Complexes of Aminophosphonates. Part 7.† Copper(II) Complexes of Some Aliphatic, Alicyclic and Aromatic Aminophosphonous and Aminophosphinic Acids

Tamas Kiss,*[a] Malgorzata Jezowska-Bojczuk,[b] Henryk Kozlowski,[b] Pawel Kafarski[c] and Kazimierz Antczak[d]

[a] *Department of Inorganic and Analytical Chemistry, Kossuth University, 4010 Debrecen, Hungary*
[b] *Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland*
[c] *Institute of Organic and Physical Chemistry, Technical University, 50-370 Wroclaw, Poland*
[d] *Institute of Chemistry, Technical University, 80-952 Gdansk, Poland*

pH-Metric and spectroscopic (visible and ESR) studies were made of the proton and copper(II) complexes of various bidentate aliphatic, alicyclic and aromatic aminophosphonous and aminophosphinic acids, and of the α- and β-phosphinic acid derivatives of aspartic acid, at 25 °C and at an ionic strength of 0.20 mol dm^{-3} (KCl). It was found that the metal-binding abilities of these bidentate ligands are weaker than those of their aminocarboxylate analogues, which is due mainly to the differences in basicity of the PO_2R^- and the CO_2^- groups. The potentially terdentate aspartic acid derivatives are co-ordinated mainly *via* their aminocarboxylate moieties and the participation of the phosphinate group in the co-ordination is significant only for the α-phosphinic acid derivative. The metal-binding abilities of amino-phosphonates, -phosphinates and -carboxylates are compared.

Aminophosphonates are analogues of aminocarboxylates in which a carboxylic moiety is replaced by a phosphonic, $PO(OH)_2$, or related [phosphonous, PO(H)(OH), or phosphinic, PO(R)(OH)] groups. Many of these compounds act as antagonists of amino acids, inhibit (metallo)enzymes involved in the peptide and amino acid metabolisms and thus affect the physiological activity of cells. These actions may be exerted as antibacterial, plant-growth regularity or neuromodulatory effects.

We recently reported results on transition-metal complexes of several bidentate aliphatic and aromatic aminophosphonates[1] and of the potentially terdentate aminophosphonate analogues of aspartic acid and glutamic acid.[2] The differences between the complex-forming properties of aminophosphonates and their aminocarboxylate analogues were explained in terms of the differences in basicity, charge and size of the PO_3^{2-} and CO_2^- groups. In the present work, the study has been extended to several phosphonous $R^1CH(NH_2)$–PO(H)(OH) (R^1 = CH_3 or C_6H_5) and phosphinic $R^1CH(NH_2)$–$PO(R^2)(OH)$ [R^1 = CH_3, C_2H_5, C_3H_7, $CH(CH_3)_2$ or $CH_2CH(CH_3)_2$; R^2 = CH_3, C_2H_5 or C_6H_5] analogues of simple aliphatic and aromatic aminocarboxylates, alicyclic phosphinic and phosphonic acids, $CH_2(CH_2)_3C(NH_2)PO(R^2)(OH)$ (R^2 = CH_3 or OH), and the α-and β-phosphinic derivatives of aspartic acid. The stoichiometries, stability constants and bonding modes of the complexes formed in the equilibrium systems of the above-mentioned ligands with the copper(II) ion are presented in this paper.

Experimental

The racemic aminophosphonous and aminophosphinic acids were obtained by the methods described in refs. 3 and 4. The purity of the ligands was checked and the exact concentrations of their solutions were determined by the method of Gran.[5] The concentration of the metal chloride stock solution was measured gravimetically *via* precipitation of the quinolin-8-olate.

The stability constants of the proton and metal complexes of the ligands were determined by pH-metric titration of 5.00 cm^3 samples. The experimental parameters were as follows: solution composition (in mol dm^{-3}), ligand concentration 0.002–0.004, copper(II) ion concentration 0.001–0.002, ionic strength 0.20 (KCl); pH range studied, protonation 2.2–10.2, metal complexation 2.2–10.0 or until precipitation; method, pH-titration, calibrated in concentrations;[6] T 25.0 ± 0.1 °C.

The pH was measured with a Radiometer pHM 64 instrument, with G2040B glass and K4040 calomel electrodes, using a TTA 80 titration unit.

Visible absorption spectra were recorded with a Beckman UV5240 spectrophotometer, while ESR spectral measurements were carried out on a RADIOPAN SE/X spectrometer in X-band (9.3 GHz) at 120 K in ethylene glycol–water (1:2) mixtures.

The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated with the aid of the PSEQUAD computer program.[7] Depending on the type of ligand, the fully deprotonated forms have different charges, *i.e.* A^- refers to bidentate aminocarboxylates and aminophosphinates, A^{2-} to aminophosphonates, aspartic acid and its phosphinic derivatives, and A^{3-} to phosphonic derivatives of aspartic acid. Hence, species with the same stoichiometric composition may have different charges. For this reason, the charges of the complexes refer only to the aminophosphinate analogues.

Results and Discussion

Simple Aminophosphonous and Aminophosphinic Acids.— Phosphonous acids can be derived from phosphonic acids by substituting one acidic OH by a H, while in the phosphinic acids the OH is replaced by an alkyl (R) group. Hence, both types of ligands contain only one acidic OH in the phosphoric moiety, but this is very acidic; similarly to the dissociation of the first proton in phosphonic acids, pK is ≈1.0, and thus full

† Part 6, J. Balla, T. Kiss, M. Jezowska-Bojczuk, H. Kozlowski and P. Kafarski, *J. Chem. Soc., Dalton Trans.*, 1990, 1861.

Table 1 Proton dissociation constants (pK) and copper(II) complex[a] formation constants (log β) of amino-phosphonous acids, -phosphinic acids and -phosphonic acids at 25.0 ± 0.1 °C and I = 0.20 mol dm^{-3} (KCl)

$CH_3CH(NH_2)PO(R^2)$-(OH)[b]	R^2 = H	CH_3	C_6H_5	OH
pK_1	8.03(1)	8.29(2)	8.21(1)	10.11
pK_2	1.0	1.0	1.0	5.55
pK_3	—	—	—	1.0
$[CuAH]^+$	—	—	—	12.29
$[CuA]^+$	4.87(2)	5.45(2)	5.13(2)	8.29
$[CuA_2]$	8.91(3)	9.99(3)	9.58(2)	14.94
$[CuA_2H_{-1}]^-$	0.64(6)	1.20(7)	0.96(3)	—
Fitting[c]	3.66 × 10^{-3}	3.61 × 10^{-3}	2.62 × 10^{-3}	
log K_1 − pK_2 − pK_1	−4.16	−3.84	−4.08	−7.37
log K_2 − pK_2 − pK_1	−4.99	−4.75	−4.76	−9.04
log(K_1/K_2)	0.83	0.91	0.68	1.64
$CH_2(CH_2)_3C(NH_2)PO(R^2)(OH)$				
pK_1			8.16(1)	10.17(1)
pK_2			1.0	5.83(2)
pK_3			—	1.0
$[CuAH]^+$			—	13.05(5)
$[CuA]^+$			4.95(2)	8.46(2)
$[CuA_2]$			9.13(2)	15.56(3)
$[CuA_2H_{-1}]^-$			0.63(5)	3.81(7)
Fitting[c]			1.63 × 10^{-3}	3.73 × 10^{-3}
log K_1 − pK_2 − pK_1			−4.09	−7.54
log K_2 − pK_2 − pK_1			−4.96	−8.90
log(K_1/K_2)			0.77	1.36
$C_6H_5CH(NH_2)PO(R^2)(OH)$[b]				
pK_1	7.18(3)	7.41(1)	7.39(1)	9.62
pK_2	1.0	1.0	1.0	6.21
pK_3	—	—	—	1.0
$[CuAH]^+$	—	—	—	12.30
$[CuA]^+$	4.46(3)	5.00(2)	4.75(2)	8.30
$[CuA_2]$	8.28(4)	9.14(2)	8.82(7)	15.18
$[CuA_2H_{-1}]^-$	prec	0.02(9)	prec	—
Fitting[c]	3.68 × 10^{-3}	1.52 × 10^{-3}	3.06 × 10^{-3}	
log K_1 − pK_2 − pK_1	−3.72	−3.41	−3.64	−6.75
log K_2 − pK_2 − pK_1	−4.36	−4.27	−4.32	−8.18
log(K_1/K_2)	0.64	0.86	0.68	−1.42

[a] Charges of the complexes refer only to aminophosphinate analogues (see text). [b] For R^2 = OH, see ref. 1. [c] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant; prec = precipitation

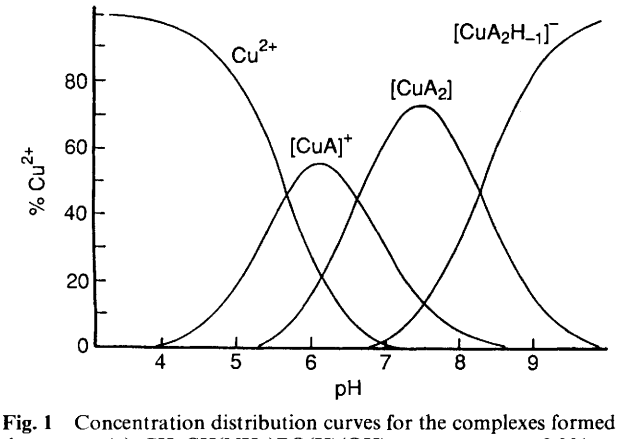

Fig. 1 Concentration distribution curves for the complexes formed in the copper(II)–$CH_3CH(NH_2)PO(H)(OH)$ system; c_{Cu} = 0.001 mol dm^{-3}, c_{ligand} = 0.004 mol dm^{-3}

deprotonation occurs in the pH range studied (2.2 < pH < 10.2). As the pK values show (see Table 1), the acidity of the NH_3^+ group of these ligands is higher than that of the aminophosphonate analogue, due to the weaker electron-withdrawing effect of the phosphonate group, but it is lower than that of the aminocarboxylate analogue, ($pK_{NH_3^+}$ = 9.68 for alanine and 9.08 for phenylalanine[8]), due to the stronger electron-withdrawing effect of the phosphinate.[9] The data reveal the following sequence for the −I (inductive) effect of these ligands: $PO_3^{2-} < CO_2^- < PO_2R^- < PO_2H^-$.

The stability constants obtained for the copper(II) complexes of the ligands, together with those for the corresponding phosphonic acid analogues, are listed in Table 1.

These simple aminophosphonous acids and aminophosphinic acids contain only two donor groups and are able to bind copper(II) in a bidentate manner forming five-membered [NH_2, $PO(R)O^-$] chelates of composition $[CuA]^+$ and $[CuA_2]$. Besides these species the formation of a hydroxo 1:2 complex of composition $[CuA_2H_{-1}]^-$ {or more precisely $[CuA_2(OH)]^-$} was also assumed in the calculation as a further base-consuming process occurred at pH ≈9 in the case of an excess of ligand. The assumption of this species improved the fit between the experimental and the calculated titration data by ≈20–30%, resulting in the fitting parameters[7] given in Table 1. The early precipitation at pH ≈6 at a metal ion to ligand ratio of 1:1 prevented the detection and characterization of the hydroxo complex [CuA(OH)]. For the aromatic phosphonous and phosphinic acids, precipitation occurred at lower pH than for the aliphatic derivatives, presumably due to the presence of the hydrophobic aromatic rings. In contrast with the aminophosphonate analogues, there was no formation of the protonated complex $[CuAH]^{2+}$, because of the lower basicity of the phosphinate group.

As an illustration, the concentration distribution curves for the complexes formed in the copper(II)–$CH_3CH(NH_2)PO(H)(OH)$ system are depicted in Fig. 1.

For a comparison of the metal ion-binding abilities of the aminocarboxylates and their various phosphorous analogues, the proton-displacement constants (log K_n − pK_1 − pK_2; also known as basicity-adjusted constants, or relative stability constants, which take into account the difference in basicity of the co-ordinating donor groups) for the formation of their complexes $[CuA]^+$ and $[CuA_2]$, together with the characteristic visible and ESR spectral parameters, are listed in Table 2.

The equilibrium data in Table 2 show that the relative stabilities of the aminophosphinate complexes are about the same as those of the corresponding aminocarboxylate derivatives, but much larger than those of the aminophosphonate analogues. That is, the lower overall stability of the phosphonous and phosphinic complexes is due purely to the lower basicity of the donor groups (*cf.* $pK_{PO_3H^-}$ for the aminophosphonic acid and $pK_{PO(R)(OH)}$ for the aminophosphonous or aminophosphinic acids, which are 5.5 and ≈1.0, respectively), and there is practically no 'overcompensation effect' due to the charge and steric effects, which were the decisive factors in the stability of the aminophosphonate complexes.[1,2] The smallest log (K_1/K_2) values obtained for the phosphonous and phosphinic derivatives suggests that the difference in geometry of the negatively charged donor groups (planar for CO_2^- and tetrahedral for PO_2R^-) results in a somewhat more favoured co-ordination of the second aminophosphinate molecule.

The spectral parameters in Table 2 are consistent with the speciation model obtained from the pH-metric titration data and with the proposed bonding modes of the complexes. Both the visible spectral and the ESR behaviour of the complex $[CuA]^+$ of each ligand clearly indicate a 1N species. It is noteworthy, however, that the energy of the d–d transition of the $[CuA_2]$ complexes of the aminophosphinates is significantly lower than that of the corresponding complexes of $CH_3CH(NH_2)PO(OH)_2$ or alanine (Ala), and the ESR parameters of

Table 2 Derived equilibrium constants[a] and spectral parameters[b] for copper(II) complexes of alanine (Ala) and its phosphonous, phosphinic and phosphonic analogues

	Ala[c]	$CH_3CH(NH_2)PO(H)(OH)$	$CH_3CH(NH_2)PO(CH_3)(OH)$	$CH_3CH(NH_2)PO(OH)_2$[c]
$\log K_1 - pK_2 - pK_1$	−3.99	−4.16	−3.84	−7.37
$\log K_2 - pK_2 - pK_1$	−5.34	−4.99	−4.75	−9.04
$\log(K_1/K_2)$	1.35	0.83	0.91	1.64
Visible spectra: $\lambda_{max}(\varepsilon)$				
$[CuA]^+$	690(50)	695(45)	702(42)	700(40)
$[CuA_2]$	615(56)	667(62)	670(61)	645(50)
$[CuA_2H_{-1}]^-$	—	675(43)	678(48)	—
ESR spectra: $g_{\|}$, $A_{\|}$				
$[CuA]^+$	2.32, 156	2.346, 137	2.341, 140	2.32, 150
$[CuA_2]$	2.26, 172	2.296, 128	2.293, 135	2.26, 160
$[CuA_2H_{-1}]^-$	—	2.271, 171	2.266, 166	

[a] Charges of the complexes refer only to aminophosphinate analogues (see text). [b] The A values are in G(10^{-4} T), λ_{max} in nm, and ε in $dm^3\ mol^{-1}\ cm^{-1}$; ε values were calculated for the total copper(II) concentration for the pH at which the respective species is a major complex. [c] See ref. 1.

Table 3 ESR spectral data* for the CuA_2 complexes of the ligands $[R^1CH(NH_2)PO(R^2)(OH)]$ studied

	$R^2 = H$		CH_3		C_2H_5		C_6H_5	
	$g_{\|}$	$A_{\|}$	$g_{\|}$	$A_{\|}$	$g_{\|}$	$A_{\|}$	$g_{\|}$	$A_{\|}$
R^1								
CH_3	2.296	128	2.293	135	2.293	138	2.288	144
C_2H_5			2.293	140	2.287	143	2.284	144
n-C_3H_7			2.287	140				
iso-C_3H_7			2.283	148	2.282	150		
n-C_4H_9					2.287	143	2.279	147
iso-C_4H_9			2.287	148				
C_6H_5			2.295	140	2.289	150		

* The A values are in G.

these complexes partly differ from those of typical 2N species with square-bipyramidal geometry. Namely, the $g_{\|}$ value [= 2.288(5), the average for the 16 different aminophosphinate derivatives] is about the usual value for normal 2N species, the $A_{\|}$ value [= 143(6)] is significantly smaller than those for the 2N complexes of $CH_3CH(NH_2)PO(OH)_2$ or Ala. These $g_{\|}$ and $A_{\|}$ values, however, are in full agreement with those of the species bis(β-alaninato)-copper(II), which is also a 2N species ($g_{\|}$ = 2.28 and $A_{\|}$ = 139).[10,11] The low value of $A_{\|}$ indicates some rather strong distortion of the usual square-bipyramidal structure of the copper(II) complexes. In the case of the copper(II)–bis(2-aminoethyl) ether system, a square-pyramidal structure with a chromophore CuN_2O_3 was suggested to explain a similar experimental finding.[12] As the ESR parameters listed in Table 3 show, the stronger electron-repelling and the bulkier the substituent R^2 on the phosphorus atom, the smaller is $g_{\|}$ and the larger is $A_{\|}$, indicating stronger metal–ligand interaction and somewhat less distortion with increasing size of the substituent R^2. Similarly, the relative stabilities of the complexes of the ligands with R^2 = H are a little lower than those of the complexes of the ligands with the stronger electron-repelling substituents $R^2 = CH_3$ or C_6H_5 (see Table 1). Hence, it can be established that the ESR parameters of the $[CuA_2]$ complexes given in Table 3 are influenced by the electronic and steric effects of the substituents R^1 and R^2, but we are unable to separate these two effects.

At higher pH the species $[CuA_2H_{-1}]^-$ is formed in most systems with a pK of ≈9.0, this pK being much smaller than those for copper(II)–aminophosphonate or –aminocarboxylate complexes ($pK_{CuA_2} \approx 12.0$).[13] With the formation of $[CuA_2H_{-1}]^-$ the ESR parameters change significantly; the average values for eight different derivatives are $g_{\|}$ = 2.268(3) and $A_{\|}$ = 168(5), which indicate a stronger metal ion–ligand interaction and a more symmetrical geometry, and are characteristic of a 2N species which the usual square-bipyramidal structure and a CuN_2O_4 chromophore. Since water molecules in the axial positions of the copper(II) co-ordination sphere are much less acidic than those in the equatorial positions, the low values of pK_{CuA_2} may suggest that OH^- displacement of the PO_2H^- group is involved in the deprotonation of the species $[CuA_2]$. In the resulting complex one of the two aminophosphinate ligands is bound in a monodentate manner to the metal ion, *via* equatorial co-ordination of the amino moiety, or in a bidentate manner *via* axial–equatorial co-ordination of the amino group and the phosphinate group, and a hydroxy ion is co-ordinated to the fourth equatorial position of the copper(II).

The group R^1 has practically no effect on the stability or the structure of the copper(II) complexes (see Tables 1 and 3) if the aliphatic side-chain is substituted with an alicyclic side-chain. The presence of an aromatic ring, however, results in a slight increase in the relative stability of both $[CuA]^+$ and $[CuA_2]$, similarly as for the aminophosphonate and aminocarboxylate complexes.[1] The slight decrease in the $\log(K_1/K_2)$ values of the aromatic derivatives may be explained by some hydrophobic interaction between the aromatic rings, which makes the co-ordination of the second ligand molecule somewhat more favoured.[14]

Complexes of $HO_2CCH_2CH(NH_2)PO(C_2H_5)OH$ *and* $HO(CH_3)OPCH_2CH(NH_2)CO_2H$.—Two phosphinic derivatives of aspartic acid were studied, in which the α-CO_2H was replaced by the $PO(C_2H_5)OH$ group or the β-CO_2H was replaced by a $PO(CH_3)OH$ group. Due to the higher acidity of the PO(R)(OH) groups ($pK \approx 1.0$), these ligands contain only two dissociable protons in the pH range studied (2.2 < pH < 10.2). A comparison of the pK values of the phosphinic and phosphonic derivatives given in Table 4 indicates that the $PO_2(R)^-/PO_3^{2-}$ substitution has practically no effect on the dissociation of the distant carboxylic group, whereas the acidity of the nearby ammonium group is increased significantly; the effect is more marked when the ammonium group is in the nearer α position.

The processes of copper(II) complexation of these potentially terdentate aminophosphinate derivatives are simple; the best fit between the experimental and the calculated titration data is obtained by the assumption of the same species as for the simple aminophosphinates (see Fig. 2). There is no possibility of the formation of protonated complexes (which is significant with the aminophosphonate complexes of aspartic acid, Asp),[2] again because of the higher acidity of the PO(R)(OH) group.

Table 4 Proton dissociation constants (pK) and copper(II) complex[a] formation constants (log β) of aspartic acid (Asp) and its phosphinic and phosphonic analogues at 25.0 ± 0.1 °C and I = 0.20 mol dm^{-3} (KCl)

	Asp[b]	α-Phosphonic acid[b]	α-Phosphonic acid	β-Phosphinic acid[b]	β-Phosphinic acid
pK_1 (NH_3^+)	9.63	10.07	8.16(1)	10.79	9.34(1)
pK_2 (α-H)	1.95	5.52	1.0	2.40	2.52(2)
pK_3 (β-H)	3.68	3.44	3.49(2)	6.07	1.0
[$CuAH_2$]	—	18.01	—	—	—
[CuAH]	12.48	14.20	—	15.51	—
[CuA]	8.80	9.34	6.53(2)	9.60	8.15(2)
[CuA_2H_2]	—	—	—	29.1	—
[CuA_2H]	—	—	—	22.4	—
[CuA_2]$^{2-}$	15.76	16.15	11.62(4)	15.49	14.47(7)
[CuA_2H_{-1}]$^{3-}$	—	—	1.68(7)	—	2.72(9)
Fitting[c]			5.51×10^{-3}		5.88×10^{-3}

[a] Charges on the complexes refer only to aminophosphinate analogues (see text). [b] See ref. 2. [c] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant.

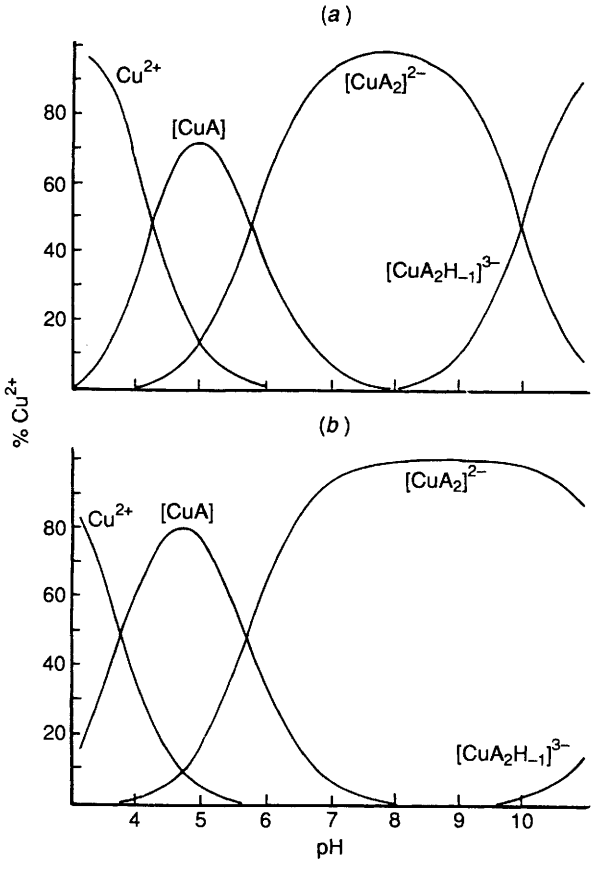

Fig. 2 Concentration distribution curves for the complexes formed in the (*a*) copper(II)–$HO_2CCH_2CH(NH_2)PO(C_2H_5)OH$ and (*b*) copper(II)–$HO(CH_3)OPCH_2CH(NH_2)CO_2H$ systems; c_{Cu} = 0.001 mol dm^{-3}, c_{ligand} = 0.004 mol dm^{-3}

The basicity-adjusted equilibrium constants of the 1:1 and 1:2 copper(II) complexes of the β-phosphinic acid derivative are very close to those of complexes of α-Ala, and much smaller than those of Asp, suggesting that the co-ordination is basically bidentate and of α-Ala type, and terdentate co-ordination of the first molecule is very limited. Only the ≈0.3 log unit difference between the log K_1 − pK_1 − pK_2 values of the β derivative and α-Ala and the somewhat less favoured co-ordination of the second ligand molecule [see the log(K_1/K_2) values in Table 5] indicate some weak involvement of the phosphinate group in the co-ordination. In a comparison of these data with those on the aminophosphonate analogue of Asp the most striking difference is that the log(K_1/K_2) value is much lower. This means that the co-ordination of the second aminophosphinate ligand is much less hindered than that of the aminophosphonate derivative. This can be explained by the lack of strong electrostatic repulsion between the PO_3^{2-} groups. The spectral parameters confirm 1N co-ordination in the complex [CuA]$^+$ and 2N co-ordination in the complex [CuA_2] in all metal–ligand systems.

The high pK value (11.75) of the complex [CuA_2]$^{2-}$ also supports the strong α-Ala type chelation of the β-phosphinic acid derivative of Asp in the equatorial plane of the copper(II) ion and the ionization of a weakly acidic axial water molecule in its deprotonation process (see Table 4 and Fig. 2).

When the phosphinic group is in the α position of Asp, comparison of the spectral parameters (see Table 5) suggests β-Ala type co-ordination with the formation of a six-membered chelate ring in the complex [CuA]$^+$. However, the greater than one order of magnitude increase in the basicity-adjusted equilibrium constant as compared with that of Cu^{II}–β-Ala indicates a more stable bonding mode, presumably the significantly terdentate binding of the α derivative. The co-ordination of the second ligand molecule is rather of aminophosphinate type than of β-Ala type. This bonding mode results in the formation of a (5 + 6)-membered chelate system, which is usually more favoured than when both chelates have the same number of ring atoms.[14] Both the larger relative stability constants (log K_2 − pK_1 − pK_2 = −6.56 for the α-derivative of Asp and −8.26 for β-Ala) and the visible spectral parameters, which are fairly similar to those of $HO_2CCH_2CH(NH_2)PO(OH)_2$, confirm this assumption. In a complex [CuA_2]$^{4-}$ of the latter ligand a mixed bonding mode of a five-membered aminophosphonate (NH_2, PO_3^{2-}) chelate and a six-membered aminocarboxylate (NH_2, CO_2^-) chelate has been suggested.[2] It is noteworthy that the similar co-ordination mode of the second α-phosphinate or -phosphonate derivative of Asp is not reflected in a similar value of the basicity-adjusted stability constant log K_2 − pK_1 − pK_2. However, this can be explained by the differences in charge of the PO_3^{2-} and the $PO_2(R)^-$ groups, which makes the co-ordination of the second aminophosphonate molecule less favoured, due to the electrostatic repulsion between the binegative PO_3^{2-} groups.

Fig. 2 clearly indicates that complex [CuA_2]$^{2-}$ of the α-phosphinic acid derivative of Asp deprotonates more readily than that of the β, again suggesting a partly aminophosphinate type co-ordination of the former ligand (*cf.* deprotonation of [CuA_2] of simple aminophosphinates).

Conclusion

The differences in basicity, charge, electron-releasing effect and size of the phosphinate, phosphonate and carboxylate groups

Table 5 Derived equilibrium constants[a] and spectral parameters[b] for copper(II) complexes of aspartic acid derivatives and other reference ligands

	Asp[c]	β-Phosphonic acid[c]	β-Phosphinic acid	α-Ala[d]	α-Phosphonic acid[d]	α-Phosphinic acid	β-Ala[d]
$\log K_1 - pK_2 - pK_1$	−2.78	−3.59	−3.71	−3.99	−6.25	−5.12	−6.65
$\log K_2 - pK_2 - pK_1$	−4.62	−7.30	−5.54	−5.34	−8.78	−6.56	−8.26
$\log(K_1/K_2)$	1.84	3.71	1.83	1.35	2.53	1.44	1.61
Visible spectra: λ_{max} (ε)							
[CuA]	700(34)	690(44)	690(46)	680(48)	690(41)	700(51)	700(50)
$[CuA_2]^{2-}$	626(53)	640(62)	630(71)	615(56)	650(59)	650(80)	638(56)
ESR soectra– $g_{\|}$, $A_{\|}$							
[CuA]	—	—	2.332, 155	2.32, 156	—	2.320, 150	2.32, 150[f]
$[CuA_2]^{2-}$	2.262, 181[e]	2.262, 170	2.263, 174	2.26, 172	2.272, 172	2.280, 156	2.28, 139[f]

[a] Charges of the complexes refer only to aminophosphinate analogues (see text). [b] The A values are in G, λ_{max} in nm, and ε in $dm^3\ mol^{-1}\ cm^{-1}$; ε values were calculated for total copper(II) concentration for the pH at which the respective species is a major complex. [c] See ref. 2. [d] See ref. 1. [e] See ref. 15. [f] See ref. 10.

result in the following differences in the complex-forming properties of simple aminocarboxylic acids and their aminophosphonous, -phosphinic and -phosphonic analogues.

(*i*) The basicity sequence $PO_3^{2-} > CO_2^- > PO_2(R)^-$ will result in the same sequence of stability of their copper(II) complexes.

(*ii*) The electrostatic and steric hindrance due to the binegative charge and the larger size of the PO_3^{2-} group will overcompensate the stability increase of the aminophosphonate complexes arising from the higher basicity of this group.

(*iii*) The basicity-adjusted stabilities of the aminocarboxylate and aminophosphinate complexes are practically the same; thus, besides the same charge, the space requirements of the two groups are also similar, even if the carboxylate is planar and the phosphinate is tetrahedral.

(*iv*) As a result of the above effects the following sequence can be derived for the metal-binding abilities of these ligands: aminocarboxylates > aminophosphonates > aminophosphinates.

(*v*) When a carboxylate and a phosphinate group are present in the same molecule (as the α- and β-phosphinic acid derivatives of Asp), the participation of the phosphinic moiety in the coordination becomes subordinate. A five-membered [NH_2, $PO_2(R)^-$] chelate, however, can be a competitor with a six-membered (NH_2, CO_2^-) chelate, which results in a mixed-type bonding mode, *e.g.* in the copper(II) complexes of the α-phosphinic acid derivative of Asp.

Acknowledgements

This work was supported by the Hungarian Academy of Sciences (Project No. 240/86) and by the Polish Ministry of National Education. The authors thank Dr. M. Soroka for the phosphinic ligands and Mrs. A. Gönczy for valuable assistance in the experimental work.

References

1 T. Kiss, J. Balla, G. Nagy, H. Kozlowski and J. Kowalik, *Inorg. Chim. Acta*, 1987, **138**, 25.
2 T. Kiss, E. Farkas and H. Kozlowski, *Inorg. Chim. Acta*, 1989, **155**, 281.
3 E. K. Baylis, C. D. Campbell and J. G. Dingwall, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2845.
4 M. Soroka and P. Mastlerz, *Rocz. Chem.*, 1976, **50**, 661; J. Oleksyszyn, J. Rachon and M. Soroka, *Chimia*, 1978, **32**, 253; B. Lejczak, P. Kafaraski, M. Soroka and P. Mastalerz, *Synthesis*, 1984, 577.
5 G. Gran, *Acta Chem. Scand.*, 1950, **29**, 599.
6 H. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475.
7 L. Zékány and I. Nagypál, in *Computational Methods for the Determination of Stability Constants*, ed. D. Leggett, Plenum, New York, 1985.
8 A. Gergely and T. Kiss, *Inorg. Chim. Acta*, 1976, **16**, 51.
9 D. D. Perrin, Boyd Dempsey and E. P. Serjeant, *pK Prediction for Organic Acids and Bases*, Chapman and Hall, London, 1981.
10 H. Yokoi, M. Sai and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2189.
11 B. Jezowska-Trzebiatowska, A. Antonow and H. Kozlowski, *Bull. Acad. Pol. Sci.*, 1974, **22**, 399.
12 R. Barbucci and M. J. M. Campbell, *Inorg. Chim. Acta*, 1976, **16**, 113.
13 R. D. Gillard, R. J. Lancashire and P. O'Brien, *Transition Met. Chem.*, 1980, **5**, 340.
14 H. Sigel, in *Coordination Chemistry-20*, ed. D. Banerjea, Pergamon, New York, 1980.
15 S. T. Show and C. A. McAuliffe, in *Prog. Inorg. Chem.*, 1975, **19**.

Received 13*th November* 1990; *Paper* 0/05102K