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Chemistry of Tetravalent Nickel and Related Species. 4. The Situation Where Nickel(III) Is Stabilized by Amine–Imine–Oxime Ligands and Nickel(IV) Is Not Formed

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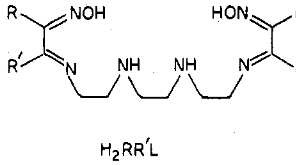
New hexadentate ligands (HRR′Y) generated by reaction of isonitroso ketones with tetraethylenepentamine in 1:1 ratio yield pseudooctahedral nickel(II) complexes $Ni(HRR'Y)(ClO_4)_2$ ($Dq \approx 1250$ cm^{-1}; $\mu_{eff} \approx 3\ \mu_B$). These are oxidized by alkaline ammonium persulfate to produce red crystals of $Ni(RR'Y)(ClO_4)_2$ which (i) oxidize iron(II) to iron(III), the reaction stoichiometry being Fe:Ni = 1:1, (ii) have $\mu_{eff} \approx 2.1\ \mu_B$, (iii) exhibit polycrystalline EPR spectra characteristic of $S = {}^1/_2$ in axial field ($g_\parallel \approx 2.04$; $g_\perp \approx 2.14$), and (iv) undergo a one-electron electrochemical reduction but no oxidation. Thus $Ni(RR'Y)^{2+}$ contains nickel in the oxidation state +3. Extensive cyclic voltammetric studies have led to the identification of the following quasi-reversible process near pH 6: $Ni(RR'Y)^{2+} + e^- + H^+ \rightleftharpoons Ni(HRR'Y)^{2+}$ with $E^{\circ\prime}_{298} \approx 0.68$ V vs. SCE. No sign of the formation of nickel(IV) species could be detected up to +0.9 V. Comparison of the complexing behavior of the various amine–imine–oxime ligands described in this paper and elsewhere and the various oxidation states of nickel achievable with each suggests that for each unit increase (above +2) in the oxidation state of the metal, the presence of at least one oxime function is needed. The HRR′Y ligand system having only one oxime function stabilizes nickel(III) but *not* nickel(IV). The low-spin iron(II) complexes $Fe(HRR'Y)(ClO_4)_2$ are also reported. The IR and electronic spectra of these and the nickel(II) and nickel(III) complexes are described and compared. The iron(II) and nickel(III) complexes exhibit MLCT and LMCT transitions, respectively, in the visible region (~500 nm).

Introduction

In the previous papers[1-3] of this series, the emphasis has been on nickel(IV) since the ligands described, **1** and **2**, preferentially stabilized this oxidation state rather than nickel(III). The latter state was detected as an intermediate in voltammetric experiments,[2,3] but it could not be isolated in the form of pure compounds. It was suggested[1-3] that the negative charge on the oximato anion plays a significant role in stabilizing the highly electrophilic +4 oxidation state. In all the complexes reported earlier,[1-3] the coordination sphere is pseudooctahedral NiN_6 with *two* oximato groups. In order to investigate what happens when the number of oxime groups per metal ion is decreased to 1, the nickel (and briefly iron(II)) complexes of the new hexadentate system **3** were explored, and the results are reported in this paper. The ligand **3** is abbreviated as HRR′Y where H is the dissociable oxime proton.



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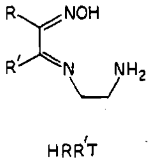

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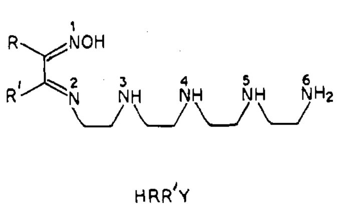

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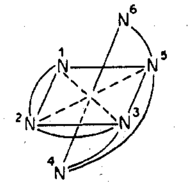

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Table I. Molar Electrical Conductivity[a,b] (Λ, Ω^{-1} cm^2 mol^{-1}) in Solution, Magnetic Moment[a] (μ_{eff}, μ_B) in the Solid State, and Frequencies (ν, cm^{-1}) and Extinction Coefficients (ε, M^{-1} cm^{-1}) of Electronic Bands in Solution[c]

compd	Λ	μ_{eff}	ν (ε)
$Ni(HMe_2Y)(ClO_4)_2$	171 (303)	3.00 (293)	815 (29), 510 (75)[d]
$Ni(HEtMeY)(ClO_4)_2$	168 (303)	2.97 (293)	810 (33), 510 (60)[d]
$Ni(HPhMeY)(ClO_4)_2$	148 (303)	3.11 (293)	800 (36), 510 (94)[d]
$Ni(HMePhY)(ClO_4)_2$	157 (303)	3.11 (293)	800 (36), 510 (102)[d]
$Fe(HMe_2Y)(ClO_4)_2$	261 (301)	diamagnetic	525 (6691), 445 (1920)[d]
$Fe(HEtMeY)(ClO_4)_2$	263 (301)	diamagnetic	530 (6158), 450 (2053)[d]
$Fe(HMeEtY)(ClO_4)_2$	268 (301)	diamagnetic	530 (5956), 445 (1930)[d]
$Ni(Me_2Y)(ClO_4)_2$	170 (303)	2.12 (291)	500 (2400), 400 (1703)[d]
$Ni(EtMeY)(ClO_4)_2$	159 (303	2.12 (292.5)	520 (2404), 410 (1803)[d]
$Ni(PhMeY)(ClO_4)_2$	148 (303)	2.17 (292.5)	510 (2617) 400 (1812)[d]
$Ni(MePhY)(ClO_4)_2$	155 (303)	2.20 (292.5)	510 (2385), 410 (1839)[d]

[a] Temperatures (K) of measurements are shown in parentheses. [b] Molar electrical conductivities of $Ni(HRR'Y)(ClO_4)_2$ and $Ni(RR'Y)(ClO_4)_2$ are measured in nitromethane and those of $Fe(HRR'Y)(ClO_4)_2$ in acetonitrile solution. [c] Electronic spectra of $Ni(HRR'Y)(ClO_4)_2$ in 0.1 N NaOH; $Ni(RR'Y)(ClO_4)_2$ in aqueous solution and $Fe(HRR'Y)(ClO_4)_2$ in methanol solution. Solids run in Nujol mull gave nearly identical spectra. The ligand-field spectrum of $Ni(HMe_2Y)(ClO_4)_2$ in neutral water was essentially the same (except for small differences in intensities) as that in 0.1 N NaOH, showing that proton dissociation, if any, only marginally affects such spectra. [d] Shoulder.

Results and Discussion

A. Nickel(II) and Iron(II) Complexes. Ligands of type **3** have not been obtained in the pure state. Reaction of isonitroso ketones with tetraethylenepentamine yields a gummy mass which readily reacts with nickel(II) perchlorate hexahydrate, producing brown crystals of $Ni(HRR'Y)(ClO_4)_2$. Violet $Fe(HRR'Y)(ClO_4)_2$ was similarly prepared. All complexes behave as 1:2 electrolytes (Table I).

The nickel(II) complexes are high spin and display characteristic ν_1 and ν_2 ligand-field transitions in the visible region (Table I). Clearly a pseudooctahedral NiN_6 coordination sphere **4** is implicated. The iron(II) complexes are diamagnetic

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(3) Part 3: A. N. Singh, Rajendra P. Singh, J. G. Mohanty, and A. Chakravorty, *Inorg. Chem.*, **16**, 2597 (1977).

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Table II. Selected Infrared Frequencies (cm^{-1}) of Nickel(II), Iron(II), and Nickel(III) Complexes in Halocarbon Mull

		Ni(HRR'Y)-$(ClO_4)_2$		Fe(HRR'Y)-$(ClO_4)_2$		Ni(RR'Y)-$(ClO_4)_2$	
R	R'	$\nu_{C=N}$	δ_{NH_2}	$\nu_{C=N}$	δ_{NH_2}	$\nu_{C=N}$	δ_{NH_2}
CH_3	CH_3	1660	1630	1520	1590	1645	1610
C_2H_5	CH_3	1660	1610	1515	1590	1635	1600
CH_3	C_2H_5	[a]		1515	1585	[a]	
C_6H_5	CH_3	1650	1600	[a]		1640	1595
CH_3	C_6H_5	1665	1605	[a]		1640	1600

[a] Not synthesized.

Table III. Titration of $Ni(RR'Y)(ClO_4)_2$ by Fe^{2+} [a]

		vol, mL	
compd	concn × 10^3	exptl	calcd[b]
$Ni(Me_2Y)(ClO_4)_2$	2.02	4.95	4.94
$Ni(EtMeY)(ClO_4)_2$	2.00	5.04	5.00
$Ni(PhMeY)(ClO_4)_2$	2.00	5.02	5.00
$Ni(MePhY)(ClO_4)_2$	2.00	4.96	5.00

[a] Strength of Fe^{2+} 2.00×10^{-3} M, volume of Fe^{2+} 5 mL. [b] On the basis that each mol of Ni^{3+} consumes 1 mol of Fe^{2+}.

(spin-paired; d^6) and have an allowed MLCT transition at ~530 nm with a shoulder on the higher energy side.

Both $Ni(HRR'Y)(ClO_4)_2$ and $Fe(HRR'Y)(ClO_4)_2$ show ν_{NH_2} and broad ν_{OH} at ~3000 cm^{-1} and ionic perchlorate bands at ~1100 and 620 cm^{-1} in addition to δ_{C-H} (1400–1300 cm^{-1}) and ν_{C-N} (1200 cm^{-1}). There are considerable differences in the $\nu_{C=N}$ frequencies of the nickel(II) and iron(II) complexes (Table II). The $\nu_{C=N}$ frequency is markedly shifted to lower values in the iron(II) complexes due possibly to MLCT contribution to the ground state.

In gross magnetic and spectroscopic properties, the nickel(II) and iron(II) complexes of **3** are closely analogous[1-4] to those of **1** and **2**. However, the chemical and electrochemical redox behavior of $Ni(HRR'Y)^{2+}$ is *qualitatively* different from those of the complexes of **1** and **2**. Only nickel(III) complexes of type $Ni(RR'Y)(ClO_4)_2$ are produced[5] as a result of such oxidation, and no evidence whatsoever could be obtained for the existence of a nickel(IV) state.

B. Nickel(III) Complexes. (a) Synthesis and Characterization. Attempted oxidation of $Ni(HRR'Y)(ClO_4)_2$ by concentrated nitric acid led to decomposition. However, dark red crystals of $Ni(RR'Y)(ClO_4)_2$ are readily obtained by using alkaline ammonium persulfate as the oxidizing agent.

The complexes behave as 1:2 electrolytes in nitromethane solution (Table I). These can be titrated quantitatively with iron(II) in acidic aqueous solution according to the stoichiometry (Table III)

$$Fe^{2+} + Ni(RR'Y)^{2+} + H^+ \rightarrow Fe^{3+} + Ni(HRR'Y)^{2+} \quad (1)$$

The electronic spectrum of $Ni(RR'Y)^{2+}$ in the visible region (Table I) is dominated by a band at ~500 nm with ϵ ~2500 M^{-1} cm^{-1}. This is probably of LMCT ($\pi \rightarrow e_g^*$) origin. The complex $Ni(RR'Y)(ClO_4)_2$ shows the expected IR absorptions due to ν_{NH_2} (no ν_{OH}), ν_{ClO_4}, etc. at the usual frequencies. In going from nickel(II) to nickel(III), $\nu_{C=N}$ decreases (Table II) considerably due to LMCT contribution to the ground state. The order of $\nu_{C=N}$ is Ni(II) > Ni(III) (LMCT) > Fe(II) (MLCT).

(b) Magnetic Susceptibility and EPR Spectra. The above results suggest that $Ni(RR'Y)(ClO_4)_2$ contains nickel in oxidation state +3. Magnetic susceptibility data (Table I) are in full agreement with such an oxidation state (d^7) in low-spin configuration ($S = {}^1/_2$). Further, polycrystalline samples give strong axial EPR spectra at room temperature. The spectra (Table IV) which are in accord[6] with an axial $S = {}^1/_2$ state ($g_\perp > g_\parallel$; i.e., $(d_{z^2})^1$ ground state) compare very well with spectra of other low-spin axial nickel(III) complexes derived from the nitrogenous ligands.[7-14]

Table IV. EPR Parameters of $Ni(RR'Y)(ClO_4)_2$ Complexes in Solid State at Room Temperature

compd	$g_\parallel$	$g_\perp$	compd	$g_\parallel$	$g_\perp$
$Ni(Me_2Y)(ClO_4)_2$	2.030	2.134	$Ni(PhMeY)(ClO_4)_2$	2.040	2.145
$Ni(EtMeY)(ClO_4)_2$	2.054	2.142	$Ni(MePhY)(ClO_4)_2$	2.040	2.143

Table V. Cyclic Voltammetric Data[a,b] of $Ni(RR'Y)(ClO_4)_2$ Complexes

compd	pH	E_{pa}, V	E_{pc}, V	ΔE_p, V	$\bar{E}_p$, V	$\Delta\bar{E}_p/\Delta pH$
$Ni(Me_2Y)(ClO_4)_2$	5.00	0.295	0.433	0.138	0.364	
	5.95	0.205	0.315	0.110	0.260	0.109
$Ni(EtMeY)(ClO_4)_2$	5.00	0.287	0.433	0.146	0.360	
	5.95	0.232	0.327	0.095	0.279	0.085
$Ni(PhMeY)(ClO_4)_2$	5.00	0.335	0.429	0.094	0.382	
	5.95	0.287	0.366	0.079	0.326	0.059
$Ni(MePhY)(ClO_4)_2$	5.00	0.335	0.429	0.094	0.382	
	5.95	0.299	0.362	0.063	0.330	0.055

[a] Anodic (E_{pa}) and cathodic (E_{pc}) peak potentials are recorded relative to the SCE. [b] $C = 2.00 \times 10^{-3}$ M; scan rate = 0.012 V s^{-1} and T = 298 K.

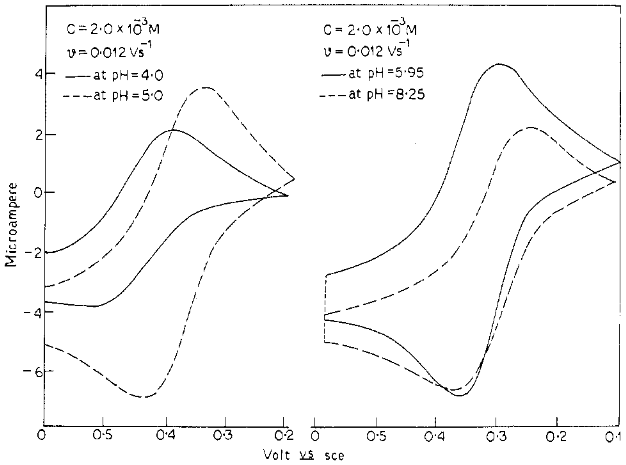

Figure 1. Cyclic voltammograms of $Ni(MePhY)(ClO_4)_2$ in 0.1 M NaCl.

(c) Electrochemistry. Having convincingly demonstrated the nickel(III) character of $Ni(RR'Y)(ClO_4)_2$, we attempted electrochemical characterization of its redox activity using cyclic voltammetry (CV). If nickel(IV) species are formed even transiently at high potential, this technique is likely to disclose this. Voltage at the platinum working electrode was scanned in the interval −0.2 to +0.9 V vs. the saturated calomel

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Table VI. Formal Electrode Potential Data for Nickel(III)–Nickel(II) Couples

couples	pH	$E°'_{298}$, V	ref
$Ni(PhMeY)^{2+} + e^- + H^+ \rightleftharpoons Ni(HPhMeY)^{2+}$	5.00	0.68	this work
	5.95	0.68	
$Ni(MePhY)^{2+} + e^- + H^+ \rightleftharpoons Ni(HMePhY)^{2+}$	5.00	0.68	this work
	5.95	0.68	
$Ni(Me_2L)^+ + e^- + H^+ \rightleftharpoons Ni(Hme_2L)^+$	7.00	0.64	2
$Ni(Me_2T)_2{}^+ + e^- + H^+ \rightleftharpoons Ni(HMe_2T)(Me_2T)^+$	8.00	0.66	3

electrode (SCE). No more than one cathodic and one anodic peak were seen in a full cycle. Under these conditions, it is not possible to oxidize $Ni(RR'Y)^{2+}$; it only undergoes cathodic reduction. Thus no evidence for the formation of nickel(IV) species could be obtained.

In general the reversibility of the nickel(II)–nickel(III) oxidation (Table V) is lower than that[2,3] of the complexes of **1** and **2**. This problem becomes more serious at low and high pH (Figure 1). By trial and error the best cyclic voltammograms are obtained at the narrow range of pH 5–6.5. Data at two pH values within this range are collected in Table V. The peak-to-peak separation (ΔE_p) reflects better quasi-reversibility in systems having a phenyl group. A minimum ΔE_p of 63 mV is observed in the case of $Ni(MePhY)^{2+}$ at pH 5.95. Identical voltammograms are obtained with the nickel(II) species $Ni(HRR'Y)^{2+}$ by starting from the anodic limit of the cycle. This observation together with overall consideration of ΔE_p and $\Delta \bar{E}_p/\Delta pH$ ($\Delta \bar{E}_p$ = shift of the average peak potential; ΔpH = change in pH) is suggestive of a quasi-reversible one-electron electrode process into which a one-proton process is coupled:

$$Ni(RR'Y)^{2+} + e^- + H^+ \rightleftharpoons Ni(HRR'Y)^{2+} \qquad (2)$$

Under a reversible situation the following relations hold for reaction 2:

$$\Delta \bar{E}_p/\Delta pH = 59\ mV \qquad (3)$$

$$E°'_{298} = \bar{E}_p + 0.059\ pH \qquad (4)$$

where $E°'_{298}$ is the formal electrode potential at 298 K. In the two cases ($Ni(PhMeY)_2{}^+$ and $Ni(MePhY)^{2+}$) where the reversibility criterion is better satisfied, consistent values of $E°'_{298}$ (Table VI) can be obtained for the couple of eq 2 by using eq 4. Interestingly the observed values of $E°'_{298}$ are close to those of proton-dependent nickel(III)–nickel(II) couples identified[2,3] in complexes of ligands **1** and **2** (Table VI).

C. Concluding Remarks. It is convincingly established that $Ni(RR'Y)(ClO_4)_2$ contains nickel(III) which can be reduced to nickel(II) chemically and electrochemically. However, it has not been possible to bring about oxidation to the nickel(IV) state. On the other hand the complexes of ligands **1** and **2** readily yield crystalline nickel(IV) complexes; the nickel(III) chemistry is, however, evidenced in electrochemical experiments. The data of Table VI show that there is no vast difference in the electron-transfer thermodynamics of the nickel(III)–nickel(II) couples of ligands **1**, **2**, and **3**. The difference seems to lie in the stability of nickel(IV). It may be significant that in the systems (ligands **1** and **2**) where nickel(IV) is stabilized there are two oximato groups per nickel atom. HRR'Y with only one oxime function appears to be unable to support a two-electron oxidation of nickel(II) although the nickel(III) species are readily formed. *It seems that, in amine–imine–oxime type ligands, under consideration, for each unit increase in the oxidation states of metal (beyond +2) the presence of at least one oxime function is needed.* This generalization falls in line with the earlier conjecture[1-3] that negative charge on the oximato oxygen plays an important role in stabilizing the higher oxidation states of nickel through σ donation and inductive transmission.

Experimental Section

A. Preparation of Complexes. (a) Nickel(II) Complexes. $Ni(HMe_2Y)(ClO_4)_2$. Biacetyl monoxime (0.01 mol) and 0.01 mol of tetraethylenepentamine in 20 mL of *n*-hexane were heated at reflux for 2 h. The mixture was cooled, and the solvent was decanted. The brown gummy residue was dissolved in 30 mL of ethanol, and an ethanolic solution of nickel(II) perchlorate hexahydrate (0.01 mol) was added slowly with constant stirring. The resulting brown mixture was heated to reflux for 3 h and treated with 100 mL of diethyl ether. A gummy dark brown product separated. This was dissolved in 50% aqueous ethanol, and the solution was concentrated. When the solution was cooled, brown crystals separated which were collected and were recrystallized from 50% aqueous ethanol. The crystals were dried over fused calcium chloride under vacuum. The yield was 65%.

$Ni(HRR'Y)(ClO_4)_2$: (i) $R = C_2H_5$, $R' = CH_3$; (ii) $R = C_6H_5$, $R' = CH_3$; (iii) $R = CH_3$, $R' = C_6H_5$. These complexes were synthesized in good yield in the same way as that described for $Ni(HMe_2Y)(ClO_4)_2$.

(b) Iron(II) Complexes. $Fe(HRR'Y)(ClO_4)_2$: (i) $R = R' = CH_3$; (ii) $R = C_2H_5$, $R' = CH_3$; (iii) $R = CH_3$, $R' = C_2H_5$. These complexes were prepared by the same procedure as that described for $Ni(HRR'Y)(ClO_4)_2$ by reaction of an ethanolic solution of iron(II) perchlorate hexahydrate with HRR'Y ligands.

(c) Nickel(III) Complexes. $Ni(Me_2Y)(ClO_4)_2$. $Ni(HMe_2Y)(ClO_4)_2$ (0.529 g, 0.001 mol) was dissolved in 10 mL of aqueous sodium hydroxide (0.001 mol). This was filtered, and to the filtrate was added 0.114 g of ammonium persulfate (0.0005 mol) with continuous shaking. The color of the reaction mixture became dark violet. It was cooled and kept at 273 K for 3 h, after which a saturated solution of sodium perchlorate was added. On further cooling of the solution, dark red crystals deposited. These were then collected by filtration and were washed with cold water, with 95% ethanol, and finally with ether. The product was dried over fused calcium chloride under vacuum. The yield was ~65%.

$Ni(RR'Y)(ClO_4)_2$: (i) $R = C_2H_5$, $R' = CH_3$; (ii) $R = C_6H_5$, $R' = CH_3$; (iii) $R = CH_3$, $R' = C_6H_5$. These complexes were prepared by procedures similar to that described above.

All complexes have been analyzed satisfactorily. (Analytical data are given as supplementary material.)

B. Titration of Nickel(III) Species with Fe^{2+}. The nickel(III) complexes were titrated with Fe^{2+} in the same manner[1] as for $Ni(RR'L)^{2+}$.

C. Physical Measurements. Magnetic moments, infrared spectra, electronic spectra, and electrical conductivities were studied as before.[1,15] Cyclic voltammetry was performed with an instrument fabricated[2,16] by Mohanty and Chakravorty used in conjunction with a Pacific Precision Instruments MP-1502B electroanalyzer. The powder EPR spectra were recorded on a Varian 4502 EPR spectrometer operating at the X-band microwave frequency.

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Registry No. $Ni(HMe_2Y)(ClO_4)_2$, 69022-06-6; $Ni(HEtMeY)(ClO_4)_2$, 72622-90-3; $Ni(HPhMeY)(ClO_4)_2$, 72638-44-9; $Ni(HMePhY)(ClO_4)_2$, 72638-46-1; $Fe(HMe_2Y)(ClO_4)_2$, 72638-48-3; $Fe(HEtMeY)(ClO_4)_2$, 72638-50-7; $Fe(HMeEtY)(ClO_4)_2$, 72638-52-9; $Ni(Me_2Y)(ClO_4)_2$, 69022-08-8; $Ni(EtMeY)(ClO_4)_2$, 72638-54-1; $Ni(PhMeY)(ClO_4)_2$, 72638-56-3; $Ni(MePhY)(ClO_4)_2$, 72638-58-5; biacetyl monoxime, 57-71-6; tetraethylenepentamine, 112-57-2; Fe^{2+}, 15438-31-0.

Supplementary Material Available: A listing of analytical data (1 page). Ordering information is given on any current masthead page.

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