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Equilibrium and Structural Studies on Metal Complexes of Oxime Ligands. Formation of Nickel(II) Complexes of Two Methyl-Substituted Pyridine Oxime Ligands in Aqueous Solution

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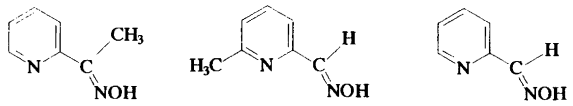
The nickel(II) complex formation equilibria of 1-(2-pyridinyl)ethanone oxime (HL=**1**) and 6-methylpyridine-2-carboxaldehyde oxime (HL=**2**) have been studied at 25 °C in aqueous 0.1 M NaCl solution by potentiometric titration with the use of a glass electrode. The experimental data were analysed with respect to the complexes formed and their stability constants, by using the least-squares computer program SUPERQUAD. In the ligand **1** system the experimental data can be explained in terms of the stepwise formation of binary mononuclear complexes $Ni(HL)_r^{2+}$ ($r=1, 2, 3$) together with a series of hydrolysed oximato complexes $H_pNi(HL)_r^{2+p}$, where $r=2, 3$ and $-p=1, 2, \ldots, r$. At low metal-to-ligand ratios a further dinuclear hydrolysed species $H_{-3}Ni_2(HL)_3^+$ is formed in alkaline solutions. With ligand **2** the formation of the tris complexes is hindered by the presence of the 6-methyl group on the pyridine ring, and the best model was that including the mononuclear complexes $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$ and $H_{-2}Ni(HL)_2$, together with the hydrolysed dinuclear $H_{-3}Ni_2(HL)_3^+$ and trinuclear $H_{-5}Ni_3(HL)_3^+$ species. The values of the stability constants of the complexes are several orders of magnitude lower for the Ni–ligand **2** system than the Ni^{2+}–ligand **1** system, indicating the weakening effect of the 6-methyl group on the complex stability.

The complexation in aqueous solution between several transition metal ions and oxime ligands has been described in earlier papers from this laboratory.[1–4] Our particular interest has been the copper(II) and nickel(II) complexes formed by aminoamidoxime and pyridine oxime ligands which contain an additional nitrogen donor atom in a position with respect to the oxime function that may allow stable five- or six-membered chelate rings to be generated. In the complexes described, the amino, amide, oxime and pyridine nitrogen as well as the oxime oxygen are involved in the coordination around the metal ions. In addition to the series of stepwise mononuclear oxime and oximato complexes we also reported a variety of polynuclear complexes. In the case of the polymeric complexes, which are potential model compounds for the study, for example, of redox and magnetic interactions, the nuclearity is very sensitive to small variations in the ligand, such as the location and number of the alkyl groups in the molecule.

Since the potentiometric data cannot give any direct information on the structure of aqueous species, we sought support for the proposed coordination modes by isolating several of the complexes from the equilibrium solution in the solid state and determining their structures by X-ray diffraction methods.

Here we report a study of the aqueous complex formation between nickel(II) and two methyl substituted pyridine oxime ligands **1** and **2**.



HL = 1 HL = 2 HL = 3

The complexation between nickel and the parent compound pyridine-2-aldoxime (HL=3) has been studied earlier, and all aqueous complexes verified were found to be members of the mononuclear series $Ni(HL)_r^{2+}$ ($r=1, 2, 3$) or deprotonated complexes derived from it.[1] The structure of the solid complex $Ni(HL)L_2 \cdot 6\frac{1}{2}H_2O$ (HL=**3**) determined by use of X-ray diffraction methods,

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conformed that coordination is through the oxime and pyridine nitrogen atoms.[1] This is in apparent contrast to results reported for copper(II), where the systems with all these ligands **1**–**3**, both in aqueous solution and in the solid state, are characterized by the presence of trinuclear complex species $Cu_3L_3OH^{2+}$ containing Cu_3OH central cores.[5–7]

To facilitate interpretation of the coordination models in the present systems, we also determined the X-ray structure of a complex isolated from an equilibrium solution containing ligand **2** and nickel(II) ions under conditions where polymerization prevailed. The complex proved to have a very complicated nonanuclear structure. Details of this structure analysis will be presented later.

Experimental

The preparations of the pyridine oxime ligands have been described in Ref. 6. The nickel(II) chloride stock solution was standardized against standard EDTA. The concentration of nickel(II) was also determined by precipitation with dimethylglyoxime.

In the Ni^{2+}–ligand **1** system, favourable conditions for the formation of the polynuclear complexes were obtained when the pH of the aqueous solution containing nickel(II) chloride and ligand **2** in molar ratio 1:1 was adjusted to 8 with NaOH. Attempts to isolate a crystalline complex from such solutions were unsuccessful, but when the counter chloride ion was changed to perchlorate ion, a light green crystalline complex of composition $Ni_9L_{10}(OH)_6(H_2O)_{12}(ClO_4)_2$ was obtained. The structure of the compound was determined by X-ray analysis. Crystal data: $C_{70}H_{108}Cl_2N_{20}Ni_9O_{40}$, $a=15.920(7)$, $b=16.673(8)$, $c=20.583(10)$ Å $\alpha=77.80(6)$, $\beta=81.00(6)$, $\gamma=72.60(4)°$, $V=5070(4)$ Å^3, $Z=2$, triclinic, space group $P(1)$, $R=0.109$ for 12584 reflections. Details of the structure analysis are given in Ref. 8.

Potentiometric measurements. The complex formation equilibria were studied in aqueous 0.1 M NaCl by means of potentiometric EMF measurements using a glass electrode. Because of the poor solubility of some of the most interesting complexes in perchlorate solutions, NaCl was chosen as the inert salt instead of the more common $NaClO_4$. The electrode system used in the measurements and its calibration to hydrogen ion concentration, h, have been described in detail earlier.[9]

During the measurements the ratio between the total concentrations of nickel(II), C_M, and ligand, C_L, was held constant. The initial concentrations were varied within the limits $0.002 \leqslant C_M \leqslant 0.010$ M and $0.005 \leqslant C_L \leqslant 0.016$ M, covering the metal-to-ligand ratios 1:1, 1:1.5, 1:2; 1:3, 1:4 and 1:8. The pH ($= -\log h$) ranges were 2.0–9.5 (ligand **1**) and 3.0–8.4 (ligand **2**). In both systems the upper pH values were largely determined by the appearance of a precipitate or very slow attainment of equilibria.

Both forward (increasing pH) and backward titrations were performed to test the reproducibility and reversibility of the equilibria.

In evaluating the equilibrium constants the two-component equilibria (1)–(3) were considered:

$$H^+ + HL = HL^+; \quad \beta_{101} \tag{1}$$

$$HL = L^- + H^+; \quad k_a \tag{2}$$

$$pH^+ + qNi^{2+} = (H^+)_p(Ni^{2+})_q; \quad \beta_{pq0} \tag{3}$$

The binary equilibria (1)–(3) have been studied earlier. The values of the protonation constant, $\log \beta_{101}$, of the pyridine nitrogen and the values of the acid dissociation constant, pk_a, of the oxime group used in the calculations were the following: 3.968 and 10.87 (ligand **1**) and 4.258 and 9.94 (ligand **2**).[6] For the hydrolytic equilibrium of nickel(II), reaction (3), we used the value $-\log \beta_{-110} = 9.26$.[10]

The acid strengths of the oxime groups are very weak, and thus the value of the corresponding constant, reaction (2), is not very accurate. This caused us, in evaluating the ternary equilibria, to choose the ligand as a component in the form of the neutral oxime (HL):

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

The mathematical analysis used to search for the complex models (pqr) and the corresponding stability constants β_{pqr} was carried out with use of the computer program SUPERQUAD.[11] The best fit to the experimental data was determined by minimizing the error squares sum

$$U = \sum w_i(E_i^{obs} - E_i^{calc})^2 \tag{5}$$

The weighting factor w_i is defined by the equation

$$w_i = 1/(\sigma_E^2 + \delta E_i/\delta V_i)\sigma_V^2 \tag{6}$$

where σ_E (0.1 mV) and σ_V (0.02 ml) are estimated uncertainties in the electrode and volume readings and δ_E/δ_V is the slope of the titration curve.

The reader is referred to Ref. 12 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.

Data treatment. Sets Z_H versus pH were calculated as a means of visualizing the experimental results. The plots are shown in Fig 1. Z_H is defined as the average number of OH^- ions reacted per ligand 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 Ni^{2+}–ligand **1** *system.* It can be directly concluded that, besides the stepwise mononuclear oxime complexes $Ni(HL)_r^{2+}$, there are some deprotonated oximato complexes formed as well. This is already evident from the negative values of the total concentration of proton (as calculated over the zero level HL, Ni^{2+} and H_2O) readily achieved in the measurements (cf. Fig. 1).

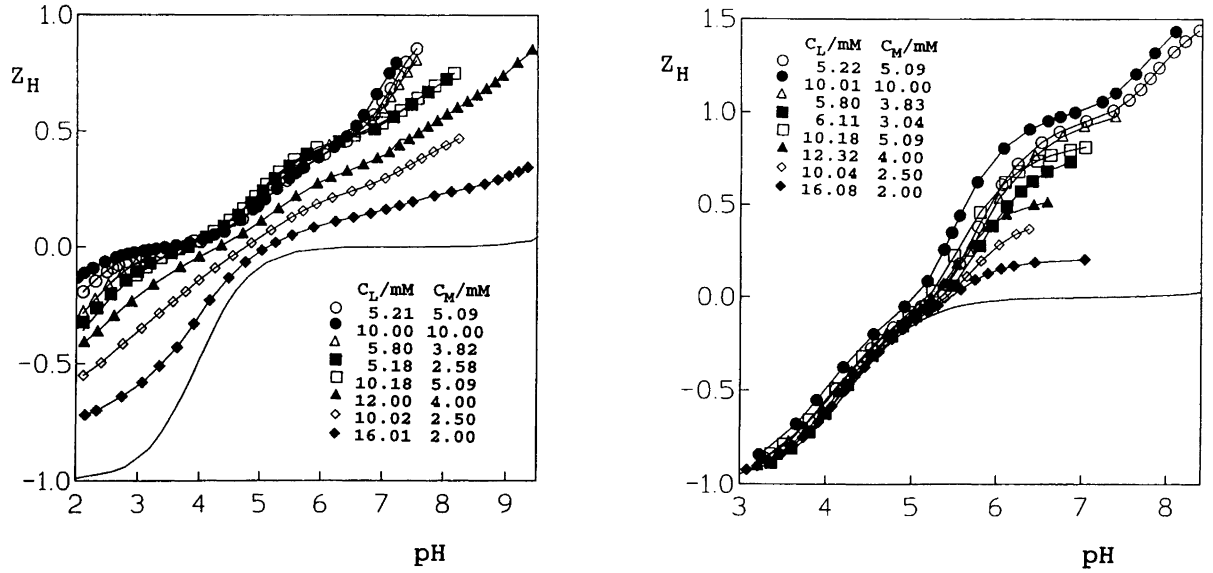

Fig. 1. Some of the experimental data plotted as curves Z_H vs. pH for the Ni^{2+}–ligand **1** (left) and the Ni^{2+}–ligand **2** systems (right). The full lines have been calculated using the sets of of proposed constants in Table 1. The lowest lines refer to the ligands alone.

In the computational analysis, all mononuclear species $Ni(HL)_rL_s^{2-s}$ with $r+s \leqslant 3$ were tested in SUPERQUAD calculations, in which the complexes and the corresponding equilibrium constants were systematically varied. At least the following eight mononuclear species had to be included in the model: $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, $Ni(HL)L^+$, NiL_2, $Ni(HL)_3^{2+}$, $Ni(HL)_2L^+$, $Ni(HL)L_2$, NiL_3^-. The fit to the experimental data was still quite unsatisfactory ($s=7.8$, $\chi^2=142$): in particular the titrations with low C_L/C_M ratios showed considerable deviations from the ideal curve, implying that some polynuclear complexes are present in such solutions. After this finding a number of polynuclear complexes were included in the calculations. A considerably better fit to the data was obtained by adding a dinuclear species with the p, q, r combination $-3, 2, 3$ to the model. None of the additional polynuclear complexes tested in subsequent calculations made any significant contribution to the complex model. The analysis was ceased at a total standard error of residuals $s=2.1$ and $\chi^2=35$ which can be considered to provide a fairly good explanation of the data (s values lower than 3 are often regarded as acceptable for comparable systems).[12]

The stability constants for the complexes proposed in final calculations which encompass 8 titrations and 433 data points are given in Table 1.

The Ni^{2+}–ligand **2** *system.* The complex formation occurs at markedly higher pH ranges than in the previous case, indicating the complexes to be considerably less stable than those formed with ligand **1**. Here the presence of polynuclear species was more obvious than with **1**, and also detectable in solutions with high C_L/C_M ratio. The inflection point which appears in the titration curves at $C_H=-1.67C_M$ further suggests that a major polynuclear species with $p/q=-5/3$ is present. In the subsequent calculations several polynuclear complexes in addition to mononuclear $Ni(HL)^{2+}$ and $Ni(HL)_2^{2+}$ oxime com-

Table 1. Stability constants ($\log \beta_{pqr} \pm 3\sigma$) relating to the reaction $pH^+ + qNi^{2+} + r(HL) = (H^+)_p(Ni^{2+})_q(HL)_r$ and the proposed formulas of the complexes. The values for HL=**3** are taken from Ref. 1 and are valid for 25 °C and 1.0 M NaCl.

		$\log \beta_{pqr} \pm 3\sigma$		
p, q, r	Proposed formula	Ligand **1**	Ligand **2**	Ligand **3**
0, 1, 1	$Ni(HL)^{2+}$	4.98±0.03	1.94±0.06	4.19±0.02
0, 1, 2	$Ni(HL)_2^{2+}$	9.39±0.04	3.86±0.12	7.62±0.02
0, 1, 3	$Ni(HL)_3^{2+}$	12.88±0.04		10.42±0.02
−1, 1, 2	$Ni(HL)L^+$	4.57±0.05		2.80±0.05
−2, 1, 2	NiL_2	−3.55±0.06	−7.43±0.09	−3.68±0.06
−1, 1, 3	$Ni(HL)_2L^+$	7.28±0.06		5.58±0.04
−2, 1, 3	$Ni(HL)L_2$	−0.09±0.06		−0.70±0.05
−3, 1, 3	NiL_3^-	−9.31±0.06		−8.42±0.04
−3, 2, 3	$Ni_2L_3^+$	−1.33±0.08	−7.28±0.04	
−5, 3, 3	$Ni_3L_3(OH)_2^+$		−20.11±0.06	

plexes were tested systematically. The single polynuclear species with $p/q = -5/3$ proved to a trimer with the p, q, r combination $-5, 3, 3$, but it was soon evident that a mononuclear bis complex $-2, 1, 2$ and a dimer $-3, 2, 3$ were also needed to explain the experimental data. It may be noted that summation of the last two species gives just the same p/q ratio $-5/3$. In all, the best fit ($s = 3.3$, $\chi^2 = 20$; 8 titrations/366 data points) was obtained by assuming the complexes $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, NiL_2, $Ni_2L_3^+$ and $Ni_3L_3(OH)_2^+$ with the stability constants given in Table 1. The value of the sample standard deviation s was somewhat high but still indicates a quite satisfactory explanation of the data.

Results and discussion

By comparing the present results with those obtained previously for other pyridine oxime ligands the methyl substituent near the oxime group (ligand **1**) can be found to have only a marginal effect in the complexation. Excluding the dimeric species which appears at low C_L/C_M ratios the complexation between Ni^{2+} and ligand **1** is dominated by formation of a series of mononuclear oxime $Ni(HL)_r^{2+}$ ($r = 1, 2, 3$) and of oximato species which derive from the stepwise deprotonation of the NOH groups from the parent bis and tris complexes. This complex model is identical with the one reported earlier for ligand **3** as well as for pyridine carboxamidoxime, a ligand which contains an NH_2 group in place of the CH_3 group in **2**. Interestingly, with all these ligands it is the deprotonated mono species NiL^+ which is missing from otherwise complete complexation scheme. This is a clear indication of similar chelation with nickel(II) bound to the ligand through the oxime and pyridine nitrogen atoms in all these systems. In the solid state this kind of coordination are verified in the octahedral six-coordinate complex $[Ni(HL)L_2] \cdot 6\frac{1}{2}H_2O$ (HL = **3**).[1]

The stepwise formation and hydrolysis of the Ni^{2+}–ligand **1** complexes is illustrated in Fig. 2, which shows the distribution of the different complex species vs. pH. The following scheme, together with the log values of the respective steps, can be calculated:

$$Ni^{2+}$$

$$\downarrow 4.98$$

$$Ni(HL)^{2+}$$

$$\downarrow 4.41$$

$$Ni(HL)_2^{2+} \xrightarrow{-4.82} Ni(HL)L^+ \xrightarrow{-8.12} NiL_2$$

$$\downarrow 3.49$$

$$Ni(HL)_3^{2+} \xrightarrow{-5.60} Ni(HL)_2L^+ \xrightarrow{-7.37} Ni(HL)L_2 \xrightarrow{-9.40} NiL_3^-$$

The values of the stability constants of the oxime complexes $Ni(HL)_r^{2+}$ obtained here are close to the corresponding values reported for ligand **3** and for pyridine-2-carboxamidoxime. The difference between the conventional pk_a-values of the comparable complexes in these three systems is somewhat larger: in general the lowest pk_a-values are detected with ligand **3**, and the highest values with pyridine-2-carboxamidoxime.

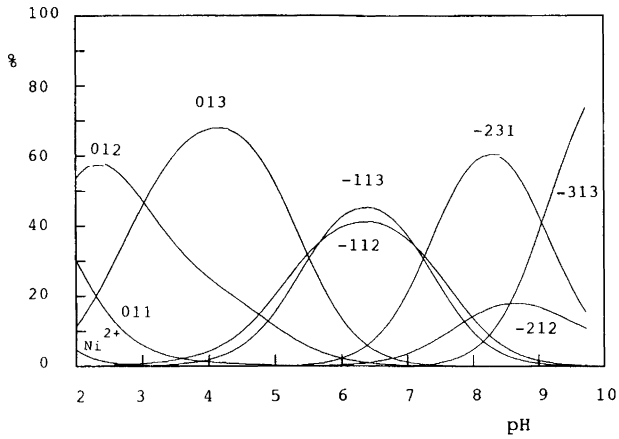

Fig. 2. An example of the concentration distribution of the nickel(II) species $(H^+)_p(Ni^{2+})_q(HL)_r$ vs. pH for the Ni^{2+}–ligand **1** system ($C_L = 30$ mM, $C_M = 10$ mM).

The 6-CH_3 on the pyridine ring has a pronounced effect on the complexation. The trend is already evident with the mononuclear complex. With ligand **2** the stability of the mono complex $Ni(HL)^{2+}$ is of several order of magnitude lower than the corresponding species with HL = **1**, formation of the bis complexes is strongly hindered, and the tris complexes are no longer detectable. The weakened tendency of ligand **2** towards complex formation, which has been observed with other comparable species, e.g. with methylated pyridine and pyridine 2-carboxylate complexes,[13,14] cannot be predicted from the different basicities of the ligands, and must arise from the steric requirements of the 6-CH_3 group.

Both of the polymeric complexes, $-3, 2, 3$ and $-5, 3, 3$, formed by ligand **2** are major species in solution as illustrated in Fig. 3. It is obvious that the power of ligand **2** to form polynuclear nickel complexes originates

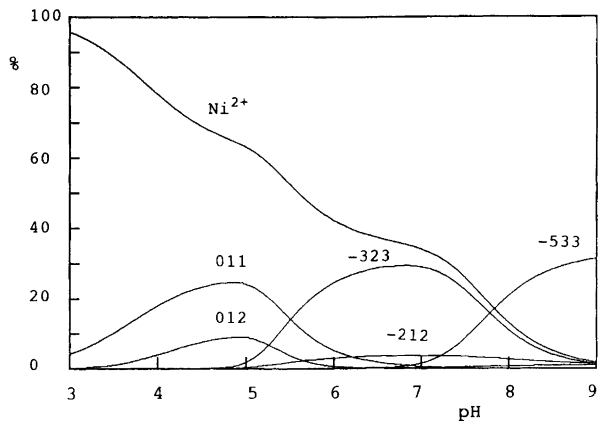

Fig. 3. An example of the concentration distribution of the nickel(II) species $(H^+)_p(Ni^{2+})_q(HL)_r$ vs. pH for the Ni^{2+}–ligand **2** system ($C_L = C_M = 10$ mM).

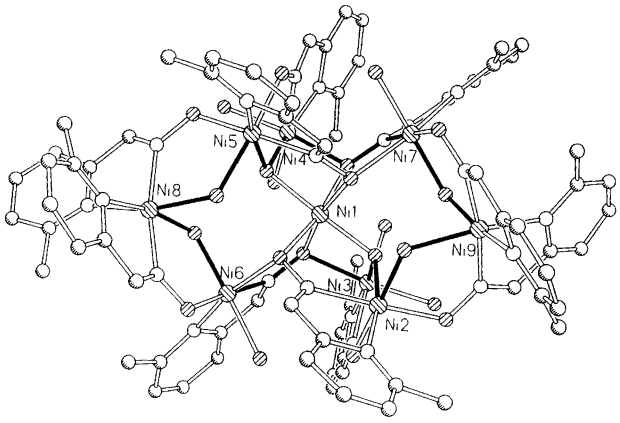

Fig. 4. The structure of the nonameric complex unit $[Ni_9L_{10}(OH)_6(H_2O)_6]^{2+}$ in $Ni_9L_{10}(OH)_6(H_2O)_{12}(ClO_4)_2$, where HL = **2**. Dotted circles, N; striped circles, O.

from its inability to form stable bis and tris complexes. This gives several alternative ways for nickel(II) to complete its octahedral coordination sphere.

With ligand **2** the only mononuclear deprotonated complex found here has the *p*, *q*, *r* notation of −2, 1, 2. Whether this is an oximato complex or a hydroxo species cannot be judged from potentiometric data. It may be noted, however, that the species does not appear in the solution until the formation of the hydrolysed dimeric species −2, 3, 3 has begun.

Neither it is possible to give any reliable proposal for the actual structure of the hydrolysed polynuclear complexes detected. The crystalline species isolated as perchlorate from solution where the trinuclear species −5, 3, 3 predominates proved to have a very complicated $[Ni_9L_{10}(OH)_6(H_2O)_6]^{2+}$ complex moiety which in our formulation corresponds to the *p*, *q*, *r* notation of −16, 9, 10. This metallacrown[15] structure contains an octahedral NiO_6 central core, and two different NiN_4O_2 and two different NiN_2O_4 environments. All of the oxime groups are deprotonated, and the nine nickel atoms are linked together via several bi- or trifurcated oximato and hydroxo bridges, as may be found in Fig. 4.

It is not reasonable to make any attempt to compile the nonanuclear species from the lower fragments found in this study. For this kind of complex which contains an extensive bridging network and numerous coordinated aqua molecules, the structure obtained must be very sensitive to precipitation circumstances, and any direct resemblance between the aqueous and solid phases can hardly be expected.

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