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# Synthesis and Dimer Cleavage Reactions of the $N_2S$ Thiolate Bridged Dimer $[(mmp\text{-}dach)_2Ni_2]Cl_2$

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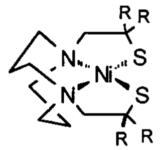
The facile synthesis of a monoderivatized $N_2S$ ligand based on the cyclic diamine diazacycloheptane provides a tridentate donor which coordinates nickel(II), yielding a dithiolate bridged nickel dimer with a hinge angle of 135.7° and acute N−Ni−N bite angles of ca. 80°. Dimer splitting occurs on reaction with iodoacetamide, producing an S-alkylated octahedral complex. Cyanide also cleaves the dimer, resulting in a cyanide-bound $N_2S$ square planar monomer with two nucleophilic sites, thiolate-S and cyanide-N. Molecular structures of the dimeric cation, $[(mmp\text{-}dach)_2Ni_2]Cl_2$, the iodoacetamide derivative, $[(dtp\text{-}dach)Ni(MeCN)_2]Cl_2$, and an S-oxygenate, [(smp-dach)-Ni(CN)], are reported.

## Introduction

The role of nickel−thiolates in the function of cysteine-rich nickel enzymes[1] has prompted the synthesis and characterization of model nickel−thiolate complexes. Two well-studied ligands in this regard are the tetradentate $N_2S_2$ ligands bme-daco and bme*-daco, which employ a cyclic diamine backbone with two pendant thiolate arms.[2,3] The diazacyclooctane (daco) ring enforces an ∠N−M−N of ∼90° and substantially restricts the ligand to a planar $N_2S_2$ donor geometry. The nickel complexes, [1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctanato]nickel(II), (bme-daco)Ni, and [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II), (bme*-daco)Ni, demonstrate a variety of S-based reactivity including oxygenation,[4] alkylation,[2,5] and metalation.[6,7] The cis orientation of the thiolates has permitted molecular $O_2$ addition across the thiolates,[8] alkylation with dihalocarbon reagents to yield a series of macrocyclic complexes,[5] and bidentate coordination to a second metal to yield heteropolymetallics.[7] While some of this chemistry is observed with the open-chain $N_2S_2$ analogues,[9−11] the bme- and bme*-daco ligands appear to be especially predisposed to yield very stable, crystallizable complexes.



R = H (bme-daco)Ni
R = Me (bme*-daco)Ni

Our attempts to control the degree of alkylation of daco by stoichiometry (to prepare the monomercapto daco derivative) have resulted in mixtures of the dialkylated diamine and starting material. Via a lengthy procedure, Tolman et al. synthesized such an $N_2S$ daco derivative by protecting and selectively deprotecting the amine nitrogens of daco.[12] Coordination of $Cu^{2+}$ yielded a thiolate bridged dimeric complex which is an appropriate model of $Cu_A$ type sites in metalloenzymes.[13] We describe below the derivatization of a cheaper, commercially available cyclic diamine, homopiperazine (diazacycloheptane or dach), to intentionally, and easily, obtain a monothiolate $N_2S$ ligand. On coordination to nickel a bimetallic compound is obtained, and this compound is shown to undergo cleavage with both nucleophiles and electrophiles. Schemes 1 and 2 show an overview of this chemistry and abbreviations of complex names. A similar ligand and mononuclear complex is derived from *N*-methylhomopiperazine.

## Experimental Section

**General Procedures.** Where anaerobic conditions were required, standard Schlenk techniques using argon and an argon glovebox (Vacuum Atmospheres) were used.

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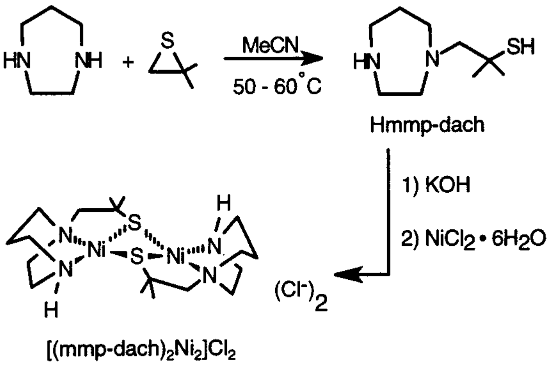
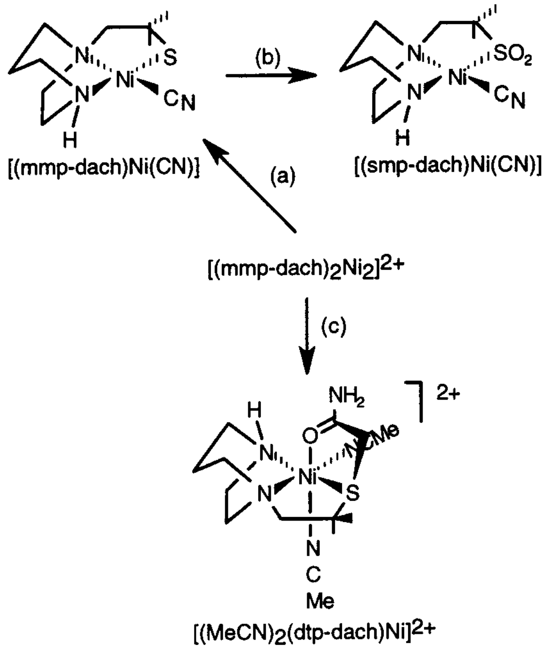
10.1021/ic990106z CCC: $18.00

**Scheme 1.** Synthesis of Hmmp-dach and $[(mmp\text{-}dach)_2Ni_2]Cl_2$



**Scheme 2**[a]



[a] (a) KCN, MeOH; (b) $H_2O_2$, $H_2O$; (c) $ICH_2C(O)NH_2$, MeCN.

Solvents were dried and distilled using standard methods.[14] Acetonitrile was distilled once from $CaH_2$ and once from $P_2O_5$ and was freshly distilled from $CaH_2$ immediately before use. The following starting materials were reagent grade and used as received: homopiperazine, iodoacetamide, and Rose Bengal (Aldrich Chemical Company); potassium cyanide and nickel(II) chloride hexahydrate (Fisher Scientific); methyl iodide (MeI) (Lancaster). Isobutylene sulfide was synthesized according to published procedures,[15] as was sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate, $NaB[C_6H_4(CF_3)_2]_4$ or NaBArF.[16]

**Physical Measurements.** UV−vis spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer using quartz cells (1.00 cm path length). An IBM IR/32 Fourier transform spectrometer was used to record infrared spectra (KBr pellets). Cyclic voltammograms were recorded on a BAS-100A electrochemical analyzer with a glassy carbon stationary electrode and a platinum wire auxiliary electrode. Samples were measured in acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (TBAHP) (0.1 M) as the supporting electrolyte and a $Ag^0/AgNO_3$ reference electrode. Potentials were standardized with $Cp_2Fe^+/Cp_2Fe$. Mass spectral analyses were performed at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Positive ion fast atom bombardment mass spectra were recorded in thioglycerol and 4-nitrobenzyl alcohol (NBA) matrixes using a VG-70S spectrometer with a xenon source having a particle energy of 10 keV. Data were collected by a VG11-250J data system. Conductivity measurements were in aqueous solution or pure acetonitrile solution using an ORION conductivity meter Model 160. Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Delta, British Columbia, Canada.

**X-ray Crystal Structure Analyses.** The X-ray crystal structures were solved at the Crystal & Molecular Structure Laboratory Center for Chemical Characterization and Analysis at Texas A&M University. For $[(mmp\text{-}dach)_2Ni_2][BArF]_2{\cdot}Et_2O$, $[(dtp\text{-}dach)Ni][PF_6]_{1.6}\ I_{0.4}$, and [(smp-dach)Ni(CN)], X-ray data were obtained on a Rigaku AFC5R diffractometer, operating at 55 kV and 180 mA, Mo K$\alpha$ ($\lambda = 0.710\ 73$ Å) radiation. Structures were solved using SHELXT-PLUS.[17,18] Experimental conditions for the X-ray crystal structure determinations of $[(mmp\text{-}dach)_2Ni_2][BArF]_2{\cdot}Et_2O$, $[(dtp\text{-}dach)Ni][PF_6]_{1.6}I_{0.4}$, and [(smp-dach)Ni(CN)] are given in Table 1.

**Synthesis of 1-(2-Mercapto-2-methylpropyl)-1,4-diazacycloheptane, Hmmp-dach.** Anaerobic techniques were used to charge a 100 mL Schlenk flask with 5.06 g (0.0505 mol) of homopiperazine which dissolved in 50 mL of dry acetonitrile. With stirring the solution was heated to 50 °C under Ar and 4.6 mL (0.047 mmol) of isobutylene sulfide was added. Heating was continued for 20 h, after which the solvent was removed. The remaining residue was transferred to a short-path distillation apparatus, and Hmmp-dach was collected at 110 °C (2 mmHg) as a light yellow or colorless oil, 2.53 g, 27% yield, following the unreacted homopiperazine as the first fraction, 1.20 g, 24% (50 °C, 2 mmHg). FAB/MS parent peak ($m/z$) = 189. $^1$H NMR: $\delta$ (ppm) = 1.27 (s, 6.0 H), 1.70 (m, 3.7 H), 2.58 (s, 2.1 H), 2.81 (m, 8.2 H).

**Synthesis of [1-(2-Mercapto-2-methylpropyl)-1,4-diazacycloheptane]nickel(II) Chloride or $[(mmp\text{-}dach)_2Ni_2]Cl_2$.** In a 100 mL Schlenk flask under Ar or $N_2$, 1.87 g (9.89 mmol) of Hmmp-dach was dissolved in 20 mL of dry, degassed methanol. To this solution was added, via cannula, 0.57 g (10 mmol) of KOH in 10 mL of MeOH. The solution was stirred for 1 h. Addition of 2.33 g (9.80 mmol) $NiCl_2{\cdot}6H_2O$ in 15 mL of methanol immediately produced a dark red solution. After 4 h of stirring the solvent was removed under vacuum, and the resulting red solid was extracted with 25 mL of dry MeCN. The solution was filtered in air to remove the solid KCl. The solvent was then removed by rotary evaporation to yield a tacky, red oil, which was dissolved in a minimum of MeOH. $[(mmp\text{-}dach)Ni_2]Cl_2$ was obtained as a red, powdery solid upon addition of diethyl ether. The crude product (1.19 g, 43%) is hygroscopic, but air stable. Crude samples of $[(mmp\text{-}dach)Ni_2]Cl_2$ were purified by alumina column chromatography. With MeCN as eluent a small, unidentified brown band was obtained. Elution with a mixture of MeOH/MeCN (1:50) yielded a small yellow band followed by a red band of pure $[(mmp\text{-}dach)Ni_2]Cl_2$ (1.03 g, 37%). IR (KBr pellet), cm$^{-1}$: 3123 (s), 3082 (s), 2880 (w), 2856 (w), 1474 (m), 1456 (m), 1441 (w), 1429 (m), 1369 (m), 1309 (m), 1126 (m), 987 (m), 787 (m), 638 (m) cm$^{-1}$. UV−vis (acetonitrile), nm: 514 (520), 348 (2930), 300 (9140), 216 (16 200) nm. Elemental anal. Calcd (found) for $Ni_2C_{18}H_{38}N_4S_2Cl_2$: C, 38.4 (36.8); N, 9.95 (11.3); H, 6.80 (6.53). Mass spectrum ($m/z$): 527 $[(mmp\text{-}dach)_2Ni_2]Cl^+$; 490 $[(mmp\text{-}dach)_2Ni_2]^+$; 245 $[(mmp\text{-}dach)_2Ni_2]^{2+}$.

**Ion Exchange of NaBArF with $[(mmp\text{-}dach)_2Ni_2]Cl_2$.** In a 100 mL Schlenk flask was dissolved 0.102 g (0.363 mmol) of $[(mmp\text{-}dach)Ni_2]Cl_2$ in 10 mL of MeOH followed by addition of 0.674 g (0.762 mmol) of NaBArF in 15 mL of MeOH. The solution was stirred for 1 h. Solvent was reduced to a minimum under vacuum, and 20 mL of diethyl ether was added, precipitating NaCl and yielding a red solution of $[(mmp\text{-}dach)Ni_2][BArF]_2$. Anion exchange produced no significant differences in the UV−vis spectrum although the solubility of the BArF salt was greater than that of the chloride salt. X-ray quality crystals were obtained by pentane diffusion into an ether solution. $\Lambda_m$ (23 °C) = 244 S cm$^2$ mol$^{-1}$ in MeCN.

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**Table 1.** Summary of X-ray Crystal Data for $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2\cdot\text{Et}_2\text{O}$, $[(\text{MeCN})_2(\text{dtp-dach})\text{Ni}][\text{PF}_6]_{1.6}\text{I}_{0.4}$, and [(smp-dach)NiCN]

| | $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2\cdot\text{Et}_2\text{O}$ | $[(\text{MeCN})_2(\text{dtp-dach})\text{Ni}][\text{PF}_6]_{1.6}\text{I}_{0.4}$ | [(smp-dach)NiCN] |
|---|---|---|---|
| empirical formula | $C_{86}H_{72}B_2F_{48}N_4Ni_2OS_2$ | $C_{15}H_{29}F_{9.6}I_{0.4}N_5NiOS$ | $C_{11}H_{23}N_3NiO_3S$ |
| fw | 2292.64 | 668.91 | 336.09 |
| space group | $P\bar{1}$ | $P2_1/c$ | *P*2(1)2(1)2(1) |
| *a* (Å) | 13.009(3) | 8.691 (3) | 6.4223(16) |
| *b* (Å) | 13.626(3) | 203789(6) | 11.454(2) |
| *c* (Å) | 16.031(3) | 14.396(4) | 20.892(2) |
| α (°) | 73.06(3) | 90 | 90 |
| *β* (°) | 74.12(3) | 90 | 90 |
| *γ* (°) | 86.48(3) | 95.28(3) | 90 |
| *V* ($Å^{-3}$) | 2614.1(9) | 2589(1) | 1536.8(5) |
| *Z* | 1 | 4 | 4 |
| *ρ* (calcd g/$cm^3$) | 1.456 | 1.715 | 1.453 |
| temp (K) | 293 (2) | 293 (2) | 193(2) |
| radiation (*λ*) | Mo Kα (0.710 73 Å) | Mo Kα (0.710 73 Å) | Mo Kα (0.710 73 Å) |
| abs coeff ($mm^{-1}$) | 0.529 | 1.493 | 1.405 |
| $R^a$ | 0.0810 | 0.0817 | 0.0373 |
| $R_w$ | 0.2153 | 0.1694 | 0.0833 |

[a] Residuals: $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

**Synthesis of [Diacetonitrile(1-(4,4-dimethyl-3-thiapentanamide)-1,4-diazacycloheptane)nickel] Chloride Iodide or $[(\text{MeCN})_2$(dtp-dach)Ni][Cl][I].** In a 50 mL Schlenk flask were dissolved 135 mg (0.241 mmol) of $[(\text{mmp-dach})\text{Ni}]_2\text{Cl}_2$ and 142 mg (0.767 mmol) of iodoacetamide in 20 mL of acetonitrile. The solution was heated to 50−60 °C and stirred overnight, during which time a light green solid precipitated. The mixture was filtered in air to obtain 211 mg (80%) of product. IR (KBr pellet), $cm^{-1}$: 3094 (s), 2980 (m), 2874 (m), 1659 (vs), 1599 (s), 1419 (m), 1385 (m), 1064 (m), 775 (m), 652 (m). UV−vis (methanol), nm: 818 (12), 640 (16), 386 (38), 236 (4330). Elemental anal. Calcd (found) for $NiC_{11}H_{23}N_3SOClI$: C, 28.3 (29.5); N, 9.01 (9.40); H, 4.97 (5.10). Mass spectrum parent peak (*m/z*): 302. $\Lambda_m$ (23 °C) = 242 S $cm^2$ $mol^{-1}$ in MeCN.

**Synthesis of [1-(2-Mercapto-2-methylpropyl)-1,4-diazacycloheptane]nickel(II) Cyanide or [(mmp-dach)Ni(CN)].** The following synthesis did not require anaerobic techniques. Into a 50 mL round-bottom flask was weighed 56.7 mg (0.872 mmol) of KCN, which was subsequently dissolved in 10 mL of dry MeOH. To this flask was transferred via cannula a $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ (0.250 g, 46 mmol in 10 mL of MeOH) solution. After stirring overnight, the orange solution was filtered in air, yielding an orange filtrate and a light orange solid. The solid was dissolved in 20 mL of hot MeCN and filtered to give a white solid, KCl, and an orange filtrate. The two filtrates were combined and reduced to a minimum, and diethyl ether was added to yield 158.1 mg (65.4%) of a yellow solid. IR (KBr pellet), $cm^{-1}$: 3169 (s), 2952 (m), 2909 (m), 2121 (vs), 1450 (m), 1055 (m), 783 (w). UV−vis (acetonitrile), nm: 418 (225), 280 (4300), 254 (10 200), 218 (9300). Elemental anal. Calcd (found) for $NiC_{10}H_{19}N_3S$: C, 44.15 (43.2); N, 15.4 (14.6); H, 7.04 (6.93). Mass spectrum parent peak (*m/z*): 272.

**Synthesis of [N-(2-Sulfinato-2-methylpropyl)-1,4-diazacycloheptanatocyanonickel(II)] or [(smp-dach)Ni(CN)].** A mixture of 0.059 g (0.218 mmol) of [(smp-dach)Ni(CN)] in 20 mL of water with 56.0 *μ*L of 30% $H_2O_2$ (0.548 mmol) was stirred overnight, producing a color change from orange to bright yellow. Upon removal of solvent the resulting solid was washed with a minimum of methanol. The methanolic solution was reduced to dryness, giving 30.0 mg (0.0987 mmol) of the yellow sulfinato complex. IR (KBr pellet), $cm^{-1}$: 2929 (s), 2118 (m), 1462 (m), 1198 (s), 1049 (s), 914 (m). UV−vis (acetonitrile), nm: 383 (350), 303 (4500), 252 sh (3000), 234 sh (5500), 211 (7900). Elemental anal. Calcd (found) for $NiC_{10}H_{19}N_3O_2S$: C, 36.5 (36.0); H, 6.30 (6.21); N, 13.8 (12.3). Mass spectrum parent peak plus sodium (*m/z*): 326.

## Results and Discussion

**Synthesis and Structure of $[(\text{mmp-dach})_2\text{Ni}_2]^{2+}$.** Whereas the eight-membered cyclic 1,5-diamine, daco, readily and regardless of stoichiometry undergoes double N-alkylation with episulfides to yield $N_2S_2$ ligands, under identical conditions homopiperazine will be alkylated at only one of the two nitrogens. Successive N,N′-alkylation occurs only with much longer reaction times or with heat. As shown in Scheme 1, addition of $NiCl_2\cdot 6H_2O$ to the potassium salt of the purified mmp-dach ligand yielded a hygroscopic, air-stable, red powder. Halide exchange with NaBArF allowed isolation of dark red crystals of $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ as its etherate, which were subjected to X-ray crystal structure analysis.

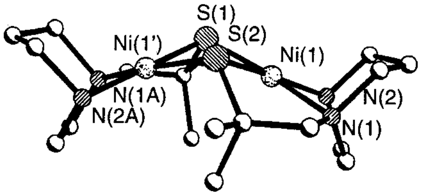

**Figure 1.** Representation of the X-ray crystal structure of $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2\cdot\text{Et}_2\text{O}$. Counterion, solvent, and hydrogen atoms have been omitted. Shown is the *R,R* isomer of the cation. Selected bond lengths (Å): Ni(1)−S(1), 2.197(3); Ni(1)−S(2), 2.150(3); Ni(1)−N(1), 2.040(4); Ni(1)−N(2), 1.965(4); Ni(1′)−S(1), 2.147(3); Ni(1′)−S(2), 2.205(3); Ni(1′)−N(1A), 1.904(4); Ni(1′)−N(2A), 1.894(4); Ni···Ni, 3.034. Selected bond angles (deg): N(1)−Ni(1)−S(2), 91.4(1); N(1)−Ni(1)−S(1), 174.2(1); N(1A)−Ni(1′)−N(2A), 83.7(2); N(1)−Ni(1)−N(2), 78.3(2); S(1)−Ni(1′)−S(2), 83.3(3); S(1)−Ni(1)−S(2), 83.5(1); Ni(1)−S(1)−Ni(1′), 88.6(2); Ni(1)−S(2)−Ni(1′), 88.3(3).

The BArF anions are electronically and sterically the largest feature in the crystal structure of $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$. In Figure 1 is a ball-and-stick representation of the relatively small, dinuclear dicationic complex in one of its possible isomeric forms. The $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ complex, refined in the space group $P\bar{1}$, was found to be disordered about a crystallographic inversion center. Attempts to refine the structure in the noncentrosymmetric space group *P*1, indicated that there are at most four and at least two isomers of the nickel complex present. Refined in the $P\bar{1}$ space group, the structure of $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ was modeled with 50% occupation of each of two isomeric models (the other two models generated by inherent symmetry). The possible isomers are presented in the Supporting Information.

As shown in Figure 1, each nickel is coordinated in a nearly planar $N_2S_2$ environment with a standard deviation from the respective planes of 0.0266 and 0.0381 Å. The $Ni_2S_2$ core is bent such that the best $N_2S_2$ coordination planes intersect at an angle of 135.7° resulting in a Ni···Ni distance of 3.034 Å. Dithiolate bridged nickel dimers typically have more acute hinge angles, ∼110°, and correspondingly shorter Ni···Ni distances, 2.7−2.9 Å.[19,20] Molecular modeling using $\text{Cerius}^2$ suggests that

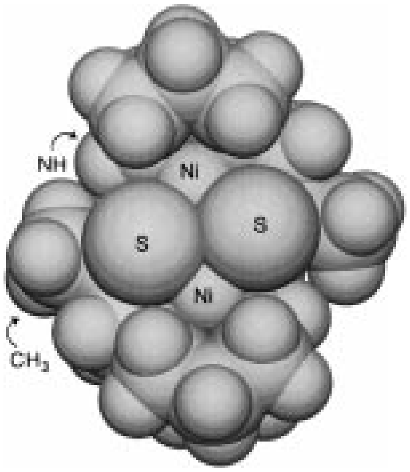

**Figure 2.** Space-filling representation of $[(\text{mmp-dach})_2\text{Ni}_2]^{2+}$ prepared using Cerius$^2$ molecular mechanics system. Heavy-atom coordinates obtained from X-ray crystal structure. Geometry optimizations were done with Cerius$^2$ using the universal force field.[12]

the longer Ni···Ni distance results from steric repulsions between the methyl substituents on the carbon $\alpha$ to sulfur and the amine hydrogen (Figure 2); indeed, substitution of the methyl groups by hydrogen using Cerius$^2$ modeling allows the hinge angle to decrease by 8°.[21] The $(\text{N}_2\text{S})\text{Cu}$ dimer reported by Tolman et al. and described above has a flat $\text{Cu}_2\text{S}_2$ core with a Cu···Cu distance of 2.903 Å.[12] The $\text{N}_2\text{SCu}$ atom arrangement is, however, not planar, unlike the nickel analogue.

The Ni−S bond distance within one mmp-dach unit of $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ is 2.148(3) Å, while that to the bridging thiolate of the neighboring ligand is slightly longer, 2.201(3) Å. These Ni−S distances are comparable to the terminal Ni−S in the monomeric dithiolate complex (bme*-daco)Ni, 2.152(1) Å,[3] and likewise, the average Ni−N distance, 2.005(3) Å, for $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ is similar to that of Ni(bme*-daco), 1.995(3) Å.[3] The ∠N−Ni−N angles in $[(\text{mmp-dach})_2\text{Ni}_2][\text{BArF}]_2$ are quite acute, 78.3(2)° and 83.7(2)°, and within the 76.2−83.8° range found for several dach derivatives;[22] daco-based ligands show the ideal 90° for square planar complexes.

**Solution Properties.** At room temperature in water, conductivity measurements find the $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ complex to behave as a 2:1 electrolyte ($\Lambda_\text{m} = 299$ S cm$^2$ mol$^{-1}$) as expected for an intact dicationic dimer with two uninegative ions free in solution, the overall results of eqs 1 and 2. In acetonitrile, the molar conductance value ($\Lambda_\text{m} = 105$ S cm$^2$ mol$^{-1}$) is more consistent with a 1:1 electrolyte.[23] The latter results can be interpreted as ion pairing of chloride with the dicationic dimer in the less polar acetonitrile or alternatively an equilibrium as expressed by eq 3. Since halide exchange with the noncoordinating BArF anion produces a 2:1 electrolyte in MeCN ($\Lambda_\text{m} = 244$ S cm$^2$ mol$^{-1}$), again consistent with a dimeric dication, the equilibrium expressed by eq 3 is considered unlikely for the halide salt. That is, the dimer retains its structural integrity.

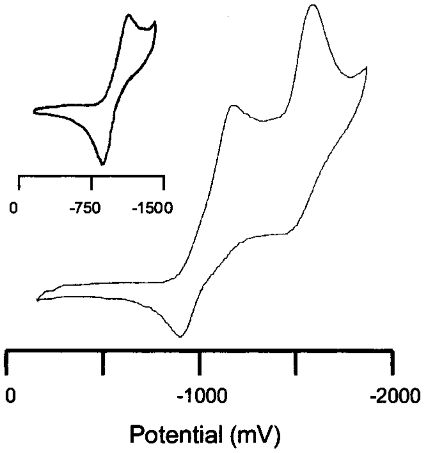

**Figure 3.** Cyclic voltammogram of $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ in 0.1 M TBAHFP in acetonitrile. Referenced to NHE via ferrocene/ferrocenium. Inset: Potential switched at −1400 mV.

$$[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2 \rightleftharpoons [(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}^+ + \text{Cl}^- \quad (1)$$

$$[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}^+ \rightleftharpoons [(\text{mmp-dach})_2\text{Ni}_2]^{2+} + \text{Cl}^- \quad (2)$$

$${}^1/_2[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2 \rightleftharpoons [(\text{mmp-dach})\text{Ni}]^+ + \text{Cl}^- \quad (3)$$

Shown in Figure 3 is the cyclic voltammogram of $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ recorded in $\text{CH}_3\text{CN}$ solution. Two distinct reduction events are observed at −1.06 and −1.50 V. The first reduction is reversible if the potential scan is reversed at −1400 mV, Figure 3 inset. As expressed by eqs 4 and 5, the reductions are assigned to a $\text{Ni}^\text{II}\text{Ni}^\text{II}/\text{Ni}^\text{II}\text{Ni}^\text{I}$ couple and a $\text{Ni}^\text{II}\text{Ni}^\text{I}/\text{Ni}^\text{I}\text{Ni}^\text{I}$ couple yielding a monocationic and a neutral dimeric complex. An irreversible oxidation is observed at +1670 mV.

$$\begin{array}{ccc} [(\text{mmp-dach})_2\text{Ni}_2]^{2+} & \xrightleftharpoons[-1057\text{ mV}]{\pm e^-} & [(\text{mmp-dach})_2\text{Ni}_2]^{+} \\ \text{Ni}^\text{II}\text{Ni}^\text{II} & & \text{Ni}^\text{II}\text{Ni}^\text{I} \end{array} \quad (4)$$

$$\begin{array}{ccc} [(\text{mmp-dach})_2\text{Ni}_2]^{+} & \xrightleftharpoons[-1503\text{ mV}]{\pm e^-} & [(\text{mmp-dach})_2\text{Ni}_2]^{0} \\ \text{Ni}^\text{II}\text{Ni}^\text{I} & & \text{Ni}^\text{I}\text{Ni}^\text{I} \end{array} \quad (5)$$

The $\text{N}_2\text{S}_2$ bridging thiolate donor environment of $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ is aptly compared to the trimetallic complex $[((\text{bme-daco})\text{Ni})_2\text{Ni}]\text{Cl}_2$, Scheme 3.[24] Each complex displays two reduction events which have be assigned to $\text{Ni}^{\text{II/I}}$ couples in $\text{N}_2\text{S}_2$ ligation.[7] Whereas the two reduction events described in eqs 4 and 5 for the dimeric dication are separated by 446 mV, a greater separation of 950 mV is observed for the trimetallic dication. The greater separation of the latter reflects the greater delocalization of charge. The first reduction event of the trimetallic dication is some 1250 mV more accessible than the first reduction of the monomeric neutral (bme-daco)Ni. In contrast the first reduction of $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ is only ca. 900 mV more positive than the reduction of the monomeric dithiolate (bme-daco)Ni, consistent with the differences in complex ion charge and the poorer electron-donating ability of bridging versus terminal thiolates.[25]

**Dimer Splitting by Iodoacetamide.** Iodoacetamide reacts slowly (days) with $[(\text{mmp-dach})_2\text{Ni}_2]\text{Cl}_2$ in warm acetonitrile to produce [diacetonitrile(1-(4,4-dimethyl-3-thiapentanamide)-

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(19) Fackler, J. P., Jr. *Prog. Inorg. Chem.* **1976**, *21*, 55.

(20) Colpas, G. J.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1990**, *29*, 4779.

(21) Cerius$^2$ User Guide, April 1997, San Diego: Molecular Simulations Inc.

(22) A search of the Cambridge Database revealed 23 rings in the 17 reported structures with a range of N−M−N angles of 76.2−83.8°.

(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

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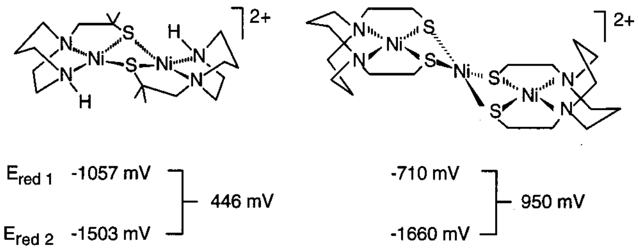
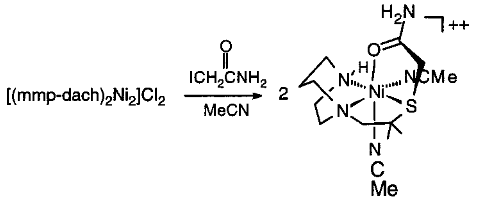
**Scheme 3**



1,4-diazacycloheptane)nickel]chloride iodide, $[(MeCN)_2(dtp\text{-}dach)Ni](Cl)(I)$, as a light green solid, eq 6. The complex is soluble in methanol/acetonitrile and water/acetonitrile mixtures.



(6)

The IR spectrum of $[(MeCN)_2(dtp\text{-}dach)Ni](Cl)(I)$ displays a $\nu$(CO) band at 1659 $cm^{-1}$ which is comparable with observations made for other oxygen-bound acetamide metal complexes.[26] The UV−vis spectrum has three weak d−d transitions at 386, 640, and 818 nm consistent with nickel(II) in an octahedral environment.[27] The complex is electrochemically inactive within the methanol solvent window, +1500 to −1500 mV, with the exception of halide oxidation. Ion exchange of the halide counterion with $PF_6^-$ does not significantly change the UV−vis spectrum and allows isolation of blue crystalline product. Unfortunately the ion exchange was incomplete, vide infra.

X-ray quality crystals of $[(MeCN)_2(dtp\text{-}dach)Ni][(PF_6)_{1.6}I_{0.4}]$ were obtained by layering of ether onto a methanol/acetonitrile solution of the acetamide complex. The unusual chemical formula for the counterion can be attributed to iodine contamination that replaces one $PF_6^-$ ion at the 40% level. As shown in Figure 4, the nickel adopts an octahedral geometry with four of the donor atoms (2 N, 1 S, 1 O) from the dtp-dach ligand and two coordinated, cis acetonitrile molecules. Alkylation of the thiolate sulfur coupled with the expansion of the nickel coordination from 4 to 6 results in a significant lengthening of the Ni−S bond from 2.148(3) in the four-coordinate $[(mmp\text{-}dach)_2Ni_2]Cl_2$ to 2.452(3) Å. (A similar Ni−S distance is observed in the octahedral bis-acetamide derivative of (bme*-daco)Ni; the pendant sulfur bound acetamide coordinates to nickel via the carbonyl oxygen with a Ni−O distance of 2.094(6) Å.[26]) The average $Ni-N_{dach}$ distance is also slightly expanded, 2.065(8) Å. The N−Ni−N angle of 76.8(3)° is relatively unchanged from $[(mmp\text{-}dach)_2Ni_2]^{2+}$.

**Dimer Splitting by Cyanide and Subsequent Reactivity. Characterization of [(mmp-dach)Ni$^{II}$(CN)] and [(smp-dach)-Ni$^{II}$(CN)].** As precedented for a neutral dimeric, $NS_2$ thiolate bridged nickel dimer,[20,28] addition of 2 equiv of KCN to a MeOH solution of $[(mmp\text{-}dach)_2Ni_2]Cl_2$ results in an immediate color change from maroon to orange. The very low conductivity of an acetonitrile solution of the isolated yellow solid and the parent peak at $m/z = 272$ in the $FAB^+$ mass spectrum are consistent with the formulation of the complex as the monomer, [(mmp-dach)Ni(CN)]. The infrared spectrum displays a single intense peak in the $\nu$(CN) region at 2121 $cm^{-1}$, which is comparable to that of a related thiolato nickel(II) cyanide reported by Maroney et al.[20,28]

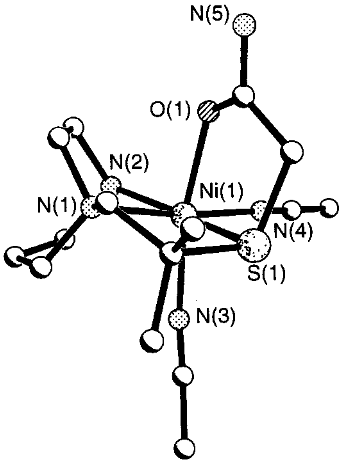
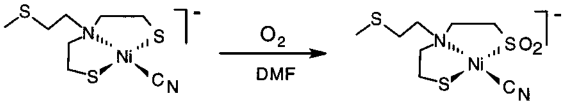


**Figure 4.** Representation of the X-ray crystal structure of $[(dtp\text{-}dach)Ni][(PF_6)_{1.6}I_{0.4}]$. Counterions are not shown. Hydrogen atoms have been omitted. Selected bond distances (Å): Ni(1)−S(1), 2.452(3); Ni(1)−O(1), 2.094(6); Ni(1)−N(1), 2.095(8); Ni(1)−N(2), 2.060(8); Ni(1)−N(3), 2.067(9); Ni(1)−N(4), 2.063(9). Selected bond angles (deg): N(2)−Ni(1)−N(4), 95.3(3); N(2)−Ni(1)−N(3), 97.5(3); N(3)−Ni(1)−N(4), 87.3(3); N(2)−Ni(1)−O(1), 93.8(3); N(2)−Ni(1)−N(1), 76.8(3); N(3)−Ni(1)−N(1), 98.2(3); O(1)−Ni(1)−N(1), 87.3(3); N(3)−Ni(1)−S(1), 87.5(2); O(1)−Ni(1)−S(1), 82.5(2); N(1)−Ni(1)−S(1), 87.3(2).

The similarity in reduction potentials of the Ni$^{II/I}$ couple of the neutral monomer [(mmp-dach)Ni(CN)], −2038 mV, and (bme*-daco)Ni, −2119 mV, suggests that the "electron-richness" of the complexes and resultant nucleophilicities of the thiolates should likewise be similar. Indeed, reaction of [(mmp-dach)Ni(CN)] with MeI produces only a minor shift in $\nu$(CN) of the product, suggesting that alkylation occurs at the thiolate sulfur rather than at the cyanide nitrogen. The more reactive and less discriminating alkylating agent, $Me_3OBF_4$, results in the disappearance of the $\nu$(CN) band with formation of a transient species at 2192 $cm^{-1}$. Ultimately all color is lost from the solution as all bands in the 2000−2200 $cm^{-1}$ region disappear. This result is interpreted as alkylation at the CN nitrogen with subsequent loss of $CNCH_3$ and complex degradation.

**Oxygenation of [(mmp-dach)Ni(CN)] by $H_2O_2$.** According to the similarity in the Ni$^{II/I}$ redox potentials, discussed above, the S-based oxygenation activity established for (bme-daco)Ni complexes[4,8] is expected to be viable in [(mmp-dach)Ni(CN)]. Nevertheless methanolic or acetonitrile solutions of [(mmp-dach)Ni(CN)] purged with $O_2$ resulted in oxygenation of the thiolates. Even upon standing under an atmosphere of $O_2$ for a week no oxygen uptake was observed. Such a negative result for our *neutral* thiolato cyanide contrasts to the *anionic* dithiolato cyanide of Maroney et al. for which reaction with ground-state $O_2$ readily leads to the sulfinate complex, eq 7.[29]



(7)

As shown in Scheme 2, reaction of [(mmp-dach)Ni(CN)] with the stronger O-atom donor, $H_2O_2$, yielded the yellow sulfone

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(26) Smee, J. J.; Goodman, D. C.; Reibenspies, J. H.; Darensbourg, M. Y. *Eur. J. Inorg. Chem.* **1999**, 539.

(27) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier Publishing Company: Amsterdam, 1968; p 333.

(28) Kumar, M.; Colpas, G. J.; Day, R. O.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8323.

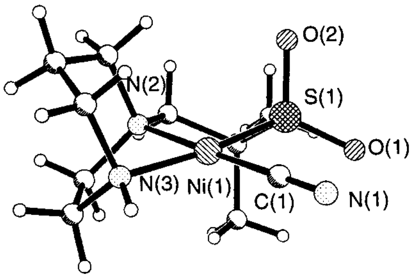


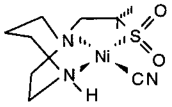
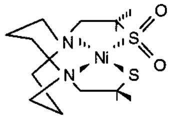
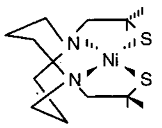
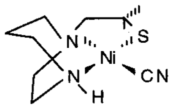
**Figure 5.** Representation of the X-ray crystal structure of [(smp-dach)-NiCN]. Counterions are not shown. Hydrogen atoms have been omitted. Selected bond distances (Å): Ni(1)−N(2), 1.950(5); Ni(1)−N(3), 1.921(5); Ni(1)−C(1), 1.865(6); Ni(1)−S(1), 2.1223(17); S(1)−O(1), 1.465 (4); S(1)−O(2), 1.474(4); C(1)−N(1), 1.503(8). Selected bond angles (deg): N(2)−Ni(1)−N(3), 82.2(2); C(1)−Ni(1)−S(1), 94.49(19); C(1)−Ni(1)−N(3), 95.9(2); N(2)−Ni(1)−S(1), 87.41(14); N(3)−Ni(1)−S(1), 169.46(16); N(2)−Ni(1)−C(1), 177.0(2); N(1)−C(1)−Ni(1), 178.7(6); O(1)−S(1)−O(2), 114.7(3); O(1)−S(1)−Ni(1), 120.65(18); O(2)−S(1)−Ni(1), 108.43(18).

cyanide complex. That the yellow product was an S-oxygenate was indicated by $\nu$(SO) stretches at 1198 and 1049 cm$^{-1}$, and the X-ray crystal structure described below confirmed the presence of the metallosulfone. The thermodynamic stability of the metallosulfone thus demonstrated suggests a deactivating effect of the cyanide ligand toward the nucleophilicity of the thiolato sulfur in the [(mmp-dach)Ni(CN)] when molecular O$_2$ is the electrophile or oxygen source. The reactivity shown in eq 7 derives from the presence of a second thiolate positioned to enhance the S$_{\text{lone pair}}$−Ni$_d$ antibonding interaction. It is notable that the remaining thiolate in the cyano nickel sulfone product is unreactive with molecular oxygen.

**X-ray Crystal Structure Analysis of [(smp-dach)Ni$^{II}$(CN)].** Suitable crystals of [(smp-dach)Ni$^{II}$(CN)] for X-ray analysis were obtained by ether diffusion into a saturated methanol solution. The ball-and-stick representation of the structure, Figure 5, shows a four-coordinate square planar nickel in a N$_2$S-(CN) donor environment (tetrahedral twist of only 0.3°). Unlike [(mmp-dach)$_2$Ni$_2$][BArF]$_2$, [(smp-dach)Ni(CN)] has only one isomer in the crystal structure. The Ni−N distances average to 1.936 Å, which is substantially the same as the Ni−N average in the four-coordinate complex [(mmp-dach)$_2$Ni$_2$]$^{2+}$ but significantly shorter than in the hexacoordinate [(dtp-dach)Ni]$^{2+}$. Consistent with previous observations, the dach framework enforces a relatively acute ∠NNiN of 82.2°. The nickel−sulfur distance of 2.122 Å is slightly shorter than those observed in [(mmp-dach)$_2$Ni$_2$]$^{2+}$ and [(dtp-dach)Ni]$^{2+}$, and the average S−O bond distance of ca. 1.47 Å is similar to that observed for the previously characterized Ni−SO$_2$R complexes.[25] The Ni−CN and Ni−SO$_2$R metric parameters of [(smp-dach)Ni(CN)] are very similar to the Maroney et al. anionic complex shown in eq 7.[20]

**Electrochemical and Spectral Comparison of N$_2$SX Nickel Complexes.** Listed in Table 2 are infrared and electrochemical data of four neutral analogous N$_2$SNi(X) complexes of interest to our study. From this data it may be concluded that relative to a thiolate sulfur donor the effect of the anionic ligands on the electron richness of the nickel (as implied by the Ni$^{II/I}$ reduction accessibility) varies as follows: RSO$_2^-$ < CN$^-$ < RS$^-$. That is, conversion of a thiolate sulfur to a sulfinato sulfur has the effect of shifting the Ni$^{II/I}$ couple positively by 283 mV whereas exchange of a thiolate-S donor by a CN$^-$ donor shifts the couple by only 74 mV.

**Table 2.** Comparison of RSO$^-$, CN$^-$, and RS$^-$ as Ligands to Square Planar N$_2$SNi

| | ν(SO) (cm$^{-1}$)$^a$ | Ni$^{II/I}$ (mV)$^b$ | ν(CN) (cm$^{-1}$)$^a$ |
|---|---|---|---|
|  | 1198<br>1049 | -1655$^c$ | 2118 |
|  | 1181<br>1044 | -1829 | |
|  | | -2112 | |
|  | | -2038 | 2121 |

$^a$ KBr pellet. $^b$ All potentials scaled to NHE referenced to ferrocene. Samples measured in acetonitrile solutions with 0.1 M TBAHP as supporting electrolyte and Ag$^0$/AgNO$_3$ as a reference electrode. $^c$ Irreversible reduction.

## Conclusions

The tridentate N$_2$S ligand was easily prepared and coordinated to Ni$^{II}$, yielding a dimeric dithiolate bridged cation. The ligand is based on the cyclic diamine diazacycloheptane, which has a N−M−N bite angle some 10° more acute than its more expensive and labor intensive analogue diazacyclooctane. The dimeric complex is susceptible to cleavage by the strong field donor cyanide, and by alkylation agents with tethered functionalities, such as the protein modification reagent iodoacetamide. Clearly the dimer holds promise for cleavage by other ligands such as thiolates or alkoxides, thus permitting a systematic study of Ni−X complexes with a common N$_2$S component.

**Acknowledgment.** Financial support from the National Science Foundation for this work (CHE 94-15901 and CHE 98-12355) and the X-ray diffractometer and crystallographic computing system (CHE 8513273) and contributions from the R. A. Welch Foundation are gratefully acknowledged. C.A.G. acknowledges additional funding from a DOW Teacher/Scholar Fellowship. The assistance of Erica Lyon with the Cerius$^2$ modeling is much appreciated.

**Supporting Information Available:** A figure depicting isomers of [(mmp-dach)$_2$Ni]$^{2+}$ and a packing diagram for [(mmp-dach)$_2$Ni$_2$]-[BArF]$_2$. X-ray crystallographic files in CIF format for the structures of [(mmp-dach)$_2$Ni$_2$][BArF]$_2$, [(dtp-dach)Ni(CH$_3$CN)$_2$][PF$_6$]$_{1.6}$I$_{0.4}$, and [(smp-dach)Ni(CN)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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