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Complexes of aminophosphonates—10.† Copper(II) complexes of phosphonic derivatives of iminodiacetate and nitrilotriacetate

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Abstract—pH-Metric and spectroscopic (absorption and EPR) studies were made on the proton and copper(II) complexes of phosphonic and mixed carboxylic–phosphonic derivatives of iminodiacetic acid and nitrilotriacetic acid. The stoichiometries and stability constants of the complexes formed were determined at 25°C and at an ionic strength of 0.20 mol dm^{-3} (KCl). Stability data and spectroscopic measurements revealed that in spite of the increased basicity of the coordinating phosphonate donors, the carboxylic analogues remain more efficient copper(II) binders as the larger space requirement and higher electrostatic repulsion between the binegative phosphonate donors overcompensate the former effect. The PO_3^{2-}/CO_2^- substitution results in a significant rhombic distortion in the geometry of the complexes. © 1997 Elsevier Science Ltd

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Aminopolycarboxylates and their phosphonic derivatives, being multidentate complexing agents with high specificity for various cations, are widely used for various purposes. They are applied among others in analytical chemistry, in the paper and textile industry for the removal of trace amounts of metal ions from bleaching baths, in medicine as antidotes for metal overload in living organisms [2–8]. Due to their biological activities, some representatives of this group are widely used as efficient herbicides [9], and plant growth regulators [10]. Their interaction with soil metal ions alters significantly metal ion speciation which could be either beneficial or detrimental.

The metal-binding capability of iminodiacetate (IDA), nitrilotriacetate (NTA) and their phosphonic derivatives (when one or more carboxylate functions of the molecules are replaced by phosphonate groups) has been widely studied both with divalent and trivalent metal ions [11–16]. Due to the high denticity of these ligands, the equimolar complex MA and its protonated forms are the predominant species for all metal ions studied. The PO_3^{2-}/CO_2^- substitution generally increases the stability of the complexes [2]. However, this stability increase is much lower than would be expected from the increase in basicity of the potentially coordinating group: the more carboxylates are replaced by phosphonates the higher the electrostatic and steric hindrance, compensating or overcompensating the former effect [3]. These effects may result in strong distortion of the geometry of copper–aminophosphonate complexes with respect to the carboxylate analogues [16]. In some cases even the

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denticity of the aminophosphonates may be lowered [2,3].

We report here the results of a comparative study of the Cu^{II} complexes of IDA and NTA and their phosphonic derivatives, such as *N*-(phosphonomethyl)glycine (PMG), iminodimethylenephosphonic acid (IDP), as well as *N*-(phosphonomethyl) iminodiacetic acid (PMI), *N*,*N*-bis(phosphonomethyl)glycine (BPG) and nitrilotrimethylenphosphonic acid (NTP). Besides detailed pH-metric speciation studies, spectral (UV-VIS and EPR) measurements are used to determine the binding modes of copper(II) in the complexes formed.

EXPERIMENTAL

Chemicals

The ligands all were Fluka products and were used without further purification. Their purity was checked and the exact concentration of their stock solutions was determined by the Gran method [17]. The concentration of the metal chloride stock solution was measured gravimetrically *via* precipitation of the quinoline-8-olate.

Potentiometric studies

The stability constants of the proton and the copper(II) complexes of the ligands were determined by pH-metric titration of 25 cm^3 samples. The concentration of the ligand in each sample was 0.004 and 0.002 mol dm^{-3} and the metal ion to the ligand ratio was 0:1, 1:1, 1:2 and 1:4. The ionic strength was adjusted to 0.20 mol dm^{-3} with KCl. The titrations were performed over the pH range 2–11, with carbonate-free KOH solution of known concentration (*ca* 0.2 mol dm^{-3}).

The pH was measured with a Radiometer PHM 84 instrument and GK2321C combined glass electrode, calibrated for hydrogen ion concentration according to Irving *et al.* [18]. A pK_w value of 13.76 was determined from a strong acid strong base titration. The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated by the PSEQUAD computer program [19]. Depending on the ligands the fully deprotonated forms have different charges. Thus, charges of the complexes are omitted throughout the text.

Spectroscopic studies

In order to establish the metal ion binding sites in metal complexes, electronic absorption and EPR studies were performed. Absorption spectra were recorded on a Beckman UV5420 spectrometer. EPR spectral measurements were performed on a Bruker ESP 300E spectrometer at the X-band frequency (9.3 GHz) at 120 K in ethylene glycol–water (1:2 v/v) solutions. The comparison of the samples and experimental conditions were the same as described for the potentiometric titrations.

RESULTS AND DISCUSSION

Iminodiacetate derivatives

IDA and its phosphonic derivatives PMG and IDP contain three, four or five acidic protons, respectively. However, only three of them dissociate in the measurable pH range. The first proton of the phosphonic groups dissociates at around pH ~ 1. As is seen from the protonation constants, the basicity of the imino group increases by ~0.7–0.9 log unit as the carboxylate functions are replaced by phosphonate ones due to the larger electron-repelling effect of the binegatively charged phosphonate groups.

The overall stability constants calculated from the potentiometric data are presented in Table 1 together with relevant derived equilibrium constants characteristic of some stepwise processes of complex formation. The stability constants reported here are in reasonable agreement with those of Motekaitis and Martell [12]; the differences in the protonation constants never exceed 0.2 log unit, while those of the proton displacement constants (which are the primarily measured equilibrium constants) are ≤0.4 log unit. Probably, because we carried out measurements also at higher ligand excesses, we could detect formation of protonated bis complexes, which were not considered previously [12]. Apparent differences in speciation (see Fig. 1 and Table 1) of the $Cu^{(II)}$ complexes of IDA, PMG and IDP result from the presence of an extra dissociable proton on each phosphonic group, which makes possible the formation of protonated species. If allowance is made for this, the three systems behave more or less similarly. A comparison of the complexing properties of mixed phosphonate and carboxylate ligands (see Table 1) indicates that the stability of the complexes increases with the number of phosphonate moieties (due to the increase in the basicity of the donor groups, see log K_{HA} values). In order to demonstrate this, the stability constants of the CuA complexes of IDA and NTA and their mixed phosphono derivatives are plotted against the number of substituted phosphate groups in Fig. 2.

Although the overall stability constants of the phosphonic derivatives are higher, the carboxylic derivatives are more effective chelating agents and the PO_3^{2-}/CO_2^- substitution decreases slightly the Cu^{II} binding capability of the ligands. The speciation diagrams clearly demonstrate this as the free metal ion concentration at a given pH decreases in the order of IDA < PMG < IDP. Similarly, the pH of the formation maximum of each corresponding species (e.g. CuA or CuA_2) is shifted to higher pH values. This is reflected in the derived equilibrium constants, too.

Table 1. Proton and copper(II) complex formation constants of imino-diacetate (IDA) and its phosphonic derivatives at 25°C and at $I = 0.20$ mol dm^{-3} (KCl)

	IDA^{2-} [a]	MPG^{3-}	IDP^{4-}
$\log K(NH_2)$	9.34	10.03(2)	10.97(3)
$\log K(PO_3^{2-})$	—	5.37(1)	6.12(1)
$\log K(PO_3^{2-})$	—	—	4.85(1)
$\log K(COO^-)$	2.6	2.13(3)	—
$\log K(COO^-)$	1.8	—	—
$CuAH_2$	—	—	21.50(3)
CuAH	12.9	15.53(2)	17.75(2)
CuA	10.56	11.68(1)	12.90(1)
$CuAH_{-1}$	2.0	2.16(3)	2.16(3)
CuA_2H_4	—	—	41.9(1)
CuA_2H_3	—	—	37.92(5)
CuA_2H_2	—	29.37(4)	32.52(4)
CuA_2H		24.61(4)	26.73(4)
CuA_2	16.4	16.42(3)	16.86(4)
Fitting[b]		0.0048	0.0057
No. of points		220	307
$\log K_{CuA} - \Sigma \log K_H$	−3.18	−5.85	−9.04
$\log K_{CuA_2} - \Sigma \log K_H$	−7.9	−12.79	−17.98
$\log (K_{CuA}/K_{CuA_2})$	4.72	6.94	8.94
$pK(CuAH_2)$		—	3.75
pK(CuAH)	2.3	3.85	4.85
pK(CuA)	8.6	9.52	10.74
$pK(CuA_2H_4)$	—	—	4.0
$pK(CuA_2H_3)$		—	5.40
$pK(CuA_2H_2)$		4.76	5.79
$pK(CuA_2H)$		8.19	9.87
$CuA + A \rightleftharpoons CuA_2$	5.8	4.74	3.96
$Cu + HA_{PO_3H} \rightleftharpoons CuAH$	—	10.16	11.63
$CuA + HA_{NH_2} \rightleftharpoons CuA_2H$	—	2.90	2.86

[a] [15].

[b] Average difference between experimental and calculated titration curves expressed in cm^3 of titrant.

Namely, the basicity adjusted stability constants ($\log K_n - \Sigma \log K_{H,A}$), which take into account the differences in basicities of the coordinating donor groups, decrease in the same order. The reason for this is the larger space requirement and the higher charge of the PO_3^{2-} group. The charge neutralization favours formation of the complex CuA for IDA but not for PMG and IDP. For similar reasons, coordination of the second ligand molecule, which is not very favoured for IDA ($\log K_{CuA}/K_{CuA_2}) = 4.72$) is even more hindered for PMG ($\log K_{CuA}/K_{CuA_2}) = 6.94$) and IDP ($\log K_{CuA}/K_{CuA_2}) = 9.06$). The charge of the bis complex $[CuA_2]$ is 2−, 4− and 6−, respectively. The spectral parameters of the complexes listed in Table 2 unambiguously indicate the tridentate (1N, 2O) coordination of ligand in the equatorial plane of the mono complex CuA. As the EPR parameters do not change upon protonation and formation of the complex CuAH, it is reasonable to assumed that one of the O donor groups (carboxylate or phosphonate) is protonated, but the central amino group remains coordinated in this complex. The further protonation of CuAH and IDP resulting in species $CuAH_2$ takes place on the amino group as it is reflected in the significant decrease in A and increase of $g_\parallel$ values (see Table 2).

In the case of ligand excess all three ligands form bis complexes. The fully deprotonated complex CuA_2 is very likely a 2N species. In the case of IDA and PMG this complex preserves the normal tetragonal bipyramidal geometry, probably with tridentate coordination of one of the ligand molecules in the equatorial plane. The relatively low energy of the d–d transition and also the EPR parameters suggest that in the complex $[CuA_2]^{4-}$ of PMG, the ligand molecules occupy five coordination sites around Cu^{II}: the second ligand molecule binds in an equatorial-(NH_2) axial-(PO_3^{2-}) manner to the tridentately bound [CuA]. With IDP^{4-} which is much more bulky and more highly negatively charged, the coordination mode of the second ligand molecule is similar. However, the much larger spatial and electrostatic hindrance causes a very strong rhombic distortion, which is unambiguously reflected in the significant decrease in $A_\parallel$ and increase in $g_\perp$ parameter and also in the occurrence of a characteristic shoulder at ~ 960 nm in the visible

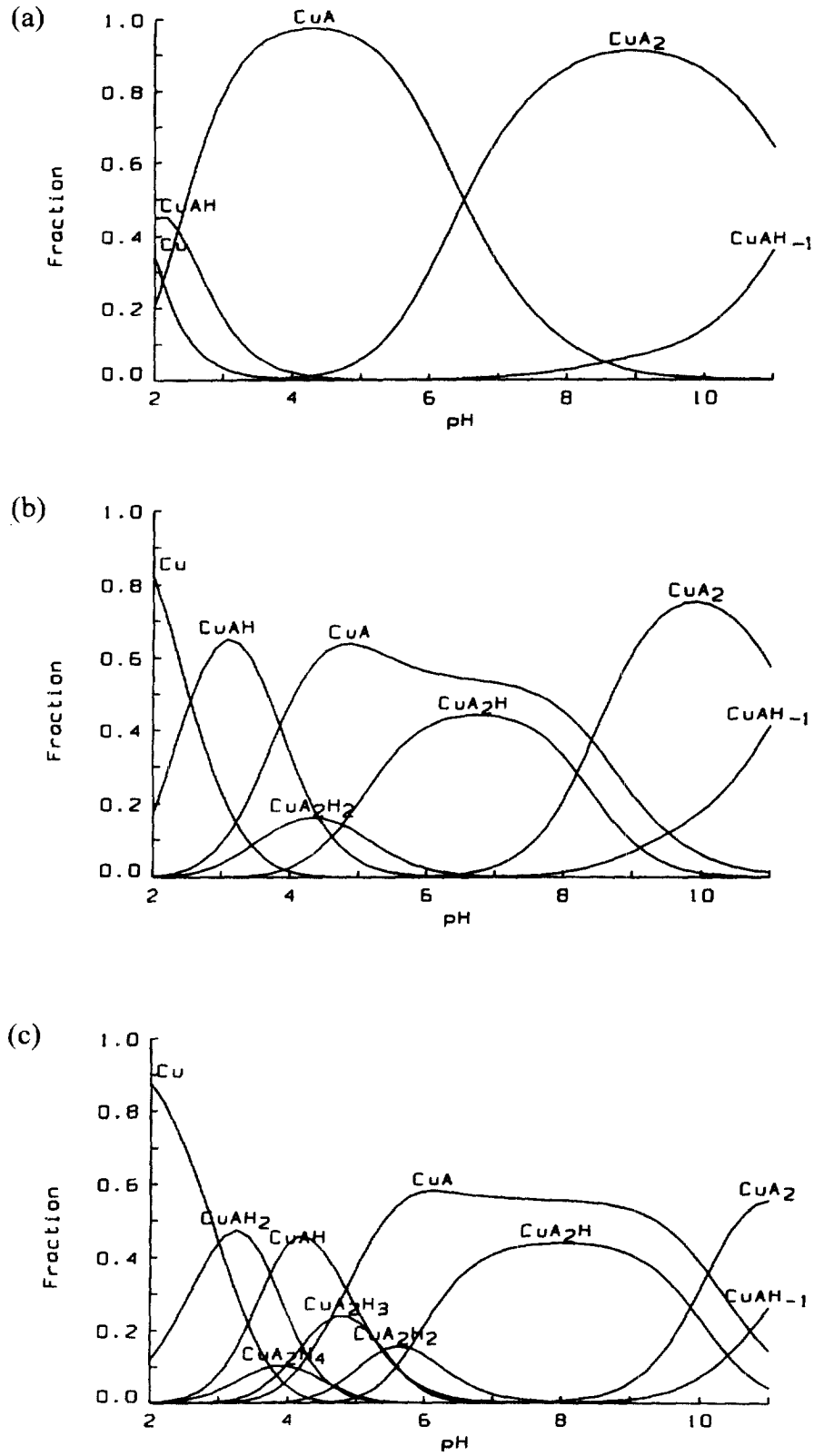

Fig. 1. Species distribution diagram for (a) Cu^{II}-IDA, (b) Cu^{II}-PMG and (c) Cu^{II}-IDP; $c_{Cu} = 0.002$ mol dm^{-3}, $c_{ligand} = 0.004$ mol dm^{-3}.

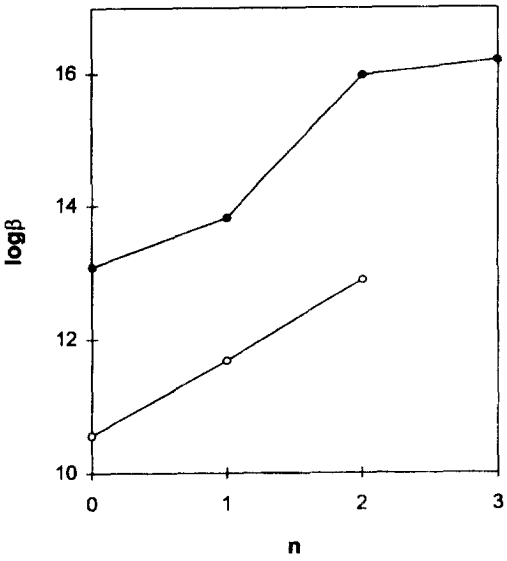

Fig. 2. Log β_{CuA} values for Cu^{II} complexes of mixed phosphonic-carboxylic derivatives of (a) IDA $HN(CH_2PO_3H_2)_n(CH_2COOH)_{2-n}$ and (b) NTA, $N(CH_2PO_3H_2)_n(CH_2COOH)_{3-n}$.

spectra. The tridentate + bidentate bonding mode also explains the fact that a pH increase at pH > 9 leads to the formation of a mixed hydroxo complex $CuAH_{-1}$ even in the case of an excess of ligand. The displacement of one ligand molecule by OH^- indicates its weaker binding to the metal ion. Such a process is generally not observed for the bidentate aminophosphonate or aminocarboxylate complexes containing two five-membered chelate rings in the equatorial plane around Cu^{II} [20,21]. Both PMG and IDP form protonated bis complexes. The first protonation process is characterized by $\log K_H = 8.19$ and 9.87, respectively, which suggests the protonation of the imino group of the complex. Thus, it is very likely that in this process only the binding mode of the second ligand changes to monodentate PO_3^{2-} coordination with a possible weak axial involvement of the other O donor carboxylate or phosphonate function (see the equilibrium constants for the process $CuA + HA_{NH_2^+} \rightleftharpoons CuA(HA)$ in Table 1). Further protonations would occur on the remaining O-donor moieties of the ligand molecules(s).

Nitrilotriacetate derivatives

NTA and its phosphonic derivatives PMI, BPG, and NTP contain four, five, six or seven dissociable protons, respectively. The first proton of each phosphonic function, however, is very acidic, its $pK < 1$ and thus, it fully dissociates by pH ~ 2 which is the lower limit of the pH range studied. Similarly to IDA and its derivatives (*vide supra*), due to the electronic effects of the substituents, the PO_3^{2-}/CO_2^- substitution increases gradually the basicity of the tertiary amino groups and the first phosphonate functions, while the basicity of the further phosphonates decreases.

The stability constants obtained for the copper(II) complexes together with some derived equilibrium constants are listed in Table 3. Our data obtained for PMI are in good agreement with those of Dhansay and Linder [14] measured at 0.1 (NaCl) ionic strength, however, the agreement is much poorer with those reported in the review of Rizkalla [2] for NTP.

The species distribution diagrams shown in Fig. 3 demonstrate that 1 : 1 complexes are the predominant species in all systems with the exception of NTA, where the bis complex $[CuA_2]^{4-}$ is the major species at around pH 9–10 in the case of ligand excess. When substituting COO^- donors by PO_3^{2-} groups in the ligand series, again the larger space requirement and higher charge deriving from the phosphonate groups hinders the coordination of the second ligand molecule. The charge of the bis complex would be 6−, 8− or 10−, respectively, in the series.

Table 2. Spectral parameters (EPR, Visible) for copper(II) complexes of IDA and its phosphonic derivatives

Complex	Ligand	$g_{\parallel}$	$A_{\parallel}G$	λ_{max}nm (ε/dm^3 mol^{-1} cm^{-1})
$CuAH_2$	IDP	2.39	137	810(30)
CuAH	IDP	2.33	150	757(45)
	PMG	2.32	149	740(63)
CuA	IDP	2.33	150	740(49)
(1N species)	PMG	2.32	149	730(60)
	IDA	2.30	150	722(58)
$CuAH_{-1}$	IDP	2.29	173	720(50)
	PMG	not detected		705(82)
	IDA	2.26	173	690(57)
CuA_2	IDP	2.33	128	739(51) 960(40)sh
(2N species)	PMG	2.27	170	720(65)
	IDA	2.27	166	675(40)

Table 3. Proton and copper(II) complex formation constants of nitrilo-triacetate (NTA) and its phosphonic derivatives at $I = 0.2$ mol dm^{-3} and $t = 25$ °C

	NTA[1-a]	PMI[4-]	BPG[5-]	NTP[6-]
log K(NH_2)	9.67	10.54(2)	11.49(5)	12.30(9)
log K(PO_3^{2-})	—	5.47(2)	6.28(1)	6.98(1)
log K(PO_3^{2-})	—	—	4.85(1)	5.69(1)
log K(PO_3^{2-})	—	—	—	4.46(1)
log K(COO^-)	2.52	2.29(2)	1.76(6)	—
log K(COO^-)	1.9	1.2(2)	—	—
log K(COO^-)	1.0	—	—	—
$CuAH_3$	—	—	—	30.23(2)
$CuAH_2$	—	—	24.67(7)	26.84(1)
CuAH	14.8	18.52(2)	21.14(6)	22.37(2)
CuA	13.1	13.83(2)	15.97(5)	16.19(2)
$CuAH_{-1}$	3.9	3.98(2)	5.56(6)	4.72(3)
CuA_2	17.5	—	—	—
Fitting[b]		0.0049	0.0067	0.0086
No. of points		312	289	309
$\log K_{CuA} - \Sigma \log K_H$	−3.99	−5.67	−8.41	−13.24
pK($CuAH_3$)	—	—	—	3.39
pK($CuAH_2$)	—	—	3.53	4.47
pK(CuAH)	1.7	4.69	5.17	6.18
pK(CuA)	9.2	9.85	10.41	11.47

[a] [15].

[b] Average difference between experimental and calculated titration curves expressed in cm^3 of titrant.

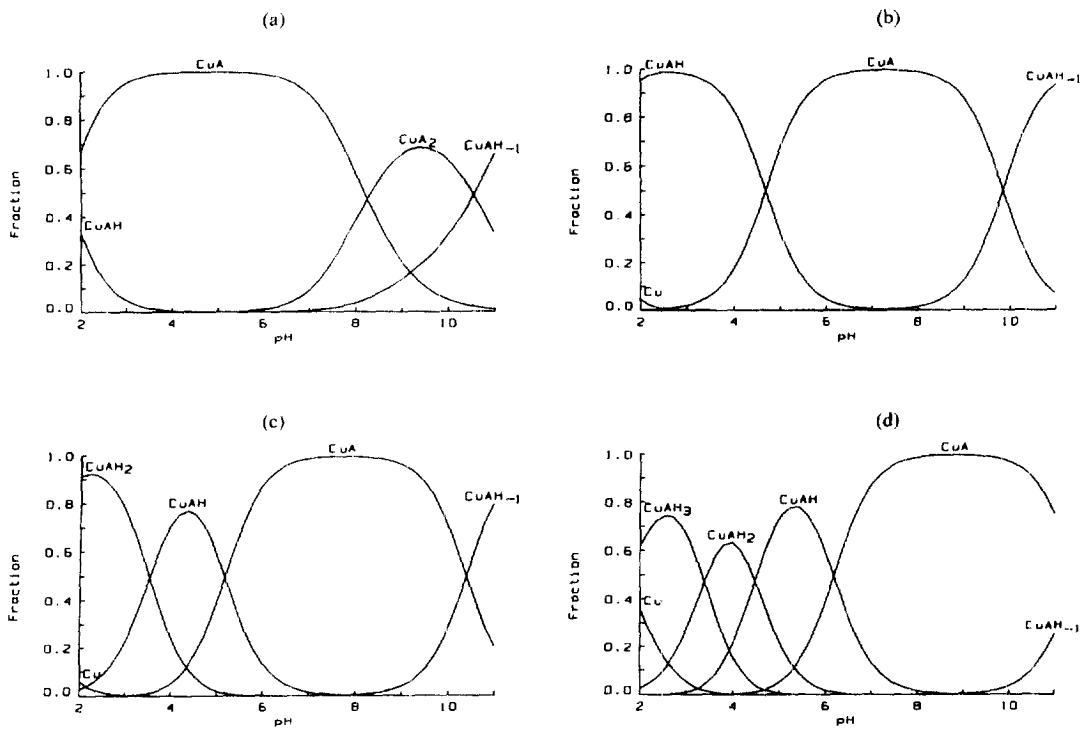

Fig. 3. Species distribution diagram for (a) Cu^{II}-NTA, (b) Cu^{II}-PMI and (c) Cu^{II}-BPG; (d) Cu^{II}-NTP; $c_{Cu} = 0.002$ mol dm^{-3}, $c_{ligand} = 0.004$ mol dm^{-3}.

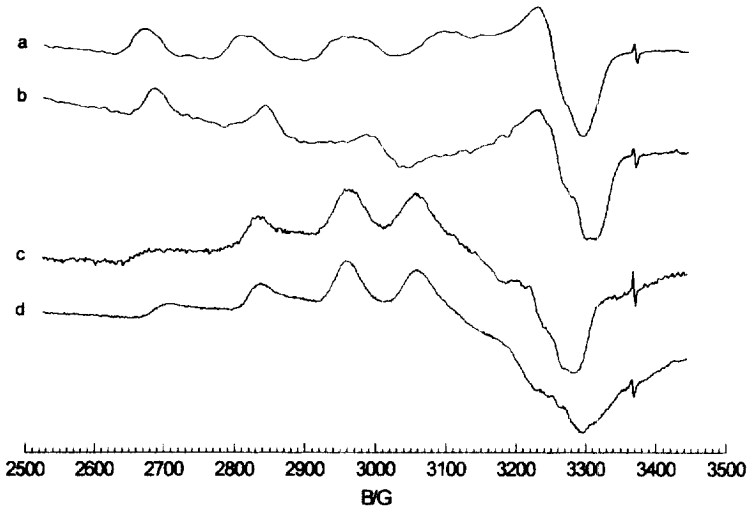

Fig. 4. X-Band EPR spectra of (a) Cu^{II}-NTA, (b) Cu^{II}-PMI and (c) Cu^{II}-BPG; (d) Cu^{II}-NTP systems at 1 : 1 metal ion to ligand ratio and at pH values optimal for CuA, recorded at 120 K.

The substitution of the COO^- functions by PO_3^{2-} results in an increase in the overall stability constants of the NTA analogues, too. However, as is seen in Fig. 2, this increase is not so smooth as for the IDA analogues and is much less than would otherwise be expected concerning the significant increase in the overall basicity of the coordinating donors [3]. The "step-like" feature of the relationship shown in Fig. 2 should suggest some change in coordination geometry or in coordination number of the CuA complexes formed with the NTA analogues. Characteristic EPR spectra of the CuA complexes (see Fig. 4 and Table 4) support this assumption. A profound change is seen also in the electronic spectra: rather low energy of the *d–d* transition and splitting of the *d–d* band. Such changes are characteristic of deviation from tetra-

Table 4. Spectral parameters (ESR, Visible) for copper(II) complexes of NTA and its phosphonic derivatives

Complex	Ligand	g	A_1/G	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$CuAH_3$	NTP	2.31	107	793(41), 997(51)
		$g_2 = 2.12, g_3 = 2.07$		
$CuAH_2$	NTP	2.34	117	790(46), 997(54)
		$g_2 = 2.11, g_3 = 2.05$		
	BPG	2.34	141	820(63), 950(46)
CuAH	NTP	2.34	122	786(48), 982(51)
		$g_2 = 2.11, g_3 = 2.05$		
	BPG	2.31	153	820(80), 950(67)
	PMI	2.33	148	774(53)
	NTA	2.30	153	775(63)
CuA	NTP	2.33	123	789(5), 1015(82)
		$g_2 = 2.10, g_3 = 2.05$		
	BPG	2.32	126	820(70), 965(90)
	PMI	2.31	157	771(47), 961(64)
	NTA	2.33	145	810(75), 900(68)
$CuAH_{-1}$	NTP	2.32	82	779(59), 983(80)
	BPG[a]	$g_1 = 2.279$	48	820(120), 940(125)
		$g_2 = 2.202$	42	
		$g_3 = 2.047$	11	
	PMI	2.27	171	743(54), 931(67)
	NTA	2.29	168	750(87), 915(90)

[a] Values obtained through simulation of the spectra [16].

gonal symmetry towards distorted square pyramid. The most likely binding mode of the ligands in the CuA complexes is a tetradentate (NH_2, O, O, O) coordination *via* the simultaneous formation of three five-membered chelate rings. Because of steric reasons the four donor groups can be arranged only in a square pyramid geometry (with a water molecule in the fourth equatorial position). As seen in Table 4, the CuA complex of NTA and PMI shows fairly regular EPR parameters characteristic to square pyramid geometry with 1N in the equatorial plane. With an increase in columbic repulsion between the highly negative phosphonate groups in the CuA complex of BPG and NTP a strong rhombic distortion occurs. This is reflected in the EPR behaviour: namely a large decrease in $A_{\parallel}$ and broadening of the perpendicular part of the spectra is observed.

In more basic solutions CuA complex liberates a proton from the coordinated water molecule and the species $CuAH_{-1}$ is formed. In the case of the diphosphono derivative BPG this process is accompanied by further distortion towards orthorombic symmetry (discussed in details in [16]).

In more acidic solution the CuA complexes undergo stepwise protonation processes. The relatively low protonation constants and the slight changes in EPR and VIS spectral parameters indicate that the nitrogen donor group remains coordinated and the proton(s) reside(s) on the oxygen donor phosphonate and/or carboxylate functions. This is in contrast with what was reported for the alkaline-earth complexes of these ligands, when the first protonation process was assumed to occur on the tertiary-N donor [3]. It is worthwhile to note also that in the case of BPG the extent of rhombic distortion decreases with protonation as the columbic repulsion between the phosphonic moieties decreases. This is reflected in the increase in $A_{\parallel}$ upon protonation (see Table 4).

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