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Chemistry of Tetravalent Nickel and Related Species. 2.[1] Cyclic Voltammetry of Oxidation–Reduction Equilibria Involving Protons

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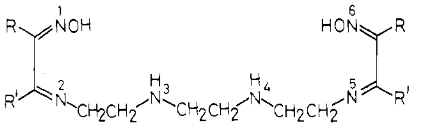
The redox behavior of nickel(II) and nickel(IV) species derived from a few hexadentate ligands of type **1** ($H_2RR'L$) have been thoroughly studied in buffered media over a wide range of pH using cyclic voltammetry and coulometry. The results for the system having R = R′ = Me are representative. At pH <5, a single reversible two-electron, two-proton couple, $Ni(Me_2L)^{2+}$–$Ni(H_2Me_2L)^{2+}$ ($E°'_{298}$ = 0.71 V vs. SCE) is observed. At pH >6, two distinct reversible one-electron processes are observed. One of these has no proton involvement: $Ni(Me_2L)^{2+}$–$Ni(Me_2L)^+$ has $E°'_{298}$ = 0.42 V vs. SCE. The second couple may or may not involve protons: pH ~7, $Ni(Me_2L)^+$–$Ni(HMe_2L)^+$, $E°'_{298}$ = 0.64 V vs. SCE; pH >8.45, $Ni(Me_2L)^+$–$Ni(Me_2L)$, $E°'_{298}$ = 0.15 V vs. SCE. The nickel(II) species involved in each couple is what is expected from acid dissociation data: pK_1 = 5.90; pK_2 = 7.80. The observed transition of the single two-electron couple into two one-electron couples as the pH is raised can be rationalized on the basis of the higher proton affinity of the nickel(II) species. It is estimated that the couple $Ni(Me_2L)^+$–$Ni(H_2Me_2L)^{2+}$ has $E°'_{298}$ = 1.01 V. The nickel(III) intermediate $Ni(Me_2L)^+$ is relatively unstable. However a paramagnetic solid containing nickel(III) has been obtained by oxidation of $Ni(H_2Me_2L)^{2+}$. In the polycrystalline phase it shows room-temperature EPR signals characteristic of axial symmetry ($g_\parallel$ = 2.04; $g_\perp$ = 2.16). The one-electron redox behavior of $Fe(H_2Me_2L)^{2+}$ is briefly reported and an empirical relationship between $E°'_{298}$ values of nickel(III)–nickel(II) and iron(III)–iron(II) couples is noted.

Introduction

Concerted electron- and proton-transfer reactions are of vital import[2] in chemistry and biochemistry. Of particular interest is the situation where a transition metal ion is bound to ligand sites which also hold dissociable protons. A redox transformation of the metal ion naturally affects the p*K* of the protons. The more oxidized the metal gets, the less tightly are the protons held. Loss of electrons and protons may thus occur simultaneously. In the present work model examples of this and related phenomena are revealed by a thorough, pH-dependent cyclic voltammetric (CV) study of the species $Ni^{II}(H_2RR'L)^{2+}$ and $Ni^{IV}(RR'L)^{2+}$ both of which are believed[1] to have the pseudooctahedral NiN_6 coordination sphere **2** (the ligand **1** is abbreviated as $H_2RR'L$ which has two dissociable oxime protons).



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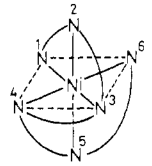

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Results and Discussion

A. Proton Dissociation of Nickel(II) Species. The pattern of CV response depends on the nature of nickel(II) species existing in solution. This in turn is dependent on the position of the equilibria

$$\mathrm{Ni(H_2RR'L)^{2+}} \overset{K_1}{\rightleftharpoons} \mathrm{Ni(HRR'L)^+ + H^+} \tag{1}$$

$$\mathrm{Ni(HRR'L)^{+}} \overset{K_2}{\rightleftharpoons} \mathrm{Ni(RR'L) + H^+} \tag{2}$$

One specific complex, viz., $Ni(H_2Me_2L)^{2+}$, was titrated pH-metrically with alkali. From the titration data the dissociation constants pK_1 and pK_2 were found to be (25 °C) 5.90 ± 0.05 and 7.80 ± 0.05, respectively. The formation curves (Figure 1) for the three species involved in eq 1 and 2 were constructed using these equilibrium constants. Examination of Figure 1 reveals that up to pH 5 $Ni(H_2Me_2L)^{2+}$ alone makes major contribution to solution composition while at pH ≥8.5 the major species is $Ni(Me_2L)$ alone. The intermediate species $Ni(HMe_2L)^+$ does not play such a singular role except in a very narrow section of pH near 7. In contrast to the nickel(II) system, the nickel(IV) species exists only in the deprotonated form $Ni(Me_2L)^{2+}$ even in strongly acidic solutions.[1]

B. Peak Potential, Formal Electrode Potential, pH, and Reaction Stoichiometry. In protic media protons are often involved in the electrode reaction. For the general reversible electrode reaction

$$\mathrm{Ox} + ne^- + m\mathrm{H}^+ \rightleftharpoons \mathrm{Red} \tag{3}$$

the Nernst equation can be readily cast into the form[3] (25 °C)

$$E_{1/2} = E^{\circ\prime}{}_{298} - \frac{0.059}{n} \log (D_{\mathrm{Ox}}/D_{\mathrm{Red}})^{1/2} - 0.059(m/n)\mathrm{pH} \tag{4}$$

where $E_{1/2}$ is the half-wave potential, $E°'_{298}$ is the formal electrode potential, and D_{Ox} and D_{Red} are respectively the diffusion coefficients of Ox and Red. In the derivation of eq 4 it is assumed that the concentration of protons at the electrode surface is equal to that in the bulk. Since protons diffuse very fast, this is expected to be true in well-buffered media.[3] By applying the usual assumption $D_{Ox} \simeq D_{Red}$ and the knowledge[4] that the CV cathodic and anodic peak potentials, E_{pc} and E_{pa}, are respectively 28.5/*n* mV more cathodic and 29.5/*n* mV more anodic than $E_{1/2}$, eq 4 can be reduced to

$$E^{\circ\prime}{}_{298} = \bar{E}_{\mathrm{p}} + 0.059(m/n)\mathrm{pH} \tag{5}$$

where

$$\bar{E}_{\mathrm{p}} = 0.5(E_{\mathrm{pc}} + E_{\mathrm{pa}}) \tag{6}$$

Strictly speaking there should be an additional term of value −0.5/*n* mV on the right-hand side of eq 5. This is neglected since it is much smaller than the accuracy (5–10 mV) with which the peak potentials can be located. In the particular case where protons are not involved (*m* = 0) in the electrode reaction, the special form of eq 5 is

$$E^{\circ\prime}{}_{298} = \bar{E}_{\mathrm{p}} \tag{7}$$

From eq 5 it is readily seen that

$$m = -(n/0.059)(\Delta\bar{E}_{\mathrm{p}}/\Delta\mathrm{pH}) \tag{8}$$

where $\Delta\bar{E}_p$ is the shift of $\bar{E}_p$ due to the change in pH by ΔpH.

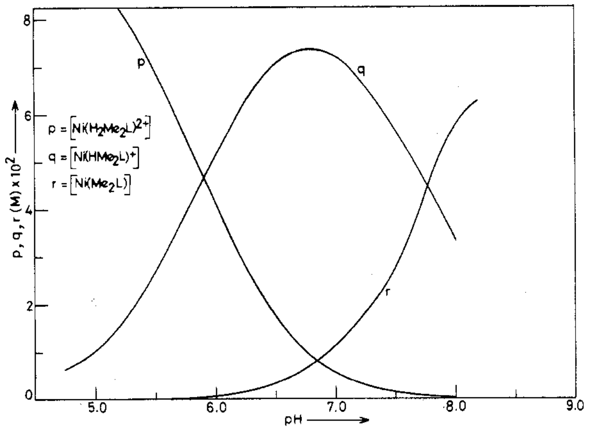

Figure 1. Formation curves of nickel(II) species.

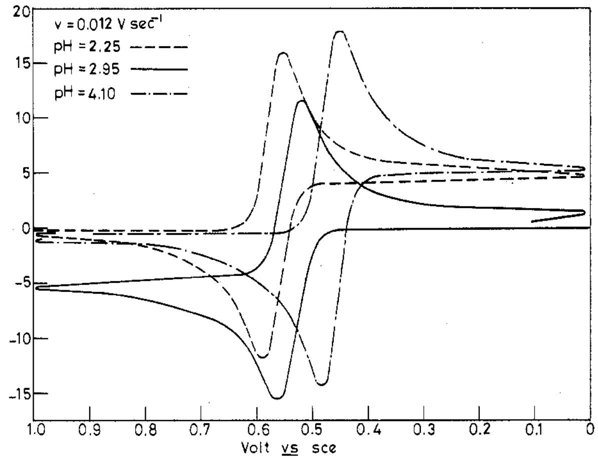

Figure 2. Cyclic voltammograms of $Ni(H_2Me_2L)(ClO_4)_2$ (1.01×10^{-3} M, –) and $Ni(Me_2L)(ClO_4)_2$ (1.01×10^{-3} M, - - -; 1.23×10^{-3} M, · — · –) at pH <5.

Table I. Cyclic Voltammetric Data[a,b] for Couple A, $Ni(Me_2L)^{2+}$–$Ni(H_2Me_2L)^{2+}$, in Acetate Buffer at 25 °C

pH	$\bar{E}_p$, V	ΔE_p, V	ΔpH	$\Delta\bar{E}_p$, V	m	$E^{\circ\prime}_{298}$, V
		Starting with $Ni(Me_2L)^{2+}$				
1.15	0.640	0.030				0.71[c]
2.25	0.573	0.035	1.10	0.067	2.1 ± 0.1	0.70
2.95	0.530	0.040	1.80	0.110	2.1 ± 0.1	0.71
3.45	0.510	0.035	2.30	0.130	1.9 ± 0.1	0.71
4.10	0.468	0.035	2.95	0.172	2.0 ± 0.1	0.71
		Starting with $Ni(H_2Me_2L)^{2+}$				
2.00[d]	0.595	0.040				0.71
2.95	0.540	0.040	0.95	0.055	2.0 ± 0.2	0.71

[a] Concentration range (0.98–1.23) × 10^{-3} M. [b] Scan rate 0.012 V s^{-1}. [c] $E^{\circ\prime}_{298}$ values at this and other pH's are calculated with $m = 2$ and $n = 2$. [d] At this pH or less, nickel(II) species appear to decompose slowly.

The negative sign of eq 8 signifies that as pH increases, $\bar{E}_p$ decreases. Equation 8 provides a method for determination of m if n is known.

C. Cyclic Voltammetry of $Ni(H_2Me_2L)^{2+}$ and $Ni(Me_2L)^{2+}$. 1. At pH < 5. Experiments were performed at several scan rates starting from either the nickel(II) or the nickel(IV) species in well-buffered media. Selected results are displayed in Table I and Figure 2. *All potentials in this paper are referenced to the saturated calomel electrode (SCE).* A single-step voltammogram is observed in the potential range 0–1 V. The separation ΔE_p between cathodic and anodic peaks lies in the range 30–40 mV. This clearly establishes[4] the presence of a reversible single-step two-electron-transfer process without the involvement of any nickel(III) intermediate. The reversibility of the process is maintained up to a scan rate of 0.14 V s^{-1}. Beyond this, progressive irreversibility sets in. As an illustration the data for pH 1.15 are set out in Table II.

Table II. Effect of Scan Rate in the Case of $Ni(Me_2L)^{2+}$ and $Ni(H_2Me_2L)^{2+}$

pH	v, V s^{-1}	Couple	E_{pa}, V	E_{pc}, V	ΔE_p, V
		Starting with $Ni(Me_2L)^{2+}$			
1.15	0.012	A[a]	0.655	0.625	0.030
	0.024	A	0.660	0.630	0.030
	0.080	A	0.655	0.625	0.030
	0.140	A	0.655	0.625	0.030
	0.240	A	0.670	0.615	0.055
	0.800	A	0.725	0.570	0.155
		Starting with $Ni(H_2Me_2L)^{2+}$			
9.00	0.012	B[b]	0.455	0.385	0.070
		C[c]	0.180	0.110	0.070
	0.072	B	0.455	0.385	0.070
		C	0.190	0.100	0.090
	0.240	B	0.460	0.385	0.075
		C	0.205	0.095	0.110

[a] Couple A, eq 9. [b] Couple B, eq 10. [c] Couple C, eq 12.

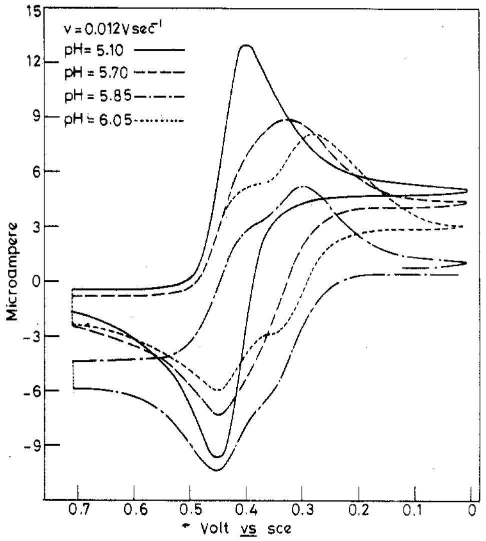

Figure 3. Cyclic voltammograms of $Ni(Me_2L)(ClO_4)_2$ (1.05×10^{-3} M, –; 1.07×10^{-3} M, - - -; 1.03×10^{-3} M, - - - -) and $Ni(H_2Me_2L)(ClO_4)_2$ (1.07×10^{-3} M, · — · –) in the pH range 5.10–6.05.

The two-electron involvement is fully corroborated by constant-potential coulometry at pH 3.25. For complete reduction (at 0.35 V) of 1.183×10^{-5} mol of $Ni(Me_2L)(ClO_4)_2$, 2.16 C was required. Reoxidation (at 0.80 V) of this solution needed 2.25 C. The value calculated for $n = 2$ is 2.28 C.

The peak potentials and hence $\bar{E}_p$ values are pH dependent (Table I, Figure 2) showing that protons are involved in the electron-transfer step. Using eq 8 and $n = 2$, values of m were computed (Table I). The quantities $\Delta\bar{E}_p$ and ΔpH are subject to experimental errors of 5 mV and 0.02 pH unit, respectively. The limits of error on m as shown in Table I correspond to these limits of error in $\Delta\bar{E}_p$ and ΔpH. The value of m is 2. The electrode reaction (couple A) is thus

$$Ni(Me_2L)^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni(H_2Me_2L)^{2+} \qquad (9)$$

The occurrence of the nickel(II) species in the fully protonated form at pH <5 is in full agreement with the results of section A. With $m = 2$ and $n = 2$, eq 5 was used to compute $E^{\circ\prime}_{298}$ for the couple (9). The observed value of 0.71 ± 0.01 V (Table I) is in excellent agreement with the value 0.70 ± 0.01 determined[1] by using a static potentiometric null method on

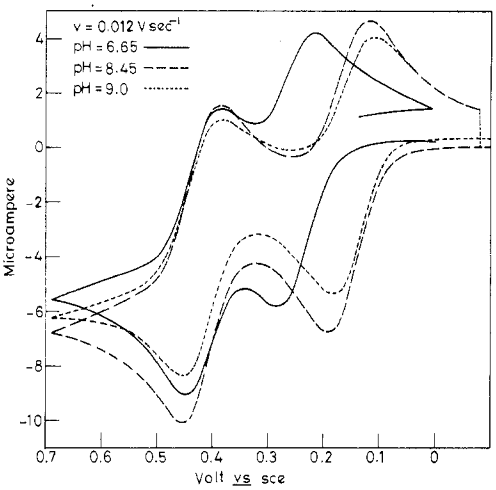

Figure 4. Cyclic voltammograms of $Ni(H_2Me_2L)(ClO_4)_2$ (1.04×10^{-3} M, –; 1.06×10^{-3} M, – – –; 1.00×10^{-3} M, - - - -) at pH >6.5.

Table III. Cyclic Voltammetric Data[a,b] of $Ni(H_2Me_2L)(ClO_4)_2$ in Phosphate and Borate Buffers at 25 °C: Couple B, $Ni(Me_2L)^{2+}$-$Ni(Me_2L)^+$; Couple C, $Ni(Me_2L)^+$-$Ni(HMe_2L)^+$ or $Ni(Me_2L)^+$-$Ni(Me_2L)$

pH	Couple	$\bar{E}_p$, V	ΔE_p, V	m	$E^{\circ\prime}_{298}$, V
6.65	B	0.417	0.065	0	0.42
	C	0.240	0.070	1	0.63
7.55	B	0.420	0.060	0	0.42
	C	0.198	0.075	1	0.64
8.45	B	0.420	0.060	0	0.42
	C	0.155	0.070	0	0.16
9.00	B	0.420	0.070	0	0.42
	C	0.145	0.070	0	0.15
9.35	B	0.420	0.070	0	0.42
	C	0.148	0.075	0	0.15

[a] Concentration range (1.00–1.15) × 10^{-3} M. [b] Scan rate 0.012 V s^{-1}.

solutions containing known concentrations of $Ni(H_2Me_2L)^{2+}$ and $Ni(Me_2L)^{2+}$.

2. At pH >5. Just above pH 5, ΔE_p begins to increase. When pH 6 is reached, it is evident that a change from couple A to two distinct couples is taking place (Figure 3). The peak position of the couple at higher potential (couple B) remains invariant with pH. On the other hand, the peak of the couple at lower potential (couple C) undergoes progressive cathodic shift with increase of pH till pH ~8.5 is reached. Beyond this pH little further change is observed (Figure 4). The above pattern is true irrespective of whether the starting complex is that of nickel(II) or that of nickel(IV). For brevity, only results obtained with the nickel(II) starting complex will be presented (Table III).

For couple B, ΔE_p is 60–70 mV when scan rates are low (Tables II and III). Clearly a reversible one-electron electrode reaction is involved. Since peak potentials are pH independent, protons do not participate in the reaction ($m = 0$). The electrode reaction is

$$Ni(Me_2L)^{2+} + e^- \rightleftharpoons Ni(Me_2L)^+ \tag{10}$$

The species $Ni(Me_2L)^+$ has nickel in the formal oxidation state III. The $E^{\circ\prime}_{298}$ of the couple (10) as obtained from application of eq 7 is 0.42 ± 0.01 V (Table III).

The ΔE_p values of couple C (Table III) suggest a reversible (or very nearly so) one-electron step. Evidently the nickel(III) species is now being reduced to the nickel(II) species. The data at pH 6.65 and 7.55 will be considered first. Formation curves (Figure 1) show that the major nickel(II) species at these pH values is $Ni(HMe_2L)^+$, although other species make some contribution. Indeed the shift (0.047 V) of $\bar{E}_p$ between the above two pH values roughly corresponds to that calculated (0.053 V) from eq 8 with $m = n = 1$. Around pH 7, the couple C can therefore be written mainly as

$$Ni(Me_2L)^+ + e^- + H^+ \rightleftharpoons Ni(HMe_2L)^+ \tag{11}$$

with $E^{\circ\prime}_{298} \approx 0.64$ V. At pH 8.45 and above, couple C no longer involves any proton since the peak potentials are independent of pH. Formation curves (Figure 1) also require that the nickel(II) species in this pH range is $Ni(Me_2L)$. The electrode reaction

$$Ni(Me_2L)^+ + e^- \rightleftharpoons Ni(Me_2L) \tag{12}$$

has $E^{\circ\prime}_{298} = 0.15 \pm 0.01$ V (eq 7 and Table III).

3. Critique. The reason that the two one-electron couples B and C become a single two-electron couple A at low pH can be understood on the basis of the expected (and observed) greater proton affinity of $Ni(Me_2L)$ compared to that of $Ni(Me_2L)^+$ and $Ni(Me_2L)^{2+}$. As the pH is lowered, $Ni(Me_2L)$ goes to $Ni(HMe_2L)^+$ and finally to $Ni(H_2Me_2L)^{2+}$ while the nickel(III) and nickel(IV) species are still unprotonated. $(\bar{E}_p)_C$ (subscript refers to couple C) consequently shifts progressively (eq 5) to higher potentials with decrease of pH while $(\bar{E}_p)_B$ remains unaffected. The shift of $(\bar{E}_p)_C$ toward $(\bar{E}_p)_B$ continues till they get superposed on each other at pH ~5. At pH <5, $(\bar{E}_p)_C$ "should occur" at potentials higher than $(\bar{E}_p)_B$. In other words in an anodic scan nickel(III) should be oxidized before it is generated from nickel(II)! The only physically tenable proposition is that it should be oxidized "as soon as" it is generated. A single-step two-electron process in which nickel(II) goes directly to nickel(IV) should thus occur at pH <5 (couple A). The arguments presented above are of general applicability. As more and more electrons are added to a substrate, the proton affinities of the reduced products would progressively increase. This would lead to decreasing separation of $\bar{E}_p$'s of the one-electron couples with decreasing pH. Eventually a single-step multielectron redox couple is all that is observed. Such a situation has been observed in the voltammetric studies of organic substrates such as diketones[5] and azo compounds.[6]

At pH 5 where the two couples just superpose, the nickel(II) species is $Ni(H_2Me_2L)^{2+}$ (Figure 1). The couple C at this pH is thus expected to be

$$Ni(Me_2L)^+ + e^- + 2H^+ \rightleftharpoons Ni(H_2Me_2L)^{2+} \tag{13}$$

while couple B is still given by eq 10. Applying eq 5 to these two couples which have equal $\bar{E}_p$ values at this pH, relation 14 is readily derived. Since $(E^{\circ\prime}_{298})_B$ is 0.42 V (Table III),

$$(E^{\circ\prime}_{298})_C - (E^{\circ\prime}_{298})_B = 0.59 \text{ V} \tag{14}$$

$(E^{\circ\prime}_{298})_C$ is computed to be 1.01 V. Simple thermodynamic considerations require that $E^{\circ\prime}_{298}$ of couple (9) should be equal to the average of the $E^{\circ\prime}_{298}$ values of couples (10) and (13). This is indeed true (average 0.72 V; observed 0.71 V (Table I)).

D. Other Systems. Nickel systems derived from a few other ligands of type **1** were also studied at different pH values. The pattern of behavior is parallel with the system considered above. Formal potential data are displayed in Table IV. The pH-dependent CV response of the iron(II) system[1,7] $Fe(H_2Me_2L)^{2+}$ was also studied. A one-electron Nernstian iron(III)–iron(II) process is involved over the studied range of pH. However, the number of protons participating in the electrode reaction depends on pH. The observed couples are summarized and compared with the corresponding nickel couples in Table V. Details will be published elsewhere. Comparison of $E^{\circ\prime}_{298}$ values (Table V) leads to the empirical relationship

$$(E^{\circ\prime}_{298})_{Ni} \simeq (E^{\circ\prime}_{298})_{Fe} + 0.32\ (\pm 0.04) \text{ V} \tag{15}$$

Table IV. Cyclic Voltammetric Data[a,b] of Other Nickel(II) Complexes in Buffers at 25 °C: Couple A, $Ni(RR'L)^{2+}$-$Ni(H_2RR'L)^{2+}$; Couple B, $Ni(RR'L)^{2+}$-$Ni(RR'L)^+$; Couple C, $Ni(RR'L)^+$-$Ni(RR'L)$

System R, R'	pH	Couple	$E^{\circ\prime}_{298}$, V
CH_3, C_2H_5	1.65; 3.05	A[c]	0.68
	⩾6.6	B	0.40
	⩾9.3	C	0.10
C_2H_5, CH_3	1.60; 2.55	A[c]	0.69
	⩾6.4	B	0.39
	⩾9.2	C	0.09
CH_3, C_6H_5	1.90; 3.45	A[c]	0.70
	⩾5.7	B	0.45
	⩾9.3	C	0.16
C_6H_5, CH_3	1.80; 3.70	A[c]	0.69
	⩾5.7	B	0.47
	⩾9.3	C	0.14

[a] Concentration range (1.03–1.16) × 10^{-3} M. [b] Scan rate 0.012 V s^{-1}. [c] Couple A was studied only at two selected pH values.

Table V. Comparison of the Corresponding Couples of Iron(II) and Nickel(II) Complexes

	pH range		$E^{\circ\prime}_{298}$, V	
Couple	Ni	Fe	Ni	Fe
$M(Me_2L)^+$-$M(H_2Me_2L)^{2+}$	~5	4.10	1.0[a]	0.65
$M(Me_2L)^+$-$M(HMe_2L)^+$	~7	5.65–6.55	0.63	0.34
$M(Me_2L)^+$-$M(Me_2L)$	⩾8.45	⩾8.20	0.15	−0.13

[a] Estimated (see text).

for every pair of couples involving the same number of protons.

The results on the nickel systems taken collectively with those of iron systems prove that the observed redox processes primarily involve the metal ion and not the bound ligand system. This is further augmented by the fact that cobalt(III) systems[1] based on H_2Me_2L are not reduced in the potential range 0–1 V.

In the literature there are several examples of voltammetric studies on Ni(II), -(III), and -(IV) systems such as those derived from dimethylglyoxime,[8] *o*-phenylenebis(dimethylphosphine),[9] *N,N*-dialkyldithiocarbamates,[10] cyclopentadienyl anion,[11] dicarbollide anion,[12] and tetraaza[16]annulene.[13] However in none of these cases do protons participate in the electrode reactions.

E. Concluding Observations. The present results further strengthen our assertion[1] that $Ni(RR'L)^{2+}$ contain nickel in the tetravalent state. Its reduction proceeds step by step to the nickel(II) state except at low pH where a single step is observed due to high proton affinity of the fully reduced oxidation state. Experiments in aprotic media should be interesting in this regard. Such experiments are under way. The excellent Nernstian character of the electrode reactions is a good indication that only minor stereochemical readjustments are needed during the redox processes: an octahedral NiN_6 coordination sphere[1] is implicated for all the oxidation states. Earlier[1] we have suggested that the negative charge on the oximate oxygen may play an important role in stabilizing the higher oxidation states of nickel. It may also be possible that the redox electron-transfer pathway is the Ni–N–O σ frame.

A significant feature of the present work is the identification of the nickel(III) intermediate $Ni(RR'L)^+$ at alkaline pH. This intermediate does not appear to be stable in solution. Constant-potential coulometry of nickel(II) at potentials high enough for oxidation to nickel(III) (but not to nickel(IV)) required more coulombs than predicted. We also have good evidence for the existence of nickel(III) in the solid state. Oxidation of $Ni(H_2Me_2L)(ClO_4)_2$ by $(NH_4)_2S_2O_8$ (0.5–1 mol for each mole of complex) in borate buffer, followed by acidification (pH ~5) and addition of $NaClO_4$, yields a black solid, whose chemical analysis corresponds to Ni:ligand:ClO_4 = 1:1:2. This solid is paramagnetic (1.6–2.3 μ_B). The exact magnetic moment, however, depended on the conditions of preparation (amount of oxidant, pH, time of reaction, etc.). The true nature of the solid remains to be established; it is probably a mixture. The significant point to note here is that every polycrystalline preparation gave the same strong EPR signals characteristic[14] of an axially symmetric $S = 1/2$ species (at room temperature and at liquid nitrogen temperature). The pure nickel(II) complex $Ni(H_2Me_2L)(ClO_4)_2$ does not show any EPR signals at room temperature.[15] It is indeed reasonable to propose that the EPR signals originate from a nickel(III) species, presumably $Ni(HMe_2L)(ClO_4)_2$. The g values are $g_\parallel = 2.04$ and $g_\perp = 2.16$ ($g_{av} = 2.12$). In a fresh solution of the black solid in nitromethane an isotropic signal with $g = 2.12$ is observed at room temperature. The observed spectra are closely akin to those of other nickel(III) species,[13,16,17] particularly[16] $Ni(Hdmg)_2(py)_2^+$ (Hdmg = dimethylglyoxime minus a proton) which has $g_\parallel \approx 2.03$ and $g_\perp \approx 2.17$. At present we are conducting experiments to obtain the nickel(III) species in pure form.

Experimental Section

A. **Preparation of Compounds.** All compounds were prepared as described earlier.[1]

B. pH-metric Titrations. These were done in a nitrogen atmosphere on 40 ml of 0.01 M $Ni(H_2Me_2L)(NO_3)_2\cdot H_2O$ using a Systronics pH meter, Type 322, in a double-walled glass vessel thermostated to 25 ± 0.1 °C. Carbonate-free sodium hydroxide solution (0.01 N) was added from a buret which could be read accurately to 0.01 ml. Relation 16 holds[18] for eq 1 and 2 where $\bar{h} = [Na^+]/C$. $[Na^+]$ is

$$\frac{\bar{h}}{2-\bar{h}}[H^+]^2 = \frac{1-\bar{h}}{2-\bar{h}}[H^+]K_1 + K_1K_2 \qquad (16)$$

the concentration of Na^+ coming from added NaOH and C is the total concentration of the complex. Values of K_1 and K_2 were obtained from eq 16. These were then slightly adjusted by trial and error to obtain best fit with the experimental titration curve.[19] The formation curves of Figure 1 were computed using the relations

$$[Ni(H_2Me_2L)^{2+}] = C(1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1} \qquad (17)$$

$$[Ni(HMe_2L)^+] = [Ni(H_2Me_2L)^{2+}]K_1/[H^+] \qquad (18)$$

$$[Ni(Me_2L)] = [Ni(H_2Me_2L)^{2+}]K_1K_2/[H^+]^2 \qquad (19)$$

which can be readily derived from considerations of equilibria 1 and 2 and the equation of mass balance of the three complex species.

C. Cyclic Voltammetry. 1. Instrumentation. The potentiostat and the signal generator were fabricated in this laboratory using indigenous components. The potentiostatic circuit was a modified version of that described by Spitzer,[20] while in the function generator, a modification of the circuit of Myers and Shain[21] was used. Details[19] will be published elsewhere. The cyclic voltammograms were recorded on a Mosley Autograf Model 7030AM X-Y recorder. The usual three-electrode cell configuration was used in this work. To eliminate non-Faradaic effects (which are particularly important for platinum electrodes in aqueous solution) an assembly of two three-electrode cells of identical design was used.[22] One of the cells contains the electroactive substance in addition to the supporting electrolyte; the other cell has only the supporting electrolyte. The same potentiostat controls the potential of the two cells but the working electrodes are connected to separate current followers. The outputs of those current followers are used as inputs to a subtractor which gives the output (current contribution from electroactive species only) to be recorded. A platinum wire (99.99%; diameter 0.05 cm) sealed into a Pyrex glass tubing was used as the working electrode. The exposed end of the platinum wire was sealed in a glass bead of 1–2 mm size to eliminate end-shape effects.[23] The exposed length of the working electrode was 2-3 mm. The counterelectrode has the same design as the working electrode except that no glass bead is fixed at the end of the wire. The reference electrode was a saturated calomel electrode of appropriate design. The working electrode was pretreated using chromic acid as described by Adams.[24] A double-walled cylindrical glass vessel (thermostated to 25 ± 0.1 °C) housed the electrode assembly. All measurements were done in nitrogen atmosphere. In every case care was taken to obtain a flat current–voltage baseline over the required voltage range in the absence of the electroactive species.

For wire electrodes the diffusion process is cylindrical whereas the important equations of cyclic voltammetry[4] refer to planar electrodes (linear diffusion). It was shown by Nicholson[23] that at relatively high scan rates the observed peak positions for the two types of diffusion are the same within experimental error. We have thoroughly checked[19] that this is so in our experimental setup at and above the scan rate of 0.01 V s^{-1}.

2. Buffers. Acetate (pH 0.65–5.20), phosphate (pH 5.29–8.04), and borate (pH 7.80–10.00) buffers were prepared in the usual manner[25] in 0.1 M NaCl. The pH value of each buffer was measured experimentally just before use. The electrolytes in the buffer and the NaCl together acted as the supporting electrolyte. The measurements were made on 50.0 ml of solution.

D. Constant-Potential Coulometry. The same cell and electrode assembly as described above were used for this purpose except that the working electrode was a platinum foil of cylindrical construction (effective area ~180 cm^2). The solution was constantly stirred during electrolysis. The potential was held constant using the potentiostatic device described earlier.

E. EPR Spectra and Magnetic Moments. The powder and solution spectra were recorded on a Varian V4502 EPR spectrometer operating at the X-band microwave frequency. Magnetic moments were measured as described earlier.[1]

Registry No. $Ni(Me_2L)^{2+}$, 55188-33-5; $Ni(H_2Me_2L)^{2+}$, 55188-31-3; $Ni(Me_2L)^+$, 59980-37-9; $Ni(HMe_2L)^+$, 60306-03-8; $Ni(Me_2L)$, 59980-38-0; $Ni(RR'L)^{2+}$ (R = Me, R′ = Et), 55758-52-6; $Ni(H_2RR'L)^{2+}$ (R = Me, R′ = Et), 55822-46-3; $Ni(RR'L)^+$ (R = Me, R′ = Et), 60338-53-6; Ni(RR′L) (R = Me, R′ = Et), 60306-04-9; $Ni(RR'L)^{2+}$ (R = Et, R′ = Me), 55758-50-4; $Ni(H_2RR'L)^{2+}$ (R = Et, R′ = Me), 55758-44-6; $Ni(RR'L)^+$ (R = Et, R′ = Me), 60306-05-0; Ni(RR′L) (R = Et, R′ = Me), 60306-06-1; $Ni(RR'L)^{2+}$ (R = Me, R′ = Ph), 55758-54-8; $Ni(H_2RR'L)^{2+}$ (R = Me, R′ = Ph), 55758-46-8; $Ni(RR'L)^+$ (R = Me, R′ = Ph), 60306-07-2; Ni(RR′L) (R = Me, R′ = Ph), 60306-08-3; $Ni(RR'L)^{2+}$ (R = Ph, R′ = Me), 55822-44-1; $Ni(H_2RR'L)^{2+}$ (R = Ph, R′ = Me), 55758-48-0; $Ni(RR'L)^+$ (R = Ph, R′ = Me), 60306-09-4; Ni(RR′L) (R = Ph, R′ = Me), 60306-10-7; $Fe(Me_2L)^+$, 60325-45-3; $Fe(H_2Me_2L)^{2+}$, 60306-11-8; $Fe(HMe_2L)^+$, 60306-12-9; $Fe(Me_2L)$, 60306-13-0.

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Spectral and Magnetic Properties of Copper(II) 1,5-Naphthyridine 1,5-Dioxide Complexes

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The di-*N*-oxide of 1,5-naphthyridine has been prepared and coordination compounds with copper(II) chloride, bromide, and nitrate have been prepared. Infrared, electronic, and electron paramagnetic resonance spectroscopies have been used to determine the binding properties of the ligand and anions. Magnetic susceptibilities support antiferromagnetic exchange through the extended π system of the heterocyclic ligand. The magnetic data can be fit to the isotropic Heisenberg model for linear chains with $S = {}^1/_2$ coupled magnetic ions with $J \approx -3.5$ cm^{-1} in all three complexes.

Introduction

Extended π pathways have recently been shown to propagate spin coupling of magnetic ions over long distances.[2-6] The pyrazine-bridged copper(II) nitrate[2,3,6] and the 1,5-naphthyridine-bridged copper(II) nitrate[4] complexes have measurable spin exchange even though the magnetic centers are separated in the linear chains by 6.7 and ~9 Å, respectively. In fact, the naphthyridine complex exhibits a greater spin coupling than does the pyrazine complex. Interchain coupling may be suspected of contributing to the interactions but it has been conclusively shown[6] that no such mechanism operates significantly in the pyrazine linear-chain complex.

In this present work extension of the π system has been accomplished by preparing the di-*N*-oxide of 1,5-naphthyridine (NDO), I, and complexing it with copper(II) chloride,