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Chemistry of Tetravalent Nickel and Related Species. I.
MN6 Coordination Octahedra Generated from Hexadentate Oxime Ligands

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Hexadentate ligands (H2RR'L) of type 1 readily yield high-spin nickel(II) complexes, Ni(H2RR'L)X2 (X = ClO4, NO3), in which the coordination polyhedron is octahedral NiN6 and Dq is $\sim$1300 cm^{-1}. These are readily oxidized to red diamagnetic Ni(RR'L)X2 by chemical and electrochemical means. The oxidized complexes contain tetravalent nickel held in an octahedral NiN6 core. They show two intense ligand $\rightarrow$ metal charge transfer transitions in the visible region. The charge transfer state also makes some contribution to the ground state (ir data). Ni(RR'L)$^{2+}$ oxidizes quantitatively 2 mol of Fe^{2+} to Fe^{3+}. The potential of the half-cell reaction Ni(RR'L)$^{2+}$ + 2H$^+$ + 2e$^-$ $\rightleftharpoons$ Ni(H2RR'L)$^{2+}$ is determined using a direct potentiometric method. $E°_{298}$ (vs. normal hydrogen electrode) is found to lie in the range 0.90–0.94 V for the systems studied. The possible role of the negative charge on the $=$N—O$^-$ moiety in minimizing the effective positive charge on the metal in Ni(RR'L)$^{2+}$ is discussed. The spectroscopic properties of the low-spin complexes of H2Me2L with two other d^6 ions, viz., iron(II) and cobalt(III) are compared with those of the nickel(IV) species.

Introduction

Uncommon oxidation states of elements, transition elements in particular, have always fascinated inorganic chemists.[1] Such oxidation states are often implicated as transient intermediates in chemical and biochemical redox reactions. To obtain "stable" compounds containing such oxidation states is then of obvious interest. In the particular case of nickel the most common oxidation state is nickel(II). The higher oxidation states, nickel(III) and nickel(IV), are scarce and have aroused considerable interest. The existing literature was recently summarized elsewhere.[2,3] It has been postulated[4,5] that higher oxidation states of nickel are favored by localized accumulation of negative charge on donor atoms and by formation of strong metal–ligand σ bonds. The roles of these factors were illustrated using pyridine–oxime type ligands.[4,5] In general, oxime ligands appear to be particularly suitable for stabilization of higher oxidation states of nickel.[3]

In the present work, hexadentate ligands of type 1 simultaneously containing oxime, azomethine, and amine functions are shown to yield cationic nickel(II) and nickel(IV) species, both of which are quite stable. Selected properties of iron(II) and cobalt(III) complexes are also reported for the purpose of comparison. Directly determined thermodynamic redox potential data for nickel(IV)–nickel(II) couples are virtually unobtainable in literature. For the systems described in this paper, it has been possible to obtain such data. In what follows the ligand system 1 will be abbreviated as H2RR'L; when R = R', the abbreviation will be H2R2L.

1

2
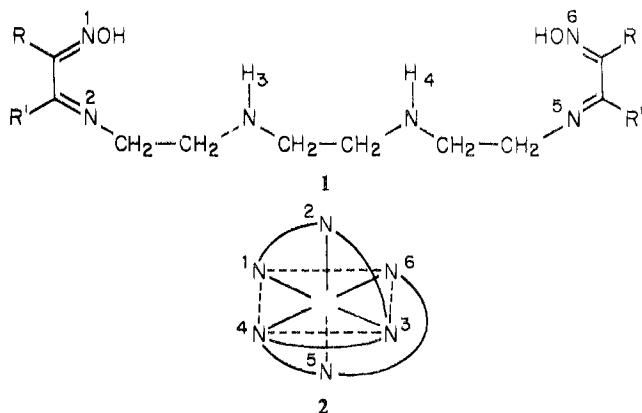
Results and Discussion

A. Nickel(II) Species. The ligand H2Me2L and its cobalt(III) complexes were reported recently.[6,7] The nickel(II) complexes of this and other ligands of type 1 are brown crystalline solids of composition Ni(H2RR'L)X2 (X = ClO4, NO3) (Table I). These are obtained by reacting 1 with NiX2 or by the in situ reaction of NiX2 with the appropriate isonitroso ketone and triethylenetetramine.

Electrical conductivity data (Table II) require[8] that the chelates are 1:2 electrolytes. The complexes are all high spin with magnetic moments lying close to 3.1 BM (Table II). In aqueous solution an electronic band is seen at $\sim$12,800 cm^{-1} and a shoulder appears at $\sim$20,000 cm^{-1} superimposed on a rising ultraviolet tail (Table III). These are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) respectively in idealized O_h symmetry. We therefore have $Dq \sim$ 1280 cm^{-1} and B(found)/B(free ion) $\sim$ 0.85 where B is the Racah parameter. The above physical data show that Ni(H2RR'L)$^{2+}$ contains pseudooctahedral nickel(II) most probably of the structural type 2, which has been shown to be present in Co(HMe2L)Br2·4H2O and Co(H2Me2L)Br3·3H2O from X-ray work.[7] H2RR'L produces a Dq which is larger than those of many other NiN6 species.[5,9,10]

B. An Iron(II) Complex. For comparison with nickel(II), nickel(IV), and cobalt(III) species, we synthesized the iron(II) complex Fe(H2Me2L)(ClO4)2 which is red and diamagnetic both in the crystalline state and in aqueous solution. It is a 1:2 electrolyte[8] in acetonitrile (molar conductivity at 305°K = 285 ohm^{-1} cm^2 mol^{-1}). It gives rise to two intense electronic bands (Figure 1) in aqueous solution (19,400 cm^{-1}, ϵ 6300; $\sim$23,000 cm^{-1} (shoulder), ϵ 2000). The same bands also appear in the crystalline state. The band at 19,400 cm^{-1} can be safely assigned to a charge transfer transition from the metal t$_{2g}$ orbital (idealized O_h) to the lowest empty diimine π^* orbital.[10–13] The origin of the shoulder at 23,000 cm^{-1} is less certain.[14]

C. Nickel(IV) Species.[15] **(a) Synthesis and Characterization.** When H2Me2L is treated with concentrated HNO3 a violent reaction occurs with the evolution of nitrous fumes. The solution thus obtained has no chelating properties toward metal ions. It has not been possible to isolate any definite compound from the oxidized solution. Evidently the free ligand is destroyed by concentrated HNO3. On the other hand, on

Table I. Characterization Data of Ligands and Complexes

| Compd	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Metal Calcd	% Metal Found
H₂EtMeL	$C_{16}H_{32}N_6O_2$	56.43	56.83	9.48	8.80	24.68	24.80		
H₂MePhL	$C_{24}H_{32}N_6O_2$	66.01	65.66	7.39	7.50	19.25	19.40		
Ni(H₂Me₂L)(ClO₄)₂	$C_{14}H_{28}N_6Cl_2O_{10}Ni$	29.49	29.80	4.91	4.85	14.70	15.10	10.30	10.31
Ni(H₂Me₂L)(NO₃)₂·H₂O	$C_{14}H_{30}N_8O_9Ni$	32.75	32.19	5.89	6.28	21.84	21.80	11.44	11.57
Ni(H₂EtMeL)(ClO₄)₂	$C_{16}H_{32}N_6Cl_2O_{10}Ni$	32.10	32.15	5.40	5.50	14.05	13.70	9.82	9.83
Ni(H₂MePhL)(ClO₄)₂	$C_{24}H_{32}N_6Cl_2O_{10}Ni$	41.50	41.81	4.65	4.93	12.10	12.70	8.46	8.80
Ni(H₂PhMeL)(ClO₄)₂	$C_{24}H_{32}N_6Cl_2O_{10}Ni$	41.50	40.97	4.65	4.80	12.10	12.10	8.46	8.93
Ni(Me₂L)(ClO₄)₂	$C_{14}H_{26}N_6Cl_2O_{10}Ni$	29.60	29.42	4.62	4.82	14.80	15.00	10.34	10.58
Ni(EtMeL)(ClO₄)₂	$C_{16}H_{30}N_6Cl_2O_{10}Ni$	32.23	32.31	5.42	5.10	14.10	14.10	9.85	9.55
Ni(MeEtL)(ClO₄)₂	$C_{16}H_{30}N_6Cl_2O_{10}Ni$	32.23	32.45	5.42	5.39	14.10	14.60	9.85	10.02
Ni(MePhL)(NO₃)(ClO₄)	$C_{24}H_{30}N_7ClO_9Ni$	44.04	44.37	4.61	4.69	14.97	14.60	8.97	8.85
Ni(PhMeL)(NO₃)(ClO₄)	$C_{24}H_{30}N_7ClO_9Ni$	44.04	44.16	4.61	4.79	14.97	15.38	8.97	9.02
Fe(H₂Me₂L)(ClO₄)₂	$C_{14}H_{28}N_6Cl_2O_{10}Fe$	29.57	29.56	4.93	5.09	14.78	15.00	9.65	9.60

Table II. Molar Electrical Conductivity (Λ, ohm⁻¹ cm² mol⁻¹) in Nitromethane Solution and Magnetic Moment (μ_{eff}, BM) in the Solid State[a]

Compd	Λ	μ_{eff}
Ni(H₂Me₂L)(ClO₄)₂	143 (303)	3.12 (302)
Ni(H₂Me₂L)(NO₃)₂·H₂O	b	3.13 (302)
Ni(H₂EtMeL)(ClO₄)₂	147 (304)	3.07 (307)
Ni(H₂MeEtL)(ClO₄)₂	157 (304)	3.07 (307)
Ni(H₂MePhL)(ClO₄)₂	178 (304)	3.06 (307)
Ni(H₂PhMeL)(ClO₄)₂	168 (304)	3.15 (306)
Ni(Me₂L)(ClO₄)₂	137 (303)	Diamagnetic
Ni(EtMeL)(ClO₄)₂	137 (308)	Diamagnetic
Ni(MeEtL)(ClO₄)₂	137 (310)	Diamagnetic
Ni(PhMeL)(NO₃)(ClO₄)	Insoluble	Diamagnetic

[a] Temperatures (°K) of measurement are shown in parentheses.
[b] Measurement not done.

treatment of Co(Me₂L)ClO₄ with concentrated HNO₃, no reaction occurs and the complex can be isolated in the protonated form Co(H₂Me₂L)³⁺ from the reaction mixture. The bound ligand is thus not necessarily destroyed or oxidized by concentrated HNO₃.

When crystalline Ni(H₂Me₂L)(ClO₄)₂ is suspended into concentrated HNO₃ at room temperature, the solid progressively dissolves, nitrous fumes are evolved, and a deep red solution results. On dilution of the reaction mixture followed by cooling, dark violet needles of composition Ni(Me₂L)-(ClO₄)₂ deposit in 75% yield. The same product could also be obtained by electrolytic oxidation of a magnetically stirred aqueous suspension of Ni(H₂Me₂L)(ClO₄)₂ in a platinum
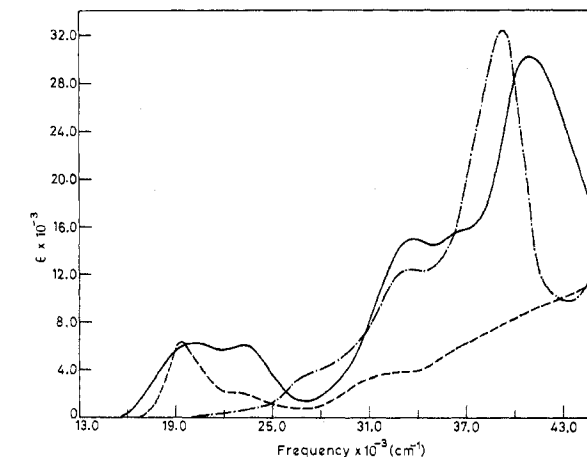
Figure 1. Electronic spectra of Ni(Me₂L)(ClO₄)₂ (—), Fe(H₂Me₂L)(ClO₄)₂ (- - -), and Co(H₂Me₂L)(ClO₄)₃ (- · · -) in aqueous solution.

vessel (anode) using a platinum wire cathode which was dipped into dilute perchloric acid. The anode and cathode compartments were separated by a porous glass diaphragm. On passing current at 2–10 V, the liquid in the anode compartment changes from orange to deep red, Ni(H₂Me₂L)(ClO₄)₂ dissolves progressively, and the needles of Ni(Me₂L)(ClO₄)₂ deposit on the walls of the anode. By using the electrolytic method Ni(Me₂L)(ClO₄)₂ can be obtained in >50% yield.

Table III. Frequencies (ν, cm⁻¹) and Extinction Coefficients (ϵ, M^{-1} cm⁻¹) of Electronic Bands of Nickel(II) and Nickel(IV) Complexes in Visible Region

Compd	Medium	ν (ϵ)
A. Nickel(II) Species		
Ni(H₂Me₂L)(ClO₄)₂	Nujol	13,160; 20,000[a]
	Water	12,820; 20,000 (75)[a]
Ni(H₂Me₂L)(NO₃)₂·H₂O	Nujol	12,900; 20,400[a]
	Water	12,820 (37); 20,000 (73)[a]
Ni(H₂EtMeL)(ClO₄)₂	Nujol	13,330; 20,400;[a] 23,809
	Water	12,820 (35); 20,000 (84)[a]
Ni(H₂MeEtL)(ClO₄)₂	Nujol	13,700;[a] 20,830;[a] 24,390[a]
	Water	12,820 (34); 19,600 (73)[a]
Ni(H₂MePhL)(ClO₄)₂	Nujol	13,330; 19,230[a]
	Water	12,990 (30); 19,230 (99)[a]
Ni(H₂PhMeL)(ClO₄)₂	Nujol	13,160; 19,600;[a] 23,800
	Water	12,820 (27); 19,230 (84)[a]
B. Nickel(IV) Species		
Ni(Me₂L)(ClO₄)₂	Water	20,000 (6300); 23,260 (5960)
	Nitromethane	18,940 (6560); 23,260 (6030)
	0.001 N HClO₄	20,000 (5430); 23,260 (5310)
Ni(EtMeL)(ClO₄)₂	Water	20,000 (6150); 23,260 (6000)
Ni(MeEtL)(ClO₄)₂	Water	20,000 (5440); 23,260 (5440)
Ni(MePhL)(NO₃)(ClO₄)	Water	19,420 (3360); 23,530 (3200)
Ni(PhMeL)(NO₃)(ClO₄)	6 N HNO₃[b]	19,230 (2850); 22,730 (2510)

[a] Shoulder. [b] Insoluble in other media.

Table IV. Selected Infrared Stretching Frequencies (cm⁻¹) of Some Ligands and Complexes [a,b]

| Compd | Assignment | | |
	NH	OH	C⁼N + C⁼C
H_2Me_2L	3300 (vs, w)	2650 (vb, st)	1685 (s, w), 1625 (s, st)
$Ni(H_2Me_2L)(ClO_4)_2$[c]	3300 (s, m)	3300 (vb, m)	1670 (s, m), 1600 (b, m)
$Fe(H_2Me_2L)(ClO_4)_2$	3280 (s, m)	3320 (vb, m)	1620 (s, w), 1540 (s, m)
$Co(H_2Me_2L)(ClO_4)_3$	3260 (b, m)	3520 (vb, m)	1640 (s, m), 1580 (s, w)
$Co(Me_2L)(ClO_4)$	3200 (b, m)		1650 (b, w), 1620 (s, m)
$Ni(Me_2L)(ClO_4)_2$	3200 (b, m)		1610 (s, w), 1500 (s, st)
H_2EtMeL	3340 (s, w)	2700 (vb, st)	1710 (b, w), 1650 (s, st)
$Ni(H_2EtMeL)(ClO_4)_2$[c]	3320 (b, st)	3320 (b, st)	1690 (s, m), 1610 (b, m)
$Ni(EtMeL)(ClO_4)_2$	3270 (b, m)		1635 (s, w), 1520 (s, st)
$Ni(H_2MeEtL)(ClO_4)_2$[c]	3360 (s, m)	3360 (s, m)	1690 (s, m), 1615 (s, m)
$Ni(MeEtL)(ClO_4)_2$	3270 (b, m)		1630 (s, w), 1510 (b, st)
H_2MePhL	3340 (s, w)	2800 (vb, st)	1640 (s, m), 1620 (s, m)
$Ni(H_2MePhL)(ClO_4)_2$[c]	3340 (b, m)	3340 (b, m)	1675 (s, m), 1600 (b, m)
$Ni(H_2PhMeL)(ClO_4)_2$[c]	3360 (s, st)	3360 (s, st)	1690 (s, m), 1630 (s, w), 1610 (s, m)
$Ni(PhMeL)(NO_3)(ClO_4)$	3140 (b, m)		1625 (s, w), 1500 (s, st)

[a] All measurements are done in Nujol mull except that those on the free ligands were done in KBr disk. [b] Meaning of symbols given in parentheses is as follows: b, broad; vb, very broad; s, sharp; vs, very sharp; st, strong; w, weak; m, medium. [c] NH and OH stretches badly overlap (see text).

However, the product is often slightly contaminated by Ni-$(H_2Me_2L)(ClO_4)_2$ because of its poor solubility in water. By far the best synthetic method is that using concentrated HNO_3 as the oxidizing agent. Several other chemical oxidizing agents such as ammonium persulfate and lead peroxide were also examined, but none match the efficacy of concentrated HNO_3 in bringing about the conversion of $Ni(H_2Me_2L)(ClO_4)_2$ to $Ni(Me_2L)(ClO_4)_2$.

The chelates $Ni(EtMeL)(ClO_4)_2$ and $Ni(MeEtL)(ClO_4)_2$ were similarly obtained in good yields by concentrated HNO_3 oxidation of the corresponding nickel(II) complexes. Similar oxidation of $Ni(H_2PhMeL)(ClO_4)_2$ yielded a mixed nitrate–perchlorate of composition $Ni(PhMeL)(NO_3)(ClO_4)$. Oxidation of $Ni(H_2MePhL)(ClO_4)_2$ similarly yielded Ni-$(MePhL)(NO_3)(ClO_4)$ though in a slightly impure form (vide infra).

The results of elemental analyses for the oxidized complexes are set out in Table I. The chelates having only alkyl substituents are fairly soluble in water, nitromethane, methanol, acetone etc. The solubility of systems having a phenyl substituent is lower. The crystalline complexes are indefinitely stable under vacuum, but in moist atmosphere they progressively change color until an orange-brown solid is left which is identical with the corresponding nickel(II) complex of the type $Ni(H_2RR'L)^{2+}$. When an aqueous solution of Ni-$(RR'L)^{2+}$ is boiled, it is quantitatively converted in a few minutes to the $Ni(H_2RR'L)^{2+}$. These experiments demonstrate that no fundamental change in the ligand backbone occurs during concentrated HNO_3 oxidation of $Ni(H_2RR'L)^{2+}$ to $Ni(RR'L)^{2+}$.

The electrical conductivity data for the chelates (Table II) demonstrate that they are 1:2 electrolytes. All oxidized complexes are diamagnetic.[16] The stoichiometry, conductivity, and diamagnetism of these complexes strongly suggest that they contain nickel in the formal oxidation state IV. We believe that $Ni(RR'L)^{2+}$ belongs to the general structure type **2**.

(b) Infrared Spectra. Characteristic OH and NH stretching frequencies in selected ligands and complexes are collected in Figure 2 and Table IV. As expected the $Ni(RR'L)^{2+}$ species show only NH and no OH stretch. Nickel(II) complexes containing an α-diimine function show[17] two distinct bands in the region 1600–1700 cm⁻¹, which are due to coupled C⁼N and C⁼C stretching modes. In the corresponding iron(II) complexes the bands are shifted to lower frequencies (1620–1500 cm⁻¹) due to metal → ligand (antibonding) charge transfer contribution[11,12,17] to the ground state. The chelates under investigation behave in a similar manner. For example,
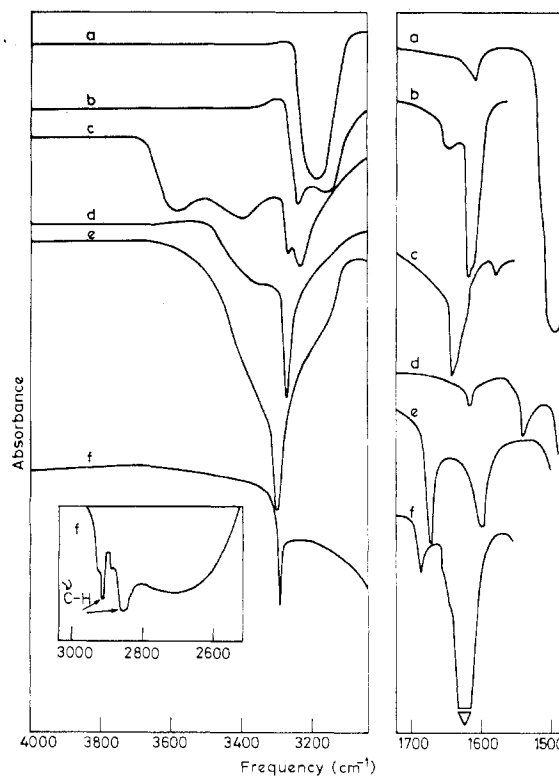

Figure 2. Infrared spectra showing NH, OH, and C⁼N + C⁼C stretches: $Ni(Me_2L)(ClO_4)_2$, a; $Co(Me_2L)ClO_4$, b; $Co(H_2Me_2L)(ClO_4)_3$, c; $Fe(H_2Me_2L)(ClO_4)_2$, d; $Ni(H_2Me_2L)$-$(ClO_4)_2$, e; H_2Me_2L, f, the OH stretching region is shown in the inset.

$Ni(H_2Me_2L)(ClO_4)_2$ has two bands at 1670 and 1600 cm⁻¹; the bands in $Fe(H_2Me_2L)(ClO_4)_2$ are at 1620 and 1540 cm⁻¹ (Figure 2). In $Ni(Me_2L)(ClO_4)_2$ the major stretch is shifted even further (~1500 cm⁻¹). We believe that this is due to strong ligand(bonding) → metal charge transfer (vide infra). Such charge transfer effects are not important in the cobalt(III) complexes (Figure 2).

(c) Electronic Spectra. The allowed electronic transitions of $Fe(H_2Me_2L)(ClO_4)_2$ in the visible region were assigned to metal → ligand charge transfer (CT) earlier in this paper (Figure 1). Both the cobalt(III) species, $Co(H_2Me_2L)^{3+}$ and $Co(Me_2L)^+$, are orange-yellow in color; the absorption at lowest energy for both species[18] is a shoulder at 27,000 cm⁻¹

(Figure 1). The position of this band is not incompatible[19-21] with the $^1A_{1g} \rightarrow {}^1T_{1g}$ (ν_1) transition in idealized O_h symmetry.

The nickel(IV) complexes show two closely spaced allowed transitions in the visible region (Figure 1, Table III). It is reasonable to assume that these are due to ligand → metal CT transition. Thus the metal → ligand CT state in the iron(II) complex and the ligand → metal CT state in the nickel(IV) complex are relatively close to the respective ground states; in the cobalt(III) complex neither situation exists. This trend is expected since the metal d orbitals get progressively depressed in energy relative to the ligand orbitals in the isoelectronic series iron(II), cobalt(III), and nickel(IV). When a CT state is close to the ground state, appreciable CT contribution may be expected in the latter state. The conclusions drawn from ir data discussed earlier (vide supra) and those drawn from electronic spectral data are thus in complete harmony with each other.

(d) Reactions with Reducing Agents. In aqueous solution the nickel(IV) species instantly oxidizes many reducing agents, e.g., Fe^{2+}, $Fe(CN)_6^{4-}$, $S_2O_3^{2-}$. The reaction with Fe^{2+} in acidic aqueous solution was studied quantitatively. The experimental molar equivalents of Fe^{2+} consumed per mole of the nickel(IV) species are: $Ni(Me_2L)^{2+}$, 2.00; $Ni(EtMeL)^{2+}$, 1.95; and $Ni(MeEtL)^{2+}$, 2.05. The reaction between Fe^{2+} and Ni-$(RR'L)^{2+}$ is therefore:

$$2Fe^{2+} + Ni(RR'L)^{2+} + 2H^+ \rightarrow 2Fe^{3+} + Ni(H_2RR'L)^{2+}$$
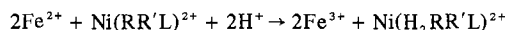
The presence of Fe^{3+} and $Ni(H_2RR'L)^{2+}$ in the reaction mixture can be demonstrated.

(e) Oxidation Potential. Since both $Ni(H_2RR'L)^{2+}$ and $Ni(RR'L)^{2+}$ were stable in acidic aqueous solutions, we determined the formal oxidation potential of such couples. In the literature, there is acute paucity of data on oxidation potentials of nickel(IV)–nickel(II) couples.[2]

For the half-cell reaction

$$Ni(RR'L)^{2+} + 2H^+ + 2e^- \rightleftharpoons Ni(H_2RR'L)^{2+} \qquad (1)$$
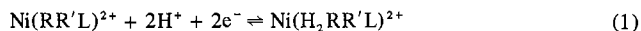
the potential E at 298°K is

$$E = E^\circ_{298} + 0.0295\,[\log\,(p/q) - 2pH] \qquad (2)$$

where p and q are respectively the concentrations of Ni-$(RR'L)^{2+}$ and $Ni(H_2RR'L)^{2+}$ and E°_{298} has its usual meaning.

In Table V, the E°_{298} (vs. SCE) values are computed for every measured set of E, p/q, and pH. It is seen that E°_{298} (vs. SCE) is a constant within small limits of fluctuation in spite of the considerable variations in p/q and pH. The E°_{298} values suitably rounded off *after conversion to the normal hydrogen electrode standard are*: $Ni(Me_2L)^{2+}$–Ni-$(H_2Me_2L)^{2+}$, 0.94 ± 0.01 V; $Ni(EtMeL)^{2+}$–$Ni(H_2EtMeL)^{2+}$, 0.92 ± 0.01 V; $Ni(MeEtL)^{2+}$–$Ni(H_2MeEtL)^{2+}$, 0.90 ± 0.01 V. The nickel(IV) species are thus moderately strong oxidizing agents, stronger than aqueous acidic Fe^{3+} but considerably weaker than aqueous acidic $Cr_2O_7^{2-}$. It is significant that $Ni(RR'L)^{2+}$ oxidizes Fe^{2+} (E°_{298}; 0.77 V) in aqueous acidic medium, but it fails to oxidize $Fe(o\text{-phen})_3^{2+}$ (E°_{298}; 1.13 V).[22]

Concluding Remarks

We believe that the evidence presented above convincingly demonstrates the presence of nickel in the formal oxidation state IV in $Ni(RR'L)^{2+}$. Restatements of some chemical observations are pertinent in this context. With metal(II) the species $M(H_2RR'L)^{2+}$ are readily obtained in neutral aqueous solutions; appreciable proton dissociation occurs only on addition of alkali.[23] As expected such dissociation becomes more facile in complexes of metal(III), e.g., $Co(H_2RR'L)^{3+}$. This trend should continue and proton dissociation should become even more facile in going to a metal(IV) complex. Indeed the protonated species $Ni(H_2RR'L)^{4+}$ has not been

Table V. Oxidation Potential Data[a] for Nickel(IV)–Nickel(II) Couples

p/q	pH	$-Y$	E vs. SCE, V	E°_{298} vs. SCE, V^b
Couple A: $Ni(Me_2L)^{2+}$–$Ni(H_2Me_2L)^{2+}$				
1.308	4.35	8.583	0.449	0.702
2.186	4.35	8.360	0.462	0.708
1.094	3.55	7.061	0.488	0.696
2.173	3.30	6.263	0.510	0.695
1.077	3.05	6.068	0.517	0.696
1.362	2.95	5.766	0.524	0.694
1.077	2.60	5.168	0.542	0.694
Couple B: $Ni(EtMeL)^{2+}$–$Ni(H_2EtMeL)^{2+}$				
0.825	4.20	8.484	0.425	0.675
0.515	4.05	8.388	0.428	0.672
0.515	3.30	6.888	0.474	0.677
1.088	2.75	5.463	0.504	0.665
1.813	2.80	5.342	0.514	0.662
0.740	2.50	5.131	0.518	0.669
0.925	2.50	5.034	0.522	0.677
Couple C: $Ni(MeEtL)^{2+}$–$Ni(H_2MeEtL)^{2+}$				
0.784	3.90	7.906	0.412	0.645
0.785	3.50	7.105	0.432	0.642
1.570	3.40	6.604	0.455	0.650
3.135	3.30	6.104	0.474	0.654
1.570	2.80	5.404	0.492	0.651
3.135	2.80	5.104	0.502	0.653
1.570	2.55	4.904	0.508	0.653

^{a} For meaning of symbols see text. ^{b} Can be converted to E°_{298} (vs. normal hydrogen electrode) by adding 0.246 V.

isolated; only $Ni(RR'L)^{2+}$ obtains even in acidic solution.[24]

The present results add further evidence toward the evolving generalization that oxime ligands after proton dissociation are particularly suitable for stabilization of higher (>2) oxidation states of nickel. We suspect that the negative charge on oximate oxygen (i.e., $=N\!-\!O^-$) plays a very important role in partial neutralization of the excessive positive charge on the metal ion through inductive transmission and σ donation. Certain spectroscopic observations pertaining to the iron complex may be significant in this regard. In $Fe(H_2Me_2L)^{2+}$ the metal → ligand CT band is at 19,400 cm^{-1} while[14] in $Fe(Me_2L)$ the band shifts to 17,240 cm^{-1}. A significant part of the observed shift in going from $Fe(H_2Me_2L)^{2+}$ to Fe-(Me_2L) could be due to smaller effective charge[11,12] (flow of negative charge from $=N\!-\!O^-$ to metal) on the metal atom in the latter.

At present we are studying the nickel(IV)–nickel(II) couples described in this paper using rapid-sweep voltammetric techniques. Nearly reversible two-step voltammograms are observed. Current studies also include new complexes of the type $Ni(HRR'L')_2^{2+}$ and $Ni(RR'L')_2^{2+}$, where $HRR'L'$ is the tridentate ligand **3**. The results of these and related researches
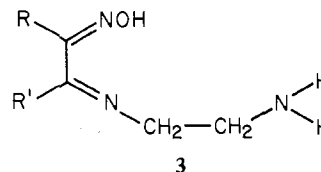
3

will constitute the subject matter of the next paper in the series.

Experimental Section

A. Preparation of Compounds. (a) Isonitroso Ketones. Biacetyl monoxime was prepared by a procedure reported elsewhere.[25] **Isonitrosopropyl methyl ketone** (3-oximinopentan-2-one) was prepared in good yield (60–70%) from methyl propyl ketone by using the same procedure. **Isonitrosopropiophenone** was prepared[26] from propiophenone. **Isonitrosoethyl ethyl ketone** and **α-isonitrosobenzyl methyl ketone** (1-oximino-1-phenylpropan-2-one) were similarly prepared starting from diethyl ketone and benzyl methyl ketone, respectively.

(b) Ligands. H_2Me_2L was prepared by a procedure reported

elsewhere.[6] H2EtMeL was prepared as follows. Triethylenetetramine (7.3 g; 0.05 mol) was added to 11.5 g of isonitrosopropyl methyl ketone (0.1 mol) suspended in 40 ml of *n*-hexane. The mass was heated to reflux for 0.5 hr. The reaction mixture was then cooled to 273°K and then kept in a stoppered flask. After 24 hr white crystals were formed. The solvent was decanted off. A few milliliters of 95% ethanol was added to the crystals which were then collected by filtration. The white solid was washed with 95% ethanol followed by ether and was dried over fused calcium chloride (yield 50%); mp 442°K. It is insoluble in ethanol and ether. H2MePhL was prepared as follows: triethylenetetramine (5.85 g; 0.04 mol) was added to a suspension of 13.04 g of isonitrosopropiophenone (0.08 mol) in 40 ml of *n*-hexane. The mixture was heated to reflux for 15 min and was then cooled (273°K) in a stoppered flask for an hour. A few milliliters of 95% ethanol was added to the mixture which had a reddish viscous layer. On stirring, the viscous matter solidified to white crystals. These were filtered off and washed with 95% ethanol followed by ether. Drying was done over fused calcium chloride: mp 440°K; yield ∼50%.

(c) Nickel(II) Complexes. Ni(H2Me2L)(ClO4)2: 1 g of H2Me2L (0.003 mol) was added slowly to an ethanolic solution of 1.22 g of nickel(II) perchlorate hexahydrate (0.003 mol) which was being warmed and stirred continuously. Gradually the color of the solution changed to orange red and soon orange brown crystals deposited on scratching the sides of the reaction vessel. The crystals were filtered off and were recrystallized from water to give shining light orange hexagonal plates (∼50% yield). Ni(H2Me2L)(NO3)2·H2O was prepared in an analogous manner from H2Me2L and nickel(II) nitrate hexahydrate. Ni(H2EtMeL)(ClO4)2 and Ni(H2MePhL)(ClO4)2: these two compounds were prepared in good yields by reacting nickel(II) perchlorate hexahydrate with H2EtMeL and H2MePhL respectively in the same manner as that described for Ni(H2Me2L)(ClO4)2. Ni(H2MeEtL)(ClO4)2: 1.46 g of triethylene-tetramine (0.01 mol) was added to an ethanolic solution of 2.3 g of isonitrosoethyl ethyl ketone (0.2 mol). An ethanolic solution of 3.65 g of nickel(II) perchlorate hexahydrate (0.01 mol) was added to the above mixture. The mixture was heated to reflux for 4–5 hr with constant stirring. Shining brown crystals were deposited in ∼50% yield. They were filtered off and were washed with alcohol followed by ether. Ni(H2PhMeL)(ClO4)2: this was prepared in the same manner as above from triethylenetetramine, isonitrosobenzyl methyl ketone, and nickel(II) perchlorate hexahydrate. Brown crystals formed in good yield were recrystallized from a 1:1 mixture of water and 95% ethanol.

(d) Nickel(IV) Complexes. Ni(Me2L)(ClO4)2: 5 ml of concentrated nitric acid was added to 2 g of Ni(H2Me2L)(ClO4)2. Soon brown nitrous fumes evolved and the compound dissolved to give a deep red solution. The mixture was cooled to 273°K and was then diluted to twice its volume with cold water. Dark violet needles deposited which were filtered off and were then washed with ethanol followed by ether. The crystals were dried over fused calcium chloride under vacuum. Some more crystals of Ni(Me2L)(ClO4)2 could be obtained from the mother liquor by adding a few milliliters of saturated sodium perchlorate solution to it. Total yield was 75%. Ni(Et-MeL)(ClO4)2 and Ni(MeEtL)(ClO4)2: these were prepared in the same manner as above by treating Ni(H2EtMeL)(ClO4)2 and Ni(H2MeEtL)(ClO4)2, respectively, with concentrated HNO3. However, these two compounds being more soluble than Ni(Me2L)(ClO4)2 had to be precipitated out (50% yield) by adding saturated sodium perchlorate solution to the reaction mixture. Ni(MePhL)(ClO4)(NO3) and Ni(PhMeL)(ClO4)(NO3): these were synthesized by dissolving Ni(H2MePhL)(ClO4)2 and Ni(H2PhMeL)(ClO4)2, respectively, in concentrated HNO3 and then diluting the solution with water as in the case of Ni(Me2L)(ClO4)2. These compounds are only slightly soluble in aqueous acidic medium and the yield was 90–95%.

(e) Fe(H2Me2L)(ClO4)2. H2Me2L (1 g; 0.003 mol) was added slowly to a solution of 0.93 g of ferrous sulfate heptahydrate (0.003 mol) in 20 ml of water with constant stirring. A deep red solution was formed. Violet rhombic plates were obtained when aqueous saturated sodium perchlorate solution was added to the above solution. The crystals were filtered off and were washed successively with cold water, 95% ethanol, and ether. These were then dried under vacuum. Yield was ∼75%.

(f) Co(H2Me2L)(ClO4)3, Co(H2Me2L)Br3·3H2O, and Co-(Me2L)ClO4. These were prepared by following procedures as described in the literature.[6]

B. Titration of Nickel(IV) Species with Fe2+. Standard (5 ml;

3 × 10⁻³ *M*) Fe²⁺ was titrated with Ni(RR'L)²⁺ to a sharp red end point. The solutions were 0.01 *N* in H2SO4 and 0.3 ml of concentrated H3PO4 was added to mask the color of Fe³⁺.

C. Physical Measurements. Magnetic moments were studied using a sensitive Gouy balance.[27] Infrared spectra were recorded on a Perkin-Elmer 521 recording spectrophotometer. Electronic spectra were studied on a Cary Model 14 recording spectrophotometer. Solution electrical conductivities of samples were determined with the help of a Systronics (India) conductivity meter Type 302.

For $E°_{298}$ determination Ni(H2RR'L)²⁺ and Ni(RR'L)²⁺ solutions were separately prepared in pure water with concentrations of ∼1 × 10⁻³ and 3.0 × 10⁻³ *M*, respectively. Required amounts of both solutions were pipetted into a double-walled glass vessel thermostated to 298 ± 0.1°K. The vessel was fitted with a saturated calomel electrode (SCE), a platinized platinum foil electrode, a glass electrode, a gas bubbler, and a thermometer. The pH was adjusted to various values by addition of 1 *N* H2SO4. Nitrogen gas was bubbled through the solution and a sensitive galvanometer (sensitivity = 0.633 μA per 100 mm) was brought to a stable null position by slowly applying a known voltage (correct to ±0.001 V) opposite to the cell voltage. Then pH of the experimental solution was determined with the help of the glass electrode using a Systronics (India) pH meter.

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(14) It could be of ligand field origin (¹A₁g → ¹T₁g)(ν₁) or it could be another component of the metal → ligand charge transfer transition arising from the low-symmetry splitting of the t2g orbital. Such splitting has been observed for terimine complexes.¹³ We prefer the former assignment for the following reasons. (i) In Co(H2Me2L)³⁺ the ν₁ band is at ∼27,000 cm⁻¹ (vide infra). In the isoelectronic Fe(H2Me2L)²⁺, ν₁ may be expected¹² to lie ∼3000 cm⁻¹ below this figure. (ii) In alkaline medium Fe(Me2L) is formed and the major charge transfer band moves to 17,240 cm⁻¹ (ε 6200). However, the shoulder under discussion still remains at 23,000 cm⁻¹. The frequencies of ligand field bands of Ni(H2Me2L)²⁺ and Co(H2Me2L)³⁺ are known to remain unaffected by deprotonation and the same may be expected to be true for the iron(II) complex.
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(19) The Dq values of Ni(NH3)6[2+] and Co(NH3)6[3+] are 1080 and 2490 cm^{-1}, respectively.[20,21] Assuming that the Dq is amplified in the same ratio in going from Ni(H2Me2L)[2+] to Co(H2Me2L)[3+], the calculated value of ν_1 for the latter complex is ~26,000 cm^{-1}. In this calculation $(Dq)_{Ni}$ (i.e., Dq of Ni(H2Me2L)[2+]) is taken as 1300 cm^{-1} so that $(Dq)_{Co}$ is ~3000 cm^{-1}; ν_1 is obtained from the relationship $\nu_1 = 10(Dq)_{Co} - C$, where[21] C, the interelectronic repulsion parameter, is ~4000 cm^{-1}.

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Skeletal Vibrational Spectra, Force Constants, and Bond Properties of Transition Metal Ammine Complexes

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A systematic investigation of skeletal ir and Raman data, force constants, and bond properties has been carried out for all octahedral hexaammine and tetrahedral and square-planar tetraammine complexes of the transition metals (including zinc and cadmium) for which reliable vibrational frequencies are known. The calculations are based on critically selected spectral data reported in the literature and on vibrational frequencies measured by ourselves. A correlation of the metal–nitrogen stretching force constants to other physical properties as well as to symmetry of the complexes, oxidation numbers, and position of the central atoms in the periodic system yields reasonable results.

Introduction

Although transition metal ammine complexes are among the best known complex compounds and although a great deal of vibrational spectroscopic work has been done in this field during the last two decades, reliable Raman data for most of the complexes of divalent metals have not yet been reported. Previous normal coordinate analyses for ammine complexes have been based mainly upon infrared vibrational frequencies using the Urey–Bradley potential function. For many complexes a comparison of the force constants reported in the literature reveals large discrepancies. In some cases the metal–nitrogen stretching force constants, which are very useful for understanding the nature of bonding in complexes, differ by more than 100%.[1]

It is the aim of this paper to report trustworthy skeletal force constants of ammine complexes determined from reliable infrared and Raman frequencies and by use of appropriate models. We will inspect whether the metal–nitrogen stretching force constants calculated by us can be correlated with other physical data and whether a comparison of the bond properties of the complexes with regard to symmetry, oxidation number, and position of the central atom in the periodic system yields reasonable results. The calculations for all octahedral hexaammine and tetrahedral and square-planar tetraammine complexes of the transition metals (including zinc and cadmium), for which skeletal vibrational frequencies are known, will be made on the basis of critically selected literature data and of frequencies measured by ourselves. Some skeletal vibrational frequencies (particularly Raman data) will be presented here for the first time.

Experimental Section

[Cr(NH3)6]Cl3, [Co(NH3)6]Cl2, [Ni(NH3)6]Cl2, [Cu(NH3)4]SO4·H2O, and [Pd(NH3)4]Cl2·H2O were prepared by standard methods[2-4] and [Mn(NH3)6]Cl2 and [Fe(NH3)6]Cl2 by introducing gaseous ammonia into aqueous solutions of NH4Cl, MnCl2·4H2O, and FeCl2·4H2O, respectively (cf. ref 5). [Cd(NH3)4](ReO4)2 was prepared according to ref 6 and 7. [Mn(NH3)6][2+], [Co(NH3)6][2+], [Ni(NH3)6][2+], and [Cd(NH3)6][2+] in aqueous solutions have been

obtained by adding concentrated aqueous ammonia to solutions of the corresponding chlorides. In the case of the manganese and cobalt complexes, small quantities of hydrazine were necessary to stabilize the divalent state of the metals.

Infrared spectra of Nujol mulls were measured on a Perkin-Elmer IR-180 spectrometer. Raman spectra of the aqueous solutions mentioned above and of [Cd(NH3)4](ReO4)2 were scanned with a Coderg laser Raman spectrometer PHO using a Kr[+] laser from Spectra-Physics (excitation lines 6471 and 4762 Å). Raman lines due to intermediate steps of complex formation in aqueous solution were not observed. The laser Raman spectra of the solid hexaammine-manganese, -iron, -cobalt, -nickel, and -cadmium complexes could not be measured (not even with the rotating cell technique) because of sample decomposition. Even in the presence of reducing agents, the central atom in solutions containing [Fe(NH3)6][2+] was oxidized to the trivalent state (Fe(OH)3 precipitate) in the course of the Raman measurement. The spectrometers were calibrated with water vapor and krypton plasma lines, respectively.

Vibrational Spectra

Hexaammine Complexes of Divalent Metals. No skeletal Raman frequencies for octahedral hexaammine complexes of divalent transition metals in aqueous solution other than the totally symmetric metal–nitrogen stretching vibrations of [Ni(NH3)6][2+] and [Cd(NH3)6][2+] have been previously reported.[8,9] In a recent publication,[1] we could confirm the position of ν_s(NiN) in the Raman spectrum of [Ni(NH3)6][2+]. Furthermore, a new line at 235 cm^{-1} appearing as a shoulder in the slope of the laser exciting line was observed and assigned to δ(NNiN)(F2g). Damaschun[9] erroneously assigned a line of [Zn(NH3)4][2+] to the corresponding hexaammine complex, which does not exist in aqueous solution.

The Raman solution data determined by us are presented in Table I. Unfortunately, only one line (instead of three lines expected) in the region of the skeletal vibrations could be observed for [Mn(NH3)6][2+] and [Cd(NH3)6][2+] (unequivocally assigned to the totally symmetric stretching vibration ν_s(MN)(A1g) from depolarization measurements). A careful investigation of the Raman spectra of [Co(NH3)6][2+] and [Ni(NH3)6][2+] revealed (in addition to the lines corresponding