

Equilibrium and Structural Studies on Metal Complexes of Oxime Ligands. Formation of Copper(II) and Nickel(II) Complexes of Pyridine-2-carboxamidoxime and Pyridine-2-acetamidoxime in Aqueous Solution

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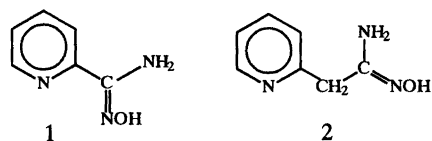
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Orama, M. and Saarinen, H., 1996. Equilibrium and Structural Studies on Metal Complexes of Oxime Ligands. Formation of Copper(II) and Nickel(II) Complexes of Pyridine-2-carboxamidoxime and Pyridine-2-acetamidoxime in Aqueous Solution. – Acta Chem. Scand. 50: 1087–1091 © Acta Chemica Scandinavica 1996.

The protonation and complex formation equilibria of pyridine-2-carboxamidoxime (HL=1) and pyridine-2-acetamidoxime (HL=2) with copper(II) and nickel(II) ions were studied at 25 °C in aqueous 0.1 mol dm⁻³ NaCl solution by potentiometric titration. Experimental data were analysed with respect to the complexes formed and their stability constants, by using the least-squares computer program SUPERQUAD. In the ligand 1 systems the data for copper(II) can be explained in terms of the mononuclear binary complexes Cu(HL)_r²⁺ (r=1, 2) and Cu(HL)L⁺, and the data for nickel(II) in terms of the stepwise binary complexes Ni(HL)_r²⁺ (r=1, 2, 3) together with a series of hydrolysed species H_pNi(HL)_r^{2+p}, where r=2, 3 and -p=1, 2, 3. With ligand 2 the best model for copper(II) was that including the mononuclear complexes Cu(HL)_r²⁺ (r=1, 2) and the dimeric species H₋₂Cu₂(HL)₂²⁺, and the best model for nickel(II) consisted of the mononuclear complexes Ni(HL)_r²⁺ (r=1, 2) and Ni(HL)L⁺ together with the dimeric species H₋₃Ni₂(HL)₂⁺. The effect of py substituent in amidoxime compounds was studied by comparing the complex models with those reported earlier for similar aminoamidoxime systems, and it is concluded that the amide group of these py-substituted ligands does not take part in the coordination to the metal.

In our earlier equilibrium and structural studies on metal complexes, we have shown that aminoamidoximes of the type RR'N(CH₂)_nC(NH₂)NOH have a pronounced tendency to form stable tetra- and pentanuclear complexes with copper(II) and nickel(II) ions.¹⁻³ In these polynuclear structures the amino, oxime and amide nitrogens as well as the oxime oxygen are coordinated to the metal. The different nuclearity of the complexes seems to depend on the number of alkyl groups on the amino nitrogen and on the value of *n*, i.e. on the length of the alkyl chain between the oxime and amino nitrogen donor atoms.

We have now extended our studies to find the aqueous complexation models of copper(II) and nickel(II) with the amidoxime ligands 1 and 2, which contain aromatic



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pyridine nitrogen in place of the amino nitrogen donors of previously investigated compounds.¹⁻³ Both of the ligands are new for equilibrium studies. It is interesting, however, that pyridine-2-aldoxime, which disregarding the amide function is structurally very similar to 1, forms highly stable trinuclear copper(II) complexes characterized by the presence of Cu₃O and Cu₃OH central cores both in aqueous solution as well as in the solid state.⁴⁻⁶

With nickel(II), on the other hand, the same ligand shows no tendency towards polymerization and all aqueous complexes verified have been members of the mononuclear series Ni(HL)_r²⁺ (r=1, 2, 3) or deprotonated species derived from these.⁷ Thus it was not easy to predict the nature of the possible polynuclear complexes in the present systems from the results of previous studies on comparable ligands.

Experimental

The amidoximes were prepared by reaction of the corresponding nitriles with hydroxylamine.

Pyridine-2-carboxamidoxime (1) was synthesised by refluxing a suspension of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.2 mol), Na_2CO_3 (0.1 mol) and 2-cyanopyridine (0.2 mol) in 1:1 ethanol/water solution for several hours. The white crystalline product that separated was recrystallized twice from ethanol. M.p. 116°C (lit. 116°C).⁸

Pyridine-2-acetamidoxime (2) was prepared from 2-pyridylacetoneitrile (0.2 mol) and hydroxylamine liberated from $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.2 mol) with sodium ethoxide. After filtration of the precipitated sodium chloride the reaction mixture was kept at 40°C for 24 h. The pale brown solid that formed was collected and recrystallized twice from ethanol. M.p. 107°C .

The purity of the ligands was checked by potentiometric titration and DSC methods. The solutions of the metal chlorides were standardized against standard EDTA. The concentration of Cu^{II} was also determined electrometrically and that of Ni^{II} by precipitation with dimethylglyoximate.

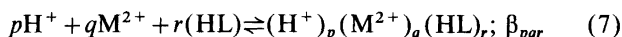
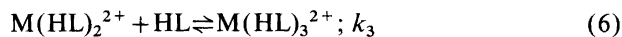
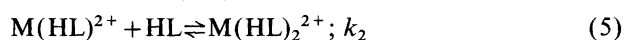
Methods

The complex formation equilibria were studied in aqueous 0.1 M NaCl by means of potentiometric EMF titrations using a glass electrode. The electrode system used in the measurements and its calibration to hydrogen ion concentration, h , have been described earlier.¹ It may be noted that the metal complexes studied here are even formed in very acidic solutions where the junction potential may amount to several millivolts. For the liquid junction potential we used $E_j = j_H h$; the value of the parameter j_H determined separately for each different run varied slightly, the average value being $-508(15) \text{ mV mol}^{-1} \text{ dm}^{-3}$.

The total concentrations of metal, C_M , and ligand, C_L , were varied within the limits $0.002 \leq C_M \leq 0.010 \text{ M}$ and $0.004 \leq C_L \leq 0.016 \text{ M}$ covering the C_L/C_M ratios 1:2, 1:1, 2:1, 3:1, 4:1 and 6:1. The available concentration and pH ($= -\log h$) ranges defined by the formation of a precipitate or very slow attainment of equilibria were relatively narrow, which made the determination of the polynuclear complexes in the systems quite difficult. To test the reproducibility and reversibility of the equilibria, both forward (NaOH) and backward (HCl) titrations were performed. In some measurements also the metal ions were used as the titrant.

The binary titrations concerning the protonation constants of the ligands were carried out in separate measurements within the concentration range 0.005–0.015 M and the pH range 2–10.5.

In evaluation of the acidity and complex equilibrium constants the reactions (1)–(7) were considered:



In evaluation of the metal complex equilibria the protonation equilibria of the ligands (1) and (2) were considered as known. The acid strengths of the oxime groups are so weak ($\text{p}k_a \approx 12$) that only rough estimates could be obtained for the equilibrium constant of reaction (3). This constant was not used in the calculations of the complex models, where the ligand was chosen as a component in the form of neutral oxime ($=\text{HL}$). The binary hydrolytic equilibria of metal ions could be neglected in our conditions.⁹ No attempts were made to adjust for the stability constants of the possible chloro complexes.

The least-squares computer program SUPERQUAD¹⁰ was used to obtain the complexation models (pqr -triplets) and the corresponding equilibrium constants β_{pqr} . The reader is referred to Ref. 10 for the definitions of the sample standard deviation s , the χ^2 -statistics and the weighting factor w_i (which comprises the estimated uncertainties in the electrode and volume readings $\sigma E = 0.1 \text{ mV}$ and $\sigma V = 0.02 \text{ ml}$) used as criteria in evaluating the complex models that best describe the experimental data.

Data treatment

The equilibrium constants relating to the protolytic reactions of the ligands, given in Table 1, were evaluated from the experimental data of five titrations and 144 points for ligand 1 and five titrations and 242 points for 2. The refinement was terminated at $\chi^2 = 43.9$, $s = 2.6$ (ligand 1) and $\chi^2 = 49.5$, $s = 3.4$ (ligand 2).

To visualize the experimental results for the copper(II) and nickel(II) complexation sets Z_H vs. pH were calcu-

Table 1. Equilibrium constants and the proposed formulas of the metal complexes.

	Proposed formula	$\log(\beta_{pqr} \pm 3\sigma)$	
		Ligand 1	Ligand 2
k_{a1}	H_3L^{2+}		-2.29 ± 0.01
k_{a2}	H_2L^+	-3.798 ± 0.006	-5.017 ± 0.003
k_{a3}	HL	$(-11.7)^a$	$(-12.3)^a$
k_1	$\text{Cu}(\text{HL})^{2+}$		5.31 ± 0.01
k_2	$\text{Cu}(\text{HL})_2^{2+}$	4.72 ± 0.03	4.24 ± 0.02
k_{2a}	$\text{Cu}(\text{HL})\text{L}^+$	-4.61 ± 0.03	
β_{-222}	$\text{H}_{-2}\text{Cu}_2(\text{HL})_2^{2+}$		4.7 ± 0.1
k_1	$\text{Ni}(\text{HL})^{2+}$	4.93 ± 0.10	3.59 ± 0.01
k_2	$\text{Ni}(\text{HL})_2^{2+}$	4.59 ± 0.06	3.27 ± 0.01
k_3	$\text{Ni}(\text{HL})_3^{2+}$	4.40 ± 0.06	
β_{-112}	$\text{Ni}(\text{HL})\text{L}^+$	1.76 ± 0.18	-1.56 ± 0.05
β_{-212}	NiL_2	6.84 ± 0.12	
β_{-113}	$\text{Ni}(\text{HL})_2\text{L}^+$	5.69 ± 0.09	
β_{-213}	$\text{Ni}(\text{HL})\text{L}_2$	-3.99 ± 0.09	
β_{-313}	NiL_3^-	-14.84 ± 0.09	
β_{-322}	$\text{H}_{-3}\text{Ni}_2(\text{HL})_2^+$		-13.82 ± 0.02

^a Approximate values.

lated. These plots are shown in Fig 1. Z_H is defined as the average number of OH^- ions reacted per ligand (HL) and is given by the relation $Z_H = (h - C_H - k_w h^{-1})/C_L$, where C_H denotes the total concentration of protons calculated over the zero level HL, H_2O and M^{2+} .

The Cu^{2+} -ligand 1 system. The complex formation occurs even in very acidic conditions. As can be seen from Fig. 1, the formation of the first complex is virtually complete at the beginning of the measurements. It can also be concluded that some deprotonated complexes are present. The best fit to the data from seven titrations and 191 points was obtained with a simple model consisting of species $\text{Cu}(\text{HL})^{2+}$, $\text{Cu}(\text{HL})_2^{2+}$ and $\text{Cu}(\text{HL})\text{L}^+$ ($\chi^2 = 58.9$, $s = 2.7$) with the stability constants given in Table 1. The useful experimental data were restricted to $\text{pH} < 4.8$ and $C_H > 0$, which prevented any further analysis.

Because of the high stability of the mono complex, an accurate value of the formation constant k_1 could not be obtained. Hence, some of the equilibrium constants in Table 1 are reported in the form of stepwise stability constants (which can be determined with better precision) instead of the conventional overall stability constants.

The Cu^{2+} -ligand 2 system. Owing to the appearance of a precipitate when $C_H \approx 0$, the pH range that could be used was again narrow ($\text{pH} < 5.9$). From the plot in Fig. 1 it is evident that, besides the mononuclear complexes, some deprotonated/polynuclear species are present. The best fit was obtained by adding the p,q,r combination $-2,2,2$ to the model ($\chi^2 = 29.8$, $s = 3.0$). It may be noted, however, that the difference from the mononuclear complex $-1,1,1$ is not very marked ($\chi^2 = 42.1$, $s = 3.2$). When combinations $-2,2,2$ and $-1,1,1$ were refined simultaneously, however, the latter species was rejected, providing further argument for the presence of the dimeric complex. No significant improvement in the goodness of fit to the data was obtained when several additional complex species were included in the model.

The values of the final refinement (7 titrations and 259 data points) are given in Table 1. It should be mentioned that stabilization of potential readings is very slow in the region where deprotonation and subsequent polymerization occur and this may be reflected in the relatively large standard deviation in the value of $\log \beta_{-222}$.

The Ni^{2+} -ligand 1 system. In this case, data readings with negative C_H values can easily be obtained (up to ca. $\text{pH} 10.5$). The mathematical p,q,r analysis (7 titrations/407 points, $\chi^2 = 30.3$, $s = 1.7$) showed the mononuclear bis and tris complexes $\text{Ni}(\text{HL})_n^{2+}$ to react as polyprotic acids in such a way that a model comprising the following eight species was obtained: $\text{Ni}(\text{HL})^{2+}$, $\text{Ni}(\text{HL})_2^{2+}$, $\text{Ni}(\text{HL})\text{L}^+$, NiL_2 , $\text{Ni}(\text{HL})_3^{2+}$, $\text{Ni}(\text{HL})_2\text{L}^+$, $\text{Ni}(\text{HL})\text{L}_2$ and NiL_3^- . The stability constants of the complexes are given in Table 1.

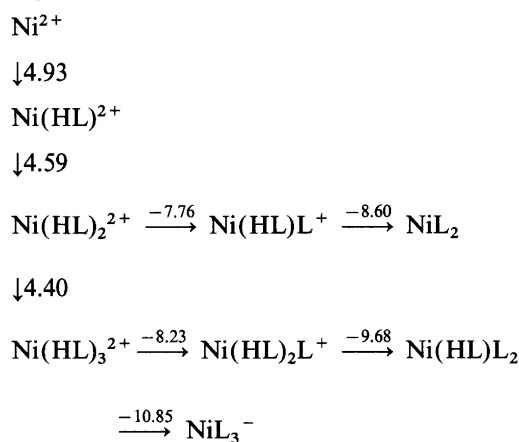
The Ni^{2+} -ligand 2 system. The inflection point which appears in the titration curves at $C_H = -1.5 C_M$ suggests the presence of a species with $p,q,r = -3,2,2$ (or $-6,4,4$) in addition to the mononuclear species. In calculations where several deprotonated mononuclear complexes were tested, the dimer proved to be more plausible than the tetramer. In all, the best fit to the experimental data ($\chi^2 = 74$, $s = 2.6$, 8 titrations/400 points, $\text{pH} < 8.8$) was obtained by assuming the complexes $\text{Ni}(\text{HL})^{2+}$, $\text{Ni}(\text{HL})_2^{2+}$, $\text{Ni}(\text{HL})\text{L}^+$ and $\text{H}_{-3}\text{Ni}_2(\text{HL})_2^+$ with the stability constants given in Table 1. Even though the χ^2 -value was abnormally high, because of the relatively low value of the sample standard deviation s , this model was considered to provide a satisfactory explanation of the data (s values lower than 3 are often regarded as acceptable for comparable systems).¹¹

Results and discussion

The acid strength of the protonated amide group in amidoxime ligands is generally very high; with ligand 2 the $\text{p}k_a$ value of the amide $-\text{NH}_3^+$ function was 2.77, but with 1, in our conditions, the dissociation of this group was so complete that no accurate value for the corresponding acidity constant could be determined. This trend was expected since our previous studies had clearly shown a considerable increase in the acidity of the protonated amide $-\text{NH}_3^+$ group when its distance from the nearby protonated amine donor (here the pyridine nitrogen) was decreased.³

The pyridyl substituent can be seen to have a marked influence in the complexation schemes: instead of the tetra- and pentanuclear complexes which dominated in the previous studies on aminoamidoximes,¹⁻³ the replacement of the amino nitrogen by the pyridine nitrogen donor results in complexation schemes where most of the major complexes are mononuclear.

The most complete complex model was that obtained for the Ni^{2+} -ligand 1 system. The hydrolysed members turn out to derive from the parent bis and tris complexes $\text{Ni}(\text{HL})_n^{2+}$ ($n = 2, 3$) in which all of the oxime NOH groups are dissociated stepwise to give the corresponding oximato species. This is illustrated in the following scheme, together with the log values of the respective steps:



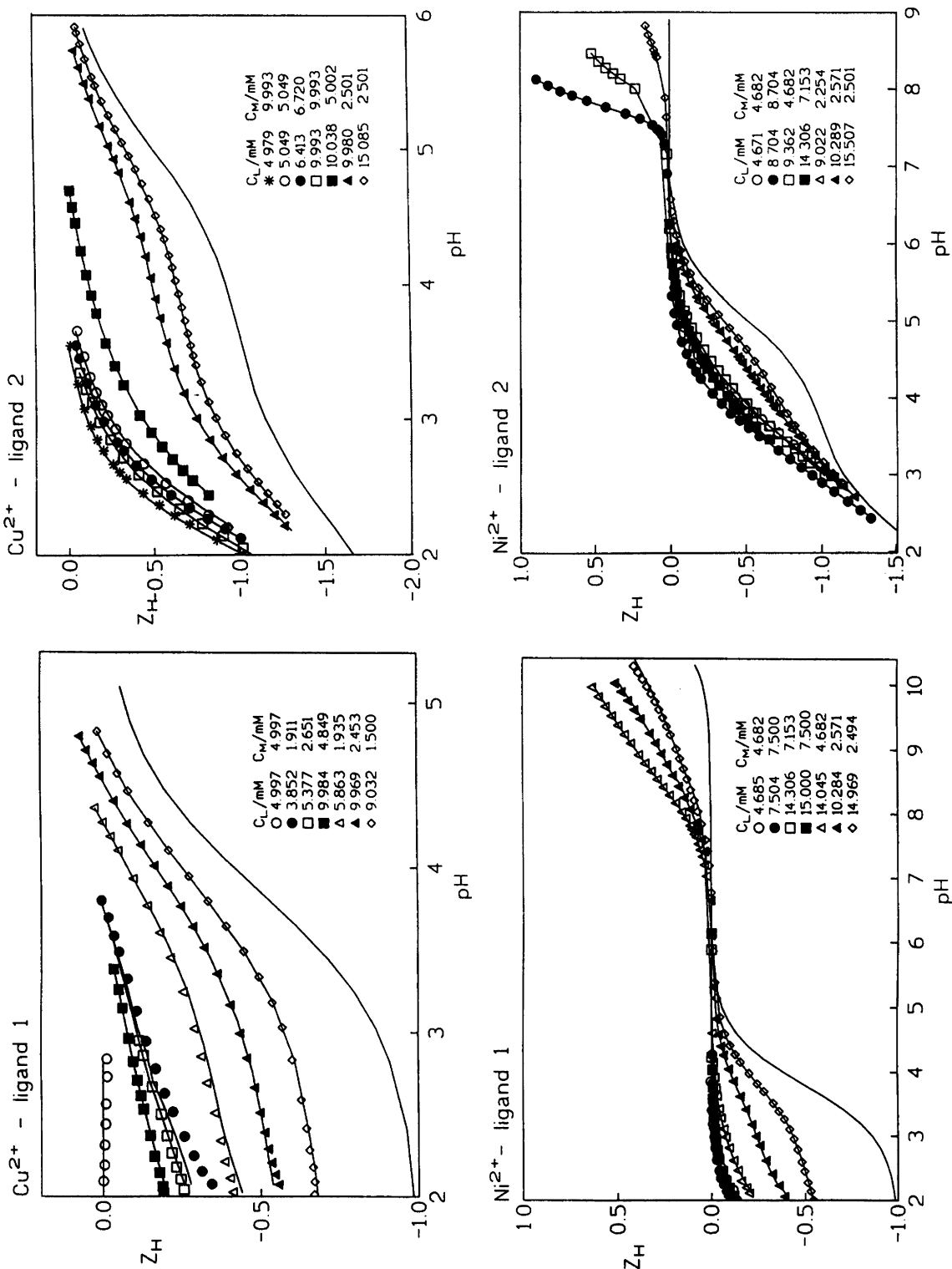


Fig. 1. Part of the experimental data plotted as curves Z_H vs. pH. The full lines have been calculated using the sets of proposed constants in Table 1. The lowest lines refer to the ligands alone.

Interestingly, this complex model is fully identical with that reported earlier for pyridine-2-aldoxime, so much so that in both systems it is the deprotonated mono complex NiL^+ that is missing from the otherwise complete system.⁷ This is an indication of similar coordination. It is also clear that the metal is bound through the oxime and pyridine nitrogen atoms of the bidentate ligands. Such a structure has been verified in the octahedral six-coordinate complex $[\text{Ni}(\text{HL})\text{L}_2] \cdot 6\frac{1}{2}\text{H}_2\text{O}$ (HL = pyridine-2-aldoxime) in the solid state.⁷ Thus the amide nitrogen is not acting as donor atom in this complexation.

It may be noted that the acid strengths are 2–3 log units weaker for the complexes given in the scheme than for the corresponding complexes formed with pyridine-2-aldoxime. Apparently this is due to the higher acidity of the oxime NOH group of the latter compound ($\text{p}K_{\text{a}} = 9.92$ at $I = 1.0 \text{ M NaCl}$).⁷

In the mononuclear complexes of ligands **1** and **2**, bonding of both nickel(II) and copper(II) evidently occurs through the pyridine and oxime nitrogen atoms. In the case of copper, the same coordination is found in the five-coordinate square-pyramidal complex $[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})(\text{ClO}_4)_2]$ (HL = **1**) and is known in several copper(II) and nickel(II) complexes of comparable ligands.^{13,14}

The structure of the hydrolysed mononuclear species $\text{Cu}(\text{HL})\text{L}^+$ with HL = **1** is clear from several studies on similar compounds: there is an intramolecular $=\text{N}-\text{O}-\text{H} \cdots \text{O}-\text{N}=\text{}$ hydrogen bridge between two oxime oxygen atoms of *cis*-oriented bidentate ligands.¹⁴

Table 1 shows that the complex species of ligand **2** are generally less stable than those of ligand **1**. With **2** the tris complex of nickel was not detected at all. The difference in stability is due to the difference between the six- and five-membered chelate rings in the respective chelates.

One important finding from this study is that the presence of the amide group in the ligand even though not taking part in the coordination, effectively prevents the formation of trinuclear copper(II) complexes, which even in very acidic conditions prevail in the Cu^{2+} -pyridine-2-aldoxime system. The reason for this is not obvious. Rather than any steric factors it is due to the electronic effects of the NH_2 group on the nearby oxime function.

It is also difficult to discover the reasons for the finding of an entirely different set of polynuclear complexes when amino nitrogen of aminoamidoxime compounds is replaced by aromatic pyridine nitrogen. With ligand **1**, the absence of tetra- and pentanuclear species in the system may arise from the conformation of the five-membered chelate ring. Because of the presence of the $\text{N}(\text{sp}^2)$ donor atom it must be distinctly less flexible than the corresponding ring formed with ligands containing an amino nitrogen donor. As a consequence, the remaining oxime oxygen and amide nitrogen atoms have limited possibilities to be active in further coordination.

With ligand **2**, dinuclear species $\text{H}_{-2}\text{Cu}_2(\text{HL})_2^{2+}$ and $\text{H}_{-3}\text{Ni}_2(\text{HL})_2^+$ form at low ligand to metal ratios when the pH of the solution is increased. In this case the six-membered chelate ring provides more freedom than the five-membered ring, and allows dimerization of the species probably via the oximato NO bridges.

References

1. Saarinen, H., Orama, M. and Korvenranta, J. *Acta Chem. Scand., Ser. A* 43 (1989) 834.
2. Orama, M., Saarinen, H., Korvenranta, J. and Raikas, T. *Acta Chem. Scand., Ser. A* 46 (1992) 1083.
3. Orama, M., Saarinen, H. and Korvenranta, J. *Acta Chem. Scand., Ser. A* 48 (1994) 127.
4. Datta, D. and Chakravorty, A. *Inorg. Chem.* 21 (1982) 363.
5. Orama, M., Saarinen, H. and Korvenranta, J. *J. Coord. Chem.* 22 (1990) 183.
6. Beckett, R. and Hoskins, B. F. *J. Chem. Soc., Dalton Trans.* (1972) 291.
7. Orama, M., Saarinen, H. and Korvenranta, J. *Acta Chem. Scand., Ser. A* 43 (1989) 407.
8. Bernasek, E., *J. Org. Chem.* 22 (1957) 1263.
9. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations*, Wiley, New York 1976, p. 272.
10. Gans, P., Sabatini, A. and Vacca, A. *J. Chem. Soc., Dalton Trans.* (1985) 1195.
11. Bologni, L., Sabatini, A. and Vacca, A. *Inorg. Chim. Acta* 69 (1983) 71.
12. Näsäkkälä, M., Saarinen, H., Korvenranta, J. and Orama, M. *Acta Crystallogr., Sect. C* (1989) 1514.
13. Pearse, G. A., Raithby, P. R. and Lewis, J. *Polyhedron* 8 (1989) 301.
14. Saarinen, H., Orama, M., Raikas, T. and Korvenranta, J. *Acta Chem. Scand., Ser. A* 40 (1986) 396.

Received January 10, 1996.