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Equilibrium and Structural Studies on Metal Complexes of Oxime Ligands. Polynuclear Complex Formation of Copper(II) with 3-Aminopropanamidoxime and its *N*-Alkyl Derivatives

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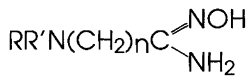
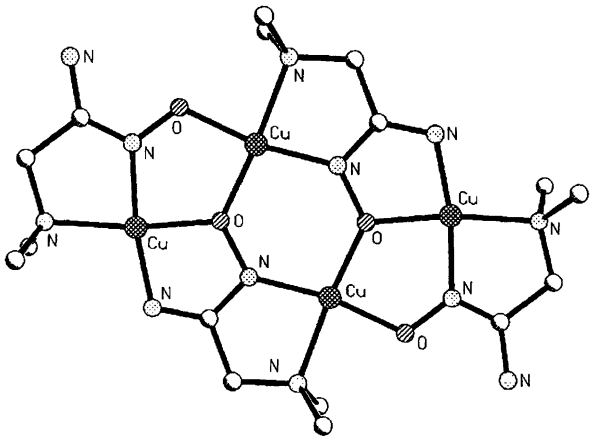
The complex formation equilibria of copper(II) with 3-aminopropanamidoxime (HL = **1**), 3-(methylamino)propanamidoxime (HL = **2**) and 3-(diethylamino)-propanamidoxime (HL = **3**) were studied in aqueous 0.1 M NaCl at 25 °C by a potentiometric method. Experimental data were analyzed with respect to the possible complexes and their stability constants, using the least-squares computer program SUPERQUAD. With all three ligands the best model was that including the mononuclear complexes $Cu(HL)^{2+}$ and $Cu(H_2L)^{3+}$ and the pentanuclear species $H_{-7}Cu_5(HL)_4^{3+}$ and $H_{-8}Cu_5(HL)_4^{2+}$. In addition, a mononuclear bis complex $Cu(HL)_2^{2+}$ was found for ligands **1** and **2** and a tetranuclear species $H_{-6}Cu_4(HL)_4^{2+}$ for ligand **2**. The crystal structure was determined by X-ray diffraction methods for the solid complex $H_{-8}Cu_5(HL)_4Br_2 \cdot 2H_2O$ (HL = **2**) isolated from the equilibrium solution. The compound crystallizes in the monoclinic space group $P2_1/c$ with the following cell parameters: $a = 10.880(5)$, $b = 5.930(3)$, $c = 23.836(11)$ Å, $\beta = 100.06(4)°$, and $Z = 2$. The structure consists of nearly planar divalent $[Cu_5(L-H)_4]^{2+}$ complex moieties, bromide ions, and water of hydration. From a comparison of the compositions of the polynuclear complex in the aqueous and solid phases it was concluded that deprotonation of the aqueous complexes starts from the coordinated oxime and amide groups and that the formulas $H_{-8}Cu_5(HL)_4^{2+}$ and $H_{-6}Cu_4(HL)_4^{2+}$ should be written as $[Cu_5(L-H)_4]^{2+}$ and $[Cu_4(L-H)_2L_2]^{2+}$, respectively.

In aqueous solution, complexation between copper(II) and aminoamidoximes of the type shown in Scheme 1



(= HL, $n = 1,2$) may give rise to various polynuclear complexes. When $n = 1$ and the ligand contains a dialkylated amino group (R = R′ = CH_3 and C_2H_5), the complex formation is dominated by the tetranuclear species $Cu_4L_2(L-H)_2^{2+}$ in which all four oxime NOH groups and two of the four amide NH_2 groups are deprotonated.[1,2] An unusual feature of this tetramer, confirmed in the solid state, is that the four copper(II) atoms are nearly coplanar instead of having their usual cubane-like or step-like configuration (Scheme 2).



With $n = 1$ the tetranuclear structure of the complexes seems to be connected with the presence of tertiary amino function, since in the case of ligands containing primary and secondary amino groups ($n = 1$, R = H, R′ = H, CH_3)

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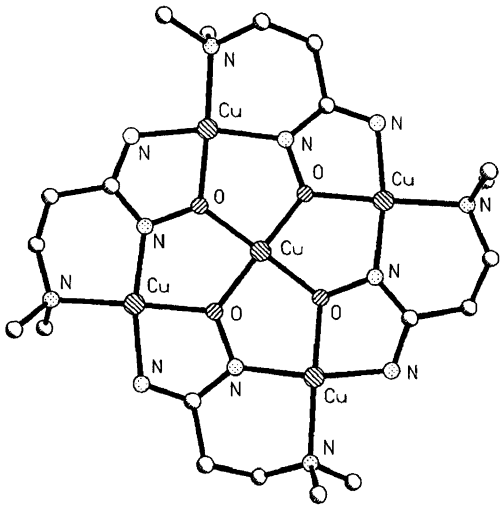
no polymerization reactions occur and only mononuclear species are formed.[1]

Evidently, too, the number of atoms in the chelate ring affects the mode of complexation: lengthening of the carbon chain from $n = 1$ to 2 ($R = R' = CH_3$) results in a series of complexes in which the main polynuclear species has the pentanuclear structure $Cu_5(L-H)_4^{2+}$.[3] The notation used indicates that all oxime NOH protons and one proton from each of the amide NH_2 groups have been displaced on coordination. In the solid state this complex moiety has been verified by X-ray structure determination of $Cu_5(L-H)_4Br_2 \cdot 8H_2O$ ($R = R' = CH_3$), which further revealed a circular copper(II)-centered body in which all five copper atoms are bound together by strong oxime NO bridges. Altogether eight five-membered and four six-membered chelate rings are formed around coplanar copper atoms (Scheme 3).



The planarity of the structure makes these tetra- and pentanuclear chelates important model compounds in the study of magnetic and redox interactions between copper atoms. So far, however, investigations with $n = 2$ have been limited to a dialkylated derivative ($R = R' = CH_3$), and the role of the 3-amino group in the formation and structure of the complexes is uncertain. To clarify the effect of the 3-amino group we now extend our study to three new ligands of the series $n = 2$, each containing a different type of amino function. The aqueous complex formation equilibria of copper(II) with 3-aminopropanamidoxime ($R = R' = H$), 3-(methylamino)propanamidoxime ($R = H$, $R' = CH_3$) and 3-(diethylamino)propanamidoxime ($R = R' = C_2H_5$) are described in this paper. The complexation models and the values of the stability constants of the species formed are reported. To facilitate interpretation of the structure of the aqueous complexes, we also isolated one of the polynuclear complexes predominating in solution and determined its solid-state structure by X-ray diffraction methods.

Experimental

Ligand preparation. 3-Aminopropanamidoxime (HL = **1**), 3-(methylamino)propanamidoxime (HL = **2**), and 3-(diethylamino)propanamidoxime (HL = **3**) were prepared by action of hydroxylamine on corresponding aminopropionitriles as described earlier.[3] The oximes were precipitated in the form of the corresponding monohydrochloride (**2**) or dihydrochloride (**1** and **3**). Recrystallization was done from ethanol (**2** and **3**) or methanol (**1**). The ligand contents of the solutions determined both potentiometrically and gravimetrically showed good agreement with the values expected from weighing.

*Preparation of the complex $Cu_5(L-H)_4Br_2 \cdot 2H_2O$, (HL = **2**).* Conditions for the formation of the polynuclear complexes are suitable in solutions containing copper(II) chloride, HL·HCl and NaOH in molar ratio 1:1:2. Attempts to isolate crystalline products from such solutions proved unsuccessful, but when the counter chloride ion was replaced by the heavier bromide ion tabular dark-brown crystals suitable for X-ray diffraction analysis were obtained. Recrystallization was done from water.

Methods. The complex formation equilibria were studied in aqueous 0.1 M NaCl at 25.0 °C by potentiometric EMF measurements in which the hydrogen ion concentration, h, was varied by adding sodium hydroxide or hydrogen chloride to the solution. The solubility of the polynuclear complexes formed in these systems was relatively low in concentrated electrolyte solutions and especially in solutions containing perchlorate ions. Thus employment of low ionic strength adjusted with sodium chloride, rather than sodium perchlorate, was necessary.

The free hydrogen ion concentration, h, was determined by measuring the EMF of cell (I),

$$- \text{RE} \mid \text{equilibrium solution} \mid \text{GE} + \qquad \text{(i)}$$

where GE and RE represent a glass electrode and reference electrode (Hg, Hg_2Cl_2|0.10 M NaCl), respectively. Assuming the activity coefficients to be constant, eqn. (1) is valid.

$$E = E^\circ + 59.157 \log h + j_h h \qquad (1)$$

The protonation constants of the ligands were determined in separate titrations with ligand concentration, C_L, 10–20 mM and pH ($= -\log h$) from 3 to ca. 11. During the three-component measurements the total concentrations of copper(II), C_M, and ligand, C_L, were varied within the limits $2.5 < C_M < 10$ mM and $5 < C_L < 20$ mM covering the ligand to metal ratios 1:2, 0.8:1, 1:1, 2:1, 3:1 and 4:1.

In evaluation of the acidity constants of the ligand equilibria (2)–(4) were considered:

$$H^+ + HL \rightleftharpoons H_2L^+ \quad (2)$$

$$2H^+ + HL \rightleftharpoons H_3L^{2+} \quad (3)$$

$$HL \rightleftharpoons L^- + H^+ \quad (4)$$

The acid strength of the oxime group is very weak ($pk_a \approx 12$), and thus only a rough estimate could be obtained for the equilibrium constant for reaction (4). This value was not used in the calculations of the stabilities of the metal complexes, where the ligand was chosen as a component in the form of the neutral acid HL. The rest of the protonation model and the corresponding constants (2) and (3) were considered as known during the evaluation of the three-component system (5).

$$pH^+ + qCu^{2+} + r(HL) \rightleftharpoons (H^+)_p(Cu^{2+})q(HL)_r;\ \beta_{pqr} \quad (5)$$

For the binary hydrolytic equilibria of copper(II) we used the results summarized by Baes and Mesmer.[4]

Data sets Z_H vs. pH were calculated to visualize the experimental results. Z_H is defined as the average number of OH^- ions reacted per ligand (HL) and is given by eqn. (6),

$$Z_H = (h - C_H - k_w h^{-1})/C_L \quad (6)$$

where the total concentration of proton, C_H, has been calculated over the zero level HL, H_2O, Cu^{2+}.

The mathematical analysis used to search for the model (*p,q,r*) and for the corresponding equilibrium constants β_{pqr} giving the best fit to the experimental data was carried out with the least-squares computer program SUPERQUAD.[5] The reader is referred to Ref. 5 for the definitions of the sample standard deviation *s* and the χ^2 statistics used in the evaluation of the complex model that best describes the experimental data.

Treatment of the potentiometric data. The protonation constants according to reactions (2)–(4) are given in Table 1. The number of titration points/titrations used in the calculations, and the values of the sample standard deviation and χ^2-statistics, were as follows for ligands **1**, **2** and **3**: 201/4, $s = 1.88$, $\chi^2 = 30.6$; 231/4, $s = 2.92$, $\chi^2 = 25.9$; 196/5, $s = 2.33$, $\chi^2 = 28.0$.

Analyses of the metal–ligand systems were begun by considering the plots Z_H(pH). An example is presented in Fig. 1. From these plots it could be directly concluded that deprotonated polynuclear complexes are present in all three systems.

The search for the composition and stability of the complexes was performed as a *p,q,r* analysis (systematic testing of different *p,q,r* combinations), during which the number of complex species in each system was increased one at a time as long as significant improvement in the goodness of fit to the data was obtained.

For **1** the lowest sample standard deviation *s* was found for the composition $Cu(HL)^{2+}$, $Cu(HL)_2^{2+}$, $Cu_5(HL)_4H_{-7}^{3+}$, $Cu_5(HL)_4H_{-8}^{2+}$ and $Cu(H_2L)^{3+}$ ($s = 1.74$, $\chi^2 = 23.0$, $\sigma V = 0.02$ ml, $\sigma E = 0.1$ mV). This five-component model is considered to provide a satisfactory explanation of the data, since *s* values lower than 3 have often be regarded as acceptable for comparable systems.[6] Although the presence of the minor species $Cu(H_2L)^{3+}$ is somewhat uncertain, it was accepted because its inclusion resulted in a significant decrease in the *s*-value from the best four-component alternative ($s = 2.13$). The proposed formulas of the complexes, with the corresponding stability constants (from 7 titrations and 345 experimental points), are given in Table 1.

For **2** the best model obtained was that consisting of six species: the complexes proposed for **1** plus the new species $Cu_4(HL)_4H_{-6}^{2+}$. Inclusion of this tetrameric complex in the five-component model improved the *s*-value from 3.89 to 1.90 ($\chi^2 = 38.0$). Correspondingly there was a striking decrease in the values of the standard deviations of the complexes.

The dissimilarity of these two systems was already apparent in the different color shades of the solutions in the area where polynuclear complex formation occurs. This is clearly visible in the spectra of the compounds. For ligand **1** the prevailing polynuclear species $Cu_5(HL)_4H_{-8}^{2+}$ gives a single absorption maximum at $\lambda = 352$–356 nm, whereas for **2** the spectra show two maxima: one at $\lambda = 356$–360 nm ($Cu_5(HL)_4H_{-8}^{2+}$) and the other at $\lambda = 330$–340 nm ($Cu_4(HL)_4H_{-6}^{2+}$).

The final values of the stability constants for the Cu-ligand **2** are given in Table 1. The results are based on the

Table 1. Equilibrium constants relating to reaction (5).[a]

				$\log(\beta_{pqr} \pm 3\sigma)$		
p	*q*	*r*	Proposed formula	HL=**1**	HL=**2**	HL=**3**
1	0	1	H_2L^+	9.061±0.004	9.375±0.005	9.148±0.005
2	0	1	H_3L^{2+}	13.066±0.006	13.198±0.006	12.899±0.008
−1	0	1	L^-	−11.5 ±0.1	−12.2 ±0.2	−12.2 ±0.2
1	1	1	$Cu(H_2L)^{3+}$	10.3 ±0.1	10.5 ±0.1	9.99 ±0.06
0	1	1	$Cu(HL)^{2+}$	7.53 ±0.01	6.82 ±0.01	5.49 ±0.02
0	1	2	$Cu(HL)_2^{2+}$	13.58 ±0.02	12.9 ±0.1	
−7	5	4	$Cu_5(L-H)_3L^{3+}$	4.98 ±0.06	4.13 ±0.06	−1.84 ±0.04
−8	5	4	$Cu_5(L-H)_4^{2+}$	0.01 ±0.05	−0.62 ±0.03	−6.99 ±0.02
−6	4	4	$Cu_4(L-H)_2L_2^{2+}$		6.16 ±0.06	

[a] **1**=$NH_2CH_2CH_2C(NH_2)(NOH)$; **2**=$CH_3NHCH_2CH_2C(NH_2)(NOH)$; **3**=$(C_2H_5)_2NCH_2CH_2C(NH_2)(NOH)$.

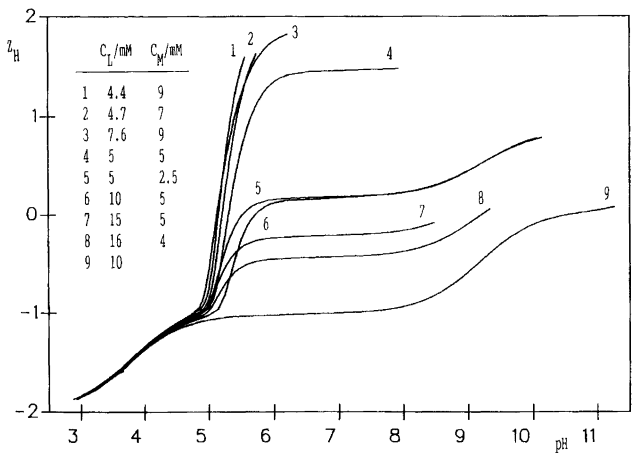


Fig. 1. Part of the experimental data plotted as curves Z_H(pH) for different C_L:C_M ratios (HL=**3**). The bottom curve refers to the ligand alone.

data from 7 different titrations and 300 experimental points.

The model that best describes the complexation between copper(II) and ligand **3** is the same as for ligand **1** except that the bis complex $Cu(HL)_2^{2+}$ is now missing. The fit to the experimental data was even better than for **1** ($s = 1.49$, $\chi^2 = 13.9$). The four complex species with the corresponding stability constants (9 independent titrations and 448 data points) are included in Table 1.

Crystal structure determination and refinements. Unit cell dimensions and diffraction data for $[Cu_5(L–H)_4]Br_2 \cdot 2H_2O$ were measured with a Nicolet P3 four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation. Details of the X-ray diffraction study are listed in Table 2.

X-Ray intensities were measured by the ω-scan technique with variable scan speeds. No significant intensity variations were observed throughout the data collection. Lorentz and polarization corrections were applied, but no corrections were made for absorption.

The structure of the complex was solved by direct methods using Siemens SHELXTL-Plus (PC-Version) programs,[7] and by successive electron-density calculations. All non-hydrogen atoms were refined with anisotropic parameters by full-matrix least-squares techniques. Atomic scattering factors were taken from Ref. 8. The hydrogen atoms were inserted at calculated positions. The final cycles of refinement gave an R-value of 0.071 ($R_w = 0.075$) for 1110 observed reflections.

Fractional coordinates for the non-hydrogen atoms are given in Table 3, and the bond lengths around copper atoms are collected in Table 4. Lists of the structure factors and anisotropic temperature factors are available from the authors on request.

Table 2. Crystal data for $[Cu_5(L–H)_4]Br_2 \cdot 2H_2O$ (HL=**2**).

M_r	974.1
Crystal system	Monoclinic
a/Å	10.880(5)
b/Å	5.930(3)
c/Å	23.836(11)
β/°	100.06(4)
V/Å^3	1514.2(12)
Space group	$p2_1/c$
Z	2
D_c/g cm^{-3}	2.136
D_m/g cm^{-3} (by flotation)	2.13
Dimensions/mm	0.20×0.20×0.20
μ(Mo$K\alpha$)/mm^{-1}	6.1
Scan rate/° min^{-1}	4.0–30.0
2Θ range/°	4–51
Unique reflections	2806
Obsd. reflections $I > 2\sigma(I)$	1110
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0014F^2$
R(obs. data)	0.071
wR(obs.data)	0.075
Largest difference/e Å^{-3}	1.2
Largest shift/e.s.d.	0.023
Goodness-of-fit	1.24

Discussion

The lengthening of the carbon chain in $RR'N(CH_2)_nC(NH_2)(NOH)$ from $n = 1$ to 2 has a marked effect on the acidity of the amine and amide nitrogens.[1–3,9] The additional CH_2 can be found to weaken the acid strength of the protonated amine $-NRR'H^+$ group by 1.0–1.1 log units. The acid-weakening influence on the protonated amide $-NH_3^+$ group is even stronger: 1.5–2.1 log units. Another result is the smaller difference

Table 3. Atomic coordinates and equivalent isotropic displacement coefficients.

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U(eq)[a]/Å^2
Cu(1)	0	10000	0	45(1)
Cu(2)	1928(3)	14340(4)	−48(1)	51(1)
Cu(3)	1682(3)	8355(4)	1224(1)	49(1)
Br(1)	3980(3)	2342(4)	3596(1)	70(1)
O(1)	−425(12)	12234(22)	−565(5)	48(5)
O(2)	1452(13)	11560(24)	285(6)	69(6)
O(3)	1135(16)	3346(31)	2747(7)	90(7)
N(1)	450(16)	13963(26)	−651(6)	45(6)
N(2)	2675(20)	16711(39)	−481(9)	99(10)
N(3)	−783(16)	14004(27)	−1516(7)	54(7)
N(4)	2155(16)	11053(28)	842(7)	54(7)
N(5)	3153(19)	8741(28)	1868(7)	70(8)
N(6)	3135(16)	14282(28)	638(7)	52(7)
C(1)	200(20)	14781(36)	−1171(8)	48(8)
C(2)	965(22)	16689(37)	−1338(9)	77(11)
C(3)	1970(25)	17778(48)	−926(10)	104(14)
C(4)	3742(24)	17908(42)	−222(10)	86(12)
C(5)	3045(19)	12554(35)	971(8)	39(7)
C(6)	3911(19)	12256(33)	1519(8)	47(8)
C(7)	3448(25)	11004(39)	1979(8)	76(11)
C(8)	2966(20)	7515(36)	2407(8)	63(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (in Å) around the copper atoms.

Cu1–Cu2	3.335(2)	Cu1–Cu3	3.309(2)	Cu1–O1	1.888(12)
Cu1–O2	1.854(14)	Cu2–O2	1.940(15)	Cu2–N1	1.973(15)
Cu2–N2	1.999(23)	Cu2–N6	1.910(15)	Cu3–O1a	1.927(11)
Cu3–N3a	1.907(27)	Cu3–N4	1.954(17)	Cu3–N5	2.028(17)
O1–N1	1.438(21)	O2–N4	1.443(20)		

between the successive pK_a-values when the distance between the two dissociable sites increased. Interestingly, too, the acidity of the $-NRR'H^+$ group does not change in a regular manner in going from primary to tertiary amino function, but rather ligand **2**, with its secondary amine group, exhibits the lowest acidity. This trend is the same whether $n = 1$ or 2 and is evidently due to the changes in the network and strength of the hydrogen bonds in the three systems.

For the most part the complex formation models we propose accord well with each other: in addition to the mononuclear species $Cu(HL)^{2+}$ and $Cu(H_2L)^{3+}$ the pentanuclear complexes $H_{-7}Cu_5(HL)_4^{3+}$ and $H_{-8}Cu_5(HL)_4^{2+}$ are common for the three ligand systems. The mononuclear bis complex $Cu(HL)_2^{2+}$ was found with ligands **1** and **2** but not with **3**, which is not surprising considering the steric requirements of the two ethyl groups in **3**. Absence of this bis complex was already noted for the corresponding *N*-dimethylated ligand. The decrease in stability of the complexes is also evident in the values of the formation constants of the mono complexes $Cu(HL)^{2+}$ in going from H_2N through $(CH_3)HN$ to $(C_2H_5)_2N$.

The mononuclear complex $Cu(H_2L)^{3+}$ formed with all three of the present ligands was not found for the corresponding ligands where $n = 1$. The most probable explanation lies in the magnitude of the values of the acid constants of the complexes. When $n = 2$ the acidity of $Cu(H_2L)^{3+}$ is relatively weak: for ligands **1**, **2** and **3** the pK_a-values are 2.8, 3.7 and 4.5, respectively. When $n = 1$ the corresponding values should be considerably lower, so that the experimental conditions do not allow formation of such a species.

In our previous studies with ligands where $n = 1$, polymerization was found only for ligands containing tertiary amino groups and led to the formation of tetranuclear species $H_{-6}Cu_4(HL)_4^{2+}$. With $n = 2$ the main complex was pentameric $H_{-8}Cu_5(HL)_4^{2+}$; however, the earlier studies had been restricted to the case where $R = R' = CH_3$.[3] A prevailing complex of similar pentanuclear composition was established for all three ligands studied here. Additionally, a tetranuclear species analogous to that noted above was formed here with ligand **2**.

Figure 2 shows the distribution of copper(II) among different complex species vs. pH in the studied systems when $C_M/C_L = 1$. In each case, the polynuclear complexes prevail in solution from ca. pH 5 upwards.

Comparison of the systems $n = 1$ and $n = 2$ reveals some discrepancies. First, with $n = 2$ polymerization seems to be independent of the nature of the amino function, since pentanuclear species were similarly formed with ligands containing tertiary, secondary and primary 3-amino groups. Secondly, the behavior of ligand **2** is exceptional as it is capable of forming both tetra- and pentanuclear species. It may be added that both of these polymers are major species formed extensively in suitable solutions (cf. Fig. 2).

Existence or non-existence of the polynuclear species apparently is due to the structure of the bis complex $Cu(HL)_2^{2+}$. Deprotonation of this species may lead to the formation of the mononuclear complex $Cu(HL)L^+$, which contains stable five-membered in-plane chelate rings and strong intramolecular $=N-O-H\cdots O-N=$ hydrogen bridges between two *cis* oxime groups. Such a species has been verified as a major component when $n = 1$ and $R = H$, $R' = H$ or CH_3.[1] With these ligands, the stability of this complex effectively suppresses any further complexation reactions, and polymerization is prevented. Formation of this kind of intramolecularly stabilized species is not possible if the chelate ring in the mononuclear complex is six-membered ($n = 2$) or two bulky dialkylsubstituted 2-amino groups are located in the *cis*-position. In these cases deprotonation would result in polynuclear complex formation.

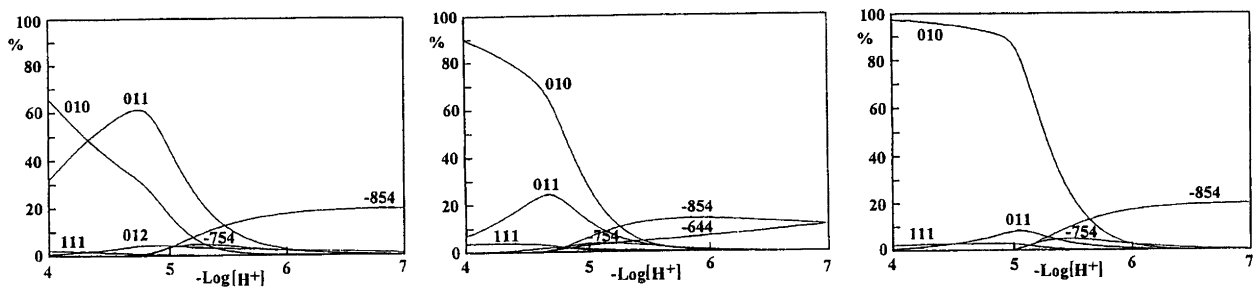


Fig. 2. Concentration distribution of the copper(II) species for C_L/C_M ratios 1 ($C_L = C_M = 5$ mM) in the different copper–ligand systems. The ligands from right to left are **1**, **2** and **3**.

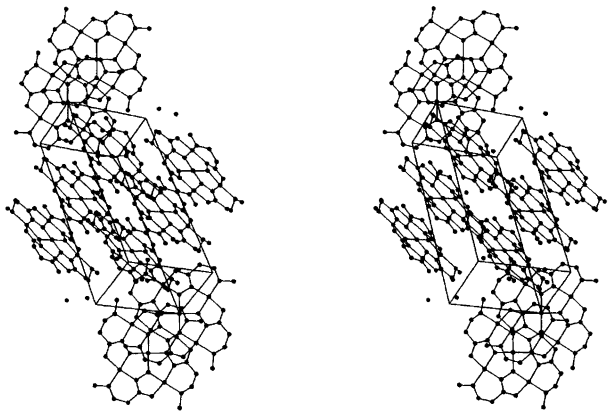


Fig. 3. Stereoscopic view of the molecular packing of $[Cu_5(L–H)_4]Br_2 \cdot 2H_2O$ (HL = **2**) with the hydrogen atoms omitted.

There is no obvious reason for the different nuclearity of the complexes when $n = 1$ and $n = 2$. Studies on the solid complexes have revealed that the difference between the tetra- and pentanuclear species derives from the ability of the deprotonated amide NH_2 group to coordinate to the metal: in the pentanuclear complexes all four amide NH_2 groups, derived from four separate ligands, act as donor groups (in the form of an NH^- anion), whereas in the tetranuclear species only two of them deprotonate, while the other two do not and remain uncoordinated. The dissociation of the NH_2 group upon coordination to copper(II) is of interest, since in the free state it shows no noticeable acidity.

Possibly the actual acid strength of the amide NH_2 group in the $n = 1$ and $n = 2$ ligands is very different, and the dissimilar tendency of the group to participate in the coordination may arise from this difference. Another possible explanation is the more suitable conformation of $n = 2$ ligands for polynuclear complex formation, arising from the greater flexibility of the six-membered chelate ring ($n = 2$) than of the five-membered ring ($n = 1$). In fact, though, the difference between the two series of ligands cannot be very decisive since both tetra- and pentanuclear complexes are simultaneously formed with **2**.

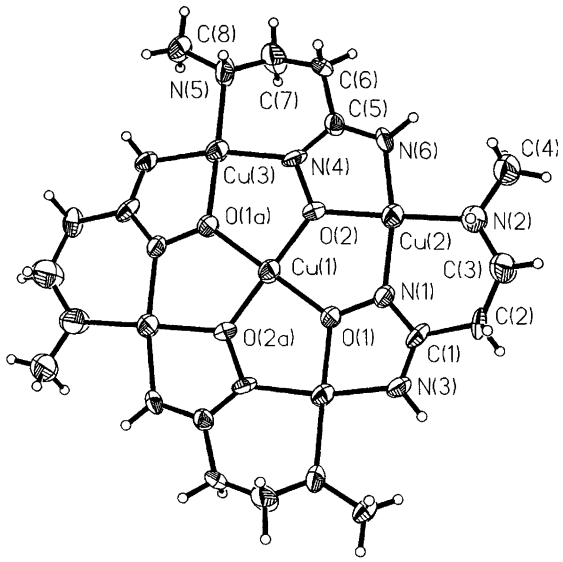


Fig. 4. A view of the complex cation $[Cu_5(L–H)_4]^{2+}$ (HL = **2**) and numbering of atoms.

Table 5. Deviation of atoms (in Å) from the plane defined by the copper atoms.

Atom	Deviation	Atom	Deviation
O1	0.243(15)	N1	0.069(16)
O2	−0.110(15)	N2	−0.345(17)
N3	−0.274(17)	N5	−0.002(17)
N4	0.015(19)	N6	0.099(18)

The crystalline complex isolated from a copper(II) – ligand **2** solution consists of divalent complex moieties $[Cu_5(L–H)_4]^{2+}$, uncoordinated bromide ions, and waters of hydration. Packing of the constituents in the unit cell illustrated in Fig. 3 shows that in-plane four-coordination of copper atoms is completed by the nitrogen and oxygen atoms from the neighbouring complex units.

The complex unit shown in Fig. 4 is closely similar to that reported earlier for $Cu_5(L–H)_4Br_2 \cdot 8H_2O$ ($n = 2$, $R = R' = CH_3$) and referred to in the introduction. All oxime NOH and amide NH_2 groups have been deprotonated on complexation, and a copper-centered body involving an extensive ring system with several five- and six-membered chelate rings is formed. The donor atoms and the copper atoms in the structure are nearly coplanar (Table 5). Selected bond lengths are shown in Table 4; the copper–copper distances included in the table vary from 3.309(2) to 3.333(2) Å.

In principle, results obtained in the solid state cannot be applied as such to species in aqueous media. However, in this case there can be little doubt about the actual structures of the aqueous species: the analogy between the formulas of the crystalline and aqueous species $H_{-8}Cu_5(HL)_4^{2+}$ is so striking that the basic structure of the complex moiety $[Cu_5(L–H)_4]^{2+}$ must be the same in the two phases. This is also valid for the tetranuclear species found with HL = **2** and, although we were unable to isolate the complex from solution for X-ray structure determination, the composition $H_{-8}Cu_4(HL)_4^{2+}$ is analogous to the tetranuclear structures verified earlier when $n = 1$, and it is quite clear that the present aqueous tetramer can also be formulated as $[Cu_4(L–H)_2L_2]^{2+}$.

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