4354 *Inorg. Chem.* **1991**, *30*, 4354-4360

Contribution from the Department of Inorganic Chemistry, Indian Association
for the Cultivation of Science, Calcutta 700 032, India

Sulfur-Ligated Nickel Oxidation States. Chemistry of a Family of $Ni^zS_2N_4$ ($z = +2, +3, +4$) Complexes Incorporating Hexadentate Thioether-Imine-Oxime Binding

Suranjan Bhanja Choudhury, Debashis Ray, and Animesh Chakravorty*

Received March 7, 1991

The title ligands $RC(=NOH)C(Me)=N(CH_2)_2S(CH_2)_xS(CH_2)_2N=C(Me)C(=NOH)R$ (R = Me, Ph; x = 2, 3) abbreviated as H_2RxS (**1**) afford the brown, paramagnetic ($S = 1$) complexes $Ni^{II}(H_2RxS)(ClO_4)_2{\cdot}pH_2O$ (R = Me, p = 1; R = Ph, p = 0). Structure determination of the two R = Me, p = 1 complexes has revealed hexadentate distorted octahedral NiS_2N_4 coordination: $a = 7.382$ (1) Å, $b = 17.598$ (4) Å, $c = 19.646$ (5) Å, $\beta = 93.28$ (2)°, $V = 2548.2$ (10) Å^3, $R = 0.0865$, and $R_w = 0.0790$ for $x = 2$ and $a = 7.536$ (2) Å, $b = 17.925$ (7) Å, $c = 19.579$ (7) Å, $\beta = 91.73$ (3)°, $V = 2643.5$ (15) Å^3, $R = 0.0741$, and $R_w = 0.0738$ for $x = 3$; space group $P2_1/c$ and $Z = 4$ for both complexes. Upon oxidation of the nickel(II) complexes with concentrated HNO_3 in the cold, violet diamagnetic $Ni^{IV}(RxS)^{2+}$ is formed. The salts $Ni^{IV}(MexS)(ClO_4)_2$ (x = 2, 3) decompose slowly in moist environments regenerating the nickel(II) complexes via $Ni^{III}(HMexS)^{2+}$ and/or $Ni^{III}(MexS)^+$. The EPR spectra of the latter in frozen solution (77 K) correspond to $g_\perp > g_\parallel$ ($d_{z^2}{}^1$ ground state). The following couples (illustrated with R = Me, x = 2) are observed in buffered aqueous media: couple A, $Ni^{IV}(Me2S)^{2+} + 2H^+ + 2e^- \rightleftharpoons Ni^{II}(H_2Me2S)^{2+}$, $E° = 0.82$ V; couple B, $Ni^{IV}(Me2S)^{2+} + e^- \rightleftharpoons Ni^{III}(Me2S)^+$, $E° = 0.56$ V; couple C, $Ni^{III}(Me2S)^+ + mH^+ + e^- \rightleftharpoons Ni^{II}(H_mMe2S)^{m+}$ ($m = 0$, $E° = 0.33$ V; $m = 1$, $E° = 0.79$ V; $m = 2$, $E° = 1.16$ V). Couple A operates below pH 5. At higher pH this is replaced by couples B and C. Comparison with related NiN_6 species has revealed that replacement of amine coordination by thioether coordination increases $E°$. This is attributed to the lower thermodynamic stability of the Ni-S(thioether) bond.

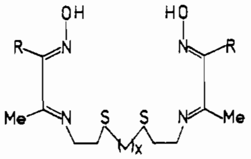
Introduction

This work forms part of our program on the chemistry of bivalent and higher valent nickel coordinated to sulfur-donor sites.[1,2] Such species are of bioinorganic interest in relation to hydrogenases containing sulfur-ligated nickel.[1-5] In recent years nickel-sulfur chemistry has progressed very well for the bivalent metal but the development of the higher valent counterpart remains plagued with an extreme paucity of tractable species.[1-3,6-11]

Herein we explore the binding of nickel oxidation states by thioether sulfur. A family of NiS_2N_4 complexes spanning the metal oxidation levels +2, +3, and +4 is described. These are derived from new hexadentate ligands bearing thioether as well as oxime and imine functions as donor sites. The bivalent and tetravalent species have been isolated in the pure state, and the X-ray structures of two bivalent compounds have authenticated NiS_2N_4 binding. The EPR-active trivalent state has been identified, but it could not be obtained pure. Variable-pH voltammetry in aqueous solution has revealed a reversible redox series interlinking the three metal oxidation states. Comparison of the NiS_2N_4 system with a related NiN_6 system reveals that thioether coordination disfavors metal oxidation in comparison to amine coordination.

Results

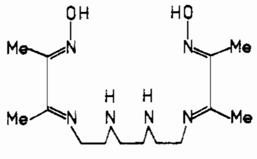
A. Synthesis and Characterization. a. Ligands. The ligands, abbreviated H_2RxS, are of type **1**, where the two oxime hydrogen atoms are dissociable. The method of synthesis is stated in Scheme I. Ligand **1** is related to the oxime-imine-amine ligand **2** (abbreviated H_2Me2N). Some years ago we used **2** and cognate species for binding oxidation states of nickel in the N_6 environment.[12-15] This fascinating system has been a subject of numerous studies by others.[16-27]



H_2RxS

R = Me, Ph ; x = 2, 3

1



H_2Me2N

2

---

(1) Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2674-2676.
(2) Bhanja Choudhury, S.; Ray, D.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 4603-4611 and references therein.
(3) Krüger, H.-J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955-2963 and references therein.
(4) Lancaster, J. R., Jr. *The Bioinorganic Chemistry of Nickel*; VCH Publishers: New York, 1988.
(5) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297-333.
(6) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87-147.
(7) Krüger, H.-J.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 3645-3647.
(8) Kumar, M.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5974-5976.
(9) (a) Fabbrizzi, L.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **1989**, 229-232. (b) Fortier, D. G.; McAuley, A. *Inorg. Chem.* **1989**, *28*, 655-662.
(10) Avdeef, A.; Fackler, J. P., Jr.; Fischer, R. G., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6972-6974.
(11) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*, 2980-2985.
(12) (a) Mohanty, J. G.; Chakravorty, A. *Ind. J. Chem.* **1974**, *12*, 883-884. (b) Mohanty, J. G.; Singh, R. P.; Chakravorty, A. *Inorg. Chem.* **1975**, *14*, 2178-2183.
(13) (a) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1976**, *15*, 2912-2916. (b) Singh, A. N.; Singh, R. P.; Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 2597-2601.
(14) (a) Singh, A. N.; Chakravorty, A. *Inorg. Chem.* **1980**, *19*, 969-971. (b) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 1561-1563. (c) Mukherjee, R. N.; Goswami, S.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 4528-4533.
(15) (a) Chakravorty, A. *Isr. J. Chem.* **1985**, *25*, 99-105. (b) Chakravorty, A. *Comments Inorg. Chem.* **1985**, *4*, 1-16.
(16) (a) Korvenranta, J.; Saarinen, H.; Näsäkkälä, M. *Inorg. Chem.* **1982**, *21*, 4296-4300. (b) Martone, D. P.; Osvath, P.; Eigenbrot, C.; Laranjeira, M. C. M.; Peacock, R. D.; Lappin, A. G. *Inorg. Chem.* **1985**, *24*, 4693-4699.
(17) McAuley, A.; Preston, K. F. *Inorg. Chem.* **1983**, *22*, 2111-2113.
(18) (a) Munn, S. F.; Lannon, A. M.; Laranjeira, M. C. M.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **1984**, 1371-1375. (b) Macartney, D. H.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1984**, 103-107. (c) Lappin, A. G.; Laranjeira, M. C. M.; Owei, L. Y. *J. Chem. Soc., Dalton Trans.* **1981**, 721-725.
(19) (a) Macartney, D. H.; McAuley, A. *Can. J. Chem.* **1982**, *60*, 2625-2628. (b) Macartney, D. H.; McAuley, A. *Can. J. Chem.* **1983**, *61*, 103-108.
(20) Lappin, A. G.; Osvath, P.; Baral, S. *Inorg. Chem.* **1987**, *26*, 3089-3094.
(21) (a) Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1983**, *22*, 2062-2066. (b) Allan, A. E.; Lappin, A. G.; Laranjeira, M. C. M. *Inorg. Chem.* **1984**, *23*, 477-482.
(22) (a) Lappin, A. G.; Laranjeira, M. C. M.; *J. Chem. Soc., Dalton Trans.* **1982**, 1861-1865. (b) Lappin, A. G.; Martone, D. P.; Osvath, P.; Marusak, R. A. *Inorg. Chem.* **1988**, *27*, 1863-1868.
(23) (a) Lappin, A. G.; Laranjeira, M. C. M.; Peacock, R. D. *Inorg. Chem.* **1983**, *22*, 786-791. (b) Martone, D. P.; Osvath, P.; Lappin, A. G. *Inorg. Chem.* **1987**, *26*, 3094-3100.
(24) Heaney, P. J.; Lappin, A. G.; Peacock, R. D.; Stewart, B. *J. Chem. Soc., Chem. Commun.* **1980**, 769-770.

Scheme I[a]

A. Ligands

$$HSCH_2CH_2NH_2\cdot HCl \xrightarrow{i,\,ii} H_2NCH_2CH_2S(CH_2)_xSCH_2CH_2NH_2 \xrightarrow{iii} H_2RxS$$

B. Complexes

$$H_2RxS \xrightarrow{iv} Ni(H_2RxS)(ClO_4)_2\cdot nH_2O\ (n = 0, 1) \xrightarrow{v,\,vi} Ni(RxS)(ClO_4)_2$$

[a] Conditions: (i) NaOEt in EtOH at 15 °C; (ii) $Cl(CH_2)_xCl$ (x = 2, 3) in EtOH at 40 °C; (iii) RC(:NOH)C(:O)Me (R = Me, Ph) in Et_2O (R = Me) or hexane (R = Ph), reflux; (iv) $Ni(H_2O)_6(ClO_4)_2$ in aqueous ethanol at 25 °C; (v) concentrated HNO_3 at 0 °C; (vi) saturated aqueous aqueous $NaClO_4$, triturate.

Table I. Characterization Data for Nickel(II) and Nickel(IV) Complexes

		electronic spectral data[b]	
compd	μ_{eff},[a,b] μ_B	medium	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$Ni(H_2Me2S)(ClO_4)_2\cdot H_2O$	3.14	MeCN	965[c] (20), 780 (52), 530[c] (181)
$Ni(H_2Me3S)(ClO_4)_2\cdot H_2O$	3.12	MeCN	965[c] (24), 800 (62), 525[c] (59)
$Ni(H_2Ph2S)(ClO_4)_2$	3.15	MeCN	930[c] (31), 780 (57), 400[c] (873)
$Ni(H_2Ph3S)(ClO_4)_2$	3.14	MeCN	970[c] (32), 780 (64), 395[c] (694)
$Ni(Me2S)(ClO_4)_2$	diamagnetic	H_2O[d]	506 (8310), 470 (8470)
$Ni(Me3S)(ClO_4)_2$	diamagnetic	H_2O[d]	514 (10 700)

[a] Measured in the solid state. [b] Temperature of measurement is 298 K. [c] Shoulder. [d] 1 M H_2SO_4 at 277 K. The species $Ni(Ph2S)^{2+}$ and $Ni(Ph3S)^{2+}$ were obtained only as solutions, and their spectra in 1 M H_2SO_4 at 277 K have the bands 520 (10 560) and 480 (10 800) for $Ni(Ph2S)^{2+}$ and 525 (10 500) and 480 (10 850) for $Ni(Ph3S)^{2+}$.

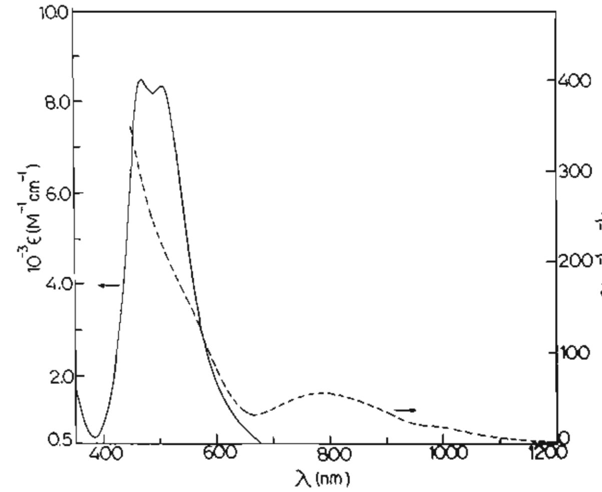


Figure 1. Electronic spectra of $Ni(H_2Me2S)(ClO_4)_2\cdot H_2O$ in acetonitrile at 298 K (- - -) and $Ni(Me2S)(ClO_4)_2$ in 1 M H_2SO_4 at 298 K (—).

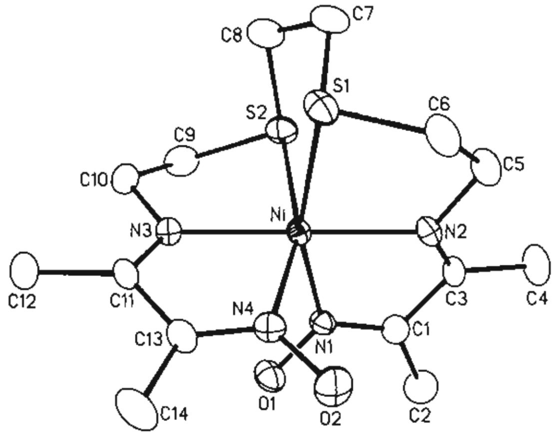


Figure 2. ORTEP plot of the cation of $Ni(H_2Me2S)(ClO_4)_2\cdot H_2O$, showing 50% thermal probability ellipsoids.

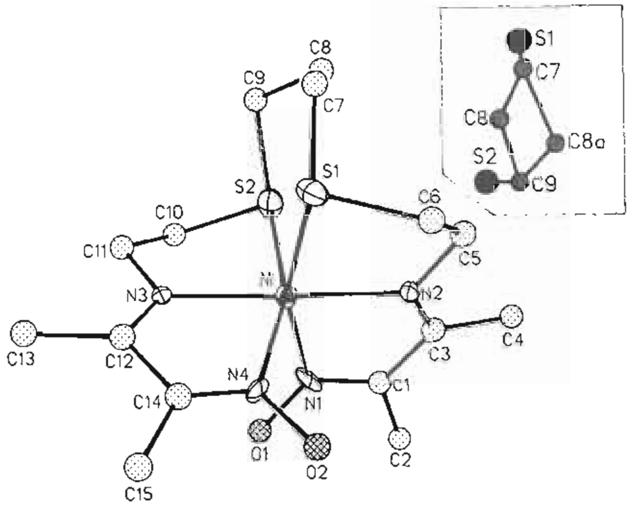


Figure 3. Perspective plot of the cation of $Ni(H_2Me3S)(ClO_4)_2\cdot H_2O$, showing 50% thermal probability ellipsoids for the atoms within the coordination sphere (inset shows the disorder of the trimethylene bridge).

Table II. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Ni(H_2Me2S)(ClO_4)_2\cdot H_2O$

	Distances		
Ni–S(1)	2.408 (2)	N(1)–C(1)	1.279 (10)
Ni–S(2)	2.418 (2)	N(2)–C(3)	1.265 (10)
Ni–N(1)	2.069 (6)	N(2)–C(5)	1.471 (10)
Ni–N(2)	2.031 (6)	N(3)–C(10)	1.453 (11)
Ni–N(3)	2.017 (6)	N(3)–C(11)	1.267 (10)
Ni–N(4)	2.077 (6)	N(4)–O(2)	1.385 (9)
N(1)–O(1)	1.387 (8)	N(4)–C(13)	1.295 (10)
	Angles		
S(1)–Ni–S(2)	87.5 (1)	S(2)–Ni–N(4)	161.4 (2)
S(1)–Ni–N(1)	161.5 (2)	N(1)–Ni–N(2)	76.9 (2)
S(1)–Ni–N(2)	84.6 (2)	N(1)–Ni–N(3)	101.6 (2)
S(1)–Ni–N(3)	96.8 (2)	N(1)–Ni–N(4)	92.6 (2)
S(1)–Ni–N(4)	93.1 (2)	N(2)–Ni–N(3)	177.2 (2)
S(2)–Ni–N(1)	92.7 (2)	N(2)–Ni–N(4)	105.0 (2)
S(2)–Ni–N(2)	93.6 (2)	N(3)–Ni–N(4)	77.3 (2)
S(2)–Ni–N(3)	84.1 (2)		

b. Complexes. The complexes were prepared according to Scheme I. The brown nickel(II) chelates contain the intact neutral ligands, while in the violet nickel(IV) species formed via nitric acid oxidation of nickel(II) congeners the ligands are deprotonated. Both types of complexes are thus dicationic, and these were generally isolated as perchlorates. In the case of nickel(IV), isolation was limited to the two R = Me complexes; the R = Ph complexes could be prepared in solution by the procedure of Scheme I, but these could not be crystallized as salts. Upon storage in a moist environment the nickel(IV) complexes decompose affording the nickel(II) complexes. Nickel(III) species are formed as intermediates; vide infra. Only freshly prepared nickel(IV) complexes were utilized in all studies.

Selected characterization data for the complexes are listed in Table I. The nickel(II) complexes are paramagnetic (S = 1) and

---

(25) (a) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530–3534. (b) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883–892.

(26) (a) Lappin, A. G.; Martone, D. P.; Osvath, P. *Inorg. Chem.* **1985**, *24*, 4187–4191. (b) Marusak, R. A.; Sharp, C.; Lappin, A. G. *Inorg. Chem.* **1990**, *29*, 4453–4456. (c) Osvath, P.; Lappin, A. G. *Inorg. Chem.* **1987**, *26*, 195–202.

(27) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988**, *32*, 241–295.

Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Ni(H_2Me3S)(ClO_4)_2{\cdot}H_2O$

	Distances		
Ni-S(1)	2.419 (7)	N(1)-C(1)	2.310 (26)
Ni-S(2)	2.410 (7)	N(2)-C(3)	1.287 (24)
Ni-N(1)	2.062 (16)	N(2)-C(5)	1.436 (26)
Ni-N(2)	2.015 (14)	N(3)-C(11)	1.432 (26)
Ni-N(3)	2.033 (13)	N(3)-C(12)	1.304 (23)
Ni-N(4)	2.089 (17)	N(4)-O(2)	1.371 (22)
N(1)-O(1)	1.353 (22)	N(4)-C(14)	1.241 (24)
	Angles		
S(1)-Ni-S(2)	98.0 (2)	S(2)-Ni-N(4)	160.2 (5)
S(1)-Ni-N(1)	160.1 (5)	N(1)-Ni-N(2)	77.4 (6)
S(1)-Ni-N(2)	83.8 (5)	N(1)-Ni-N(3)	101.2 (6)
S(1)-Ni-N(3)	98.0 (4)	N(1)-Ni-N(4)	94.5 (6)
S(1)-Ni-N(4)	88.0 (5)	N(2)-Ni-N(3)	176.1 (6)
S(2)-Ni-N(1)	89.1 (5)	N(2)-Ni-N(4)	107.5 (6)
S(2)-Ni-N(2)	91.9 (5)	N(3)-Ni-N(4)	76.1 (6)
S(2)-Ni-N(3)	84.4 (4)		

display a ligand-field feature (split octahedral ν_1) consisting of a band at ~800 nm and a shoulder near 960 nm. The nickel(IV) complexes are diamagnetic (spin-paired d^6). One or two intense LMCT band(s) occur near 500 nm (Table I, Figure 1). In acidic aqueous solution the complexes act as two-electron oxidants as in eq 1.

$$Ni(RxS)^{2+} + 2H^+ + 2Fe^{2+} \rightarrow Ni(H_2RxS)^{2+} + 2Fe^{3+} \quad (1)$$

B. Structures of $Ni(H_2MexS)(ClO_4)_2{\cdot}H_2O$ (x = 2, 3). In both complexes the ligands bind the metal in hexadentate N_4S_2 fashion. Views of the cations are shown in Figures 2 and 3, and selected bond parameters are listed in Tables II and III.

Both coordination spheres are severely distorted from idealized octahedral geometry, as can be seen from the angles subtended by the donor atoms at the metal centers. The bite angle of the chelate ring incorporating the two sulfur atoms shows a large increase with expansion of the ring size from five membered to six membered: 87.5 (7)° in $Ni(H_2Me2S)^{2+}$ and 98.0 (9)° in $Ni(H_2Me3S)^{2+}$.

The ligands coordinate in two meridional segments of type N_2S. Each NiN_2S fragment is a good plane (mean deviation, 0.01–0.05 Å). The dihedral angle between the two NiN_2S plane is 91.8 (2)° in $Ni(H_2Me2S)^{2+}$ and 86.7 (7)° in $Ni(H_2Me3S)^{2+}$. The five-membered oxime–imine chelate rings along with oxime oxygen and methyl carbons form satisfactory planes (mean deviation, 0.04–0.08 Å). All the dimethylene bridges in the complexes are gauche in configuration. The central carbon atom of the trimethylene bridge in $Ni(H_2Me3S)^{2+}$ is disordered between two conformations (inset in Figure 3).

The bond distances in the two complexes are similar and follow the same trends. We therefore scrutinize only one case viz. $Ni(H_2Me2S)^{2+}$. Here the average Ni–S distance is 2.413 (2) Å. The sum of ionic radii is 2.44 Å.[28] In structurally characterized pseudooctahedral complexes, the Ni(II)–S(thioether) distance is known to span the range 2.39–2.44 Å.[29] The average Ni–N(oxime) distance, 2.073 (6) Å, is longer than the average Ni–N(imine) distance, 2.024 (6) Å. The structure of $Ni(H_2Me2S)(ClO_4)_2{\cdot}H_2O$ can be compared with that[16] of $Ni(H_2Me2N)(ClO_4)_2$. Here the average Ni–N(oxime) and Ni–N(imine) distances are 2.119 (5) and 2.005 (3) Å, respectively.

One perchlorate ion, the water molecule, and their symmetry-related congeners form a centrosymmetric eight-membered cyclic hydrogen-bonding network, which bridges two symmetry-related cations via oximato oxygen atoms (Figure 4). The hydrogen bonds are weaker in $Ni(H_2Me3S)(ClO_4)_2{\cdot}H_2O$. The nonbonded intramolecular O···O distances in the two complexes are similar: $Ni(H_2Me2S)^{2+}$, 4.245 (6) Å, and $Ni(H_2Me3S)^{2+}$, 4.156 (8) Å.

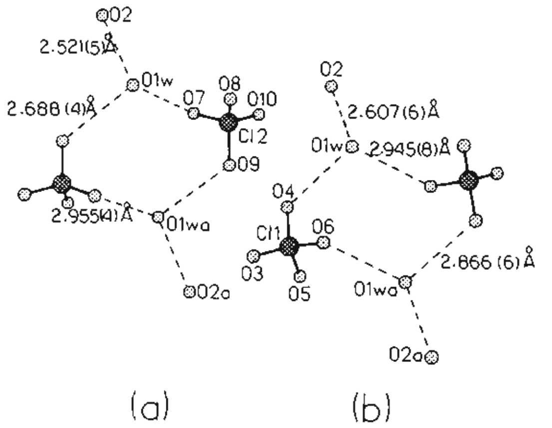


Figure 4. Hydrogen-bonding networks of (a) $Ni(H_2Me2S)(ClO_4)_2{\cdot}H_2O$ and (b) $Ni(H_2Me3S)(ClO_4)_2{\cdot}H_2O$.

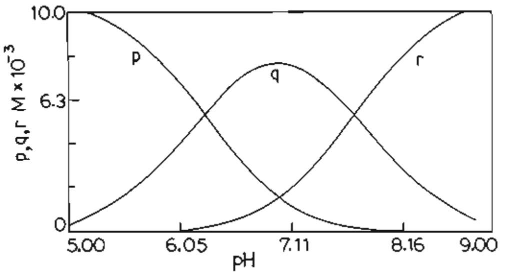


Figure 5. Equilibrium distribution of $Ni(H_mMe2S)^{m+}$ as a function of pH at 298 K. p, q, and r represent the concentrations of the species with m = 2, 1, and 0, respectively.

C. Solution Equilibria. a. Protic Dissociation of $Ni(H_2MexS)(ClO_4)_2{\cdot}H_2O$. The nickel(II) complexes act as dibasic acids in aqueous solution (eqs 2 and 3). The values of pK_1 (±0.05)

$$Ni(H_2MexS)^{2+} \overset{K_1}{\rightleftharpoons} Ni(HMexS)^+ + H^+ \quad (2)$$

$$Ni(HMexS)^+ \overset{K_2}{\rightleftharpoons} Ni(MexS) + H^+ \quad (3)$$

and pK_2 (±0.05) are as follows: $Ni(H_2Me2S)^{2+}$, 6.28 and 7.69, and $Ni(H_2Me3S)^{2+}$, 6.22 and 7.75, respectively. The pK values of the two complexes are expectedly equal within experimental error. The pH dependence of the equilibrium distribution shows that the predominant species contributing to solution composition are $Ni(H_2MexS)^{2+}$ at pH <5, $Ni(HMexS)^+$ near pH 7, and $Ni(MexS)$ at pH ≥8.5 (Figure 5).

b. Electroprotic Equilibria. In buffered aqueous solution the complexes display electroprotic equilibria,[15b] which have been studied electrochemically at platinum working electrodes. Reduction potential data are summarized in Table IV; Table V containing coulometric data is deposited as supplementary material. Representative voltammograms are shown in Figure 6. All potentials were measured at 298 K and are referred to the saturated calomel electrode (SCE). The following discussion relates specifically to the complexes of H_2Me2S. The other complexes behave similarly.

Below pH 5 a single cyclic response characterized by a peak-to-peak separation (ΔE_p) of 40–50 mV is observed. The peak potentials (average = $\bar{E}_p$) are pH-dependent, the slope, $\Delta\bar{E}_p/\Delta pH$, being 60 mV. Exhaustive constant-potential electrolysis at 100 mV past the anodic peak potential affords a coulomb count corresponding to the transfer of two electrons. After electrolysis the solution contains only $Ni(Me2S)^{2+}$. Thus, the cyclic response at pH <5 corresponds to the couple A given by eq 4. The formal

$$\text{Couple A:} \quad Ni^{IV}(Me2S)^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni^{II}(H_2Me2S)^{2+} \quad (4)$$

potential of the couple will be designated $E°(A)$, and its value is 0.82 V, as calculated from eq 5, where m and n are respectively

---

(28) Murrey, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365–414.

(29) Cooper, S. R.; Rawle, S. C.; Hartman, J. A. R.; Hintsa, E. J.; Admans, G. A. *Inorg. Chem.* **1988**, *27*, 1209–1214.

Table IV. Electrochemical Data[a,b] for Nickel(II) Complexes at 298 K in Buffered[c] Aqueous Media

compd	pH	couple(s)	E_p,[d] V (ΔE_p,[d] mV)	$E°_{298}$, V
$Ni(H_2Me2S)(ClO_4)_2·H_2O$	3.05	A	0.64 (40)	0.82
	3.55	A	0.61 (40)	0.82
	4.06	A	0.58 (40)	0.82
	7.10	C2, B	0.37 (50), 0.56 (60)	0.79, 0.56
	8.60	C3, B	0.33 (50), 0.56 (60)	0.33, 0.56
	9.00	C3, B	0.33 (60), 0.56 (60)	0.33, 0.56
$Ni(H_2Me3S)(ClO_4)_2·H_2O$	3.05	A	0.68 (40)	0.86
	3.55	A	0.65 (40)	0.86
	4.06	A	0.62 (40)	0.86
	7.10	C2, B	0.39 (50), 0.60 (60)	0.81, 0.60
	8.50	C3, B	0.37 (50), 0.60 (60)	0.37, 0.60
	9.00	C3, B	0.37 (60), 0.60 (60)	0.37, 0.60
$Ni(H_2Ph2S)(ClO_4)_2$	2.58	A	0.65 (40)	0.80
$Ni(H_2Ph3S)(ClO_4)_2$	2.70	A	0.64 (40)	0.80

[a] The meanings of the symbols used are the same as in the text. [b] The working electrode is platinum, the reference electrode is the SCE, the solute concentration is 10^{-3} M, and the scan rate is 50 mV s^{-1}. [c] The following buffers, all 0.1 M in KCl, were used: acetate buffer for pH 2.5–4.25; phosphate buffer for pH 4.50–7.75; borate buffer for pH 8.00–9.50. [d] $\bar{E}_p$ is the average of anodic and cathodic peak potentials, and ΔE_p is the difference of anodic and cathodic peak potentials.

the number of protons and electrons transferred ($m = n = 2$ in eq 5).

$$E° = \bar{E}_p + 0.059(m/n)(pH) \qquad (5)$$

Above pH 5, the voltammograms begin to broaden, and above pH 6, two distinct couples become observable. Current height data demonstrate that the electron stoichiometries for the two couples are equal. Near pH 7 $\bar{E}_p$ of the couple at lower potential (couple C2, eq 7) has $\Delta\bar{E}_p/\Delta pH$ ~60 mV, while that at higher potential (couple B, eq 6) is pH-independent. Consequently, the separation between the couples increases with increasing pH. Constant-potential coulometry performed at 100 mV beyond the anodic peak potential of couple C2 is consistent with one-electron stoichiometry. The formal potentials $E°(B)$ and $E°(C2)$ are 0.56 and 0.79 V, respectively.

$$\text{Couple B:} \quad Ni^{IV}(Me2S)^{2+} + e^- \rightleftharpoons Ni^{III}(Me2S)^+ \qquad (6)$$

$$\text{Couple C2:} \quad Ni^{III}(Me2S)^+ + e^- + H^+ \rightleftharpoons Ni^{II}(HMe2S)^+ \qquad (7)$$

At pH ≥8.5 two pH-independent one-electron couples are observed: B and C3 (eq 8). The formal potential $E°(C3)$ is 0.33 V.

$$\text{Couple C3:} \quad Ni^{III}(Me2S)^+ + e^- \rightleftharpoons Ni^{II}(Me2S) \qquad (8)$$

For later discussion we also need the formal potential of couple C1 (eq 9), which cannot be separately observed due to species overlap in the relevant pH range (Figure 5). The required potential can however be calculated by adding $0.059(pK_1)$ to $E°(C2)$ or $0.059(pK_1 + pK_2)$ to $E°(C3)$. The two values agree to within 10 mV, and we set $E°(C1) = 1.16$ V.

$$\text{Couple C1:} \quad Ni^{III}(Me2S)^+ + e^- + 2H^+ \rightleftharpoons Ni^{II}(H_2Me2S)^{2+} \qquad (9)$$

D. Nickel(III) Species. Apart from the electrochemical results a strong second line of evidence exists for the occurrence of the trivalent state. Freshly prepared pure samples of $Ni^{IV}(MexS)(ClO_4)_2$ are EPR-silent as expected. Upon storage of the solid in a moist environment, an EPR signal developes within 40 h. On prolonged keeping of the solid (4 days), the signal disappears. At this stage the metal oxidation state has become entirely bivalent.

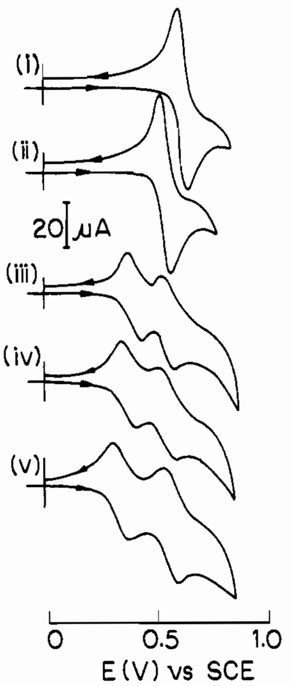


Figure 6. Cyclic voltammograms (scan rate 50 mV s^{-1}) of 10^{-3} M solutions of $Ni(H_2Me2S)(ClO_4)_2·H_2O$ in buffered aqueous media (0.1 M KCl) at 298 K at a platinum electrode at pH (i) 3.05, (ii) 4.40, (iii) 6.45, (iv) 7.10, and (v) 9.00.

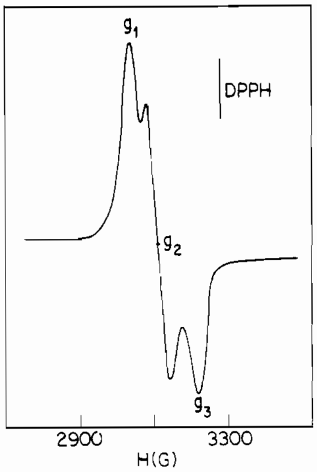
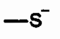


Figure 7. X-Band (9.105 GHz) 77 K EPR spectrum in 1:1 acetonitrile–toluene of the nickel(III) species formed from $Ni(Me3S)(ClO_4)$.

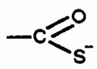
The spectrum of the EPR-active stage is consistent with the presence of nickel(III) (low-spin d^7). The solid itself gives a broad signal near $g = 2.1$. In frozen 1:1 MeCN/toluene glass (77 K) anisotropic features are observed (Figure 7) . The spectrum of the complex with R = Me, $x = 3$ is rhombic, $g_1 = 2.168$, $g_2 = 2.112$, and $g_3 = 2.039$, and that of the R = Me, $x = 2$ complex, axial, $g_\perp = 2.112$ and $g_\parallel = 2.046$.

Discussion

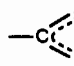
A. Thioether Binding of Oxidation States. Among sulfur-donor groups employed so far for binding higher oxidation states of nickel, the more important ones are[1-3,6-10] thiolates (3), thiocarboxylates (4), dithioates (5), and thioethers (6). The only pure species isolated so far are nickel(III) bonded by 4 (at S only)[3] and nickel(IV) by 5 (S,S-chelated).[10] The present work has augmented this meager list by adding pure nickel(IV) species involving coordination by 6.



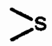
3



4



5



6

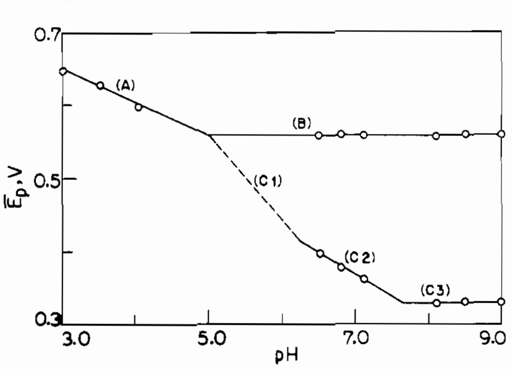


Figure 8. Plot of $\bar{E}_p$ vs pH for the couples A, B, C1, C2, and C3 at 298 K for H_mMe2S complexes. The C1 values are calculated (see text).

The severe stability limitation of the sulfur-ligated higher oxidation states is often due to internal redox leading to metal reduction and formation of disulfide species (eq 10). The

$$2Ni^{III}S- \rightarrow 2Ni^{II} + -S-S- \qquad (10)$$

thermodynamic factors controlling this process have been analyzed.[2] The process can be blocked by lowering the metal reduction potential via coligand or other controls. In nickel hydrogenases the nickel(III)-nickel(II) potential is <-0.4 V and here the Ni^{III}-S- moiety is well sustained.[2-5]

In the present work we have employed the thioether function in order to circumvent facile disulfide formation. But thioethers are poor coordinating agents[28] except under the compulsion of other factors such as macrocyclic ligation.[29,30] To strengthen thioether coordination we have employed multiple chelation implicit in hexadentate binding. We have simultaneously employed binding by the oxime-imine function, which is well tested for stabilizing higher oxidation states of nickel.[12-15,31] The NiS_2N_4 binding mode has been authenticated for the nickel(II) complexes. Lack of X-ray-quality single crystals has vitiated complete structural characterization of the nickel(IV) species. Gross $Ni^{IV}S_2N_4$ coordination is however not in any doubt. The excellent reversibility of voltammetric interconversions of oxidation states is a very strong indication that the nature and geometry of the coordination sphere is conserved in the entire redox series. We also note that, in the case of ligand **2**, the structures of both $Ni(H_2Me2N)^{2+}$ and $Ni(Me2N)^{2+}$ are known and these have similar NiN_6 spheres.[16]

The EPR spectra ($g_\perp > g_\parallel$) of the nickel(III) species imply effective axial elongation ($d_{z^2}{}^1$ ground state), which is normal for octahedral nickel(III) complexes. The *g* values of the H_2Me3S complex (2.168, 2.112, 2.039) can be compared with those of tris(methylxanthate) (2.141, 2.123, 2.033),[2] bis(pyridine-2,6-bis(monothiocarboxylate)) (2.137, 2.137, 2.033),[3] and the Ni-C form of the *Desulfovibrio gigas* hydrogenase (2.19, 2.16, 2.02).[32] In aqueous solution the nickel(III) complex exists in the deprotonated form $Ni(RxS)^+$ at pH > 5. A monoprotonated state $Ni(HRxS)^{2+}$ similar to $Ni(HMe2N)^{2+}$ (pK = 4.05)[15a] may exist at a lower pH. The nickel(III) complexes formed during solid-state decomposition of the nickel(IV) species could therefore be one or both of the above types.

B. Redox Behavior. a. Two-Electron and One-Electron Couples. The origin of the pH evolution of two one-electron couples (nickel(IV)-nickel(III), nickel(III)-nickel(II)) from one two-electron couple (nickel(IV)-nickel(II)) (Figure 6) is revealed by Figure 8, where the $\bar{E}_p$ values of redox couples are plotted against pH.

As the pH is progressively decreased from the high side, Ni^{II}(Me2S) gets protonated first to $Ni^{II}(HMe2S)^+$ and then to $Ni^{II}(H_2Me2S)^{2+}$. On the other hand $Ni^{IV}(Me2S)^{2+}$ does not protonate at all over the pH range examined and $Ni^{III}(Me2S)^+$ also does not protonate above pH 5. Consequently $\bar{E}_p$ of the nickel(III)-nickel(II) couple (C3, C2, C1) progressively increases as pH is lowered (eq 5) till it becomes equipotential with $\bar{E}_p$ of couple B. After that, only couple A involving direct two-electron oxidation of nickel(II) to nickel(IV) remains. At this stage $Ni^{III}(Me2S)^+$ would spontaneously disproportionate (eq 11). The values of log K_d (eq 12) are calculated to be 6.2 and 4.2 at pH 2 and 3, respectively.

$$2Ni^{III}(Me2S)^+ + 2H^+ \overset{K_d}{\rightleftharpoons} Ni^{IV}(Me2S)^{2+} + Ni^{II}(H_2Me2S)^{2+} \qquad (11)$$

$$\log K_d = [(E°(C1) - E°(B))/0.059] - 2pH \qquad (12)$$

The equipotential transfer of two electrons is unusual for a mononuclear complex. Under ideal reversibility ΔE_p of couple A should be 30 mV. In the present system the observed value is 40-50 mV.

b. Reduction Potentials: Thioether versus Amine Coordination. The redox behavior of the present NiS_2N_4 complexes is qualitatively similar to that[13,15] of the NiN_6 complexes afforded by ligand **2**. The NiN_6 formal potentials are however systematically lower: 0.71, 0.42, 1.00, 0.64, and 0.15 V for couples corresponding to A, B, C1, C2, and C3, respectively. The potentials are linearly related to the NiS_2N_4 $E°$ values (Table IV). The intercept on the NiS_2N_4 axis is 170 mV. Thus, thioether coordination makes the nickel oxidation levels more oxidizing than amine coordination. We attribute this to the inherent thermodynamic weakness of the metal-thioether bond compared to the metal-amine bond in a primarily σ-bonded situation. The inferior σ-donor strength of thioethers as compared to amines is reflected in the pK values:[33] Me_2SH^+, -5.2, and $Me_2NH_2^+$, ~10.0.[33] When comparisons are limited to similarly constituted molecules, $E°$ of a couple can be expressed[34] as $E° = -\Delta H_f°/F + k$. Here F is a faraday, k is a constant, and $\Delta H_f°$ is the difference between the enthalpies of formation of the reduced and the oxidized complexes *taken in that order*. Taking couple C3 as an example, these complexes are of $Ni^{II}L$ and $Ni^{III}L^+$, respectively (L = $Me2S^{2-}$, $Me2N^{2-}$). Generally $\Delta H_f°$ will be positive (endothermic)—more so when bonds are stronger. Hence, NiS_2N_4 has a smaller $\Delta H_f°$ than NiN_6 and $E°$ is correspondingly larger.

The thioether function has limited efficacy in depressing nickel reduction potentials. The anionic sulfur donor centers **3**-**5** are more potent in this regard.[2,3,10] Among these only **3** is directly relevent to the actual state of metal binding in nickel hydrogenases. All others including **6** are models useful for assessment of the effects of sulfur binding on nickel oxidation states. The bioinorganic significance of the present work rests at this level.

C. Concluding Remarks. The main features of this work will now be summarized. A family of hexadentate ligands, H_2RxS (**1**), has been designed and successfully employed for thioether binding of bi-, tri-, and tetravalent nickel in the NiS_2N_4 mode both in the solid state and in aqueous solution. Two of the nickel(II) complexes, $Ni(H_2MexS)(ClO_4)_2$ (x = 2, 3), have been structurally characterized as monohydrates. The corresponding nickel(IV) complexes, $Ni^{IV}(MexS)(ClO_4)_2$, are the first examples of pure compounds having a thioether-coordinated higher (>2) oxidation state of nickel. The nickel(III) complexes could not be isolated in the pure form. These are however observable both in solution and in the solid state. Their EPR spectra ($g_\perp > g_\parallel$) have certain similarities to the Ni-C spectrum of the *D. gigas* hydrogenase.

The aqueous solution voltammetry of the complexes reveals synchronous transfer of electron(s) and proton(s) at metal and oxime sites, respectively. At pH values <5 a single-step $2e^-$-$2H^+$ transfer connects $Ni^{II}(H_2RxS)^{2+}$ and $Ni^{IV}(RxS)^{2+}$ directly. At

---

(30) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1-80.

(31) (a) Boucom, E. I.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6469-6475. (b) Sproul, G.; Stucky, G. D. *Inorg. Chem.* **1973**, *12*, 2898-2902.

(32) Teixeira, M.; Moura, I.; Xavier, A. V.; Huynh, B. H.; Dervartanian, D. V.; Peck, H. D., Jr.; LeGall, J.; Moura, J. J. G. *J. Biol. Chem.* **1985**, *260*, 8942-8950.

(33) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S.; *Organic Chemistry*, 3rd ed.; McGraw-Hill Book Co.: Tokyo, 1970.

(34) Mukherjee, R. N.; Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 785-790.

Table VI. Crystallographic Data for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$

	$Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$	$Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$
chem formula	$C_{14}H_{28}N_4O_{11}S_2Cl_2Ni$	$C_{15}H_{30}N_4O_{11}S_2Cl_2Ni$
fw	622.19	636.22
space group	$P2_1/c$	$P2_1/c$
a, Å	7.382 (1)	7.536 (2)
b, Å	17.598 (4)	17.925 (7)
c, Å	19.646 (5)	19.579 (7)
β, deg	93.28 (2)	91.73 (3)
V, Å^3	2548.2 (10)	2643.5 (15)
Z	4	4
T, °C	23 ± 1	23 ± 1
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.622	1.598
μ, cm^{-1}	11.89	11.48
transm coeff	0.6210–0.8713	0.4960–0.7485
R^a	0.0865	0.0741
$R_w{}^b$	0.0790	0.0738

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2|F_o| + g|F_o|^2$; $g = 0.0005$ for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and 0.00 for $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$.

Table VII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O^a$

atom	x	y	z	U(eq)	sof^b
atom	−2337 (1)	−3341 (1)	2422 (1)	38 (1)	1.00
Cl(1)	−1179 (3)	−5913 (1)	978 (1)	60 (1)	1.00
Cl(2)	4335 (4)	8434 (2)	441 (1)	77 (1)	1.00
S(1)	−4172 (3)	−2216 (1)	2275 (1)	61 (1)	1.00
S(2)	284 (3)	−2540 (1)	2297 (1)	57 (1)	1.00
N(1)	−791 (8)	−4205 (3)	2873 (3)	43 (2)	1.00
N(2)	−2441 (8)	−3120 (3)	3433 (3)	45 (2)	1.00
N(3)	−2101 (8)	−3558 (3)	1423 (3)	44 (2)	1.00
N(4)	−4513 (8)	−4062 (3)	2192 (3)	48 (2)	1.00
O(1)	−107 (8)	−4049 (3)	2573 (3)	66 (2)	1.00
O(2)	−5722 (8)	−4354 (4)	2638 (3)	78 (2)	1.00
C(1)	−504 (11)	−4167 (5)	3521 (4)	54 (3)	1.00
C(2)	492 (14)	−4749 (5)	3945 (5)	84 (4)	1.00
C(3)	−1326 (11)	−3485 (3)	3822 (3)	50 (3)	1.00
C(4)	−862 (13)	−3304 (6)	4559 (4)	83 (4)	1.00
C(5)	−3436 (11)	−2453 (5)	3666 (4)	62 (3)	1.00
C(6)	−4882 (11)	−2241 (5)	3139 (4)	70 (4)	1.00
C(7)	−2487 (14)	−1472 (5)	2329 (5)	81 (4)	1.00
C(8)	−815 (14)	−1686 (5)	1950 (5)	81 (4)	1.00
C(9)	915 (12)	−3027 (5)	1537 (5)	70 (4)	1.00
C(10)	−638 (12)	−3233 (5)	1052 (4)	63 (3)	1.00
C(11)	−3404 (11)	−3910 (4)	1116 (3)	46 (3)	1.00
C(12)	−3626 (13)	−4023 (5)	367 (4)	72 (4)	1.00
C(13)	−4791 (10)	−4240 (4)	1555 (4)	48 (3)	1.00
C(14)	−6253 (12)	−4750 (5)	1273 (5)	78 (4)	1.00
O(1W)	5839 (26)	−4721 (12)	3886 (10)	80 (7)	0.50
O(7)	5763 (13)	8927 (6)	654 (5)	140 (5)	0.50
O(7A)	3766 (144)	8924 (56)	−43 (53)	114 (37)	0.50
O(8)	2800 (11)	8622 (5)	791 (4)	107 (4)	0.50
O(8A)	3436 (110)	7780 (50)	374 (40)	94 (24)	0.50
O(9)	3971 (14)	8504 (7)	−280 (4)	116 (5)	1.00
O(10)	4973 (17)	7703 (5)	566 (5)	135 (5)	1.00
O(1A)	−1281 (59)	−6761 (22)	1129 (22)	87 (15)	0.20
O(1B)	−541 (54)	−5082 (17)	1158 (16)	37 (8)	0.20
O(1C)	−2210 (44)	−6085 (19)	388 (15)	45 (7)	0.20
O(1D)	−1092 (43)	−6390 (19)	1596 (15)	49 (8)	0.20
O(1E)	−774 (49)	−6638 (20)	1362 (20)	40 (7)	0.20
O(2A)	823 (37)	−5915 (18)	885 (14)	75 (8)	0.25
O(2B)	−3124 (33)	−5802 (15)	1107 (15)	63 (6)	0.25
O(2C)	−2123 (73)	−5810 (32)	1603 (25)	142 (23)	0.25
O(2D)	−28 (47)	−6458 (20)	1148 (18)	89 (10)	0.25
O(3A)	−2936 (69)	−6261 (30)	775 (26)	115 (16)	0.20
O(3B)	−2033 (63)	−5518 (29)	1462 (22)	66 (11)	0.20
O(3C)	−2858 (46)	−5875 (20)	653 (19)	54 (8)	0.20
O(3D)	324 (53)	−6181 (21)	602 (20)	77 (10)	0.20
O(3E)	−1199 (56)	−5177 (21)	1315 (17)	45 (8)	0.20
O(4A)	−85 (49)	−5302 (21)	1319 (19)	92 (13)	0.25
O(4B)	−933 (51)	−5904 (20)	256 (16)	85 (9)	0.25
O(4C)	−63 (77)	5368 (33)	629 (30)	195 (19)	0.25
O(4D)	−1844 (53)	−5708 (20)	259 (17)	86 (11)	0.25
O(1WA)	5268 (29)	−4546 (14)	3875 (12)	72 (6)	0.50

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupation factor of an atom.

a higher pH the bivalent complex undergoes progressive protic dissociation and two discrete one-electron couples involving all the three nickel oxidation states become observable. Comparison with complexes of ligand **2** has revealed that the NiS_2N_4 reduction potentials are systematically higher than the corresponding NiN_6 potentials. This is attributed to the weakness of the metal–thioether link.

Experimental Section

Materials. Commercially available pure diacetyl monoxime, 2-aminoethanethiol hydrochloride, benzyl methyl ketone, 1,2-dichloroethane, and 1,3-dichloropropane were used for ligand synthesis. 2-Isonitrosobenzyl methyl ketone was synthesized according to a reported procedure.[35] Buffers were prepared from pure-quality acetic acid, boric acid, potassium dihydrogen phosphate, and sodium hydroxide.

Physical Measurements. Microanalytical data (C, H, N) were obtained with Perkin-Elmer Model 240C elemental analyzer. Electronic spectra were recorded with a Hitachi 330 spectrophotometer. EPR spectra were recorded in the X-band with a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurements at 77 K (liquid nitrogen). The spectra were calibrated with respect to DPPH ($g = 2.0037$). Electrochemical measurements were done by using the PAR Model 370-4 electrochemistry system as before.[2] All pH measurements were performed by using a Systronics Model 335 digital pH meter standardized with standard buffer solutions.

Preparation of the Dithia Diamines. a. 1,10-Diaza-4,7-dithiadecane. This amine was previously synthesized[36] from ethane-1,2-dithiol. Our synthetic route starts from 2-aminoethanethiol hydrochloride. To a cooled (15 °C) and stirred ethanolic solution of sodium ethoxide (obtained by dissolving 2.30 g of sodium metal in 40 mL of dry ethanol) was added dry 2-aminoethanethiol hydrochloride (5.68 g; 5 × 10^{-2} mol). After the mixture was stirred for 15 min, 1,2-dichloroethane (2.0 mL; 2.5 × 10^{-2} mol) was added. The solution was warmed (40 °C) and stirred for 4 h. The solvent was removed under vacuo, and the yellowish mass was dissolved in a minimum volume of water (ca. 15 mL). It was then made strongly alkaline with solid NaOH (~5 g), and the resulting solution was kept in a refrigerator overnight. A pale yellow oil separated, which was extracted with dichloromethane (2 × 30 mL). The extract was evaporated under reduced pressure to get the diamine as a yellow oil (yield, 76%). It rapidly absorbs carbon dioxide from the air and was used immediately after synthesis.

b. 1,11-Diaza-4,8-dithiaundecane. This diamine was synthesized and isolated by following the same procedure as described above except that 1,3-dichloropropane was used instead of 1,2-dichloroethane.

Syntheses of Ligands. a. 3,14-Dimethyl-4,13-diaza-7,10-dithiahexadeca-3,13-diene-2,15-dione Dioxime, H_2Me2S. To a solution of diacetyl monoxime (1.70 g; 1.68 × 10^{-2} mol) in 40 mL of dry diethyl ether was added 1,10-diaza-4,7-dithiadecane (1.50 g; 8.33 × 10^{-3} mol), and the mixture was heated to reflux under dry dinitrogen for 2 h to get a clear solution. The reaction mixture was then kept overnight under refrigeration. Upon shaking of the clear cold solution vigorously, the ligand was deposited as a white solid (yield, 72%). Anal. Calcd for $C_{14}H_{26}N_4O_2S_2$: C, 48.56; H, 7.51; N, 16.19. Found: C, 48.42; H, 7.60; N, 16.10.

b. 3,15-Dimethyl-4,14-diaza-7,11-dithiaheptadeca-3,14-diene-2,16-dione Dioxime, H_2Me3S. This was synthesized by the condensation of diacetyl monoxime and 1,11-diaza-4,8-dithiaundecane in 2:1 molar ratio in dry diethyl ether medium by following the same procedure as for H_2Me2S to get the white solid ligand (yield, 66%). Anal. Calcd for $C_{15}H_{28}N_4O_2S_2$: C, 50.00; H, 7.78; N, 15.56. Found: C, 49.83; H, 7.87; N, 15.41.

c. 2,13-Dimethyl-1,14-diphenyl-3,12-diaza-6,9-dithiatetradeca-2,12-diene-1,14-dione Dioxime, H_2Ph2S, and 2,14-Dimethyl-1,15-diphenyl-3,13-diaza-6,10-dithiapentadeca-2,13-diene-1,15-dione Dioxime, H_2Ph3S. These ligands were synthesized by condensing α-isonitrosobenzyl methyl ketone with 1,10-diaza-4,7-dithiadecane and 1,11-diaza-4,8-dithiaundecane, respectively, in 2:1 mole ratio in n-hexane. The details are the as those used for H_2MexS. The ligands were isolated as red gummy masses, and these were used as such for the syntheses of complexes.

Syntheses of Nickel(II) Complexes, $Ni(H_2RxS)(ClO_4)_2$ (R = Me, Ph; x = 2, 3). All the complexes were synthesized by following the same general procedure. We report below the method of synthesis of the compound $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ as an example.

---

(35) Hartung, W. H.; Crossley, F. In *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1943; Collect. Vol. II.

(36) Dwyer, F. P. J.; Lions, F. *J. Am. Chem. Soc.* **1950**, *72*, 1545–1550.

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$[a,b]

atom	*x*	*y*	*z*	*U* (eq)
Ni	2391 (3)	6663 (1)	2424 (1)	31 (1)
Cl(1)	1114 (10)	3421 (5)	4656 (3)	78 (3)
Cl(2)	3866 (9)	4159 (3)	988 (3)	59 (2)
S(1)	191 (8)	7640 (3)	2291 (3)	52 (2)
S(2)	5003 (8)	7427 (3)	2323 (3)	57 (2)
N(1)	3945 (21)	5844 (9)	2877 (9)	45 (6)
N(2)	2230 (21)	6901 (8)	3426 (7)	35 (6)
N(3)	2728 (20)	6447 (8)	1417 (7)	32 (5)
N(4)	391 (23)	5895 (10)	2177 (8)	44 (6)
O(1)	4650 (20)	5227 (9)	2594 (7)	64 (4)
O(2)	−793 (20)	5595 (8)	2619 (7)	58 (4)
C(1)	4215 (28)	5919 (12)	3538 (11)	45 (6)
C(2)	5284 (34)	5330 (13)	3941 (12)	71 (7)
C(3)	3343 (26)	6554 (12)	3824 (9)	38 (5)
C(4)	3791 (32)	6798 (14)	4550 (10)	73 (7)
C(5)	1227 (28)	7529 (12)	3658 (10)	53 (6)
C(6)	−412 (29)	7604 (13)	3190 (10)	59 (6)
C(7)	1138 (36)	8550 (14)	2221 (13)	86 (8)
C(8)	2695 (47)	8718 (19)	2371 (18)	54 (10)
C(8A)	2645 (44)	8503 (22)	1596 (21)	71 (11)
C(9)	4427 (37)	8366 (16)	1985 (13)	91 (8)
C(10)	5674 (29)	6932 (12)	1563 (10)	57 (6)
C(11)	4198 (27)	6763 (13)	1072 (10)	57 (6)
C(12)	1431 (25)	6086 (10)	1110 (9)	31 (5)
C(13)	1304 (30)	5979 (12)	345 (10)	56 (6)
C(14)	119 (24)	5749 (10)	1563 (9)	31 (5)
C(15)	−1350 (35)	5244 (14)	1291 (12)	72 (7)
O(3)	2612 (32)	3610 (12)	4278 (11)	126 (8)
O(4)	−247 (36)	3980 (14)	4559 (11)	137 (8)
O(5)	298 (31)	2778 (15)	4459 (11)	126 (8)
O(6)	1546 (26)	3442 (11)	5369 (10)	107 (6)
O(7)	1923 (99)	4074 (35)	1067 (35)	185 (23)
O(8)	4090 (85)	4313 (30)	331 (28)	151 (18)
O(9)	4595 (55)	3513 (23)	1277 (19)	99 (12)
O(10)	4382 (34)	4884 (13)	1202 (12)	129 (8)
O(1W)	9716 (24)	376 (9)	1119 (9)	85 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] The site occupation factor (sof) is 0.50 of both C(8) and C(8A); the sof of all other atoms is 1.00.

To an ethanolic solution of $Ni(H_2O)_6(ClO_4)_2$ (1.25 g; 3.42×10^{-3} mol), H_2Me2S (1.20g; 3.47×10^{-3} mol) was gradually added while the mixture was stirred and warmed. The reaction was allowed to proceed for 1 h, and the solution was filtered. The deep brown solution was then subjected to slow evaporation in air to produce the complex as a deep brown crystalline solid compound in good (90%) yield. This was washed with cold water and dried over P_4O_{10} in vacuo. (*Caution! Perchlorate salts are explosive in nature.*) Anal. Calcd for $C_{14}H_{28}N_4O_{11}S_2Cl_2Ni$: C, 27.03; H, 4.50; N, 9.01. Found: C, 27.09; H, 4.59; N, 9.11.

Syntheses of Nickel(IV) Complexes, $Ni(MexS)(ClO_4)_2$ (x = 2, 3). These complexes were synthesized by following a general method. The procedure of synthesis of $Ni(Me2S)(ClO_4)_2$ is cited below.

Solid $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ (1 g) was added to 2 mL of cold concentrated nitric acid in one lot, and the mixture was kept in a refrigerator for 30 min. This produced a deep violet solution, to which a saturated aqueous solution of sodium perchlorate was gradually added. The mixture was triturated with a glass rod to get the complex as a dark solid. This was collected by filtration and washed with a cold dilute solution of sodium perchlorate. The compound was dried over P_4O_{10} in vacuo (yield, 65%). Anal. Calcd for $C_{14}H_{24}N_4O_{10}S_2Cl_2Ni$: C, 27.92; H, 3.99; N, 9.31. Found: C, 27.88; H, 4.03; N, 9.22.

pH-Metric Titration. The nickel(II) complexes were titrated in aqueous 10^{-2} M solutions with standard sodium hydroxide solution (0.10 M). Titration data were processed for p*K* determination according to methods reported earlier.[13a]

X-ray Structure Determination. Single crystals of $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$ were grown by slow evaporation of the respective aqueous ethanolic solutions. Data collections were performed on a Nicolet R3m/V automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Significant crystal data and data collection parameters are listed in Table VI. The unit cell parameters were determined by least-squares fit of 25 machine-centered reflections selected from rotation photographs. Lattice dimensions and Laue groups were verified by using axial photographs. Data collections on both the crystals were done in ω–2θ scan mode with 3 check reflections, measured after every 97 reflections, to monitor the crystal stability. No significant decay of crystals was observed. The crystal of $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$ was weakly diffracting, and the number of observed reflections was relatively small. Systematic absences led to the unambiguous identification of the space group to be $P2_1/c$ for both the crystals. All data were subjected to Lorentz–polarization corrections. An empirical absorption correction was done on the basis of azimuthal scans.[37] The criteria used for observed data are $I > 1.5\sigma(I)$ for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and $I > 3\sigma(I)$ for $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer with the programs of SHELXTL-PLUS.[38] The structures were solved by direct methods. The models were refined by full-matrix least-squares procedures. All the non-hydrogen atoms except the oxygen atoms of the disordered perchlorate ions were made anisotropic for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$. In the case of $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$ only the atoms within the coordination sphere were made anisotropic due to the small volume of available data. Hydrogen atoms were included at their idealized positions with fixed thermal parameters. The final convergence refinement gave residuals as summarized in Table VI. The highest difference Fourier peaks were 0.29 and 0.33 e $Å^{-3}$ near the metal atoms for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$, respectively. Atomic coordinates and isotropic thermal parameters for the two structures are listed in Tables VII and VIII.

Acknowledgment. We are very thankful to the Department of Science and Technology, New Delhi, for establishing a National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Financial support received from the Council of Scientific and Industrial Research is also acknowledged.

Registry No. **1** (R = Me, X = 2), 136617-43-1; **1** (R = Me, X = 3), 136617-44-2; **1** (R = Ph, X = 2), 136617-45-3; **1** (R = Ph, X = 3), 136617-46-4; $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$, 136599-96-7; $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$, 136599-99-0; $Ni(H_2Ph2S)(ClO_4)_2$, 136600-01-6; $Ni(H_2Ph3S)(ClO_4)_2$, 136600-03-8; $Ni(Me2S)(ClO_4)_2$, 136600-05-0; $Ni(Me3S)(ClO_4)_2$, 136600-07-2; $Ni(Ph2S)(ClO_4)_2$, 136600-09-4; $Ni(Ph3S)(ClO_4)_2$, 136600-11-8; $Ni^{II}(Me2S)$, 136600-12-9; $Ni^{II}(HMe3S)^+$, 136600-13-0; $Ni^{III}(Me3S)^+$, 136600-14-1; $Ni^{II}(Me3S)^+$, 136600-15-2; $Ni^{II}(HMe2S)^+$, 136600-16-3; $Ni^{III}(Me2S)^+$, 136600-17-4; $HSCH_2CH_2NH_2 \cdot HCl$, 156-57-0; $Cl(CH_2)_2Cl$, 107-06-2; $Cl(CH_2)_3Cl$, 142-28-9; $H_2NCH_2CH_2S(CH_2)_2SCH_2CH_2NH_2$, 21057-05-6; $H_2NCH_2CH_2S(CH_2)_3SCH_2CH_2NH_2$, 57383-24-1; biacetyl monoxime, 57-71-6; α-isonitrosobenzyl methyl ketone, 25355-34-4.

Supplementary Material Available: Coulometric data (Table V), structure determination summaries (Tables IX and X), complete bond distances (Tables XI and XII) and angles (Tables XIII and XIV), anisotropic thermal parameters (Tables XV and XVI), and hydrogen atom positional parameters (Tables XVII and XVIII) for $Ni(H_2Me2S)(ClO_4)_2 \cdot H_2O$ and $Ni(H_2Me3S)(ClO_4)_2 \cdot H_2O$ (14 pages); listings of observed and calculated structure factors for the above two complexes (17 pages). Ordering information is given on any current masthead page.

---

(37) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351–359.

(38) Sheldrick, G. M. *SHELXTL-Plus 88, Structure Determination Software Programms*; Nicolet Instrument Corp.: 5225-2 Verona Rd, Madison, WI 53711, 1988.