Structural and Electrochemical Comparison of Ni^{II} in an N_2S_2 Plane with Two, One and No Axial Ligands: Isolation and Characterization of a Five-Coordinate Nickel(II) Complex

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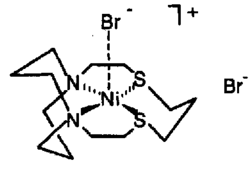
Addition of two equivalents of benzyl bromide to [*N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**) produced the green dibenzyl dithioether complex **[Ni-1-Bzl$_2$Br$_2$]** structurally characterized by X-ray crystallography as a six-coordinate octahedral complex in a monoclinic crystal system and the *P*21/*c* space group. Benzylation of the methyl thioether/thiolate **[(Ni-1-Me)$^+$I$^-$** yielded the mixed benzyl/methyl dithioether **[(Ni-1-BzlMe)Br]I**, structurally characterized by X-ray crystallography as a five-coordinate square pyramidal nickel(II) complex with a Ni−Br distance of 2.451 Å. The complex crystallizes in the orthorhombic *Cmca* space group. The latter is the first nickel(II) pentacoordinate complex isolated for the *N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane (daco) ligand. Structural comparison of these two complexes with the square-planar dimethyl compound **[Ni-1-Me$_2$]I$_2$** found an expansion of the N_2S_2 plane upon addition of axial ligands. The five-coordinate nickel complex showed a displacement of the Ni ion from the N_2S_2 plane by 0.43 Å toward the axial bromide ligand, a common observation of pentacoordinate complexes of this ligand with metals such as Zn and Fe. Electrochemical studies as well as the X-ray crystal structures for complex **[Ni-1-Bzl$_2$Br$_2$]** and **[(Ni-1-BzlMe)Br]I** are presented and discussed in detail.

The complex [*N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**) reacts with methyl iodide sequentially to produce monomethylated[1] and dimethylated[2] derivatives. In both cases, the nickel product is four-coordinate square planar with the iodides present as noninteracting counterions. Reaction of **Ni-1** with 1,3-dibromopropane forms the 14-membered macrocycle **Ni-1(bicycle)Br$_2$** in which one of the bromides is 2.947(2) Å from the nickel center[3]. Although this is ca. 0.5 Å beyond the Ni−Br bonding distance (average 2.41 Å)[4], the bromide's position as a long range axial ligand in a square pyramid is inferred by the Br−Ni−S and the Br−Ni−N angles of approximately 88 and 98°, respectively[3]. Further, the Ni$^{II/I}$ redox potential of −0.71 V (referenced to NHE in CH_3CN) is some 0.3 V less accessible than **[Ni-1(bicycle)][BPh$_4$]$_2$**, suggesting that the Br^---Ni^{II} interaction is retained in solution and destabilizes Ni^I.



Ni-1(bicycle)Br$_2$

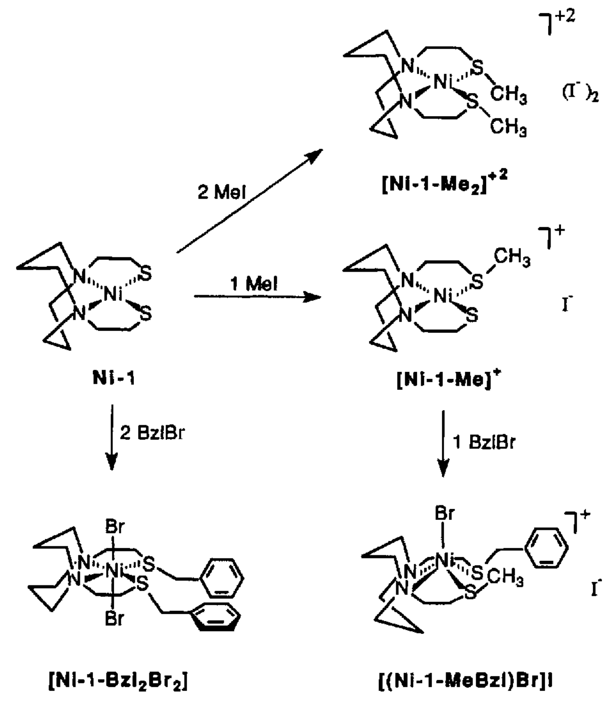
Since the benzyl group would, relative to simple aliphatics, create a less electron-donating thioether S-donor, and since the balance of 4/6 coordination in nickel(II) complexes is delicate[3], we endeavored to examine structures of compounds derived from benzylation of **Ni-1**. Thus the reaction of **Ni-1** with two equivalents of benzyl bromide is studied here in detail, including the synthesis and structural characterization of a mixed methyl/benzyl dithioether in which the nickel is in a definite five-coordinate square-pyramidal geometry.

Results and Discussion

Syntheses, Spectral Data and X-ray Structures: The molecular structures of **[(Ni-1-MeBzl)Br]I** and **[Ni-1-Bzl$_2$Br$_2$]** are shown in Figures 1 and 2, respectively. Figure 3 shows a packing diagram for complex **[Ni-1-Bzl$_2$Br$_2$]**. Selected bond lengths and bond angles for both complexes as well as **[Ni-1-Me$_2$]I$_2$**[2] are listed in Table 2. Scheme 1 summarizes the synthetic routes to these compounds.

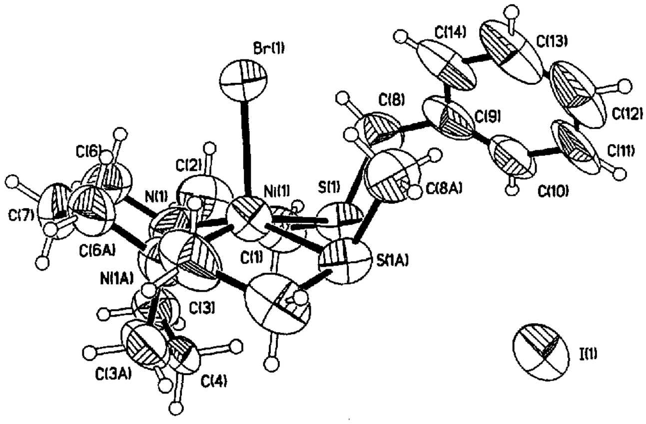
The **[(Ni-1-MeBzl)Br]I** compound (Figure 1) is one of the sparse examples of bona fide five-coordinate N_2S_2 nickel(II) complexes and the first one to be isolated and structurally characterized for the *N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane ligand (**bme-daco**). The synthesis of this complex (Scheme 1) is a two-step one-pot reaction that takes advantage of the decreased rate of addition of the second alkyl to the thiolate sulfurs[5]. Successive addition to **Ni-1** of one equiv. of MeI and one equiv. of BzlBr afforded the mixed methyl/benzyl complex in very high yields (89%). This compound is green in the solid state and in solution (acetonitrile and methanol), where it is slightly air-sensitive; it is air-stable in the solid state. The molar conductance in solution of **[(Ni-1-MeBzl)Br]I** (161.5 ± 0.6 $\Lambda^{-1}M^{-1}$ at

Scheme 1



23 °C) is consistent with a 1:1 electrolyte[6] therefore maintaining pentacoordination in solution.

Figure 1. Molecular structure of **[(Ni-1-MeBzl)Br]I** showing the atomic labelling scheme (thermal ellipsoid plot at 50% probability)



As seen in Figure 1, the **[(Ni-1-MeBzl)Br]**$^+$ ion is square-pyramidal with the nickel atom out of the N_2S_2 plane by 0.437 Å; the apical bromide ion, with a Ni−Br distance of 2.451(3) Å, is well within the range of NiBr single bonds[4]. The fused metalladiazacyclohexane rings are in a boat/chair conformation with the axial hydrogen of C4 directed at the sixth coordination site of the nickel with Ni−C4 distance of 2.313 Å. The structure is similar to another pentacoordinate complex containing the daco framework: diacetatoaquo(1,5-diazacyclooctane-*N,N′*)nickel(II) · H_2O or **(dacoda)Ni^{II} · H$_2$O**[7a]. Here the fifth coordination site is occupied by the oxygen atom of a water molecule, with the nickel located above the N_2S_2 plane by 0.36 Å.

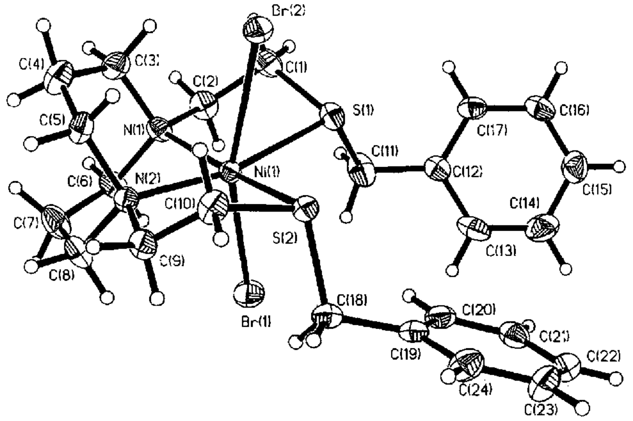
Table 1. Crystal data and structure refinement for **[(Ni-1-BzlMe)Br]I** and **[Ni-1-Bzl$_2$Br$_2$]**

Complex	**[(Ni-1-BzlMe)Br]I**	**[Ni-1-Bzl$_2$Br$_2$]**
Chemical formula	$C_{12}H_{26}BrIN_2NiS_2$	$C_{24}H_{34}Br_2N_2NiS_2$
Formula mass (amu)	527.99	633.18
Temperature	293(2) K	193(2) K
Crystal system	orthorhombic	monoclinic
Space group	*Cmca*	*P*21/*c*
a [Å]	10.096(2)	15.066(3)
b [Å]	21.194(4)	12.084(2)
c [Å]	21.378(4)	13.676(3)
α [°]	90	90
β [°]	90	94.45(3)
γ [°]	90	90
Volume, *Z*	4574(2) Å^3, 16	2482.3(9) Å^3, 4
Density (calculated)	1.917 Mg/m ^{3}	1.694 Mg/m^3
Goodness-of-fit on F^2	1.025	1.076
$R(F)$, $wR(F^2)$[a] (%)	6.78 (16.68)	3.16 (7.05)

[a] Residuals: $R = \Sigma F_o - F_c/\Sigma F_o$; $wR(F^2) = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)_2]\}^{1/2}$.

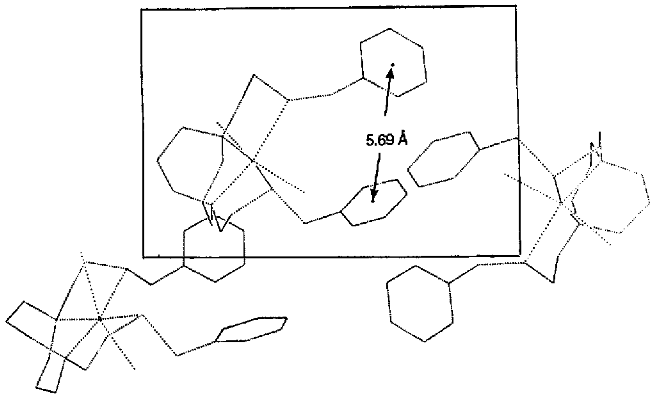
The addition of two benzyl groups to **Ni-1** produces the six-coordinate complex **[Ni-1-Bzl$_2$Br$_2$]** where the bromides occupy the axial positions of the distorted octahedron, Figure 2. Relative to the pentacoordinate complex, the nickel has dropped back into the N_2S_2 plane, albeit an expanded plane. Carbon atoms C7 and C4 are directed away from the metal center making space for both axial ligands and resulting in the chair/chair conformation of the fused nickeldiazacyclohexane rings. The two benzylic carbon atoms are on the same side of the N_2S_2 plane as the shorter Ni−Br bond. That is, the Ni−Br distances are significantly different, Ni−Br(1) = 2.513 and Ni−Br(2) = 2.762 Å, with a Br−Ni−Br angle of 162.01(2)°. Less sterically restricted $N_2S_2X_2$ octahedral complexes find the halides in a *cis* relationship[8–13].

Figure 2. Molecular structure of **[Ni-1-Bzl$_2$Br$_2$]** showing the atomic labelling scheme (thermal ellipsoid plot at 50% probability)



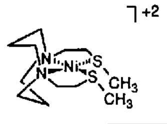
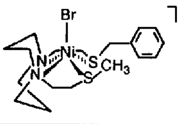
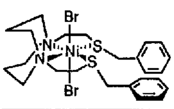
The packing of **[Ni-1-Bzl$_2$Br$_2$]** (Figure 3) shows no tendency for aromatic ring stacking or intercalation either intra- or intermolecularly. Intramolecularly, the normal of the centroids between the aromatic rings is 72°, i.e., the ring planes are nearly perpendicular to each other. The intramolecular distance between the centroids is 5.69 Å, while the closest intermolecular centroid to centroid distance is 3.8 Å.

Figure 3. Packing diagram of complex **[Ni-1-Bzl$_2$Br$_2$]** showing the intramolecular distance between the centroids of the least square planes of the aromatic rings



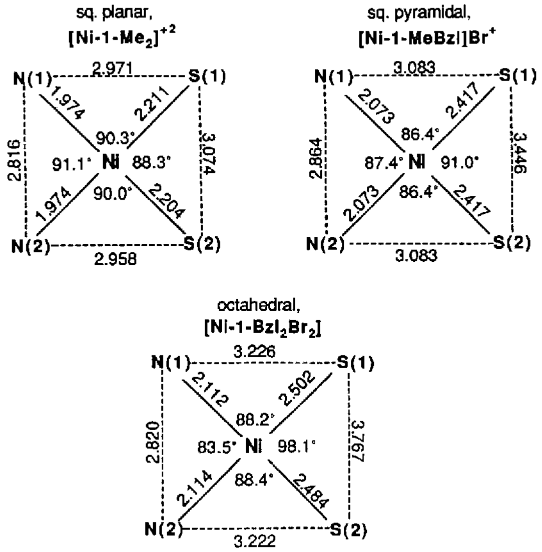
Bond lengths and bond angles for compounds **[Ni-1-Me$_2$]I$_2$**, **[(Ni-1-MeBzl)Br]I**, and **[Ni-1-Bz]$_2$Br$_2$]** are compared in Table 2. The expansion in the N_2S_2 plane cavity resulting from the increase of coordination number is represented in Figure 4.

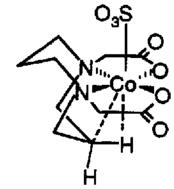
Table 2. Selected bond lengths [Å] and bond angles [°] for compounds **[Ni-1-Me$_2$]$^{+2}$**, **[(Ni-1-MeBzl)Br]$^+$**, and **[Ni-1-Bzl$_2$Br$_2$]** (estimated standard deviations are given in parentheses)

			
Ni–S$_1$ [Å]	2.211(3)	2.417(4)	2.5026(11)
Ni–S$_2$ [Å]	2.204(3)	2.417(4)	2.4842(10)
Ni–N$_1$ [Å]	1.974(7)	2.073(13)	2.114(3)
Ni–N$_2$ [Å]	1.974(7)	2.073(13)	2.122(3)
Ni–Br$_1$ [Å]		2.451(3)	2.5130(7)
Ni–Br$_2$ (Å)			2.7621(8)
S---S (Å)	3.074	3.446	3.767
S$_1$–Ni–S$_2$ [°]	88.3(1)	91.0(2)	98.14(3)
Br$_1$–Ni–Br$_2$ [°]			162.01(2)
Br–Ni–N [°]		101.2(3)	96.08(8)
Br–Ni–S$_{avg}$Me [°]		101.50(12)	
Br–Ni–S$_{avg}$Bzl [°]		101.50(12)	92.93(4)

Given in Figure 5 are overlays of the daco ring and *S*-substituents as hydrocarbon stick projections from the least squares fit of the N and S atoms of **Ni-1(bicycle)Br$_2$** and **[(Ni-1-MeBzl)Br]I**; the N_2S_2 plane centroid is the common point. Major differences are seen in the deviation of nickel from the N_2S_2 plane as well as the orientation of the daco rings with respect to the nickel atom. With the axial coordination of bromide and the nickel elevation from the N_2S_2 plane in **[(Ni-1-MeBzl)Br]I**, a tilting of daco framework is required to maintain good directional overlap of the N–Ni coordinate covalent bond. This moves the chair portion of the nickeldiazacyclohexane ring away from the bromide while the central methylene carbon (C4) of the boat form moves underneath the N_2S_2 plane, resulting in a C4-Ni distance of 2.71 Å and an axial Ni--H$_{axial}$ distance of 2.313 Å. In contrast, the analogous distances for the planar **Ni-1(bicycle)Br$_2$** are 2.83 Å (Ni–C4 distance) and 2.61 Å (Ni--H$_{axial}$). While the Ni--H distance of 2.313 Å in **[(Ni-1-MeBzl)Br]I** is the same as in an "agostic" Co^{III}--H$_{axial}$ interaction [2.31(5) Å]$^{[7b]}$ observed for **[Co^{III}(dacoda)SO$_3$]$^-$**, the Co--C$_{axial}$ distance is 2.531(4) Å, i.e., significantly shorter than the Ni--C$_{axial}$ distance of **[(Ni-1-MeBzl)Br]I**. The "agostic" C–H interaction of **[Co^{III}(dacoda)SO$_3$]$^-$**, is further intimated by substantial strain in the boat CoN$_2$C$_3$ cyclohexane ring. However, stick projection overlays of the analogous boat NiN$_2$C$_3$ of **[(Ni-1-MeBzl)Br]I$^+$** and **[Ni-1(bicycle)]$^{+2}$** show no significant deviations.

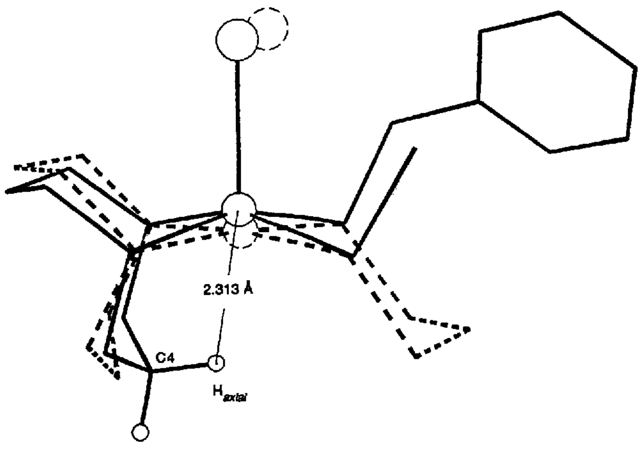
Figure 4. Summary of N_2S_2 plane data for three complexes. The *trans* N–S distances [Å] are: **[Ni-1-Me$_2$]I$_2$** N(1)–S(2) 4.178, N(2)–S(1) 4.176; **[[Ni-1-MeBzl]Br]I** N(1)–S(2) 4.401, N(2)–S(1) 4.401; **[Ni-1-Bzl$_2$Br$_2$]** N(1)–S(2) 4.599, N(2)–S(1) 4.570





[Co^{III}(dacoda)SO$_3$]$^-$

Figure 5. Overlays of selected hydrocarbon stick projections from the least squares fit of the N and S atoms of **Ni-1(bicycle)Br$_2$** (– – – –) and **[(Ni-1-MeBzl)Br]I** (——). See text



Electrochemistry: The preparation of square planar **[Ni-1-Me$_2$I$_2$**[2] and **[Ni-1-Me]$^+$I$^-$**[1], their crystal structures and electrochemistry have been reported previously. Cyclic voltammograms for dialkylated **Ni-1** derivatives show two waves, one reversible reduction wave assigned by EPR results to the Ni$^{II/I}$ couple[1] and an oxidation event, sometimes fully reversible and assigned to the Ni$^{II/III}$ couple[1]. Table 3 compares the Ni$^{II/I}$ redox couple potentials and reversibility data for complexes **[Ni-1-Me$_2$]I$_2$**, **[(Ni-1-MeBzl)-Br]I**, **[Ni-1-Bzl$_2$Br$_2$]**, and **[Ni-1-Me]$^+$I$^-$** in acetonitrile solution, and Scheme 2 summarizes the Ni$^{II/I}$ accessibility dependence on *S*-alkylation. Addition of a methyl group to the parent compound, with the creation of the cationic thioether/thiolate **[Ni-1-Me]$^+$I$^-$**, shifts the Ni$^{II/I}$ reduction potential from −1.94 to −1.20 V, while the second methylation further raises the potential to −0.48 V. This apparently additive effect of ca. 0.7 V per thiolate conversion to a methyl thioether S-donor is due to the change in the donor character of the sulfur site (alleviating the Ni$_{d\pi}$−S$_{p\pi}$ antibonding interaction) as well as the increase in the overall charge of the complex.

The addition of two benzyl groups to **Ni-1** shifts the Ni$^{II/I}$ potential from −1.94 to −0.67 V overall, stabilizing the Ni$^{II/I}$ couple by approximately 1.3 V, or 0.65 V per benzylation. Benzylation of **[Ni-1-Me]$^+$I$^-$** to produce complex **[(Ni-1-MeBzl)Br]I** shifts the Ni$^{II/I}$ reduction potential from −1.2 to 0.65 V; a stabilization of only 0.55 V in this case.

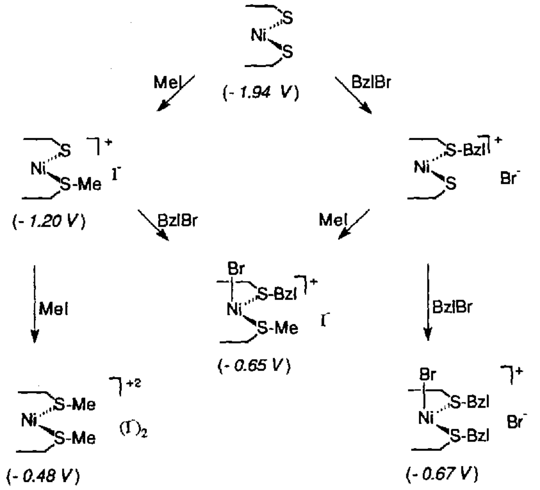
Table 3. Potential and reversibility data from cyclic voltammetry for complexes **Ni-1**, **[Ni-1-Me$_2$]I$_2$**, **[(Ni-1-MeBzl)Br]I**, **[Ni-1-Bzl$_2$Br$_2$]** and **[Ni-1-Me]$^+$I$^-$** in CH$_3$CN[a]

	Reduction Ni$^{II/I}$			Oxidation Ni$^{II/III}$		
	$E_{1/2}$ (mV)	ΔE (mV)	i_{pa}/i_{pc}	$E_{1/2}$ (mV)	ΔE (mV)	i_{pa}/i_{pc}
Ni-1	−1944	65	1.01	+360[e]		
[Ni-1-Me$_2$]I$_2$	−482[b]	72	0.98	+1568	76	0.97
[(Ni-1-MeBzl)Br]I	−657[c]	41	0.79	+1624	69	0.68
[Ni-1-Bzl$_2$Br$_2$]	−671[c]	58	0.80	+1565	78	0.85
[Ni-1-Me]$^+$	−1204[b]	60	0.87	Obscured[d]		

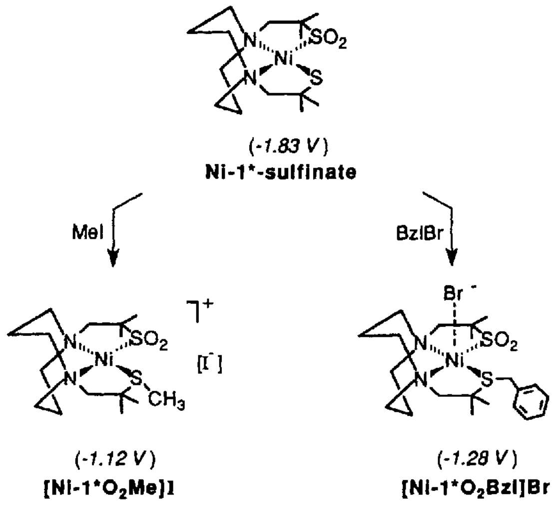
[a] All potentials measured in CH$_3$CN solutions, 0.1 M TBAHFP electrolite, measured vs. Ag/AgNO$_3$ electrode. – [b] Potentials scaled to NHE referenced to a MeV^{2+}/MeV$^+$ standard ($^{NHE}_{1/2}$ = −440 mV). – [c] Potentials scaled to NHE referenced to a ferrocene standard ($E^{NHE}_{1/2}$ = +400 mV). – [d] Oxidation peak obscured by those assigned to halide counterion. – [e] Thiolate oxidation.

A further check of the consistency of methylation and benzylation on Ni$^{II/I}$ couple stabilization may be based on the alkylation of **Ni-1*-sulfinate** and is presented in Scheme 3. The product of methylation has been fully characterized as a square-planar complex with the iodide far removed from the nickel(II) center; it is a uni-unielectrolyte in solution. The benzyl thioether/sulfinate has been characterized by elemental analysis, UV/Vis spectroscopy and electrochemical measurements, vide supra. Addition of a methyl group to form the sulfinate/thioether **[Ni-1*O$_2$Me]I** stabilizes the reduction potential, once again, by 0.70 V, shifting the Ni$^{II/I}$ from −1.83 to −1.12 V (vs. NHE in CH$_3$CN). In contrast, benzylation with BzlBr to form **[Ni-1*O$_2$Bzl]Br** shifts the Ni$^{II/I}$ reduction potential from −1.83 m to −1.28 V, a difference of 0.55 V. Clearly, *S*-benzylation with the formation of a bromide salt is less stabilizing of the Ni$^{II/I}$ couple as compared to *S*-methylation forming the iodide salt. Since the benzyl thioether is expected, based on electronic effects, to be less electron-donating than the methyl group, the anomaly of the *S*-substituent effect on Ni^I stability must attributed to differences in halide/Ni^{+2} interactions. The strong ligation of bromide to Ni^{II} (as compared to iodide) has been demonstrated in the X-ray crystal structures described above. The fact that this ligation is retained in solution was probed by conductivity measurements in acetonitrile over a concentration range of 9.43 · 10^{-6} through 5.56 · 10^{-5} M. The molar conductance of **[Ni-1-Bzl$_2$Br$_2$]** was determined to be 123.9 ± 0.8 Λ^{-1}M^{-1}, a value corresponding to a 1:1 electrolyte[6]. For this reason, Schemes 2 and 3 represent the iodide anions as non-interacting with the cationic complexes, while the bromide derivatives are depicted either as Ni−Br coordinate covalent bonds or tightly bound site-specific ion pairs. Of all the compounds, the benzyl thioether is expected to create the

Scheme 2. ($E_{1/2}$Ni$^{II/I}$ vs NHE)



Scheme 3. ($E_{1/2}$Ni$^{II/I}$ vs NHE)



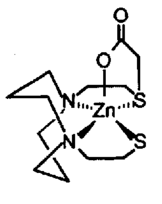
most electrophilic site at nickel(II) and the strongest Ni−Br interaction.

Conclusions

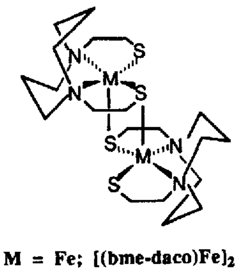
Although the daco ring framework was originally adopted in the synthesis of polydentate ligands to serve as a steric block of one site (in the chair/boat conformation), numerous studies have shown that the flexibility of the ring permits access to both axial sites via the chair/chair conformation. We do not expect small differences in conformational energies[1,14] to determine the coordination number adopted by the complexes prepared here.

It is noteworthy that pentacoordinate complexes of **bme-daco** with metals other than nickel have been isolated and structurally characterized. The monoacetate complex of [*N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane]zinc(II), **(bme-daco)Zn-OAc**, has a square-pyramidal geometry around the zinc with one of the oxygen atoms of the acetate occupying the fifth position[14]. The zinc atom is out of the N_2S_2 plane by 0.431 Å. Other examples of pentacoordination are found in the dimeric isostructural complexes **[(bme-daco)M]$_2$** (M = Fe, Zn)[15,16]. The apical site of each metal center is occupied by a sulfur from a second **[(bme-daco)M]** unit giving rise to a 2M−2S core. The Fe(II) ion is displaced out of the N_2S_2 basal plane by 0.59 Å, while the Zn^{II} is 0.49 Å above the plane. The nickel complex **Ni-1(bicycle)Br$_2$**, which has a long-range ionic interaction with a bromide in the axial position, finds the nickel coplanar with the N_2S_2 donor set. From this it can be concluded that only a truly five-coordinate complex will find the nickel displaced out of the plane cavity.

The expansion of the N_2S_2 plane upon addition of axial ligands is remarkable given that the trans N−S distance spans 0.41 Å on going from the dithioether square planar complex **[Ni-1-Me$_2$]I$_2$**, having no axial ligands, to the hexacoordinate **[Ni-1-Bzl$_2$Br$_2$]** (Figure 4). The pentacoordinate species has both an expanded N_2S_2 plane (the *trans* N−S distance increases by 0.23 Å relative to **[Ni-1-Me$_2$]I$_2$**) as well as displacement of Ni^{II} by 0.43 Å toward the axial bromide ligand. Addition of a second axial ligand to achieve hexacoordination returns the Ni(II) ion to coplanarity with the N_2S_2 cavity resulting in an axial ligation metric effect reminiscent that of O_2 binding to Fe^{II} of hemoglobin.



(bme-daco)Zn-OAc



M = Fe; [(bme-daco)Fe]$_2$
M = Zn; [(bme-daco)Zn]$_2$

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Experimental

General Procedures: Solvents were reagent grade and purified according to published procedures[17]. Acetonitrile was distilled once from CaH_2, twice from P_2O_5 and again freshly distilled from CaH_2 immediately before use in each experiment. Methyl iodide (MeI) and benzyl bromide (BzlBr) were purchased from Aldrich and used as received. **Ni-1**[2] and [*N*-(2-mercapto-2-methylpropyl)-*N'*-(2-methyl-2-sulfinylpropyl)-1,5-diazacyclooctane]nickel(II)[18] (**Ni-1*-sulfinate**) were synthesized by published procedures and purified by silica gel column chromatography using ethanol as eluant and isolated on removal of the solvent by rotary evaporation. Where anaerobic conditions were required, standard Schlenk techniques using nitrogen (passed through a drying tube of $CaSO_4$, molecular sieves, and NaOH) and an argon glovebox (Vacuum Atmospheres) were employed. − Elemental analyses: Galbraith Laboratories, Knoxville, TN. − Conductivity measurements: pure acetonitrile solution, ORION Conductivity Meter Model 160. Plots of conductance vs. (1/concentration) and extrapolation to zero concentration yielded the molar conductance values in units of $\Lambda^{-1}M^{-1}$.

{N-[2-(Benzylthio)ethyl]-N'-[2-(methylthio)ethyl]-1,5-diazacyclooctane}bromonickel(II) Iodide, **[(Ni-1-MeBzl)Br]I**: Methyl iodide (15.4 µl, 0.24 mmol) was added to a 20-ml purple solution of **Ni-1** (0.0718 g, 0.24 mmol) in acetonitrile under N_2. After 1 h of stirring, benzyl bromide (29 µl, 0.24 mmol) was added, and the solution was stirred overnight at 23 °C. The resulting green solution was concentrated in vacuo to about 1 ml, and 10 ml of ether was added slowly. The dark green solid which precipitated out of solution was filtered anaerobically and washed with 3 × 3 ml of ether. X-ray quality green crystals were grown by ether diffusion into a methanolic solution of the complex; yield 0.128 g (89%). − $C_{18}H_{30}BrIN_2NiS_2$ (477.2): calcd. C 35.7, H 5.01, N 4.64; found C 35.3, H 5.03, N 4.62. − UV/Vis (CH_3CN): λ_{max} (ε): 432 (118), 660 (66). − Molar conductance (CH_3CN) at 23 °C: 161.5 ± 0.6 $\Lambda^{-1}M^{-1}$.

{N,N'-Bis[2-(benzylthio)ethyl]-1,5-diazacyclooctane}-dibromonickel(II), **[Ni-1-Bzl$_2$Br$_2$]**, was prepared by dissolving 0.036 g (0.124 mmol) of **Ni-1** in 10 ml of acetonitrile and adding 0.09 ml (0.756 mmol) of benzyl bromide by means of a syringe. The mixture was stirred under N_2 overnight. The resulting green solution was concentrated to about 1 ml, and 10 ml of dry ether was added slowly. A bright green solid precipitated out of solution, was filtered anaerobically, and washed with 2 × 3 ml of ether. X-ray quality green crystals were grown by ether diffusion into a methanolic solution of the complex; yield 0.076 g (97%). − $C_{24}H_{34}Br_2N_2NiS_2$ (633.2): calcd C 45.5, H 5.41, N 4.42; found C 45.4, H 5.23, N 4.37. − UV/Vis (CH_3CN): λ_{max} (ε): 430 (425), 654 (149). − Molar conductance in CH_3CN at 23 °C: 123.9 ± 0.8 $\Lambda^{-1}M^{-1}$.

{N-[2-Methyl-2-(methylthio)propyl]-N'-(2-methyl-2-sulfinylpropyl)-1,5-diazacyclooctane}nickel(II) Iodide, **[Ni-1*O$_2$Me]I**: Methyl iodide (0.4 ml, 6.4 mmol) was added to a solution of **Ni-1*-sulfinate** (0.100 g, 0.265 mmol) in 10 ml of dry dichloromethane. Orange needles precipitated immediately, were filtered anaerobically, and washed with 3 × 5 ml of ether. The solid compound is soluble in methanol and ethanol, slightly soluble in acetonitrile and is air-stable. It was characterized by elemental analysis and by X-ray crystallography[19]. − Molar conductance in CH_3CN at 23 °C: 167.9 ± 0.5 $\Lambda^{-1}M^{-1}$.

{N-[2-(Benzylthio)-2-methylpropyl]-N'-(2-methyl-2-sulfinylpropyl)-1,5-diazacyclooctane}nickel(II) Bromide, **[Ni-1*O$_2$Bzl]Br**, was prepared by dissolving 0.100 g (0.310 mmol) of **Ni-1*-sulfinate** in 10 ml of acetonitrile and adding 74 µl (6.4 mmol) of benzyl bromide by means of a syringe. The solution was stirred under N_2

for 2 h. The solvent was concentrated to 1 ml, and 10 ml of ether was added slowly while stirring. The yellow precipitate obtained was filtered anaerobically and washed with 2 × 5 ml of anhydrous ether. The solid compound is soluble in methanol and ethanol, slightly soluble in acetonitrile and highly hygroscopic. – $C_{17}H_{27}BrN_2NiO_2S_2 \cdot CH_3CN \cdot H_2O$ (553.2): calcd. C 41.2, H 5.83, N 7.60; found C 41.1, H 6.10, N 7.45. – Molar conductance in CH_3CN at 23 °C: 80.9 ± 0.3 $\Lambda^{-1}M^{-1}$.

Cyclic Voltammetry: Cyclic voltammograms were obtained using a Bio-Analytical Systems 100A electrochemical analyzer with a glassy carbon stationary electrode and a platinum wire auxiliary electrode. Samples were measured in acetonitrile solution (~2.5 mM) with a 0.1 M solution of TBAHPF as the supporting electrolyte and a Ag/AgNO$_3$ reference electrode. Potentials were standardized to either ferrocene or methylviologen and referenced to NHE.

X-ray Structure Determination of **[(Ni-1-MeBzl)Br]I** *and* **[Ni-1-Bzl$_2$Br$_2$]**: All crystal structures were solved at the Crystal and Molecular Structure Laboratory, Center for Chemical Characterization and Analysis, at Texas A & M University. X-ray crystallographic data were obtained with a Nicolet R3m/V single-crystal X-ray diffractometer operating at 50 kV and 30 mA, Mo-K_α (λ = 0.71073 Å) radiation, equipped with a Nicolet LT-2 cryostat. Diffractometer control software P3VAX 3.42 was supplied by Nicolet Analytical X-ray instruments. Structures were solved by using SHELXT-PLUS and refined with SHELXL-93[8]. In both cases, crystals were mounted on a glass fiber with epoxy cement. X-ray experimental conditions for complexes **[(Ni-1-MeBzl)Br]I** and **[Ni-1-Bzl$_2$Br$_2$]** are given in Table 1[20].

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[20] The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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