Role of the NH_3^+ Moiety in Iron(III)–, Aluminium(III)– and Gallium(III)–Aminohydroxamate Interactions

Etelka Farkas,[*,a] **Emese Kozma,**[a] **Tamás Kiss,**[a] **Imre Tóth**[a] **and Barbara Kurzak**[b]
[a] *Department of Inorganic and Analytical Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary*
[b] *Institute of Chemistry, Pedagogical University, Siedlce, Poland*

Stability constants have been determined and the bonding modes and effects caused by the side-chain NH_3^+ moiety in aminohydroxamic acids evaluated for complexes formed in aqueous solution in between iron(III), aluminium(III) and gallium(III) with α-alaninehydroxamic acid (α-Alaha), β-alaninehydroxamic acid (β-Alaha), aspartic acid-β-hydroxamic acid (Asp-β-ha) and glutamic acid-γ-hydroxamic acid (Glu-γ-ha). The iron(III)–, aluminium(III)– and gallium(III)–acetohydroxamic acid (aha) systems were studied as models. Co-ordination of hydroxamate oxygens occurs in the cases of aha, α- and β-Alaha, while Asp-β-ha and Glu-γ-ha are co-ordinated *via* their hydroxamate and carboxylate oxygens. The OH^- ion was found to be an effective ligand in these systems (especially for Ga^{III}) causing the formation of both binary and ternary hydroxo complexes. The presence of NH_3^+ in the hydroxamic acids favours the hydrolysis to an extent which depends on the distance between the hydroxamate moiety and NH_3^+. These findings can be explained by the electron-withdrawing effect of NH_3^+ and electrostatic repulsion between it and the co-ordinating M^{3+} ion.

It is well known that siderophores synthesised by micro-organisms, containing primarily either hydroxamate or catecholate groups as chelators, are able to protect the classical 'hard' metal ion Fe^{III} against hydrolysis.[1] The same behaviour has been found with interesting synthetic analogues prepared in different laboratories.[2–4] The simple monohydroxamic acids are also effective ligands of Fe^{III} and other high-oxidation-state cations. However, aminohydroxamic acids, such as hydroxamic acid derivatives of simple amino acids, exhibit significant differences in their complex formation as compared with the monohydroxamic acids. They are able to form chelates *via* the amino and hydroxamate nitrogens; this type of chelate is preferred by many metal ions,[5] except by typical hard metal ions, which prefer chelation through the hydroxamate oxygens. The very few papers relating to the complexes formed with hard metal ions reveal contradictions and unsolved problems.[5] In our laboratory, studies have already been performed on the complexes in the Fe^{III}– and Al^{III}–α-Alaha,[6,†] Fe^{III}–Asp-β-ha[7] and Fe^{III}–Glu-γ-ha systems.[8] The surprising result was obtained that hydrolysis of the metal ion is much more suppressed in the systems containing Asp-β-ha and Glu-γ-ha, than in the case of α-Alaha, where numerous mixed hydroxo species are found even if a fairly large excess of hydroxamic acid is used. Moreover, the complexes formed with Glu-γ-ha were found to be more stable than those of Asp-β-ha. The present work was carried out to clarify these, at first sight, unexpected results; detailed equilibrium and structural studies were performed on the complexes of Fe^{III}, Al^{III} and Ga^{III} formed with acetohydroxamic acid (aha) as reference, and with α-Alaha, β-Alaha, Asp-β-ha and Glu-γ-ha, using pH-metric, ^1H, ^{27}Al NMR and spectrophotometric methods. For comparison, results published earlier[5–8] are included as reference data.

Experimental

The compounds Asp-β-ha, Glu-γ-ha and aha were obtained from Sigma, while α-Alaha and β-Alaha were prepared *via* the methyl ester of the respective amino acid.[9] The purities of the hydroxamic acids and the exact concentrations of the stock solutions were determined by the Gran method.[10]

Solutions of Al^{III} and Fe^{III} were prepared by dissolving an appropriate amount of the metal chloride in doubly distilled water or in hydrochloric acid of known concentration. Their exact concentrations were determined gravimetrically *via* precipitation of the quinolin-8-olate or oxide. Gallium(III) solution was prepared by dissolution of the pure (99.99%) metal in a known amount of HCl. The exact concentration of the metal was established by complexometric titration with ethylenediamine-*N,N,N′,N′*-tetraacetate (edta) and the amount of acid was determined by the method of Harris and Martell.[11] pH-Metric titrations were performed at five or six different metal ion : hydroxamic acid ratios in the range 1 : 1–1 : 10. The concentrations of the hydroxamic acids were $(1–3) \times 10^{-3}$ mol dm^{-3}. All pH-metric measurements were carried out at 25.0 ± 0.1 °C, at an ionic strength of 0.2 mol dm^{-3} KCl, with KOH solutions of known concentration (*ca.* 0.2 mol dm^{-3}). The ionisation constant of water under these conditions is $10^{-13.756}$ mol^2 dm^{-6}. The measurements were made with a Radiometer PHM 84 instrument with a GK 2421 C combined electrode, and a Radiometer PHM 64 instrument with a GK 2401 B electrode, throughout the range pH 2.0–11.0, using 10.00 cm^3 samples. The electrode system was calibrated by the method of Irving *et al.*[12] so that the pH-metric readings could be converted into hydrogen-ion concentrations. Concentration stability constants ($\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$) were calculated from pH-metric data with the aid of the PSEQUAD computer program,[13] using literature data on the metal hydroxo complexes.[14–17]

Visible absorption spectra were recorded on a Beckman Acta MIV double-beam recording spectrophotometer over the range *ca.* 300–800 nm. The concentration of Fe^{III} was 5×10^{-4} or 1×10^{-3} mol dm^{-3}, and the metal : hydroxamic acid (aha or β-Alaha) ratio was 1 : 20 or 1 : 10.

The ^1H NMR measurements on the Al^{III}–aha system were made on Bruker AM400 and WP 200SY FT instruments. The aluminium(III) concentration was 2×10^{-3} mol dm^{-3}, and the

---

† For example, α-Alaha = α-alaninehydroxamic acid (2-amino-*N*-hydroxypropanamide).

Table 1 Overall stability constants (log β) for the hydroxamic acids and hydroxo metal ions at 298 K and I = 0.2 mol dm^{-3} (KCl)

Species	aha[a]	α-Alaha[b]	β-Alaha[b]	Asp-β-ha[c]	Glu-γ-ha[a]
HA	9.26	9.16	9.42	9.42	9.50
H_2A	—	16.50	17.91	17.71	18.05
H_3A	—	—	—	19.83	20.26

Species	Fe^{III}[d]	Al^{III}[e]	Ga^{III}[f]
$[MH_{-1}]^{2+}$	−3.21	−5.52	−2.46
$[MH_{-2}]^{+}$	−6.73	—	−5.92
$[M_2H_{-2}]^{4+}$	−4.09	−7.70	
$[M_3H_{-4}]^{5+}$	−7.58	−13.57	
$[MH_{-3}]$	—	—	−10.63
$[MH_{-4}]^{-}$	—	−23.46	−16.87
$[M_{13}H_{-32}]^{7+}$	—	−109.1	—

[a] Ref. 8. [b] Ref 19. [c] Ref. 7. [d] Ref. 15. [e] Ref. 16. [f] Ref. 17.

Al^{III} : aha ratio was 1 : 3 or 1 : 5. The ^{27}Al NMR spectra were recorded on a Bruker AC200 spectrometer equipped with a selective broad-band probe and operating at 52.148 MHz. The chemical shift reference was 0.1 mol dm^{-3} aqueous $AlCl_3$. The concentration of the Al^{III} was 0.04 mol dm^{-3} and the Al^{III} : aha ratio was 1 : 3. All NMR measurements were made in D_2O. The pD values were calculated *via* expression (1).[18]

$$pD = pH_{\text{meter reading}} + 0.4 \qquad (1)$$

Results and Discussion

Dissociation constants for all of the hydroxamic acids involved in the present work had already been determined in our laboratory.[6–8] Not only the macroconstants, but also the dissociation microconstants, are available for α- and β-Alaha.[19] The macro dissociation constants are listed in Table 1, which also contains stability constants for metal ion–hydroxo complexes.[14–17] The tabulated data reveal a strong tendency to hydrolysis in the case of these metal ions, and especially Ga^{III}. For this reason different hydroxo species were included in our speciation models. Initially they were included with fixed stability constants, but if their concentrations were found to be significant in a system these values were refined too {as was the case with the gallium(III)–hydroxo complexes and $[Al(OH)_4]^-$}.

Metal Ion–aha *Systems*.—The model aha ($CH_3CONHOH$) contains only one hydroxamate moiety for co-ordination. Three such ligands, each forming a five-membered chelate, saturate an octahedral co-ordination sphere in stepwise processes. In addition to pH-metry, various spectroscopic measurements (UV/VIS for Fe^{III}–aha, and ^1H and ^{27}Al NMR for Al^{III}–aha) were made to establish the best equilibrium model.

The absorbance spectra were registered as a function of pH at Fe^{III} : aha ratios of 1 : 10 and 1 : 20. The spectra exhibit maximum absorbance in the ranges pH 5–7.5 and 5–8, respectively, with ε_{max} = *ca.* 2800 dm^3 mol^{-1} cm^{-1} at λ_{max} = *ca.* 420 nm. This ε_{max} value suggests the co-ordination of three hydroxamates per iron(III) ion[4,20] in this pH region. Above this pH range a decrease in the absorbance is observed, indicating the formation of complexes containing less than three hydroxamates (mixed hydroxo complexes). Decreasing the ligand excess favours hydrolysis. If the hydroxamic acid : metal ion ratio is 1 : 5 or less, precipitation occurs at below or *ca.* pH 7.

In the calculations on Fe^{III}–aha the experimental pH-metric points were used taken from pH ranges where measurable hydrolysis did not occur. The models yielding the best fitting, together with the related constants, are given in Table 2.

Evaluation of the experimental pH-metric data on Al^{III}–aha demonstrated that two different speciation models yielded acceptable fittings. One involved only the species $[MA]^{2+}$, $[MA_2]^+$ and $[MA_3]$, in addition to the binary hydroxo complexes (see Table 1), while the formation of mixed hydroxo species ($[MA_2H_{-1}]$ and $[MA_2H_{-2}]^-$) too was postulated in the second model. To differentiate between the two models, ^1H and ^{27}Al NMR measurements were carried out. The ^1H NMR measurements were performed in the same concentration range as used in pH-metry. For comparison, the pH dependence of the spectrum of aha (containing only one singlet resonance line) was also measured. When the isotope effect is taken into account,[21] the pK_D calculated from the pD dependence of the chemical shifts for aha correlates well with the value determined by pH-metry. The Al^{III} : aha ratios were 1 : 3 and 1 : 5. Some representative spectra recorded at different pH values at a ratio of 1 : 3 are depicted in Fig. 1.

Table 2 Stability constants (log β) for the complexes of Fe^{III}, Ga^{III} and Al^{III} formed with aha at 298 K and I = 0.2 mol dm^{-3} (KCl)

	M		
Species	Fe^{III}*	Ga^{III}	Al^{III}
$[MA]^{2+}$	11.42	9.51(5)	8.15(2)
$[MA_2]^{+}$	21.10	18.42(4)	15.77(2)
$[MA_3]$	28.30	26.21(5)	21.5(2)
$[MA_2H_{-1}]$	—	—	10.40(3)
$[MA_2H_{-2}]^{-}$	—	—	1.04(5)

* Ref. 8.

As Fig. 1 shows, resonance lines with different chemical shifts are to be found for the aha species throughout the whole measured pH range. The separated signals of free aha (δ 1.94 and 1.80 for HA and A^-, respectively) clearly demonstrate a 'slow exchange regime' between the free and co-ordinated hydroxamic acid. At lower pH values [Fig. 1(*a*)–(*c*)] more than one signal of the complexes can be seen. It can be explained by 'slow exchange' on the ^1H NMR time-scale not only between the free hydroxamic acid and the complexes but also for the ligand exchange between the different complexes. At higher pH [Fig. 1(*c*)–(*e*)] some broadening of the signal of the complex or complexes can be seen. This cannot be attributed to a mutual exchange with the free aha, because it does not broaden. The broadening observed might be related to some chemical exchange between different complexes, but the appearance of two signals with almost identical chemical shifts cannot be ruled out. A detailed study of the ligand-exchange reactions is under progress.

The above results and fittings give greater support to the second speciation model. Representative concentration distribution curves are depicted in Fig. 2. From a comparison of the results in Figs. 1 and 2, the species $[MA]^{2+}$, $[MA_2]^+$ and $[MA_2H_{-2}]^-$ can easily be identified, but in the pH range where the parallel existence of $[MA_3]$ and $[MA_2H_{-1}]$ can be assumed

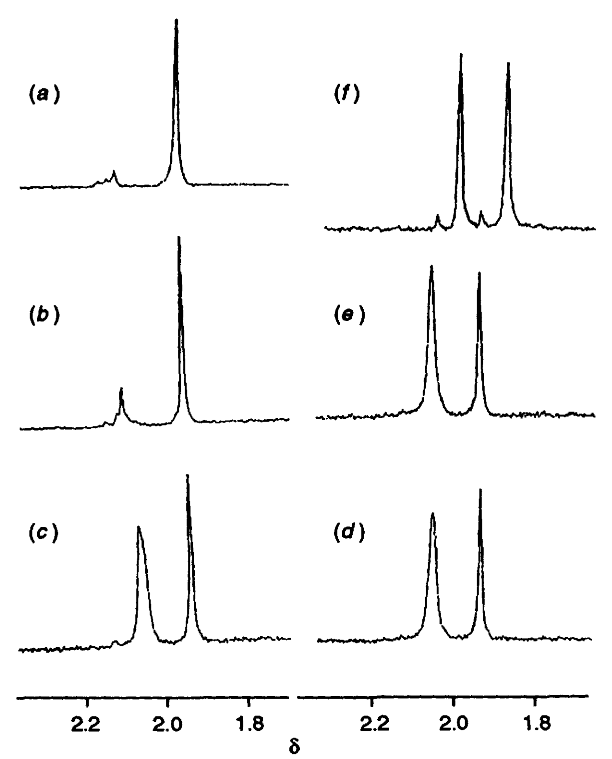

Fig. 1 The 400 MHz ^1H NMR spectra recorded for Al^{III}–aha at 1 : 3 ratio at different pD values: 3.46 (*a*), 4.43 (*b*), 6.37 (*c*), 7.66 (*d*), 8.47 (*e*), and 10.22 (*f*)

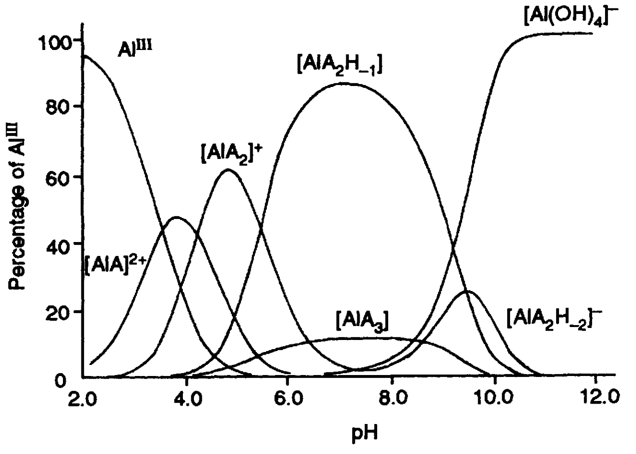

Fig. 2 Concentration distribution curves for complexes formed in tne Al^{III}–aha system at 1 : 3 ratio at $c_{Al} = 2 \times 10^{-3}$ mol dm^{-3}

from pH-metry only one NMR peak is observed at 298 K. However, at 273 K (where chemical exchange is even slower) it is split into two lines (a representative example is given in Fig. 3), indicating the existence of at least two different aha-containing species.

Aluminium-27 NMR spectroscopy requires much higher analytical concentrations than those sufficient for ^1H NMR, and this causes significant changes in concentration distribution (the hydrolytic reactions are appreciably hindered in the latter case), as is seen on comparison of the distribution curves in Figs. 2 and 4. The NMR spectra show that Al^{III} can be detected in two extremely different chemical environments in the range pH 5–9.5. As an illustration, a ^{27}Al NMR spectrum is shown in Fig. 5. The relatively sharp band at δ 36.7 indicates Al^{III} in a fairly symmetrical complex; this can probably be ascribed to the octahedral tris complex $[AlA_3]$, while the very broad band (*ca.* 3000 Hz) with maximum at around δ 56 is characteristic of mixed hydroxo complexes having much lower symmetry.

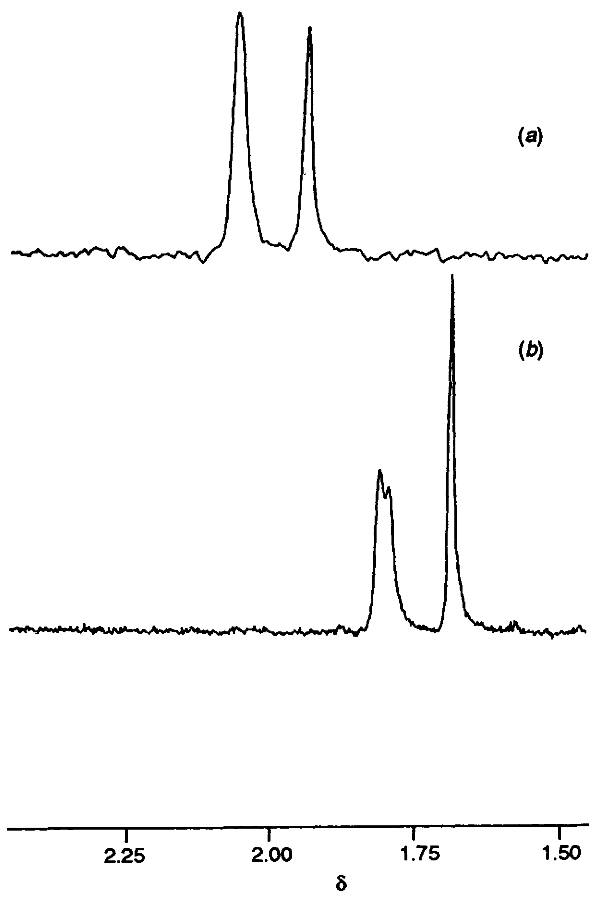

Fig. 3 Temperature dependence of 200 MHz ^1H NMR spectra recorded for Al^{III}–aha at 1 : 3 ratio, at pD 6.4: (*a*) 298, (*b*) 273 K

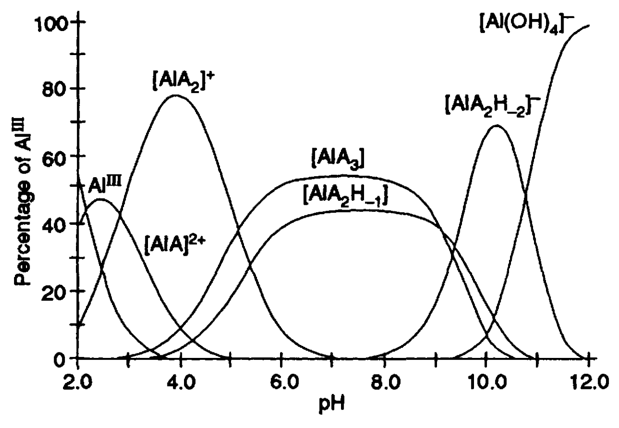

Fig. 4 Concentration distribution curves of complexes formed in the Al^{III}–aha system at 1 : 3 ratio at $c_{Al} = 4 \times 10^{-2}$ mol dm^{-3}

Formation of the tetrahedral, very symmetric species $[Al(OH)_4]^-$ can also be detected by the observation of a sharp signal (*ca.* 5 Hz) at δ 80.8 at pH > 10. These conclusions are in good agreement with the speciation model listed in Table 2.

All the above findings show that aha is an effective chelator of these metal ions and suppresses their hydrolysis to an extent determined by the metal : aha ratio, the analytical concentration and the pH. The highest stability constants were found for iron(III) complexes and the lowest those for Al^{III}. The same stability sequence was observed earlier for other hydroxamates.[22]

*Metal Ion–α-*Alaha $[CH_3CH(NH_3^+)CONHOH]$ *and* -β-Alaha $(NH_3^+CH_2CH_2CONHOH)$ *Systems.*—The systems

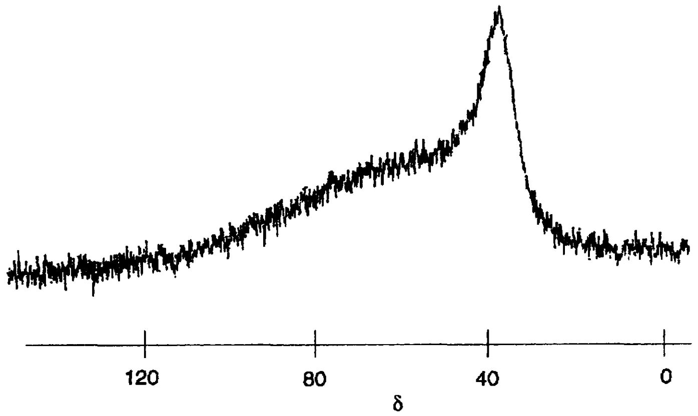

Fig. 5 A ^{27}Al NMR spectrum recorded for Al$^{\mathrm{III}}$–aha at 1 : 3 ratio at *ca.* pD 7.0

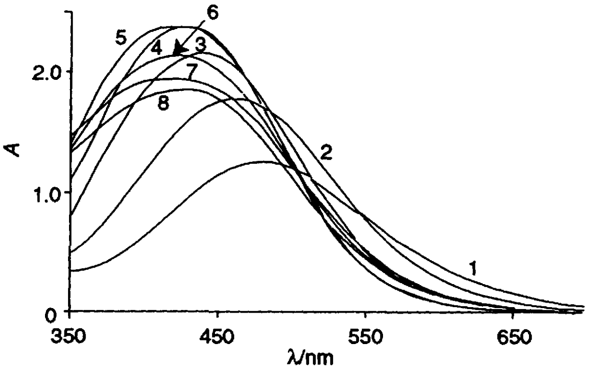

Fig. 6 Visible spectra registered in the Fe$^{\mathrm{III}}$–β-Alaha system at 1 : 10 ratio, at different pH values: 1.97 (1), 2.94 (2), 4.03 (3), 5.03 (4), 6.01 (5), 6.94 (6), 8.00 (7) and 10.0 (8). $c_{\mathrm{Fe}} = 1 \times 10^{-3}$ mol dm^{-3}

Fe$^{\mathrm{III}}$–α-Alaha and Al$^{\mathrm{III}}$–α-Alaha were studied in our laboratory earlier.[6] It was found that both Fe$^{\mathrm{III}}$ and Al$^{\mathrm{III}}$ prefer chelation at the hydroxamate binding site and, due to the high hydrolytic tendencies of these metal ions, mixed hydroxo complexes too were formed in the pH range where the unco-ordinated NH_3^+ group of the ligand is still protonated. This leads to the formation of protonated mixed hydroxo complexes.[6] With regard to the above, only the Ga$^{\mathrm{III}}$-containing system was studied in the present work with α-Alaha. The results showed that the formation of gallium(III) hydroxo complexes is favoured even in the acidic pH range. Besides the binary hydroxo species, a stability constant could be calculated only for $[GaAH]^{3+}$. On the basis of this result Ga$^{\mathrm{III}}$ was not included in our studies on β-Alaha.

To choose the appropriate equilibrium models for the studied systems, we again used spectrophotometry for the Fe$^{\mathrm{III}}$–β-Alaha and ^{27}Al NMR spectroscopy for the Al$^{\mathrm{III}}$–β-Alaha system. Additionally, our previous work[6] on Al$^{\mathrm{III}}$–α-Alaha was supplemented with NMR measurements.

The pH dependence of the visible spectrum of the iron(III) system at a metal : hydroxamic acid ratio of 1 : 10 can be seen in Fig. 6. The value of $\varepsilon_{\max}$ calculated from the spectral data in the range pH 5–6 at $\lambda_{\max}$ *ca.* 420 nm is *ca.* 2600 dm^3 mol^{-1} cm^{-1}, suggesting the formation of complexes containing three hydroxamate chelates in quite high percentage.[20] The decrease in absorbance above this pH might be due to the lowering of the average number of hydroxamate groups co-ordinated by an OH^- displacement reaction.

The equilibrium model based on the pH-metric results yielded a good fitting and correlated acceptably with the spectrophotometric results. These stability data are listed in Table 3. The model relating to Al$^{\mathrm{III}}$–β-Alaha (see Table 3) was chosen with the aid of ^{27}Al NMR measurements. A comparative study of the Al$^{\mathrm{III}}$–α-Alaha and –β-Alaha systems revealed little differences in NMR behaviour between the two hydroxamic acids. In both systems only very broad, highly overlapping bands were observed in the range pH 3–9, with a dominating maximum at around δ 60–65, indicating octahedral Al$^{\mathrm{III}}$ in low symmetrical environments. In contrast with the Al$^{\mathrm{III}}$–aha system, no sharp signal characteristic of Al$^{\mathrm{III}}$ in a highly symmetric co-ordination sphere was observed. Thus speciation models which included tris complexes involving hydroxamate-type co-ordination (O$^-$, =O) were rejected. The formation of $[Al(OH)_4]^-$ was detected in both systems at pH > 10.0.

Table 3 Stability constants (log β) for the Fe$^{\mathrm{III}}$–, Ga$^{\mathrm{III}}$–[a] and Al$^{\mathrm{III}}$–α-Alaha and Fe$^{\mathrm{III}}$– and Al$^{\mathrm{III}}$–β-Alaha complexes at 298 K and I = 0.2 mol dm^{-3} (KCl)

Hydroxamic acid	Species	M Fe$^{\mathrm{III}}$	 Al$^{\mathrm{III}}$
α-Alaha[b]	$[MAH]^{3+}$	17.15	14.35
	$[MA]^{2+}$	13.92	—
	$[M_2A_2]^{4+}$	—	22.21
	$[M_2A_2H_{-1}]^{3+}$	—	17.59
	$[M_2A_2H_{-2}]^{2+}$	—	12.63
	$[M_2A_2H_{-3}]^{+}$	—	5.85
	$[M_2A_2H_{-4}]$	—	−2.44
	$[MA_2H]^{2+}$	28.36	—
	$[MA_2]^{+}$	21.99	16.7
	$[MA_2H_{-1}]$	14.54	9.62
	$[MA_2H_{-2}]^{-}$	—	−0.16
	$[MA_3]$	33.90	—
β-Alaha	$[MAH]^{3+}$	19.95(6)	16.72(2)
	$[MA]^{2+}$	16.99(5)	—
	$[MA_2H_2]^{3+}$	38.30(4)	32.07(2)
	$[MA_2H]^{2+}$	—	27.04(2)
	$[MA_2]^{+}$	—	19.87(2)
	$[MA_2H_{-1}]$	22.11(7)	10.74(2)
	$[MA_2H_{-2}]^{-}$	12.12(8)	0.04(32)
	$[MA_3H_3]^{3+}$	55.47(4)	—
	$[MA_3H_2]^{2+}$	50.24(5)	—
	$[MA_3H]^{+}$	42.75(7)	—

[a] Only one complex, $[GaAH]^{3+}$, was formed in measurable concentration with α-Alaha. The log β value is 16.4(4). [b] Ref. 6.

Comparison of the results calculated for the metal(III)–α-Alaha and –β-Alaha systems both with each other and with those obtained for metal(III)–aha reference systems led to the following findings. The stability constants for the reaction $M + HA \rightleftharpoons MAH$, characteristic of the interaction of the metal(III) ion with the hydroxamate binding site, were derived from the overall stability data ($\log K_{\mathrm{MAH}} = \log \beta_{\mathrm{MAH}} - \log K_{\mathrm{HA}}$). Since HA contains the amino group in protonated form and the two deprotonation processes of the free hydroxamic acids overlap, the corresponding microconstants had to be used

Table 4 Stability constants (log β) for the complexes of Fe^{III}, Ga^{III} and Al^{III} formed with Asp-β-ha and Glu-γ-ha at 298 K and $I = 0.2$ mol dm^{-3} (KCl)

	Fe^{III}		Ga^{III}		Al^{III}	
Species	Asp-β-ha[a]	Glu-γ-ha[b]	Asp-β-ha	Glu-γ-ha	Asp-β-ha	Glu-γ-ha
$[MAH]^{2+}$	18.82	18.92	18.33(4)	18.5(1)	16.27(5)	16.65(5)
$[MA_2H_2]^+$	36.35	36.65	35.53(8)	35.0(2)	31.76(7)	32.79(7)
$[MA_2H]$	31.63	31.70	31.61(1)	30.8(1)	26.80(4)	27.62(5)
$[MA_2]^-$	24.25	24.10	24.23(6)	24.2(3)	19.26(3)	19.89(5)
$[MA_2H_{-1}]^{2-}$	15.32	14.70	15.6(3)	—	10.36(4)	9.9(5)
$[MA_2H_{-2}]^{3-}$	—	—	—	—	—	1.10(15)

[a] Ref. 7. [b] Ref. 8.

in these calculations.[19] The log K_{MAH} values (7.99, 10.53, 5.19 and 7.30 for Fe^{III}–α-Alaha, Fe^{III}–β-Alaha, Al^{III}–α-Alaha and Al^{III}–β-Alaha, respectively) show that the complexes formed with β-Alaha are more stable than those formed with α-Alaha, and both are less stable than those formed with aha (see constants for $[MA]^{2+}$ in Table 2). This means that the presence of the NH_3^+ group in the side-chain decreases the stability of the hydroxamate chelate, and the extent of the decrease depends on the distance between the NH_3^+ group and the hydroxamate moiety. As to the origin of this effect, the following conclusion can be drawn: at least two effects result from the presence of the NH_3^+ group. First, an electron-withdrawing effect, which makes the hydroxamic acid group more acidic, as is known from the acid–base properties of these ligands.[19] Secondly, there is an electrostatic repulsion between the NH_3^+ group and the co-ordinating M^{3+} ion. These two superimposed effects result in the significant difference in the equilibrium models discussed above for the α-Alaha-and β-Alaha-containing systems. Hydrolysis of the metal ions is more favoured in the presence of the former hydroxamic acid.

Metal Ion–Asp-β-ha $[HO_2CCH(NH_3^+)CH_2CONHOH]$ *and* –Glu-γ-ha $[HO_2CCH(NH_3^+)CH_2CH_2CONHOH]$ *Systems*.—Besides the chelate-forming hydroxamate moiety, these hydroxamic acids contain an extra carboxylate group which is a new potential site for co-ordination. Our earlier results on Fe^{III}–Asp-β-ha and –Glu-γ-ha showed that the hydroxamate oxygens are the main donor atoms, but that co-ordination of the carboxylate group can also be assumed.[6,7] It was also found that the non-co-ordinating amino group containing a dissociable proton in the protonated complexes deprotonates in a process overlapping with ionisation of the co-ordinated water molecules. The complexes of Ga^{III} and Al^{III} with Asp-β-ha and Glu-γ-ha were studied in the present work. The speciation models yielding the best fitting of the pH-metric experimental data were the same as for the Fe^{III}-containing systems.[6,7] They involve neither polynuclear species nor any complex with a metal : hydroxamic acid ratio of 1 : 3, as can be seen in Table 4. The results obtained for Ga^{III}–Asp-β-ha, Ga^{III}–Glu-γ-ha, Al^{III}–Asp-β-ha and Al^{III}–Glu-γ-ha are in complete agreement with those found for Fe^{III}–Asp-β-ha[6] and Fe^{III}–Glu-γ-ha.[7] The tridentate co-ordination *via* the hydroxamate function and the carboxylate oxygens is the preferred binding mode in both the 1 : 1 and 1 : 2 complexes.

Since the appropriate dissociation microconstants are not available, the equilibrium constants for the reaction $M + HA \rightleftharpoons MAH$, characteristic of the interaction between the metal(III) ion and the tridentate hydroxamic acids, cannot be derived and hence their comparison with those for α- and β-Alaha is not possible. A simple comparison of the data in Table 4, however, clearly indicates that the complexes of Glu-γ-ha are somewhat more stable than those of Asp-β-ha. These differences can again be explained if the effects of the side-chain NH_3^+ group (electrostatic repulsion and electron-withdrawing effects) are taken into account. These effects result in the formation of more stable complexes with Glu-γ-ha, in which the NH_3^+ group is situated farther away from the hydroxamate moiety, than those with Asp-β-ha in which the two positively charged centres are nearer each other.

Acknowledgements

This work was supported by the Hungarian Academy of Sciences (Projects OTKA 04 09604, OTKA 1647 and US–Hungarian Joint Fund No. 182/92b).

References

1 A. Chimiak, R. C. Hilder, A. Liu, J. B. Neilands, K. Nomoto and Y. Sugiura, *Struct. Bonding (Berlin)*, 1984, **58**.

2 C. Yuen Ng, S. J. Rodgers and K. N. Raymond, *Inorg. Chem.*, 1989, **28**, 2062.

3 I. Dayan, J. Libman, Y. Agi and A. Shanzer, *Inorg. Chem.*, 1993, **32**, 1467; P. Yakirevitch, N. Rochel, A.-M. Albrecht-Gary, J. Libman and A. Shanzer, *Inorg. Chem.*, 1983, **32**, 1779.

4 M. A. Santos, M. A. Esteves, M. Candida, T. Vaz and M. L. S. Goncalves, *J. Chem. Soc., Dalton Trans.*, 1993, 927.

5 B. Kurzak, H. Kozlowski and E. Farkas, *Coord. Chem. Rev.*, 1992, **114**, 169.

6 E. Farkas, J. Szöke, T. Kiss, H. Kozlowski and W. Bal, *J. Chem. Soc., Dalton Trans.*, 1989, 2247.

7 E. Farkas and P. Buglyó, *J. Chem. Soc., Dalton Trans.*, 1990, 1549.

8 E. Farkas, D. A. Brown, R. Cittaro and W. K. Glass, *J. Chem. Soc., Dalton Trans.*, 1993, 2803.

9 C. R. Hauser and W. B. Renfrow, jun., *Org. Synth.*, 1943, **2**, 67.

10 G. Gran, *Acta Chem. Scand.*, 1950, **4**, 559.

11 W. R. Harris and A. E. Martell, *Inorg. Chem.*, 1976, **15**, 713.

12 H. M. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475.

13 L. Zékány and I. Nagypál, in *Computational Methods for the Determination of Stability Constants*, ed. D. Leggett, Plenum, New York, 1985.

14 G. H. Khoe, P. L. Brown, R. N. Sylva and R. G. Robins, *J. Chem. Soc., Dalton Trans.*, 1986, 1901.

15 C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976.

16 L. O. Öhman and W. Forschling, *Acta Chem. Scand., Ser. A*, 1981, **35**, 795.

17 I. Tóth, E. Brücher and L. Zékány, *Magy. Kém. Foly.*, 1984, **90**, 149.

18 R. G. Bates, *Determination of pH*, Wiley, New York, 1964.

19 E. Farkas, T. Kiss and B. Kurzak, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1255.

20 S. J. Barlcay, P. E. Riley and K. N. Raymond, *Inorg. Chem.*, 1984, **23**, 2005; S. J. Barclay, B. H. Huynh and K. N. Raymond, *Inorg. Chem.*, 1984, **23**, 2011.

21 R. F. Jameson, G. Hunter and T. Kiss, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1105.

22 A. Evers, R. D. Hancock, A. E. Martell and R. J. Motekaitis, *Inorg. Chem.*, 1989, **28**, 2189.

Received 10*th August* 1994; *Paper* 4/04923C