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Trivalent Nickel. The Quinone Oximate Family: Synthesis and Redox Regulation of Isomerism and Ligand Redistribution

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Received February 4, 1988

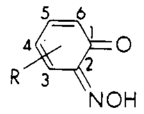
The anionic N_3O_3 tris chelates $Ni^{II}(RQ)_3^-$, derived from 1,2-quinone 2-oximes (HRQ, **1**), occur as equilibrium mixtures of *fac* (**2a**) and *mer* (**2b**) isomers in acetonitrile solution and display the reversible nickel(III)–nickel(II) couples *fac*-$Ni(RQ)_3$–*fac*-$Ni(RQ)_3^-$ and *mer*-$Ni(RQ)_3$–*mer*-$Ni(RQ)_3^-$ (^1H NMR and voltammetry). The former couple has a higher (by ~0.12 V) formal potential. These potentials are also sensitive to the substituent R, and the range 0.3–0.7 V vs SCE is covered by the present complexes. The *fac*-$Ni(RQ)_3$ isomer is spontaneously transformed into the *mer* form in solution. In the case R = Me, the rate constant is estimated to be 0.02 s^{-1} at 258 K. Due to this isomerization pure $Ni(RQ)_3$ could be isolated only in the *mer* form via coulometric oxidation of $Ni(RQ)_3^-$. The dark-colored $Ni(RQ)_3$ chelates behave as one-electron paramagnets and in frozen solution (77 K) display rhombic EPR spectra ($g \approx 2.04, 2.14, 2.19$) characterizing the *mer* geometry. Upon reduction, *mer*-$Ni(RQ)_3$ is reconverted into the equilibrium mixture of *fac*- and *mer*-$Ni(RQ)_3^-$. At 258 K, the *mer* → *fac* isomerization of $Ni(RQ)_3^-$ is slow on the cyclic voltammetric time scale and the *mer*-$Ni(RQ)_3$–*mer*-$Ni(RQ)_3^-$ couple alone is observable. Mixed complexes of type $Ni(RQ)_2L_2$ undergo quasi-reversible cyclic voltammetric oxidation to $Ni^{III}(RQ)_2L_2^+$ (L = two pyridine ligands or one 2,2′-bipyridine ligand). The oxidized complex is unstable and reacts spontaneously with the parent nickel(II) complex, affording *mer*-$Ni(RQ)_3$ via ligand redistribution. By coulometric oxidation of $Ni(BuQ)_2(bpy)$ at 263 K, a measurable concentration of $Ni(BuQ)_2(bpy)^+$ can be produced in dichloromethane solution, and in the frozen state this affords an EPR spectrum characteristic of axial compression ($g_\parallel = 2.169$, $g_\perp = 2.083$). Five-line nitrogen hyperfine ($a_\perp \approx 15$ G) is observed in the $g_\perp$ region, and a structure (**5**) having bpy on the *xy* plane is suggested. The formal nickel(III)–nickel(II) potentials (0.49–0.80 V vs SCE) of $Ni(MeQ)_2L_2$ are found to correlate linearly with the donor strength (pK_a) of L (L = pyridine, 4-methylpyridine, 4-aminopyridine, and pyrazole).

Introduction

High oxidation levels of nickel are of current interest.[1-6] The trivalent state occurs in bacterial hydrogenases.[2,7] Biological donor atoms usually come from the group N, O, S. The synthesis, characterization, and redox potency of model nickel(III) complexes in the coordination environments of one or more of these atoms have concerned us.[2,8,9] The present work stems from our search for high oxidation states of nickel coordinated to ligands of the 1,2-quinone family. The quinones themselves have not been effective, but their monooximes (HRQ, see below) are found to act as good bidentate N,O chelators toward trivalent nickel. Herein we report the synthesis of the tris chelates $Ni^{III}(RQ)_3$ by electrooxidation of $Ni^{II}(RQ)_3^-$. The complexes have afforded an unique opportunity for voltammetric and spectroscopic examination of geometrical isomerism and isomer preferences of the two oxidation states of nickel in a N_3O_3 environment. We also describe a redox-driven ligand redistribution reaction that furnishes $Ni(RQ)_3$ following electrooxidation of $Ni^{II}(RQ)_3(N,N)$ to $Ni^{III}(RQ)_2(N,N)^+$, where N,N represents amine coordination. The effects of geometric structure, substituents, and ligands on the nickel(III)–nickel(II) reduction potential in $Ni(RQ)_3$ and $Ni(RQ)_2(N,N)^+$ are noted.

Results and Discussion

A. Nickel(II) Tris Chelates, $Ni(RQ)_3^-$. a. Synthesis and Characterization. Four HRQ ligands (**1**) were used in the present work. The anions $Ni(ClQ)_3^-$ and $Ni(BzQ)_3^-$ are already known.[10,11] We have also prepared $Ni(MeQ)_3^-$ and $Ni(BuQ)_3^-$ with the help of the reaction of eq 1 carried out in ethanol. These



R = 4-Me, HMeQ
4-Bu^t, HBuQ
4-Cl, HClQ
3,4-benzo, HBzQ

1

$$Ni(RQ)_2 + HRQ + OH^- \rightarrow Ni(RQ)_3^- + H_2O \qquad (1)$$

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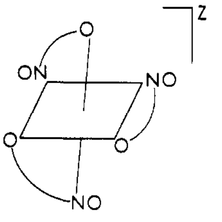
Table I. ^{1}H NMR Chemical Shifts[a] of Isomeric $Ni(RQ)_3^-$ in CD_3CN at 298 K

compd	isomer	$\delta_{4\text{-Me}}$	$\delta_{6\text{-H}}$
$K[Ni(MeQ)_3]$	*mer*	-3.43, -3.49, -4.03	26.15, 25.51, 24.26
	fac	-4.11	24.26
$Ph_4As[Ni(MeQ)_3]$	*mer*	-3.48, -3.48, -4.10	25.88, 25.08, 24.14
	fac	-4.28	24.32
$K[Ni(ClQ)_3]$	*mer*		23.56, 21.86, 21.45
	fac		21.69

[a] Tetramethylsilane is used as an internal standard.

were isolated as K^+ and Ph_4As^+ salts. Analytical, spectral (octahedral ν_1 band, 1050–1100 nm), and magnetic (μ_{eff} = 2.75–3.11 μ_B) data for the brownish red complexes are deposited as supplementary material. Their stereochemistry is revealed by ^{1}H NMR spectra as shown below.

b. Stereochemistry and Isomerism in Solution. The X-ray structure of an acetone adduct of $K[Ni(ClQ)_3]$ has been reported.[10a] In the crystal lattice, $Ni(ClQ)_3^-$ exists exclusively in the *fac* geometry (**2a**) and the metal ion is chelated as in **4**. This mode of chelation is present in all structurally characterized complexes of 1,2-quinone 2-oximes.[12]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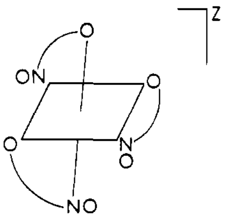
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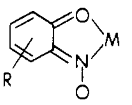
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When salts of $Ni(RQ)_3^-$ are dissolved in organic solvents, a mixture of two distinct nickel(II) species is invariably formed. This phenomenon was first disclosed by voltammetry in MeCN (vide infra). The two species are diagnosed as *fac* (**2a**) and *mer* (**2b**) isomers with the help of 270-MHz ^{1}H NMR spectra in CD_3CN. Selected results pertaining to 6-H and 4-Me protons are in Table I and Figure 1.

In the 6-H region of $K[Ni(ClQ)_3]$ four signals are observed and the chemical shifts vary inversely with temperature as expected for paramagnetic systems[13] (Figure 1). The *fac* isomer has a 3-fold axis of symmetry while the *mer* form has no symmetry. In a mixture of the two isomers four signals are indeed expected for each kind of proton—the three signals of the *mer* form being equal in intensity.[14] Thus, $K[Ni(ClQ)_3]$, which is exclusively *fac* in the crystalline state,[10a] forms an isomeric mixture upon dissolution. In the case of $K[Ni(MeQ)_3]$, the presence of two isomers is seen in both the 4-Me and 6-H regions. The spectrum of $Ph_4As[Ni(MeQ)_3]$ is very closely similar (Table I).

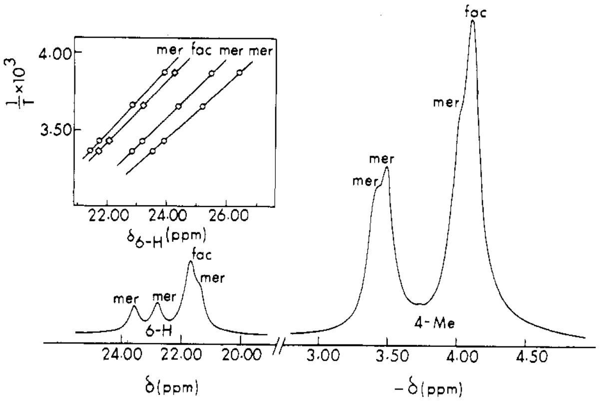

Figure 1. ^{1}H NMR spectrum of $K[Ni(MeQ)_3]$ and $K[Ni(ClQ)_3]$ in CD_3CN at 298 K. The inset shows a plot of the inverse of absolute temperature against the 6-H chemical shift.

Integration of signals shows that the relative populations of the two isomers of $Ni(RQ)_3^-$ remain invariant for each complex from preparation to preparation as expected of an equilibrium process (eq 2). For $Ni(MeQ)_3^-$ the values of K^{II} at 298 and 258 K are

$$fac\text{-}Ni(RQ)_3^- \rightleftharpoons mer\text{-}Ni(RQ)_3^- \qquad (2)$$

$$K^{II} = [mer]/[fac] \qquad (3)$$

0.87 and 0.75, respectively. The isomerization process is slow on the NMR time scale as revealed by the observation of distinct *fac* and *mer* signals. For random ligand distribution, K^{II} = 3. The experimental K^{II} values demonstrate that in solution the *fac* isomer is energetically very favorable. This is also consistent with the exclusive *fac* population in the crystalline state of one complex examined.[10a] The reason for this stability is unclear, but concentration of the anionic charge near one face of the coordination octahedron (**2a**) may conceivably provide more effective electrostatic stabilization via anion–cation or anion–solvent interaction. Interestingly, $Fe(RQ)_3^-$ complexes are exclusively *fac* both in the crystalline state and in solution phases[12a,15] and the same applies to some other related anionic tris(oximato) species.[16] Upon oxidation of $Ni(RQ)_3^-$ to neutral $Ni(RQ)_3$, the equilibrium distribution of geometrical isomers undergoes a dramatic change as has been disclosed by the studies described below.

B. Nickel(III) Tris Chelates. a. Voltammetry of $Ni(RQ)_3^-$: Evidence for Isomeric $Ni^{III}(RQ)_3$. Selected results are in Figure 2 and Table II. We first examine the 258 K cyclic and differential pulse voltammograms. All $Ni(RQ)_3^-$ species display two distinct oxidative responses on the positive side of the SCE. Collective rationalization of NMR, EPR (see below), and electrochemical data has led us to conclude that the two voltammetric responses correspond to the couples of eq 4 and 5, the response at lower

$$mer\text{-}Ni^{III}(RQ)_3 + e^- \rightleftharpoons mer\text{-}Ni^{II}(RQ)_3^- \qquad (4)$$

$$fac\text{-}Ni^{III}(RQ)_3 + e^- \rightleftharpoons fac\text{-}Ni^{II}(RQ)_3^- \qquad (5)$$

potential being due to the *mer* form. The relationship of formal potentials stated in eq 6 is approximately valid for all the complexes

$$E°_{258}(fac) \approx E°_{258}(mer) + 0.12 \text{ V} \qquad (6)$$

studied. Interestingly, in some tricarbonyl triphosphine complexes of chromium the formal potential of the chromium(I)–chromium(0) couple is higher in the *fac* isomer compared to that of the *mer* isomer.[17]

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Table II. Electrochemical Data[a,b]

		mer			*fac*			
compd	temp, K	E_{pa}, V	E_{pc}, V	$E°$,[c,d] V	E_{pa}, V	E_{pc}, V	$E°$,[c,d] V	n (E, V)[h,i]
$K[Ni(MeQ)_3]$	258	0.41	0.34	0.38	0.52	0.46	0.49	0.98 (0.72)
	298	0.42[e]	0.35	0.39	0.52	0.46[e]	0.49	0.97 (0.72)
$K(Ni(BuQ)_3]$	258	0.43	0.36	0.40	0.55	0.49	0.52	1.02 (0.75)
	298	0.44[e]	0.36	0.40	0.55	0.49[e]	0.52	0.93 (0.75)
$K[Ni(ClQ)_3]$	258	0.64	0.58	0.61	0.75	0.69	0.72	0.95 (0.97)
	298	0.66[e]	0.60	0.63	0.77	0.71[e]	0.74	0.98 (0.97)
$Na[Ni(BzQ)_3]$	258	0.33	0.26	0.30	0.46	0.40	0.43	1.00 (0.66)
	298	0.34[e]	0.27	0.31	0.46	0.40[e]	0.43	0.92 (0.66)
$Ni(MeQ)_3$	258	0.41	0.33	0.37				0.98 (0.13)
	298	0.42	0.33	0.38	0.51	f	0.48[g]	0.96 (0.13)
$Ni(BuQ)_3$	258	0.45	0.36	0.41				0.97 (0.15)
	298	0.44	0.35	0.40	0.52	f	0.49[g]	1.03 (0.15)
$Ni(ClQ)_3$	258	0.65	0.57	0.61				0.99 (0.35)
	298	0.64	0.57	0.62	0.75	f	0.72[g]	0.90 (0.35)
$Ni(BzQ)_3$	258	0.33	0.24	0.29				0.96 (0.05)
	298	0.34	0.25	0.30	0.44	f	0.41[g]	0.91 (0.05)

[a] Unless otherwise stated, meanings of the symbols are the same as in the text. [b] The solvent is acetonitrile, the supporting electrolyte is TEAP (0.1 M), the working electrode is platinum, and the reference electrode is the SCE. [c] Cyclic voltammetric data: scan rate 50 mV s^{-1}. [d] $E°$ calculated as the average of anodic and cathodic peak potentials. [e] Shoulder on cyclic voltammogram. [f] Not observed. [g] Calculated by assuming that peak-to-peak separation is 60 mV. [h] Constant-potential coulometric data. [i] $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated coulomb count for one-electron transfer; E is the constant potential at which electrolysis was performed.

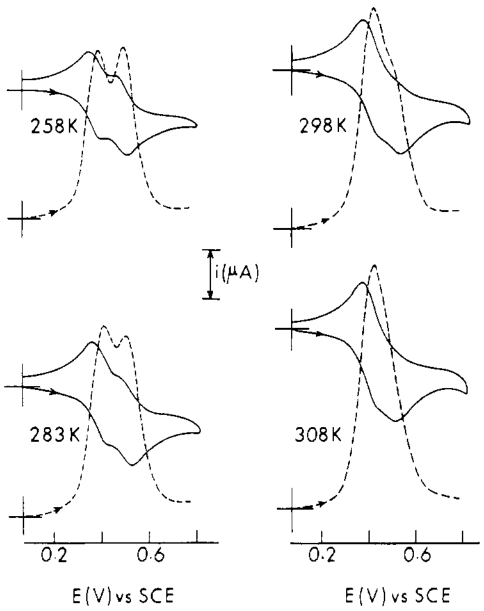

Figure 2. Variable-temperature cyclic voltammograms (CV) (—) and differential pulse voltammograms (DPV) (---) of a ~10^{-3} M $K[Ni(MeQ)_3]$ solution in acetonitrile (0.1 M in TEAP) at a platinum electrode with scan rates of 50 mV s^{-1} (CV) and 10 mV s^{-1} (DPV) and modulation amptitude (DPV) of 25 mV. The marked current range is 20 μA (CV) or 40 μA (DPV).

The R substituent affects the formal potentials in a predictable manner. Thus, the Me substituent lowers the potential significantly more than does the Cl substituent. For the entire group of complexes covering both isomeric and substituent differences the nickel(III)–nickel(II) formal potentials cover a substantial range: 0.3–0.7 V (Table II).

Both the *mer* and the *fac* couples are nearly reversible, having cyclic voltammetric peak-to-peak separations (ΔE_p) of 60–70 mV. Coulometric data (Table II) demonstrated that the two couples together correspond to the transfer of one electron/mol of $Ni(RQ)_3^-$ (*mer* + *fac*). This as well as forthcoming EPR results militate against the possibility that sequential electron transfer within the same species is the origin of the two couples.

In the case of $Ni(MeQ)_3^-$, the ratio of the anodic peak current of the *mer* isomer to that of the *fac* isomer is 0.75 by cyclic voltammetry and 0.77 by differential pulse voltammetry. These results match very well with the NMR K^{II} value of 0.75. This implies that at 258 K the isomer interconversion rate is slow on the voltammetric time scale as well (scan rate v = 5–50 mV s^{-1}). However, the ratio of the cathodic and anodic peak currents of the *fac* isomer is only 0.6–0.7, depending on the switching potential (v = 10 mV s^{-1}). This is attributed to the homogeneous rate process *fac*-$Ni(MeQ)_3$ → *mer*-$Ni(MeQ)_3$, which follows the formation of *fac*-$Ni(MeQ)_3$ (**3a**) by electron transfer at the electrode surface. From current ratios the rate constant (k) of the homogeneous process is estimated to be 0.02 s^{-1} at 258 K with the help of available procedures.[18] At higher temperatures, determination of k is complicated by the faster rate of isomer interconversion in the bivalent state. The effect of temperature on k can however be qualitatively seen in the voltammograms of Figure 2. The cathodic peak of the *fac* isomer progressively diminishes with increasing temperature, and at 308 K it is virtually unobservable. Due to the spontaneous nature of *fac* → *mer* conversion, pure $Ni(RQ)_3$ can be isolated only in the *mer* form (vide infra).

The thermodynamic stability of *mer*-$Ni(MeQ)_3$ with respect to the *fac* isomer has been assessed with the help of the cycle of eq 2 and 7. If the net free energy change over the cycle is set

$$\begin{tikzcd}
fac\text{-}Ni^{II}(MeQ)_3^- \arrow[r, shift left, "K^{II} = 0.87"] \arrow[d, shift left, "0.49\ V"] & mer\text{-}Ni^{II}(MeQ)_3^- \arrow[l, shift left] \arrow[d, shift left, "0.39\ V"] & (2) \\
fac\text{-}Ni^{III}(MeQ)_3 \arrow[r, shift left, "K^{III}"] \arrow[u, shift left] & mer\text{-}Ni^{III}(MeQ)_3 \arrow[l, shift left] \arrow[u, shift left] & (7)
\end{tikzcd}$$

to zero and the stated K^{II} and $E°_{298}$ values are used, K^{III} is estimated to be 43 at 298 K.

b. Electrosynthesis and Characterization of *mer*-$Ni(RQ)_3$. Three $Ni(RQ)_3$ species were isolated in the pure state in 65–70% yield by constant-potential electrolysis of $K[Ni(RQ)_3]$ in MeCN with NH_4PF_6 as supporting electrolyte.[19] The initial red color of $Ni(RQ)_3^-$ changed to brown and $Ni(RQ)_3$ was obtained as a dark powder after removal of solvent and supporting electrolyte. We have not been able to devise a practical chemical oxidation of $Ni(RQ)_3^-$ to $Ni(RQ)_3$. Single crystals of $Ni(RQ)_3$ have eluded us so far. The $Ni^{III}N_xO_{6-x}$ coordination sphere is known among amino acid and peptide complexes usually in the solution phase.[3c–f,20a] Only one example of a crystalline complex appears

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(19) In the case of $Ni(BzQ)_3$ studies were made on a coulometrically produced solution in dimethylformamide. The insolubility of $Na[Ni(BzQ)_3]$ in acetonitrile precluded isolation of $Ni(BzQ)_3$ in pure form.

Table III. Characterization Data of *mer*-$Ni(RQ)_3$

compd	anal.,[a] % C	H	N	μ_{eff},[b] μ_B	g values[c]
mer-$Ni(MeQ)_3$	54.19 (54.11)	4.00 (3.86)	8.94 (9.01)	1.95	2.038, 2.138, 2.188
mer-$Ni(BuQ)_3$	60.82 (60.74)	6.08 (6.07)	6.85 (7.09)	2.03	2.035, 2.138, 2.188
mer-$Ni(ClQ)_3$	41.77 (41.67)	1.87 (1.74)	8.20 (8.10)	1.90	2.041, 2.138, 2.188

[a] Calculated values are in parentheses. [b] In the solid state at 298 K. [c] In acetonitrile–toluene glass at 77 K.

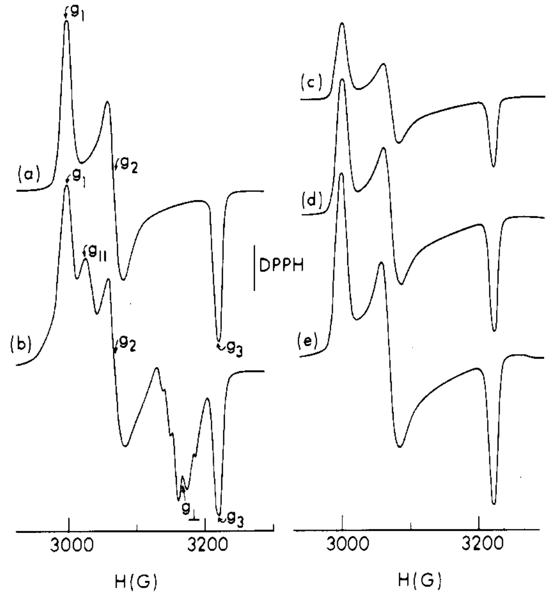

Figure 3. EPR spectra (X-band) at 77 K: (a) *mer*-$Ni(MeQ)_3$ in 1:1 acetonitrile–toluene glass; (b) 30% electrooxidized (263 K) solution of $Ni(BuQ)_2(bpy)$ in dichloromethane glass showing the presence of both $Ni(BuQ)_2(bpy)^+$ and *mer*-$Ni(BuQ)_3$; (c) 25% electrooxidized (300 K) solution of $Ni(BuQ)_2(bpy)$ in dichloromethane; (d) same as (c) except that the level of electrooxidation is 45%; (e) same as (c) except that the level of electrooxidation is 67%. Identical spectrometer settings were used in spectra c–e.

to be known.[20b] The $Ni(RQ)_3$ chelates provide new examples.

Characterization data for the isolated complexes are set out in Table III. Magnetic moments correspond to one unpaired electron, and this fits with low-spin nickel(III) (d^7). Pure $Ni(RQ)_3$ powder generally displays a broad EPR signal near $g = 2.12$ both at room temperature and at 77 K. In frozen acetonitrile–toluene or dichloromethane glass (77 K), however, the spectra are neatly rhombic (Figure 3a), characterizing the *mer* geometry of the complex. No nitrogen hyperfine structure is observed. For the *fac* geometry the spectra would have been axial. The two EPR resonances of $Ni(RQ)_3$ at lower fields are relatively closely spaced and can be considered as components of $g_\perp$ split by a meridional rhombic field. In this idealization the $Ni(RQ)_3$ complexes belong to the $g_\perp > g_\|$ class corresponding to axial elongation (d_{z^2} ground state).[2]

The exclusive meridional geometry of isolated $Ni(RQ)_3$ is similar to the behavior of other $M^{III}(RQ)_3$ chelates (M = Mn,[15] Fe,[15] Co[21]). We note that the *mer* form is sterically favored since here the pendant oximato oxygen atoms have greater separations than in the *fac* form. This factor is expected to be more important for trivalent than for bivalent ions because of the smaller size of the former. Further, $M(RQ)_3$ being electrically neutral, the *fac* isomer would not be subject to electrostatic stabilization of the type invoked earlier in the case of *fac*-$M(RQ)_3^-$.

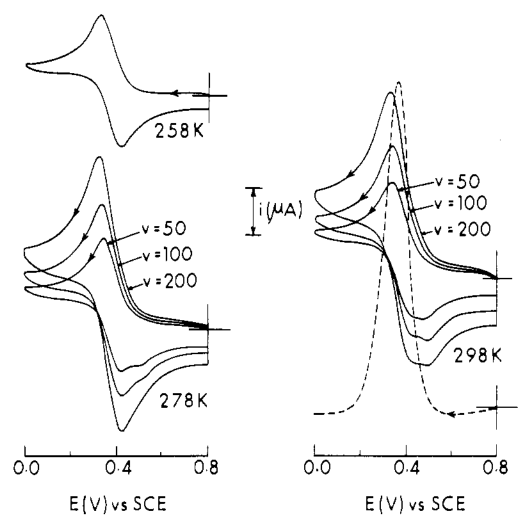

Figure 4. Variable-temperature and variable-scan-rate (v, mV s^{-1}) cyclic voltammograms of 10^{-3} M $Ni(MeQ)_3$ in acetonitrile (0.1 M in TEAP) at a platinum electrode. The superimposed differential pulse voltammogram (---) on the right side has $v = 10$ mV s^{-1} and modulation amptitude 25 mV. The marked current range is 20 μA (CV) or 40 μA (DPV).

Table IV. Mixed Complexes and Their Nickel(III)–Nickel(II) Formal Potentials[a]

compd	$E°_{298}$,[b] V (ΔE_p,[c] mV)	compd	$E°_{298}$,[b] V (ΔE_p,[c] mV)
$Ni(MeQ)_2(bpy)$	0.71 (90)	$Ni(MeQ)_2(mpy)_2$	0.65 (100)
$Ni(BuQ)_2(bpy)$	0.71 (90)	$Ni(MeQ)_2(apy)_2$	0.49 (100)
$Ni(ClQ)_2(bpy)$	0.88 (90)	$Ni(MeQ)_2(pz)_2$	0.80 (120)
$Ni(MeQ)_2(py)_2$	0.70 (120)		

[a] Collected in acetonitrile solutions with use of a platinum working electrode at 298 K, TEAP supporting electrolyte (0.1 M), and SCE reference electrode. [b] Cyclic voltammetric data at a scan rate of 50 mV s^{-1} and solute concentration of ~10^{-3} M. $E°_{298}$ is calculated as the average of anodic and cathodic peak potentials. [c] ΔE_p is the peak-to-peak separation.

c. Reductive Isomerization. A variable-temperature cyclic voltammogram of $Ni(MeQ)_3$ is displayed in Figure 4. At low temperature a *single* one-electron couple is observed. The anodic and cathodic peak potentials are identical with those of the *mer* isomer monitored in the oxidation of $Ni(MeQ)_3^-$ (Table II). Two conclusions can be drawn: (i) $Ni(MeQ)_3$ exists exclusively in the *mer* form and (ii) *mer*-$Ni(MeQ)_3^-$ produced by reduction of *mer*-$Ni(MeQ)_3$ retains stereochemical purity over the cyclic voltammetric time scale at 258 K.

When the temperature is raised, electrogenerated *mer*-$Ni(MeQ)_3^-$ isomerizes faster at the electrode surface and the anodic peak corresponding to the *fac* isomer also becomes observable (eq 8). At 278 K isomerization can still be virtually suppressed by

$$mer\text{-}Ni(MeQ)_3 + e^- \rightleftharpoons mer\text{-}Ni(MeQ)_3^- \rightleftharpoons fac\text{-}Ni(MeQ)_3^- \quad (8)$$

raising the scan rate to 200 mV s^{-1}. Voltammograms at higher temperature follow the expected pattern. The isomeric purity of *mer*-$Ni(MeQ)_3$ is also confirmed by the single differential pulse voltammetric response it displays throughout the studied temperature range (298 K response is shown in Figure 4). The coulomb count in exhaustive reduction of *mer*-$Ni(MeQ)_3$ corresponds to the transfer of one electron. Irrespective of the temperature used, an equilibrium mixture of *fac*- and *mer*-$Ni(MeQ)_3^-$ is produced. Cyclic voltammograms of the reduced solution are identical with those of Figure 2. The electrochemical behavior of other $Ni(RQ)_3$ complexes is entirely analogous to that of *mer*-$Ni(MeQ)_3$.

C. Mixed Complexes: Oxidative Ligand Redistribution. In the reaction of eq 1, alkaline HRQ can be replaced by amines of the pyridine family such as pyridine (py), 4-methylpyridine (mpy),

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(20) (a) Lati, J.; Koresh, J.; Meyerstein, D. *Chem. Phys. Lett.* **1975**, *33*, 286–288. (b) van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489–3491.

(21) Kalia, K. C.; Kumar, A. *Indian J. Chem., Sect. A* **1978**, *16A*, 49–51.

4-aminopyridine (apy), pyrazole (pz), and 2,2′-bipyridine (bpy). Selected complexes of the type $Ni(RQ)_2(N,N)$ formed in this manner are listed in Table IV. The complex $Ni(MeQ)_2(py)_2$ is already known.[22] All the complexes of Table IV behave as two-electron paramagnets (μ_{eff} = 2.79–3.15 μ_B) and display the octahedral ν_1 crystal field band near 1030 nm. Characterization data are collected in the supplementary material. The complexes are stable in solutions of dichloromethane and acetonitrile. Thus, addition of bpy to $Ni(RQ)_2(bpy)$ does not affect the electronic spectrum or voltammogram (see below) and upon addition of bpy to $Ni(RQ)_2$ all spectral changes level off at $Ni(RQ)_2$:bpy = 1:1. Our interest in the mixed complexes lies in their possible oxidation to nickel(III) species.

The complexes indeed display a straightforward quasi-reversible cyclic voltammetric response whose current height corresponds to one-electron transfer and metal oxidation is implied by EPR results (see below). The formal potentials of the couples (eq 9)

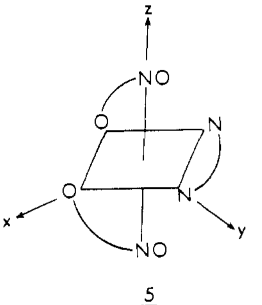
$$Ni^{III}(RQ)_2(N,N)^+ + e^- \rightleftharpoons Ni^{II}(RQ)_2(N,N) \qquad (9)$$

correlate linearly with the pK_a's of L[23,24] in the series $Ni(MeQ)_2L_2$ (L = py, mpy, apy, pz) (Table IV). A stronger donor (larger pK_a) provides better stabilization for nickel(III). In general, the formal potentials of the mixed complexes are higher than those of the tris chelates.

Even though $Ni(RQ)_2(N,N)^+$ exists on the cyclic voltammetric time scale, all attempts to isolate salts of the cation produced coulometrically in acetonitrile and dichloromethane solutions have failed. Irrespective of the amine ligand present, the solution coulometrically oxidized at room temperature (~300 K) invariably displays an EPR spectrum identical with that of *mer*-$Ni(RQ)_3$. The primary reaction responsible for this behavior is stated in eq 10, in which the metal oxidation equivalents are transferred from a higher to a lower potential situation via ligand redistribution.

$$2Ni(RQ)_2(N,N)^+ + Ni(RQ)_2(N,N) \rightarrow 2\ mer\text{-}Ni(RQ)_3 + Ni(N,N)_3^{2+} \qquad (10)$$

Some details will be considered with $Ni(BuQ)_2(bpy)$ as the example. By performing low-temperature (263 K) coulometry at 0.9 V in dichloromethane[25] and immediately freezing (77 K) the partially oxidized solution, it is possible to observe an EPR spectrum that has two prominent resonances in addition to those of *mer*-$Ni(BuQ)_3$ (Figure 3b). These resonances ($g_\parallel$ = 2.169, $g_\perp$ = 2.083) are assigned to $Ni(BuQ)_2(bpy)^+$. Since $g_\parallel > g_\perp$, an axially compressed structure with the unpaired electron in the $d_{x^2-y^2}$ orbital is indicated.[9] Nitrogen hyperfine due to the oxime ligand is not observable in *mer*-$Ni(RQ)_3$, and the same is assumed to be true for $Ni(BuQ)_2(bpy)^+$. The observed five-line hyperfine splitting ($a_\perp \approx$ 15 G) in the perpendicular region is attributed to the two bpy nitrogen atoms. The probable structure of the complex is shown by **5**. We prefer the location of oximato nitrogen (as opposed to quinone oxygen) on axial sites since this can be a reason for axial compression. Quinone oxime complexes of known structures generally have M–N distances shorter than M–O distances.[12] When the oxidized solution is warmed to ~300 K, the spectrum of $Ni(BuQ)_2(bpy)^+$ disappears and an intensified spectrum of *mer*-$Ni(BuQ)_3$ is all that remains.



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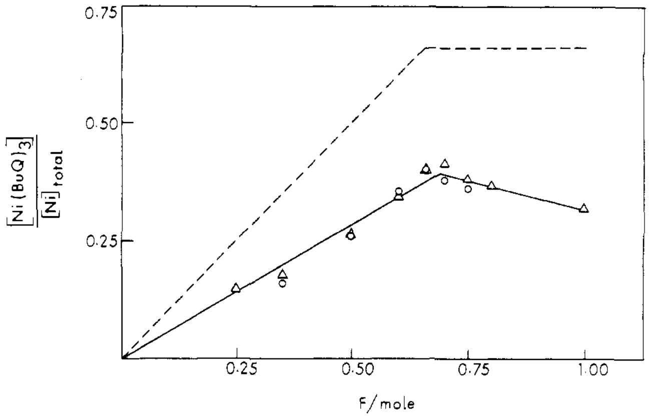

Figure 5. Formation of *mer*-$Ni(BuQ)_3$ (as a fraction of the total nickel present) in the course of constant-potential electrolysis of $Ni(BuQ)_2(bpy)$ in dichloromethane solution at 300 K: concentration of *mer*-$Ni(BuQ)_3$ measured coulometrically (○) and spectrophotometrically (△).

From the EPR intensity, the coulometric count at 0.1 V due to reduction of $Ni(BuQ)_3$ to $Ni(BuQ)_3^-$, and optical spectra,[26] it is observed that the maximum concentration of *mer*-$Ni(BuQ)_3$ is produced when ~67% of $Ni(BuQ)_2(bpy)$ has been oxidized at 0.9 V at 300 K[27] (Figures 3c–e and 5). This is in accord with the reaction of eq 10. In Figure 5, the concentration of *mer*-$Ni(BuQ)_3$ (as a fraction of the total nickel concentration) is plotted as a function of the faradays passed. The dotted line corresponds to the case where eq 10 is the only mode of disappearance of $Ni(BuQ)_2(bpy)^+$. It is clear that $Ni(BuQ)_2(bpy)^+$ is consumed by other unidentified reaction(s) as well. But a major reaction appears to be that of eq 10.

The condition for the spontaneity of the reaction of eq 10 can be defined with the help of the cycle stated in eq 11 and 12. At

$$\begin{tikzcd}
\begin{array}{c} 2Ni^{III}(BuQ)_2(bpy)^+ \\ + \\ Ni^{II}(BuQ)_2(bpy) \end{array} \arrow[r, shift left, "K_m^{III}"] \arrow[d, shift left, "0.71\ V"] & \begin{array}{c} 2Ni^{III}(BuQ)_3 \\ + \\ Ni^{II}(bpy)_3^{2+} \end{array} \arrow[l, shift left] \arrow[d, shift left, "0.40\ V"] & (11) \\
3Ni^{II}(BuQ)_2(bpy) \arrow[r, shift left, "K_m^{II}"] \arrow[u, shift left] & \begin{array}{c} 2Ni^{II}(BuQ)_3^- \\ + \\ Ni^{II}(bpy)_3^{2+} \end{array} \arrow[l, shift left] \arrow[u, shift left] & (12)
\end{tikzcd}$$

298 K, $K_m^{III} \simeq 3 \times 10^{10} K_m^{II}$. Earlier we have stated that $Ni(RQ)_2(bpy)$ is stable in solution. This suggests that K_m^{II} is small. The required condition of spontaneity requires that K_m^{II} should only be large compared to 10^{-11}.

D. Concluding Remarks. It is demonstrated that RQ^- is an excellent stabilizer for nickel(III). The favored geometries of $Ni(RQ)_3$ and $Ni(RQ)_3^-$ are respectively *mer* and *fac*. Synthesis of *mer*-$Ni(RQ)_3$ has been achieved by electrooxidation of $Ni(RQ)_3^-$. The *fac* isomer and *fac* → *mer* isomerization of $Ni(RQ)_3$ are observable in the cyclic voltammetric oxidation of $Ni(RQ)_3^-$, which exists in solution as an equilibrium mixture of *fac* and *mer* isomers. This work provides the first demonstration of *fac–mer* isomerism in the two oxidation states of nickel.

The mixed complex $Ni(RQ)_2(bpy)^+$, produced electrochemically, has been observed in solution. It has an axially compressed

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(22) Charalambous, J.; Frazer, M. J.; Taylor, F. B. *J. Chem. Soc. A* **1971**, 602–605.

(23) The following pK_a values[24] were used: py, 5.17; mpy, 6.02; apy, 9.20; pz, 2.53.

(24) (a) Badger, G. M. *The Chemistry of Heterocyclic Compounds*; Academic: New York and London, 1961. (b) Albert, A. *Heterocyclic Chemistry. An Introduction*; Athlone: London, 1959.

(25) Coulometry in acetonitrile is complicated by the formation of sizable proportions of iminooxy radicals in addition to the trivalent complex.

(26) The $Ni(BuQ)_3$ complex has a characteristic strong band at 690 nm (ϵ = 2990 M^{-1} cm^{-1}), which can be used for monitoring its concentration. A similar band occurs in *mer*-$Ni(RQ)_3$ complexes in general.

(27) Slow coulomb accumulation continues beyond the said (~67%) level of oxidation due to unidentified processes, but the amount of *mer*-$Ni(BuQ)_3$ does not increase any further. In fact, it decreases slowly (Figure 5).

geometry ($d_{x^2-y^2}$ ground state) and, like *fac*-Ni(RQ)$_3$, it spontaneously affords *mer*-Ni(RQ)$_3$–in this case by ligand redistribution. In both the cases, oxidation equivalents pass from higher to lower reduction potentials.

Ongoing studies include the oxidation of substrates by *mer*-Ni(RQ)$_3$ as well as Ni(RQ)$_2$(bpy)$^+$ and the generation of binuclear nickel(III) species using multifunctional quinone oximes as bridging ligands.

Experimental Section

Materials. The purification of acetonitrile and dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical/spectroscopic work were done as before.[28] For synthetic experiments commercially available solvents and chemicals were used.

Physical Measurements. Variable-temperature ^{1}H NMR spectra were measured in CD$_3$CN on a Bruker 270-MHz spectrometer. Electronic spectra were recorded with a Hitachi 330 spectrophotometer. Magnetic susceptibilities were measured with a PAR vibrating-sample magnetometer (Model 155) fitted with a Walker Scientific magnet (Model L75 FBAL). X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar. The spectra were calibrated with the help of DPPH (g = 2.0037). The microwave power level was maintained around 0.2 mW. Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating a Model 174A polarographic analyzer, a Model 175 universal programmer, a Model RE0074 X-Y recorder, a Model 173 potentiostat, a Model 179 digital coulometer, and a Model 377A cell system. The three-electrode measurements were carried out with use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). A platinum-wire-gauze working electrode was used in coulometric experiments. All experiments were done under a dinitrogen atmosphere, and the reported potentials are uncorrected for junction contribution. Low-temperature electrochemical measurements were done with the help of a Haake Model F3-K digital cryostat and circulator connected with jacketed cell bottoms. Microanalytical data (C, H, N) were obtained with use of a Perkin-Elmer Model 240C elemental analyzer.

The data points of Figure 5 were obtained as follows. A 20-mL solution of Ni(BuQ)$_2$(bpy) of exactly known concentration ($\sim 10^{-3}$ M) in dichloromethane (0.1 M in TEAP) was electrolyzed at a constant potential of 0.9 V, and the temperature was kept fixed at 300 K. Electrolysis was discontinued after passing a certain number of faradays. Fifteen minutes was allowed for all reactions to subside. The concentration of *mer*-Ni(BuQ)$_3$ in the resultant solution was determined either by coulometry at 0.1 V (reduction to Ni(BuQ)$_3^-$) or by the spectral intensity of the 690-nm band of *mer*-Ni(BuQ)$_3$.[26] For each data point a fresh solution was used.

Preparation of Ligands and Complexes. Free ligands (HRQ), except HBzQ, which is available commercially, were synthesized from phenols via copper complexes according to the procedure of Cronheim.[29] The ligands are unstable and were used immediately after preparation. Bis(1,2-quinone 2-oximato)nickel(II) was synthesized by a reported method.[22] The complex Na[Ni(BzQ)$_3$] was obtained as before.[11] A general method was used for the synthesis of all K[Ni(RQ)$_3$] complexes. These were converted to tetraphenylarsonium salts by double decomposition. The nickel(III) complexes, *mer*-Ni(RQ)$_3$, were generally prepared from K[Ni(RQ)$_3$] by constant-potential coulometry. The mixed complexes of type Ni(RQ)$_2$(N,N) were syntheiszed by reacting Ni(RQ)$_2$ with the appropriate tertiary amines in stoichiometric ratios. Details are given below for representative examples in each class.

Potassium Tris(4-methyl-1,2-benzoquinone 2-oximato)nickelate(II), K[Ni(MeQ)$_3$]. To an ethanolic solution (30 mL) of HMeQ (0.15 g, 1.10 mmol) and KOH (0.1 g, 1.79 mmol) was added a solution (30 mL) of bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II) (0.35 g, 1.06 mmol) in the same solvent. The mixture was stirred at room temperature for 0.5 h. The resulting red solution was filtered and was then slowly evaporated at room temperature. After the solution was concentrated to 20 mL, a crystalline red-brown solid separated. It was collected by filtration, washed with water, dried, and finally washed with hexane. This was recrystallized from acetonitrile–water (4:1), affording the required complex, yield 0.37 g (70%).

Tetraphenylarsonium Tris(4-methyl-1,2-benzoquinone 2-oximato)nickelate(II), [Ph$_4$As][Ni(MeQ)$_3$]. To a solution containing K[Ni(MeQ)$_3$] (0.25 g, 0.49 mmol) in 20 mL of ethanol was added dropwise with magnetic stirring a solution of Ph$_4$AsCl (0.3 g, 0.72 mmol) in 5 mL of water. The mixture was stirred at room temperature (298 K) for 1 h. The solution was slowly evaporated. The precipitated complex was filtered and washed thoroughly with water and finally with petroleum ether (boiling range 40–60 °C). The dark crystalline compound thus obtained was dried in vacuo over P$_4$O$_{10}$; yield 0.33 g (80%) (based on the potassium salt).

***mer*-Tris(4-methyl-1,2-benzoquinone 2-oximato)nickel(III), *mer*-Ni(MeQ)$_3$.** An acetonitrile solution (25 mL) of K[Ni(MeQ)$_3$] (0.1 g, 0.2 mmol) and NH$_4$PF$_6$ (0.05 g, supporting electrolyte) was exhaustively electrolyzed coulometrically at 0.72 V vs SCE. During electrolysis the solution changed from red to brown. The electrolyzed solution was evaporated to dryness under vacuum at room temperature. The dark solid residue was washed thoroughly with water to remove NH$_4$PF$_6$ and dried under vacuum over P$_4$O$_{10}$; yield 0.065 g (70%). The following constant potentials were used for the synthesis of the other complexes: *mer*-Ni(BuQ)$_3$, 0.75 V; *mer*-Ni(ClQ)$_3$, 0.95 V.

Bis(4-methyl-1,2-benzoquinone 2-oximato)(2,2′-bipyridine)nickel(II), Ni(MeQ)$_2$(bpy). Bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II) (0.17 g, 0.51 mmol) was suspended in acetonitrile (30 mL) and treated with 2,2′-bipyridine (0.09 g, 0.58 mmol) under magnetic stirring at room temperature (298 K). Stirring was continued for 1 h, and the solution was then filtered. Upon slow evaporation the filtrate deposited the deep red crystalline complex, which was collected by filtration and was then washed successively with acetonitrile and diethyl ether. It was dried under vacuum over P$_4$O$_{10}$; yield 0.15 g (60%).

Bis(4-methyl-1,2-benzoquinone 2-oximato)bis(pyrazole)nickel(II), Ni(MeQ)$_2$(pz)$_2$. To an acetone solution (30 mL) of bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II) (0.17 g, 0.51 mmol) was added solid pyrazole (0.08 g, 1.18 mmol). The solution was heated under reflux for 1 h. The mixture was then filtered, and on slow evaporation of the solvent at room temperature, the red-brown crystalline complex precipitated. The compound was collected by filtration, washed with light petroleum (boiling rate 40–60 °C), and then dried under vacuum over P$_4$O$_{10}$. The compound was recrystallized from dichloromethane–hexane (1:3), affording dark crystals, yield 0.14 g (60%).

Acknowledgment. Financial assistance received from the Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi, India, is gratefully acknowledged.

Registry No. *mer*-K[Ni(MeQ)$_3$], 115889-95-7; *fac*-K[Ni(MeQ)$_3$], 115940-60-8; *mer*-K[Ni(BuQ)$_3$], 115889-96-8; *fac*-K[Ni(BuQ)$_3$], 115940-61-9; *mer*-K[Ni(ClQ)$_3$], 115889-97-9; *fac*-K[Ni(ClQ)$_3$], 115940-62-0; *mer*-Na[Ni(BzQ)$_3$], 115889-98-0; *fac*-Na[Ni(BzQ)$_3$], 115940-63-1; *mer*-Ni(MeQ)$_3$, 115890-07-8; *fac*-Ni(MeQ)$_3$, 115940-68-6; *mer*-Ni(BuQ)$_3$, 115890-08-9; *fac*-Ni(BuQ)$_3$, 115940-69-7; *mer*-Ni(ClQ)$_3$, 115890-09-0; *fac*-Ni(ClQ)$_3$, 115940-70-0; *mer*-Ni(BzQ)$_3$, 115890-10-3; *fac*-Ni(BzQ)$_3$, 115940-71-1; [Ni(MeQ)$_2$(bpy)]$^+$, 115890-11-4; [Ni(BuQ)$_2$(bpy)]$^+$, 115890-12-5; [Ni(ClQ)$_2$(bpy)]$^+$, 115890-13-6; [Ni(MeQ)$_2$(py)$_2$]$^+$, 32630-77-6; [Ni(MeQ)$_2$(mpy)$_2$]$^+$, 115890-14-7; [Ni(MeQ)$_2$(apy)$_2$]$^+$, 115890-15-8; [Ni(MeQ)$_2$(pz)$_2$]$^+$, 115890-16-9; *mer*-Ph$_4$As[Ni(MeQ)$_3$], 115890-00-1; *fac*-Ph$_4$As[Ni(MeQ)$_3$], 115940-65-3; Ph$_4$As[Ni(ClQ)$_3$], 115940-67-5; Ni(MeQ)$_2$(bpy), 115890-01-2; Ni(BuQ)$_2$(bpy), 115890-02-3; Ni(ClQ)$_2$(bpy), 115890-03-4; Ni(MeQ)$_2$(py)$_2$, 32680-77-6; Ni(MeQ)$_2$(mpy)$_2$, 115890-04-5; Ni(MeQ)$_2$(apy)$_2$, 115890-05-6; Ni(MeQ)$_2$(pz)$_2$, 115890-06-7; Ni(BuQ)$_2$, 115890-17-0; Ni(ClQ)$_2$, 30993-27-2; Ni(BzQ)$_2$, 115912-11-3; bis(4-methyl-1,2-benzoquinone 2-oximato)nickel(II), 30993-30-7.

Supplementary Material Available: A table showing the analytical, magnetic, and spectral data of the nickel(II) complexes (3 pages). Ordering information is given on any current masthead page.

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(28) Lahiri, G. K.; Bhattacharya, S.; Ghosh, B. K.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 4324–4331.

(29) Cronheim, G. *J. Org. Chem.* **1947**, *12*, 7–19.