Coordination modes of hydroxamic acids in copper(II), nickel(II) and zinc(II) mixed-ligand complexes in aqueous solution

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Abstract

The stability constants and coordination modes of the mixed-ligand complexes formed by Cu(II), Ni(II), Zn(II), ethylenediamine (en), 2,2′-bipyridine (bpy), glycinate (Gly), disodium salt of 4,5-dihydroxybenzene 1,3-disulfonate (Tiron), diethylenetriamine (dien) or 2,2′:6,2″-terpyridine (terpy) (= ligand B) and acetohydroxamate (Aha), N-methylacetohydroxamate (MeAha) or N-phenylacetohydroxamate (PhAha) (= ligand A) were determined in water (25°C, $I = 0.2$ M KCl) by pH-metric, spectrophotometric, EPR and calorimetric methods. Mixed-ligand complexes with typical hydroxamate type chelation mode involving the NHO^- moiety are formed in all systems. However, further copper(II) induced deprotonation of the NHO^- moiety of Aha in the presence of en or bpy results in the formation of mixed-ligand complexes with hydroximato chelates at high pH. The results show the favoured coordination of a hydroxamate to metal(II)–en and especially to a metal(II)–bpy moiety. If ligand B is Gly, the increase of stability of the mixed-ligand complexes is as expected on statistical basis, whereas the formation of complexes involving O,O-coordinated hydroxamate and O,O-coordinated Tiron is unfavoured. The tridentate coordination of dien or terpy results in five-coordinated mixed-ligand copper(II) complexes in which, most probably, the hydroxamate moiety adopts an equatorial–axial coordination mode. This quite unstable hydroxamate chelate can not hinder the hydrolysis of the complex above pH 8. Under very basic conditions acetohydroximato moieties ($-CONO^{2-}$) displace the rigid terpy ligand from the coordination sphere and complexes, $[Cu(AhaH_{-1})_2]^{2-}$ involving hydroximato chelates are formed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mixed-ligand complexes; Solution equilibrium; Hydroxamic acid; Copper(II), nickel(II) and zinc(II) complexes

1. Introduction

Hydroxamate molecules, one of the major classes of naturally occurring metal complexing agents, have been thoroughly studied as ligands. Numerous papers showed that monohydroxamic acids adopt a typical
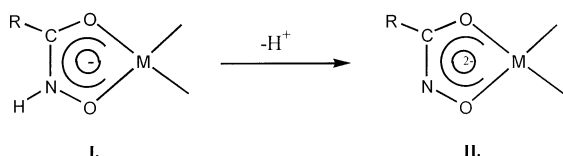
Scheme 1.

binding mode. As disclosed first by an X-ray diffraction study of the benzohydroxamate complex of iron(III), the chelation involves the oxygens belonging to carbonyl and NHOH groups [1]. Complexes of simple hydroxamic acids have been studied both in solution and in solid state [2–9]. First of all Fe(III) but also some other metal ions, e.g. Co(II), Co(III), Ni(II), Zn(II), Cu(II) and V(IV) were involved in studies. The relevancy of the results to siderophore-mediated iron uptake by microorganisms was discussed in reviews [10,11].

Investigations on the complex formation with simple primary hydroxamic ligands in aqueous solution demonstrated clearly that, depending on pH, two (O,O) bonding modes of the ligands are accessible to metal ions like Cu(II) and VO(IV) [8,9]. The hydroxamato(1 −) type mode arises from the first deprotonation step and involves the coordination of the NHO^- moi-

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ety (**I**, see Scheme 1). The hydroximato(2 −) form of the ligand is produced by further metal-induced deprotonation of NHO^- (**II**).

The coordination of the nitrogen atom of hydroxamic moiety was never found in metal complexes formed by simple hydroxamic acids even if this nitrogen atom can be converted into very effective binding site in aminohydroxamates, as demonstrated by studies on aminohydroxamates both in solution and in the solid state [12].

In contrast with binary systems of hydroxamic acids or aminohydroxamic acids, their ternary systems have been studied only in a few cases [12–15]. Nevertheless, mixed ligand complexes are better models for understanding the reactivity of hydroxamic acids in biological systems (e.g. inhibition of metalloenzymes). We have performed a systematic study in solution aimed at establishing the coordination modes of hydroxamic acids and the stability of the resulting chelates in the presence of additional ligands. The ternary systems examined involve metal(II), hydroxamate (ligand A) and an additional ligand (ligand B) like ethylenediamine (en), 2,2′-bipyridine (bpy), glycinate (Gly), the disodium salt of 4,5-dihydroxybenzene 1,3-disulfonate (Tiron), diethylenetriamine (dien), or 2,2′:6,2″-terpyridine (terpy).

2. Experimental

2.1. Chemicals

Acetohydroxamic acid (Aha), en, bpy, Gly, Tiron, dien, and terpy were pure commercially available chemicals (Sigma, Reanal, Aldrich and Fluka). N-Methylacetohydroxamic (MeAha) and N-phenylacetohydroxamic (PhAha) acids were prepared by standard procedures from the corresponding carboxylic esters and hydroxylamine [16]. Freshly distilled en and dien were dissolved in known amounts of HCl solutions. The purity of the ligands and the concentration of the ligand stock solutions were determined by Gran's method [17]. The metal ion stock solutions were prepared from $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 5H_2O$ (Reanal). ZnO (Reanal) was dissolved in a known amount of HCl solution. The concentrations of the copper(II), nickel(II) and zinc(II) stock solutions were determined gravimetrically via the precipitation of quinolin-8-olates.

2.2. Potentiometric, spectrophotometric, calorimetric and EPR studies

All the measurements were carried out at 0.2 M ionic strength (KCl) and 25°C. Carbonate-free KOH solution of known concentration (ca. 0.2 M) was used as titrant.

The binary systems were studied previously [8,18–22], however most of the constants were redetermined in the present work. The pH-metric titrations were performed over the pH range 2.0–10.5, or below precipitation, on 10.00 cm³ samples. The ligand concentration varied in the range 2×10^{-3}–8×10^{-3} M. In the binary systems, the metal–ligand ratios were, generally, in the range 1:1–1:8, and samples at four or five different ratios were measured. The metal:ligand A:ligand B ratios were 1:1:1, 1:2:1, 1:1:2 and 1:2:2. The pH-metric titrations were made with a Radiometer pHM84 instrument equipped with a Metrohm 6.0234.100 combined electrode. The titrant was added from a Metrohm 715 Dosimat autoburette. The electrode system was calibrated by the method of Irving et al. [23] so that the pH-meter readings could be converted into hydrogen ion concentration. A pK_w value of 13.756 was determined in the present work. The pH-metric results were used to establish the stoichiometry of the species and to calculate the stability constants. Calculations were performed with the program PSEQUAD [24]. In the pH regions where the experimental findings indicated hydrolysis (a continuous decrease in the pH or the formation of a precipitate) calculations were not performed. The volume of the titrant was fitted and the accepted fittings were below 1×10^{-2} cm³.

UV–Visible measurements were carried out on systems containing copper(II) and nickel(II). The metal ion to ligand ratios were 1:1, 1:2 and 1:5 for the binary systems and the metal:ligand A:ligand B ratios were 1:1:1 and 1:2:1 for the ternary systems. Titrations were made on samples containing the metal(II) ion at $3–5 \times 10^{-3}$ M. A HP 8453 spectrophotometer was used to record the spectra in the region of 300–800 nm.
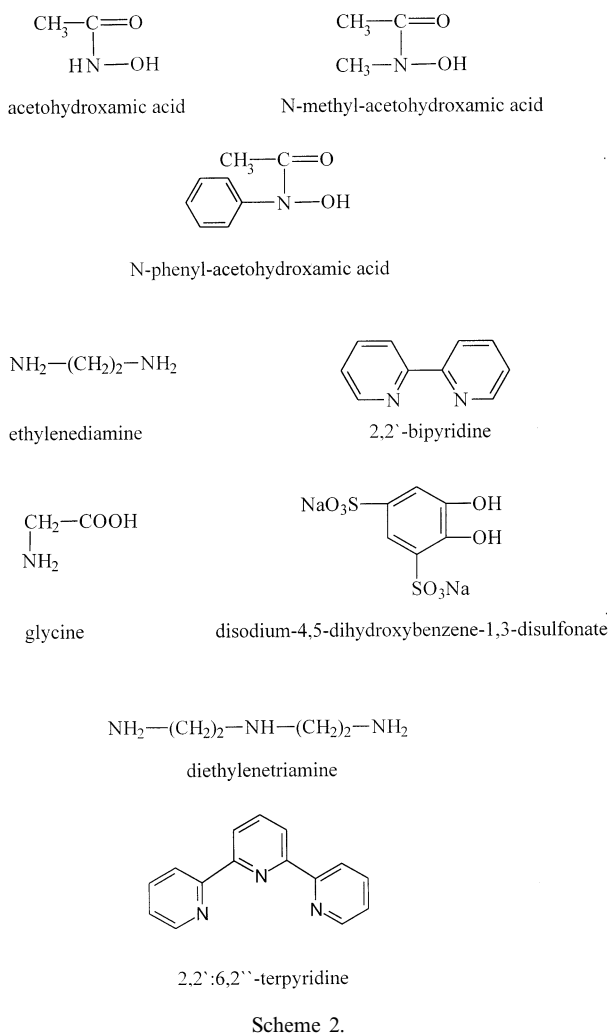
Calorimetric measurements were performed to determine the enthalpy changes of the reaction of the [CuB] complex (B = bpy, dien or terpy) with Aha and KOH using an LKB 8700 solution calorimeter. Samples of the [CuB] species (25 cm³, $c = 3.0 \times 10^{-3}$ M, pH 10) were reacted with ampoules containing a known amount of Aha or KOH.

EPR spectra were recorded on a Varian E9 spectrometer at the X-band frequency (9.15 GHz) at 120 K. Ethylene glycol was added to aqueous samples to ensure glass formation.

## 3. Results and discussion

3.1. Solution equilibria

Among the hydroxamic acids (ligand A), the primary derivative Aha was studied with copper(II), nickel(II) and zinc(II), whereas the secondary ones, MeAha and PhAha were studied only with copper(II). The type of donor atom (nitrogen donors, oxygen donors or mixed,

acetohydroxamic acid

N-methyl-acetohydroxamic acid

N-phenyl-acetohydroxamic acid

ethylenediamine

2,2`-bipyridine

glycine

disodium-4,5-dihydroxybenzene-1,3-disulfonate

diethylenetriamine

2,2`:6,2``-terpyridine

Scheme 2.

in alyphatic or in aromatic compounds) and number of donor atoms (two or three) were varied in ligands B. The formulae of the neutral ligands are shown in Scheme 2.

3.1.1. Binary systems

The copper(II), nickel(II) and zinc(II) complexes of the hydroxamic ligands were already studied in previous works of ours and most of the systems containing copper(II) were characterised by EPR, too [8,18]. Stability constants for the metal ion–ligand B complexes were determined in former works [19–22], but those for the copper(II)–dien, copper(II)–terpy, nickel(II)–Tiron and zinc(II)–Tiron complexes were redetermined in the present work. Owing to oxidation reactions involving the ligand, the copper(II)–Tiron system could not be investigated. On the other hand, as the formation of $[Cu(terpy)]^{2+}$ occurs below the measurable pH range, overall stability constant was not obtained for this species. Instead, the equilibrium process

$$[Cu(terpy)]^{2+} + H_2O \rightleftharpoons [Cu(terpy)(OH)]^+ + H^+ \quad (1)$$
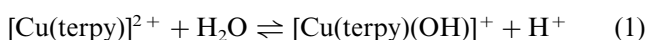
what takes place in a measurable pH range (ca. 7–10) was characterised. The equilibrium models and corresponding stability constants ($\log \beta$) are summarised in Table 1. EPR and electron absorption parameters for copper(II) simple complexes are shown in Table 2 (Cu(II)–Aha hydroximate species which formed beyond the capability of glass electrode potentiometry were detected only by EPR).

The main conclusions drawn for the coordination modes of hydroxamic ligands in the binary systems are as follows: exclusively hydroxamate-type (O,O) coordination (the ligand chelates the metal ion via the monoanionic form $R–CO–NR'–O^-$) exists in all the nickel(II)– and zinc(II)–hydroxamate complexes as well as in copper(II)–MeAha ($R' = Me$) and –PhAha ($R' = Ph$) complexes [18]. Hydroximate-type chelated complexes arising from a further deprotonation process of the hydroxamic moiety (the dianionic form $R–CO–N–O^{2-}$ is involved) exist only in the copper(II)–Aha ($R' = H$) system at high pH [8]. The hydroximate chelation is significantly more stable than the hydroxamate one and is clearly indicated by EPR spectra. The decrease of $g_\parallel$ and increase of $A_\parallel$ parameters of EPR spectra, in comparison to the hydroxamate species (see Table 2), substantiate a significant strengthening of the in plane bonds in the copper(II) coordination sphere.

3.1.2. Ternary systems

The stability constants for mixed-ligand complexes giving the best fit of the pH-metric titration curves are listed in Table 3.

Table 3 lists the logarithmic overall constants expressed by the equation

$$pM + qA + rB + sH \rightleftharpoons M_pA_qB_rH_s \quad (2)$$
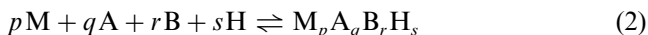
except for mixed-ligand complexes containing terpy, for which data related to the equilibrium

$$MB + A \rightleftharpoons MAB \quad (3)$$

have been determined. As Table 3 shows, mixed-ligand complexes with stoichiometry [MAB] are formed in all systems. In addition, $[MABH_{-1}]$ species exist in metal(II)–Aha–bpy/en systems, and also $[MA_2B]$ and/or $[MAB_2]$ complexes exist in some nickel(II) and zinc(II) containing systems.

The relative stability of the mixed-ligand complexes, as compared with the corresponding binary species, could be evaluated in different ways. In most cases the relative stability of [MAB] is expressed in terms of $\Delta \log K_{MAB}$, the logarithmic stability constant for the equilibrium

$$MA + MB \rightleftharpoons MAB + M \quad (4)$$

The equilibrium constant for Eq. (4) can be calculated from the experimentally measured stability constants according to equation:

Table 1
Models and stability constants (log β) for the complexes formed in proton–, copper(II)–, nickel(II)– and zinc(II)–ligand A and B binary systems * ($T = 25°C$; $I = 0.2$ M KCl)

Log β	M_p	L_q	H_r	Aha[a]	MeAha[a]	PhAha[a]	en	bpy	Gly	Tiron	dien	terpy
H$^+$	0	1	1	9.27	8.70	8.44	10.12(1)	4.43(1)	9.60(1)	11.93(1)	9.91(6)	4.54(3)
	0	1	2				17.37(2)		11.92(1)	19.34(1)	19.04(6)	8.11(2)
	0	1	3								23.50(1)	
Cu(II)	1	1	1								18.42(4)	
	1	1	0	7.89	7.40	7.31	10.57[b]	9.06[d]	8.07[b]		16.10(2)	
	1	2	1								29.50(4)	
	1	2	0	13.80	13.3	12.90	19.68[b]	14.96[d]	14.84[b]		20.98(2)	
	1	3	0					18.21[d]				
	1	1	−1								6.86(1)	8.60(1)[f]
	1	1	−2					−9.10[d]				
	1	2	−1	4.4				5.38[d]				
	2	2	−2					7.27[d]				
	2	4	−1					23.46[d]				
Ni(II)	1	1	0	5.37	4.73	4.68	7.36[e]	7.07[e]	5.65[e]	9.21(1)		
	1	2	0	9.50	8.27	8.28	13.52[e]	13.93[e]	10.40[e]	15.87(3)		
	1	3	0	13.32		10.16	17.78[e]	20.13[e]	13.78[e]	18.8(1)		
	1	1	−1							−0.1(2)		
	1	2	−1	−0.87	−3.2	−2.42						
Zn(II)	1	1	0	5.32	4.51	4.34	5.75[e]	5.04[e]	4.84[e]	9.65(1)		
	1	2	0	9.64	8.35	8.12	10.79[e]	9.39[e]	9.02[e]	17.70(1)		
	1	3	0	12.8				12.96[e]		20.3(4)		
	1	2	−1	−0.32		−1.9						

[a] Ref. [18].
[b] Ref. [19].
[c] Ref. [20].
[d] Ref. [21].
[e] Ref. [22].
[f] Log K value relates to the process: $[Cu(terpy)] + H_2O \rightleftharpoons [Cu(terpy)OH] + H^+$.
* Standard deviations are shown in parentheses for the complexes determined in the present work.

Table 2
EPR and absorption parameters for the complexes formed in the copper(II)–ligand A and B binary systems

Ligand	Species	$g_\parallel$	$A_\parallel$ ($\times 10^{-4}$ cm^{-1})	Coordination mode[a]	λ_{max} (nm)	ε (M^{-1} cm)
Aha	[MA]$^+$	2.336	168	ha (O,O)		
	[MA$_2$]	2.282	181	2×ha (O,O)	653	30
	[MA$_2$H$_{-1}$]$^-$	2.258	192	ha (O,O, hi (O,O)		
	[MA$_2$H$_{-2}$]$^{2-}$	2.219	206	2×hi (O,O)		
	[MAH$_{-1}$(OH)$_2$]$^{2-}$	2.230	204	hi (O,O), 2 (OH$^-$)		
MeAha	[MA]$^+$	2.327	169	ha (O,O)		
	[MA$_2$]	2.267	185	2×ha (O,O)	647	36
PhAha	[MA$_2$]			2×ha (O,O)	651	42
en	[MB$_2$]$^{2+}$			2×2 (N)	548	75
bpy	[MB]$^{2+}$	2.307	170	2 (N)	700	32
	[MB$_2$]$^{2+}$	2.263	162	2×2 (N)	731	91
	[MBH$_{-1}$]	2.253	177	2 (N); (OH$^-$)	640	42
	[MBH$_{-2}$]	2.233	197	2 (N); 2 (OH$^-$)	619	49
Gly	[MB$_2$]			2×(N,O)	615	38
dien	[MB]$^{2+}$	2.230	191	3 (N)	615	70
	[MBOH]$^+$	2.240	171	3 (N), (OH$^-$)	608	65
terpy	[MB]$^{2+}$	2.262	178	3 (N)	685	90
	[MBOH]$^+$	2.262	156	3 (N), (OH$^-$)	674	72

[a] ha, hydroxamato; hi, hydroximato.

Table 3
Models and stability constants (log β) for the mixed-ligand complexes formed in metal ion–ligand A–ligand B systems [a]

Ligand B	Ligand A	Cu(II)		Ni(II)				Zn(II)			
		[MAB]	[MABH$_{-1}$]	[MAB]	[MA$_2$B]	[MAB$_2$]	[MABH$_{-1}$]	[MAB]	[MA$_2$B]	[MAB$_2$]	[MABH$_{-1}$]
en	Aha	17.65(1)	7.49(2)	12.62(1)	15.89(9)	17.85(4)	1.8(2)	11.15(1)	14.07(9)	14.4(1)	1.77(6)
	MeAha	17.07(2)									
	PhAha	17.38(2)									
bpy	Aha	16.90(2)	7.31(2)	12.78(4)	17.31(3)			10.65(4)	14.3(1)	14.93(3)	2.08(8)
	MeAha	16.67(1)									
	PhAha	16.52(1)									
Gly	Aha	14.92(1)		10.20(2)		14.18(2)		9.78(4)		13.08(5)	
	MeAha	14.36(3)									
	PhAha										
Tiron	Aha			13.36(5)				13.57(5)			
	MeAha										
	PhAha										
dien	Aha	19.70(1)									
	MeAha	19.30(1)									
	PhAha	19.85(1)									
terpy	Aha	4.21 [b]									
	MeAha	3.89 [b]									
	PhAha	3.67 [b]									

[a] Standard deviations are shown in parenthesis for the complexes determined in the present work.
[b] Log K values related to the following process: MB+A $\rightleftharpoons$ MAB.

$$\Delta\log K_{MAB} = \log\beta_{MAB} - (\log\beta_{MA} + \log\beta_{MB}) \qquad (5)$$

The differences between $\Delta\log K_{MAB}$ data calculated by Eq. (5) and its statistical values are evaluated. If bidentate ligands are coordinated to the metal ion, depending on the geometry of the complex, the following statistical values can be calculated for $\Delta\log K_{MAB}$: -0.4 for complexes with nearly octahedral geometry, e.g. nickel(II) and zinc(II) complexes, and -0.9 for distorted copper(II) complexes [25]. $\Delta\log K_{MAB}$ values calculated by Eq. (5) are listed in Table 4.

The results in Table 4 substantiate that the formation of mixed-ligand complexes with N-donor bidentate ligands B is favoured ($\Delta\log K_{MAB}$ values are higher than statistical). It is true especially with the aromatic bpy. Formation of mixed-ligand complexes involving hydroxamate and an other O-donor ligand B like Tiron is unfavoured ($\Delta\log K_{MAB}$ values are significantly lower than statistical).

The relative stability of the mixed-ligand complexes with compositions [MA$_2$B] and [MAB$_2$], could be also evaluated in different ways, e.g. it is possible to calculate the stability constants expected on a statistical basis [26] through the equations:

$$\log\beta^{stat}_{MA_2B} = 2/3\log\beta_{MA_3} + 1/3\log\beta_{MB_3} + \log 3 \qquad (6)$$

$$\log\beta^{stat}_{MAB_2} = 2/3\log\beta_{MB_3} + 1/3\log\beta_{MA_3} + \log 3 \qquad (7)$$

The values of $\log\beta^{stat}_{MA_2B}$ (15.28 for [Ni(Aha)$_2$(en)] and 16.07 for [Ni(Aha)$_2$(bpy)]) and $\log\beta^{stat}_{MAB_2}$ (16.77 for

[Ni(Aha)(en)$_2$]$^+$ and 14.10 for [Ni(Aha)(Gly)$_2$]$^-$) are calculated by use of the corresponding constants listed in Table 1. From a comparison of these data with the experimentally measured constants (log β^{meas}) in Table 3 we conclude that the formation of [Ni(Aha)(Gly)$_2$]$^-$ is as expected on the statistical basis, but the formation of en and bpy containing mixed-ligand species is much more favoured. Similar calculations for the zinc(II) containing species lead to the same conclusion. Concentration distribution curves for zinc(II)–Aha–bpy (a) and zinc(II)–Aha–Tiron (b) are shown in Fig. 1.

Fig. 1 clearly indicates that mixed-ligand species dominate in zinc(II)–Aha–bpy above pH 7, whereas no significant mixed-ligand complex formation occurs in the zinc(II)–Aha–Tiron system. These results are in agreement with the general finding that the formation

Table 4
$\Delta\log K_{MAB}$ values calculated for copper(II)–, nickel(II)– and zinc(II)–ligand A–bidentate ligand B complexes

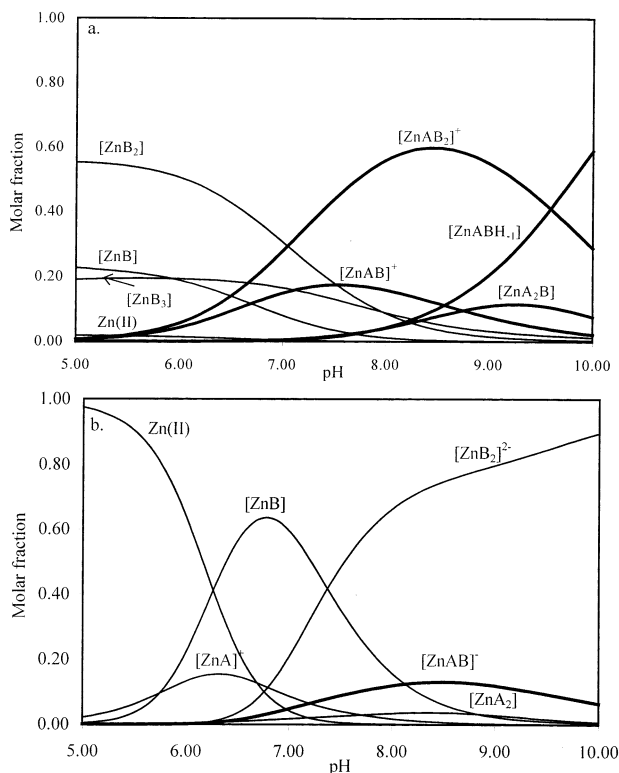|	Cu(II)			Ni(II)	Zn(II)
Ligands	Aha	MeAha	PhAha	Aha	Aha
en	-0.81	-0.90	-0.50	-0.11	0.08
bpy	-0.05	0.21	0.15	0.34	0.29
Gly	-1.04	-1.11		-0.82	-0.38
Tiron				-1.22	-1.40

Fig. 1. Concentration distribution curves for zinc(II)–Aha–bpy (a) and zinc(II)–Aha–Tiron (b) mixed-ligand complexes ($c_{Zn(II)} = 2 \times 10^{-3}$ M, $c_{Aha} = 4 \times 10^{-3}$ M, $c_{bpy} = c_{Tiron} = 4 \times 10^{-3}$ M).

Table 5
Stepwise equilibrium constants (log K) for the mixed-ligand complexes containing copper(II)

Equilibrium process	Log K	Equilibrium process	Log K
$[Cu(en)]^{2+} + Aha$	7.08	$[Cu(dien)]^{2+} + Aha$	3.60
$[Cu(en)]^{2+} + MeAha$	6.50	$[Cu(dien)]^{2+} + MeAha$	3.20
$[Cu(en)]^{2+} + PhAha$	6.81	$[Cu(dien)]^{2+} + PhAha$	3.75
$[Cu(bpy)]^{2+} + Aha$	7.84	$[Cu(terpy)]^{2+} + Aha$	4.21
$[Cu(bpy)]^{2+} + MeAha$	7.61	$[Cu(terpy)]^{2+} + MeAha$	3.89
$[Cu(bpy)]^{2+} + PhAha$	7.46	$[Cu(terpy)]^{2+} + PhAha$	3.67
$[Cu(Gly)]^{+} + Aha$	6.85		
$[Cu(Gly)]^{+} + MeAha$	6.29		

of mixed-ligand complexes is favoured with ligands having different types of donor atom [27].

The situation is somewhat different when the coordinating ligand B is tridentate, terpy or dien. $\Delta \log K_{MAB}$ values were not calculated in these cases (equilibrium constant for Cu + terpy $[Cu(terpy)]^{2+}$ is not available which prevents the calculation of $\Delta \log K_{MAB}$ for the copper(II)–hydroxamate–terpy complexes); however, a comparison of the stepwise stability constants of the mixed-ligand species (see Table 5) shows much lower constants for the complexes involving dien or terpy than for the species containing en, bpy or Gly. There are significant differences in the calorimetric results,

too. Namely, the ΔH value is -19.4 kJ mol^{-1} for the process $[Cu(bpy)]^{2+} + Aha$ and those of $[Cu(terpy)]^{2+} + Aha$ and $[Cu(dien)]^{2+} + Aha$ are $+2.8$ and -0.2 kJ mol^{-1}, respectively. The corresponding ΔS values, in turn, are 87, 90 and 68 J mol^{-1} K^{-1}.

In order to interpret the above results one must take into account that tridentate terpy and dien ligands occupy three equatorial positions of copper(II) in their [CuB] complexes. It means that only one position remains available for the coordination of a second ligand in the plane. Possible modes of coordination of a hydroxamate ligand in the mixed-ligand complexes are: (i) monodentate coordination at the fourth equatorial position; (ii) formation of a (O,O) chelate in the plane by the replacement of one of the three N atoms of dien/terpy; (iii) formation of a (O,O) chelate through equatorial–axial binding mode. Thermodynamic results do not allow us to differentiate the above three possibilities. It is known, however, that the axial coordination in copper(II) complexes results in a red shift of the electron absorption maximum λ_{max} [28]. The pH dependence of λ_{max} in the visible spectra collected on all copper(II)–terpy/dien–hydroxamate systems indicates a significant red shift in the pH region corresponding to the formation of species CuAB. This is clearly demonstrated in Fig. 2 which shows the pH–λ_{max} plot together with the species distribution curves for the copper(II)–Aha–dien. The value of λ_{max} increases from 615 (at pH ca. 7) to 685 nm (at pH 8.8), but starts to decrease above pH 9. Consequently, the red shift which parallels the formation of $[Cu(Aha)(dien)]^{+}$ supports a significant axial interaction in copper(II)–terpy/dien–hydroxamate mixed-ligand complexes.

$[MABH_{-1}]$ is detected only with the Aha ligand in which hydrogen is the R_N substituent, but it is not formed in measurable concentration with MeAha and PhAha secondary derivatives. As an illustration of the different behaviour of the complexes formed by primary and secondary hydroxamates, Fig. 3 shows the electron absorption spectra obtained as a function of pH for copper(II)–Aha–en (a) and copper(II)–MeAha–en (b) systems.

In nickel(II)– and zinc(II)–Aha systems, the species $[MABH_{-1}]$ is formed just before the precipitation so that it can be considered a mixed hydroxo species, denotated better as $[MAB(OH)]$. Instead, the complex remains in solution and is a dominant species in copper(II)–Aha–en/bpy systems. Parallel with its formation, a significant blue shift in the λ_{max} values is observed (see Fig. 3(a)) which supports the strengthening of the equatorial bonds in the chelated species. A comparison of the above findings with the results for the corresponding binary systems supports that the coordinated hydroxamate moiety of Aha looses a proton in the $[CuAB]^{+} \rightleftharpoons [CuABH_{-1}] + H^{+}$ process resulting in the formation of very stable copper(II)–hydroximato–en/bpy complexes.
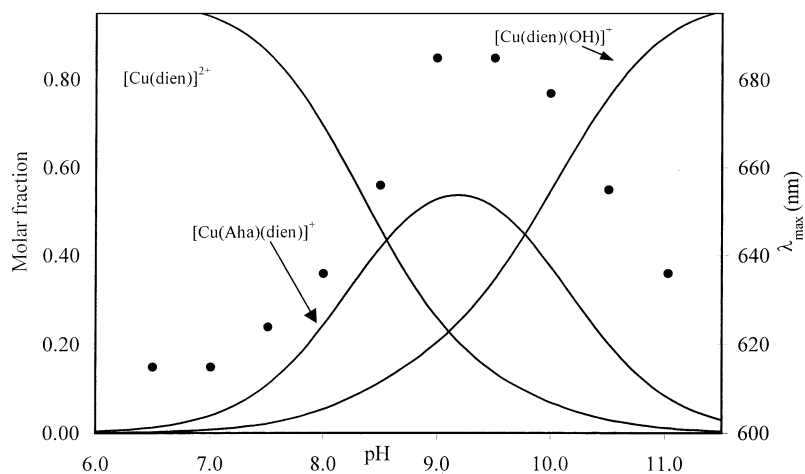
Fig. 2. Concentration distribution curves for copper(II)–Aha–dien mixed-ligand complexes are plotted together with the λ_{max} values in dependence of pH (●) ($c_{Cu(II)} = c_{terpy} = 3 \times 10^{-3}$ M, $c_{Aha} = 6 \times 10^{-3}$ M).
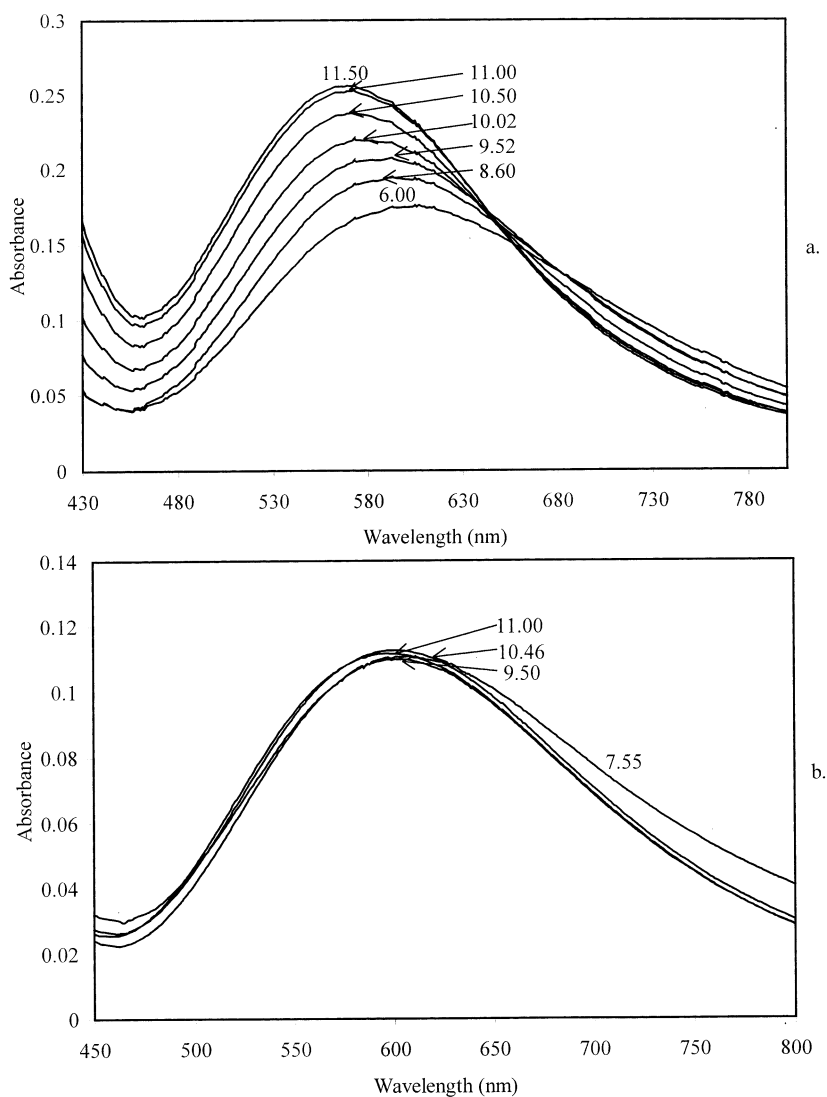

Fig. 3. UV–Vis spectra for copper(II)–Aha–en (a) and copper(II)–MeAha–en (b) at different pH values in the range 430–800 nm ($c_{Cu(II)} = 5 \times 10^{-3}$ M, $c_{Aha} = c_{en} = c_{MAha} = 5 \times 10^{-3}$ M).
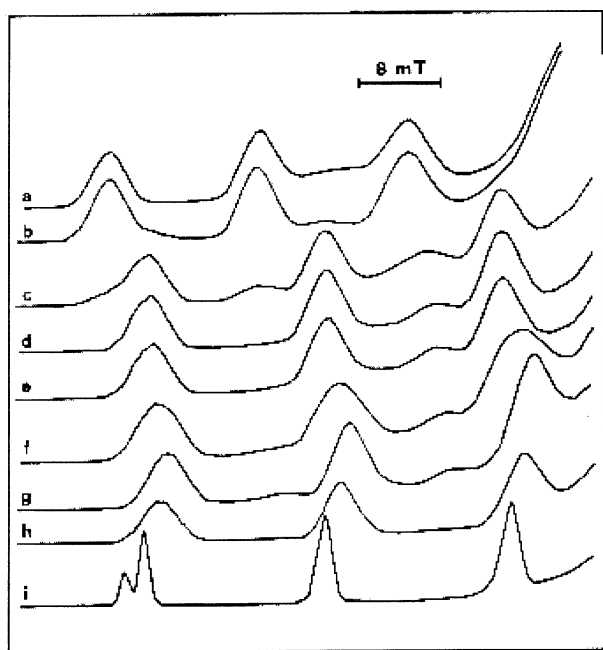
Fig. 4. Parallel region of frozen-solution EPR spectra recorded on copper(II)–Aha–bpy system at the 1:2:1 molar ratio ($c_{Cu(II)} = 5 \times 10^{-3}$ M) at different pH values: (a) 2.55, (b) 3.60, (c) 4.60, (d) 6.50, (e) 9.50, (f) 10.45, (g) 11.25 and (h) 12.48. Spectrum (i) belongs to $[Cu(OH)_4)]^{2-}$. Main species: (a,b) $[CuB]^{2+}$, (c–f) $[CuAB]^+$, (g) $[CuABH_{-1}]$ and (h) $[CuBH_{-2}]$.

3.2. EPR results

In order to get more complete information about the bonding modes in mixed ligand complexes formed in the copper(II)–Aha/MeAha–bpy/terpy/dien systems, EPR measurements were also performed and spectra were recorded at different pH values. Selected spectra for the Cu(II)–Aha–bpy system at the 1:2:1 molar ratio are shown in Fig. 4.

The measured $g_\parallel$ and $A_\parallel$ parameters and the proposed bonding modes in the various complexes are listed in Table 6.

The conclusions that can be drawn from the EPR results are substantially in agreement with those derived from equilibrium studies, but interesting new information has been got also in some cases. Details for the individual systems are described below.

3.2.1. Copper(II)–Aha/MeAha–bpy systems

Following the formation of the monochelated copper(II)–bpy complex, a new species starts to form at pH ca. 4.5 in copper(II)–Aha–bpy (see Fig. 4) and at pH lower than 3 in copper(II)–MeAha–bpy. This species, $[CuAB]^+$, predominates until pH 10.5 in the latter system and only the hydrolysis of this species can be found at higher pH. The donor atoms in the equatorial plane are the same in the $[Cu(Aha)(bpy)]^+$ and $[Cu(MeAha)(bpy)]^+$ species, as indicated by their similar spectral values. A further complex $[CuABH_{-1}]$ is formed in the copper(II)–Aha–bpy system at pH ca. 10. For this species, $g_\parallel$ is lower and $A_\parallel$ higher (see Table 5), supporting the presence of a stronger in-plane field than in the preceding complex $[CuAB]^+$. Therefore, the spectral changes could be assumed as the distinctive features for the second proton dissociation from the hydroxamic group of Aha and the formation of a hydroximato-type chelate in the species $[CuABH_{-1}]$. All the above findings are in complete agreement with equilibrium studies.

In both ternary systems involving MeAha and Aha EPR spectra show the signals due to a dimeric species present as a minor component in solution over the pH range 6–11. The species is distinguished, in the region of the spectrum corresponding to $\Delta M = 1$ resonances, by two peaks centred at 0.295 and 0.338 T attributable to the perpendicular features. A g factor of 2.07 is measured at the middle point between these two resonances and a value of 0.042 cm^{-1} is calculated for the 'zero-field splitting' value, D. A $\Delta M = 2$ transition, without resolved hyperfine structure, is observed in the range 0.150–0.170 T. Similar spectral features were not observed in the binary systems; therefore, it is likely

Table 6
EPR parameters for the Cu(II)–ligand A–ligand B mixed complexes [a]

Ligand A	Ligand B	Species	$g_\parallel$	$A_\parallel$ ($\times 10^{-4}$ cm^{-1})	Donor atoms
Aha	bpy	[MAB]	2.239	192	ha (O,O), 2 (N)
		[MABH$_{-1}$]	2.219	199	hi (O,O), 2 (N)
		[M$_2$AB]			
		[M$_2$A$_2$B$_2$]			
MeAha	bpy	[MAB]	2.235	193	ha (O,O), 2 (N)
Aha	dien	[MAB]	2.240	181	ha (O,O), 3 (N)
MeAha	dien	[MAB]	2.241	182	ha (O,O), 3 (N)
Aha	terpy	[MAB]	2.267	158	ha (O,O), 3 (N)
MeAha	terpy	[MAB]	2.266	160	ha (O,O), 3 (N)

[a] ha, hydroxamato; hi, hydroximato.

that the dimer is a mixed-ligand species. As judged from the signal intensity, the concentration of the dimer is quite low and this could be the reason why the species was not detected by solution equilibrium studies and their structure not fully characterised.

The most likely hypothesis is that the dimer is formed by bridging of $[Cu(bpy)]^{2+}$ and $[Cu(Aha)]^{+}$ by two OH^{-} ions. In the copper(II)–bpy binary system the hydrolysis starts at pH 6 with the formation of a dimeric complex $[Cu_2(bpy)_2(OH)_2]^{2+}$. In the presence of hydroxamate it is probable that one of the bpy molecules is replaced by a hydroxamate ligand. Since the species is observed both with Aha and MeAha, the hydroxamate form of the ligands seems involved.

An examination of molecular models shows that the interatomic distance in a $[(bpy)Cu(\mu\text{-}OH)_2Cu(Aha)]^{+}$ complex is of ca. 3 Å. If we assume that the structure is nearly planar, we can apply the Steven's equation [29] (a value of 90° for ϑ, the angle formed by Cu–Cu axis and the direction of the magnetic field is used) to correlate the D parameter to the Cu–Cu distance R in the dimer.

$$R^3 = \frac{0.325 g_\perp^2}{D}\left|1 - 3\cos^2\vartheta\right|$$

By use of this equation we calculate a Cu–Cu distance of 3.2 Å.

For the sake of comparison, it must be observed that in $[Cu_2(\mu\text{-}OH)_2(bpy)_2]SO_4\cdot5H_2O$, the copper separation is ca. 2.9 Å in the solid state [30–32], while it changes to ca. 3.4 Å in solution [33].

3.2.2. Copper(II)–Aha/MeAha–dien/terpy systems

The dien and terpy ligands chelate the metal ion in the $[CuB]^{2+}$ species by use of three nitrogen atoms. The basicity of their nitrogens is, however, significantly different from each other (see Table 1). As a result, their mixed-ligand complexes are formed in significantly different pH ranges. Namely, the EPR parameters that can be calculated from the spectra recorded in copper(II)–Aha/MeAha–terpy at 1:3:1 molar ratio below pH 7 are consistent with the presence of the $[Cu(terpy)]^{2+}$ complex (see Table 2) and signals characteristic of complexes $[CuAB]^{+}$ are observed above pH 7. Instead, the monochelated $[Cu(hydroxamato)]^{+}$ species predominates in the pH range 4–4.5 if dien is ligand B, and is replaced by $[Cu(dien)]^{2+}$ and, to a smaller extent, by the bis chelated hydroxamato complex $[CuA_2]$ as the pH is raised. Mixed-ligand complexes $[CuAB]^{+}$ are formed above pH 8. The EPR spectra for these complexes are of the tetragonal type and substantiate a five-coordinated metal ion with approximate square pyramidal geometry. As EPR results show (Table 6), the geometry is more distorted with the more sterically rigid terpy ligand. However, to establish which groups are bound in the plane and which are in an axial position is a rather difficult task.

If the pH is increased further, the replacement of hydroxamates by OH^{-} is documented by both pH-metric and spectrophotometric results (see Fig. 2). The EPR results indicate again the significant differences existing at very high pH (above 11) between the behaviour of Aha and MeAha and also between dien and terpy. The formation of the hydroximato bis-chelated complex $[CuA_2H_{-2}]^{2-}$ takes place in the copper(II)–Aha–terpy system, as it is supported by its characteristic EPR parameters ($g_\parallel = 2.217$ and $A_\parallel = 203 \times 10^{-4}$ cm^{-1}) and the hydrolysed species of terpy $[CuBH_{-1}]^{+}$ appears only as a minor species. At pH values higher than 12, the formation of the hydrolysed species of Aha, $[CuAH_{-1}(OH)_2]^{2-}$, is observed. However, in the copper(II)–Aha–dien system the hydrolysed complex of dien is the predominant species. With MeAha $[CuBH_{-1}]$ is formed in both the copper(II)–MeAha–dien and copper(II)–MeAha–terpy systems at high pH.

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