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A Comparison of the Structural Chemistry of Scandium, Yttrium, Lanthanum and Lutetium: A contribution to the Group 3 debate

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Abstract

Data deposited in the Cambridge Structural Database (CSD) for compounds of scandium, yttrium, lanthanum and lutetium(III) have been analysed to assess the structural similarities of complexes of the different metal ions. 29 sets of compounds of Sc, Y, La and Lu where at least three of the elements form compounds with the same ligands have been identified and their crystal structures analysed. In 14 of them, scandium and lutetium have the same coordination number; in the remaining 15 they do not. Similarly, there are 10 examples where there is a difference in coordination number between Lu and Y for compounds with the same ligands. For the other 19 either the coordination numbers are the same or that compounds for both the elements under consideration have not been reported. Overall structural differences correlate well with the size of the metal ions and provide no true chemical basis for arranging Lu rather than La in one triad with Sc and Y.

Keywords: Scandium(III), Yttrium(III), Lanthanum(III), Lutetium(III), Structural Chemistry, Coordination number, Coordination Geometry, Cambridge Structural Database

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1. Introduction

Traditionally, scandium, yttrium and lanthanum have been considered as a triad due to their occupation of successive vertically arranged boxes in Group 3 of the Periodic Table [1]. In recent years, the suggestion has been made, not without controversy, that lutetium is better fitted to be member of this group than lanthanum [2-8] and the arrangement of the Periodic Table is under current debate as a IUPAC project [9, 10]. In the current IUPAC version of the Periodic Table the 'box' under yttrium contains the word "lanthanoids", rather than either La or Lu, reflecting the lack of consensus at the present time. Most recently, Vernon has presented 'a series of ten interlocking arguments' for La belonging in Group 3 [10]. But how similar are scandium and lutetium in their chemistry, particularly as manifest in the structures of their compounds?

In general, the size of successive atoms increases as groups are descended in the Periodic Table, although with heavier elements, including La - Lu, relativistic effects counterbalance this to some extent [11, 12], and it is remarkable that atomic radii vary by only a factor of approximately two over the whole Table. Nonetheless, yttrium is larger than scandium, and lanthanum is larger than yttrium, but in the elements immediately following lanthanum this trend is reversed. Because of the poor shielding by the 4 f electrons of the increasing nuclear charge, as the lanthanide series is traversed from La to Lu, the ionic radius of the M^{3+} ions decrease by some 16%, the effect well-known as the "lanthanide contraction". The resulting change in ionic radius from La^{3+} (radius 1.172 Å for six coordination) to Lu^{3+} (radius 1.001 Å) causes lutetium to be smaller than Y^{3+} (1.040 Å), the latter having virtually the same ionic radius as Ho^{3+} (1.041 Å) and thus very similar chemistry [13].

As Victor Moritz Goldschmidt pointed out, the decreasing ionic radii of the lanthanide ions with increasing atomic number affects not just the properties of the lanthanides but also the succeeding 5d metals, and this is the context in which Goldschmidt originally coined the term 'lanthanide contraction' [14]. Thus Zr^{4+} ions are virtually the same size as those of Hf^{4+} , with ionic (crystal) radii for six coordination of 0.86 Å and 0.85 Å respectively, the effect of the greater effective nuclear charge almost exactly counterbalancing the effect of the extra electronic subshell, and their chemistry is very similar [15]. Zirconium is much more abundant than hafnium and so because they occur together hafnium was not discovered until 1923. Some properties of these metals are different, however. For example, as the hafnium atom is nearly twice as heavy as a zirconium atom, though of (virtually) identical size, its density is 13.35 g cm⁻³, compared with the value of 6.51 g cm⁻³ for zirconium. Likewise, there are very close resemblances in the chemistry of platinum and palladium, most notably in the (+2) oxidation state [16-18]. Similarly, the Au^+ ion is smaller than the Ag^+ ion (experimental radii are 1.25 and 1.33 Å respectively), [19-21] though, once again, there are major differences in their properties

such as in their ligand substitution rates, and these differences are often attributed to relativistic effects [22].

So where does Sc^{3+} fit in? Although it has a significantly smaller ionic radius (0.885 Å) than Y^{3+} or even Lu^{3+} , the smallest Ln(III), it is sometimes compared to Lu^{3+} .

Certain aspects of the chemistry of the compounds of scandium, yttrium, and of the series lanthanum to lutetium, such as their lattice energies, solvation energies and complex stability constants, are closely related to the size of the metal atom or ion, and also to the charge density of the metal ions. In this article a survey of the structures of a range of the compounds of Sc, Y, La and Lu is presented. Metal-ligand bond parameters as well as their coordination numbers and coordination geometries have been analysed with the intent of providing new insights into the relationships between lutetium and the Group 3 elements.

2. The Radii of the +3 ions of Sc, Y, La and Lu

The largest single repository of structural data for lanthanide complexes is the Cambridge Structural Database (CSD) [23] which contains entries for 45,191 compounds of La and Ce to Lu (CSD Version 5.41(November 2019) + 3 updates). In the same version of the CSD there are 1490 entries for Sc-containing compounds and 3959 entries for Y-containing compounds. It should be noted that all these complexes contain at least one “organic” carbon atom so that simple salts such as $[\text{Ln}(\text{H}_2\text{O})_9][\text{CF}_3\text{SO}_3]_3$, the oxides Ln_2O_3 or the binary halides $[\text{LnX}_3; \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}]$ are omitted unless accompanied in the crystal structure by a species containing an organic carbon. However information on these salts can be found in the Inorganic Crystal Structure Database (ICSD) [24] provided by FIZ Karlsruhe GmbH. The CSD, with its sophisticated search and analysis software, is an appropriate tool for an investigation of the structural chemistry of the structural chemistry of the Group 3 elements and of the lanthanides.

The +3 ions of Sc, Y, La and Lu, and indeed all the lanthanide(III) ions, are classed as “hard” metal ions and, as such, have a preference for bonding to “hard” bases with oxygen or nitrogen donor atoms as illustrated in Figure 1 (CSD Version 5.41(November 2019) + 3 updates). The lanthanides have been important in providing a basis for attempts to establish a quantitative scale for “oxophilicity” [25]. Since M-O bonds are somewhat more prevalent in the structures being considered, the analysis was carried out on these CSD hits. The results of a search for Sc, Y, La and Lu complexes that contain at least one M-O bond for coordination numbers 6 to 9 are presented in Table 1 (additional material is available in the Supporting Information). The mean M-O distance with the associated esd and the variance are shown and, assuming a radius of 0.66 Å for the coordinated O atom (O atom covalent

radius), the radius of the M ions in the complexes is obtained by subtraction. For comparison, the atomic radii for the four elements, determined empirically from crystals by J. C. Slater in the 1960s [26], are included in the final column. The comparison shows the improvement in the ability to fine tune the radii values, including accounting for different coordination numbers, over the last sixty years as the number of structural examples of each type that can be used in the analysis has increased.

Figure 2 shows a plot of the M-O mean bond lengths for the 6-, 7-, 8- and 9-coordinate complexes of the four 3+ metal ions, which indicates that across the complexes with different coordination numbers the M-O bonds in Lu³⁺ and Y³⁺ complexes are similar. This would suggest that for chemical and physical properties of compounds of these elements, where the size of the metal ion is important, the chemistry of Lu complexes might most closely resemble that of Y complexes.

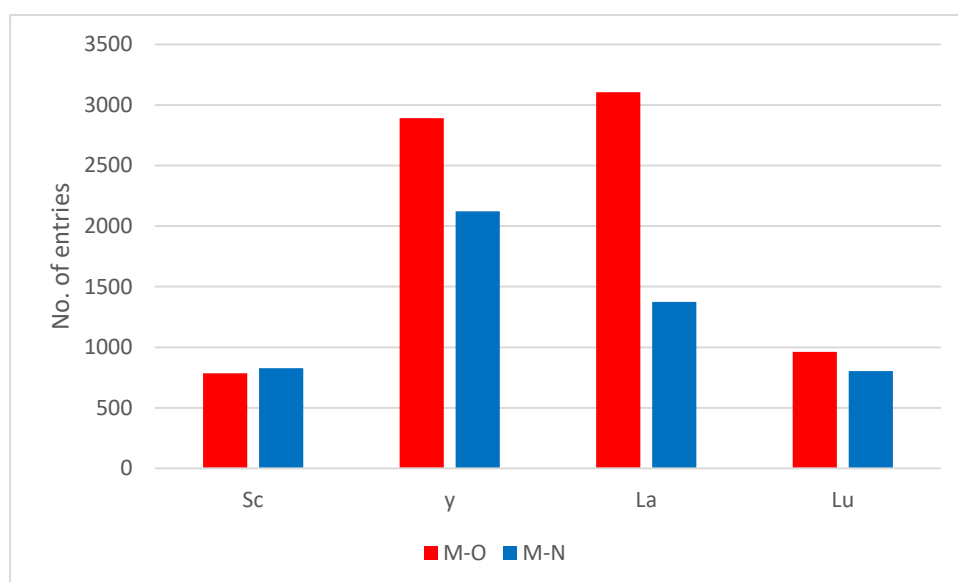


Figure 1. The distribution of structural hits for complexes of Sc, Y, La and Lu in the CSD for which there is at least one M-O or M-N bond (complexes containing both M-O and M-N bonds will appear in both records of the element).

Table 1. Mean M-O (M = Sc, Y, La, Lu) bond lengths in 6-9 coordinate complexes

Metal ion	Coordination number	No. of CSD hits	Mean M-O bond length (esd) Å	Variance	Resultant M radius (Å) [†]	Empirical atomic radii (Å) [‡]
Sc ³⁺	6	193	2.10(9)	0.008	1.44	
	7	55	2.15(9)	0.007	1.49	
	8	46	2.20(8)	0.007	1.54	
	9 [§]	5	2.31(10)	0.011	1.65	1.60

Y ³⁺	6	401	2.28(12)	0.016	1.62	
	7	270	2.30(12)	0.015	1.64	
	8	603	2.35(9)	0.007	1.69	
	9	349	2.40(11)	0.012	1.74	1.85
La ³⁺	6	90	2.45(14)	0.014	1.79	
	7	102	2.45((14)	0.019	1.79	
	8	316	2.50(8)	0.006	1.84	
	9	658	2.54(8)	0.007	1.88	1.95
Lu ³⁺	6	112	2.25(11)	0.012	1.59	
	7	88	2.29(13)	0.016	1.63	
	8	210	2.30(8)	0.006	1.64	
	9	132	2.34(10)	0.009	1.68	1.75

[†]This radius was calculated by subtracting 0.66 Å from the mean M-O bond length. [§] There are not enough examples for these data to be meaningful. [‡]Radii for the metal ions taken from *Atomic Radii in Crystals* [26].

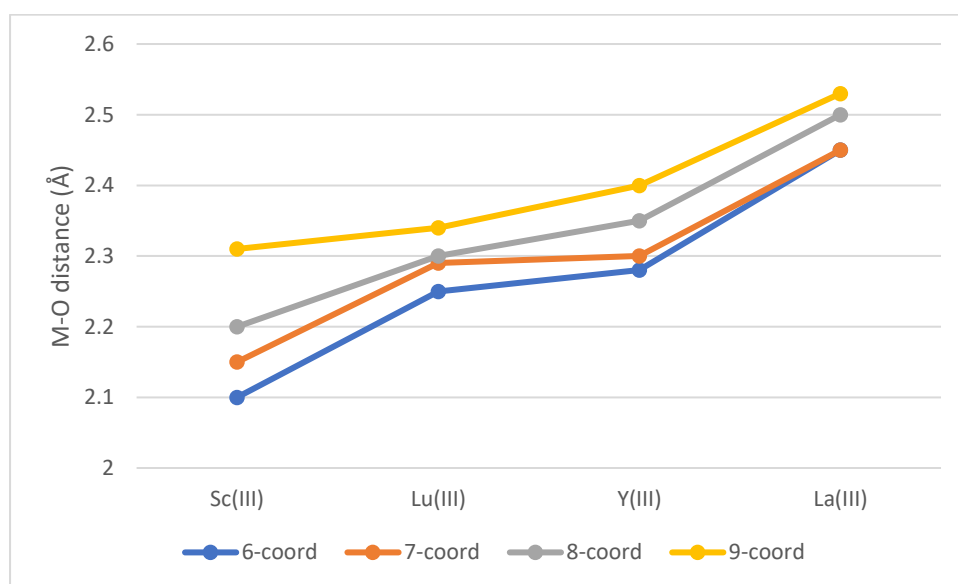


Figure 2. The mean M-O bond lengths (M = Sc, Y, La and Lu) for all the 6-, 7-, 8- and 9-coordinated complexes that contain at least one M-O bond whose structures have been deposited in the CSD.

The analysis of the M-O bond lengths in the complexes of the 3+ ions of the four elements is also consistent with the trends in ionisation energies (Table 2) and in the electronegativities (on both the Pauling and Allred-Rochow scales [27, 28]) with the data for Lu most closely resembling that of Y, with Sc showing a higher value for the formation of the 3+ ion and higher electronegativity than that of Lu.

Table 2. The sum of the first three ionisation energies (KJ/mole) and Pauling and Allred-Rochow Electronegativities for Sc, Y, La and Lu

	Sum of the first three ionisation energies (KJ/mole)	Electronegativities	
		Pauling	Allred-Rochow
Sc	4257	1.36	1.20
Y	3777	1.22	1.11
La	3455	1.10	1.08
Lu	3896	1.27	1.14

3. Binary compounds

One reason for the perceived similarity of scandium and lutetium lies in the structures of simple binary compounds [29, 30]. Certainly, the oxide and the halides - except the fluoride – all have the same coordination number (though not necessarily adopting the same structure). Thus, scandium, yttrium and lutetium all have a coordination number of 6 in their oxides M_2O_3 ($M = Sc, Y, Lu$) and in all the halides, save the fluoride. Apart from the fluoride (six coordinate WO_3 structure), all ScX_3 ($X = F, Cl, Br, I$) have the $FeCl_3$ structure, also adopted by LuX_3 ($X = Br, I$) whilst $LuCl_3$ has the $AlCl_3$ structure. Lutetium fluoride adopts the 9 coordinate YF_3 structure.

As expected, lanthanum has higher coordination numbers in its halides than either of the other two metals, with 11-coordination in LaF_3 , 9 coordination in LaX_3 ($X = Cl, Br$) and 8 coordination in LaI_3 . Lanthanum oxide has capped octahedral seven-coordination.

4. Complexes of monodentate ligands

4.1 Hydrated salts and the aqua ions

It has been known for some 80 years that a number of hydrated lanthanide salts [31, 32] such as the bromates and ethyl sulfates contain $[M(OH_2)_9]^{3+}$ ions with tricapped trigonal prismatic coordination [33].

Subsequently it was established that a series of isomorphous trifluoromethane sulfonates (triflates) $[M(OH_2)_9] (CF_3SO_3)_3$ ($M = Y, La-Lu$ except Pm) similarly exists [34, 35]. When hydrated scandium trifluoromethane sulfonate was found to be isomorphous with the lanthanide series, it was assumed to contain $[Sc(H_2O)_9]^{3+}$ ions [36].

It is now known that in the solid-state, the hydrated triflates of the later part of the lanthanide series, as well as scandium and lutetium, exhibit a water deficiency, randomly distributed over the capping positions. For scandium the hydration number in the solid salts

is approximately 8.0 and for lutetium 8.2. The earlier lanthanides (La-Dy inclusive) do have $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ ions in their solid triflate salts (Figure 3a) [37], as in the bromates and ethylsulfates. In solution, EXAFS measurements indicate that scandium is strongly bound to the six prism water molecules (Sc–O bond distance of 2.17(1) Å), to a capping water at 2.32(4) Å and possibly to another less strongly bound capping water at approx. 2.5 Å. The solution hydration number approximates [38] to seven. In solution, lutetium triflate is believed to contain eight coordinate Lu^{3+} ions, on account of the similarity of the EXAFS and XANES spectra of solid $[\text{Lu}(\text{OH}_2)_n](\text{CF}_3\text{SO}_3)_3$ ($n \sim 8.2$) and the solution spectra [39, 40], whilst solutions of lanthanum triflate contain the $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ ions found in the crystal [41]. Various $[\text{Ln}(\text{OH}_2)_8]^{3+}$ species (Figure 3b), not the whole series but including $[\text{Lu}(\text{OH}_2)_8]^{3+}$, have been characterised in the solid state in association with other anions, e.g. iodide [42, 43].

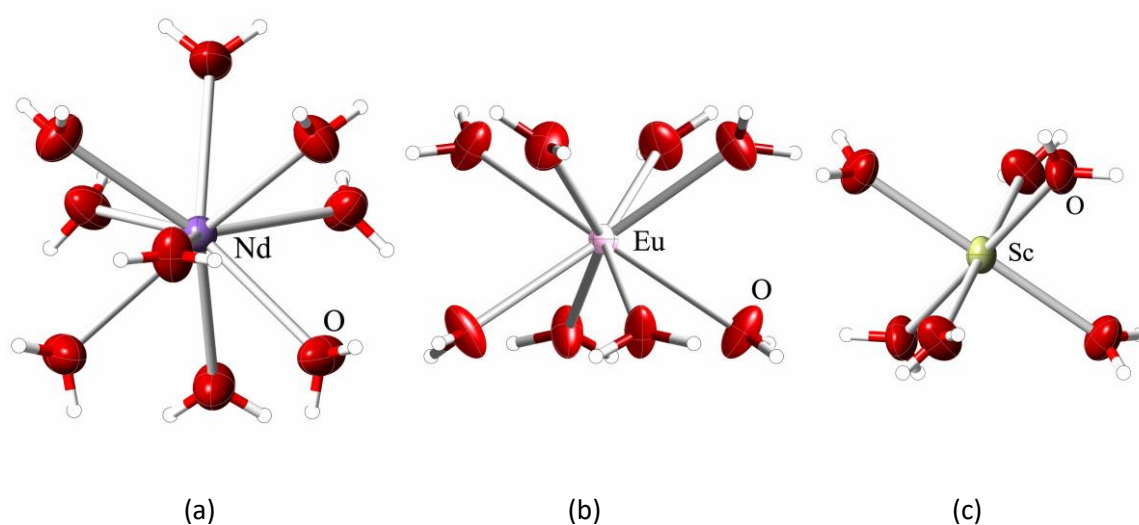


Figure 3 Aqua-cations of tricapped trigonal prismatic (nonacoordinate), square-antiprismatic (octa-coordinate) and octahedral (hexacoordinate) coordination geometry, as found in the crystals of (a) $[\text{Nd}(\text{OH}_2)_9](\text{CF}_3\text{SO}_3)_3$ [37] (b) $[\text{Eu}(\text{OH}_2)_8]\text{I}_3$ [43] and (c) $[\text{Sc}(\text{OH}_2)_6][\text{Sc}(\text{O}_3\text{SCH}_3)_6]$ [45], respectively. (Nd = violet; Eu = pink; Sc = yellow; O = red; H atoms are shown as small spheres of an arbitrary 0.1 Å radius)

In contrast to the triflate salts, the hydrated perchlorates demonstrate another facet of behaviour. All lanthanides form $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{La-Lu}$ except Pm), containing the octahedral $[\text{Ln}(\text{H}_2\text{O})_6]^{3+}$ ion [44], just as $\text{Sc}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ ($x = 6, 9$) both contain $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ ions (Figure 3c) [38, 45]. $\text{Y}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ is isomorphous and is presumed to contain $[\text{Y}(\text{H}_2\text{O})_6]^{3+}$ ions, but its structure has not been investigated in detail [44]. In general, the H-bonding ability of $[\text{Ln}(\text{OH}_2)_n]^{3+}$ appears often to play a significant role in determining the exact species found in association with a given anion [46-50].

Clearly the solubility of these salts is the factor driving their isolation, removing from solution what may be an ion of very low abundance compared with those of higher coordination number. Studies of water ligand exchange rates [51] on the lanthanide(III)

aqua cations in solution have been interpreted in terms of both nona-aqua and octa-aqua species being present, with the former predominating for the early lanthanides and the latter for the later.

4.2 Other monodentate ligands

Dimethylsulfoxide (DMSO) and N,N'-dimethylpropylene urea (DMPU) are two ligands bulkier than water which form homoleptic complexes with both scandium and the lanthanide (III) ions for which both solution and solid state structural data are available.

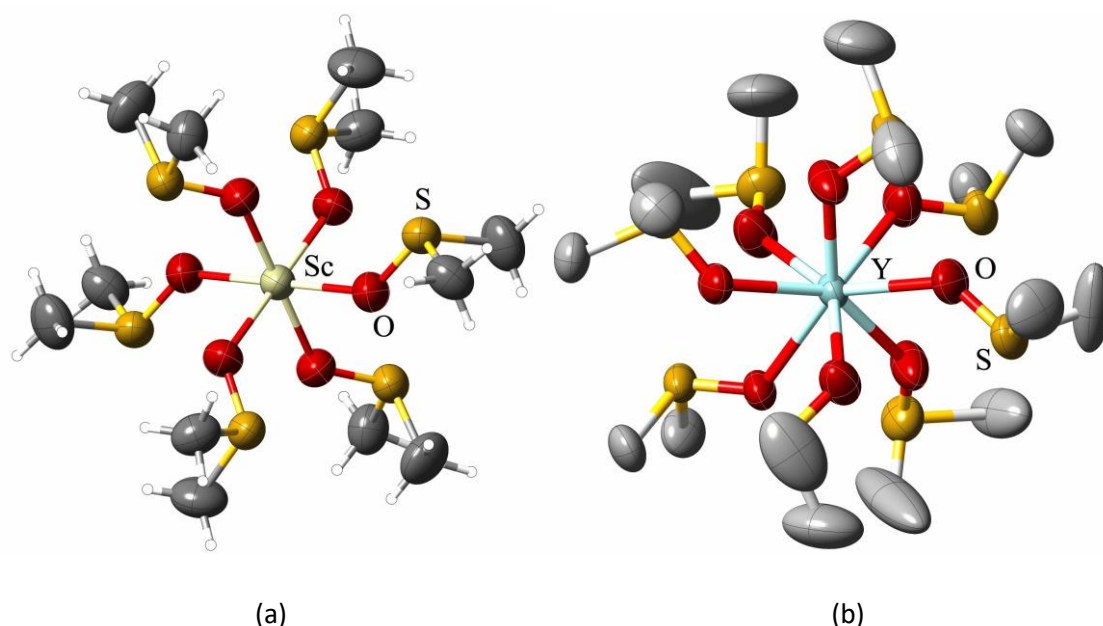


Figure 4. Dimethylsulfoxide-coordinated cations present in the crystals of (a) $[\text{Sc}(\text{DMSO})_6]\text{I}_3$ and (b) $[\text{Y}(\text{DMSO})_8]\text{I}_3$. (Sc = yellow; Y = blue; O = red; S = apricot; partial disorder of the Y structure, in which H-atoms were not located, is not shown.)

X-ray diffraction studies of crystalline $[\text{Sc}(\text{DMSO})_6]\text{I}_3$ (Figure 4a) show it to contain octahedral $[\text{Sc}(\text{DMSO})_6]^{3+}$ ions (Sc-O 2.069(3) Å), whilst the bond length of 2.09(1) Å indicated by EXAFS measurements for solvated scandium(III) ions in DMSO solution implies that six co-ordinate species are also present there [52]. The yttrium(III) ion in the complex $[\text{Y}(\text{DMSO})_8]\text{I}_3$ (Figure 4b) is eight coordinate with a distorted square antiprismatic geometry and an average Y-O bond length of 2.38 Å [53].

All the lanthanides form complexes $[\text{Ln}(\text{DMSO})_8]\text{I}_3$ (Ln = La-Lu except Pm) and X-ray diffraction confirms the presence in the crystal of $[\text{Ln}(\text{DMSO})_8]^{3+}$ ions, with distorted square antiprismatic coordination [54]. The average metal–oxygen bond length decreases from 2.49 Å (La) to 2.30 Å (Lu). EXAFS spectra of the solids indicate very similar Ln-O distances to these and show a close correspondence with the spectra of DMSO solutions of the lanthanide ions, suggesting the presence of eight coordination in solution as well [55].

N,N-dimethylpropylene urea is more demanding sterically. Limited published data indicate that the DMPU-solvated scandium ion is six-coordinate [41], while a crystal structure of $[\text{Y}(\text{DMPU})_6]\text{I}_3$ (Figure 5) confirms that the cation adopts an octahedral geometry with an average Y-O bond length of 2.23 Å [53]. The X-ray diffraction-data on the crystalline complexes show that the octahedrally coordinated $[\text{Ln}(\text{DMPU})_6]\text{I}_3$ complexes are formed across the lanthanide series (La-Lu except Pm). In solution, however, EXAFS spectra of DMPU solutions of the lanthanides are, with the exception of lutetium, quite different to those of solid $[\text{Ln}(\text{DMPU})_6]\text{I}_3$, with Ln-O distances 0.08 Å longer than those in the solid state, but shorter than the values expected for eight-coordination, consistent with seven coordinate $[\text{Ln}(\text{DMPU})_7]^{3+}$ ions [56]. In the case of lutetium, solid $[\text{Ln}(\text{DMPU})_6]\text{I}_3$ and solutions of LuI_3 in DMPU give identical EXAFS spectra, showing that the smaller Lu^{3+} ion is six coordinate in DMPU solution [56]. Once again, it is clear that the close ion association enforced in a solid can influence the form of the species isolated and that this form may not be that apparently dominant in solution. In turn, this raises the question of how, in solution, a secondary coordination sphere of solvent may influence the form of the primary coordination sphere.

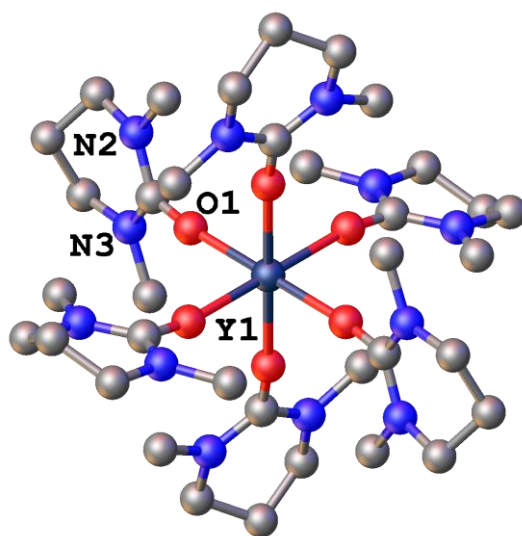


Figure 5. The structure of the $[\text{Y}(\text{DMPU})_6]^{3+}$ cation in the $[\text{Y}(\text{DMPU})_6]\text{I}_3$ salt. H-atoms have been omitted for clarity (Y = dark grey; O = red; N = blue; C = pale grey).

4.3 THF complexes of the chlorides

The THF complexes of the lanthanide chlorides are a case where stoichiometry does not always give a clear indication of structure [57]. This, in general, is one of the reasons why X-ray crystallography is so important in characterising lanthanide ion coordination chemistry, since electronic spectra of the complexes, where available, are rather insensitive to the nature of the primary coordination sphere and it has been observed in many crystal structures that good ligands incorporated in the crystals are not necessarily bound directly to the metal ions [58]. Both *mer*- $[\text{ScCl}_3(\text{THF})_3]$ [59] (Figure 6) and *mer*- $[\text{LuCl}_3(\text{THF})_3]$ [60]

feature octahedral six coordination and there is no crystal structure of the analogous yttrium complex.

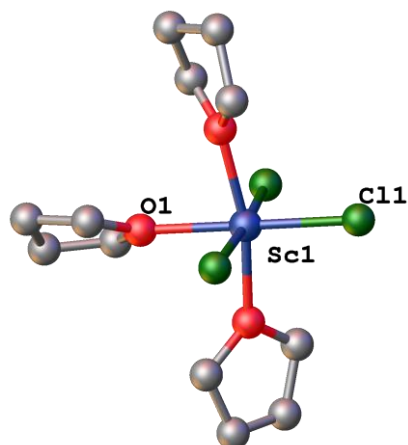


Figure 6. The structure of *mer*-[ScCl₃(THF)₃] with H-atoms removed for clarity (Sc = blue; Cl = green; O = red and C = light grey).

Seven coordination is found in [LnCl₃(THF)₄] (Ln = Nd-Gd) but earlier in the series [LnCl₃(THF)₂]_n (Ln = La-Nd) are obtained. Most have the structure [LnCl(μ-Cl)₂(THF)₂]_n (Ln = Ce-Nd) but the lanthanum compound is eight coordinate [La(μ-Cl)₃(thf)₂]_n [61] (Figure 7) with, perhaps, the larger size of the La³⁺ ion accommodating the additional bridging chloride ligand.

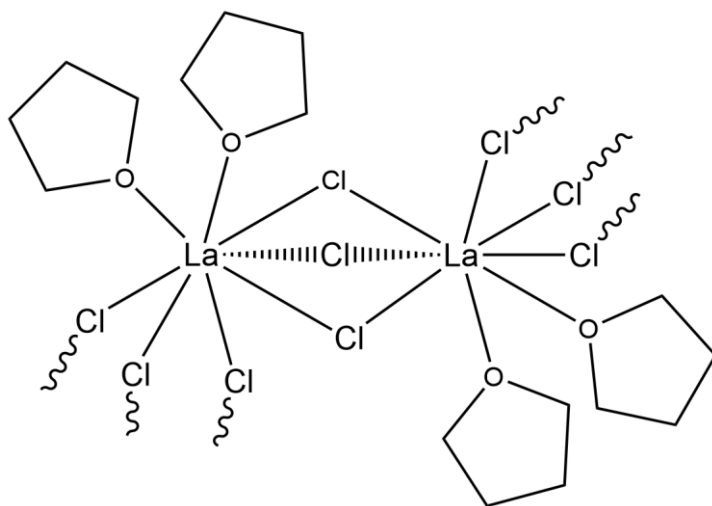


Figure 7. A schematic of the structure of [La(μ-Cl)₃(thf)₂]_n showing the polymeric nature of the structure (the polymeric links are shown as wiggly lines).

4.4 Triphenylphosphine oxide complexes

Triphenylphosphine oxide complexes of the lanthanide nitrates afford structural variety with different coordination numbers. [La(Ph₃PO)₄(NO₃)₃] attains nine coordination (Figure 8a) through one monodentate and two bidentate nitrates, but although Lu(Ph₃PO)₄(NO₃)₃ has a

similar molecular formula the presence of one ionic nitrate leads [62] to the lower coordination number of eight in $[\text{Lu}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_2]^+ \text{NO}_3^-$ (Figure 8b). The yttrium complex, $[\text{Y}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_2]^+ \text{NO}_3^-$, is also eight coordinate with one ionic nitrate [63]. The scandium complex has a different stoichiometry, and the presence of just two phosphine oxide ligands means that all three nitrates can adopt the bidentate mode in eight coordinate $[\text{Sc}(\text{Ph}_3\text{PO})_2(\text{NO}_3)_3]$ [64] (Figure 8c). Thus, the higher number of nitrates in its coordination sphere helps scandium to attain the same coordination number as lutetium and yttrium.

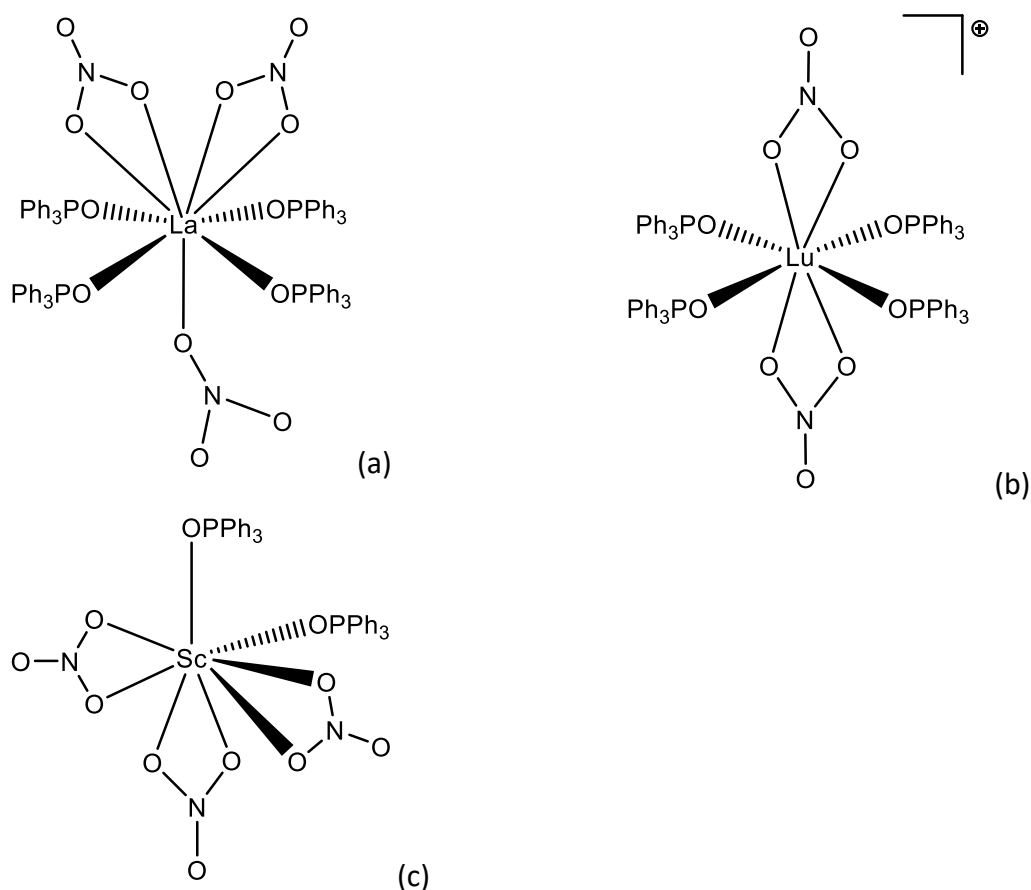


Figure 8. Schematic structures of the triphenylphosphine oxide clusters of (a) $[\text{La}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_3]$, (b) the $[\text{Lu}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_2]^+$ cation, and (c) $[\text{Sc}(\text{Ph}_3\text{PO})_2(\text{NO}_3)_3]$.

Triphenylphosphine oxide complexes of the triflates have also been examined. They have the same stoichiometry $[\text{M}(\text{Ph}_3\text{PO})_4(\text{CF}_3\text{SO}_3)_2]^+ (\text{CF}_3\text{SO}_3)^-$, but differ in the binding of the triflate groups. While the Y complex has not been reported the Sc and Lu compounds are both six coordinate (Figure 9a), with two monodentate triflates, whilst in the lanthanum complex (Figure 9b) (likewise elements as far as neodymium) one triflate is bidentate, affording seven coordination [65, 66].

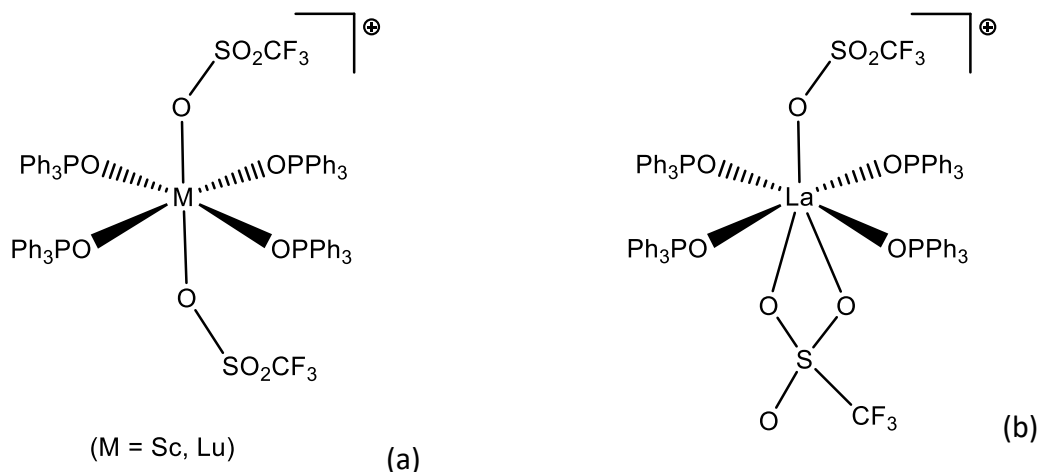


Figure 9. Schematic structures of the triphenylphosphine oxide complex salts of the triflates (a) $[M(\text{Ph}_3\text{PO})_4(\text{CF}_3\text{SO}_3)_2]^+ (\text{CF}_3\text{SO}_3)^-$ ($M = \text{Sc, Lu}$) and (b) $[\text{La}(\text{Ph}_3\text{PO})_4(\text{CF}_3\text{SO}_3)_2]^+ (\text{CF}_3\text{SO}_3)^-$

4.5 Alkylamides

Transition metal bis(trimethylsilyl)amides $[\text{M}(\text{N}(\text{SiMe}_3)_2)_3]$ ($M = \text{Ti to Co}$) are a well-known family of three coordinate compounds with planar MN_3 cores. In contrast to the compounds of the succeeding 3d metals, $[\text{Sc}(\text{N}(\text{SiMe}_3)_2)_3]$ has a pyramidal MN_3 core [67] as does the yttrium analogue [68] both showing disorder of the metal atom above and below the plane of the three N-donor atoms. This structural feature is also found in the crystal structures of their lanthanide analogues (La to Lu except Pm) with N–Ln–N angles around 114° rather than the 120° expected for a planar structure [69, 70]. Electron diffraction results indicate that the pyramidal structure is retained in the gas phase [71, 72], but the complexes are evidently planar in solution as they have no dipole moment. Theoretical calculations [73] suggest that it is $\beta\text{-Si-C}$ agostic interactions with the central metal that cause this small pyramidal distortion (Figure 10).

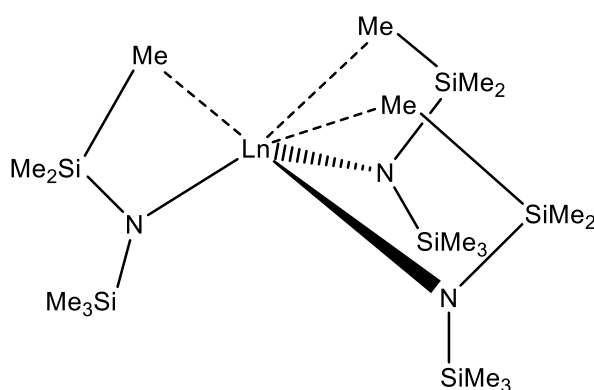


Figure 10. A schematic of the structure of the $[\text{Ln}(\text{N}(\text{SiMe}_3)_2)_3]$ (La to Lu except Pm) showing the proposed agostic interactions.

Lanthanum compounds with even bulkier amide ligands, $[\text{La}(\text{N}(\text{SiMe}_2\text{Bu}^t)_2)_3]$ and $[\text{La}(\text{N}(\text{SiMe}_2\text{Bu}^t)(\text{SiMe}_3))_3]$, do not show this distortion, both having planar LaN_3 cores [74]. In contrast to the bis(trimethylsilyl)amides, the less bulky diisopropylamides form isolable THF adducts, and here there is a significant difference between the metals. Lanthanum and yttrium form five coordinate $[\text{Ln}(\text{N}^i\text{Pr}_2)_3(\text{THF})_2]$ [75] (Figure 11a), whilst scandium and lutetium form four coordinate $[\text{M}(\text{N}^i\text{Pr}_2)_3(\text{THF})]$ [75, 76] (Figure 11b). However, these amides were synthesized and crystallized under differing conditions, which may render strict comparisons difficult.

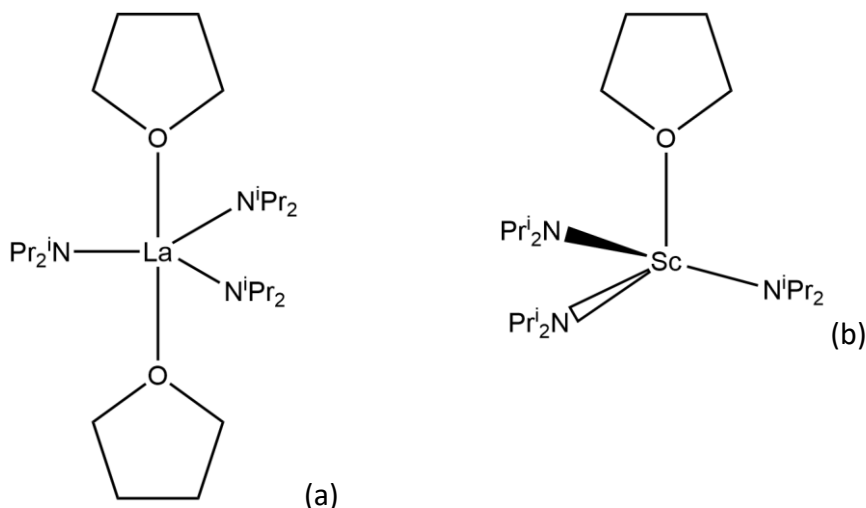


Figure 11. The schematic structures of (a) $[\text{La}(\text{N}^i\text{Pr}_2)_3(\text{THF})_2]$ and (b) $[\text{Sc}(\text{N}^i\text{Pr}_2)_3(\text{THF})]$

5. Compounds of bidentate ligands

5.1 Nitrate complexes

These exhibit the expected difference in coordination numbers. $[\text{Me}_4\text{N}]_3[\text{La}(\text{NO}_3)_6] \cdot \text{MeOH}$ has six nitrates arranged octahedrally round lanthanum (Figure 12a), resulting in 12 coordination; this coordination geometry is found in other hexanitrate complexes of the lanthanides [77]. $(\text{NH}_4)_2[\text{Lu}(\text{NO}_3)_5]$ has 10 coordinate lutetium, the nitrates being arranged in a trigonal bipyramidal arrangement round the metal [78] (Figure 12b).

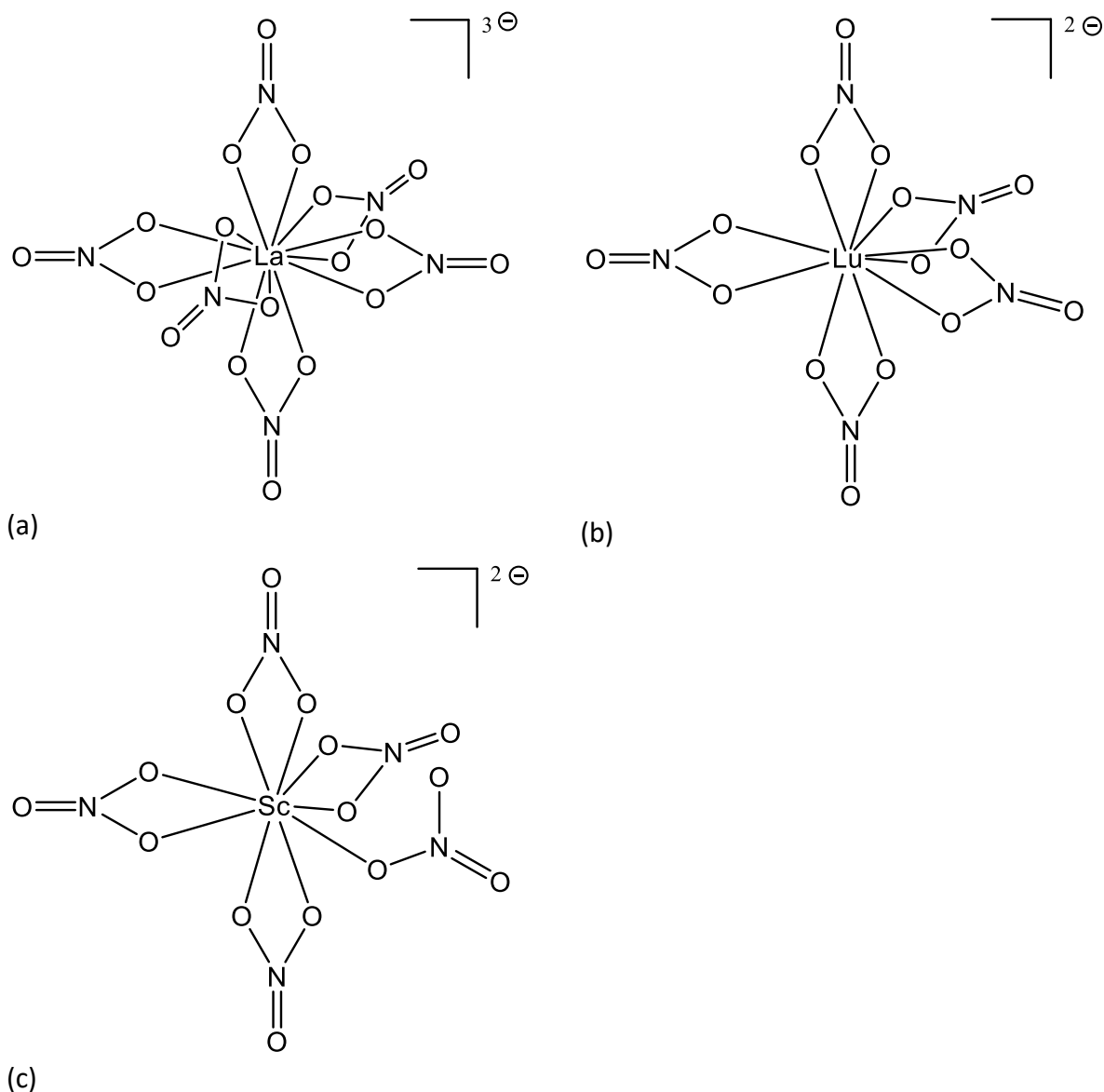


Figure 12. The schematic structures of (a) the $[La(NO_3)_6]^{3-}$ anion, (b) the $[Lu(NO_3)_5]^{2-}$ anion and (c) the $[Sc(NO_3)_5]^{2-}$ anion.

The complex $(NO)_2[Sc(NO_3)_5]$ again has a structure based on a trigonal bipyramid (Figure 12c). There are four bidentate nitrates with one of the equatorial nitrates being monodentate, leading to nine coordination, whereas in the yttrium analogue the five nitrate groups are symmetrically bidentate, giving an overall coordination number of ten [79] similar to that of the lutetium complex. In $Rb_2[Sc(NO_3)_5]$, however, there are three bidentate and two monodentate nitrates, resulting in eight coordinate scandium [80].

5.2 Carbonate complexes

The carbonate complexes of these metals are less well studied than the nitrates, though similarly they involve bidentate carbonates. Early lanthanides form $[Ln(CO_3)_4(H_2O)]^{5-}$ (Ln = Pr- Tb) whilst the heavier metals form $[Ln(CO_3)_4]^{5-}$ (Dy-Lu, Y). Structures of nine coordinate

$[\text{C}(\text{NH}_2)_3]_5 [\text{Ln}(\text{CO}_3)_4(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$) and of eight coordinate $[\text{C}(\text{NH}_2)_3]_5 [\text{Ln}(\text{CO}_3)_4] \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ and Y) have been determined [81]. Scandium [82] resembles lutetium in forming $[\text{Sc}(\text{CO}_3)_4]^{5-}$, present in $\text{K}_5[\text{Sc}(\text{CO}_3)_4] \cdot 5\text{H}_2\text{O}$ although the Sc-O bond lengths (mean 2.21 Å) are significantly shorter than Lu-O (mean 2.32 Å). The yttrium analogue, $[\text{Y}(\text{CO}_3)_4]^{5-}$ [83] (Figure 13), as the $[\text{C}(\text{NH}_2)_3]^+$ salt, also adopts a distorted dodecahedral geometry with an average Y-O bond length of 2.348(15) Å which is similar to the value for the Lu anion. No corresponding lanthanum complex has been reported in the solid state, though the $[\text{La}(\text{CO}_3)_4]^{5-}$ ion (degree of hydration not known) has been identified in aqueous solution [84], and lanthanum is known to be 10 coordinate in $\text{Na}_4\text{La}_2(\text{CO}_3)_5$ [83].

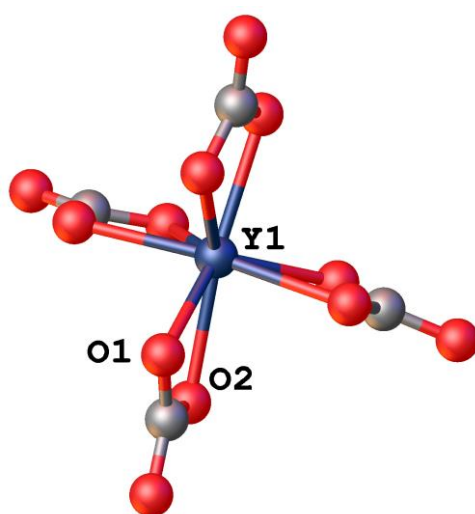


Figure 13. The structure of the $[\text{Y}(\text{CO}_3)_4]^{5-}$ anion (Y = dark blue; O = red; C = dark grey)

5.3 Complexes of bis(diphenylphosphino)methane dioxide

Complexes of bis(diphenylphosphino)methane dioxide ($\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$) with the triflates $\text{M}(\text{CF}_3\text{SO}_3)_3$ ($\text{M} = \text{Sc}, \text{Lu}$, and La) display a nice progression in the structures [85] (Figure 14). The scandium complex $[\text{ScL}_3](\text{CF}_3\text{SO}_3)_3$ exhibits approximately octahedral six-coordination (Figure 14a), whilst the slightly larger lutetium ion permits additional coordination of one water molecule in $[\text{LuL}_3(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_3$ with distorted pentagonal seven-coordination (Figure 14b). The crystal structure of the yttrium analogue has not been reported. The even larger lanthanum ion allows four ligands to bind to it in $[\text{LaL}_4](\text{CF}_3\text{SO}_3)_3$, in which lanthanum is in distorted square antiprismatic coordination (Figure 14c). Related eight-coordinate lanthanide complexes $[\text{Ln}(\text{dppmO}_2)_4]\text{Cl}_3$ and a six-coordinate Lu complex, $[\text{Lu}(\text{dppmO}_2)_2\text{Cl}_2]\text{Cl}$, have been synthesised [86], but scandium and yttrium analogues have not yet been characterised so that a full comparison is lacking.

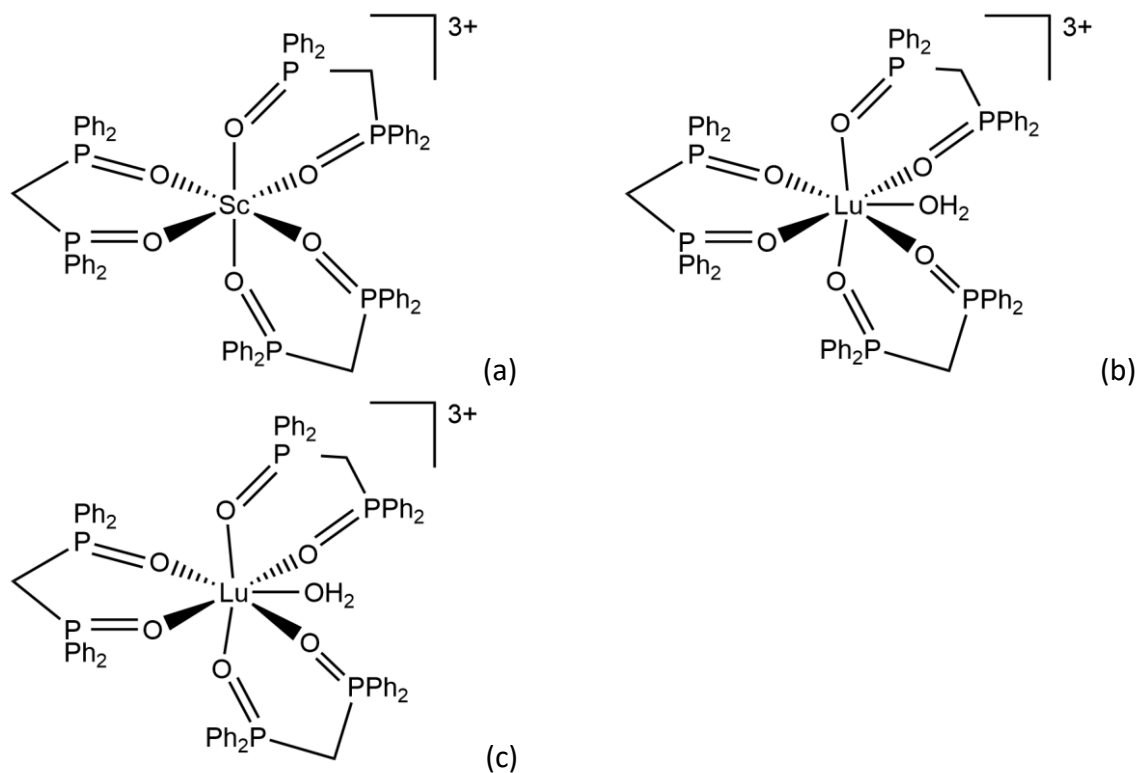
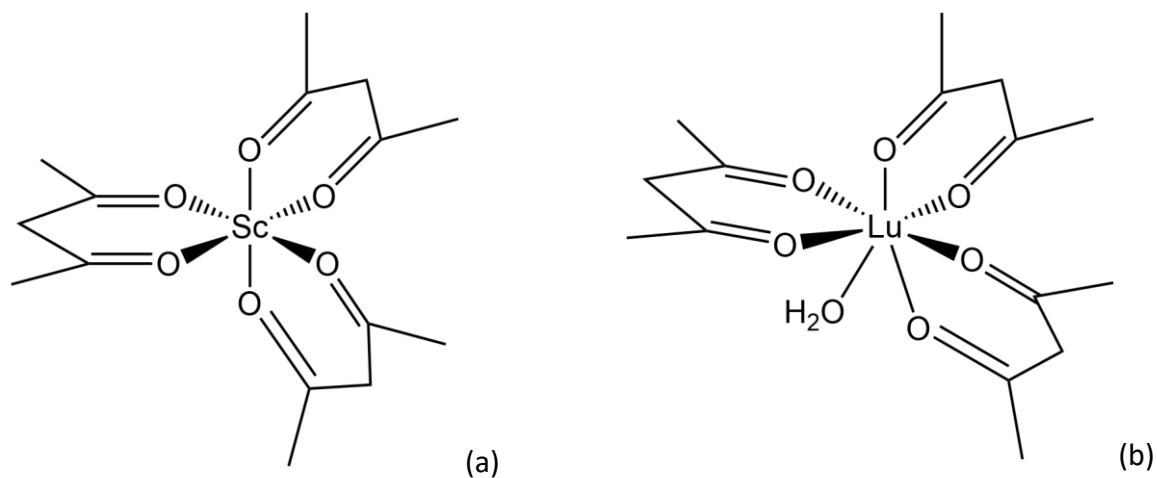
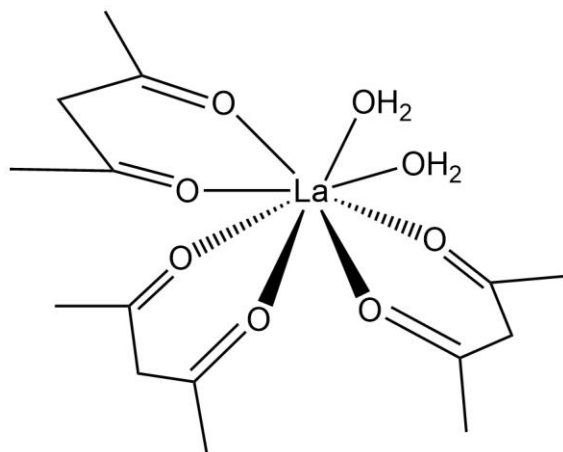


Figure 14. Schematic structures of the trications (a) $[\text{ScL}_3]^{3+}$, (b) $[\text{LuL}_3(\text{H}_2\text{O})]^{3+}$ and (c) $[\text{LaL}_4]^{3+}$ where $\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$.

5.4 β -diketonate complexes

For the simplest of these, the acetylacetonates, there is a clear progression in coordination number. $[\text{Sc}(\text{acac})_3]$ has distorted octahedral six coordination [87, 88] (Figure 15a); whilst the structure of $[\text{Lu}(\text{acac})_3(\text{H}_2\text{O})]$ has not been reported, it is believed to be very similar [89] (Figure 15b) to seven coordinate $[\text{Yb}(\text{acac})_3(\text{H}_2\text{O})]$. The yttrium(III) complex, $[\text{Y}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ is eight coordinate with an additional water molecule in the crystal lattice [90]. The La(III) complex, $[\text{La}(\text{acac})_3(\text{H}_2\text{O})_2]$, is also eight coordinate [91] (Figure 15c).





(c)

Figure 15. Schematic structures of the carboxylate complexes (a) $[\text{Sc}(\text{acac})_3]$, (b) $[\text{Lu}(\text{acac})_3(\text{H}_2\text{O})]$ and (c) $[\text{La}(\text{acac})_3(\text{H}_2\text{O})_2]$.

The tertiary-butyl groups make tetramethylheptanedioate bulkier than the acetylacetonate ligand. $[\text{M}(\text{tmhd})_3]$ ($\text{M} = \text{Sc}$ [92], Lu [93] and Y [68]) are all six coordinate (Figure 16), with very distorted octahedral coordination spheres, whilst the lanthanum compound is a dimer, with two chelating diketonates also involved as bridging ligands, resulting in seven coordinate lanthanum [94] (Figure 17).

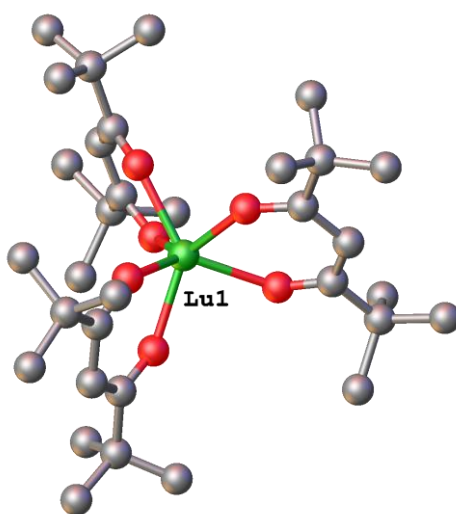


Figure 16. The structure of $[\text{M}(\text{tmhd})_3]$. H-atoms have been omitted for clarity (Lu = green; O = red; C = light grey).

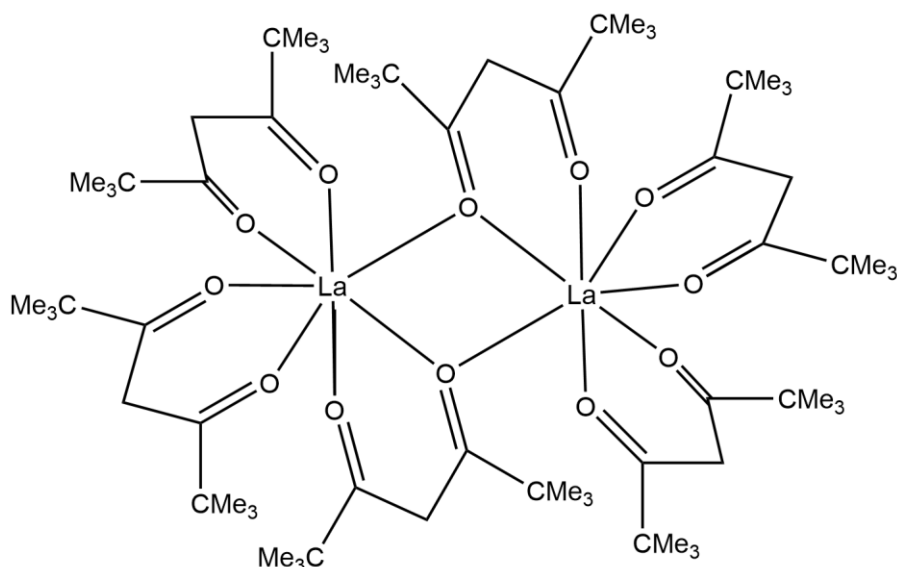


Figure 17. Schematic structure of the La(III) dimer $[La(tmhd)_3]_2$.

5.5 Acetates

The anhydrous lanthanide acetates $[Ln(OAc)_3]$ have structures [95] involving several types of bridging and chelating acetate, displaying a decrease in coordination number from 10 at the beginning of the series to 7 at the end. The $[Sc((OAc)_3)]$ complex has a simple polymeric structure with a linear chain of metal ions connected by three bridging acetate groups on either side, affording octahedral six coordination [96] (Figure 18a). $[Ln(OAc)_3]$ ($Ln = Tm-Lu$) are similar, except that two of the bridging acetates have a single oxygen bridging the two metals, whilst the acetate group acts as a chelating ligand to one lutetium, resulting in seven coordination [97] (Figure 18b). The acetates of yttrium and the lanthanides from Sm to Er are eight coordinate and involve both chelating and chelating bridging acetates. $[Nd(OAc)_3]$ has both 8 and 9 coordinate metal ions, whilst praseodymium is 9 and 10 coordinate in $Pr(OAc)_3$. Finally $[Ln(OAc)_3]$ ($Ln = La, Ce$) have 10 coordination, with tetradentate double-bridging and bridging bidentate acetate groups [98].

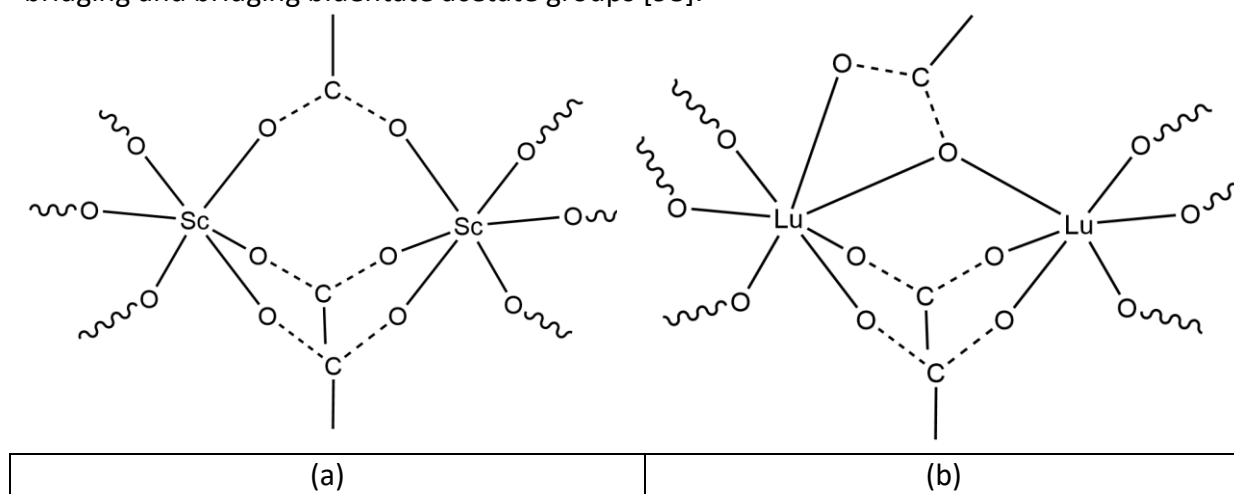
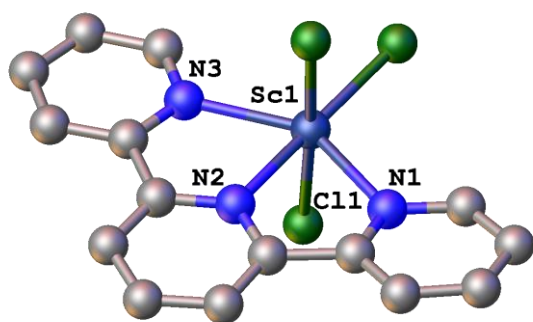


Figure 18. Schematic diagrams of $[\text{Sc}(\text{OAc})_3]_\infty$ and $[\text{Lu}(\text{OAc})_3]_\infty$ showing the polymeric nature of the structures (the wiggly lines showing the connections to the next Lu atoms in the chain and the dashed lines emphasise the delocalisation within the acetate groups).

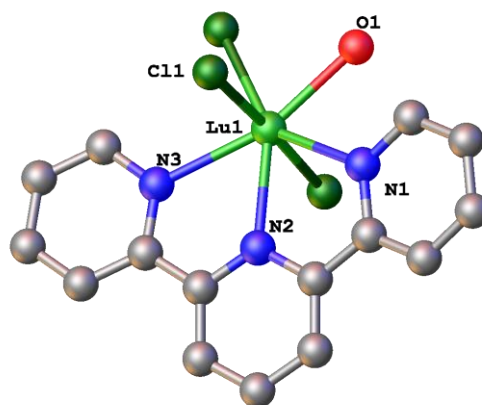
6. Ligands with N-donor atoms

6.1 2,2': 6',2''-terpyridine complexes of the metal chlorides

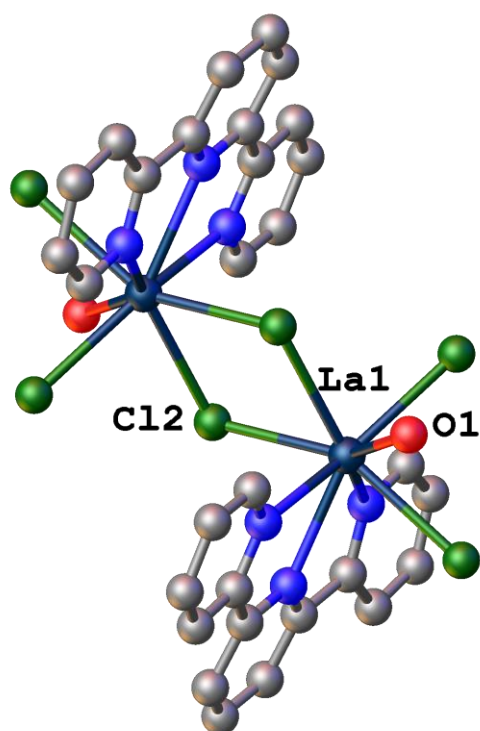
Scandium exhibits *mer*-octahedral coordination in *mer*- $[\text{ScCl}_3(\text{terpy})]$ (Figure 19a), where the terdentate ligand is responsible for imposing that geometry. The increased size of the lutetium and yttrium ions additionally permits a water molecule to bind in the seven coordinate $[\text{MCl}_3(\text{terpy})(\text{H}_2\text{O})]$ (M = Y, Lu) complex (Figure 19b). The even larger lanthanum does not coordinate a second water molecule, but instead adopts a dimeric structure with two bridging chlorides to attain eight coordination in $[(\text{La}(\text{terpy})(\text{H}_2\text{O})\text{Cl}_2)_2(\mu\text{-Cl})_2]$ (Figure 19c). Clearly coordination number increases in line with increasing ionic radius of the metal [99].



(a)



(b)



(c)

Figure 19. The structures of (a) $[\text{ScCl}_3(\text{terpy})]$, (b) $[\text{LuCl}_3(\text{terpy})(\text{H}_2\text{O})]$ and (c) $[(\text{La}(\text{terpy})(\text{H}_2\text{O})\text{Cl}_2)_2(\mu\text{-Cl})_2]$. H-atoms have been omitted for clarity (Sc = dark blue; Lu = light green; La = dark blue; Cl = green; N = blue; O = red; C = light grey).

6.2 Terpyridine complexes of the metal nitrates, $[\text{M}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})_n]$

As already noted, the bidentate nitrate group with its small bite angle is often associated with high coordination numbers, and these complexes are no exception [100].

The majority of lanthanides form 10-coordinate $[\text{Ln}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$ (Ln = Ce-Ho except Pm), but exceptionally lanthanum forms 11-coordinate $[\text{La}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ (Figure 20) whilst the four smallest lanthanides adopt 9 coordinate $[\text{Ln}(\text{terpy})(\text{NO}_3)_3]$ (Ln = Er-Lu) [101, 102], in keeping with the decreasing radius of the Ln^{3+} ions with increasing atomic number.

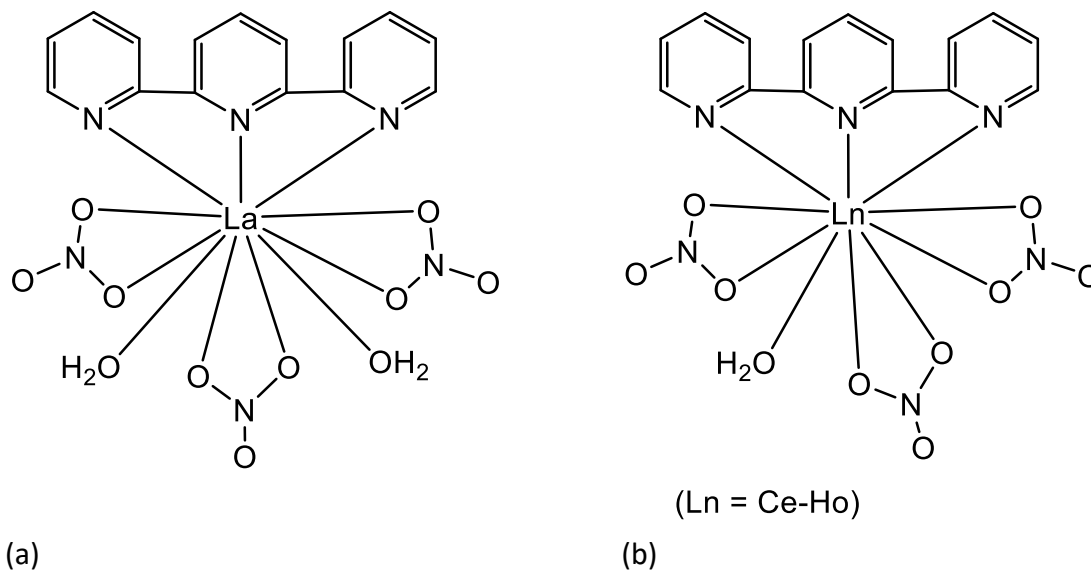


Figure 20. Schematic structures of (a) [La(terpy)(NO₃)₃(H₂O)₂] and (b) Ln(terpy)(NO₃)₃(H₂O) (Ln = Ce-Ho except Pm).

The compounds show smooth progression in bond length with decreasing ionic radius of Ln³⁺, clearly seen in the short series [Ln(terpy)(NO₃)₃] (Ln = Er to Lu) which makes a cogent point about congestion in the coordination sphere. Comparing Er(terpy)(NO₃)₃ with Lu(terpy)(NO₃)₃, the average Ln-N bond length decreases from 2.424 Å in the erbium compound to 2.394 Å in the lutetium compound, corresponding changes in Ln-O (nitrate) being from 2.406 Å to 2.380 Å, in keeping with a decrease from 1.030 to 1.001 Å in ionic radius for the nine-coordinate ions [13]. The spread of Ln-O distances involving the coordinated nitrate groups increases from 0.070 Å in the erbium complex to 0.090 Å in the lutetium compound, which may indicate growing congestion.

The scandium compound (Figure 21a) has the same stoichiometry as those of the later lanthanides, but examination of its molecular structure [103] reveals a significant increase in congestion over the lutetium compound (Figure 21b). The Sc-O distances in [Sc(terpy)(NO₃)₃] range from 2.232(2) Å to 2.458(2) Å, a considerably bigger spread of distances (0.226 Å) than observed even in [Lu(terpy)(NO₃)₃], reflecting the difficulty in arranging the nine donor atoms round the small Sc³⁺ ion. Here the longest Sc-O distance of 2.458 Å is over 0.14 Å longer than the next longest (2.315 Å), and nine-coordinate is an optimistic description of the complex (‘8.5 coordinate’ is a possible description). The mean Sc-N bond length (2.30 Å) is significantly shorter than that of Lu-N bond (2.394 Å), a factor which may contribute to partial displacement of the nitrate ligands. Interestingly, depending on the recrystallisation conditions, two different structures have been obtained for the yttrium terpy *tris*-nitrate complex by recrystallisation from acetonitrile. One complex [Y(terpy)(NO₃)₃(H₂O)] is nine co-ordinate with two bidentate nitrates and one

monodentate nitrate, and the last coordination site being occupied by a water molecule. The Y-O(nitrate) distances range from 2.330(2) to 2.504(2) Å, and the Y-O(water) distance is 2.311(3) Å. The second isomer of the complex is ten coordinate but with the formula $[\text{Y}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{MeCN} \cdot \text{terpy}$, having both an acetonitrile molecule and a free terpyridine molecule in the crystal lattice. In this case the three nitrate groups are considered to be bidentate although one is distinctly more asymmetric (2.414(3) vs. 2.736(2) Å) than the other two (2.444(3) to 2.523(3) Å) [104].

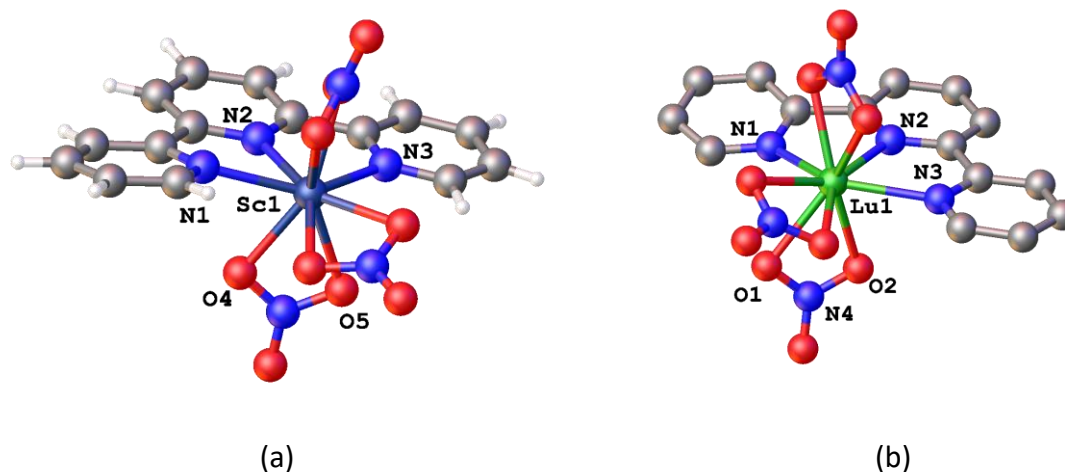


Figure 21. The structures of (a) $[\text{Sc}(\text{terpy})(\text{NO}_3)_3]$ and (b) $[\text{Lu}(\text{terpy})(\text{NO}_3)_3]$. H-atoms have been omitted for clarity (Sc = dark blue; Lu = green; N = blue; O = red; C = light grey).

6.3 Complexes of EDTA ($\text{EDTAH}_4 = \text{Ethylenediaminetetraacetic acid}$) and related ligands

EDTA forms strong complexes with scandium, yttrium and all the lanthanides.

$\text{NH}_4[\text{Sc}(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ contains eight coordinate $[\text{Sc}(\text{EDTA})(\text{H}_2\text{O})_2]^-$ ions [105] (Figure 22a); similarly $\text{C}(\text{NH}_2)_3[\text{Lu}(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, isomorphous with its ytterbium analogue [106], has eight coordinate $[\text{Lu}(\text{EDTA})(\text{H}_2\text{O})_2]^-$. $\text{K}[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$ has nine coordinate $[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3]^-$ ions (Figure 22b). In all of these complexes, the EDTA is hexadentate, binding through two nitrogen donor and four oxygen donor atoms and wrapping itself round the metal ions, leaving space for additional water molecules to come into the coordination sphere.

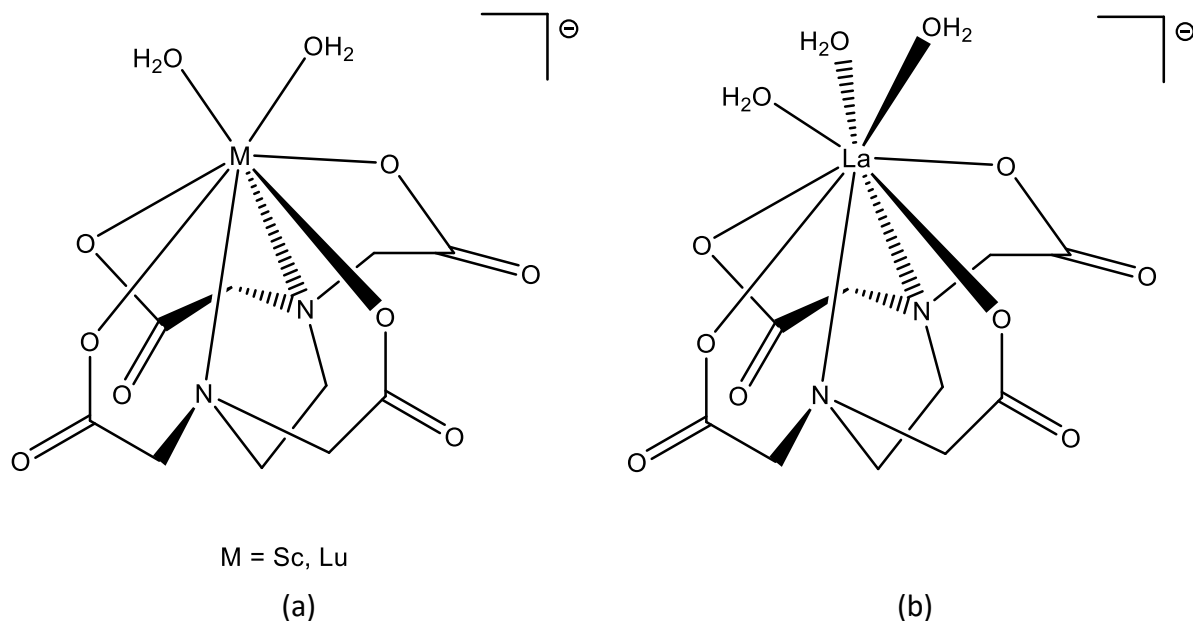


Figure 22. Schematic diagrams of the anions (a) $[\text{Sc}(\text{EDTA})(\text{H}_2\text{O})_2]^-$ and (b) $[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3]^-$.

It is pertinent to remark again that, allowing for solubility effects, the counter-ion can influence the thermodynamic product that crystallises from solution, so that sodium ions crystallise the $[\text{Er}(\text{EDTA})(\text{H}_2\text{O})_3]^-$ ion, with NH_4^+ cation favouring $[\text{Er}(\text{EDTA})(\text{H}_2\text{O})_2]^-$. However, this complication is only likely to occur around the point (Ho-Er) where both the eight and nine-coordinate anions are present in solution in significant amounts, and is unlikely to affect metals at the extremes of the series [108].

In contrast to the situation with EDTA, scandium exhibits a different coordination number to its yttrium and lutetium analogues in its complex with DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate). In $\text{K}[\text{Sc}(\text{DOTA})][\text{H}_6\text{DOTA}]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ scandium binds to four nitrogen donors and four carboxylate oxygen atoms [109] but there is no space in the coordination sphere to bind a water molecule to the $[\text{Sc}(\text{DOTA})]^-$ ion (Figure 23). A similar situation exists in $3(\text{Na}[\text{Sc}(\text{DOTA})])$, $\text{NaOH} \cdot 18\text{H}_2\text{O}$ [110].

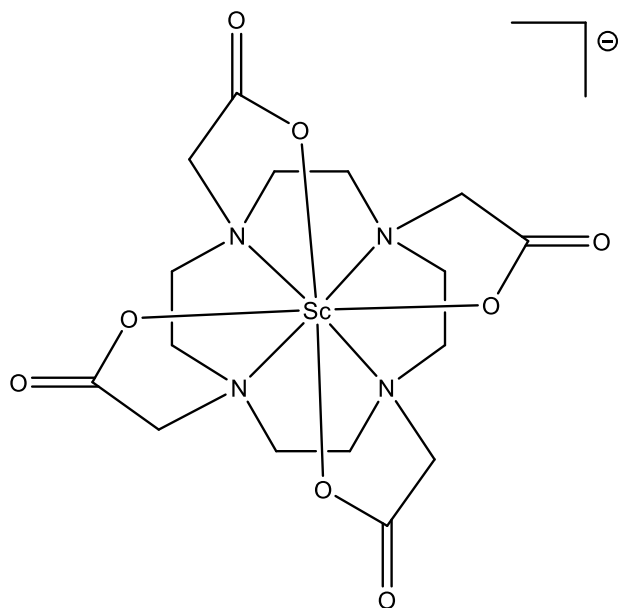


Figure 23. The schematic structure of the $[\text{Sc}(\text{DOTA})]^-$ anion.

In contrast, $\text{Na}[\text{Lu}(\text{DOTA})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ and $\text{Na}[\text{Y}(\text{DOTA})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ both have nine-coordinate metal centres in the solid state [111, 112] adopting a monocapped square antiprism with a coordinated water molecule occupying the capping site (Figure 24). However, in the case of lutetium EXAFS measurements have failed to locate a coordinated water molecule in solution [113].

The solid state structure of $\text{Na}[\text{La}(\text{HDOTA})\text{La}(\text{DOTA})]\cdot 10\text{H}_2\text{O}$ shows it [114] to contain a dimerised unit with a bridging carboxylate group, but in solution it is believed to exist as a $[\text{La}(\text{DOTA})(\text{H}_2\text{O})]^-$ ion, similar to cerium and other lanthanides [115, 116].

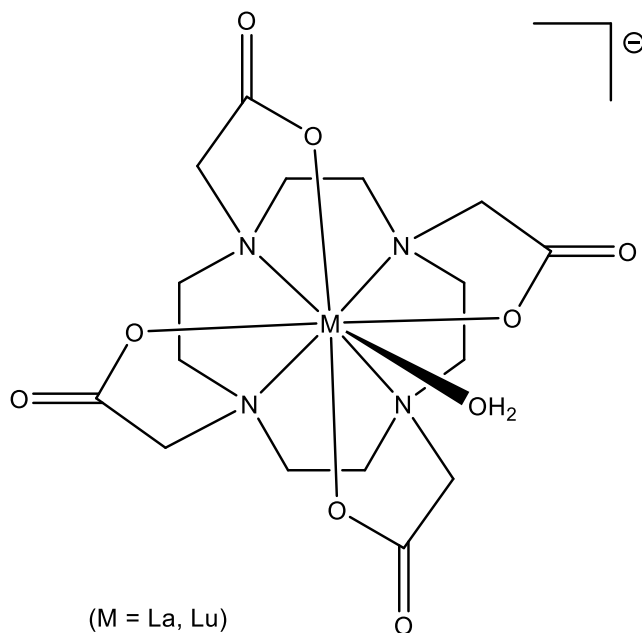


Figure 24. A schematic of the generic structure for the $[M(\text{DOTA})(\text{H}_2\text{O})]^-$ anions $M = \text{Y, La, Ce}$ and Lu .

7. Organometallic compounds

7.1 Benzyls

Tribenzyls are formed by scandium, yttrium and all the lanthanides; they are isolated as THF adducts with the formula $[M(\text{benzyl})_3(\text{THF})_3]$. There is more to this than at first meets the eye. $[\text{Sc}(\text{benzyl})_3(\text{THF})_3]$, $[\text{Y}(\text{benzyl})_3(\text{THF})_3]$ and $[\text{Lu}(\text{benzyl})_3(\text{THF})_3]$ are all six-coordinate with η^1 -benzyls [117, 118] (Figure 25a), but the greater size of the lanthanum ion means that the adoption of this structure would leave space around the ion to accommodate additional ligands. In this case three additional *ipso*-interactions are observed (with La-C distances some 0.3 Å longer than the other La-C bonds) and this results in the benzyl groups adopting η^2 -coordination (Figure 25b) [119].

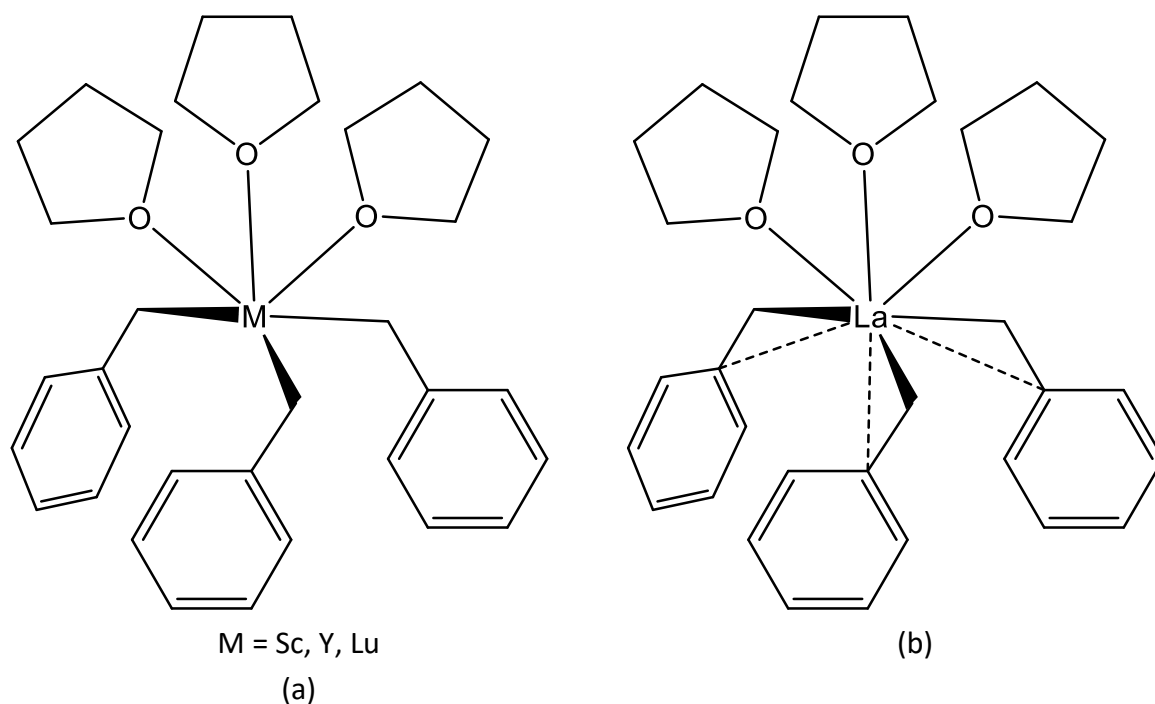


Figure 25. Schematic structures of the $[M(\text{benzyl})_3(\text{THF})_3]$ complexes, (a) $M = \text{Sc, Y, Lu}$ and (b) La

When triturated with hexane or recrystallised from toluene, $[M(\text{benzyl})_3(\text{THF})_3]$ ($M = \text{Sc, Lu}$) lose one molecule of THF, forming $[M(\text{benzyl})_3(\text{THF})_2]$. These have different structures. All the benzyl groups remain η^1 - in the five coordinate Sc compound [117] (Figure 26a), but one benzyl has an *ipso*-interaction in the lutetium compound (Figure 26b), evidently on account of the slightly greater size of lutetium(III) [120].

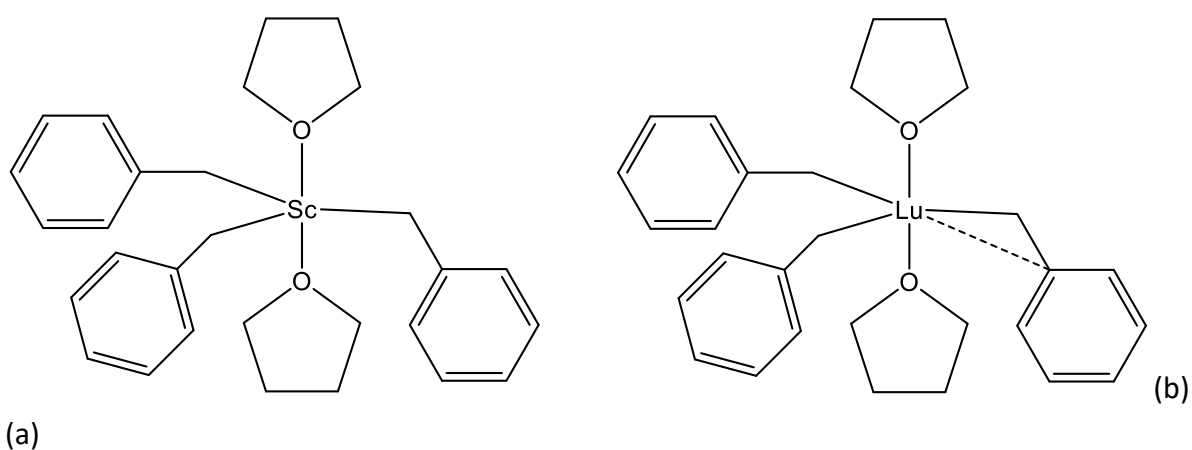


Figure 26. Schematic structures of the (a) Sc and (b) Lu examples of the $[M(\text{benzyl})_3(\text{THF})_2]$ complexes.

7.2 Tris(trimethylsilyl)methyl complexes

Lanthanide *tris*(trimethylsilyl)methyl complexes are too unstable to be crystallised for the early lanthanides, and isolable compounds can only be obtained (e.g. as THF adducts) from samarium onwards [121]. Crown ether adducts $[\text{Ln}(12\text{-crown-4})(\text{CH}_2\text{SiMe}_3)_3]$ (Ln e.g. Y, Lu) all have seven coordinate 'piano-stool structures' (Figure 27a) [122]. The scandium analogue is, however, only six-coordinate (Figure 27b), as evidently scandium is too small to span all four ether oxygen atoms [123].

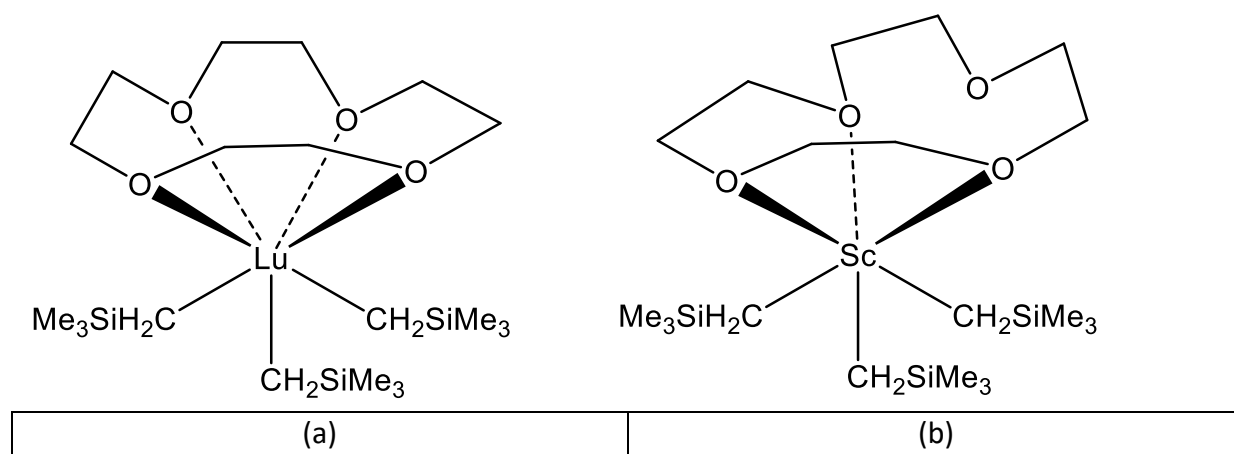


Figure 27. Schematic structures of the $[\text{M}(12\text{-crown-4})(\text{CH}_2\text{SiMe}_3)_3]$ complexes, (a) $\text{M} = \text{Y}, \text{Lu}$ and (b) $\text{M} = \text{Sc}$.

7.3 Tris(cyclopentadienyl) compounds

The tris(cyclopentadienyl) compounds of the rare earths, $[(\text{C}_5\text{H}_5)_3\text{Ln}]$, display an interesting variety of structures (Figure 28). Essentially molecular structures are only displayed by the yttrium compound [124] and those of a few lanthanides of similar size (e.g. Ho, Er, Tm). Larger lanthanides have polymeric structures, illustrated by the lanthanum compound [125], where lanthanum is attached to three η^5 -rings, one of which also participates in a η^2 attachment to a neighbouring lanthanum. If a Cp ring is thought of as occupying three coordination sites, then this approximates to 11-coordinate lanthanum. It should be noted that our use of coordination number assignments for Cp-rings differs from the more rigid IUPAC/Werner guidelines that are based on the number of atoms that form dative bonds. At the other end of the lanthanide series, lutetium can only bind to two η^5 -rings, also forming two η^1 -attachments to bridging rings, approximating to eight-coordination [126]. The scandium compound is isostructural [127].

The metal ion evidently attains the highest coordination number possible consistent with its size, making use of the ability of the cyclopentadienyl ligand to adopt more than one bonding mode.

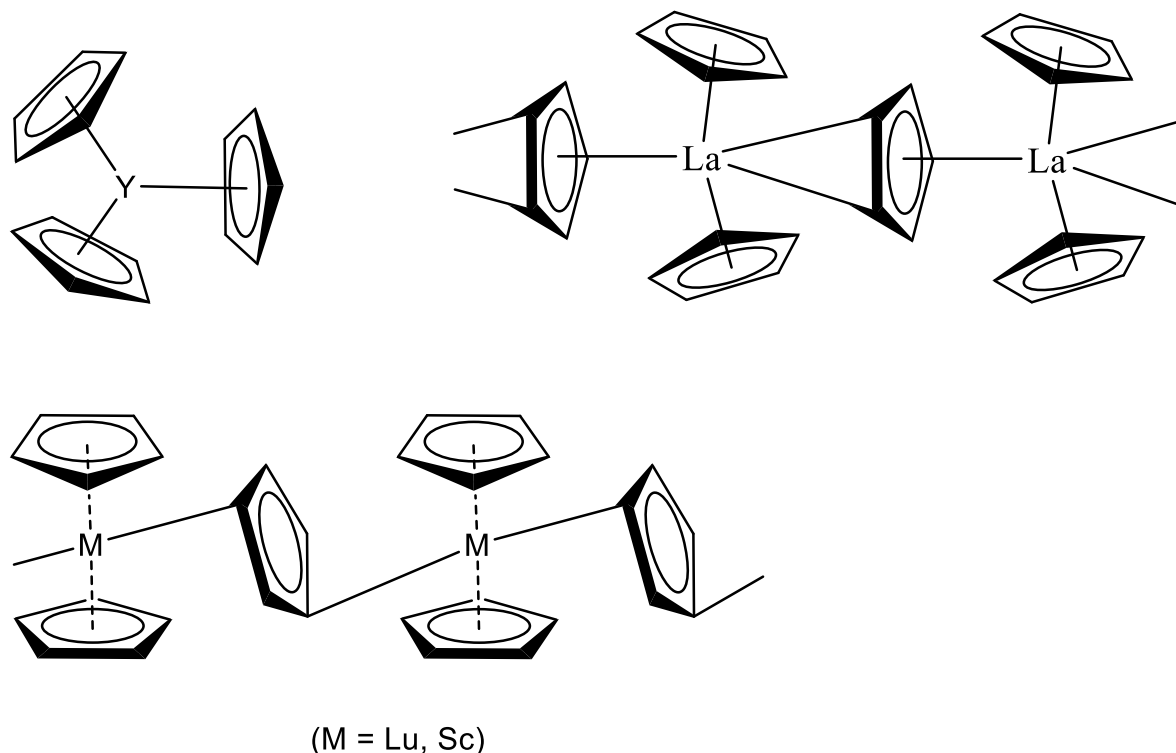


Figure 28. Schematic structures of the Tris(cyclopentadienyl) complexes of Sc, Y and the lanthanides.

Cyclopentadienyl derivatives of the lanthanides have been studied for many years, but it is only relatively recently that more bulky ligands have been investigated. It was believed for a long while that compounds $[(C_5Me_5)_3Ln]$ were not likely to be isolable on account of the bulk of the substituted ring, but following a breakthrough in the synthesis of the samarium compound, imaginative synthetic techniques have led to the synthesis of the series up to $[(C_5Me_5)_3Er]$ [128]. There is no report of the isolation of the lutetium or scandium compounds.

Use of the less demanding C_5Me_4H ligand affords interesting comparisons. $[(C_5Me_4H)_3Ln]$ ($Ln = La$ [129], Lu [130]) (Figure 29a) are isostructural, with three *pentahapto* cyclopentadienyl rings. Assuming that a Cp ring takes up three coordination sites, this corresponds to nine coordination. The metal-to-ring centroid distance decreases from 2.616 Å in the lanthanum compound to 2.406 Å in the lutetium compound, rather more than the 0.164 Å predicted from ionic radii [13]. It is notable (and counter-intuitive) that lutetium can accommodate three *pentahapto*- C_5Me_4H rings, but not three of the less bulky C_5H_5 , in the solid state, at least. The yttrium complex, $[(C_5Me_4H)_3Y]$, also accommodates three *pentahapto*- C_5Me_4H rings [131, 132].

However, in the solid state the corresponding scandium compound has the structure $[(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)]$ with one *monohapto* C_5Me_4H ligand, a consequence of the

smaller size of scandium (Figure 29b). Only one type of C_5Me_4H ring is seen in the solutions down to $-80\text{ }^\circ\text{C}$, evidently due to fluxional behaviour [133].

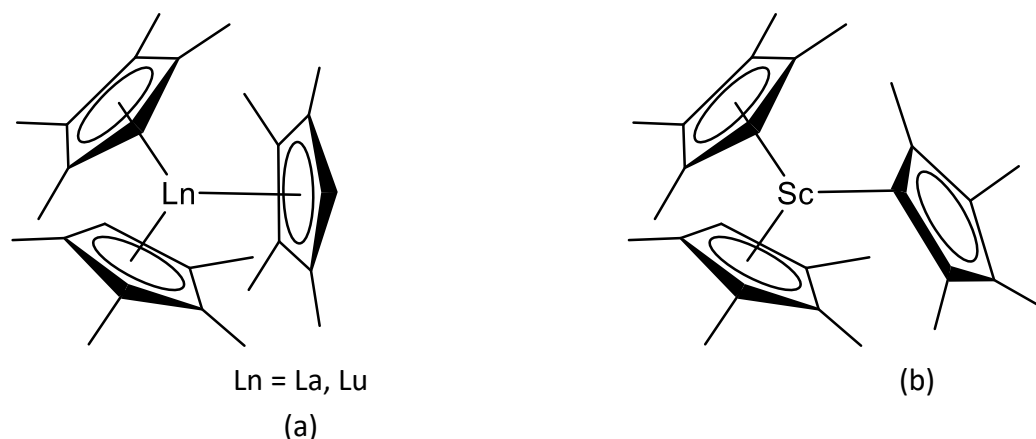


Figure 29. Schematic structures of the $[(C_5Me_4H)_3Ln]$ complexes (a) ($Ln = La, Lu$) and of the (b) Sc analogue showing the difference in coordination.

Discussion and Conclusions

Table 3 contains a summary of the structures of the compounds and complexes of Sc^{3+} , Y^{3+} , La^{3+} and Lu^{3+} metal ions giving details of the coordination numbers of the metals and highlighting differences between the coordination numbers for each class of compound for the four elements. The Table lists 29 sets of compounds of Sc, Y, La and Lu where at least three of the elements form compounds with the same ligands. In 14 of them, scandium and lutetium have the same coordination number; in the remaining 15 they do not. The 15 examples where there are differences in coordination number for Sc and Lu are highlighted in yellow. Similarly, there are 10 examples where there is a difference in coordination number between Lu and Y for compounds with the same ligands and these are highlighted in grey. For the other 19 either the coordination numbers are the same or that compounds for both the elements under consideration do not exist. This comparative data provides a more comprehensive analysis across the coordination chemistry of these elements than does a selective choice of one or two series of complexes.

Table 3. Co-ordination Numbers for Compounds and Co-ordination Complexes of the Sc³⁺, Y³⁺, La³⁺ and Lu³⁺ Ions

Compound	Sc compound/complex		Ref	Y compound/complex		Ref
	Formula	C.N.		Formula	C.N.	
Oxide	Sc ₂ O ₃	6	[30]	Y ₂ O ₃	6	[134]
Fluoride	ScF ₃	6	[30]	YF ₃	9	[30]
Chloride	ScCl ₃	6	[30]	YCl ₃	6	[30]
Bromide	ScBr ₃	6	[30]	YBr ₃	6	[30]
Iodide	ScI ₃	6	[30]	YI ₃	6	[30]
Hydrated triflate M(CF ₃ SO ₃) ₃ .nH ₂ O	[Sc(H ₂ O) ₈](CF ₃ SO ₃) ₃	8	[36]	[Y(H ₂ O) ₉](CF ₃ SO ₃) ₃	9	[37]
Aqua ion	[Sc(H ₂ O) _n] ³⁺	7	[36]	[Y(H ₂ O) ₈] ³⁺	8	[135]
DMSO complex	[Sc(DMSO) ₆] ³⁺	6	[52]	[Y(DMSO) ₈] ³⁺	8	[53]
N,N-dimethylpropylene urea complex	[Sc(DMPU) ₆] ³⁺	6	[41]	[Y(DMPU) ₆] ³⁺	6	[53]
Tris(diisopropyl)amide)	[Sc(N ⁱ Pr ₂) ₃ (THF)]	4	[76]	[Y(N ⁱ Pr ₂) ₃ (THF) ₂]	5	[136]
Bis(trimethylsilyl)amide	Sc(N(SiMe ₃) ₂) ₃	3	[67]	Y(N(SiMe ₃) ₂) ₃	3	[68]
THF adduct of trichloride	ScCl ₃ (THF) ₃	6	[59]	YCl ₃ (THF) _{3.5}	7,6	[137]
				[YCl ₃ (THF) ₂] _n	7	[137]
Terpy complex of chloride	ScCl ₃ (terpy)	6	[99]	[YCl ₃ (terpy)(H ₂ O)]	7	[99]
Terpy complex of nitrate	Sc(NO ₃) ₃ (terpy)	8.5	[103]	Y(NO ₃) ₃ (terpy)(H ₂ O)	10	[104]
Ph ₃ PO complex of nitrate	[Sc(η ² -NO ₃) ₃ (Ph ₃ PO) ₂]	8	[64]	[Y(η ² -NO ₃) ₃ (Ph ₃ PO) ₃]	9	[64]
Ph ₃ PO complex of triflate	[Sc(Ph ₃ PO) ₄ (η ¹ -OTf) ₂] ⁺ OTf ⁻	6	[66]			
Ph ₂ P(O)CH ₂ P(O)Ph ₂ complex of triflate	[ScL ₃](OTf) ₃	6	[85]			
Acetylacetonate	Sc(acac) ₃	6	[87]	Y(acac) ₃ (H ₂ O) ₂	8	[90]
Tetramethylheptanedionate	Sc(tmhd) ₃	6	[92]	Y(tmhd) ₃	6	[138]
Acetate (anhydrous)	Sc(OAc) ₃	6	[96]	Y(OAc) ₃	8	[97]
Nitrate complex	[Sc(NO ₃) ₅] ²⁻	9	[80]	[Y(NO ₃) ₅] ²⁻	10	[139]

Carbonate complex ³	[Sc(CO ₃) ₄] ⁵⁻	8	[82]	[Y(CO ₃) ₄] ⁵⁻		
EDTA complex	[Sc(EDTA)(H ₂ O) ₂] ⁻	8	[105]	[Y(EDTA)(H ₂ O) ₃] ⁻	9	[140]
DOTA complex	[Sc(DOTA)] ⁻	8	[109]	[Y(DOTA)(H ₂ O)] ⁻	9	[112]
Benzyl tris(THF) adduct	fac-[ScBz ₃ (THF) ₃]	6	[117]	fac-[YBz ₃ (THF) ₃]	6	[118]
Benzyl bis(THF) adduct	fac-[ScBz ₃ (THF) ₂]	5	[117]			
Tris(cyclopentadienyl) ⁴	[(η ⁵ -C ₅ H ₅) ₂ Sc(μ-η ¹ :η ¹ -C ₅ H ₅)] _∞	8	[127]	[(η ⁵ -C ₅ H ₅) ₃ Y]	9	[124]
Tris(tetramethylcyclopentadienyl) ⁴	[(η ⁵ -C ₅ Me ₄ H) ₂ Sc(η ¹ -C ₅ Me ₄ H)]	7	[133]	[(η ⁵ -C ₅ Me ₄ H) ₃ Y]	9	[141]
12-crown-4 adduct of M(CH ₂ SiMe ₃) ₃	[Sc(CH ₂ SiMe ₃) ₃ (12-crown-4)]	6 ⁵	[123]	[Y(CH ₂ SiMe ₃) ₃ (12-crown-4)]	7	[122]
	La compound/complex			Lu compound/complex		
Compound	Formula	C.N.	Ref	Formula	C.N.	
Oxide	La ₂ O ₃	7	[30]	Lu ₂ O ₃	6	[30]
Fluoride	LaF ₃	9+2	[30]	LuF ₃	9	[30]
Chloride	LaCl ₃	9	[29, 30]	LuCl ₃	6	[29, 30]
Bromide	LaBr ₃	9	[29, 30]	LuBr ₃	6	[29, 30]
Iodide	LaI ₃	8	[29, 30]	LuI ₃	6	[29, 30]
Hydrated triflate M(CF ₃ SO ₃) ₃ .nH ₂ O	[La(H ₂ O) ₉](CF ₃ SO ₃) ₃	9	[35]	[Lu(H ₂ O) _{8.2}](CF ₃ SO ₃) ₃	8.2	[35]
Aqua ion	[La(H ₂ O) ₉] ³⁺	9	[37]	[Lu(H ₂ O) ₈] ³⁺	8	[42]
DMSO complex	[La(DMSO) ₈] ³⁺	8	[54]	[Lu(DMSO) ₆] ³⁺	8	[54]
N,N-dimethylpropylene urea complex	[La(DMPU) ₇] ³⁺	7 ²	[56]	[Lu(DMPU) ₆] ³⁺	6 ²	[56]
Tris(diisopropyl)amide)	[La(N ⁱ Pr ₂) ₃ (THF) ₂]	5	[75]	[Lu(N ⁱ Pr ₂) ₃ (THF)]	4	[75, 76]
Bis(trimethylsilyl)amide	La(N(SiMe ₃) ₂) ₃	3	[69, 70]	Lu(N(SiMe ₃) ₂) ₃	3	[68]
THF adduct of trichloride	[La(μ-Cl) ₃ (THF) ₂ La(μ-Cl) ₃] _n	8	[61]	LuCl ₃ (THF) ₃	6	[60]

Terpy complex of chloride	$[\text{LaCl}_3(\text{terpy})(\text{H}_2\text{O})]_2$	8	[99]	$[\text{LuCl}_3(\text{terpy})(\text{H}_2\text{O})]$	7	[99]
Terpy complex of nitrate	$\text{La}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})_2$	11	[101]	$\text{Lu}(\text{NO}_3)_3(\text{terpy})$	9	[101]
Ph_3PO complex of nitrate	$\text{La}(\eta^1\text{-NO}_3)(\eta^2\text{-NO}_3)_2(\text{Ph}_3\text{PO})_4$	9	[62]	$[\text{Lu}(\eta^2\text{-NO}_3)_2(\text{Ph}_3\text{PO})_4]\text{NO}_3$	8	[62]
Ph_3PO complex of triflate	$[\text{La}(\text{Ph}_3\text{PO})_4(\eta^1\text{-OTf})(\eta^2\text{-OTf})]^+ \text{OTf}^-$	7	[65]	$[\text{Lu}(\text{Ph}_3\text{PO})_4(\eta^1\text{-OTf})_2]^+ \text{OTf}^-$	6	[66]
$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ complex of triflate	$[\text{LaL}_4] (\text{OTf})_3$	8	[85]	$[\text{LuL}_3(\text{H}_2\text{O})] (\text{OTf})_3$	7	[85]
Acetylacetonate	$\text{La}(\text{acac})_3(\text{H}_2\text{O})_2$	8	[91]	$\text{Lu}(\text{acac})_3(\text{H}_2\text{O})$	7	[89]
Tetramethylheptanedionate	$[\text{La}(\text{tmhd})_3]_2$	7	[94]	$\text{Lu}(\text{tmhd})_3$	6	[93]
Acetate (anhydrous)	$\text{La}(\text{OAc})_3$	10	[98]	$\text{Lu}(\text{OAc})_3$	7	[97]
Nitrate complex	$[\text{La}(\text{NO}_3)_6]^{3-}$	12	[77]	$[\text{Lu}(\text{NO}_3)_5]^{2-}$	10	[78]
Carbonate complex ³	$[\text{Pr}(\text{CO}_3)_4(\text{H}_2\text{O})]^{5-}$	9	[81]	$[\text{Lu}(\text{CO}_3)_4]^{5-}$	8	[81]
EDTA complex	$[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3]^-$	9	[107]	$[\text{Lu}(\text{EDTA})(\text{H}_2\text{O})_2]^-$	8	[106]
DOTA complex	$[\text{La}(\text{DOTA})(\text{H}_2\text{O})]^-$	9 ²	[115]	$[\text{Lu}(\text{DOTA})(\text{H}_2\text{O})]^-$	9	[111]
Benzyl tris(THF) adduct	$\text{fac-}[\text{LaBz}_3(\text{THF})_3]$	6+3	[119]	$\text{fac-}[\text{LuBz}_3(\text{THF})_3]$	6	[118]
Benzyl bis(THF) adduct				$[\text{LuBz}_3(\text{THF})_3]$	5+1	[120]
Tris(cyclopentadienyl) ⁴	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{La}(\mu\text{-}\eta^5\text{:}\eta^2\text{-C}_5\text{H}_5)]_\infty$	11	[125]	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Lu}(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_5\text{H}_5)]_\infty$	8	[126]
Tris(tetramethylcyclopentadienyl) ⁴	$[(\eta^5\text{-C}_5\text{Me}_4\text{H})_3\text{La}]$	9	[129]	$[(\eta^5\text{-C}_5\text{Me}_4\text{H})_3\text{Lu}]$	9	[130]
12-crown-4 adduct of $\text{M}(\text{CH}_2\text{SiMe}_3)_3$	Not isolated ⁶			$[\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$	7	[122]

Difference between Sc and Lu

Difference between Lu and Y

¹ gas phase (electron diffraction)

² in solution

³ Structure of La complex not known

⁴ assuming that a $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5\text{Me}_4\text{H}$ ligand occupies three coordination sites while $\eta^5\text{-C}_5\text{H}_5$ occupies one coordination site

⁵ 12-crown-4 is tetradentate

⁶ Such compounds unstable for metals larger than Sm

Generally, when considering the coordination numbers and geometry of the closed-shell Sc^{3+} , Y^{3+} , La^{3+} and Lu^{3+} metal ions ligand-field effects are not significant. Instead, steric effects are largely responsible [30, 142, 143]. These may be divided into ‘first order’ effects, where it is inter-donor atom repulsions between the atoms directly bound to the metal – cases where it is impossible to pack more atoms around the metal - that are most important, and ‘second order effects’, where very bulky groups like $-\text{SiMe}_3$ are attached to the donor atoms, and the interactions between these groups that determine how many ligands can coordinate to the metal. As is also apparent from the structures discussed above, is that in the solid-state interactions additional to those within the complex unit can have an influence upon the coordination number and geometry of a given complex. These interactions may be repulsive, as in "steric" effects but can also be attractive, as, for example in the H-bonding of a bound water molecule to perchlorate counterions occurring in $[\text{Ln}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ species.

So, ligands like halide or water, which feature a small donor atom with non-bulky groups attached, produce compounds with high coordination numbers, in which the coordination number is dictated by packing considerations. Very bulky ligands such as $\text{N}(\text{SiMe}_3)_2$ lead to three coordinate compounds $[\text{M}(\text{N}(\text{SiMe}_3)_2)_3]$ with a range of 3+ metals of varying size (M e.g. Sc-Co, Y, La-Lu, U-Pu) [144] where the first coordination sphere is not fully satisfied but the second coordination sphere is congested by the trimethylsilyl groups, preventing access to the metal by further donors. Other bonding forces, such as Si-C...M interactions, together with ‘London’ ligand-ligand interactions are also present in these formally low-coordinate complexes and effectively saturate the coordination sphere.

It needs to be borne in mind that the species isolated in the solid-state may not be that favoured in other phases. Most strikingly, scandium, lanthanum and lutetium (and the intervening lanthanides) all form crystalline perchlorate salts containing octahedral $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ions, whilst the coordination number of the metal in the aqua ions in solution varies from seven (Sc) through 8 (Lu) to 9 (La) (Section 4.1).

The fact that 7-coordination is observed in crystalline $[\text{Ln}(\text{diketonato})_3(\text{H}_2\text{O})]$ species [90, 145, 146] while 8- or 9-coordination is found in solution can be rationalised [147] as due to H-bonding interactions of the aqua ligand in the solid which block access to a possible eighth coordination site. Even dispersion interactions between ligands on separate molecules in the solid state appear to be sufficient to enforce 7-coordination in analogous $[\text{Ln}(\text{diketonato})_3(\text{solvent})]$ complexes [147].

Where anion coordination accompanies that of water or various dipolar, aprotic solvents, differences between Sc(III) and Lu(III) are again apparent. The hydrated picrate (pic

= 2,4,6-trinitrophenoxide), $\text{Lu}(\text{pic})_3 \cdot 11.5\text{H}_2\text{O}$, isomorphous with those of the larger cations Dy(III), Er(III) and Y(III) [148], contains 8-coordinate, square-antiprismatic $[\text{Lu}(\text{pic-O})(\text{H}_2\text{O})_7]^{2+}$ cations (pic-O denoting the phenoxide-bound, unidentate form of picrate), whereas $\text{Sc}(\text{pic})_3 \cdot 11.3\text{H}_2\text{O}$ [149] contains 7-coordinate, capped trigonal prismatic $[\text{Sc}(\text{pic-O})(\text{H}_2\text{O})_6]^{2+}$ while in $\text{Sc}(\text{pic})_3 \cdot \text{Hpic} \cdot 12.2\text{H}_2\text{O}$ [150], octahedral (6-coordinate) *trans*- $[\text{Sc}(\text{pic-O})_2(\text{H}_2\text{O})_4]^+$ is found, providing another illustration of the operation of factors outside the primary coordination sphere. In contrast to what is seen in homoleptic solvates of the lanthanides where substitution of dimethylsulfoxide (DMSO) for water is associated with a diminution in coordination number, the solvates $\text{Ln}(\text{pic})_3(\text{DMSO})_3$ contain 9-coordinate, tricapped trigonal-prismatic cations across the whole series [151], as do the analogues with trimethylphosphate [152] and dimethylacetamide [153], although the solvates of $\text{Lu}(\text{pic})_3$ with hexamethylphosphoramide [154] and N-methylpyrrolidinone [153] do contain different forms of the 8-coordinate metal ion. Solvates of $\text{Sc}(\text{pic})_3$ with the same group of ligands all contain 6-coordinate Sc(III) in their crystals [153], seemingly reflecting an effect of ligand bulk not seen with the lanthanides. It should be borne in mind that the chemistry of scandium has been less studied than any of the other metals discussed in this article, and that new discoveries showing the richness of its chemistry are continually being made [155, 156].

In the majority of structural series of coordination complexes with bidentate or polydentate ligands described in this article there is a clear progression in coordination number as the size of the metal ion decreases. Several cases are known where this occurs by loss of a water molecule. Thus, lanthanum forms an eight coordinate acetylacetonate complex $[\text{La}(\text{acac})_3(\text{H}_2\text{O})_2]$ [91] as does yttrium in $[\text{Y}(\text{acac})_3(\text{H}_2\text{O})_2]$. The lutetium complex, $[\text{Lu}(\text{acac})_3(\text{H}_2\text{O})]$, is seven coordinate [89] and $\text{Sc}(\text{acac})_3$ is six coordinate [87] (Section 5.5). Likewise, terpyridine complexes include seven coordinate $[\text{LuCl}_3(\text{terpy})(\text{H}_2\text{O})]$ [99] and $[\text{YCl}_3(\text{terpy})(\text{H}_2\text{O})]$, but six coordinate $[\text{ScCl}_3(\text{terpy})]$ [59] (Section 6.1). Among complexes of EDTA, lanthanum and the larger, early lanthanides form complexes with nine coordinate ions, including $[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3]^-$ [107]; the lutetium and yttrium complex $[\text{M}(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (M= Lu, Y) [106] have eight coordinate $[\text{M}(\text{EDTA})(\text{H}_2\text{O})_2]^-$ ions, similar to those containing scandium found in $\text{NH}_4[\text{Sc}(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ [105] (Section 6.3). To extend the principle further, the even smaller Fe^{3+} ion forms a number of complexes containing the seven coordinate $[\text{Fe}(\text{EDTA})(\text{H}_2\text{O})]^-$ ion, with just one bound water [157].

Other factors also contribute, with bidentate ligands such as nitrate able to exert a subtle influence. Among the terpyridine complexes of lanthanide nitrates, the lanthanum complex is 11-coordinate $[\text{La}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ [101]. Slightly smaller metals form 10-coordinate $[\text{Ln}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$ (Ln = Ce-Ho) and the last few lanthanides form 9-coordinate $[\text{Ln}(\text{terpy})(\text{NO}_3)_3]$ (Ln = Er-Lu) [101] (Section 6.2). The yttrium analogue, $[\text{Y}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$ [104], has been crystallised in two isomeric forms, one with three

bidentate nitrates and one with two bidentate and one monodentate nitrate, giving ten and nine coordinate Y centres, respectively. The scandium complex $[\text{Sc}(\text{terpy})(\text{NO}_3)_3]$ [103] is at first sight very similar to the lutetium compound, but one Sc-O bond is substantially longer than the others. This reflects the severe congestion around the small scandium ion, relieved by the presence of one weak Sc-O bond. A striking example of constancy in stoichiometry and coordination number across the lanthanide series is provided by the two families of complexes $[\text{Ln}(\text{bipy})_2(\text{NO}_3)_3]$ and $[\text{Ln}(\text{phen})_2(\text{NO}_3)_3]$ (Ln = La-Lu except Pm; bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline). The scandium analogues to these complexes do not seem to have been isolated. All contain five bidentate ligands; as the lanthanide ion becomes smaller, so increasing asymmetry becomes evident in the Ln-O distances (though not in Ln-N), with the range in Ln-O bond lengths increasing from 0.04 Å (La complex), through 0.067 Å (Eu) and 0.105 Å (Er) to 0.130 Å (Lu) [100, 158, 159].

The analysis of the structural data for the complexes of the Sc^{3+} , Y^{3+} , La^{3+} and Lu^{3+} ions and, by implication, the rest of the lanthanide series described in the preceding pages is more complex than perhaps the common generalisations would suggest and, often, the "devil is in the detail". That the size of a cation is a factor limiting its coordination number may seem obvious on the basis of minimising donor atom repulsions but it is not so obvious when regarding actual structures how great the difference in cation radius must be before a change in coordination number occurs. Lanthanide(III) complexes provide numerous examples of changes in solid state coordination number at various points across the series depending seemingly on the size of the ligand [100] but there are also examples where a given ligand provides an isostructural series across the complete range of lanthanides [151-153, 160, 161], indicating that cation size alone must be an influence in competition with others [161]. In comparing Sc^{3+} and Lu^{3+} , an obvious source of differences is the valence shell, with d-orbital involvement more important for Sc than Lu, and it is course possible that the electronic interactions between metal ion and ligand can affect the interactions of the ligand with its "external" environment within a crystal. In this context it is informative to look at the solution pK_a values of the 3+ aqua ions (Sc^{3+} pK_a 4.3; Y^{3+} pK_a 7.7; Lu^{3+} pK_a 7.6; La^{3+} pK_a 8.5) [162] and note the similarity between the values for Y^{3+} and Lu^{3+} , matching the similarities in their radii.

In summary, because of their ionic character the structural chemistry of the Group 3 metal ions and that of the lanthanides is governed by the size of the metal ions and the steric requirements of the ligands, with the largest of the +3 ions, La^{3+} , displaying the highest coordination number for a given set of ligands. As illustrated by the examples discussed above it is the ligand set that is the dominant factor in determining the coordination number and geometry of the metal ion. For the coordination numbers greater than six, where there are several limiting geometries with similar energies, such as square antiprismatic or trigonal dodecahedral arrangements for 8-coordinate complexes, the

geometry adopted can be determined by the ligand set or indeed the crystal environment, and the complexes are fluxional in solution. Chemical properties such as lattice energies, solvation energies and complex stability constants of the complexes are closely related to the size of the metal ions. In the direct comparison of the Group 3 metals with Lu the analysis of M-O bonds shows that the radius of Lu^{3+} is closest in size to that of Y^{3+} and in more than half of the comparative series of 29 sets of structures analysed above these two elements have similar coordination numbers and geometries for the same ligand set; whereas, for complexes of the smaller Sc^{3+} when compared to Lu^{3+} there are about equal numbers of similarities and differences in coordination number and geometry between complexes of the two ions. Whilst in many of these comparative series lutetium resembles scandium in its behaviour, there are more cases where lutetium resembles yttrium. So, in the discussion of whether the order of the elements for Group 3 should be Sc, Y and La, or whether Lu should replace La in the group, this detailed review of the structural chemistry indicates that there is a logical progression in chemistry as the size of the Sc, Y and La ions increase. The structural chemistry of Lu most closely matches that of Y and not of La, so we feel that the case for replacing La by Lu in Group 3 has not been made on structural grounds. In the absence of more compelling evidence, the Periodic Table as presented currently, not least in the IUPAC form, gives the most appropriate description of the chemistry of Group 3 and of the lanthanides.

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Conflicts of Interest

The authors declare no competing financial interests.

References

- [1] P. Thyssen, K. Binnemans, Accommodation of the Rare Earths in the Periodic Table, in: K.A. Gschneidner Jr., J.-C. Bünzli, V.K. Pecharsky (Eds.) Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 2011, pp. 1-93.
- [2] D.C. Hamilton, *Am. J. Phys.*, 33 (1965) 637-640.
- [3] W.B. Jensen, *J. Chem. Ed.*, 59 (1982) 634.
- [4] W.B. Jensen, *J. Chem. Ed.*, 86 (2009) 1186.
- [5] W.B. Jensen, *Found Chem*, 17 (2015) 23-31.
- [6] L. Lavelle, *J. Chem. Ed.*, 85 (2008) 1482-1483.
- [7] L. Lavelle, *J. Chem. Ed.*, 86 (2009) 1187.
- [8] E. Scerri, *J. Chem. Ed.*, 86 (2009) 1188.
- [9] E. Scerri, *Chem. International*, 43 (2021) 31-34.
- [10] R.E. Vernon, *Found Chem*, 23 (2021) 155-197.
- [11] P. Pyykko, *Chem. Rev.*, 88 (1988) 563-594.
- [12] M. Seth, M. Dolg, P. Fulde, P. Schwerdtfeger, *J. Am. Chem. Soc.*, 117 (1995) 6597-6598.
- [13] R.D. Shannon, *Acta Crystallogr. A*, 32 (1976) 751-767.
- [14] V.M. Goldschmidt, T. Barth, G. Lunde, Isomorphie und Polymorphie der Sesquioxyde. Die Lanthaniden-Kontraktion und ihre Konsequenzen, in: *Geochemische Verteilungsgesetze der Elemente*, Part V Skrifter Norske Videnskaps-Akademi i, Oslo, 1925.
- [15] C.M. Kozak, P. Mountford, Zirconium & Hafnium: Inorganic & Coordination Chemistry Based in part on the article Zirconium & Hafnium: Inorganic & Coordination Chemistry by Grigorii L. Soloveichik which appeared in the *Encyclopedia of Inorganic Chemistry*, First Edition, in: R.B. King, R.H. Crabtree, C.M. Lukehart, D.A. Atwood, R.A. Scott (Eds.) *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2006, pp. 263.
- [16] A.C. Albéniz, P. Espinet, Palladium: Inorganic & Coordination Chemistry, in: R.A. Scott (Ed.) *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2011, pp. eibc0164.
- [17] S.A. Cotton, Palladium and Platinum, in: *Chemistry of Precious Metals*, Springer Netherlands, Dordrecht, 1997, pp. 173-272.
- [18] R.H. Crabtree, H. Torrens, Platinum: Inorganic & Coordination Chemistry, in: R.A. Scott (Ed.) *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2011, pp. eibc0179.
- [19] A. Bayler, A. Schier, G.A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.*, 118 (1996) 7006-7007.
- [20] M.S. Liao, W.H.E. Schwarz, *Acta Crystallogr. B*, 50 (1994) 9-12.
- [21] P. Schwerdtfeger, P.D.W. Boyd, A.K. Burrell, W.T. Robinson, M.J. Taylor, *Inorg. Chem.*, 29 (1990) 3593-3607.
- [22] P. Schwerdtfeger, *Heteroatom Chem.*, 13 (2002) 578-584.
- [23] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, *Acta Crystallogr. B*, 72 (2016) 171-179.
- [24] D. Zagorac, H. Muller, S. Ruehl, J. Zagorac, S. Rehme, *J. Appl. Crystal.*, 52 (2019) 918-925.
- [25] K.P. Kepp, *Inorg. Chem.*, 55 (2016) 9461-9470.
- [26] J.C. Slater, *J. Chem. Phys.*, 41 (1964) 3199-3204.
- [27] A.L. Allred, E.G. Rochow, *J. Inorg. & Nucl. Chem.*, 5 (1958) 264-268.
- [28] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press Ithaca, NY, 1960.
- [29] T.J. Boyle, L.A.M. Steele, Lanthanides: Halides, in: R.A. Scott (Ed.) *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2012, pp. eibc2021.
- [30] S. A. Cotton, *Lanthanide and Actinide Chemistry*, Chichester : John Wiley, Chichester, 2006.
- [31] J.A.A. Ketelaar, *Physica*, 4 (1937) 619-630.
- [32] L. Helmholz, *J. Am. Chem. Soc.*, 61 (1939) 1544-1550.
- [33] J. Albertsson, I. Elding, *Acta Crystallogr. B*, 33 (1977) 1460-1469.
- [34] A. Chatterjee, E.N. Maslen, K.J. Watson, *Acta Crystallogr B*, 44 (1988) 386-395.
- [35] J.M. Harrowfield, D.L. Kepert, J.M. Patrick, A.H. White, *Aust. J. Chem.*, 36 (1983) 483-492.

- [36] C.B. Castellani, O. Carugo, M. Giusti, N. Sardone, *Eur. J. Solid State and Inorg. Chem.*, 32 (1995) 1089-1099.
- [37] A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandström, S. Lidin, I. Persson, M. Sandström, *Chem. Eur. J.*, 11 (2005) 4065-4077.
- [38] P. Lindqvist-Reis, I. Persson, M. Sandström, *Dalton Trans.*, (2006) 3868-3878.
- [39] P. D'Angelo, A. Zitolo, V. Migliorati, I. Persson, *Chem. Eur. J.*, 16 (2010) 684-692.
- [40] I. Persson, P. D'Angelo, S. De Panfilis, M. Sandstrom, L. Eriksson, *Chem. Eur. J.*, 14 (2008) 3056-3066.
- [41] J. Näslund, P. Lindqvist-Reis, I. Persson, M. Sandström, *Inorg. Chem.*, 39 (2000) 4006-4011.
- [42] J.M. Harrowfield, *Metal ions in biological systems*, 40 (2003) 105-159.
- [43] K.C. Lim, B.W. Skelton, A.H. White, *Aust. J. Chem.*, 53 (2000) 867-873.
- [44] J. Glaser, G. Johansson, T. Lundström, L. Nordenskiöld, O. Wahlberg, *Acta Chem. Scand.*, 35a (1981) 639-644.
- [45] A.G. Davidian, O.N. Pestova, G.L. Starova, V.V. Gurzhii, L.A. Myund, M.K. Khripun, *Russ J Gen Chem*, 82 (2012) 621-625.
- [46] Y. Toshihiro, N. Haruo, W.A.M.S. José, K. Masahiko, *Chem. Let.*, 27 (1998) 1281-1282.
- [47] C.J. Kepert, B.W. Skeleton, A.H. White, *Aust. J. Chem.*, 47 (1994) 391-396.
- [48] F.J. Waller, A.G.M. Barrett, D.C. Braddock, D. Ramprasad, R.M. McKinnell, A.J.P. White, D.J. Williams, R. Ducray, *J. Org. Chem.*, 64 (1999) 2910-2913.
- [49] P.C. Junk, L.I. Semenova, B.W. Skelton, A.H. White, *Aust. J. Chem.*, 52 (1999) 531-538.
- [50] J.L. Atwood, L.J. Barbour, M.J. Hardie, C.L. Raston, *Coord. Chem. Rev.*, 222 (2001) 3-32.
- [51] L. Helm, A.E. Merbach, *Coord. Chem. Rev.*, 187 (1999) 151-181.
- [52] M.Y. Skripkin, P. Lindqvist-Reis, A. Abbasi, J. Mink, I. Persson, M. Sandström, *Dalton Trans.*, (2004) 4038-4049.
- [53] P. Lindqvist-Reis, J. Näslund, I. Persson, M. Sandström, *J. Chem. Soc., Dalton Trans.*, (2000) 2703-2710.
- [54] A. Abbasi, E. D. Risberg, L. Eriksson, J. Mink, I. Persson, M. Sandström, Y.V. Sidorov, M.Y. Skripkin, A.-S. Ullström, *Inorg. Chem.*, 46 (2007) 7731-7741.
- [55] I. Persson, E. D. Risberg, P. D'Angelo, S. De Panfilis, M. Sandström, A. Abbasi, *Inorg. Chem.*, 46 (2007) 7742-7748.
- [56] D. Lundberg, I. Persson, L. Eriksson, P. D'Angelo, S. De Panfilis, *Inorg. Chem.*, 49 (2010) 4420-4432.
- [57] G.R. Willey, T.J. Woodman, M.G.B. Drew, *Polyhedron*, 16 (1997) 351-353.
- [58] S.A. Cotton, J.M. Harrowfield, L.I. Semenova, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 73 (2020) 434-446.
- [59] J.L. Atwood, K.D. Smith, *J. Chem. Soc., Dalton Trans.*, (1974) 921-923.
- [60] G.K.-I. Magomedov, A.Z. Voskoboinikov, N.I. Kirillova, A.I. Gusev, I.N. Parshina, I.P. Bele, *Metallorg. Khim. (Organomet. Chem. USSR)*, 5 (1992) 679.
- [61] G.B. Deacon, T. Feng, P.C. Junk, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 51 (1998) 75-89.
- [62] W. Levason, E.H. Newman, M. Webster, *Polyhedron*, 19 (2000) 2697-2705.
- [63] Y.-H. Jiang, W.-J. Kong, Z.-F. Li, Q.-H. Jin, C.-L. Zhang, *Zeit. Krist.*, 227 (2012) 9-11.
- [64] L. Deakin, W. Levason, M.C. Popham, G. Reid, M. Webster, *J. Chem. Soc., Dalton Trans.*, (2000) 2439-2447.
- [65] J.C. Berthet, M. Nierlich, M. Ephritikhine, *Polyhedron*, 22 (2003) 3475-3482.
- [66] J. Fawcett, A.W.G. Platt, D.R. Russell, *Polyhedron*, 21 (2002) 287-293.
- [67] J.S. Ghotra, M.B. Hursthouse, A.J. Welch, *J. Chem. Soc., Chem. Commun.*, (1973) 669-670.
- [68] M. Westerhausen, M. Hartmann, A. Pfitzner, W. Schwarz, *Z. anorg. allg. Chem.*, 621 (1995) 837-850.
- [69] W.S. Rees, O. Just, D.S. Van Derveer, *J. Mater. Chem.*, 9 (1999) 249-252.

- [70] G. Scarel, C. Wiemer, M. Fanciulli, I.L. Fedushkin, G.K. Fukin, G.A. Domrachev, Y. Lebedinskii, A. Zenkevich, G. Pavia, *Z. anorg. allg. Chem.*, 633 (2007) 2097-2103.
- [71] T. Fjeldberg, R.A. Andersen, *J. Mol. Struct.*, 128 (1985) 49-57.
- [72] T. Fjeldberg, R.A. Andersen, *J. Mol. Struct.*, 129 (1985) 93-105.
- [73] E.D. Brady, D.L. Clark, J.C. Gordon, P.J. Hay, D.W. Keogh, R. Poli, B.L. Scott, J.G. Watkin, *Inorg. Chem.*, 42 (2003) 6682-6690.
- [74] C.A.P. Goodwin, K.C. Joslin, S.J. Lockyer, A. Formanuik, G.A. Morris, F. Ortu, I.J. Vitorica-Yrezabal, D.P. Mills, *Organometallics*, 34 (2015) 2314-2325.
- [75] F. Estler, G. Eickerling, E. Herdtweck, R. Anwander, *Organometallics*, 22 (2003) 1212-1222.
- [76] T. Spallek, O. Heß, M. Meermann-Zimmermann, C. Meermann, M.G. Klimpel, F. Estler, D. Schneider, W. Scherer, M. Tafipolsky, K.W. Törnroos, C. Maichle-Mössmer, P. Sirsch, R. Anwander, *Dalton Trans.*, 45 (2016) 13750-13765.
- [77] A.S.R. Chesman, D.R. Turner, G.B. Deacon, S.R. Batten, *Acta Crystallogr. E*, 62 (2006) m1942-m1943.
- [78] E. Manek, G. Meyer, *Z. Anorg. Allg. Chem.*, 619 (1993) 1237-1240.
- [79] C.C. Addison, A.J. Greenwood, M.J. Haley, N. Logan, *J. C. S. -Chem. Comm.*, (1978) 580-581.
- [80] G. Meyer, S. Stockhause, *Zeit. Krist.*, 209 (1994) 180.
- [81] R. Janicki, P. Starynowicz, A. Mondry, *Eur. J. Inorg. Chem.*, 2011 (2011) 3601-3616.
- [82] M. Dahm, A. Adam, *Zeit. Natur. B*, 57 (2002) 1439-1445.
- [83] M. Luo, G.X. Wang, C.S. Lin, N. Ye, Y.Q. Zhou, W.D. Cheng, *Inorg. Chem.*, 53 (2014) 8098-8104.
- [84] V. Philippini, T. Vercouter, P. Vitorge, *J Solution Chem*, 39 (2010) 747-769.
- [85] J. Fawcett, A.W.G. Platt, *Polyhedron*, 22 (2003) 967-973.
- [86] R.D. Bannister, W. Levason, G. Reid, *Chem.*, 2 (2020).
- [87] T.J. Anderson, M.A. Neuman, G.A. Melson, *Inorg. Chem.*, 12 (1973) 927-930.
- [88] Y.S. Ezhov, S.A. Komarov, V.G. Sevast'yanov, *J. Struct. Chem.*, 39 (1998) 514-519.
- [89] J.A. Cunningham, D.E. Sands, W.F. Wagner, M.F. Richardson, *Inorg. Chem.*, 8 (1969) 22-28.
- [90] J.A. Cunningham, D.E. Sands, W.F. Wagner, *Inorg. Chem.*, 6 (1967) 499-503.
- [91] T. Phillips, D.E. Sands, W.F. Wagner, *Inorg. Chem.*, 7 (1968) 2295-2299.
- [92] A.J. Rossini, R.W. Schurko, *J. Am. Chem. Soc.*, 128 (2006) 10391-10402.
- [93] S. Onuma, H. Inoue, S. Shibata, *Bull. Soc. Japan*, 49 (1976) 644-647.
- [94] L. Yuikhan, S.A. Mosyagina, P.A. Stabnikov, N.I. Alferova, I.V. Korol'kov, N.V. Pervukhina, N.B. Morozova, *J. Struct. Chem.*, 58 (2017) 843-846.
- [95] S. Gomez Torres, G. Meyer, *Z. anorg. allg. Chem.*, 634 (2008) 231-233.
- [96] R. Fuchs, J. Strähle, *Zeit. für Natur. B*, 39 (1984) 1662-1663.
- [97] A. Lossin, G. Meyer, *Z. Anorg. Allg. Chem.*, 619 (1993) 1609-1615.
- [98] G. Meyer, D. Gieseke-Vollmer, *Z. Anorg. Allg. Chem.*, 619 (1993) 1603-1608.
- [99] E. Curnock, W. Levason, M.E. Light, S.K. Luthra, G. McRobbie, F.M. Monzittu, G. Reid, R.N. Williams, *Dalton Trans.*, 47 (2018) 6059-6068.
- [100] S.A. Cotton, P.R. Raithby, *Coord. Chem. Rev.*, 340 (2017) 220-231.
- [101] B. Ahrens, S.A. Cotton, N. Feeder, O.E. Noy, P.R. Raithby, S.J. Teat, *J. Chem. Soc., Dalton Trans.*, (2002) 2027-2030.
- [102] M.G.B. Drew, P.B. Iveson, M.J. Hudson, J.O. Liljenzin, L. Spjuth, P.V. Cordier, A. Enarsson, C. Hill, C. Madic, *J. Chem. Soc. Dalt. Trans.*, (2000) 821-830.
- [103] A.M. Arif, F.A. Hart, M.B. Hursthouse, M. Thornton-Pett, W.X. Zhu *J. Chem. Soc. Dalt. Trans.* (1984) 2449-2454.
- [104] A.K. Boudalis, V. Nastopoulos, A. Terzis, C.P. Raptopoulou, S.P. Perlepes, *Zeit. Natur. B*, 56 (2001) 122-128.
- [105] Y.W. Zhang, Z.M. Wang, J.T. Jia, C.S. Liao, C.H. Yan, *Acta Crystallogr. C*, 55 (1999) 1418-1420.
- [106] R. Janicki, P. Starynowicz, A. Mondry, *Eur. J. Inorg. Chem.*, 2008 (2008) 3075-3082.
- [107] J.L. Hoard, B. Lee, M.D. Lind, *J. Am. Chem. Soc.*, 87 (1965) 1612-1613.
- [108] R. Janicki, A. Mondry, *Phys. Chem. Chem. Phys.*, 16 (2014) 26823-26831.

- [109] M. Pniok, V. Kubíček, J. Havlíčková, J. Kotek, A. Sabatie-Gogová, J. Plutnar, S. Huclier-Markai, P. Hermann, *Chem. Eur. J.*, 20 (2014) 7944-7955.
- [110] F. Benetollo, G. Bombieri, L. Calabi, S. Aime, M. Botta, *Inorg. Chem.*, 42 (2003) 148-157.
- [111] S. Aime, A. Barge, M. Botta, M. Fasano, J. Danilo Ayala, G. Bombieri, *Inorganica Chimica Acta*, 246 (1996) 423-429.
- [112] D. Parker, K. Pulukkody, F.C. Smith, A. Batsanov, J.A.K. Howard, *J. Chem. Soc., Dalton Trans.*, (1994) 689-693.
- [113] M.A. Brown, T. Brossard, D.A. Rotsch, *Inorg. Chim. Acta*, 482 (2018) 118-121.
- [114] S. Aime, A. Barge, F. Benetollo, G. Bombieri, M. Botta, F. Uggeri, *Inorg. Chem.*, 36 (1997) 4287-4289.
- [115] S. Aime, M. Botta, M. Fasano, M.P.M. Marques, C.F.G.C. Geraldes, D. Pubanz, A.E. Merbach, *Inorg. Chem.*, 36 (1997) 2059-2068.
- [116] N. Viola-Villegas, R.P. Doyle, *Coord. Chem. Rev.*, 253 (2009) 1906-1925.
- [117] N. Meyer, P.W. Roesky, S. Bambirra, A. Meetsma, B. Hessen, K. Saliu, J. Takats, *Organometallics*, 27 (2008) 1501-1505.
- [118] D.P. Mills, O.J. Cooper, J. McMaster, W. Lewis, S.T. Liddle, *Dalton Trans.*, (2009) 4547-4555.
- [119] S. Bambirra, A. Meetsma, B. Hessen, *Organometallics*, 25 (2006) 3454-3462.
- [120] K.O. Saliu, J. Takats, R. McDonald, *Acta Crystallogr. E*, 74 (2018) 88-90.
- [121] H. Schumann, D.M.M. Freckmann, S. Dechert, *Z. anorg. allg. Chem.*, 628 (2002) 2422-2426.
- [122] S. Arndt, P.M. Zeimentz, T.P. Spaniol, J. Okuda, M. Honda, K. Tatsumi, *Dalton Trans.*, (2003) 3622-3627.
- [123] B.R. Elvidge, S. Arndt, P.M. Zeimentz, T.P. Spaniol, J. Okuda, *Inorg. Chem.*, 44 (2005) 6777-6788.
- [124] M. Adam, U. Behrens, R.D. Fischer, *Acta Crystallogr. C*, 47 (1991) 968-971.
- [125] S.H. Eggers, J. Kopf, R.D. Fischer, *Organometallics*, 5 (1986) 383-385.
- [126] S.H. Eggers, H. Schultze, J. Kopf, R.D. Fischer, *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 656-657.
- [127] J.L. Atwood, K.D. Smith, *J. Am. Chem. Soc.*, 95 (1973) 1488-1491.
- [128] D.H. Woen, C.M. Kotyk, T.J. Mueller, J.W. Ziller, W.J. Evans, *Organometallics*, 36 (2017) 4558-4563.
- [129] H. Schumann, M. Glanz, H. Hemling, F. E. Hahn, *Z. Anorg. Allg. Chem.*, 621 (1995) 341-345.
- [130] W.J. Evans, D.S. Lee, M.A. Johnston, J.W. Ziller, *Organometallics*, 24 (2005) 6393-6397.
- [131] W.J. Evans, B.L. Davis, T.M. Champagne, J.W. Ziller, *Proceedings of the National Academy of Sciences*, 103 (2006) 12678-12683.
- [132] B.S. Soller, Q. Sun, S. Salzinger, C. Jandl, A. Pöthig, B. Rieger, *Macromolecules*, 49 (2016) 1582-1589.
- [133] S. Demir, T.J. Mueller, J.W. Ziller, W.J. Evans, *Angew. Chem. Int. Ed.*, 50 (2011) 515-518.
- [134] M.G. Paton, E.N. Maslen, *Acta Crystallogr.*, 19 (1965) 307-310.
- [135] P. Lindqvist-Reis, K. Lamble, S. Pattanaik, I. Persson, M. Sandstrom, *J. Phys. Chem. B*, 104 (2000) 402-408.
- [136] D.C. Bradley, J.S. Ghotra, F.A. Hart, *Inorg. & Nucl. Chem. Let.*, 12 (1976) 735-737.
- [137] P. Sobota, J. Utko, S. Szafert, *Inorg. Chem.*, 33 (1994) 5203-5206.
- [138] A. Gleizes, S. Sanslenain, D. Medus, N. Hovnanian, P. Miele, J.D. Foulon, *Inorg. Chim. Acta*, 209 (1993) 47-53.
- [139] P.C. Jiao, Y. Zhang, W.L. Yuan, G.H. Tao, H.Q. Cai, *J. Mol. Struct.*, 1222 (2020).
- [140] J. Wang, Y. Wang, Z.H. Zhang, X.D. Zhang, J. Tong, X.Z. Liu, X.Y. Liu, Y. Zhang, Z.J. Pan, *J. Struct. Chem.*, 46 (2005) 895-905.
- [141] S.E. Lorenz, B.M. Schmiede, D.S. Lee, J.W. Ziller, W.J. Evans, *Inorg. Chem.*, 49 (2010) 6655-6663.
- [142] S.A. Cotton, *Comptes Rendus Chimie*, 8 (2005) 129-145.
- [143] X.Z. Feng, A.L. Guo, Y.T. Xu, X.F. Li, *Polyhedron*, 6 (1987) 1041-1048.
- [144] M. F. Lappert, A. Protchenko, P. Power, A. Seeber, *Metal Amide Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2008.

- [145] F. A. Cotton, P. Legzdins, *Inorg. Chem.*, 7 (1968) 1777-1783.
- [146] A. Lennartson, M. Vestergren, M. Håkansson, *Chem. Eur. J.*, 11 (2005) 1757-1762.
- [147] E.J. Chan, J.M. Harrowfield, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 73 (2020) 455-461.
- [148] J.M. Harrowfield, W.M. Lu, B.W. Skelton, A.H. White, *Aust. J. Chem.*, 47 (1994) 339-348.
- [149] M.C. Sanchez, P.C. Isolani, J. Zukerman-Schpector, G. Vicentini, *J. Alloys and Compounds*, 344 (2002) 298-303.
- [150] J. Harrowfield, B. Skelton, A. White, *Aust. J. Chem.*, 47 (1994) 397-403.
- [151] Z. Asfari, E.J. Chan, J.M. Harrowfield, B.W. Skelton, A.N. Sobolev, P. Thuery, A.H. White, *Aust. J. Chem.*, 73 (2020) 447-454.
- [152] E.J. Chan, J.M. Harrowfield, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 73 (2020) 462-467.
- [153] E.J. Chan, J.M. Harrowfield, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 73 (2020) 488-496.
- [154] E.J. Chan, J.M. Harrowfield, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.*, 73 (2020) 477-487.
- [155] J.M. Sears, T.J. Boyle, *Coord. Chem. Rev.*, 340 (2017) 154-171.
- [156] T.J. Boyle, R.E. Cramer, F.A. Fasulo, N. Padilla, *Polyhedron*, 208 (2021) 115437.
- [157] X. Solans, M. Font Altaba, J. Garcia-Oricain, *Acta Crystallogr. C*, 40 (1984) 635-638.
- [158] D. Kepert, L. Semenova, A. Sobolev, A. White, *Aust. J. Chem.*, 49 (1996) 1005-1008.
- [159] H. Yang, *Acta Crystallogr. E*, 68 (2012) m577-m577.
- [160] K. Matsumoto, K. Suzuki, T. Tsukuda, T. Tsubomura, *Inorg. Chem.*, 49 (2010) 4717-4719.
- [161] M. Seitz, A.G. Oliver, K.N. Raymond, *J. Am. Chem. Soc.*, 129 (2007) 11153-11160.
- [162] T.I. Kostelnik, C. Orvig, *Chem. Rev.*, 119 (2019) 902-956.