Studies on Tetranuclear Metal Complexes of 2-(Dialkylamino)-acetamidoxime [R₂NCH₂C(NH₂)NOH]. Formation of Aqueous Copper(II) and Nickel(II) Complexes (R = C₂H₅) and X-Ray Structural Characterization of the Solid Copper(II) Complexes (R = CH₃, C₂H₅)

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Saarinen, H., Orama, M. and Korvenranta, J., 1989. Studies on Tetranuclear Metal Complexes of 2-(Dialkylamino)acetamidoxime [R₂NCH₂C(NH₂)NOH]. Formation of Aqueous Copper (II) and Nickel(II) Complexes (R = C₂H₅) and X-Ray Structural Characterization of the Solid Copper(II) Complexes (R = CH₃, C₂H₅). – Acta Chem. Scand. 43: 834–841.

The complex formation equilibria of copper(II) and nickel(II) with 2-(diethylamino)-acetamidoxime (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. With each metal the best model was that including the mononuclear complex $M(HL)^{2+}$ together with the hydrolyzed dinuclear $H_{-2}M_2(HL)_2^{2+}$ and tetranuclear $H_{-6}M_4(HL)_4^{2+}$ species (M = Cu, Ni). Crystal structures were determined by an X-ray diffraction method for the complexes $[Cu_4L_2(L\text{-}H)_2](ClO_4)_2$ and $[Cu_4Y_2(Y\text{-}H)_2](ClO_4)_2 \cdot H_2O$ [HY = 2-(dimethylamino)acetamidoxime]. The crystals of the former compound are monoclinic, $P2_1/n$, $a = 12.627(4)$, $b = 7.344(2)$, $c = 22.250(9)$ Å, $\beta = 90.38(3)°$, $Z = 2$. The latter compound is monoclinic, $C2/c$, $a = 24.703(14)$, $b = 5.887(5)$, $c = 28.998(15)$ Å, $\beta = 126.50(4)°$, $Z = 4$. The two compounds are basically similar, consisting of centrosymmetric tetranuclear complex cations and perchlorate anions. In forming the tetramers the oxime groups and two of the four amide groups of the ligand molecules are deprotonated. The copper(II) atoms have a square-planar coordination environment in which each ligand is bound to copper(II) through its amino and oxime nitrogen atoms. The coordination of the two crystallographically independent copper(II) atoms is completed by an oximate oxygen atom and a nitrogen atom from a deprotonated amide group of another ligand (Cu 1), or by two oximate oxygens of the two other ligands in the tetramer (Cu 2). The complex moieties themselves are nearly planar, the maximum deviation of the coordinating atoms from the Cu₄ plane (symmetry required) being 0.08(1) Å (ligand L) and 0.37(1) Å (ligand Y). From comparison of the compositions of the tetranuclear complexes in the aqueous and solid phases it is concluded that deprotonation of the aqueous complexes originates from coordinated oxime and amide groups and that the formula $H_{-6}M_4(HL)_4^{2+}$ should be written as $[M_4L_2(L\text{-}H)_2]^{2+}$ rather than in the form of a mixed hydroxo complex.

In earlier investigations on the complex formation equilibria of copper(II) and nickel(II) with N-methylated 2-aminoacetamidoximes we showed that hydrolysis of the mononuclear metal complexes formed by 2-(dimethylamino)acetamidoxime (HY) gives an aqueous tetranuclear species of composition $H_{-6}M_4(HY)_4^{2+}$ (M = Cu, Ni) as major product.[1,2] Preliminary results obtained for the solid state suggested that the formula of the complex should be written $M_4Y_2(Y\text{-}H)_2^{2+}$, which means that all four oxime groups and two of the four amide groups are deprotonated on complexation. It was also proposed that the compounds possess a highly uncommon planar structure in which all metal ions and coordinating atoms are coplanar.[2]

The tendency of HY towards polynuclear complex formation has been attributed to the presence of the tertiary amino group in the ligand. By restraining the formation of

stable intramolecularly hydrogen-bonded bis complexes it facilitates a scheme of hydrolysis markedly different from that found for complexes with corresponding ligands containing primary or secondary amino groups.[2]

To find out whether the tetrameric complex moiety is characteristic for the N-dialkylated ligand type, we have now studied the complex formation of copper(II) and nickel(II) with 2-(diethylamino)acetamidoxime (HL) in aqueous solution. In this paper we will also summarize the results of X-ray structure determinations of the solid state tetranuclear complexes isolated from the aqueous Cu-HL and Cu-HY systems. Unfortunately, we failed in several attempts to obtain the tetranuclear nickel(II) complexes in the crystalline state and were unable to carry out X-ray diffraction analyses of these structures.

Experimental

Materials. Preparation of 2-(dimethylamino)acetamidoxime (HY) has been described earlier.[1] 2-(Diethylamino)-acetamidoxime (HL) was prepared similarly to HY, using 2-(diethylamino)acetonitrile as starting material. The product was further converted to its monohydrochloride with anhydrous HCl and was recrystallized from hot ethanol. The formula weight of the air-dried needles as determined by potentiometric titration was 182.0 (calc. 181.7 for $C_6H_{15}N_3O \cdot HCl$).

The stock solutions of $CuCl_2$ and $NiCl_2$ were standardized against standard EDTA. The copper(II) content was also determined electrogravimetrically and the nickel(II) content by precipitation with dimethylglyoxime. The agreement between the different methods was within 0.1 %.

The black-green complexes of formulae $CuYH_{-0.5}$ $(ClO_4)_{0.5}$ $(H_2O)_{0.25}$ and $CuLH_{-0.5}$ $(ClO_4)_{0.5}$ were isolated in the solid state by adding copper(II) perchlorate to an aqueous solution of the respective ligand (1:1 molar ratios) and adjusting the pH of the resulting solution to about 6. The needle-like crystals used for X-ray diffraction analyses were obtained by recrystallization from water. The compound $CuLH_{-0.5}$ $Cl_{0.5}$ used in the conductometric measurements was obtained by slow evaporation of the aqueous solution containing HL, $CuCl_2$ and NaOH in molar ratio 1:1:1.5.

Potentiometric measurements and data treatment. The investigation was carried out as a series of titrations at 25 °C and in constant 1.0 M Na(Cl) medium. In our earlier studies on aqueous amidoxime complexes we used $NaClO_4$ as inert electrolyte.[1,2] The change here to NaCl was necessary because of the sparing solubility of the present complexes in perchlorate solutions. Nevertheless, the concentrations of the reactants that could be used in the measurements were still rather low, especially in the regions where polymerization reactions occur, and this lowered the accuracy of the equilibrium constants for the corresponding complexes to some extent.

The cell arrangement for the measurement of the free hydrogen ion concentration, h, was the following:

$$-RE \mid \text{equilibrium solution} \mid GE+$$
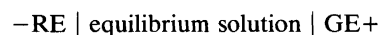
where GE denotes a glass electrode (Beckman, type 40495) and $RE = Hg,Hg_2Cl_2|1.0\ M\ NaCl|$. The procedure used in the calibration of the glass electrode was as described in Ref. 1.
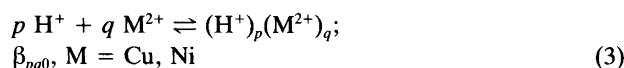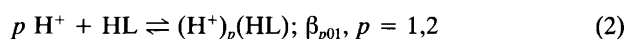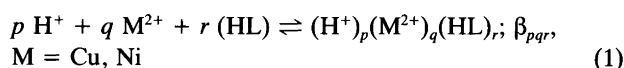
During the measurements, h was varied by adding sodium hydroxide or hydrochloric acid to the solution. The total concentrations of copper(II) or nickel(II), C_M, and ligand, C_L, were varied within the limits $0.001 \le C_M \le 0.011$ M and $0.004 \le C_L \le 0.020$ M, covering the ligand to metal ratio from 1 to 10.

The titrations carried out to determine the protonation constants of the ligand were made on solutions with $C_M = 0$. In the presence of metal ions the measurements were carried out at a constant C_L/C_M ratio. The starting solutions were generally prepared by weighing HL into the metal chloride solution. In some measurements crystalline copper(II) complexes $[Cu_4L_2(L-H)_2](ClO_4)_2$ and $[Cu_4L_2(L-H)_2]Cl_2$ were also used as starting reagent. In this way double control of C_M and C_L was achieved.

Owing to the formation of precipitates or uncertainty in attainment of equilibria, the $-\log h$ ranges used in the calculations were restricted to the upper limits of ca. 6 (M = Cu) and 9 (M = Ni).

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

$$p\ H^+ + q\ M^{2+} + r\ (HL) \rightleftharpoons (H^+)_p(M^{2+})_q(HL)_r;\ \beta_{pqr},$$
$$M = Cu, Ni \tag{1}$$

$$p\ H^+ + HL \rightleftharpoons (H^+)_p(HL);\ \beta_{p01},\ p = 1,2 \tag{2}$$

$$p\ H^+ + q\ M^{2+} \rightleftharpoons (H^+)_p(M^{2+})_q;$$
$$\beta_{pq0},\ M = Cu, Ni \tag{3}$$

No attention was paid to the possible formation of chloro complexes. The equilibrium constants for the binary protonation reactions (2) were determined from separate experiments, and these equilibria were assumed to be exactly known in the subsequent calculations. For the hydrolytic reactions (3) of the metal ions we used the results given in the literature.[3] Metal hydrolysis was found to be negligible under our conditions. Deprotonation of HL could be ignored because of the low acid strength of the oxime group $(pK_a > 12)$.[1] In this way all effects above the level of the protonation equilibria (2) could be treated as being due to the formation of the ternary metal complexes $(H^+)_p(M^{2+})_q$ $(HL)_r$.

The calculational problem is to find the sets of pqr-triplets and respective equilibrium constants β_{pqr} that give the best fit to the experimental data. The mathematical analyses were performed with the least-squares computer program SUPERQUAD,[4] which minimizes the sum of the squared residuals between the observed and calculated emf values

$$U = \Sigma\ w_i\ (E_i^{obs} - E_i^{calc})^2 \tag{4}$$

The weighting factor w_i is defined by the equation

$$w_i = 1/(\sigma_E^2 + \delta E_i/\delta V_i)\sigma_V^2 \tag{5}$$

where 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.

Conductometric measurements. The conductometric measurements were made with a Radiometer conductivity meter, model CDM 3. The cell constant was determined by

Table 1. Crystal data for [Cu$_4$L$_2$(L-H)$_2$]ClO$_4$)$_2$ and [Cu$_4$Y$_2$(Y-H)$_2$]ClO$_4$)$_2$ · H$_2$O (HL = 2-(diethylamino)acetamidoxime and HY = 2-(dimethylamino)acetamidoxime).

Formula	[Cu$_4$(C$_{24}$H$_{54}$N$_{12}$O$_4$)](ClO$_4$)$_2$	[Cu$_4$(C$_{16}$H$_{38}$N$_{12}$O$_4$)](ClO$_4$)$_2$ · H$_2$O
M	1027.84	933.62
Reflections used for cell refinement	22 (7<2Θ<24)	17 (9<2Θ<21)
Crystal system	Monoclinic	Monoclinic
a/Å	12.627(4)	24.703(14)
b/Å	7.344(2)	5.887(5)
c/Å	22.250(9)	28.998(15)
β/°	90.38(3)	126.50(4)
V/Å^3	2063(1)	3390(4)
Space group	P2$_1$/n	C2/c
Z	2	4
D$_c$/g cm^{-3}	1.655	1.829
D$_m$/g cm^{-3} (by flotation)	1.66	1.84
Dimensions/mm	0.15×0.15×0.30	0.20×0.25×0.40
μ(MoKα)/cm^{-1}	23.1	28.1
Scan rate/° min^{-1}	3.0–30.0	3.0–30.0
2Θ range/°	5–53	3–50
Unique reflections	4274	2889
Obsd. reflections I>2σ(I)	2676	1445
R=Σ||F$_o$| − |F$_c$||/Σ|F$_o$|	0.065	0.079
w	1.0/19.0 + F$_o$ +0.061F$_o$^{2}	1/σ^2(F$_o$)
Largest shift/esd	0.14	0.71
Δϱ/eÅ^{-3}	1.1	1.2

use of an aqueous potassium chloride standard. The measurements of conductivity of [Cu$_4$L$_2$(L-H)$_2$]Cl$_2$ were made in the concentration range 7.7·10^{-4} to 1.0·10^{-2} M. Solutions of KCl, CaCl$_2$ and LaCl$_3$ of known concentration were used to represent the behaviour of the electrolytes of different ionic type.

Crystal structure determination and refinements. Unit cell dimensions and diffraction data were measured with a Nicolet P3 four-circle diffractometer using graphite-monochromated MoKα radiation. Details of the X-ray diffraction studies are listed in Table 1.

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

The structures of the complexes were solved by direct methods using the MULTAN program.[5] Full-matrix least-squares refinement with the X-RAY system[6] was completed with anisotropic thermal parameters for the non-hydrogen atoms. Atomic scattering factors and corrections for anomalous dispersion were taken from Refs. 7 and 8. The hydrogen atoms were not included in the calculations since it was not possible to locate them all on the difference Fourier maps. The final cycles of refinement gave R values of 0.065 (R$_w$ = 0.076) and 0.079 (R$_w$ = 0.067) for [Cu$_4$L$_2$(L-H)$_2$](ClO$_4$)$_2$ and [Cu$_4$Y$_2$(Y-H)$_2$](ClO$_4$)$_2$ · H$_2$O, respectively. The rather high agreement indexes are attributed to one or both of the following factors: (i) the qualities of the crystals and (ii) disorder of the perchlorate groups. For the purpose

of this study the accuracy obtained can, however, be regarded as being sufficient.

Fractional coordinates for the non-hydrogen atoms in both complexes are given in Table 2, the bond lengths and angles of interest being collected in Table 3. The numbering of the atoms can be seen in Fig. 5. Lists of the structure factors and anisotropic temperature factors are available from the authors on request.

Equilibrium analyses

The Cu-HL system. SUPERQUAD calculations readily confirmed that the only mononuclear complex Cu(HL)$_2^{2+}$ formed under our conditions was Cu(HL)$^{2+}$. The distinct potential jump in the titration data when C$_H$/C$_M$ approached −1.5 (C$_H$ is calculated over the zero level HL, H$_2$O, M^{2+}) was a clear demonstration that some dominant polynuclear hydrolyzed species H$_p$Cu$_q$(HL)$_r^{p+2q}$ with the relation p/q = −1.5 was present in the system.

The search for the polynuclear/hydrolyzed complexes was similar to that performed in connection with HY.[2] The results of the calculations showed that the N-methylated and N-ethylated ligands behave identically: The best fit of the experimental data was obtained by assuming the presence of a tetranuclear complex of composition H$_{-6}$Cu$_4$ (HL)$_4^{2+}$ together with a dimeric species H$_{-2}$Cu$_2$(HL)$_2^{2+}$. None of the additional complexes tested made a significant contribution to the model. The analysis ended at s = 3.2 and χ^2 = 57, which values indicate a satisfactory fit. For the definitions of these statistics the reader is referred to the program.[4] No other parameters besides β$_{pqr}$ were varied in

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\mathring{A}^3 \times 10^3$).

Atom	[Cu$_4$L$_2$(L-H)$_2$](ClO$_4$)$_2$				[Cu$_4$Y$_2$(Y-H)$_2$](ClO$_4$)$_2\cdot$H$_2$O			
	x	y	z	U_{eq} [a]	x	y	z	U_{eq}
Cu1	456(1)	2133(2)	6280(1)	36(1)	5719(1)	475(3)	6028(1)	29(1)
Cu2	1275(1)	5582(2)	4567(1)	33(1)	5520(1)	5750(3)	4725(1)	27(1)
Ligand A								
O1	−1744(5)	3150(11)	6130(3)	52(4)	4531(4)	2454(15)	5840(4)	31(6)
N1	1014(5)	2254(12)	6460(4)	43(4)	5041(5)	965(17)	6135(4)	46(7)
N2	565(6)	594(10)	7048(3)	37(4)	6143(5)	−1600(18)	6726(5)	55(8)
N3	−2353(7)	1456(15)	7127(4)	55(5)	4668(5)	75(20)	6695(5)	52(9)
C1	−1332(7)	1467(14)	6935(4)	39(4)	5105(6)	−222(23)	6560(5)	39(9)
C2	−502(9)	495(18)	7325(5)	60(7)	5631(7)	−1974(25)	6845(7)	49(10)
C3	1035(9)	−1234(14)	6917(6)	56(6)	6365(8)	−3865(22)	6640(7)	49(12)
C4	438(15)	−2209(25)	6398(8)	103(13)				
C5	1314(11)	1622(17)	7459(5)	60(7)	6742(7)	−420(29)	7220(6)	65(12)
C6	1523(11)	726(19)	8061(5)	66(8)				
Ligand B								
O2	149(4)	3632(9)	5585(3)	40(3)	5268(4)	2772(14)	5442(4)	36(6)
N4	1086(5)	4096(11)	5261(4)	39(4)	5653(6)	3426(20)	5245(5)	53(9)
N5	2872(6)	4943(11)	4703(3)	45(5)	6419(5)	4550(19)	4932(4)	35(7)
N6	1854(6)	2325(12)	6010(4)	48(5)	6371(6)	511(22)	5877)6)	62(10)
C7	1922(7)	3331(14)	5521(5)	44(5)	6206(8)	2234(30)	5498(8)	76(25)
C8	2977(8)	3787(17)	5250(5)	57(7)	6718(19)	3002(42)	5389(10)	157(25)
C9	3308(9)	4033(19)	4144(6)	68(9)	6317(12)	3328(46)	4453(8)	166(23)
C10	2588(8)	2322(27)	4001(10)	123(14)				
C11	3468(15)	6726(17)	4780(5)	58(6)	6899(9)	6257(32)	5101(13)	149(23)
C12	2946(15)	7943(23)	5250(8)	29(11)				
Perchlorate ion								
Cl	4843(2)	678(4)	6564(1)	39(2)	8281(2)	1251(8)	1697(2)	61(3)
O3	3773(6)	748(12)	6733(4)	70(5)	8228(11)	−993(29)	1545(9)	165(21)
O4	5386(12)	−196(39)	7028(12)	231(21)	8360(8)	2547(39)	1364(7)	199(20)
O5	5027(14)	−396(36)	6109(12)	269(23)	7718(7)	1960(30)	1649(7)	141(15)
O6	5370(10)	2337(16)	6588(7)	118(10)	8869(6)	1549(24)	2239(6)	106(11)
Water molecule								
O7					5000	3890(24)	2500	56(11)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3$.

the calculations, and the errors in the measured potential and added volume were estimated as 0.1 mV and 0.02 ml, respectively.

The stability constants for the copper(II) complexes obtained (8 titrations, 272 data points) as well as the values of the protonation constants for HL determined separately (5 titrations, 185 experimental points, $s = 1.9$ and $\chi^2 = 29$) are given in Table 3.

In the Cu-HY system studied earlier we made use of the Onsager equation[9,10]

$$\Lambda_o - \Lambda_e = (A + w \, B\Lambda_o)\sqrt{C_{eq}} \qquad (6)$$

to allow a choice between the tetrameric H$_{-6}$Cu$_4$(HY)$_4^{2+}$ and dimeric H$_{-3}$Cu$_2$(HY)$_2^+$ species, which were found to describe the potentiometric data equally well. For checking purposes we followed the same practice in this investigation and made conductometric measurements on a series of solutions with different concentrations of the complex CuLH$_{-0.5}$Cl$_{0.5}$. Fig. 1 shows the difference between the conductivity at infinite dilution and the equivalent conductivity, $\Lambda_o - \Lambda_e$, plotted against the square root of the equivalent concentration C_{eq} for CuLH$_{-0.5}$Cl$_{0.5}$ and some other electrolytes. From the different slopes it can be reliably concluded that the complex is a 2:1 electrolyte, which is in accordance with the results given in the foregoing.

The Ni^{2+}-HL system. Collection of potentiometric data on the nickel(II) complexes was troublesome owing to the formation of precipitates that were difficult to observe in the dark green solutions and the slow kinetics of the reactions, especially in the -log h range in which polymerization occurs. Thus, stable potential readings were not obtained until 5–25 min after every change in the composition of the solution. The attainment of equilibrium was monitored by use of a high-sensitivity servo-recorder with which any systematic drift in the potential value with time can be revealed. To test the reproducibility and reversibility of equilibria, both forward (increasing -log h) and backward (decreasing -log h) titrations were performed.

Table 3. Selected interatomic distances (Å) and angles (°).[a]

	[Cu$_4$L$_2$(L-H)$_2$](ClO$_4$)$_2$	[Cu$_4$Y$_2$(Y-H)$_2$](ClO$_4$)$_2$·H$_2$O
Interatomic distances		
Cu1−N1	1.904(7)	1.90(1)
Cu1−N2	2.054(8)	2.04(1)
Cu1−N6	1.873(8)	1.90(2)
Cu1−O2	1.934(7)	1.93(1)
Cu2−N4	1.909(8)	1.92(1)
Cu2−N5	2.090(7)	2.05(1)
Cu2−O1'	1.9096(7)	1.89(1)
Cu2−O2'	1.917(6)	1.91(1)
Cu1−Cu2'	3.329(1)	3.334(3)
Cu2−Cu2'	3.861(1)	3.847(3)
N1−O1	1.347(10)	1.34(1)
N1−C1	1.272(12)	1.34(2)
N3−C1	1.361(12)	1.36(3)
N4−O2	1.431(9)	1.42(2)
N4−C7	1.325(12)	1.31(2)
N6−C7	1.318(13)	1.37(2)
Bond angles		
N1−Cu1−N2	84.8(3)	84.9(5)
N1−Cu1−O2	87.2(3)	86.3(5)
N6−Cu1−O2	83.4(3)	85.1(5)
O1−N1−C1	117.1(7)	119(1)
N4−Cu2−N5	83.1(3)	82.9(6)
O1'−Cu2−O2	90.3(3)	89.7(5)
N4−Cu2−O2'	101.1(3)	101.2(6)
O2−N4−C7	109.8(7)	111(1)

[a]Symmetry code:' 1−x, 1−y, 1−z.

The only mononuclear complex Ni(HL)$_r^{2+}$ found in the solution was Ni(HL)$^{2+}$. No inflection points could be observed in the titration curves for this system, and thus no
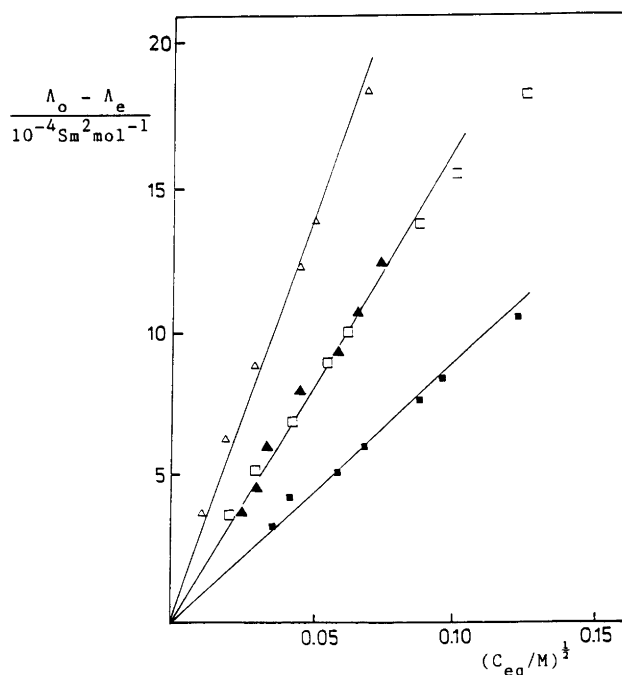

Fig. 1. The behaviour of Λ_o-Λ_e for electrolytes representing different electrolytes in water. ■ KCl, □ CaCl$_2$, ▲ [Cu$_4$L$_2$(L-H)$_2$]Cl$_2$, △ LaCl$_3$.

preliminary information on the nature of the other complexes was available. In systematic SUPERQUAD analysis, and in analogy with the Cu^{2+}-HL system, H$_{-6}$Ni$_4$(HL)$_4^{2+}$ was found to be the single additional complex which best explained the data. As with copper, the remaining systematic errors were easily corrected by assuming the presence of a single dinuclear species H$_{-2}$Ni$_2$(HL)$_2^{2+}$. The analysis, which was based on 200 experimental points from 6 forward and backward titrations terminated at s = 2.7 and χ^2 = 27, which indicate a good explanation of the data. In the calculations, the values of the adjustable error parameters and the refinement strategy were the same as in the Cu^{2+}-HL system. The stability constants of the complexes are given in Table 4.

Discussion

The present equilibrium analyses confirm our earlier assumption that deprotonation of the mononuclear complexes of copper(II) and nickel(II) with N-dialkylated 2-aminoacetamidoximes leads to polynuclear complex formation. A tetranuclear species of composition H$_{-6}$M$_4$(HL)$_4^{2+}$ has now been established as the main hydrolytic product of the complexation between both copper(II) and nickel(II) and the dimethyl- and diethyl-substituted ligands. As shown in Fig. 2, this complex is the predominant species in the alkaline regions of the titration curves.

Change from methyl groups (ligand HY) to ethyl groups

Table 4. Values of the complex formation constants relating to the reaction $p\text{H}^+ + q\text{M}^{2+} + r\,(\text{HL}) \rightleftharpoons (\text{H}^+)_p(\text{M}^{2+})_q(\text{HL})_r$ (HL = 2-(diethylamino)acetamidoxime, M = Cu, Ni) I = 1.0 M Na(Cl).

p, q, r	Proposed structural formula	$\log(\beta_{pqr} \pm 3\sigma)$
1, 0, 1	H_2L^+	8.138±0.004
2, 0, 1	H_3L^{2+}	9.839±0.009
0, 1, 1	$[\text{Cu(HL)}]^{2+}$	6.583±0.015
−2, 2, 2	$[\text{Cu}_2\text{L}_2]^{2+}$	5.38 ±0.04
−6, 4, 4	$[\text{Cu}_4\text{L}_2(\text{L-H})_2]^{2+}$	3.53 ±0.06
0, 1, 1	$[\text{Ni(HL)}]^{2+}$	2.21 ±0.04
−2, 2, 2	$[\text{Ni}_2\text{L}_2]^{2+}$	−8.34 ±0.05
−6, 4, 4	$[\text{Ni}_4\text{L}_2(\text{L-H})_2]^{2+}$	−28.96 ±0.04

(ligand HL) does, however, bring about some minor alterations in the complex formation schemes. With both metals the obvious difference is the suppression of the formation of the bis complex M(HL)_2^{2+}. This is hardly due to the difference in the ionic medium used in the investigations but can evidently be attributed to the greater steric requirements of the ethyl groups than the methyl groups. In going from $(\text{CH}_3)_2\text{N}$ to $(\text{C}_2\text{H}_5)_2\text{N}$ the decrease in stability of the complexes is already evident in the values of the formation constants for the mono complexes M(HL)^{2+}. The effect is expected and has been documented, for example, for N-alkylated ethylenediamine ligands.[11]

In this study the same dimeric $\text{H}_{-2}\text{M}_2\,(\text{HL})^{2+}$ composition was found for the first hydrolytic complex of the two metals. This is in agreement with the results obtained for the complex formation between Cu^{2+} and HY; however, in the Ni^{2+}-Hy system the mononuclear species $\text{H}_{-1}\text{Ni(HY)}_2^+$ was found instead.[1] The difference is clearly related to the fact that no detectable amounts of the parent undissociated bis complex Ni(HL)_2^{2+} are found in the case of the diethylated ligand.

The crystal structures determined here are essentially similar, consisting of tetranuclear $\text{Cu}_4\text{L}_2(\text{L-H})_2^{2+}$ and Cu_4Y_2 $(\text{Y-H})_2^{2+}$ complex cations and discrete perchlorate anions. With ligand Y, uncoordinated water molecules are also present in the structure. Stereoscopic views of the molecular packing of the compounds are shown in Figs. 3 and 4.

The ionic charge of the complex unit necessitates the dissociation of six protons for each four ligand molecules. Clearly, four of them are the oxime protons of the four HL and HY ligands, and the remaining two derive from deprotonation of two of the amide NH_2 groups.

The reason for the different amide functions of the separate ligands becomes evident from the schematic illustration of the structures shown in Fig. 5. The two crystallographically independent copper(II) atoms are seen to have different coordination arrangements. The coordination about Cu 1 is square-planar with the CuN_3O plane formed by the amine and oximate nitrogen atoms from one ligand (A) and the oximate oxygen and amide nitrogen of the deprotonated amide group of the second ligand (B). The coordination about Cu 2 is also square-planar, but in this case the plane is CuN_2O_2 made up of the amine and oximate nitrogens of ligand B and the oximate oxygens from the symmetry-related ligands A' and B'. Thus, the amide NH_2 group of ligand A does not participate in the coordination and is preserved unaltered, while the same group in ligand B is bonded to the metal and upon removal of a proton occurs in the form of the negative -NH^- donor group.

In forming the coordination network, the contribution of the oximate groups of the ligands is decisive: each nitrogen and oxygen atom of the oximate anion plays an active role in the coordination. The NO group of ligand A bridges two
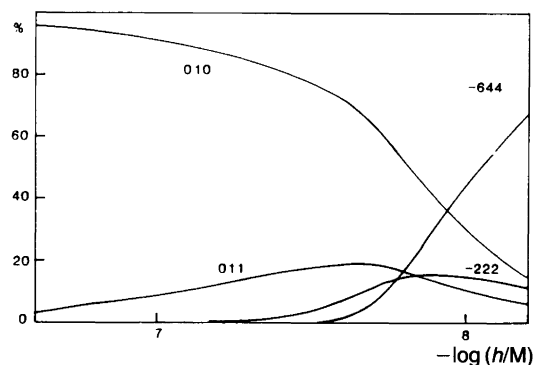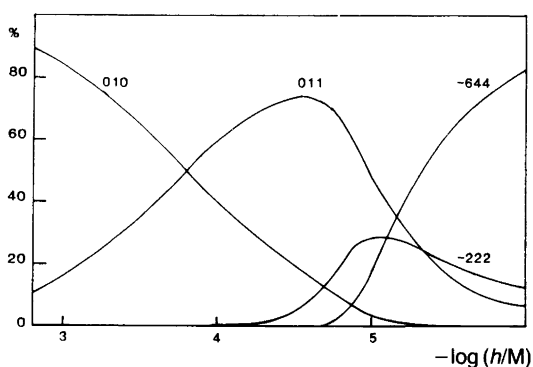

Fig. 2. Percentage distribution of copper(II) (left) and nickel(II) (right) among different $\text{H}_p\text{M}_q(\text{HL})_r^{(2q+p)+}$ complexes versus -log h (C_M = 5 mM and C_L = 10 mM).
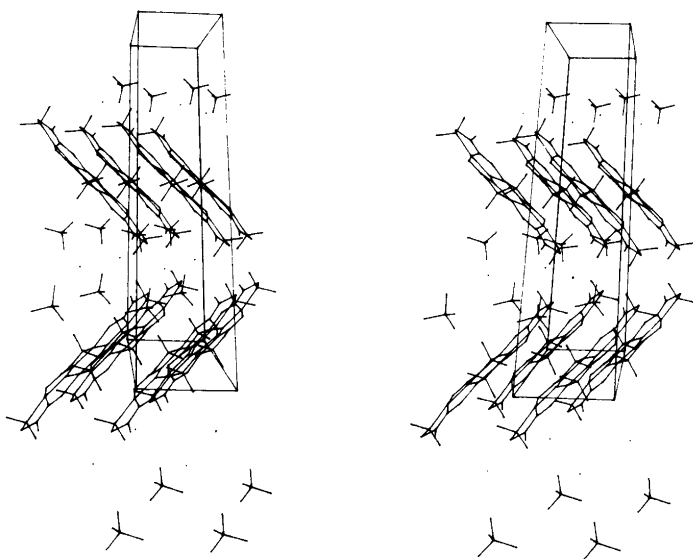
Fig. 3. Stereoscopic view of the molecular packing of
$[Cu_4Y_2(Y\text{-}H)_2](ClO_4)_2 \cdot H_2O$ with the hydrogen atoms omitted.

copper(II) atoms, while that of ligand B serves as a link between three copper(II) atoms.

The vast majority of known tetranuclear copper(II) complexes have cubane-like or step-like structures, which can be thought of as two dimers joined together through longer bonds. Such is not the case here; no smaller fragments can be distinguished within the tetramer, and it adopts a configuration that is nearly planar, the maximum deviations of the coordinated atoms from the symmetry-imposed Cu_4 plane being 0.37(1) Å for ligand Y and 0.08(1) Å for ligand L (Table 5). The unique planarity and the several possibilities for magnetic coupling between the copper(II) atoms make the complexes suitable model compounds for studying in-plane exchange interactions. Characterization of the magnetic properties of the complexes is in progress in our laboratory.

In deciding upon the structures of the different aqueous complexes there can be little doubt about the mononuclear

species $M(HL)^{2+}$. Comparison of the values of the complex formation constants with those reported for similar compounds for which structural information is available shows that HL acts as a bidentate ligand and that coordination to the metal is through the oxime and amine nitrogens.[12]

In formation of the dinuclear species $H_{-2}M_2(HL)_2^{2+}$, deprotonation would plausibly occur from the coordinated oxime groups rather than from the coordinated water molecules. The resulting dinuclear oximato complex most probably would contain a six-membered $M_2N_2O_2$ ring. Such a ring system is frequently found in dimeric copper(II) complexes with oxime ligands, and is not uncommon in nickel(II) complexes.[12,13] It may be noted that the $Cu_2N_2O_2$ ring is also present as a central ring in the tetranuclear structure in Fig. 5.

In principle, the crystal structure determinations of the present tetranuclear copper(II) complexes give no direct information about the structure of the aqueous species.
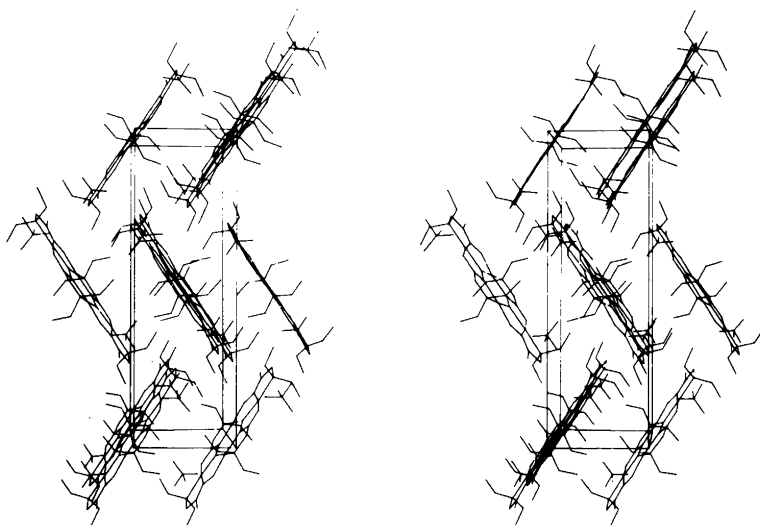

Fig. 4. Stereoscopic view of the molecular packing of $[Cu_4L_2(L\text{-}H)_2](ClO_4)_2$ with the hydrogen atoms omitted.
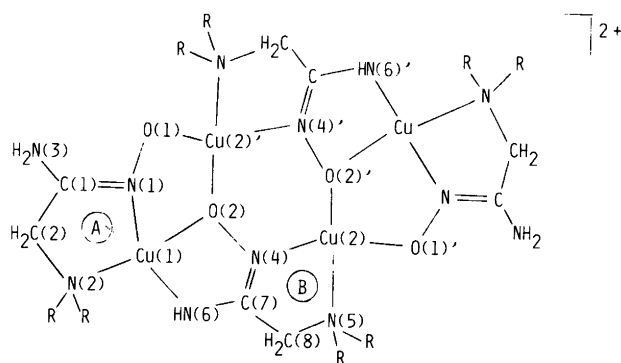
Fig. 5. Schematic representation of the complex ion showing numbering of the atoms. $R = CH_3$ and C_2H_5.

is no evidence to suggest that it does not occur in the aqueous phase as well.

Among other plausible formulations for the aqueous tetramers, the ternary hydroxo species $Cu_4(OH)_2L_4^{2+}$ and $Ni_4(OH)_4(HL)_2L_2^{2+}$ would seem most reasonable. Such compositions would be in accord with the close connection frequently found between the binary metal hydrolysis and ternary hydrolytic complexes formed in a system.[15,16] With the ligand L, however, the hydroxo complex alternatives are highly improbable, since the differences in the stereochemistries of copper(II) and nickel(II) complexes make it unlikely that the presence of structures with dominant binary hydrolytic cores $Cu_2(OH)_2^{2+}$ and $Ni_4(OH)_4^{4+}$ would give rise to complexes of the same tetranuclear $H_{-6}M_4(HL)_4^2$ composition.

Neither is it possible to establish the source of the dissociated protons in $H_{-6}M_4(HL)_4^{2+}$ from potentiometric data. The identical complex formation schemes for nickel (II) and copper(II), and the compositional similarity of the tetranuclear $H_{-6}M_4(HL)_4^{2+}$ species with the solid copper(II) complexes, however, strongly suggest that the formulae of the aqueous compounds should be written as $[Cu_4L_2 (L\text{-}H)_2]^{2+}$ and $[Ni_4L_2(L\text{-}H)_2]^{2+}$.

No comparisons of the equilibrium constants for the present tetramers with the values for similar complexes of known structure can be made. Nevertheless, the high thermodynamic stabilities of the complexes of this study are clearly due to the presence of an extensive ring system. Certainly the M_4L_2 (L-H)$_2^{2+}$ structure shown in Fig. 5, with its eight five-membered chelate rings in addition to the six-membered central ring, would qualify as a compound containing an extensive ring system. A complex unit like this is apparently very specific for the ligand type, and there

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Table 5. Deviation of the coordinated atoms (Å) from the Cu1Cu2Cu1'Cu2' plane.

Atom	$[Cu_4L_2(L\text{-}H)_2](ClO_4)_2$	$[Cu_4Y_2(Y\text{-}H)_2](ClO_4)_2 \cdot H_2O$
N1	0.064(9)	0.186(10)
N2	0.081(8)	0.374(11)
N4	−0.030(8)	−0.072(12)
N5	0.051(8)	0.078(11)
N6	−0.004(6)	−0.054(14)
O1	0.059(8)	0.184(10)
O2	−0.044(7)	−0.121(9)