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Structural Investigations of Nickel Complexes with Nitrogen and Sulfur Donor Ligands

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The synthesis of five novel Ni(II) complexes with N donor and/or thiolate S donor ligands and the structure of each compound are reported. Reaction of dichloro[tris(2-aminoethyl)amine]nickel(II), [Ni(tren)Cl_2], with sodium maleonitriledithiolate, Na_2(mnt), yields a salt composed of the novel complex cation bis[tris(2-aminoethyl)amine]nickel(2+), $[Ni(tren)_2]^{2+}$, and bis(maleonitriledithiolato)nickelate(2−), $[Ni(mnt)_2]^{2-}$. Crystals of a DMF disolvate of this salt, **1**·2DMF, crystallize in monoclinic space group $P2_1/n$ with cell dimensions $a = 13.086$ (2) Å, $b = 11.260$ (3) Å, $c = 14.083$ (2) Å, $\beta = 106.69$ (1)°, $V = 1988$ (1) Å^3, and $Z = 2$. The cation contains two tridentate tren ligands in a facial arrangement. The anion is the familiar planar Ni(II) complex with four S donor atoms. An independent synthesis of bis[tris(2-aminoethyl)amine]nickel(2+) tetrafluoroborate, $[Ni(tren)_2](BF_4)_2$ (**2**), confirms that the structure of the cation is not dependent on the anion in any way, and allows the electronic absorption spectroscopy of the cation to be examined in detail. Crystals of **2** form in the triclinic space group $P\bar{1}$ with cell dimensions $a = 7.909$ (1) Å, $b = 8.788$ (1) Å, $c = 8.919$ (1) Å, $\alpha = 108.45$ (1)°, $\beta = 96.32$ (1)°, $\gamma = 104.03$ (1)°, $V = 558.6$ (3) Å^3, and $Z = 1$. The structure of the cation in **2** is essentially the same as was found in **1**·2DMF. Reaction of chloro[tris(2-(dimethylamino)ethyl)amine]nickel(II) chloride, [Ni(Me_6tren)Cl]Cl, with tetraethylammonium (*p*-chlorothio)phenolate leads to a salt containing two $[Ni(Me_6tren)Cl]^+$ cations and a dimeric anion, tetrakis(*p*-chlorothiophenolato)bis(μ-*p*-chlorothiophenolato)dinickelate, $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$. Crystals of a diacetonitrile solvate, **3**·2CH_3CN, form in the triclinic space group $P\bar{1}$ with cell dimensions $a = 11.778$ (4) Å, $b = 13.799$ (3) Å, $c = 14.774$ (3) Å, $\alpha = 65.65$ (2)°, $\beta = 77.86$ (2)°, $\gamma = 64.94$ (2)°, $V = 1979.8$ (9) Å^3, and $Z = 1$. The dianion is the first example of an arenethiolate complex with essentially planar Ni coordination geometry. The cation has approximate trigonal-bipyramidal geometry with an axial chloride ligand. The factors involved in stabilizing this structure are discussed. In solution, the planar structure persists and is not easily converted to the known tetrahedral $[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]^{2-}$ anion upon addition of more thiolate ligand. However, addition of methanol to solutions of the tetrahedral anion will convert it to the diamagnetic, planar, dimeric anion in **3**. Cyclic voltammetric studies of the dianion reveal two irreversible oxidations with anodic peak potentials near the Fc/Fc$^+$ couple. When the ligand bis(2-mercaptoethyl)(2-(methylthio)ethyl)amine (NS_2SMe) is reacted with anhydrous nickel(II) acetate in methanol, a neutral dimeric complex, $[Ni(NS_2SMe)]_2$ (**4**), is obtained. Crystals of **4** from DMF/methanol solution form in the monoclinic space group $C2/c$ with cell dimensions $a = 32.391$ (9) Å, $b = 8.473$ (3) Å, $c = 16.500$ (4) Å, $\beta = 107.17$ (2)°, $V = 4327$ (4) Å^3, and $Z = 8$. The structure is best described as containing two planar Ni(II) centers in NS_3 coordination environments that share an edge formed by two bridging thiolates. The molecule is folded along the shared edge, and each Ni(NS_3) unit has an unbound arm containing the thioether. This structure is compared with a number of other dimeric Ni complexes with similar structures. Evidence is presented that supports an analogous structure (with a pendant thiol) for the dimeric complex formed with the trithiol ligand tris(2-mercaptoethyl)amine. A monomeric complex, **5**, is obtained from the reaction of the ligand *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine with 1 equiv of Ni(OAc)$_2$·4H_2O in methanol. Crystals of **5** were obtained that formed in monoclinic space group $P2_1/n$ with cell dimensions $a = 8.865$ (1) Å, $b = 12.172$ (2) Å, $c = 11.729$ (2) Å, $\beta = 103.71$ (1)°, $V = 1229.6$ (6) Å^3, and $Z = 4$. The neutral complex is best described as containing planar Ni(N_2S_2) units with cis geometry. Two of these monomeric units react with additional Ni(II) ions to form a trinuclear species. Cyclic voltammetric studies of **5** reveal an irreversible oxidation with $E_{p_a} = -25$ mV (vs Fc/Fc$^+$). This oxidation is not observed in the trinuclear complex, which instead exhibits a pseudoreversible reduction ($E_{1/2} = -1110$ mV).

The recent identification of redox-active Ni complexes with S donor ligands in many hydrogenases (H_2ases)[1] and carbon monoxide dehydrogenases[2] has stimulated interest in the chemistry of nickel thiolates. In the case of H_2ases, the Ni is believed to be in a five- or six-coordinate environment,[3] and ligation by a N donor ligand has also been detected.[4] With the notable exception of distorted tetrahedral arenethiolate complexes, Ni(SAr)$_4$,[5] nickel thiolates are generally planar, four-coordinate species with a tendency to form dimers,[6] trimers,[6a-c,7] tetramers,[8] and higher polymers[8a,9] involving bridging thiolates and resulting in compounds consisting of edge-sharing planar NiS_4 units. The same tendency is known to occur in cases involving mixed N, O, and S ligation,[10] and few five- or six-coordinate complexes with any degree of thiolate ligation have been characterized.[11] The results presented here detail reactions leading to four novel Ni complexes. The structures of these compounds illustrate the interplay of the established trends in nickel thiolate chemistry and the structural diversity that can result. The structures described herein include the description of a Ni(II) complex with *tridentate* tren ligands,

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the first example of an arenethiolate complex with *planar* Ni coordination geometry ($[Ni(S\text{-}p\text{-}C_6H_4Cl)_3]_2^{2-}$), the structure of a dimer that possesses unusual redox properties,[12] and the structure of a monomeric $Ni(N_2S_2)$ complex with cis geometry.

Experimental Section

Preparation of Compounds. All solvents were dried by using conventional methods and distilled and stored under N_2 atmosphere. Although none of the isolated compounds are air-sensitive in the solid state, all synthetic procedures involving manipulations of solutions were carried out under an N_2 atmosphere by using standard Schlenk techniques. Practical grade (>97%) tris(2-aminoethyl)amine (tren) was obtained from Fluka and used without further purification. Other starting materials, $[Ni(H_2O)_6]Cl_2$, $[Ni(H_2O)_6](BF_4)_2$, $Ni(OAc)_2\cdot 4H_2O$, and 4-chlorothiophenol (HS-*p*-C_6H_4Cl), were of reagent grade and used without further purification. Anhydrous $Ni(OAc)_2$ was prepared by heating samples of the tetrahydrate at 100 °C over P_4O_{10} in vacuo overnight. The ligands tris(2-(dimethylamino)ethyl)amine (Me_6tren),[13] bis(2-mercaptoethyl)(2-(methylthio)ethyl)amine (NS_2SMe),[14] tris(2-mercaptoethyl)amine (NS_3),[15] *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine (N_2S_2),[16] Et_4N(S-*p*-C_6H_4Cl),[5c] and sodium maleonitriledithiolate (Na_2mnt)[17] were prepared by literature methods. The Et_4N(S-*p*-C_6H_4Cl) was further purified by recrystallization from acetonitrile and ether. The Ni(II) complexes $[Ni(tren)Cl_2]$[18] and $[Ni(Me_6tren)Cl]Cl$[13] were also prepared according to literature procedures.

$[Ni(tren)_2][Ni(mnt)_2]\cdot 2DMF$ (1·2DMF). A solution of $[Ni(tren)Cl_2]$ (1.94 g, 7.0 mmol) in 20 mL of methanol was added to a solution of Na_2mnt (2.62 g, 14.1 mmol) in 55 mL of methanol. An orange microcrystalline solid formed. The mixture was stored at −20 °C overnight and then filtered, yielding 0.66 g (11%) of crude product. Polyfaceted red-orange crystals that were used in the X-ray structure determination were produced by dissolving 100 mg of the crude product in DMF (10 mL) and allowing a layer of 10 mL of ethanol to slowly diffuse into the solution. The product was filtered, washed several times with ethanol, and dried by passing dry N_2 over the sample. (Drying in vacuo causes decrepitation of the crystals.) Yield = 50 mg. Anal. Calcd for $C_{26}H_{50}N_{14}O_2S_4Ni_2$: C, 37.34; H, 6.03; N, 23.44. Found: C, 37.36; H, 6.04; N, 23.43. IR (cm^{-1}): 3297 m (ν_{NH}), 3118 m (ν_{NH}), 2208 s (ν_{CN}), 1663 vs ($\nu_{C=C}$), 1583 m (δ_{NH}), 1495 m, 1150 m, 1103 m, 1065 m, 912 m, 662 m, 505 m.

$[Ni(tren)_2](BF_4)_2$ (2). The synthesis of this compound does not involve thiolates and was carried out entirely in air. To a filtered solution of $[Ni(H_2O)_6](BF_4)_2$ (5.0 g, 15 mmol) in absolute EtOH was added tren (4.4 mL, 30 mmol), dissolved in 95 mL of absolute EtOH, with stirring. A purple precipitate formed immediately. The mixture was heated to boiling, and 25.5 mL of water was added to dissolve the compound. When the mixture was cooled to room temperature, a mixture of blue and violet crystals were isolated by suction filtration. Yield = 4.25 g. The crude product was dissolved in boiling acetonitrile (500 mL) containing 1 mL of tren and filtered. When the solution was cooled to room temperature, well-formed purple crystals of **2** with rhomboidal faces were isolated by suction filtration, washed several times with absolute EtOH, and dried by passing air through the sample. Yield = 2.41 g (31%). These crystals were used for the X-ray structure determination. A sample submitted for elemental analysis was further dried over P_4O_{10} in vacuo. Anal. Calcd for $C_{12}H_{36}N_8B_2F_8Ni$: C, 27.46; H, 6.91; N, 21.35. Found: C, 27.46; H, 6.83; N, 21.29. UV–vis (0.1 M tren/H_2O), λ_{max} in nm (ϵ in cm^{-1} M^{-1}): 885 (3.6), 800 (sh), 540 (3.7), 344 (16). IR (cm^{-1}): 3387 m (ν_{NH}), 3348 s (ν_{NH}), 3308 m (ν_{NH}), 3136 s (ν_{NH}), 1602 s (δ_{NH}), 1290 m, 1060 vs (br, BF_4^-), 915 m, 885 m, 797 w, 615 m, 516 m, 439 m. Magnetic susceptibility: μ = 3.35 μ_B at 20 °C.

$[Ni(Me_6tren)Cl]_2[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]\cdot 2CH_3CN$ (3·2CH_3CN). A solution of Et_4N(S-*p*-C_6H_4Cl) (273 mg, 1.0 mmol) in acetonitrile (5 mL) was added slowly, dropwise with rapid stirring to a solution of $[Ni(Me_6tren)Cl]Cl$ (361 mg, 1.0 mmol) in acetonitrile (10 mL) resulting in a dark red-brown solution. When this solution was allowed to stand overnight at 5 °C, large black (dark brick-red) crystals of **3**·2CH_3CN formed. These crystals were collected by filtration, dried in vacuo, and used without further purification for the X-ray structure determination. Yield = 182 mg (67% based on $^-$S-*p*-C_6H_4Cl content). A sample for microanalysis was dried overnight over P_4O_{10} in vacuo. Anal. Calcd for $C_{60}H_{84}N_8S_6Cl_8Ni_4$: C, 44.26; H, 5.20; N, 6.88. Found: C, 44.21; H, 5.23; N, 7.17. UV–vis (CH_3CN), λ_{max} in nm (ϵ in cm^{-1} M^{-1}): 335 (sh), 480 (5460). IR (cm^{-1}): 1561 w($\nu_{C=C}$), 1283 m, 1087 s, 1007 m, 935 w, 808 m, 775 m, 735 w, 535 m, 487 m. Magnetic susceptibility: μ = 4.53 μ_B at 21 °C. ^1H NMR (CD_3CN): $[Ni(Me_6tren)Cl]^+$, δ = 89; $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$, δ = 7.57 (m, 12 H), δ = 6.85 (m, 12 H).

$[Ni(NS_2SMe)]_2$ (4). The free ligand (100 mg, 0.47 mmol) was dissolved in methanol (10 mL) and cooled to 5 °C in an ice bath. Anhydrous $Ni(OAc)_2$ (84 mg, 0.47 mmol) was dissolved in methanol (10 mL) and added dropwise to the rapidly stirring ligand solution. The red-black microcrystalline solid that formed immediately was collected by filtration, washed several times with small amounts of methanol, and dried in vacuo. Yield = 160 mg (65%). Anal. Calcd for $C_{14}H_{30}N_2S_6Ni_2$: C, 31.36; H, 5.64; N, 5.22. Found: C, 31.34; H, 5.03; N, 5.19. UV–vis (CH_2Cl_2), λ_{max} in nm (ϵ in cm^{-1} M^{-1}) 547 (705), 440 (970), 384 (sh). IR (cm^{-1}): 1295 w, 1258 w, 1017 m, 968 w, 740 m, 571 m.

Crystals used in the X-ray structure determination were obtained from a solution of **4** (100 mg) in DMF (5 mL) and methanol (5 mL) upon cooling at −22 °C for 3 days.

$[Ni(NS_3)]_2$. This compound is prepared from the trithiol ligand, tris(2-mercaptoethyl)amine, using a procedure analogous to that used to prepare **4**. The ligand (0.66 g, 3.3 mmol) was dissolved in methanol (15 mL), and a solution of $Ni(OAc)_2\cdot 4H_2O$ (0.82 g, 3.3 mmol) in methanol (15 ml) was added dropwise. The red-brown microcrystalline product formed and was stirred for 0.5 h before collection by filtration. The product was washed with methanol (2 × 5 mL) and dried under vacuum. Yield = 0.75 g, 90%. Anal. Calcd for $C_{12}H_{26}N_2S_6Ni_2$: C, 28.37; H, 5.16; N, 5.51. Found: C, 29.35; H, 5.44; N, 5.52. IR (cm^{-1}): 2475 w (ν_{S-H}), 1304 m, 1274 w, 1249 w, 1216 m, 1200 w, 1097 w, 1066 w, 1047 m, 938 s, 918 m, 670 w, 663 w, 577 w.

$Ni(N_2S_2)$ (5). A solution of $Ni(OAc)_2\cdot 4H_2O$ (250 mg, 1.0 mmol) was prepared in 50% ethanol/methanol (20 mL) by gently warming the mixture. This solution was added to a solution of the ligand (222 mg, 1.0 mmol) in ethanol (5 mL), resulting in the formation of a red-brown solution. The volume of the solution was reduced to ca. 8 mL under vacuum, ether (10 mL) was added, and the mixture was stored at −20 °C overnight. Dark brown laths of **5** that were used in the X-ray structure determination formed and were isolated by filtration, washed with ether, and dried in vacuo. Yield = 100 mg (37%). Anal. Calcd for $C_9H_{20}N_2S_2Ni$: C, 38.73; H, 7.22; N, 10.04. Found: C, 38.89; H, 7.02; N, 10.03. UV–vis (CH_3OH), λ_{max} in nm (ϵ in cm^{-1} M^{-1}): 472 (122), 365 (sh). IR (cm^{-1}): 1304 m, 1245 w, 1190 m, 1150 m, 1057 m, 1024 m, 994 m, 972 m, 939 w, 912 w, 782 s, 751 s, 720 s, 501 m, 448 m.

$\{[Ni(N_2S_2)]_2Ni\}(BF_4)_2$. Crystals of the trinuclear complex were obtained by mixing a solution of $[NiH_2O)_6](BF_4)_2$ (102 mg, 0.3 mmol) in 20 mL of MeOH with a solution of **5** (168 mg, 0.6 mmol) in EtOH. Upon addition of 15 mL of Et_2O, 120 mg (51%) of black (dark green) crystals of $[Ni_3(N_2S_2)](BF_4)_2$ were isolated by filtration, washed with Et_2O, and air-dried. A sample for elemental analysis was further dried in vacuum over P_4O_{10} overnight. Anal. Calcd for $C_{18}H_{40}N_4S_4B_2F_8Ni_3$: C, 27.35; H, 5.10; N, 7.09. Found: C, 27.31; H, 5.25; N, 6.61. UV–vis (CH_3CN), λ_{max} in nm (ϵ in cm^{-1} M^{-1}): 610 (sh), 502 (2100), 423 (6900), 313 (18 100). IR (cm^{-1}): 1312 m, 1195 m, 1065 vs (BF_4^-), 782 m, 750 m, 725 m, 522 m (BF_4^-).

Physical Measurements. Electronic absorption spectra were obtained by using an OLIS 4300 Cary-14 system. Infrared spectra were taken as Nujol mulls between KBr plates on a Perkin-Elmer 783 IR spectrophotometer and calibrated with polystyrene. Relative intensities of the bands in a spectrum are indicated (w = weak, m = medium, s = strong, vs = very strong), and assignments are indicated when they can be made with confidence. ^1H-NMR spectra were obtained on a Varian XL-200 instrument and are referenced to external TMS. Magnetic measurements were made at ambient temperature by using a Johnson Matthey susceptibility balance and are uncorrected for diamagnetic contributions (error ±2%). Cyclic voltammetric measurements were made by using a BAS-100 electrochemical analyzer on ca. 1 mM solutions of complexes in a 0.1 M $Bu_4N(ClO_4)$ in CH_3CN solution at room temperature by using a Pt-button working electrode, a Pt-wire auxiliary electrode, and a Ag-wire pseudoreference electrode. Potentials were obtained at a sweep rate of 250 mV/s and referenced to internal ferrocene/ferrocenium, which for conversion purposes has a potential of ca. +400 mV vs. NHE. Microanalyses were performed by the University of Massachusetts Microanalysis Laboratory.

X-ray Structure Determinations. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\bar{\alpha})$ = 0.710 73 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental

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Table I. Crystallographic Data for Compounds 1–5

	1·2DMF	**2**	**3**·2CH$_3$CN	**4**	**5**
formula	$C_{26}H_{50}O_2N_{14}S_4Ni_2$	$C_{12}H_{36}N_8F_8B_2Ni$	$C_{64}H_{90}N_{10}S_6Cl_8Ni_4$	$C_{14}H_{30}N_2S_6Ni_2$	$C_9H_{20}S_2N_2Ni$
fw	836.46	524.79	1710.34	536.22	279.11
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a, Å	13.086 (2)	7.909 (1)	11.778 (4)	32.391 (9)	8.865 (1)
b, Å	11.260 (3)	8.788 (1)	13.799 (3)	8.473 (3)	12.172 (2)
c, Å	14.083 (2)	8.919 (1)	14.774 (3)	16.500 (4)	11.729 (2)
α, deg		108.45 (1)	65.65 (2)		
β, deg	106.69 (1)	96.32 (1)	77.86 (2)	107.17 (2)	103.71 (1)
γ, deg		104.03 (1)	64.94 (2)		
V, Å^3	1988 (1)	558.6 (3)	1979.8 (9)	4327 (4)	1229.6 (6)
Z	2	1	1	8	4
D_{calc}, g/cm^3	1.397	1.560	1.434	1.646	1.508
μ, cm^{-1}	11.958	9.512	14.091	23.122	18.8
relative trans coeff	0.8708–0.9989	0.8673–0.9993	0.8770–0.9987	0.8439–0.9989	0.9327–0.9986
$R(F)$	0.044	0.043	0.043	0.059	0.028
$R_w(F)$	0.064	0.068	0.058	0.074	0.036

Table II. Selected Atomic Coordinates in Crystalline [Ni(tren)$_2$](BF$_4$)$_2$ (**2**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
Ni	0.0000	0.0000	0.0000	2.582 (9)
N1	−0.1075 (3)	0.1359 (3)	0.1966 (3)	3.21 (5)
N2	−0.0983 (4)	−0.2004 (3)	0.0852 (3)	3.72 (5)
N3	0.2363 (3)	0.1004 (3)	0.1820 (3)	3.54 (5)
N4	−0.4397 (4)	0.3769 (3)	0.1771 (4)	4.80 (7)
C1	−0.1953 (5)	0.0164 (4)	0.2715 (4)	5.71 (8)
C2	−0.2134 (7)	−0.1531 (5)	0.1925 (5)	8.7 (1)
C3	0.0490 (4)	0.2659 (4)	0.3124 (4)	3.99 (7)
C4	0.2029 (5)	0.1972 (5)	0.3391 (4)	4.40 (8)
C5	−0.2314 (4)	0.2132 (4)	0.1369 (4)	4.18 (7)
C6	−0.2927 (5)	0.3429 (4)	0.2616 (4)	4.65 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

procedures have been described previously.[19]

Crystals were mounted in thin-walled glass capillaries that were sealed as a precaution against moisture/air sensitivity. Data were collected by using the θ–2θ scan mode. Empirical absorption corrections based on ψ scans were applied.

The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares techniques.[20]

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.

1·2DMF. The wedge-shaped crystal used for the study was cut to approximate dimensions of 0.33 × 0.45 × 0.50 mm. A total of 3492 independent reflections ($+h,+k,\pm l$; $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 50°$) were measured. The 20 independent non-hydrogen atoms comprising the two nickel species were refined anisotropically. The DMF of solvation is disordered with unique positions for the oxygen and nitrogen atoms but with two sets of positions for the three independent carbon atoms, which were refined as six atoms in half-occupancy. All non-hydrogen atoms of the disordered solvent were refined isotropically. Sixteen of the eighteen independent hydrogen atoms of the cation were included in the refinement as fixed isotropic scatterers in ideal positions. Hydrogen atoms of the dangling amino group and all DMF hydrogen atoms were omitted from the refinement. The final agreement factors[21] (Table I) were based on the 2230 reflections having $I \geq 3\sigma_I$.

2. The crystal used for the study had dimensions of 0.35 × 0.35 × 0.50 mm. A total of 1971 independent reflections ($+h,\pm k,\pm l$; $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 50°$) were measured. The 16 independent nonhydrogen atoms were refined anisotropically. The 18 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers with ideal positions (C–H) or difference Fourier positions (N–H). The final refinement was based on the 1902 reflections with $I \geq 3\sigma_I$. Selected atomic positions are given in Table II.

3·2CH$_3$CN. Large coal-like, black, partially faceted crystals of **3** diffract poorly. The crystal used for the study was cut to dimensions of 0.25 × 0.35 × 0.50 mm. A total of 4259 independent reflections ($+h,\pm k,\pm l$; $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$) was measured. Large isotropic thermal parameters for many of the carbon atoms of the cation suggested disorder in this species, but only one set of positions for the atoms in question could be resolved. The 46 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the anion and those hydrogen atoms of the cation bonded to carbon atoms C1, C5, and C9 (18 H atoms) were included as fixed isotropic scatterers in ideal positions. The remaining 24 independent H atoms were omitted from the refinement. The final refinement was based on the 3457 reflections having $I \geq 3\sigma_I$. Selected atomic positions are given in Table III.

Table III. Selected Atomic Coordinates in Crystalline [Ni(Me$_6$tren)Cl]$_2$[Ni$_2$(S-*p*-C$_6$H$_4$Cl)$_6$]·2CH$_3$CN (**3**·2CH$_3$CN)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
Ni1	0.01405 (6)	0.11618 (5)	−0.00761 (4)	3.88 (2)
Ni2	0.02700 (6)	−0.33704 (5)	0.65105 (4)	4.08 (2)
S1	0.1375 (1)	−0.0646 (1)	0.01515 (9)	4.07 (3)
S2	−0.1073 (1)	0.2990 (1)	−0.0424 (1)	5.16 (4)
S3	0.1630 (1)	0.1607 (1)	0.0160 (1)	5.40 (4)
N1	0.1104 (4)	−0.2345 (4)	0.6663 (4)	6.2 (1)
N2	0.0353 (5)	−0.4116 (4)	0.8059 (3)	5.8 (1)
N3	−0.1681 (4)	−0.2835 (4)	0.6776 (4)	6.6 (2)
N4	0.1263 (4)	−0.5140 (3)	0.6616 (3)	5.5 (1)
C1	0.1061 (7)	−0.3647 (5)	0.8381 (5)	9.4 (2)
C2	0.1080 (8)	−0.2553 (7)	0.7688 (6)	15.6 (3)
C3	0.0487 (9)	−0.1098 (6)	0.6154 (9)	13.9 (4)
C4	0.2371 (7)	−0.2640 (7)	0.6198 (6)	10.6 (3)
C5	−0.0977 (8)	−0.3809 (8)	0.8458 (5)	10.3 (3)
C6	−0.1895 (8)	−0.340 (1)	0.7854 (7)	16.4 (6)
C7	−0.2274 (6)	−0.3215 (6)	0.6281 (6)	9.2 (2)
C8	−0.2269 (7)	−0.1587 (6)	0.6475 (6)	9.5 (3)
C9	0.1037 (7)	−0.5371 (5)	0.8342 (5)	7.6 (2)
C10	0.167 (1)	−0.5773 (7)	0.7607 (5)	17.7 (6)
C11	0.2376 (8)	−0.5282 (7)	0.5957 (7)	12.5 (4)
C12	0.0513 (8)	−0.5671 (6)	0.6464 (7)	14.6 (3)
C21	−0.2119 (5)	0.3519 (4)	−0.1360 (4)	4.0 (1)
C22	−0.3272 (5)	0.4386 (4)	−0.1363 (4)	4.9 (2)
C23	−0.4072 (5)	0.4904 (4)	−0.2132 (4)	5.2 (2)
C24	−0.3709 (5)	0.4546 (4)	−0.2922 (4)	5.1 (2)
C25	−0.2588 (5)	0.3686 (4)	−0.2954 (4)	4.7 (2)
C26	−0.1796 (5)	0.3169 (4)	−0.2175 (3)	4.4 (1)
C31	0.2487 (5)	0.0527 (4)	0.1212 (4)	4.5 (1)
C32	0.3681 (5)	0.0455 (4)	0.1302 (4)	5.5 (2)
C33	0.4345 (5)	−0.0315 (5)	0.2145 (4)	6.1 (2)
C34	0.3826 (6)	−0.1009 (4)	0.2903 (4)	6.1 (2)
C35	0.2666 (6)	−0.0957 (4)	0.2843 (4)	5.7 (2)
C36	0.1991 (5)	−0.0182 (4)	0.2001 (3)	4.7 (1)
C41	0.2113 (4)	−0.0591 (4)	−0.1046 (3)	4.1 (1)
C42	0.1724 (5)	0.0376 (4)	−0.1903 (4)	5.4 (2)
C43	0.2320 (6)	0.0367 (5)	−0.2817 (4)	6.3 (2)
C44	0.3313 (5)	−0.0578 (5)	−0.2867 (4)	5.3 (2)
C45	0.3741 (5)	−0.1541 (5)	−0.2048 (4)	5.8 (2)
C46	0.3122 (5)	−0.1558 (4)	−0.1120 (4)	5.1 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

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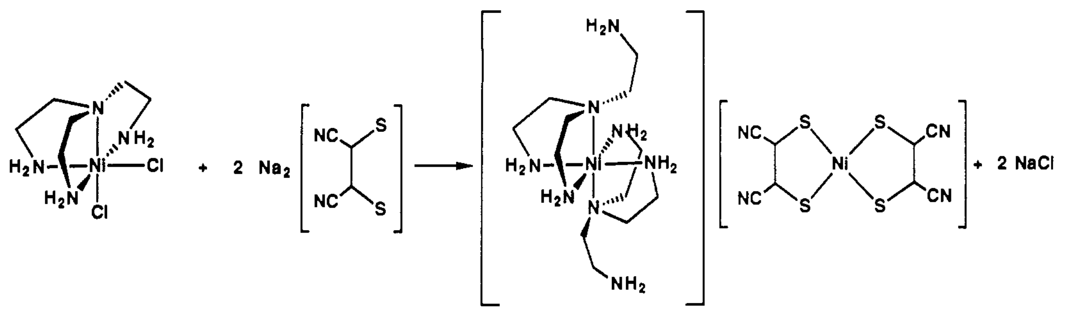
[19] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[20] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

[21] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

Scheme I



1

Table IV. Atomic Coordinates in Crystalline $[Ni(NS_2SMe)]_2$ (**4**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
Ni1	0.11814 (3)	0.1088 (1)	0.13814 (6)	2.58 (2)
Ni2	0.12588 (3)	−0.1333 (1)	0.24178 (6)	2.48 (2)
S1	0.07501 (6)	0.0505 (3)	0.2139 (1)	3.22 (4)
S2	0.16793 (7)	0.0723 (3)	0.2612 (1)	3.30 (5)
S3	0.06880 (7)	0.1417 (3)	0.0189 (2)	3.83 (5)
S4	0.17464 (8)	−0.3132 (3)	0.2832 (2)	4.75 (6)
S5	0.23093 (9)	0.5250 (4)	0.0560 (2)	6.10 (7)
S6	0.05929 (9)	−0.4416 (3)	−0.0580 (2)	4.63 (6)
N1	0.1631 (2)	0.1208 (8)	0.0821 (4)	3.1 (1)
N2	0.0828 (2)	−0.2957 (8)	0.1912 (4)	2.9 (1)
C1	0.1988 (3)	0.004 (1)	0.1268 (6)	4.3 (2)
C2	0.2144 (3)	0.034 (1)	0.2205 (6)	4.6 (2)
C3	0.1448 (3)	0.068 (1)	−0.0077 (6)	3.8 (2)
C4	0.1034 (3)	0.150 (1)	−0.0492 (5)	4.0 (2)
C5	0.1787 (3)	0.288 (1)	0.0858 (5)	3.6 (2)
C6	0.2140 (3)	0.323 (1)	0.0461 (6)	5.0 (2)
C7	0.1909 (5)	0.614 (2)	−0.026 (1)	8.0 (4)
C8	0.0934 (4)	−0.444 (1)	0.2389 (6)	4.8 (2)
C9	0.1406 (4)	−0.487 (1)	0.2491 (6)	5.0 (3)
C10	0.0386 (3)	−0.237 (1)	0.1933 (6)	4.1 (2)
C11	0.0296 (3)	−0.075 (1)	0.1571 (6)	4.0 (2)
C12	0.0843 (3)	−0.308 (1)	0.1013 (5)	3.4 (2)
C13	0.0509 (3)	−0.421 (1)	0.0452 (6)	4.6 (2)
C14	0.0359 (4)	−0.260 (1)	−0.1075 (7)	6.3 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 5. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

4. Dark brownish black opaque laths of **4** diffracted poorly and had broad peaks. The crystal used for the study had dimensions of 0.20 × 0.25 × 0.50 mm. A total of 3782 independent reflections ($+h,+k,\pm l$; $3° \leq 2\theta_{MoK\alpha} \leq 50°$) was measured. The 24 independent non-hydrogen atoms were refined anisotropically. The 30 independent hydrogen atoms were included as fixed isotropic scatterers in ideal positions. The final refinement was based on the 2369 reflections with $I \geq 3\sigma_I$. Selected atomic positions are given in Table IV.

5. The crystal used for the study had dimensions of 0.11 × 0.12 × 0.43 mm. A total of 1917 independent reflections ($+h,+k,\pm l$; $3° \leq 2\theta_{MoK\alpha} \leq 48°$) were measured. The 14 independent nonhydrogen atoms were refined anisotropically. The 20 independent hydrogen atoms were treated as described for **4**. The final refinement was based on the 1463 reflections having $I \geq 3\sigma_I$. Selected atomic positions are given in Table V.

Table V. Atomic Coordinates in Crystalline $Ni(N_2S_2)$ (**5**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
Ni	0.42885 (4)	0.35327 (3)	0.35573 (3)	2.342 (7)
S1	0.3375 (1)	0.30843 (9)	0.50592 (8)	4.17 (2)
S2	0.5960 (1)	0.22217 (9)	0.41378 (9)	4.35 (2)
N1	0.2536 (3)	0.4593 (2)	0.3055 (2)	2.83 (6)
N2	0.5369 (3)	0.3860 (2)	0.2274 (2)	2.59 (5)
C1	0.1679 (4)	0.3957 (4)	0.4806 (3)	4.36 (9)
C2	0.1980 (4)	0.4934 (3)	0.4110 (3)	4.39 (8)
C3	0.2913 (4)	0.5641 (3)	0.2515 (3)	4.01 (8)
C4	0.3669 (5)	0.5483 (3)	0.1491 (3)	4.56 (9)
C5	0.5292 (4)	0.5026 (3)	0.1884 (3)	4.01 (8)
C6	0.7061 (4)	0.3598 (4)	0.2712 (3)	4.04 (8)
C7	0.7273 (4)	0.2448 (4)	0.3192 (4)	4.52 (9)
C8	0.1254 (4)	0.4009 (4)	0.2224 (4)	4.43 (9)
C9	0.4738 (4)	0.3133 (3)	0.1254 (3)	3.81 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 6. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Selected Distances (Å) and Angles (deg) for $[Ni(tren)_2](BF_4)_2$ (**2**)[a]

	Distances		
Ni–N1	2.172 (2)	N2–C2	1.428 (6)
Ni–N2	2.145 (3)	N3–C4	1.481 (4)
Ni–N3	2.129 (2)	N4–C6	1.458 (5)
N1–C1	1.491 (5)	C1–C2	1.395 (5)
N1–C3	1.480 (3)	C3–C4	1.512 (6)
N1–C5	1.464 (5)	C5–C6	1.535 (5)
	Angles		
N1–Ni–N2	81.8 (1)	Ni–N2–C2	108.7 (2)
N1–Ni–N3	82.03 (9)	Ni–N3–C4	111.1 (2)
N2–Ni–N3	91.7 (1)	N1–C1–C2	117.0 (3)
Ni–N1–C1	108.4 (2)	N2–C2–C1	119.8 (4)
Ni–N1–C3	105.0 (2)	N1–C3–C4	112.2 (3)
Ni–N1–C5	110.2 (2)	N3–C4–C3	110.0 (3)
C1–N1–C3	110.5 (2)	N1–C5–C6	117.9 (3)
C1–N1–C5	111.8 (3)	N4–C6–C5	108.0 (3)
C3–N1–C5	110.6 (2)	N1–Ni–N2′	98.2 (1)
N1–Ni–N3′	97.97 (9)	N2–Ni–N3′	88.3 (1)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

Results and Discussion

Ni(tren) Complexes. Metal complexes containing the tetradentate tripod ligand tren have been prepared for a number of transition metals, including Ni.[22] By far the most common geometry is six-coordinate, with tren enforcing a cis geometry that leaves two cis positions available for binding other ligands. This type of structure is found in $[Ni(tren)(NCS)_2]$.[23] Reaction of $[Ni(tren)Cl_2]$ with Na_2mnt (Scheme I) does not lead to simple substitution of the Cl^- ligands but rather to the formation of a salt, $[Ni(tren)_2][Ni(mnt)_2]$ (**1**), where both the cation and anion are Ni(II) complexes. The anion, $Ni(mnt)_2^{2-}$, has been structurally characterized as R_4N^+ salts[24] and differs in only subtle ways from the published structures. The cation is a novel complex, $Ni(tren)_2^{2+}$, that contains two tridentate tren ligands, where each

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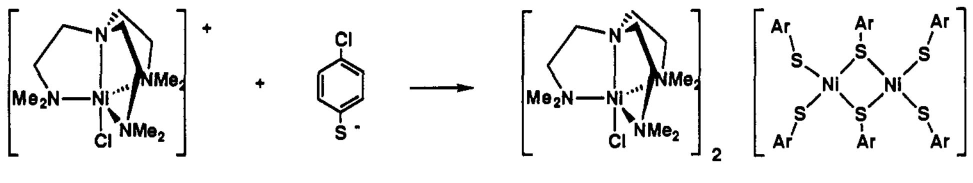
Scheme II



3

tren ligand has one primary amine that is not bound. This is a bonding mode of tren that has not previously been structurally characterized. The closest analogue to this structure is a dinuclear Mn complex where tren is bound to one metal center by two primary amines and the tertiary amine with the remaining primary amine bound to the second metal.[25]

One possible explanation for the formation of this cation is the apparent stability of the planar $Ni(S_4)$ unit found in $Ni(mnt)_2^{2-}$, coupled with the kinetic lability characteristic of Ni(II). To test this idea, we attempted to synthesize the cation in the absence of thiolate-type ligands and with the use of weakly coordinating anions. The formation of $[Ni(tren)_2](BF_4)_2$ (**2**) demonstrates that the formation of a NiS_4 unit is not the driving force for the formation of the cation.

The structure of the cation in **2** is illustrated in Figure 1, and selected bond lengths and angles may be found in Table VI. The ligands utilize two primary amines and the tertiary N atom to occupy trigonal faces of a distorted octahedron with the tertiary nitrogen donors of the two ligands in trans positions. The Ni atom lies on a crystallographic inversion center, and thus the angles between trans ligand donor atoms are required by symmetry to be 180°. The angles at Ni in the five-membered chelate rings are substantially less than 90°. The chelate rings are best described as having envelope conformations with C2 and C3 as flap atoms.

Although the packing is very different in **1**·2DMF and **2**, the geometries of the cations are nearly identical. Both Ni atoms lie on crystallographic inversion centers, and the tren ligands adopt a facial arrangement. The largest difference in the Ni geometry between the cations involves the angle between the ligand arms, N2–Ni–N3, which is essentially 90° in **1**·2DMF (89.7 (1)°) and somewhat larger in **2** (91.7°). A meridonal (rather than facial) arrangement of the tridentate tren ligands is logically possible, but is not observed in either compound despite the differences in packing. This is in contrast to the geometry observed for the Ni(II) complexes of the related ligand, bis(2-aminoethyl)amine (den), which differs from tren by having a secondary amine rather than a tertiary amine. In the complex $[Ni(den)_2](ClO_4)_2$, only the meridional isomer has been structurally characterized.[26] A meridional ligand arrangement is also observed in [bis(3-aminopropyl)amine]nickel(II) perchlorate.[26]

It is possible that the additional hydrogen-bonding interactions that arise from the presence of the dangling primary amines in the tren complexes favor the facial arrangement of the ligands. In both **1**·2DMF and **2**, there are hydrogen-bonding interactions involving the amino hydrogen atoms. In both cations, there is an intermolecular hydrogen-bonding interaction between the dangling amino groups (acceptors) and the N atoms of chelating amino groups (donors). In addition, in **1**·2DMF each of the chelating amino groups is involved in a hydrogen bonding interaction with an oxygen atom of the solvent, while in **2** each of the F atoms of the BF_4^- anions is involved in a hydrogen-bonding interaction with an amino group.

The Ni atom of the $Ni(mnt)_2^{2-}$ anion in **1**·2DMF also lies on a crystallographic inversion center, and thus the Ni atom and the four S donor atoms of the ligands are required by symmetry to be coplanar. The five-membered chelate rings in the anion are also nearly coplanar (±0.011 Å).

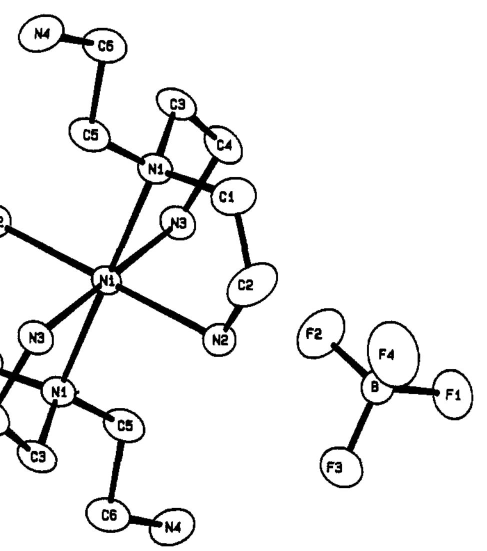


Figure 1. ORTEP plot of the cation and the independent anion in $[Ni(tren)_2](BF_4)_2$ (**2**) with the thermal ellipsoids at the 30% probability level. Atoms of the cation with the same labels are related by a crystallographic inversion center. The coordinates of the anion shown are related to those in the coordinate list by (*x*, *y* − 1, *z*). Hydrogen atoms are omitted for clarity.

Electronic absorption spectra of **2** in aqueous solution containing 0.1 M tren reveal three d–d transitions characteristic of octahedral Ni(II) complexes: λ_{max} (cm^{-1}) = 11 300, 18 500, and 29 100, leading to values of the ligand field parameters *Dq* and *β*° for tridentate tren of 1130 cm^{-1} and 16.6. These parameters are similar to those calculated for $Ni(en)_3^{2+}$ (1120 cm^{-1}, 16.1)[27] and slightly larger than those obtained for $Ni(NH_3)_6^{2+}$ (1060 cm^{-1}, 15.3).[28] The values obtained for *mer*-$Ni(den)_2^{2+}$ (1150 cm^{-1}, 19.3)[29] are larger than for *fac*-$Ni(tren)_2^{2+}$.

$[Ni(Me_6tren)Cl]_2[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]\cdot 2CH_3CN$. Methylation of the primary amines of tren produces Me_6tren, where all of the amines are tertiary amines. In analogy with the formation of **1**, reaction of $[Ni(Me_6tren)Cl]Cl$ complex salt with 1 equiv of $Et_4N(S\text{-}p\text{-}C_6H_4Cl)$ in acetonitrile leads to the formation of the salt **3**·$2CH_3CN$ (Scheme II), where the cation contains all of the N donor ligands and the anion contains all of the S donor ligands and consists of planar NiS_4 units. Selected bond lengths and angles for the complex cation and complex anion are contained in Table VII. The anion, $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$ (Figure 2), consists of two approximately planar NiS_4 units (±0.095 Å) joined along an S–S edge such that the two NiS_4 planes are essentially coplanar. The central Ni_2S_2 rhomb is required by symmetry to be planar. The terminal S donor atoms (S2 and S3) are displaced from this plane in opposite directions by distances of 0.164 and 0.216 Å, respectively. The structure is essentially that of the $[Ni_2(SEt)_6]^{2-}$ anion[6a] where the Me_4N^+ salt consists of two crystallographically independent anions that differ only slightly in M–S and M–M distances and in the S–Ni–S angles from those of **3**. The Ni-S

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(29) Calculated from values contained in: Jorgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 887.

Table VII. Selected Distances (Å) and Angles (deg) for [Ni(Me$_6$tren)Cl]$_2$[Ni$_2$(S-*p*-C$_6$H$_4$Cl)$_6$]·2CH$_3$CN (3·2CH$_3$CN)^a

	Distances		
Ni1-S1	2.212 (1)	Ni2-N4	2.168 (4)
Ni1-S1′	2.220 (2)	Ni2-N2	2.090 (4)
Ni1-S2	2.204 (1)	Ni2-N3	2.098 (5)
Ni1-S3	2.219 (2)	S3-C31	1.769 (4)
Ni2-Cl4	2.295 (2)	S1-C41	1.786 (5)
Ni2-N1	2.134 (7)	S2-C21	1.758 (6)
Ni1-Ni1′	3.273 (1)	S1-S1′	2.988 (2)
	Angles		
S1-Ni1-S1′	84.78 (6)	N1-Ni2-N3	115.4 (2)
S1-Ni1-S2	175.70 (6)	N1-Ni2-N4	124.8 (2)
S1-Ni1-S3	94.48 (6)	N2-Ni2-N3	85.1 (2)
S1′-Ni1-S2	94.73 (6)	N2-Ni2-N4	82.8 (2)
S1′-Ni1-S3	174.38 (5)	N3-Ni2-N4	116.3 (2)
S2-Ni1-S3	86.43 (6)	Ni1-S1-Ni1′	95.22 (5)
Cl4-Ni2-N1	96.2 (1)	Ni1-S1-C41	104.0 (1)
Cl4-Ni2-N2	178.5 (1)	Ni1′-S1-C41	98.2 (2)
Cl4-Ni2-N3	96.4 (1)	Ni1-S2-C21	112.9 (2)
Cl4-Ni2-N4	96.2 (1)	Ni1-S3-C31	110.6 (2)
N1-Ni2-N2	83.5 (2)		

^{a}Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

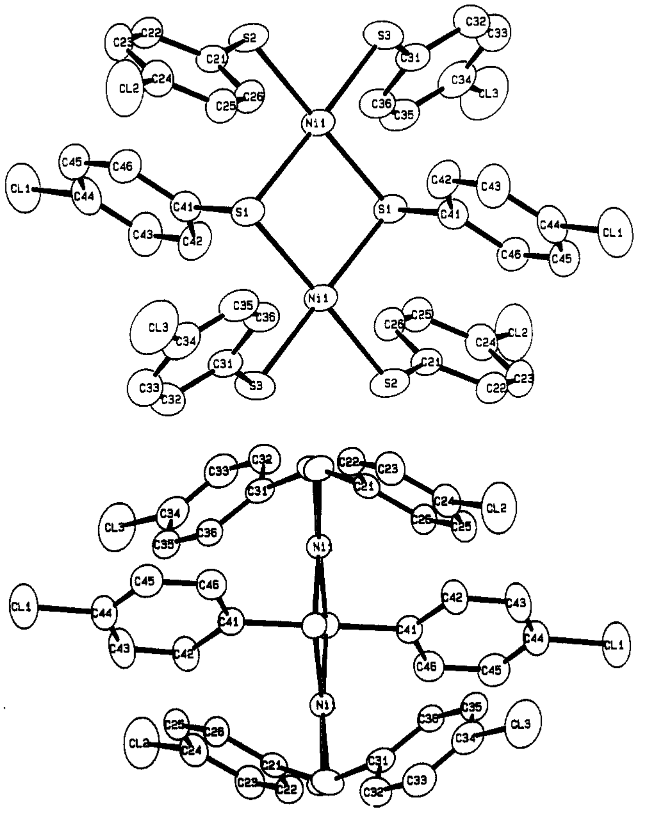

Figure 2. ORTEP plot of the anion in [Ni(Me$_6$tren)Cl]$_2$[Ni$_2$(S-*p*-C$_6$H$_4$Cl)$_6$]·2CH$_3$CN (3·CH$_3$CN) with thermal ellipsoids at the 30% probability level: (a, top) view showing the complete atom-labeling scheme; (b, bottom) view roughly parallel to the Ni$_2$S$_6$ plane. Atoms with the same labels are related by a crystallographic inversion center. Hydrogen atoms are omitted for clarity.

distances (>2.2 Å) lie at the upper end of the range that has been observed in planar nickel thiolate complexes (2.16–2.21 Å).[30] The C–S–Ni bond angles of the S donor ligands are such that the alkyl or aryl substituents are alternately directed above and below the plane of the Ni$_2$S$_2$ rhomb in both anions.

The structure of [Ni$_2$(S-*p*-C$_6$H$_4$Cl)$_6$]$^{2-}$ is unusual in that it constitutes the first example of an arenethiolate complex of Ni(II) that has planar rather than tetrahedral geometry about Ni. The distorted tetrahedral anions Ni(SAr)$_4$$^{2-}$ (Ar = Ph, *p*-C$_6$H$_4$Cl) are known from crystallographic studies,[5] and other analogues with similar properties (e.g. paramagnetic ground states) are believed to have similar structures.[5c] The characterization of a distorted tetrahedral complex with the same thiolate ligand as 3·2CH$_3$CN, allows the direct structural comparison between the two geometries. The average Ni–S distance in Ni(S-*p*-C$_6$H$_4$Cl)$_4$$^{2-}$ is 2.281 (1) Å[5c] and is longer than the Ni–S bonds in 3·2CH$_3$CN (average Ni–S = 2.214 (2) Å). Both of the tetrahedral complexes are distorted in the same manner; two of the S–Ni–S angles are ca. 90°, while the other four are ca. 120°. It has been observed that the Ni–S bonds tend to lie in the plane of the phenyl ring attached to the S donor atom.[31,32] Given this preference of electronic origin, it has been suggested that a tetrahedral or a square-planar structure would give rise to unfavorable steric interactions between the ortho H atoms of the phenyl rings and the S and Ni atoms. Thus, the distortions have been interpreted as arising from a compromise that allows the Ni–S bonds to be coplanar with the phenyl rings without giving rise to unfavorable steric interactions.[5c,31,32] The original suggestion that this distortion arose from crystal packing forces in (Ph$_4$P)$_2$[Ni(SPh)$_4$] was based on the observation of similar distortions in isomorphous complexes of Co, Zn, and Cd.[5b] This suggestion was discounted in view of the persistence of the same distortion in (Et$_4$N)$_2$[Ni(S-*p*-C$_6$H$_4$Cl)$_4$], where the counterion and arenethiolate involved have been changed.[5c] The characterization of 3·2CH$_3$CN demonstrates that a structure with planar Ni geometry can form at the expense of the orientation of the phenyl groups. The calculated angles between the Ni–S bonds and the least-squares planes of the phenyl ring bound to the S donor (Table VIII) reveal that none of the phenyl groups of 3·2CH$_3$CN are coplanar with the Ni–S vectors, in contrast with (Et$_4$N)$_2$[Ni(S-*p*-C$_6$H$_4$Cl)$_4$], where three of the rings are essentially coplanar with Ni–S bonds (Table VIII). In the case of the bridging thiolates, the two phenyl groups are oriented parallel to each other and are more nearly coplanar with the shorter of the two Ni–S bonds. It is clear that the geometry of nickel arenethiolates is fairly plastic and that a number of subtle factors are involved in stabilizing a particular geometry.

Table VIII. Ring Orientations in Nickel(II) Arenethiolate Complexes

compd	Ni-S vector	ring	angle, deg
3	Ni1-S1	C41-C46	12.0 (5)
	Ni1-S2	C21-C26	33.8 (3)
	Ni1-S3	C31-C36	23.4 (4)
(Et$_4$N)$_2$[Ni(S-*p*-C$_6$H$_4$Cl)$_4$]^{5c}	Ni-S1	no. 1	5.4
	Ni-S2	no. 2	0.2
	Ni-S3	no. 3	0.3
	Ni-S4	no. 4	26.7

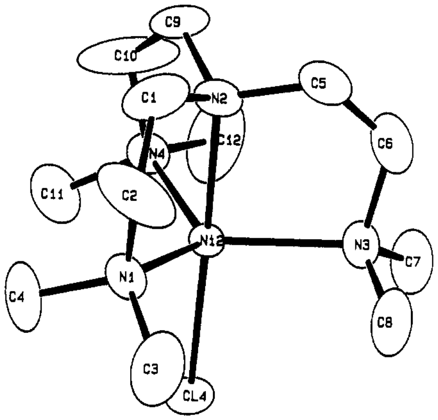

Figure 3. ORTEP plot of the cation in [Ni(Me$_6$tren)Cl]$_2$[Ni$_2$(S-*p*-C$_6$H$_4$Cl)$_6$]·2CH$_3$CN (3·CH$_3$CN) with thermal ellipsoids at the 20% probability level. Hydrogen atoms are omitted for clarity.

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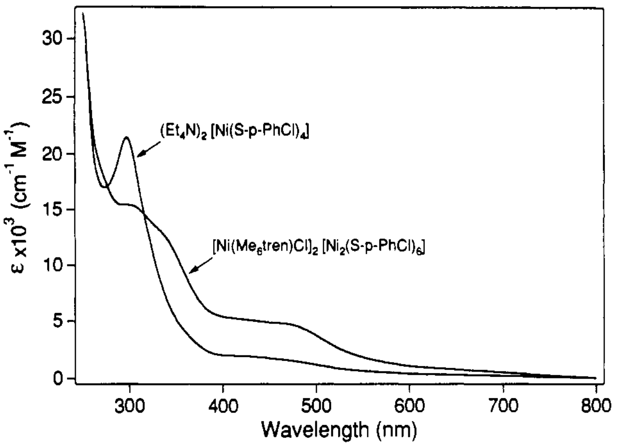

Figure 4. Electronic absorption spectra of 0.05 mM solutions of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ and $[Ni(Me_6tren)Cl]_2[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]$ in acetonitrile.

The coordination chemistry of the Me_6tren tripodal ligand is dominated by the formation of high-spin, five-coordinate complexes with approximate trigonal-bipyramidal geometry.[33] The room-temperature susceptibility of **3**·$2CH_3CN$ ($\mu = 4.53\ \mu_B$, uncorrected) can be attributed to two high-spin, $S = 1$, Ni(II) cations and a diamagnetic anion ($\mu = 3.42\ \mu_B$ for $Ni(Me_6tren)Cl^+$ in $[Ni(Me_6tren)Cl]Cl$).[13] The structures of the $Ni(Me_6tren)Cl^+$ cations (Figure 3, Table VII) do not differ significantly from those found in the analogous Br^-,[34] I^-,[35] and NCS^-[36] complexes, with the exception of the Ni–anion bond. The Ni–Cl bonds in the cations of **3**·$2CH_3CN$ have a bond length of 2.295 (2) Å, compared with Ni–X bond lengths of 1.97 (2), 2.467 (2), and 2.665 (1) Å for X = NCS^-, Br^-, and I^-, respectively. The Ni atom is displaced 0.232 Å out of the plane of the equatorial N donor atoms in the direction of the Cl^- ligand, a distortion similar to those observed in the analogous NCS^-, Br^-, and I^- complexes.

Electronic absorption spectra (Figure 4) obtained for acetonitrile solutions of **3** are dominated by the absorption spectrum of the $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$ anion ($\lambda_{max} = 483$ nm ($\epsilon = 4500$ M^{-1} cm^{-1}) with a shoulder on a maximum in the UV at 343 nm). Absorptions associated with $Ni(Me_6tren)Cl^+$ are comparatively weak.[13] The spectrum is distinct from that obtained for $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ in the same solvent (Figure 4). The presence of the planar, diamagnetic anion in acetonitrile solution is confirmed by ^1H NMR spectra that reveal peaks assigned to the aryl proton resonances that are not hyperfine-shifted (δ = 7–8 ppm), in contrast to those observed for the paramagnetic tetrahedral compound $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ (δ = 1.9, 22.3 ppm).[5c] The ^1H NMR spectrum shown in Figure 5 reveals resonances due to the $Ni(Me_6tren)Cl^+$ cation at 89 ppm and resonances at 7.57 and 6.85 ppm that account for all of the $^-S\text{-}p\text{-}C_6H_4Cl$.

In the ^1H NMR study of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$,[5c] the authors noted the presence of peaks in the diamagnetic region of the spectrum that were present under a variety of conditions and were not affected by the presence of additional thiolate ligand. It was suggested that one possible assignment of these resonances is to planar, polymeric, thiolate-bridged species that would be diamagnetic. Such species are known to form under synthetic conditions employing either protic solvents or reactions corresponding to high Ni:thiolate ratios (i.e. adding the thiolate to a Ni solution). The reaction conditions leading to the formation of **3** employ high Ni:thiolate ratios but lead to the formation of a soluble product, perhaps mediated by the presence of the tripod ligand. The resonances observed in the diamagnetic region of solutions of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ can now be assigned to the diamagnetic anion $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$. Spectra obtained on fresh solutions of **3** show no more than a trace amount of paramagnetic thiolate complex.

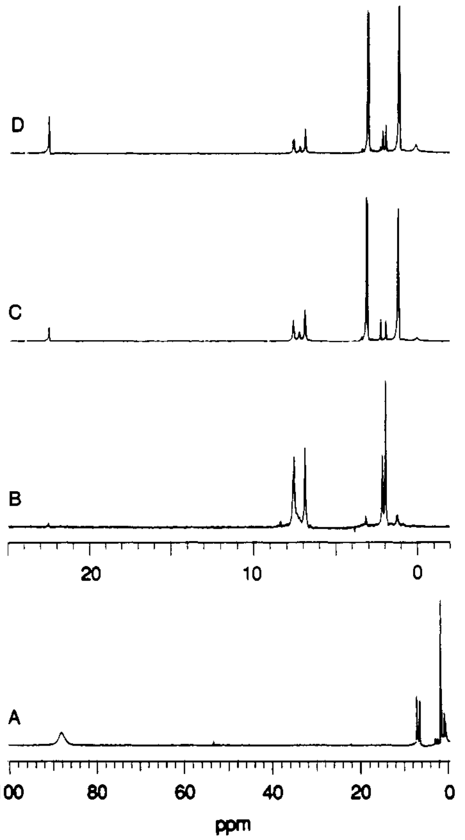

Figure 5. ^1H NMR spectra of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ and $[Ni(Me_6tren)Cl]_2[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]$ in CD_3CN: (A) a solution of **3** showing the presence of a hyperfine-shifted resonance assigned to the paramagnetic $Ni(Me_6tren)Cl$ cation at 89 ppm; (B) the same solution of **3** showing only a minute trace of a peak near 22.3 ppm assigned to meta protons of $^-S\text{-}p\text{-}C_6H_4Cl$ in the paramagnetic $[(Ni(S\text{-}p\text{-}C_6H_4Cl)_4]^{2-}$ anion and resonances assigned to $^-S\text{-}p\text{-}C_6H_4Cl$ in **3** at 7.57 and 6.85 ppm with peaks near 1.93 ppm assigned to solvent and trace water in the sample; (C) a solution of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ containing a drop of CD_3OD, showing the conversion of some of the paramagnetic, tetrahedral anion to the diamagnetic, planar, dimeric anion with the peak at 7.10 ppm attributable to free $DS\text{-}p\text{-}C_6H_4Cl$ and additional peaks near 3.2 and 1.2 ppm due to tetraethylammonium cations; (D) a solution of $(Et_4N)_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ showing the thiophenolate peaks at 22.3 ppm (meta) and 0.2 ppm (ortho).

It has been noted that the diamagnetic species is not readily converted to the paramagnetic complex.[5c] We can confirm these results and suggest that the situation is of kinetic origin. The paramagnetic thiolate is kinetically labile and rapidly generates some diamagnetic complex in solution via loss of one of the thiolate ligands. However, the dianionic, diamagnetic complex is kinetically more inert and does not readily add two thiolate ligands to form the tetrahedral complex even under conditions employing excess thiolate. Protic solvents encourage thiolate dissociation,[6c] leading to higher concentrations of "$Ni(SAr)_3$" units in solutions of $[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]^{2-}$ that can subsequently oligomerize. Addition of a drop of methanol to an acetonitrile solution of $[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]^{2-}$ results in the rapid conversion of some of the paramagnetic thiolate into the diamagnetic, dimeric anion (Figure 5). Under synthetic conditions employing low Ni:thiolate ratios, the formation of species that can readily oligomerize is suppressed. The solution speciation of these and analogous nickel thiolate complexes is the subject of future investigations.

Interest in the redox chemistry of nickel thiolate complexes has been stimulated by the low potentials observed in hydrogenase chemistry that have been interpreted as involving interconversions between formally Ni(II) and Ni(III) species.[1] The electrochemistry of simple nickel thiolate complexes is dominated by irreversible oxidations that can arise from the oxidation of the thiolate

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Table IX. Selected Distances (Å) and Angles (deg) for $[Ni(NS_2SMe)]_2$ (**4**)[a]

Distances			
Ni1–S1	2.189 (3)	Ni2–N2	1.961 (6)
Ni1–S2	2.210 (2)	S1–C11	1.833 (8)
Ni1–S3	2.156 (2)	S2–C2	1.85 (1)
Ni1–N1	1.945 (7)	S3–C4	1.81 (1)
Ni2–S1	2.214 (2)	S4–C9	1.82 (1)
Ni2–S2	2.176 (2)	Ni1–Ni2	2.635 (1)
Ni2–S4	2.156 (3)	S1–S2	2.884 (3)

Angles			
S1–Ni1–S2	81.92 (9)	S4–Ni2–N2	90.0 (2)
S1–Ni1–S3	97.15 (9)	Ni1–S1–Ni2	73.50 (8)
S1–Ni1–N1	167.8 (2)	Ni1–S1–C11	112.9 (3)
S2–Ni1–S3	179.0 (1)	Ni2–S1–C11	97.7 (3)
S2–Ni1–N1	89.9 (2)	Ni1–S2–Ni2	73.84 (7)
S3–Ni1–N1	90.9 (2)	Ni1–S2–C2	98.2 (3)
S1–Ni2–S2	82.12 (9)	Ni2–S2–C2	110.4 (3)
S1–Ni2–S4	173.5 (1)	Ni1–S3–C4	98.2 (3)
S1–Ni2–N2	90.7 (2)	Ni2–S4–C9	98.8 (3)
S2–Ni2–S4	98.71 (9)	C6–S5–C7	101.7 (5)
S2–Ni2–N2	163.7 (2)	C13–S6–C14	100.5 (5)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 5.

ligand and subsequent formation of disulfides.[12,30] A few examples of nickel thiolate complexes with reversible one-electron oxidations have recently begun to emerge.[12,37,38] The electrochemistry of **3** in CH_3CN is dominated by irreversible processes characteristic of both the $[Ni(Me_6tren)Cl]^+$ cation and the $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$ dianion. The cyclic voltammogram of a sample of $[Ni(Me_6tren)Cl]Cl$ reveals an irreversible oxidation (E_{p_a} = 640 mV vs Fc/Fc$^+$) and an irreversible reduction (E_{p_c} = −1820 mV). The analogous features in the cyclic voltammogram of **3** are assigned to the cation. These extreme potentials are characteristic of the redox chemistry of Ni(II) coordination complexes with N donor ligands.[39] In addition to these features, **3** also reveals two irreversible oxidations (E_{p_a} = −195 and +125 mV) that are associated with the $[Ni_2(S\text{-}p\text{-}C_6H_4Cl)_6]^{2-}$ dianion. Presumably, this oxidation product also ultimately oxidizes the thiolate ligands to form disulfides. This behavior differs dramatically from that observed for the monomeric, planar nickel tetrathiolate $[Ni(S_2\text{-norbornane})_2]^{2-}$,[38] which exhibits a reversible one-electron oxidation at −760 mV vs SCE in DMF. Apparently, the redox chemistry of nickel thiolates is sensitive to a number of factors that remain to be clearly defined.

$[Ni(NS_2SMe)]_2$. Reaction of the dithiol, bis(2-mercaptoethyl)(2-(methylthio)ethyl)amine, and anhydrous $Ni(OAc)_2$ in cold methanol causes the precipitation of a neutral dimeric Ni complex with mixed N/S ligand, **4**. The structure of the dimer in crystals obtained from DMF/methanol is shown in Figure 6 and selected bond lengths and angles are contained in Table IX. The structure is similar to a large number of dimeric Ni complexes with dithiolato bridges. Structural elements of these dimers are compared in Table X. Our interest in this molecule stems from its unusual redox properties; the dimer undergoes a reversible one-electron oxidation to form an $S = {}^1/_2$ radical that is stable below room temperature and has an EPR spectrum that is reminiscent of those obtained from hydrogenases.[12]

The structure of **4** is best described as containing two planar[40] Ni(II) complexes with NS_3 ligation that are joined along an edge via two bridging thiolates. To our knowledge, this is the only known Ni structure featuring this ligation using exclusively thiolato S donor atoms. In contrast to the structure of **3**, the two planes composed of the Ni and bridging S atoms are not coplanar, but meet with an angle (referred to hereafter as the folding angle) of 105.2 (1)°. This angle is the most acute angle known for dimers of this type that contain four-coordinate Ni atoms (Table X). The folding apparently arises from a combination of factors that include Ni–Ni interactions, S–S interactions, the total charge provided by the ligands, and steric constraints involving both ligand–ligand interactions and constraints on the pyramidal geometry of the bridging S atoms imposed by chelate rings.[6b,g] Although it is not possible to clearly separate the role played by each of these components in determining the geometry of **4**, it is likely that constraints imposed by the chelate rings involving the bridging S atoms play an important role in determining the overall structure. These constraints arise because the bridging S atoms in five-membered chelate rings cannot position their alkyl substituents above and below a planar dimer, as is found in **3** and in $[Ni(SEt)_3]_2$.[6a] With few exceptions,[6f,g] anti stereochemistry is characteristic of the bridging monodentate thiolates and contrasts with the syn–endo stereochemistry that is observed for every known dimer involving bridging by chelating thiolates (Table X).

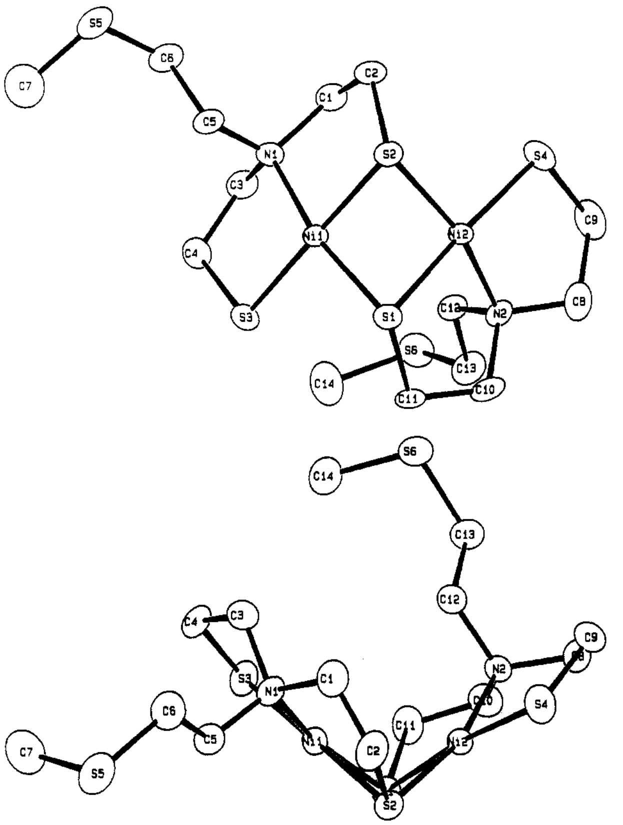

Figure 6. ORTEP plot of $[Ni(NS_2SMe)]_2$, **4**, with thermal ellipsoids at the 30% probability level: (a, top) view normal to the plane defined by the vectors Ni1–Ni2 and S1–S2; (b, bottom) view showing the fold along S1–S2. Hydrogen atoms are omitted for clarity.

The folding along the S–S edge brings the two Ni atoms into close contact (2.635 (1) Å) and decreases the S–S distance slightly from 2.91 Å in $[Ni(SEt)_3]_2$[6a] to 2.88 Å in **4**. Both of the Ni–Ni and S–S distances are well below the sum of the van der Waals radii of the atoms involved and suggest that increased Ni–Ni and S–S interactions that result from the folding may also be important factors in the electronic structure of the dimer. Clearly, since folded dimers with syn–endo stereochemistry are known that involve simple nonchelating bridging thiolates,[6f,g] the folding of these μ-dithiolato dimers can be driven by factors other than steric constraints.

In **4**, the bridging S atoms are involved in five-membered chelate rings. The bridging Ni–S distances for each S atom divide into two groups, with the Ni–S bonds from the monomeric units containing the chelate rings being slightly longer than those in-

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(40) Ni1, S1, S2, and N2 are coplanar to within ±0.084 Å. For the corresponding plane containing Ni2 the coplanarity is less good (±0.200 Å). The NiS_3 groupings are more nearly planar (Ni1, ±0.004 Å; Ni2, ±0.062 Å) with the N atoms displaced from their respective planes by 0.298 Å (N1) and 0.628 Å (N2).

Table X. Structural Comparisons of Thiolate-Bridged Ni Dimers[a]

compd	Ni–Ni, Å	$Ni–S_{br}$,[b] Å	S–S, Å	Ni–S–Ni, deg	fold angle, deg	stereochem	ref
A	2.733 (5)	2.220 (5), 2.183 (5) 2.217 (5), 2.183 (5)	2.903 (5)[c]	76.7 (2), 76.8 (2)	111.3	syn–endo	6d
B	2.941	2.166 (2), 2.209 (2) 2.158 (2), 2.221 (2)	2.819 (3)	83.7 (1), 83.2 (1)	121.1	syn–endo	6b,c
C	2.763 (2)	2.179 (4), 2.184 (3) 2.186 (4), 2.196 (3)	2.84[d]	78.3 (1), 78.4 (1)	110.2[e]	syn–endo	6f
D	2.795 (3)	2.188 (4), 2.190 (4)	2.862 (5)	79.5	115.5	syn–endo	6g
E	2.647	2.215, 2.225		73.2		syn–endo	6h
F	2.739 (1)	2.169 (1), 2.186 (1)	2.786 (2)	77.94 (5)	110	syn–endo	10b
G[f]	2.839 (2)	2.244 (4), 2.257 (3) 2.192 (3), 2.208 (3)		79.2 (1), 79.3 (1)	90[g]	syn–endo	10g
4	2.635 (1)	2.210 (2), 2.189 (3) 2.214 (2), 2.176 (2)	2.884 (3)	73.50 (8), 73.84 (7)	105.2	syn–endo	this work
H	3.3355 (2)	2.214 (2), 2.224 (1)	2.906 (4)	98.2 (1)	180	anti	6a
3	3.273 (1)	2.212 (1), 2.220 (2)	2.988 (2)	95.22 (5)	180	anti	this work

[a] Structures: A, bis(μ-(bis(2-mercaptoethyl) sulfide)dinickel(II); B, bis(μ-1,2-ethanedithiolato)(1,2-ethanedithiolato)dinickelate(2−); C, bis(μ-ethanethiolato)bis(ethanetrithiocarbonato)dinickel(II); D, bis(μ-phenylmethanethiolato)bis(phenylmethanetrithiocarbonato)dinickel(II); E, bis[μ-(tris(2-mercaptoethyl)phosphine]dinickel(II); F, bis{μ-2-[(2-pyridylethyl)amino[ethanethiolato}dinickelate(2−); G, bis{2-[(2-pyridylethyl)(2-(methylthio)ethyl)amino]ethanethiolato}dinickel(+); H, bis(μ-ethanethiolato)tetrakis(ethanethiolato)dinickelate(2−). [b] Complexes A, B, E, F, G, and 4 involve bridging thiolates that are involved in a chelate ring. In these cases, the first Ni–S bond length of the pair is the intrachelate Ni–S bond and the second bond length is the extrachelate Ni–S bond. [c] Calculated from parameters given in ref 6d. [d] From ref 6b. [e] Angle represents that between the Ni coordination planes as opposed to the folding angle as defined in the text. [f] Ni atoms are in ca. square-pyramidal coordination environments with axial ligation of thioether groups. [g] Calculated from bond lengths and angles given in ref 10g.

Table XI. Selected Distances (Å) and Angles (deg) for $Ni(N_2S_2)$ (5)[a]

	Distances		
Ni–S1	2.176 (1)	N1–C2	1.495 (5)
Ni–S2	2.174 (1)	N1–C3	1.496 (5)
Ni–N1	1.999 (3)	N1–C8	1.491 (4)
Ni–N2	2.006 (3)	N2–C5	1.487 (5)
S1–C1	1.807 (4)	N2–C6	1.500 (4)
S2–C7	1.810 (4)	N2–C9	1.487 (4)
	Angles		
S1–Ni–S2	85.37 (4)	Ni–N1–C8	107.7 (2)
S1–Ni–N1	89.31 (9)	C2–N1–C3	105.3 (3)
S1–Ni–N2	173.14 (7)	C2–N1–C8	108.9 (3)
S2–Ni–N1	172.28 (9)	C3–N1–C8	110.0 (3)
S2–Ni–N2	88.26 (8)	Ni–N2–C5	115.2 (2)
N1–Ni–N2	97.3 (1)	Ni–N2–C6	108.5 (2)
Ni–S1–C1	100.0 (1)	Ni–N2–C9	109.3 (2)
Ni–S2–C7	100.7 (1)	C5–N2–C6	106.1 (3)
Ni–N1–C2	108.7 (2)	C5–N2–C9	109.8 (2)
Ni–N1–C3	116.0 (2)	C6–N2–C9	107.7 (3)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 6.

volved in forming the dimer. A similar situation is observed for the analogous dimer formed with the ligand bis(2-mercaptoethyl) sulfide, where no N donor atom exists. However, inspection of Table X reveals no clear trend in this regard.

Another structural feature of 4 are the pendant thioether arms. A similar situation exists in the structure of the dimer obtained by using tris(2-mercaptoethyl)phosphine.[6h] This structure features a Ni–Ni distance of 2.65 Å and unbound thioethyl arms. The arms containing potential thiolate ligands are protonated, giving rise to a neutral dimer with pendant thiols. Results obtained for tris(2-mercaptoethyl)amine complexes of Ni suggest that the same situation obtains in this case as well (vide supra).[41] These structures contrast with that obtained by using the ligand N-2-([2-(2-pyridyl)ethyl][2-(methylthio)ethyl]amino)ethanethiol, which contains the same (methylthio)ethyl arms as 4.[10f] In this case the thioethers are bound, forming pyramidal Ni(II) complexes with Ni–S(thioether) distances of 2.563 (4) and 2.797 (4) Å, leading to a complex that is paramagnetic at room temperature. All of the other dimeric complexes contain roughly planar Ni coordination environments and are diamagnetic. Clearly, the Lewis acidity of the Ni(II) center is enhanced by the replacement of an anionic thiolate ligand by a neutral pyridine donor.

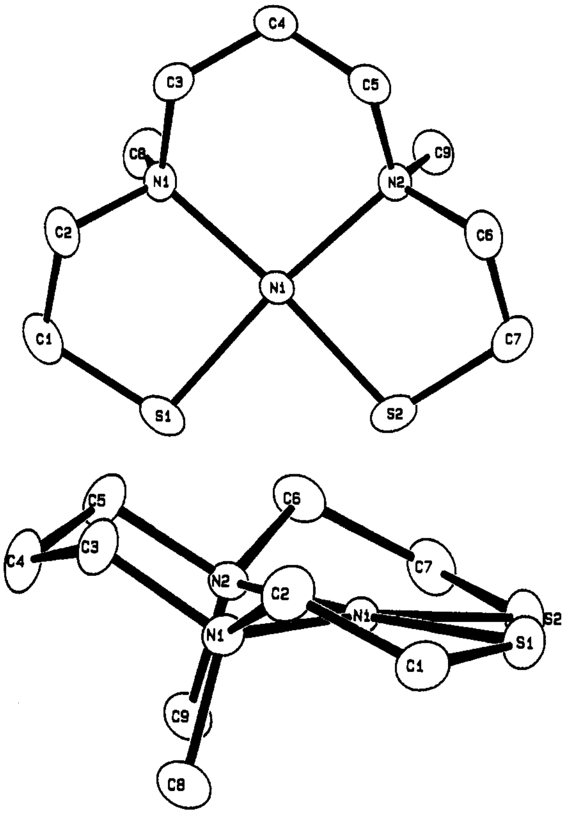

Figure 7. ORTEP plot of $Ni(N_2S_2)$ (5) with thermal ellipsoids at the 30% probability level: (a, top) view roughly perpendicular to the $Ni(N_2S_2)$ plane; (b, bottom) side view emphasizing planarity of the Ni coordination sphere, the conformation of the rings, and the stereochemistry of the N donor atoms. Hydrogen atoms are omitted for clarity.

$Ni(N_2S_2)$. Reaction of the dithiol ligand *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine with 1 equiv of $Ni(OAc)_2 \cdot 4H_2O$ produces a monomeric complex with planar Ni coordination and cis geometry. The structure of 5 is shown in Figure 7, and selected bond lengths and angles are collected in Table XI. Compound 5 exists in the solid state as discreet monomeric units in which there is no evidence of intermolecular Ni–S interactions. Atoms Ni, N1, N2, S1, and S2 are co-planar to within ±0.071 Å, and the sum of the angles at Ni in this plane is 360.2°.

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(41) The elemental analysis of this compound is consistent with a neutral, dimeric structure. The infrared spectrum contains a band at 2475 cm^{-1} that is consistent with the presence of a pendant thiol.

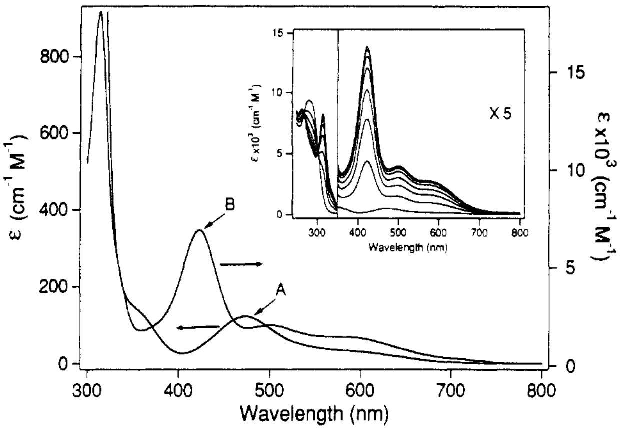

Figure 8. Electronic absorption spectra of Ni(N_2S_2) complexes: (A) 0.40 mM solution of **5** in MeOH (extinction coefficients on left side); (B) 0.10 mM solution of [$Ni_3(N_2S_2)_2$]$(BF_4)_2$ in acetonitrile (extinction coefficients on right side). Inset: Titration of a 0.40 mM solution of **5** with [Ni($H_2O)_6$]Cl_2 in MeOH. Spectra recorded from the bottom to the top correspond to the addition of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 equiv of [Ni($H_2O)_6$]Cl_2.

The six-membered chelate ring is in a chair conformation. Atoms N1, N2, C3, and C5 are coplanar to within ±0.007 Å with atoms C4 and Ni displaced in opposite directions from this plane by distances of 0.735 and 0.687 Å, respectively. The two methyl groups are both axial and are therefore on the same side of the N1–N2–C3–C5 plane. The cis disposition of the methyl groups appears to be required if the Ni coordination geometry is planar and the geometry at the N atoms is tetrahedral. (The intraring distance of 2.681 (4) Å between S1 and C2 is spanned by the single methylene, C1. However, the distance between S1 and C8 is 3.591 (4) Å. If the positions of C2 and the axial methyl group, C8, were interchanged, a single methylene group would not be able to span this distance. The same reasoning can be followed for the second five-membered chelate ring, since the ideal symmetry of the molecule is C_s with Ni and C4 on the mirror plane.) The five-membered chelate rings are best described as being in envelope conformations with C2 and C6 as flap atoms.

Complexes of this ligand with Fe(II),[42] Co(II),[43] and Zn(II)[44] have been previously reported. Interestingly, all three of these metals produced multinuclear complexes with bridging thiolates. The Fe compound exists in the solid state as a centrosymmetric dimer where the Fe–S interactions between inversion related monomers forms a central Fe_2S_2 rhomb, leading to pentacoordinated Fe atoms with approximate trigonal-bipyramidal geometry. However, the basic nature of the monomeric unit in the Fe compound is the same as in **5**. The six-membered ring is in a chair conformation with cis axial methyl groups. Although the formation of an analogous dimeric Ni(II) complex with five-coordinate pyramidal Ni centers is easily visualized, the combination of the stability of square-planar complexes of d^8 metals and a dianionic tetradentate ligand leading to a neutral Ni(II) complex apparently favors the monomeric planar structure over the dimeric pyramidal alternative.

Ligands like the one in **5** that adopt a cis geometry about Ni are frequently found to form trinuclear complexes, where a Ni atom featuring NiS_4 coordination derived solely of bridging thiolates connects two Ni(N_2S_2) units. Jicha and Busch reported the synthesis of such a trinuclear complex of 2-aminoethanethiolate, {Ni[Ni($NH_2CH_2CH_2S)_2$]$_2$}.[45] The structure of this trinuclear complex was determined by Wie and Dahl.[10a] Here again the molecule is folded along each S–S edge with folding angles of 109°, leading to a staircaselike structure for the trinuclear complex that brings the Ni–Ni separation to 2.733 (7) Å. Another example of a trinuclear compound with a very similar structure has recently come to light.[46] In this case, the ligand *N,N'*-dimethyl-*N,N'*-bis(*β*-mercaptoethyl)ethylenediamine leads to the formation of a Ni(II) trinuclear complex with a corresponding folding angle of 107.84 (7)° and a Ni–Ni distance of 2.748 (1) Å. The electronic absorption spectra obtained for these trinuclear complexes reveals an intense absorption at ca. 420 nm that is not observed in the spectra of the monomers and is thus an absorption that is associated with the planar NiS_4 unit. Addition of [Ni($H_2O)_6$]$(BF_4)_2$ in MeOH to MeOH solutions of **5** lead to spectra that contain a similar band at 423 nm (ϵ = 6900 cm^{-1} M^{-1}), indicating the formation of the analogous trinuclear complex (Figure 8). Titrations of **5** with Ni($H_2O)_6Cl_2$ proceed through the formation of isosbestic points at 302 and 267 nm, demonstrating the clean conversion of mononuclear to trinuclear complex with a stoichiometry of 2:1 (**5**:additional Ni(II) ion). The trinuclear complex $Ni_3(N_2S_2)_2^{2+}$ may be isolated in crystalline form as a BF_4^- salt upon addition of Et_2O to the MeOH solution.

The redox chemistry of **5** is similar to that of **3** and most other Ni complexes of simple thiolate ligands (vide supra). Cyclic voltammetric studies of **5** reveal an irreversible oxidation (E_{p_a} = −25 mV vs Fc/Fc$^+$). Upon addition of Ni and the formation of the trinuclear complex, this oxidation is no longer observed. Instead, a pseudoreversible reduction ($E_{1/2}'$ = −1110 mV) is observed. The loss of the oxidations upon conversion of the terminal thiolate ligands of **5** into the bridging thiolates of the trinuclear complex suggest that the oxidative chemistry of **5** is more closely associated with the S donor atoms than with the Ni center and point to an important role for the nickel cysteinethiolate ligands in the redox chemistry of the Ni center in hydrogenase.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S4), **2** (Tables S5–S8), **3** (Tables S9–S12), **4** (Tables S13–S16), and **5** (Tables S17–S20) (31 pages); observed and calculated structure factor amplitudes for **1–5** (50 pages). Ordering information is given on any current masthead page.

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