

119207-67-9; 28, 119207-42-0; 29, 119207-54-4; 29-K⁺, 119207-68-0; Gu₂SO₄, 594-14-9.

Supplementary Material Available: Tables S1.1-1.4, listing positional and isotropic thermal parameters, Tables S2.1-2.4, listing bond distances, Tables S3.1-3.4, listing bond angles, Table S4.1-4.4, listing bond distances of the coordinated transition-metal cations, Tables S5.1-5.4, listing

bond angles of the coordinated transition-metal cations, Tables S6.1-6.4, listing anisotropic thermal parameters, and Tables S7.1-7.4, listing least-squares planes and deviations therefrom, and figures showing the structures, respectively, for the complexes **3**-MeOH, **10**-H₂O, **14**-Na⁺Pic⁻, and **25**-3DMF (37 pages); Tables S8.1-8.4, listing calculated and observed structure factors (120 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Chemical and Electrochemical Reactivity of Nickel(II,I) Thiolate Complexes: Examples of Ligand-Based Oxidation and Metal-Centered Oxidative Addition

H.-J. Krüger and R. H. Holm*

Received September 29, 1988

The first extensive study of the reactivity of nickel in a classical coordination environment containing mainly thiolate ligands is described and was undertaken to examine the factors affecting the stability of Ni(III) in hydrogenases. Reaction of Ni(acac)₂ with pyridine-2,6-dimethanethiol (H₂pdmt) in toluene afforded dimeric [Ni(pdmt)]₂ (**1**). This compound can be electrochemically reduced at $E_{1/2} = -1.21$ V vs SCE in DMF solution to [Ni(pdmt)]₂⁻ (**1**⁻), a mixed-valence Ni(II,I) complex, and can be cleaved with thiolate to afford [Ni(pdmt)(SR)]⁻ (R = Ph (**2**), Et (**3**)). (*n*-Bu₄N)[**2**] crystallizes in the monoclinic space group *P*2₁/*a* with *a* = 15.256 (7) Å, *b* = 9.610 (4) Å, *c* = 21.340 (9) Å, β = 95.15 (4)°, and *Z* = 4. (Me₄N)[**3**] crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 7.628 (4) Å, *b* = 20.014 (8) Å, *c* = 12.800 (4) Å, β = 98.53 (4)°, and *Z* = 4. Both complexes are planar with unexceptional metric features. Complexes **2** and **3** undergo the irreversible ligand-based oxidation [Ni(pdmt)(SR)]⁻ → ¹/₂[**1**] + ¹/₂RSSR + e⁻ at $E_{pa} = +0.01$ (**2**) and -0.08 (**3**) V. The reverse of this reaction was also demonstrated. The reduced dimer exhibits the oxidative-addition reaction **1**⁻ + RSSR → [**2/3**] + ¹/₂[**1**] + ¹/₂RSSR. Plausible pathways for these reactions are presented. These results and related observations show that ligand-based oxidation of classical nickel(II) thiolate complexes with irreversible formation of disulfide is a pervasive process that extends to unidentate and chelating thiolate ligands. Nickel sites in certain hydrogenases contain ca. three anionic sulfur ligands and are characterized by extremely low Ni(III)/Ni(II) potentials. Factors contributing to the stability of the Ni(III) enzyme sites are considered, and the general type of ligand that should be effective in stabilizing Ni(III) at low potentials is described.

Introduction

The purposeful exploration of structures and reactions of nickel thiolate complexes¹⁻⁵ has most recently been motivated by the discovery of nickel in a large number of hydrogenases.⁶ The EPR signals with *g* values near 2.3, 2.2, and 2.0 usually observed in most "as prepared" hydrogenases have been ascribed to Ni(III) in a tetragonal environment. Recent MCD results, which indicate a dissimilarity in coordination geometry of paramagnetic, distorted tetrahedral Ni(II)-substituted rubredoxins vs diamagnetic Ni(II) in hydrogenases,⁷ add further support to tetragonal coordination in the latter. However, the more provocative property of these centers is their low Ni(III/II) redox potentials of ca. -150 to -400 mV vs NHE (-390 to -640 mV vs SCE), values remarkably depressed compared to the normal values of ca. +500 mV or higher vs SCE for synthetic complexes.⁸ There are a few such complexes

with substantially lower potentials than the latter value.^{2,9,10} Several of these, prepared in this laboratory, are classical amide thiolate complexes with potentials in the -330- to -35-mV interval.^{2,11} These results are of apparent relevance to the enzymes inasmuch as the Ni EXAFS of the latter have been interpreted in terms of (at least) three anionic sulfur ligands.¹² One means of lowering Ni(III/II) potentials, therefore, is to incorporate around the metal negative, polarizable ligands.

A promising initial model for the Ni site in hydrogenases would be a mononuclear tetragonal complex containing three or more thiolate ligands and exhibiting a low, reversible Ni(III/II) potential. Because of the highly anisotropic EPR spectra of the enzymes, a dithiolene-type nickel cofactor appears to be an unlikely candidate for the model.¹³ Certain difficulties attend the preparation of such model complexes. One is the decided tendency of nickel(II) thiolates to form polynuclear complexes,^{1,3,4,5b,14,15} especially in protic media. Two types of mononuclear thiolates are known. The first and more common, [Ni(SR)₄]²⁻, is derived

- (1) Snyder, B. S.; Rao, Ch. P.; Holm, R. H. *Aust. J. Chem.* **1986**, *39*, 963.
- (2) Krüger, H.-J.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 3645; unpublished results.
- (3) Yamamura, T.; Miyamae, H.; Katayama, Y.; Sasaki, Y. *Chem. Lett.* **1985**, 269.
- (4) Yamamura, T. *Chem. Lett.* **1986**, 801.
- (5) (a) Rosenfield, S. G.; Armstrong, W. H.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3014. (b) Rosenfield, S. G.; Wong, M. L. Y.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 4119.
- (6) (a) Hausinger, R. P. *Microbiol. Rev.* **1987**, *51*, 22. (b) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297.
- (7) Kowal, A. T.; Zambrano, I. C.; Moura, I.; Moura, J. J. G.; LeGall, J.; Johnson, M. K. *Inorg. Chem.* **1988**, *27*, 1162.
- (8) (a) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87. (b) Haines, R. J.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77. (c) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988**, *32*, 241.

- (9) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.
- (10) Chakravorty, A. *Isr. J. Chem.* **1985**, *25*, 99.
- (11) Hereafter, all potentials are referenced to the SCE.
- (12) (a) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062. (b) Scott, R. A.; Wallin, S. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864. (c) Scott, R. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *Rev. Port. Quim.* **1985**, *27*, 67.
- (13) The EPR spectra of [Ni(S₂C₂R₂)₂]²⁻ complexes are much less anisotropic; cf., e.g.: Maki, A. H.; Edelman, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.
- (14) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.
- (15) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.

from arenethiolate ligands whose steric properties promote a mononuclear tetrahedral structure.^{3,5a,16} The second type consists of only one example, planar $[\text{Ni}(\text{edt})_2]^{2-}$ ($\text{edt} = \text{ethane-1,2-dithiolate}$), which, however, can be converted to $[\text{Ni}_n(\text{edt})_{n+1}]^{2-}$ ($n = 2, 3$) under aprotic and mild protic conditions.^{1,3} An additional difficulty in achieving model complexes is made evident by the pervasive tendency of nickel(II) thiolates to undergo irreversible oxidation.^{1,3,4,17,18} In such cases, the Ni(III) state (if formed at all) has never been detected, and the nature of the oxidized product has rarely been determined.

Our current research on synthetic analogues of the Ni site in hydrogenases deals in part with an investigation of the factors that stabilize (or destabilize) Ni(III) in a coordination environment containing largely or exclusively thiolate ligands. In this connection, we became interested in the reported cleavage reaction of dimeric or polymeric (pyridine-2,6-dimethanethiolato)nickel(II) by tertiary phosphines to yield monomeric $\text{Ni}(\text{pdmt})(\text{PR}_3)$.¹⁹ A similar reaction with thiolate would afford $[\text{Ni}(\text{pdmt})(\text{SR})]^-$, a complex with three thiolate ligands and a planar structure, anticipated from the steric features of the pdmt ligand when acting as a tridentate. As observed, both features are pertinent to the hydrogenase site. Further, if oxidation of the complex were ligand- instead of metal-centered, it would likely involve the unidentate thiolate, whose oxidation product would be easily identified. We report here the preparation, structures, and reactions of the complexes $[\text{Ni}(\text{pdmt})(\text{SR})]^-$, results that bear on the ultimate attainment of an analogue of the Ni(II,III) site in hydrogenases.

Experimental Section

Preparation of Compounds. Pyridine-2,6-dimethanethiol^{20,21} (H_2pdmt) was prepared from pyridine-2,6-dimethanol²² after isolation and purification of the intermediate bis(2,6-bromomethyl)pyridine.²² The compounds 8-quinolinethiol²³ (Hqt), 2,4,6-triisopropylbenzenethiol²⁴ (Htpbt), and bis(2-mercaptoethyl) sulfido nickel(II)^{25,26} ($[\text{Ni}(\text{mes})_2]$) were prepared according to published methods. Other thiols and disulfides were obtained from Aldrich. Diphenyl disulfide was recrystallized from ethanol and diethyl disulfide was distilled prior to use. Nickel metal enriched 86.44% in ^{61}Ni was obtained from the Oak Ridge National Laboratory. All operations in the following preparations were performed under a pure dinitrogen atmosphere.

$[\text{Ni}(\text{pdmt})_2]$ (1). To a solution of 2.57 g (10.0 mmol) of bis(acetylacetonato)nickel(II) in 100 mL of toluene was added dropwise with stirring a solution of 1.71 g (10.0 mmol) of H_2pdmt in 20 mL of toluene. The brown amorphous precipitate, which immediately separated, was collected by filtration and washed with toluene and ether to afford 2.07 g (91%) of product. $^1\text{H NMR}$ (CDCl_3): δ 3.71 (s, 2), 4.10 (s, 2), 7.08 (d, 2), 7.47 (t, 1). $^1\text{H NMR}$ (Me_2SO): δ 3.61 (s, 2), 3.92 (s, 2), 7.19 (2), 7.62 (1). Absorption spectrum (Me_2SO): λ_{max} (ϵ_{M}) 307 (13 700), 334 (12 900), 410 (4960), 540 (sh, 920) nm. A ^{61}Ni -enriched sample was prepared on a 41- μm scale from hydrated NiCl_2 (from the metal and concentrated HCl) and H_2pdmt in ethanol.

$(n\text{-Bu}_4\text{N})[\text{Ni}(\text{pdmt})(\text{SPh})]$ (2). A suspension of 0.58 g (1.27 mmol) of **1**, 0.83 g (2.57 mmol) of $n\text{-Bu}_4\text{NBr}$, and 0.34 g (2.58 mmol) of NaSPh in 150 mL of acetonitrile was stirred for 20 h. The green-red dichroic solution was filtered, the solid was washed with a small amount of acetonitrile, and the combined filtrate was reduced in volume to 10–20 mL. Ether (ca. 30 mL) was cautiously introduced until turbidity and the solution was stored at -20°C for 1 day. Ether (100 mL) was added, and after another day at -20°C the reaction mixture was filtered to afford 0.604 g (41%) of pure product as a black microcrystalline product. Anal. Calcd for $\text{C}_{25}\text{H}_{48}\text{N}_2\text{NiS}_3$: C, 60.10; H, 8.35; Ni, 10.13; N, 4.83; S, 16.59.

Table I. Crystallographic Data for Compounds 2 and 3

	2	3
chem formula	$\text{C}_{25}\text{H}_{48}\text{NiN}_2\text{S}_3$	$\text{C}_{15}\text{H}_{27}\text{NiN}_3\text{S}_3$
fw	579.58	404.28
a , Å	15.256 (7)	7.628 (4)
b , Å	9.610 (4)	20.014 (8)
c , Å	21.340 (9)	12.800 (4)
β , deg	95.15 (4)	98.53 (4)
V , Å ³	3116 (2)	1933 (1)
Z	4	4
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
T , K	298	298
λ , Å	0.710 69	0.710 69
ρ_{calcd} (ρ_{obsd}), g/cm ³	1.24 (1.24) ^a	1.39 (1.39) ^a
μ , cm ⁻¹	8.4	13.2
$R(F_o)$	0.045	0.042
$R_w(F_o^2)$	0.055	0.044

^a Determined by neutral buoyancy in $\text{CCl}_4/\text{hexane}$.

Found: C, 59.98; H, 8.14; Ni, 10.39; N, 4.92; S, 16.71. $^1\text{H NMR}$ (CD_3CN , anion): δ 3.89 (s, 4), 6.75 (t, 1), 6.85 (t, 2), 6.95 (d, 2), 7.36 (t, 1), 7.72 (d, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_{M}) 242 (18 500), 254 (sh, 17 400), 300 (20 800), 384 (sh, 3490), 476 (sh, 824), 560 (520), 752 (sh, 81) nm.

$(\text{Me}_4\text{N})[\text{Ni}(\text{pdmt})(\text{SEt})]\text{MeCN}$ (3). A suspension of 0.685 g (1.50 mmol) of **1**, 0.468 g (3.04 mmol) of Me_4NBr , and 0.264 g (3.14 mmol) of NaSEt in 200 mL of acetonitrile was stirred for 20 h. The green-red dichroic solution was filtered, the solid was washed (2×5 mL) with acetonitrile, and the combined filtrate was reduced in volume to 150 mL. The solution was filtered again to remove a white solid, and the filtrate was reduced in volume to ca. 100 mL. The solution was warmed and slowly cooled to room temperature and then to -20°C , at which temperature it was maintained for 1 day. The pure product was obtained as 0.75 g (62%) of long black needles. Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{N}_3\text{NiS}_3$: C, 44.56; H, 6.73; N, 10.39; Ni, 14.52; S, 23.79. Found: C, 44.51; H, 6.80; N, 10.36; Ni, 14.62; S, 23.71. $^1\text{H NMR}$ (CD_3CN , anion): δ 1.01 (t, 3), 1.68 (q, 2), 3.85 (s, 4), 6.91 (d, 2), 7.32 (t, 1). Absorption spectrum (acetonitrile): λ_{max} (ϵ_{M}) 246 (17 500), 291 (14 500), 308 (sh, 13 400), 414 (2900), 574 (sh, 209) nm.

Cleavage of $[\text{Ni}(\text{pdmt})_2]$ by Other Thiolates. The complexes $[\text{Ni}(\text{pdmt})(\text{tpbt})]^-$ and $[\text{Ni}(\text{pdmt})(\text{qt})]^-$ were generated in solution by a procedure similar to the preceding preparations by using stoichiometric quantities of **1**, $n\text{-Bu}_4\text{NBr}$, and the sodium thiolate in acetonitrile (mole ratio of 1:2:2). The solutions were filtered, adjusted to the desired concentrations, and examined spectrophotometrically and electrochemically.

X-ray Structural Determinations. Single crystals of **2** and **3** were obtained by slow addition of ether to an acetonitrile solution and directly from the preparative procedure, respectively. Crystals were mounted in glass capillaries, which were sealed under dinitrogen. Data collections were carried out on a Nicolet P3F four-circle automated diffractometer using graphite-monochromatized $\text{Mo K}\alpha$ radiation. Parameters of the data collections are listed in Table I. The unit cell parameters and final orientation matrices were obtained from least-squares refinement of 25 machine-centered reflections in the range $15^\circ < 2\theta < 25^\circ$ for **2** and $25^\circ < 2\theta < 30^\circ$ for **3**. Three standard reflections measured every 123 reflections indicated no decay of the crystals during data collection. Data sets were processed with the program XTAPE of the SHELXTL program package (Nicolet XRD Corp., Madison, WI), and empirical absorption corrections were applied with use of the program PSICOR. The systematic absences $h0l$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$) for **2**, and $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$) for **3** uniquely determine the space groups as $P2_1/a$ and $P2_1/n$, respectively. The structures were solved by a combination of direct methods (MULTAN) and Fourier techniques. Atom scattering factors were taken from a standard source.²⁷ The trial positions for the Ni atoms were taken from the E map derived from the phase set with the highest figure of merit for **2** and the second highest for **3**. All other non-hydrogen atoms were located by means of Fourier refinements with the program CRYSTALS. Isotropic refinement converged at $R = 10.2\%$ (**2**) and 9.2% (**3**). All non-hydrogen atoms were described anisotropically. In the final stages of the refinements, hydrogen atoms were introduced at 0.98 Å from and with 1.2 times the thermal parameters of the bonded carbon atoms. Final R factors are given in Table I and positional parameters are collected in Tables II and III.²⁸

- (16) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932.
 (17) Fabre, P.-L.; Poilblanc, R. *Bull. Soc. Chim. Fr.* **1986**, 740.
 (18) Nakabayashi, Y.; Matsuda, Y.; Sekido, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *205*, 209.
 (19) op den Brouw, P. M.; van der Linden, J. G. M. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 149.
 (20) Weber, E.; Vögtle, F. A. *Liebigs Ann. Chem.* **1976**, 891.
 (21) Partyka, R. A. U.S. Patent 3,290,319; *Chem. Abstr.* **1967**, *66*, 115609k.
 (22) Newcomb, M.; Timko, J. M.; Walba, D. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6392.
 (23) Kealey, D.; Freiser, H. *Talanta* **1966**, *13*, 1381.
 (24) Pearson, D. E.; Caine, D.; Field, L. *J. Org. Chem.* **1960**, *25*, 867.
 (25) Harley-Mason, J. *J. Chem. Soc.* **1952**, 146.
 (26) (a) Barclay, G. A.; McPartlin, E. M.; Stephenson, N. C. *Acta Crystallogr.* **1969**, *B25*, 1262. (b) Baker, D. J.; Goodall, D. C.; Moss, D. S. *J. Chem. Soc. D* **1969**, 325.

- (27) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.
 (28) See the paragraph at the end of this article concerning supplementary material available.

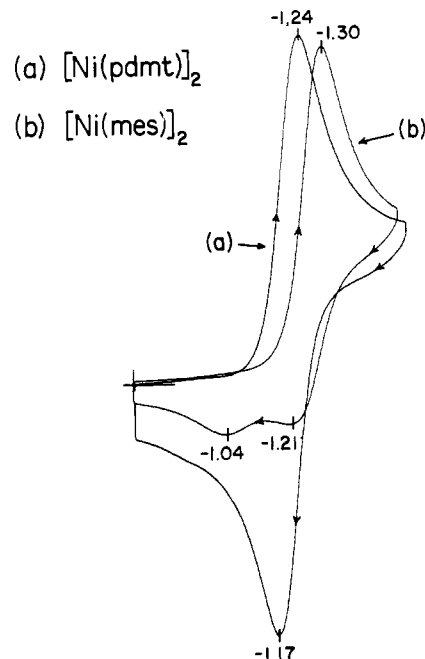
Table II. Positional Parameters ($\times 10^4$) for the Non-Hydrogen Atoms in $\text{NBu}_4[\text{Ni}(\text{pdmt})(\text{SPh})]$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	2646.6 (4)	792.6 (6)	6859.0 (3)
S(1)	1758 (1)	24 (2)	6084.2 (7)
S(2)	3611.0 (9)	1526 (2)	7592.5 (6)
N(1)	3319 (3)	1652 (4)	6259 (2)
C(1)	2135 (4)	1092 (7)	5476 (3)
C(2)	2973 (4)	1808 (6)	5657 (3)
C(3)	3389 (6)	2586 (8)	5246 (3)
C(4)	4165 (6)	3225 (7)	5427 (4)
C(5)	4556 (4)	3026 (6)	6031 (4)
C(6)	4115 (3)	2219 (5)	6446 (3)
C(7)	4475 (3)	1881 (6)	7086 (3)
S(3)	1764 (1)	-169 (2)	7476.5 (7)
C(8)	2014 (3)	229 (6)	8275 (2)
C(9)	2025 (4)	1582 (6)	8491 (3)
C(10)	2169 (5)	1849 (9)	9129 (4)
C(11)	2288 (6)	770 (12)	9551 (3)
C(12)	2295 (6)	-569 (11)	9339 (3)
C(13)	2146 (4)	-842 (7)	8702 (3)
N(2)	970 (2)	1503 (4)	2359 (2)
C(14)	1961 (3)	1363 (6)	2508 (3)
C(15)	2236 (3)	276 (7)	2996 (3)
C(16)	3218 (3)	314 (9)	3154 (3)
C(17)	3508 (5)	-547 (9)	3706 (4)
C(18)	505 (3)	1615 (6)	2955 (2)
C(19)	796 (4)	2799 (6)	3389 (2)
C(20)	438 (4)	2603 (6)	4016 (2)
C(21)	707 (4)	3747 (6)	4476 (3)
C(22)	593 (4)	227 (5)	2014 (2)
C(23)	865 (4)	-68 (7)	1364 (3)
C(24)	310 (5)	-1246 (8)	1074 (3)
C(25)	536 (6)	-1683 (11)	444 (4)
C(26)	837 (3)	2808 (6)	1962 (3)
C(27)	-104 (4)	3119 (7)	1733 (3)
C(28)	-112 (6)	4287 (9)	1248 (5)
C(29)	-976 (7)	4712 (13)	995 (6)

Table III. Positional Parameters ($\times 10^4$) for the Non-Hydrogen Atoms in $\text{NMe}_4[\text{Ni}(\text{pdmt})(\text{SEt})]\cdot\text{MeCN}$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	2518.4 (6)	1241.8 (2)	8086.3 (4)
S(1)	2942 (2)	438.6 (5)	6997.7 (8)
S(2)	2009 (2)	2005.4 (5)	9200.6 (8)
N(1)	2343 (4)	582 (1)	9145 (2)
C(1)	3024 (7)	-262 (2)	7889 (3)
C(2)	2745 (5)	-65 (2)	8983 (3)
C(3)	2913 (6)	-529 (2)	9778 (4)
C(4)	2607 (7)	-334 (2)	10781 (4)
C(5)	2110 (7)	317 (2)	10939 (3)
C(6)	1984 (5)	769 (2)	10120 (3)
C(7)	1446 (6)	1472 (2)	10247 (3)
S(3)	3041 (1)	1929.4 (5)	6844.7 (8)
C(8)	2513 (6)	2792 (2)	7115 (3)
C(9)	542 (6)	2944 (2)	6885 (4)
N(2)	7549 (4)	991 (1)	5564 (2)
C(10)	5825 (5)	1069 (2)	4850 (3)
C(11)	9048 (5)	1116 (2)	4944 (3)
C(12)	7702 (6)	303 (2)	6007 (4)
C(13)	7643 (6)	1482 (2)	6440 (4)
N(3)	1877 (6)	1293 (3)	3244 (4)
C(14)	1966 (6)	1823 (3)	3540 (3)
C(15)	2033 (7)	2501 (3)	3934 (4)

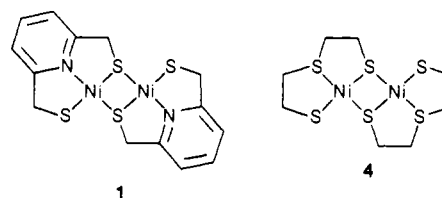
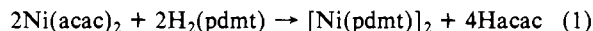
Other Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were recorded on a Varian 2390 spectrophotometer and a Perkin-Elmer Lambda 4C spectrophotometer interfaced with a Perkin-Elmer 7000 Professional Computer. EPR spectra were determined with use of Varian E Line spectrometer operating at X-band frequencies. Solutions of the reduction product of $[\text{Ni}(\text{pdmt})_2]$ were electrochemically generated and immediately frozen at liquid-nitrogen temperature. Electrochemical measurements were performed with standard PAR instrumentation. Solutions were prepared in acetonitrile (distilled from CaH_2) or DMF (Burdick and Jackson) and contained 0.2 M (*n*-Bu₄N)(ClO₄) supporting electrolyte. A glassy carbon or platinum foil electrode was used as the working electrode. The Pt electrode was cleaned by immersion in 6 N HNO₃ followed by rinsing

**Figure 1.** Cyclic voltammograms (100 mV/s) of $[\text{Ni}(\text{pdmt})_2]$ and $[\text{Ni}(\text{mes})_2]$ in DMF solutions at 25 °C; peak potentials vs SCE are indicated.

with deionized water and acetonitrile. All potentials were referenced to a SCE. Under these conditions, the potential of the ferrocenium/ferrocene couple was 0.40 V in acetonitrile and 0.48 V in DMF. Coulometric experiments were performed by using a Pt-gauze electrode and a PAR Model 179 digital coulometer.

Results and Discussion

(Pyridine-2,6-dimethanethiolato)nickel(II). This compound, $[\text{Ni}(\text{pdmt})_2]$ (**1**), is the starting point for the reactivity studies described below. A brown diamagnetic material of composition $\text{Ni}(\text{pdmt})$ was first prepared by op den Brouw and van der Linden¹⁹ by reaction of the dithiol with a nickel salt in water, ethanol, or Me_2SO . On the basis of its low solubility, the compound was considered to be a polymer, but the possibility of the binuclear structure **1** was recognized. Constable et al.²⁹ have reported a hydrated form of this compound, which was described as dimeric on the basis of its mass spectrum. Because of the tendency of $\text{Ni}(\text{II})$ thiolates to oligomerize in protic solvents, reaction 1 as



a preparative method for the dimeric form was carried out here in toluene solution. The product is a brown solid sufficiently soluble in chloroform, DMF, and Me_2SO for further characterization, which supports structure **1**. The ¹H NMR spectra in CDCl_3 and Me_2SO contain two equally intense methylene signals near 3.6 and 4.0 ppm, consistent with **1**, which is assumed hereafter. We have not been able to obtain suitable single crystals of the compound for a structure determination. Formulation **1** is closely related to the proven binuclear structure **4** for $[\text{Ni}(\text{mes})_2]$.²⁶ As such, a nonplanar conformation bent along the vector connecting the bridging sulfur atoms is probable. In **4**, this deformation places the two $\text{Ni}(\text{II})$ atoms only 2.73 Å apart; similar distortions from overall planarity have been observed in other

(29) Constable, E. C.; Lewis, J.; Marquez, V. E.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1986**, 1747.

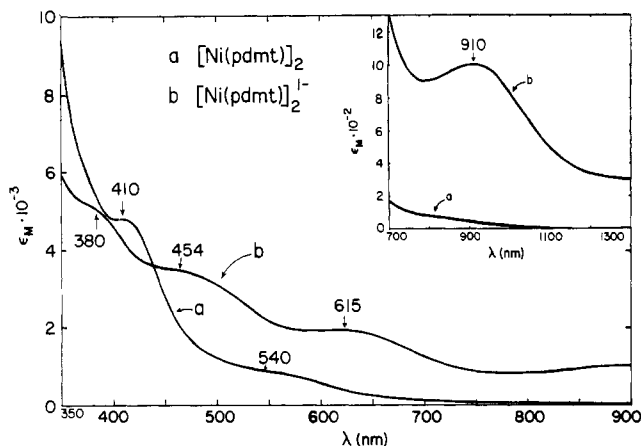


Figure 2. Electronic absorption spectra of $[\text{Ni}(\text{pdmt})_2]_2^-$ (a) and $[\text{Ni}(\text{pdmt})_2]_2^-$ (b), generated by controlled-potential electrolysis, in DMF solutions. The extinction coefficients of spectrum b may be low by 10–20% owing to the instability of the reduced complex over the 30-min period required for its generation.

thiolate-bridged acyclic Ni(II) complexes.^{30,31}

Reduction of $[\text{Ni}(\text{pdmt})_2]_2^-$. As shown in Figure 1, complex **1** is reduced at $E_{1/2} = -1.21$ V in DMF solution in a process that closely approaches reversible charge transfer. At 50 mV/s, $\Delta E_p = 60$ mV and increases slightly with scan rate v , $i_p/v^{1/2}$ is independent of scan rate, and $i_{pc}/i_{pa} \approx 1$. Complex **4** reduces at nearly the same potential ($E_{pc} = -1.30$ V), but the reaction is irreversible, implying that electron delocalization on the pyridine ring is a stabilizing feature. Additional reduction steps were observed at $E_{pc} \lesssim -1.8$ V, but these are irreversible.

Coulometry of **1** at an applied potential of -1.4 V in DMF solution produced a dark olive green solution. Multiple determinations gave a mean value of 1.03 ± 0.03 e/2 Ni. Reoxidation gave 0.78 e/2 Ni, indicating that over the 30-min time of electrolysis there had been some decay of the reduced complex. The absorption spectra of $[\text{Ni}(\text{pdmt})_2]_2^-$ and its reduction product are compared in Figure 2. The neutral complex exhibits relatively weak features in the region (ca. 500–650 nm) expected for the ligand field transitions of a planar Ni(II) chromophore and is essentially transparent at lower energies. The reduced complex absorbs more strongly in the visible interval and in the near-IR region possesses a band at 910 nm. We assign this feature as an intervalence transfer band, and from it we estimate the intramolecular electron-transfer rate constant³² as 6×10^9 s⁻¹.

The EPR spectrum of the electrochemically generated reduced complex in frozen DMF solution is shown in Figure 3. It consists of an axial signal with $g_{\perp} = 2.058$, $g_{\parallel} = 2.196$, and $g_{av} = 2.104$. The unpaired spin is clearly metal-centered because of the substantial g anisotropy; from $g_{\parallel} > g_{\perp}$, the electron is described by an orbital of mainly $d_{x^2-y^2}$ character.^{8c} Similar configurations are observed in nearly all other Ni(I) complexes. The g values are quite comparable to those of, e.g., $[\text{Ni}(\text{mnt})_2]^{3-}$.³³ Substitution of 86% ⁶¹Ni ($I = 3/2$) causes significant broadening of the spectrum, especially of the g_{\parallel} signal. Resolution of this spectral portion is poor, but six hyperfine features separated by about 30 G can be discerned. Only four such features would arise if the electron were localized on one Ni atom.

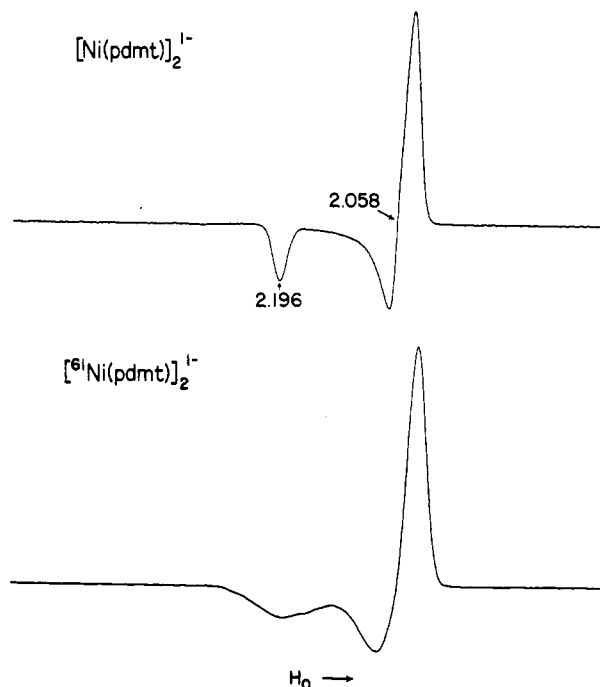


Figure 3. X-Band EPR spectra of electrochemically generated $[\text{Ni}(\text{pdmt})_2]_2^-$ and $[\text{Ni}(\text{pdmt})_2]_2^-$ in DMF solutions at 100 K. Apparent g values are indicated.

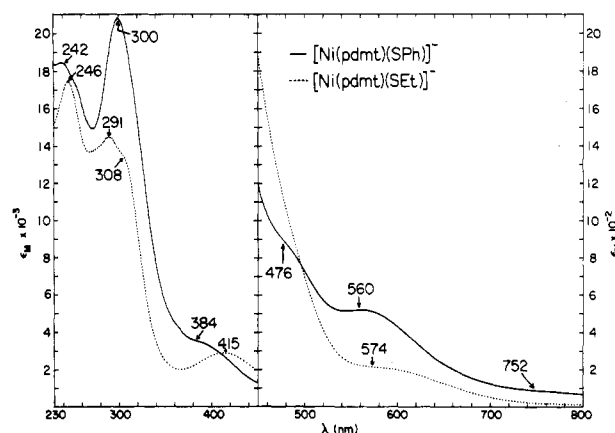
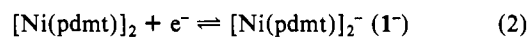


Figure 4. Electronic absorption spectra of $[\text{Ni}(\text{pdmt})(\text{SR})]_2^-$ ($R = \text{Ph}$, Et) in acetonitrile solutions.

We conclude that the reduction of **1** is represented by reaction 2. The product 1^- is a mixed-valence Ni(II,I) complex in which the odd electron is delocalized over both metal centers. Complex



1^- is formed at potentials that are quite comparable to those for reduction of neutral or cationic complexes to the Ni(I) state.⁸ Among sulfur-ligated complexes, the nickel(II) dithiolenes such as $[\text{Ni}(\text{mnt})_2]^{2-}$ ^{33,34} are further reduced to authentic Ni(I) at more negative potentials (< -1.7 V). The complexes $\text{Ni}(\text{qt})_2$,¹⁸ $\text{Ni}(\text{SacSac})_2$,³⁵ and $\text{Ni}(\text{S}_2\text{CNR}_2)_2$ ^{36,37} undergo one-electron reductions at -1.1 to -1.5 V. Reduction of $\text{Ni}(\text{SacSac})_2$ is apparently ligand-based. The EPR spectra of $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]^-$ complexes demonstrate that these are Ni(I) species which, however, are decidedly unstable.³⁷ These results underscore the current uni-

- (30) (a) Fackler, J. P.; Zegarski, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 8566. (b) Vance, T. B., Jr.; Warner, L. G.; Seff, K. *Inorg. Chem.* **1977**, *16*, 2106. (c) Tremel, W.; Krebs, B.; Henkel, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1527.
- (31) This type of folding along S–S bridging atoms is an obligatory feature of cyclic nickel(II) thiolates with planar NiS_4 coordination units: (a) Miyamae, H.; Yamamura, T. *Acta Crystallogr.* **1988**, *C44*, 686. (b) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1985**, *24*, 1201. (c) Gaete, W.; Ros, J.; Solans, X.; Font-Altaba, M.; Brianso, J. L. *Inorg. Chem.* **1984**, *23*, 39.
- (32) Meyer, T. J. *Chem. Phys. Lett.* **1979**, *64*, 417.
- (33) (a) Mines, T. E.; Geiger, W. E., Jr. *Inorg. Chem.* **1973**, *12*, 1189. (b) Geiger, W. E., Jr.; Allen, C. S.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1977**, *16*, 2003. mnt = maleonitriledithiolate(2-).

- (34) Geiger, W. E., Jr.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1975**, *14*, 2141.
- (35) (a) Bond, A. M.; Heath, G. A.; Martin, R. L. *Inorg. Chem.* **1971**, *10*, 2026. (b) Bowden, W. L.; Holloway, J. D.; Geiger, W. E., Jr. *Inorg. Chem.* **1978**, *17*, 256. SacSac = dithioacetetylacetonate(1-).
- (36) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*, 2980.
- (37) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K.; Hope, J. M.; Martin, R. L. *Inorg. Chem.* **1982**, *21*, 1152.

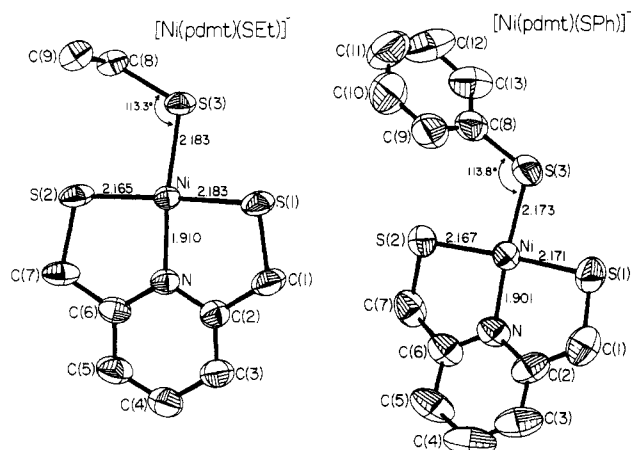


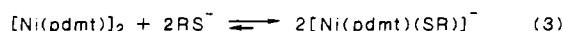
Figure 5. Structures of $[\text{Ni}(\text{pdmt})(\text{SEt})]^-$ and $[\text{Ni}(\text{pdmt})(\text{SPh})]^-$ showing 50% thermal ellipsoids and selected bond distances (Å) and angles.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{Ni}(\text{pdmt})(\text{SR})]^-$ (R = Ph, Et)

distance/angle	R = Ph	R = Et
Ni-S(1)	2.171 (2)	2.183 (1)
Ni-S(2)	2.167 (1)	2.165 (1)
Ni-S(3)	2.173 (2)	2.183 (1)
Ni-N(1)	1.901 (4)	1.910 (3)
C(1)-S(1)	1.789 (7)	1.803 (4)
C(7)-S(2)	1.811 (5)	1.814 (4)
C(8)-S(3)	1.755 (5)	1.818 (4)
C(1)-C(2)	1.473 (8)	1.500 (5)
C(7)-C(6)	1.461 (8)	1.482 (6)
N(1)-C(2)	1.352 (7)	1.355 (5)
N(1)-C(6)	1.357 (6)	1.369 (5)
C(8)-C(9)		1.519 (6)
S(1)-Ni-N(1)	88.4 (1)	88.7 (1)
S(2)-Ni-N(1)	88.4 (1)	89.0 (1)
S(1)-Ni-S(3)	86.5 (1)	86.5 (1)
S(2)-Ni-S(3)	96.8 (1)	96.0 (1)
S(1)-Ni-S(2)	175.9 (1)	177.1 (1)
S(3)-Ni-N(1)	174.3 (1)	172.5 (1)
Ni-S(1)-C(1)	97.9 (2)	99.4 (1)
Ni-S(2)-C(7)	96.5 (2)	99.0 (1)
Ni-S(3)-C(8)	113.8 (2)	113.0 (1)

queness of $[\text{Ni}(\text{pdmt})]_2^-$, which is the first example of a Ni(II,I) mixed-valence complex of any kind.

Cleavage of $[\text{Ni}(\text{pdmt})]_2^-$. We have confirmed that reaction of **1** and excess Ph_3P in a heterogeneous system in chloroform results in cleavage and formation of $\text{Ni}(\text{pdmt})(\text{PPh}_3)$.¹⁹ Thereafter, it was found that reaction 3, homogeneous in Me_2SO and hetero-



geneous in acetonitrile owing to the low solubility of **1**, proceeds smoothly with cleavage of the dimer to form the mononuclear, diamagnetic thiolate complexes with R = Ph (**2**) and Et (**3**). The solvent of choice for preparative reactions is acetonitrile owing to the easier workup conditions. There is no reaction in ethanol where, as already noted, nickel(II) thiolates tend to oligomerize. Absorption spectra of the two complexes are provided in Figure 4. While their spectra and that of **1** are similar, the differences are sufficient to distinguish them. In particular, the d-d bands of **2** and **3** in the visible region are red-shifted with respect to the shoulder at 540 nm in the spectrum of the dimer.

Cleavage reaction 3 in acetonitrile and DMF also proceeded cleanly with sterically hindered 2,4,6-triisopropylbenzenethiolate and with 8-quinolinethiolate. Products were detected in solution by their spectral similarities to **2** and by their electrochemical behavior (vide infra). No reaction was observed with *p*-nitrobenzenethiolate, which is apparently insufficiently nucleophilic to cleave the bridge bonds of **1**. Similarly, there was no reaction with excess phenolate, pyridine, 2,2'-bipyridyl, acetate, and carbon monoxide in acetonitrile at ambient temperature.

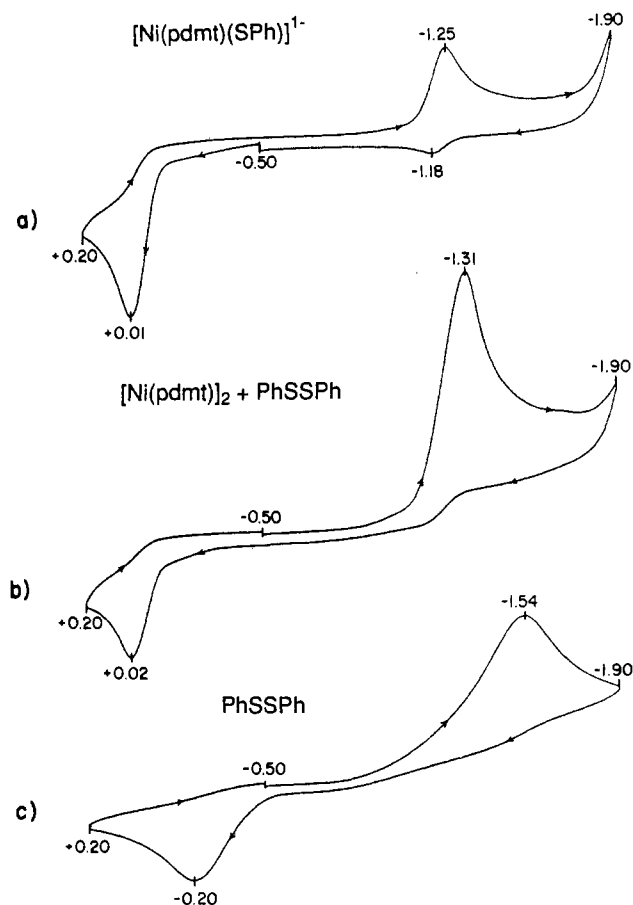


Figure 6. Cyclic voltammograms (100 mV/s) in DMF solutions at 25 °C with a glassy-carbon electrode: (a) 4.4 mM $[\text{Ni}(\text{pdmt})(\text{SPh})]^-$; (b) 2.2 mM $[\text{Ni}(\text{pdmt})]_2 + 2.2$ mM PhSSPh; (c) 2.2 mM PhSSPh. Peak, switching, and rest potentials are indicated.

Structures of $[\text{Ni}(\text{pdmt})(\text{SR})]^-$. The structures of **2** and **3** are set out in Figure 5, and selected metric parameters are listed in Table IV. The complexes are essentially square planar. The Ni atom deviates by 0.002 (**2**) and 0.029 (**3**) Å from the least-squares NiNS₃ planes. The chelate rings are slightly puckered, with the result that the coordination plane and the plane of the pyridyl group are disposed at dihedral angles of 14.4° (**2**) and 12.8° (**3**). The ethyl and phenyl groups are tilted toward atoms S(2) such that the torsional angles S(2)-Ni-S(3)-C(8) are 10.2° (**2**) and 9.3° (**3**). Steric interactions between thiolate phenyl and ethyl groups and atoms S(2) result in a distortion from a square arrangement whereby the angles S(2)-Ni-S(3) are larger, and S(1)-Ni-S(3) are smaller, than 90°. Similarly, the angles S(3)-Ni-N(1) show the larger deviations from 180°. The remaining angles in the structure more closely approach the ideal values for a square planar structure.

The Ni-S distances fall in the usual range of 2.16–2.21 Å for bond lengths between planar nickel(II) and terminal thiolates.^{1,30c,38,39} Similarly, the Ni-N distances are nearly identical with those in planar Ni(II) complexes containing pyridine ligands.⁴⁰ No structure of a complex containing the pdmt ligand has been reported previously.

Redox Reactions. The redox chemistry of complexes **2** and **3** has been investigated electrochemically. Initial cathodic scans of both complexes reveal minor occurrence of reaction 2, consistent with a small extent of disproportionation, the reverse of reaction

(38) Watson, A. D.; Rao, Ch. Pulla; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2820.

(39) Tremel, W.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 634.

(40) (a) Madaule-Aubry, F.; Busing, W. R.; Brown, G. M. *Acta Crystallogr.* **1968**, *B24*, 754. (b) Bose, N.; Lynton, H. *Can. J. Chem.* **1973**, *51*, 1952. (c) Morrison, R. M.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 238.

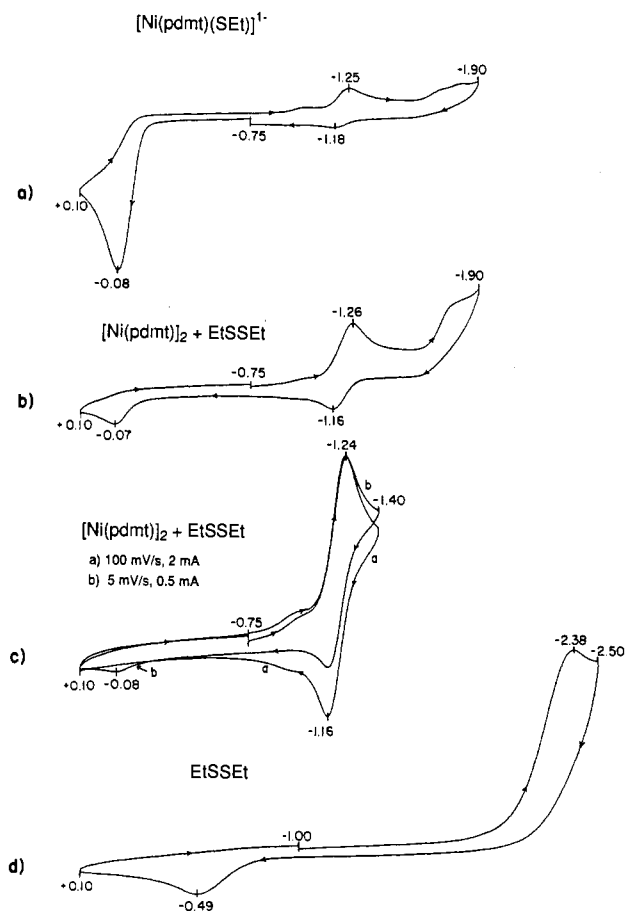
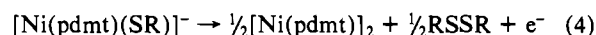


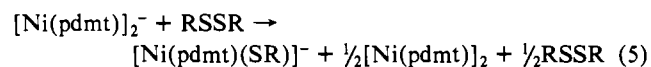
Figure 7. Cyclic voltammograms under the conditions of Figure 6: (a) 4.2 mM $[\text{Ni}(\text{pdmt})(\text{SEt})]^-$; (b) 2.2 mM $[\text{Ni}(\text{pdmt})_2] + 2.2$ mM EtSSEt; (c) solution from part b at 100 mV/s (trace a) and 5 mV/s (trace b) scan rates; (d) 2.2 mM EtSSEt.

3. The presence of free thiolate raises the possibility of its oxidation, and a rapid displacement of reaction 3 to the left, in certain of the reactions discussed below. Note from Figures 6c and 7d that, at a glassy-carbon electrode, irreversible oxidations of PhS^- and EtS^- , generated by reduction of the corresponding disulfides, occur at $E_{\text{pa}} = -0.20$ and -0.49 V, respectively. These were checked by oxidation of $(\text{Et}_4\text{N})(\text{SPh})$ (-0.19 V) and NaSEt (-0.54 V). Oxidation potentials are shifted in the positive direction at a Pt electrode; the behavior and potentials of PhSSPh at this electrode agree with earlier results.⁴¹

Cyclic voltammograms of complexes **2** and **3** at a glassy-carbon electrode in DMF solutions are presented in Figures 6a and 7a; scans were initiated at rest potentials of -0.50 (**2**) and -0.75 V (**3**). Initial anodic scans reveal irreversible oxidations at $E_{\text{pa}} = +0.01$ (**2**) and -0.08 V (**3**). Coulometric oxidation of **2** and **3** at $+0.20$ and $+0.12$ V, respectively, gave mean values of 0.98 and 1.00 e/Ni, respectively, from three experiments on each complex. Reverse scans reveal a feature at $E_{\text{pc}} = -1.25$ V in both cases. Consequently, the oxidative process is reaction 4, followed by



reaction 2 on the reverse scan. The unequal peak currents for this otherwise reversible reaction (Figure 1) are proposed to be a consequence of overall reaction 5, proceeding at a rate com-



petitive with electrochemical oxidation of I^- . In this involved

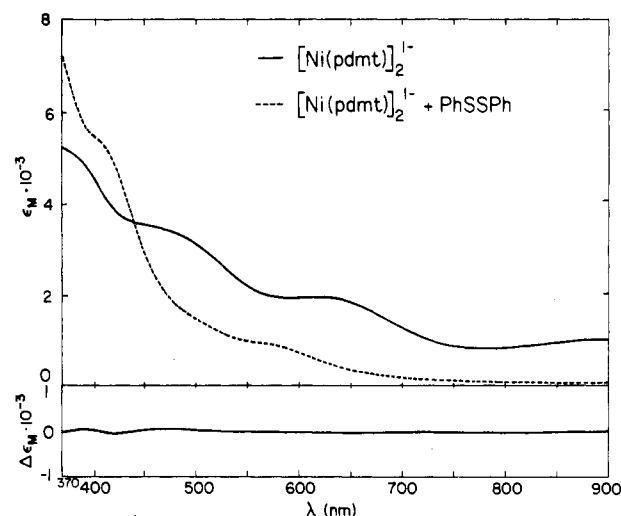


Figure 8. Absorption spectra of DMF solutions of electrochemically generated $[\text{Ni}(\text{pdmt})_2]^-$ and the reaction product of equimolar $[\text{Ni}(\text{pdmt})_2]^-$ and PhSSPh. The bottom panel contains the difference spectrum of the spectra of the reaction product and $[\text{Ni}(\text{pdmt})(\text{SPh})]^- + [\text{Ni}(\text{pdmt})_2]$ in a 2:1 mole ratio. (The molar extinction coefficients of the reaction product and the difference spectrum are based on the concentration of generated monoanion.)

process, complex **1**⁻ undergoes an oxidative addition with disulfide affording **2** or **3**, the half-dimer of **1**, and a thiyl radical of which the last two both dimerize to yield products. Note that the oxidative-addition step is equivalent to the demonstrated cleavage reaction 3. This reaction accounts for the failure to detect PhSSPh, whose reduction occurs in the potential region scanned.

When complexes **2** and **3** are examined at a Pt electrode, their irreversible oxidations occur at 0.00 and -0.09 V, respectively. That for **2** is indistinguishable from the oxidation of PhS^- at this electrode. Inasmuch as this situation is not observed for **2** at glassy carbon or for **3** at either electrode and the potentials of the complexes are not electrode-dependent, it seems likely that the process observed at Pt is oxidation of coordinated benzenethiolate. Neither complex shows a well-defined reduction to at least -2.0 V.

Reaction 5 is subject to additional verification. When an equimolar solution of **1** and PhSSPh is reduced (Figure 6b), there is no detectable reoxidation of I^- owing to its being rapidly scavenged by the disulfide. The situation is not improved by using a less negative switching potential (not shown). Related but somewhat different behavior is found with **1** and EtSSEt (Figure 7b,c). At 100 mV/s, the anodic current at $E_{\text{pa}} = -1.16$ V increases when the switching potential is decreased from -1.90 to -1.40 V. With the latter potential, decreasing the scan rate from 100 to 5 mV/s leads to a detectable quantity of **3** at $E_{\text{pa}} = -0.08$ V. These observations are consistent with competitive chemical and electrochemical oxidation of reduced dimer I^- . At the slower scan rate, the rate of reoxidation of I^- is insufficient to prevent formation of chemical product **3** in small amount. The much more negative reduction potential of EtSSEt (-2.4 V) accounts for the much slower reaction with I^- than in systems containing PhSSPh, whose reduction potential is -1.5 V.

Further independent demonstrations of reaction 5 are found in Figures 8 and 9. If this reaction is correctly described, the visible spectrum of the products should be the spectral composite of **2** or **3** and **1** in the mole ratio of 2:1. Complex I^- was electrochemically generated and treated with equimolar PhSSPh or EtSSEt. The final spectra are considerably different from the spectrum of I^- but are virtually identical with the computed spectral composites, as shown by the difference spectra. Finally, when an equimolar solution of **1** and EtSSEt was subjected to coulometric reduction at -1.40 V, 1.93 e/dimer (mean of four determinations) was absorbed. This result is consistent with the reverse of reaction 4, which is the pathway by which thiolate complexes are formed in reaction 5, but differs from it in being a two-electron process overall, such that all dimer is converted

(41) (a) Magno, F.; Bontempelli, G.; Pilloni, G. *J. Electroanal. Chem.* **1971**, *30*, 375. (b) Bradbury, J. R.; Masters, A. F.; McDonnell, A. C.; Brunette, A. A.; Bond, A. M.; Wedd, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1959.

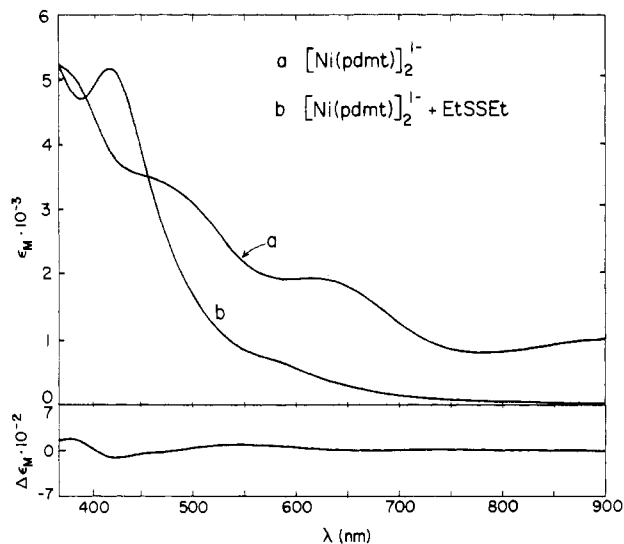


Figure 9. Absorption and difference spectra under the conditions of Figure 8 but with use of EtSSEt in producing the chemical reaction product with spectrum b.

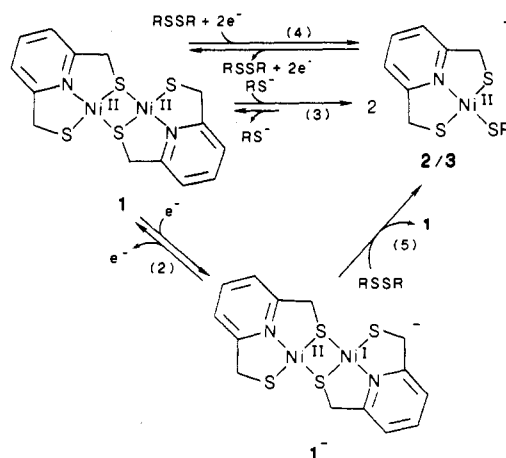
to product. In the corresponding PhSSPh system, 2.2–2.5 e/dimer were passed in multiple runs, presumably because of shifting of the disproportionation reaction due to reduction of **1** to **1**⁻.

In the reactions 4, the oxidized product is disulfide. Because we have no means of detecting the instantaneous oxidation product, the point is moot as to its containing, in the extreme, a coordinated thiyl radical or Ni(III). Several attempts were made to bias the oxidation in favor of the latter species. On the basis of the stabilization of higher oxidation states by hindered thiolates including 2,4,6-triisopropylbenzenethiolate,⁴² [Ni(pdmt)(tpbt)]⁻ was generated in DMF solution by reaction 3 and identified by its spectral similarity to **2**.⁴³ This complex has the electrochemical characteristics of **2** and is oxidized irreversibly at $E_{pa} = -0.02$ V (glassy-carbon electrode). It was also generated by reverse reaction 4 and oxidized, with the same result. Under the same conditions, the free thiolate is oxidized at $E_{pa} = -0.10$ V. Ligand-based oxidation is not prevented in this case. We have not taken this approach further in view of the observation that immensely hindered 2,4,6-triadamantylbenzenethiol can be oxidized to its disulfide.⁴⁴

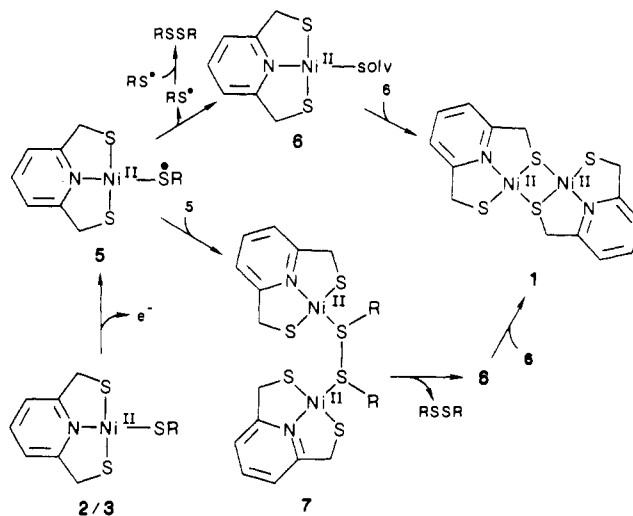
In a related experiment, the rigid bidentate ligand 8-quinolinethiolate was employed as a potential means of preventing release from the metal center of any thiyl radical produced in oxidation. [Ni(pdmt)(qt)]⁻ was generated in DMF and acetonitrile solutions⁴³ by the two reactions used for the preceding complex. Potentials for irreversible oxidation varied from -0.12 to -0.26 V, depending on solvent and electrode. The lack of metal-centered oxidation is consistent with the previous result that Ni(qt)₂ undergoes ligand-based oxidation to disulfide at $E_{pa} \approx +0.5$ V.¹⁸ The far more positive potential than for complexes of the [Ni(pdmt)(SR)]⁻ type is a reflection of overall negative charge and chelate ring stability. Indeed, dimer **1** exhibits an irreversible ligand oxidation at $E_{pa} = +0.56$ V.

Summary. Reactions 2–5 are summarized in the form of Scheme I. Plausible pathways for the irreversible oxidation of [Ni(pdmt)(SR)]⁻ complexes in reaction 4 are set out in Scheme II. The products of the oxidation implicate a coordinated thiyl radical complex **5**, which may react in several ways. Loss of the coordinated radical affords disulfide and solvated monomer **6**. Each of these recombines with another radical or monomer to yield disulfide and dimer **1**. Alternatively, two radical complexes **5** may

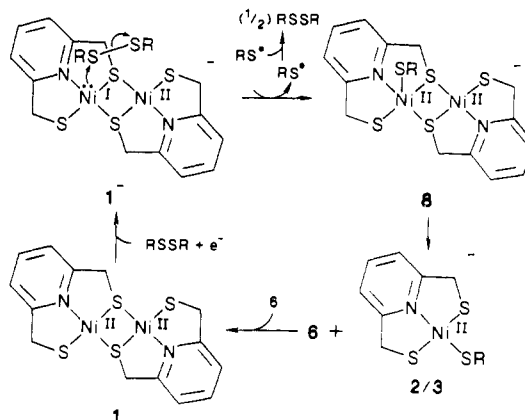
Scheme I



Scheme II



Scheme III



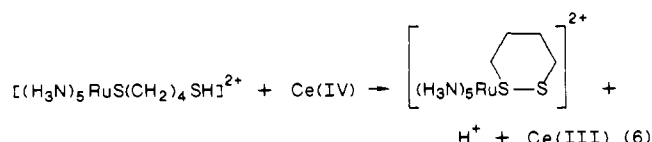
dimerize to form the dimeric disulfide complex **7**. Dissociation of RSSR and recombination of **6** generates products.⁴⁵ Coordinated thiyl radical complexes have been implicated in oxidations of thiols or thiolates by metals,^{46–49} but no such intermediate has

(42) (a) Millar, M.; Koch, S. A.; Fikar, R. *Inorg. Chim. Acta* **1984**, *88*, L15. (b) Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311.
 (43) Spectra of complexes generated in solution: for [Ni(pdmt)(tpbt)]⁻, $\lambda_{max} = 311$ (13.6), 406 (sh, 4.48), 570 (sh, 1) nm; for [Ni(pdmt)(qt)]⁻, $\lambda_{max} = 307$ (sh, 12.5), 380 (4.02), 540 (sh, 1) nm. Relative intensities are given in parentheses.
 (44) Rundel, W. *Chem. Ber.* **1969**, *102*, 1649.

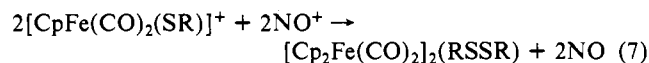
(45) A third pathway (not shown) involves nucleophilic attack of thiolate in **2/3** at the radical site in **5** to give a dimeric disulfide-bridged Ni(II)/Ni(I) complex, which is oxidized to **7**; this species passes to products as described. This pathway involves more steps than the two above and is otherwise discounted because of the intermediacy of Ni(I) in an oxidation process.

(46) (a) Wechsler, C. J.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1974**, *13*, 2360. (b) Woods, M.; Sullivan, J. C.; Deutsch, E. *J. Chem. Soc., Chem. Commun.* **1975**, 749. (c) Woods, M.; Karbwang, J.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1976**, *15*, 1678.

been clearly detected. Two observations, among the many made, are particularly pertinent to Scheme II. Reaction 6, by Stein and



Taube,⁴⁷ is difficult to rationalize without development of radical character on the coordinated sulfur atom. Likewise, reaction 7,



by Treichel et al.,⁴⁸ requires a coordinated radical and provides a particularly clear case of the coupling of radical species to afford a binuclear disulfide-bridged product.

The proposed pathway for reaction 5 is presented in Scheme III. In an oxidative-addition process, the nucleophilic Ni(I) center in reduced dimer **1**⁻ attacks disulfide with release of a thyl radical and association of thiolate with Ni(II). Thereafter, cleavage reaction 3 occurs to generate **2/3** and solvated monomer **6** which, as in Scheme II, combines with another to yield dimer **1**. While we are unaware of any prior examples of disulfide cleavage by Ni(I), the reaction is analogous to that with alkyl halides, where the immediate products are Ni^{II}-X (or Ni(II) + X⁻) and R[•].^{50,51}

On the basis of this investigation and related observations, the ligand-based oxidation of classical nickel(II) thiolate complexes with irreversible formation of disulfide is a pervasive process that extends to unidentate thiolates, as in [Ni(pdmt)(SR)]⁻ and [Ni(SR)₄]²⁻,^{3,4} and chelating mono- and dithiolates, as in **1**, Ni(qt)₂,¹⁸ and complexes of ethane-1,2-dithiolate.^{1,3} The nickel dithiolenes represent a special case and, as a class, are an exception. Oxidized species of the type [Ni(S₂C₂R₂)₂]⁻ do have Ni(III) character (EPR criteria¹³), but the odd electron is extensively delocalized over the unsaturated ligands. The vast majority of

Ni(III) complexes have oxygen and/or nitrogen ligand sets^{8,52} that, relative to thiolate sulfur, minimize the possibility of autoreduction. In virtually all synthetic nickel thiolates, this difficulty is not avoided. Autoreduction in Ni(III) sites of hydrogenases may be thwarted by the inability of a putative thyl radical to couple with another owing to protein structural constraints. If so, this situation would appear to be similar to that in blue Cu proteins such as plastocyanin, where protein folding dictates metal site structure⁵³ and presumably prevents autoreduction of Cu(II) by coordinated cysteinate. Additionally, protein constraints prevent formation of polynuclear nickel thiolate species, stable examples of which have been characterized.^{1,3,14,15,38,39} Prevention of the autoredox reaction in model complexes by steric blockage is a formidable task in ligand design and synthesis.

While this study did not afford any identifiable Ni(III) thiolates, it does provide well-documented examples of ligand-based oxidation and provides direction to ongoing work intended to stabilize Ni(III) in coordination units containing one or more thiolates. The following guidelines are suggested: use of a relatively rigid multidentate ligand that stabilizes tetragonal stereochemistry, affords a net negative charge for the complex in the Ni(II) state, and contains a complement of polarizable anionic donor sites sufficient to place Ni(II) in an electron-rich condition but insufficient to cause autoreduction in the Ni(III) state. All factors will tend to lower the Ni(III)/Ni(II) potential. One solution to this problem has been obtained by employment of a tetradentate amide thiolate ligand that affords a potential of -0.035 V.² Other approaches to the stabilization of Ni(III) in a (partly) anionic sulfur environment are in progress, and the results will be the subjects of future reports.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 85-21365. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank Y.-P. Zhang for experimental assistance.

Supplementary Material Available: Crystallographic data for compounds **2** and **3** including a summary of the crystal data and intensity collection and refinement parameters and tables of interatomic distances and angles, anisotropic temperature factors, and calculated hydrogen atom positions (7 pages); tables of calculated and observed structural factors (36 pages). Ordering information is given on any current masthead page.

- (47) Stein, C. A.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2212.
 (48) (a) Treichel, P. M.; Rosenhein, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 691. (b) Treichel, P. M.; Rosenhein, L. D.; Schmidt, M. S. *Inorg. Chem.* **1983**, *22*, 3960.
 (49) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.
 (50) (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713, 719, 5353. (b) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.
 (51) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 3082 and references therein.

- (52) Kimura, E. *J. Coord. Chem.* **1986**, *15*, 1.
 (53) (a) Guss, J. M.; Freeman, H. C. *J. Mol. Biol.* **1983**, *169*, 521. (b) Church, W. B.; Guss, J. M.; Potter, J. J.; Freeman, H. C. *J. Biol. Chem.* **1986**, *261*, 234.