# Subtle Bite-Angle Influences on N₂S₂Ni Complexes

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A new N₂S₂Ni complex based on the 1,4-diazacycloheptane (dach) framework allows the study of the effects of ring size, in fused diamines, on the structural and chemical properties of nickel(II) dithiolate and dithioether complexes. Compared to its 1,5-diazacyclooctane (daco) derivatives, the dithiolate complex (bmedach)Ni and the S-templated, macrocyclic dithioether complex (propyl-bmedach)NiBr₂ show decreased cavity sizes with narrower ∠N−Ni−N angles (by ca. 6°) and wider ∠S−Ni−S angles (also by ca. 6°). The electrochemical properties of the dithiolate complexes based on dach and daco are nearly identical, while the (propyl-bmedach)NiBr₂ complex shows a 140 mV destabilization of the Niᴵ oxidation state relative to its daco analogue. Molecular structures for the (bmedach)Ni and (propyl-bmedach)NiBr₂ complexes and their respective electrochemical and spectroscopic properties are reported.

## Introduction

A broad series of ligands based on the diazacyclooctane (daco) framework derivatized with episulfides have been useful for delineating square-planar nickel(II) coordination chemistry.[1−3] The study of these complexes has led to a better understanding of the scope of nickel-bound, thiolate-sulfur modification and how such changes influence the redox accessibility of the Niᴵ and Niᴵᴵᴵ oxidation states, in particular as they might pertain to the redox properties measured in [NiFe]hydrogenase.[1] It was verified that the Niᴵ oxidation state is stabilized upon conversion of the thiolates to thioethers (ca. +600 mV per alkylation),[1] to RSOₓ by oxygenation (by ca. +150 mV per O atom),[3] and on their interaction with metal cations.[2] This stabilization is due to the relief of the $S_{p\pi}-Ni_{d\pi}$ antibonding interaction in the Ni−SR HOMO,[4−6] as well as the increase in the positive charge on the complex. In contrast, the Niᴵᴵᴵ oxidation state is destabilized in the cationic thioether derivatives, but gains stability when those derivatives contain additional ligating sites leading to N₂S₂O₂ octahedral complexes.[7,8]

While the N₂S₂Ni complexes based on the daco framework have produced an extremely useful body of work, the synthesis of the daco diazacycle is not trivial. Hence we explored the use of the commercially available diazacycloheptane (dach) as a platform for further N₂S₂ ligand development.[9] In addition, the

**Scheme 1**
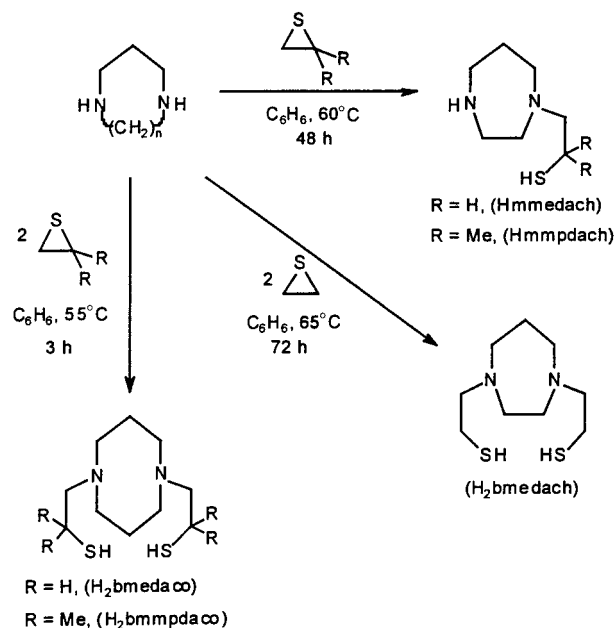


dach diazacycle would permit an assessment of decreasing scaffold ring size on the formation of the N₂S₂ ligand and the physicochemical properties of the resulting nickel(II) complexes.

An important difference was found in the reactivity of dach vs daco with episulfides to yield the mixed N/S ligands (Scheme 1). Two equivalents of episulfide, ethylene sulfide, or isobutylene sulfide readily add to the daco diamine, yielding *N,N'*-bis-(mercaptoethyl)-1,5-diazacyclooctane (H₂bmedaco) and *N,N'*-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane (H₂bmmp-daco), respectively. In contrast, under similar conditions, only one equivalent of episulfide will add to the dach diamine and forms N₂S tridentate ligands. With significantly longer reaction times, 2 equiv of the less sterically hindered ethylene sulfide adds, producing H₂bmedach. In this paper we present the X-ray crystal structures and chemical properties of the (bmedach)Ni and the S-templated macrocyclic (propyl-bmedach)NiBr₂ com-

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(9) Grapperhaus, C. A.; Bellefeuille, J. A.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1999**, *38*, 3698.

plexes. The structural features of these compounds are discussed in relation to their magnetic, spectroscopic, and electrochemical properties; these properties are then compared to those of the analogous daco derivatives.

## Experimental Section

**General Methods.** Nickel acetylacetonate (Strem Chemical Company), 1,3-dibromopropane (Lancaster Synthesis Ltd.), 1,4-diazacycloheptane, ethylene sulfide, and methyl iodide (Aldrich Chemical Co.) were used as received. Benzene, methanol, toluene, and diethyl ether were dried according to standard procedures and freshly distilled prior to use.[11] NMR solvents were purchased from Cambridge Isotopes Laboratories and used as received. The ligand H$_2$bmedach formed disulfide species upon long (hours) exposure to O$_2$, necessitating that the syntheses of the ligand and the (bmedach)Ni complex be carried out using dry and degassed solvents under dry N$_2$ or Ar atmosphere. Once isolated, the (bmedach)Ni showed little sensitivity toward O$_2$ or water. Due to the hygroscopic nature of the alkylated derivatives of (bmedach)Ni, their syntheses required careful exclusion of water.

**Physical Methods.** Proton NMR spectra were recorded in $d_4$-MeOH on a Varian XL-200 FT-NMR. Mass spectral analyses were done at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Positive ion fast atom bombardment mass spectra were recorded in a 4-nitrobenzyl alcohol (NBA) matrix using a VG-70S spectrometer with a xenon source having a particle energy of 10 keV. The data were collected by a VG11−250J data system. UV−vis spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer using quartz cells (1.00 cm path length). Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Delta, British Columbia, Canada. Cyclic voltammograms were recorded on a BAS-100A electrochemical analyzer with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag$^0$/AgNO$_3$ reference electrode. Samples (ca. 2.5 mM) were measured in CH$_3$CN with tetra-$n$-butylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. Potentials were standardized with Cp$_2$Fe$^+$/Cp$_2$-Fe (+400 mV vs NHE). It should be noted that the preferred reference potential for ferrocene in acetonitrile solutions is +600 mV.[12] However, to facilitate comparisons with complexes previously characterized in our laboratory, we will continue to use the +400 mV reference.

**X-ray Crystal Structure Analysis.** The X-ray crystal structures were solved at the Crystal Structure Laboratory Center for Chemical Characterization and Analysis at Texas A&M University. Cell parameters and data collection summaries for (bmedach)Ni and (propyl-bmedach)NiBr$_2$ are given in Table 1. The X-ray crystal data of (bmedach)Ni were obtained on a Siemens P-4 single-crystal X-ray diffractometer operating at 50 kV and 30 mA, Mo Kα ($\lambda$ = 0.71073 Å). The X-ray crystal data of (propyl-bmedach)NiBr$_2$ were obtained on a Bruker SMART-1000 single-crystal X-ray diffractometer operating at 50 kV and 40 mA, Mo Kα ($\lambda$ = 0.71073 Å) radiation. For both complexes, data reduction was done with SAINTPLUS (Bruker);[13] structure solution, with SHELXS-86 (Sheldrick);[14] and structure refinement, with SHELXL-97 (Sheldrick).[15] Both crystal structures were solved by direct methods, and anisotropic refinement for all non-hydrogen atoms was done by a full-matrix least-squares method.

**Syntheses.** The (bmedaco)Ni[16] and its corresponding (propyl-bmedaco)NiBr$_2$ bicyclic complex[17] were prepared according to published procedures that served as the guide for the syntheses of the analogous dach complexes that follow.

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(15) Sheldrick, G. *SHELXL-97*, Program for Crystal Structure Refinement; Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400, Göttingen, Germany, 1997.

**Table 1.** Experimental Data for the X-ray Crystal Structures of (bmedach)Ni and (propyl-bmedach)NiBr$_2$

| | (bmedach)Ni | (propyl-bmedach)NiBr$_2$ |
|---|---|---|
| chemical formula | C$_9$H$_{18}$N$_2$S$_2$Ni | C$_{12}$H$_{22}$Br$_2$N$_2$NiS$_2$·H$_2$O |
| fw | 277.08 | 494.98 |
| space group | orthorhombic | monoclinic |
| | *Pnma* | *P2$_1$/c* |
| $a$, Å | 10.056(4) | 14.0180(9) |
| $B$, Å | 14.796(6) | 10.4274(6) |
| $C$, Å | 7.526(2) | 13.3327(8) |
| $\beta$, deg | 90.000 | 113.1340(10) |
| $V$, Å$^3$ | 1119.8(7) | 1792.15(19) |
| $\rho$, g/cm$^3$ | 1.644 | 1.835 |
| Z | 4 | 4 |
| temp, K | 193 | 110 |
| radiation ($\lambda$, Å) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| $\mu$, mm$^{-1}$ | 2.068 | 5.772 |
| $R(F)^a$ | 0.0576 | 0.0593 |
| $R_w(F^2)^{a,b}$ | 0.1478 | 0.1449 |

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

***N,N′*-Bis(2-mercaptoethyl)-1,4-diazacycloheptanenickel(II), (bmedach)Ni.** In a 250 mL Schlenk flask equipped with a magnetic stir bar, 5.24 g of 1,4-diazacycloheptane, dach (52.4 mmol), were dissolved in 100 mL of dry benzene. The mixture was heated to 65 °C under Ar, after which time 8 mL (134 mmol) of ethylene sulfide was added. The mixture was stirred for 72 h at 65 °C. A fine white powder that precipitated from solution was removed by anaerobic filtration through Celite in a glass-fritted funnel. The solvent was removed from the filtrate in vacuo while maintaining the temperature at 60−65 °C; continued heating under vacuum removed any unreacted dach. The resulting pale yellow to colorless H$_2$bmedach liquid was transferred to a 500 mL Schlenk flask and dissolved in 50 mL of dry toluene. To this was added, dropwise via cannula, a solution containing an equimolar amount (relative to that of the dach diamine) of Ni(acac)$_2$ dissolved in 250 mL of dry toluene. During this time a tan-colored precipitate formed. Upon complete addition of the Ni(acac)$_2$, the mixture was stirred for an additional hour and the crude (bmedach)Ni precipitate was collected by filtration (anaerobic conditions are not required). The complex was purified by recrystallization from a hot (60 °C) 50:50 MeOH/H$_2$O solvent mixture. Yield: 1.53 g (10.5% based on dach). UV−vis spectrum in MeOH [$\lambda_{max}$, ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 457(290), 278(12500), 236-(11500). Mass spectrum ($m/z$) = 277. Anal. Calcd (found): C, 39.02 (39.08); H, 6.55 (6.47); N, 10.11 (10.13).

**4-8-Dithia-1,11-diazabicyclo[9.3.2]hexadecanenickel(II) bromide, (propyl-bmedach)NiBr$_2$.** To a 25 mL CH$_3$CN slurry of 110 mg (0.40 mmol) of (bmedach)Ni was added 0.5 mL (4.1 mmol) of 1,3-dibromopropane. The solution changed from a light yellow to red-orange as the (bmedach)Ni was consumed. The few crystals that formed overnight from the stirred solution were augmented by precipitation upon addition of diethyl ether. The liquid was decanted and the solid washed with an additional 2 × 10 mL of diethyl ether; the orange powder was dried overnight in vacuo. Yield: 103 mg (53.7%). UV−vis spectrum in MeCN [$\lambda_{max}$, ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 495(320), 271(9900), 218sh(15500), 203(17800). Molar conductivity measured in CH$_3$CN: 320 S/cm·mol. Mass spectrum ($m/z$) = 318. Anal. Calcd (found): C, 30.1 (29.1); H, 5.05 (5.02); N, 5.85 (5.61).

**1,4-Bis[2-(methylsulfanyl)ethyl]-1,4-diazacycloheptanenickel-(II) Iodide, (Me$_2$-bmedach)NiI$_2$.** To a 50 mL CH$_3$CN slurry of 190 mg (0.69 mmol) of (bmedach)Ni was added 3 equiv (135 μL, 2.2 mmol) of MeI via syringe. The solution was stirred overnight, during which time black crystals formed on the bottom of the flask. Addition of a large excess of ether precipitated the remainder of the product as a brown solid, which was collected by filtration (aerobic) and dried in vacuo. The product thus obtained was used without further purification

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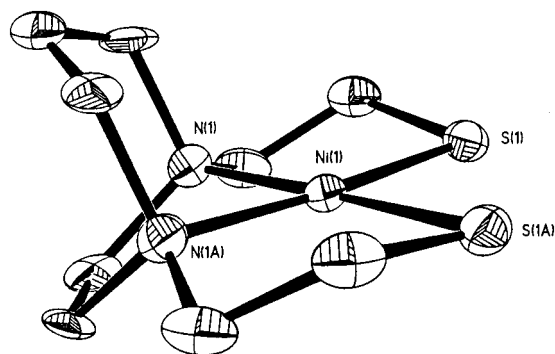(17) Musie, G.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 302.

**Figure 1.** Thermal ellipsoid plot (at 50% probability) of (bmedach)-Ni. The hydrogen atoms are omitted.
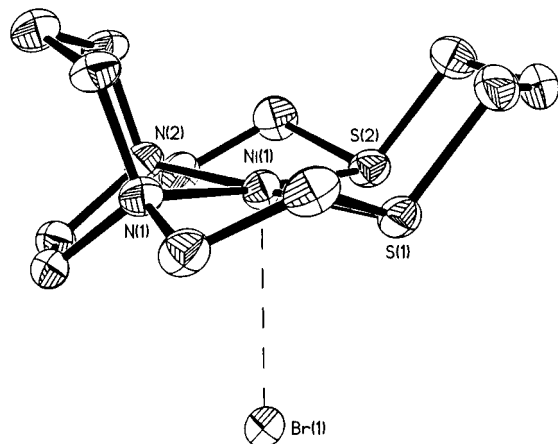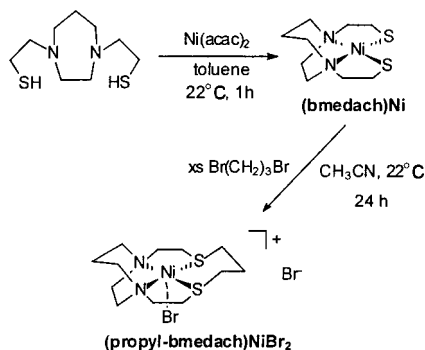


**Figure 2.** Thermal ellipsoid plot (at 50% probability) of the monocationic unit of (propyl-bmedach)NiBr₂. The noninteracting bromide counterion, the single water of crystallization, and all hydrogen atoms are omitted.

and was stored in a desiccator prior to use. Yield: 239 mg (62.1%). Anal. Calcd (found): C, 23.6 (22.9); H, 4.31 (4.34); N, 4.99 (5.67).

**Scheme 2**



**Table 2.** Comparison of Metric Parameters from the dach and daco[a] Derivatives



| | (bmedach)Ni | (propyl-bmedach) NiBr₂ |
|---|---|---|

| | (bmedaco)Ni | (propyl-bmedaco) NiBr₂ |
|---|---|---|
| Ni-N (Å) | 1.940(4) | 1.924(4) |
| | 1.940(4) | 1.923(4) |
| | *1.979(7)* | *1.990(8)* |
| | *1.979(7)* | *1.979(9)* |
| Ni-S (Å) | 2.164(1) | 2.163(1) |
| | 2.164(1) | 2.160(1) |
| | *2.159(3)* | *2.188(3)* |
| | *2.159(3)* | *2.202(3)* |
| Ni···Br (Å) | n/a | 3.039 |
| | n/a | *2.944* |
| Ni···N₂S₂ (Å)[b] | n/a | 0.065 |
| | n/a | *0.110* |
| ∠N-Ni-N (°) | 82.5(2) | 82.8(2) |
| | *89.3(4)* | *89.3(3)* |
| ∠S-Ni-S (°) | 95.4(1) | 93.8(1) |
| | *89.4(1)* | *89.9(1)* |
| Td twist (°)[c] | 0.0 | 0.8 |
| | *13.3* | *0.2* |
| Arm conformation[d] | eclipsed | eclipsed |
| | *staggered* | *eclipsed* |

[a] The metric parameters for the daco derivative, given in italics, are taken from refs 16 and 17. [b] Defined as the nickel displacement from the best N₂S₂ plane. [c] Defined as the intersection of the normals of the S−X−S and N−X−N planes where X is the centroid of the N₂S₂ plane. As the nickel atom is not necessarily equidistant from the nitrogen and sulfur atoms, the centroid rather than the nickel is used to define the planes. [d] As viewed across the N₂S₂Ni plane.

## Results and Discussion

**Preparation and Structures of the dach Complexes.** Summarized in Scheme 2 are the details for the syntheses of (bmedach)Ni and (propyl-bmedach)NiBr₂.

Both products were crystalline and suitable for X-ray diffraction studies; details of the collection and refinement are presented in Table 1, and molecular structures are given in Figures 1 and 2. Listings of selected metric data and structural features are given in Table 2 for the new compounds of this study and for the diazacyclooctane analogues, (bmedaco)Ni and (propyl-bmedaco)NiBr₂.[16,17] The N₂S₂ donor ligands of (bmedach)Ni and (propyl-bmedach)NiBr₂ maintain square planarity

in both thiolate and thioether forms. The structures shown in Table 2 illustrate that the chair conformation predominates in the six-membered nickel-diazacyclohexane and nickel-dithiacyclohexane rings. For the (bmedaco)Ni complex, there is a pronounced Td twist distortion from square planarity of ca.

**Table 3.** Comparison of Electronic Spectroscopy[a] and Electrochemistry[a] of the dach and daco[b] Derivatives

| | (bmedach)Ni<br>*(bmedaco)Ni* | (propyl-bmedach)NiBr$_2$<br>*(propyl-bmedaco)NiBr$_2$* |
|---|---|---|
| color[c] | red-brown/yellow-brown<br>*purple/purple* | orange/orange-red<br>*purple/violet* |
| $\lambda_{max}$ (nm) ($\epsilon$) | 457(290)[d]<br>*506(640)*<br>*602 sh* | 495(320)<br>*410(151)*<br>*581(142)* |
| $E_{1/2}$ Ni$^{II/I}$ | −2051 mV<br>*−2048 mV* | −813 mV<br>*−670 mV* |
| $E_{pa}$ | +254 mV<br>*+246 mV* | +882 mV<br>*+869 mV* |
| $E_{1/2}$, rev | +756 mV<br>*+801 mV* | +1138 mV<br>*+1108 mV* |

[a] Unless specified otherwise, all results were obtained from acetonitrile solutions. [b] The parameters for the daco derivatives are given in italics and are taken from refs 16 and 17. [c] In the solid state/solution (acetonitrile or methanol). [d] The electronic spectrum of (bmedach)Ni was measured in methanol.

13.3°.[16] In contrast the (bmedach)Ni complex is essentially square planar, which accounts for sharper signals in the ¹H NMR spectrum as compared to the (bmedaco)Ni complex.

Whereas the differences in the Ni−N and Ni−S bond distances are of little statistical significance, the Ni−N and the Ni−S distances in the dach derivatives are shorter than those in the daco derivatives. Larger metric differences are in the ∠N−Ni−N angles enforced by the two diazacycles, which are observed at 83° and 89° for the dach and daco derivatives, respectively. As a result, the ∠S−Ni−S angles open to 95° and 94° for (bmedach)Ni and (propyl-bmedach)NiBr$_2$, respectively; in contrast, both daco derivatives have ∠S−Ni−S angles of 89°.

In the (propyl-bmedach)NiBr$_2$ and (propyl-bmedaco)NiBr$_2$ analogues, a single bromide is positioned to interact with nickel(II) in an axial fashion, generating a quasi-square-pyramidal coordination geometry. The comparative data of Table 2 show this to be a long-range Br⁻···Ni$^{II}$ interaction, ca. 2.9−3.0 Å. A bona fide Ni−Br bond in a similar N$_2$S$_2$NiBr complex is 2.45 Å.[18] Also supporting this description is the fact that the nickel atoms in both the (propyl-bmedach)NiBr$_2$ and (propyl-bmedaco)NiBr$_2$ complexes are slightly pulled out of the best-fit N$_2$S$_2$ plane and oriented toward Br⁻. This pseudo-square-pyramidal geometry accounts for the observed paramagnetism, vide infra. A cocrystallized water molecule appears to be H-bonded to both Br⁻ counterions, as seen by the O···Br distances of 3.46 and 3.37 Å for the Br⁻ interacting with the Ni center and the noninteracting Br⁻, respectively.

**Electronic Properties.** The daco dithiolate derivative is more richly colored than its dach analogue; the UV−vis solution spectra and molar absorptivity coefficients in CH$_3$CN reflect these differences, suggesting that the distortions seen in the solid-state structures are maintained in the solution samples (Table 3). The solution spectroscopic properties of the derivatives (propyl-bmedaco)NiBr$_2$ and (propyl-bmedach)NiBr$_2$ are more similar, most likely on account of the restrictions in the N$_2$S$_2$ macrocyclic plane, as well as the tendency for axial interactions of anion or solvent for the dicationic complexes, which prevent tetrahedral distortions. Since the conductivity of (propyl-bmedach)NiBr$_2$ in CH$_3$CN is consistent with a uni-dielectrolyte,[19] a replacement of the interacting Br⁻ by CH$_3$CN or adventitious water, freeing both Br⁻ counterions, is suggested.

It should be noted that the ¹H NMR spectra of both propyl macrocycles display somewhat broadened peaks, with the daco derivative significantly more broadened than its dach analogue. While broadened peaks are consistent with a thermally accessible paramagnetic state resulting from pentacoordination, variable-temperature ¹H NMR spectra showed no changes in line widths for either complex.

**Electrochemical Properties.** A summary and comparison of the electrochemical properties of (bmedach)Ni, (bmedaco)Ni, (propyl-bmedach)NiBr$_2$, and (propyl-bmedaco)NiBr$_2$ are given in Table 3. The four complexes all show reversible waves assigned to the Ni$^{II/I}$ redox couple. Irreversible anodic events are ascribed to thiolate oxidation in the case of the dithiolate derivatives and bromide counterion oxidation for the salts of the macrocyclic derivatives. A quasi-reversible wave is observed for all four complexes centered in the range of +700 to +1200 mV. A Ni$^{III/II}$ redox couple is expected to be in this region; however the species that gives rise to this couple has not been defined.

There is no difference in the Ni$^{II/I}$ redox potential for (bmedach)Ni and (bmedaco)Ni; however the (propyl-bmedaco)NiBr$_2$ derivative displays a 140 mV stabilization of the Ni$^I$ oxidation state relative to (propyl-bmedach)NiBr$_2$. This observation could be attributed to the smaller cavity size of the (propyl-bmedach)NiBr$_2$ macrocycle or to a decreased Ni$^{II}$-axial ligand or specific counterion interaction in (propyl-bmedaco)NiBr$_2$. Since conductivity measurements indicate that the latter is not the case, the decreased N$_2$S$_2$ cavity size and accompanying decreased flexibility would appear to be the more likely explanation. In support of the cavity-size/flexibility argument, the open-chain dithioether derived from double MeI alkylation of (bmedach)Ni, (Me$_2$-bmedach)NiI$_2$, shows the most accessible Ni$^{II/I}$ couple (−712 mV) of the three dach derivatives, while the daco analogue, (Me$_2$-bmedaco)NiI$_2$, with its larger cavity size, has a Ni$^{II/I}$ redox couple at −482 mV.[16] This lowest of all values is consistent with the greater flexibility of the open-chain tetradentate, dithioether ligand.

## Summary and Remarks

The effects of ring size, and of fused rings, in doubly bridged tertiary N donors in open-chain ligands on complex stability have been extensively explored and recently reviewed by Martell and Hancock.[20] Pertinent to the subject of this paper are references to square-planar nickel(II) complexes of the following ligands:
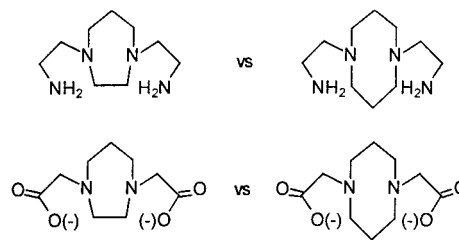


Both comparisons of dach versus daco frameworks find the latter to form more stable complexes with nickel(II), a result that is ascribed to a more favorable N−Ni size match or orbital orientation match for daco. On the basis of qualitative results (ease of isolation and stability on storage) we see no difference in the stability of the dithiolate and macrocyclic dithioether complexes thus far derived from daco versus dach.

According to the analysis of Hancock et al.,[20] the ideal geometry for a metallodiazacyclopentane ring should have a

(18) Buonomo, R. M.; Reibenspies, J. H.; Darensbourg, M. Y. *Chem. Ber.* **1996**, *129*, 779.
(19) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

N$-$M distance of 2.5 Å and a N$-$M$-$N angle of 69°; for a metallodiazacyclohexane ring the optimal parameters are 1.6 Å and 109.5°, respectively. Neither of these metric sets is congruent with the data presented here. The Ni$-$N and Ni$-$S distances vary by less than 0.1 Å. While the (bmedaco)Ni complex shows regular 90° angles in the N$_2$S$_2$ plane, and a significant T$_d$ twist distortion, the dach diamine imparts a narrowing of the N$-$Ni$-$N angle to 83° and an expansion of the S$-$Ni$-$S to 95°, keeping a more regular square plane. These changes evidently compensate and place the Ni$^{II}$ in an environment equally conducive to the acceptance of an electron to form a Ni$^I$ species. While the angle data are consistent with the Hancock prediction, the trend in the distance data is the opposite, with the Ni$-$N and Ni$-$S distances being shorter in the dach derivatives. That is, the N$_2$S$_2$ cavity is slightly smaller in the open-chain bmedach(Ni) as well as in the macrocyclic (propyl-bmedach)NiBr$_2$ as compared to the daco analogues.

The principal difference in the physical properties between the complexes lies in the ease or accessibility of the Ni$^{II/I}$ redox couple of the N$_2$S$_2$ dithioether macrocycle complexes (propyl-bmedaco)NiBr$_2$ and (propyl-bmedach)NiBr$_2$. The 140 mV stabilization of the former relative to the latter may be attributed to a greater flexibility of the larger cavity to accommodate the increased size and geometry preference of Ni$^I$. As noted above, values for the Ni$^{II/I}$ couple of the dimethylated complexes (Me$_2$-bmedaco)NiI$_2$ and (Me$_2$-bmedach)NiI$_2$ show an even more dramatic difference. The redox couples in both open-chain, dithioether complexes are more easily accessed than those of the more rigid closed-chain macrocycles, with the daco derivatives again providing more stabilization of the Ni$^I$ oxidation state than those of the dach.

We conclude that the (bmedach)Ni complexes are minimally different from those derived from (bmedaco)Ni, and the rich S-based reactivity found for the latter should be available to the former. Clearly the use of (bmedach)Ni as a templating reagent in the preparation of the S$-$S linked macrocycle is not impaired by the N$_2$S$_2$ angle differences. Preliminary studies of oxygen reactivity find the (bmedach)Ni complex to be less reactive with ground-state O$_2$ than is (bmedaco)Ni. Nevertheless with limited amounts of H$_2$O$_2$, a sulfone, the [*N*,*N*′-(mercapto-ethyl)(sulfinatoethyl)diazacycloheptane]Ni(II), has been obtained. Both constrained N$_2$S$_2$ frameworks do not show the extensive S-oxygenation that has been reported for a more flexible ethylenediamine-based N$_2$S$_2$Ni complex.[21]

**Supporting Information Available:** Tables of crystallographic data, collection parameters, atomic coordinates, packing diagrams, a complete listing of bond lengths and bond angles, and the cyclic voltammograms for (bmedach)Ni and (propyl-bmedach)NiBr$_2$; also included is the cyclic voltammogram of (Me$_2$-bmedach)NiI$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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