Formation, Redox and Structural Properties of Nickel Complexes of Pyridine-2-aldoxime

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The nickel(II) complex formation of pyridine-2-aldoxime (= HL) has been studied at 25 °C in aqueous 1.0 mol dm^{-3} Na(Cl) solution by emf titrations. The experimental data, analyzed by use of the least-squares computer program SUPERQUAD, can be explained in terms of the stepwise formation of binary complexes, Ni(HL)$_r^{2+}$ (r = 1,2,3), together with a series of hydrolyzed mononuclear complexes, Ni(HL)$_r$L$_s^{2-s}$, where s = 1, 2, 3 and $r + s$ = 2,3. The values of the stability constants for the complexes are given. Oxidation of the set of the tris complexes was studied as a function of pH using cyclic voltammetric measurements. Above pH ca. 7, the occurrence of a pH-independent one-electron couple Ni(III)L$_3$ + e$^-$ $\rightleftharpoons$ Ni(II)L$_3^-$ with the formal electrode potential $E_{298}^{\circ\prime}$ = 0.59 ± 0.01 V vs. NHE was established. The structure of the neutral crystalline tris complex with the formula Ni(HL)L$_2$· 6$\frac{1}{2}$ H$_2$O, isolated as a solid from an equilibrium solution, was determined from X-ray diffraction data. The compound was found to consist of two monomeric Ni(HL)L$_2$ units held together by two O$\cdots$O hydrogen bridges between the oxime oxygen atoms. The distorted octahedral coordination sphere around the nickel, made up of three pyridine and three oxime nitrogen atoms, was verified.

The complexation in aqueous solution between nickel(II) and 2-aminoacetamidoximes of the type RR'NCH$_2$C(NH$_2$)-NOH (= HY) has been discussed in earlier papers from this laboratory.[1-3] When R = H and R' = H or CH$_3$, the systems are dominated by the presence of stable square-planar Ni(HY)Y$^+$ complexes with an intramolecular hydrogen bridge between cis oxime oxygen atoms. When R = R' = CH$_3$ or C$_2$H$_5$ the formation of this hydrogen bond is hindered, and deprotonation of the oxime groups in the mononuclear complexes leads to polynuclear species in which amide nitrogen acts as donor atom. To clarify the role of the different nitrogen donors in these structures, we have also studied comparable bidentate oximes containing aromatic nitrogen in place of the amino function. Here we describe the complexation between nickel(II) and pyridine-2-aldoxime (= HL) in aqueous solution. To obtain additional support for the proposed coordination model, one of the tris complexes was isolated as a solid from solution and analyzed by X-ray diffraction methods. Also, finding the structures to possess characteristics presumed effective in stabilizing oxidation states of Ni higher than +II, we studied the oxidation of Ni(II) in the aqueous complexes by cyclic voltammetric methods.

Experimental

The purity of the pyridine-2-aldoxime employed (99+ %; Aldrich, gold label) (= HL), was checked by potentiometric titration and DSC methods.

The solid tris complex, Ni(HL)L$_2$· 6$\frac{1}{2}$ H$_2$O, subjected to X-ray analysis was obtained by evaporation of a 1:3 aqueous solution of NiCl$_2$ and HL; the pH value of the solution was adjusted to about 7. Crystals suitable for measurement were obtained by recrystallization from water. The stoichiometry of the complex was checked by thermal and elemental analyses. Thermogravimetric studies showed that some of the water molecules are relatively loosely bound in the structure, and dehydration of the compound begins already at about 30 °C.

Potentiometry. The potentiometric investigations were carried out as a series of titrations at 25 °C. To avoid variations in activity coefficients, a constant ionic medium of 1.0 mol dm^{-3} Na(Cl) was used. The free hydrogen ion concentration, h, was determined by measuring the emf of the cell

$-$RE | equilibrium solution | GE$+$
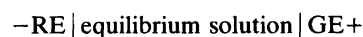
where GE denotes a glass electrode (Beckman, type 40495) and RE = Hg, Hg$_2$Cl$_2$ ‖ 1.00 mol dm^{-3} Na(Cl). Assuming the activity coefficients to be constant, the following expression is valid:

$$E = E^{\circ} + 59.157 \log h + E_{\mathrm{j}} \qquad (1)$$

For each separate titration the electrode system was calibrated against the background electrolyte by means of E°, E_{j} titration, after which the main run was started. For the
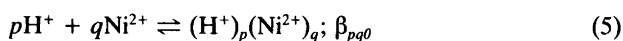
liquid junction potential we used $E_j = j_H h$; the value of the coefficient j_H varied slightly in separate measurements, and the average value was -60 mV mol^{-1} dm^3.

During the measurements h was varied by adding hydroxide or hydrogen ions to the solution. Both forward and backward titrations were carried out to ascertain the reversibility of the equilibria. The titrations used to obtain the acidity constants for pyridine-2-aldoxime were performed in four separate runs comprising a total of 147 experimental points within the concentration range 0.005–0.015 mol dm^{-3}. In the three-component systems, the ratio between the total concentration of nickel(II), C_M, and ligand, C_L, was held constant. The initial concentrations were varied within the limits $0.002 \leqq C_M \leqq 0.009$ mol dm^{-3} and $0.007 \leqq C_L \leqq 0.026$ mol dm^{-3}, and the ligand-to-metal ratio was within $1 \leqq C_L/C_M \leqq 10$. Owing to the formation of precipitate or, in other cases, a very slow attainment of equilibria, the $-\log h$ (= pH) value was restricted to an upper value of ca. 8.6.

In evaluating the equilibrium constants we assumed the presence of a three-component system of the form

$$p\text{H}^+ + q\text{Ni}^{2+} + r(\text{HL}) \rightleftharpoons (\text{H}^+)_p(\text{Ni}^{2+})_q(\text{HL})_r; \; \beta_{pqr} \qquad (2)$$
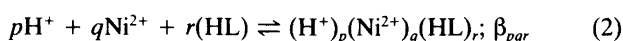
in addition to the two-component systems

$$\text{H}^+ + \text{HL} \rightleftharpoons \text{H}_2\text{L}^+; \; \beta_{101} \qquad (3)$$

$$\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^-; \; k_a \qquad (4)$$

$$p\text{H}^+ + q\text{Ni}^{2+} \rightleftharpoons (\text{H}^+)_p(\text{Ni}^{2+})_q; \; \beta_{pq0} \qquad (5)$$

The values of the equilibrium constants for binary proton-ligand equilibria (3) and (4) were obtained in separate experiments. For the equilibrium (5) we used the results summarized by Baes and Mesmer,[4] but later found that the Ni^{2+} hydrolysis was negligible under our conditions.

In the search for the complexation model, the problem is to find the sets of pqr-triplets and corresponding equilibrium constants giving the best fit to the experimental data. In these calculations we used the least-squares computer program SUPERQUAD.[5]

Cyclic voltammetry. All cyclic voltammograms were recorded using a Metrohm Polarographic Instruments apparatus in conjunction with a VA scanner and a three-electrode system consisting of a platinum wire working electrode, a glassy-carbon auxiliary electrode and a saturated calomel reference electrode (SCE). The measurements were carried out in aqueous 1.0 mol dm^{-3} Na(Cl) solutions under nitrogen over the pH range 2–9, using a metal-to-ligand ratio of 1:3. The voltage at the Pt electrode was scanned within the interval -0.1 to $+0.8$ V vs. SCE. At higher voltage values irreversible oxidation of ligand occurs. All the redox potential values in the following text are quoted relative to SCE.

The reduction potential $\bar{E}$ for a complex ML_r^{m+} involving n electrons and p protons, eqn. (6), depends on pH according to eqn. (7):

$$\text{ML}_r^{m+} + ne^- + p\text{H}^+ \rightleftharpoons \text{ML}_r\text{H}_p^{m-n+p} \qquad (6)$$
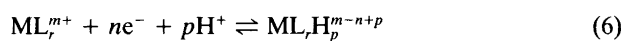
$$\bar{E} = E_{298}^{o\prime} - 0.059\,\frac{p}{n}\,\text{pH} \qquad (7)$$

The number of electrons, n, is established from the peak-to-peak separation in a cyclic voltammetry experiment. For a reversible couple, the peak-to-peak separation is $0.059/n$ V. When reduction is independent of pH, the formal electrode potential $E_{298}^{o\prime}$ can be calculated from the equation

$$E_{298}^{o\prime} = \bar{E} = \tfrac{1}{2}(E_a + E_c) \qquad (8)$$

where $\bar{E}$ is the midpoint potential, i.e. the average of the anodic and cathodic peak potentials E_a and E_c, respectively.

X-Ray crystallography. An orange-red crystal of maximum dimension 0.3 mm was mounted on a glass fibre and covered with epoxy adhesive. Unit cell parameters were obtained by least-squares fit to the automatically centred settings for 22 reflections collected on a Nicolet P3 four-circle diffractometer. Cell dimensions and intensity data are listed in Table 1.

X-ray intensities were measured by the ω-scan technique with variable scan speeds. The data were corrected for

Table 1. Crystal and intensity data for [Ni(HL)L$_2$] · 6½H$_2$O.

Molecular formula	NiC$_{18}$H$_{16}$N$_6$O$_3$ · 6½H$_2$O
Cell refinement	22 reflections
2 θ range/°	10–21
Cryst. system	Monoclinic
a/Å	14.688(6)
b/Å	12.921(5)
c/Å	25.775(9)
β/deg	92.09(3)
V/Å^3	4888(3)
Z	8 (monomer)
Space group	C2/c
d_o/g cm^{-3}	1.44(2)
d_c/g cm^{-3}	1.468(1)
Radiation	MoK$_\alpha$(λ = 0.71069 Å)
Method	ω-scan technique
Standards	2 every 58 reflections
μ/cm^{-1}	8.5
Rate/° min^{-1}	2.2–30.0
2 θ range/°	4.0–50.0
Unique reflections	4307
Obsd. reflections	
$I > 3.0\sigma(I)$	2799
R^a	0.046
$R_w^{b,c}$	0.051
Largest shift/esd	0.070

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. $^c w = 1/[\sigma^2|F_o| + 0.0013|F_o|^2]$.

Table 2. Positional parameters (×10⁴) and equivalent isotropic thermal parameters (×10³) for [Ni(HL)L₂]·6½H₂O.

Atom	x	y	z	U_{eq}[a]
Ni	3950(1)	347(1)	1120(1)	38
Ligand 1				
C1	2784(3)	588(3)	191(2)	46
C2	2100(4)	893(5)	−160(2)	64
C3	1444(4)	1599(5)	0(3)	73
C4	1497(4)	1971(5)	496(3)	69
C5	2199(4)	1627(4)	832(2)	57
C6	3491(3)	−152(4)	61(2)	50
N1	2831(2)	952(3)	684(1)	44
N2	4089(2)	−364(3)	412(1)	42
O1	4783(2)	−1051(3)	317(1)	51
Ligand 2				
C7	4754(4)	−1409(4)	1645(2)	51
C8	5368(5)	−2100(5)	1865(2)	73
C9	6280(5)	−1835(6)	1894(3)	82
C10	6569(5)	−903(6)	1700(3)	77
C11	5916(4)	−245(5)	1483(2)	58
C12	3774(4)	−1612(4)	1605(2)	58
N3	5027(3)	−480(3)	1462(1)	44
N4	3255(3)	−930(3)	1393(1)	50
O2	2359(2)	−1118(3)	1349(2)	71
Ligand 3				
C13	4130(3)	2188(4)	1753(2)	47
C14	4013(5)	2899(5)	2153(2)	62
C15	3538(4)	2694(6)	2573(2)	67
C16	3156(4)	1682(6)	2604(2)	67
C17	3263(4)	996(4)	2197(2)	57
C18	4682(4)	2372(4)	1305(2)	52
N5	3735(3)	1240(3)	1777(1)	45
N6	4737(2)	1661(3)	966(1)	42
O3	5289(2)	1836(3)	566(1)	57
Water molecules				
O$_w$1	2851(4)	1937(5)	4011(3)	144
O$_w$2	1093(5)	121(7)	1755(4)	178
O$_w$3	3961(5)	3982(7)	4480(3)	191
O$_w$4	3806(7)	3213(7)	5436(4)	211
O$_w$5	288(7)	230(7)	4049(6)	248
O$_w$6	9018(9)	731(8)	2243(5)	281
O$_w$7[b]	8329(10)	424(10)	1400(6)	139

$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3$. [b]Population parameter 0.5.

Lorentz and polarization factors, but no absorption corrections were deemed necessary.

The structure was solved by heavy-atom procedures and refined by use of the full-matrix least-squares method using the SHELX76 computer program.[6] Anisotropic thermal parameters were refined for all non-hydrogen atoms. The thermal parameters for some of the water O atoms were

quite high, evidently due to the weak bonding of water molecules in the structure. Hydrogen atoms of the complex unit were clearly located on difference electron density maps and included in the refinement with isotropic thermal parameters. The final R value was 0.046 ($R_w = 0.051$) and the highest peak in the final $\Delta\varrho$ map was 0.64 Å⁻³.

Fractional coordinates of the non-hydrogen atoms are given in Table 2. Lists of hydrogen atom positions and structure factors are available from the authors on request.

Equilibrium analysis

In SUPERQUAD calculations the following values for the binary proton-ligand equilibria relating to the reactions (3) and (4) were obtained: $\log(\beta_{101}\pm3\sigma) = 3.865\pm0.006$ and $\log(k_a\pm3\sigma) = -9.922\pm0.006$. In the subsequent calculations these equilibria were assumed to be exactly known, and no attempts were made to adjust the equilibrium constants.

The treatment of the three-component data was initiated by drawing the conventional Bjerrum plot, $\bar{n}(\log[HL])$, shown in Fig. 1. It could immediately be concluded that besides the stepwise complexes Ni(HL)$_r^{2+}$ with $r = 1,2,3$, several deprotonated species were formed as well. The presence of deprotonated complexes in the system was also evident from the negative values of the total concentration of protons (as calculated relative to the zero level HL, Ni²⁺ and H₂O) readily obtained in the titrations.

The search for the best model was started with calculations in which the data points falling on the single mononuclear curve in Fig. 1 were treated together. SUPER-QUAD analysis of 145 experimental points from 9 different titrations gave a satisfactory fit, and yielded the following formation constants with their standard deviations (3σ): $\log \beta_{011} = 4.19(2)$, $\log \beta_{012} = 7.62(2)$ and $\log \beta_{013} = 10.42(2)$. The values of these parameters were then assumed as known during the search for the additional complexes, and were not varied until the final calculations.

As initial considerations indicated HL and L⁻ to act as ligands, it was logical to test all of the complexes Ni(HL)$_r$(L)$_s^{2-s}$ with $r + s \leq 3$ against the whole data set. This was done in calculations in which the equilibrium constants were systematically varied. SUPERQUAD analysis showed that the best fit to the experimental data was obtained when the deprotonated complexes Ni(HL)L⁺, NiL₂, Ni(HL)₂L⁺, Ni(HL)L₂ and NiL₃⁻ were included in the model. After this, a number of polynuclear species were tested against the whole data set, but none of these made any significant difference to the model. Table 3 lists the formation constants for the complexes proposed in final

Table 3. Final values of the equilibrium constants (β_{pqr}) relating to the reaction (2). The errors given are 3σ($\log \beta_{pqr}$).

$\log \beta_{011}$	4.190±0.024			$\log \beta_{-113}$	5.58±0.04
$\log \beta_{012}$	7.620±0.015	$\log \beta_{-112}$	2.80±0.05	$\log \beta_{-213}$	−0.70±0.05
$\log \beta_{013}$	10.416±0.021	$\log \beta_{-212}$	−3.68±0.06	$\log \beta_{-313}$	−8.42±0.04

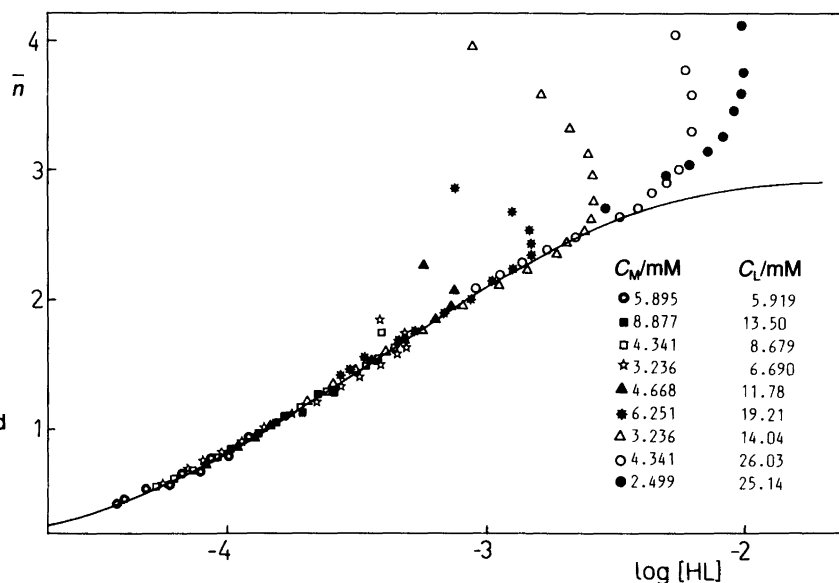Fig. 1. A part of the experimental data plotted as curves $\bar{n}$(log [HL]). The full curve was calculated with log β_{011}, log β_{012} and log β_{013} values according to Table 3. Symbols O, ▲ and ■ refer to back titrations.

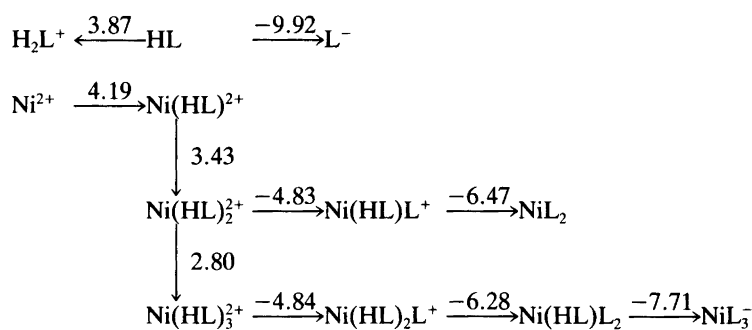|	C_M/mM	C_L/mM
O	5.895	5.919
■	8.877	13.50
□	4.341	8.679
☆	3.236	6.690
▲	4.668	11.78
✱	6.251	19.21
△	3.236	14.04
○	4.341	26.03
●	2.499	25.14

calculations encompassing 9 different titrations and 455 experimental points. The analysis was ceased at a total standard error of residuals S = 2.1 and χ^2 = 47. Standard errors were used for weighting by least-square calculations.[5] The values σ_V = 0.02 ml and σ_E = 0.10 mV were used for titre volume and measured potential errors [cf. formula (4) in Ref. 5].

Discussion

Earlier studies on the speciation in the aqueous Ni^{2+} − HL system are few, and the complexation models proposed must be regarded as unreliable.[7] The present emf investigation shows several deprotonated complexes to be formed in addition to the stepwise complexes $Ni(HL)_r^{2+}$ with r = 1,2,3. These deprotonated species can be observed to derive from the parent bis and tris oxime complexes, which behave as polyprotic acids and dissociate into the corresponding oximato species. The model is illustrated in Scheme 1, in which the log values of the respective equilibrium constants are included. Differences between the values of the stepwise formation constants for the oxime complexes, and the closely similar acidities of the species

$Ni(HL)_2^{2+}$ and $Ni(HL)_3^{2+}$, suggest that no coordination shift occurs during the complex formation. This means that probably all the present complexes, including $Ni(HL)L^+$, are octahedral and that the effect of the pyridine nitrogen on the complexation resembles the effect of the tertiary R_2N grouping. The same conclusion is supported by the magnetic and thermal properties of the complexes.[8,9] In the case of pyridine-2-aldoxime, as with aliphatic amino-oxime ligands with primary and secondary amino groups, the formation of the square-planar complex $Ni(HL)L^+$ stabilized by a strong intramolecular O$\cdots$O hydrogen bridge between the oxime oxygen atoms, must result in a considerable strain in the complex molecule. Not only do the *cis* C(6)-H groups have large spatial requirements but the *cis* oxime oxygens are strongly repelling.

Interestingly, the structure of the solid tris complex $Ni(HL)_2 \cdot 6\frac{1}{4}$ H_2O analyzed here is dimeric, the two halves of the molecule being held together at the oxime ends by two O$\cdots$H$\cdots$O hydrogen bridges (cf. Fig. 2). The intermolecular hydrogen bond formed in this way is relatively short, 2.491(5) Å, like the corresponding intramolecular hydrogen bond in square-planar nickel(II) complexes. No polymeric complex species were detected in solution, per-

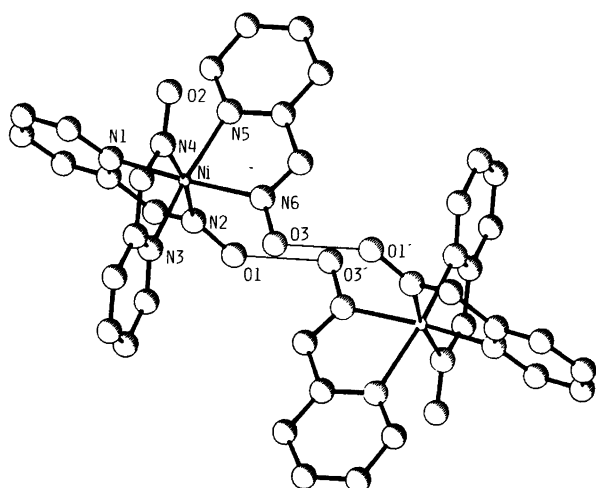$$H_2L^+ \xleftarrow{\;3.87\;} HL \xrightarrow{\;-9.92\;} L^-$$

$$Ni^{2+} \xrightarrow{\;4.19\;} Ni(HL)^{2+}$$

$$\Big\downarrow 3.43$$

$$Ni(HL)_2^{2+} \xrightarrow{\;-4.83\;} Ni(HL)L^+ \xrightarrow{\;-6.47\;} NiL_2$$

$$\Big\downarrow 2.80$$

$$Ni(HL)_3^{2+} \xrightarrow{\;-4.84\;} Ni(HL)_2L^+ \xrightarrow{\;-6.28\;} Ni(HL)L_2 \xrightarrow{\;-7.71\;} NiL_3^-$$

Scheme 1.

Fig. 2. The structure of the dimeric complex unit in Ni(HL)L$_2$·6½ H$_2$O.

haps because the aforementioned hydrogen bonds were dissociated in water, or because the limited solubility ranges did not permit their formation in measurable amounts under our conditions.

It may be noted that the present complexation model is entirely different from that for the copper(II)- HL system, which in aqueous solution as well as in the solid state is characterized by the presence of very stable trinuclear species Cu$_3$L$_3$(OH)$^{2+}$ and Cu$_3$L$_3$(OH)$_2^+$.[10,11]

In the solid state the coordination about the nickel atom is distorted octahedral, involving three oxime and three pyridine nitrogens. The most important bond lengths and angles of the complex moiety are given in Table 4. In comparison with the dimensions reported for other octahedral nickel(II) complexes with oxime ligands, the present structure shows some clear discrepancies. In particular, the Ni-N(4) and N(4)-O(2) distances can be regarded as exceptionally long for a coordinated oximato group.[3] The lengthenings of these bonds may be explained in terms of the

Table 4. Selected bond lengths (Å) and angles (°).

Bond lengths			
Ni–N1	2.107(3)	C6–N2	1.266(6)
Ni–N2	2.062(3)	N2–O1	1.380(5)
Ni–N3	2.079(4)	C12–N4	1.276(6)
Ni–N4	2.077(4)	N4–O2	1.339(5)
Ni–N5	2.081(4)	C18–N6	1.271(6)
Ni–N6	2.100(4)	N6–O3	1.354(5)
Bond angles			
N1–Ni–N2	78.0(1)	N3–Ni–N4	79.8(2)
N1–Ni–N3	169.6(1)	N3–Ni–N5	94.3(1)
N1–Ni–N4	95.3(1)	N3–Ni–N6	94.6(1)
N1–Ni–N5	95.2(1)	N4–Ni–N5	94.3(1)
N1–Ni–N6	91.3(1)	N4–Ni–N6	170.9(1)
N2–Ni–N3	92.7(1)	N5–Ni–N6	78.8(1)
N2–Ni–N4	90.6(1)	C6–N2–O1	120.7(4)
N2–Ni–N5	172.0(1)	C12–N4–O2	118.8(4)
N2–Ni–N6	96.9(1)	C18–N6–O3	117.2(4)

hydrogen bond formation with the nearby water molecules: O(2)···O(4) = 2.692(6) Å, O(2)···O(5) = 2.693(6) Å. Also, the remaining two CNO(H) groups exhibit minor deviations from the ideal geometry of the oxime group. These distortions are possibly closely related to the shortness of the "intermolecular" hydrogen bond between the oxime oxygens.
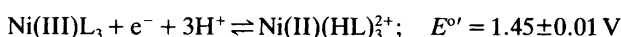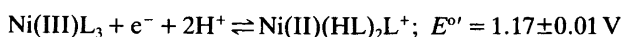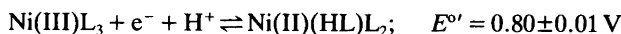
Although the results obtained for the solid state cannot give direct information about the structure of the corresponding aqueous species, it seems likely that the present tris complexes have a similar octahedral six-coordination in these two phases. A structure such as this, with at least one oximato nitrogen, is of particular interest since it has proved effective in stabilizing nickel ion in its formal oxidation states +III and +IV. So far, in the structurally and electrochemically best characterized compounds of this type, the coordination sphere above nickel has been derived from tri- and hexadentate amine-imine-oxime ligands. Directly determined redox potential data for various nickel(IV)/(III)/(II) couples involved in these systems are also available.[12,13]

In this study the oxidation of nickel was studied by cyclic voltammetry using a titration technique in which the pH of the system was varied by adding NaOH to the solution containing nickel(II) and HL in the molar ratio 1:3. The distribution of nickel(II) between different complex species vs. pH in the studied system is illustrated in Fig. 3.

From the CV measurements a single reversible or pseudo-reversible redox equilibrium can be detected at pH>6.9. The increase in the anodic and cathodic currents as a function of pH (Fig. 4) is clearly associated with the simultaneous increase in the relative amount of the fully deprotonated tris complex, NiL$_3^-$ (cf. Fig. 3). The constancy of the peak positions and the peak-to-peak separations indicate that the pH-independent one-electron

$$\text{Ni(III)L}_3 + \text{e}^- \rightleftharpoons \text{Ni(II)L}_3^- \tag{9}$$

couple is involved. The value of the formal electrode potential, E°_{298}, obtained here for eqn. (9) is +0.34±0.01 V vs. SCE. The neutral nickel(III) species is thus a moderately strong oxidizing agent, and considerably stronger than the aforementioned amine-imine-oxime complexes, for which the values for the proton-independent nickel(III)/(II) couples are between 0.07 and 0.16 V (vs. SCE at 25°C and in 0.1 M NaCl).[13]

Experimental potential values for the nickel(III)/(II) system involving protonated forms of the ligand could not be obtained directly from CV data. The relevant potentials can, however, be readily calculated with the aid of the deprotonation constants for the Ni(II)L$_3$H$_n^{n-1}$ complexes, and the folloving values are obtained:

$$\text{Ni(III)L}_3 + \text{e}^- + \text{H}^+ \rightleftharpoons \text{Ni(II)(HL)L}_2; \quad E^{\circ\prime} = 0.80\pm0.01 \text{ V}$$

$$\text{Ni(III)L}_3 + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{Ni(II)(HL)}_2\text{L}^+; \quad E^{\circ\prime} = 1.17\pm0.01 \text{ V}$$

$$\text{Ni(III)L}_3 + \text{e}^- + 3\text{H}^+ \rightleftharpoons \text{Ni(II)(HL)}_3^{2+}; \quad E^{\circ\prime} = 1.45\pm0.01 \text{ V}$$
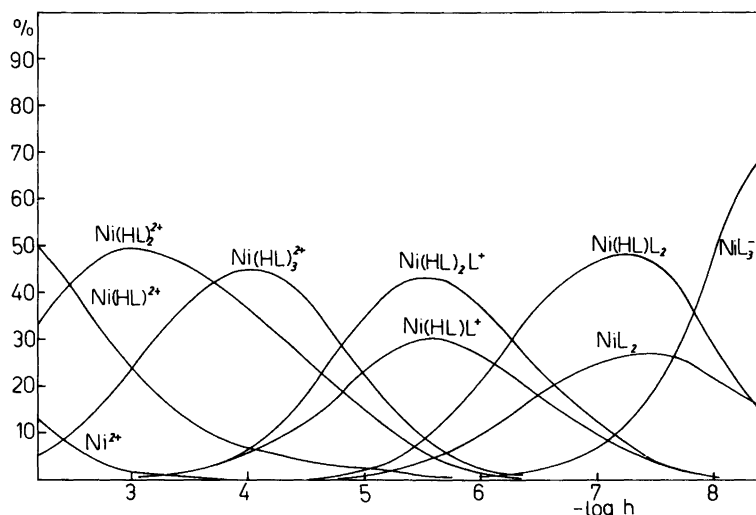
Fig. 3. Percentage distribution of nickel(II) among different complex species vs. pH in the Ni^{2+}-pyridine-2-aldoxime system with $C_M = 6.25$ mM and $C_L = 19.21$ mM.

The values of the derived potentials indicate that protonation of these complexes stabilizes the lower oxidation state of metal. The coordinated oximato group acts as a one-electron oxidant, and complexes with two or more oximato functions permit oxidation at the nickel centre to the tetravalent state.[14] We were not able to obtain quantitative information about the further oxidation of $Ni(III)L_3$; the CV measurements suggested that the complex undergoes an anodic oxidation at $+0.70\pm0.01$ V, but the cathodic peak could not be detected. This is in agreement with

the results of Drago and Baucom, who found no visual or chemical evidence of a more highly oxidized species when oxidation of $Ni(III)L_3$ was attempted.[15]

In all, the nickel(III) atom in the present complex seems to be considerably more stable towards oxidation to the tetravalent state than is the nickel(III) atom in comparable amine-imine-oxime complexes. This may be due to the lower thermodynamic stability of the present complex with three bidentate ligands than that of the amine-imine-oxime complexes which are formed by two tridentate or one hexadentate ligand.
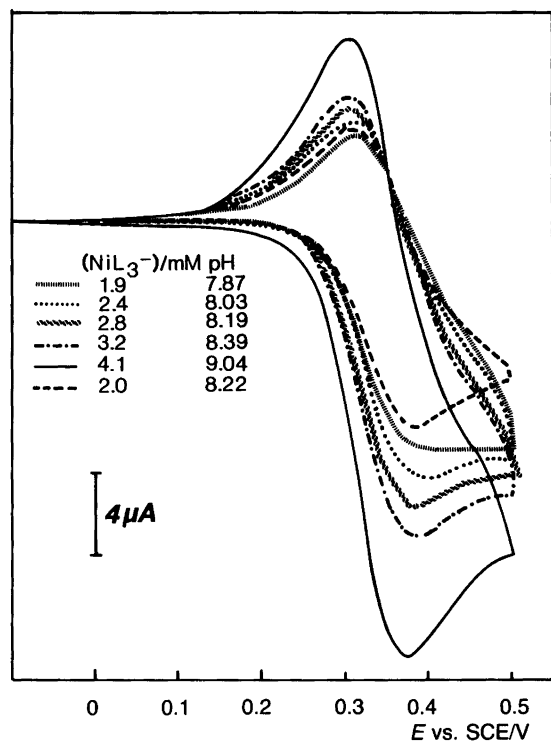

Fig. 4. The cyclic voltammograms for Ni(II)-pyridine-2-aldoxime complexes in 1 M Na(Cl) solutions. Scan rate 10 mV s^{-1}. The concentrations of the complex were calculated using the values of the stability constants given in Table 3. (—–) measured in borate buffer.

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