga(his)(ida)] is of interest. However, the complex is not soluble at neutral pH levels, hence triethylamine was added to obtain a solution with a pH of 8.0–8.5. This affects the significance of NMR-spectroscopic studies, as mentioned before (Subsections 2.2.10 and 2.3.6).

In contrast to every other spectrum of basic solutions shown up to this point, the signals in the $^{13}C\{^{1}H\}$ NMR (Figure 2.49) and ^{1}H NMR spectrum of this solution are broadened to such an extent that signal assignment was not possible even with 2D NMR experiments. To be specific, this means that the signals of the C1 and C2 atom of the two ligands could not be distinguished and an overall assignment of signals to different species in solution was also not feasible. A detailed interpretation of the spectra was not possible and, with the information at hand, it could not be determined which complexes were present in solution. There might only be different complex isomers of [Ga(his)(ida)], though the existence of homoleptic complexes cannot be ruled out. Due to this fact, no NMR-spectroscopic data of the $^{13}C\{^{1}H\}$ NMR and ^{1}H NMR spectra are listed in the experimental part of this work.

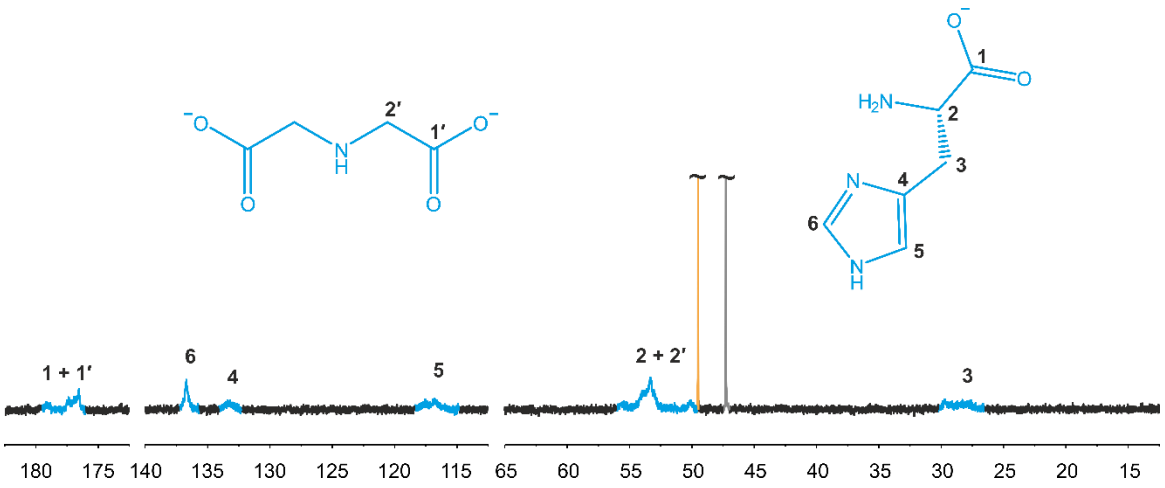


Figure 2.49: $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(his)(ida)] + 0.40 H_2O in D_2O and triethylamine* (c = 0.25 mol L^{-1}). Cyan: signals of L-histidinato and iminodiacetato ligands, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Despite the obstacles to an exhaustive analysis of the spectrum, a few assertions can nevertheless be made. Since no defined sharp signals are found in the $^{13}C\{^{1}H\}$ NMR spectrum, different complexes and/or complex isomers might exist in solution. Also, no sharp signals of the ligands can be seen. In this work, the signals of free ligands were well-defined in every $^{13}C\{^{1}H\}$ NMR spectrum of neutral or basic solutions. Therefore, it seems that no free ligand is present in solution, which indicates that the complexes are stable against hydrolysis, at least in basic solution.

This is an important difference in comparison to the complexes with tetra- and bidentate aminecarboxylato ligands and shows that the investigation of further gallium(III) complexes with tridentate aminecarboxylato ligands is reasonable.

2.4.2 Gallium(III) complexes with tridentate aa ligands

The successful synthesis of [Ga(his)(ida)] showed that L-histidine is a suitable tridentate ligand for gallium(III). To form a comparable complex with L-histidine, ida had to be substituted with a similar tridentate ligand. As stated in subsection 2.4.1, L-aspartic acid is such a ligand. The main difference when comparing L-aspartic acid with iminodiacetic acid is the additional CH_2-group, which would necessitate the formation of two six-membered and four five-membered chelate rings to form the target complex [Ga(asp)(his)]. This complex was synthesised in water with stoichiometric amounts of the starting materials and triethylamine as base (Figure 2.50, pH 7.5). After the reaction the product was precipitated by addition of ethanol and examined by elemental analysis.

$$GaCl_3 + H_2asp + Hhis + 3\ NEt_3 \xrightarrow[-\ 3\ HNEt_3Cl]{H_2O} [Ga(asp)(his)]$$

Figure 2.50: Chemical equation for the synthesis of [Ga(asp)(his)].

The elemental analysis (Table 2.23) of this reaction's crude product indicates that the synthesis of [Ga(asp)(his)] was, most likely, successful. The compound shows excellent solubility in neutral aqueous solution, which is a striking difference when compared to [Ga(his)(ida)]. Unfortunately, crystallisation experiments of this compound failed despite several attempts. Therefore, a structural examination of the obtained complex by crystallography was not possible.

To obtain crystals of a [Ga(asp)(his)] complex, D-histidine and L-aspartic acid were used as a ligand combination. The reaction was done with an excess of triethylamine as no solution was obtained at neutral pH levels. Aside from that, the procedure was identical to that of the reaction with L-histidine and L-aspartic acid. According to an elemental analysis (Table 2.23) of this product, the target complex [Ga(asp)(D-his)] was obtained. A subsequent crystallisation experiment with an aqueous solution of triethylamine and [Ga(asp)(D-his)] (pH 10.0) yielded a few crystals which were suitable for X-ray diffraction.

Table 2.23: Interpretation of elemental analyses: [Ga(asp)(his)] complexes. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

complex-salt	contamination	max. diff.
[Ga(asp)(his)]	2.40 H_2O + 0.05 $HNEt_3Cl$	0.23
[Ga(asp)(D-his)]	1.95 H_2O	0.04

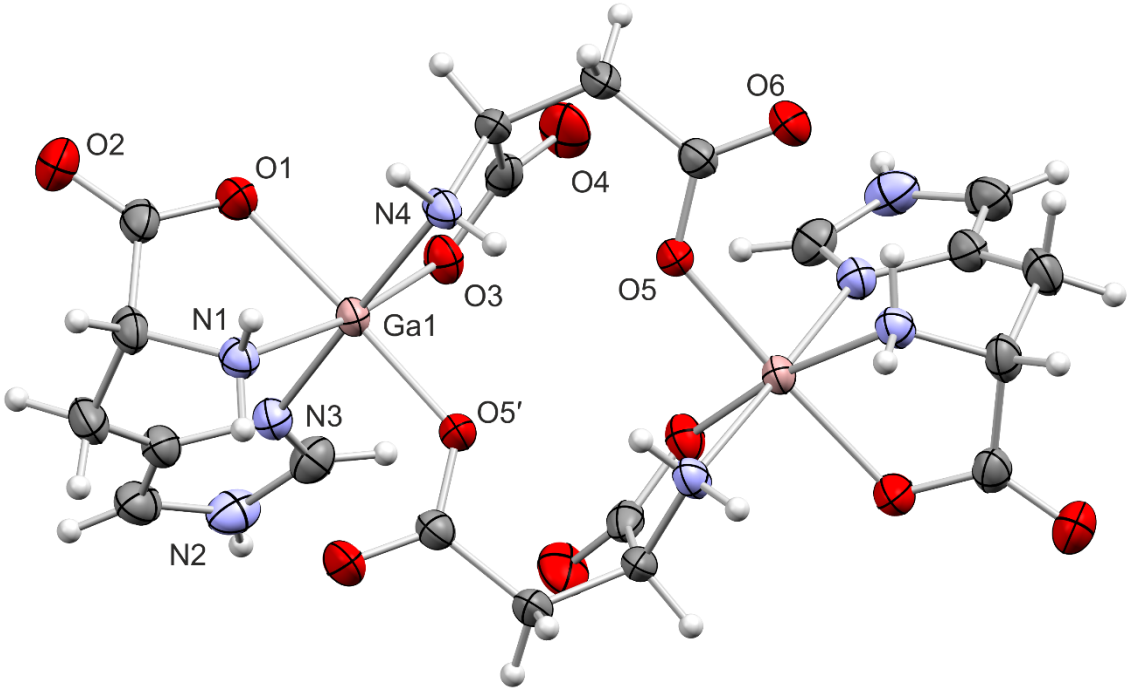


Figure 2.51: Plot of [{Ga(μ-asp)(D-his)}$_2$] in crystals of **4b**·1.61H_2O. Space group: $P4_12_12$. $CShM_{OC-6}$: 0.449. The thermal ellipsoids are drawn at 50% probability (room temperature data collection). Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.039(3), Ga1–N3 2.044(2), Ga1–N4 2.048(3), Ga1–O1 2.045(2), Ga1–O3 1.945(2), Ga1–O5′ 1.958(2), N3–Ga1–N4 173.99(10), N1–Ga1–O3 170.53(10), O1–Ga1–O5′ 175.06(9), N1–Ga1–N4 97.52(11), N1–Ga1–N3 88.36(10), N1–Ga1–O1 80.18(10), N3–Ga1–O1 89.25(10), N3–Ga1–O3 90.92(9), N3–Ga1–O5′ 91.93(9).

Surprisingly, no mononuclear complex [Ga(asp)(D-his)] was crystallised. Instead, the binuclear complex [{Ga(μ-asp)(D-his)}$_2$] (Figure 2.51) was obtained. The octahedral GaN_3O_3 coordination of the gallium(III) atoms is slightly distorted, and the interatomic distances and angles are in the expected range. The N- and O-atoms show a meridional arrangement, while the histidinato ligands are coordinated facially. Since this complex resembles the targeted mononuclear complex when it comes to its charge and composition, it is not distinguishable from the target complex by elemental analysis.

Apparently, the crystallisation of a binuclear complex with two bridging aspartato ligands instead of the mononuclear complex is favoured. It might be possible that the formation of the mononuclear complex does not occur as it would require the formation of a second six-membered chelate ring which might, in turn, cause a higher distortion of the octahedral coordination sphere of gallium(III) in the complex. This would be averted by the formation of the binuclear complex. However, since the overall yield of crystals was very low and the crystals that feature this complex were the only ones that were obtained, it is not possible to determine if this complex was the only one that was formed. Hence, it cannot be ruled

out that the mononuclear complex exists in solution. In fact, molecular structures of gallium(III) complexes with tridentate N/O ligands that feature four six-membered chelate rings and two five-membered chelate rings have already been reported.[49] Therefore, the crystallisation or even the formation of a mononuclear complex might just not be favoured in this case.

One striking difference when comparing [Ga(asp)(his)] with [{Ga(μ-asp)(D-his)}$_2$] is the excellent solubility of [Ga(asp)(his)] in neutral aqueous solution. This might indicate that, at least in aqueous solution, the [Ga(asp)(his)] complex has a different structural configuration than [{Ga(μ-asp)(D-his)}$_2$]. Hence, [Ga(asp)(his)] might actually be mononuclear and therefore resemble the targeted complex. On a side note, when racemic mixtures of both ligands were used for complex formation, the composition of the product remained unknown. However, it was soluble in water, hence the formation of the insoluble [{Ga(μ-asp)(D-his)}$_2$] was not favoured.

To further investigate the compositions of those complexes in solution, $^{13}C\{^1H\}$ and ^1H NMR spectroscopy in combination with 2D NMR techniques was used. Unfortunately, since [{Ga(μ-asp)(D-his)}$_2$] is soluble only at basic pH level, a direct comparison of $^{13}C\{^1H\}$ and ^1H NMR spectra of this complex with spectra of [Ga(asp)(his)] solutions is not possible. In addition, the solubility of [{Ga(μ-asp)(D-his)}$_2$] is very low even at higher pH levels, therefore the spectra are not interpretable and not displayed.

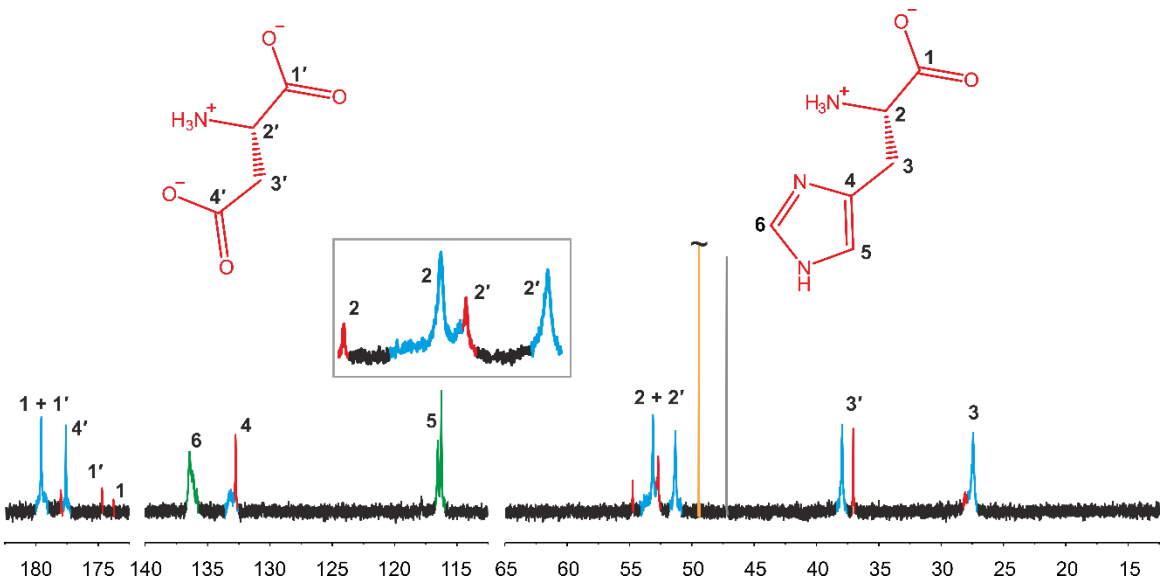


Figure 2.52: $^{13}C\{^1H\}$ NMR spectrum of [Ga(asp)(his)] + 2.40 H_2O + 0.05 $HNEt_3Cl$ in D_2O* (c = 0.25 mol L^{-1}). Cyan: signals of L-histidinato and L-aspartato ligands, red: signals of free AA, green: signals that are to be assigned to either bound or free AA, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

The $^{13}C\{^{1}H\}$ NMR spectrum of [Ga(asp)(his)] + 2.40 H_2O + 0.05 $HNEt_3Cl$ depicted in Figure 2.52 (pH 7.0) shows at least two signal sets of both amino acids. Since two different aa ligands were used in the synthesis, some of the signals in the spectra are found in close proximity. Therefore, the assignment of signals and a detailed evaluation of the spectrum is difficult without comparing it to spectra of similar compounds. Subsequently, two of the signal sets in the $^{13}C\{^{1}H\}$ NMR spectrum were assignable to free amino acid. The signals of the aa ligands are broadened and seem to be formed by overlapping signals in most cases. This indicates that different isomers of [Ga(asp)(his)] or maybe even overall different complexes are present in solution. Nevertheless, the intensities of the signal sets reveal that equal amounts of the two amino acids are bound to gallium(III). This indicates that the complexes in solution are, most likely, heteroleptic [Ga(asp)(his)] complexes of some sort, since it seems unlikely that two homoleptic complexes with different charges and quite different ligands are by chance equally stable in solution. Regrettably, it was not possible to conclude if mono- or binuclear complexes are present in solution with the available data.

An important aspect which can be derived from this spectrum is that over 80% of amino acids in solution are bound to gallium(III) at neutral pH levels. However, ligand exchange reactions are still present, most likely by the incorporation of hydroxido ligands.

This example shows that with the information gathered about complexes with aa ligands in solution, it is possible to draw conclusions about the stability and formation of unknown gallium(III) complexes with aa ligands, at least to some extent, without the absolute necessity of molecular structures. Previous investigations of aminecarboxylatogallium(III) complexes with $^{13}C\{^{1}H\}$ and ^{1}H NMR spectroscopy shown in this work provide useful pointers for the investigation of other gallium(III) complexes with aa ligands. For example, the signal of the atom C2 of proteinogenic amino acids was—with only very few exceptions—shifted to high field when coordinated to a gallium(III) centre. In addition, the signals of the carboxylate functions were almost always shifted to low field when coordinated to gallium(III). Furthermore, the sharpness of the signals in the spectra can be used to gather information as well. If broadening of the signals occurs at neutral pH levels, these signals should, most likely, be assigned to a ligand, while the opposite is true for the signals of uncoordinated AA. By combining this knowledge with 2D NMR experiments, solid information about the composition in solution can be gained.

2.5 Gallium(III) complexes with tetradentate amine ligands

The successful synthesis of gallium(III) complexes with aminecarboxylato ligands led to the conclusion that a combination of amine ligands with carboxylate ligands might be a feasible way of synthesising further gallium(III) complexes. With tris(2-aminoethyl)amine (tren) and triethylenetetramine (trien), two structural analogues of nta and edda are available. According to the experiences with aminecarboxylato ligands, trien and tren should, in combination with bidentate dicarboxylic or hydroxycarboxylic acids, allow the synthesis of heteroleptic complexes at neutral pH levels. The choice of bidentate ligands was based on the following considerations: first, only the formation of five- and six-membered chelate rings should lead to complex formation. Therefore, the complexing oxygen atoms must be three atoms apart at most. Furthermore, the ligands should be simple, nontoxic and not sterically demanding. Apart from oxalic and malonic acid a few hydroxycarboxylic acids like L-malic acid were considered uitable ligands. Since tren itself is a toxic substance—which contradicts the purpose of finding substances suitable for pharmacological applications—experiments with this ligand should be seen as a proof of concept. While trien is considered toxic through contact with skin but not when administered orally[50] it is already used in pharmacological applications[51,52]. Hence, trien might be an appropriate ligand for the intended purpose.

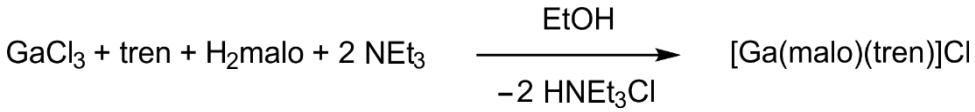


Figure 2.53: Chemical equation for the synthesis of [Ga(malo)(tren)]Cl.

A few experiments with tren and different bidentate ligands were done, but only one experiment generated crystals suitable for X-ray diffraction. The synthetic approach of [Ga(malo)(tren)]Cl was slightly different when compared to every other compound in this work, as the synthesis was done in ethanol instead of water. While water also worked as a solvent of the reaction, the product was obtained with higher purity when ethanol was used. Another difference compared to the usual reaction conditions was the huge excess of triethylamine used as base. Apart from that, the other starting materials were used in stoichiometric ratios (Figure 2.53). The product precipitated over the course of the reaction and was separated by filtration.

According to elemental analysis of the crude product (Table 2.24), [Ga(malo)(tren)]Cl was synthesised. Crystallisation experiments with this raw product in methanolic solution yielded crystals of this complex (Figure 2.54).

Table 2.24: Interpretation of elemental analyses: tren and trien compounds. The maximum difference (max. diff.) is given between the found and calculated percentages of the listed compositions.

compounds	contamination	max. diff.
[Ga(malo)(tren)]Cl	1.10 H_2O + 0.05 EtOH	0.16
[Ga(mal)(trien)]	0.85 EtOH + 0.30 H_2O + 0.20 $Ga(OH)_3$	0.07
[Ga(malo)(trien)]Cl	1.65 H_2O + 0.05 $Ga(OH)_3$	0.20
[Ga(ox)(trien)]Cl	2.75 H_2O	0.12

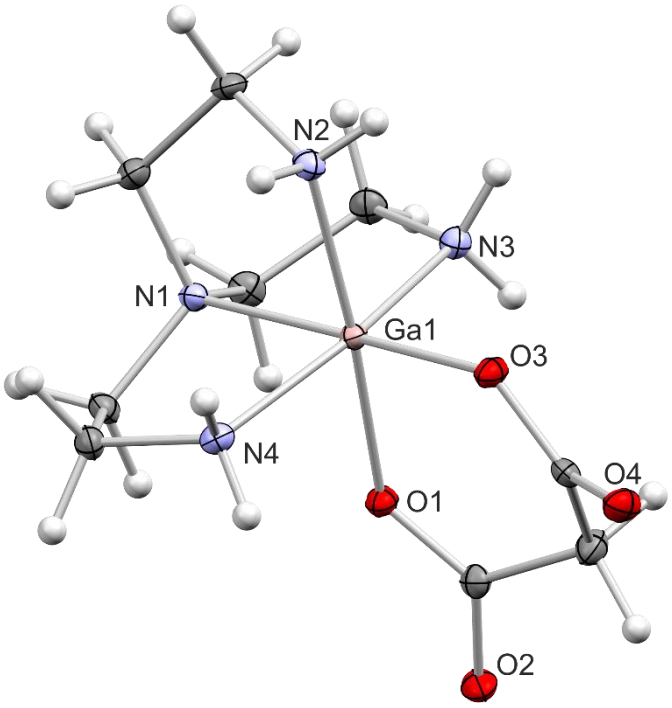


Figure 2.54: Plot of $[Ga(malo)(tren)]^+$ in crystals of **5a**Cl·MeOH. Space group: $P2_1/c$. $CShM_{OC-6}$: 0.378. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0925(12), Ga1–N2 2.0450(12), Ga1–N3 2.0728(13), Ga1–N4 2.0708(13), Ga1–O1 1.9844(10), Ga1–O3 1.9268(10), N3–Ga1–N4 164.81(5), N1–Ga1–O3 175.63(5), N2–Ga1–O1 174.75(5), N1–Ga1–N4 82.94(5), N1–Ga1–O1 89.56(4), N3–Ga1–O1 88.27(5), N3–Ga1–O3 100.75(5), N4–Ga1–O1 85.64(5), O1–Ga1–O3 92.60(4).

This is proof that complexes with the tetradentate ligand tren and a bidentate dianionic ligand can be formed. The octahedral GaN_4O_2 coordination of gallium(III) in this complex is slightly distorted and the Ga–N/O distances and angles are in the expected range. The complex is therefore comparable with similar complexes which feature aminecarboxylato ligands. Unfortunately, the solubility of the compound is very low both in methanol and water. Therefore, an NMR-spectroscopic examination of the complex in solution was not feasible.

In contrast to tren, the synthesis and the procedure to obtain trien complexes were done the usual way. Water was used as solvent and triethylamine as base. The synthesis of [Ga(ox)(trien)]Cl was done with stoichiometric ratios of the starting materials (Figure 2.55). Water had to be removed after the reaction to allow for the separation of the byproduct and the target complex with organic solvents.

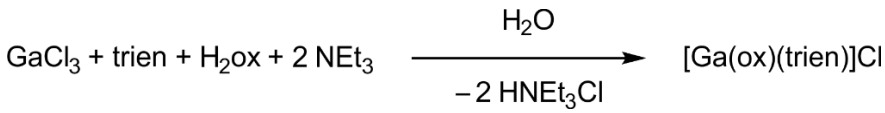


Figure 2.55: Chemical equation for the synthesis of [Ga(ox)(trien)]Cl.

According to the elemental analysis of the obtained product, [Ga(ox)(trien)]Cl was contaminated only with residual water and, therefore, obtained with high purity (Table 2.24). Since the compound is hygroscopic, a contamination with water was almost impossible to avoid under the conditions of the synthesis.

Crystals of $[Ga(ox)(trien)]Cl \cdot 2H_2O$ (Figure 2.56) were obtained from aqueous solution. The solubility of the compound was increased by addition of a very small amount of triethylamine. This raised the pH of the solution to 7.0, which was only slightly acidic due to the high concentration of the solution. In contrast to the other crystallisations in this section, the yield of crystals was quite high with a recovery rate of 37.8%.

The interatomic distances and angles between gallium(III) and the nitrogen and oxygen atoms of this complex are in the expected ranges. Gallium(III) features the expected GaN_4O_2 environment and with a $CShM_{OC\text{-}6}$ value of 1.111, the distortion of the octahedral coordination sphere is more significant than in most other complexes of this work.

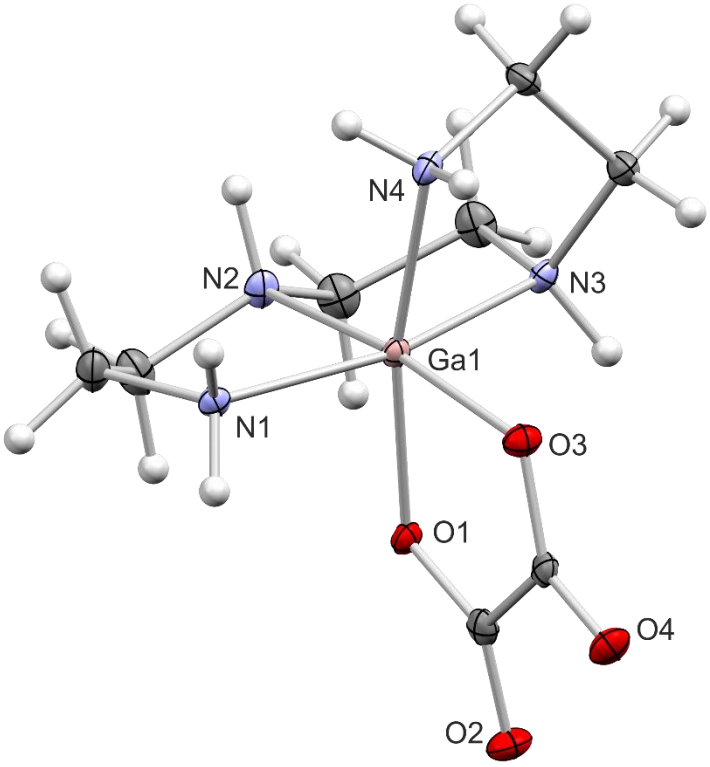


Figure 2.56: Plot of $[Ga(ox)(trien)]^+$ (**5b**) in crystals of **5b**·**5c**·2Cl·4H_2O. Space group: *Pn*. $CShM_{OC-6}$: 1.111. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.056(3), Ga1–N2 2.068(3), Ga1–N3 2.082(3), Ga1–N4 2.048(3), Ga1–O1 1.992(3), Ga1–O3 1.979(2), N1–Ga1–N3 164.79(10), N2–Ga1–O3 171.52(10), N4–Ga1–O1 168.08(11), N2–Ga1–N4 100.00(12), N1–Ga1–O1 92.05(11), N2–Ga1–O1 89.56(11), N3–Ga1–O1 90.67(9), O1–Ga1–O3 82.01(11).

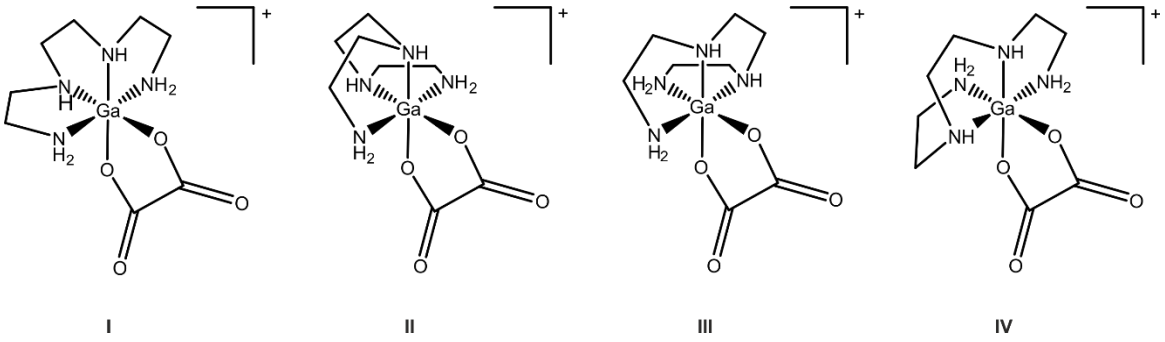


Figure 2.57: The four possible constitutional isomers of $[Ga(ox)(trien)]^+$.

The isomers found in crystals of this compound (isomer **III** and **IV**) are two of four different potential isomers (Figure 2.57). When compared, the C_2-symmetric complex isomers **I** and **II** should allow for a less strained arrangement of the trien ligand, which would, in turn, lead to lesser distortion of the octahedral coordination sphere. These isomers would also

be similar to the isomers that were found in every crystal of edda complexes. Yet, these isomers of $[Ga(ox)(trien)]^+$ are not observed in the crystal structure, a difference which is surprising since trien and edda are very similar ligands.

$^{13}C\{^1H\}$ and ^1H NMR spectra of a solution of [Ga(ox)(trien)]Cl + 2.75 H_2O in D_2O (pH 7.0) were examined. The $^{13}C\{^1H\}$ NMR spectrum of this compound (Figure 2.58a) features three signals of oxalic acid, either of the oxalato ligand or uncoordinated oxalate and about a dozen signals of trien. The many signals of trien indicate the existence of different complexes or complex isomers in solution. This was expected due to the experiences with [Ga(aa)(edda)] complexes. Unfortunately, despite the overall high quality of the spectrum and significantly fewer signals and lesser signal overlap when compared to spectra of [Ga(aa)(edda)] complexes, it was not possible to determine if free oxalic acid was present in solution with the information of only this spectrum. In addition, 2D NMR experiments were of no use due to the lack of C–H bonds in oxalic acid. Consequently, it was not even possible to figure out if the oxalato ligand in one $[Ga(ox)(trien)]^+$ complex isomer showed two different signals in the spectrum. While this is unlikely, it is possible since the chemical environments of the carboxylato functions do not necessarily have to be exactly similar.

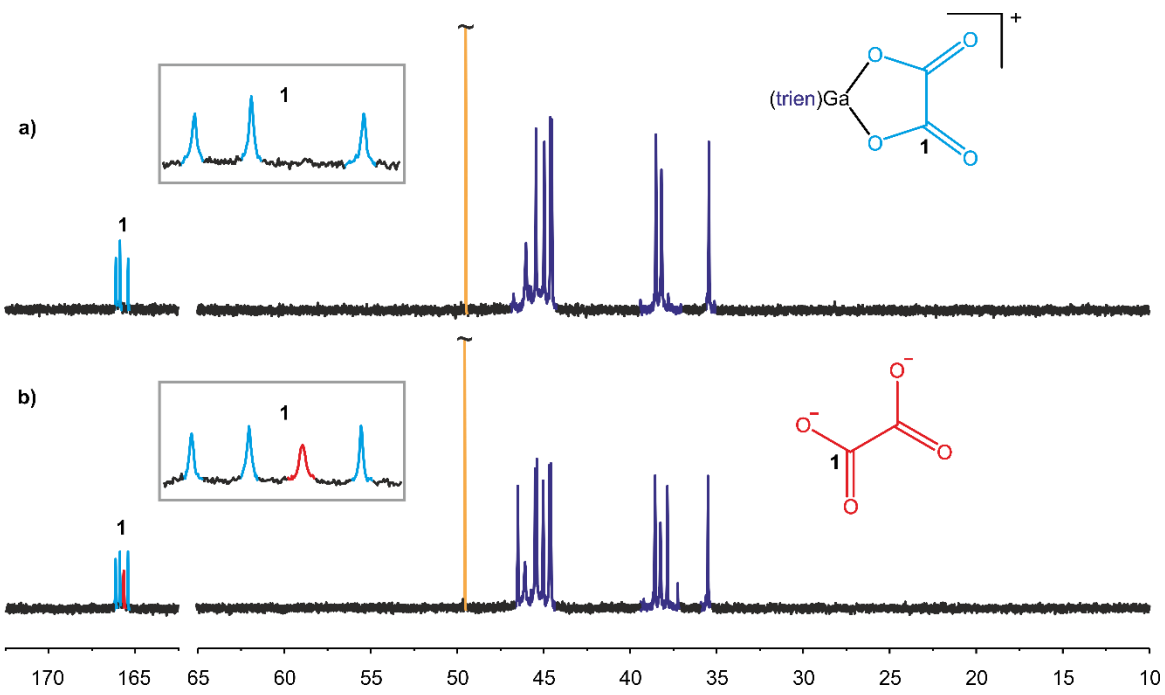


Figure 2.58: [Ga(ox)(trien)]Cl + 2.75 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: $^{13}C\{^1H\}$ NMR spectrum of [Ga(ox)(trien)]Cl + 2.75 H_2O in D_2O*, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(ox)(trien)]Cl + 2.75 H_2O with 0.25 equ. of oxalic acid in D_2O*. Cyan: oxalato in $[Ga(ox)(trien)]^+$, blue: trien in $[Ga(ox)(trien)]^+$, red: oxalate, orange: MeOH. * One drop of MeOH was added for referencing.

To at least determine if free oxalic acid is present, 0.25 equivalents (5 mg) of oxalic acid were added to the solution of [Ga(ox)(trien)]Cl + 2.75 H_2O in D_2O and the NMR spectra were re-measured.

The amount of oxalic acid had to be chosen carefully. It had to be as low as possible to not change the pH of the solution too drastically while still allowing for a discernible signal. With these measures taken, the pH of the solution still changed, but dropped only from 7.0 to 6.0. The $^{13}C\{^1H\}$ NMR spectrum of this experiment is displayed in Figure 2.58b. Indeed, with the addition of free oxalic acid, a fourth signal in close proximity to the already present signals of the oxalato ligands occurs. It is thereby proven that a solution of [Ga(ox)(trien)]Cl in D_2O does not contain free oxalic acid. Hence, the complex seems to be stable against hydrolysis at physiological pH levels.

Still, it must be mentioned that the signals of trien are not only affected by the addition of oxalic acid, but even the emergence of new signals can be observed. It seems that the change of the solution's pH only has a significant effect on the trien ligand. A probable explanation for this might be found in the pK_a values of the ligands. The pK_a of the carboxylic functions is much lower than the pK_a of the amine groups. Therefore, it seems plausible that partial protonation of the amine functions of trien and, therefore, changes in gallium(III) bonding occur while the oxalato ligand is unaffected.

In conclusion, it seems that this is the first complex synthesised in this work which is stable against hydrolysis in aqueous solution at neutral pH levels. In addition—or as a result—the complex is easy to synthesise and crystallise.

It is possible to investigate this issue further with a very similar complex. [Ga(malo)(trien)]Cl should show the same characteristics as [Ga(ox)(trien)]Cl since the only difference between the two complexes can be found in the formation of one six-membered chelate ring instead of a five-membered one. The synthesis and procedure to obtain this complex was the same as for [Ga(ox)(trien)]Cl, with the exception that the basic compound was used in excess (Figure 2.59, pH 9.0) and the product was precipitated directly by addition of organic solvents.

$$GaCl_3 + trien + H_2malo + 2\ NEt_3 \xrightarrow[-\,2\ HNEt_3Cl]{H_2O} [Ga(malo)(trien)]Cl$$

Figure 2.59: Chemical equation for the synthesis of [Ga(malo)(trien)].

According to the elemental analysis of the crude product obtained, [Ga(malo)(trien)]Cl was successfully synthesised. Unfortunately, no crystals of this compound were yielded in crystallisation experiments. Therefore, further analytical data was obtained only by NMR spectroscopy. The aqueous solutions of [Ga(malo)(trien)]Cl + 1.65 H_2O + 0.05 $Ga(OH)_3$ and [Ga(ox)(trien)]Cl + 2.75 H_2O both have a pH of 7.0 which enabled the comparison of their spectra. It should be noted that a saturated solution of [Ga(malo)(trien)]Cl was used as an NMR sample because of the low solubility of this compound in water. The $^{13}C\{^1H\}$ NMR spectrum of the aqueous solution of [Ga(malo)(trien)]Cl + 1.65 H_2O + 0.05 $Ga(OH)_3$ is shown in Figure 2.60. Just as in the spectrum of [Ga(ox)(trien)]Cl + 2.75 H_2O, about a dozen signals of trien are visible. Therefore, different complex isomers or complexes must be present. In contrast to the spectrum of [Ga(ox)(trien)]Cl + 2.75 H_2O, the signals of the malonato ligand are broadened clusters. This indicates the existence of different complex isomers, but does not enable their identification. However, no signal of free malonate is visible, hence it seems that the complex is stable against hydrolysis in aqueous solution, just as the $[Ga(ox)(trien)]^+$ complex. Since this characteristic was found for two similar complexes, the conclusion concerning their stability could be reached with more confidence.

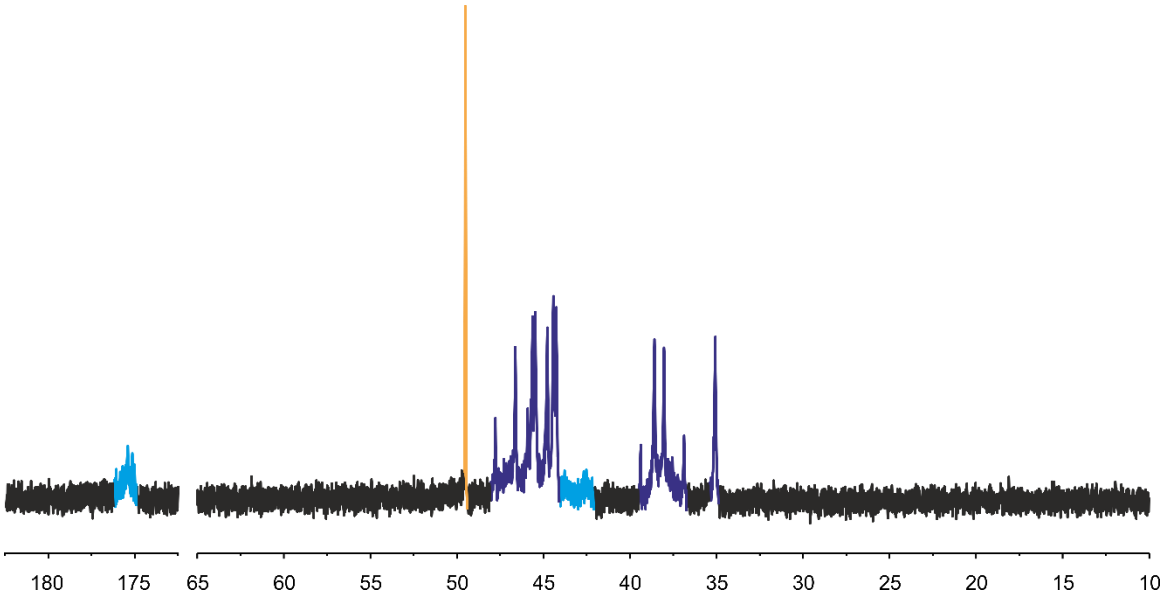


Figure 2.60: $^{13}C\{^1H\}$ NMR spectrum of [Ga(malo)(trien)]Cl + 1.65 H_2O + 0.05 $Ga(OH)_3$ in D_2O*. Cyan: malonato in $[Ga(malo)(trien)]^+$, blue: trien in $[Ga(malo)(trien)]^+$, orange: MeOH. * One drop of MeOH was added for referencing.

As stated earlier, some experiments with a combination of hydroxycarboxylic acids—for example L-malic acid—and trien were performed. The synthesis of [Ga(Hmal)(trien)]Cl was

done by reacting stoichiometric ratios of starting materials (Figure 2.61), while the amount of triethylamine proved to be excessive for the obtained product. According to elemental analysis, [Ga(Hmal)(trien)]Cl was contaminated with water, ethanol and gallium(III) hydroxide and therefore by no means pure.

$$GaCl_3 + trien + H_3mal + 2\ NEt_3 \xrightarrow[-2\ HNEt_3Cl]{H_2O} [Ga(Hmal)(trien)]Cl$$

Figure 2.61: Chemical equation for the synthesis of [Ga(Hmal)(trien)]Cl.

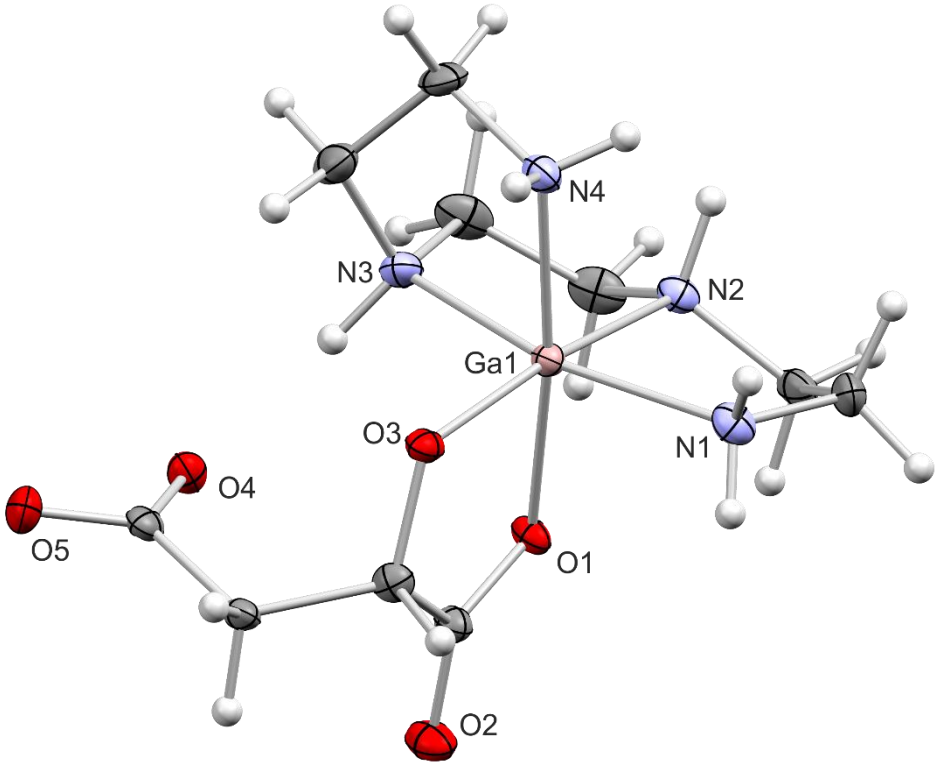


Figure 2.62: Plot of [Ga(mal)(trien)] in crystals of **5d**·3H$_2$O. Space group: $P2_1$. CShM$_{OC-6}$: 0.870. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.068(6), Ga1–N2 2.109(5), Ga1–N3 2.090(5), Ga1–N4 2.054(4), Ga1–O1 2.002(3), Ga1–O3 1.907(5), N1–Ga1–N3 162.3(2), N2–Ga1–O3 170.3(2), N4–Ga1–O1 172.8(2), N2–Ga1–N3 81.1(2), N1–Ga1–O3 99.9(2), N3–Ga1–O3 97.7(2), N4–Ga1–O3 93.5(2), O1–Ga1–O3 84.7(2).

Crystallisation experiments with this raw product in a mixture of methanol and water yielded crystals, but those were comprised of [Ga(mal)(trien)]. The molecular structure of this complex is very similar to the structure of [Ga(ox)(trien)]$^+$. It features an isomer similar to isomer **III** of the oxalato complex (Figure 2.57). Hence, trien is, once again, not coordinated in a C_2-symmetric fashion. The distortion of the octahedral GaN_4O_2

coordination is slightly lower than in $[Ga(ox)(trien)]^+$ and the interatomic distances and angles of [Ga(mal)(trien)] are in the expected range.

The difference between the crystalline compound and the crude product concerning its composition caused problems when it came to the reliable synthesis of a specific compound and a potential NMR-spectroscopic analysis, since differing protonation states of a functional group can cause chaotic spectra. In combination with the fact that the malato ligand can bind to gallium(III) in two different ways—resulting in the potential formation of twelve different isomers of [Ga(mal)(trien)]—the interpretation of spectra is not a feasible task.

However, the compound is soluble at neutral pH levels and malic acid is non-hazardous[53], wherefore it might still be applicable as a pharmaceutical. In general, it seems that experiments with further hydroxycarboxyliato ligands in combination with tetradentate amine ligands might be a promising endeavour.

2.6 HDIPEA[Ga(edda)(malo)]

The successful use of aminecarboxylato, amine and dicarboxylato ligands to form gallium(III) complexes pointed to even more possible ligand combinations. For example, the combination of the tetradentate ligand edda with a dicarboxylato ligand has not been tried yet. This mix of ligands should lead to the formation of a monoanionic octahedral complex which is, therefore, comparable to the $[Ga(aa)(nta)]^-$ complexes. As described before, the replacement of nta with edda while still obtaining a monoanionic complex is advantageous as edda—in contrast to nta[45]—is not classified as potentially carcinogenic. To obtain HDIPEA[Ga(edda)(malo)], the ligands and $GaCl_3$ were used in stoichiometric ratios and the basic compound was used in excess (Figure 2.63, pH 8.0).

$$GaCl_3 + H_2edda + H_2malo + 4\ DIPEA \xrightarrow[-\,3\ HDIPEACl]{H_2O} HDIPEA[Ga(edda)(malo)]$$

Figure 2.63: Chemical equation for the synthesis of HDIPEA[Ga(edda)(malo)].

The procedure was done in the already established manner and the elemental analysis indicated that the target compound was obtained. According to this analysis, the target complex was formed with a small amount of residual water still present in the product: HDIPEA[Ga(edda)(malo)] + 0.95 H_2O. The maximum difference between the found and calculated percentages of this composition is 0.10.

To crystallise HDIPEA[Ga(edda)(malo)], an aqueous solution of the raw product was stored over dimethyl sulfoxide for one month. As can be seen in the plot of the complex salt (Figure 2.64), the octahedral GaN_2O_4 coordination is slightly distorted. This is backed by the distances and angles between gallium(III) and the nitrogen and oxygen atoms of the ligands, which are in the expected range. The complex isomer in the crystal structure is one of four possible isomers. Also, the binding pattern of edda is C_2-symmetric and, therefore, equivalent to those found in molecular structures of [Ga(aa)(edda)] complexes.

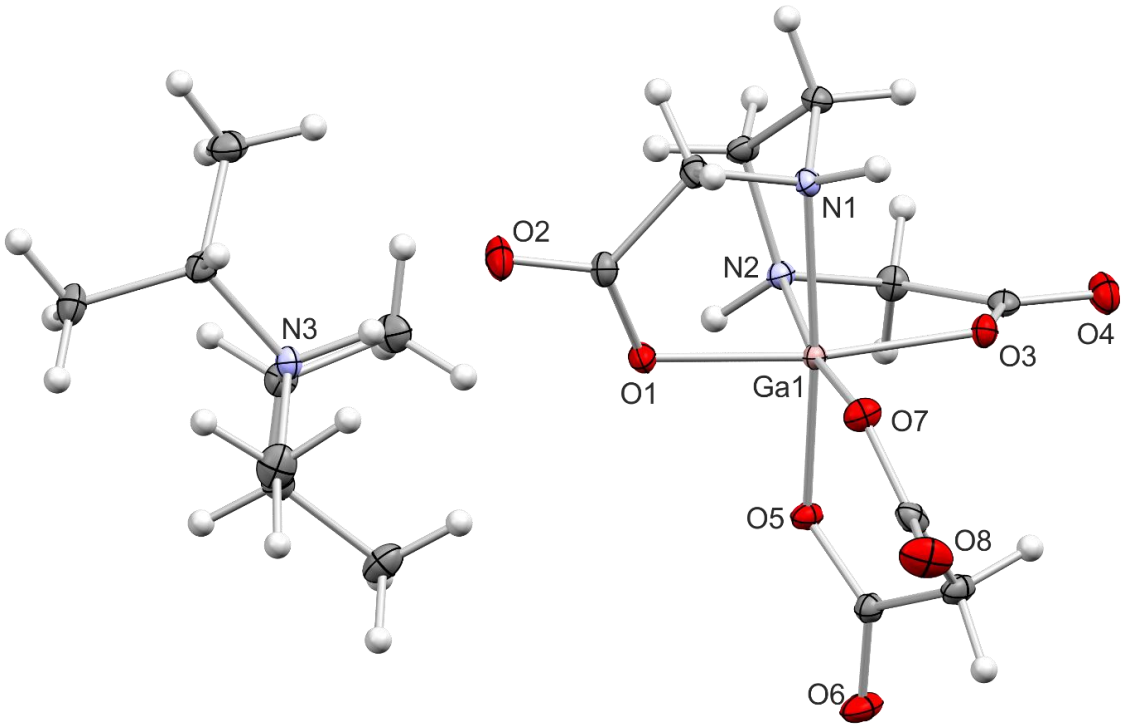


Figure 2.64: Plot of HDIPEA[Ga(edda)(malo)] in crystals of (HDIPEA)**3k**·H_2O. Space group: $P\bar{1}$. $CShM_{OC-6}$: 0.233. The thermal ellipsoids are drawn at 50% probability. Interatomic distances (in Å) and angles (in °) with standard deviation of the last digit in parentheses: Ga1–N1 2.0764(9), Ga1–N2 2.0933(9), Ga1–O1 1.9635(8), Ga1–O3 1.9855(8), Ga1–O5 1.9377(8), Ga1–O7 1.9231(8), N1–Ga1–O5 174.56(4), N2–Ga1–O7 172.10(4), O1–Ga1–O3 171.33(3), N2–Ga1–O3 82.15(4), N2–Ga1–O5 91.78(3), O1–Ga1–O5 92.23(3), O3–Ga1–O5 93.62(3), O5–Ga1–O7 93.95(3), N3–O2 2.7643(13).

The result of this experiment confirms that further combinations of ligands which were already used in this work are feasible to obtain new gallium(III) complexes.

3 Discussion

3.1 Applicability and validity of analytical methods

Different analytical methods were tried in the course of this work and most of them were dismissed as not expedient. As described in subsection 2.2.6, techniques like UV-Vis and IR spectroscopy as well as potentiometric titration were ruled out as sensible methods for the examination of gallium(III) complexes in solution.

UV-Vis and IR spectroscopy were also not applicable for the analysis of solid compounds since the problems encountered in solution and in the solid state are identical. In addition, mass spectrometry was unsuccessfully tried with different compounds. This led to the use of elemental analysis as a first method for characterising product compositions, despite its obvious shortcomings. With the help of the online-program *JASPER*, even contaminated products—which was the usual case—were analysable. However, the interpretation of those product compositions would have remained dubious without X-ray diffraction experiments with single crystals.

X-ray diffraction experiments were, to a large extent, only used to prove the existence of the respective compound as this was one of the main goals of this work. Since solution studies showed the presence of equilibria between different compounds in aqueous solution, the crystallisation of a specific compound is largely dependent on its solubility and not necessarily on its superior stability when compared to other compounds in solution. Hence, molecular structures of complexes are used only to discuss preferences in the formation of certain complex isomers if those are striking.

The combination of these two analytical methods already led to quite accurate impressions about the composition of aqueous solutions of gallium(III) compounds. With the use of NMR spectroscopy, these assumptions were consolidated and enhanced. In general, most compounds were very soluble in water, a very positive aspect which allowed for a combination of elemental analysis, X-ray diffraction experiments and NMR spectroscopy. This was a reasonable mix of methods to obtain comprehensive information about most compounds. That being said, a more in-depth look into the NMR-spectroscopic analyses is appropriate due to some challenges that are faced when gallium(III) complexes are examined with this method.

3.2 Aqueous solutions of gallium(III) complexes: NMR studies

NMR-spectroscopic analyses of gallium(III) complexes are challenging in general. One reason is found in the overall small CIS gallium(III) causes in the ligands. For that reason it is not easy to determine if a ligand is bound to gallium(III) or not and NMR spectra of gallium(III) complexes quickly become inconclusive without the possibility of exact referencing. If signals of free and bound ligand exist simultaneously, their signals are found in close proximity which impedes the interpretation of 2D NMR spectra to some extent. Still, the existence of both bound and free ligand is not only a disadvantage as described later on.

Measuring different NMR-active nuclei was tried as an option to circumvent the problems caused by the low CIS. However, ^{14}N NMR spectra proved to be inconclusive due to broad indistinguishable signals in the spectra. Without using ^{15}N labelled ligands, nitrogen based NMR spectroscopy is not possible with these compounds. A further potential approach was to use ^{71}Ga and ^{69}Ga NMR spectroscopy. Unfortunately, these spectra proved to be inapplicable to characterise or even distinguish different octahedral complexes in solution. The signals in these spectra are broadened to such an extent that they are no longer visible. This problem was encountered with gallium(III) complexes before.[54]

In this work, NMR-spectroscopic examinations were, therefore, done by measuring ^{13}C{^{1}H} and ^{1}H NMR spectra in combination with DEPT135, ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-HMQC and ^{1}H-^{13}C-HMBC. The spectra of compounds in D_2O were always referenced against methanol to provide precise absolute values of chemical shifts and enable their assignment.

These efforts allowed a reasonable interpretation of most spectra. When it came to the analysis of their NMR spectra, one major advantage of most complexes in this work was their limited stability in aqueous solution. This seems counterintuitive at first, but it does eliminate the problems caused by the small CIS of gallium(III) to some extent. Due to the fact that ligands are present both in their free form and bound in a gallium(III) complex, discernible signals of both are visible in the spectra. Therefore, even tiny coordination-induced shifts are identifiable and the formation of the complexes can be confirmed more easily. This would have not been possible by just comparing spectra of the complexes with those of free ligands, as in many cases the error would have been bigger than the CIS. To get the same effect in solutions of stable complexes, excess ligand would have to be added.

Different examples in this work have shown that the pH level of the solution has a significant effect on the signals and the chemical shifts in NMR spectra. The signal shifts are dependent on the pH level in solution, as is the position of the equilibrium. Therefore, spectra of different compounds are comparable only if the pH levels are approximately equal.

The solvent in use also proved to have a major effect on the NMR spectra. A solution of $[Ga(ala)(nta)]^-$ in MeOD shows no equilibrium (Subsection 2.2.6). This is due to the absence of water/D_2O which would act as both solvent and reactant in the equilibrium reaction. However, the position of the equilibrium is affected even by the small amounts of methanol which are added to aqueous solutions to allow for proper referencing. It seems that the change of the solutions' polarity already has a significant effect on the equilibria. This has to be kept in mind when ratios of compounds in equilibria are discussed. Without the addition of methanol the equilibria are slightly shifted to the side of the hydroxido-bridged complexes. It would have been possible to separate the sample and the reference by the use of methanol-filled capillaries, however this would have led to lower resolutions of the spectra.

If the addition of triethylamine is necessary to obtain analysable solutions, the spectra are drastically altered as well. Not only does triethylamine raise the pH of solution, it also changes its polarity, both affecting the shift of signals as well as the equilibria.

In summary, the use of NMR spectroscopy to gain information about the gallium(III) complexes of this work is feasible. However, a high level of accuracy is needed to reach reliable conclusions. In addition, the solvent in use and the pH of the solutions have huge impacts on the position of the equilibria and the quality of the analyses.

3.3 Aminecarboxylato complexes

3.3.1 Gallium(III) complexes with aa ligands

The synthesis and characterisation of complexes with aa ligands was a major focus of this work. As mentioned in section 1.4, only two crystal structures with aa ligands coordinated to gallium(III) were available before.[36,37] Since those complexes were obtained under inert conditions and feature a tetrahedral coordination sphere, they are not equivalent to gallium(III) complexes with aa ligands synthesised under non-inert or aqueous conditions.

The latest publication on the topic of gallium(III) complexes with bidentate aa ligands suggested that octahedral [Ga(aa)$_3$] complexes are formed.[34] However, no molecular structures of such compounds have yet confirmed this hypothesis.

In order to change this, the synthesis and crystallisation of [Ga(gly)$_3$] from aqueous solution was tried. While crystals of [Ga(gly)$_3$] (**1b**) were obtained by chance, the direct synthesis of this complex by using stoichiometric amounts of starting material was not possible (Section 2.1) and, instead, resulted in the formation of [{Ga(gly)$_2$(μ-OH)}$_2$]—contaminated with unreacted glycine—which was subsequently crystallised (**1a**). Hence, the first molecular structures of octahedral complexes with Ga(aa)$^{2+}$ fragments were obtained, but the synthesis of [Ga(aa)$_3$] compounds proved to be not as straightforward as expected. This led to the utilisation of co-ligands in combination with aa ligands in order to generate more information about the chemistry of gallium(III) in combination with aa ligands.

Complexes with a combination of bidentate aa ligands and tetradentate ligands—nta and edda—were synthesised, characterised and, in some cases, crystallised. Thereby, molecular structures of nine different [Ga(aa)(nta)]$^-$ and eight different [Ga(aa)(edda)] complexes and complex isomers were obtained by re-crystallising raw products of the respective complexes from aqueous or methanolic solutions or mixtures of methanol and water under non-inert conditions. However, not only the target complexes were obtained. Frequently only crystalline AA or hydroxido-bridged di- and hexanuclear complexes [{Ga(nta)(μ-OH)}$_2$] and [{Ga(edda)(μ-OH)}$_n$] were crystallised. In addition, the yields of target complexes by crystallisation were low in most cases. NMR-spectroscopic analyses of aqueous solutions of those compounds showed that equilibrium reactions between the target complexes, free AA and the hydroxido-bridged complexes exist. The equilibrium reaction explains the different compounds obtained in crystallisation experiments.

In the equilibria, water is not only the solvent, but also a reactant. Hence, the concentration of [Ga(aa)(nta)]$^-$ and [Ga(aa)(edda)] solutions has a significant effect on the composition of such solutions. In hindsight, this explains why precipitating the target complexes by addition of organic solvents is, in most cases, an effective procedure only if done slowly. The addition of the solvent leads to a shift of the equilibrium to the side of the target complexes and, with rising concentration, to the precipitation of these compounds. The equilibrium reaction is also influenced by the pH of the solutions. A slight excess of basic compounds leads to higher yields since it results in a higher ratio of the target complex in solution.

This might also explain why the complex formation with L-tyrosine as a ligand was not successful with the otherwise effective procedure. The solubility of this specific AA is very

low, even in water.[41] Presumably, the addition of organic solvent leads to precipitation of L-tyrosine and not the target complex, which, in turn, affects the equilibrium and results in the formation of more L-tyrosine. Eventually, no target complex is left in solution, and the precipitate contains mostly L-tyrosine.

Since aqueous solutions of gallium(III) complexes with aa ligands were found to feature free AA and bound aa ligand, it is reasonable to assume that this happens in solutions with gallium(III) complexes which feature only aa ligands as well. Therefore, the attempt to synthesise $[Ga(aa)_3]$ from aqueous solution might result in the formation of product mixtures. In particular, the formation of a hydroxido-bridged dinuclear complex while free aa ligand remains might even be favoured. This was encountered when glycine was used. Hence, it seems reasonable to assume that homoleptic $[Ga(aa)_3]$ complexes are not stable against hydrolysis in aqueous solutions, which might cause the problems in the synthesis of well-defined products and with the crystallisation of target complexes.

If the solubilities of starting materials allow for it, the synthesis of $[Ga(aa)_3]$ complexes as well as other complexes featuring aa ligands should be favoured in non-aqueous media like methanol or ethanol. This was discarded as a viable option at the beginning of this work, since first tests showed that the use of water as a solvent was more promising and practicable.

All the data suggests that the formation of polynuclear species with hydroxido bridges between gallium(III) centres is a significant competing reaction in aqueous solutions at neutral pH levels when aa ligands are involved. If water is present, especially in excess, the chelating effect of bidentate and tridentate aa ligands cannot prevent the formation of such species. This phenomenon was not described before, and renders the applicability of such compounds as pharmaceuticals questionable. A more detailed discussion of this issue and a comparison with other ligands is found in section 3.6.

Finally, it should be mentioned that the NMR-spectroscopic studies of gallium(III) complexes with aa ligands in aqueous solutions did show characteristics which are potentially useful for future investigations of such complexes. As discussed in subsection 2.4.2, the signal of the C2 atom of an aa ligand in the $^{13}C\{^1H\}$ NMR spectrum is almost always shifted to high field when coordinated to gallium(III), while the signal of the carboxylato function is shifted to low field. In combination with the fact that the signals of bound aa ligands are less sharp than those of free aa ligand in most cases, even mixtures of different aa ligands in combination with gallium(III) might be interpretable by NMR spectroscopy. If this analytical approach is chosen, the purity of the tested samples is key and compositions need to be determined, for example, by using elemental analysis as a

second analytical method.

3.3.2 Stability of aminecarboxylato complexes

With the issues of bidentate aa ligands established, a closer look at the other aminecarboxylato ligands and their characteristics is necessary.

The two tetradentate ligands nta and edda were, without exception, bound to gallium(III) (Sections 2.2 and 2.3). This stable bonding to gallium(III) can be explained by the chelating effect, but might also be due to the fact that it is not necessary to separate these ligands from the gallium(III) centre in order to form hydroxido-bridged gallium(III) complexes. Since the hydroxido ligands in such complexes are bound *cis* to each other, even if no tetradentate ligands are present (Section 2.1), four binding sites seem to be unaffected in general. Therefore, the only potential competing reactions with the binding of the utilised tetradentate ligands is the formation of gallium(III) hydroxide or the formation of complexes with the bidentate ligands instead, which is highly unlikely and indeed not observed. A further property which might factor into the bonding stability of the tetradentate ligands is the location of the amine function in the ligand. If the carboxylate functions are bound to the positively charged gallium(III) centre, the amine functions are forced to bind to gallium(III) as well due to their resulting close proximity to gallium(III). Simultaneously, the binding of another ligand in the specific position is prevented through steric hindrance.

This might explain the issues encountered when the tridentate aa ligands asp and his are used in combination (Section 2.4). In case of the histidinato ligand, the amine functions are not necessarily forced to bind when the carboxylate function is bound to the gallium(III) centre. Also, the formation of dinuclear complexes with bridging asp ligands was observed when D-his and asp were used in combination. Therefore, the formation of dinuclear complexes is possible even without hydroxido-bridges. The bridging behaviour of the asp ligand may be favoured since only one instead of two six-membered chelate rings has to be formed this way.

However, hydroxido-bridged complexes were also formed with this ligand combination since free aa ligands are present in aqueous solution according to NMR spectroscopy. As stated before, only four binding sites were shown to be unaffected when hydroxido ligands are bound to gallium(III). The chelating effect of tridentate ligands seems to not be strong enough to overcome the tendency of forming hydroxido-bridged complexes. At first, combinations of tridentate aminecarboxylato ligands were thought to be more stable than

combinations of tetra- and bidentate ligands. However, this is, at least, not the case when only tridentate aa ligands are used. In basic solutions of [Ga(his)(ida)], a comparable complex, no free ligand seems to be present. Unfortunately, it was not possible to obtain conclusive NMR-spectroscopic data of this complex, hence the bonding of the more symmetric tridentate ligand ida to gallium(III) cannot be further analysed. Subsequently, the assertion that the use of ida instead of asp is beneficial for complex formation cannot be made, especially since an examination at neutral pH levels was not possible.

In conclusion, hydroxido-bridged gallium(III) complexes seem to form in aqueous solutions whenever bi-, tri- or tetradentate aminecarboxylato ligands are used. Ligand combinations, which are not solely comprised of aminecarboxylates, might not show this behaviour. The synthesis and crystallisation of HDIPEA[Ga(edda)(malo)] (Section 2.6) proved that such complexes are feasible. This issue was not further examined in this work, but might be an interesting topic for future investigations.

3.3.3 Crystallisation of complexes: the influence of the counter-ion

A peculiar characteristic of $[Ga(aa)(nta)]^-$ complexes was encountered when trying to replace the tertiary ammonium ions with alkali cations to potentially reduce disorder in crystal structures (Subsection 2.2.5). The elemental analyses showed that the target complexes were, indeed, formed after a simple cation exchange reaction with CsOH, however most of the products did also contain the dinuclear complex $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$, sometimes even as the main component. Re-crystallisation of such products did not yield Cs[Ga(aa)(nta)] compounds. Instead, only crystals of free aa ligands or $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ were obtained. Since tests with further alkali cations did not indicate a different outcome, the substitution of the tertiary ammonium ions was not pursued. However, these results were a main reason for in-depth solution studies by NMR spectroscopy of $[Ga(aa)(nta)]^-$ complexes. With the data gathered the appearance of $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ in experiments with caesium cations can be explained.

An equilibrium between the targeted $[Ga(aa)(nta)]^-$ complexes and the dinuclear complex as well as free aa ligand is present in the reaction mixture. The target compounds as well as the dinuclear complex salt $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ are almost insoluble in organic solvents. Therefore, even slow addition of ethanol to such reaction mixtures leads to precipitation of both the target complexes and the dinuclear complex. If tertiary ammonium

cations are present instead of the alkali cations, the addition of organic solvent leads to a shift of the equilibrium to the target complex first, followed by the precipitation of these.

Throughout this work, $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ compounds with tertiary ammonium cations were not crystallised. In contrast, $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ crystallised readily and apparently better than any Cs[Ga(aa)(nta)] compound. This may be due to the ionic bond network in crystals of $Cs_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ which cannot be formed with tertiary ammonium cations. Therefore, crystallisation experiments with the product mixtures yielded only crystals of the dinuclear complex while no target complexes were crystallised.

3.4 Amine complexes

As complex formation with aminecarboxylato ligands was possible, combinations of amine and carboxylato ligands were also examined. While experiments with tren as a ligand were done only as a proof of concept due to its toxicity, the ligand trien was seen as a viable option to meet every requirement set as a goal in this work. It is considered non-toxic when applied orally[50] and is already used as a chelating agent for copper(II) to treat Wilson's disease[51,52]. In addition, it has been shown that trien can be used in the treatment of cancer[52].

As shown in section 2.5, the synthesis and crystallisation of compounds like [Ga(malo)(tren)]Cl, [Ga(ox)(trien)]Cl and [Ga(mal)(trien)] is possible. Furthermore, according to NMR-spectroscopic studies, the complexes [Ga(ox)(trien)]Cl and [Ga(malo)(trien)]Cl were stable against hydrolysis at neutral pH levels, which is a decisive difference when compared to the aminecarboxylato complexes examined in this work. While only a few experiments with such ligand combinations were done, the results are intriguing and further investigation of such compounds seem promising, for example with combinations of amine and hydroxycarboxylato ligands. However, one shortcoming of trien as a ligand is the range of different complex isomers it can form. This limits the significance of NMR spectroscopy, and may cause problems concerning the formation of distinct complexes. If pharmacological applications of complexes are targeted, the toxicity of many amines does limit the variety of potential ligands. Hence, further experiments with trien may be advised despite potential analytical problems with this ligand.

3.5 Stability and binding patterns: GaN_xO_y

The molecular structures of complexes presented feature different gallium(III) surroundings: $GaNO_5$, GaN_2O_4, GaN_3O_3 and even GaN_4O_2. It would be advantageous for the future design of gallium(III) complexes if the stability of complexes were directly dependent on the respective gallium(III) environment.

The quantity of each different gallium(III) surrounding in this work is not meaningful, as the complexes were obtained via the use of specific ligand combinations and, thereby, their formation was to some extent forced. However, the fact that different gallium(III) surroundings are possible already indicates that these may not influence the stability of complexes to such an extent that they are the only important factor. Direct evidence of this can be found in the equilibria in aqueous solutions: equilibria between $[Ga(aa)(nta)]^-$ complexes and $[\{Ga(nta)(\mu\text{-}OH)\}_2]$ feature GaN_2O_4 and $GaNO_5$ binding patterns. The ratio of these complexes in solution is influenced by different effects, for example the concentration or the pH level (Section 3.3). Due to the different influences, it is not possible to determine if the binding patterns have any impact in these cases. At least, no strong preference for one of the gallium(III) surroundings could be observed. The same reasoning can be applied to the equilibria between [Ga(aa)(edda)] and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ complexes which feature GaN_3O_3 and GaN_2O_4 environments. If anything, the [Ga(aa)(edda)] complexes with GaN_3O_3 binding patterns seem to be less favoured in the equilibria. This might be due to the steric requirements of edda in addition to the aforementioned influences. The difference in ratios is also not prominent enough to allow for even a tentative hypothesis in this regard.

In addition, NMR-spectroscopic analyses of the complexes [Ga(ox)(trien)]Cl and [Ga(malo)(trien)]Cl with GaN_4O_2 surroundings indicate that those are stable in aqueous solutions at neutral pH levels (Section 2.5) which would imply that more nitrogen in the vicinity of gallium(III) is beneficial for the stability of such complexes. This also matches a statement of Petrosyants[38] who mentions that gallium(III) has a tendency to form complexes with a GaN_4O_2 environment. However, it is not possible to say whether this statement is true under every circumstance. For example, the NMR spectra of [Ga(Hmal)(trien)]Cl (Section 2.5), a further complex featuring a GaN_4O_2 binding pattern, show the existence of so many different species that no sensible assignment of signals is possible. This is caused by the tridentate malic acid bound as a bidentate ligand. Hence, the potential formation of different complexes and many different complex isomers leads to insignificant data and prevents the determination whether a specific binding pattern is

preferred. The current state of research does not allow a definite hypothesis, but it may be possible that the double negative charge of the bidentate ligands ox, malo and mal in combination with a tetradentate neutral ligand is advantageous for the stability of these complexes.

It should be mentioned that further experiments with different ligand combinations from those shown were done. In some of these attempts of synthesis—with procedures similar to those in this work—the target complexes would have carried a double negative charge. As those attempts were not successful and resulted in non-interpretable results, they are not displayed. A similar issue was encountered with acidic aa ligands in section 2.2. It seems that the resulting charge of the complex is an important factor when it comes to the formation of gallium(III) compounds, especially when the synthesis is done in aqueous media at close to neutral pH levels. Whenever possible, a charge higher than minus one seems to have been omitted by formation of different compounds. This is easy to achieve in aqueous solution, as hydroxido-bridging is possible. Also, the formation of five-coordinated gallium(III) complexes is an option.

While the results of this work are by no means extensive enough to allow for definite assertions, some tentative advice concerning the successful syntheses of gallium(III) complexes in aqueous solutions can be given. In approximately neutral solutions, charges of the target complexes should be neutral or +/− 1. Also, GaN_4O_2 binding patterns seem to be advantageous for the stability of the complexes in general. If amine functions are present, those should be part of the ligand with higher denticity to ensure that the bond formation is complete, as bidentate aminecarboxylato ligands are prone to ligand exchange reactions with hydroxido ligands. To ensure that a bidentate ligand is bound, two anionic functions seem to be beneficial. However, this is not always necessary. Literature about, for example, tris(maltolato)gallium(III) and tris(8-hydroxychinolinato)-gallium(III) shows that these are, most likely, entirely stable in aqueous solution at neutral pH levels.[55] Finally, it seems that the formation of more than one six-membered chelate ring is avoided if possible. This should be kept in mind, especially when the reaction mixtures allow for various ligand combinations.

3.6 Applicability of synthesised compounds as pharmaceuticals

Currently it is possible only to evaluate which compounds might feature the necessary characteristics to be applicable as therapeutic agents, since, so far, no pharmaceutical tests of the synthesised compounds have been carried out.

The stability of compounds in aqueous solutions is important for therapeutic applicability. As already outlined in the introduction, complexes should be stable enough to keep gallium(III) in solution, hence the formation of gallium(III) hydroxide must be prevented. This can be phrased in another way: If gallium(III) hydroxide is formed instead of the target complex or as a sizeable concurring product, the combination of ligands in use is not suitable for the intended purpose. The persistent presence of solid during the synthesis was therefore avoided if possible to rule out the formation of gallium(III) hydroxide. However, sometimes gallium(III) hydroxide was found as a contaminant in raw products. This indicated that the reaction conditions for the synthesis of the target complexes were not optimised. If aqueous solutions of raw products did not show the formation of precipitate after the removal of gallium(III) hydroxide, the compounds are nevertheless stable enough to not degrade to gallium(III) hydroxide. In general, if aqueous solutions of gallium(III) compounds did not show the formation of precipitate over time at neutral pH levels, a first stability requirement was met.

Most gallium(III) complexes shown in this work fulfil this demand. However, certain exceptions have to be mentioned. The solubility of some complexes at neutral pH levels was too low for a proper NMR-spectroscopic analysis. Thus, no assertions concerning their stability at neutral pH levels are possible. While the very low solubility of some complexes hinders meaningful solution studies, it is not necessarily a criterion which, in itself, renders such compounds inapplicable as pharmaceuticals. Tris(maltolato)-gallium(III) and tris(8-hydroxyquinolinato)gallium(III) exhibit very low solubility in aqueous solutions, yet those are the gallium(III) complexes which are described as most promising in clinical trials.[24,55]

Only one successfully synthesised complex shown in this work definitely does not fulfil the minimal stability criterion. As mentioned (Subsection 2.2.7), $[Ga(cys)(nta)]^-$ is not stable in aqueous solution due to the degradation of L-cysteine.

Hence, with the exception of this compound, every other compound examined might be applicable as a therapeutic agent. However, there are further requirements which should be fulfilled. For example, to allow for oral application, it seems that the compounds should

be stable in aqueous solution. The biodistribution of tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III) is speculated to be rooted in their stability.[55] Whenever aa ligands are involved in complex formation (Section 3.3) the resulting complexes are not stable against hydrolysis. Only [Ga(ox)(trien)]Cl, [Ga(malo)(trien)]Cl and possibly the hydroxido-bridged species $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ might fulfil this requirement. The latter are, however, multinuclear species, a characteristic not shared with tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III). Hence, out of all compounds examined, [Ga(ox)(trien)]Cl and [Ga(malo)(trien)]Cl might be the most promising options for pharmacological applications.

In addition to oral administration, some tests regarding the antimicrobial use of gallium(III) compounds were done by releasing gallium(III) locally[56] or intravenously[25]. In both cases, the use of gallium(III) nitrate in such experiments has been reported. Since gallium(III) nitrate forms gallium(III) hydroxide in aqueous solutions[8,21], gallium(III) complexes which fulfil the minimal stability requirements might still be applicable and would keep gallium(III) in solution more efficiently when compared to those compounds. Hence, most complexes shown in this work might raise the bioavailability of gallium(III) when compared to more simple gallium(III) salts, presumably just not via oral administration.

There are, of course, further characteristics of gallium(III) compounds which have an impact on their applicability as pharmaceuticals. Throughout chapter 2, the search for non-hazardous compounds was outlined and described as an important matter. One of the main reasons to examine proteinogenic amino acids as ligands in detail is that they are endogenous. Hence, they are non-hazardous ligands, which would be a favourable characteristic for gallium(III) complexes used as pharmaceuticals. As described in section 1.3, the therapeutic effect of gallium(III) compounds is based entirely on the reactions of gallium(III). The ligands are released in the process, therefore toxic or carcinogenic ligands are disadvantageous. This is also true for counter ions, if present. As mentioned before, nta is potentially carcinogenic and tren as well as the cations $HNEt_3^+$ and $HDIPEA^+$ are hazardous.[43-45] The tetradentate ligands edda, which is not yet classified, and trien, which is considered non-toxic when applied orally and not classified as carcinogenic[50], might be applicable. Also, the bidentate ligands ox[57], malo[58] and mal[53] as well as all aa ligands are non-toxic and not carcinogenic. In the case of the tridentate ligand ida[59], just as with edda, no data to classify its toxicity is available. As mentioned, trien is already used pharmacologically as a chelating agent, therefore complexes containing this ligand might be the most promising option of the compounds examined.

3.7 Complex isomers

In section 2.2, the two complex isomers **I** and **II** (Figure 2.6) were shown to exist and discussed to some extent. In isomer **I**, the nitrogen atom of the aa ligand and the nitrogen atom of nta are coordinated trans to each other, while the oxygen atom of the aa ligand is coordinated trans to the nitrogen atom of nta in isomer **II**. Only one crystal structure of $[Ga(aa)(nta)]^-$ complexes contained isomer **II,** while isomer **I** was found in 13 different crystal structures. Since only one molecular structure of isomer **II** is available, the informative value which can be obtained by comparison with isomer **I** is limited.

As shown extensively in section 2.2, an equilibrium with free AA and $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$ on one side and the target complexes on the other is present in aqueous solutions of the nitrilotriacetatogallium(III) complexes. Those solutions usually display only one signal set of the aa ligand. Though, in very few cases (Subsections 2.2.6 and 2.2.8), a second signal set of an aa ligand is visible. The intensity of this signals set is low, and it can be identified with certainty only in two NMR spectra of aqueous solutions (Figure 2.28 and Figure 2.29). Due to its rare occurrence—and the lack of a sensible different option—this signal set was assigned to isomer **II**, since this is the isomer which is the most uncommon in crystal structures. While this assumption seems reasonable, it is unfortunately not possible to prove its validity. However, this hypothesis would explain the low abundancy of isomer **II** in crystal structures, as it is already practically non-existent in solution.

Regardless of signal assignment, one of the two isomers is formed in vastly superior amounts in every case. The investigations of solutions and crystalline compounds indicate that one isomer is formed to only very small, most of the time even undetectable, amounts. To reach such a high disparity, a substantial difference between the two isomers is expected. However, according to the characteristics of the crystal structures, the preferred occurrence of isomer **I** seems to not be rooted in the properties of the crystalline compounds. The molecular structures do not show significant steric hindrance in one of the two potential isomers. When comparing isomer **I** and **II** found in molecular structures of $[Ga(met)(nta)]^-$, isomer **II** actually features a higher distortion of the octahedral coordination sphere of gallium(III), however the difference seems to be too small to have such a significant impact (Subsection 2.2.4). Subsequently, a calculation with *ORCA** based on the molecular structure of $[Ga(gly)(nta)]^-$ was carried out to get information about the stability of both isomers. However, the difference between the isomers **I** and **II** was

found to be only 3 kJ/mol with isomer **I** being slightly more stable. This is not enough disparity to explain such a significant difference in complex formation.

It seems that a mechanistic cause is the most reasonable explanation for the preferred formation of one isomer. However, no intermediates of the reaction were identifiable, neither by NMR spectroscopy nor by X-ray diffraction experiments, therefore it is impossible to propose a proper reaction mechanism. Since this issue is not important for the scope of this work, no further efforts were made to find an explanation.

It should be noted that the occurrence of different isomers was not only a concern with nta but with edda and trien as well. As the latter two ligands enable the formation of many different isomers, no assignment of signals in NMR spectra to specific isomers was possible. In crystal structures, two different binding patterns of both ligands were found. While molecular structures of edda complexes featured only the C_2-symmetric binding pattern (Section 2.3), trien was found only in the non-C_2-symmetric binding pattern (Section 2.5). This is curious, since both ligands can potentially bind in the C_2-symmetric pattern. However, this should just be noted, since trying to find an explanation for this issue is futile with the scarce information at hand.

* The quantum-chemical calculations were done by Prof. Dr. Peter Klüfers with *ORCA*4 (version 4.1.0) at DFT level. Initial geometries were taken from molecular structures obtained by X-ray diffraction experiments. Wave functions were calculated at the RI-DFT level using the functional BP86 and def2-TZVP basis set. Dispersion correction was applied by using Grimme's D3-correction with Becke-Johnson-damping as implemented in *ORCA*4.[60]

4 Summary

Past investigations have shown that both gallium(III) nitrate and gallium(III) citrate display antimicrobial activity[20,21], while gallium(III) compounds like tris(maltolato)gallium(III) and tris(8-hydroxy-quinolinato)gallium(III) were studied in clinical trials for their antineoplastic activity[24]. In another publication[34] on the subject of potential gallium(III)-based pharmaceuticals, $[Ga(aa)_3]$ complexes with bidentate proteinogenic aminecarboxylato (aa) ligands were described. Since no structural information on gallium(III) complexes with aa ligands at non-inert conditions has been available yet, a major goal of this work was the synthesis, crystallisation and characterisation of such complexes.

The molecular structures of $[\{Ga(gly)_2(\mu\text{-}OH)\}_2]$ (**1a**) and $[Ga(gly)_3]$ (**1b**) are first examples of gallium(III) complexes with aa ligands which were obtained from aqueous solutions. However, the synthesis of such complexes was not as straightforward as anticipated, even though the formation of octahedral $[Ga(aa)_3]$ complexes with bidentate aa ligands has been described in the latest publication on this topic[34]. Acquiring further information on the formation of gallium(III) complexes with aa ligands was therefore advised. By utilising the two tetradentate ligands nta and edda as co-ligands in combination with aa ligands, nine $[Ga(aa)(nta)]^-$ (**2a**–**2i**) and eight [Ga(aa)(edda)] (**3a**–**3h**) complexes and complex isomers with bidentate aa ligands were crystallised and characterised by X-ray diffraction. According to elemental analyses, complexes of these kinds were obtained with each polar or nonpolar aa ligand except L-tyrosinate. The combination of acidic as well as basic aa ligands with nta or edda led to the formation of slightly different complexes. While octahedral complexes were synthesised, elemental analysis of the isolated products revealed that the basic and acid functions of the aa ligands' side chains are protonated and adducts with the respective tertiary amine used as a basic compound were formed. This led to ill-defined products with the exception of [Ga(Harg)(edda)]Cl, [Ga(edda)(Hhis)]Cl and [Ga(edda)(Hlys)]Cl.

NMR-spectroscopic analyses of the Ga(aa)-bearing compounds at neutral pH levels revealed an equilibrium between the target complex, free AA and hydroxido-bridged complexes—$[\{Ga(nta)(\mu\text{-}OH)\}_2]$ and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ (n = 2 or 6, **3i**, **3j**)—in aqueous solution. Hence, while the synthesis of gallium(III) complexes with aa ligands was feasible and the simultaneous existence of free AA and bound aa ligands simplified the assignment of signals in NMR spectra, those compounds are prone to ligand exchange reactions in aqueous solution.

The equilibria are influenced by the characteristics of the solvent in use, the pH value and the concentration of the solution as well as the respective aa ligand of the complexes. While a shift of the equilibrium position towards the target complexes was noticeable when L-threoninato and L-cysteinato were compared to other aa ligands, the pH of the solution has a much higher influence. For example, in acidic solutions the ratio of target complexes was significantly reduced. In case of [Ga(aa)(edda)] complexes, the influence of basic pH values was demonstrated: the ratio of the target complexes peaked at neutral and slightly basic pH levels. At higher pH levels (around 9.5 and above), no [Ga(aa)(edda)] complex was left. Since water is a reactant in the equilibrium reactions, the concentration of the aqueous solutions had a further major influence on the position of the equilibria. Furthermore, even the addition of small amounts of methanol to aqueous solutions led to a shift of the equilibrium positions, while the formation of hydroxido-bridged complexes and therefore an equilibrium reaction is not possible in dry organic solvents.

The results of the NMR-spectroscopic studies can be used for the characterisation of further gallium(III) complexes with aa ligands in future experiments. For example, the signal of the C2 atom was, with only very few exceptions, shifted to high field when the aa ligand is bound to gallium(III). The opposite is true for the C1 atom in most cases. These characteristics, along with other features like the broadening of signals enhanced the assignability of signals in spectra.

In addition to the use of bi- and tetradentate aminecarboxylato ligands, gallium(III) complexes with combinations of tridentate aminecarboxylato ligands were examined. [Ga(his)(ida)] (**4a**) was synthesised and crystallised, and the synthesis of [Ga(asp)(his)] was achieved according to elemental analysis and NMR spectroscopy. To get structural information on the latter complex, a combination of asp and D-his ligands was used. This resulted in the synthesis and crystallisation of [{Ga(μ-asp)(D-his)}$_2$] (**4b**), a dinuclear complex. [Ga(asp)(his)] showed different characteristics than **4b**, hence it is considered to be mononuclear.

As the syntheses and characterisation of gallium(III) complexes with bi-, tri- and tetradentate aminecarboxylato ligands were successful—despite the reactivity of these complexes with water—complexes with combinations of amine and carboxylato ligands were synthesised. In this process, [Ga(malo)(tren)]Cl (**5a**Cl), [Ga(ox)(trien)]Cl (**5b**·**5c**·2Cl) and [Ga(mal)(trien)] (**5d**) were crystallised and [Ga(malo)(trien)]Cl was characterised. NMR-spectroscopic analyses of [Ga(ox)(trien)]$^+$ and [Ga(malo)(trien)]$^+$ indicated that these two complexes are stable against hydrolysis at physiological pH levels, while the spectra of [Ga(mal)(trien)] remained inconclusive.

During the course of this work, reaction conditions and choice of basic compounds proved to be essential. Tertiary amines were used, since the separation of the respective hydrochlorides from the target complexes after the reaction proved to be efficient. While this in itself is a very convenient and important characteristic, it turned out that $[Ga(aa)(nta)]^-$ complexes were only crystallisable with triethylammonium and *N*,*N*-diisopropylethylammonium ions. The presence of alkali cations M resulted in the crystallisation of the respective $M_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$ instead. Consequently, without the use of the tertiary amines, a main source of information about the characteristics of aa ligands in gallium(III) complexes would not have been available.

Due to the lack of tests regarding the applicability of the synthesised gallium(III) compounds as antimicrobial or antineoplastic agents, only the observed characteristics of the compounds can be used to consider their potential as such. Most compounds are stable enough to not precipitate gallium(III) hydroxide in aqueous solutions. This fulfils a first stability requirement in order to raise bioavailability, if administered locally or parenterally. Therefore, most compounds might be applicable as therapeutic agents. However, only two complexes—$[Ga(ox)(trien)]^+$ and $[Ga(malo)(trien)]^+$—seem to be stable against hydrolysis in aqueous solution at neutral pH levels. Since both share this characteristic with tris(maltolato)gallium(III) and tris(8-hydroxyquinolinato)gallium(III), those may be considered to be the most promising compounds when it comes to potential pharmaceutical use. In addition, none of the components of these compounds are considered hazardous, which is a further positive characteristic. Some of the examined gallium(III) compounds contain toxic or potentially carcinogenic ligands or cations. Consequently, those compounds might not be applicable as pharmaceuticals. In this work, only complexes which feature combinations of trien, edda, ida, ox, malo, mal or aa ligands could be considered as non-hazardous.

If gallium(III) complexes should be synthesised at neutral pH levels in aqueous solution, a few tentative advices to raise their stability based on the experiences in this work can be given. The charge of the target complex should not exceed +/− 1. In addition, an octahedral GaN_4O_2 environment seems to be beneficial, as stated before[38]. Also, the formation of six-membered chelate ring is not guaranteed, while five-membered chelate rings are formed readily. As shown, the stability of the complexes is largely based on the kind of ligand in use, too. If amine functions are present, those should be incorporated in the ligand with higher denticity, while the ligand with lower denticity should carry the higher negative charge. Different ligand combinations can potentially form in the reaction mixture if those requirements are not met, and the resulting compounds are likely to differ from

expectation. One general concern is the formation of hydroxido-bridged complexes by ligand exchange reactions with ligands of low denticity.

Bearing that in mind, further use of tetradentate amine ligands like trien in combination with divalent bidentate ligands seems to be a reasonable endeavour. Additionally, combining those divalent bidentate ligands with tetradentate aminecarboxylato ligands like edda to form gallium(III) complexes is feasible. This was demonstrated by the synthesis and characterisation of $[Ga(edda)(malo)]^-$ (**3k**).

5 Experimental Part

5.1 Common working techniques

All reactions were carried out under air at room temperature. Methanol, ethanol and ethyl acetate were purified by rotary evaporation before use. Gallium(III) chloride was only added from aqueous stock solutions prepared of anhydrous gallium(III) chloride and deionised water. The concentration of the solutions ranged between 504 g L^{-1} and 506 g L^{-1}. Due to the minimal differences in volume the following procedures do not contain the added volume of gallium(III) chloride solution but the mass and the amount of added gallium(III) chloride salt.
All products were analysed by elemental analysis. Crystallisation was attained by vapour diffusion of less polar solvents into aqueous or methanolic solutions of the raw products or by slow evaporation of these solutions.

5.2 Analytical methods

5.2.1 Elemental analysis

CHNS analyses were done with an *Elementar vario EL* and an *Elementar vario micro tube*. The interpretation of the elemental analyses was done with *JASPER*[61].

5.2.2 X-ray diffraction

Crystals were selected with a *Leica MZ6* polarisation microscope. Suitable crystals were measured on a *Bruker D8 Venture* or an *Oxford XCalibur 3* diffractometer using Mo-K_α irradiation (λ = 0.71073 Å). The structure solutions were done by direct methods using *SHELXT*[62] and the structures were refined by full-matrix least-squares calculations on F^2 using *SHELXL-2016*[63] and *ShelXle*[64]. For visualisation the programmes *POV-Ray*[65] and *Mercury*[66] were used. Further details and packing diagrams of every crystal structure are listed in the appendix (Section 6.2 and 6.3).

5.2.3 NMR spectroscopy

NMR spectra were recorded on *Bruker 400* and *Bruker 400 TR* spectrometers. All ^{13}C NMR spectra were recorded broad band proton decoupled ($^{13}C\{^{1}H\}$ NMR). The chemical shift δ is given in ppm and refers to the signal of non-deuterated methanol which was added to every solution in D_2O as a reference. An exception for this is only found when deuterated methanol was used as solvent, in that case the shift refers to the signal of deuterated methanol. ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-HMQC, ^{1}H-^{13}C-HMBC and DEPT135 experiments were used for signal-assignment if possible. Interpretation of the spectra was done with the software *MestReNova*[67].

The NMR-spectroscopic analyses were done with solutions of obtained raw products—their compositions are specified with the empirical formulas—with a concentration of 0.25 mol L^{-1} whenever comparability regarding the ratios of compounds in solution is targeted. If no concentrations are specified below illustrations of NMR spectra, the examined solutions were almost saturated. This was done to enhance the examination by 2D NMR methods.

5.3 Signal shifts of recurring compounds in NMR spectra

Due to the nature of this work almost every solution which was examined by ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR contained recurring compounds. The chemical shifts of these compounds remained roughly the same in every experiment. For convenience and to emphasise this fact those signals are summarised here and not cited separately in each of the experiments.

The signals of the triethylammonium ($HNEt_3^+$) and *N*,*N*-diisopropylethylammonium ($HDIPEA^+$) cations are listed hereafter. Only the signals in ^{1}H NMR spectra of $[Ga(nta)(trp)]^-$ and $[Ga(nta)(phe)]^-$ salts differ slightly when compared to every other spectrum and are therefore displayed separately.

$HNEt_3^+$ ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.19 (q, 6H, H1, $^{3}J_{1,2}$ = 7.3 Hz), 1.26 or 1.27 (t, 9H, H2, $^{3}J_{1,2}$ = 7.3–7.4 Hz) ppm.

$HNEt_3$[Ga(nta)(phe)] ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.16 (q, 6H, H1, $^3J_{1,2}$ = 7.3 Hz), 1.25 (t, 9H, H2, $^3J_{1,2}$ = 7.3 Hz) ppm.

$HNEt_3$[Ga(nta)(trp)] ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.03 (q, 6H, H1, $^3J_{1,2}$ = 7.3 Hz), 1.17 (t, 9H, H2, $^3J_{1,2}$ = 7.3 Hz) ppm.

$HNEt_3^+$ ^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 47.2 or 47.3 (C1), 8.9 (C2) ppm.

HDIPEA$^+$ ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.64–3.74 (sp, 2H, H1), 3.18 or 3.19 (q, 2H, H4, $^3J_{4,5}$ = 7.4 Hz), 1.28–1.37 (sp, 15H, H2/H3/H5) ppm.

HDIPEA[Ga(nta)(phe)] ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.61–3.71 (sp, 2H, H1), 3.15 (q, 2H, H4, $^3J_{4,5}$ = 7.4 Hz), 1.25–1.34 (sp, 15H, H2/H3/H5) ppm.

HDIPEA[Ga(nta)(trp)] ^{1}H NMR (400 MHz, D_2O)**:** δ = 3.52–3.60 (sp, 2H, H1), 3.05 (q, 2H, H4, $^3J_{4,5}$ = 7.4 Hz), 1.23–1.38 (sp, 15H, H2/H3/H5) ppm.

HDIPEA$^+$ ^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 54.9 or 55.0 (C1), 43.1 or 43.2 (C4), 18.3 or 18.4 (C2), 16.8 or 16.9 (C3), 12.7 or 12.8 (C5) ppm.

^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy revealed equilibria between different complexes as well as free ligand in aqueous solutions. In case of [Ga(aa)(nta)]$^-$- and [Ga(aa)(edda)]-complexes only the respective aa ligand was observed in its free form and with the state of protonation appropriate for the pH value of the individual solution. The signals of the free and bound proteinogenic amino acids of the solutions are listed in the individual experimental descriptions of the respective complexes.

The tetradentate ligands were not observed in their uncoordinated form. As the chemical shifts of nta in [Ga(aa)(nta)]$^-$ complexes remained roughly the same in every experiment the corresponding signals are summarised in Table 5.1–Table 5.4. This is also true for the signals of nta in the [{Ga(nta)(μ-OH)}$_2$]$^{2-}$ complex which are found in those aqueous solutions, therefore those signals are also given in Table 5.1–Table 5.4.

Table 5.1: *δ* in ppm of nta in ^{1}H NMR spectra (400 MHz, D_2O): compounds containing triethylamine and triethylammonium ions.

complex	H2	complex	H2
$[Ga(ala)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
[Ga(Harg)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(asn)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(Hasp)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.77 (s, 6H)
$[Ga(cys\text{-}\kappa^2S,X)(nta)]^-$	3.73 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.73 (s, 6H)
$[Ga(cys\text{-}\kappa O,N)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.73 (s, 6H)
$[Ga(gln)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(Hglu)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.78 (s, 6H)
$[Ga(gly)(nta)]^-$	3.83 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
[Ga(Hhis)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.76 (s, 6H)
$[Ga(ile)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(leu)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.70 (s, 6H)
[Ga(Hlys)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(met)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(phe)]^-$	3.78 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.67 (s, 6H)
$[Ga(nta)(pro)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(ser)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(thr)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(trp)]^-$	3.68 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.54 (s, 6H)
$[Ga(nta)(val)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)

Table 5.2: *δ* in ppm of nta in $^{13}C\{^{1}H\}$ NMR spectra (101 MHz, D_2O): compounds containing triethylamine and triethylammonium ions. The descriptors A and B are used in visual representations of spectra throughout this work to clarify signal assignments.

complex	C1 (A)	C2 (B)	complex	C1 (A)	C2 (B)
$[Ga(ala)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
[Ga(Harg)(nta)]	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.7	63.3
$[Ga(asn)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(Hasp)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(cys\text{-}\kappa^2S,X)(nta)]^-$	176.0	63.4	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.4
$[Ga(cys\text{-}\kappa O,N)(nta)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.4
$[Ga(gln)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(Hglu)(nta)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.4
$[Ga(gly)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
[Ga(Hhis)(nta)]	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.7	63.3
$[Ga(ile)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(leu)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
[Ga(Hlys)(nta)]	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.7	63.2
$[Ga(met)(nta)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(nta)(phe)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(nta)(pro)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(nta)(ser)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(nta)(thr)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(nta)(trp)]^-$	175.0	63.1	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.2
$[Ga(nta)(val)]^-$	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3

Table 5.3: δ in ppm of nta in ^{1}H NMR spectra (400 MHz, D_2O): compounds containing *N*,*N*-diisopropylethylamine and *N*,*N*-diisopropylethylammonium ions.

complex	H2	complex	H2
$[Ga(ala)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
[Ga(Harg)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(asn)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.74 (s, 6H)
$[Ga(Hasp)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.77 (s, 6H)
$[Ga(cys\text{-}\kappa^2S,X)(nta)]^-$	3.72 (sp, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(cys\text{-}\kappa O,N)(nta)]^-$	3.82 (sp, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(gln)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(Hglu)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.78 (s, 6H)
$[Ga(gly)(nta)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
[Ga(Hhis)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.76 (s, 6H)
$[Ga(ile)(nta)]^-$	3.80 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.70 (s, 6H)
$[Ga(leu)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.70 (s, 6H)
[Ga(Hlys)(nta)]	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(met)(nta)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(phe)]^-$	3.77 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.67 (s, 6H)
$[Ga(nta)(pro)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.72 (s, 6H)
$[Ga(nta)(ser)]^-$	3.82 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.71 (s, 6H)
$[Ga(nta)(thr)]^-$	3.81 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.70 (s, 6H)
$[Ga(nta)(trp)]^-$	3.71 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.58 (s, 6H)
$[Ga(nta)(val)]^-$	3.80 (s, 6H)	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	3.70 (s, 6H)

Table 5.4: δ in ppm of nta in $^{13}C\{^{1}H\}$ NMR spectra (101 MHz, D_2O): compounds containing *N*,*N*-diisopropylethylamine and *N*,*N*-diisopropylethylammonium ions. The descriptors A and B are used in visual representations of spectra instead of numbers throughout this work to clarify signal assignments.

complex	C1 (A)	C2 (B)	complex	C1 (A)	C2 (B)
$[Ga(ala)(nta)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.4	63.3
[Ga(Harg)(nta)]	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.2
$[Ga(asn)(nta)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(Hasp)(nta)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.4	63.3
$[Ga(cys\text{-}\kappa^2S,X)(nta)]^-$	176.0	63.4	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.4
$[Ga(cys\text{-}\kappa O,N)(nta)]^-$	175.1	63.3	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.4
$[Ga(gln)(nta)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(Hglu)(nta)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.4
$[Ga(gly)(nta)]^-$	174.9	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.3	63.2
[Ga(Hhis)(nta)]	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.3
$[Ga(ile)(nta)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(leu)(nta)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
[Ga(Hlys)(nta)]	175.2	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.6	63.2
$[Ga(met)(nta)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(nta)(phe)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(nta)(pro)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(nta)(ser)]^-$	175.0	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(nta)(thr)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3
$[Ga(nta)(trp)]^-$	175.0	63.1	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.2
$[Ga(nta)(val)]^-$	175.1	63.2	$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$	175.5	63.3

Since the signals of edda in [{Ga(edda)(μ-OH)}$_n$) are not distinguishable from those of edda in [Ga(aa)(edda)] complexes and furthermore resemble large signal clusters in $^{13}C\{^1H\}$ NMR as well as ^1H NMR spectra the signals of edda are listed as ranges without further distinction in Table 5.5 and Table 5.6. Note that significant differences of signal shifts are only found when pH-differences of the measured solutions are sizeable.

Table 5.5: *δ* in ppm of edda in ^1H NMR spectra (400 MHz, D_2O). * only the [{Ga(edda)(μ-OH)}$_n$] complex is present in the spectrum, the [Ga(aa)(edda)] complex is only given to state the origin of the solution.

complexes	H2–H5
[Ga(ala)(edda)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.25 (sp), 2.38–3.38 (sp).
[Ga(Harg)(edda)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	3.51–4.27 (sp), 2.38–3.38 (sp).
[Ga(asn)(edda)], [{Ga(edda)(μ-OH)}$_n$]	3.47–4.24 (sp), 2.39–3.40 (sp).
[Ga(Hasp)(edda)], [{Ga(edda)(μ-OH)}$_n$]	3.72–4.04 (sp), 2.81–3.30 (sp).
[Ga(cys)(edda)], [{Ga(edda)(μ-OH)}$_n$]	-
[Ga(edda)(gln)], [{Ga(edda)(μ-OH)}$_n$]	3.64–4.02 (sp), 2.62–3.40 (sp).
[Ga(edda)(Hglu)], [{Ga(edda)(μ-OH)}$_n$]	3.66–4.07 (sp), 2.79–3.38 (sp).
[Ga(edda)(gly)], [{Ga(edda)(μ-OH)}$_n$]	3.61–4.25 (sp), 2.39–3.38 (sp).
[Ga(edda)(Hhis)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	3.51–4.24 (sp), 2.40–3.40 (m).
[Ga(edda)(ile)], [{Ga(edda)(μ-OH)}$_n$]	3.43–4.18 (m), 2.38–3.38 (m).
[Ga(edda)(leu)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.25 (sp), 2.38–3.38 (sp).
[Ga(edda)(Hlys)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	3.51–4.25 (sp), 2.38–3.38 (sp).
[Ga(edda)(met)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.25 (sp), 2.40–3.40 (m).
[Ga(edda)(phe)], [{Ga(edda)(μ-OH)}$_n$]*	3.67–3.95 (m), 2.52–3.30 (sp).
[Ga(edda)(pro)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.26 (sp), 2.40–3.40 (m).
[Ga(edda)(ser)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.26 (sp), 2.40–3.40 (m).
[Ga(edda)(thr)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.26 (sp), 2.40–3.40 (m).
[Ga(edda)(trp)], [{Ga(edda)(μ-OH)}$_n$]*	3.63–3.94 (sp), 2.46–3.46 (sp).
[Ga(edda)(val)], [{Ga(edda)(μ-OH)}$_n$]	3.51–4.25 (sp), 2.40–3.40 (m).

Table 5.6: δ in ppm of edda in $^{13}C\{^{1}H\}$ NMR spectra (101 MHz, D_2O). The descriptors A and B are used in visual representations of spectra instead of numbers throughout this work to clarify signal assignments. * only the [{Ga(edda)(μ-OH)}$_n$] complex is present in the spectrum, the [Ga(aa)(edda)] complex is only given to state the origin of the solution.

complexes	C1, C6 (A, ms)	C2–C5 (B, ms)
[Ga(ala)(edda)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.4	50.0–52.9, 44.2–47.3.
[Ga(Harg)(edda)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	177.0–178.4	49.6–52.9, 44.2–47.3.
[Ga(asn)(edda)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.4	49.6–52.9, 44.2–47.3.
[Ga(Hasp)(edda)], [{Ga(edda)(μ-OH)}$_n$]	-	50.8–51.4, 46.3.
[Ga(cys)(edda)], [{Ga(edda)(μ-OH)}$_n$]	-	-
[Ga(edda)(gln)], [{Ga(edda)(μ-OH)}$_n$]	177.0–179.0	50.8–51.9, 45.8–46.6.
[Ga(edda)(Hglu)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.0	50.9–51.4, 46.1–47.3.
[Ga(edda)(gly)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.4	46.9–52.9, 44.2–47.3.
[Ga(edda)(Hhis)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	177.0–178.5	50.0–52.9, 44.2–47.4.
[Ga(edda)(ile)], [{Ga(edda)(μ-OH)}$_n$]	177.0–178.5	50.0–52.9, 44.2–47.4.
[Ga(edda)(leu)], [{Ga(edda)(μ-OH)}$_n$]	177.0–178.4	50.1–52.9, 44.2–47.4.
[Ga(edda)(Hlys)]$^+$, [{Ga(edda)(μ-OH)}$_n$]	177.0–178.5	50.1–52.9, 44.2–47.4.
[Ga(edda)(met)], [{Ga(edda)(μ-OH)}$_n$]	177.0–178.5	50.1–52.9, 44.2–47.4.
[Ga(edda)(phe)], [{Ga(edda)(μ-OH)}$_n$]*	178.1–179.0	51.2–52.3, 46.0–46.8.
[Ga(edda)(pro)], [{Ga(edda)(μ-OH)}$_n$]	176.9–178.4	50.0–52.9, 44.2–47.4.
[Ga(edda)(ser)], [{Ga(edda)(μ-OH)}$_n$]	176.9–178.4	50.0–52.9, 44.1–47.3.
[Ga(edda)(thr)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.4	50.0–52.9, 44.1–47.3.
[Ga(edda)(trp)], [{Ga(edda)(μ-OH)}$_n$]*	177.9–179.1	51.2–52.1, 45.9–46.8.
[Ga(edda)(val)], [{Ga(edda)(μ-OH)}$_n$]	177.1–178.4	49.7–52.9, 44.2–48.0.

5.4 Reagents and solvents

Name	Purity [%]	Distributor
acetone	99.5 (technical grade)	Bernd Kraft
acetonitrile	99.99	VWR
L-alanine	99	Acros Organics
L-arginine	≥98	Sigma-Aldrich
L-asparagine monohydrate	99	Acros Organics
L-aspartic acid	≥98	Acros Organics
caesium hydroxide monohydrate	99.95	Acros Organics
choline hydroxide aqueous solution	48–50	TCI
L-cysteine	≥99	Acros Organics
deuterium oxide	99.9	Aldrich
diethyl ether	99.7 (technical grade)	Brenntag
N,*N*-diisopropylethylamine	99	ABCR
dimethyl sulfoxide	99.7	Acros Organics
1,4-dioxane	99.9 (technical grade)	Brenntag
ethanol	99 (technical grade)	BfB
ethyl acetate	99.7 (technical grade)	Staub
ethylenediamine-*N*,*N*′-diacetic acid	≥98	TCI
gallium(III) chloride	99.999	ABCR
L-glutamic acid	99	Aldrich
L-glutamine	98	Aldrich
glycine	99	Acros Organics
glycylglycylglycine	99	ABCR
n-hexane	95 (technical grade)	Grüssing
D-histidine	99	Alfa Aesar
L-histidine	≥99	Sigma-Aldrich
iminodiacetic acid	98	Aldrich
L-isoleucine	99	Acros Organics
L-leucine	≥99.5	Fluka
L-lysine hydrochloride	≥99	Acros Organics
L-malic acid	≥99	Fluka
malonic acid	99	Sigma-Aldrich

Name	Purity [%]	Distributor
methanol	99.9 (technical grade)	Staub
methanol-d_4	99.5	Eurisotop
L-methionine	≥98	Sigma-Aldrich
nitrilotriacetic acid	≥99	Fluka
oxalic acid anhydrous	≥99	Fluka
L-phenylalanine	98.5	Acros Organics
L-proline	99	Acros Organics
L-serine	99	Acros Organics
L-threonine	98	Acros Organics
toluene	99.5 (technical grade)	Brenntag
triethylamine	98	Acros Organics
triethylenetetramine	≥97	Fluka
tris(2-aminoethyl)amine	≥98	TCI
L-tryptophan	99	Acros Organics
L-tyrosine	99	Sigma-Aldrich
L-valine	≥98	Aldrich
water	deionized	house installation

5.5 Synthesis of gallium(III) complexes

5.5.1 [{Ga(gly)$_2$(μ-OH)}$_2$]

Starting material: Glycine, water, gallium(III) chloride, triethylamine, ethanol, diethyl ether, 1,4-dioxane.

Procedure:

Glycine (161 mg, 2.15 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (126 mg, 0.71 mmol) and triethylamine (499 μL, 3.58 mmol) resulted in a colourless solution (pH 10.0). A colourless slurry was obtained after addition of ethanol (2 mL) and stirring at 0 °C for 30 min. The colourless amorphous solid was separated by filtration and washed with ethanol and diethyl ether.

Empirical formula: $C_8H_{18}Ga_2N_4O_{10}$ + 0.65 $C_2H_5NO_2$ + 0.40 H_2O + 0.10 C_2H_6O.

Yield: 189 mg (0.326 mmol, 91.1%).

Elemental analysis: Calcd. (%): C 21.52, H 4.31, N 12.28.

Found (%): C 21.44, H 4.41, N 12.20.

Calcd. $C_8H_{18}Ga_2N_4O_{10}$ (%): C 20.46, H 3.86, N 11.93.

Crystals of [{Ga(gly)$_2$(μ-OH)}$_2$] (**1a**) were obtained after six weeks by storing an aqueous solution (adjusted with triethylamine to pH 10.0) of the raw product over 1,4-dioxane.

Empirical formula: $C_8H_{18}Ga_2N_4O_{10}$, 469.70 g mol^{-1}.

Yield: Few crystals.

5.5.2 [Ga(gly)$_3$]

Starting material: Gallium(III) chloride, glycylglycylglycine, glycine, choline hydroxide, water, ethanol.

Procedure: Gallium(III) chloride solution (165 mg, 0.94 mmol) was added to a solution of glycylglycylglycine (178 mg, 0.94 mmol), glycine (71 mg, 0.94 mmol) and choline hydroxide (842 µL, 3.75 mmol, 50% solution in water) in water (1 mL). The yellow slurry (pH 9.0) was stirred for 16 h and after addition of ethanol (40 mL) the yellow solid was separated by filtration. Storing an aqueous solution of this product for one year while allowing for slow evaporation of the solvent yielded crystals of [Ga(gly)$_3$]·H_2O (**1b**·H_2O).

Empirical formula: $C_6H_{12}GaN_3O_6 \cdot H_2O$, 291.92 g mol^{-1}.

Yield: Few crystals.

5.5.3 $HNEt_3[Ga(ala)(nta)]$

Starting material: L-Alanine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Alanine (89 mg, 1.0 mmol) was dissolved in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{15}H_{28}GaN_3O_8$ + 0.60 H_2O.

Yield: 302 mg (0.658 mmol, 65.8%).

Elemental analysis: Calcd. (%): C 39.26, H 6.41, N 9.16.

Found (%): C 39.35, H 6.50, N 9.16.

Calcd. $C_{15}H_{28}GaN_3O_8$ (%): C 40.20, H 6.30, N 9.38.

$[Ga(ala)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.75–3.82 (sp, 1H, H2), 1.51 (d, 3H, H3, $^3J_{2,3}$ = 7.3 Hz) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 180.0 (C1), 50.3 (C2), 18.0 (C3) ppm.

L-Alanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.75–3.82 (sp, 1H, H2), 1.46 (d, 3H, H3, $^3J_{2,3}$ = 7.3 Hz) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 176.3 (C1), 51.1 (C2), 16.8 (C3) ppm.

5.5.4 [Ga(Harg)(nta)]·0.10NEt_3

Starting material: L-Arginine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Arginine (174 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{12}H_{20}GaN_5O_8 \cdot 0.10C_6H_{15}N + 1.55\ H_2O + 0.10\ C_2H_6O$.

Yield: 362 mg (0.763 mmol, 76.3%).

Elemental analysis: Calcd. (%): C 32.39, H 5.35, N 15.05.

Found (%): C 32.41, H 5.42, N 15.02.

Calcd. $C_{12}H_{20}GaN_5O_8$ (%): C 33.36, H 4.67, N 16.21.

[Ga(Harg-κ*O*,*N*)(nta)] (isomer I):

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.74–3.80 (sp, 1H, H2), 3.21–3.26 (sp, 2H, H5), 1.97–2.11 (m, 1H, H3), 1.78–1.87 (sp, 1H, H3), 1.69–1.86 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.6 (C1), 157.4 (C6), 54.1 (C2), 41.2 (C5), 29.3 (C3), 25.3 (C4) ppm.

[Ga(Harg-κ*O*,*N*)(nta)] (isomer II):

^{1}H NMR (400 MHz, D_2O)**:** δ = -

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.7 (C1), 53.6 (C2), 41.2 (C5), 29.7 (C3), 25.5 (C4) ppm.

L-Arginine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.74–3.80 (sp, 1H, H2), 3.21–3.26 (sp, 2H, H5), 1.83–1.94 (sp, 2H, H3), 1.59–1.72 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.9 (C1), 157.4 (C6), 54.9 (C2), 41.1 (C5), 28.2 (C3), 24.5 (C4) ppm.

5.5.5 $HNEt_3[Ga(asn)(nta)]$

Starting material: L-Asparagine monohydrate, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Asparagine monohydrate (150 mg, 1.00 mmol) was suspended in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (5 mL) and ethyl acetate (10 mL). The colourless solid was separated by filtration and suspended in ethanol (5 mL) and ethyl acetate (10 mL) again. After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 4 h.

Empirical formula: $C_{16}H_{29}GaN_4O_9 + 0.20\ Ga(OH)_3 + 0.15\ C_4H_8O_2$.

Yield: 302 mg (0.576 mmol, 57.6%).

Elemental analysis: Calcd. (%): C 37.58, H 5.85, N 10.69.

Found (%): C 37.70, H 5.96, N 10.56.

Calcd. $C_{16}H_{29}GaN_4O_9$ (%): C 39.13, H 5.95, N 11.41.

$[Ga(asn)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97 (t, 1H, H2, $^3J_{2,3}$ = 5.5 Hz), 2.95–2.97 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 177.6 (C1), 175.3 (C4), 51.4 (C2), 36.2 (C3) ppm.

L-Asparagine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.00–4.03 (m, 1H, H2), 2.82–2.96 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 174.9 (C4), 173.7 (C1), 51.8 (C2), 35.0 (C3) ppm.

5.5.6 $HNEt_3[Ga(Hasp)(nta)]\cdot 0.30NEt_3$

Starting material: L-Aspartic acid, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, acetone, diethyl ether.

Procedure: L-Aspartic acid (133 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (767 µL, 5.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL), ethyl acetate (250 mL) and acetone (100 mL). After filtration and washing with acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{16}H_{28}GaN_3O_{10}\cdot 0.30C_6H_{15}N + 1.40\ H_2O$.

Yield: 273 mg (0.498 mmol, 49.8%).

Elemental analysis: Calcd. (%): C 39.03, H 6.50, N 8.44.

Found (%): C 39.04, H 6.72, N 8.43.

Calcd. $C_{16}H_{28}GaN_3O_{10}$ (%): C 39.05, H 5.74, N 8.54.

$[Ga(Hasp)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.90–3.93 (m, 1H, H2), 2.79–2.93 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 177.9 (C1), 176.7 (C4), 51.8 (C2), 37.5 (C3) ppm.

L-Aspartic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.96–4.02 (m, 1H, H2), 2.79–2.93 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 176.7 (C1), 173.9 (C4), 52.1 (C2), 36.7 (C3) ppm.

5.5.7 $HNEt_3[Ga(cys)(nta)]$

Starting material: L-Cysteine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, acetone, diethyl ether.

Procedure: L-Cysteine (121 mg, 1.00 mmol) was dissolved in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (5 mL) and ethyl acetate (15 mL). After filtration and washing with acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 5 h.

Empirical formula: $C_{15}H_{28}GaN_3O_8S + 1.25\ H_2O + 0.10\ C_3H_7NO_2S$.

Yield: 264 mg (0.513 mmol, 51.3%).

Elemental analysis: Calcd. (%): C 35.70, H 6.11, N 8.43, S 6.85.

Found (%): C 35.65, H 6.06, N 8.42, S 6.81.

Calcd. $C_{15}H_{28}GaN_3O_8S$ (%): C 37.52, H 5.88, N 8.75, S 6.68.

$[Ga(cys\text{-}\kappa^2S,X)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 174.5 (C1), 56.1 (C2), 24.6 (C3) ppm.

$[Ga(cys\text{-}\kappa O,N)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 57.8 (C2) ppm.

L-Cysteine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 172.9 (C1), 56.4 (C2), 25.3 (C3) ppm.

5.5.8 $HNEt_3[Ga(gln)(nta)]$

Starting material: L-Glutamine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Glutamine (146 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{17}H_{31}GaN_4O_9 + 0.75\ H_2O$.

Yield: 405 mg (0.781 mmol, 78.1%).

Elemental analysis: Calcd. (%): C 39.37, H 6.32, N 10.80.

Found (%): C 39.46, H 6.25, N 10.72.

Calcd. $C_{17}H_{31}GaN_4O_9$ (%): C 40.42, H 6.19, N 11.09.

$[Ga(gln)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.71–3.82 (sp, 1H, H2), 2.48–2.52 (m, 2H, H4), 2.25–2.34 (m, 1H, H3), 2.04–2.12 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.4 (C5), 178.1 (C1), 54.0 (C2), 32.1 (C4), 28.0 (C3) ppm.

L-Glutamine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.71–3.82 (sp, 1H, H2), 2.41–2.46 (m, 2H, H4), 2.08–2.15 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.1 (C5), 174.5 (C1), 54.7 (C2), 31.4 (C4), 26.8 (C3) ppm.

5.5.9 $HNEt_3[Ga(Hglu)(nta)]\cdot 0.10NEt_3$

Starting material: L-Glutamic acid, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, acetone, diethyl ether.

Procedure: L-Glutamic acid (147 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (767 µL, 5.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL), ethyl acetate (130 mL) and acetone (50 mL). After filtration and washing with acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{17}H_{30}GaN_3O_{10}\cdot 0.10C_6H_{15}N + 0.55\ H_2O$.

Yield: 352 mg (0.669 mmol, 66.9%).

Elemental analysis: Calcd. (%): C 40.17, H 6.25, N 8.25.

Found (%): C 40.22, H 6.25, N 8.21.

Calcd. $C_{17}H_{30}GaN_3O_{10}$ (%): C 40.34, H 5.97, N 8.30.

$[Ga(Hglu)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.57 (sp, 2H, H4), 1.98–2.18 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 54.1 (C2), 32.4 (C4), 28.1 (C3) ppm.

L-Glutamic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.57 (sp, 2H, H4), 1.98–2.18 (sp, 2H, H3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 179.5 (C5), 174.5 (C1), 54.7 (C2), 32.4 (C4), 26.9 (C3) ppm.

5.5.10 $HNEt_3[Ga(gly)(nta)]$

Starting material: Glycine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, diethyl ether, acetone.

Procedure: Glycine (75 mg, 1.0 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{14}H_{26}GaN_3O_8$ + 0.20 H_2O.

Yield: 353 mg (0.806 mmol, 80.6%).

Elemental analysis: Calcd. (%): C 38.42, H 6.08, N 9.60.

Found (%): C 38.46, H 6.11, N 9.52.

Calcd. $C_{14}H_{26}GaN_3O_8$ (%): C 38.74, H 6.04, N 9.68.

$[Ga(gly)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.55 (sp, 2H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 177.1 (C1), 42.1 (C2) ppm.

Glycine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.55 (sp, 2H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 172.9 (C1), 42.0 (C2) ppm.

Crystals of $HNEt_3[Ga(gly)(nta)]$ (($HNEt_3$)**2c**) were obtained after two weeks by storing an aqueous solution (pH 6.5) of the raw product over acetone.

Empirical formula: $C_{14}H_{26}GaN_3O_8$, 434.10 g mol^{-1}.

Yield: 263 mg (0.606 mmol, 60.6%).

Elemental analysis: Calcd. (%): C 38.74, H 6.04, N 9.68.

Found (%): C 38.58, H 5.95, N 9.61.

5.5.11 [Ga(Hhis)(nta)]·0.30NEt_3

Starting material: L-Histidine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Histidine (155 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (55 mL) and ethyl acetate (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{12}H_{15}GaN_4O_8 \cdot 0.30C_6H_{15}N + 1.60\ H_2O$.

Yield: 243 mg (0.515 mmol, 51.5%).

Elemental analysis: Calcd. (%): C 35.10, H 4.85, N 12.76.

Found (%): C 34.99, H 4.95, N 12.81.

Calcd. $C_{12}H_{15}GaN_4O_8$ (%): C 34.90, H 3.66, N 13.57.

[Ga(Hhis)(nta)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 8.34–8.44 (sp, 1H, H6), 7.15–7.31 (sp, 1H, H5), 4.01–4.07 (sp, 1H, H2), 3.24–3.47 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.9 (C1), 133.2 (C6), 129.0 (C4), 116.5 (C5), 53.7 (C2), 26.9 (C3) ppm.

L-Histidine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 8.34–8.44 (sp, 1H, H6), 7.15–7.31 (sp, 1H, H5), 4.01–4.07 (sp, 1H, H2), 3.24–3.47 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 173.5 (C1), 136.2 (C6), 129.0 (C4), 118.2 (C5), 54.5 (C2), 27.7 (C3) ppm.

5.5.12 $HNEt_3$[Ga(ile)(nta)]

Starting material: L-Isoleucine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Isoleucine (131 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on under fine vacuum for 3 h.

Empirical formula: $C_{18}H_{34}GaN_3O_8$, 490.21 g mol^{-1}.

Yield: 329 mg (0.671 mmol, 67.1%).

Elemental analysis: Calcd. (%): C 44.10, H 6.99, N 8.57.

Found (%): C 44.06, H 6.92, N 8.53.

[Ga(ile)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.66–3.68 (sp, 1H, H2), 2.17–2.26 (m, H1, H3), 1.25–1.33 (sp, 2H, H4), 1.06 (d, 3H, H6, $^3J_{3,6}$ = 7.0 Hz), 0.88–0.94 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.7 (C1), 59.5 (C2), 37.2 (C3), 24.1 (C4), 16.3 (C6), 12.0 (C5) ppm.

L-Isoleucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.66–3.68 (sp, 1H, H2), 1.92–2.01 (m, H1, H3), 1.41–1.51 (m, 1H, H4), 1.19–1.26 (sp, 1H, H4), 0.99 (d, 3H, H6, $^3J_{3,6}$ = 7.0 Hz), 0.88–0.94 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.6 (C1), 60.1 (C2), 36.5 (C3), 25.1 (C4), 15.3 (C6), 11.7 (C5) ppm.

5.5.13 $HNEt_3[Ga(leu)(nta)]$

Starting material: L-Leucine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Leucine (131 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was dissolved in ethanol (5 mL). Colourless solid was precipitated by addition of ethyl acetate (20 mL) and separated by filtration. Afterwards, the solid was suspended in ethanol (5 mL) and ethyl acetate (10 mL) again. After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{18}H_{34}GaN_3O_8$ + 0.05 $Ga(OH)_3$.

Yield: 158 mg (0.318 mmol, 31.8%).

Elemental analysis: Calcd. (%): C 43.57, H 6.94, N 8.47.

Found (%): C 43.54, H 6.80, N 8.37.

Calcd. $C_{18}H_{34}GaN_3O_8$ (%): C 44.10, H 6.99, N 8.57.

$[Ga(leu)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.67–3.74 (sp, 1H, H2), 1.72–1.81 (sp, 2H, H3), 1.64-1.81 (sp, 1H, H4), 0.93–0.97 (sp, 6H, H5/H6) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 179.7 (C1), 52.9 (C2), 41.4 (C3), 25.1 (C4), 23.1 (C5), 20.7 (C6) ppm.

L-Leucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.67–3.74 (sp, 1H, H2), 1.64–1.81 (sp, 1H, H4), 1.64–1.73 (sp, 2H, H3), 0.93–0.97 (sp, 6H, H5/H6) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 176.0 (C1), 54.0 (C2), 40.4 (C3), 24.8 (C4), 22.7 (C5), 21.6 (C6) ppm.

5.5.14 [Ga(Hlys)(nta)]·0.10NEt_3

Starting material: L-Lysine hydrochloride, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Lysine hydrochloride (183 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (767 µL, 5.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (40 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{12}H_{20}GaN_3O_8 \cdot 0.10C_6H_{15}N + 2.15\ H_2O$.

Yield: 356 mg (0.786 mmol, 78.6%).

Elemental analysis: Calcd. (%): C 33.42, H 5.74, N 9.59.

Found (%): C 33.62, H 5.79, N 9.78.

Calcd. $C_{12}H_{20}GaN_3O_8$ (%): C 42.79, H 6.98, N 11.09.

[Ga(Hlys-κ*O*,*N*)(nta)] (isomer I):

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.70–3.79 (sp, 1H, H2), 2.98–3.07 (sp, 2H, H6), 1.97–2.09 (m, 2H, H3), 1.66–1.76 (sp, 2H, H5), 1.47–1.60 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.9 (C1), 54.2 (C2), 39.7 (C6), 31.6 (C3), 26.9 (C5), 22.8 (C4) ppm.

[Ga(Hlys-κ*O*,*N*)(nta)] (isomer II):

^{1}H NMR (400 MHz, D_2O)**:** δ = -

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 180.0 (C1), 53.7 (C2), 22.9 (C4) ppm.

L-Lysine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.70–3.79 (sp, 1H, H2), 2.98–3.07 (sp, 2H, H6), 1.80–1.93 (m, 2H, H3), 1.66–1.76 (sp, 2H, H5), 1.37–1.54 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.1 (C1), 55.1 (C2), 39.7 (C6), 30.5 (C3), 27.0 (C5), 22.0 (C4) ppm.

5.5.15 $HNEt_3[Ga(met)(nta)]$

Starting material: L-Methionine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether, acetone.

Procedure: L-Methionine (149 mg, 1.00 mmol) was suspended in 3 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (40 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{17}H_{32}GaN_3O_8S + 0.70\ H_2O$.

Yield: 407 mg (0.781 mmol, 78.1%).

Elemental analysis: Calcd. (%): C 39.20, H 6.46, N 8.07, S 6.16.

Found (%): C 39.13, H 6.33, N 8.02, S 6.20.

Calcd. $C_{17}H_{32}GaN_3O_8S$ (%): C 40.18, H 6.35, N 8.27, S 6.31.

$[Ga(met)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.84–3.89 (sp, 1H, H2), 2.66–2.78 (m, 2H, H4), 2.26–2.36 (m, 1H, H3), 2.13 (s, 3H, H5), 2.02–2.11 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.5 (C1), 53.5 (C2), 31.2 (C3), 30.3 (C4), 14.6 (C5) ppm.

L-Methionine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.84–3.89 (sp, 1H, H2), 2.62 (t, 2H, H4, $^3J_{3,4}$ = 7.6 Hz), 2.08–2.23 (sp, 2H, H3), 2.11 (s, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.7 (C1), 54.5 (C2), 30.3 (C3), 29.4 (C4), 14.5 (C5) ppm.

Crystals of $HNEt_3[Ga(met)(nta)]$ ($(HNEt_3)$**2f**) were obtained after two weeks by an aqueous solution (pH 7.0) of the raw product over acetone.

Empirical formula: $C_{17}H_{32}GaN_3O_8S$, 508.24 g mol^{-1}.

Yield: Few crystals.

5.5.16 $HNEt_3[Ga(nta)(phe)]$

Starting material: L-Phenylalanine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Phenylalanine (165 mg, 1.00 mmol) was suspended in 2 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (40 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{21}H_{32}GaN_3O_8$ + 1.10 H_2O.

Yield: 334 mg (0.614 mmol, 61.4%).

Elemental analysis: Calcd. (%): C 46.36, H 6.34, N 7.72.

Found (%): C 46.37, H 6.27, N 7.74.

Calcd. $C_{21}H_{32}GaN_3O_8$ (%): C 48.12, H 6.15, N 8.02.

$[Ga(nta)(phe)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.40–7.45 (sp, 2H, H6), 7.34–7.39 (sp, 1H, H7), 7.32–7.38 (sp, 2H, H5), 3.95–4.01 (sp, 1H, H2), 3.39–3.45 (m, 1H, H3), 3.00–3.08 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.9 (C1), 137.1 (C4), 129.8 (C5), 129.7 (C6), 128.0 (C7), 55.8 (C2), 37.7 (C3) ppm.

L-Phenylalanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.35–7.42 (sp, 2H, H6), 7.34–7.39 (sp, 1H, H7), 7.29–7.34 (sp, 2H, H5), 3.95–4.01 (sp, 1H, H2), 3.23–3.29 (m, 1H, H3), 3.07–3.14 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.4 (C1), 135.7 (C4), 130.0 (C5), 129.7 (C6), 128.3 (C7), 56.6 (C2), 37.0 (C3) ppm.

5.5.17 $HNEt_3[Ga(nta)(pro)]$

Starting material: L-Proline, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether, methanol, toluene.

Procedure: L-Proline (115 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{17}H_{30}GaN_3O_8$ + 0.75 H_2O.

Yield: 199 mg (0.408 mmol, 40.8%).

Elemental analysis: Calcd. (%): C 41.87, H 6.51, N 8.62.

Found (%): C 41.77, H 6.38, N 8.53.

Calcd. $C_{17}H_{30}GaN_3O_8$ (%): C 43.06, H 6.38, N 8.86.

$[Ga(nta)(pro)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.10–4.16 (sp, 1H, H2), 3.27–3.44 (sp, 2H, H5), 2.29–2.41 (sp, 1H, H3), 1.95–2.10 (sp, 2H, H4), 1.87–1.98 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.2 (C1), 61.4 (C2), 48.7 (C5), 30.4 (C3), 26.8 (C4) ppm.

L-Proline:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.10–4.16 (sp, 1H, H2), 3.27–3.44 (sp, 2H, H5), 2.29–2.41 (sp, 1H, H3), 1.95–2.10 (sp, 2H, H4), 1.87–1.98 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.1 (C1), 61.8 (C2), 46.7 (C5), 29.6 (C3), 24.4 (C4) ppm.

Crystals of $HNEt_3[Ga(nta)(pro)]\cdot H_2O$ ($(HNEt_3)$**2g**$\cdot H_2O$) were obtained after ten months by storing a methanolic solution of the raw product over toluene.

Empirical formula: $C_{17}H_{30}GaN_3O_8\cdot H_2O$, 492.18 g mol^{-1}.

Yield: Few crystals.

5.5.18 $HNEt_3[Ga(nta)(ser)]$

Starting material: L-Serine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether, methanol, *n*-hexane.

Procedure: L-Serine (105 mg, 1.00 mmol) was suspended in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (5 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{15}H_{28}GaN_3O_9$ + 0.15 $Ga(OH)_3$ + 0.10 H_2O.

Yield: 282 mg (0.583 mmol, 58.3%).

Elemental analysis: Calcd. (%): C 37.22, H 5.97, N 8.68.

Found (%): C 37.19, H 5.91, N 8.64.

Calcd. $C_{15}H_{28}GaN_3O_9$ (%): C 38.82, H 6.08, N 9.05.

$[Ga(nta)(ser)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.04 (sp, 2H, H3), 3.81–3.88 (sp, 1H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 176.6 (C1), 61.4 (C3), 56.2 (C2) ppm.

L-Serine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.04 (sp, 2H, H3), 3.81–3.88 (sp, 1H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 172.8 (C1), 60.8 (C3), 57.0 (C2) ppm.

Crystals of $HNEt_3[Ga(nta)(ser)]\cdot 0.14H_2O$ ($(HNEt_3)$**2h**$\cdot 0.14H_2O$) were obtained after two weeks by storing a methanolic solution of the raw product over *n*-hexane.

Empirical formula: $C_{17}H_{30}GaN_3O_8\cdot 0.14H_2O$, 468.66 g mol^{-1}.

Yield: Few crystals.

5.5.19 $HNEt_3[Ga(nta)(thr)]$

Starting material: L-Threonine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Threonine (119 mg, 1.00 mmol) was suspended in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (15 mL) and ethyl acetate (30 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{16}H_{30}GaN_3O_9 + 0.15\ H_2O$.

Yield: 194 mg (0.403 mmol, 40.3%).

Elemental analysis: Calcd. (%): C 39.97, H 6.35, N 8.74.

Found (%): C 40.03, H 6.33, N 8.66.

Calcd. $C_{16}H_{30}GaN_3O_9$ (%): C 40.19, H 6.32, N 8.79.

$[Ga(nta)(thr)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.53–4.59 (m, 1H, H3), 3.58–3.63 (sp, 1H, H2), 1.30–1.34 (sp, 3H, H4) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 177.0 (C1), 66.4 (C3), 59.7 (C2), 20.1 (C4) ppm.

L-Threonine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.22–4.27 (m, 1H, H3), 3.58–3.62 (sp, 1H, H2), 1.30–1.34 (sp, 3H, H4) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 173.3 (C1), 66.5 (C3), 61.0 (C2), 20.1 (C4) ppm.

5.5.20 $HNEt_3[Ga(nta)(trp)]/[Ga(nta)(Htrp)]$

Starting material: L-Tryptophan, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, acetone, diethyl ether.

Procedure: L-Tryptophan (181 mg, 1.00 mmol) was suspended in 8.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (5 mL) and ethyl acetate (40 mL). After filtration and washing with acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{23}H_{33}GaN_4O_8 + 0.10\ C_{17}H_{18}GaN_3O_8 + 1.65\ H_2O$.

Yield: 194 mg (0.334 mmol, 33.4%).

Elemental analysis: Calcd. (%): C 46.41, H 6.01, N 9.42.

Found (%): C 46.41, H 5.97, N 9.46.

Calcd. $C_{23}H_{33}GaN_4O_8$ (%): C 49.05, H 5.91, N 9.95.

$[Ga(nta)(trp)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.64–7.68 (sp, 1H, H8), 7.47–7.50 (sp, 1H, H11), 7.29 (s, 1H, H5), 7.21–7.25 (sp, 1H, H10), 7.12–7.16 (sp, 1H, H9), 4.00–4.04 (sp, 1H, H2), 3.44–3.56 (sp, 1H, H3), 3.16–3.24 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.3 (C1), 137.0 (C6), 127.3 (C7), 125.4 (C5), 122.8 (C10), 120.0 (C9), 119.0 (C8), 112.6 (C11), 109.2 (C4), 54.6 (C2), 27.9 (C3) ppm.

L-Tryptophan:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.64–7.68 (sp, 1H, H8), 7.47–7.50 (sp, 1H, H11), 7.25 (s, 1H, H5), 7.21–7.25 (sp, 1H, H10), 7.12–7.16 (sp, 1H, H9), 4.00–4.04 (sp, 1H, H2), 3.73–3.45 (sp, 1H, H3), 3.22–3.28 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.8 (C1), 136.9 (C6), 127.3 (C7), 125.6 (C5), 122.7 (C10), 120.1 (C9), 119.0 (C8), 112.6 (C11), 108.1 (C4), 55.5 (C2), 27.0 (C3) ppm.

5.5.21 Attempt of synthesis: $HNEt_3[Ga(nta)(tyr)]$

Starting material: L-Tyrosine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Tyrosine (181 mg, 1.00 mmol) was suspended in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_9H_{11}NO_3 + 1.15\ H_2O + 0.35\ C_{24}H_{46}Ga_2N_4O_{14}$.

Yield: 380 mg.

Elemental analysis: Calcd. (%): C 44.86, H 6.36, N 7.22.

Found (%): C 45.00, H 6.52, N 7.37.

5.5.22 $HNEt_3[Ga(nta)(val)]$

Starting material: L-Valine, water, gallium(III) chloride, nitrilotriacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Valine (117 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (15 mL) and ethyl acetate (5 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{17}H_{32}GaN_3O_8$ + 0.15 H_2O.

Yield: 221 mg (0.461 mmol, 46.1%).

Elemental analysis: Calcd. (%): C 42.64, H 6.80, N 8.77.

Found (%): C 42.61, H 6.74, N 8.79.

Calcd. $C_{17}H_{32}GaN_3O_8$ (%): C 42.88, H 6.77, N 8.82.

$[Ga(nta)(val)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.66 (d, 1H, H2, $^3J_{2,3}$ = 3.5 Hz), 2.46–2.53 (m, 1H, H3), 1.08 (d, 3H, H4, $^3J_{3,4}$ = 7.0 Hz), 0.91 (d, 3H, H5, $^3J_{3,5}$ = 7.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.7 (C1), 59.8 (C2), 30.2 (C3), 19.2 (C4), 15.9 (C5) ppm.

L-Valine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.60 (d, 1H, H2, $^3J_{2,3}$ = 4.3 Hz), 2.21–2.31 (m, 1H, H3), 1.03 (d, 3H, H4, $^3J_{3,4}$ = 7.0 Hz), 0.98 (d, 3H, H5, $^3J_{3,5}$ = 7.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.7 (C1), 60.9 (C2), 29.7 (C3), 18.6 (C4), 17.3 (C5) ppm.

5.5.23 $(HNEt_3)_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$

Starting material: Nitrilotriacetic acid, water, gallium(III) chloride, triethylamine, ethanol, diethyl ether.

Procedure: Nitrilotriacetic acid (191 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 2 days.

Empirical formula: $C_{24}H_{46}Ga_2N_4O_{14} + 1.60\ H_2O$.

Yield: 310 mg (0.396 mmol, 79.2%).

Elemental analysis: Calcd. (%): C 36.82, H 6.33, N 7.16.

Found (%): C 36.80, H 6.32, N 7.15.

Calcd. $C_{24}H_{46}Ga_2N_4O_{14}$ (%): C 38.23, H 6.15, N 7.43.

$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.71 (s, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 175.5 (C1), 63.2 (C2) ppm.

5.5.24 HDIPEA[Ga(ala)(nta)]

Starting material: L-Alanine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, dimethyl sulfoxide.

Procedure: L-Alanine (89 mg, 1.0 mmol) was dissolved in 2 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The colourless solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (10 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{17}H_{32}GaN_3O_8$ + 0.85 H_2O.

Yield: 358 mg (0.728 mmol, 72.8%).

Elemental analysis: Calcd. (%): C 41.54, H 6.91, N 8.55.

Found (%): C 41.57, H 6.91, N 8.54.

Calcd. $C_{17}H_{32}GaN_3O_8$ (%): C 42.88, H 6.77, N 8.82.

[Ga(ala)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.76–3.82 (sp, 1H, H2), 1.51 (d, 3H, H3, $^3J_{2,3}$ = 7.3 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.7 (C1), 50.3 (C2). 18.1 (C3) ppm.

L-Alanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.76–3.82 (sp, 1H, H2), 1.46 (d, 3H, H3, $^3J_{2,3}$ = 7.2 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.1 (C1), 51.1 (C2), 16.8 (C3) ppm.

[Ga(ala-κ*O*,*N*)(nta)]$^-$ (isomer I):

^{1}H NMR (400 MHz, MeOD)**:** δ = 3.63–3.71 (sp, 1H, H2), 3.70 (s, 6H, nta), 1.53 (d, 3H, H3, $^3J_{2,3}$ = 7.3 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, MeOD)**:** δ = 179.4 (C1), 175.0 (C1, A, nta), 64.7 (C2, B, nta), 51.5 (C2). 19.0 (C3) ppm.

[Ga(ala-κ*O*,*N*)(nta)]$^-$ (isomer II):

^{1}H NMR (400 MHz, MeOD)**:** δ = -

^{13}C{^{1}H} NMR (101 MHz, MeOD)**:** δ = 179.4 (C1), 51.6 (C2). 19.1 (C3) ppm.

HDIPEA$^+$:

^{1}H NMR (400 MHz, MeOD)**:** δ = 3.69–3.79 (sp, 2H, H1), 3.24 (q, 2H, H4, $^3J_{4,5}$ = 7.4 Hz), 1.36–1.40 (sp, 15H, H2/H3/H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, MeOD)**:** δ = 56.2 (C1), 44.2 (C4), 19.2 (C2), 17.8 (C3), 13.6 (C5) ppm.

Crystals of HDIPEA[Ga(ala)(nta)]·2H_2O ((HDIPEA)**2a**·2H_2O) were obtained after one week by storing an aqueous solution (pH 7.0) of the raw product over dimethyl sulfoxide.

Empirical formula:	$C_{16}H_{30}GaN_3O_8$·2H_2O, 512.22 g mol^{-1}.
Yield:	189 mg (0.369 mmol, 36.9%).
Elemental analysis:	Calcd. (%): C 39.86, H 7.08, N 8.20.
	Found (%): C 39.78, H 6.84, N 8.22.

5.5.25 [Ga(Harg)(nta)]·0.05DIPEA

Starting material: L-Arginine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, diethyl ether.

Procedure: L-Arginine (174 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{12}H_{20}GaN_5O_8 \cdot 0.05C_8H_{19}N + 2.45\ H_2O$.

Yield: 344 mg (0.713 mmol, 71.3%).

Elemental analysis: Calcd. (%): C 30.86, H 5.40, N 14.66.

Found (%): C 30.94, H 5.30, N 14.57.

Calcd. $C_{12}H_{20}GaN_5O_8$ (%): C 33.36, H 4.67, N 16.21.

[Ga(Harg-κ*O*,*N*)(nta)] (isomer I):

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.77–3.83 (sp, 1H, H2), 3.21–3.26 (sp, 2H, H5), 1.98–2.12 (m, 1H, H3), 1.78–1.86 (sp, 1H, H3), 1.69–1.87 (sp, 2 H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.6 (C1), 157.3 (C6), 54.1 (C2), 41.2 (C5), 29.3 (C3), 25.3 (C4) ppm.

[Ga(Harg-κ*O*,*N*)(nta)] (isomer II):

^{1}H NMR (400 MHz, D_2O)**:** δ = -

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.6 (C1), 53.6 (C2), 41.2 (C5), 29.7 (C3), 25.5 (C4) ppm.

L-Arginine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.73–3.79 (sp, 1H, H2), 3.21–3.26 (sp, 2H, H5), 1.83–1.95 (sp, 2H, H3), 1.58–1.74 (sp, 2 H, H4) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 174.9 (C1), 157.3 (C6), 54.9 (C2), 41.1 (C5), 28.2 (C3), 24.5 (C4) ppm.

5.5.26 HDIPEA[Ga(asn)(nta)]

Starting material: L-Asparagine monohydrate, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, methanol, acetone.

Procedure: L-Asparagine monohydrate (150 mg, 1.00 mmol) was suspended in 7 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless suspension (pH 7.5) which was stirred for 16 h. The colourless slurry was concentrated by rotary evaporation and the obtained oil diluted with 1 mL of water. The raw product was precipitated by addition of ethanol (40 mL) and ethyl acetate (60 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{18}H_{33}GaN_4O_9$ + 0.20 $Ga(OH)_3$ + 0.05 C_2H_6O.

Yield: 322 mg (0.590 mmol, 59.0%).

Elemental analysis: Calcd. (%): C 39.84, H 6.26, N 10.27.

Found (%): C 39.77, H 6.37, N 10.36.

Calcd. $C_{18}H_{33}GaN_4O_9$ (%): C 41.64, H 6.41, N 10.79.

$[Ga(asn)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97 (t, 1H, H2, $^{3}J_{2,3}$ = 5.5 Hz), 2.95–2.97 (sp, 2H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 177.6 (C1), 175.2 (C4), 51.4 (C2), 36.2 (C3) ppm.

L-Asparagine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.03 (dd, 1H, H2), 2.82–2.95 (sp, 2H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 174.8 (C4), 173.7 (C1), 51.8 (C2), 35.0 (C3) ppm.

Crystals of HDIPEA[Ga(asn)(nta)] ((HDIPEA)**2b**) were obtained after one week by storing a methanolic solution of the raw product over acetone.

Empirical formula: $C_{18}H_{33}GaN_4O_9$, 519.20 g mol^{-1}.

Yield: Few crystals.

5.5.27 HDIPEA[Ga(Hasp)(nta)]·0.10DIPEA

Starting material: L-Aspartic acid, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Aspartic acid (133 mg, 1.00 mmol) was suspended in 2.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (909 µL, 5.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The colourless solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (10 mL) and ethyl acetate (50 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{18}H_{32}GaN_3O_{10}·0.10C_8H_{19}N$ + 0.10 $Ga(OH)_3$.

Yield: 470 mg (0.862 mmol, 86.2%).

Elemental analysis: Calcd. (%): C 41.42, H 6.32, N 7.96.

Found (%): C 41.20, H 6.19, N 8.13.

Calcd. $C_{18}H_{32}GaN_3O_{10}$ (%): C 41.56, H 6.20, N 8.08.

[Ga(Hasp)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.93 (t, 1H, H2, $^3J_{2,3}$ = 5.5 Hz), 2.83–2.96 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.7 (C1), 176.2 (C4), 51.7 (C2), 37.3 (C3) ppm.

L-Aspartic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.98–4.07 (m, 1H, H2), 2.83–2.96 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.2 (C1), 173.6 (C4), 51.9 (C2), 36.5 (C3) ppm.

5.5.28 HDIPEA[Ga(cys)(nta)]

Starting material: L-Cysteine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, acetone, diethyl ether.

Procedure: L-Cysteine (121 mg, 1.00 mmol) was dissolved in 3.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless slurry (pH 7.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (70 mL). After filtration and washing with acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 15 h.

Empirical formula: $C_{17}H_{32}GaN_3O_8S + 0.10\ Ga(OH)_3 + 0.10\ H_2O + 0.05\ C_2H_6O$.

Yield: 448 mg (0.854 mmol, 85.4%).

Elemental analysis: Calcd. (%): C 39.16, H 6.30, N 8.01, S 6.11.

Found (%): C 39.17, H 6.33, N 8.08, S 6.05.

Calcd. $C_{17}H_{32}GaN_3O_8S$ (%): C 40.18, H 6.35, N 8.27, S 6.31.

[Ga(cys-κ^2*S*,*X*)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.5 (C1), 56.1 (C2), 24.6 (C3) ppm.

[Ga(cys-κ*O*,*N*)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 57.8 (C2), 26.5 (C3) ppm.

L-Cysteine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.97–4.01 (sp, 1H, H2), 2.97–3.03 (sp, 1H, H3), 2.81–2.85 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 172.8 (C1), 56.4 (C2), 25.3 (C3) ppm.

5.5.29 HDIPEA[Ga(gln)(nta)]

Starting material: L-Glutamine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Glutamine (146 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL) and ethyl acetate (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{19}H_{35}GaN_4O_9 + 0.2\ H_2O + 0.05\ C_2H_6O$.

Yield: 464 mg (0.861 mmol, 86.1%).

Elemental analysis: Calcd. (%): C 42.55, H 6.67, N 10.39.

Found (%): C 42.51, H 6.61, N 10.34.

Calcd. $C_{19}H_{35}GaN_4O_9$ (%): C 42.80, H 6.62, N 10.51.

[Ga(gln)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.71–3.82 (sp, 1H, H2), 2.46–2.54 (m, 2H, H4), 2.24–2.35 (m, 1H, H3), 2.02–2.12 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.3 (C5), 178.0 (C1), 54.0 (C2), 32.2 (C4), 28.1 (C3) ppm.

L-Glutamine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.71–3.82 (sp, 1H, H2), 2.41–2.46 (m, 2H, H4), 2.08–2.17 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.0 (C5), 174.4 (C1), 54.7 (C2), 31.4 (C4), 26.8 (C3) ppm.

5.5.30 HDIPEA[Ga(Hglu)(nta)]·0.05DIPEA

Starting material: L-Glutamic acid, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Glutamic acid (147 mg, 1.00 mmol) was suspended in 2.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (909 µL, 5.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The colourless solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (10 mL) and ethyl acetate (50 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{19}H_{34}GaN_3O_{10}\cdot 0.05C_8H_{19}N + 0.30\ H_2O + 0.05\ Ga(OH)_3$.

Yield: 524 mg (0.949 mmol, 94.9%).

Elemental analysis: Calcd. (%): C 42.20, H 6.52, N 7.74.

Found (%): C 40.02, H 6.31, N 7.80.

Calcd. $C_{19}H_{34}GaN_3O_{10}$ (%): C 42.72, H 6.42, N 7.87.

[Ga(Hglu)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.57 (sp, 2H, H4), 1.98–2.18 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 54.0 (C2), 32.2 (C4), 28.0 (C3) ppm.

L-Glutamic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.57 (sp, 2H, H4), 1.98–2.18 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.9 (C5), 174.2 (C1), 54.6 (C2), 32.1 (C4), 26.8 (C3) ppm.

5.5.31 HDIPEA[Ga(gly)(nta)]

Starting material: Glycine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, methanol, acetone, dimethyl sulfoxide.

Procedure: Glycine (75 mg, 1.0 mmol) was dissolved in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The colourless solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (15 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{16}H_{30}GaN_3O_8$ + 0.95 H_2O.

Yield: 401 mg (0.837 mmol, 83.7%).

Elemental analysis: Calcd. (%): C 40.10, H 6.71, N 8.77.

Found (%): C 40.02, H 6.58, N 8.86.

Calcd. $C_{16}H_{30}GaN_3O_8$ (%): C 41.58, H 6.54, N 9.09.

$[Ga(gly)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.57 (s, 2H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 176.7 (C1), 42.1 (C2) ppm.

Glycine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.55 (s, 2H, H2) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 172.7 (C1), 42.0 (C2) ppm.

Crystals of HDIPEA[Ga(gly)(nta)]·H_2O ((HDIPEA)**2c**· H_2O) were obtained after two weeks by storing a methanolic solution of the raw product over acetone.

Empirical formula: $C_{16}H_{30}GaN_3O_8 \cdot H_2O$, 480.17 g mol^{-1}.

Yield: 178 mg (0.371 mmol, 37.1%).

Elemental analysis: Calcd. (%):C 40.02, H 6.72, N 8.75.

Found (%): C 39.97, H 6.70, N 8.65.

Crystals of HDIPEA[Ga(gly)(nta)]·MeOH ((HDIPEA)**2c**·MeOH) were obtained after one week by storing a methanolic solution of the raw product over dimethyl sulfoxide.

Empirical formula: $C_{16}H_{30}GaN_3O_8 \cdot CH_4O$, 494.19 g mol^{-1}.

Yield: Few crystals.

5.5.32 [Ga(Hhis)(nta)]·0.25DIPEA

Starting material: L-Histidine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, diethyl ether.

Procedure: L-Histidine (155 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{12}H_{15}GaN_4O_8 \cdot 0.25C_8H_{19}N + 2.10\ H_2O + 0.05\ C_2H_6O$.

Yield: 234 mg (0.482 mmol, 48.2%).

Elemental analysis: Calcd. (%): C 34.89, H 5.04, N 12.26.

Found (%): C 34.76, H 5.13, N 12.43.

Calcd. $C_{12}H_{15}GaN_4O_8$ (%): C 34.90, H 3.66, N 13.57.

[Ga(Hhis)(nta)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 8.34–8.43 (sp, 1H, H6), 7.14–7.30 (sp, 1H, H5), 4.02–4.08 (sp, 1H, H2), 3.24–3.47 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.9 (C1), 133.3 (C6), 129.6 (C4), 116.5 (C5), 53.7 (C2), 26.8 (C3) ppm.

L-Histidine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 8.34–8.43 (sp, 1H, H6), 7.14–7.30 (sp, 1H, H5), 4.02–4.08 (sp, 1H, H2), 3.24–3.47 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 173.5 (C1), 136.2 (C6), 129.6 (C4), 118.2 (C5), 54.4 (C2), 27.7 (C3) ppm.

5.5.33 HDIPEA[Ga(ile)(nta)]

Starting material: L-Isoleucine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Isoleucine (131 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (15 mL) and ethyl acetate (50 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{20}H_{38}GaN_3O_8$ + 0.20 H_2O.

Yield: 421 mg (0.807 mmol, 80.7%).

Elemental analysis: Calcd. (%): C 46.03, H 7.42, N 8.05.

Found (%): C 46.05, H 7.36, N 7.98.

Calcd. $C_{20}H_{38}GaN_3O_8$ (%): C 46.35, H 7.39, N 8.11.

[Ga(ile)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.65–3.72 (sp, 1H, H2), 2.16–2.26 (m, H1, H3), 1.25–1.35 (sp, 2H, H4), 1.06 (d, 3H, H6, $^3J_{3,6}$ = 7.0 Hz), 0.88–0.95 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.5 (C1), 59.5 (C2), 37.2 (C3), 24.1 (C4), 16.3 (C6), 12.0 (C5) ppm.

L-Isoleucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.65–3.72 (sp, 1H, H2), 1.92–2.02 (m, H1, H3), 1.40–1.51 (sp, 1H, H4), 1.20–1.31 (sp, 1H, H4), 0.99 (d, 3H, H6, $^3J_{3,6}$ = 7.0 Hz), 0.88–0.95 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.5 (C1), 60.1 (C2), 36.5 (C3), 25.1 (C4), 15.3 (C6), 11.8 (C5) ppm.

5.5.34 HDIPEA[Ga(leu)(nta)]

Starting material: L-Leucine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, methanol, acetone.

Procedure: L-Leucine (131 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL) and ethyl acetate (40 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{20}H_{38}GaN_3O_8 + 0.15\ H_2O + 0.05\ C_4H_8O_2$.

Yield: 356 mg (0.678 mmol, 67.8%).

Elemental analysis: Calcd. (%): C 46.18, H 7.43, N 8.00.

Found (%): C 46.20, H 7.38, N 7.98.

Calcd. $C_{20}H_{38}GaN_3O_8$ (%): C 46.35, H 7.39, N 8.11.

[Ga(leu)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.65–3.74 (sp, 1H, H2), 1.72–1.80 (sp, 2H, H3), 1.64–1.80 (sp, 1H, H4), 0.93–0.98 (sp, 6H, H5/H6) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.6 (C1), 52.9 (C2), 41.4 (C3), 25.1 (C4), 23.1 (C5), 20.7 (C6) ppm.

L-Leucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.65–3.74 (sp, 1H, H2), 1.64–1.80 (sp, 1H, H4), 1.64–1.72 (sp, 2H, H3), 0.93–0.98 (sp, 6H, H5/H6) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.9 (C1), 54.0 (C2), 40.4 (C3), 24.8 (C4), 22.7 (C5), 21.6 (C6) ppm.

Crystals of HDIPEA[Ga(leu)(nta)] ((HDIPEA)**2d**) were obtained after 2 days by storing a methanolic solution of the raw product over acetone.

Empirical formula: $C_{20}H_{38}GaN_3O_8$, 518.26 g mol^{-1}.

Yield: Few crystals.

5.5.35 [Ga(Hlys)(nta)]·0.05DIPEA

Starting material: L-Lysine hydrochloride, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, diethyl ether.

Procedure: L-Lysine hydrochloride (183 mg, 1.00 mmol) was dissolved in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (909 µL, 5.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{12}H_{20}GaN_3O_8 \cdot 0.05C_8H_{19}N + 2.25\ H_2O + 0.15\ C_2H_6O$.

Yield: 305 mg (0.666 mmol, 66.6%).

Elemental analysis: Calcd. (%): C 33.31, H 5.80, N 9.33.

Found (%): C 33.16, H 5.87, N 9.50.

Calcd. $C_{12}H_{20}GaN_3O_8$ (%): C 35.67, H 4.99, N 10.40.

[Ga(Hlys-κ*O*,*N*)(nta)] (isomer I):

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.70–3.79 (sp, 1H, H2), 2.98–3.07 (sp, 2H, H6), 1.95–2.10 (m, 2H, H3), 1.64–1.77 (sp, 2H, H5), 1.50–1.60 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.8 (C1), 54.2 (C2), 39.7 (C6), 31.6 (C3), 26.9 (C5), 22.8 (C4) ppm.

[Ga(Hlys-κ*O*,*N*)(nta)] (isomer II):

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.9 (C1), 53.7 (C2), 39.7 (C6), 31.9 (C3), 22.9 (C4) ppm.

L-Lysine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.70–3.79 (sp, 1H, H2), 2.98–3.07 (sp, 2H, H6), 1.80–1.95 (m, 2H, H3), 1.64–1.77 (sp, 2H, H5), 1.37–1.54 (sp, 2H, H4) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 175.1 (C1), 55.0 (C2), 39.7 (C6), 30.5 (C3), 27.0 (C5), 22.0 (C4) ppm.

5.5.36 HDIPEA[Ga(met)(nta)]

Starting material: L-Methionine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, diethyl ether, acetone.

Procedure: L-Methionine (149 mg, 1.00 mmol) was suspended in 3 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{19}H_{36}GaN_3O_8S + 0.05\ H_2O$.

Yield: 505 mg (0.940 mmol, 94.0%).

Elemental analysis: Calcd. (%): C 42.48, H 6.77, N 7.82, S 5.97.

Found (%): C 42.52, H 6.66, N 7.87, S 5.86.

Calcd. $C_{19}H_{36}GaN_3O_8S$ (%): C 42.55, H 6.77, N 7.84, S 5.98.

$[Ga(met)(nta)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.83–3.88 (sp, 1H, H2), 2.65–2.78 (m, 2H, H4), 2.25–2.36 (m, 1H, H3), 2.13 (s, 3H, H5), 2.02–2.12 (sp, 1H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 178.4 (C1), 53.5 (C2), 31.3 (C3), 30.3 (C4), 14.6 (C5) ppm.

L-Methionine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.83–3.88 (sp, 1H, H2), 2.62 (t, 2H, H4, $^{3}J_{3,4}$ = 7.5 Hz), 2.09–2.23 (sp, 2H, H3), 2.11 (s, 3H, H5) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 174.6 (C1), 54.5 (C2), 30.3 (C3), 29.4 (C4), 14.5 (C5) ppm.

Crystals of HDIPEA[Ga(met)(nta)] ((HDIPEA)**2e**) were obtained after two weeks by storing an aqueous solution (pH 7.0) of the raw product over acetone.

Empirical formula: $C_{19}H_{36}GaN_3O_8S$, 536.29 g mol^{-1}.

Yield: 177 mg (0.330 mmol, 33.0%).

Elemental analysis: Calcd. (%): C 42.55, H 6.77, N 7.84, S 5.98.

Found (%): C 42.49, H 6.47, N 7.89, S 6.00.

5.5.37 HDIPEA[Ga(nta)(phe)]

Starting material: L-Phenylalanine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Phenylalanine (165 mg, 1.00 mmol) was suspended in 2.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (13 mL) and ethyl acetate (70 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 3 h.

Empirical formula: $C_{23}H_{36}GaN_3O_8$ + 0.90 H_2O.

Yield: 375 mg (0.660 mmol, 66.0%).

Elemental analysis: Calcd. (%): C 48.59, H 6.70, N 7.39.

Found (%): C 48.52, H 6.60, N 7.40.

Calcd. $C_{23}H_{36}GaN_3O_8$ (%): C 50.02, H 6.57, N 7.61.

[Ga(nta)(phe)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.40–7.46 (sp, 2H, H6), 7.34–7.39 (sp, 1H, H7), 7.32–7.38 (sp, 2H, H5), 3.95–4.01 (sp, 1H, H2), 3.39–3.46 (m, 1H, H3), 2.99–3.08 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.9 (C1), 137.1 (C4), 129.8 (C5), 129.7 (C6), 128.0 (C7), 55.8 (C2), 37.8 (C3) ppm.

L-Phenylalanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.35–7.42 (sp, 2H, H6), 7.34–7.39 (sp, 1H, H7), 7.29–7.34 (sp, 2H, H5), 3.95–4.01 (sp, 1H, H2), 3.23–3.29 (m, 1H, H3), 3.07–3.14 (sp, 1H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 174.4 (C1), 135.7 (C4), 130.0 (C5), 129.7 (C6), 128.3 (C7), 56.6 (C2), 37.0 (C3) ppm.

5.5.38 HDIPEA[Ga(nta)(pro)]

Starting material: L-Proline, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, methanol, dimethyl sulfoxide.

Procedure: L-Proline (115 mg, 1.00 mmol) was suspended in 2.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The colourless solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (3 mL) and ethyl acetate (50 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{19}H_{34}GaN_3O_8$ + 0.05 $Ga(OH)_3$ + 0.05 H_2O.

Yield: 478 mg (0.939 mmol, 93.9%).

Elemental analysis: Calcd. (%): C 44.82, H 6.78, N 8.25.

Found (%): C 44.74, H 6.69, N 8.25.

Calcd. $C_{19}H_{34}GaN_3O_8$ (%): C 45.44, H 6.82, N 8.37.

$[Ga(nta)(pro)]^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.10–4.16 (sp, 1H, H2), 3.27–3.44 (sp, 2H, H5), 2.29–2.41 (sp, 1H, H3), 1.95–2.10 (sp, 2H, H4), 1.87–1.98 (sp, 1H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 179.1 (C1), 61.4 (C2), 48.7 (C5), 30.4 (C3), 26.7 (C4) ppm.

L-Proline:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.10–4.16 (sp, 1H, H2), 3.27–3.44 (sp, 2H, H5), 2.29–2.41 (sp, 1H, H3), 1.95–2.10 (sp, 2H, H4), 1.87–1.98 (sp, 1H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 175.0 (C1), 61.8 (C2), 46.7 (C5), 29.6 (C3), 24.4 (C4) ppm.

Crystals of HDIPEA[Ga(nta)(pro)] ((HDIPEA)**2g**) were obtained after two days by storing a methanolic solution of the raw product over dimethyl sulfoxide.

Empirical formula: $C_{19}H_{34}GaN_3O_8$, 502.22 g mol^{-1}.

Yield: Few crystals.

5.5.39 HDIPEA[Ga(nta)(ser)]

Starting material: L-Serine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Serine (105 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL) and ethyl acetate (70 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{17}H_{32}GaN_3O_9$ + 0.80 H_2O.

Yield: 420 mg (0.829 mmol, 82.9%).

Elemental analysis: Calcd. (%): C 40.31, H 6.69, N 8.29.

Found (%): C 40.26, H 6.60, N 8.25.

Calcd. $C_{17}H_{32}GaN_3O_9$ (%): C 41.49, H 6.55, N 8.54.

[Ga(nta)(ser)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.04 (sp, 2H, H3), 3.81–3.88 (sp, 1H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.4 (C1), 61.4 (C3), 56.2 (C2) ppm.

L-Serine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.04 (sp, 2H, H3), 3.81–3.88 (sp, 1H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 172.8 (C1), 60.8 (C3), 56.9 (C2) ppm.

5.5.40 HDIPEA[Ga(nta)(thr)]

Starting material: L-Threonine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Threonine (165 mg, 1.00 mmol) was suspended in 1.0 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL) and ethyl acetate (40 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{18}H_{34}GaN_3O_9$ + 0.50 H_2O.

Yield: 291 mg (0.565 mmol, 56.5%).

Elemental analysis: Calcd. (%): C 41.96, H 6.85, N 8.16.

Found (%): C 41.80, H 6.67, N 8.28.

Calcd. $C_{18}H_{34}GaN_3O_9$ (%): C 42.71, H 6.77, N 8.30.

[Ga(nta)(thr)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.54–4.58 (m, 1H, H3), 3.57–3.63 (sp, 1H, 2H), 1.29–1.36 (sp, 3H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.9 (C1), 66.4 (C3), 59.7 (C2), 20.1 (C4) ppm.

L-Threonine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.21–4.28 (m, 1H, H3), 3.57–3.63 (sp, 1H, 2H), 1.29–1.36 (sp, 3H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 173.2 (C1), 66.5 (C3), 61.0 (C2), 20.1 (C4) ppm.

5.5.41 HDIPEA[Ga(nta)(trp)]

Starting material: L-Tryptophan, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Tryptophan (204 mg, 1.00 mmol) was suspended in 16 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol), *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) and ethanol (10 mL) resulted in a yellow solution (pH 7.0) which was stirred for 16 h. The solution was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (10 mL) and ethyl acetate (60 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{25}H_{37}GaN_4O_8 + 0.25\ H_2O + 0.20\ Ga(OH)_3$.

Yield: 343 mg (0.553 mmol, 55.3%).

Elemental analysis: Calcd. (%): C 48.43, H 6.19, N 9.04.

Found (%): C 48.44, H 6.21, N 9.06.

Calcd. $C_{25}H_{37}GaN_4O_8$ (%): C 50.78, H 6.31, N 9.48.

[Ga(nta)(trp)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.66–7.69 (sp, 1H, H8), 7.48–7.52 (sp, 1H, H11), 7.30 (s, 1H, H5), 7.22–7.26 (sp, 1H, H10), 7.13–7.18 (sp, 1H, H9), 4.02–4.05 (sp, 1H, H2), 3.46–3.54 (sp, 1H, H3), 3.16–3.24 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.4 (C1), 137.1 (C6), 127.3 (C7), 125.4 (C5), 122.8 (C10), 120.1 (C9), 119.0 (C8), 112.6 (C11), 109.2 (C4), 54.6 (C2), 28.0 (C3) ppm.

L-Tryptophan:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.66–7.69 (sp, 1H, H8), 7.48–7.52 (sp, 1H, H11), 7.26 (s, 1H, H5), 7.22–7.26 (sp, 1H, H10), 7.13–7.18 (sp, 1H, H9), 4.02–4.05 (sp, 1H, H2), 3.39–3.45 (m, 1H, H3), 3.22–3.29 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.9 (C1), 136.9 (C6), 127.3 (C7), 125.6 (C5), 122.7 (C10), 120.1 (C9), 119.0 (C8), 112.6 (C11), 108.1 (C4), 55.5 (C2), 27.0 (C3) ppm.

5.5.42 Attempt of synthesis: HDIPEA[Ga(nta)(tyr)]

Starting material: L-Tyrosine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Tyrosine (181 mg, 1.00 mmol) was suspended in 4.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (774 µL, 4.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_9H_{11}NO_3 + 0.05\ C_{23}H_{36}GaN_3O_9 + 0.05\ Ga(OH)_3$.

Yield: 135 mg.

Elemental analysis: Calcd. (%): C 56.53, H 6.05, N 7.47.

Found (%): C 56.42, H 5.91, N 7.28.

Calcd. $C_{23}H_{36}GaN_3O_9$ (%): C 48.61, H 6.39, N 7.39.

5.5.43 HDIPEA[Ga(nta)(val)]

Starting material: L-Valine, water, gallium(III) chloride, nitrilotriacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Valine (117 mg, 1.00 mmol) was suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), nitrilotriacetic acid (191 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL) and ethyl acetate (60 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{19}H_{36}GaN_3O_8$ + 0.15 H_2O.

Yield: 312 mg (0.615 mmol, 61.5%).

Elemental analysis: Calcd. (%): C 45.02, H 7.22, N 8.29.

Found (%): C 45.01, H 7.14, N 8.24.

Calcd. $C_{19}H_{36}GaN_3O_8$ (%): C 45.26, H 7.20, N 8.33.

[Ga(nta)(val)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.65 (d, 1H, H2, $^3J_{2,3}$ = 3.4 Hz), 2.46–2.54 (m, 1H, H3), 1.08 (d, 3H, H4, $^3J_{3,4}$ = 7.0 Hz), 0.91 (d, 3H, H5, $^3J_{3,5}$ = 7.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.5 (C1), 59.8 (C2), 30.2 (C3), 19.2 (C4), 15.9 (C5) ppm.

L-Valine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.60 (d, 1H, H2, $^3J_{2,3}$ = 4.3 Hz), 2.21–2.31 (m, 1H, H3), 1.03 (d, 3H, H4, $^3J_{3,4}$ = 7.0 Hz), 0.98 (d, 3H, H5, $^3J_{3,5}$ = 7.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.6 (C1), 60.9 (C2), 29.7 (C3), 18.6 (C4), 17.3 (C5) ppm.

Crystals of HDIPEA[Ga(nta)(val)]·H_2O ((HDIPEA)**2i**·H_2O) were obtained after one year by storing an aqueous solution (pH 7.0) of the raw product.

Empirical formula: $C_{19}H_{36}GaN_3O_8 \cdot H_2O$, 522.25 g mol^{-1}.

Yield: Few crystals.

5.5.44 $HDIPEA_2[\{Ga(nta)(\mu\text{-}OH)\}_2]$

Starting material: Nitrilotriacetic acid, water, gallium(III) chloride, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: Nitrilotriacetic acid (191 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (744 µL, 4.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL) and ethyl acetate (50 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1.5 h.

Empirical formula: $C_{28}H_{54}Ga_2N_4O_{14}$ + 0.25 $Ga(OH)_3$.

Yield: 271 mg (0.322 mmol, 64.5%).

Elemental analysis: Calcd. (%): C 40.02, H 6.57, N 6.67.

Found (%): C 39.99, H 6.40, N 6.73.

Calcd. $C_{28}H_{54}Ga_2N_4O_{14}$ (%): C 41.54, H 6.72, N 6.92.

$[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.72 (s, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 175.3 (C1), 63.2 (C2) ppm.

5.5.45 Cs[Ga(ala)(nta)]

Starting material: $HNEt_3$[Ga(ala)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether, methanol.

Procedure: A solution of $HNEt_3$[Ga(ala)(nta)] (0.65 mmol) and caesium hydroxide monohydrate (110 mg, 0.65 mmol) in 6 mL of water (pH 9.0) was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min. The product was dissolved in a water/methanol mixture and then dried on a lyophilizer for 4 days.

Empirical formula: $C_9H_{12}CsGaN_2O_8$ + 0.25 $C_{12}H_{14}Cs_2Ga_2N_2O_{14}$ + 1.00 CH_4O + 1.00 H_2O.

Yield: 167 mg (0.228 mmol, 35.1%).

Elemental analysis: Calcd. (%): C 21.31, H 2.96, N 4.78.

Found (%): C 21.34, H 2.97, N 4.78.

Calcd. $C_9H_{12}CsGaN_2O_8$ (%): C 22.58, H 2.53, N 5.85.

[Ga(ala)(nta)]$^-$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.82 (s, 6H, H2, nta), 3.75–3.82 (sp, 1H, H2, ala), 1.51 (d, 3H, H3, $^3J_{2,3}$ = 7.4 Hz, ala) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 180.0 (C1, ala), 175.2 (C1, nta), 63.2 (C2, nta), 50.3 (C2, ala), 18.0 (C3, ala) ppm.

L-Alanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.75–3.82 (sp, 1H, H2), 1.46 (d, 3H, H3, $^3J_{2,3}$ = 7.3 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.3 (C1), 51.1 (C2), 16.8 (C3) ppm.

[{Ga(nta)(μ-OH)}$_2$]$^{2-}$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.70 (s, 6H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.7 (C1), 63.2 (C2) ppm.

5.5.46 Cs[Ga(asn)(nta)]

Starting material: $HNEt_3$[Ga(asn)(nta)], caesium hydroxide monohydrate, triethylamine, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(asn)(nta)] (0.32 mmol), caesium hydroxide (56 mg, 0.34 mmol) and triethylamine (44 µL, 0.32 mmol) in 2 mL of water was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{13}CsGaN_3O_9 + 2.35\ H_2O + 0.25\ Ga(OH)_3$.

Yield: 133 mg (0.224 mmol, 70.0%).

Elemental analysis: Calcd. (%): C 20.21, H 3.13, N 7.07.

Found (%): C 20.19, H 3.16, N 7.10.

Calcd. $C_{10}H_{13}CsGaN_3O_9$ (%): C 23.02, H 2.51, N 8.05.

5.5.47 Cs[Ga(gln)(nta)]

Starting material: $HNEt_3$[Ga(gln)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(gln)(nta)] (0.97 mmol) and caesium hydroxide monohydrate (171 mg, 1.02 mmol) in 2 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{11}H_{15}CsGaN_3O_9 + 0.25\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 2.80\ H_2O$.

Yield: 378 mg (0.478 mmol, 49.3%).

Elemental analysis: Calcd. (%): C 21.28, H 3.07, N 6.20.

Found (%): C 21.38, H 3.13, N 6.09.

Calcd. $C_{11}H_{15}CsGaN_3O_9$ (%): C 24.65, H 2.82, N 7.84.

5.5.48 Cs[Ga(gly)(nta)]

Starting material: $HNEt_3$[Ga(gly)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(gly)(nta)] (0.80 mmol) and caesium hydroxide monohydrate (141 mg, 0.84 mmol) in 1.5 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (15 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_8H_{10}CsGaN_2O_8 + 0.35\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 5.20\ H_2O$.

Yield: 145 mg (0.172 mmol, 21.5%).

Elemental analysis: Calcd. (%): C 17.36, H 3.02, N 4.48.

Found (%): C 17.21, H 2.88, N 4.64.

Calcd. $C_8H_{10}CsGaN_2O_8$ (%): C 20.67, H 2.17, N 6.03.

5.5.49 Cs[Ga(ile)(nta)]

Starting material: $HNEt_3$[Ga(ile)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(ile)(nta)] (0.42 mmol) and caesium hydroxide monohydrate (75 mg, 0.45 mmol) in 1.5 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{12}H_{18}CsGaN_2O_8 + 0.65\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 3.15\ H_2O$.

Yield: 118 mg (0.107 mmol, 25.5%).

Elemental analysis: Calcd. (%): C 21.47, H 3.04, N 4.17.

Found (%): C 21.64, H 3.22, N 3.99.

Calcd. $C_{12}H_{18}CsGaN_2O_8$ (%): C 27.67, H 3.48, N 5.38.

5.5.50 Cs[Ga(leu)(nta)]

Starting material: $HNEt_3$[Ga(leu)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(leu)(nta)] (0.11 mmol) and caesium hydroxide monohydrate (19 mg, 0.11 mmol) in 0.5 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{12}H_{18}CsGaN_2O_8 + 3.4\ H_2O + 0.25\ C_2H_6O$.

Yield: 15 mg (0.025 mmol, 22.7%).

Elemental analysis: Calcd. (%): C 25.29, H 4.47, N 4.72.

Found (%): C 25.28, H 4.44, N 4.71.

Calcd. $C_{12}H_{18}CsGaN_2O_8$ (%): C 27.67, H 3.48, N 5.38.

5.5.51 Cs[Ga(met)(nta)]

Starting material: $HNEt_3$[Ga(met)(nta)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(met)(nta)] (0.30 mmol) and caesium hydroxide monohydrate (52 mg, 0.31 mmol) in 1.5 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{11}H_{16}CsGaN_2O_8S + 0.15\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 3.05\ H_2O$.

Yield: 75 mg (0.105 mmol, 35.0%).

Elemental analysis: Calcd. (%): C 21.47, H 3.41, N 4.50, S 4.48.

Found (%): C 21.48, H 3.29, N 4.38, S 4.58.

Calcd. $C_{11}H_{16}CsGaN_2O_8S$ (%): C 24.51, H 2.99, N 5.20, S 5.95.

5.5.52 Cs[Ga(nta)(phe)]

Starting material: $HNEt_3$[Ga(nta)(phe)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(phe)] (0.44 mmol) and caesium hydroxide monohydrate (77 mg, 0.46 mmol) in 1 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{15}H_{16}CsGaN_2O_8 + 0.05\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 3.25\ H_2O$.

Yield: 59 mg (0.090 mmol, 20.5%).

Elemental analysis: Calcd. (%): C 28.64, H 3.57, N 4.50.

Found (%): C 28.86, H 3.45, N 4.28.

Calcd. $C_{15}H_{16}CsGaN_2O_8$ (%): C 32.47, H 2.91, N 5.05.

5.5.53 Cs[Ga(nta)(pro)]

Starting material: $HNEt_3$[Ga(nta)(pro)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(pro)] (0.44 mmol) and caesium hydroxide monohydrate (77 mg, 0.46 mmol) in 0.5 mL of water was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (4 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{11}H_{14}CsGaN_2O_8 + 0.05\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 1.60\ H_2O$.

Yield: 45 mg (0.078 mmol, 17.7%).

Elemental analysis: Calcd. (%): C 24.25, H 3.14, N 5.12.

Found (%): C 24.35, H 3.18, N 5.01.

Calcd. $C_{11}H_{14}CsGaN_2O_8$ (%): C 26.17, H 2.80, N 5.55.

5.5.54 Cs[Ga(nta)(ser)]

Starting material: $HNEt_3$[Ga(nta)(ser)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(ser)] (0.28 mmol) and caesium hydroxide monohydrate (55 mg, 0.33 mmol) in 0.5 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_9H_{12}CsGaN_2O_9$ + 0.30 $C_{12}H_{14}Cs_2Ga_2N_2O_{14}$ + 3.10 H_2O.

Yield: 110 mg (0.138 mmol, 49.3%).

Elemental analysis: Calcd. (%): C 19.03, H 2.84, N 4.58.

Found (%): C 18.99, H 2.87, N 4.63.

Calcd. $C_9H_{12}CsGaN_2O_9$ (%): C 21.85, H 2.44, N 5.66.

5.5.55 Cs[Ga(nta)(thr)]

Starting material: $HNEt_3$[Ga(nta)(thr)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(thr)] (0.63 mmol) and caesium hydroxide monohydrate (110 mg, 0.66 mmol) in 1 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{14}CsGaN_2O_9$ + 0.15 $C_{12}H_{14}Cs_2Ga_2N_2O_{14}$ + 3.05 H_2O.

Yield: 238 mg (0.347 mmol, 55.1%).

Elemental analysis: Calcd. (%): C 20.66, H 3.26, N 4.70.

Found (%): C 20.61, H 3.33, N 4.77.

Calcd. $C_{10}H_{14}CsGaN_2O_9$ (%): C 23.60, H 2.77, N 5.51.

5.5.56 Cs[Ga(nta)(trp)]

Starting material: $HNEt_3$[Ga(nta)(trp)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(trp)] (0.69 mmol) and caesium hydroxide monohydrate (121 mg, 0.72 mmol) in 2 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{17}H_{17}CsGaN_3O_8 + 1.65\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 4.00\ H_2O$.

Yield: 170 mg (0.085 mmol, 12.4%).

Elemental analysis: Calcd. (%): C 21.97, H 2.41, N 4.39.

Found (%): C 22.20, H 2.63, N 4.15.

Calcd. $C_{17}H_{17}CsGaN_3O_8$ (%): C 34.38, H 2.89, N 7.07.

5.5.57 Cs[Ga(nta)(val)]

Starting material: $HNEt_3$[Ga(nta)(val)], caesium hydroxide monohydrate, water, ethanol, diethyl ether.

Procedure: A solution of $HNEt_3$[Ga(nta)(val)] (0.60 mmol) and caesium hydroxide monohydrate (105 mg, 0.63 mmol) in 1 mL of water was stirred for 16 h. The raw product was precipitated by addition of ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{11}H_{16}CsGaN_2O_8 + 0.35\ C_{12}H_{14}Cs_2Ga_2N_2O_{14} + 3.85\ H_2O$.

Yield: 208 mg (0.241 mmol, 40.2%).

Elemental analysis: Calcd. (%): C 21.19, H 3.35, N 4.39.

Found (%): C 21.24, H 3.32, N 4.32.

Calcd. $C_{11}H_{16}CsGaN_2O_8$ (%): C 26.07, H 3.18, N 5.53.

5.5.58 [Ga(ala)(edda)]

Starting material: L-Alanine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Alanine (89 mg, 1.0 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (30 mL) and ethyl acetate (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min and then on a lyophilizer for 7 days.

Empirical formula: $C_9H_{16}GaN_3O_6$ + 0.20 H_2O.

Yield: 318 mg (0.948 mmol, 94.8%).

Elemental analysis: Calcd. (%): C 32.21, H 4.93, N 12.52.

Found (%): C 32.28, H 5.01, N 12.49.

Calcd. $C_9H_{16}GaN_3O_6$ (%): C 32.56, H 4.86, N 12.66.

[Ga(ala)(edda)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.74–3.81 (sp, 1H, H2), 1.45–1.50 (sp, 3H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 180.3–180.5 (2s, C1), 49.8–50.5 (2s, C2), 18.0–18.2 (3s, C3) ppm.

L-Alanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.77 (q, 1H, H2, $^3J_{2,3}$ = 7.2 Hz), 1.47 (d, 3H, H3, $^3J_{2,3}$ = 7.2 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.3 (C1), 51.1 (C2), 16.8 (C3) ppm.

5.5.59 [Ga(Harg)(edda)]Cl

Starting material: L-Arginine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Arginine (174 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (40 mL). After filtration the colourless amorphous solid was washed with ethanol and diethyl ether and dried at 80 °C for 10 min and then on a lyophilizer for 8 days.

Empirical formula: $C_{12}H_{24}ClGaN_6O_6$ + 2.00 H_2O + 0.05 $C_6H_{16}ClN$.

Yield: 307 mg (0.618 mmol, 61.8%).

Elemental analysis: Calcd. (%): C 29.76, H 5.85, N 17.07.

Found (%): C 29.83, H 5.86, N 16.98.

Calcd. $C_{12}H_{24}ClGaN_6O_6$ (%): C 34.56, H 5.56, N 20.15.

[Ga(Harg)(edda)]Cl:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.64–3.75 (sp, 1H, H2), 3.20–3.28 (sp, 2H, H5), 1.94–2.12 (sp, 2H, H3), 1.71–1.90 (sp, 2 H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D2O): δ = 178.9–179.1 (3s, C1), 157.3 (C6), 53.8–54.3 (3s, C2), 41.2 (2s, C5), 29.3–29.4 (2s, C3), 25.3–25.6 (2s, C4) ppm.

L-Arginine·HCl:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.77 (t, 1H, H2, $^3J_{2,3}$ = 6.1 Hz), 3.24 (t, 2H, H5, $^3J_{4,5}$ = 6.9 Hz), 1.88–1.95 (sp, 2H, H3), 1.58–1.80 (sp, 2 H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D2O): δ = 174.9 (C1), 157.3 (C6), 54.9 (C2), 41.1 (C5), 28.1 (C3), 24.5 (C4) ppm.

5.5.60 [Ga(asn)(edda)]

Starting material: L-Asparagine monohydrate, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic, triethylamine, ethanol, diethyl ether, acetone.

Procedure: L-Asparagine monohydrate (150 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL). After filtration the colourless amorphous solid was washed with ethanol and diethyl ether and dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{17}GaN_4O_7$ + 0.15 H_2O.

Yield: 324 mg (0.858 mmol, 85.8%).

Elemental analysis: Calcd. (%): C 31.80, H 4.62, N 14.83.

Found (%): C 31.96, H 4.64, N 14.67.

Calcd. $C_{10}H_{17}GaN_4O_7$ (%): C 32.03, H 4.57, N 14.94.

[Ga(asn)(edda)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.98–4.01 (sp, 1H, H2), 2.89–2.97 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.1–178.6 (2s, C1), 175.4–175.5 (3s, C4), 50.4–51.6 (2s, C2), 36.2–36.4 (3s, C3) ppm.

L-Asparagine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.98–4.01 (sp, 1H, H2), 2.82–2.97 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.0 (C4), 173.8 (C1), 51.9 (C2), 35.1 (C3) ppm.

Crystals of [Ga(asn)(edda)]·2H_2O (**3a**·2H_2O) were obtained after four weeks by storing an aqueous solution (pH 7.0) of the raw product over acetone.

Empirical formula: $C_{10}H_{17}GaN_4O_7 \cdot 2H_2O$, 411.03 g mol^{-1}.

Yield: Few crystals.

5.5.61 [Ga(Hasp)(edda)]·0.30NEt_3

Starting material: L-Aspartic acid, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Aspartic acid (133 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (30 mL) and ethyl acetate (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 4 days.

Empirical formula: $C_{10}H_{16}GaN_3O_8 \cdot 0.30C_6H_{15}N + 1.30\ H_2O$.

Yield: 251 mg (0.584 mmol, 58.4%).

Elemental analysis: Calcd. (%): C 32.98, H 5.42, N 10.76.

Found (%): C 32.95, H 5.35, N 10.82.

Calcd. $C_{10}H_{16}GaN_3O_8$ (%): C 31.95, H 4.29, N 11.18.

[Ga(Hasp)(edda)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.93–3.99 (sp, 1H, H2), 2.81–2.90 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 52.1 (1s, C2). 37.9 (1s, C3) ppm.

L-Aspartic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.93–3.99 (sp, 1H, H2), 2.81–2.90 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 52.2 (C2), 36.6 (C3) ppm.

5.5.62 [Ga(cys)(edda)]

Starting material: L-Cysteine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Cysteine (146 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 7.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 3 days.

Empirical formula: $C_9H_{16}GaN_3O_6S + 1.05\ H_2O + 0.10\ C_6H_{16}ClN$.

Yield: 360 mg (0.907 mmol, 90.7%).

Elemental analysis: Calcd. (%): C 29.07, H 5.01, N 10.95, S 8.08.

Found (%): C 29.03, H 4.91, N 11.06, S 7.98.

Calcd. $C_9H_{16}GaN_3O_6S$ (%): C 29.07, H 4.43, N 11.54, S 8.81.

5.5.63 [Ga(edda)(gln)]

Starting material: L-Glutamine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Glutamine (146 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. Ethanol (10 mL) was added to the obtained slurry. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 7 days.

Empirical formula: $C_{11}H_{19}GaN_4O_7$ + 0.80 H_2O + 0.05 $C_6H_{16}ClN$.

Yield: 269 mg (0.656 mmol, 65.6%).

Elemental analysis: Calcd. (%): C 33.08, H 5.26, N 13.83.

Found (%): C 32.94, H 5.45, N 14.00.

Calcd. $C_{11}H_{19}GaN_4O_7$ (%): C 33.96, H 4.92, N 14.40.

[Ga(edda)(gln)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.59 (t, 1H, H2, $^3J_{2,3}$ = 6.2 Hz), 2.33–2.44 (sp, 2H, H4), 1.96–2.11 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.7 (C5), 177.4 (C1), 55.2 (C2), 31.8 (C4), 28.4 (C3) ppm.

L-Glutamine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.14–4.18 (m, 1H, H2), 2.41–2.53 (sp, 2H, H4), 1.99–2.43 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 182.3 (C5), 180.8 (C1), 59.0 (C2), 30.3 (C4), 26.0 (C3) ppm.

5.5.64 [Ga(edda)(Hglu)]·0.15NEt_3

Starting material: L-Glutamic acid, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Glutamic acid (147 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (30 mL) and ethyl acetate (10 mL). After filtration and washing with ethanol, ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 4 days.

Empirical formula: $C_{11}H_{18}GaN_3O_8 \cdot 0.15C_6H_{15}N + 1.25\ H_2O$.

Yield: 215 mg (0.503 mmol, 50.3%).

Elemental analysis: Calcd. (%): C 33.42, H 5.36, N 10.32.

Found (%): C 33.35, H 5.31, N 10.37.

Calcd. $C_{11}H_{18}GaN_3O_8$ (%): C 33.88, H 4.65, N 10.77.

[Ga(edda)(Hglu)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.48 (sp, 2H, H4), 1.98–2.20 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 54.6 (1s, C2), 32.9 (1s, C4). 28.1 (1s, C3) ppm.

L-Glutamic acid:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.78–3.82 (sp, 1H, H2), 2.41–2.48 (sp, 2H, H4), 1.98–2.20 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 180.0 (C5), 174.8 (C1), 54.9 (C2), 32.8 (C4), 26.9 (C3) ppm.

5.5.65 [Ga(edda)(gly)]

Starting material: Glycine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether, acetone.

Procedure: Glycine (75 mg, 1.0 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min, then under fine vacuum for 2 h and finally on a lyophilizer for 3 days.

Empirical formula: $C_8H_{14}GaN_3O_6$ + 1.40 H_2O + 0.10 $Ga(OH)_3$.

Yield: 287 mg (0.808 mmol, 80.8%).

Elemental analysis: Calcd. (%): C 27.05, H 4.85, N 11.83.

Found (%): C 27.03, H 4.84, N 11.85.

Calcd. $C_8H_{14}GaN_3O_6$ (%): C 30.22, H 4.44, N 13.22.

[Ga(edda)(gly)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.45–3.57 (sp, 2H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.0–177.1 (2s, C1), 41.7–42.4 (2s, C2) ppm.

Glycine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.55 (s, 2H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 173.0 (C1), 42.0 (C2) ppm.

Crystals of [Ga(edda)(gly)]·2H_2O (**3b**·2H_2O) were obtained after one week by storing an aqueous solution (pH 7.0) of the raw product over acetone.

Empirical formula: $C_8H_{14}GaN_3O_6$·2H_2O, 353.97 g mol^{-1}.

Yield: 277 mg (0.783 mmol, 78.3%).

Elemental analysis: Calcd. (%): C 27.15, H 5.13, N 11.87.

Found (%): C 27.38, H 5.08, N 11.77.

5.5.66 [Ga(edda)(Hhis)]Cl

Starting material: L-Histidine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, acetone, diethyl ether.

Procedure: L-Histidine (155 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless slurry (pH 9.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL) and acetone (80 mL). After filtration and washing with ethanol, acetone and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min and then on a lyophilizer for 4 days.

Empirical formula: $C_{12}H_{19}ClGaN_5O_6$ + 0.10 H_2O + 0.05 $C_6H_{16}ClN$.

Yield: 217 mg (0.490 mmol, 49.0%).

Elemental analysis: Calcd. (%): C 33.34, H 4.55, N 15.96.

Found (%): C 33.41, H 4.68, N 15.95.

Calcd. $C_{12}H_{19}ClGaN_5O_6$ (%): C 33.17, H 4.41, N 16.12.

[Ga(edda)(Hhis)]Cl:

^{1}H NMR (400 MHz, D2O): δ = 8.00–8.16 (m, 1H, H6), 7.06–7.19 (sp, 1H, H5), 3.88–3.99 (sp, 1H, H2), 3.14–3.28 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** *δ* = 173.7–177.1 (2s, C1), 136.2–137.8 (2s, C6), 132.4–133.2 (2s, C4), 117.4–124.0 (2s, C5), 54.3–54.4 (2s, C2), 26.5–28.8 (2s, C3) ppm.

L-Histidine·HCl:

^{1}H NMR (400 MHz, D2O): δ = 7.95 (s, 1H, H6), 7.12 (s, 1H, H5), 3.88–3.99 (sp, 1H, H2), 3.14–3.28 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** *δ* = 174.2 (C1), 136.5 (C6), 131.8 (C4), 117.7 (C5), 55.1 (C2), 28.2 (C3) ppm.

5.5.67 [Ga(edda)(ile)]

Starting material: L-Isoleucine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Isoleucine (131 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL) and ethyl acetate (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 3 days.

Empirical formula: $C_{12}H_{22}GaN_3O_6$ + 0.80 H_2O + 0.05 $C_6H_{16}ClN$.

Yield: 333 mg (0.842 mmol, 84.2%).

Elemental analysis: Calcd. (%): C 37.37, H 6.22, N 10.81.

Found (%): C 37.42, H 6.32, N 10.85.

Calcd. $C_{12}H_{22}GaN_3O_6$ (%): C 38.53, H 5.93, N 11.23.

[Ga(edda)(ile)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.58–3.68 (sp, 1H, H2), 2.11–2.26 (sp, H1, H3), 1.21–1.31 (sp, 2H, H4), 1.00–1.04 (sp, 3H, H6), 0.86–0.95 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.2–179.3 (2s, C1), 59.2–59.8 (3s, C2), 37.2–37.5 (2s, C3), 24.0–24.2 (2s, C4), 15.9–16.4 (3s, C6), 11.9–12.0 (2s, C5) ppm.

L-Isoleucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.66 (d, 1H, H2, $^3J_{2,3}$ = 4.0 Hz), 1.92–2.02 (m, H1, H3), 1.40–1.51 (m, 1H, H4), 1.19–1.33 (sp, 1H, H4), 1.00 (d, 3H, H6, $^3J_{3,6}$ = 7.0 Hz), 0.93 (t, 3H, H5, $^3J_{4,5}$ = 7.4 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.7 (C1), 60.2 (C2), 36.5 (C3), 25.1 (C4), 15.3 (C6), 11.7 (C5) ppm.

5.5.68 [Ga(edda)(leu)]

Starting material: L-Leucine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, acetone, diethyl ether, acetonitrile.

Procedure: L-Leucine (131 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless slurry (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (30 mL) and acetone (30 mL). After filtration and washing with ethanol, acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 4 days.

Empirical formula: $C_{12}H_{22}GaN_3O_6$ + 1.50 H_2O.

Yield: 239 mg (0.596 mmol, 59.6%).

Elemental analysis: Calcd. (%): C 35.94, H 6.28, N 10.48.

Found (%): C 35.94, H 6.24, N 10.43.

Calcd. $C_{12}H_{22}GaN_3O_6$ (%): C 38.53, H 5.93, N 11.23.

[Ga(edda)(leu)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.69–3.74 (sp, 1H, H2), 1.59–1.79 (sp, 3H, H3/H4), 0.91–1.01 (sp, 6H, H5/H6) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 180.2–180.3 (2s, C1), 53.1–53.2 (2s, C2), 41.5 (1s, C3), 25.0–25.2 (3s, C4), 23.0–23.1 (3s, C5), 20.6–20.8 (3s, C6) ppm.

L-Leucine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.69–3.74 (sp, 1H, H2), 1.59–1.79 (sp, 3H, H3/H4), 0.91–1.01 (sp, 6H, H5/H6) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 176.1 (C1), 54.0 (C2), 40.4 (C3), 24.8 (C4), 22.7 (C5), 21.5 (C6) ppm.

Crystals of [Ga(edda)(leu)]$_2$·[{Ga(edda)(µ-OH)}$_2$]·6H_2O (**3c**·**3d**·**3i**·6H_2O) were obtained after two months by storing an aqueous solution (pH 7.0) of the raw product over acetonitrile.

Empirical formula: $2C_{12}H_{22}GaN_3O_6 \cdot C_{12}H_{22}Ga_2N_4O_{10} \cdot 6H_2O$, 1377.96 g mol^{-1}.

Yield: Few crystals.

5.5.69 [Ga(edda)(Hlys)]Cl

Starting material: L-Lysine hydrochloride, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Lysine hydrochloride (183 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (627 µL, 4.50 mmol) resulted in a colourless solution (pH 9.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (40 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 7 days.

Empirical formula: $C_{12}H_{24}ClGaN_4O_6 + 0.60\ H_2O$.

Yield: 350 mg (0.802 mmol, 80.2%).

Elemental analysis: Calcd. (%): C 33.03, H 5.82, N 12.84.

Found (%): C 33.07, H 5.73, N 12.74.

Calcd. $C_{12}H_{24}ClGaN_4O_6$ (%): C 33.87, H 5.69, N 13.17.

[Ga(edda)(lys)]Cl:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.63–3.76 (sp, 1H, H2), 2.94–3.07 (sp, 2H, H6), 1.89–2.10 (sp, 2H, H3), 1.68–1.85 (sp, 2H, H5), 1.50–1.60 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.2–179.4 (3s, C1), 53.9–54.5 (3s, C2), 39.8 (C6), 31.6–31.7 (3s, C3), 26.9 (2s, C5), 22.7–23.13 (2s, C4) ppm.

L-Lysine·HCl:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.75 (t, 1H, H2, $^3J_{2,3}$ = 6.1 Hz), 2.99–3.04 (sp, 2H, H6), 1.86–1.93 (sp, 2H, H3), 1.68–1.76 (sp, 2H, H5), 1.37–1.59 (sp, 2H, H4) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.1 (C1), 55.1 (C2), 39.7 (C6), 30.5 (C3), 27.0 (C5), 22.0 (C4) ppm.

5.5.70 [Ga(edda)(met)]

Starting material: L-Methionine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Methionine (149 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 1 h.

Empirical formula: $C_{11}H_{20}GaN_3O_6S + 0.55\ H_2O + 0.15\ Ga(OH)_3$.

Yield: 340 mg (0.809 mmol, 80.9%).

Elemental analysis: Calcd. (%): C 31.45, H 5.17, N 10.00, S 7.63.

Found (%): C 31.42, H 5.13, N 10.08, S 7.65.

Calcd. $C_{11}H_{20}GaN_3O_6S$ (%): C 33.70, H 5.14, N 10.72, S 8.18.

[Ga(edda)(met)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.75–3.87 (sp, 1H, H2), 2.63–2.78 (sp, 2H, H4), 2.17–2.33 (sp, 1H, H3), 2.11–2.13 (sp, 3H, H5), 2.00–2.12 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 178.9–179.1 (3s, C1), 52.9–53.9 (3s, C2), 31.2–31.3 (3s, C3), 30.2–30.4 (3s, C4), 14.5 (3s, C5) ppm.

L-Methionine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.83–3.87 (sp, 1H, H2), 2.62 (t, 2H, H4, $^3J_{3,4}$ = 7.5 Hz), 2.08–2.22 (sp, 2H, H3), 2.12 (s, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.8 (C1), 54.5 (C2), 30.3 (C3), 29.5 (C4), 14.6 (C5) ppm.

5.5.71 [Ga(edda)(phe)]

Starting material: L-Phenylalanine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether, acetone.

Procedure: L-Phenylalanine (165 mg, 1.00 mmol) was dissolved in 11 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless slurry (pH 8.5) which was stirred for 16 h. The colourless slurry was concentrated by rotary evaporation and the raw product was precipitated by addition of ethanol (10 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 1 h.

Empirical formula: $C_{15}H_{20}GaN_3O_6$ + 1.05 H_2O.

Yield: 380 mg (0.890 mmol, 89.0%).

Elemental analysis: Calcd. (%): C 42.20, H 5.22, N 9.84.

Found (%): C 42.21, H 5.21, N 9.88.

Calcd. $C_{15}H_{20}GaN_3O_6$ (%): C 44.15, H 4.94, N 10.30.

L-Phenylalanine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.31–7.41 (sp, 2H, H6), 7.27–7.37 (sp, 1H, H7), 7.24–7.37 (sp, 2H , H5), 3.54–3.59 (m, 1H, H2), 2.99–3.13 (sp, 1H, H3), 2.81–2.91 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 181.2 (C1), 138.4 (C4), 130.0 (C5), 129.3 (C6), 127.4 (C7), 57.8 (C2), 40.6 (C3) ppm.

Crystals of 2[Ga(edda)(phe)]·3H_2O (**3e**·**3f**·3H_2O) were obtained after one week by storing an aqueous solution of the raw product (360 mg) and 200 µL of triethylamine (pH 9.5) over acetone.

Empirical formula: $C_{15}H_{20}GaN_3O_6$·1.5H_2O, 435.09 g mol^{-1}.

Yield: 191 mg (0.439 mmol, 43.9%).

Elemental analysis: Calcd. (%): C 41.41, H 5.33, N 9.66.

Found (%): C 41.21, H 5.29, N 9.65.

5.5.72 [Ga(edda)(pro)]

Starting material: L-Proline, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Proline (115 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min, then under fine vacuum for 2 h and finally on a lyophilizer for 7 days.

Empirical formula: $C_{11}H_{18}GaN_3O_6$ + 0.10 H_2O.

Yield: 306 mg (0.850 mmol, 85.0%).

Elemental analysis: Calcd. (%): C 36.72, H 5.10, N 11.68.

Found (%): C 36.78, H 5.00, N 11.57.

Calcd. $C_{11}H_{18}GaN_3O_6$ (%): C 36.90, H 5.07, N 11.74.

[Ga(edda)(pro)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.09–4.14 (sp, 1H, H2), 3.29–3.45 (sp, 2H, H5), 2.29–2.38 (sp, 1H, H3), 1.97–2.10 (sp, 2H, H4), 1.92–2.03 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.7–179.9 (3s, C1), 60.9–62.1 (3s, C2), 47.8–48.5 (3s, C5), 30.1–30.2 (2s, C3), 27.0–27.3 (3s, C4) ppm.

L-Proline:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.09–4.14 (sp, 1H, H2), 3.29–3.45 (sp, 2H, H5), 2.29–2.38 (sp, 1H, H3), 1.97–2.10 (sp, 2H, H4), 1.92–2.03 (sp, 1H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 175.2 (C1), 61.8 (C2), 46.7 (C5), 29.6 (C3), 24.4 (C4) ppm.

Crystals of [Ga(edda)(pro)]·3H_2O (**3g**·3H_2O) were obtained after one week by storing an aqueous solution (pH 7.0) of the raw product over ethanol.

Empirical formula: $C_{11}H_{18}GaN_3O_6 \cdot 3H_2O$, 412.05 g mol^{-1}.

Yield: 168 mg (0.408 mmol, 40.8%).

Elemental analysis: Calcd. (%): C 32.06, H 5.87, N 10.20.

Found (%): C 31.83, H 5.62, N 10.21.

5.5.73 [Ga(edda)(ser)]

Starting material: L-Serine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether, acetone.

Procedure: L-Serine (105 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the resulting amorphous solid was resolved in water (1 mL). A colourless precipitate was obtained by addition of ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was again dissolved in water (2 mL). The raw product was precipitated by addition of ethanol (50 mL) and ethyl acetone (20 mL). After filtration and washing with ethanol, acetone and diethyl ether the obtained colourless amorphous solid was dried on a lyophilizer for 1 day.

Empirical formula: $C_9H_{16}GaN_3O_7 + 1.55\ H_2O + 0.10\ Ga(OH)_3$.

Yield: 242 mg (0.624 mmol, 62.4%).

Elemental analysis: Calcd. (%): C 27.86, H 5.04, N 10.83.

Found (%): C 27.86, H 5.00, N 10.88.

Calcd. $C_9H_{16}GaN_3O_7$ (%): C 31.07, H 4.63, N 12.08.

[Ga(edda)(ser)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.01 (sp, 2H, H3), 3.80–3.87 (sp, 1H, H2) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.1–177.2 (2s, C1), 61.4–62.1 (3s, C3), 55.5–56.5 (4s, C2) ppm.

L-Serine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.91–4.01 (sp, 2H, H3), 3.80–3.87 (sp, 1H, H2) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 172.9 (C1), 60.8 (C3), 57.0 (C2) ppm.

5.5.74 [Ga(edda)(thr)]

Starting material: L-Threonine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether, acetone.

Procedure: L-Threonine (119 mg, 1.00 mmol) was suspendended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in water (1 mL) and ethanol (30 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was again dissolved in water (2 mL). The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried on a lyophilizer for 1 day.

Empirical formula: $C_{10}H_{18}GaN_3O_7 + 1.75\ H_2O$.

Yield: 280 mg (0.712 mmol, 71.2%).

Elemental analysis: Calcd. (%): C 30.52, H 5.51, N 10.68.

Found (%): C 30.71, H 5.35, N 10.49.

Calcd. $C_{10}H_{18}GaN_3O_7$ (%): C 33.18, H 5.01, N 11.61.

[Ga(edda)(thr)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.51–4.60 (sp, 1H, H3), 3.53–3.63 (sp, 1H, 2H), 1.26–1.33 (sp, 3H, H4) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 177.3–177.4 (2s, C1), 66.4–66.8 (3s, C3), 59.0–60.1 (4s, C2), 20.0–20.2 (3s, C4) ppm.

L-Threonine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 4.21–4.28 (m, 1H, H3), 3.53–3.63 (sp, 1H, 2H), 1.26-1.33 (sp, 3H, H4) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 173.4 (C1), 66.5 (C3), 61.0 (C2), 20.1 (C4) ppm.

Crystals of [Ga(edda)(thr)]·2H_2O (**3h**·2H_2O) were obtained after one month by storing an aqueous solution (pH 6.0) of the raw product over acetone.

Empirical formula: $C_{10}H_{18}GaN_3O_7 \cdot 2H_2O$, 398.02 g mol^{-1}.

Yield: 260 mg (0.653 mmol, 65.3%).

Elemental analysis: Calcd. (%): C 30.18, H 5.57, N 10.56.

Found (%): C 30.15, H 5.47, N 10.54.

5.5.75 [Ga(edda)(trp)]

Starting material: L-Tryptophan, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, acetone, diethyl ether.

Procedure: L-Tryptophan (204 mg, 1.00 mmol) was suspended in 3 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (432 µL, 3.10 mmol) resulted in a colourless solution (pH 8.0) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (60 mL). After filtration and washing with ethanol, acetone and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 1 day.

Empirical formula: $C_{17}H_{21}GaN_4O_6$ + 1.50 H_2O.

Yield: 385 mg (0.812 mmol, 81.2%).

Elemental analysis: Calcd. (%): C 43.07, H 5.10, N 11.82.

Found (%): C 43.03, H 5.05, N 11.76.

Calcd. $C_{17}H_{21}GaN_4O_6$ (%): C 45.67, H 4.73, N 12.53.

L-Tryptophan:

^{1}H NMR (400 MHz, D_2O)**:** δ = 7.69–7.71 (m, 1H, H8), 7.46–7.50 (m, 1H , H11), 7.22 (s, 1H, H5), 7.19–7.28 (sp, 1H, H10), 7.12–7.17 (m, 1H, H9), 3.67–3.71 (sp, 1H, H2), 3.22–3.30 (sp, 2H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 180.2 (C1), 136.8 (C6), 127.7 (C7), 125.1 (C5), 122.5 (C10), 119.8 (C9), 119.3 (C8), 112.4 (C11), 110.2 (C4), 56.6 (C2), 29.6 (C3) ppm.

5.5.76 Attempt of synthesis: [Ga(edda)(tyr)]

Starting material: L-Tyrosine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: L-Tyrosine (181 mg, 1.00 mmol) was suspended in 11 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. Ethanol (50 mL) and ethyl acetate (20 mL) were added to the slurry. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_9H_{11}NO_3 + 0.05\ H_2O$.

Yield: 147 mg.

Elemental analysis: Calcd. (%): C 59.37, H 6.14, N 7.69.

Found (%): C 59.27, H 6.14, N 7.70.

5.5.77 [Ga(edda)(val)]

Starting material: L-Valine, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, triethylamine, ethanol, diethyl ether.

Procedure: L-Valine (117 mg, 1.00 mmol) was suspended in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a colourless solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (40 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min, then under fine vacuum for 2 h and finally on a lyophilizer for 7 days.

Empirical formula: $C_{11}H_{20}GaN_3O_6$ + 0.50 H_2O.

Yield: 181 mg (0.490 mmol, 49.0%).

Elemental analysis: Calcd. (%): C 35.80, H 5.74, N 11.39.

Found (%): C 35.86, H 5.73, N 11.31.

Calcd. $C_{11}H_{20}GaN_3O_6$ (%): C 36.70, H 5.60, N 11.67.

[Ga(edda)(val)]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.57–3.67 (sp, 1H, H2), 2.38–2.53 (sp, 1H, H3), 1.02–1.06 (sp, 3H, H4), 0.85–0.92 (sp, 3H, H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 179.3–179.5 (3s, C1), 59.4–60.2 (3s, C2), 30.0–30.9 (4s, C3), 19.0–19.2 (3s, C4), 15.7–15.9 (2s, C5) ppm.

L-Valine:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.60 (d, 1H, H2, $^3J_{2,3}$ = 4.4 Hz), 2.22–2.32 (m, 1H, H3), 1.03 (d, 3H, H4, $^3J_{3,4}$ = 7.0 Hz), 0.98 (d, 3H, H5, $^3J_{3,5}$ = 7.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 174.8 (C1), 61.0 (C2), 29.7 (C3), 18.6 (C4), 17.3 (C5) ppm.

5.5.78 [{Ga(edda)(OH)}$_6$]

Starting material: Ethylenediamine-*N*,*N*′-diacetic acid, gallium(III) chloride, water, triethylamine, ethanol, ethyl acetate, diethyl ether, acetone.

Procedure: Ethylenediamine-*N*,*N*′-diacetic acid (176 mg, 1.00 mmol) was dissolved in gallium(III) chloride solution (176 mg, 1.00 mmol), 0.5 mL of water and triethylamine (488 µL, 3.50 mmol). The colourless solution (pH 8.5) was stirred for 16 h. Ethanol (30 mL) and ethyl acetate (20 mL) were added. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 2 days.

Empirical formula: $C_{36}H_{66}Ga_6N_{12}O_{30}$ + 7.60 H_2O.

Yield: 62 mg (0.036 mmol, 21.9%).

Elemental analysis: Calcd. (%): C 25.40, H 4.81, N 9.87.

Found (%): C 25.41, H 4.74, N 9.80.

Calcd. $C_{36}H_{66}Ga_6N_{12}O_{30}$ (%): C 27.62, H 4.25, N 10.74.

[{Ga(edda)(OH)}$_6$]:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.51–4.25 (sp, 2H, H2–H5), 2.38–3.38 (sp, 6H, H2–H5) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 177.2–178.5 (ms, C1, C6), 49.6–52.9 (ms, C2–C5), 44.2–47.0 (ms, C2–C5) ppm.

Crystals of [{Ga(edda)(µ-OH)}$_6$]·xH_2O (**3j**·xH_2O) were obtained after one week by storing an aqueous solution (pH 7.0) of the raw product over acetone.

Empirical formula: $C_{36}H_{66}Ga_6N_{12}O_{30}$·x$H_2O$.

Yield: Few crystals.

5.5.79 [Ga(his)(ida)]

Starting material: Iminodiacetic acid, L-histidine, water, gallium(III) chloride, triethylamine, ethanol, diethyl ether.

Procedure: Iminodiacetic acid (133 mg, 1.00 mmol) and L-histidine (155 mg, 1.00 mmol) were dissolved in 0.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol) and triethylamine (418 µL, 3.00 mmol) resulted in a solution (pH 5.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{13}GaN_4O_6$ + 0.40 H_2O.

Yield: 305 mg (0.842 mmol, 84.2%).

Elemental analysis: Calcd. (%): C 33.16, H 3.84, N 15.47.

Found (%): C 33.15, H 3.85, N 15.44.

Calcd. $C_{10}H_{13}GaN_4O_6$ (%): C 33.84, H 3.69, N 15.78.

Crystals of [Ga(his)(ida)] (**4a**) were obtained by storing a solution of the raw product in a water/triethylamine mixture (20:1, pH 8.5) in an open vessel for one week.

Empirical formula: $C_{10}H_{13}GaN_4O_6$, 354.96 g mol^{-1}.

Yield: Few crystals.

5.5.80 [Ga(asp)(his)]

Starting material: L-Aspartic acid, L-histidine, water, gallium(III) chloride, triethylamine, ethanol, diethyl ether.

Procedure: L-Aspartic acid (134 mg, 1.01 mmol) and L-histidine (156 mg, 1.01 mmol) were suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (177 mg, 1.01 mmol) and triethylamine (561 µL, 4.02 mmol) resulted in a solution (pH 7.5) which was stirred for 16 h. The raw product was precipitated by addition of ethanol (50 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then on a lyophilizer for 1 day.

Empirical formula: $C_{10}H_{13}GaN_4O_6$ + 2.40 H_2O + 0.05 $C_6H_{16}NCl$.

Yield: 149 mg (0.368 mmol, 36.4%).

Elemental analysis: Calcd. (%): C 30.54, H 4.63, N 14.00.

Found (%): C 30.38, H 4.61, N 14.23.

Calcd. $C_{10}H_{13}GaN_4O_6$ (%): C 33.84, H 3.69, N 15.78.

[Ga(asp)(his)]:

^{1}H NMR (400 MHz, D2O): δ = 7.72–8.16 (sp, 1H, H6, his), 7.07–7.19 (sp, 1H, H5, his), 4.15–4.20 (sp, 1H, H2, his), 3.89–3.97 (sp, 1H, H2, asp), 3.24–3.36 (sp, 2H, H3, his), 2.84–3.16 (sp, 2H, H3, asp) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** *δ* = 179.0–180.0 (sp, C1, asp/his), 177.3–177.9 (ms, C4, asp), 135.7–136.6 (ms, C6, his), 132.4–133.4 (ms, C4, his), 115.7–116.8 (ms, C5, his), 52.8–54.0 (ms, C2, his), 50.9–51.9 (ms, C2, asp), 37.8–38.3 (ms, C3, asp), 27.5–28.3 (ms, C3, his) ppm.

L-Aspartic acid:

^{1}H NMR (400 MHz, D_2O)**:** *δ* = 3.87–3.90 (sp, 1H, H2), 2.63–2.81 (sp, 2H, H3) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** *δ* = 178.1 (C4), 174.7 (C1), 52.8 (C2), 37.1 (C3) ppm.

L-Histidine:

^{1}H NMR (400 MHz, D2O): δ = 7.72–8.16 (sp, 1H, H6), 7.07–7.19 (sp, 1H, H5), 3.98–4.01 (m, 1H, H2), 3.18–3.26 (sp, 2H, H3) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)**:** δ = 173.1 (C1), 135.7–136.6 (sp, C6), 132.7 (C4), 115.7–116.8 (sp, C5), 54.8 (C2), 27.5 (C3) ppm.

5.5.81 [{Ga(μ-asp)(D-his)}$_2$]

Starting material: L-Aspartic acid, D-histidine, water, gallium(III) chloride, triethylamine, ethanol, diethyl ether, acetone.

Procedure: L-Aspartic acid (134 mg, 1.01 mmol) and D-histidine (156 mg, 1.01 mmol) were suspended in 1.5 mL of water. Gradual addition of gallium(III) chloride solution (177 mg, 1.01 mmol) and triethylamine (561 µL, 4.02 mmol) resulted in a slurry (pH 9.0) which was stirred for 16 h. Further solid was precipitated by addition of ethanol (20 mL). After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{13}GaN_4O_6$ + 1.95 H_2O.

Yield: 335 mg (0.859 mmol, 85.9%).

Elemental analysis: Calcd. (%): C 30.79, H 4.37, N 14.36.

Found (%): C 30.72, H 4.31, N 14.45.

Calcd. $C_{10}H_{13}GaN_4O_6$ (%): C 33.84, H 3.69, N 15.78.

Crystals of [{Ga(asp)(D-his)}$_2$]·1.61H_2O (**4b**·1.61H_2O) were obtained by storing a solution of the raw product in a water-triethylamine-mixture (20:1, pH 10.0) over acetone for two month.

Empirical formula: $C_{20}H_{26}Ga_2N_8O_{12}$·1.61$H_2O$, 738.92 g mol^{-1}.

Yield: Few crystals.

5.5.82 [Ga(malo)(tren)]Cl

Starting material: Tris(2-aminoethyl)amine, gallium(III) chloride, malonic acid, triethylamine, ethanol, diethyl ether, methanol, *n*-hexane.

Procedure: Tris(2-aminoethyl)amine (154 mg, 1.05 mmol) was added to a solution of gallium(III) chloride (185 mg, 1.05 mmol), malonic acid (109 mg, 1.05 mmol) and triethylamine (1025 µL, 7.35 mmol) in 7 mL of ethanol. The resulting suspension was stirred for 16 h. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was dried under fine vacuum for 3 h.

Empirical formula: $C_9H_{20}ClGaN_4O_4$ + 1.10 H_2O + 0.05 C_2H_6O.

Yield: 160 mg (0.426 mmol, 42.6%).

Elemental analysis: Calcd. (%): C 29.10, H 6.04, N 14.92.

Found (%): C 29.01, H 5.88, N 14.76.

Calcd. $C_9H_{20}ClGaN_4O_4$ (%): C 30.58, H 5.70, N 15.85.

Crystals of [Ga(malo)(tren)]Cl·MeOH (**5a**Cl·MeOH) were obtained after four months by storing a methanolic solution of the raw product over *n*-hexane.

Empirical formula: $C_9H_{20}ClGaN_4O_4 \cdot CH_4O$, 385.50 g mol^{-1}.

Yield: Few crystals.

5.5.83 [Ga(ox)(trien)]Cl

Starting material: Oxalic acid, water, gallium(III) chloride, triethylamine, triethylenetetramine, ethanol, ethyl acetate, diethyl ether, acetone.

Procedure: Oxalic acid (90 mg, 1.0 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), triethylamine (279 µL, 2.00 mmol) and triethylenetetramine (146 mg, 1.00 mmol) resulted in a yellowish solution (pH 8.5) which was stirred for 16 h. The solvent was removed by rotary evaporation and the residue was suspended in ethanol (10 mL) and ethyl acetate (30 mL). After filtration and washing with ethyl acetate and diethyl ether the obtained beige amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_8H_{18}ClGaN_4O_4$ + 2.75 H_2O.

Yield: 340 mg (0.874 mmol, 87.4%).

Elemental analysis: Calcd. (%): C 24.70, H 6.09, N 14.40.

Found (%): C 24.61, H 5.97, N 14.51.

Calcd. $C_8H_{18}ClGaN_4O_4$ (%): C 28.31, H 5.35, N 16.51.

[Ga(ox)(trien)]$^+$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 2.53–3.55 (sp, 12H, H1–H6, trien) ppm.

^{13}C{^{1}H} NMR (101 MHz, D_2O)**:** δ = 165.4–166.1 (3s, C1, ox), 44.5–46.7 (ms, C1–C6, trien), 37.8–39.4 (ms, C1–C6, trien), 35.0–35.8 (ms, C1–C6, trien) ppm.

Crystals of [Ga(ox)(trien)]Cl·2H_2O (**5b**·**5c**·2Cl·4H_2O) were obtained after one week by storing an aqueous solution of the raw product (pH 7.0, adjusted with triethylamine) over acetone.

Empirical formula: $C_8H_{18}ClGaN_4O_4 \cdot 2H_2O$, 375.46 g mol^{-1}.

Yield: 142 mg (0.378 mmol, 37.8%).

Elemental analysis: Calcd. (%): C 25.59, H 5.91, N 14.92.

Found (%): C 25.39, H 5.69, N 14.67.

5.5.84 [Ga(malo)(trien)]Cl

Starting material: Malonic acid, water, gallium(III) chloride, triethylenetetramine, triethylamine, ethanol, ethyl acetate, diethyl ether.

Procedure: Malonic acid (104 mg, 1.00 mmol) was suspended in 0.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), triethylenetetramine (146 mg, 1.00 mmol) and triethylamine (488 µL, 3.50 mmol) resulted in a yellowish solution (pH 9.0) which was stirred for 16 h. Addition of ethanol (30 mL) and ethyl acetate (30 mL) yielded a yellow slurry. After filtration and washing with ethyl acetate and diethyl ether the obtained beige amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_9H_{20}ClGaN_4O_4 + 1.65\ H_2O + 0.05\ Ga(OH)_3$.

Yield: 308 mg (0.791 mmol, 79.1%).

Elemental analysis: Calcd. (%): C 27.77, H 6.07, N 14.39.

Found (%): C 27.94, H 5.98, N 14.19.

Calcd. $C_9H_{20}ClGaN_4O_4$ (%): C 30.58, H 5.70, N 15.85.

$[Ga(malo)(trien)]^+$:

^{1}H NMR (400 MHz, D_2O)**:** δ = 3.15–3.25 (sp, 2H, H2, malo), 2.33–3.47 (sp, 12H, H1–H6, trien) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, D_2O)**:** δ = 175.0–176.1 (ms, C1, malo), 44.3–47.9 (ms, C1–C6, trien), 42.1–44.3 (ms, C2, malo), 36.8–39.4 (ms, C1–C6, trien), 34.9–35.9 (ms, C1–C6, trien) ppm.

5.5.85 [Ga(mal)(trien)]

Starting material: L-malic acid, water, gallium(III) chloride, triethylamine, triethylenetetramine, ethanol, diethyl ether, methanol, acetonitrile.

Procedure: L-Malic acid (134 mg, 1.00 mmol) was dissolved in 0.5 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), triethylamine (418 µL, 3.00 mmol) and triethylenetetramine (146 mg, 1.00 mmol) resulted in a yellowish solution (pH 9.0) which was stirred for 16 h. A yellow slurry was obtained which was then diluted with ethanol (10 mL). After filtration and washing with ethanol and diethyl ether the obtained beige amorphous solid was dried at 80 °C for 10 min.

Empirical formula: $C_{10}H_{22}GaClN_4O_5 + 0.85\ C_2H_6O + 0.30\ H_2O + 0.20\ Ga(OH)_3$.

Yield: 311 mg (0.688 mmol, 68.8%).

Elemental analysis: Calcd. (%): C 31.08, H 6.31, N 12.39.

Found (%): C 31.03, H 6.36, N 12.46.

Calcd. $C_{10}H_{22}GaClN_4O_5$ (%): C 31.32, H 5.78, N 14.61.

Crystals of [Ga(mal)(trien)]·3H$_2$O (**5d**·3H$_2$O) were obtained after one month by storing a solution of the raw product in a water/methanol mixture (1:1, pH 7.0) of the raw product over acetonitrile.

Empirical formula: $C_{10}H_{21}GaN_4O_5 \cdot 3H_2O$, 401.08 g mol^{-1}.

Yield: Few crystals.

5.5.86 HDIPEA[Ga(edda)(malo)]

Starting material: Malonic acid, water, gallium(III) chloride, ethylenediamine-*N*,*N*′-diacetic acid, *N*,*N*-diisopropylethylamine, ethanol, ethyl acetate, diethyl ether, dimethyl sulfoxide.

Procedure: Malonic acid (104 mg, 1.00 mmol) was dissolved in 1 mL of water. Gradual addition of gallium(III) chloride solution (176 mg, 1.00 mmol), ethylenediamine-*N*,*N*`-diacetic acid (176 mg, 1.00 mmol) and *N*,*N*-diisopropylethylamine (826 µL, 5.00 mmol) resulted in a colourless slurry (pH 8.0) which was stirred for 16 h. The solution was concentrated by rotary evaporation. Addition of ethanol (20 mL) and ethyl acetate (30 mL) yielded colourless precipitate. After filtration and washing with ethanol and diethyl ether the obtained colourless amorphous solid was first dried at 80 °C for 10 min and then under fine vacuum for 2 h.

Empirical formula: $C_{17}H_{32}GaN_3O_8$ + 0.95 H_2O.

Yield: 334 mg (0.677 mmol, 67.7%).

Elemental analysis: Calcd. (%): C 41.39, H 6.93, N 8.52.

Found (%): C 41.30, H 6.83, N 8.48.

Calcd. $C_{17}H_{32}GaN_3O_8$ (%): C 42.88, H 6.77, N 8.82.

Crystals of HDIPEA[Ga(edda)(malo)]·H_2O ((HDIPEA)**3k**·H_2O) were obtained after one month by storing an aqueous solution of the raw product (pH 7.0) over dimethyl sulfoxide.

Empirical formula: $C_{17}H_{32}GaN_3O_8$·H_2O, 494.19 g mol^{-1}.

Yield: Few crystals.

6 Appendix

6.1 Illustrations of $^{13}C\{^{1}H\}$ NMR spectra

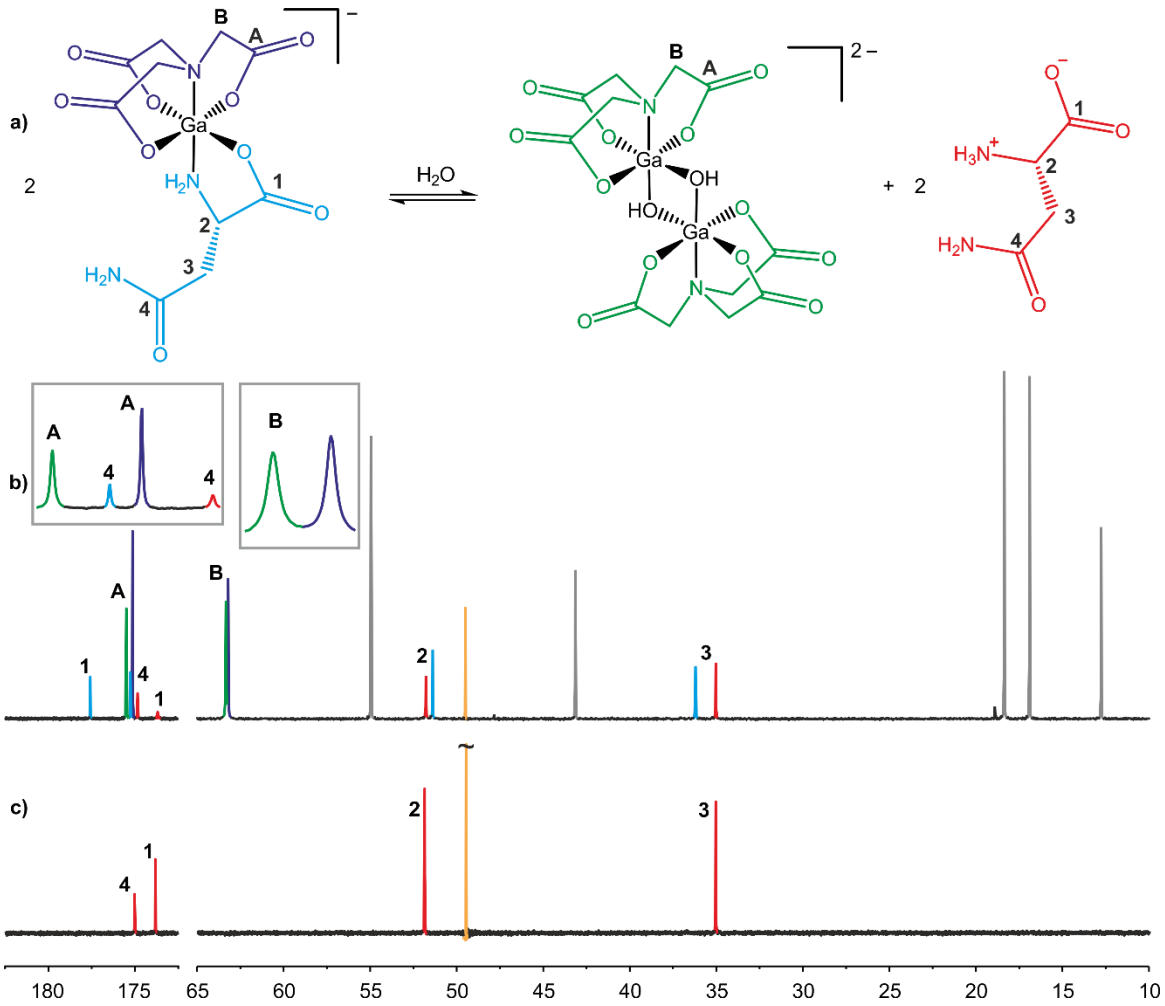


Figure 6.1: HDIPEA[Ga(asn)(nta)] + 0.20 $Ga(OH)_3$ + 0.05 EtOH in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(asn)(nta)] + 0.20 $Ga(OH)_3$ + 0.05 EtOH in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-asparagine in D_2O*. Red: L-asparagine, cyan: L-asparaginato in $[Ga(asn)(nta)]^-$, blue: nta in $[Ga(asn)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.1: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-asparagine and the L-asparaginato ligand in $[Ga(asn)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4
$HDIPEA^+$	$[Ga(asn)(nta)]^-$	δ	177.6	51.4	36.2	175.2
	L-Asparagine	δ	174.8	51.8	35.0	173.7
		$\Delta\delta$	2.8	-0.4	1.2	1.5
$HNEt_3^+$	$[Ga(asn)(nta)]^-$	δ	177.6	51.4	36.2	175.3
	L-Asparagine	δ	174.9	51.8	35.0	173.7
		$\Delta\delta$	2.7	-0.4	1.2	1.6

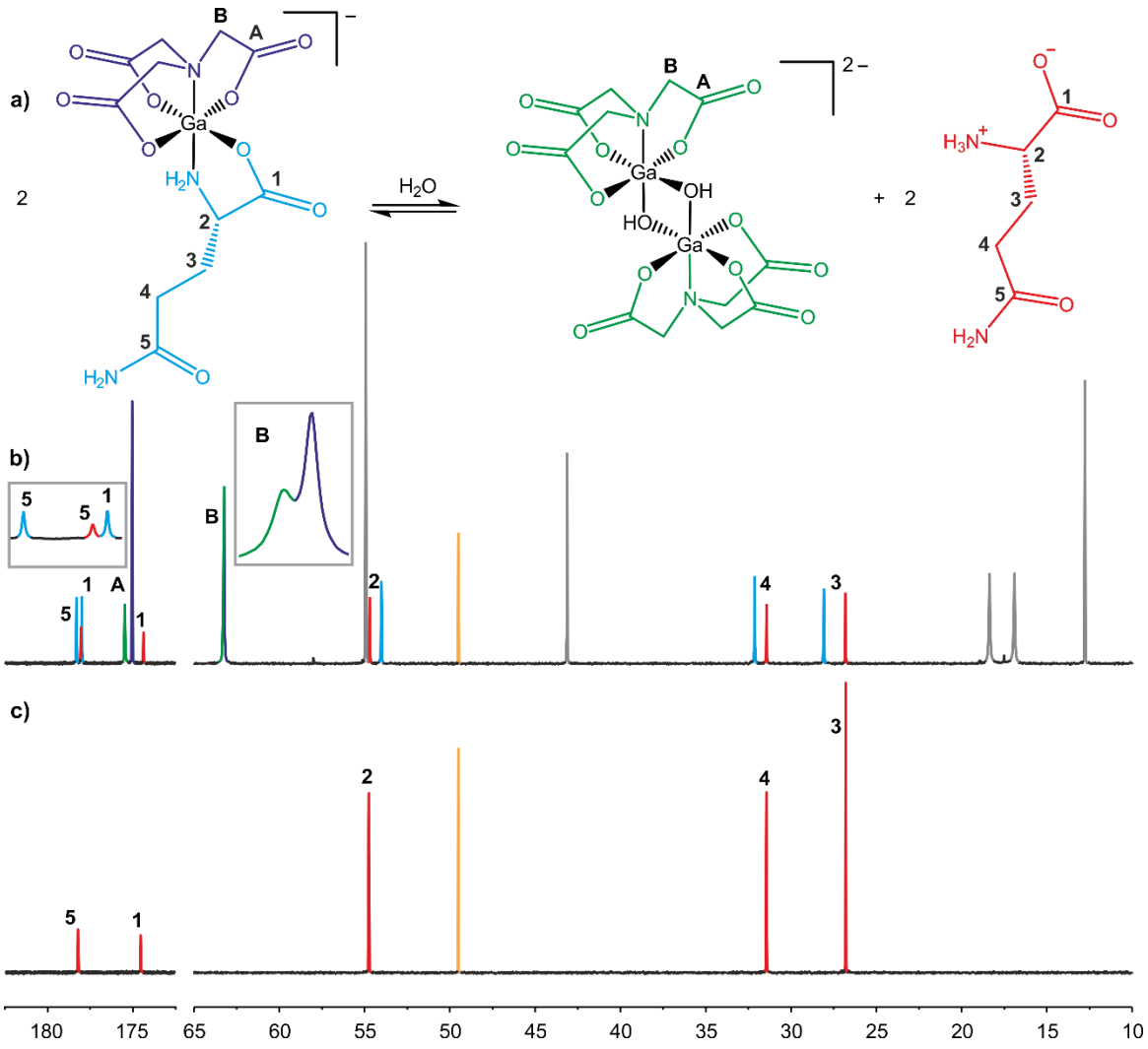


Figure 6.2: HDIPEA[Ga(gln)(nta)] + 0.20 + 0.05 EtOH in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(gln)(nta)] + 0.20 + 0.05 EtOH in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-glutamine in D_2O*. Red: L-glutamine, cyan: L-glutaminato in $[Ga(gln)(nta)]^-$, blue: nta in $[Ga(gln)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.2: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-glutamine and the L-glutaminato ligand in $[Ga(gln)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5
$HDIPEA^+$	$[Ga(gln)(nta)]^-$	δ	178.0	54.0	28.1	32.2	178.3
	L-Glutamine	δ	174.4	54.7	26.8	31.4	178.0
		$\Delta\delta$	3.6	-0.7	1.3	0.8	0.3
$HNEt_3^+$	$[Ga(gln)(nta)]^-$	δ	178.1	54.0	28.0	32.1	178.4
	L-Glutamine	δ	174.5	54.7	26.8	31.4	178.1
		$\Delta\delta$	3.6	-0.7	1.2	0.7	0.3

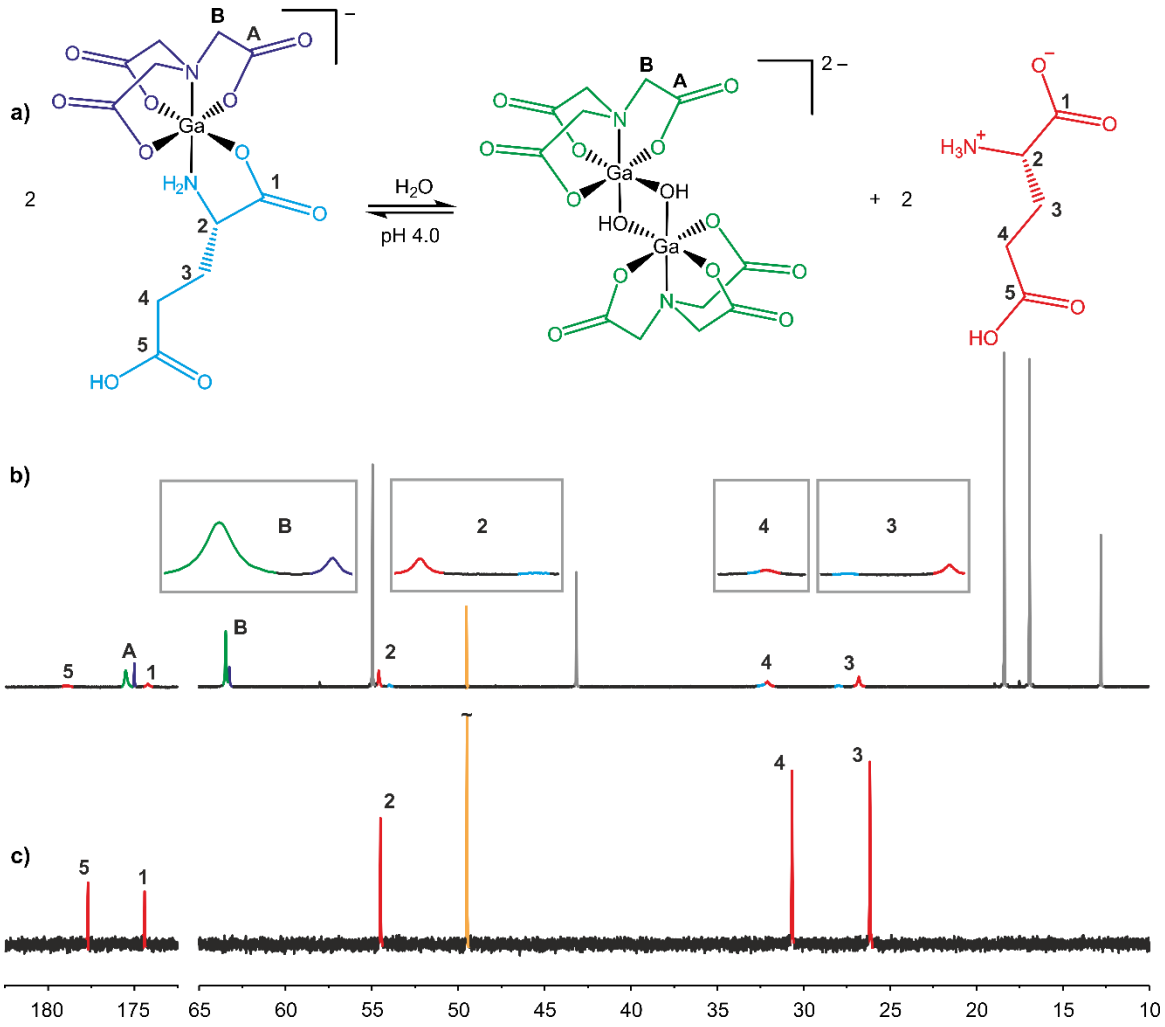


Figure 6.3: HDIPEA[Ga(Hglu)(nta)]·0.05DIPEA + 0.30 H_2O + 0.05 $Ga(OH)_3$ in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(Hglu)(nta)]·0.05DIPEA + 0.30 H_2O + 0.05 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-glutamic acid in D_2O*. Red: L-glutamic acid, cyan: L-glutamato in $[Ga(Hglu)(nta)]^-$, blue: nta in $[Ga(Hglu)(nta)]^-$, green: nta in in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, yellow: residual EtOH, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.3: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-glutamic acid and the L-glutamato ligand in $[Ga(Hglu)(nta)]^-$ complexes. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5
$HDIPEA^+$	$[Ga(Hglu)(nta)]^-$	δ	-	54.0	28.0	32.2	-
	L-Glutamic acid	δ	174.2	54.6	26.8	32.1	178.9
		$\Delta\delta$	-	-0.6	1.2	0.1	-
$HNEt_3^+$	$[Ga(Hglu)(nta)]^-$	δ	-	54.1	28.1	32.4	-
	L-Glutamic acid	δ	174.5	54.7	26.9	32.4	179.5
		$\Delta\delta$	-	-0.6	1.2	0.0	-

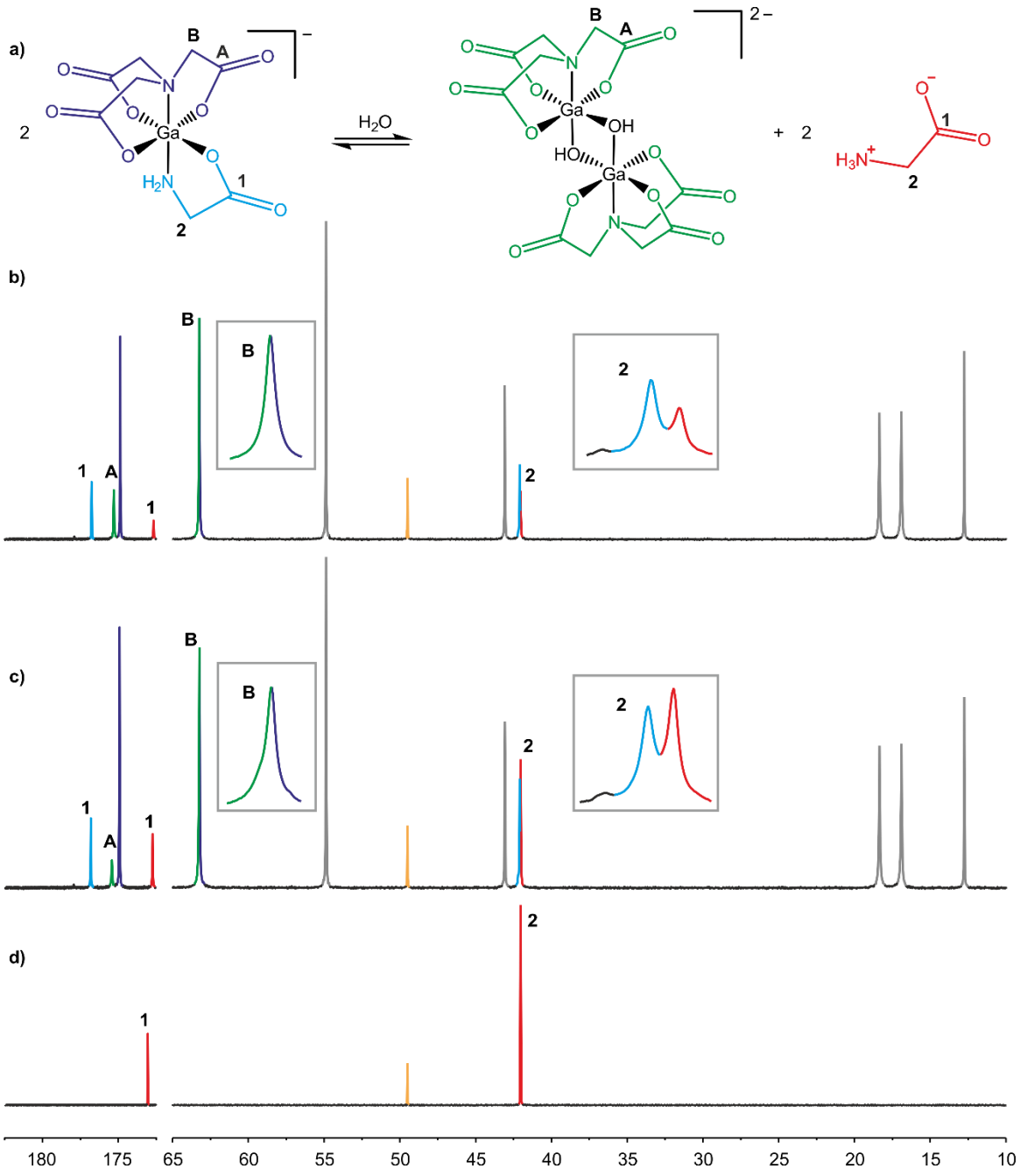


Figure 6.4: HDIPEA[Ga(gly)(nta)] + 0.95 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(gly)(nta)] + 0.95 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(gly)(nta)] + 0.95 H_2O with 0.5 equ. of glycine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of glycine in D_2O*. Red: glycine, cyan: glycinato in $[Ga(gly)(nta)]^-$, blue: nta in $[Ga(gly)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.4: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of glycine and the glycinato ligand in $[Ga(gly)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2
$HDIPEA^+$	$[Ga(gly)(nta)]^-$	δ	176.7	42.1
	Glycine	δ	172.7	42.0
		$\Delta\delta$	4.0	0.1
$HNEt_3^+$	$[Ga(gly)(nta)]^-$	δ	177.1	42.1
	Glycine	δ	172.9	42.0
		$\Delta\delta$	4.2	0.1

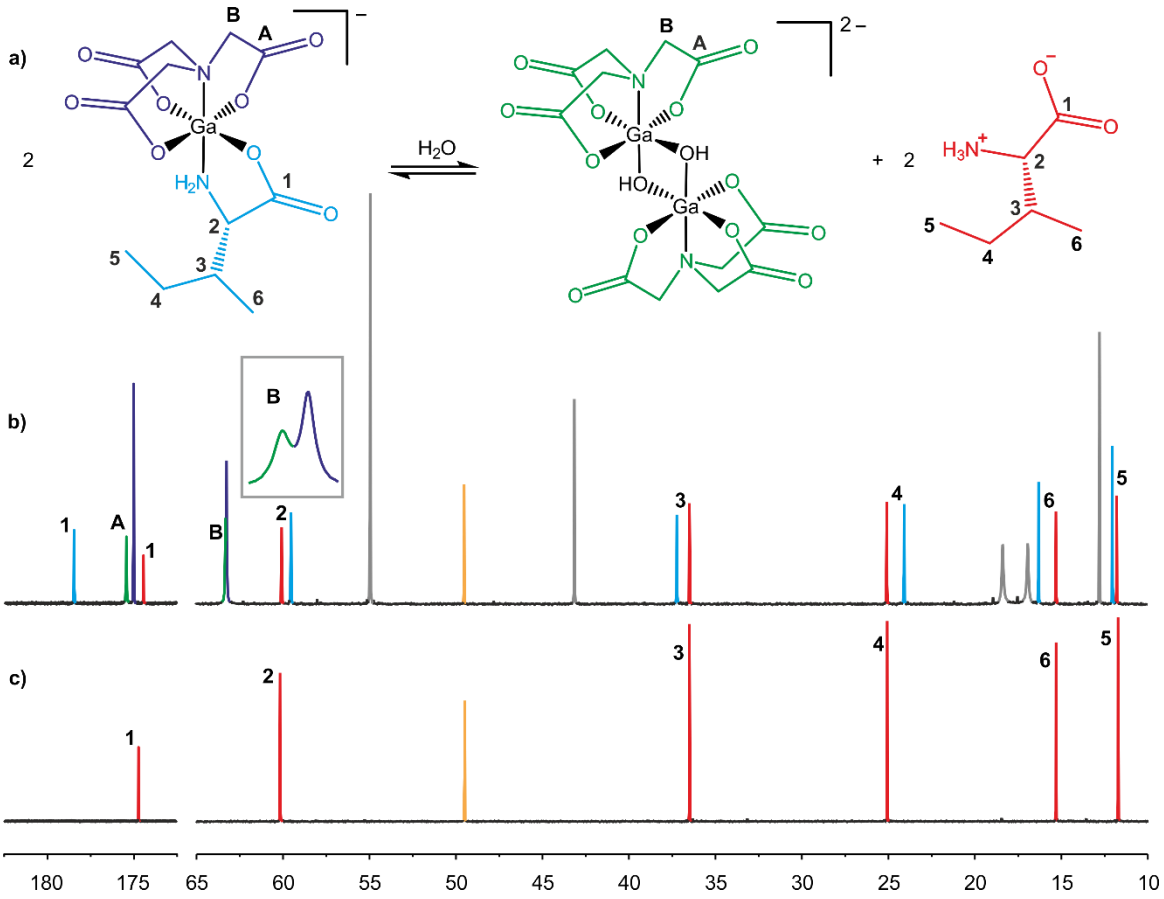


Figure 6.5: HDIPEA[Ga(ile)(nta)] + 0.20 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(ile)(nta)] + 0.20 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-isoleucine in D_2O*. Red: L-isoleucine, cyan: L-isoleucinato in $[Ga(ile)(nta)]^-$, blue: nta in $[Ga(ile)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.5: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-isoleucine and the L-isoleucinato ligand in $[Ga(ile)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5	C6
$HDIPEA^+$	$[Ga(ile)(nta)]^-$	δ	178.5	59.5	37.2	24.1	16.3	12.0
	L-Isoleucine	δ	174.5	60.1	36.5	25.1	15.3	11.8
		$\Delta\delta$	4.0	-0.6	0.7	-1.0	1.0	0.2
$HNEt_3^+$	$[Ga(ile)(nta)]^-$	δ	178.7	59.5	37.2	24.1	16.3	12.0
	L-Isoleucine	δ	174.6	60.1	36.5	25.1	15.3	11.7
		$\Delta\delta$	4.1	-0.6	0.7	-1.0	1.0	0.3

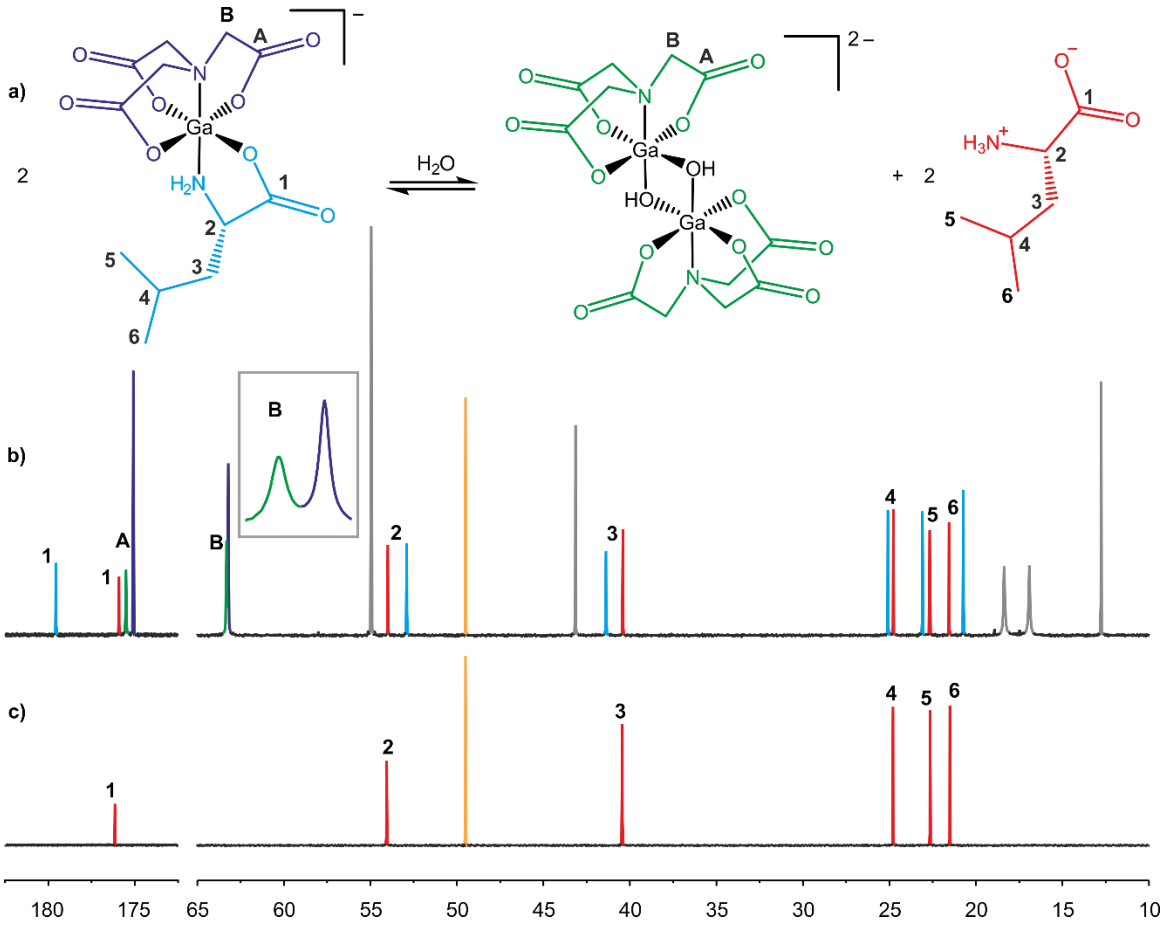


Figure 6.6: HDIPEA[Ga(leu)(nta)] + 0.15 H_2O + 0.05 EtOAc in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(leu)(nta)] + 0.15 H_2O + 0.05 EtOAc in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-leucine in D_2O*. Red: L-leucine, cyan: L-leucinato in $[Ga(leu)(nta)]^-$, blue: nta in $[Ga(leu)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.6: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-leucine and the L-leucinato ligand in $[Ga(leu)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5	C6
$HDIPEA^+$	$[Ga(leu)(nta)]^-$	δ	179.6	52.9	41.4	25.1	23.1	20.7
	L-Leucine	δ	175.9	54.0	40.4	24.8	22.7	21.6
		$\Delta\delta$	3.7	-1.1	1.0	0.3	0.4	-0.9
$HNEt_3^+$	$[Ga(leu)(nta)]^-$	δ	179.7	52.9	41.4	25.1	23.1	20.7
	L-Leucine	δ	176.0	54.0	40.4	24.8	22.7	21.6
		$\Delta\delta$	3.7	-1.1	1.0	0.3	0.4	-0.9

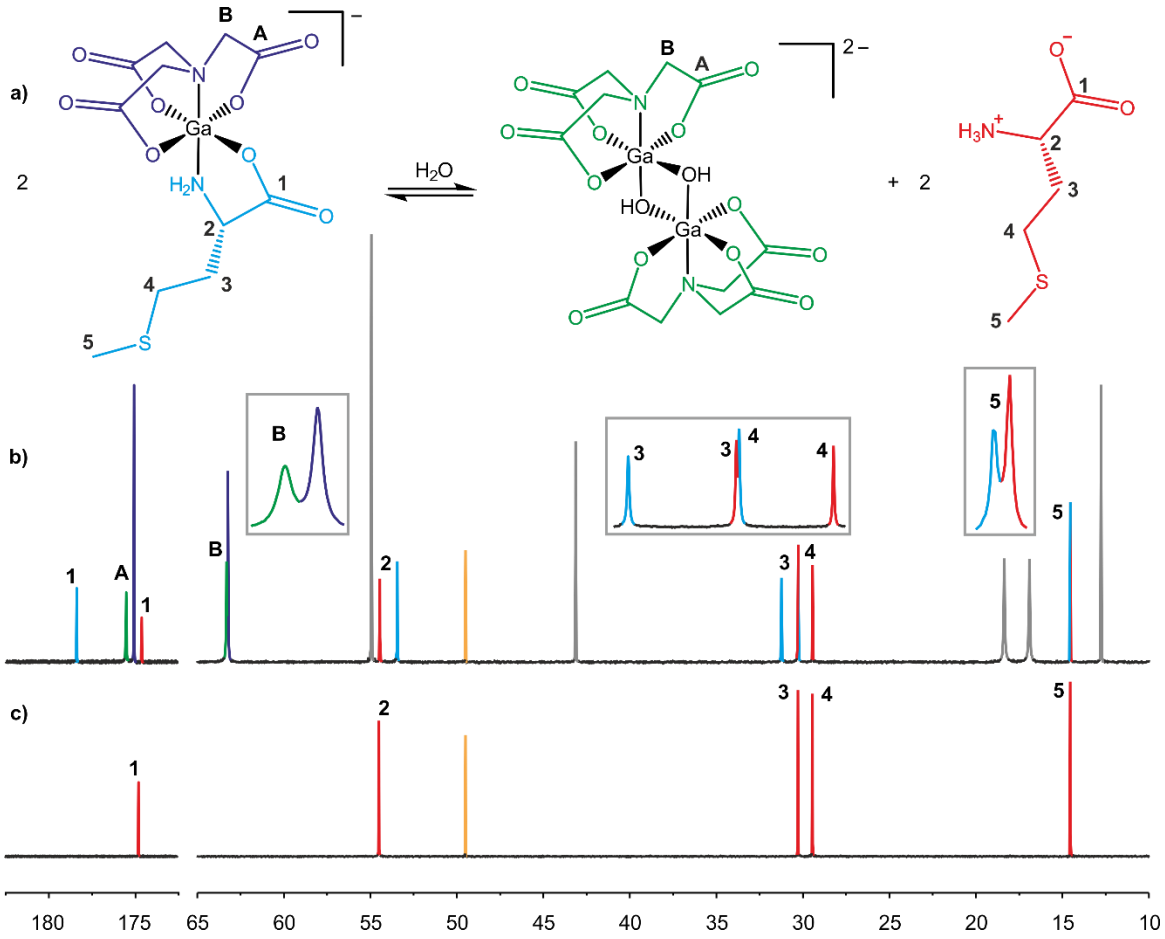


Figure 6.7: HDIPEA[Ga(met)(nta)] + 0.05 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(met)(nta)] + 0.05 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-methionine in D_2O*. Red: L-methionine, cyan: L-methioninato in $[Ga(met)(nta)]^-$, blue: nta in $[Ga(met)(nta)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.7: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-methionine and the L-methioninato ligand in $[Ga(met)(nta)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5
$HDIPEA^+$	$[Ga(met)(nta)]^-$	δ	178.4	53.5	31.3	30.3	14.6
	L-Methionine	δ	174.6	54.5	30.3	29.4	14.5
		$\Delta\delta$	3.8	-1.0	1.0	0.9	0.1
$HNEt_3^+$	$[Ga(met)(nta)]^-$	δ	178.5	53.5	31.2	30.3	14.6
	L-Methionine	δ	174.7	54.5	30.3	29.4	14.5
		$\Delta\delta$	3.8	-1.0	0.9	0.9	0.1

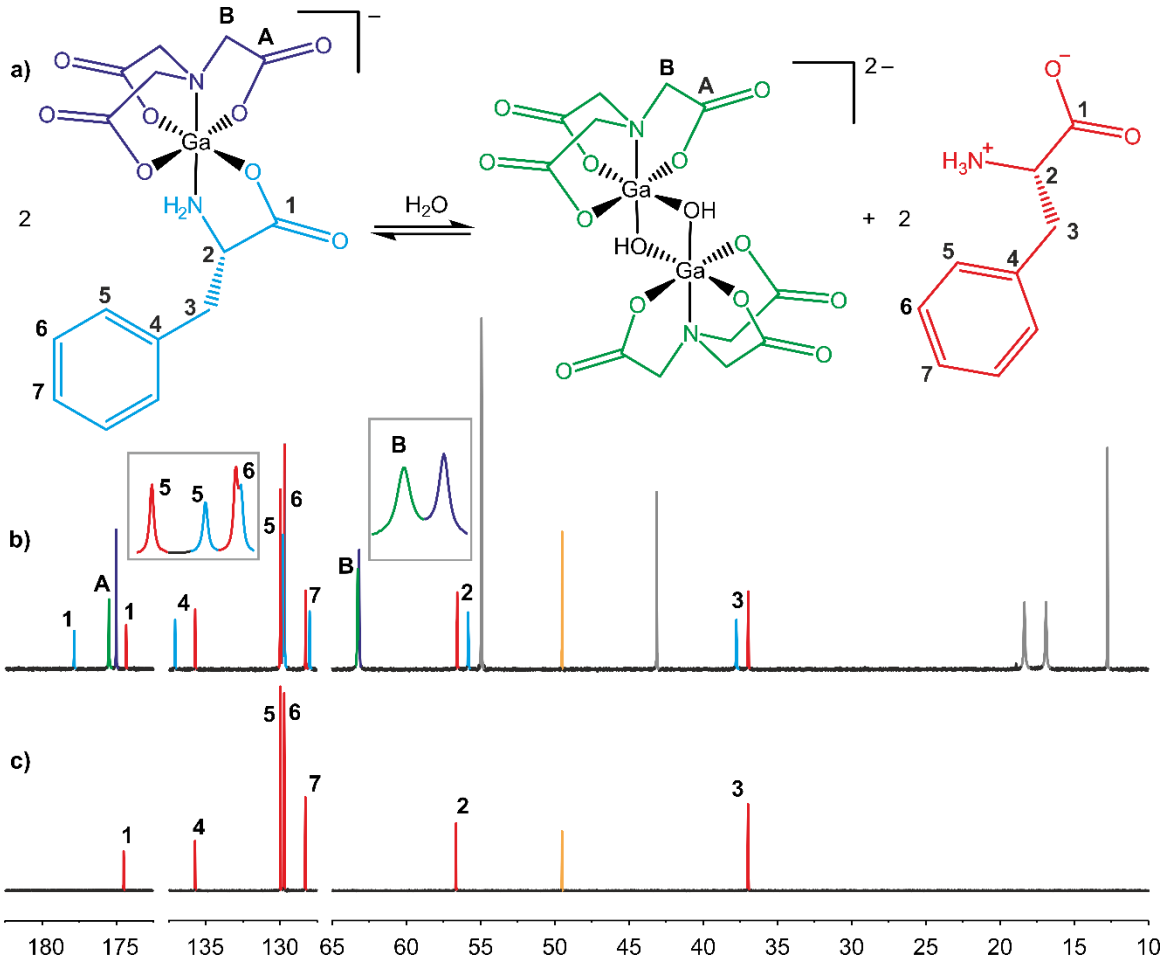


Figure 6.8: HDIPEA[Ga(nta)(phe)] + 0.90 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(phe)] + 0.90 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-phenylalanine in D_2O*. Red: L-phenylalanine, cyan: L-phenylalaninato in $[Ga(nta)(phe)]^-$, blue: nta in $[Ga(nta)(phe)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.8: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-phenylalanine and the L-phenylalaninato ligand in $[Ga(nta)(phe)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
$HDIPEA^+$	$[Ga(nta)(phe)]^-$	δ	177.9	55.8	37.8	137.1	129.8	129.7	128.0
	L-Phenylalanine	δ	174.4	56.6	37.0	135.7	130.0	129.7	128.3
		$\Delta\delta$	3.5	-0.8	0.8	1.4	-0.2	0.0	-0.3
$HNEt_3^+$	$[Ga(nta)(phe)]^-$	δ	177.9	55.8	37.7	137.1	129.8	129.7	128.0
	L-Phenylalanine	δ	174.4	56.6	37.0	135.7	130.0	129.7	128.3
		$\Delta\delta$	3.5	-0.8	0.7	1.4	-0.2	0.0	-0.3

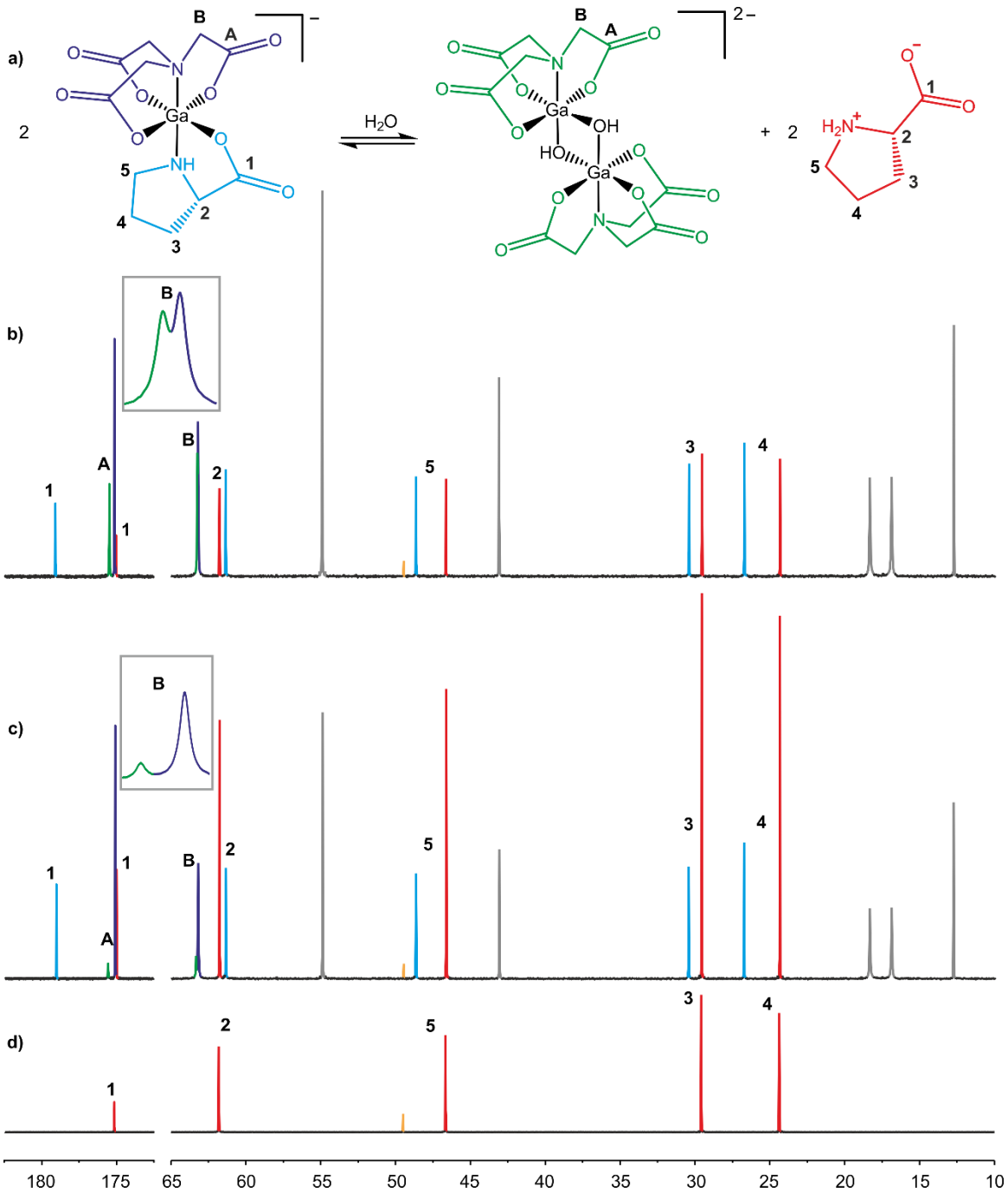


Figure 6.9: HDIPEA[Ga(nta)(pro)] + 0.05 $Ga(OH)_3$ + 0.05 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(pro)] + 0.05 $Ga(OH)_3$ + 0.05 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(pro)] + 0.05 $Ga(OH)_3$ + 0.05 H_2O with 0.5 equ. of L-proline in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-proline in D_2O*. Red: L-proline, cyan: L-prolinato in $[Ga(nta)(pro)]^-$, blue: nta in $[Ga(nta)(pro)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.9: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-proline and the L-prolinato ligand in $[Ga(nta)(pro)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5
$HDIPEA^+$	$[Ga(nta)(pro)]^-$	δ	179.1	61.4	30.4	26.7	48.7
	L-Proline	δ	175.0	61.8	29.6	24.4	46.7
		$\Delta\delta$	4.1	-0.4	0.8	2.3	2.0
$HNEt_3^+$	$[Ga(nta)(pro)]^-$	δ	179.2	61.4	30.4	26.8	48.7
	L-Proline	δ	175.1	61.8	29.6	24.4	46.7
		$\Delta\delta$	4.1	-0.4	0.8	2.4	2.0

Table 6.10: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-serine and the L-serlinato ligand in $[Ga(nta)(ser)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3
$HDIPEA^+$	$[Ga(nta)(ser)]^-$	δ	176.4	56.2	61.4
	L-Serine	δ	172.8	56.9	60.8
		$\Delta\delta$	3.6	-0.7	0.6
$HNEt_3^+$	$[Ga(nta)(ser)]^-$	δ	176.6	56.2	61.4
	L-Serine	δ	172.8	57.0	60.8
		$\Delta\delta$	3.8	-0.8	0.6

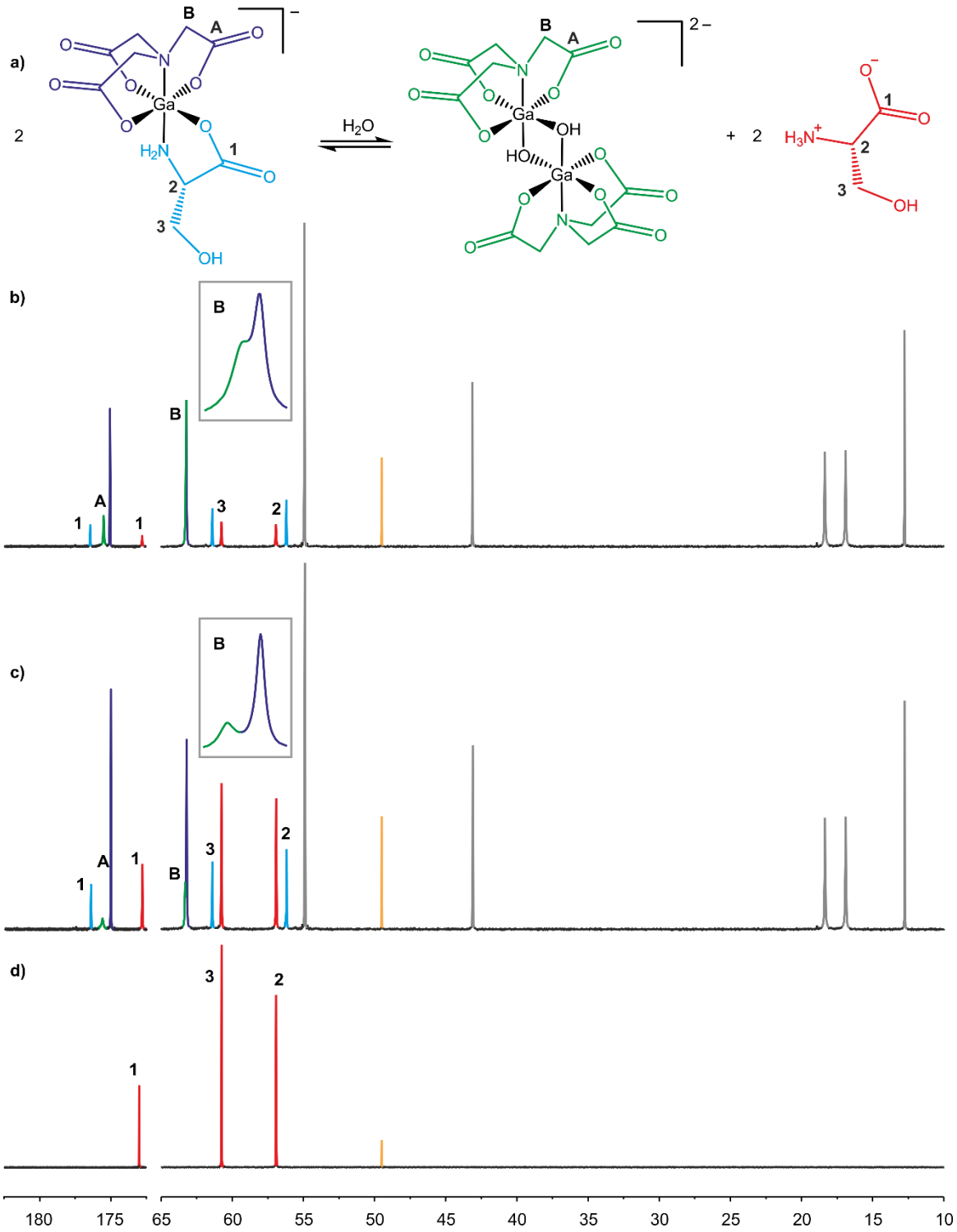


Figure 6.10: HDIPEA[Ga(nta)(ser)] + 0.80 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(ser)] + 0.80 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(ser)] + 0.80 H_2O with 0.5 equ. of L-serine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-serine in D_2O*. Red: L-serine, cyan: L-serinato in $[Ga(nta)(ser)]^-$, blue: nta in $[Ga(nta)(ser)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

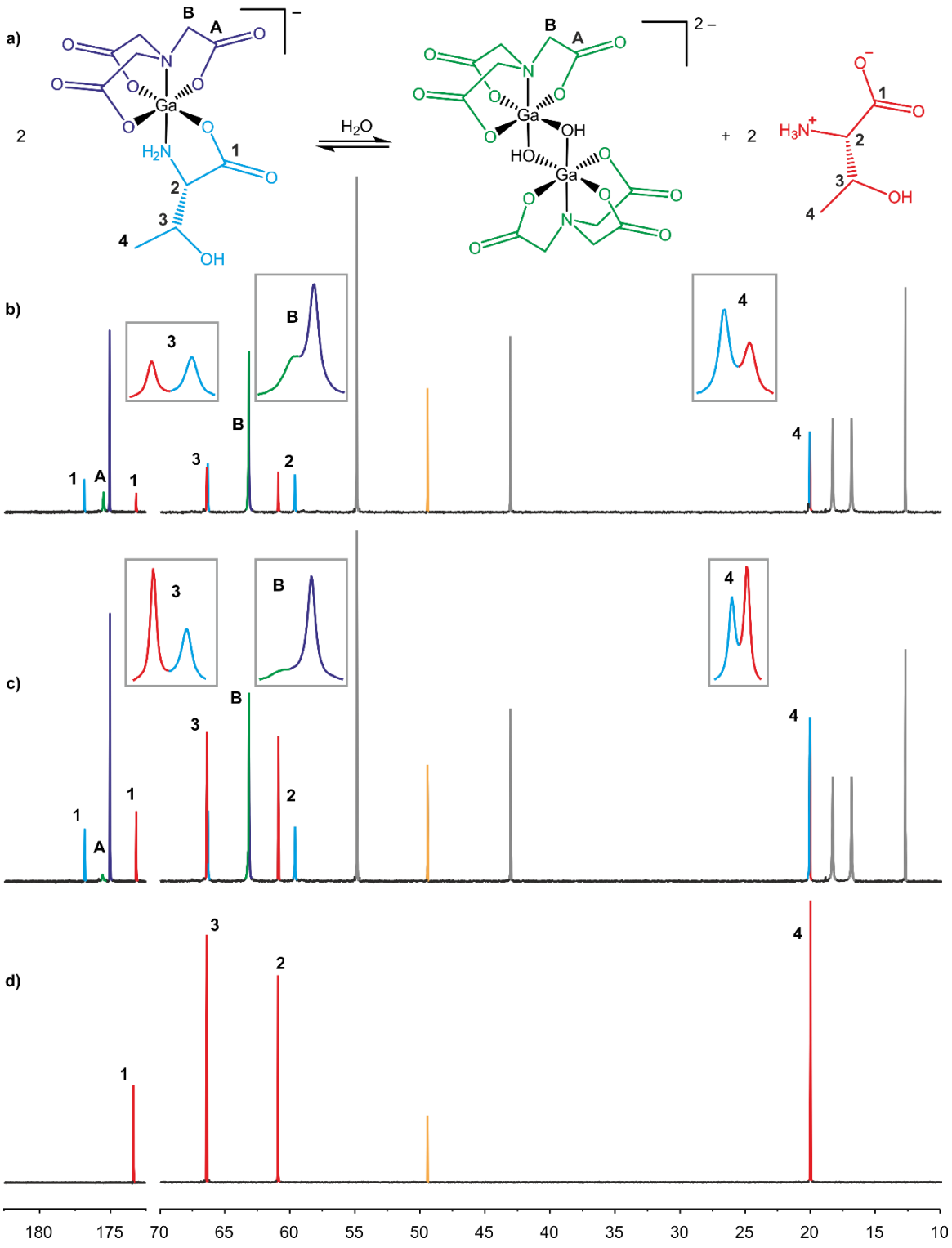


Figure 6.11: HDIPEA[Ga(nta)(thr)] + 0.50 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(thr)] + 0.50 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(thr)] + 0.50 H_2O with 0.5 equ. of L-threonine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-threonine in D_2O*. Red: L-threonine, cyan: L-threoninato in $[Ga(nta)(thr)]^-$, blue: nta in $[Ga(nta)(thr)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.11: $^{13}C\{^1H\}$ NMR shifts (δ/ppm, D_2O) of L-threonine and the L-threoninato ligand in $[Ga(nta)(thr)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4
$HDIPEA^+$	$[Ga(nta)(thr)]^-$	δ	176.9	59.7	66.4	20.1
	L-Threonine	δ	173.2	61.0	66.5	20.1
		$\Delta\delta$	3.7	-1.3	-0.1	0.0
$HNEt_3^+$	$[Ga(nta)(thr)]^-$	δ	177.0	59.7	66.4	20.1
	L-Threonine	δ	173.3	61.0	66.5	20.1
		$\Delta\delta$	3.7	-1.3	-0.1	0.0

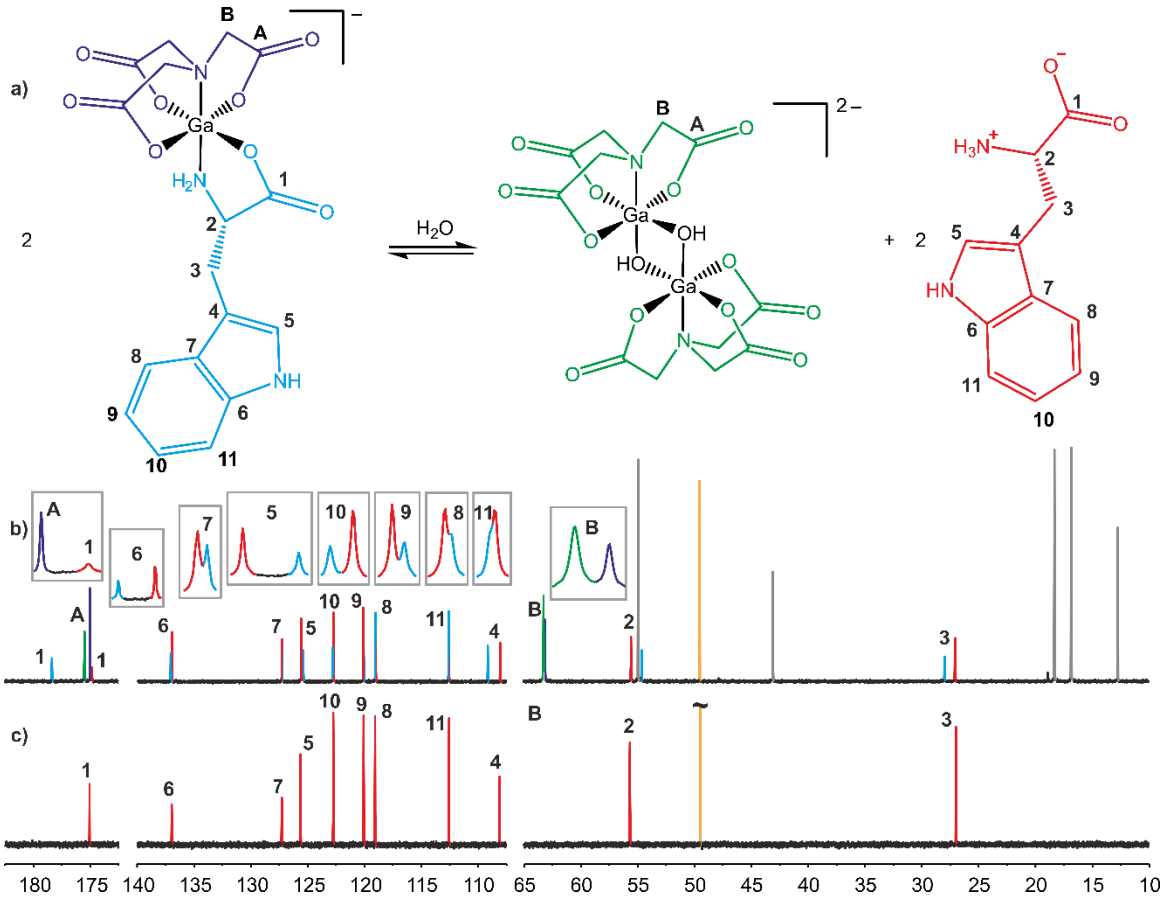


Figure 6.12: HDIPEA[Ga(nta)(trp)] + 0.25 H_2O + 0.20 $Ga(OH)_3$ in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(trp)] + 0.25 H_2O + 0.20 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-tryptophan in D_2O*. Red: L-tryptophan, cyan: L-tryptophanato in $[Ga(nta)(trp)]^-$, blue: nta in $[Ga(nta)(trp)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

Table 6.12: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-tryptophan and the L-tryptophanato ligand in $[Ga(nta)(trp)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
$HDIPEA^+$	$[Ga(nta)(trp)]^-$	δ	178.4	54.6	28.0	109.2	125.4	137.1	127.3	119.0	120.1	122.8	112.6
	L-Tryptophan	δ	174.9	55.5	27.0	108.1	125.6	136.9	127.3	119.0	120.1	122.7	112.6
		$\Delta\delta$	3.5	-0.9	1.0	1.1	-0.2	0.2	0.0	0.0	0.0	0.1	0.0
$HNEt_3^+$	$[Ga(nta)(trp)]^-$	δ	178.3	54.6	27.9	109.2	125.4	137.0	127.3	119.0	120.0	122.8	112.6
	L-Tryptophan	δ	174.8	55.5	27.0	108.1	125.6	136.9	127.3	119.0	120.1	122.7	112.6
		$\Delta\delta$	3.5	-0.9	0.9	1.1	-0.2	0.1	0.0	0.0	-0.1	0.1	0.0

Table 6.13: $^{13}C\{^{1}H\}$ NMR shifts (δ/ppm, D_2O) of L-valine and the L-valinato ligand in $[Ga(nta)(val)]^-$. The relative shift is given in $\Delta\delta$ (CIS).

			C1	C2	C3	C4	C5
$HDIPEA^+$	$[Ga(nta)(val)]^-$	δ	178.5	59.8	30.2	19.2	15.9
	L-Valine	δ	174.6	60.9	29.7	18.6	17.3
		$\Delta\delta$	3.9	-1.1	0.5	0.6	-1.4
$HNEt_3^+$	$[Ga(nta)(val)]^-$	δ	178.7	59.8	30.2	19.2	15.9
	L-Valine	δ	174.7	60.9	29.7	18.6	17.3
		$\Delta\delta$	4.0	-1.1	0.5	0.6	-1.4

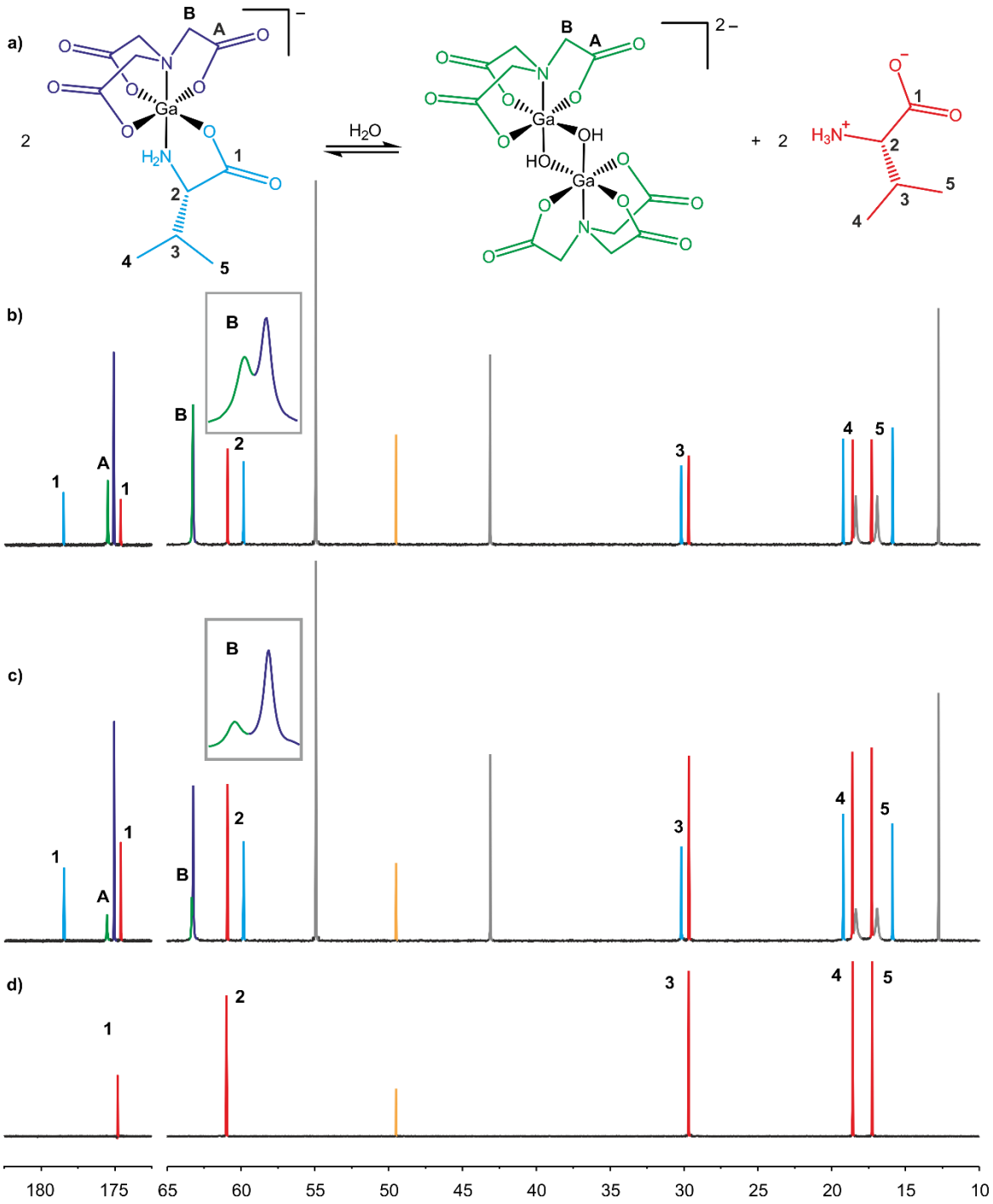


Figure 6.13: HDIPEA[Ga(nta)(val)] + 0.15 H_2O in aqueous solution. a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(val)] + 0.15 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of HDIPEA[Ga(nta)(val)] + 0.15 H_2O with 0.5 equ. of L-valine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-valine in D_2O*. Red: L-valine, cyan: L-valinato in $[Ga(nta)(val)]^-$, blue: nta in $[Ga(nta)(val)]^-$, green: nta in $[\{Ga(nta)(\mu\text{-}OH)\}_2]^{2-}$, grey: $HDIPEA^+$, orange: MeOH. * One drop of MeOH was added for referencing.

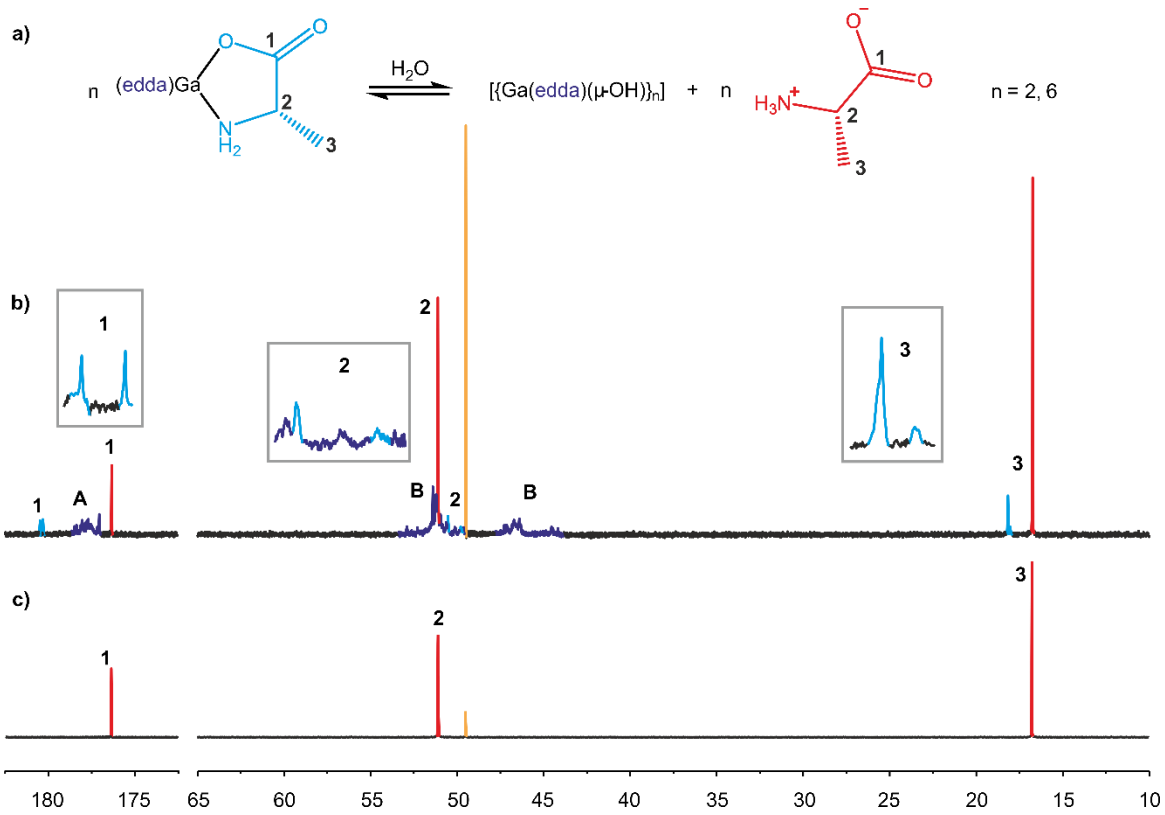


Figure 6.14: [Ga(ala)(edda)] + 0.20 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(ala)(edda)] + 0.20 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-alanine in D_2O*. Red: L-alanine, cyan: L-alaninato in [Ga(ala)(edda)], blue (**A** and **B**): edda in [Ga(ala)(edda)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

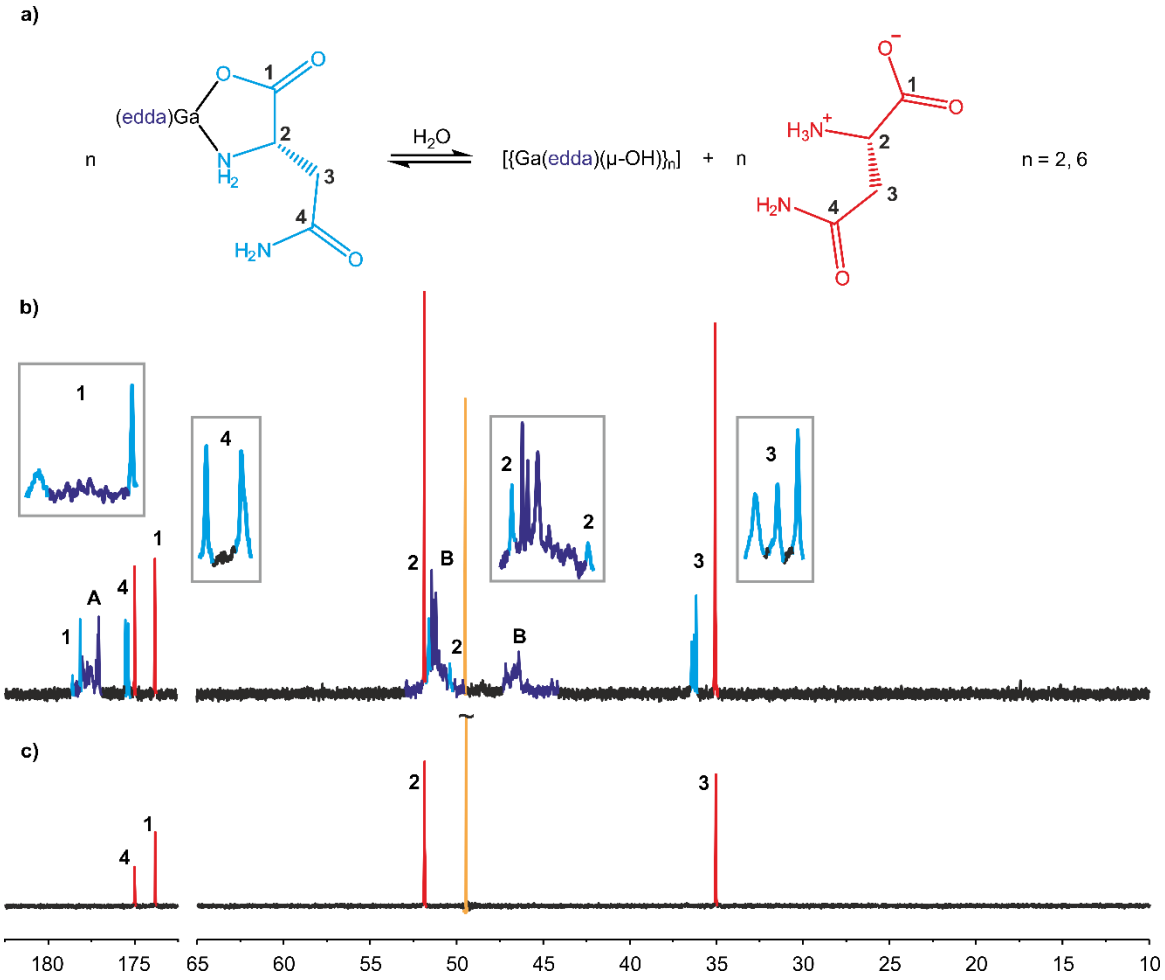


Figure 6.15: [Ga(asn)(edda)] + 0.15 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(asn)(edda)] + 0.15 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-asparagine in D_2O*. Red: L-asparagine, cyan: L-asparaginato in [Ga(asn)(edda)], blue (**A** and **B**): edda in [Ga(asn)(edda)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

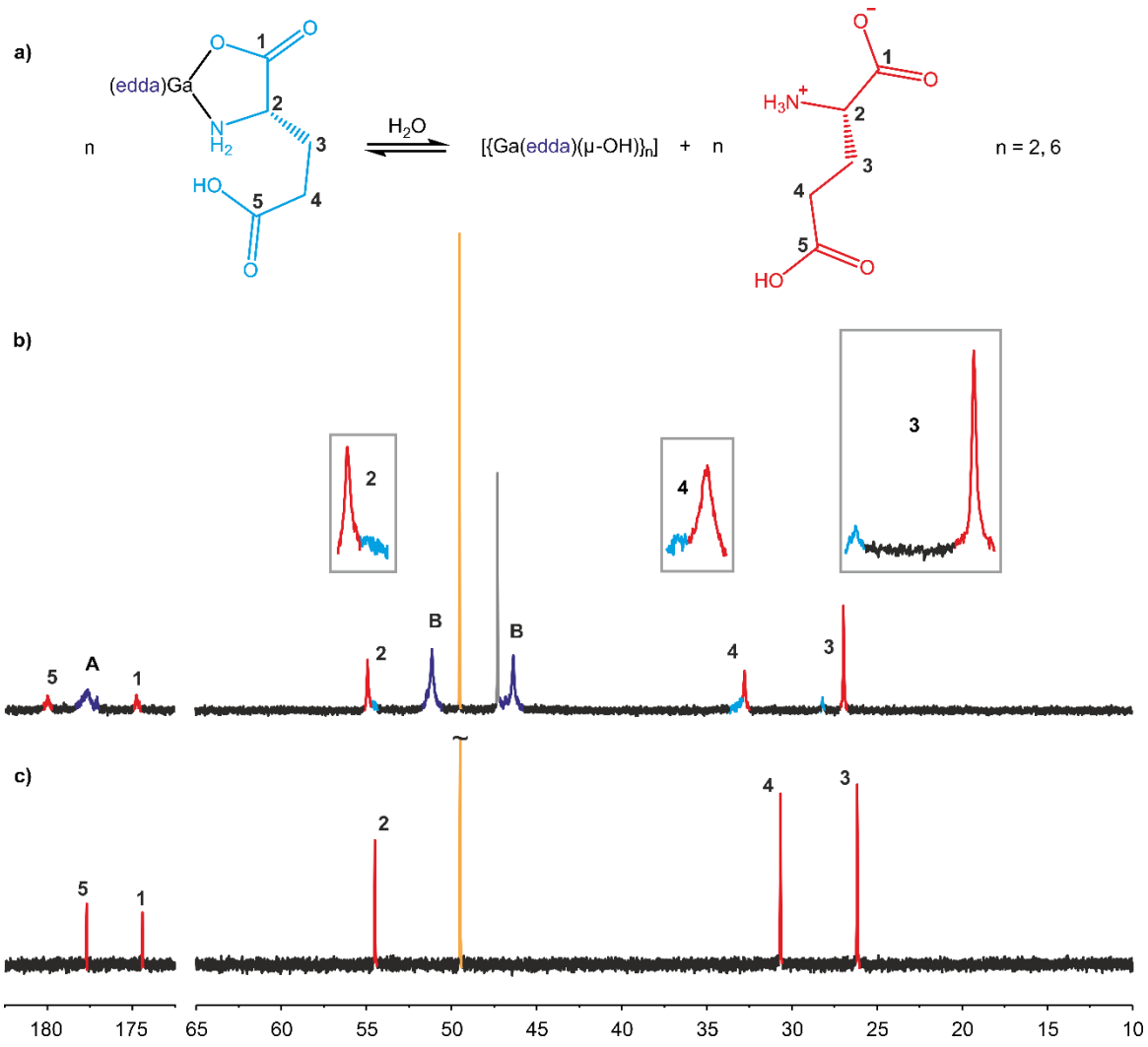


Figure 6.16: [Ga(edda)(Hglu)]·0.30NEt_3 + 1.25 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(Hglu)]·0.30NEt_3 + 1.25 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-glutamic acid in D_2O*. Red: L-glutamic acid, cyan: L-glutamato in [Ga(edda)(Hglu)], blue (**A** and **B**): edda in [Ga(edda)(Hglu)] and [{Ga(edda)(μ-OH)}$_n$] complexes, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

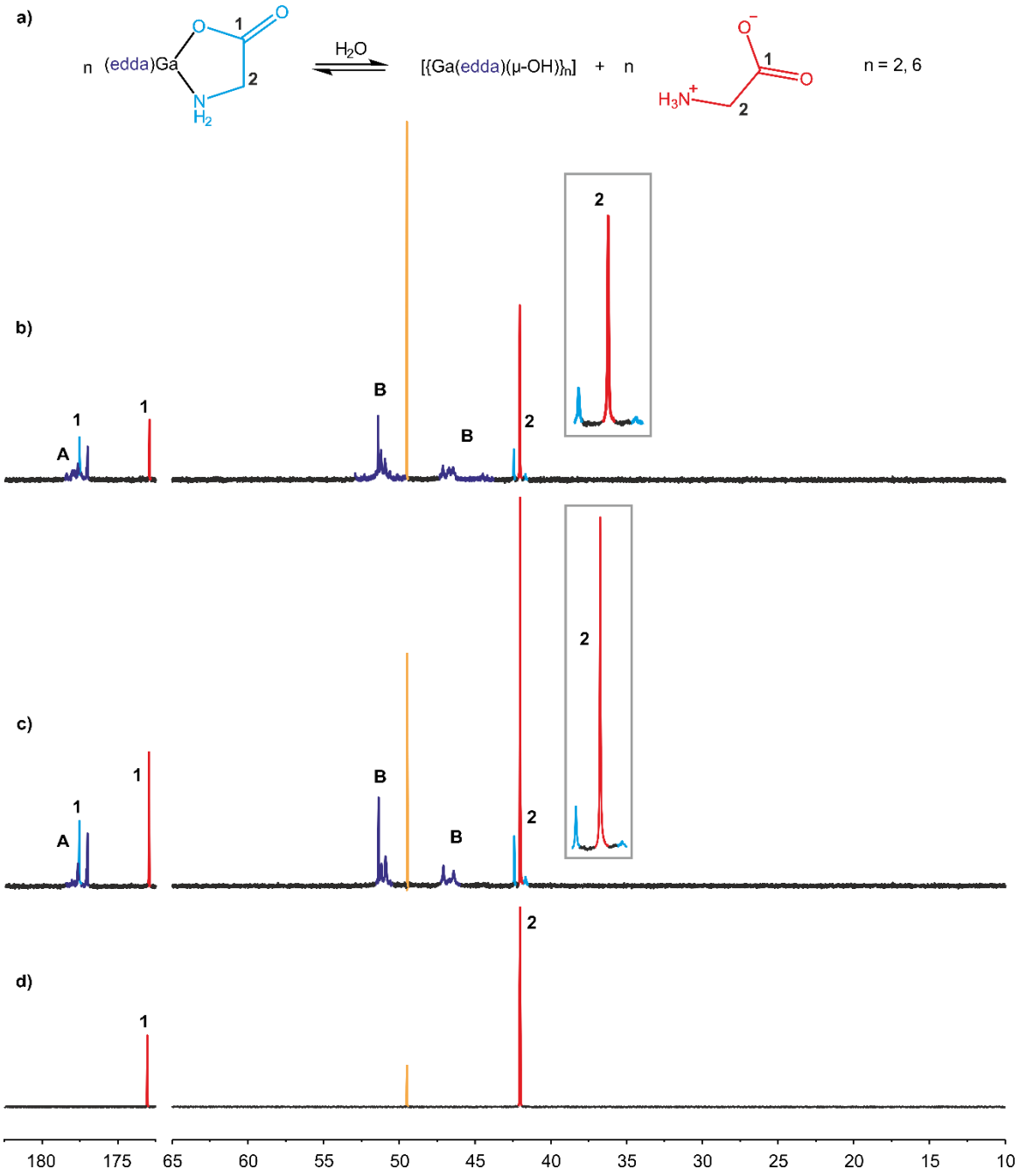


Figure 6.17: [Ga(edda)(gly)] + 1.40 H_2O + 0.10 $Ga(OH)_3$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(gly)] + 1.40 H_2O + 0.10 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(gly)] + 1.40 H_2O + 0.10 $Ga(OH)_3$ with 1.0 equ. of glycine in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of glycine in D_2O*. Red: glycine, cyan: glycinato in [Ga(edda)(gly)], blue (**A** and **B**): edda in [Ga(edda)(gly)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

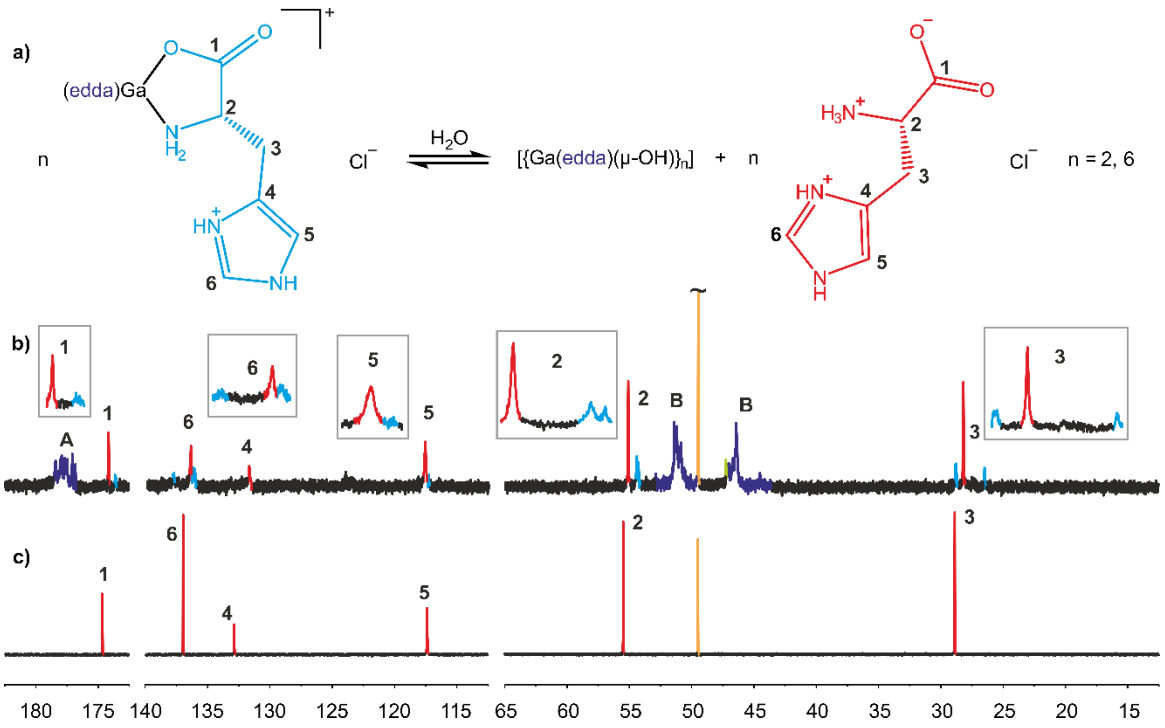


Figure 6.18: [Ga(edda)(Hhis)]Cl + 0.10 H_2O + 0.05 $HNEt_3Cl$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(Hhis)]Cl + 0.10 H_2O + 0.05 $HNEt_3Cl$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-histidine in D_2O*. Red: L-histidine, cyan: L-histidinato in $[Ga(edda)(Hhis)]^+$, blue (**A** and **B**): edda in $[Ga(edda)(Hhis)]^+$ and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ complexes, orange: MeOH. * One drop of MeOH was added for referencing.

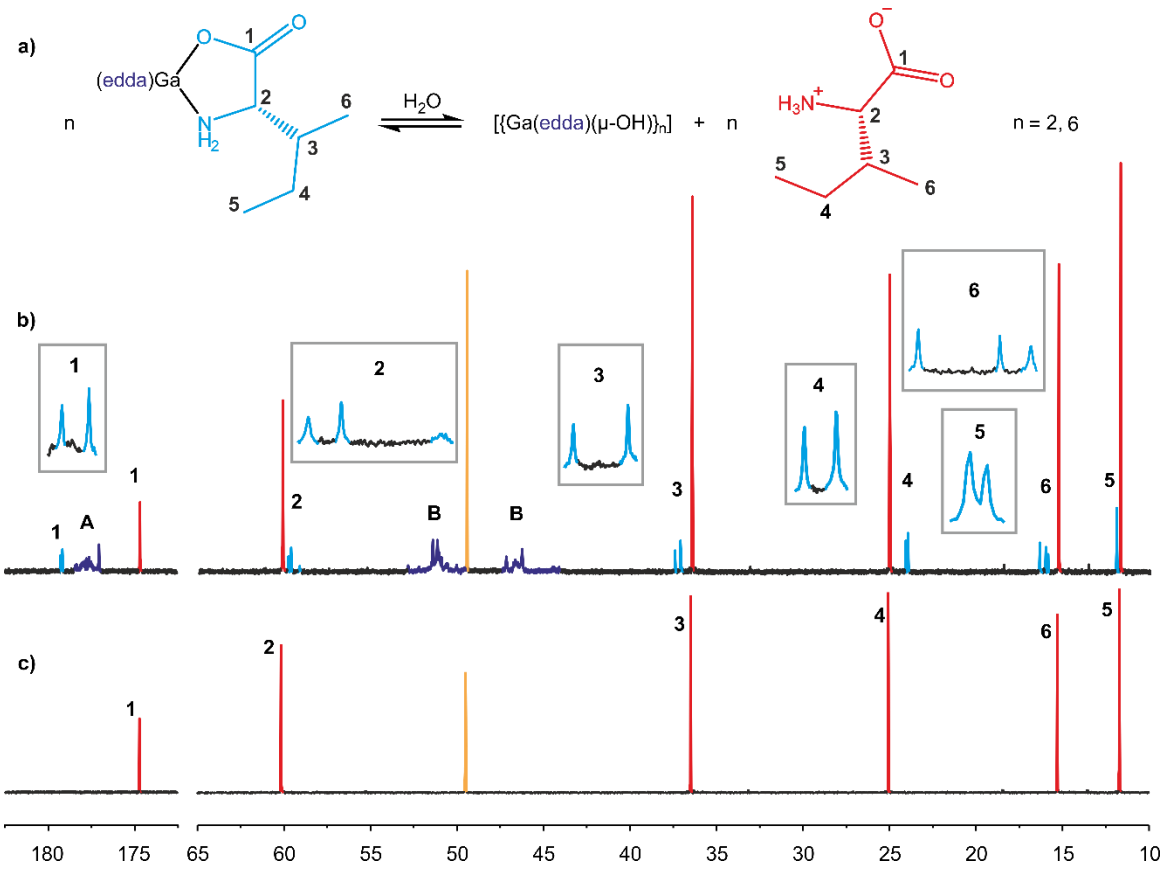


Figure 6.19: [Ga(edda)(ile)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(ile)] + 0.80 H_2O + 0.05 $HNEt_3Cl$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-isoleucine in D_2O*. Red: L-isoleucine, cyan: L-isoleucinato in [Ga(edda)(ile)], blue (**A** and **B**): edda in [Ga(edda)(ile)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

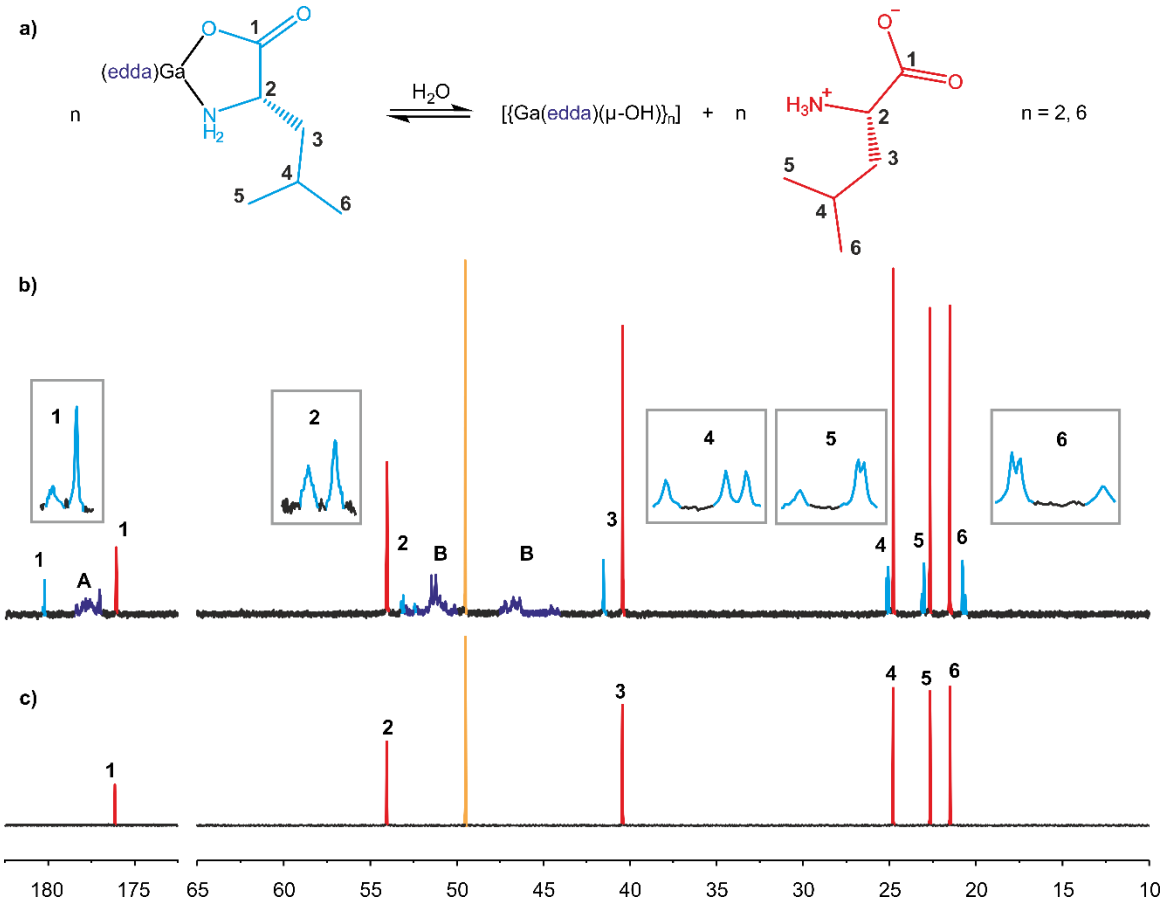


Figure 6.20: [Ga(edda)(leu)] + 1.50 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(leu)] + 1.50 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-leucine in D_2O*. Red: L-leucine, cyan: L-leucinato in [Ga(edda)(leu)], blue (**A** and **B**): edda in [Ga(edda)(leu)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

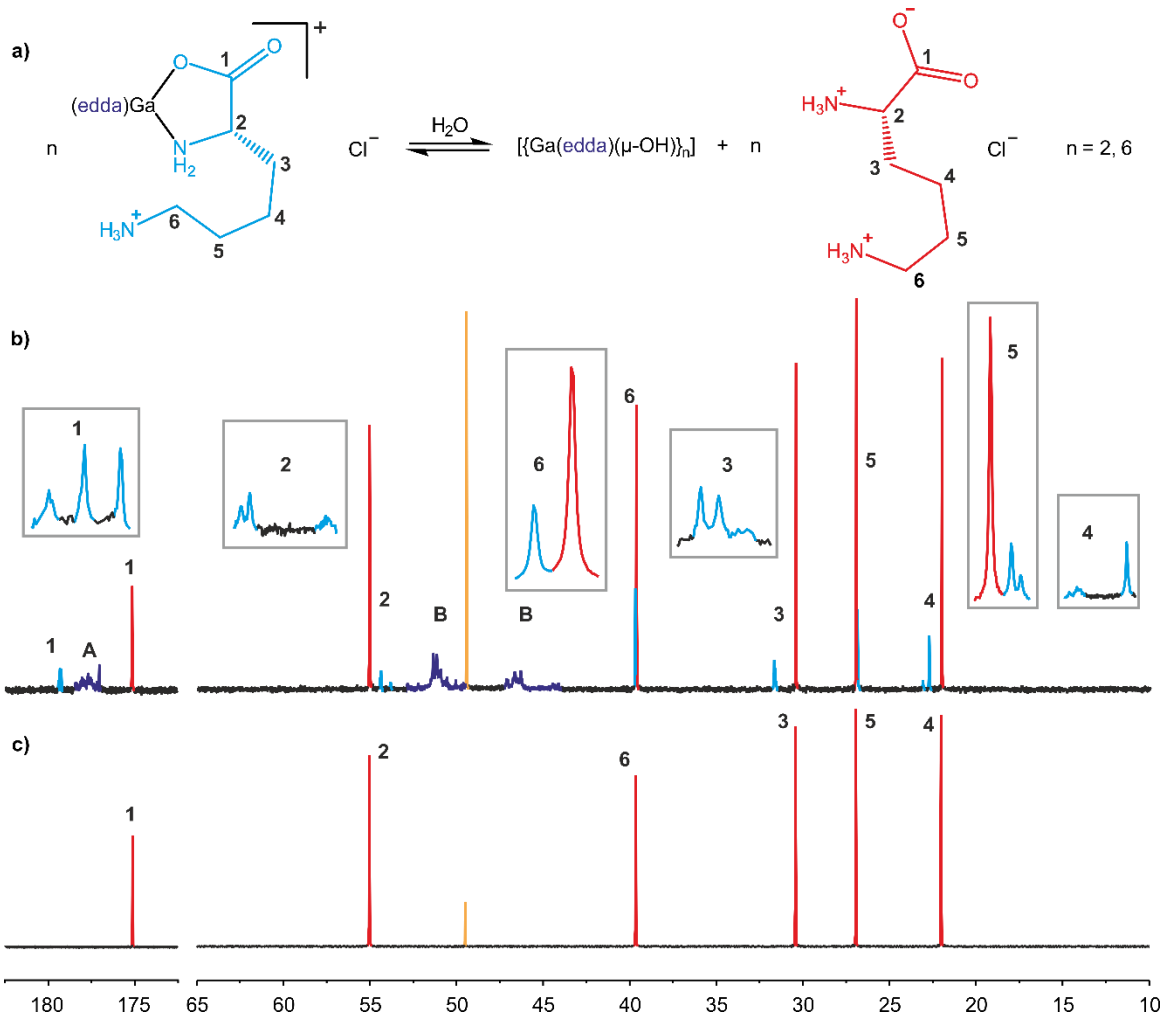


Figure 6.21: [Ga(edda)(Hlys)]Cl + 0.60 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(Hlys)]Cl + 0.60 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-lysine hydrochloride in D_2O*. Red: L-lysine, cyan: L-lysinato in $[Ga(edda)(Hlys)]^+$, blue (**A** and **B**): edda in $[Ga(edda)(Hlys)]^+$ and $[\{Ga(edda)(\mu\text{-}OH)\}_n]$ complexes, orange: MeOH. * One drop of MeOH was added for referencing.

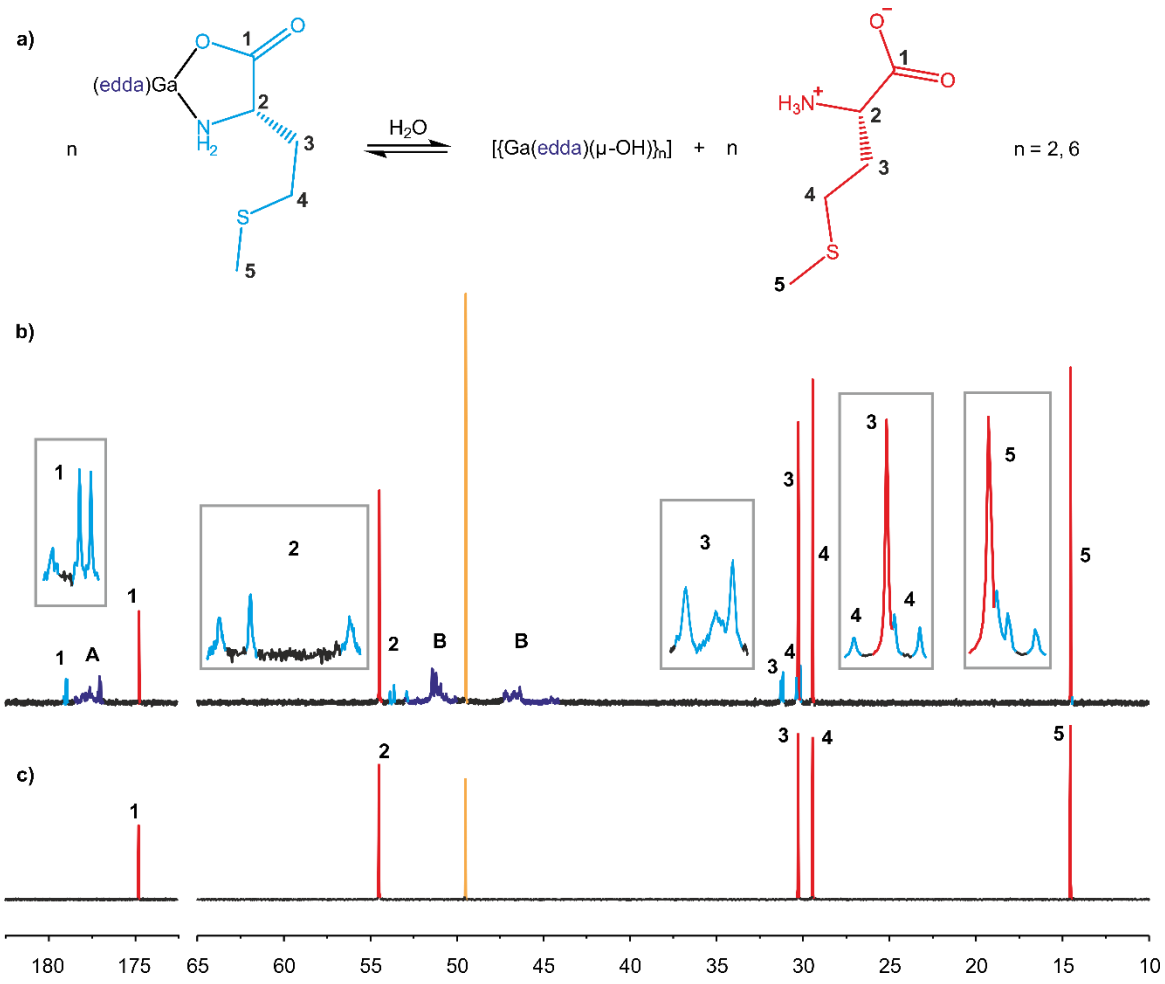


Figure 6.22: [Ga(edda)(met)] + 0.55 H_2O + 0.10 $Ga(OH)_3$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(met)] + 0.55 H_2O + 0.10 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-methionine in D_2O*. Red: L-methionine, cyan: L-methioninato in [Ga(edda)(met)], blue (**A** and **B**): edda in [Ga(edda)(met)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

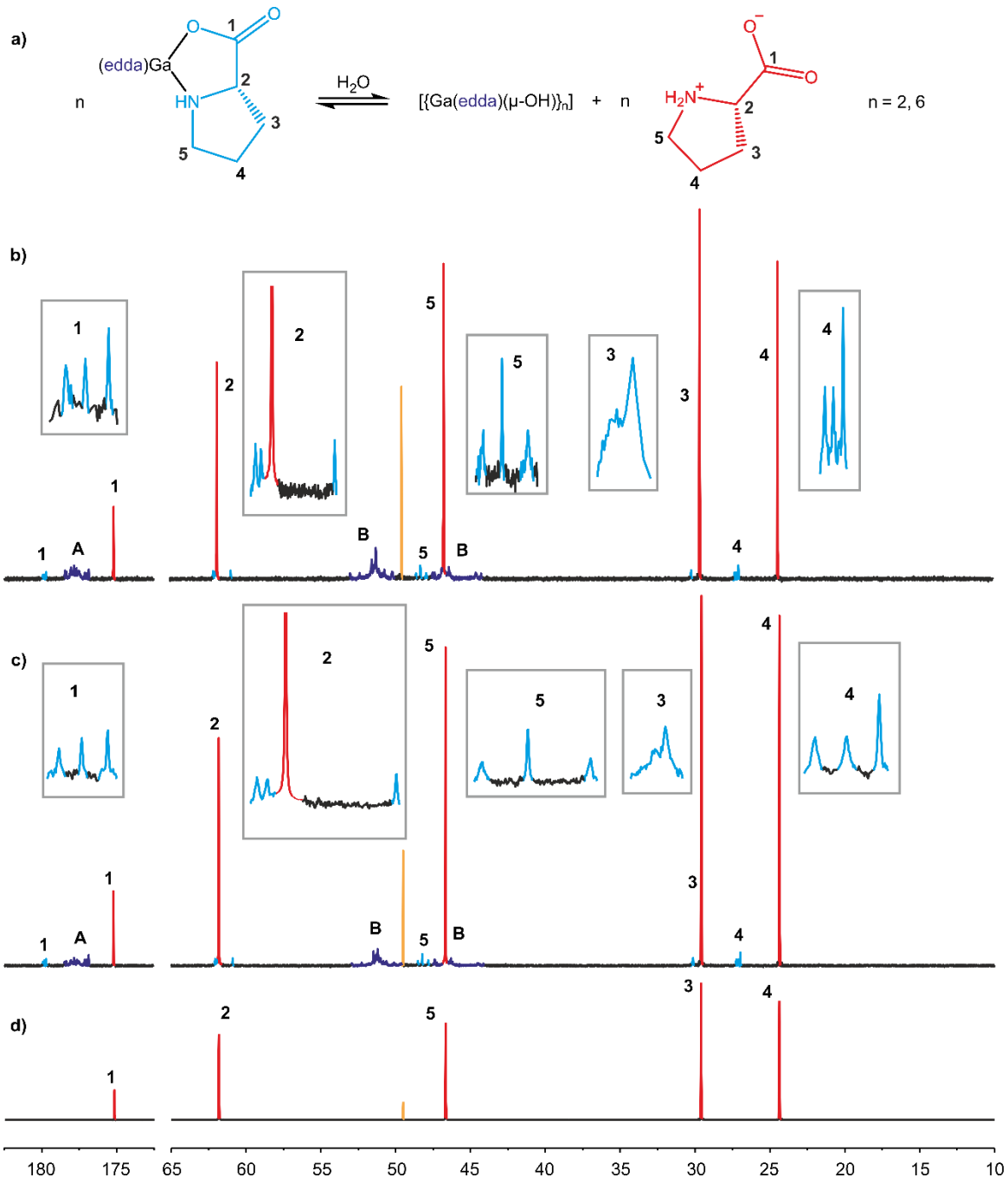


Figure 6.23: [Ga(edda)(pro) + 0.10 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(pro)] + 0.10 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(pro)] + 0.10 H_2O with 1.0 equ. of L-proline in D_2O*, d: $^{13}C\{^1H\}$ NMR spectrum of L-proline in D_2O*. Red: L-proline, cyan: L-prolinato in [Ga(edda)(pro)], blue (**A** and **B**): edda in [Ga(edda)(pro)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

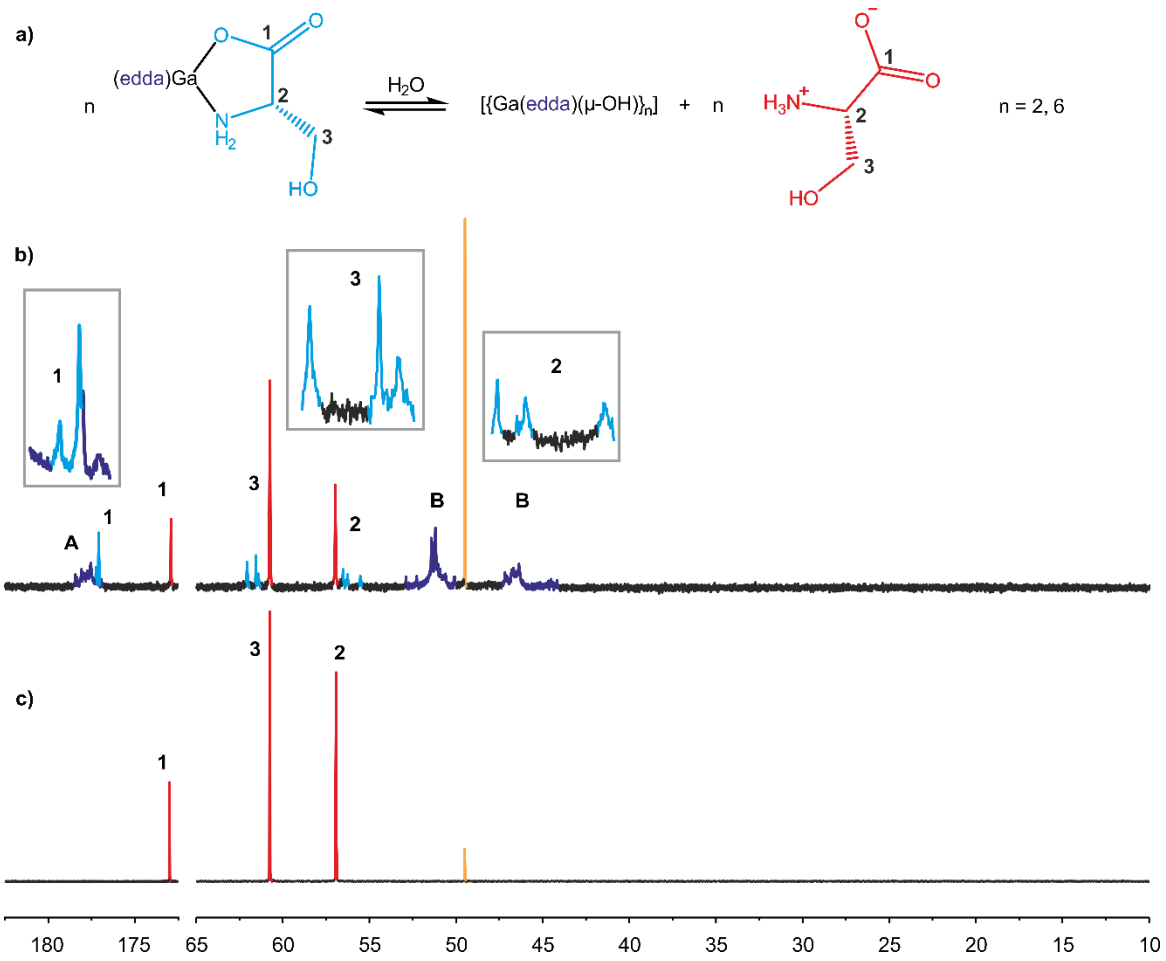


Figure 6.24: [Ga(edda)(ser)] + 1.55 H_2O + 0.10 $Ga(OH)_3$ in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(ser)] + 1.55 H_2O + 0.10 $Ga(OH)_3$ in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-serine in D_2O*. Red: L-serine, cyan: L-serinato in [Ga(edda)(ser)], blue (**A** and **B**): edda in [Ga(edda)(ser)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

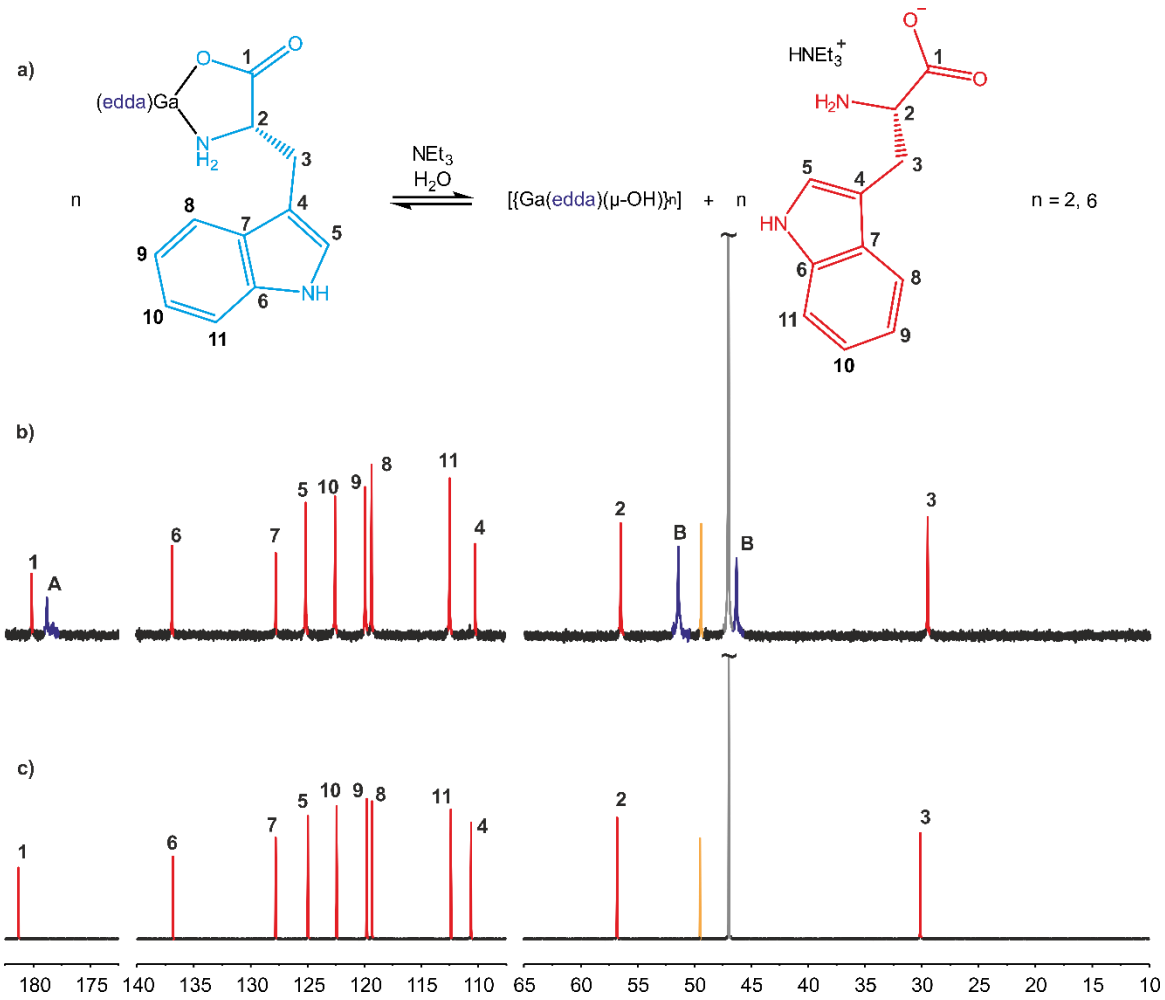


Figure 6.25: [Ga(edda)(trp)] + 1.50 H_2O in basic aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(trp)] + 1.50 H_2O in D_2O and triethylamine*, c: $^{13}C\{^1H\}$ NMR spectrum of L-tryptophan in D_2O and triethylamine*. Red: L-tryptophanate, blue (**A** and **B**): edda in [{Ga(edda)(μ-OH)}$_n$] complexes, grey: $HNEt_3^+$, orange: MeOH. * One drop of MeOH was added for referencing.

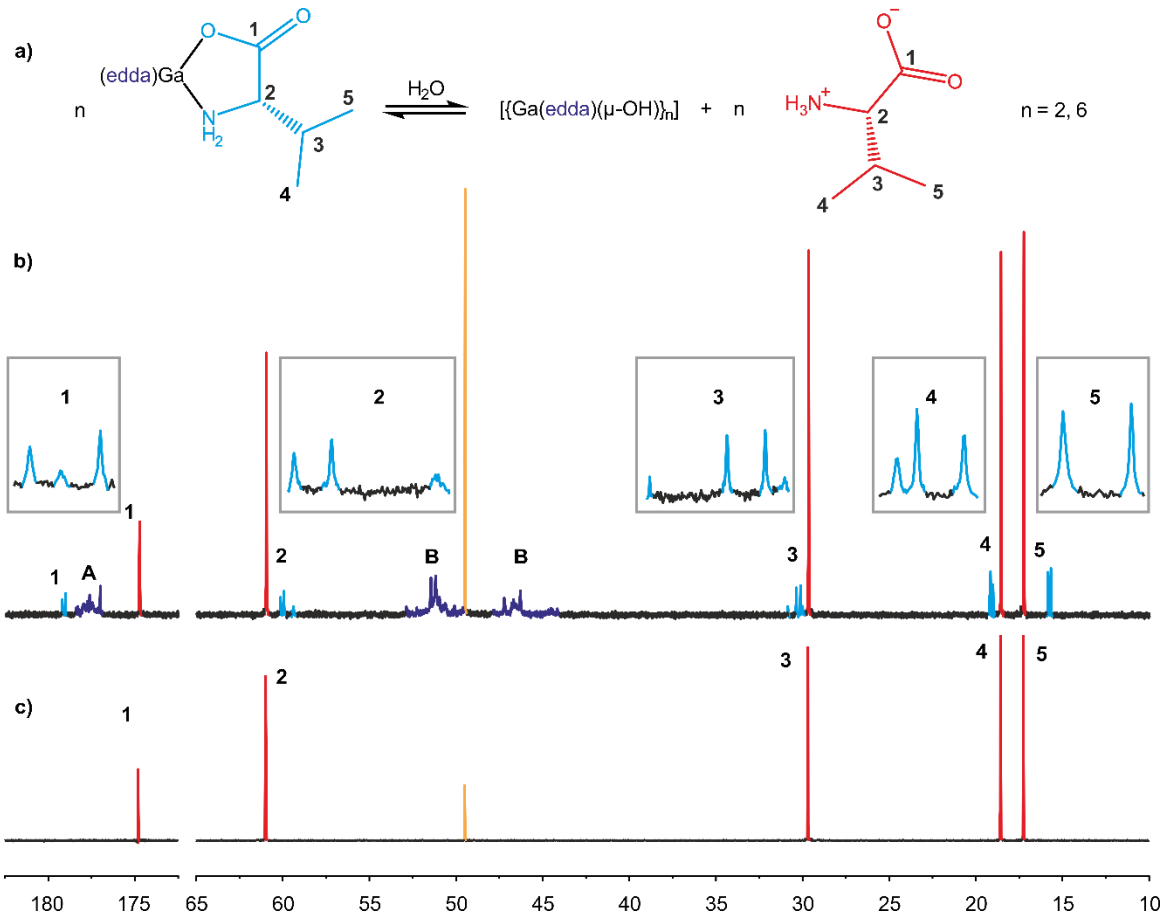


Figure 6.26: [Ga(edda)(val)] + 0.50 H_2O in aqueous solution (c = 0.25 mol L^{-1}). a: equilibrium reaction, b: $^{13}C\{^1H\}$ NMR spectrum of [Ga(edda)(val)] + 0.50 H_2O in D_2O*, c: $^{13}C\{^1H\}$ NMR spectrum of L-valine in D_2O*. Red: L-valine, cyan: L-valinato in [Ga(edda)(val)], blue (**A** and **B**): edda in [Ga(edda)(val)] and [{Ga(edda)(μ-OH)}$_n$] complexes, orange: MeOH. * One drop of MeOH was added for referencing.

6.2 Packing diagrams of crystal structures

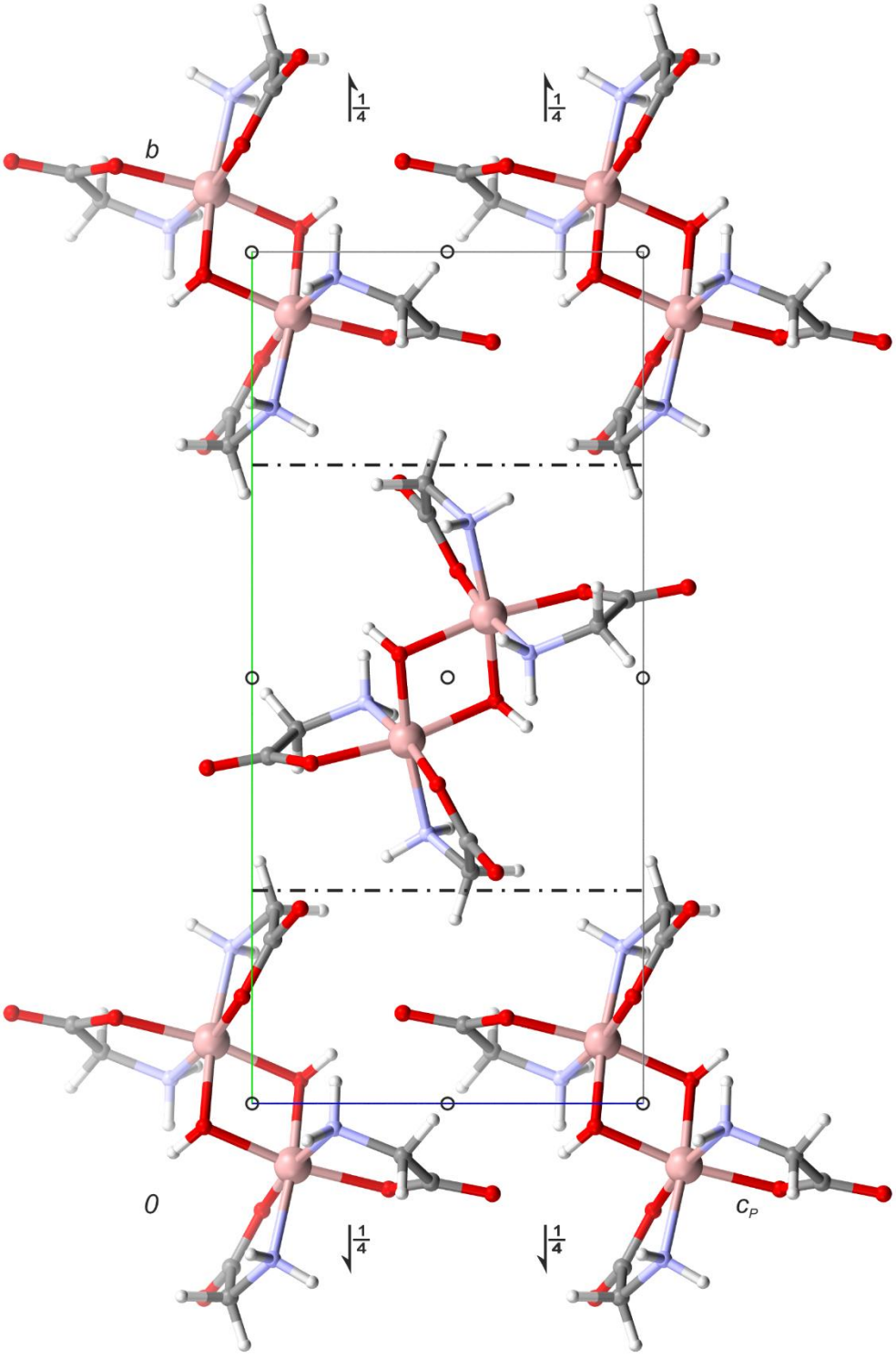


Figure 6.27: Packing diagram of **1a** (uv174) in the monoclinic space group $P2_1/n$ with view along [100]. The symmetry elements of the space group $P2_1/n$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

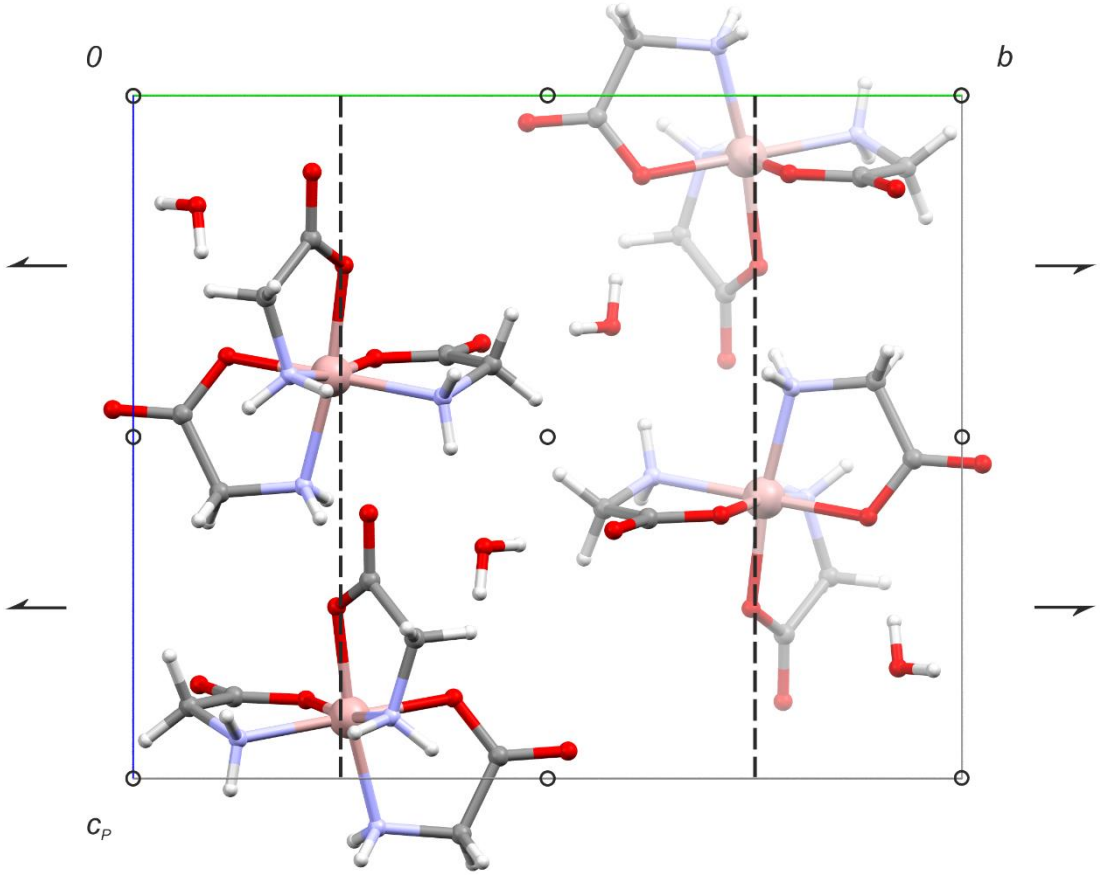


Figure 6.28: Packing diagram of **1b**·H_2O (wv552) in the monoclinic space group $P2_1/c$ with view along [100]. The symmetry elements of the space group $P2_1/c$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

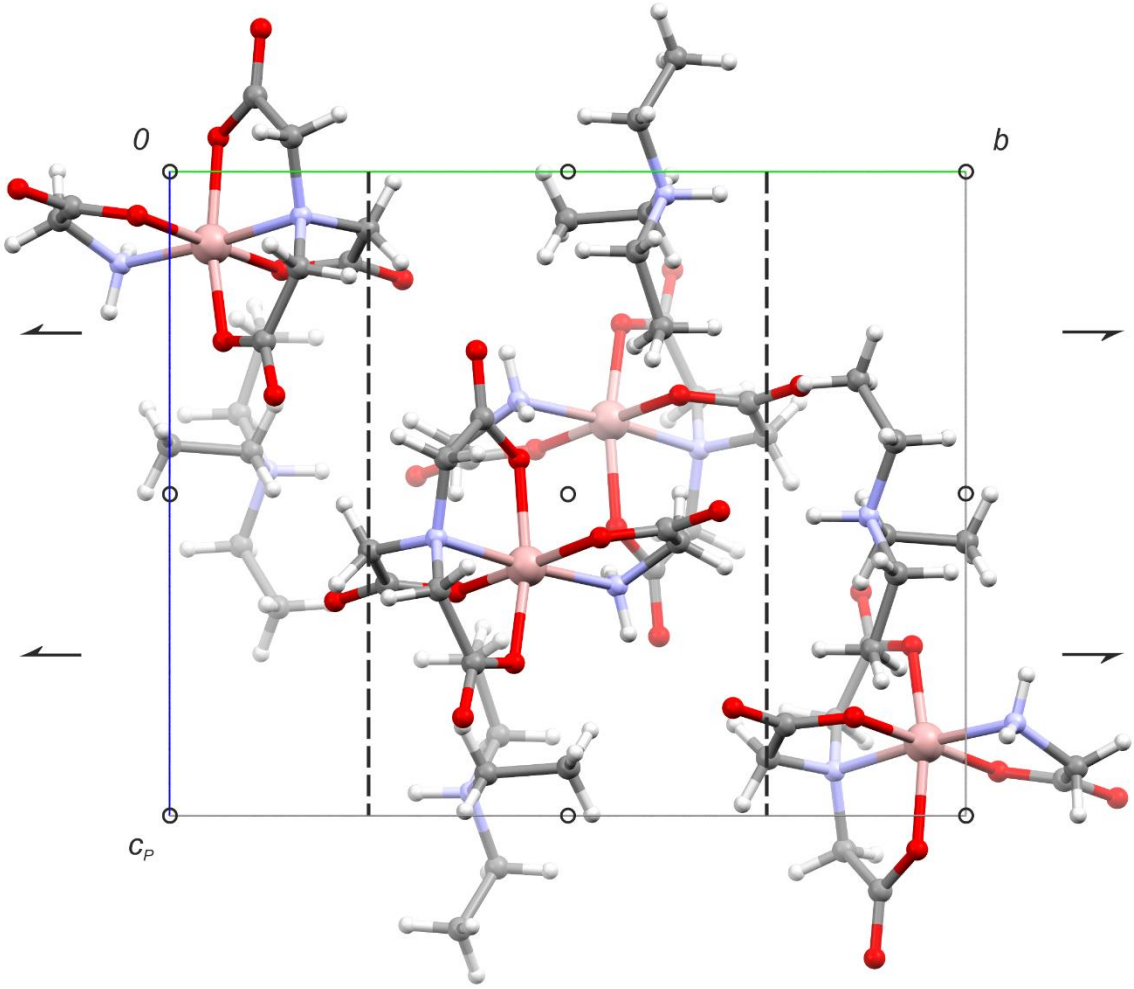


Figure 6.29: Packing diagram of ($HNEt_3$)**2c** (uo063) in the monoclinic space group $P2_1/c$ with view along [100]. The symmetry elements of the space group $P2_1/c$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

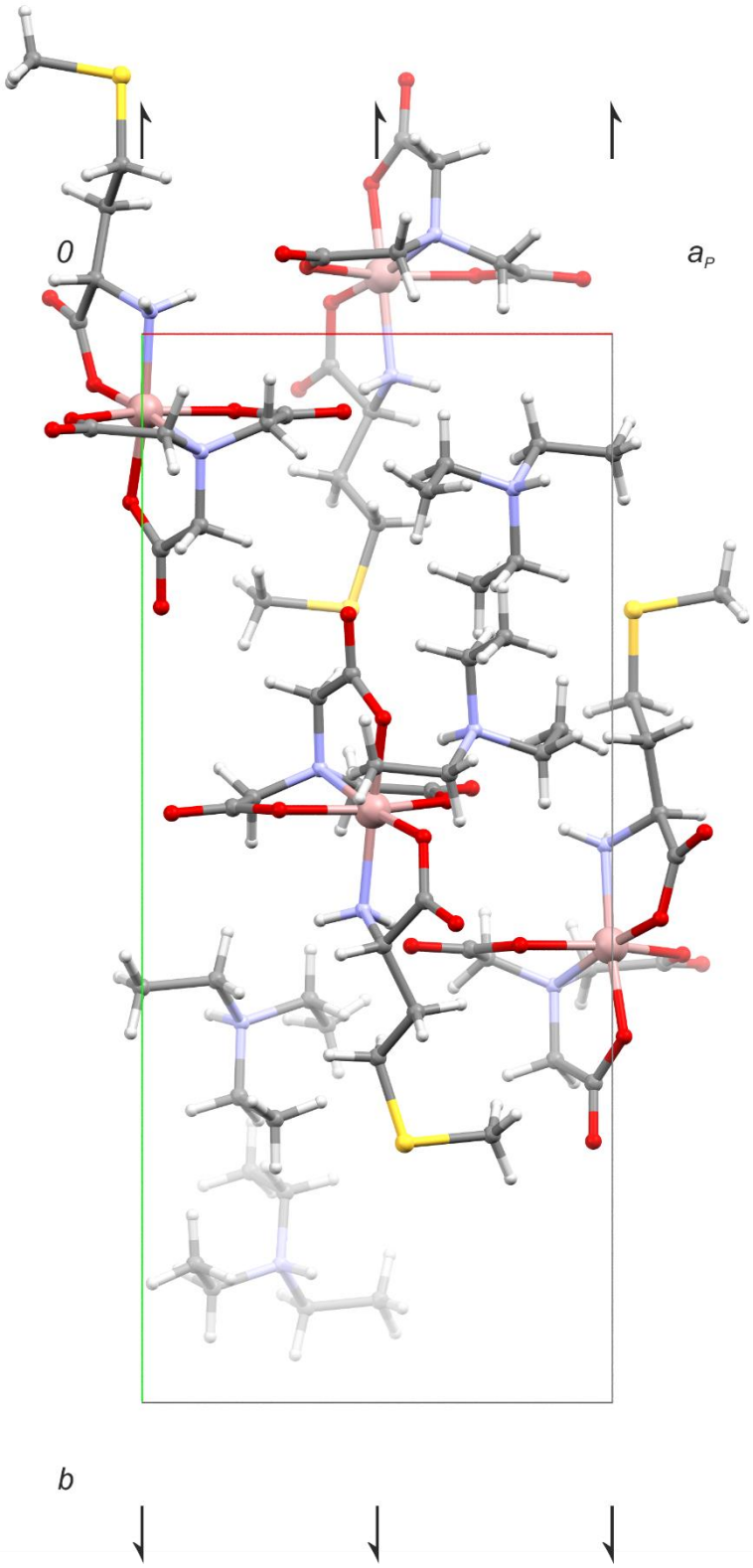


Figure 6.30: Packing diagram of ($HNEt_3$)**2f** (uv281) in the monoclinic space group $P2_1$ with view along [001]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red), gallium (puce) and sulphur (yellow).

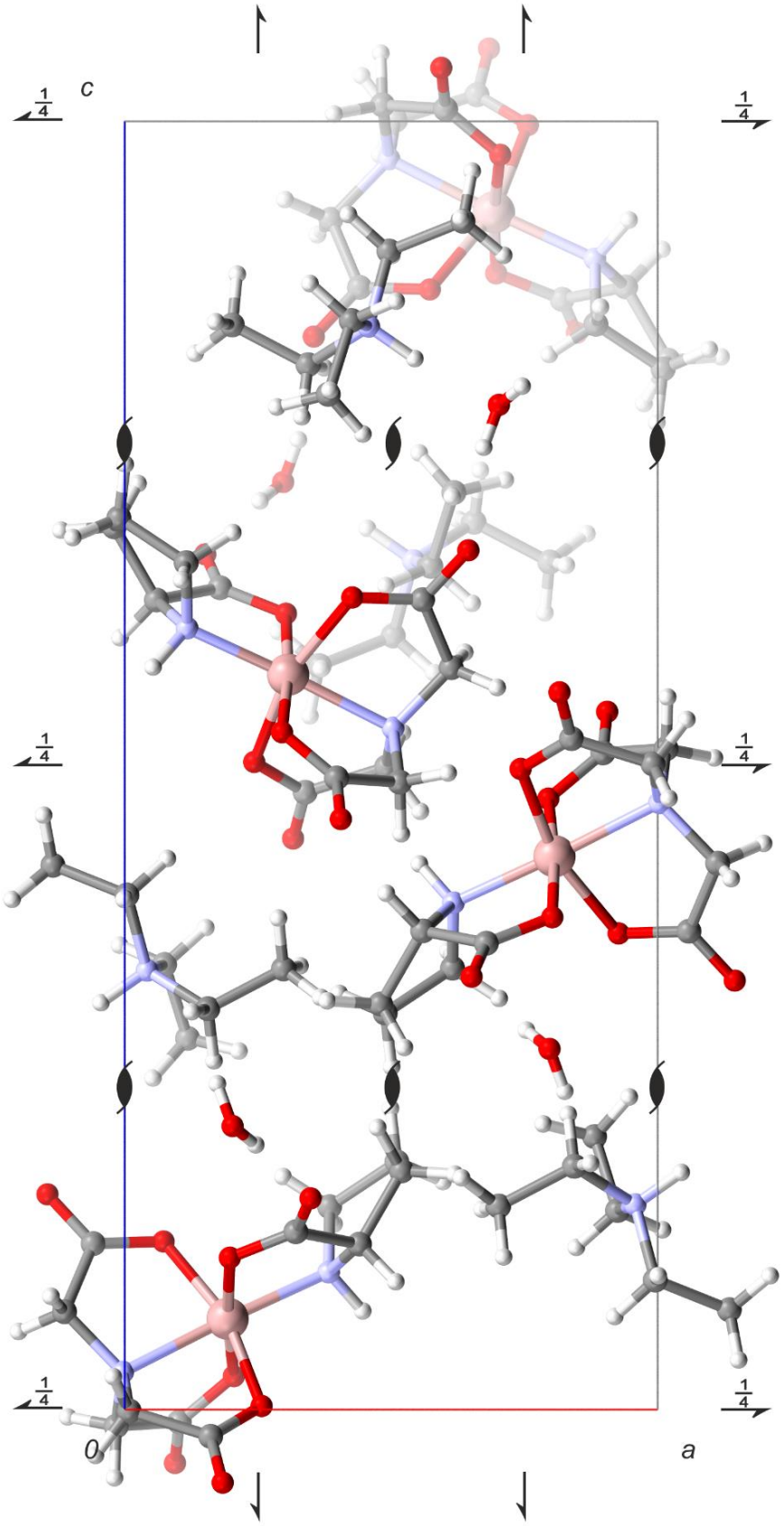


Figure 6.31: Packing diagram of (HNEt$_3$)**2g**·H$_2$O (vv202) in the orthorhombic space group $P2_12_12_1$ with view along [010]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

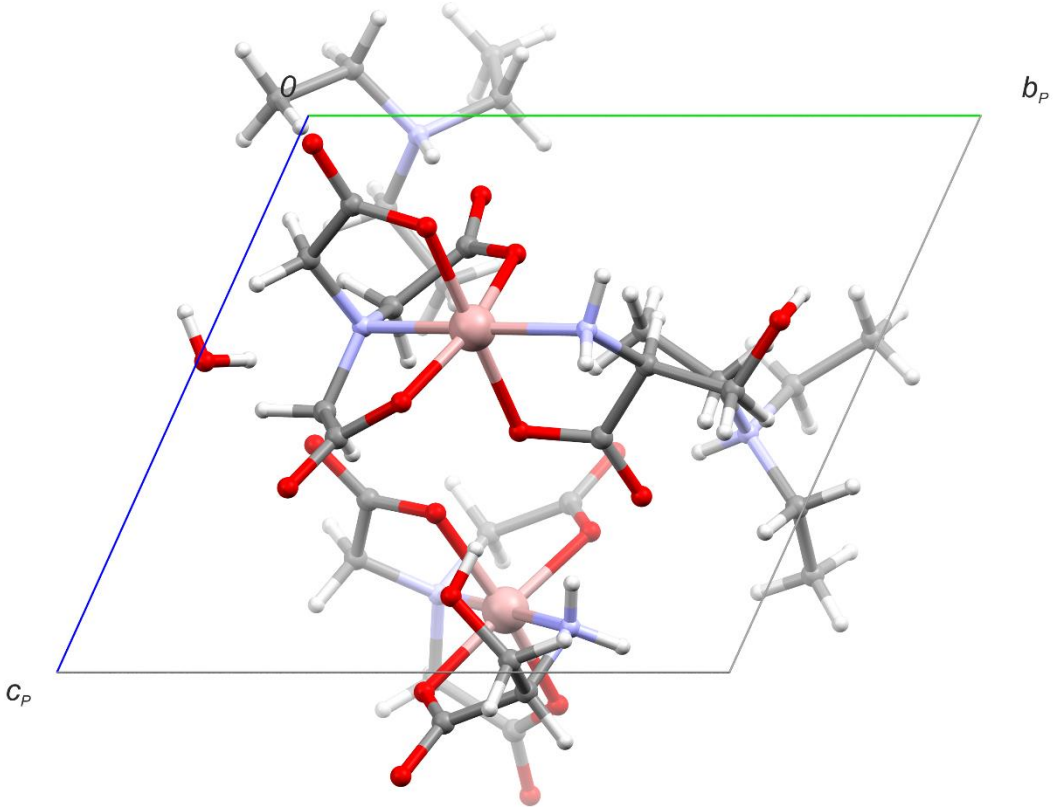


Figure 6.32: Packing diagram of (HNEt$_3$)**2h**·0.14H$_2$O (uv170) in the triclinic space group *P*1 with view along [100]. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

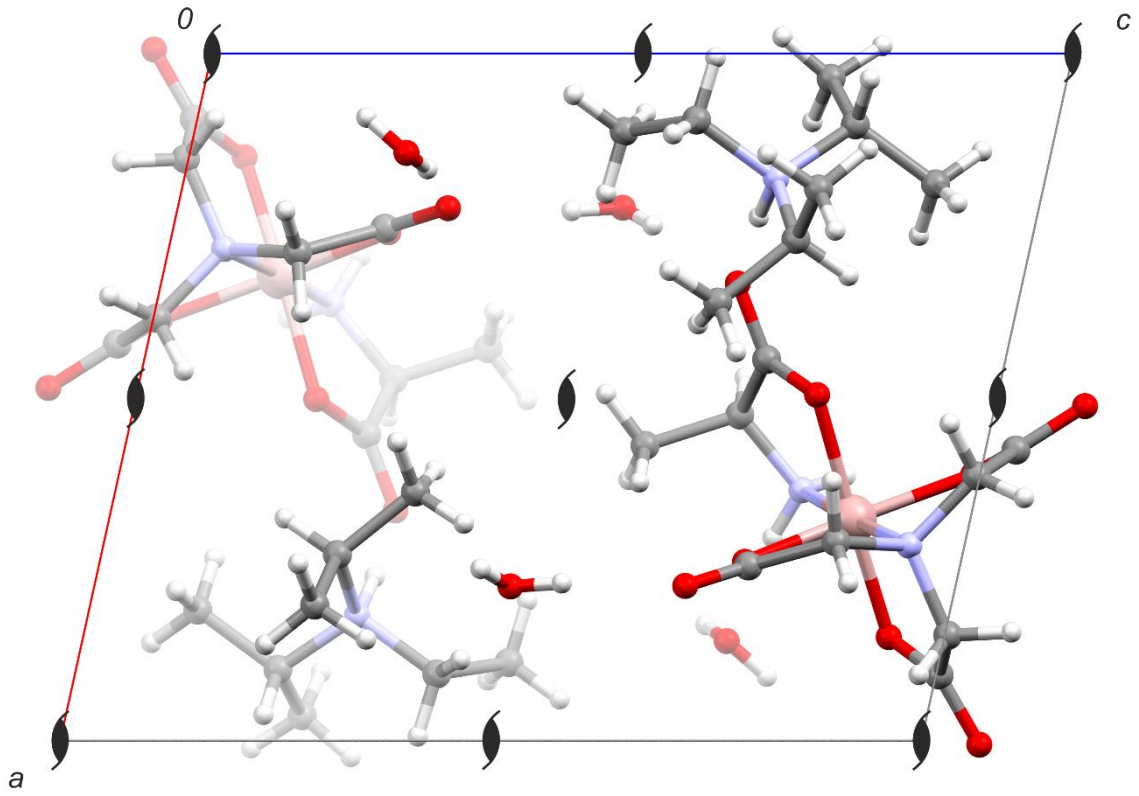


Figure 6.33: Packing diagram of (HDIPEA)**2a**·2H_2O (vv373) in the monoclinic space group $P2_1$ with view along [010]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

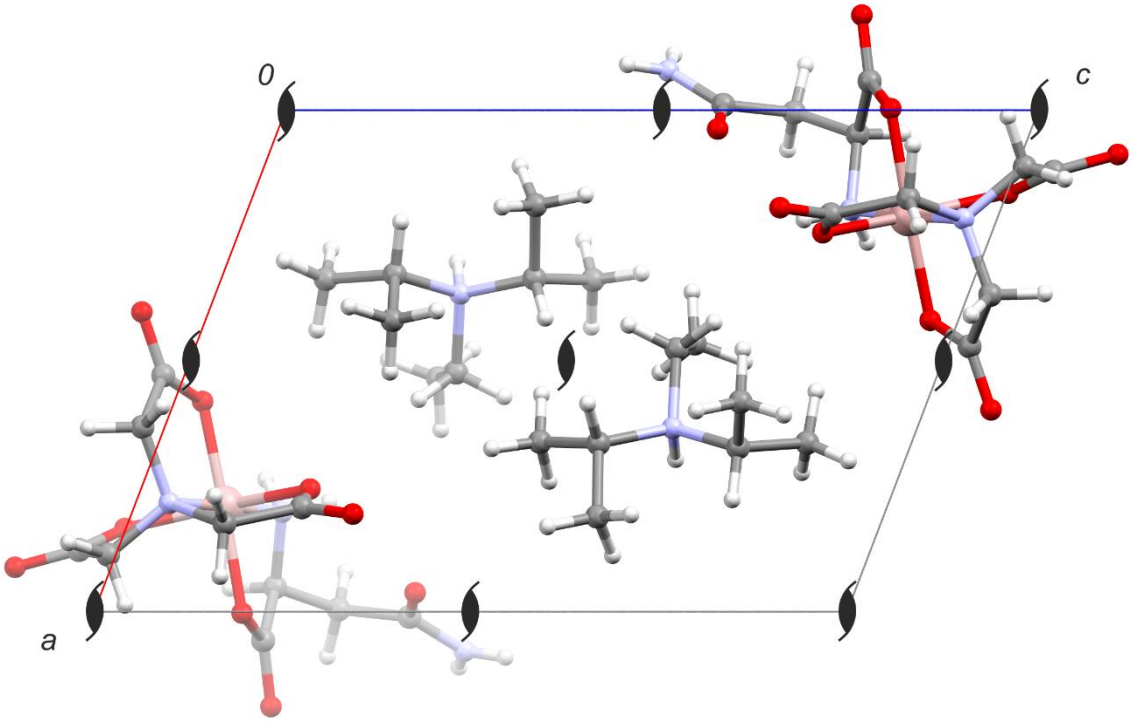


Figure 6.34: Packing diagram of (HDIPEA)**2b** (vv753) in the monoclinic space group $P2_1$ with view along [010]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

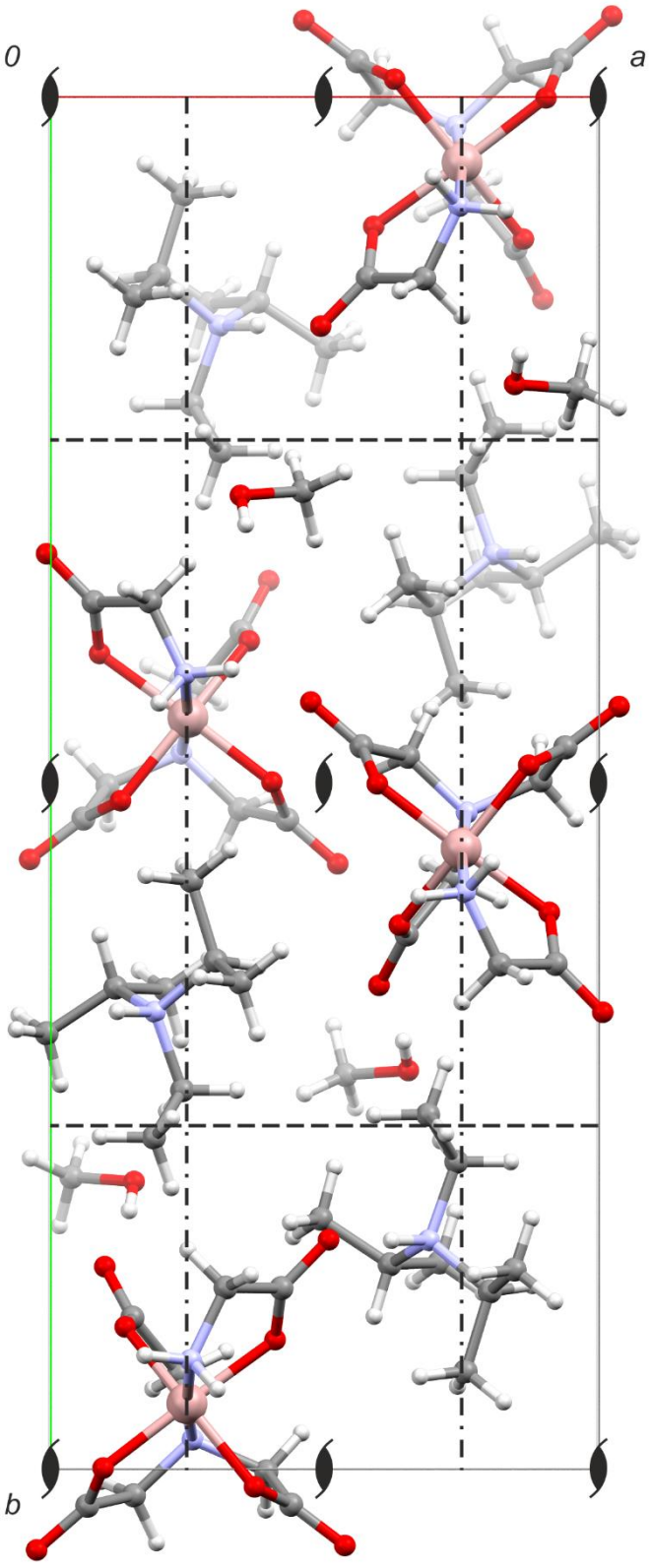


Figure 6.35: Packing diagram of (HDIPEA)**2c**·MeOH (uv716) in the orthorhombic space group *Pna*2_1 with view along [001]. The symmetry elements of the space group *Pna*2_1 are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

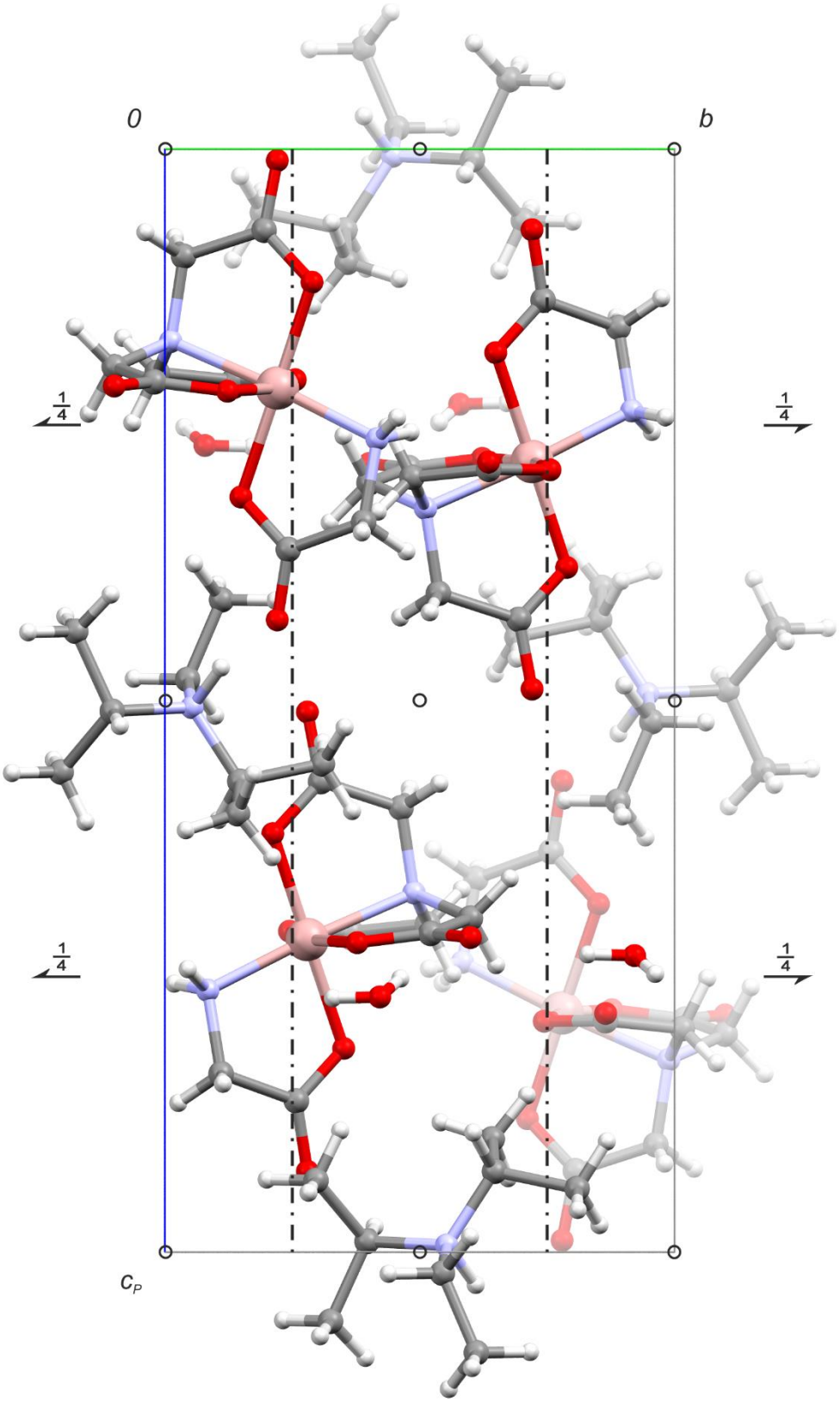


Figure 6.36: Packing diagram of (HDIPEA)**2c**·H_2O (wv334) in the monoclinic space group $P2_1/n$ with view along [100]. The symmetry elements of the space group $P2_1/n$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

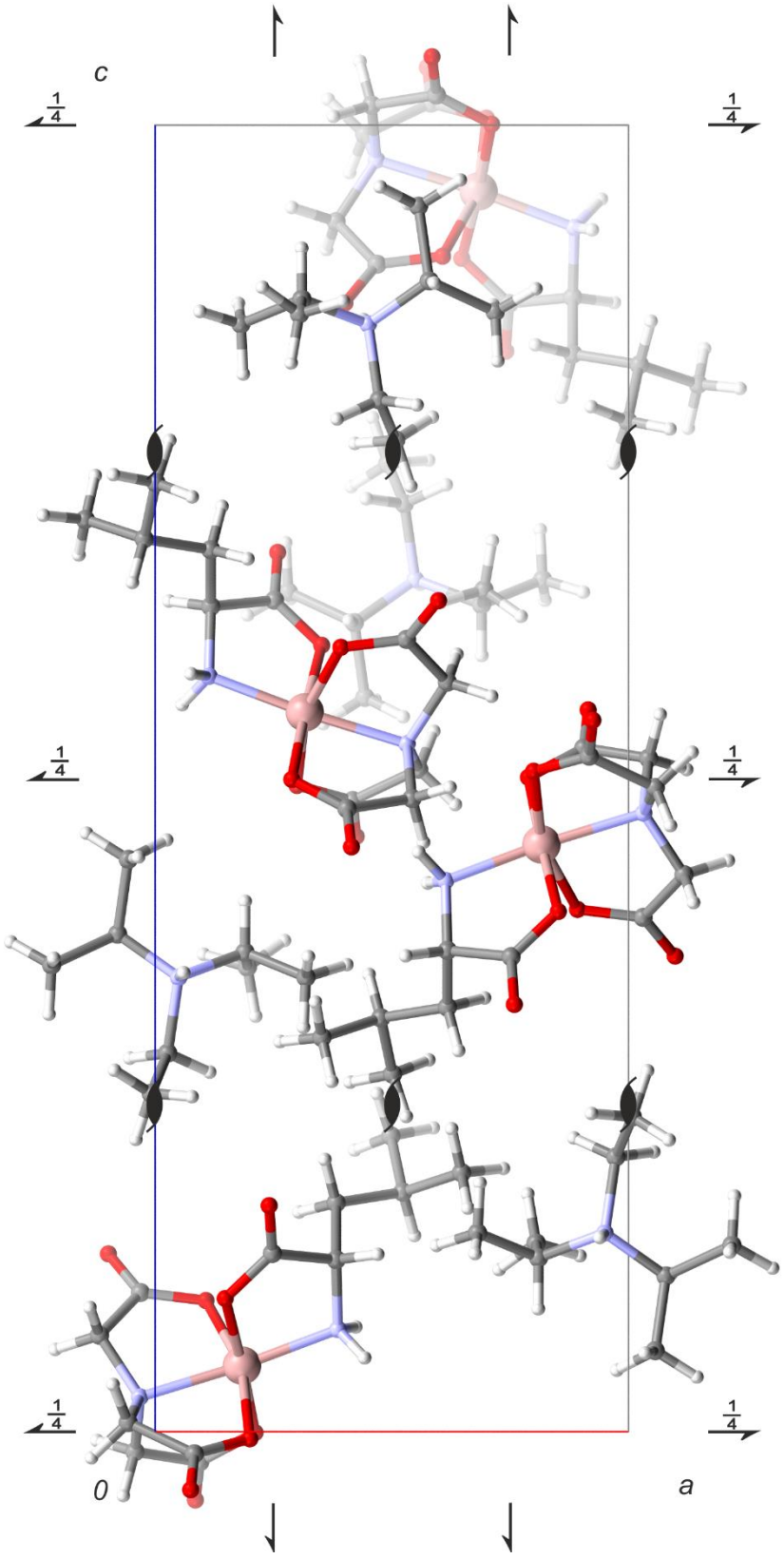


Figure 6.37: Packing diagram of (HDIPEA)**2d** (wo068) in the orthorhombic space group $P2_12_12_1$ with view along [010]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

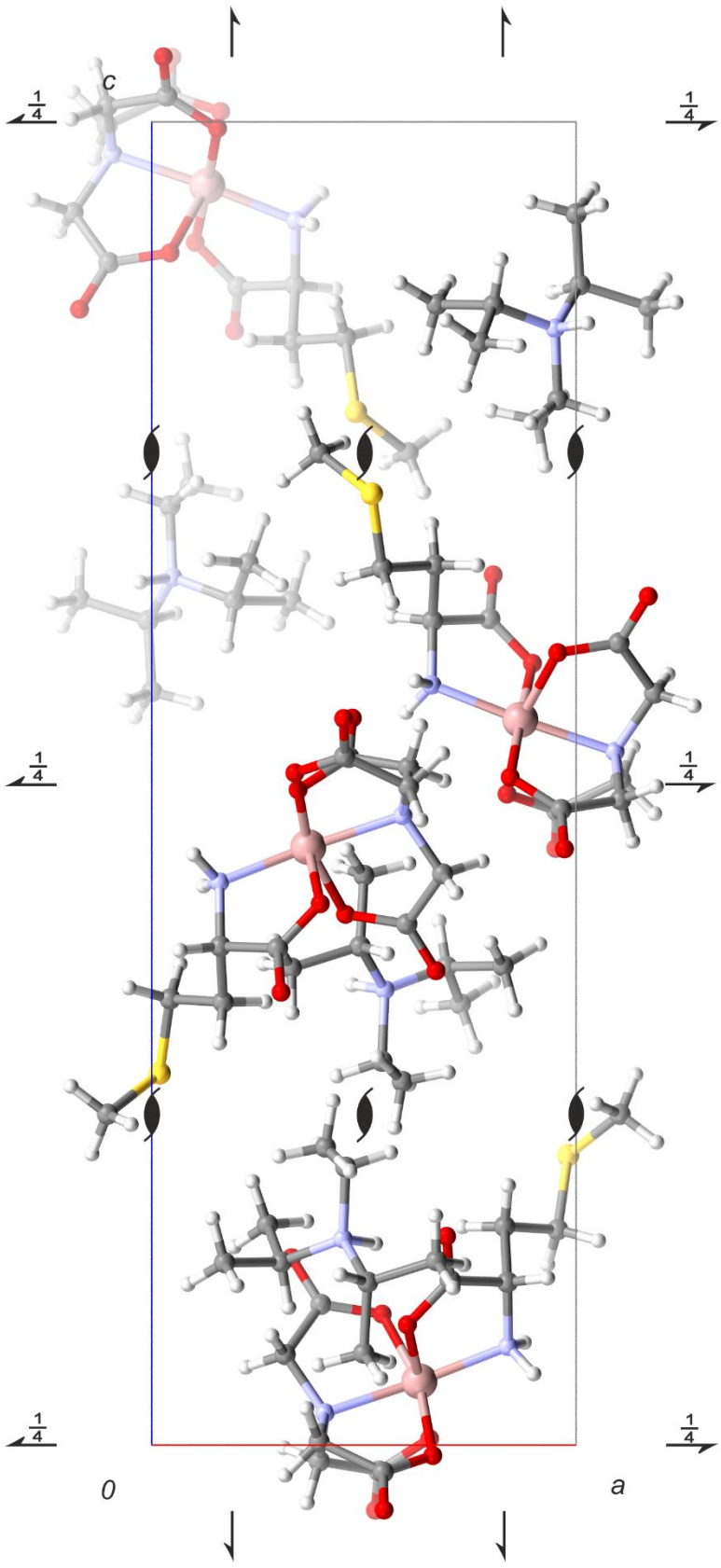


Figure 6.38: Packing diagram of (HDIPEA)**2e** (vv362) in the orthorhombic space group $P2_12_12_1$ with view along [010]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red), gallium (puce) and sulphur (yellow).

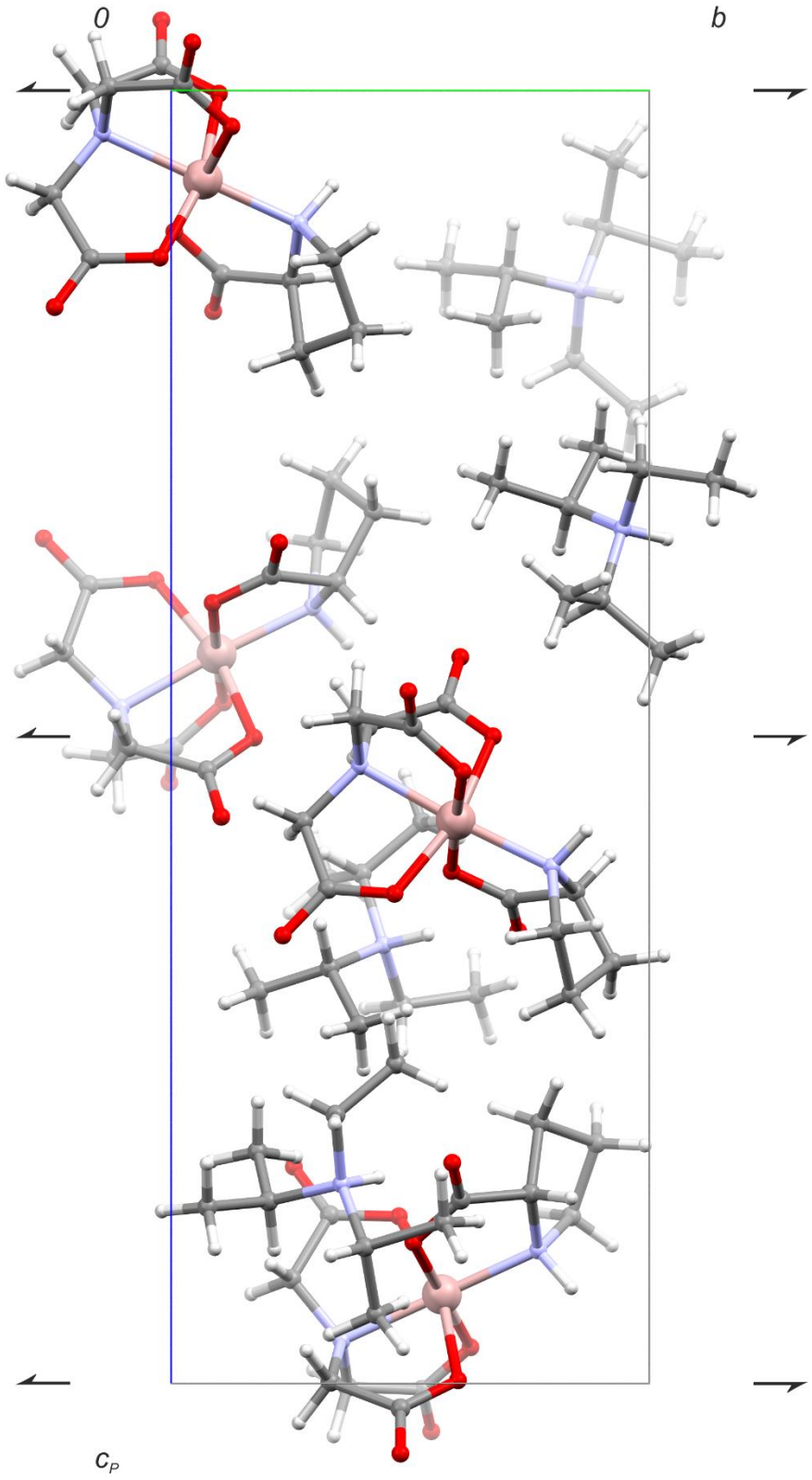


Figure 6.39: Packing diagram of (HDIPEA)**2g** (vv128) in the monoclinic space group $P2_1$ with view along [100]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

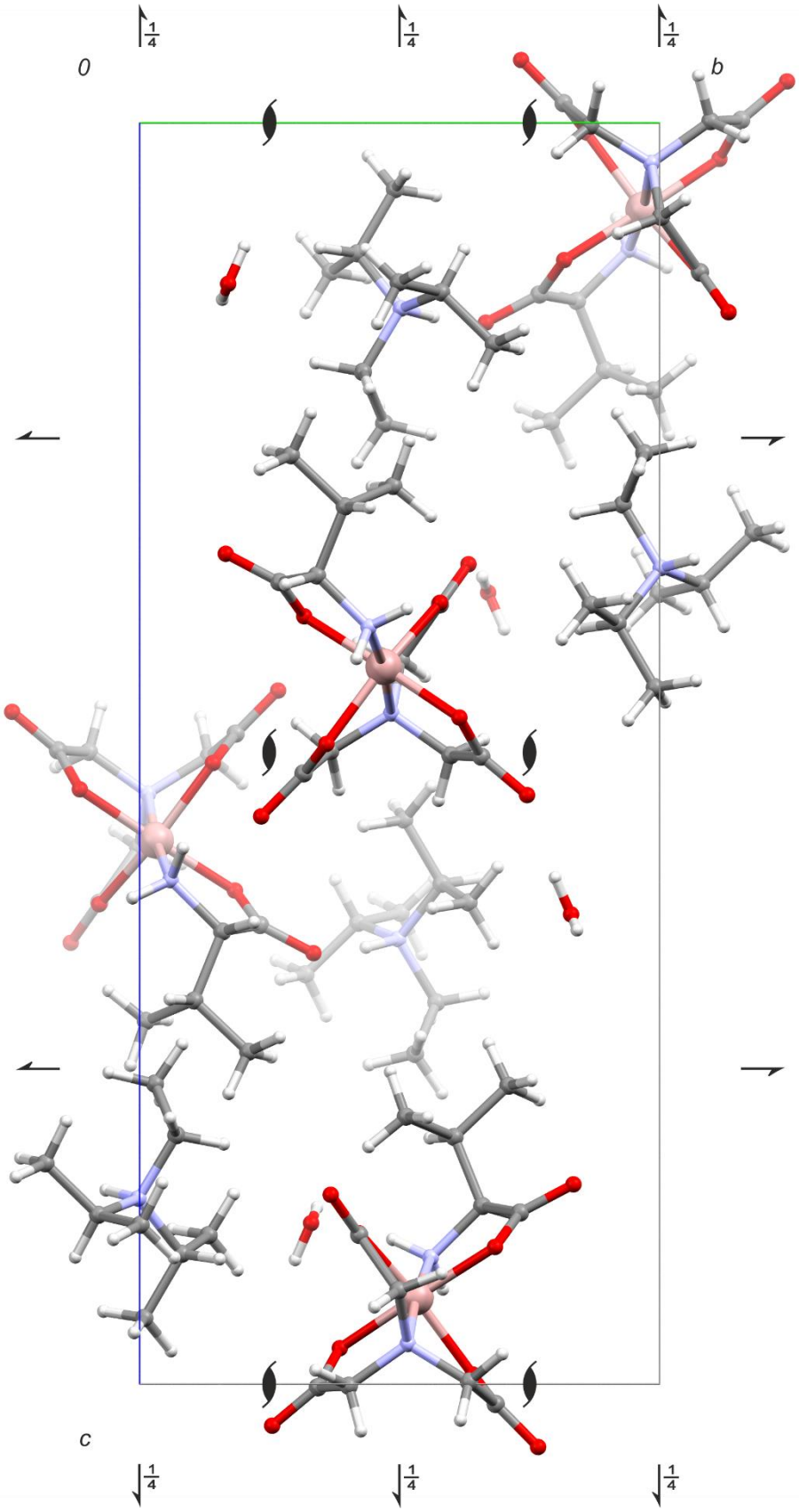


Figure 6.40: Packing diagram of (HDIPEA)**2i**·H_2O (wv547) in the orthorhombic space group $P2_12_12_1$ with view along [100]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

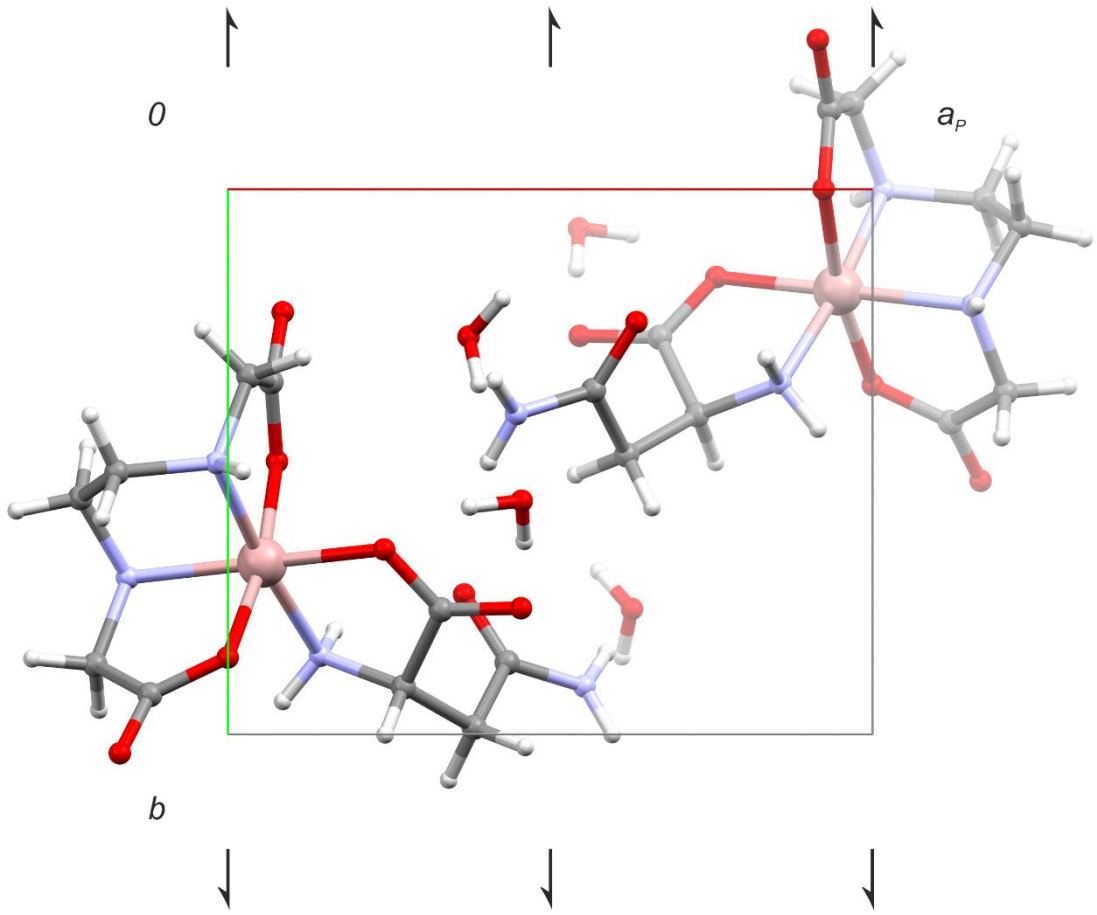


Figure 6.41: Packing diagram of **3a**·2H_2O (wv356) in the monoclinic space group $P2_1$ with view along [001]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

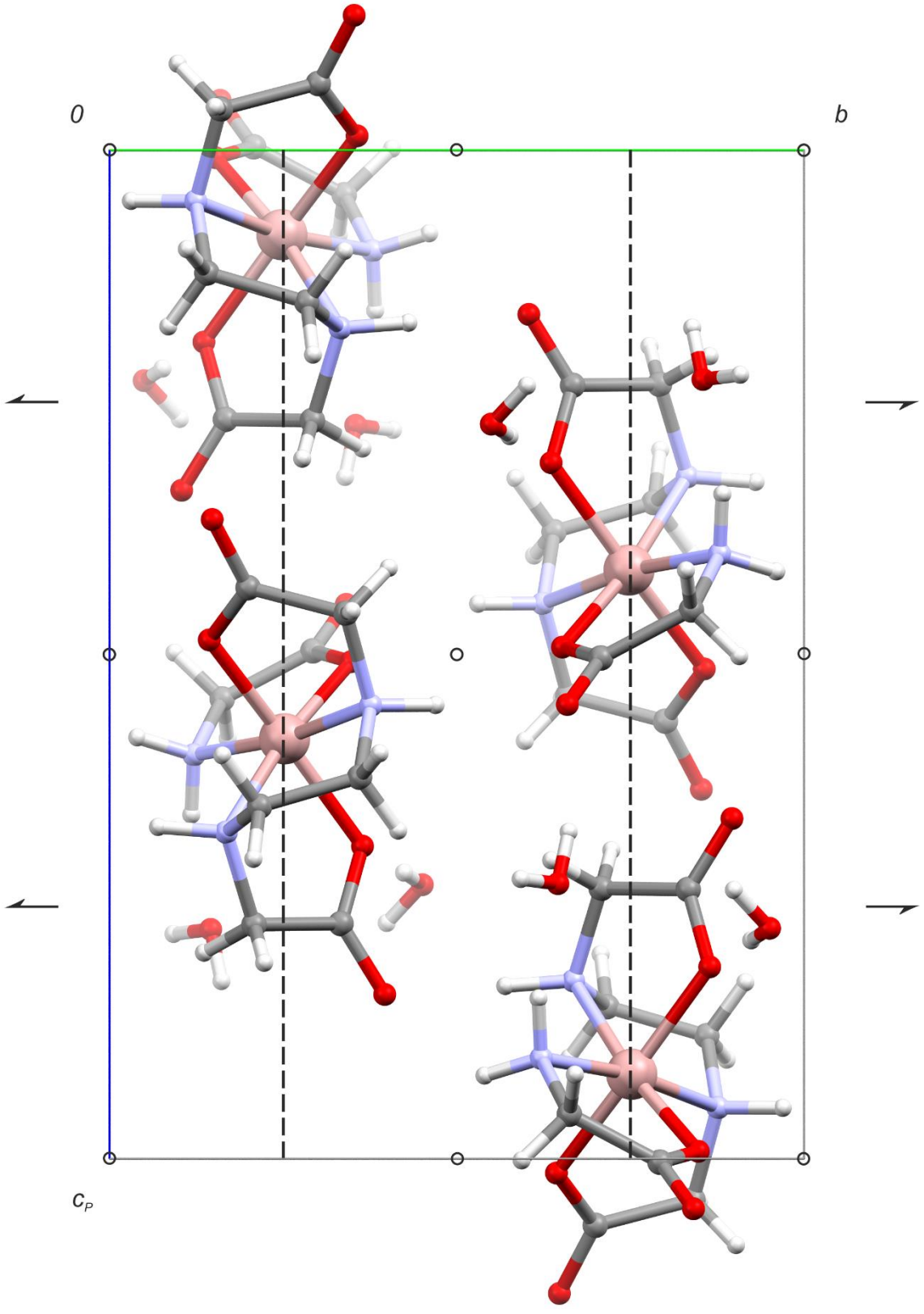


Figure 6.42: Packing diagram of **3b**·2H_2O (uv502) in the monoclinic space group $P2_1/c$ with view along [100]. The symmetry elements of the space group $P2_1/c$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

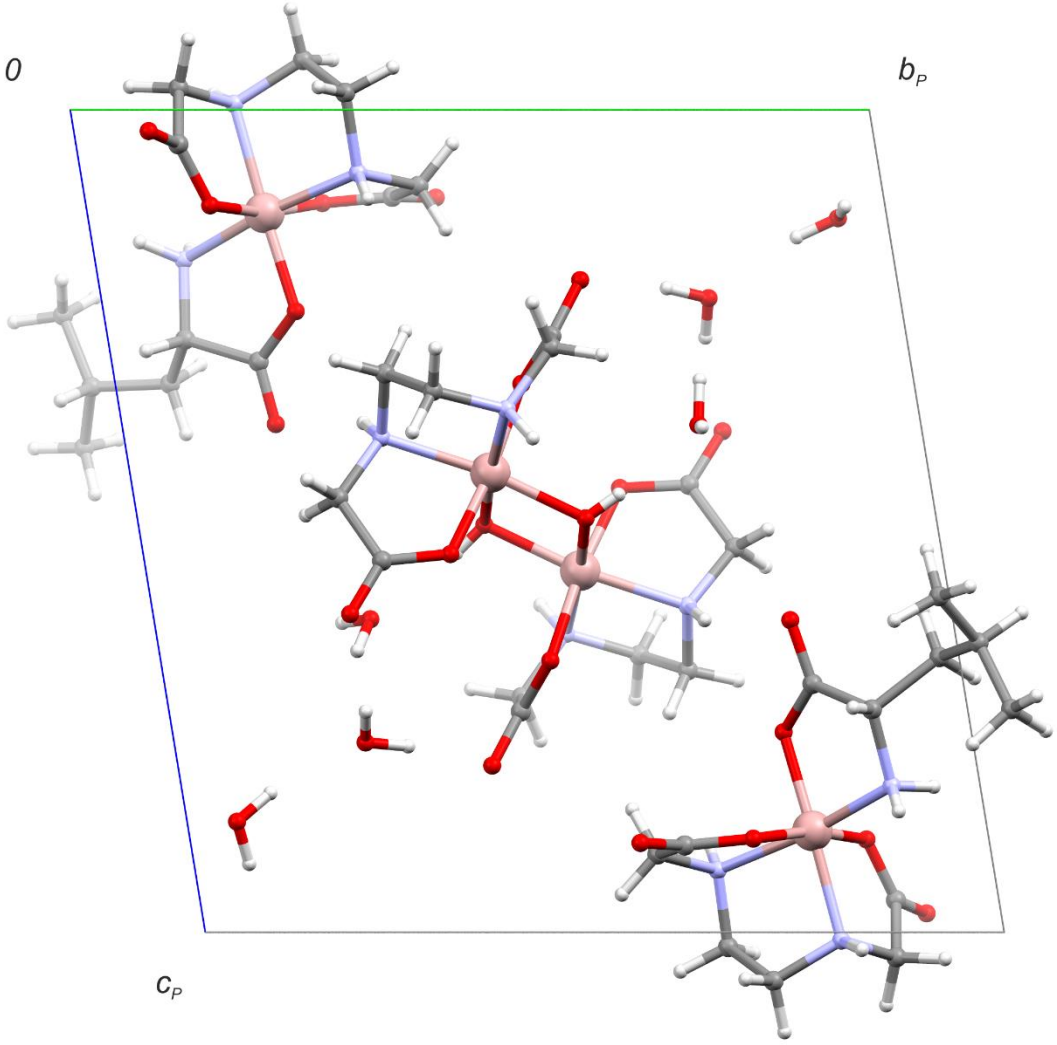


Figure 6.43: Packing diagram of **3c**·**3d**·**3i**·6H_2O (vv062) in the triclinic space group *P*1 with view along [100]. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

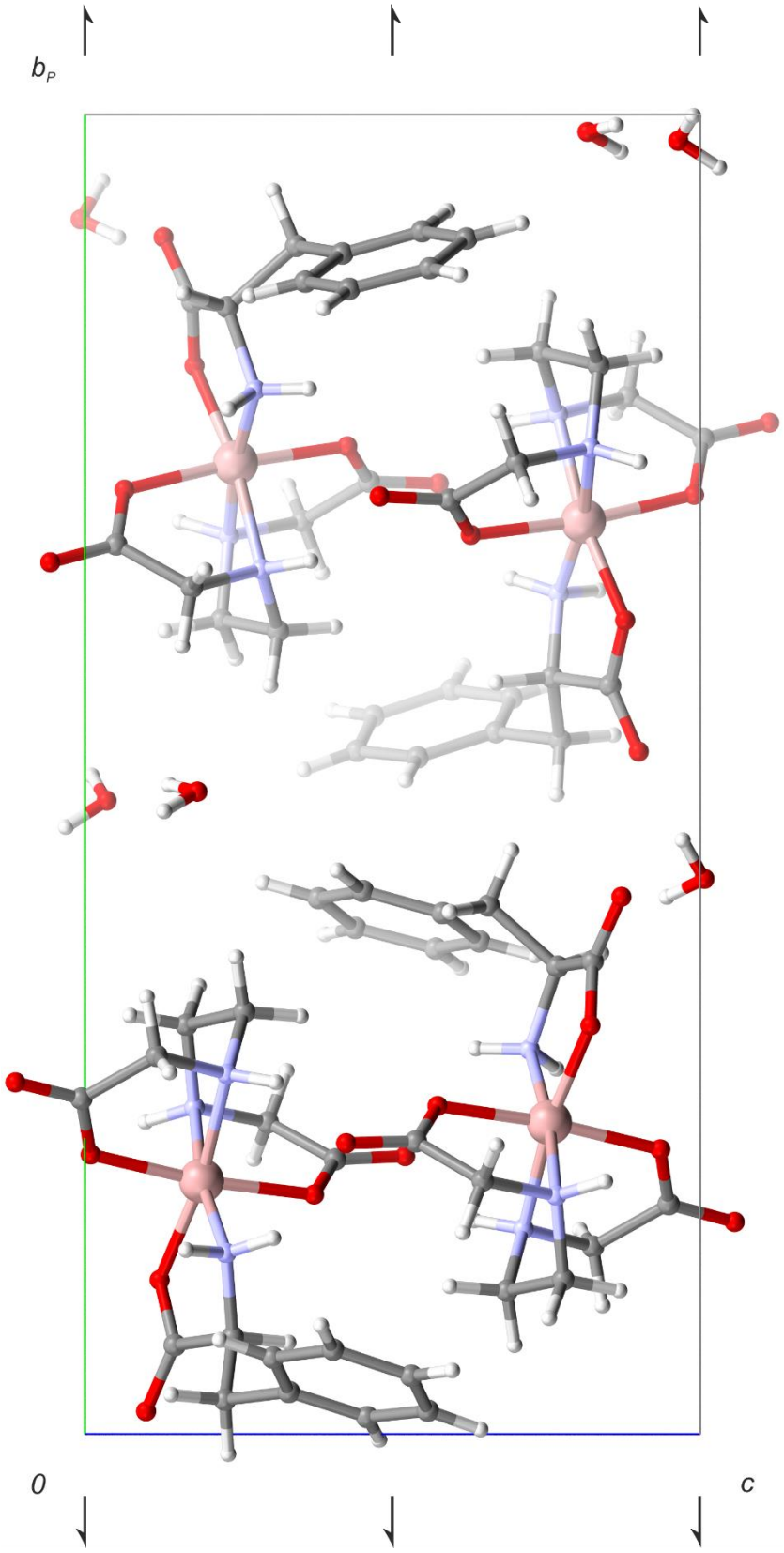


Figure 6.44: Packing diagram of **3e**·**3f**·3H_2O (uv537) in the monoclinic space group $P2_1$ with view along [100]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

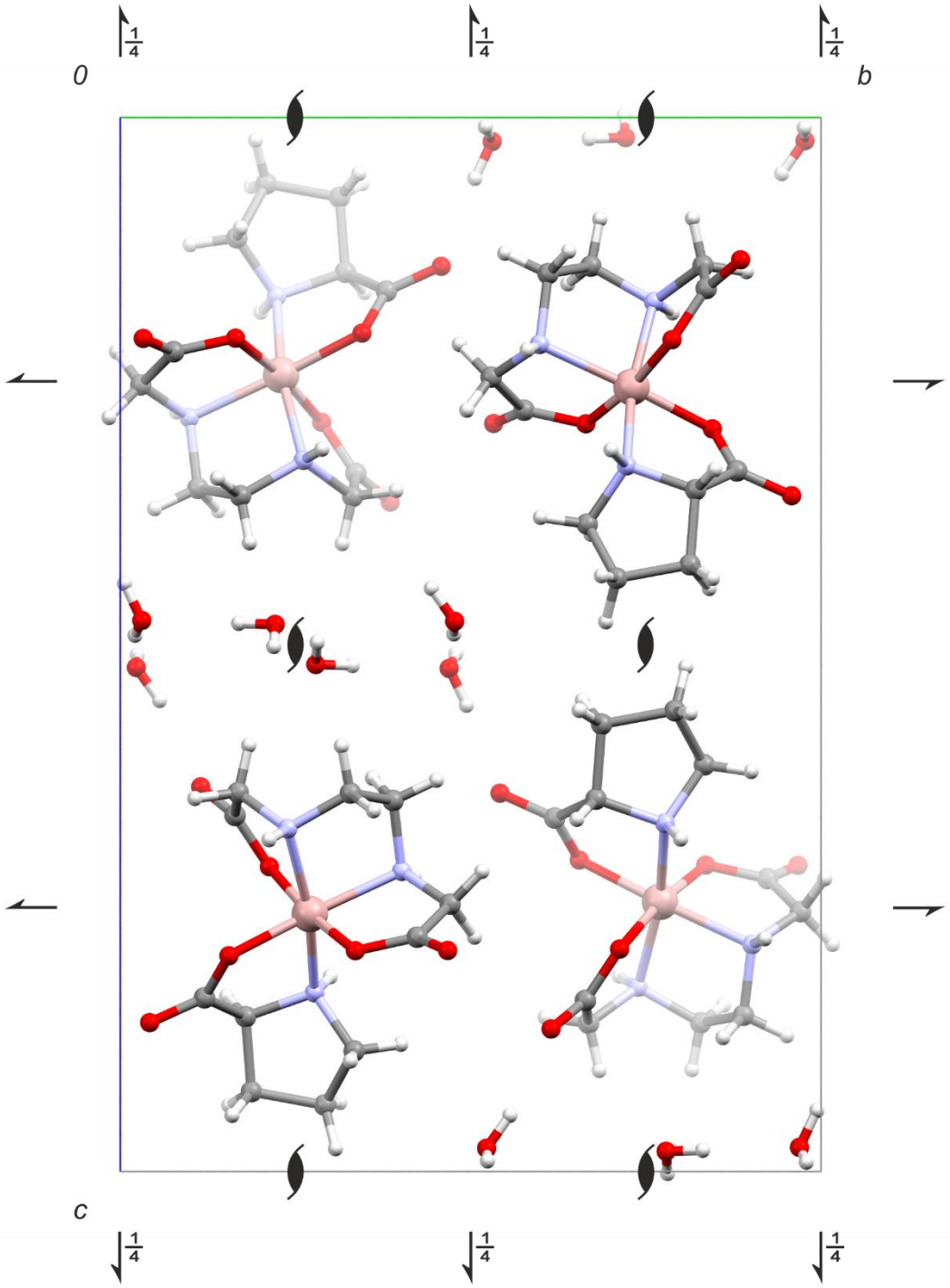


Figure 6.45: Packing diagram of **3g**·3H_2O (uo103) in the orthorhombic space group $P2_12_12_1$ with view along [100]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

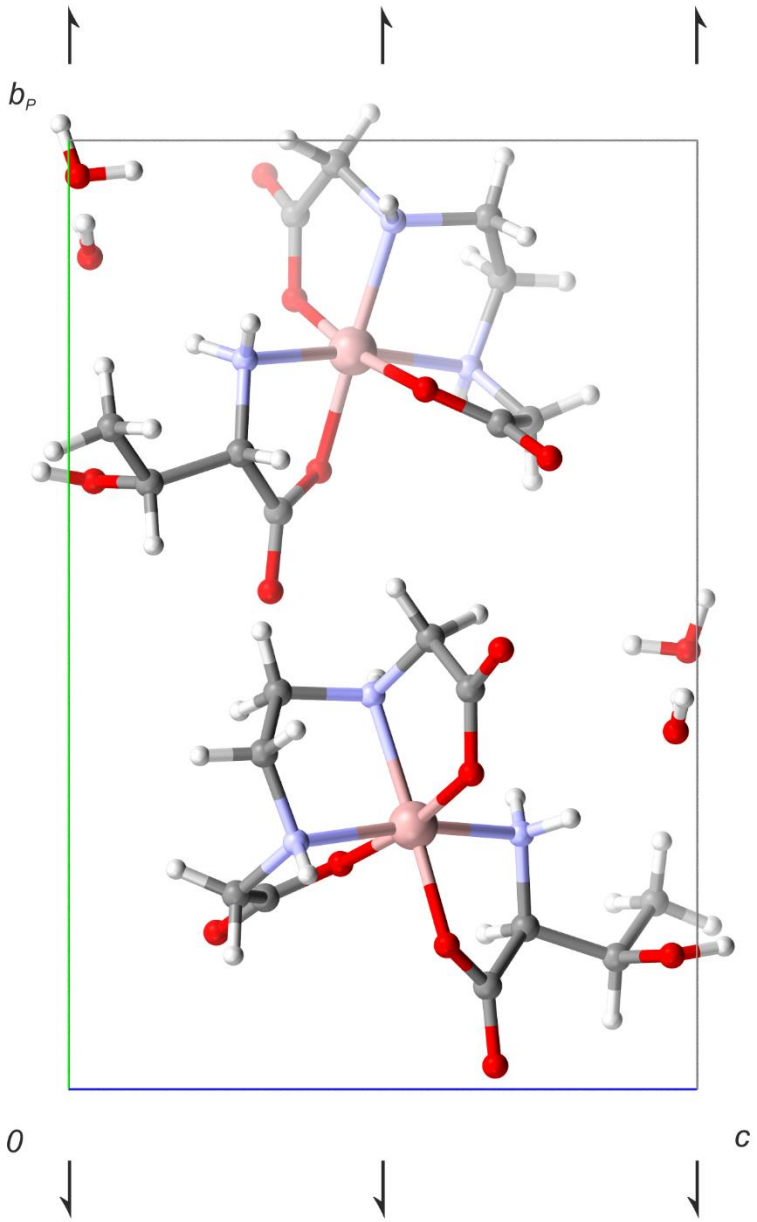


Figure 6.46: Packing diagram of **3h**·2H_2O (uv699) in the monoclinic space group $P2_1$ with view along [100]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

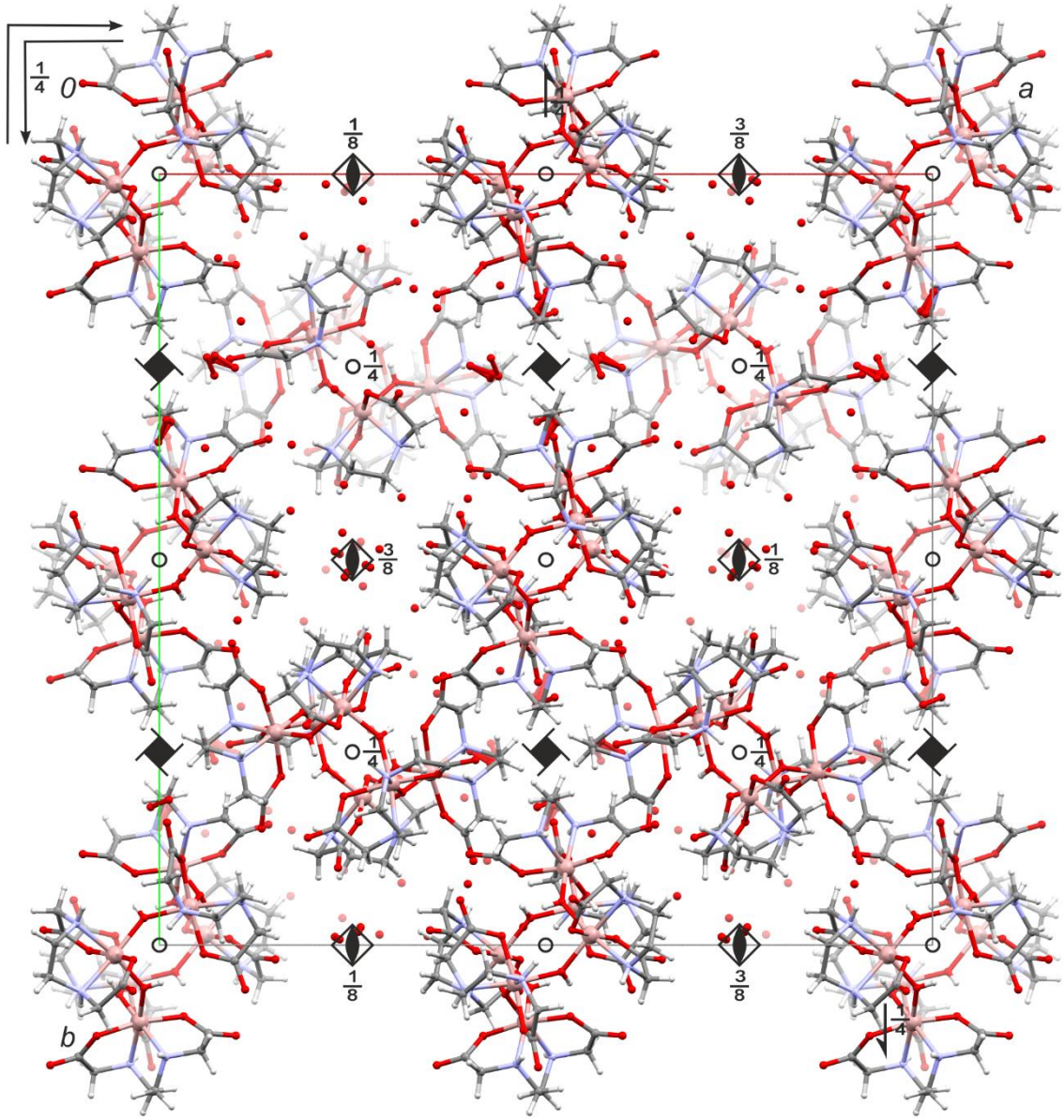


Figure 6.47: Packing diagram of **3j**·xH_2O (vv074) in the tetragonal space group $I4_1/a$ with view along [001]. The symmetry elements of the space group $I4_1/a$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

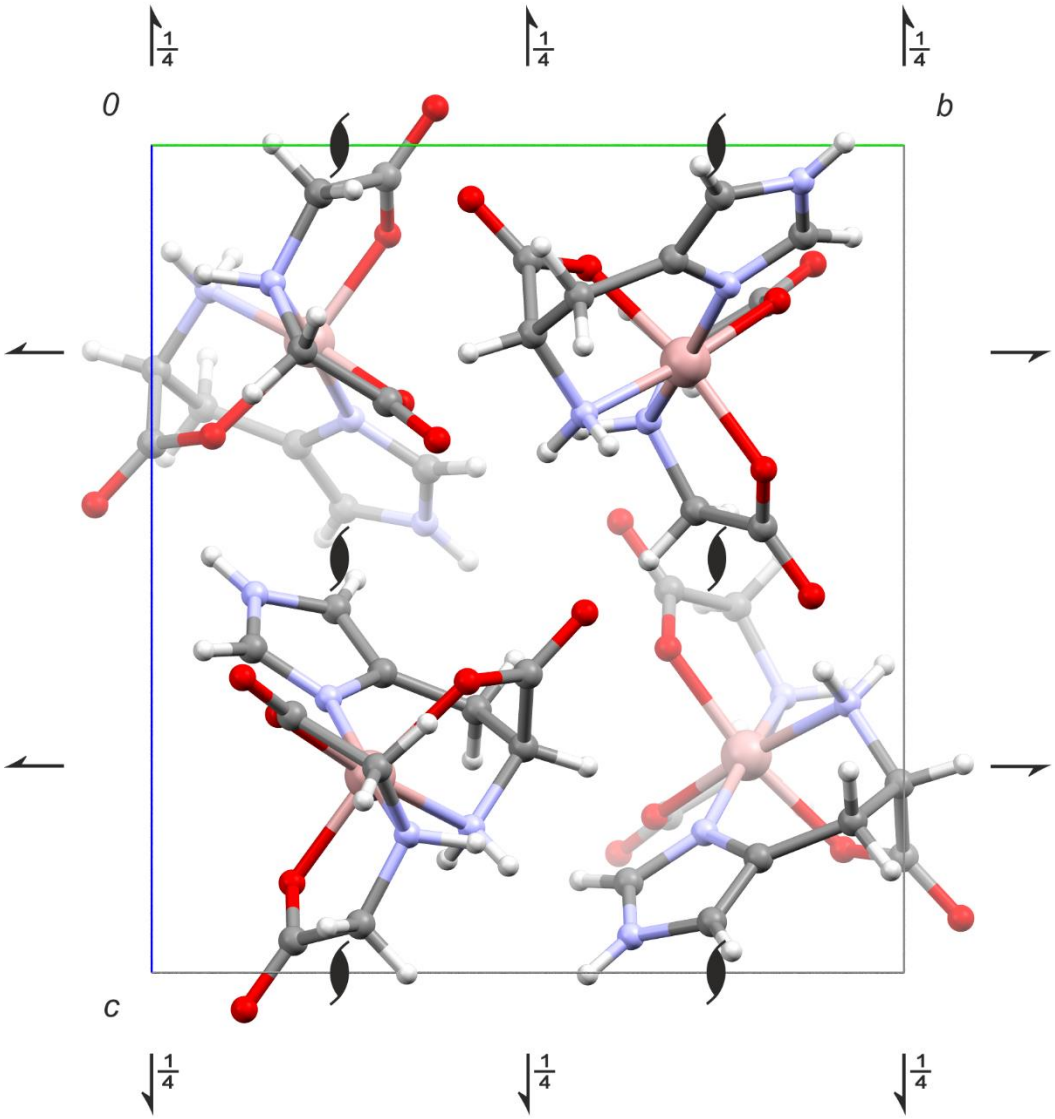


Figure 6.48: Packing diagram of **4a** (vv161) in the orthorhombic space group $P2_12_12_1$ with view along [100]. The symmetry elements of the space group $P2_12_12_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

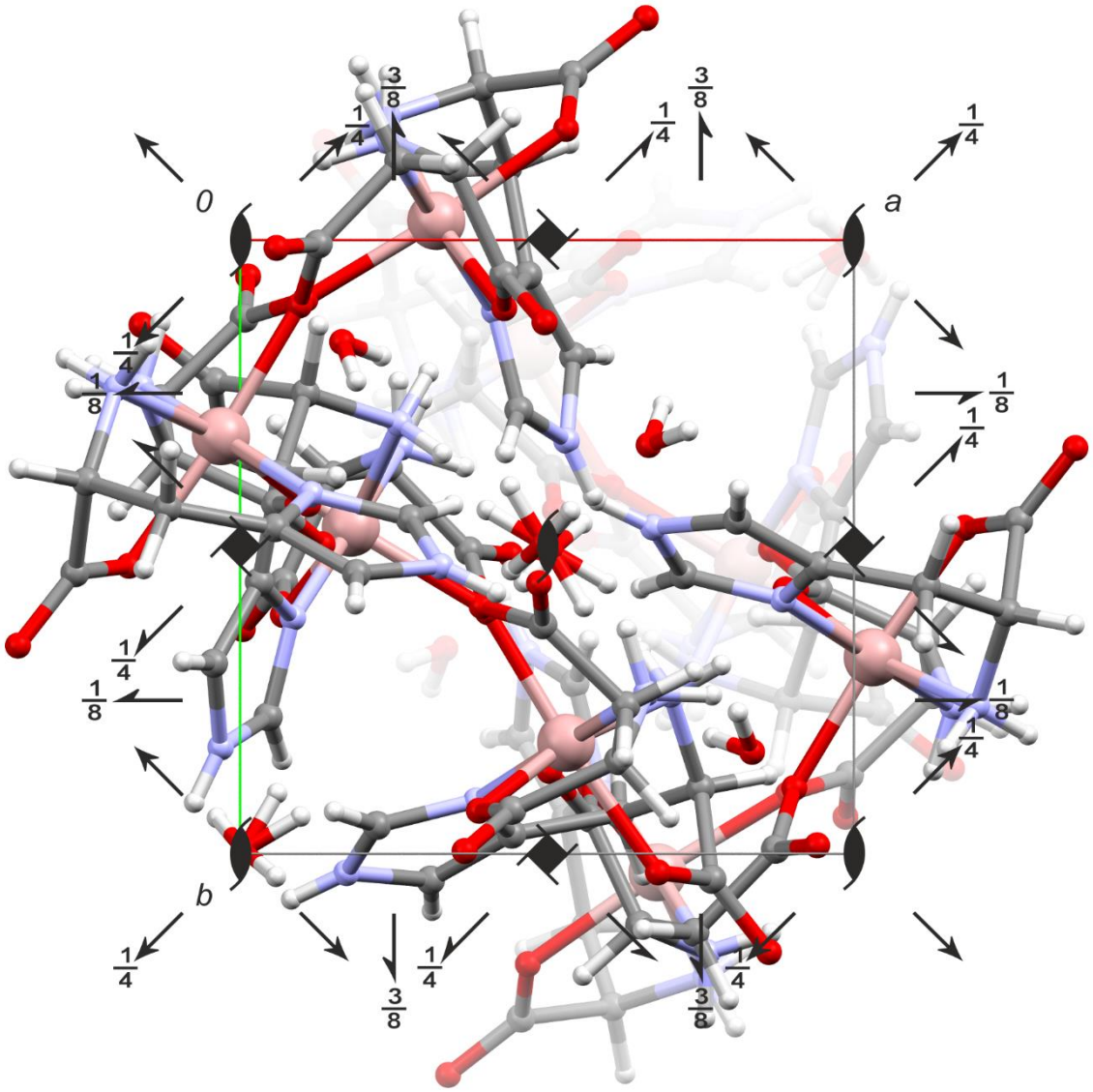


Figure 6.49: Packing diagram of **4b**·1.61H_2O (vv351) in the tetragonal space group $P4_12_12$ with view along [001]. The symmetry elements of the space group $P4_12_12$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

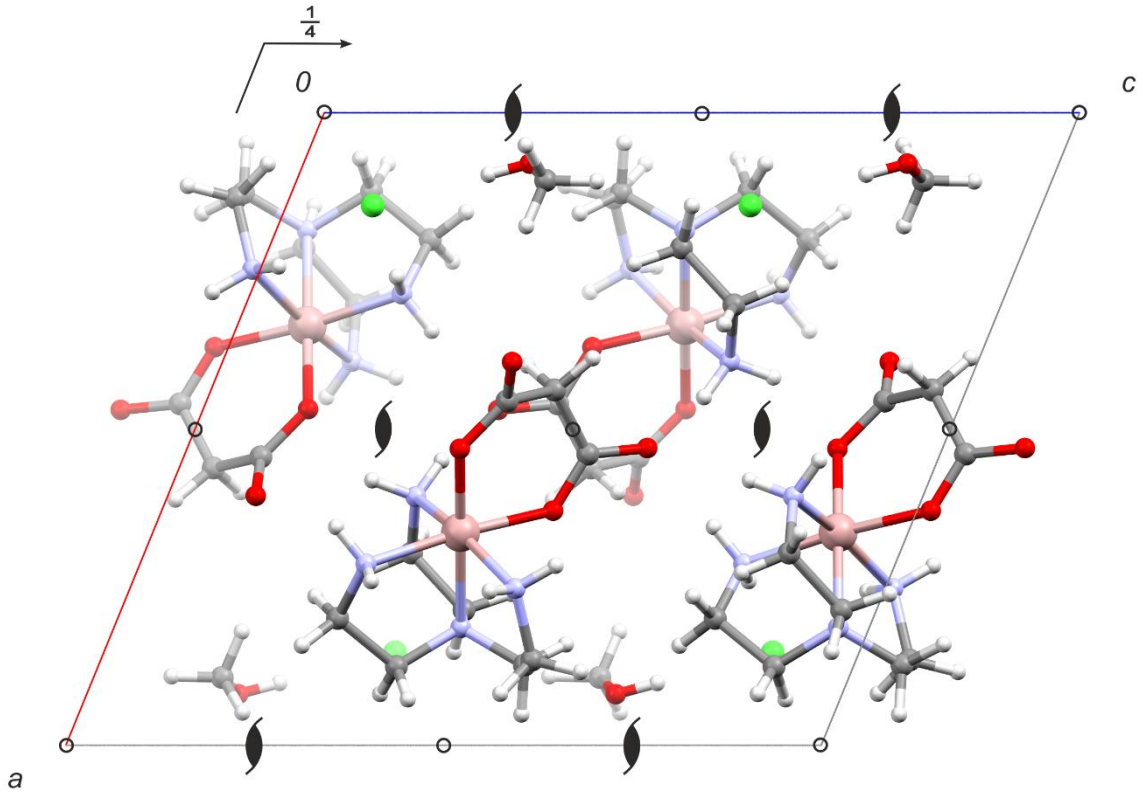


Figure 6.50: Packing diagram of **5a**Cl·MeOH (uv087) in the monoclinic space group $P2_1/c$ with view along [010]. The symmetry elements of the space group $P2_1/c$ are overlaid. Atoms: carbon (grey), hydrogen (white), chlorine (green), nitrogen (blue), oxygen (red) and gallium (puce).

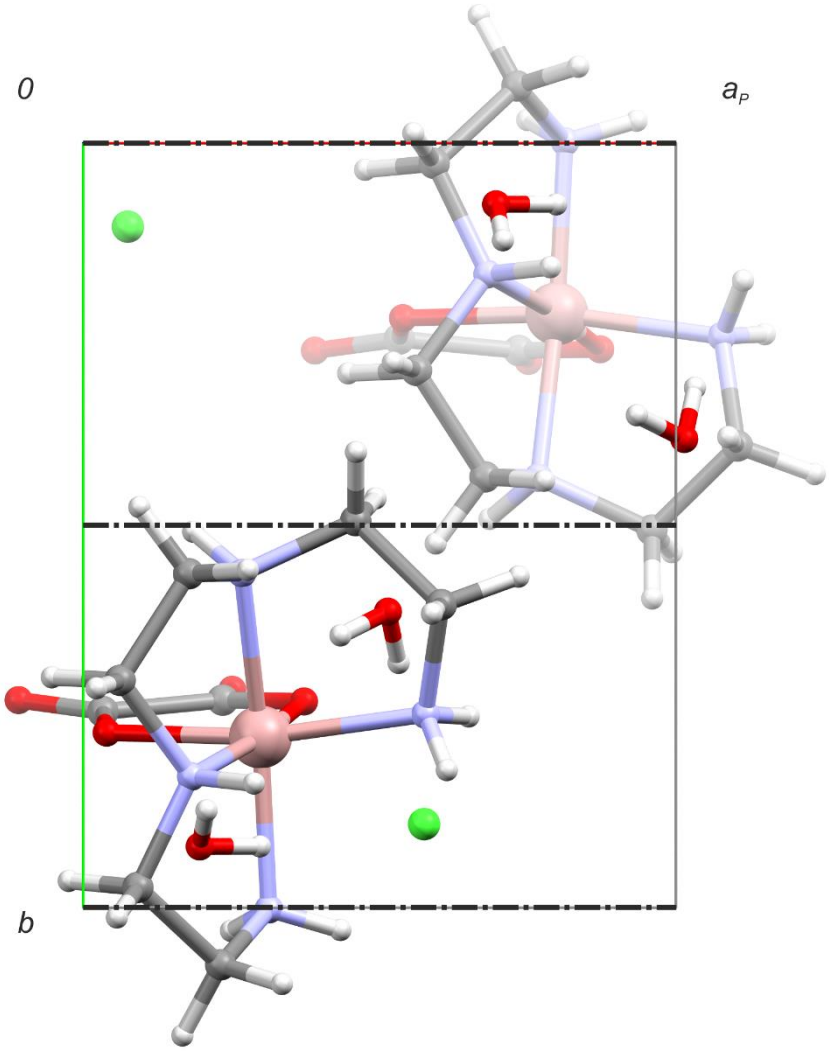


Figure 6.51: Packing diagram of **5b**·**5c**·2Cl·4H_2O (uv732) in the monoclinic space group *Pn* with view along [001]. The symmetry elements of the space group *Pn* are overlaid. Atoms: carbon (grey), hydrogen (white), chlorine (green), nitrogen (blue), oxygen (red) and gallium (puce).

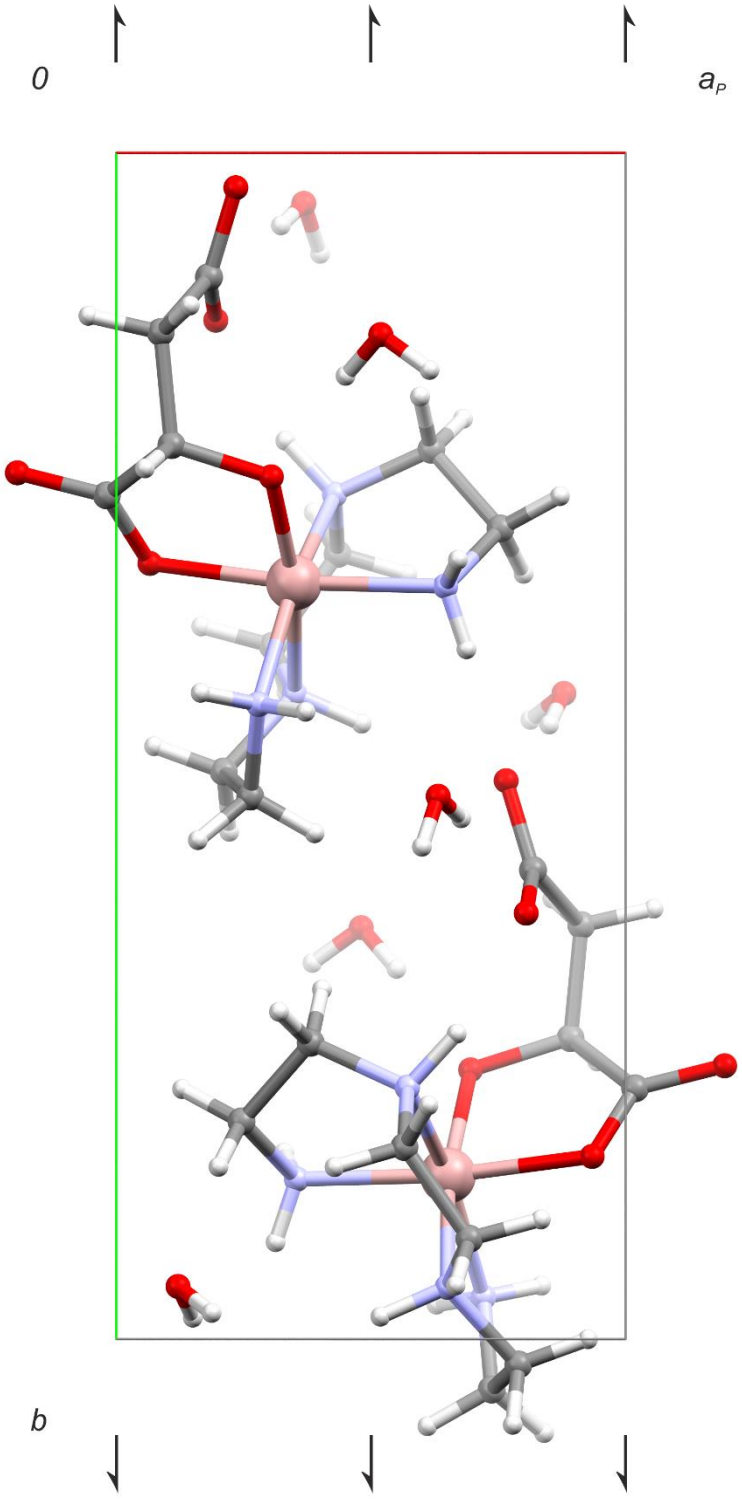


Figure 6.52: Packing diagram of **5d**·3H_2O (vv079) in the monoclinic space group $P2_1$ with view along [001]. The symmetry elements of the space group $P2_1$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

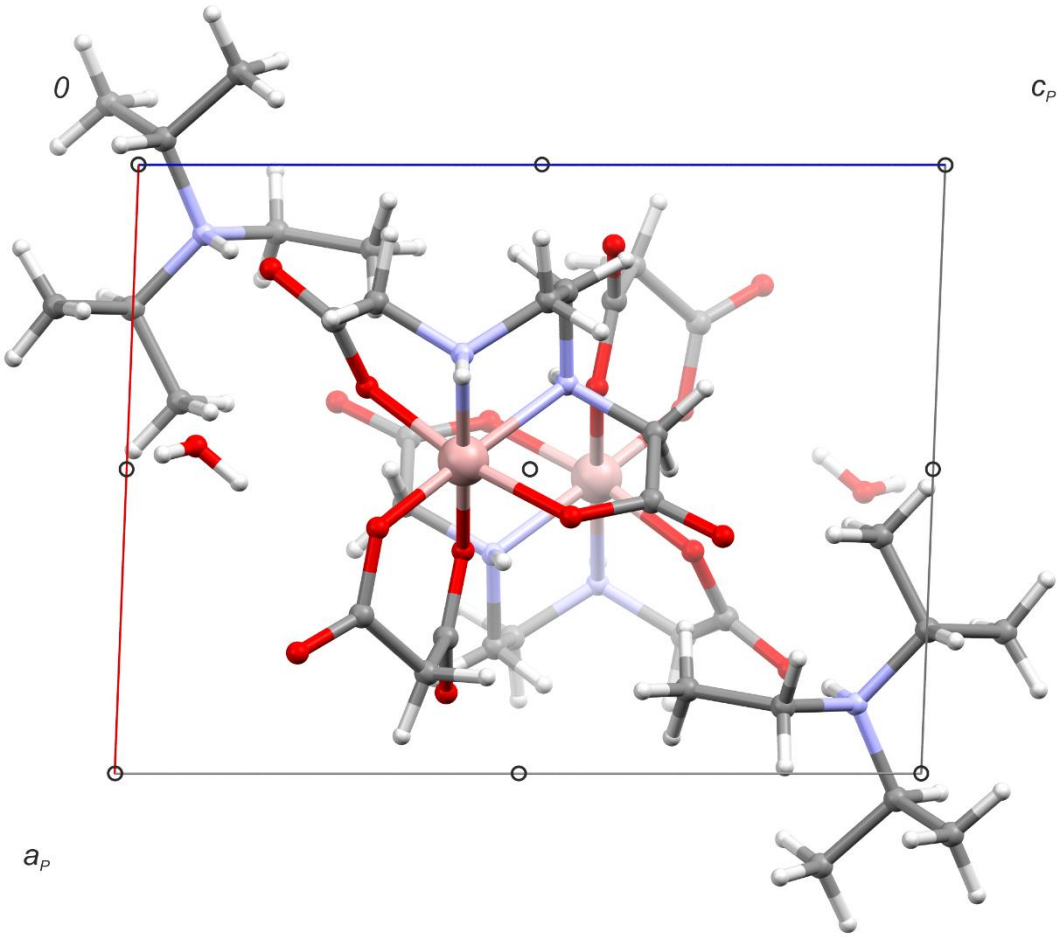


Figure 6.53: Packing diagram of (HDIPEA)**3k**·H_2O (wv137) in the triclinic space group $P\bar{1}$ with view along [010]. The symmetry elements of the space group $P\bar{1}$ are overlaid. Atoms: carbon (grey), hydrogen (white), nitrogen (blue), oxygen (red) and gallium (puce).

6.3 Crystallographic tables

Table 6.14: Crystallographic data of [{Ga(gly)$_2$(μ-OH)}$_2$] (**1a**), [Ga(gly)$_3$]·H$_2$O (**1b**·H$_2$O) and HNEt$_3$[Ga(gly)(nta)] ((HNEt$_3$)**2c**).

	1a	**1b**·H$_2$O	(HNEt$_3$)**2c**
empirical formula	$C_8H_{18}Ga_2N_4O_{10}$	$C_6H_{14}GaN_3O_7$	$C_{14}H_{26}GaN_3O_8$
M_r/g mol^{-1}	469.70	309.92	434.10
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	5.7023(2)	6.1913(2)	10.7329(3)
b/Å	16.8012(5)	14.5830(4)	14.3878(4)
c/Å	7.8405(2)	12.2156(4)	12.0805(4)
α/°	90	90	90
β/°	100.2090(10)	100.8500(10)	105.736(4)
γ/°	90	90	90
V/Å^3	739.27(4)	1083.20(6)	1795.59(10)
Z	2	4	4
ρ_{calc}/g cm^{-3}	2.110	1.900	1.606
μ/mm^{-1}	3.708	2.572	1.581
crystal size/mm	0.110 × 0.040 × 0.030	0.100 × 0.030 × 0.010	0.177 × 0.165 × 0.084
T/K	100(2)	107(2)	123(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Oxford XCalibur
radiation	MoKα	MoKα	MoKα
anode	rotating anode	rotating anode	fine-focus sealed tube
rated input/kW	2.5	2.5	2.00
θ-range/°	3.585–27.12	3.269–25.69	4.192–28.842
reflexes for metric	9990	9900	3780
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6482–0.7455	0.6901–0.7453	0.89111–1.00000
reflexes measured	29889	20716	10402
independent reflexes	1632	2067	4120
R_{int}	0.0377	0.0310	0.0329
mean $\sigma(I)/I$	0.0185	0.0203	0.0425
reflexes with $I \geq 2\sigma(I)$	1515	1964	3396
x,y (weighting scheme)	0.0106, 0.8587	0.0174, 0.9322	0.0300, 1.3611
hydrogen refinement	[a,b]	[a,c]	[a]
Flack parameter	-	-	-
parameters	110	162	238
restraints	0	3	0
$R(F_{obs})$	0.0173	0.0180	0.0335
$R_w(F^2)$	0.0435	0.0465	0.0807
S	1.129	1.069	1.046
$shift/error_{max}$	0.002	0.001	0.001
max. electron density/e Å^{-3}	0.388	0.357	0.916
min. electron density/e Å^{-3}	−0.269	−0.282	−0.604
measurement code	uv174	wv552	uo063

[a] C- and N-bonded H: constr., [b] O-bonded H: constr., [c] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.15: Crystallographic data of $HNEt_3$[Ga(met)(nta)] ($(HNEt_3)$**2f**), $HNEt_3$[Ga(nta)(pro)]·H_2O ($(HNEt_3)$**2g**·H_2O) and $HNEt_3$[Ga(nta)(ser)]·0.14H_2O ($(HNEt_3)$**2h**·0.14H_2O).

	$(HNEt_3)$**2f**	$(HNEt_3)$**2g**·H_2O	$(HNEt_3)$**2h**·0.14H_2O
empirical formula	$C_{17}H_{32}GaN_3O_8S$	$C_{17}H_{32}GaN_3O_9$	$C_{15}H_{28.28}GaN_3O_{9.14}$
M_r/g mol^{-1}	508.23	492.17	466.64
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1$	$P2_12_12_1$	$P1$
a/Å	10.4808(7)	9.4523(3)	10.5532(4)
b/Å	21.4486(15)	10.0306(4)	10.6604(3)
c/Å	11.0268(6)	22.8924(7)	10.8684(4)
α/°	90	90	107.6010(10)
β/°	115.749(2)	90	117.8210(10)
γ/°	90	90	97.2030(10)
V/Å^3	2232.7(3)	2170.48(13)	977.88(6)
Z	4	4	2
ρ_{calc}/g cm^{-3}	1.512	1.506	1.585
μ/mm^{-1}	1.373	1.321	1.462
crystal size/mm	0.090 × 0.060 × 0.030	0.100 × 0.080 × 0.050	0.130 × 0.100 × 0.060
T/K	100(2)	100(2)	100(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	2.795–25.37	2.961–25.70	3.731–27.13
reflexes for metric	9988	9898	9871
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6361–0.7452	0.6931–0.7453	0.6740–0.7455
reflexes measured	53576	37690	25503
independent reflexes	8043	4109	6954
R_{int}	0.0583	0.0433	0.0195
mean $\sigma(I)/I$	0.0430	0.0370	0.0490
reflexes with $I \geq 2\sigma(I)$	7217	3886	6746
x,y (weighting scheme)	0.0527, 3.7250	0.0261, 0.5307	0.0026, 0.4765
hydrogen refinement	[a,b]	[a,c,d]	[a,c,d]
Flack parameter	0.053(9)	0.000(4)	0.027(5)
parameters	549	285	548
restraints	49 [e]	3	7
$R(F_{obs})$	0.0414	0.0238	0.0267
$R_w(F^2)$	0.1113	0.0556	0.0628
S	1.088	1.036	1.054
$shift/error_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	1.471	0.675	1.110
min. electron density/e Å^{-3}	−0.751	−0.379	−0.538
measurement code	uv281	vv202	uv170

[a] C-bonded H: constr., [b] N-bonded H: constr., [c] N-bonded H: mixed constr. and refall, [d] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å, [e] ISOR was used for eight atoms.

Table 6.16: Crystallographic data of HDIPEA[Ga(ala)(nta)]·2H_2O ((HDIPEA)**2a**·2H_2O), HDIPEA[Ga(asn)(nta)] ((HDIPEA)**2b**) and HDIPEA[Ga(gly)(nta)]·MeOH ((HDIPEA)**2c**·MeOH).

	(HDIPEA)**2a**·2H_2O	(HDIPEA)**2b**	(HDIPEA)**2c**·MeOH
empirical formula	$C_{17}H_{36}GaN_3O_{10}$	$C_{18}H_{33}GaN_4O_9$	$C_{17}H_{34}GaN_3O_9$
M_r/g mol^{-1}	512.21	519.20	494.19
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1$	$Pna2_1$
a/Å	10.6793(5)	9.8125(4)	10.0228(2)
b/Å	8.5181(4)	9.1108(3)	25.0997(5)
c/Å	13.0630(7)	13.7554(4)	8.8022(2)
α/°	90	90	90
β/°	102.427(2)	110.881(2)	90
γ/°	90	90	90
V/Å^3	1160.47(10)	1148.96(7)	2214.36(8)
Z	2	2	4
ρ_{calc}/g cm^{-3}	1.466	1.501	1.482
μ/mm^{-1}	1.241	1.253	1.295
crystal size/mm	0.060 × 0.030 × 0.010	0.100 × 0.080 × 0.010	0.100 × 0.080 × 0.020
T/K	100(2)	103(2)	100(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	3.194–25.68	3.152–28.77	3.247–28.30
reflexes for metric	4846	9890	9966
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6741–0.7453	0.6773–0.7458	0.6831–0.7457
reflexes measured	19254	24556	38669
independent reflexes	4354	5884	5466
R_{int}	0.0505	0.0299	0.0332
mean *σ*(*I*)/*I*	0.0740	0.0446	0.0414
reflexes with $I \geq 2\sigma(I)$	3879	5464	4860
x,*y* (weighting scheme)	-, -	0.0223, 0.0054	-, 0.6689
hydrogen refinement	[a,c]	[a]	[a,b]
Flack parameter	0.025(9)	0.024(4)	0.018(5)
parameters	302	294	279
restraints	7	1	1
$R(F_{obs})$	0.0376	0.0252	0.0264
$R_w(F^2)$	0.0639	0.0586	0.0558
S	1.013	1.040	1.053
shift/error$_{max}$	0.001	0.001	0.002
max. electron density/e Å^{-3}	0.379	0.427	0.293
min. electron density/e Å^{-3}	−0.429	−0.284	−0.263
measurement code	vv373	vv753	uv716

[a] C- and N-bonded H: constr., [b] O-bonded H: constr., [c] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.17: Crystallographic data of HDIPEA[Ga(gly)(nta)]·H_2O ((HDIPEA)**2c**·H_2O), HDIPEA[Ga(leu)(nta)] ((HDIPEA)**2d**) and HDIPEA[Ga(met)(nta)] ((HDIPEA)**2e**).

	(HDIPEA)**2c**·H_2O	(HDIPEA)**2d**	(HDIPEA)**2e**
empirical formula	$C_{16}H_{32}GaN_3O_9$	$C_{20}H_{38}GaN_3O_8$	$C_{19}H_{36}GaN_3O_8S$
M_r/g mol^{-1}	480.16	518.25	536.29
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a/Å	13.1944(4)	9.2378(6)	8.8393(4)
b/Å	8.7962(3)	10.1131(5)	9.8826(4)
c/Å	19.0764(7)	25.4953(16)	27.5357(13)
α/°	90	90	90
β/°	94.1170(10)	90	90
γ/°	90	90	90
V/Å^3	2208.30(13)	2381.8(2)	2405.39(18)
Z	4	4	4
ρ_{calc}/g cm^{-3}	1.444	1.445	1.481
μ/mm^{-1}	1.296	1.205	1.279
crystal size/mm	0.090 × 0.080 × 0.040	0.239 × 0.135 × 0.112	0.100 × 0.080 × 0.010
T/K	299(2)	143(2)	100(2)
diffractometer	Bruker D8Venture	Oxford XCalibur	Bruker D8Venture
radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
anode	rotating anode	fine-focus sealed tube	rotating anode
rated input/kW	2.5	2.00	2.5
θ-range/°	3.154–27.14	4.336–28.275	3.179–26.36
reflexes for metric	9620	3041	9349
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.8195–0.8620	0.90988–1.00000	0.6379–0.7454
reflexes measured	54559	14182	35820
independent reflexes	4856	5455	4883
R_{int}	0.0317	0.0591	0.0517
mean $\sigma(I)/I$	0.0189	0.0778	0.0599
reflexes with $I \geq 2\sigma(I)$	4161	4364	4191
x,*y* (weighting scheme)	0.0302, 0.9324	0.0479, 0.2105	0.0156, 6.8760
hydrogen refinement	[a,b]	[a]	[a]
Flack parameter	-	−0.015(11)	0.039(7)
parameters	275	296	295
restraints	3	0	0
$R(F_{obs})$	0.0246	0.0489	0.0485
$R_w(F^2)$	0.0671	0.1180	0.0970
S	1.053	1.042	1.061
shift/error$_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	0.305	0.775	0.645
min. electron density/e Å^{-3}	−0.232	−0.728	−0.710
measurement code	wv334	wo068	vv362

[a] C- and N-bonded H: constr., [b] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.18: Crystallographic data of HDIPEA[Ga(nta)(pro)] ((HDIPEA)**2g**), HDIPEA[Ga(nta)(val)]·H_2O ((HDIPEA)**2i**·H_2O) and [Ga(asn)(edda)]·$2H_2O$ (**3a**·$2H_2O$).

	(HDIPEA)**2g**	(HDIPEA)**2i**·H_2O	**3a**·$2H_2O$
empirical formula	$C_{19}H_{34}GaN_3O_8$	$C_{19}H_{38}GaN_3O_9$	$C_{10}H_{21}GaN_4O_9$
M_r/g mol^{-1}	502.21	522.24	411.03
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1$	$P2_12_12_1$	$P2_1$
a/Å	10.5247(4)	8.7517(3)	9.5516(17)
b/Å	8.9515(3)	10.6239(3)	8.0803(14)
c/Å	24.2972(8)	25.7782(8)	10.3637(17)
α/°	90	90	90
β/°	96.2220(10)	90	91.898(6)
γ/°	90	90	90
V/Å^3	2275.60(14)	2396.78(13)	799.4(2)
Z	4	4	2
ρ_{calc}/g cm^{-3}	1.466	1.447	1.708
μ/mm^{-1}	1.258	1.201	1.776
crystal size/mm	0.080 × 0.070 × 0.010	0.090 × 0.080 × 0.070	0.100 × 0.030 × 0.020
T/K	100(2)	108(2)	299(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	3.021–25.71	3.118–25.68	3.198–27.48
reflexes for metric	9978	9970	9246
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6842–0.7453	0.6926–0.7453	0.6553–0.7456
reflexes measured	41874	46559	20605
independent reflexes	8525	4530	3672
R_{int}	0.0449	0.0617	0.0382
mean $\sigma(I)/I$	0.0563	0.0422	0.0414
reflexes with $I \geq 2\sigma(I)$	7490	4084	3404
x,*y* (weighting scheme)	0.0377, 2.0279	0.0205, 0.5109	0.0253, 0.0797
hydrogen refinement	[a]	[a,b]	[a,b]
Flack parameter	0.015(5)	0.003(6)	0.015(6)
parameters	569	304	225
restraints	1	3	8
$R(F_{obs})$	0.0395	0.0273	0.0276
$R_w(F^2)$	0.0931	0.0582	0.0633
S	1.049	1.054	1.066
shift/error$_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	0.735	0.278	0.441
min. electron density/e Å^{-3}	−0.682	−0.288	−0.335
measurement code	vv128	wv547	wv356

[a] C- and N-bonded H: constr., [b] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.19: Crystallographic data of [Ga(edda)(gly)]·2H$_2$O (**3b**·2H$_2$O), 2[Ga(edda)(leu)]·[{Ga(edda)(μ-OH)}$_2$]·6H$_2$O (**3c**·**3d**·**3i**·6H$_2$O) and [Ga(edda)(phe)]·3H$_2$O (**3e**·**3f**·3H$_2$O).

	3b·2H$_2$O	**3c**·**3d**·**3i**·6H$_2$O	**3e**·**3f**·3H$_2$O
empirical formula	$C_8H_{18}GaN_3O_8$	$C_{36}H_{78}Ga_4N_{10}O_{28}$	$C_{30}H_{46}Ga_2N_6O_{15}$
M_r/g mol^{-1}	353.97	1377.96	870.17
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P1$	$P2_1$
a/Å	8.7524(4)	5.8411(3)	8.0741(10)
b/Å	10.1518(5)	14.7435(7)	21.902(3)
c/Å	15.1341(7)	15.4884(8)	10.6153(15)
α/°	90	80.585(2)	90
β/°	102.723(2)	83.636(2)	106.024(4)
γ/°	90	88.522(2)	90
V/Å^3	1311.69(11)	1307.72(11)	1804.3(4)
Z	4	1	2
ρ_{calc}/g cm^{-3}	1.792	1.750	1.602
μ/mm^{-1}	2.141	2.139	1.572
crystal size/mm	0.100 × 0.050 × 0.020	0.500 × 0.040 × 0.020	0.500 × 0.500 × 0.200
T/K	100(2)	100(2)	100(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	3.118–27.13	3.220–25.65	2.825–25.79
reflexes for metric	6985	8879	7836
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6559–0.7455	0.6690–0.7453	0.5201–0.7453
reflexes measured	21581	27257	26047
independent reflexes	2879	9630	6761
R_{int}	0.0378	0.0428	0.0861
mean $\sigma(I)/I$	0.0308	0.0706	0.1025
reflexes with $I \geq 2\sigma(I)$	2316	7952	5647
x,y (weighting scheme)	0.0232, 1.2552	0.0352, 0.8506	0.0532, -
hydrogen refinement	[a,c]	[a,b,c]	[a,c]
Flack parameter	-	0.076(16)	0.058(12)
parameters	197	749	502
restraints	6	188 [d]	22 [e]
$R(F_{obs})$	0.0245	0.0422	0.0536
$R_w(F^2)$	0.0638	0.0916	0.1240
S	1.051	1.024	1.013
$shift/error_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	0.353	1.012	0.917
min. electron density/e Å^{-3}	−0.370	−0.593	−1.140
measurement code	uv502	vv062	uv537

[a] C- and N-bonded H: constr., [b] O-bonded H: refall, [c] O-bonded H: O–H of water molecules fixed to 0.83 Å, H...H fixed to 1.31 Å, [d] ISOR was used for 16 atoms, [e] ISOR was used for two atoms.

Table 6.20: Crystallographic data of [Ga(edda)(pro)]·3H$_2$O (**3g**·3H$_2$O), [Ga(edda)(thr)]·2H$_2$O (**3h**·2H$_2$O) and [{Ga(edda)(μ-OH)}$_6$]·xH$_2$O (**3j**·xH$_2$O).

	3g·3H$_2$O	**3h**·2H$_2$O	**3j**·xH$_2$O
empirical formula	$C_{11}H_{24}GaN_3O_9$	$C_{10}H_{22}GaN_3O_9$	$C_{36}H_{66}Ga_6N_{12}O_{30}$
M_r/g mol^{-1}	412.05	398.02	1498.80
crystal system	orthorhombic	monoclinic	tetragonal
space group	$P2_12_12_1$	$P2_1$	$I4_1/a$
a/Å	5.3979(2)	5.5295(2)	31.0336(4)
b/Å	14.3225(6)	14.4347(5)	31.0336
c/Å	21.5455(8)	9.5439(3)	14.9558(4)
α/°	90	90	90
β/°	90	92.4630(10)	90
γ/°	90	90	90
V/Å^3	1665.71(11)	761.06(5)	14403.7(5)
Z	4	2	8
ρ_{calc}/g cm^{-3}	1.643	1.737	1.382
μ/mm^{-1}	1.703	1.861	2.290
crystal size/mm	0.500 × 0.183 × 0.066	0.100 × 0.030 × 0.010	0.100 × 0.080 × 0.050
T/K	173(2)	100(2)	100(2)
diffractometer	Oxford XCalibur	Bruker D8Venture	Bruker D8Venture
radiation	MoK*α*	MoK*α*	MoK*α*
anode	fine-focus sealed tube	rotating anode	rotating anode
rated input/kW	2.00	2.5	2.5
θ-range/°	4.223–27.484	3.540–27.14	2.935–28.31
reflexes for metric	3937	9904	9966
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.79233–1.00000	0.6602–0.7455	0.6644–0.7457
reflexes measured	11126	21775	123508
independent reflexes	3796	3343	8928
R_{int}	0.0306	0.0317	0.0392
mean $\sigma(I)/I$	0.0341	0.0332	0.0214
reflexes with $I \geq 2\sigma(I)$	3616	3265	7761
x,*y* (weighting scheme)	0.0276, 0.1571	0.0166, 0.0306	0.0443, 99.4994
hydrogen refinement	[a,b,e]	[a,b,e]	[a,c,d]
Flack parameter	−0.008(6)	0.027(4)	-
parameters	241	225	536
restraints	9	7	0
$R(F_{obs})$	0.0251	0.0167	0.0430
$R_w(F^2)$	0.0577	0.0424	0.1144
S	1.056	1.021	1.078
shift/error$_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	0.461	0.294	2.268
min. electron density/e Å^{-3}	−0.453	−0.228	−0.998
measurement code	uo103	uv699	vv074

[a] C-bonded H: constr., [b] N-bonded H: constr., [c] N-bonded H: refall., [d] O-bonded H: refall., [e] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.21: Crystallographic data of [Ga(his)(ida)] (**4a**), [{Ga(μ-asp)(D-his)}$_2$]·1.61H_2O (**4b**·1.61H_2O) and [Ga(malo)(tren)]Cl·MeOH (**5a**Cl·MeOH).

	4a	**4b**·1.61H_2O	**5a**Cl·MeOH
empirical formula	$C_{10}H_{13}GaN_4O_6$	$C_{20}H_{29.23}Ga_2N_8O_{13.61}$	$C_{10}H_{24}ClGaN_4O_5$
M_r/g mol^{-1}	354.96	739.01	385.50
crystal system	orthorhombic	tetragonal	monoclinic
space group	$P2_12_12_1$	$P4_12_12$	$P2_1/c$
a/Å	9.3204(2)	7.8793(3)	13.1283(4)
b/Å	10.9873(3)	7.8793	8.9147(3)
c/Å	12.0573(3)	42.747(3)	14.4947(4)
α/°	90	90	90
β/°	90	90	112.1890(10)
γ/°	90	90	90
V/Å^3	1234.74(5)	2653.9(3)	1570.76(8)
Z	4	4	4
ρ_{calc}/g cm^{-3}	1.909	1.850	1.630
μ/mm^{-1}	2.267	2.117	1.948
crystal size/mm	0.100 × 0.050 × 0.010	0.100 × 0.040 × 0.030	0.120 × 0.040 × 0.020
T/K	100(2)	297(2)	100(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	2.508–26.07	2.954–26.38	3.352–27.16
reflexes for metric	9811	9779	9836
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6798–0.7453	0.6819–0.7454	0.6844–0.7455
reflexes measured	45516	68815	62749
independent reflexes	2443	2709	3471
R_{int}	0.0351	0.0282	0.0389
mean $\sigma(I)/I$	0.0184	0.0137	0.0199
reflexes with $I \geq 2\sigma(I)$	2357	2680	3152
x,*y* (weighting scheme)	0.0120, 0.5924	0.0223, 1.3967	0.0178, 1.1091
hydrogen refinement	[a,b]	[a,c,e]	[a,c,d]
Flack parameter	0.006(3)	0.017(3)	-
parameters	190	226	219
restraints	0	6	0
$R(F_{obs})$	0.0154	0.0206	0.0197
$R_w(F^2)$	0.0366	0.0522	0.0477
S	1.106	1.166	1.048
shift/error$_{max}$	0.001	0.002	0.001
max. electron density/e Å^{-3}	0.230	0.191	0.345
min. electron density/e Å^{-3}	−0.235	−0.242	−0.288
measurement code	vv161	vv351	uv087

[a] C-bonded H: constr., [b] N-bonded H: constr., [c] N-bonded H: refall, [d] O-bonded H: refall, [e] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

Table 6.22: Crystallographic data of [Ga(ox)(trien)]Cl·2H$_2$O (**5b**·**5c**·2Cl·4H$_2$O), [Ga(mal)(trien)]·3H$_2$O (**5d**·3H$_2$O) and HDIPEA[Ga(edda)(malo)]·H$_2$O ((HDIPEA)**3k**·H$_2$O).

	5b·**5c**·2Cl·4H$_2$O	**5d**·3H$_2$O	(HDIPEA)**3k**·H$_2$O
empirical formula	$C_8H_{22}ClGaN_4O_6$	$C_{10}H_{27}GaN_4O_8$	$C_{17}H_{34}GaN_3O_9$
M_r/g mol^{-1}	375.46	401.07	494.19
crystal system	monoclinic	monoclinic	triclinic
space group	*Pn*	$P2_1$	$P\bar{1}$
a/Å	7.1651(2)	7.2277(5)	9.3499(3)
b/Å	9.0775(3)	15.8606(11)	10.4273(3)
c/Å	11.3216(4)	7.5211(5)	11.7875(4)
α/°	90	90	83.2630(10)
β/°	100.8160(10)	109.684(2)	89.9540(10)
γ/°	90	90	71.1570(10)
V/Å^3	723.29(4)	811.80(10)	1079.27(6)
Z	2	2	2
ρ_{calc}/g cm^{-3}	1.724	1.641	1.521
μ/mm^{-1}	2.117	1.742	1.328
crystal size/mm	0.100 × 0.030 × 0.030	0.050 × 0.030 × 0.010	0.100 × 0.100 × 0.080
T/K	100(2)	100(2)	100(2)
diffractometer	Bruker D8Venture	Bruker D8Venture	Bruker D8Venture
radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
anode	rotating anode	rotating anode	rotating anode
rated input/kW	2.5	2.5	2.5
θ-range/°	3.663–25.71	3.150–25.68	2.553–33.13
reflexes for metric	7959	5443	9957
absorption correction	multi-scan	multi-scan	multi-scan
transmission factors	0.6537–0.7453	0.5998–0.7453	0.7124–0.7465
reflexes measured	11066	12419	37876
independent reflexes	2507	3093	8242
R_{int}	0.0296	0.0586	0.0302
mean $\sigma(I)/I$	0.0438	0.0637	0.0364
reflexes with $I \geq 2\sigma(I)$	2440	2756	7209
x,*y* (weighting scheme)	-, 0.0040	0.0335, -	0.0181, 0.4798
hydrogen refinement	[a,b,d]	[a,b,d]	[a,c,d]
Flack parameter	0.030(6)	0.025(9)	-
parameters	197	232	314
restraints	8	10	6
$R(F_{obs})$	0.0185	0.0352	0.0272
$R_w(F^2)$	0.0443	0.0753	0.0615
S	1.046	1.035	1.032
shift/error$_{max}$	0.001	0.001	0.001
max. electron density/e Å^{-3}	0.456	0.648	0.478
min. electron density/e Å^{-3}	−0.294	−0.387	−0.451
measurement code	uv732	vv079	wv137

[a] C-bonded H: constr., [b] N-bonded H: constr., [c] N-bonded H: refall, [d] O-bonded H: O–H fixed to 0.83 Å, H...H fixed to 1.31 Å.

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