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Short Communication

Equilibrium and Structural Studies on Metal Complexes of Oxime Ligands. Pentanuclear Complex Formation of 3- Aminopropanamidoxime and Its *N*-Methyl Derivatives with Nickel(II) in Aqueous Solution

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Aminoamidoximes of the type $RR'N(CH_2)_nC(NH_2)$-NOH (HL, $n=1$ and 2) readily form polynuclear copper(II) and nickel(II) complexes together with a series of mononuclear species. In the mononuclear complexes the ligand is found to bind the metal ions bidentately through its amino (RR'N-) and oxime NOH nitrogens. The oxime as well as the amide $-NH_2$ group of the coordinated ligand may, however, undergo deprotonation, and the $-NO^-$ and $-NH^-$ anions that are formed are capable of being involved in further coordination. This occurs through the generating of additional five-membered chelate rings with amide nitrogen and oxime oxygen as donor atoms and gives rise to tetra- and pentanuclear structures.[1–3] An interesting feature of these polymers is that the metal ions exhibit a nearly planar configuration, which makes them potential model compounds in the study of redox and magnetic-exchange interactions of metal ions.

The nuclearity of these polynuclear complexes has been found to depend on at least two factors: the length of the carbon chain (n) and the number of the alkyl groups on the amino nitrogen of the ligand.[1,2] When $n=1$ the copper(II) and nickel(II) complexes dominating in aqueous solution are tetrameric.[3] The formation of such species, however, seems to necessitate the presence of a tertiary amino group ($R=R'=CH_3$ and C_2H_5) on the ligand since all complexes with primary and secondary amino functions have been monomeric. This is probably due to the fact that the formation of the strong intramolecular oximato bridges which normally control these complexation reactions is sterically hindered when *N*-dialkylated amino groups are present.[3]

The same does not seem to be true when $n=2$, since with copper(II) the major polynuclear complexes have been pentanuclear regardless of the nature of the terminal amino group.[1] So far nothing has been published about nickel structures with $n=2$ ligands. In this paper we report the aqueous complex formation between nickel and three 3-aminopropanamidoxime ligands containing a primary (HL=**1**, R=R'=H), a secondary (HL=**2**, R=H, R'=CH_3) and a tertiary (HL=**3**, R=R'=CH_3) amino group. To facilitate interpretation of the structures of the complexes, some of the polynuclear species formed were also isolated from the equilibrium solution in the solid state.

Experimental

The preparations of the ligands have been described in Refs. 1 and 2.

Preparation and analyses of the solid polynuclear complexes. Dark green precipitates were formed when aqueous solutions of nickel(II) chloride and the ligands were mixed in 1:1 molar ratios, the pH was adjusted to 8–9 with NaOH, and the dark-green solutions were allowed to stand overnight. The solids are sparingly soluble in water and DMSO but practically insoluble in organic solvents. $C_{12}H_{34}N_{12}O_7Ni_5Cl_2=Ni_5(L–H)_4Cl_2\cdot 3H_2O$, HL=**1**, M=822.9 g mol^{-1}. Anal.: C, H, N, Ni, Cl, H_2O. MS *m/z* 768 $Ni_5(L–H)_4Cl_2$ (FAB), 348 $Ni_5(L\text{-}H)_4$ (ESI); $C_{16}H_{52}N_{12}O_{12}Cl_2=Ni_5(L\text{-}H)_4Cl_2\ 8H_2O$, HL=**2**,

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M = 969.1 g mol^{-1}. Anal.: C, H, N, Ni, Cl, H_2O. MS *m/z* 789 $Ni_5(L–H)_4Cl$, 752, 376 $Ni_5(L–H)_4$ (ESI).

Ligand **3** gave a green powdery mass of varying composition. This was probably a mixture of a polynuclear complex and nickel hydroxide.

The solid complexes were analysed by conventional methods: Ni (TG, AAS); Cl (potentiometric Ag^+-titration); C,H,N (microanalysis), H_2O (TG). FAB-MS were collected in DMSO with a Finnigan Mat 8400 mass spectrometer, and an ESI-MS in methanol/water mixture at pH 9 adjusted with NaOH with a Finnigan-TSO-700 spectrometer. Electrical conductivity measurements were carried out on an Amel Instruments 160 conductometer in dilute DMSO (1.8×10^{-5}–1.8×10^{-4} M).

Potentiometric measurements. The complex formation equilibria were studied in aqueous 0.1 M NaCl at 25.0 °C through a series of EMF titrations using a glass electrode. The electrode system used in the measurements has been described earlier.[1]

Use of sodium chloride rather than the more conventional sodium perchlorate, and a relatively low ionic strength, were required because of the limited solubility of the polynuclear complexes.

In order to study the nickel(II)–ligand equilibria, the total concentrations of nickel(II), C_M, and ligand, C_L, were varied within the limits $2 < C_M < 9$ mM and $4 < C_L < 17$ mM covering ligand to metal ratios between 0.5 and 4.0 and the pH ($= -\log h$) range 5.0–9.6.

The reproducibility and reversibility of the equilibria were tested by performing both forward (increasing pH) and backward (decreasing pH) titrations.

In evaluating the proton/ligand systems the following equilibria (1)–(3) were considered:

$$H^+ + HL \rightleftharpoons H_2L^+ \quad (1)$$

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

$$HL \rightleftharpoons L^- + H^+ \quad (3)$$

The acid strength of the oxime group is very weak ($pk_a \approx 12$), and an accurate value for the corresponding deprotonation constant, reaction (3), could not be obtained here. On account of this in the evaluation of the metal complex equilibria the ligand was chosen as a component in the form of neutral oxime (HL):

$$pH^+ + qNi^{2+} + r(HL) \rightleftharpoons (H^+)_p(Ni^{2+})_q(HL)_r;\ \beta_{pqr} \quad (4)$$

The metal hydrolysis proved to be negligible in our conditions.[4]

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

Treatment of potentiometric data. A trial-and-error procedure in which the different *pqr*-combinations were tested one by one, to find the compositions of the hydrolysed/polynuclear complexes together with the binary species $pqr = 01n$ ($n = 1$–3) formed in the systems. With ligands **1** and **2** the best fit to the experimental data was found for the model comprising the following five species: $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, $Ni(HL)L^+$, $H_{-8}Ni_5(HL)_4^{2+}$ and $H_{-9}Ni_5(HL)_4^+$; with ligand **3** the best fit was for the model consisting of only three complexes: $Ni(HL)^{2+}$, $H_{-8}Ni_5(HL)_4^+$ and $H_{-9}Ni_5(HL)_4^+$.

The number of titration points/titrations used in the calculations, and the values of s and χ^2-statistics, were as follows for ligands **1**, **2** and **3**: 403/8, $s = 2.85$, $\chi^2 = 36.8$; 465/8, $s = 2.71$, $\chi^2 = 59.2$; 164/8, $s = 1.45$, $\chi^2 = 39.3$.

The acidity constants have been determined earlier[1] for ligands **1** and **2** but are not known in 0.1 M NaCl for ligand **3**. The log values of equilibrium constants of the reactions (1)–(3) obtained for **3** in this study were 8.577(3), 12.237(5) and −12.01(3) ($s = 1.45$, $\chi^2 = 29.0$).

Results and discussion

The results given in Table 1 show that for the most part, the complexation models accord well with each other: excluding the bis complexes $Ni(HL)^{2+}$ and $Ni(HL)L^+$ which were not detected with **3**, the three sets of complexes are identical. The reduced tendency of ligand **3** to form higher complexes is expected, and the weakening effect of its *N*-dimethyl substitution on the stabilities of the complexes is already clear from the values of the formation constants of the mono complexes $Ni(HL)^{2+}$ in Table 1.

The type of coordination occurring in the mononuclear complexes of aminoamidoxime ligands has been discussed in earlier papers of this series.[1–3] In view of these

Table 1. Equilibrium constants (log $\beta_{pqr} \pm 3\sigma$) relating to the reaction $pH^+ + qNi^{2+} + r(HL) \rightleftharpoons (H^+)_p(Ni^{2+})_q(HL)_r$; β_{pqr}

p	*q*	*r*	Proposed formula	HL = **1**	HL = **2**	HL = **3**
0	1	1	$Ni(HL)^{2+}$	4.89 ± 0.01	4.46 ± 0.01	2.74 ± 0.01
0	1	2	$Ni(HL)_2^{2+}$	8.35 ± 0.02	6.78 ± 0.08	
−1	1	2	$Ni(HL)L^+$	−0.51 ± 0.03	−1.18 ± 0.03	
−8	5	4	$Ni_5(L–H)_4^{2+}$	−36.32 ± 0.06	−37.34 ± 0.03	−44.62 ± 0.04
−9	5	4	$Ni_5(L–H)_4(OH)^+$	−45.9 ± 0.2	−46.7 ± 0.1	−54.1 ± 0.1

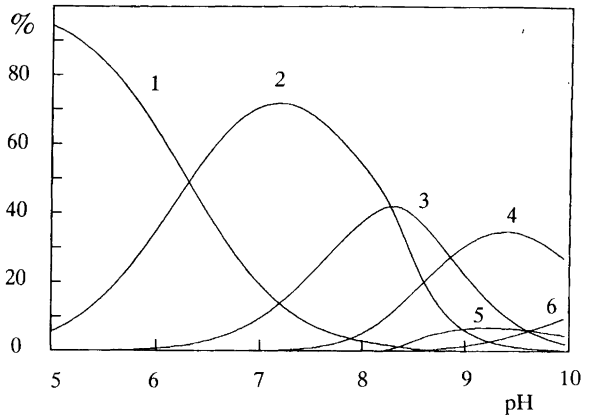

Fig. 1. An example of the concentration distribution of the nickel(II) species for the Ni^{2+}–ligand **1** system. (1) Ni^{2+}, (2) $Ni(HL)^{2+}$, (3) $Ni(HL)_2^{2+}$, (4) $Ni(HL)L^+$, (5) $Ni_5(L\text{-}H)_4^{2+}$ and (6) $Ni_5(L\text{-}H)_4(OH)^+$ ($C_L = 10$ mM and $C_{Ni} = 5$ mM).

results it is evident that bonding to the metal is through the amine and oxime nitrogen atoms, i.e. six-membered chelate rings are formed with the ligands **1–3**. This is also reflected in the values of the stability constants of the complexes, which are much lower than those of complexes formed with comparable aminoethanamidoximes which contain five-membered chelate rings.[3]

The main finding of this study is that the polynuclear complexes formed between the present 3-aminopropanamidoxime ligands and nickel(II) are pentanuclear, containing five nickel atoms for each of the four ligand molecules: species of the compositions $H_{-8}Ni_5(HL)_4^{2+}$ and $H_{-9}Ni_5(HL)_4^{+}$ are found in all three cases. The polymerization models are thus basically similar to those obtained earlier for the corresponding copper(II)–3-aminopropanamidoxime systems.[1,2] This confirms the observation that, with the $n = 2$ ligands, the length of the alkyl chain rather than the nature of the amino group plays the decisive role in the polymerization.

Figure 1 shows an example of the distribution of nickel among different complex species. As can be seen, the bis-$Ni(HL)_2^{2+}$ as well as the pentanuclear $H_{-8}Ni_5(HL)_4^{2+}$ complexes are weak acids. The pK_a-values of the mononuclear species are 8.9 (ligand **1**) and 8.0 (ligand **2**), and those of the pentanuclear complexes 9.6, 9.4 and 9.5 for ligands **1**, **2** and **3**, respectively.

The actual structures of the complexes cannot be determined from potentiometric data. To obtain supporting information we isolated two of the pentanuclear complexes with formula corresponding to the composition $H_{-8}Ni_5(HL)_4^{2+}$, as chlorides in the solid state. The equivalent conductances Λ_∞ of the compounds as measured in DMSO solutions were 99(2) (HL = **1**) and 96(2) (HL = **2**) S cm^2 mol^{-1}, which indicate the presence of a 2:1 electrolyte in the solution.[6]

All our attempts to prepare these species in the crystal-

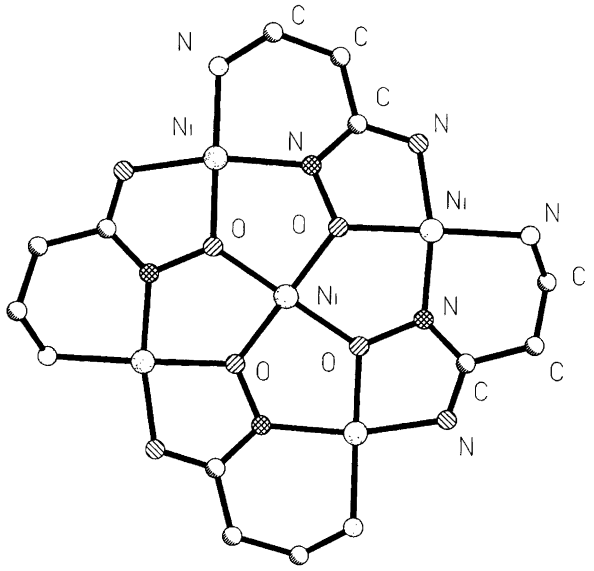

Fig. 2. Schematic representation of the pentanuclear complex cation $Ni_5(L\text{-}H)_4^{2+}$ (HL = **1**).

line state suitable for X-ray structure determination proved unsuccessful. The striking analogy between the formulas of the present nickel(II) pentamers and the copper(II) pentamers studied earlier[1] means, nevertheless, that the coordination about the two metals in these complexes is similar. Evidently, too, the molecular structures of the nickel(II) pentamers correspond to the respective copper(II) structures, in which all of the oxime and amide protons are dissociated upon coordination, as was verified in the solid state by X-ray crystallographic methods.[1] Thus the most plausible structure of the pentanuclear complex moiety of $H_{-8}Ni_5(HL)_4^{2+}$ is $Ni_5(L\text{-}H)_4^{2+}$, as illustrated in Fig. 2.

As to the structure of the complex $H_{-9}Ni_5(HL)_4^{2+}$, very probably the coordination environment remains unaltered on deprotonation and a hydroxo species of the formula $Ni_5(L\text{-}H)_4(OH)^+$ is formed.

References

1. Saarinen, H., Orama, M. and Korvenranta, J. *Acta Chem. Scand., Ser. A 48* (1994) 127.
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 43* (1994) 834.
4. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations*, Wiley, New York 1976, p. 272.
5. Gans, P., Sabatini, A. and Vacca, A. *J. Chem. Soc., Dalton Trans.* (1985) 1195.
6. Pilarczyk, M., Grzybkowski, W. and Klinszporn, L. *J. Chem. Soc., Faraday Trans. 85* (1989) 3395.

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