

Complex Formation between Copper(II) and 2-Aminoacetamidoxime and Its *N*-Methylated Derivatives

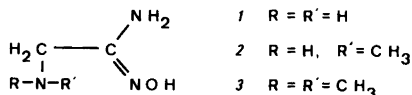
Heikki Saarinen, Marjatta Orama, Tuovi Raikas and Jorma Korvenranta

Division of Inorganic Chemistry, University of Helsinki,
SF-00100 Helsinki 10, Finland

Saarinen, Heikki, Orama, Marjatta, Raikas, Tuovi and Korvenranta, Jorma, 1986. Complex Formation between Copper(II) and 2-Aminoacetamidoxime and Its *N*-Methylated Derivatives. – Acta Chem. Scand. A 40: 396–401.

The complex formation equilibria of copper(II) with 2-aminoacetamidoxime *1*, 2-(methylamino)acetamidoxime *2* and 2-(dimethylamino)acetamidoxime *3* have been studied in 1.0M and, in part, in 0.1M NaClO₄ at 25°C by potentiometric titrations with the use of a glass electrode. Experimental data collected from acid, neutral and weak alkaline solutions were analyzed with respect to the complexes formed and their stability constants using the least-squares computer program MINQUAD. In addition to the stepwise mononuclear complexes Cu(HL)²⁺ and Cu(HL)₂⁺, a deprotonated species, H_{−1}Cu(HL)₂⁺, presumably containing an intramolecular O...O hydrogen bridge between the oxime oxygen atoms, was formed with *1* and *2* (HL is a neutral oxime ligand). With ligand *3*, the deprotonated complexes found were H_{−6}Cu₄(HL)₄²⁺ and H_{−2}Cu₂(HL)₂²⁺. The composition of the dominating tetranuclear species was confirmed by conductometric measurements and, from the results obtained in the solid state, it is suggested that it corresponds to the formula Cu₄L₂(L-H)₂²⁺ in which all the oxime protons and two of the four amide protons are deprotonated.

In earlier publications, we have reported the equilibrium and structural properties of complexes formed between the 2-aminoacetamidoxime ligands *1*–*3* and nickel(II).^{1,2} In aqueous solution, the potentiometric data were consistent with the formation of stepwise octahedral complexes Ni(HL)_{*n*}²⁺ with *n* = 1,2,3 (HL = *1* and *2*) and *n* = 1,2 (HL = *3*), and a deprotonated, presumably square planar species Ni(HL)L⁺ (HL = *1* and *2*) with an intramolecular O...O hydrogen bridge between the oxime oxygen atoms.



In all these complexes, coordination to the metal probably occurred via the 2-amino and oxime nitrogen atoms without any direct participation of the amidoxime NH₂ group. Though the suggestion concerning the mode of coordination

was tentative, it was strongly supported by X-ray diffraction analyses of the complexes in their solid state. With ligand *3*, the formation of the complexes Ni(HL)₃²⁺ and Ni(HL)L⁺ was suppressed and the dominating species in alkaline solution had the composition H_{−6}Ni₄(HL)₄²⁺. A structure like this would allow the amide NH₂ function to be involved in the coordination either as such or in the form of the deprotonated NH[−] anion. The potentiometric data alone did not provide sufficient evidence to establish the nature of the deprotonated groups and, because no auxiliary information was available, the actual structure of the tetranuclear complex remained uncertain.

In this paper, we report the complex formation between the ligands *1*–*3* and copper(II) in aqueous sodium perchlorate solutions. The starting point for our work was the finding that the solid complex obtained from an alkaline solution of Cu(ClO₄)₂ and *3* has the composition H_{−6}Cu₄(HL)₄²⁺, i.e. a composition identical to the

aforementioned nickel species. Since the X-ray analysis of the solid compound revealed the presence of deprotonated NH^- groups in the structure, a comparison of the equilibrium data for the nickel and copper systems was of great interest.

Experimental

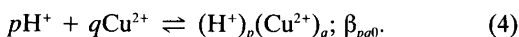
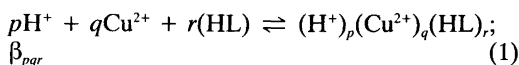
2-Aminoacetamidoxime 1, 2-(methylamino)acetamidoxime 2, and 2-(dimethylamino)-acetamidoxime 3 were prepared and purified as described earlier.¹ The following complexes were isolated in the solid state by evaporation from solution and recrystallization from water, and used as reagents in subsequent potentiometric measurements: $[\text{Cu}(\text{HL})_2](\text{ClO}_4)_2$, HL = 1, violet-blue monoclinic crystals, cell dimensions: $a = 8.160(4)$, $b = 7.904(3)$, $c = 11.527(6)\text{\AA}$, $\beta = 96.02(4)^\circ$, $Z = 2$, F.W. = 440.4 (calc. 440.6); $[\text{Cu}(\text{HL})\text{L}]\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, HL = 1, violet-red orthorhombic crystals, cell dimensions: $a = 10.045(2)$, $b = 20.670(4)$, $c = 11.930(4)\text{\AA}$, $Z = 8$, F.W. = 351.1 (calc. 349.2); $[\text{Cu}_4\text{L}_2(\text{L}-\text{H})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, HL = 3, black-green monoclinic crystals, $C2/c$, cell dimensions: $a = 24.703(5)$, $b = 5.887(2)$, $c = 28.998(5)\text{\AA}$, $\beta = 126.50(1)^\circ$, $Z = 4$, F.W. = 937.3 (calc. 933.7). The details of the diffraction data will be published in a forthcoming paper.

Method. The cell arrangement for the emf measurements and the procedure used in calibrating the glass electrode were as described in Ref. 1. During the titrations, the total concentrations of copper(II), C_M , and ligand, C_L , were varied within the limits $0.003 \leq C_M \leq 0.017\text{ M}$ and $0.006 \leq C_L \leq 0.018\text{ M}$ for ligand 1, $0.004 \leq C_M \leq 0.010\text{ M}$ and $0.010 \leq C_L \leq 0.024\text{ M}$ for ligand 2 and $0.003 \leq C_M \leq 0.011\text{ M}$ and $0.007 \leq C_L \leq 0.021\text{ M}$ for ligand 3. The ligand to metal ratios varied between $1 \leq C_L/C_M \leq 6$.

In the presence of copper(II), the measurements were carried out at a constant C_L/C_M ratio and the hydrogen ion concentration, h , was varied by adding sodium hydroxide or perchloric acid to the solution. The starting solutions were prepared by weighing HL into the metal perchlorate solutions or weighing crystallized metal complexes into the ionic medium. Thus, a double control of the analytical concentrations of C_M and C_L was achieved. Owing to the formation of pre-

cipitates or very slow attainment of equilibria, the $-\log h$ ranges used in the calculations were restricted to the upper limits of ca. 9.0 (HL = 1), 8.9 (HL = 2), 5.7 (HL = 3, $I = 1.0\text{ M}$) and 7.1 (HL = 3, $I = 0.1\text{ M}$). The conductivities were measured with a Radiometer conductivity meter, model CDM3. The cell constant was determined by use of a standard aqueous solution of potassium chloride.

Data treatment. H^+ , Cu^{2+} and HL were chosen as components in evaluating the equilibrium constants. The general three-component equilibrium (1) and the two-component equilibria (2)–(4) are the following:



For protonation of the ligand (eqn. 2) in 1.0 M $\text{Na}(\text{ClO}_4)$, we made use of the results obtained earlier.¹ The corresponding values valid for 0.1 M $\text{Na}(\text{ClO}_4)$ were determined in this study and are given in Table 2. The acidities of the oxime groups in ligands 1–3 (eqn. 3) are so weak ($\text{p}k_a \geq 12.3$)¹ that they can be neglected here. For the binary hydrolytic equilibrium (eqn. 4), we used the results summarized by Baes and Mesmer.³ Inclusion of the proposed complexes (CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$) and equilibrium constants in the calculations showed that the Cu^{2+} hydrolysis was negligible under our conditions. In the calculation of the three-component systems, the binary equilibria were assumed to be exactly known and no attempts were made to adjust the respective equilibrium constants. The mathematical analyses of the experimental data were performed with the least-squares computer programs MINIQUAD-75⁴ and MINIQUAD-76A,⁵ which minimize the sum of the squares of residuals, $U = \Sigma(\Delta C_M^2 + \Delta C_L^2 + \Delta C_H^2)$, where C_M , C_L and C_H are the total concentrations of copper(II), ligand and proton, respectively. The computations were performed on an Univac 1108 computer.

Calculations and results

The H^+ - Cu^{2+} - HL system with $HL = 1$ and 2. The schemes of complex formation were closely similar for ligands 1 and 2. In both systems, the solution changed from deep blue to violet with increasing basicity. With excess ligand, the potential readings were stable until a solid red-violet phase began to form near the inflection point that appeared in the titration data when $C_H/C_M = -1$ (the total concentrations of protons, C_H , were calculated over the zero level HL , H_2O , Cu^{2+}).

The MINQUAD refinements on the total data sets (7 titrations and 300 data points for system 1, 9 titrations and 300 points for 2) clearly showed the formation of the stepwise complexes $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$ and the deprotonated species $H_{-1}Cu(HL)_2^+$. Any of these complexes can exist as the major component in the system; the standard deviations within their stability constants were rather low [$3\sigma(\log\beta_{pqr}) < 0.014$]. Since none of the additional complexes tested in subsequent calculations was found to make a significant contribution to the model, we accordingly proposed the set of these three complexes as the final equilibrium model for both systems.

The calculations terminated in the R values 0.0018 and 0.0013 for ligands 1 and 2, respectively, indicating a good fit in both systems. The final stability constants with their standard deviations are given in Table 1.

The H^+ - Cu^{2+} - HL system with $HL = 3$. The studies with ligand 3 in 1.0 M $NaClO_4$ indicated that only mononuclear complexes $Cu(HL)_n^{2+}$ ($n = 1, 2$) exist in acid solutions ($-\log h < 5.5$). The deviations from the conventional Bjerrum plot, $\bar{n}(\log[HL])$, occurring in less acid solutions further indicated the formation of hydroxo and/or polynuclear species as well. Because of the ap-

pearance of precipitates, however, the number of data points obtainable from higher $-\log h$ values was too small to allow the composition(s) of these additional complex(es) to be established. The data used to determine the stability constants of the complexes $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$ in 1.0 M $NaClO_4$ were from 5 titrations and comprised 227 experimental points obtained in the mononuclear $Cu(HL)_n^{2+}$ region of the $\bar{n}(\log[HL])$ plot. The results are included in Table 1.

The upper $-\log h$ limit in the measurements was set by the relatively low solubility of the green complex $H_{-1.5}Cu(HL)(ClO_4)_{0.5}$ identified in its crystalline form as $[Cu_4L_2(L-H)_2](ClO_4)_2 \cdot H_2O$ (see Discussion). Since lowering of the perchlorate ion concentration was found to raise the onset of precipitation to considerably higher $-\log h$ values, we studied the complexation between Cu^{2+} and ligand 3 in 0.1 M $NaClO_4$ also. In this way, it was possible to collect more experimental data from the most interesting areas where polymerization reactions occur.

Inspection of the new titration data revealed a distinct potential jump when C_H/C_M approached -1.5 , after which a dark green precipitate separated. This implied that some predominating hydrolyzed complex which was at least dinuclear formed up to this equivalence point. Formation of the tetranuclear complex $H_{-6}Cu_4(HL)_4^{2+}$, established in the solid state, was expected in the buffer range involved, yet when only one new species in addition to $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$ was assumed in MINQUAD Acta Chem. Scand. calculations, the best fit to the experimental data ($R = 0.0032$) was obtained for the dinuclear species $H_{-3}Cu_2(HL)_2^+$ with $\log(\beta_{-322} \pm 3\sigma) = 0.25 \pm 0.03$. The agreement with the best tetranuclear species $H_{-6}Cu_4(HL)_4^{2+}$ was considerably lower ($R = 0.0060$). When β_{-322} and β_{-644} were co-varied, the latter species was insignificant. The same proved to be true for all other deprotonated and polynuclear complexes included in the model $Cu(HL)^{2+}$, $Cu(HL)_2^{2+}$ and $H_{-3}Cu_2(HL)_2^+$.

The search for the best model was next performed as a covariation between $H_{-6}Cu_4(HL)_4^{2+}$ and a new $H_pCu_q(HL)_r^{p+2q}$ species. In these calculations, the best fit of the data was found assuming $\log(\beta_{-644} \pm 3\sigma) = 3.27 \pm 0.03$ and $\log(\beta_{-222} \pm 3\sigma) = 4.98 \pm 0.03$ together with the mononuclear stepwise complexes $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$ ($R = 0.0026$). In this model, the tetranuclear species formed almost to 100% of C_M at

Table 1. Logarithmic values of the complex formation constants relating to the reaction $pH^+ + qCu^{2+} + r(HL) \rightleftharpoons (H^+)_p(Cu^{2+})_q(HL)_r$, $I = 1.0$ M $Na(ClO_4)$. The errors given are $3\sigma(\log\beta_{pqr})$.

p, q, r	Ligand 1	Ligand 2	Ligand 3
0, 1, 1	8.787 ± 0.005	8.108 ± 0.004	6.909 ± 0.005
0, 1, 2	16.824 ± 0.006	14.995 ± 0.006	11.894 ± 0.009
-1, 1, 2	10.247 ± 0.008	8.453 ± 0.014	

Table 2. Binary and ternary complexes in the system $H^+Cu^{2+}HL$, where $HL = 3$ and $l = 0.1$ M $Na(ClO_4)$. The formation constants are related to the reaction $pH^+ + qCu^{2+} + r(HL) \rightleftharpoons (H^+)_p(Cu^{2+})_q(HL)_r$.

p, q, r	Tentative structure	$\log(\beta_{pqr} \pm 3\sigma)$
1, 0, 1	H_2L^+	7.214 ± 0.004
2, 0, 1	H_3L^{2+}	8.565 ± 0.007
0, 1, 1	$[Cu(HL)]^{2+}$	6.602 ± 0.006
0, 1, 2	$[Cu(HL)_2]^{2+}$	11.284 ± 0.021
-2, 2, 2	$[Cu_2L_2]^{2+}$	4.98 ± 0.03
-6, 4, 4	$[Cu_4L_2(L-H)_2]^{2+}$	3.27 ± 0.03

the end of the titrations, while $H_{-2}Cu_2(HL)_2^{2+}$ appeared in the calculations with a presence of less than 15% relative to C_M in the area near $C_H/C_M \sim 0$. The improvement in the R factor relative to the three-component system, however, was statistically insignificant. Since none of the additional complexes tested was found to yield any significant improvement on the four-component model, and with no support obtained from χ^2 statistics,⁴ we were forced to conclude that the two sets of complexes describe our potentiometric data for the H^+Cu^{2+} -ligand 3 system equally well.

To allow a choice between the two alternative models, we performed conductometric measurements on a series of solutions in which different amounts of solid tetrameric complex $[Cu_4L_2(L-H)_2]Cl_2$ were dissolved (without any neutral salt present). The complex was added as chloride rather than perchlorate because of the greater solubility of the former. The values of the stability constants obtained in the calculations (Table 2) indicated that the nearly neutral, green solutions formed contained almost exclusively the complex $H_{-3}Cu_2(HL)_2^+$ or the complex $H_{-6}Cu_4(HL)_4^{2+}$.

A single determination of the equivalent conductivity Λ_e is not sufficient to decide between the complexes $H_{-3}Cu_2(HL)_2^+$ and $H_{-6}Cu_4(HL)_4^{2+}$. However, the change in Λ_e with concentration is a direct function of the charge of the ions involved⁶⁻⁸ and the difference between 1:1 and 2:1 electrolytes should be obvious from plots derived from the Onsager equation.

$$\Lambda_0 - \Lambda_e = (A + wB\Lambda_0)c^{\frac{1}{2}} \quad (5)$$

The measurements of the conductivity of $[Cu_4L_2(L-H)_2]Cl_2$ were made in the concentration range $7.5 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ M. The conductivity, Λ_c , was first plotted as a function of $c^{\frac{1}{2}}$, where c is the equivalent concentration. Then Λ_e was extrapolated to infinite dilution to obtain Λ_0 . In Fig. 1, the factor $(\Lambda_0 - \Lambda_e)$ is plotted against $c^{\frac{1}{2}}$ for $[Cu_4L_2(L-H)_2]Cl_2$ along with some other known electrolytes. Although some variation is seen between the slopes of different electrolytes of the same ionic type, it is clear that, when dissolved in water, the tetranuclear complex did not dissociate into dimeric species but retained its nature as a 2:1 electrolyte.

On the basis of the results from both potentiometric and conductometric studies, we suggest that the species $H_{-3}Cu_2(HL)_2^+$ represents a type of average complex and the more plausible equilibrium model in the H^+Cu^{2+} -ligand 3 system comprises the species $Cu(HL)^{2+}$, $Cu(HL)_2^{2+}$, $H_{-3}Cu_2(HL)_2^+$ and $H_{-6}Cu_4(HL)_4^{2+}$. The stability constants of these complexes determined in 0.1 M $NaClO_4$ (7 titrations, 300 data points) as well as the values of the protonation constants of 3 determined separately in 0.1 M $NaClO_4$ (4 titrations, 168 experimental points) are shown in Table 2. The relative distribution of copper(II) among the different complexes is seen in Fig. 2 for two different compositions of the system.

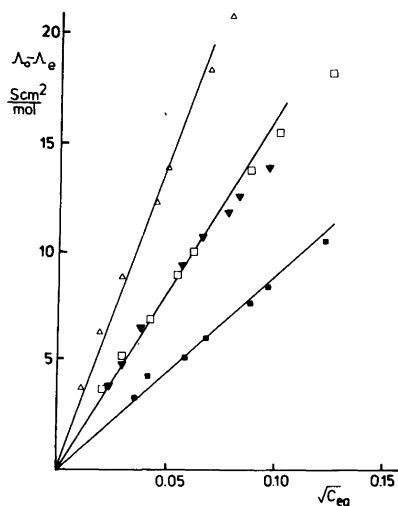


Fig. 1. The behaviour of $\Lambda_0 - \Lambda_e$ for different electrolytes in water. ■ KCl, □ $CaCl_2$, ▼ $[Cu_4L_2(L-H)_2]Cl_2$, △ $LaCl_3$.

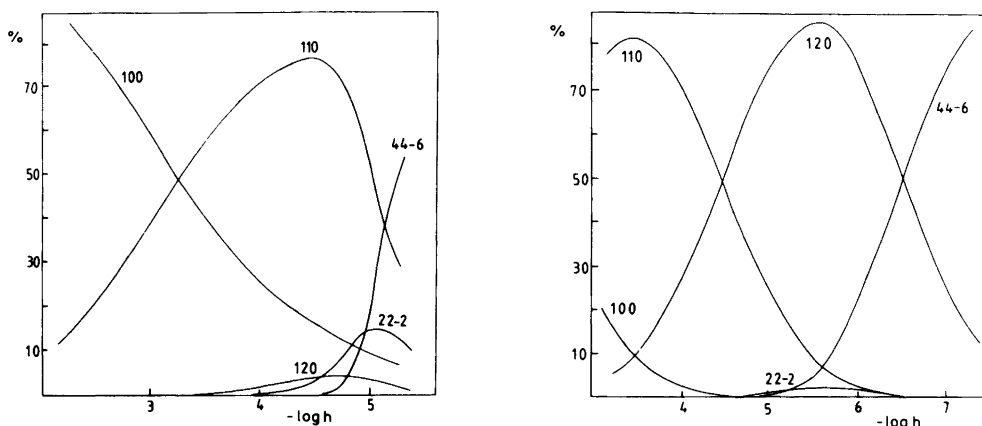


Fig. 2. Percentage distribution of copper among different complexes versus $-\log h$ in the H^+ - Cu^{2+} -ligand **3** system with $C_M = 5.67$ mM and $C_L = 5.67$ mM (left) and with $C_M = 2.81$ mM and $C_L = 16.9$ mM (right). $I = 0.1$ M $Na(ClO_4)$.

Discussion

The equilibrium analyses of the present systems confirm our earlier finding that the number of methyl groups on the amino nitrogen atom of the ligands **1**–**3** can have a decisive effect on their complex formation reactions. With **1** and **2**, the modes of complexation are identical, besides the blue complexes $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$, a violet mononuclear hydrolyzed species $H_{-1}Cu(HL)_2^+$ is formed. The two stepwise complexes are also found with **3** but in this case, the hydrolysis results in a very stable, green tetranuclear complex $H_{-6}Cu_4(HL)_4^{2+}$ evidently formed via the dimeric species $H_{-2}Cu_2(HL)_2^{2+}$. Thus the schemes of complex formation between copper(II) and ligands **1**–**3** are basically the same as those found earlier with nickel(II).¹

In the structures $Cu(HL)^{2+}$ and $Cu(HL)_2^{2+}$ the ligands **1**–**3** are all probably bonded to copper(II) through the amine and oxime nitrogen atoms. This coordination has been verified in the solid state for the nickel(II) complexes of **1** and **3**, as well as for several copper(II) complexes of comparable ligands.⁹ In aqueous solution, the function of the amino nitrogen as a donor atom is evident from the values of the stability constants of the complexes which decrease with increasing N-methylation: $1 > 2 > 3$.

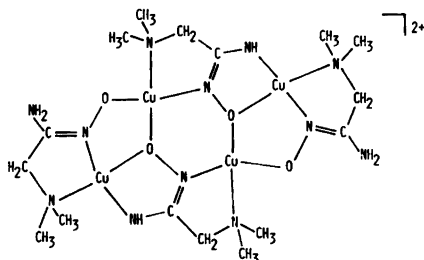
With **1** and **2**, deprotonation of $Cu(HL)_2^{2+}$ occurs in neutral $-\log h$ ranges and the acidity constants of the complexes are very similar: the cal-

culated pK_a values are 6.58 ($HL = 1$) and 6.54 ($HL = 2$), which are comparable to those found in the corresponding nickel(II) systems (6.57 and 7.10).¹ Evidently dissociation of $Cu(HL)_2^{2+}$ takes place at the coordinated oxime group. Removal of the oxime proton allows rearrangements in the coordination sphere and a bis complex, $H_{-1}Cu(HL)_2^+$, stabilized by a strong intramolecular O...O hydrogen bridge between the *cis* oxime oxygens may be formed. In that event, the complexes can be written $Cu(HL)L^+$. A vast number of such complexes have been characterized with nickel(II) in the solid state^{2,9-12} and are not uncommon with copper(II) either.^{9,13} Although, in the case of copper(II), these complexes frequently exist in the dimeric form, under our experimental conditions, no such species were found.

The unusual behaviour of **3** towards hydrolysis can be attributed to steric factors. Examination of the molecular models shows that the formation of a complex $Cu(HL)L^+$ with intramolecular O...O hydrogen bridge, as proposed for **1** and **2**, would result in a considerable strain in the structure because of the spatial requirements of the *cis*- $N(CH_3)_2$ groups and, on the other hand, of the electrostatic repulsion of the *cis* oxime oxygens.

The most interesting complex to emerge from this study was the tetranuclear species $H_{-6}Cu_4(HL)_4^{2+}$ with $HL = 3$, which started to form when C_H/C_M became negative and caused a green colouration of the solution. The dark green

crystalline compound could also be isolated as perchlorate or chloride from solutions where $C_M/C_L = 1$ and $C_H/C_M = -1.5$. When submitted to X-ray analysis a complex moiety was found¹⁴ with the structure shown in formula 2.



In this structure, the oxygen atoms from the deprotonated oxime groups and the nitrogen atoms from two deprotonated amide $-NH^-$ groups are involved in square planar coordinations about copper atoms. The unusual feature of this tetrameric compound is that the four copper atoms are in the planar arrangement with respect to each other. It is also the first amidoxime structure for which deprotonation of the amide function has been verified. The tetrameric complex built up in this way seems to be very rigid and characteristic for the ligand type. Accordingly, the aqueous species $H_{-6}Cu_4(HL)_4^{2+}$ should preferably be written as $Cu_4L_2(L-H)_2^{2+}$ and not in the form of a mixed hydroxo complex. It is reasonable to assume that the corresponding four-coordination is also present in the structure of the nickel(II) complex of the composition $H_{-6}Ni_4(HL)_4^{2+}$ found in our earlier work.¹

With regard to the dimeric complex species $H_{-2}Cu_2(HL)_2^{2+}$ which exists as an intermediate between the mononuclear and tetrameric species, it

is probably formed through the deprotonation of the oxime groups, and subsequent bonding of two copper atoms via two NO oxime bridges. Such a six-membered $(CuNO)_2$ ring is frequently found in the dimeric copper(II) compounds of comparable ligands¹⁵ and it also appears as the central ring in the structure of the solid tetrameric complex.

References

1. Saarinen, H., Orama, M., Raikas, T. and Korvenranta, J. *Acta Chem. Scand. A* 37 (1983) 631.
2. Saarinen, H., Korvenranta, J., Orama, M. and Raikas, T. *Acta Chem. Scand. A* 38 (1984) 265.
3. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations*, Wiley, New York 1976, p. 264.
4. Gans, P., Vacca, A. and Sabatini, A. *Inorg. Chim. Acta* 18 (1976) 237.
5. Micheloni, M., Sabatini, A. and Vacca, A. *Inorg. Chim. Acta* 25 (1977) 41.
6. Geary, W. J. *Coord. Chem. Rev.* 7 (1971) 81.
7. Feltham, R. D. and Hayter, R. G. *J. Chem. Soc.* (1964) 4587.
8. Hayter, R. G. and Humic, F. S. *Inorg. Chem.* 2 (1963) 306.
9. Chakravorty, A. *Coord. Chem. Rev.* 13 (1974) 1.
10. Fair, C. K. and Schlemper, E. O. *Acta Crystallogr. B* 34 (1978) 436.
11. Hussain, M. S. and Schlemper, E. O. *Inorg. Chem.* 18 (1979) 2275.
12. Endres, H., Jannack, T. and Prickner, B. *Acta Crystallogr. B* 36 (1980) 2230.
13. Gavel, D. P. and Schlemper, E. O. *Inorg. Chem.* 18 (1979) 283.
14. Korvenranta, J. and Saarinen, H. *To be published*.
15. Näsäkkälä, M., Saarinen, H., Korvenranta, J. and Näsäkkälä, E. *Acta Chem. Scand. A* 35 (1981) 569, and references therein.

Received January 28, 1986.