Pentanuclear Complex Formation between 3-(Dimethylamino)-propanamidoxime and Copper(II) in Aqueous Solution

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The complex formation equilibria of copper(II) with 3-(dimethylamino)propanamidoxime (HL) were studied in aqueous 1.0 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. The best model was that which included the mononuclear complex $Cu(HL)^{2+}$ and the hydrolyzed pentanuclear species $(Cu^{2+})_5(HL)_4H_{-7}^{3+}$ and $(Cu^{2+})_5(HL)_4H_{-8}^{2+}$. From a comparison of the compositions of the complexes in the aqueous and solid phases it is concluded that deprotonation of the aqueous complexes originates from the coordinated oxime and amide groups, and that the most probable formula of the major pentanuclear species, $(Cu^{2+})_5(HL)_4H_{-8}^{2+}$, should be written as $[Cu_5(L-H)_4]^{2+}$ rather than in the form of a mixed hydroxo complex.

Complexation between copper(II) and aminoalkanamidoximes of the type $R_2N(CH_2)_nC(NH_2)NOH$ (= HL, $n = 1$, $R = CH_3$ and C_2H_5) is characterized by the formation of highly stable tetranuclear complexes $Cu_4L_2(L-H)_2^{2+}$ in which the oxime NOH groups and two of the four amide NH_2 groups are deprotonated.[1,2] Instead of the cubane-like structure which is common for copper(II) tetramers, these compounds exhibit an unusual configuration in which all four copper atoms are nearly coplanar. This property makes them important model compounds, for instance in studying the redox and magnetic-exchange interactions of copper(II).

To clarify the effect of a lengthening of the carbon chain from $n = 1$ to 2 on the composition and structure of these polynuclear complexes, we have now studied the complex formation of 3-(dimethylamino)propanamidoxime (= HL, $n = 2$, $R = CH_3$) with copper(II) in aqueous solution. To facilitate interpretation of the structure of the aqueous complexes, we have also isolated the predominating polynuclear species from the solution in the solid state and determined its structure by X-ray diffraction methods. The results of the equilibrium study are given in this communication. There are apparently no previous reports concerning this metal–ligand system.

Experimental

Ligand preparation. 3-(Dimethylamino)propanamidoxime (HL) was prepared by action of hydroxylamine on 3-dimethylaminopropionitrile. A sodium ethoxide solution, prepared by dissolving 1 mol of sodium in 200 ml of absolute ethanol, was added with vigorous stirring to a suspension of the nitrile (1 mol) and hydroxylammonium chloride (1 mol) in absolute ethanol. The precipitated sodium chloride was filtered out and the solution was stirred for several hours at room temperature. HL was isolated in the form of the monohydrochloride HL · HCl by passing gaseous HCl through the solution. Recrystallization was made from ethanol. The HL contents of the solutions determined both potentiometrically and gravimetrically showed good agreement with the values expected from weighing.

Preparation of the pentanuclear complex $Cu_5(L-H)_4Br_2 \cdot 8H_2O$. Conditions for the formation of the polynuclear complexes are suitable in solutions containing copper(II) chloride, HL · HCl and NaOH in 1:1:2 molar ratios. Attempts to isolate crystalline products from such solutions proved unsuccessful, but when the counter chloride ion was exchanged for the heavier bromide ion tabular dark-brown crystals suitable for X-ray diffraction analysis were obtained. Recrystallization was made from water. Anal. $Cu_5(C_5H_{11}N_3O)_4(H_2O)_8Br_2$: C, H, Cu, Br. The structure of the compound was determined by X-ray diffraction methods and refined to the conventional R value 6.4%. Details of this analysis will be given in a subsequent paper.[3]

The crystalline complex was also used as a starting material in some of the titrations. In this way double control of the metal and ligand contents in the solutions was achieved.

Methods. The complex formation equilibria were studied in aqueous 1.0 M Na(Cl) at 25.0 °C by potentiometric EMF measurements using a glass electrode. Sodium chloride, rather than sodium perchlorate, was chosen as the inert salt

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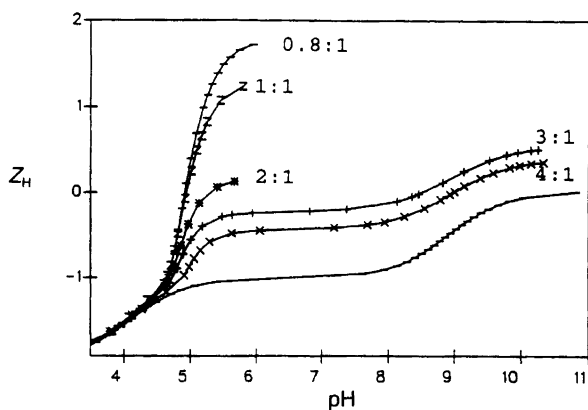* To whom correspondence should be addressed.

Fig. 1. Part of the experimental data plotted as curves Z_H(pH) for different $C_L:C_M$ values. The lowest curve refers to the ligand alone.

because of the better solubility of the polynuclear complexes formed in NaCl solutions. The titration procedure, including the procedure to calibrate the glass electrode, has been described earlier.[4]

The protonation constants of the ligand were determined in separate titrations with a ligand concentration, C_L, of 10–20 mM and pH (= $-\log[H^+]$) from 3 to ca. 11. During the three-component titrations the total concentrations of copper(II), C_M, and ligand, C_L, were varied within the limits $2 < C_M < 9$ mM and $7 < C_L < 15$ mM, covering the ligand-to-metal ratios 0.8:1, 1:1, 2:1, 3:1, 4:1 and 5:1. In these measurements the pH range was restricted to an upper value of ca. 10.

To test the reproducibility and reversibility of equilibria, both forward (increasing pH) and backward (decreasing pH) titrations were performed.

In evaluation of the acidity constants of the ligand equilibria (1)–(3) were considered. The acid strength of the

$$H^+ + HL \rightleftharpoons H_2L^+ \tag{1}$$

$$2H^+ + HL \rightleftharpoons H_3L^{2+} \tag{2}$$

$$HL \rightleftharpoons L^- + H^+ \tag{3}$$

oxime group is very weak ($pk_a > 12$), and thus only a roughly estimated value could be obtained for the equilibrium constant for reaction (3). This value was not used in the calculations of the stabilities of the metal complexes, for which the ligand was chosen as a component in the form HL. The rest of the protonation model and the corresponding constants (1) and (2) were considered as known during the evaluation of the three-component system [reaction (4)].

$$p\text{H}^+ + q\text{Cu}^{2+} + r(\text{HL}) \rightleftharpoons (\text{H}^+)_p(\text{Cu}^{2+})_q(\text{HL})_r; \ \beta_{pqr} \tag{4}$$
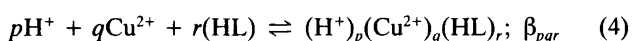
For the binary hydrolytic equilibria of copper(II) we used the results summarized by Baes and Mesmer.[5] In our experimental conditions binary hydrolysis of copper(II) was

negligible. No attention was paid to the possible formation of chloro complexes.

To visualize the experimental results, data sets Z_H vs. pH were calculated. Z_H is defined as the average number of OH^- ions reacted per ligand (HL) and is given by eqn. (5),

$$Z_H = ([H^+] - C_H - k_w[H^+]^{-1})/C_L \tag{5}$$

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

The mathematical analysis used to search for the model (p,q,r) and the corresponding equilibrium constants β_{pqr} giving the best fit to the experimental data was carried out with the least-squares computer program SUPERQUAD.[6] The program minimizes the sum of the squared residuals between the observed and calculated EMF values [eqn. (6)]. The weighting factor w_i is defined by eqn. (7), where

$$U = \Sigma w_i(E_i^{\text{obs}} - E_i^{\text{calc}})^2 \tag{6}$$

$$w_i = 1/(\sigma_E^2 + \delta E_i/\delta V_i)\sigma_V^2 \tag{7}$$

σ_E and σ_V are the estimated uncertainties in the electrode and volume readings, taken individually, and $\delta E/\delta V$ is the slope of the titration curve. For the definitions of the sample standard deviation s and the χ^2 statistics used in the evaluation of the complex model, the reader is referred to Ref. 6.

Data treatment. From the plots Z_H(pH) presented in Fig. 1 it can be directly concluded that deprotonated complexes are present in the system. The shape of the curves for the low C_L/C_M ratios further indicates polynuclear complex formation. Other information about the nature of the complexes is obtainable from the number, steepness and location of the equivalence points in the titration curves.

There is a significant potential jump near pH 6.5, which for the pure ligand corresponds to the neutralization of the acid H_3L^{2+}. The location of this point in the titrations for different C_L/C_M ratios indicates that 1.6 mol of extra protons are liberated from HL per mol of copper(II) added to the solution. The very slight but still detectable inflection point in the alkaline parts of the curves when $C_H/C_M = -1.6$ is in accordance with this observation. The existence of some predominant complex species with $p/q = -8/5$ is implied.

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), on the assumption that only one polynuclear/hydrolysed complex in addition to the mononuclear species is formed. The significantly best fit to the data (lowest sample standard deviation) was found for the compositions $Cu(HL)^{2+}$ and $Cu_5(HL)_4H_{-8}$ ($s = 6.0$, $\sigma_V = 0.02$ ml, $\sigma_E = 0.2$ mV), which is in accordance with the location of the equivalence points in the titration curves.

The remaining systematic residuals between the experimental data and complex model largely disappeared when

Table 1. Equilibrium constants of the 3-(dimethylamino)-propanamidoxime (= HL) – copper(II) system relating to reaction (4) in 1 M NaCl solution at 25 °C.

p	q	r	Proposed formula	log $(\beta_{pqr} \pm 3\sigma)$
1	0	1	H_2L^+	8.903 ± 0.003
2	0	1	H_3L^{2+}	12.974 ± 0.005
-1	0	1	L^-	-12.6 ± 0.3
0	1	1	$Cu(HL)^{2+}$	5.61 ± 0.03
-7	5	4	$Cu_5(L-H)_3L^{3+}$	-0.26 ± 0.06
-8	5	4	$Cu_5(L-H)_4^{2+}$	-5.48 ± 0.06

a new pentanuclear species $Cu_5(HL)_4H_{-7}$ ($s = 2.5$) was added to the model. The new three-component model is already quite appropriate, since s values lower than 3 can be estimated acceptable for comparable systems.[7] In these calculations the difference in the goodness of fit between this new pentamer and the next best alternatives $Cu_2(HL)_2H_{-2}^{2+}$ ($s = 3.3$) and $Cu_3(HL)_2H_{-5}^{3+}$ ($s = 4.0$) was significant. An acceptable four-complex model could not be found, and because the s-value and the χ^2-statistics ($\chi^2 = 21.9$) indicated a satisfactory explanation of the data, we suggest the compositions $Cu(HL)^{2+}$, $Cu_5(HL)_4H_{-7}^{3+}$ and $Cu_5(HL)_4H_{-8}^{2+}$ as the final result of complexation under the conditions used. The proposed formulas of the species, with their corresponding stability constants (from seven titrations and 192 experimental points), are given in Table 1.

Discussion

The lengthening of the carbon chain in $(CH_3)N(CH_2)_n$-$C(NH_2)NOH$ from $n = 1$ to $n = 2$ has a pronounced effect on the acid properties of the amine and amide nitrogen atoms: the additional CH_2 considerably weakens the acidity of the protonated amine $-NH(CH_3)_2^+$ [$pk_a = 7.61$ ($n = 1$)[1] and $pk_a = 8.90$ ($n = 2$)] and amide $-NH_3^+$ [$pk_a = 1.76$ ($n = 1$)[1] and $pk_a = 4.07$ ($n = 2$)] groups. Another result is the smaller difference between the successive pk_a values of the ligand when the distance between the dissociable groups increases.

The complex formation scheme we propose is very simple: in addition to the mononuclear species $Cu(HL)^{2+}$ there are just two pentanuclear complexes. As shown in Fig. 2, polymerization is appreciable even in fairly acidic solutions. This is possibly connected with our failure to find the 1:2 bis complex $Cu(HL)_2^{2+}$ in the present system. With $n = 1$ and $R = CH_3$ this mononuclear species was easily formed.

As regards the mononuclear complexes that are formed, there can be little doubt about the mode of coordination: several known examples of comparable structures unambiguously show that bonding to the metal is through the oxime and amine nitrogen donors.[2,8,9] An increase in the number of atoms in the chelate ring from five to six
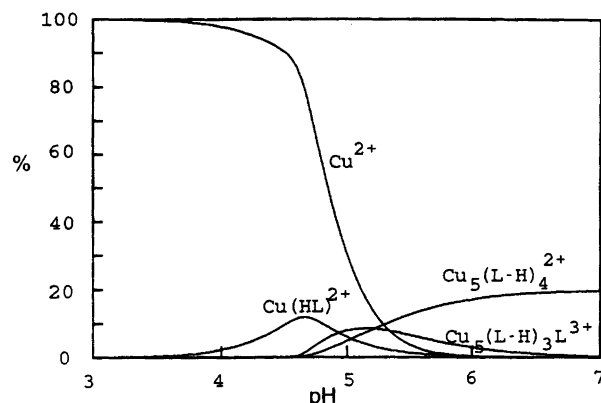

Fig. 2. Percentage distribution of copper(II) among different complexes plotted against pH ($C_M = C_L = 10$ mM).

is reflected in the values of the stability constants: $\log \beta_{011} = 6.91$ ($n = 1$) and $\log \beta_{011} = 5.61$ ($n = 2$).

We have previously pointed out that the number of alkyl groups on the amine nitrogen atom plays a decisive role in complex formation schemes for this type of ligand. Polymerization takes place only when two alkyl substituents are present, and in the case of primary and secondary amine groups complexation leads to a series of mononuclear complexes that are stabilized by strong intramolecular hydrogen bridges between the oxime oxygen atoms.[1]

When $n = 1$ the predominating polynuclear complexes are tetranuclear. The planar structure of $Cu_4L_2(L-H)_2^{2+}$ is formed in such a way that, besides the amine and oxime nitrogen atoms, the oxime oxygens and two of the four amide nitrogens are involved in a square-planar coordination system around copper(II) atoms (Fig. 3). The notation L–H implies that bonding of the amide group to the metal is accompanied by the removal of one of the amide NH_2 protons.

In this study, where $n = 2$, no tetranuclear complexes were found but the polymeric species proved to be pentameric. Although the potentiometric data do not give any direct indication of the actual structure of the compounds, it seems clear that the compositions $Cu_5(HL)_4H_{-7}^{3+}$
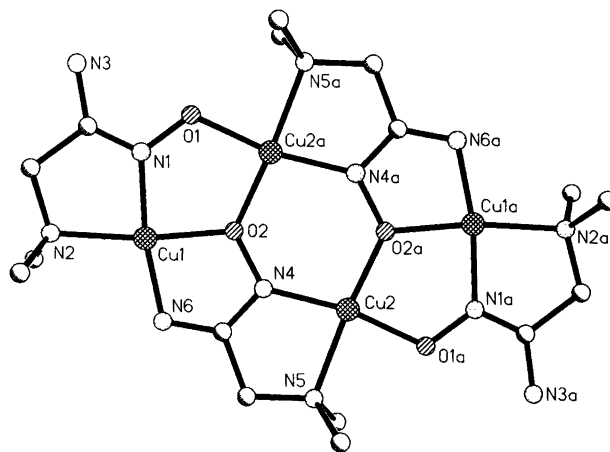

Fig. 3. Schematic representation of the tetranuclear complex ion $[Cu_4(L-H)_2L_2]^{2+}$ in the solid state.
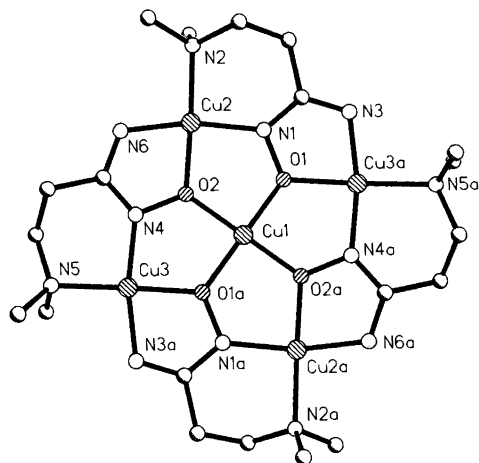
Fig. 4. Schematic representation of the pentanuclear complex ion $[Cu_5(L-H)_4]^{2+}$ in the solid state.

and $Cu_5(HL)_4H_{-8}^{2+}$ obtained should be written as $Cu_5(L-H)_3L^{3+}$ and $Cu_5(L-H)_4^{2+}$. In addition to the results obtained for $n = 1$, these formulas are supported by the results of the X-ray diffraction analysis, which showed the solid pentameric compound $Cu_5(HL)_4H_{-8}Br_2 \cdot 8H_2O$ isolated from the equilibrium solution to consist of discrete $Cu_5(L-H)_4^{2+}$ complex units (Fig. 4).

In spite of their different nuclearity, the polymeric complexes with $n = 1$ and $n = 2$ are basically similar; both structures are virtually planar and the role of the donor atoms is analogous. One reason for the different structure is obvious: with $n = 2$ the larger six-membered chelate rings allow all of the amide groups to coordinate to the copper-(II) atoms, with a simultaneous increase in the number of copper(II) atoms in the complex from four to five.

It is interesting to discover that in all these structures the amide groups directly bound to the metal are present in the

form of a negative $-NH^-$ ion. Since the $-NH_2$ function shows no detectable acidity in the free state, the coordination results in a marked lowering in the corresponding pk_a-value. Deprotonation of the complex $Cu_5(HL)_4H_{-7}$ with the pk_a-value 5.22 apparently involves the displacement of such a proton.

The formation of planar polynuclear copper complexes seems to be characteristic of the present type of ligand. The ring system formed and the nuclearity of the complexes depend on the small variations in the ligand molecule. Evidently, too, these complexes are formed through deprotonation of the oxime and amide nitrogen groups rather than deprotonation of the coordinated aqua molecules, and they exhibit the same basic structure in solution and in the solid state.

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