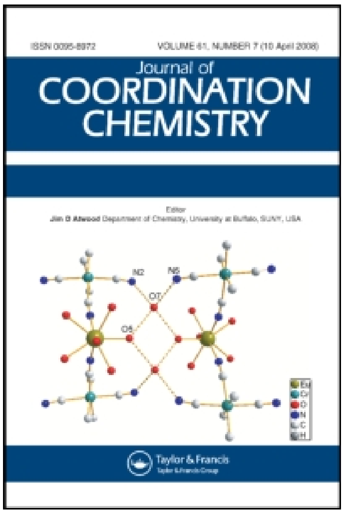


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Copper(II) Complexes of Ligands Containing Alcoholic Hydroxy Groups

Tamás Kiss[a]; Csaba Simon[b]; Zsolt Vachter[ab]
[a] Department of Inorganic and Analytical Chemistry, Lajos Kossuth University, Debrecen, Hungary [b] Alkaloida Pharmaceutical Works, Tiszavasvari, Hungary

To cite this Article Kiss, Tamás , Simon, Csaba and Vachter, Zsolt(1987) 'Copper(II) Complexes of Ligands Containing Alcoholic Hydroxy Groups', Journal of Coordination Chemistry, 16: 3, 225 — 236

To link to this Article: DOI: 10.1080/00958978708081206

URL: http://dx.doi.org/10.1080/00958978708081206

J. Coord. Chem. 1987, Vol. 16, p.225–236
Photocopying permitted by license only

COPPER(II) COMPLEXES OF LIGANDS CONTAINING ALCOHOLIC HYDROXY GROUPS

TAMÁS KISS*

Department of Inorganic and Analytical Chemistry, Lajos Kossuth University, H–4010 Debrecen, Hungary

CSABA SIMON

Alkaloida Pharmaceutical Works, H–4440 Tiszavasvári, Hungary

and ZSOLT VACHTER✣†

(Received October 14, 1986; in final form December 19, 1986)

Potentiometric and calorimetric methods were used to determine the thermodynamic parameters of formation of the copper(II) complexes of *L*-3-hydroxy-2-aminopropionic acid, *D,L*-3-amino-2-hydroxypropionic acid, *D,L*-4-amino-3-hydroxybutyric acid, 1,3-diaminopropan-2-ol and *L*-(+)-threo-2-amino-l-phenylpropane-1,3-diol at 25°C at an ionic strength $I = 0.2$ mol dm^{-3} (KCl). The thermodynamic data, together with electronic and ESR spectra and the magnetic behaviour of the complexes formed, indicated that in the monomeric complexes the deprotonation and coordination of the alcoholic hydroxy group occurs only at high pH. However, if the alcoholic hydroxy group is adjacent on both sides to further donor groups that are able to form strong coordinate bonds, then its metal ion induced deprotonation becomes more favoured and polynuclear alkoxo-bridged complexes are formed even at pH ~ 5.

INTRODUCTION

Interest is currently focussed on the coordination chemistry of transition metal ions and ligands containing alcoholic hydroxy groups. Metal complexes formed through participation of the alcoholic hydroxy group may play important roles in living organism. For instance, it is probable that in certain copper proteins of type 3, containing spin-paired Cu(II)–Cu(II) pairs that are not detectable by ESR, the active sites are formed by alkoxo-bridged dimeric units.[1]

In aqueous medium α-amino acids containing a terminal hydroxy group, such as serine or threonine, undergo deprotonation of the weakly acidic OH group and interact directly with copper(II) ion only at high pH, though it may be presumed that the protonated OH group can also be coordinated to the metal ion at lower pH.[2–6] In ligands where the alcoholic hydroxy group is adjacent on both sides to donor groups able to form strong coordinate bonds, the metal ion induced deprotonation of the OH group is more favoured; there is then a possibility for the formation of O^--bridged polynuclear species at lower pH. This bonding mode even at around pH 5–6 has been demonstrated in the interactions of the copper(II) ion with various ligands containing an ethanolamine function such as $H_2N\text{-}CH_2\text{-}CH(OH)\text{-}X$ (where $X = CH_2COOH$,[7] COOH,[8] CH_2NH_2[9–11] or $CH_2CH_2NH_2$[12,13]).

---

*To whom correspondence should be directed. †Deceased.

Kida *et al.*,[14,15] have studied the possibility of the formation of binuclear copper(II) complexes with a very large number of aminoalcohols and diaminoalcohols. From magnetic and spectral measurements of the complexes, which were also prepared in the solid state, they established that a considerable proportion of them contain antiferromagnetically coupled copper(II) pairs, and show a characteristic charge-transfer band in the near UV. In aqueous solution, however, complexes connected through terminal alkoxo oxygen as bridging donor atom were hydrolysed to monomeric units.

In the present work we have investigated the complex-forming properties of certain ligands with proton and with the copper(II) ion; these ligands contain an alcoholic hydroxy group in various positions: *L*-3-hydroxy-2-aminopropionic acid (serine, ser), *D,L*-3-amino-2-hydroxypropionic acid (isoserine, ise), *D,L*-4-amino-3-hydroxybutyric acid (ahba), 1,3-diaminopropan-2-ol (dpol) and *L*-(+)-threo-2-amino-l-phenyl-propane-1,3-diol (phenylserinol, pse). The stoichiometric compositions and the thermodynamic data of the complexes formed were determined by means of calorimetric and pH-potentiometric measurements in the pH range 3–11. Spectral (UV, visible and ESR) and magnetic measurements were also performed to establish the bonding mode in the complexes and to study dimer formation.

EXPERIMENTAL

The ligands used were Fluka or Sigma products of *puriss.* quality. The exact concentrations of the solutions prepared from them were measured by the method of Gran[16].

The stability constants of the proton and the copper(II) complexes of the ligands were determined by pH-metric titration on 25 cm^3 samples. The concentration of the ligands in the samples was 6×10^{-3} or 4×10^{-3} mol dm^{-3}. In all solutions, the ionic strength was adjusted to 0.2 mol dm^{-3} with KCl. Titrations were carried out in the pH interval 3–11 with KOH solution of known concentration ($\sim$0.2 mol dm^{-3}).

The enthalpy changes accompanying the complex-formation processes were determined calorimetrically under similar experimental conditions, by means of a continuous titration technique.[17]

pH was measured on a Radiometer PHM 64 instrument, with G202 B glass and K 104 calomel electrodes. The electrode system was calibrated by the method of Irving *et al.*[18] so as to convert the pH-meter readings to hydrogen ion concentrations. The calorimetric measurements were made on an LKB-8700 reaction and solution calorimeter. The temperature was in all cases 25.0 ± 0.1°C.

TABLE I
Thermodynamic data for the dissociation of the ligands at 25°C and I = 0.2 mol dm^{-3} (KCl).[†]

Ligand		pK	ΔG (kJ/mol)	ΔH (kJ/mol)	-ΔS (J/mol K)
Ser	COOH	2.13	12.16	1.9	34.3
	NH_3^+	9.04	51.59	43.6	26.9
Ise	COOH	2.67	15.24	4.2	36.9
	NH_3^+	9.12	52.05	44.2	26.2
Ahba	COOH	3.96	22.60	4.6	60.4
	NH_3^+	9.44	53.87	47.9	20.0
Dpol	NH_3^+	8.05	45.94	48.7	−9.4
	NH_3^+	9.54	54.44	49.3	17.3
Pse	NH_3^+	8.47	48.34	47.9	1.6

[†] Uncertainty in pK ± 0.02, in ΔH ± 0.3 kJ mol^{-1} and in ΔS ± 0.5 J K^{-1} mol^{-1}.

A Beckman ACTA MIV double-beam recording spectrophotometer was used for spectrophotometric measurements in the visible and UV range.

ESR spectral measurements were made on solutions at room temperature or on solutions frozen to the temperature of liquid nitrogen, as described previously.[19] These studies were performed on a JEOL JES-ME-3F spectrometer.

Magnetic moments were measured on a Bruker WP 200 SY NMR spectrometer by the method of Löliger and Scheffold.[20]

The enthalpy changes and the stability constants of the complexes were calculated with the PSEQUAD computer program.[211]

RESULTS AND DISCUSSION

The pH-metrically and calorimetrically determined thermodynamic data on the ligands are presented in Table I.

Since the alcoholic hydroxy groups are very weakly acidic in nature, their dissociation was studied at high ligand concentration (0.1 mol dm^{-3}) up to high pH (~ 13.4). It was found that the ligand titration curves run together with the titration curve for the strong acid of the same concentration. Accordingly, the alcoholic hydroxy groups do not undergo dissociation in the measurable pH range; this is in contrast with certain literature data, which suggest that these processes are characterized by pK values of around 12–13.[6–8]

If the thermodynamic quantities in Table I are compared with the data for the corresponding reference compounds not containing alcoholic hydroxy groups, it may be stated that these vary in accordance with the slight electron-attracting effect of the alcoholic hydroxy group.

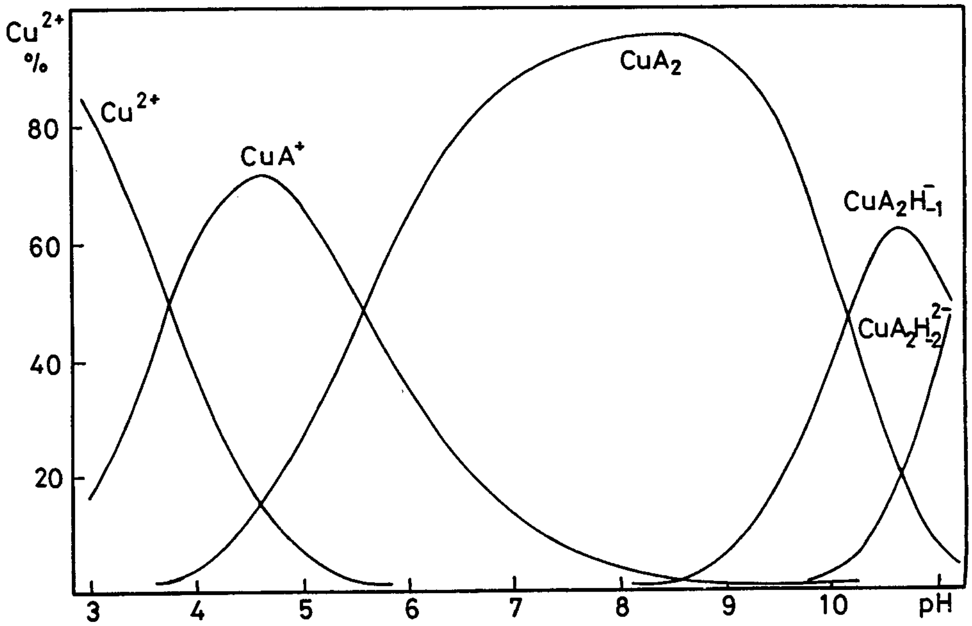


FIGURE 1 Concentration distribution curves of the complexes formed in the Cu(II)-ser system as a function of pH. $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}, $C_{lig} = 4 \times 10^{-3}$ mol dm^{-3}.

Table II

Thermodynamic data for the copper(II) complexes of the ligands at 25°C and $I = 0.2$ mol dm^{-3} (KCl); $\beta_{pqr} = [Cu_pA_qH_r]/[Cu]^p[A]^q[H]^r$.

Ligand		log β_{pqr}	-ΔG (kJ/mol)	-ΔH (kJ/mol)	ΔS (J/mol K)
Ser	CuA	7.81	44.58	22.6	74
	CuA_2	14.24	81.28	52.1	98
	CuA_2H_{-1}	4.09	23.35	19.7	12
	CuA_2H_{-2}	−7.06	−40.30	0.6	−137
Ise	CuAH	10.92	62.34	46.6	53
	CuA	6.42	36.65	23.1	45
	$Cu_2A_2H_{-2}$	8.13	46.41	23.8	76
	CuA_2H_{-2}	−6.50	−37.10	−1.3	−129
Ahba	CuA	5.88	33.56	23.5	34
	$Cu_2A_2H_{-2}$	3.01	17.18	−4.8	74
	CuA_2H_{-2}	−7.29	−41.61	−2.3	−132
Dpol	CuA	8.37	47.78	50.2	−8
	CuA_2	14.77	84.31		
	$Cu_2A_2H_{-2}$	10.25	58.51	55.3	11
Pse	CuA_2H_{-2}	−5.45	−31.11		
	CuA	4.61	26.31	24.2	7
	$CuAH_{-1}$	−1.71	−9.76	−7.8	−6
	$CuAH_{-2}$	−9.53	−54.40	−39.6	−50
	CuA_2H_{-1}	2.06	11.76	25.1	−45
	CuA_2H_{-2}	−5.78	−32.99	−2.9	−101
	CuA_2H_{-3}	−17.50	−99.89	−37.5	−209

$^+$Uncertainty in log $\beta \pm 0.04$, in ΔH ± 0.5 kJ mol^{-1} and in ΔS ± 1 J K^{-1} mol^{-1}.

The pH-metrically and calorimetrically determined thermodynamic data relating to the formation of the copper(II) complexes of the above five ligands are listed in Table II. If consideration is paid to the differing ionic strengths, and in some cases to the incorrectly determined dissociation constants for the alcoholic hydroxy groups, the tabulated stability constants in general display satisfactory agreement with the previously reported literature results.[5–8,10,11] We shall return to the more appreciable differences in our discussion of the assumed bonding modes in the various species.

Figures 1-5 depict the pH-dependence of the concentration distribution of the species formed in the various copper(II) - ligand systems, at 1:2 metal ion/ligand ratio.

To clarify the bonding modes of the complexes formed in the metal - ligand systems, electronic and ESR spectral and magnetic measurements were performed. The results of these are to be seen in Table III.

For purposes of illustration, Fig. 6 presents ESR spectra recorded on frozen solutions at 77 K for the copper(II) - ise system at various pH values.

1:1 Complexes

The species [CuAH] is formed only with isoserine as ligand; it follows from its stoichiometric composition that it contains a protonted amino group and copper(II) coordinated through the carboxylate and alcoholic hydroxy groups. This is supported by the fact that its formational enthalpy change is approximately the same as the protonation heat of the amino group (see Table I); on the basis of the nearly zero enthalpy changes of the copper(II)-carboxylate and copper(II)-alcoholic hydroxy group bonds, this is in accordance with expectations.

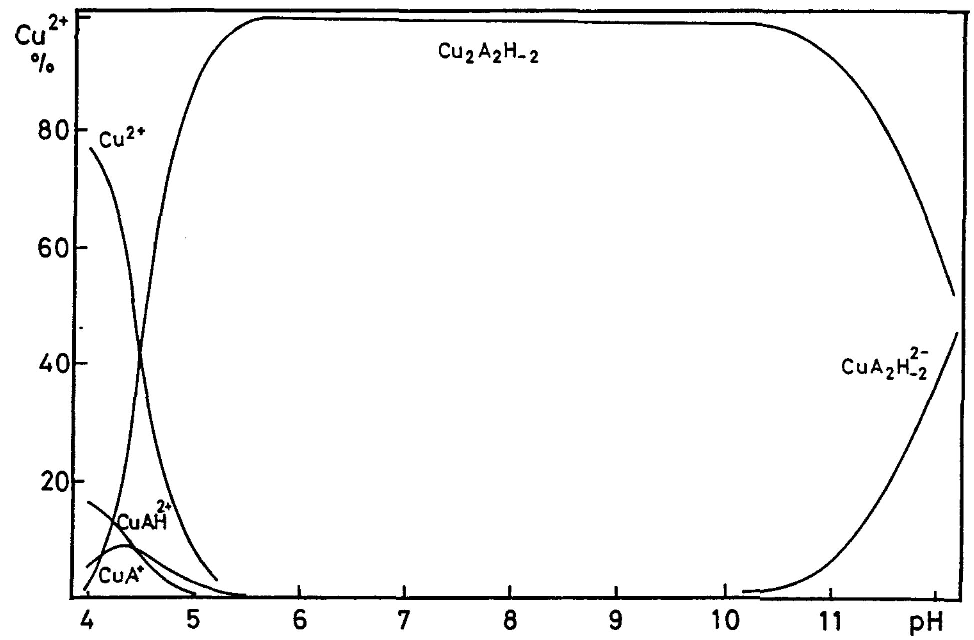


FIGURE 2 Concentration distribution curves of the complexes formed in the Cu(II)-ise system as a function of pH. $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}, $C_{lig} = 4 \times 10^{-3}$ mol dm^{-3}.

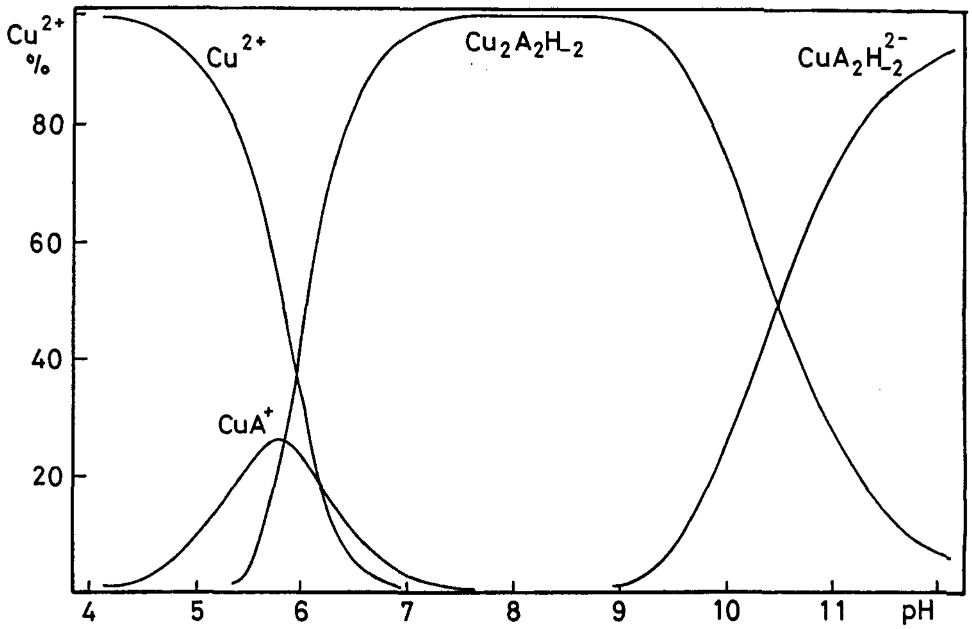


FIGURE 3 Concentration distribution curves of the complexes formed in the Cu(II)-ahba system as a function of pH. $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}, $C_{lig} = 4 \times 10^{-3}$ mol dm^{-3}.

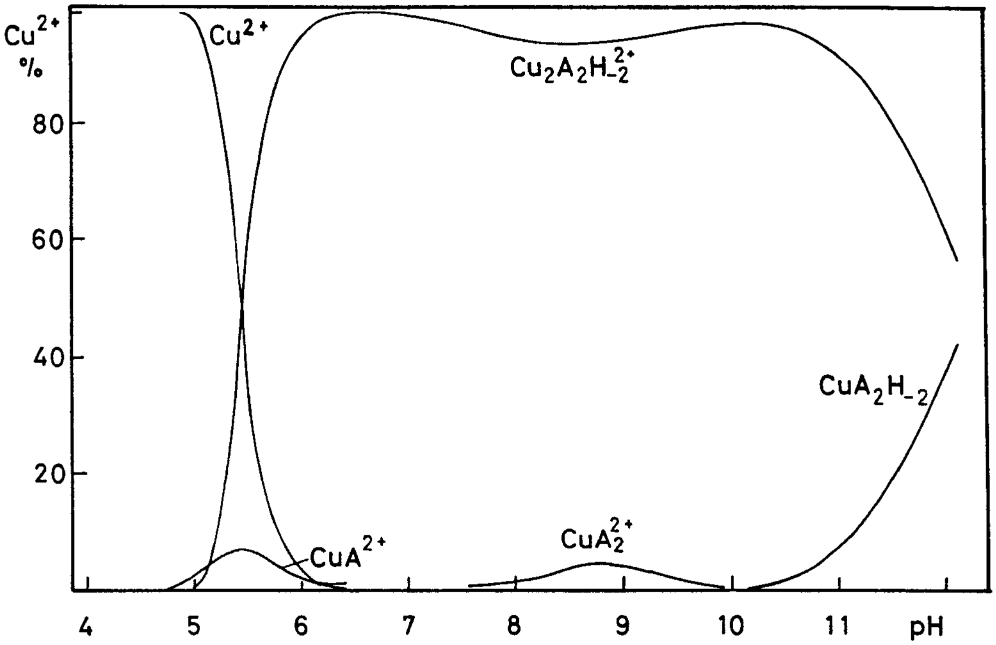


FIGURE 4 Concentration distribution curves of the complexes formed in the Cu(II)-dpol system as a function of pH. $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}, $C_{lig} = 4 \times 10^{-3}$ mol dm^{-3}.

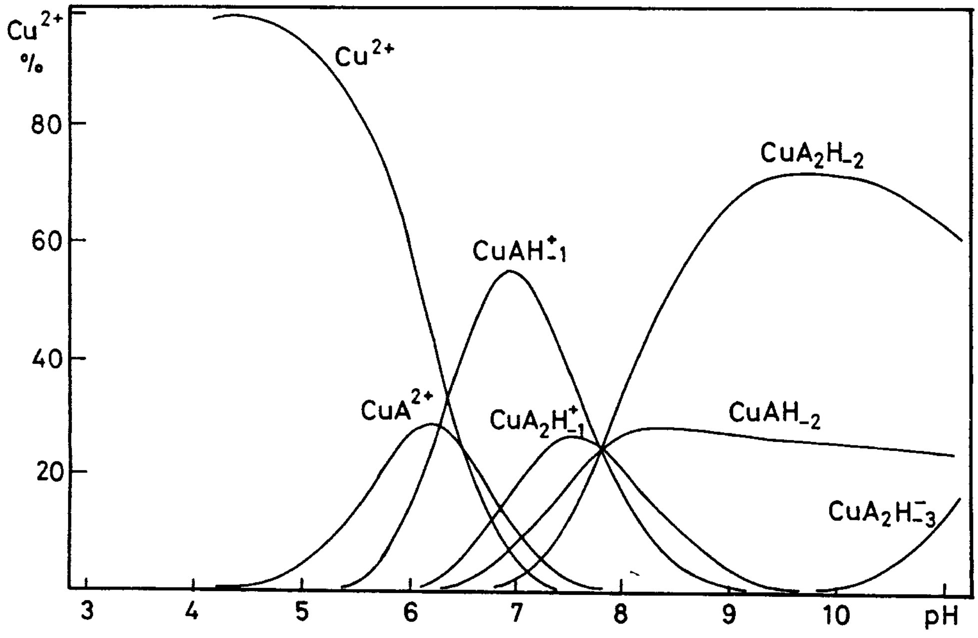


FIGURE 5 Concentration distribution curves of the complexes formed in the Cu(II)-pse system as a function of pH. $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}, $C_{lig} = 4 \times 10^{-3}$ mol dm^{-3}.

TABLE III
Spectral and magnetic data for the copper(II) complexes†.

		pH	λ_{max}	ε	$g_{\|}$	$A_{\|}$	$g_{\perp}$	$A_{\perp}$	μ
Cu(II)-Ser:OH	1:2:2	6.3	620	66	2.274	177	2.064	29	1.76
	1:2:4	11.1	608	40	2.241	190	2.049	35	
	1:2:20	12.8	595	36	2.241	190	2.049	35	
Cu(II):Ise:OH	1:1:2	7.0	650	48	No ESR signal				0.86
			250	2400					
			218	3300					
	1:2:2	6.0	650	48	No ESR signal				
	1:2:4	11.4	650	47	No ESR signal				
	1:2:20	13.2	600	37	2.240	188	2.050	34	
Cu(II):Ahba:OH	1:1:2	7.2	650	67	No ESR signal				0.95
			250	3100					
			230	3100					
	1:2:2	7.8	650	67	No ESR signal				
	1:2:4	11.4	625	41	2.238	188	2.047	35	
	1:2:20	13.2	595	38	2.238	188	2.047	35	
Cu(II):Dpol:OH	1:1:1	7.2	615	80	No ESR signal				0.96
			250	2800					
			220	2800					
	1:2:2	8.4	615	80	2.215	189	2.053	42	
	1:2:4	10.4	615	80	2.224	193	2.051	39	
	1:2:20	12.8	595	40	2.232	191	2.050	36	
Cu(II):Pse:OH	1:2:2	8.8	590	48	2.240	189	2.052	35	1.78
	1:2:4	11.4	590	45	2.240	189	2.052	35	
	1:2:20	13.1	590	42	2.236	187	2.049	35	
Cu(II):Tmen:OH	1:1:1	9.2	650	75	2.250	176	2.052	30	1.40
			355^{sh}	210					
			265	4300					
Cu(II):Etol:OH	1:2:20	13.0	585	70	2.240	189	2.050	35	

†The A values are given in G (10^{-4} T), λ_{max} in nm, ε in M^{-1} cm^{-1} and μ in B.M.; sh = shoulder.

The species [CuA] is present in each system examined in the initial pH interval of complex formation. For serine, the bonding mode can clearly only be of the glycine type. Ahba and pse are coordinated *via* the amino and the alcoholic hydroxy groups, as indicated by the fact that the stability data for the process $Cu^{2+} + HA \rightleftharpoons CuA^{+} + H^{+}$ (-3.56 and -3.86, respectively) agree well with the corresponding value of log K = -3.77 for the ethanolamine. The equivalent constant for ise is -2.70, which is closer to the value of the log K = -3.23 for β-alanine; in this case, therefore, it may be suspected that the bonding mode is rather of the β-alanine type. For the propanediamine derivative dpol, the equilibrium contant for the process $Cu^{2+} + H_2A^{2+} \rightleftharpoons CuA^{2+} + 2\ H^{+}$ is log K = -9.22; the equivalent value for the complex of 1,3-propanediamine is -9.72, which suggest (N,N) coordination in the present case. In the cases of ise and dpol, however, there is a relative stability increase of about 0.5 log unit in comparison with the appropriate reference compounds, which may be indicative of a certain degree of coordination of the alcoholic hydroxy group, in addition to the bonding mode already mentioned.

The complexes $[CuAH_{-1}]$ and $[CuAH_{-2}]$ are formed in the copper(II) - pse system, through stepwise deprotonation of the (N,OH)-bonded complex CuA. The deprotonation constants are $pK_{CuA}^{CuAH_{-1}} = 6.32$ $pK_{CuAH_{-1}}^{CuAH_{-2}} = 7.82$. The release of these two protons can presumably be ascribed to the overlapping processes of deprotonation of the water molecule coordinated to the metal ion and of one of the alcoholic hydroxy groups of the ligand.

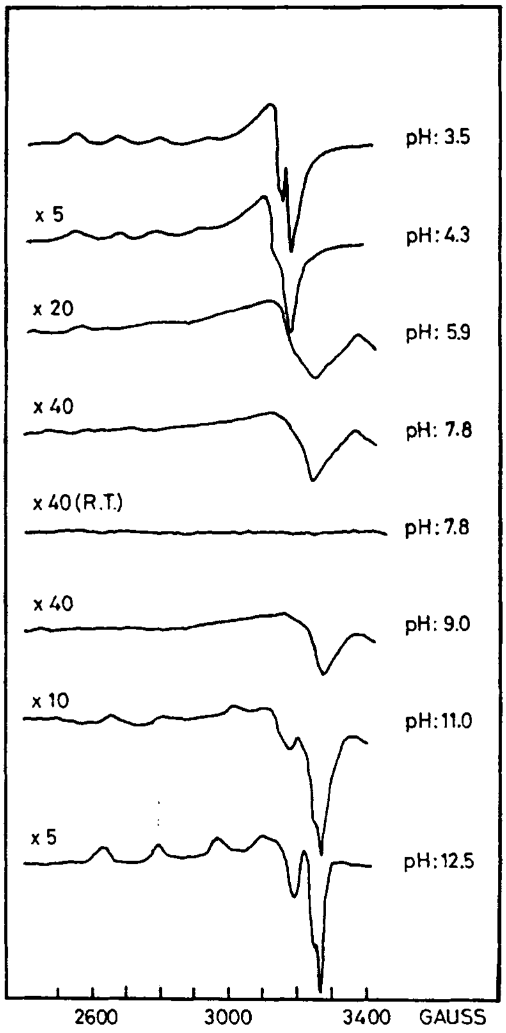
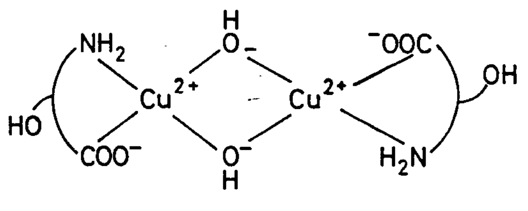


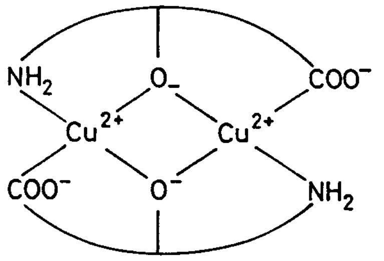
FIGURE 6 ESR spectra of the Cu(II)-ise system at 1:1 metal ion/ligand ratio and 77K.

It may be seen in Figures 2–4 that, for those ligands in which the alcoholic hydroxy group is adjacent on both sides to donor groups able to coordinate relatively strongly to copper(II), over a wide interval of pH the only species formed is the dimer $[Cu_2A_2H_{-2}]$. In the case of ahba, Braibanti *et al.*[8] assumed a dimer-monomer equilibrium on the basis of the equilibrium measurements. At Cu(II) concentrations in the interval 2×10^{-3} - 2×10^{-2} mol dm^{-3}, in the pH range of formation of the dimeric species, we found that the absorbance at 650 nm (characteristic of the d-d transition) obeyed the Beer-Lambert law, which strongly suggests that a dimer-monomer equilibrium can be excluded.

The data in Figure 6 and Table II reveal that the dimeric species $[Cu_2A_2H_{-2}]$ formed in the systems of copper(II) with ise, ahba or dpol has an anomalously low magnetic moment ($\mu = 0.86$, 0.95 and 0.96 B.M., respectively) and is ESR-inactive; this points to an antiferromagnetic spin-spin exchange interaction between the copper(II) ions. This feature and the stoichiometry of the species may possibly be explained by the two types of bonding mode, hydroxo bridging or alkoxo bridging, to be seen in Scheme 1.



(I)



(II)

There is evidence against the hydroxo-bridged structure; in the 1:1 system of copper(II) with β-alanine, γ-aminobutyric acid and 1,3-propanediamine, which have analogous structures to those of the ligands studied in the present work, but which do not contain an alcoholic hydroxy group, the formation of hydroxo-bridged dimer is insignificant, for at pH > 7 hydrolysis occurs to the accompaniment of precipitation. In the systems we have investigated here, no precipitate appears. The dimeric species is formed exclusively in a wide pH range (see Figures 2–4); this can only be attributed to the role of the alcoholic hydroxy groups. However, the *N*-substituted derivatives of ethylenediamine, which co-ordinate as five-membered chelates, tend to form hydroxo-bridged dimers.[22–24] The thermodynamic quantities relating to their formation are to be found in Table IV, together with the data calculated for the complexes $[Cu_2A_2H_{-2}]$ for the ligands we have studied, with the assumption of the hydroxo-bridged structure.

The data in Table IV reveal that the complexes of ise, ahba and dpol are about 3.5–6 orders of magnitude more stable than the definitely hydroxo-bridged complexes of the ethylenediamine derivatives. Further evidence against the hydroxo-bridged structure is the fact that the magnetic and ESR properties of the complex $[Cu_2tmen_2(OH)_2]$ differ from those of the species of type $[Cu_2A_2H_{-2}]$ for the other ligands (see Table 3).

It is difficult to interpret the visible and UV spectral properties of the complexes. Kida *et al.*, [25] assume that the charge-transfer band in the region 350–400 nm is a

TABLE IV

Thermodynamic data for olation reactions, $2\,CuA + 2OH^- \rightleftharpoons Cu_2A_2(OH)_2$, of the CuA complexes.

	log K_0	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Dmen†	15.02	85.73	46.9	130
Admn†	15.42	87.99	46.9	138
Tmen†	15.25	87.07	39.3	160
Dpol	21.02	119.98	68.3	173
Ise	22.80	130.14	91.1	131
Ahba	18.76	107.08	61.7	152

Dmen: *N,N'*-dimethylethylenediamine, Admn: *N,N*-dimethylethylene diamine, Tmen: *N,N,N',N'*-tetramethylethylenediamine; †See Ref 23.

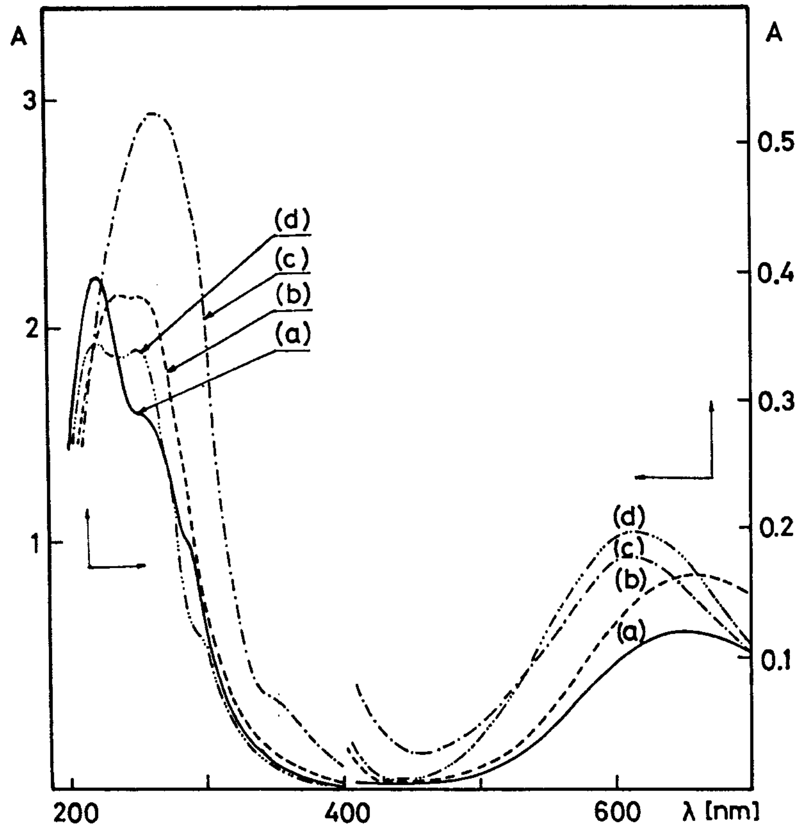


FIGURE 7 Electronic spectra of Cu(II)-binary systems at 1:2 metal ion/ligand ratio. (a) Cu(II)-ise, pH:6.3; (b) Cu(II)-ahba, pH:7.2; (c) Cu(II)-tmen, pH:9.2; (d) Cu(II)-dpol, pH:7.2.

characteristic feature of the dialkoxo- or the dihydroxo-bridged dimeric structure; it is an undisputed fact that a very large number of dimers of this type exhibit such a band. It is clear from Figure 7 and Table III that none of the complexes we have examined displays this spectral feature; there is merely a shoulder at 355 nm ($\varepsilon = 210$ M^{-1} cm^{-1}) in the spectrum of the species [$Cu_2tmen_2(OH)_2$]. At the same time, it is noteworthy that alkoxo-bridged dimers that are stable even in aqueous solution have been prepared from the ligands 1,5-diamino-3-pentanol (dpl) and 1,4-diamino-2-butanol (dbl).[12,13] These complexes differ from the dimeric complex of dpol that we have examined only insofar as the latter contains 5,5-membered chelate rings instead of 6,6- or 5,5-membered rings. However, it could be observed that the intensity of the charge-transfer band assigned to the copper(II) ← 0^- transition decreased considerably with the decrease of the number of atoms in the chelate ring; $\varepsilon = 1300$ at 352 nm for dpl, and $\varepsilon = 239$ at 357 nm for dbl (ε/M^{-1} cm^{-1}). Hence, it can not be excluded that, with the decrease of the number of ring atoms, a change occurs in the coordination sphere, such that the intensity of the charge-transfer band for dpol further decreases and it merges into the high-intensity ($\varepsilon > 2500$M^{-1}cm^{-1}) copper(II)-*N* charge transfer band at 250 nm. Our results appear to strengthen the view of Waters *et al.*,[26] that the assessment of this band as an unambiguous indicator of spin-pairing is not necessarily correct.

It is also worth of note that Näsänen *et al.*[10] made an X-ray diffraction study of the solid dpol complex [$Cu_2A_2H_{-2}$] and concluded that this probably has the alkoxo-bridged structure, though their paper does not include a detailed discussion of the results or the proof of the structure.

Although our overall results, obtained with the various methods, do not completely prove the alkoxo-bridged structure of the dimer formed in the systems under investigation, they do suggest this. It appears that detailed X-ray diffraction studies should be performed for an adequate clarification of the structure.

1:2 Complexes

With ser, the species $[CuA_2H_{-1}]$ and $[CuA_2H_{-2}]$ are formed through stepwise deprotonation (starting above pH ~ 9) of the complex $[CuA_2]$, which involves bonding of glycine type. As shown by the data in Table III, this process is accompanied by a characteristic shift of the d-d band towards lower wavelengths. Although the results to date[2–5,27] are partly contradictory, the appreciable shift of the d-d transition towards higher energies strongly suggests the deprotonation of at least one of the alcoholic hydroxy groups and its coordination to the copper(II) ion.

With pse as the ligand, the species $[CuA_2H_{-1}]$, $[CuA_2H_{-2}]$ and $[CuA_2H_{-3}]$ are formed; the corresponding pK values are 7.84 and 11.72. The spectral change observed is similar to that in the case of ser (see Table III). For the formation processes $[CuAH_{-1}]^+ + A \rightleftharpoons [CuA_2H_{-1}]^+$ and $[CuAH_{-2}] + A \rightleftharpoons [CuA_2H_{-2}]$, the equilibrium constants are log K = 3.77 and 3.75, respectively; on this basis, the coordination of the second ligand may be conceived as involving the same (N,OH) bonding mode as in [CuA] ($\log \beta_{CuA} = 4.61$; the second ligand is generally bound with lower stability). The enthalpy changes, however, are $\Delta H = -32.9$ and -36.7 kJ mol^{-1}, respectively, which are much more exothermic than in the formation of [CuA]; accordingly, it is not possible to exclude the partial deprotonation of the alcoholic hydroxy group and the development of (N,O^-) bonding. With the formation of the species $[CuA_2H_{-2}]$, neither the visible nor the ESR spectral parameters display any additional change in response to further elevation of the pH. Thus, the deprotonation of the second alcoholic hydroxy group of pse can be excluded, *i.e.*, formation of the species $(CuA_2H_{-3}]$ can presumably be attributed to the ionization of a coordinated water molecule.

In systems of copper(II) with ise, ahba and dpol, the complex $[CuA_2H_{-2}]$ is formed through decomposition of the dimeric species at high pH. At a ligand excess in the copper(II) - dpol system, the complex containing four nitrogen atoms in the equatorial plane, $[CuA_2]$, is also present; its concentration is not very high (5-10%), but it can be demonstration quite unambiguously by pH-metric and ESR spectral means. The thermodynamic data and the spectral and ESR parameters for the complexes $[CuA_2H_{-2}]$ agree well with each other and with the corresponding data on the complexes of ser, pse and ethanolamine (see Table III). Thus, for all of the species the bonding mode in the equatorial plane is of ethanolamine type, *i.e.* (N,O) (N,O) or (N,O) (N,OH), while an OH^-, H_2O or COO^- interaction may be assumed at the axial positions.

Our results show that the deprotonation of the alcoholic hydroxy group induced by copper(II) ion and its coordination in the form of monomeric complexes is hindered and occurs only above pH ~ 9. It is conceivable that in the 1:2 complexes, even at pH ~ 12, only one of these groups is deprotonated, while the other is bound in a protonated form to the metal ion. If the alcoholic hydroxy group is adjacent on both sides to further donor groups, able to form strong coordinate bonds, deprotonation of the alcoholic hydroxy group becomes more favoured and can occur at as low as pH ~ 5, polynuclear alkoxo-bridged complexes being formed. Accordingly, there is a possibility for amino acid side-chains containing alcoholic hydroxy groups to feature as metal ion binding sites in certain copper(II) proteins.

REFERENCES

1. E.I. Solomon, in "Copper Proteins", Chapter 2, Ed. T.G. Spiro, Wiley, New York, 1981.
2. J.E. Letter and J.E. Bauman, *J. Amer. Chem. Soc.*, **92,** 437 (1970).
3. A. Rossi, M. Ptak, P. Grenovillet and R.P. Martin, *J. Chim. Phys.*, **71,** 1371 (1974).
4. L.D. Pettit and J.L.M. Swash, *J. Chem. Soc. Dalton Trans.*, 2416, (1976).
5. A. Gergely, J. Mojzes and Zs. Kassai-Bazsa, *J. Inorg. Nucl. Chem.*, **34,** 1277 (1972).
6. A. Braibanti, F. Dallavalle, E. Leporati and G. Mori, *Inorg. Chim. Acta*, **5,** 449 (1971).
7. A. Braibanti, G. Mori, F. Dallavalle and E. Leporati, *J. Chem. Soc. Dalton Trans.*, 1319 (1975).
8. A. Braibanti, G. Mori and F. Dallavalle, *J. Chem. Soc. Dalton Trans.*, 826 (1976).
9. E. Mario and S.M. Bolton, *Anal. Chem.*, **37,** 165 (1965).
10. R. Näsänen, P. Tilus, H. Järvinen and I. Kowri, *Suomen Kemistilehti*, **B43,** 154 (1970); L. Lemmetti, R. Näsänen, A. Kainlauri, R. Kikeväs and K. Saastamoinen, *ibid.* **B43,** 259 (1970), R. Näsänen, L. Lemmetti and K. Saramäki, *ibid.* **B43,** 486 (1970).
11. P.O. Lumne, P. Tilus and M. Orama, *Finn. Chem. Lett.*, 11, (1981).
12. I. Murase, M. Hatano, M. Tanaka, S. Ueno, H. Okava and S. Kida, *Bull. Chem. Soc. Japan*, **55,** 2404 (1982).
13. I. Murase, S. Ueno and S. Kida, *Inorg. Chim. Acta*, **87,** 155 (1984).
14. M. Mikuriya, T. Harada, H. Okawa and S. Kida, *Inorg. Chim. Acta*, **75,** 1 (1983), and references therein.
15. Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem.*, **38,** 451 (1976), and references therein.
16. G. Gran, *Acta Chem. Scand.*, **4,** 599 (1950).
17. A. Gergely and I. Sóvágó, *J. Inorg. Nucl. Chem.*, **35,** 4355 (1973).
18. H. Irving, M.G. Miles and L.D. Pettit: *Anal. Chim. Acta*, **38,** 475 (1967).
19. A. Gergely and T. Kiss, *Inorg. Chim. Acta*, **16,** 51 (1976).
20. J. Löliger and R. Scheffold, *J. Chem. Educ.*, **49,** 646 (1972).
21. L. Zékány and I. Nagypál, in "Computational Methods for the Determination of Stability Constants", Plenum Press, New York, 1985.
22. E. Arenase, P. Paoletti, A. Dei and A. Vacca, *J. Chem. Soc. Dalton Trans.*, 736 (1972).
23. R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc. Dalton Trans.*, 740 (1972).
24. C. Arcus, K.P. Fivizzani and S.F. Pavkovicz, *J. Inorg. Nucl. Chem.*, **39,** 285 (1977).
25. S. Kida, Y. Nishida and M. Sakamoto, *Bull. Chem. Soc. Japan*, **46,** 2428 (1973).
26. N.F. Curtis, G.R. Clark, B.W. Skelton and T.N. Waters, *J. Chem. Soc. Dalton Trans.*, 1051 (1977).
27. I. Nagypál, E. Farkas and A. Gergely, *J. Inorg. Nucl. Chem.*, **37,** 2145 (1975).