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PAPER

Metallacrowns of Ni(II) with α-aminohydroxamic acids in aqueous solution: beyond a 12-MC-4, an unexpected (vacant?) 15-MC-5†

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Growing attention has been devoted in the recent years to a class of metallamacrocycles known as metallacrowns (MCs). They are structural analogues of crown ethers where the methylene bridges have been substituted by coordinative bonds formed by a transition metal ion ("ring" metal) and a nitrogen atom. The cavity of the metallacrown can accommodate an additional metal ion ("core" metal) either identical or different from the ring metal, thus forming a homo- or hetero-metallic MC. The most studied ring metal ion is certainly Cu^{2+} and the aminohydroxamic acids have proved to be very suitable ligands to form MCs. The behavioural analogies between Cu^{2+} and Ni^{2+} in forming complexes, along with recent literature data in the solid state, prompted us to investigate the possible MC formation between Ni^{2+} and both (*S*)-α-alaninehydroxamic acid and (*S*)-valinehydroxamic acid, in aqueous solution. Two metallacrowns, a 12-MC-4 and an unexpected 15-MC-5 have been detected by potentiometry and confirmed by ESI–MS results. Their structures are discussed on the basis of potentiometric, calorimetric, spectroscopic data and DFT calculations. The existence of a vacant 15-MC-5 species in solution can be put forward for the first time, making the present metal/ligand systems very interesting for their potential applications in cation recognition and separation. Finally, the crystal structure of the binary complex $K[NiL_2H_{-1}]\cdot 5/3\ H_2O$ of (*S*)-α-alaninehydroxamic acid (LH) is also reported.

Introduction

Metallacrowns (MCs) are a class of inorganic macrocycles analogues of crown ethers where a transition metal ("ring" metal) and a nitrogen atom ideally substitute for two methylene groups; a "core" metal can be present inside the cavity of the cycle.[1] Aminohydroxamic acids in their hydroximate form are particularly suitable for metallacrown assembly because they can act as bridging bis-chelating ligands in the presence of copper(II) or other transition metal ions.

Since 1989, Pecoraro and coworkers synthesized a large number of these metallamacrocycles and characterized their structures by X-ray analysis, as they have recently reported in a comprehensive review.[2] Copper metallacrowns are the most studied, and their formation requires a templating metal ion as observed in the solid state. For instance, the 12-MC-4 of β-aminohydroxamic acids (LH) contain Cu^{2+} as the core metal, while the 15-MC-5 of α-aminohydroxamic acids are assembled in presence of core metals (M) such as Ca(II), Ln(III) or UO_2(VI) (Fig. 1). Studies in solution confirmed the lack of formation of a vacant copper 15-MC-5 of formula $[Cu_5L_5H_{-5}]$: in the absence of a suitable core metal M, the 15-MC-5 rearranges to 12-MC-4 ($[Cu_5L_4H_{-4}]^{2+}$) where the central cavity is occupied by a copper(II) ion.

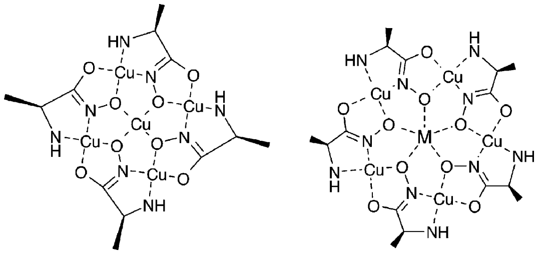

Fig. 1 Structures of 12-MC-4 (left) and 15-MC-5 (right) copper(II) metallacrowns with (*S*)-α-alaninehydroxamic acid. Charges are omitted for the sake of simplicity.

In this context, the solution chemistry of Cu(II) 12-MC-4 with aminohydroxamic acids has been fully investigated by our research

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group in the last few years by potentiometry, calorimetry, UV-Vis and CD spectrophotometry, and ESI–MS.[3–7] It has been demonstrated that not only β-, but also α- and γ-aminohydroxamates can form Cu(II) 12-MC-4 and their thermodynamic properties ($\Delta G°$, $\Delta H°$, $\Delta S°$) have been critically discussed (see Table S1, Supplementary Information†).

With regards to Ni(II) metallacrowns with α-aminohydroxamates, no 12-MC-4 species has been so far detected in solution equilibria studies,[8] although NMR titrations of DMSO solutions of two compounds $[Cu_5L_4H_{-4}]X_2$ (LH = picolinehydroxamic acid or (*S*)-phenylalaninehydroxamic acid; X = Cl^-, NO_3^-, HSO_4^-) with Ni^{2+} revealed the replacement of the central copper to form the species $[NiCu_4L_4H_{-4}]^{2+}$, which was confirmed by ESI–MS spectra.[9] However, Ni(II) resembles Cu(II) in the capability to form 15-MC-5 complexes: 15-MC-5 of picolinehydroxamate with Ni(II) as ring metal and different Ln(III) ions or Pb(II) have been so far isolated and their crystal structures described.[10,11] The interest in devising new MCs with ring metals different from Cu(II) is justified by the growing interest in the isolation of new polymetallic complexes acting as single molecule magnets or recognition agents for anions and cations.[2] In this respect, the tendency of Ni(II) to give planar coordination environments associated with low paramagnetism is an interesting feature that can be used for the synthesis of Ln(III) 15-MC-5 where the unpaired electrons are almost localized on the core metal with low contribution from the peripheral Ni(II) ions. X-Ray analysis of the Sm(III) and Pb(II) compounds revealed the presence of both octahedral and square planar Ni(II), suggesting that materials with controlled magnetic and host–guest properties can be obtained, taking advantage of these different geometries.[11] However, with the low tendency of planar Ni(II) to coordinate in the axial positions, additional ligands can be employed for the preparation of MCs as hosts for anions interacting almost exclusively with the core metal. Finally, the finding that Ni(II) can only partially substitute Cu(II) in 12-MC-4, opens up the possibility of designing new MC-based structural motifs and might led to the isolation of new homo-metallic (only Ni) or hetero-metallic (Ni/Cu, Ni/Ln or even Ni/Cu/Ln) self assembled metallacrowns. From this perspective, it is desirable to get more quantitative information on the thermodynamics of the self-assembly of Ni(II) metallacrowns in solution. On the basis of the similarities between Ni(II) and Cu(II) ions (dimensions and tendency to assume a 4-planar coordination) we considered reasonable the possibility that Ni(II) can also form homo-metallic 12-MC-4 with α-aminohydroxamates besides the hetero-metallic that have previously been reported qualitatively.[9]

We report herein the results of the investigation of the equilibria in aqueous solution of Ni(II) with two α-aminohydroxamic acids (see Scheme S1, Supplementary Information†): (*S*)-α-alaninehydroxamic acid (α-Alaha) and (*S*)-valinehydroxamic acid (Valha) by means of different techniques (potentiometry, calorimetry, UV-Vis, ESI–MS and DFT calculations). The use of different cations (arising from the background electrolyte) allowed us to demonstrate the unexpected formation of a vacant 15-MC-5 complex, and the different thermodynamic behaviour of Ni^{2+} MCs compared to Cu^{2+} ones.

Results

Potentiometry and calorimetry

α-Alaha and Valha exhibit two basic sites, corresponding to the aminic and hydroxamic groups. The protonation constants of α-Alaha and (*R*,*S*)-Valha (LH) were previously determined[7] and are reported as supporting information (Table S2†) along with the corresponding protonation enthalpies and entropies.

The complexation equilibria of Ni^{2+} with both ligands were studied by potentiometric titrations. The fitting of the measurements performed with ligand/metal molar ratios >2 was obtained with a speciation model containing only mononuclear complexes, $[NiL]^+$, $[NiL_2]$, $[NiL_2H_{-1}]^-$. This result is consistent with that previously reported in the literature for the same metal/ligand ratios.[8]

In order to investigate the possible formation of the metallacrown complexes, we carried out potentiometric measurements with ligand/metal molar ratios <2. At pH >7.5 a drift of the e.m.f. readings was observed, confirmed also by the visible spectra registered as a function of time (Figure S1, Supplementary Information†). The attainment of the equilibrium after each titrant addition was therefore carefully checked, performing titrations with long waiting intervals (see Experimental). A speciation model including the polynuclear $[Ni_5L_4H_{-4}]^{2+}$ and $[Ni_5L_5H_{-5}]$ species in addition to the mononuclear ones $[NiL]^+$, $[NiL_2]$, $[NiL_2H_{-1}]^-$ allowed a satisfactory fitting of the data with ligand/metal molar ratios <2 up to pH *ca.* 11 (see Fig. S2, Supplementary Information†).

The complexation logβ values for the systems containing Ni^{2+} and α-Alaha, Valha or acetohydroxamic acid (Acha, studied for the sake of comparison), in the presence of KCl as the background electrolyte, are presented in Table 1 and the corresponding distribution diagrams are shown in Fig. 2 and S3 (Supplementary Information†). Calorimetric measurements were

Table 1 Overall thermodynamic complex-formation parameters for the systems Ni^{2+}/ α-Alaha or Valha or Acha (acetohydroxamic acid). $T = 298.2$ K and $I = 0.1$ mol dm^{-3} (KCl). Standard deviation on the last figure in parentheses

	α-Alaha				Valha	Acha
Species	log β	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	log β	log β
$[NiL]^+$	6.88 (1)	39.2 (1)	13 (2)	92 (8)	6.72 (2)	5.42 (1)
$[NiL_2]$	14.05 (1)	80.1 (1)	24.3 (8)	187 (2)	14.16 (1)	9.90 (1)
$[NiL_2H_{-1}]^-$	4.87 (3)	27.8 (2)	4 (1)	81 (4)	5.04 (3)	—
$[NiL_3]^-$	—	—	—	—	—	13.36 (2)
$[Ni_5L_4H_{-4}]^{2+}$	15.51 (5)	88.5 (3)	−21 (4)	367 (14)	15.57 (5)	—
$[Ni_5L_5H_{-5}]$	13.53 (8)	77.2 (5)	−27 (3)	350 (11)	13.9 (1)	—
σ	1.9	—	2.7 10^{-4}	—	2.87	0.5
n	370	—	444	—	533	650

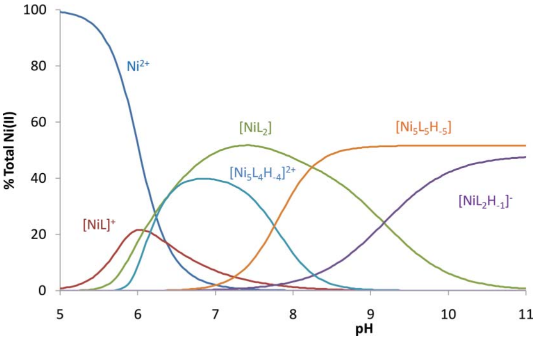

Fig. 2 Exemplificative distribution diagram for the system Ni^{2+}/ α-Alaha with ligand-to-metal ratio 1 : 1.5 and $C°_{Ni}$ = 2 mmol dm^{-3}.

performed only on the Ni(II)/α-Alaha system, since previous studies[7] demonstrated that α-Alaha and Valha possess very similar thermodynamic parameters with respect to Cu(II) complexation. Enthalpy and entropy data are also reported in Table 1.

For a ligand/metal ratio equal to or higher than 3 (Figure S4, Supplementary Information†) the complex formation starts at pH 5 with the species $[NiL]^+$ followed, at pH close to 5.5, by the bis-complex $[NiL_2]$. The latter is practically the only species which exists at neutral pH, which can further deprotonate to give $[NiL_2H_{-1}]^-$ in the alkaline pH range. On the contrary, when the ligand/metal ratio is close to 1, the two polynuclear species $[Ni_5L_4H_{-4}]^{2+}$ and $[Ni_5L_5H_{-5}]$ form in significant amounts at the expense of the mononuclear complexes. The stoichiometries of the two polynuclear species correspond to a 12-MC-4 and a 15-MC-5 respectively. As regards $[Ni_5L_5H_{-5}]$, however, it corresponds to a vacant 15-MC-5, a species that was never revealed before for Cu(II) complexes in the same experimental conditions. The presence in solution of these polymetallic complexes has been confirmed by ESI–MS spectra (see below). Calorimetric data revealed an endothermic contribution for the formation of both the MCs accompanied by a highly favourable entropic term.

In the presence of KCl as the background electrolyte, we could not exclude *a priori* the possible templating role played by the K^+ ion, owing to its high concentration. This prompted us to investigate the complex-formation equilibria of the Ni^{2+}/α-Alaha system in the presence of NaCl or tetraethylammonium chloride as background electrolytes (Table 2). These two cations (Na^+ and NEt_4^+) were chosen because Na^+ is smaller than K^+, while tetraethylammonium is larger than K^+ and with lower coordination capabilities to oxygen donor groups than alkali metals. It is worthy of note that when tetraethylammonium was employed, the titrant was tetrabutylammonium hydroxide; however, the concentration of the latter cation is negligible with respect to the former. The best fitting model with Na^+ or NEt_4^+ is the same as with K^+, while the stability of the two MCs depends on the type of cation employed (Table 2). The kinetics for attaining the equilibrium conditions in these potentiometric titrations did not change appreciably with respect to that observed with KCl as the background electrolyte. Also in these cases, the presence of the polynuclear species was confirmed by the ESI–MS results (see below).

Visible spectrophotometry

Visible spectra for the Ni^{2+}/α-Alaha system have been collected at variable pH and at different ligand/metal ratios: they are reported as Supplementary Information (Fig. S5†), while the molar absorbances for single species corresponding to the potentiometric model are shown in Fig. 3. It is worth noting the excellent agreement with literature data as far as mono-nuclear species are concerned.[12]

Table 2 Overall complex-formation constants for the system Ni^{2+}/α-Alaha T = 298.2 K and I = 0.1 mol dm^{-3} using different background electrolytes. Standard deviation on the last figure in parentheses

Titrant	KOH	NaOH	$(C_4H_9)_4NOH$
Background salt	KCl	NaCl	$(C_2H_5)_4NCl$
Species			
$[NiL]^+$	6.88 (1)	6.97 (1)	7.09 (1)
$[NiL_2]$	14.05 (1)	14.06 (2)	14.25 (2)
$[NiL_2H_{-1}]^-$	4.87 (3)	5.25 (5)	5.19 (4)
$[Ni_5L_4H_{-4}]^{2+}$	15.51 (5)	16.04 (6)	16.40 (4)
$[Ni_5L_5H_{-5}]$	13.53 (8)	13.5 (1)	11.5 (1)
σ	1.9	1.9	3.3
n	370	287	362

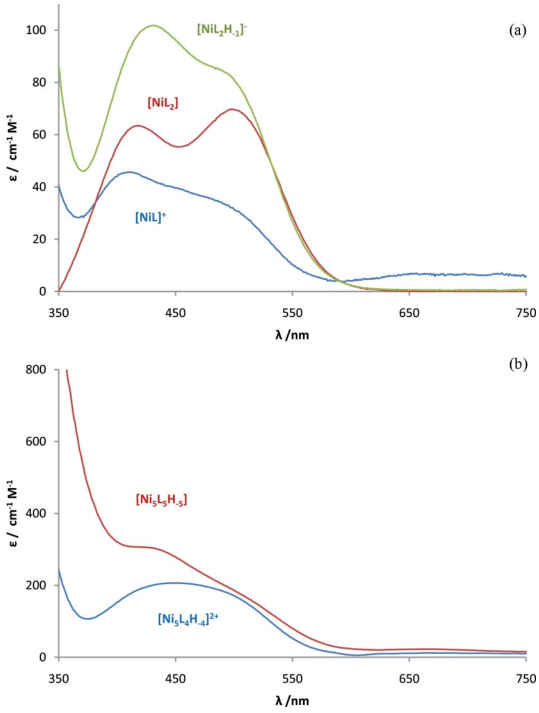

Fig. 3 Calculated UV-Vis absorption spectra for the single complex species in the Ni^{2+}/α-Alaha system. Experimental spectra registered at different pH values are shown in Fig. S5 (Supplementary Information†).

ESI–MS

Solutions of the system Ni^{2+}/α-Alaha with the same concentrations employed in the potentiometric studies, without addition of background electrolyte (which could interfere with the measurements due to its high concentration), were studied by ESI–MS at different pH values, chosen at the maximum of formation of the different metal complexes. The pH was adjusted using KOH,

Table 3 ESI–MS ions for the complex species of the systems Ni^{2+}/α-Alaha or Valha in the presence of different cations. The *m/z* values refer to the most intense peak of each multiplet

	α-Alaha			Valha	
Species	K^+ *m/z*	Na^+ *m/z*	TMA^+ *m/z*	Na^+ *m/z*	TMA^+ *m/z*
$[NiL]^+$					189.0
$[NiL_2]K^+$	303.2				
$[NiL_2]Na^+$		287.1		343.2	
$[NiL_2H_{-1}]^-$					319.2
$[NiL_2H_{-1}]K_2{}^+$	340.9				397.1
$[NiL_2H_{-1}]Na_2{}^+$		309.1		365.2	
$[Ni_5L_4H_{-4}]Cl^+$	737.0	734.8	736.8	849.0	848.9
$[Ni_5L_4H_{-4}]^{2+}$		350.0	350.0	406.1	406.1
$[Ni_5L_5H_{-5}]K^+$	841.0				
$[Ni_5L_5H_{-5}]Na^+$		825.0		965.0	

NaOH or tetramethylammonium hydroxide‡ in order to verify the role of the cation as a possible core metal in the 15-MC-5 species. All the complexes suggested by potentiometry were detected in ESI–MS spectra, as reported in Table 3 and in Fig. 4, S6 and S7 (Supplementary Information†). It is worthy of note that the complex $[Ni_5L_5H_{-5}]$ was detected as an adduct with the alkali metals, but not in systems containing tetramethylammonium.

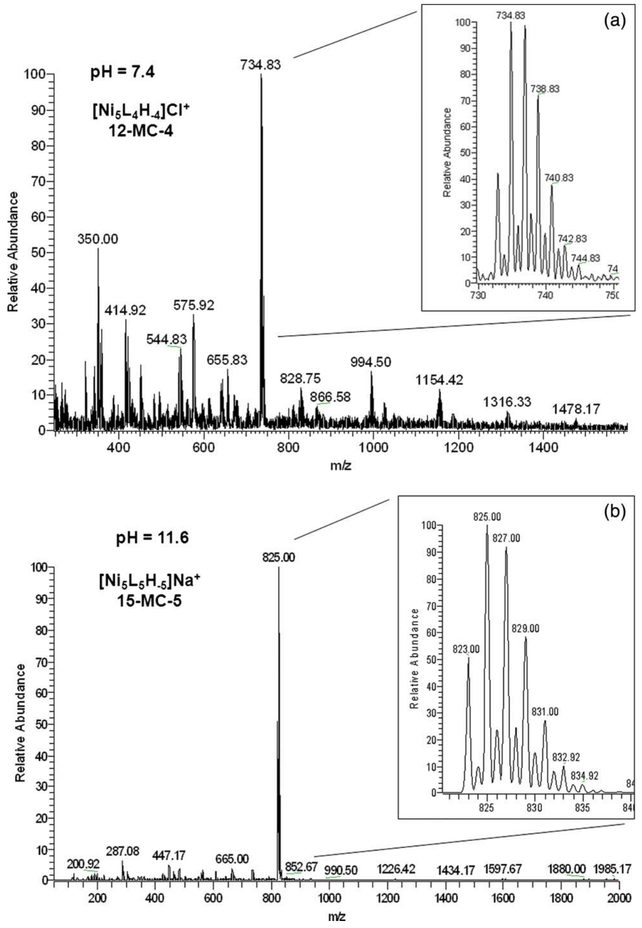

Fig. 4 ESI–MS spectra for the Ni^{2+} / α-Alaha system in aqueous solution at pH 7.4 and 11.6, respectively. Base employed to adjust pH: NaOH.

Crystal structure of $K[NiL_2H_{-1}]\cdot5/3H_2O$ with α-Alaha

The complex $K[NiL_2H_{-1}]\cdot5/3H_2O$ contains the $[NiL_2H_{-1}]^-$ species which is formed when an excess of the ligand is present at pH > 8. The asymmetric unit is made up of two *cis*-$[NiL_2H_{-1}]^-$ anionic complexes, one in a general position and the latter on a twofold axis passing through the Ni and H5 atoms, two K^+ cations, one of them laying on a twofold axis, two water molecules in general positions and one on a twofold axis. Accordingly, the ratios among the three different moieties forming the crystal: potassium, *cis*-$[NiL_2H_{-1}]^-$ complex and water are 3 : 3 : 5.

ORTEP[13] views of both the independent anionic complexes are shown in Fig. 5a and 5b. The coordination geometries around K1 and K2 cations are shown in Fig. 6a and 6b. The crystal packing diagram is displayed in Fig. S8 (Supplementary Information†). Selected interatomic distances and angles are given in Table 4. The hydrogen bond parameters are reported in Table 5.

The Ni(II) atoms are coordinated in square-planar fashion, through four nitrogens, by both a mono-deprotonated and a bi-deprotonated α-Alaha ligand, *cis* to each other. The first complex, containing the Ni1 atom and situated in a general position, displays a slight asymmetry with the OH hydrogen of a hydroxamate moiety localized on the O3 oxygen. In the latter complex the H5 hydrogen is shared and centered between the O5 and O5′ oxygens related by twofold symmetry. The Ni atoms in both complexes are surrounded by two nitrogen atoms belonging to two N-deprotonated hydroxamate groups and two aminic nitrogens of alanine moieties. The Ni–N (deprotoated nitrogen) bond lengths, in the range 1.845(3)–1.854(4) Å, are typical for square planar Ni(II) complexes with deprotonated hydroxamate ligands[14–18] and are longer than Ni–N (aminic) distances between Ni(II) and N (sp^3) nitrogens, in the range 1.920(4)–1.924(3) Å. The hydroxamate groups exhibit extended conjugation, localized mainly on the $O{=}C{-}N^- \leftrightarrow {}^-O{-}C{=}N$ group, while the $N{-}O^-$ and N–OH distances, in the range 1.389(5)–1.399(4) Å, are close to those observed in neutral oximes.[19] The O1 · · · O3 and O5 · · · O5′ hydrogen bond distances of 2.406(5) and 2.429(5) Å, respectively, are very short and exhibit parameters which are characteristic of square-planar *cis*-bis(oximato) Ni(II) complexes.[20–26] These very strong O–H · · · O interactions can be accounted for both by a compression due to the chelation around Ni(II) cations and by the homomolecular negative charge assisted (–)CAHB $[O\cdots H\cdots O]^-$ hydrogen bond.[27]

The K1 cation is seven-coordinated by a water molecule and three Ni(II) complexes, which act as bidentate ligands through two hydroxamate oxygens. The polyhedron around the K1 cation can be described as a distorted trigonal prism monocapped by the water molecule O1w (Table 4, Fig. 6a). The K2 cation, situated on a twofold axis, is five coordinated by two complex anions, acting as monodentate ligands through the hydroxamate oxygen O6, and three water molecules. The coordination geometry can be described as a distorted square planar pyramid where the vertex is occupied by the water molecule O2w and the basal plane by two water molecules O1w and two O6 oxygens of two complex anions both related by twofold axes. (Table 4, Fig. 6b).

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‡ We used tetramethylammonium hydroxide rather than the tetrabutylammonium one in ESI–MS studies to prevent matrix effects which often occur with big alkylammonium ions and which obscure the detection of the signals of other ions.

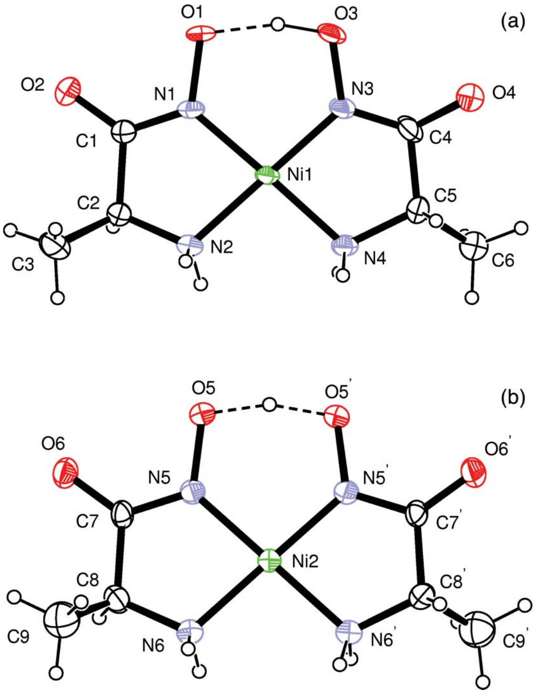

Fig. 5 (a) An ORTEP view of the anionic complex *cis*-$[NiL_2H_{-1}]^-$ with α-Alaha, in general position, showing the thermal ellipsoids at 40% probability level. (b) An ORTEP view of the anionic complex *cis*-$[NiL_2H_{-1}]^-$ with α-Alaha, situated on a twofold axis passing through Ni2 and H5 atoms, showing the thermal ellipsoids at 40% probability level. [‘] = *y*, *x*, 1 − *z*.

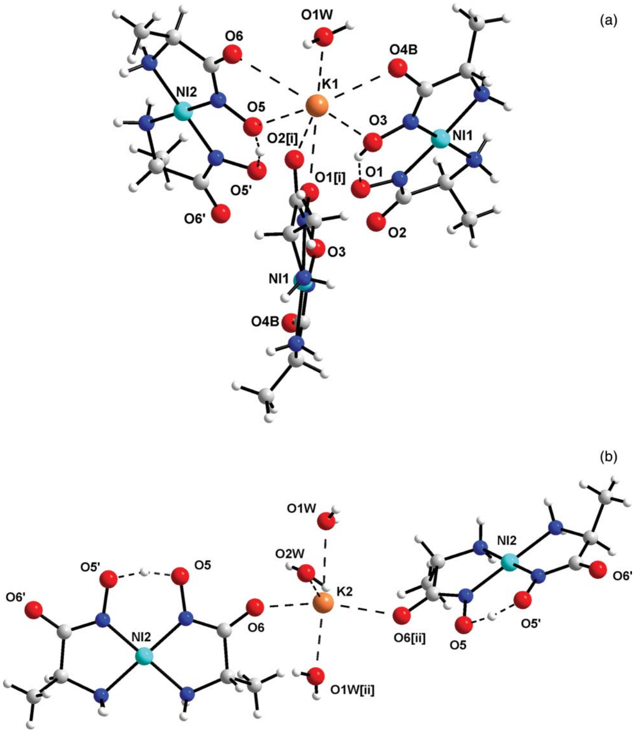

Fig. 6 (a) Coordination geometry around the K1 cation. [i] = *y*, *x*, 1 − *z*. (b) Coordination geometry around the K2 cation. [ii] = *x* − *y*, −*y*, 2/3 − *z*.

An extensive network of hydrogen bonds connects the Ni(II) anionic complexes and water molecules (Table 5).

DFT calculations on 15-MC-5 with α-Alaha

The molecular geometry of a vacant $[Ni_5L_5H_{-5}]$ of α-Alaha was optimized in order to substantiate the hypothesis that this species can form in solution (Fig. 7). The pentanuclear structure can be viewed as derived by the connection of five regular tiles that are represented by the five Ni(II)-donor atom moieties. The presence of the sp^3 hybridized systems –CH–NH_2 causes a slight distortion from the ideal planar geometry of the overall structure. However, any single Ni(II) coordination system is actually planar, even though the Ni(II) coordination planes are tilted with respect to each other with angles of 6–14°, approximately. In fact, The Ni(II)-donor atom bond distances are in agreement with those reported for square planar Ni(II) complexes with nitrogen or oxygen as donor atoms (Table 6).[28] The distance between the molecular center and the oxygen atoms that define the pentagonal cavity is 2.40 Å. Notably, taking into account an ionic radius for a tri-coordinated oxygen of 1.36 Å,[29] the calculated cavity radius results 1.04 Å, which is not different from that of the Cu(II) 15-MC-5 with phenylalaninehydroxamic acid (1.03–1.09 Å, calculated from X-ray structural data).[30] This cavity is suitable for accommodating large metal ions such as heavier lanthanides (ionic radii = 1.05–0.98 Å from Gd^{3+} to Lu^{3+}, coordination number = 8) or Na^+ (ionic radius = 1.00 to 1.18 Å for a coordination number from 5 to 8).[29] On the other hand, the cavity is too small for the in-plane accommodation of a potassium cation, which possesses a ionic radius of 1.38–1.51 Å (coordination number from 6 to 8).[29] In fact, preliminary calculations performed on $\{Na[Ni_5L_5H_{-5}]\}^+$ and $\{K[Ni_5L_5H_{-5}]\}^+$ model complexes, showed that in the former complex the Na^+ cation resides into the penta-atomic cavity, whereas in the latter complex, the K^+ cation is located outside of the metallacrown molecular plane with formation of a side-on complex (results not shown).

Discussion

Mononuclear complexes

With regards to the mononuclear complexes formed by Ni(II) with α-Alaha or Valha, structures analogous to those already proposed for the corresponding Cu(II) complexes can be considered (Fig. 8).[7] In particular, for α-Alaha the *trans*-configuration of $[NiL_2]$ (Fig. 8c) has been found in the compound $NiL_2{\cdot}2H_2O$ by X-ray analysis,[16] while the *cis*-configuration of $[NiL_2H_{-1}]^-$ is supported by the above-reported single-crystal data of $K[NiL_2H_{-1}]{\cdot}5/3H_2O$ complex, where an $(OH\cdots O^-)$ intramolecular hydrogen bond occurs, as already found in the case of the analogous species with Glyha.[15]

The thermodynamic data obtained for the formation of these complexes (Table 1) are in accordance with these structural hypotheses. The formation of mononuclear complexes is favoured from both the enthalpic and the entropic contributions, even though the latter is the prevailing one. In fact, the complex formation always leads to a partial or a total charge neutralization, with respect to the reagents, with a consequent release of water molecules from their solvation sphere.

Table 4 Selected bond distances (/Å) and angles (/degrees). Standard deviation on last figure(s) is given in parentheses

Ni1–N1	1.854(3)	Ni2–N5	1.845(3)
Ni1–N2	1.921(4)	Ni2–N6	1.920(4)
Ni1–N3	1.853(4)		
Ni1–N4	1.924(3)		
N1–O1	1.399(4)	N5–O5	1.403(5)
N1–C1	1.313(4)	N5–C7	1.322(5)
C1–O2	1.272(5)	C7–O6	1.258(5)
N3–O3	1.389(5)		
N3–C4	1.298(6)		
C4–O4A	1.338(7)		
C4–O4B	1.327(7)		
K1 ··· O5	2.722(3)	K2 ··· O6	2.613(3)
K1 ··· O6	3.050(3)	K2 ··· O6 $[x-y, -y, 2/3-z]$	2.613(3)
K1 ··· O1 $[y, x, 1-z]$	2.654(3)	K2 ··· O1w	2.752(4)
K1 . . . O2 $[y, x, 1-z]$	3.069(3)	K2 ··· O1w $[x-y, -y, 2/3-z]$	2.754(4)
K1 ··· O3	2.681(4)	K2 ··· O2w	2.678(9)
K1 ··· O4B	2.791(6)		
K1 ··· O1w	2.916(5)		
N1–Ni1–N2	83.1(2)	N5–Ni2–N6	84.1(2)
N1–Ni1–N3	97.2(2)	N5–Ni2–N5′	96.2(2)
N1–Ni1–N4	175.4(2)	N5-Ni2–N6′	179.7(2)
N2–Ni1–N3	175.5(2)	N6–Ni2–N5′	179.7(2)
N2–Ni1–N4	95.9(2)	N6–Ni2–N6′	95.7(2)
N3–Ni1–N4	84.2(2)		
Ni1–N1–O1	123.4(3)	Ni2–N5–O5	124.6(3)
Ni1–N1–C1	120.4(3)	Ni2–N5–C7	120.4(3)
O1–N1–C1	115.9(3)	O5–N5–C7	115.0(3)
Ni1–N3–O3	123.4(3)		
Ni1–N3–C4	120.3(3)		
O3–N3–C4	116.3(3)		

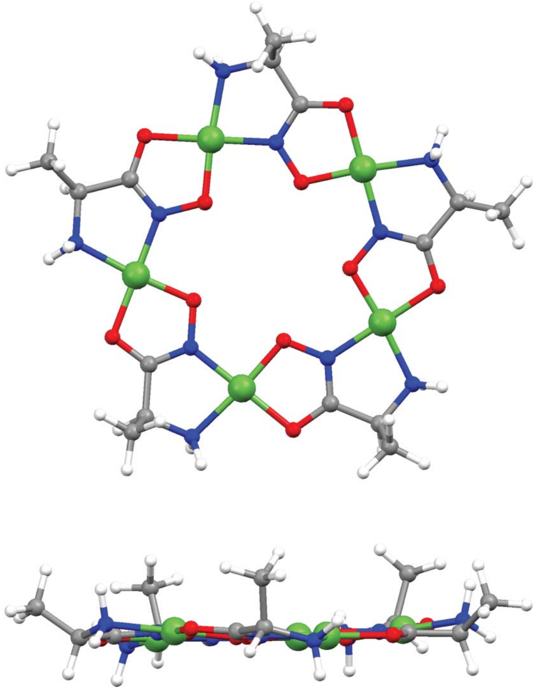

Fig. 7 Optimized molecular structure of vacant [$Ni_5L_5H_{-5}$] where the ligand is α-Alaha; top view (above), side view (below). The geometry was optimized with the B3LYP density functional and with the 6-31G(d)/(C,H,N,O) and lanl2dz/Ni basis sets.

For [NiL]$^+$ both log$K$ and ΔH° values (6.88 and −13 kJ mol^{-1}) are lower than those of [CuL]$^+$ (10.5 and −33 kJ mol^{-1}, respectively) as expected, while ΔS° values are quite similar (92 and 95 J K^{-1} mol^{-1} for Ni^{2+} and Cu^{2+}, respectively). Either {NH$_2$,N$^-$} or {O,O$^-$} chelations are possible (Fig. 8, structures a and b). Moreover, both octahedral and square-planar geometries should be allowed, considering the presence, in the visible spectra, of d-d bands both at 700 and 400–500 nm.[31] The formation of [NiL$_2$] from [NiL]$^+$ presents a logK_2 value (7.17) higher than logK_1 (6.78) and this suggests the loss of any octahedral character in favour of a {2NH$_2$,2N$^-$} pure square-planar geometry[16] (structure c). This process is mainly entropy-driven (95 J K^{-1} mol^{-1}, Table 3) owing to the release of water molecules as a consequence of the charge neutralization. The disappearance of the 700 nm signal in the visible spectrum of [NiL$_2$] supports the above conclusions. The two bands around 420 and 500 nm do not significantly change position, supporting {NH$_2$,N$^-$} coordination for both the [NiL]$^+$ and [NiL$_2$] complexes.

The reaction *trans*-[NiL$_2$] → *cis*-[NiL$_2$H$_{-1}$]$^-$ + H$^+$ presents a pK_a value (9.18) significantly lower than that observed with Cu(II)

Table 5 Hydrogen bond parameters (Å, degrees). Standard deviation on last figure(s) is given in parentheses

D–H	d(D–H)	D(H ··· A)	<D–H ··· A	d(D ··· A)	A [Symm. Op.]
N2–H200[a]	0.90	1.94	168	2.833(6)	O5 $[x+1, y, z]$
N4–H400[a]	0.90	1.98	170	2.866(7)	O2 $[y+1, x, -z+1]$
N4–H401[a]	0.90	2.19	170	3.076(7)	O6 $[x+1, y, z]$
O3–H1	1.06(9)	1.48(9)	143(8)	2.406(5)	O1
N6–H600[a]	0.90	2.05	163	2.922(3)	O3 $[x-1, y-1, z]$
O5–H5	1.23(4)	1.23(4)	161.8(2)	2.429(5)	O5 $[y, x, -z+1]$
O1W–H11W	0.88(8)	2.07(8)	145(6)	2.836(10)	O3WB
O1W–H12W	0.88(5)	1.98(6)	149(5)	2.768(12)	O3WA $[x-y+1, -y+1, -z+2/3]$
O1W–H12W	0.88(5)	2.16(4)	162(5)	3.004(8)	O3WB $[x-y+1, -y+1, -z+2/3]$
O2W–H2W	0.90(4)	1.79(4)	169(3)	2.675(8)	O3WA $[x-y+1, -y+1, -z+2/3]$
O3wA[b]				2.840(9)	O2 $[y, x, 1-z]$
O3wA[b]				2.726(11)	O4A $[x-y, 1-y, 2/3-z]$
O3wA[b]				2.577(10)	O4B $[x-y, 1-y, 2/3-z]$
O3wB[b]				2.767(7)	O2 $[y, x, 1-z]$
O3wB[b]				2.426(9)	O4A $[x-y, 1-y, 2/3-z]$
O3wB[b]				2.672(8)	O4B $[x-y, 1-y, 2/3-z]$

[a] Hydrogen calculated; [b] Hydrogen not localized

Table 6 Selected bond lengths (Å) and angles (degrees) for the DFT structure of the complex $[Ni_5L_5H_{-5}]$ with α-Alaha

Ni–$O_{external}$	Ni–$O_{internal}$	Ni–NH_2	Ni–N
1.895	1.817	1.984	1.875
1.895	1.818	1.986	1.874
1.894	1.818	1.986	1.874
1.894	1.817	1.985	1.874
1.895	1.816	1.987	1.874

O–Ni–O	N–Ni–N	O_{ext}–Ni–N_{ext}	O_{int}–Ni–N_{int}
87.55	82.57	97.11	92.75
87.45	82.83	97.16	92.56
87.57	82.72	96.91	92.84
87.60	82.47	96.99	92.93
87.57	82.56	97.18	92.70

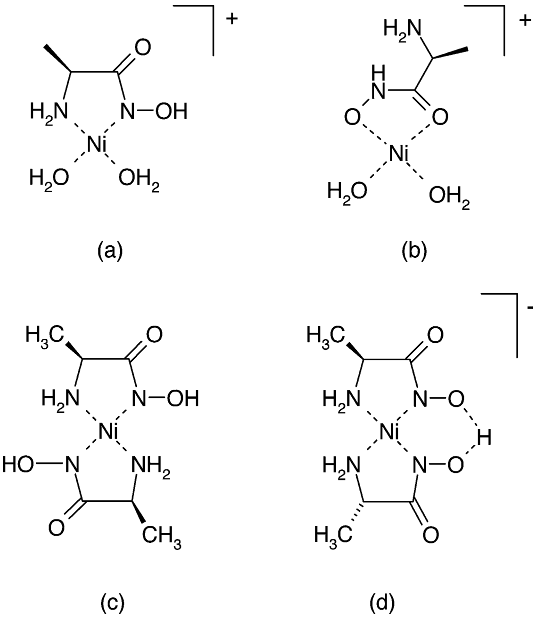

Fig. 8 Structural hypotheses for the mononuclear Ni^{2+} complexes with α-Alaha, in aqueous solution. (a) $[NiL]^+$ $\{NH_2, N^-\}$; (b) $[NiL]^+$ $\{O,O^-\}$; (c) $[NiL_2]$; (d) $[NiL_2H_{-1}]^-$.

(10.02) and for the free ligand (>11).[7] Since no water molecule is bound to the metal ion this deprotonation process must involve the hydroxyl of one hydroxamate group and the low pK_a is justified by the formation of the O···H···O intramolecular hydrogen bond observed in the solid state, with the concomitant change in configuration from *trans* to *cis*. The visible spectrum also supports this change of configuration in solution, as the two absorption bands become more intense, especially that at 420 nm. Actually, the corresponding $\Delta H°$ value (20.3 kJ mol^{-1}) for the deprotonation of $[NiL_2]$ can be considered as the sum of the endothermic deprotonation process of one NOH^- group (with a small contribution due to the unfavourable *trans*/*cis* configuration change) and the exothermic formation of the intramolecular hydrogen bond. The former can be estimated considering that $\Delta H°$ for the reaction: $Cu^{2+} + –NOH^- \rightarrow –NO–Cu + H^+$ is 35 kJ mol^{-1},[32] a value entirely attributable to the deprotonation of the hydroxamic group since the formation of a Cu–O bond is characterized by an enthalpic contribution of almost nil.[33] The difference between the latter and the former values (~15 kJ mol^{-1}) is an estimation of the hydrogen-bond strength, in solution. Finally, the large entropy diminution observed, $\Delta S° = -106$ J K^{-1} mol^{-1}, is accounted for by the reordering of the solvent around the two ions formed in the reaction.

Nickel(II) metallacrowns

Both ligands examined form two MCs of Ni(II) of similar stability; therefore, only the results concerning α-Alaha are discussed here in detail. The two MCs $[Ni_5L_4H_{-4}]^{2+}$ and $[Ni_5L_5H_{-5}]$ are formed in solution only when the ligand/metal molar ratio is lower than 2. This fact could explain why they were not detected in previous speciation studies, where an excess of ligand was employed.[8] The distribution diagram of Fig. 2 shows that the 12-MC-4 species appears at pH *ca.* 6, together with $[NiL_2]$, and it reaches its maximum (40%) at pH *ca.*7. Increasing the pH, these two complexes transform into the 15-MC-5 and $[NiL_2H_{-1}]^-$ species, respectively. Both complexes (50% each) are maintained up to pH *ca.*11. As regards the stability of the nickel 12-MC-4 compared to the corresponding MC with copper, the former ($\log\beta = 15.51$) is noticeably lower than that the latter ($\log\beta = 40.16$; Table S2, Supplementary Information†). This result is accounted for by considering the lower affinity of Ni^{2+} for O^- and N^- ligands with respect to Cu^{2+}, mainly due to enthalpic contributions (see Tables 1 and S3, Supplementary Information†). It should be taken also into account that the Cu(II) 12-MC-4 with α-Alaha[7] is not planar, having a concave shape with significant deviation from planarity for the Cu(II) equatorial coordination environment. As a consequence, the latter strained structure is less suitable for Ni^{2+} which has a preference for the planar geometry.

The formation of the 15-MC-5 species $[Ni_5L_5H\text{-}_5]$ was completely unexpected not only because the Ni(II) 15-MC-5 complexes obtained so far in the solid state had a Ln^{3+} or the Pb^{2+} ion as core metals, but also because this species was never detected for the extensively studied Cu(II) systems.[11] However, the inclusion of this complex in the speciation model dramatically improved the fitting of the potentiometric titrations. Its presence was also confirmed by ESI–MS spectra of both α-Alaha and Valha and in the presence of both KCl and NaCl.

These results suggest a possible templating role of K^+ or Na^+ as core metal ions for the 15-MC-5 self assembly. The excess of these alkali metals can actually promote the assembly of 15-MC-5, and justifies the exclusion of the Na^+ or K^+ components from the speciation models as these metallacrown complexes are formed under self-medium conditions.[34] The investigation was then extended to systems where the alkaline metal-ions are absent and substituted with non-coordinating tetraalkylammonium ions. The treatment of the potentiometric data obtained from solutions where the only cations present (besides Ni^{2+}) were tetraethyl- and tetrabutylammonium ions, still suggests the presence of the 15-MC-5 $[Ni_5L_5H_{-5}]$. The stability of this species, however, is dependent on the ionic medium employed: in presence of Na^+ and K^+ ions the $\log\beta$ is 13.5, while in their absence a lower value was determined ($\log\beta = 11.5$, Table 2). Since any tetraalkylammonium ion is obviously too large to fit the metallacrown cavity and possesses poor coordination capabilities, we put forward the hypothesis that in the presence of these ions the 15-MC-5 complex is necessarily vacant. The 15-MC-5 complex was also not detected by ESI–MS using $(CH_3)_4NOH$ as the base.‡ This is not in contrast with the hypothesis of the formation of the 15-MC-5 complex, which, being a neutral species, requires a counter-ion to form an ionic adduct detectable in MS. However, the absence of any 15-MC-5 signal is a proof of the poor tendency of the tetraalkylammonium cations to interact with the Ni^{2+} complexes. In support of this hypothesis is the absence of any signal derived from the $[NiL_2]$ complex, which is also a neutral species and the formation of which in solution is not in doubt.

As regards the $\log\beta$ values, these are higher when K^+ or Na^+ are used in place of a NR_4^+ cation, but they are substantially independent of the nature of the alkali metal. This seems in contrast with the observation, shown by DFT calculations, that only Na^+ can fit the cavity of a 15-MC-5, while K^+ is too large. On this ground, a recent thermodynamic investigation on Ca^{2+} and Ln^{3+} 15-MC-5 complexes with Cu(II) and (*S*)-phenylalaninehydroxamic acid or (*S*)-tryptophanhydroxamic acid clearly demonstrated that the size correspondence between the core metal and the cavity radii is not a key factor in the determination of the overall 15-MC-5 stability.[30] For instance, it has been reported that La^{3+} and Nd^{3+}, which possess an ionic radius larger or on the upper edge of the 15-MC-5 cavity, are capable of interacting efficiently with the oxygens of the cavity. Moreover, even if they are only partially encapsulated with significant deviations from the cavity plane (as occurs for the large La^{3+} ion), their stability is equal to or even slightly higher than that of Gd^{3+} which is quite perfectly accommodated into the MC cavity. As a matter of fact, the size correspondence is a key factor only for cations smaller than the cavity.[30] The preliminary DFT investigations on Na^+ and K^+ complexes presented here, together with the detailed DFT analysis of the $[Ni_5L_5H_{-5}]$ species, seem to suggest a similar behaviour.

The fact that the Ni(II) 15-MC-5 species is formed in solution, irrespective of the presence or the absence of alkali metals is actually a relevant result, showing that the Ni(II) ion is inherently different from Cu(II) with respect to metallacrown formation. As a matter of fact, it was demonstrated that the homometallic Cu(II) 12-MC-4 complex is, in the absence of a suitable di- or trivalent core metal ion, the only polynuclear species present in solution.[7] The assembly of a strained 12-MC-4 with a cavity occupied by a copper ion is therefore favoured over the assembly of a vacant 15-metallacrown-5.

The formation of vacant Ni(II) 15-MC-5 species besides the 12-MC-4 species should result from the balance of two main factors, namely the tendency of Ni(II) to achieve a planar coordination environment and that of aminohydroxamates to form metallacrown species where the cavity is occupied by a suitable metal ion. While the second factor promotes the formation of 12-MC-4 species, the first plays in favour of the vacant 15-MC-5 species, and in the case of Ni(II) the latter factor seems to predominate. By virtue of these considerations, the existence of the $[Ni_5L_5H_{-5}]$ can be accounted for by the inherent stability of the metallamacrocyclic scaffold, and is independent of templating effects of core metals. The presence of cations such as K^+ or Na^+ has the effect of increasing the stability of the 15-MC-5 species, but not templating its formation.

Conclusions

The present investigation on the Ni(II)/α-Alaha or Valha systems confirms that Ni(II), like Cu(II), can form in solution a 12-MC-4 with α-aminohydroxamates, although of lower stability, when the ligand/metal ratio is lower than two. At pH > 8.5 this metallacrown converts into an unexpected 15-MC-5 species, in the presence of both an alkaline metal ion (K^+ or Na^+) and a tetraalkylammonium salt as the background electrolyte. The thermodynamic, ESI–MS and DFT studies suggest that this complex can exist as a vacant 15-MC-5, a species never observed in Cu(II) systems. Our experimental data show that the alkali metals stabilize the 15-MC-5 species, although it is not clear if they play a role in templating the MC formation,

These results demonstrate how Ni(II)/α-aminohydroxamates 15-MC-5 species are a new and powerful class of metallacrowns. Actually, vacant 15-MC-5 complexes may have possible applications in cation recognition and separation, especially for large cations such as lanthanides and possibly actinides, with an impact on the field of material sciences and in the treatment of nuclear wastes, as it has been recently shown for Cu(II) MC analogues.[30]

Experimental

Reagents

(*S*)-α-Alaninehydroxamic acid (α-Alaha) and (*S*)-valinehydroxamic acid (Valha) were synthesized as previously reported.[35] Their purity was checked by potentiometric titrations and NMR. The ligands were dried *in vacuo* over P_4O_{10} and sample solutions were prepared by weight with fresh MilliQ (Millipore) water. KOH, NaOH, $(C_4H_9)_4NOH$, $(CH_3)_4NOH$, HCl, HNO_3 and $NiCl_2\cdot 6H_2O$ solutions were prepared from highly pure products, with procedures described elsewhere.[36]

Synthesis of $K[NiL_2H_{-1}]\cdot 5/3H_2O$

2.08 mg of α-Alaha (~0.02 mmol) were mixed with 0.56 cm^3 of $NiCl_2$ 0.0177 mol dm^{-3} (~0.01 mmol). After dilution with 4 cm^3 of water, the solution pH was adjusted to 10 with KOH 0.1 mol dm^{-3}. A few green crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Potentiometry

Potentiometric titrations were performed with the following equipment: Orion EA 940 pH meter (resolution 0.1 mV, accuracy 0.2 mV) equipped with a combined glass electrode (Metrohm EA125); Hamilton MicroLab M motor burette equipped with a 500 mm^3 Hamilton syringe (resolution 0.1 mm^3, accuracy 0.2 mm^3). Constant-speed magnetic stirring was applied throughout. The temperature of the titration cell was kept at 298.2 ± 0.1 K by use of a Haake F3C circulation thermostat. UPP grade nitrogen, previously saturated with H_2O (0.1 mol dm^{-3} KCl, 298.2 K) was blown over the test solution in order to maintain an inert atmosphere. The electrodic chain was calibrated on the $pH = -\log c_{H^+}$ scale by titration of HNO_3 0.01 mol dm^{-3} (I = 0.1 mol dm^{-3}, KNO_3) with standard KOH. Aliquots (2 cm^3) of sample solution, containing suitable amounts of metal, ligand, HCl and the background electrolyte (KCl, NaCl or $(C_2H_5)_4NCl$), were titrated with the corresponding standard base solution. The concentration range employed for both Ni^{2+} ion and the ligands was 1.0–8.0 mmol dm^{-3}; the metal/ligand ratios ranged from 1 : 1.5 to 1 : 8. The pH range explored was approximately 3–11. The slow kinetics characterizing the formation of MC complexes required long waiting times between the titrant additions; the suitable interval was determined from time to time, checking the stability of the voltage after each addition. This control was based on the computation of standard deviation (max. 0.05 mV) on the last nine e.m.f. readings, taken at 3 s intervals. The maximum waiting time was fixed as 30 min. Total titration times often reached 16 h when the lowest ligand/metal ratios were employed, in order to favour the MC formation.

Calorimetry

Enthalpy values for Ni^{2+} complexation with the ligands were obtained by means of calorimetric titrations performed with a Tronac 450 calorimeter equipped with a 3 cm^3 dewar titration vessel, at $T = 298.16 \pm 0.02$ °C and $I = 0.1$ mol dm^{-3} (KCl). The sample solutions had compositions similar to those employed in the potentiometry. The titrant (standard HCl) was added using a 1 cm^3 Hamilton syringe also immersed in the thermostatic bath. The pH range explored was approximately 11–3. A warming resistance (~100 Ω) and a thermistor placed in the solution respectively allowed the instrument to be electrically calibrated and temperature variations to be detected. Accuracy was checked daily by titrating a 2-amino-2-(hydroxymethyl)-1,3-propanediol (THAM) solution with nitric acid. The completely automated system was managed by a personal computer *via* a Tronac 900 interface. The potential difference at the thermistor ends was measured by a FLUKE 8840A digital multi-meter. In the case of the low ligand/metal ratios required to favour the formation of MC species, the reaction kinetics was slow and the isoperibolic calorimeter was employed in a "batch mode": each titration experiment consisted of a single, small addition of acid to the sample solution, followed by a long waiting time (up to 20 min) during which all the developed or absorbed heat was measured. At the end of the experiment, the solution was cooled again (without opening the dewar cell) and it was ready for a new addition (and measurement). In such a way, a complete titration took one working day, collecting 12–14 experimental points. This method, successfully tested on known systems (data not shown), allowed the estimation of the formation-enthalpy of the MC complexes, although with rather high standard deviations.

Home-made programs for the management of the calorimetric system, data acquisition and gross heat correction for non-chemical contributions[37] and dilution heats (computed from literature data[38]) were all in BASIC language. From experimental $\Delta H°$ values the corresponding $\Delta S°$ values were computed by means of the Gibbs–Helmholtz equation: $-\Delta G° = -\Delta H° + T\Delta S°$, where the free energy variation was calculated by the corresponding cumulative constants (β), given by potentiometry: $-\Delta G° = 2.303\ RT \log\beta$.

Visible spectrophotometry

The absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer, equipped with a 1 cm path-length quartz cuvette. Sample solutions had compositions similar to those employed in the potentiometry. Complexation equilibria were studied through visible spectrophotometric titrations by recording spectra in the range 350–900 nm (pH range 3.5–11). In order to investigate the kinetic behaviour of MC complex-formation, visible spectra on two solutions (metal/ligand ratio 1 : 1.2, $C°_{Ni}$ = 6 mmol dm^{-3}, pH = 8.4 and 9.4, respectively) were registered as a function of time (range: 0–60 min, interval: 5 min).

Electrospray-ionization mass spectrometry (ESI–MS)

ESI mass spectra were recorded either on a single quadrupole ZMD Mass Spectrometer (Micromass, Manchester, UK) fitted with a pneumatically-assisted electrospray probe or a linear ion trap LTQ XL Mass Spectrometer (Thermo Scientific, Waltham, MA, USA). Data were processed by using the spectrometer software. The measurements were performed on both Ni^{2+}/α-Alaha and Ni^{2+}/Valha solutions at appropriate pH values, chosen in order to maximize the formation of a single complex species. The samples were prepared in a similar way as described for the potentiometric studies without the addition of background electrolyte. The counter-ion was supplied by the base employed to adjust the pH value, namely KOH, NaOH or $(CH_3)_4NOH$. Direct infusion analyses were always performed at 10 µL min^{-1}. In the case of the ZMD Mass Spectrometer, the conditions were: ES capillary 3.0 kV; cone 30–110 V; extractor 4 V; source block temperature 80 °C; desolvation temperature 150 °C; cone and desolvation gas (N_2) 1.6 and 8 L min^{-1}, respectively. Scanning was performed from m/z = 100 to 1800. When using the LTQ XL mass spectrometer, experimental conditions were as follows: spray voltage 3.0 kV; sheath and auxiliary gas 50 and 5 a.u., respectively; capillary temperature 250 °C; source fragmentation auxiliary voltage 30 V; capillary voltage 20 V and tube lens 50 V for mono-nuclear complexes; capillary voltage 90 V and tube lens 110 V for poly-nuclear species.

Calculations

Ni^{2+} complexation constants were calculated from the potentiometric data with the HYPERQUAD 2006 program.[39] Least-squares treatment was performed by minimization of the sample standard deviation $\sigma = [\Sigma_i w_i(E_i° - E_i^c)^2/(n - m)]^{1/2}$, where $E_i°$ and E_i^c are the observed and calculated e.m.f. values, n is the number of observations and m is the number of parameters refined. The statistical weights w_i were put equal to $1/\sigma_i^2$, where σ_i is the expected error on each observed e.m.f. value (0.2 mV). A literature pK_w value of 13.77 was employed.[33] For each system, the data of different titrations were treated together. The speciation diagrams were plotted with the Hyss program.[40]

$\Delta H°$ values were computed from the calorimetric data by means of the least-squares computer program HypDH,[41] which minimizes the function: $U = \Sigma w_i(Q_i°-Q_i^c)^2$, where w_i are statistical weights and $Q_i°$, Q_i^c are the experimental and calculated heats, respectively, over n observations. A literature $\Delta H°_w$ value of 56.4 kJ mol^{-1}, was used in the calculations.[42]

The spectrophotometric data were treated with the pHab and HypSpec programs, using unit weights.[43]

Throughout, the precision of each thermodynamic parameter is reported as the standard deviation given by the corresponding least-squares program and it is shown in parentheses as uncertainty on the last significant figure.

DFT calculations were carried out using the Gaussian 03 program suite.[44] Geometry optimization were performed for the

Table 7 Crystal data

Compound	K[NiL$_2$H$_{-1}$]·5/3H$_2$O with α-Alaha
Formula	3(C$_6$H$_{13}$N$_4$NiO$_4$)$^-$·3K$^+$·5(H$_2$O)
M	999.12
System	Trigonal
Space Group	$P3_121$(N. 152)
a/Å	9.6236(2)
c/Å	35.6392(8)
U/Å^3	2858.5(1)
Z	3
D_c/g cm^{-3}	1.741
μ/cm^{-1}	18.77
θ_{min}–θ_{max}/°	2.51–28.00
Unique Reflns	3815
R_{int}	0.046
Obs. Reflns [$I > 2\sigma(I)$]	3343
R (Obs. Reflns)	0.0403
wR (All Reflns)	0.0978
Flack parameter	−0.01(2)
S	1.067
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	0.51; −0.45

[Ni$_5$L$_5$H$_{-5}$] species of α-Alaha. The calculations were performed with gradient-corrected hybrid density functional B3LYP[45,46] and with the 6-31G(d) basis set for C, H, N, O[47,48] and the lanl2dz basis set with Hay and Wadt effective core potential (ECP) for nickel.[49,50] Molecular orbital diagrams were generated with the GaussView program.[51]

Crystal structure determination

The crystal data of K[NiL$_2$H$_{-1}$]·5/3H$_2$O with α-Alaha were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package[52] and corrected for Lorentz, polarization and absorption effects (SORTAV).[53] The structure was solved by direct methods (SIR97)[54] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions riding on their carrier atoms, except the hydrogens H1 and H5 forming strong intramolecular O–H···O hydrogen bonds and the hydrogens of water molecules O1w and O2w which were refined isotropically with the thermal parameters 1.2 times U_{eq} of the carrier atoms. The atoms O4, C6, C9 and the water molecule O3w were found to be disordered and were refined isotropically over two positions with occupancies 0.45 and 0.55, respectively.

All calculations were performed using SHELXL-97[55] and PARST[56] implemented in WINGX[57] system of programs. The crystal data and refinement parameters are summarized in Table 7.

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