(16) J. Casanova, N. D. Weaner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).
(17) S. D. Ittel, *Inorg. Synth.*, in press.
(18) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972); W. Partenheimer and E. F. Hoy, *J. Am. Chem. Soc.*, **95**, 2840 (1973).
(19) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
(20) S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Am. Chem. Soc.*, **93**, 6462 (1971).
(21) R. U. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **91**, 1453 (1972).
(22) In Tables II and III and throughout the paper when compounds in those tables are referred to, an arabic number is used to indicate the olefin, the arabic number followed by a lower case "a" indicates the $Ni(t\text{-}BuNC)_2$ complex of that olefin and "b" indicates the $Ni(PPh_3)_2$ complex of that olefin; i.e., **20** is acrylonitrile, **20a** is $Ni(t\text{-}BuNC)(CH_2CHCN)$ and **20b** is $Ni(PPh_3)_2(CH_2CHCN)$.
(23) For an ethylene complex, the symmetry would be C_{2v} and $\nu_{NC}{}^1$ and $\nu_{NC}{}^2$ would be A_1 and B_1. Substitution reduces the symmetry to C_2 (trans disubstitution), C_s (gem or cis disubstitution), or C_1 (mono or trisubstitution).
(24) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **74**, 121 (1974).
(25) M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc. A.*, 2828 (1971).
(26) S. D. Ittel, *J. Organomet. Chem.*, in press.
(27) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).
(28) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1940.
(29) K. N. Houk and L. L. Munchausen, *J. Am. Chem. Soc.*, **98**, 938 (1976).
(30) See K. Wallenfels, K. Friedrich, J. Rieser, W. Ertel, and H. Thieme, *Angew. Chem., Int. Ed. Engl.*, **15**, 261 (1976).
(31) A. Evans, C. T. Mortimer, and R. J. Puddephatt, *J. Organomet. Chem.*, **72**, 295 (1974); **85**, 101 (1975).
(32) W. G. Kirkham, M. W. Lister, and R. B. Doyntz, *Thermochim Acta*, **11**, 89 (1975).
(33) C. T. Mortimer, M. P. Wilkinson, and P. J. Puddephatt, *J. Organomet. Chem.*, **102**, C43 (1975).

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Chemistry of Tetravalent Nickel and Related Species. 3.[1] Characterization and Cyclic Voltammetry of New NiN_6 Species Based on Tridentate Ligands

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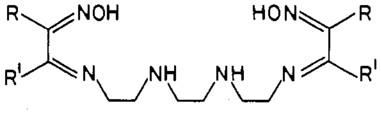
High-spin octahedral (NiN_6 core; $Dq \approx 1250$ cm^{-1}) nickel(II) complexes of type $Ni(HRR'T)_2X_2$ (where HRR′T is a tridentate ligand of class *N*-β-aminoethylisonitroso ketimine and $X = ClO_4$, NO_3) are readily oxidized by concentrated nitric acid to yield the diamagnetic nickel(IV) species $Ni(RR'T)_2X_2$. Cyclic voltammetry (CV) of $Ni(RR'T)_2(ClO_4)_2$ has been thoroughly done in well-buffered aqueous media over a wide range of pH. Below pH 6.0, CV data show a single reversible two-electron, two-proton transfer process followed by an irreversible chemical decomposition of the nickel(II) species. The rate constant for this decomposition reaction has been determined to be 0.16 s^{-1} (283 K) from CV data. In the pH range 7.0–9.0, two distinct reversible one-electron processes are observed corresponding to Ni(IV)–Ni(III) and Ni(III)–Ni(II) couples. The first of these has no proton involvement while the other involves one proton. The $E^{\circ\prime}_{298}$ values for the various couples have been accurately determined from CV data. Representative results are as follows: $Ni(Me_2T)_2{}^{2+}$–$Ni(HMe_2T)_2{}^{2+}$, 0.71 V; $Ni(Me_2T)_2{}^{2+}$–$Ni(Me_2T)_2{}^{+}$, 0.40 V; $Ni(Me_2T)_2{}^{+}$–$Ni(HMe_2T)(Me_2T)^{+}$, 0.66 V; $Ni(Me_2T)_2{}^{+}$–$Ni(Me_2T)_2$, 0.07 V (estimated). The nickel(II) species involved in each of the above couples is what is expected from acid dissociation (oxime protons) data of $Ni(HMe_2T)_2{}^{2+}$ ($pK_1 = 7.80$; $pK_2 = 10.00$).

Introduction

The highest known oxidation state of nickel is IV. Only a very limited number of nickel(IV) species have been identified to date. These include[2-7] σ complexes having NiN_6, NiO_6, NiF_6, $NiAs_4X_2$, NiP_4X_2, NiS_6, and $NiSe_6$ coordination spheres and η^5 complexes derived from cyclopentadienyl, dicarbollide, and related anions. Our present concern lies with σ-NiN_6 species.[3] The only structurally definitive works[8] done till now concern two ligand systems: tridentate 2,6-diacetylpyridine dioxime[9,10] and hexadentate[1,11-13] $H_2RR'L$, **1**. It is believed[12] that in nickel(IV) complexes of these ligands, the negative charge on the oximato oxygen plays an important role in bringing about partial neutralization of the positive charge on the metal atom through inductive transmission and σ donation. In view of the interesting chemical and electrochemical results[1,11-13] obtained with complexes of **1**, it is of interest to investigate the behavior of the closely related chelate system derived from tridentate donors of type *N*-β-aminoethylisonitroso ketimine (**2**). The major results of this investigation are presented below. In what follows, the ligand **2** will be abbreviated as HRR′T. When R = R′, the abbreviation will be HR_2T.



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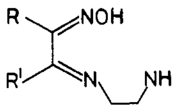

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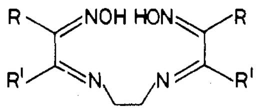

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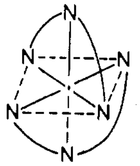

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Results and Discussion

A. Ligands and Their Nickel(II) Complexes. Three ligands of type **2**, viz., HMe_2T, HEtMeT, and HMeEtT, were obtained by condensing 1 mol of ethylenediamine with 1 mol of the appropriate isonitroso ketone. When 2 mol of isonitroso ketone is used, ligands of type **3** are obtained.[14] Ligands of type **2** are reported here for the first time. They show characteristic NH (3340–3150 cm^{-1}), OH (2650–2550 cm^{-1}), and C═N + C═C (1650–1610 cm^{-1}) stretches in the infrared spectra. The low frequency and broadness of the OH stretch suggest that the systems are strongly hydrogen bonded.

Red-brown nickel(II) species of type $Ni(HRR'T)_2{}^{2+}$ are readily obtained by reaction of nickel(II) salts with HRR′T in ethanolic solution. Nitrates and perchlorates of these cations have been isolated. These act as 1:2 electrolytes[15] in nitro-

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

Compd	Λ	μ_{eff}	ν (ϵ)
$Ni(HMe_2T)_2(ClO_4)_2$	154 (300)	3.04 (302)	12 800 (28), 19 230 (150),[b] 24 690 (850)[b]
$Ni(HMe_2T)_2(NO_3)_2 \cdot H_2O$	153 (305)	3.05 (295)	12 660 (28), 19 610 (35),[b] 24 390 (90)[b]
$Ni(HEtMeT)_2(ClO_4)_2$	136 (301)	3.16 (301)	12 660 (27), 19 610 (120),[b] 24 390 (440)[b]
$Ni(HMeEtT)_2(ClO_4)_2$	136 (300)	3.08 (301)	12 200 (16), 19 230 (24),[b] 23 810 (60)[b]
$Ni(Me_2T)_2(ClO_4)_2$	144 (305)	Diamag	20 000 (6200), 24 100 (5100), 33 900 (11 710), 41 240 (26 880)
$Ni(EtMeT)_2(ClO_4)_2$	142 (305)	Diamag	20 000 (6200), 24 100 (4980), 34 480 (11 250), 40 820 (26 500)
$Ni(MeEtT)_2(ClO_4)_2$	142 (305)	Diamag	20 000 (6750), 24 100 (5660), 34 480 (13 690), 40 000 (31 020)

[a] Temperatures (K) of measurements are shown in parentheses. [b] Shoulder.

methane solution (Table I) and are fully paramagnetic (two unpaired electrons, Table I). The two electronic bands (Table I) at 12 500 and 19 300 cm^{-1} are assigned[12] to octahedral ν_1 and ν_2 transitions. Evidently, $Ni(HRR'T)_2^{2+}$ like[12] $Ni(H_2RR'L)^{2+}$ has a pseudooctahedral NiN_6 coordination sphere (**4**). The Dq (~1250 cm^{-1}) of **4** is slightly (~50 cm^{-1}) less than that of $Ni(H_2RR'L)^{2+}$ where the ligand is hexadentate.[12] A singly hexadentate ligand appears to bind nickel(II) more compactly than two tridentate ligands. This is also manifest in the decreased acidity (dissociation of oxime protons) of $Ni(HRR'T)_2^{2+}$ compared to $Ni(H_2RR'L)^{2+}$. The dissociation constants for equilibria 1 and 2 were determined potentiometrically in aqueous solution.

$$Ni(HMe_2T)_2^{2+} \overset{K_1}{\rightleftharpoons} Ni(HMe_2T)(Me_2T)^+ + H^+ \quad (1)$$

$$Ni(HMe_2T)(Me_2T)^+ \overset{K_2}{\rightleftharpoons} Ni(Me_2T)_2 + H^+ \quad (2)$$

metrically in aqueous solution. The values (298 K) are pK_1 = 7.80 ± 0.05 and pK_2 = 10.00 ± 0.05. These may be compared with the corresponding values (5.90 and 7.80) of $Ni(H_2Me_2L)^{2+}$. In contrast to $Ni(H_2RR'L)^{2+}$ which is stable even at pH ~1.0, $Ni(HRR'T)_2^{2+}$ is unstable in acidic solution. At pH ≤5.0 the ~12 500-cm^{-1} band completely disappears showing that decomposition is complete. In pH titration with acid 4 mol of proton is consumed suggesting that the decomposition reaction may be

$$Ni(HRR'T)_2^{2+} + 4H^+ \xrightarrow{H_2O} Ni^{2+}(aq) + 2bam + 2enH_2^{2+} \quad (3)$$

where bam is biacetyl monoxime and en is ethylenediamine. The electronic spectrum of the decomposed solution shows that all nickel(II) is present in the form $Ni(H_2O)_6^{2+}$ (ν_1 band in the visible region). The kinetics of the decomposition reaction will be discussed in a later section of this paper.

B. Nickel(IV) Species. (a) Synthesis and Characterization. $Ni(HRR'T)_2(ClO_4)_2$ can be readily oxidized by concentrated HNO_3 to yield violet diamagnetic crystals of $Ni(RR'T)_2(ClO_4)_2$ which act as 1:2 electrolyte in nitromethane solution (Table I). In the electronic spectra (Table I) of $Ni(RR'T)_2(ClO_4)_2$ the ligand → metal charge-transfer transitions (Table I) are observed in the range 20 000–25 000 cm^{-1}. The major C$\overset{\dots}{=}$N + C$\overset{\dots}{=}$C stretch is at 1500 cm^{-1}. Thus the properties of $Ni(RR'T)_2^{2+}$ are very similar to those[12] of $Ni(RR'L)^{2+}$. Both contain nickel in the oxidation state IV. $Ni(RR'T)_2^{2+}$ reacts with various reducing agents. Iron(II) salts can be titrated with $Ni(RR'T)_2^{2+}$ in aqueous acidic solution to a sharp pink (color of the first excess of $Ni(RR'T)_2^{2+}$) end point. Two moles of Fe^{2+} is consumed per mole of $Ni(RR'T)_2^{2+}$ which is reduced to $Ni(HRR'T)_2^{2+}$ in this process. The latter being unstable in acid solution undergoes further decomposition.

(b) Cyclic Voltammetry of $Ni(RR'T)_2^{2+}$ in Acidic Solution. (i) General Pattern of Electrode Reaction. From a cyclic voltammetric (CV) study it has been established[1] that, for the hexadentate chelate system $Ni(RR'L)^{2+}$, the electrode reaction

$$Ni(RR'L)^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni(H_2RR'L)^{2+} \quad (4)$$

is reversible at pH <5 and $v \leq 0.14$ V s^{-1} where v is the potential scan rate. Accordingly $i_{pa}/i_{pc} = 1$ and ΔE_p = 30–40 mV. Here i_{pa} and i_{pc} are the anodic and cathodic peak currents and $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are the peak potentials.

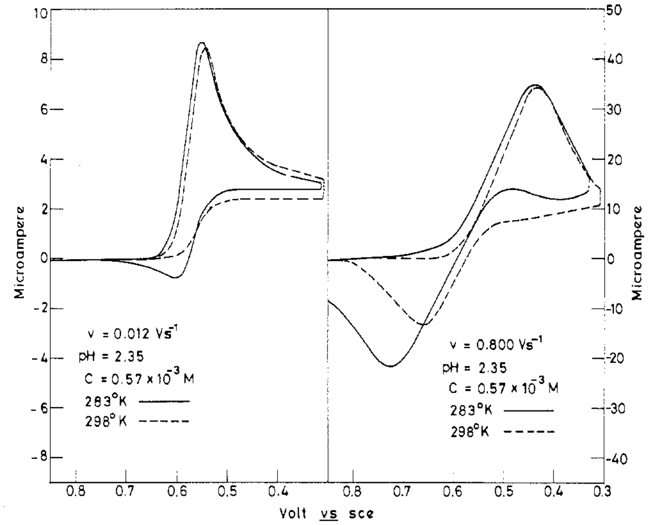


Figure 1. Cyclic voltammograms of $Ni(Me_2T)_2^{2+}$ at two different scan rates and at two different temperatures in acidic media.

The CV pattern of the tridentate system under discussion is complicated by the decomposition of the nickel(II) species in acidic media (vide supra). Cyclic voltammograms of $Ni(Me_2T)_2^{2+}$ will be discussed first. Voltammograms at pH 2.35 at two different temperatures and two different scan rates are displayed in Figure 1. *All potentials in this work are referenced to the saturated calomel electrode* (SCE). At scan rate of 0.012 V s^{-1} the anodic peak is virtually absent at 298 K but is visible at 283 K. On increasing the scan rate, the anodic peak becomes progressively larger. At 0.8 V s^{-1}, its height is very comparable to that of the cathodic peak particularly at 283 K. These results clearly suggest[16] an electrode reaction (reduction) followed by a chemical decomposition of the reduced species. As expected, the decomposition rate decreases with decreasing temperature, making the anodic peak more visible at low temperatures. At high scan rates the reduced species is oxidized before it can decompose. At 0.8 V s^{-1}, the electrode reaction is no longer reversible as judged from the high ΔE_p (~300 mV).

The couple (4) is reversible[1] in the electrochemical sense up to v = 0.14 V s^{-1}. It will be reasonable to assume that the electrode reaction involving the tridentate chelate system under consideration will also be reversible at low scan rates. This proposition is substantiated by the observation that i_{pc} of $Ni(Me_2T)_2^{2+}$ (16.5 μA) and $Ni(Me_2L)^{2+}$ (i_{pc} = 17 μA) have virtually the same value, under identical experimental conditions ($C = 1.13 \times 10^{-3}$ M, pH 3.50, T = 298 K, v = 0.011 V s^{-1}). This observation further shows that the tridentate tetravalent system $Ni(Me_2T)_2^{2+}$ also undergoes a single-step two-electron reversible electrode reaction at low scan rates. Analysis of the potentiometric titration (with alkali, vide supra)

Table II. Cyclic Voltammetric Data[a] of $Ni(RR'T)_2(ClO_4)_2$ for the Couple $Ni(RR'T)_2^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni(HRR'T)_2^{2+}$

Compd	T, K	pH	E_{pc}, V	E_{pa}, V	$(2.303 \cdot RT/F) \cdot$ pH	$E^{\circ\prime}_T$, V
R = R' = Me	298	1.70	0.585	*b*	0.10	0.70
		2.35	0.545	*b*	0.14	0.70
		3.50	0.485	*b*	0.21	0.71
		4.30	0.440	*b*	0.25	0.71
		4.85	0.400	*b*	0.29	0.71
	283	1.75	0.600	0.640	0.10	0.72
		2.35	0.550	0.600	0.13	0.71
		3.75	0.475	0.525	0.21	0.71
		4.20	0.455	0.510	0.24	0.72
		4.40	0.440	0.495	0.25	0.72
R = Et, R' = Me	298	3.50	0.465	*b*	0.21	0.69
		4.30	0.415	*b*	0.25	0.68
R = Me, R' = Et	298	3.50	0.460	*b*	0.21	0.69
		4.35	0.410	*b*	0.26	0.69

[a] Data collected at $v = 0.012$ V s^{-1} and $C \approx 1 \times 10^{-3}$ M. [b] Anodic peak is not observed and $E^{\circ\prime}_T$ is calculated using eq 8.

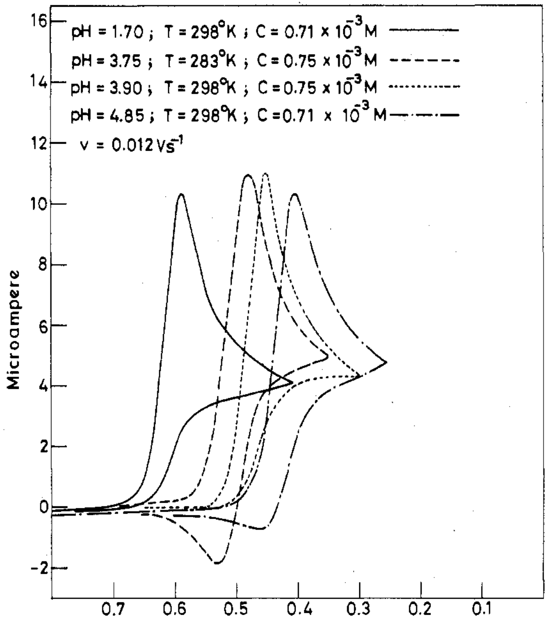


Figure 2. Effect of pH on peak position for $Ni(Me_2T)_2^{2+}$ in acidic media.

data of $Ni(HMe_2T)_2^{2+}$ in terms of the formation curves of the three species (eq 1 and 2) shows that below pH 6, only the fully protonated species $Ni(HMe_2T)_2^{2+}$ is present. In view of this it is evident that the reversible electrode reaction of $Ni(Me_2T)_2^{2+}$ corresponds to (5) in which electron transfer is

$$Ni(Me_2T)_2^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni(HMe_2T)_2^{2+} \tag{5}$$

coupled with proton transfer. This is followed by an irreversible chemical reaction in which the reduced species is decomposed (eq 3).

(ii) Formal Electrode Potentials. Since protons are involved in the electrode reaction (5), E_{pc} is expected to move to positive values with decrease in pH. That this does happen is evident from the data of Table II and Figure 2. For the general reversible electrode reaction

$$Ox + ne^- + mH^+ \rightleftharpoons H_mRed \tag{6}$$

it can be readily shown[1] that the formal electrode potential $E^{\circ\prime}_T$ is given by

$$E^{\circ\prime}_T = 0.5(E_{pc} + E_{pa}) + (2.303mRT/nF)pH \tag{7}$$

Table III. Rate of Decomposition of $Ni(HMe_2T)_2^{2+}$ Computed from CV Data of $Ni(Me_2T)_2^{2+}$ in Acidic Media (283 K)

pH	v, V s^{-1}	ΔE_p, V	$0.5(E_{pa} + E_{pc})$, V	t, s	i_{pa}/i_{pc}	k_f,[a] s^{-1}
1.75	0.010	0.040	0.620	5.70	0.536	0.15
1.75	0.021	0.040	0.615	4.00	0.573	0.18
1.75	0.021	0.040	0.615	5.50	0.521	0.16
2.35	0.012	0.055	0.578	7.20	0.492	0.14
2.35	0.022	0.055	0.573	3.81	0.582	0.18
3.75	0.066	0.065	0.503	1.50	0.802	0.15
3.75	0.066	0.065	0.503	1.50	0.802	0.15
3.75	0.066	0.065	0.503	3.22	0.679	0.14

[a] Using $k_f = 0.16$ s^{-1}, the value of k_f/a, where $a = nFv/RT$, is 0.2 at $v = 0.010$ V s^{-1}. At higher scan rates k_f/a is even smaller.

Since for the reversible two-electron reaction (5) E_{pa} is expected[16] to be 30 mV (more generally $60/n$ mV) more positive of E_{pc}, eq 7 can be recast in the form

$$E^{\circ\prime}_T = E_{pc} + 0.030/n + (2.303mRT/nF)pH \tag{8}$$

It is true[16] that when a reversible electrode reaction is followed by an irreversible chemical decomposition of reduced species, the cathodic peak potential is dependent upon the ratio k_f/a where k_f is the pseudo-first-order rate constant of the decomposition reaction and $a = nFv/RT$. However, for small values (≤ 0.5) of k_f/a the peak potential is only very slightly (<5 mV) affected.[16] In the system under consideration, we shall show in the next section (Table III), that this condition prevails even at low scan rates (~ 0.01 V s^{-1}). It is therefore justifiable to use the observed E_{pc}'s to compute $E^{\circ\prime}_T$ in terms of eq 8. Results are set out in Table II. Also included in this table are the results on $Ni(EtMeT)_2^{2+}$ and $Ni(MeEtT)_2^{2+}$. It is interesting to note that the formal potentials of the tridentate systems are virtually identical with those[1] of the corresponding hexadentate systems. From the observed invariance of $E^{\circ\prime}_T$ with temperature (Table II) it can be inferred that the nickel(IV)–nickel(II) electrode potential has approximately the same temperature coefficient as that[17] of SCE (0.67 mV/deg).

(iii) Rate of Decomposition of $Ni(HMe_2T)_2^{2+}$. Nicholson and Shain have outlined in their classic paper[16] a procedure for determination of the rate constant (k_f) for irreversible decomposition of the reduced species following a reversible charge transfer. The parameters involved in this procedure are i_{pa}/i_{pc} and $k_f t$, where t is the time in seconds from $0.5(E_{pc} + E_{pa})$ to the switching potential. The quantities i_{pa}/i_{pc} and t are computed from the experimental cyclic voltammograms.[18,19] The rate constant k_f is then obtained from a working curve.[16] Using this method the rate constant for the irreversible decomposition of $Ni(HMe_2T)_2^{2+}$ (eq 5) is readily determined. Results at several pH values are collected in Table III. The rate constant is found to be 0.16 s^{-1} (283 K).

(c) Cyclic Voltammetry in Alkaline pH. In alkaline pH two distinct couples are observed (Table IV, Figure 3) as in the case[1] of $Ni(RR'L)^{2+}$. These evidently correspond to the stepwise reactions nickel(IV)–nickel(III) and nickel(III)–nickel(II). The reason that nickel(IV)–nickel(II) reaction occurs in one step in acid pH but in two steps in alkaline pH has been delineated elsewhere.[1] The couple at higher potential is pH independent and has $\Delta E_p \approx 70$ mV. This thus corresponds to an approximately reversible one-electron electrode reaction

$$Ni(RR'T)_2^{2+} + e^- \rightleftharpoons Ni(RR'T)_2^{+} \tag{9}$$

in which protons do not participate. The species on the right-hand side of eq 9 has nickel in the formal oxidation state III. $E^{\circ\prime}_{298}$ values of this couple ($m = 0$, $n = 1$ in eq 7) are set out in Table IV. The couple at lower potential is pH

Table IV. Cyclic Voltammetric Data[a,b] of $Ni(RR'T)_2(ClO_4)_2$ in the pH Range 7.8–9.0

coupleA: $Ni(RR'T)_2^{2+}$–$Ni(RR'T)_2^{+}$
couple B: $Ni(RR'T)_2^{+}$–$Ni(HRR'T)(RR'T)^{+}$

Compd	pH	Couple	$0.5(E_{pc} + E_{pa})$, V	E_p, V	E°_{298}, V
R = R′ = Me	7.90	A	0.393	0.075	0.39
		B	0.193	0.105	0.66
	8.80	A	0.398	0.075	0.40
		B	0.145	0.130	0.66
R = Et, R′ = Me	7.90	A	0.355	0.070	0.36
		B	0.160	0.110	0.63
	8.80	A	0.368	0.075	0.37
		B	0.115	0.130	0.63
R = Me, R′ = Et	7.90	A	0.368	0.065	0.37
		B	0.158	0.095	0.62
	8.80	A	0.373	0.065	0.37
		B	0.105	0.120	0.62

[a] $v = 0.012$ V s^{-1}; $C = 1.0 \times 10^{-3}$ M. [b] $E^{\circ\prime}_{298}$ values calculated using eq 7 where $m = 0$ and $n = 1$ for couple A and $m = n = 1$ for couple B.

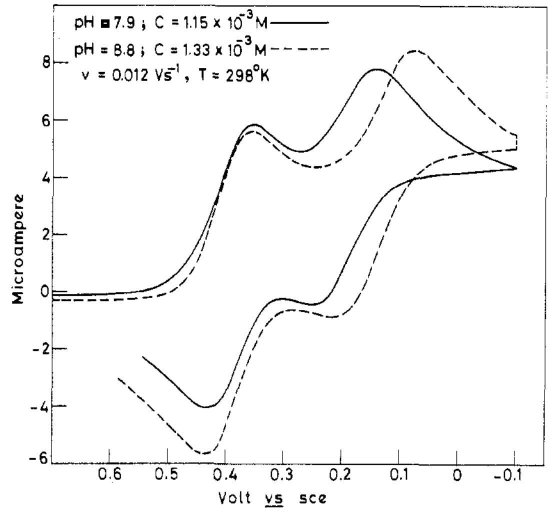


Figure 3. Cyclic voltammograms of $Ni(Me_2T)_2^{2+}$ in alkaline media.

dependent and is quasi-reversible ($\Delta E_p \approx$ 90–130 mV). Assuming that, eq 7, is still valid, consistent values of $E^{\circ\prime}_{298}$ can be obtained (Table IV) using $n = m = 1$ as required by the nickel(III)–nickel(II) couple

$$Ni(RR'T)_2^{+} + e^- + H^+ \rightleftharpoons Ni(RR'T)(HRR'T)^{+} \qquad (10)$$

Unlike the case of the hexadentate chelate system,[1] the proton-independent nickel(III)–nickel(II) couple

$$Ni(RR'T)_2^{+} + e^- \rightleftharpoons Ni(RR'T)_2 \qquad (11)$$

could not be identified in the present work. Formation curve data for the various nickel(II) species (eq 1 and 2) suggests that the deprotonated nickel(II) complex $Ni(Me_2T)_2$ becomes the major species only above pH 10.5. However, at such high pH irreversible cyclic voltammograms were obtained which could not be properly interpreted.

It is possible to estimate the $E^{\circ\prime}_{298}$ value of couple (11) in the following manner. We have shown elsewhere[20] that in couples of type (6), one can separate the observed free-energy change into electron-transfer and proton-transfer contributions. In the specific case of couple (10), these contributions correspond to the reactions (11) and (12):

$$Ni(RR'T)_2 + H^+ \rightleftharpoons Ni(RR'T)(HRR'T)^{+} \qquad (12)$$

It is then possible[20] to write

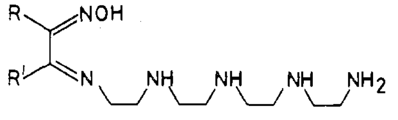
$$(E^{\circ\prime}_{298})_{10} = (E^{\circ\prime}_{298})_{11} + 0.059\mathrm{p}K_2 \qquad (13)$$

where the subscripts after parentheses refer to the equation number in the text. In the case where R = R′ = Me, $(E^{\circ\prime}_{298})_{10}$ = 0.66 V (Table II), while pK_2 = 10.00. Application of these values to eq 13 leads to $(E^{\circ\prime}_{298})_{11}$ = 0.07 V. It is possible to go one step further. It can be shown[20] that

$$(E^{\circ\prime}_{298})_5 = {}^1/_2[(E^{\circ\prime}_{298})_9 + (E^{\circ\prime}_{298})_{11} + 0.059(\mathrm{p}K_1 + \mathrm{p}K_2)] \qquad (14)$$

Using $(E^{\circ\prime}_{298})_9$ = 0.39 V (Table IV), $(E^{\circ\prime}_{298})_{11}$ = 0.07 V, and (pK_1 + pK_2) = 17.80, the value of $(E^{\circ}_{298})_5$ is computed as 0.76 V which is in good agreement with the experimental value of 0.71 V (Table II).

C. Concluding Remarks. At this stage it is appropriate to take an overview of certain features of our previous[1,11–13,20] and present works on tetravalent nickel. It has been demonstrated that with proper choice of the ligand frame, it is possible to obtain stable NiN_6 nickel(IV) species quite easily. The dual role[1,12] of the oximato group in bringing stability to nickel(IV) and in providing a pathway for facile electron transfer is reiterated. In this context it is significant that the hexadentate ligand **5** with only one oxime function readily yields[21] a 1:1 nickel(II) complex which can be oxidized chemically and electrochemically to a nickel(III) species but *not* to a nickel(IV) species. In contrast to this, the ligand **1** yields[1,12] both nickel(IV) and nickel(III) complexes. The same applies[22] to the tridentate ligands considered in this paper. It would appear that with the oxime–imine–amine ligands of types **1**, **2**, and **5** at least one oxime function is needed to stabilize each unit increase (above +2) of the oxidation number of nickel.



5

The nickel(II) complexes of **2** and **5**[21] but *not* of **1** undergo facile decomplexation in dilute acids. It would appear that in the competition between proton and the metal ion for binding the *terminal* amino function, the former wins. Once the terminal amino group is delinked from the metal ion, the next amino group will be subject to proton attack attended with delinking from the metal ion. This progressive zipper-like detachment of binding sites from the metal ion may be responsible for eventual rejection of the entire ligand.

One major feature of these works is the unequivocal characterization of coupled electron- and proton-transfer reactions. Reactions of this general class are of considerable interest to chemists and biochemists.[23] Since free-energy change of the reactions studied by us are separable (an argument[20] which has been used in the present work) into electron- and proton-transfer contributions, it is desirable to be cautious in describing such reaction as "concerted"—a term which has been loosely used in literature.[1,23] Last, we wish to note that formal potential data for couples involving various oxidation states of nickel are very few in the literature. The accurate formal potentials reported in our works are to be viewed in this perspective.

Experimental Section

A. Preparation of Compounds. (a) Ligands. ***N*-β-Aminoethylisonitrosoethyl methyl ketimine (HMe_2T)** was prepared as follows. Ethylenediamine (3 g, 0.05 mol) was added to a solution of 0.05 g of biacetyl monoxime (0.05 mol) in dry diisopropyl ether. The mixture was heated to reflux for 0.5 h and then cooled to 273 K in a stoppered flask. After 5 h yellowish white crystals were formed. These crystals were filtered off and washed with diisopropyl ether and were then dried over fused calcium chloride (yield ≥80%; mp 371 K). ***N*-β-Aminoethylisonitrosopropyl methyl ketimine (HMeEtT)** (mp 365 K) and HEtMeT (mp 371 K) were prepared in good yield by reacting ethylenediamine with isonitrosoethyl ethyl ketone and isonitrosopropyl methyl ketone in the same manner as that described for HMe_2T. These ligands are sparingly soluble in alcohol and are insoluble in ether.

(b) Nickel(II) Complexes. *Caution! Perchlorate salts of nickel complexes may explode.* $Ni(HMe_2T)_2(ClO_4)_2$ was prepared as follows. A 1.43-g sample of HMe_2T (0.01 mol) was added slowly to an ethanolic solution of 1.80 g of nickel(II) perchlorate hexahydrate (0.005 mol) which was being warmed and stirred continuously. Gradually the color of the solution changed to reddish brown. Upon concentration of this solution and scratching of the sides of the reaction vessel, reddish brown crystals deposited. The crystals were filtered off and were recrystallized from ethanol (~50% yield). These were dried over fused calcium chloride.

$\mathbf{Ni(HMe_2T)_2(NO_3)_2 \cdot H_2O}$ was prepared in an analogous manner from HMe_2T and nickel(II) nitrate hexahydrate. $\mathbf{Ni(HEtMeT)_2(ClO_4)_2}$ and $\mathbf{Ni(HMeEtT)_2(ClO_4)_2}$ were prepared in good yields by reacting nickel(II) perchlorate hexahydrate with HEtMeT and HMeEtT, respectively, in the same manner as that described for $Ni(HMe_2T)_2(ClO_4)_2$.

(c) Nickel(IV) Complexes. $\mathbf{Ni(Me_2T)_2(ClO_4)_2}$ was prepared as follows. Five to six drops of concentrated nitric acid was added to 0.5 g of $Ni(HMe_2T)_2(ClO_4)_2$. Soon brown nitrous fumes evolved and the compound changed to a deep red mass. This was cooled to 273 K and was then diluted to twice its volume with cold water. Dark violet needles deposited (yield ~50%) out of this solution, when a few milliters of saturated sodium perchlorate solution was added to it. The crystals were filtered off and were washed successively with 95% ethanol and ether. These were then dried under vacuum over fused calcium chloride.

$\mathbf{Ni(EtMeT)_2(ClO_4)_2}$ and $\mathbf{Ni(MeEtT)_2(ClO_4)_2}$ were prepared in the same manner (yield 50%) as above by treating $Ni(HEtMeT)_2(ClO_4)_2$ and $Ni(HMeEtT)_2(ClO_4)_2$, respectively, with concentrated HNO_3.

All ligands and complexes have been analyzed satisfactorily. (Analytical results are given as supplementary material.)

B. Titration of Nickel(IV) Species with $\mathbf{Fe^{2+}}$. The nickel(IV) complexes $Ni(RR'T)_2{}^{2+}$ were titrated with Fe^{2+} in the same manner[12] as done with $Ni(RR'L)^{2+}$.

C. Physical Measurements. Magnetic moments, infrared spectra, electronic spectra and electrical conductivities were studied as before.[12,24] Potentiometric titrations were done on 40 mL of 0.01 M $Ni(HMe_2T)_2(NO_3)_2 \cdot H_2O$ with carbonate-free sodium hydroxide solution (0.1 N) at 298 K. Details concerning treatment of data for obtaining K_1 and K_2 and formation curves are delineated elsewhere.[1] Cyclic voltammetry was performed in an instrument fabricated in this laboratory.[1] The i_{pa}/i_{pc} ratios were determined using procedures described in the literature.[25]

Registry No. $Ni(HMe_2T)_2(ClO_4)_2$, 63703-62-8; $Ni(HMe_2T)_2(NO_3)_2$, 63703-63-9; $Ni(HEtMeT)_2(ClO_4)_2$, 63703-65-1; $Ni(HMeEtT)_2(ClO_4)_2$, 63703-67-3; $Ni(Me_2T)_2(ClO_4)_2$, 63703-69-5; $Ni(EtMeT)_2(ClO_4)_2$, 63703-71-9; $Ni(MeEtT)_2(ClO_4)_2$, 63703-73-1; $Ni(Me_2T)_2{}^+$, 63703-74-2; $Ni(HMe_2T)(Me_2T)^+$, 63703-75-3; $Ni(EtMeT)_2{}^+$, 63703-76-4; $Ni(HEtMeT)(EtMeT)^+$, 63703-77-5; $Ni(MeEtT)_2{}^+$, 63703-78-6; $Ni(HMeEtT)(MeEtT)^+$, 63703-79-7; ethylenediamine, 107-15-3; biacetyl monoxime, 57-71-6; isonitrosoethyl ethyl ketone, 32818-79-4; isonitrosopropyl methyl ketone, 609-29-0; HMe_2T, 63702-99-8; HEtMeT, 63702-98-7; HMeEtT, 63703-00-4.

Supplementary Material Available: Table V, analytical data for ligands and complexes (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Part 2: J. G. Mohanty and A. Chakravorty, *Inorg. Chem.*, **15**, 2912 (1976).
(2) W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, **12**, 151 (1974).
(3) A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1 (1974).
(4) I. F. Warren and M. A. Bennett, *J. Am. Chem. Soc.*, **96**, 3340 (1974).
(5) D. Lachenol, *Inorg. Nucl. Chem. Lett.*, **11**, 101 (1975).
(6) R. R. Reitz, D. F. Dustin, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1580 (1974).
(7) L. O. Pont, A. R. Siedle, M. S. Lazarus, and W. L. Jolly, *Inorg. Chem.*, **13**, 483 (1974).
(8) Benzamidoxime and the trimer of formaldoxime are also believed[3] to give nickel(IV) species but little is known about their structure. Dimethylglyoxime (H_2dmg) yields[2] $Ni(dmg)_3{}^{2-}$ which probably has pseudooctahedral NiN_6 coordination.
(9) E. I. Baucom and R. S. Drago, *J. Am. Chem. Soc.*, **93**, 6469 (1971).
(10) G. Sproul and G. D. Stucky, *Inorg. Chem.*, **12**, 2898 (1973).
(11) J. G. Mohanty and A. Chakravorty, *Indian J. Chem.*, **12**, 883 (1974).
(12) J. G. Mohanty, R. P. Singh, and A. Chakravorty, *Inorg. Chem.*, **14**, 2178 (1975).
(13) J. G. Mohanty and A. Chakravorty, *Inorg. Chim. Acta*, **18**, L33 (1976).
(14) L. E. Edelman, *J. Am. Chem. Soc.*, **72**, 5765 (1950); E. Uhlig and M. Freidrich, *Z. Anorg. Allg. Chem.*, **343**, 299 (1966).
(15) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(16) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(17) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley-Interscience, New York, N.Y., 1974, p 42.
(18) J. R. Kuempel and W. B. Schaap, *Inorg. Chem.*, **7**, 2435 (1968).
(19) C. M. Elson, *Inorg. Chim. Acta*, **18**, 209 (1976).
(20) J. G. Mohanty and A. Chakravorty, *Inorg. Chem.*, **16**, 1561 (1977).
(21) J. G. Mohanty, A. N. Singh, and A. Chakravorty, unpublished results.
(22) The nickel(III) species are involved in equilibria as described in the text. An impure solid containing nickel(III) has also been obtained by procedures[1] similar to those used for the hexadentate ligand. The EPR spectrum is axial ($S = {}^1/_2$) with $g_\perp = 2.17$ and $g_\parallel = 2.05$.
(23) E. I. Steifel, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 988 (1973); G. Hamilton in "Progress in Bio-Organic Chemistry", Vol. I, Wiley-Interscience, New York, N.Y. p 83.
(24) T. S. Kannan and A. Chakravorty, *Inorg. Chem.*, **9**, 1153 (1970).
(25) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).

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Kinetic and Equilibrium Parameters for the Reaction of Neptunium(III) with Tris(ethylenediamine)ruthenium(III)

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The kinetic and equilibrium parameters for the reaction $Np^{3+} + Ru(en)_3{}^{3+} \rightleftarrows Np^{4+} + Ru(en)_3{}^{2+}$ have been determined in aqueous trifluoromethanesulfonate media. The observed forward rate constants (in $M^{-1}\ s^{-1}$, $\mu = 1.00$ M) are: 6.40 ± 0.23 (4.3 °C), 8.96 ± 0.38 (25 °C), and 9.78 ± 0.60 (40.3 °C). The enthalpy and entropy of the reaction are −12.6 ± 1.0 kcal/mol and −41.5 ± 3.3 eu, respectively. From these values, the E_f for $Ru(en)_3{}^{3+/2+}$ in 1.0 M HCF_3SO_3 at 25 °C is calculated to be 0.167 V, in close agreement with the value of 0.172 V ($\mu = 0.013$ M) previously determined electrochemically. Activation parameters and the temperature dependence of the equilibrium quotients are similar to those determined for reactions of Np^{3+} with $Ru(NH_3)_6{}^{3+}$ and $Ru(NH_3)_5H_2O^{3+}$. From the Marcus cross relation, the self-exchange rate for $Ru(en)_3{}^{2+/3+}$ is calculated to be 5 times the corresponding rate for $Ru(NH_3)_6{}^{2+/3+}$ in contrast to the value of 0.25 times this rate reported earlier. The relative exchange rate for these two species, as calculated from expected outer-sphere reorganization energy differences, is of the same order of magnitude and direction as we report.

Introduction

A previous study[1] demonstrated that the reactions of neptunium(III) with hexaammineruthenium(III) and aquopentaammineruthenium(III) in acidic aqueous media proceed to an equilibrium position that is readily measurable. We have investigated the reaction of Np(III) with tris(ethylenediamine)ruthenium(III) and the reverse reaction of Np(IV) with tris(ethylenediamine)ruthenium(II). The resulting equilibrium