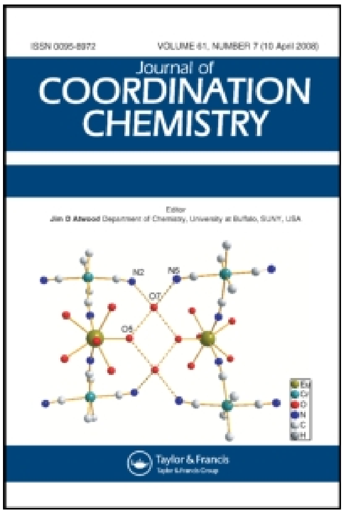

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHETIC STRATEGIES FOR N_2S_2O-PENTACOORDINATE NICKEL(II) BASED ON THE HIGHLY STERICALLY ENCUMBERED LIGAND N,N'-BIS(2-MERCAPTO-2-METHYLPROPANE)-1,5-DIAZACYCLOOCTANE

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To cite this Article Darensbourg, Marcetta Y. , Font, Ivan , Pala, Magdalena and Reibenspies, Joseph H.(1994) 'SYNTHETIC STRATEGIES FOR N_2S_2O-PENTACOORDINATE NICKEL(II) BASED ON THE HIGHLY STERICALLY ENCUMBERED LIGAND N,N'-BIS(2-MERCAPTO-2-METHYLPROPANE)-1,5-DIAZACYCLOOCTANE', Journal of Coordination Chemistry, 32: 1, 39 — 49

To link to this Article: DOI: 10.1080/00958979408024236

URL: http://dx.doi.org/10.1080/00958979408024236

J. Coord. Chem., 1994, Vol 32, pp. 39–49
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SYNTHETIC STRATEGIES FOR N_2S_2O-PENTACOORDINATE NICKEL(II) BASED ON THE HIGHLY STERICALLY ENCUMBERED LIGAND N,N'-BIS(2-MERCAPTO-2-METHYLPROPANE)-1,5-DIAZACYCLOOCTANE

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(Received August 12, 1993; in final form December 10, 1993)

An attempt to prepare a square pyramidal pentacoordinate Ni(II) complex was made by increasing steric hindrance in a N_2S_2O macrocyclic ligand derived from (bme-daco), N,N'-bis(2-mercaptoethyl)-1,5-diazacyclooctane. Thus two methyl groups were added to each carbon in a position α to sulfur atoms of the macrocycle. The resulting complex, 3,3,11,11-tetramethyl-7-oxa-4,10-dithiabicyclo[11.3.3]nonadecanenickel(II) iodide or [Ni(bmmp-ether)]I_2 or 2*I_2, shows a greater steric rigidity and a severe steric block of one side of the NiN_2S_2 pseudo-square plane. Neither iodide nor the ethereal oxygen bind to nickel. The 2*I_2 complex crystallizes in the monoclinic $P2_1/n$(No. 14) space group with $a = 11.193(3)$ Å, $b = 11.408(3)$ Å, $c = 20.129(5)$ Å, $\beta = 91.44(2)$ °, $V = 2569.5(12)$ Å^3, and $Z = 4$. The preparation and crystal structure of its precursor, N,N'-bis(2-mercapto-2-methylpropane)-1,5-diaza-cyclooctanenickel(II) or [(bmmp-daco)Ni] or 1*, is also reported. Square planar complex 1* crystallizes in orthorhombic Pnma space group with $a = 11.307(2)$ Å, $b = 19.579(3)$ Å, $c = 7.4790(10)$ Å, V = 1655.7(4) Å^3, and $Z = 4$.

KEYWORDS: square pyramidal, pentacoordinate, nickel(II), tetradentate ligand

INTRODUCTION

The design of ligands that would enforce an atypical coordination geometry on a transition metal ion has long intrigued coordination chemists in pursuit of unusual properties induced by electronically frustrated metal ions. Pendant arm derivatives of diazacyclooctane[1] held forth expectations for pentacoordinate cobalt and nickel complexes, due to the blockage of one face of the MN_2X_2 plane by the central methylene group of one metalladiazacyclohexane ring.[2] This was realized for (dacoda)(H_2O)Ni^{II} and (dacoda)LCo^{II} (dacoda = diazacyclooctanediacetate).[2] For the latter complex the result of the proximity of one CH_2 group, as illustrated below, was a unique heterolytic cleavage of the C-H bond when Co^{II} was oxidized to Co^{III} in the presence of base.[3]

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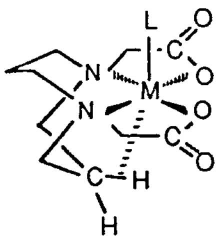
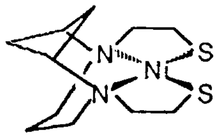
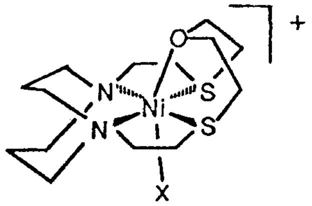


(dacoda)(L)M



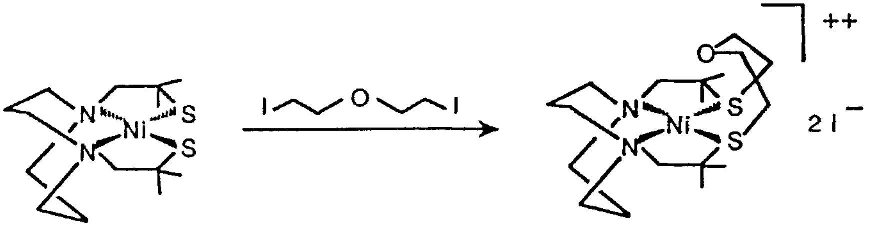
(bme-daco)Ni^{II}, **1**



[Ni(ether)X]$^+$, **2**

Although penta-coordination of the d^8 nickel(II) ion is hardly 'atypical',[4] especially in soft, organometallic-type ligation,[5] tetra- and hexa-coordinate complexes are by far the more common. Earlier we attempted to exact a square pyramidal five-coordinate N_2S_2O donor set, a donor set of interest in the biomimicry of NiFe hydrogenases,[6] from alkylation of N, N'-bis(mercaptoethyl)-diazacyclooctanenickel(II) or (bme-daco)Ni^{II} or 1,[7] by diiodoethylether. Obtained instead was the six-coordinate structure shown above, [Ni(ether)I]I,**2**.[8] In that case, both of the fused nickelladiazacyclohexane rings adopted a chair conformation in order to accommodate the binding of a sixth ligand, iodide. Electronic spectra showed that exchange of both iodides by non-coordinating BPh_4^- ions simultaneously led to a departure of the ether oxygen and the production of a four-coordinate N_2S_2Ni square planar complex.[8]

In further pursuit of sterically encumbered nickel(II) complexes we recently prepared an analogue of (bme-daco)Ni^{II}, a derivative with four methyl groups on carbon atoms in positions α to sulfur, N,N'-bis(2-mercapto-2-methyl-propane)-1,5-diazacyclooctanenickel(II) or [(bmmp-daco)Ni] (**1***). The X-ray crystal structure (*vide infra*) of this complex finds one N_2S_2Ni face to be severely crowded with hydrocarbon fragments, two methyl and one methylene groups. Hence the derivatization with 1,5-diiodoethylether was again attempted, eq 1, and the isolation and characterization of salts of **2*** are described below.



(1)

(bmmp-daco)Ni^{II}, **1***

[Ni^{II}(bmmp-ether)]I_2, **2*** I_2

EXPERIMENTAL

General

Solvents were reagent grade and used as received. Where anhydrous conditions were required, solvents were purified before use according to published procedures.[9] Acetonitrile was distilled once from CaH_2, twice from P_2O_5 and freshly distilled from CaH_2 immediately before use. Bis(2-chloroethyl) ether (Fluka), isobutylene oxide (TCI America or Lancaster), sodium iodide, and $AgBF_4$ (reagent grade from commercial sources), were used as received. NMR solvents were purchased from Cambridge Isotope Laboratories and used as received. Where anaerobic conditions were required, standard Schlenk techniques using (Airco) nitrogen or argon (passed through a drying tube of $CaSO_4$, molecular sieves, and NaOH) and an argon glove box (Vacuum Atmospheres) were employed.

NMR spectra were recorded in CD_3OD on a Varian XL-200 FT-NMR. Cyclic voltammograms were recorded in CH_3CN on a BAS-100A electrochemical analyzer using $Ag^\circ/AgNO_3$ reference and glassy carbon working electrodes with 0.1 M tetra(n-butyl)ammonium hexafluorophosphate as supporting electrolyte. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN. Magnetic susceptibility measurements were performed on an Evans balance purchased from the Johnson Matthey Company. X-ray crystallographic data were obtained on a Nicolet R3m/V single-crystal X-ray diffractometer.

Conductivity measurements were performed with an Orion Model 160 conductivity meter equipped with a Barnstead B-1 cell manufactured by Sybron Corp. Using 0.02M KCl ($K = 0.002768$ mho cm^{-1}) and the relation $K = L\theta$, the cell constant θ was determined to be 0.112 cm^{-1}. Two freshly distilled portions of CH_3CN were found to have conductivities of ($\times 10^6$ mho) 0.41 and 0.46, well within acceptable limits of pure, dry CH_3CN.

Syntheses

*N,N'-bis(2-mercapto-2-methylpropane)-1,5-diazacyclooctane-nickel(II) or [(bmmp-daco)Ni], 1**

To a solution of 1,5-diazacyclooctane[10] (6.0g, 52.6 mmol) in 100 mL of dry benzene heated at 55°C and stirred under N_2 were added 9.26 g (105 mmol) of isobutylene sulfide[11] all at once. After 12 h the benzene was evaporated yielding 9.90 g (65% yield) of a yellow oil and a small amount of white solid (an insoluble, unreactive polymer). This oil was dissolved in 100 mL of dry toluene. A green solution of $Ni(acac)_2$ (7.44 g, 28.9 mmol) in 250 mL of toluene was transferred by cannula into the ligand solution producing a purple-colored solution and dark precipitate. The solution was filtered and the purple solid washed twice with 100 mL of toluene, followed by 2 × 100 mL of diethyl ether. The solid was dissolved in 25 mL of methanol and transferred to a dry silica gel column (1" by 10"). The purple band was eluted with methanol. After evaporation of the methanol 5.17 g (52% yield based on Ni(II)) of a purple solid were obtained. Single crystals suitable for X-ray crystal structure analysis were obtained by ether diffusion into an acetonitrile solution. *Anal.* Calcd. for $C_{14}H_{28}N_2NiS_2(1^*)$: C, 48.5; H, 8.00; N, 8.00. Found: C, 48.6; H, 7.86; N, 7.83. ^{1}H NMR (CD_3OD) δ(ppm): 1.42 s (12H), 1.9–2.1 m (2H), 2.55 s(4H), 2.55–2.70 m (2H), 3.27-3.43 m (8H).

3,3,11,11-Tetramethyl-7-oxa-4,10-dithia-1,13-diazabicyclo[11.3.3]nonadecane nickel(II) iodide, [Ni(bmmp-ether)]I$_2$, or [2]I$_2$*

The ligand precursor bis(2-iodoethyl)ether was obtained by conversion of the corresponding dichloride using NaI in refluxing acetone.[12] Reaction of 0.1 g (0.29 mmol) [(bmmp-daco)Ni] in 25 mL CH_3CN with 0.2 mL (0.39 g, 1.2 mmol) of the iodoether caused a series of color changes culminating in the formation of a green solution after 24 h. Addition of 150 mL of dry ether to this acetonitrile solution caused the immediate precipitation of the product as an orange-brown solid. The supernatant was removed by cannula and the solid dried under vacuum. The product was moderately hygroscopic and manipulations were carried out in the glove box to avoid hydration. Yield: 0.16 g (80 %). Crystals suitable for single crystal X-ray analysis precipitated upon ether diffusion to a methanol solution of the diiodide salt. *Anal.* Calcd. for $C_{18}H_{36}I_2N_2NiOS_2$,: C,32.1; H, 5.34; N, 4.16. Found: C, 31.3; H, 5.31; N, 3.79. IR (KBr) $\nu_{C\text{-}O\text{-}C}$ (cm^{-1}): 1073 (s), 1100 (s); ^{1}H NMR: see Results; dec. 165°C.

Ion Exchange

The diiodide salt of **2*** was treated with $AgBF_4$ in methanol precipitating AgI which was separated by filtration. The ion exchanged product [Ni(bmmp-ether)][BF_4]$_2$, **[2*][BF$_4$]$_2$**, was obtained as a red microcrystalline solid after solvent evaporation. Yield: 80.6%; dec. 145°C; IR (KBr) $\nu_{C\text{-}O\text{-}C}$(cm^{-1}): 1073 (vs, br).

X-ray Data Collection, Structure Determination and Refinement

Crystals of [(bmmp-daco)Ni], **1***, (a purple needle) and [Ni(bmmp-ether)]I$_2$, **[2*]I$_2$**, (an orange plate) were mounted on a glass fiber with epoxy cement, at room temperature and that of **[2*]I$_2$** was cooled to 193 K in a N_2 cold stream. Cell parameters (Table 1) were calculated from the least-squares fitting of the setting angles for 25 reflections. Omega scans for several intense reflections indicated good crystal quality.

In the case of [(bmmp-daco)Ni] data were collected for $5.0° \leq 2\theta \leq 120.0°$ (θ-2θ scans] with fixed scan rate of 16.00°min^{-1} and scan range of 1.47 + 0.30·tan(theta). Three control reflections, collected every 150 reflections, showed no significant trends. Lorentz and polarization corrections were applied to 1471 reflections. A semi-empirical absorption correction was applied (T_{max} = 0.9999, T_{min} = 0.8606). All 1279 unique reflections were used in further calculations.

For [Ni(bmmp-ether)]I$_2$, data were collected for $4.0° \leq 2\theta \leq 50.0°$ [ω (Wyckoff) scans] at 193 K. Scan width, on ω, for the data collection was 1.00° with variable scan rate of 2.00 to 14.65° min^{-1}. Three control reflections, collected every 97 reflections, showed no significant trends. Lorentz and polarization corrections were applied to 5029 reflections. A semi-empirical absorption correction was applied (ellipsoid approximation; μ·r = 0.01; T_{max} = 0.9963, T_{min} = 0.5630). A total of 3565 unique reflections (R_{int} = 0.03),[13] with $|I| \geq 2.0\sigma I$, were used in further calculations.

Table 1 Experimental data for the X-ray crystal structure of [(bmmp-daco)Ni], **1***, and [Ni(bmmp-ether)]I_2CH_3Oh, **2*I_2CH_3OH**.

complex	**[(bmmp-daco)Ni]**	**[Ni(bmmp-ether)]I_2CH_3OH**
chemical formula	$C_{14}H_{28}N_2NiS_2$	$C_{19}H_{40}N_2O_2S_2NiI_2$
formula weight (g/mol)	347.2	705.2
space group	orthorhombic Pnma	monoclinic $P2_1/n$(No.14)[a]
a.(Å)	11.307(2)	11.193(3)
b.(Å)	19.579(3)	11.408(3)
c.(Å)	7.4790(10)	20.129(5)
β. (deg)	–	91.44(2)
V, ($Å^3$)	1655.7(4)	2569.5(12)
Z	4	4
ρ (calcd), (g cm^{-3})	1.393	1.823
temp.(K)	296	193
radiation	CuKα(λ = 1.54178Å)	Mo-Kα(λ = 0.71073Å)
absorption coefficient, (mm^{-1})	3.900	3.310
min./max. transmission coeff.	0.8606/0.9999	0.5630/0.9963
R(%)[b]	4.1	4.5
wR(%)[b]	4.1	4.0

[a] a nonstandard setting for the space group $P2_1/c$. [b] Residuals: $R = \Sigma|F_o\text{-}F_c|/\ \Sigma F_o$; $wR = \{[\Sigma w(F_o\text{-}F_c)^2]/[\Sigma\ w(F_o)^2]\}^{1/2}$

The molecular structures were solved by Patterson synthesis[14] for both complexes. Full-matrix least-squares isotropic refinement for O(2) in **[2*]I_2** and anisotropic refinement for all remaining non-hydrogen atoms in both complexes [quantity minimized $\Sigma w(F_o - F_c)^2$, $w^{-1} = \sigma^2 F$; number of least-squares parameters = 92 and 244 for **1*** and **[2*]I_2**, respectively][14] yielded at convergence[13] $R = 0.041$, $wR = 0.041$ and $S = 3.52$ for **1***, and $R = 0.045$, $wR = 0.040$ and $S = 2.37$ for **[2*]I_2**. In the case of [(bmmp-daco)Ni], **1***, the Ni(1), C(4), and C(6) atoms were found to only partially fill their sites in the asymmetric unit of the crystallographic unit cell and their site occupations were fixed on special positions to 50% occupation. The model, corrected for the variable site occupation, was used to refine the structure to convergence.

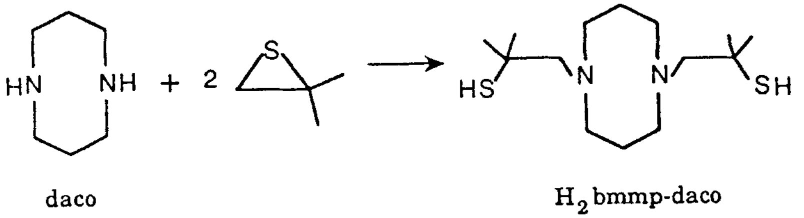
The extinction coefficient χ {where $F^* = F_c/[1 + 0.002\chi F_c^2/\sin(2\theta)^{0.25}]$} was refined to 0.0096(4) for **1*** and 0.00019(15) for **[2*]I_2**.[15] Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 $Å^2$. Neutral atom scattering factors and anomalous scattering correction terms were taken from a standard source.[16]

RESULTS AND DISCUSSION

Synthesis and characterization

The attachment of pendant arms to diazacyclooctane[7] was extended in this work utilizing the general reaction of amines with thioepoxides.[11] The ring opening of isobutylene sulfide occurs at the less hindered carbon and results in alkylation of 1,5-diazacyclooctane in 65% yield, eq 2.

Nickel(II) acetylacetonate efficiently reacts with the thiol form of N,N'-bis(2-mercapto-2-methylpropane)-1,5-diazacyclooctane producing a purple solid soluble



(2)

in protic solvents, acetonitrile, chloroform, and methylene chloride but insoluble in diethyl ether or hydrocarbons. As in the case of its non-methylated analogue, the sulfur sites are further reactive with electrophiles. Despite the steric hindrance about sulfur provided by the four methyl groups, complex **1*** exhibits the well-known template effect upon reaction with bis(2-iodoethyl)ether, eq. 1. The macrocyclic complex [Ni(bmmp-ether)]I_2, **[2*]I_2**, was obtained in good yield (80%); ion exchange in methanol produced the tetrafluoroborate analogue **[2*][BF_4]$_2$**.

Certain physical and spectroscopic properties of **1*** and the two **2*** complexes are presented in Table 3. All three compounds are diamagnetic in the solid state as well as in solution. Molar conductivity studies indicate that **[2*]I_2** and **[2*][BF_4]$_2$** are di-univalent electrolytes in acetonitrile.[4e] The UV-vis spectra for **1***, **[2*]I_2**, and **[2*][BF_4]$_2$** exhibit strong charge transfer bands below 300 nm and a weak single band in the 430–500 nm region, both in aqueous and in acetonitrile solutions. The ^1H NMR spectrum of [(bmmp-daco)Ni] in deuterated methanol contains two singlets in *ca.* 3:1 ratio assigned to the CH_3 groups and two other protons in pendant arms (1.42 and 2.56 ppm, respectively), which cannot couple with any other hydrogen atoms in the molecule. Protons from the daco ring in positions α to N atoms give rise to a multiplet at *ca.* 3.3 ppm, and those from the central methylene groups are not equivalent and appear as two multiplets at *ca.* 2.0 and 2.6 ppm. A similar pattern was observed and interpreted by Sardella *et al.* for the $[Ni(daco)]^{2+}$ cation.[17]

The observation of NMR spectra for salts of **2*** implies diamagnetism of these samples in methanol solutions. Nevertheless the spectra are difficult to interpret as arrested rotations in the macrocycle lead to several magnetically and chemically nonequivalent protons. Lowering the temperature to $-40°C$ did not change the complexity of the spectra obtained.

X-ray crystal structures

The molecular structures of **1*** and **[2*]I_2** are shown in Figures 1 and 2, respectively, and selected bond lengths and bond angles are listed in Table 2. Full structural reports for both complexes are available as supplementary material.

The (bmmp-daco)Ni^{II} compound, **I***, crystallizes in the orthorhombic crystal system. The donor atoms of the ligand form a regular plane from which the nickel deviates 0.0193 Å away from the more hindered face. The two fused nickelladiazacyclohexane rings of **1*** are in the boat/chair configuration and do not show any disorder as was observed for [(bme-daco)Ni], **1**, the non-methylated analogue.[7] The boat portion of the nickelladiazacyclohexane ring is situated on the same side of the

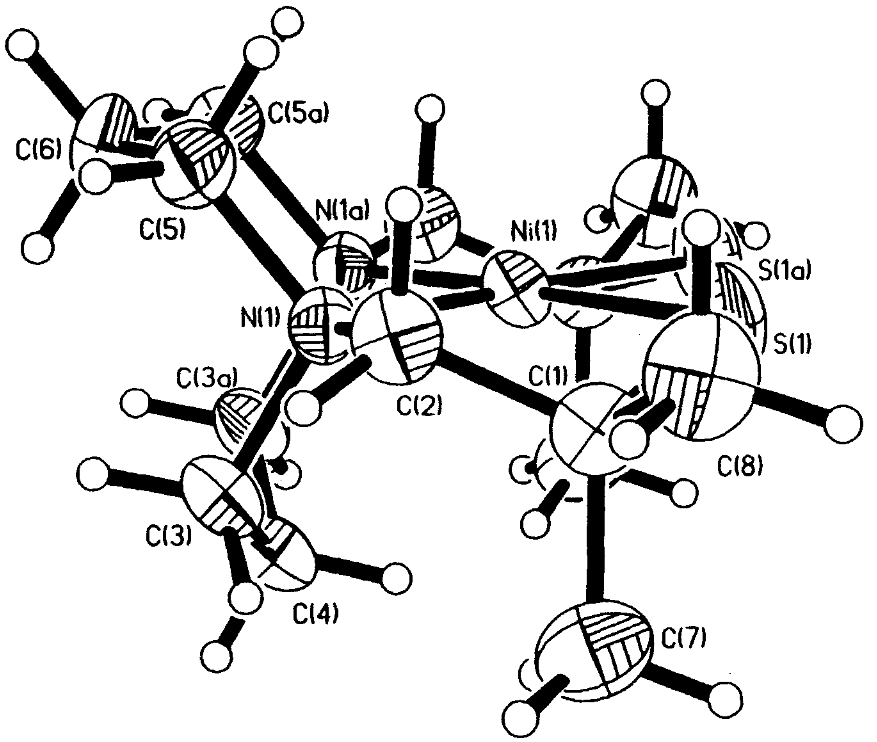


Figure 1 Molecular structure (thermal ellipsoid plot at 50% probability) of the (bmmp-daco)Ni^{II} with the atom-labeling scheme.

N_2S_2 plane as the axial methyl groups, providing a great steric shield of one face of the nickel ion. This arrangement minimizes cross-plane steric interactions of the hydrogens in the CH_2 groups α to N on daco and the axial methyl groups on the carbon α to S. This could be responsible for a greater rigidity in the daco framework. Another feature distinguishing **1*** from **1** is the position of pendant arms which are eclipsed in **1*** but staggered in **1**. The bond lengths and bond angles are virtually indistinguishable in **1*** and **1**. The sulfurs are sterically encumbered but project sites sufficiently open for further reaction, as evidenced by the production of **[2*]I_2**.

The [Ni(bmmp-ether)]I_2 compound, **[2*]I_2**, crystallizes in the monoclinic crystal system with four complexes and four methanol molecules in the asymmetric unit. Iodides are counterions, dispersed through the lattice; the closest distance to the complex cation is *ca.* 4 Å. Neither is there any H-bonding of the methanol molecule which co-crystallizes with the salt. The major features of complex **[2*]I_2** are substantially the same as **1***, with the obvious addition of the ether bridge between sulfurs. That bridge is folded in towards the open face of the NiN_2S_2 pseudo plane, yielding a Ni...O distance of 2.431(5)Å. This is only 0.044 Å longer than that of the Ni-O bond of the [Ni(ether)I][BPh_4], **2[BPh_4]**, hexacoordinate analogue, but is nevertheless beyond the metal-oxygen bonding distances observed for nickel

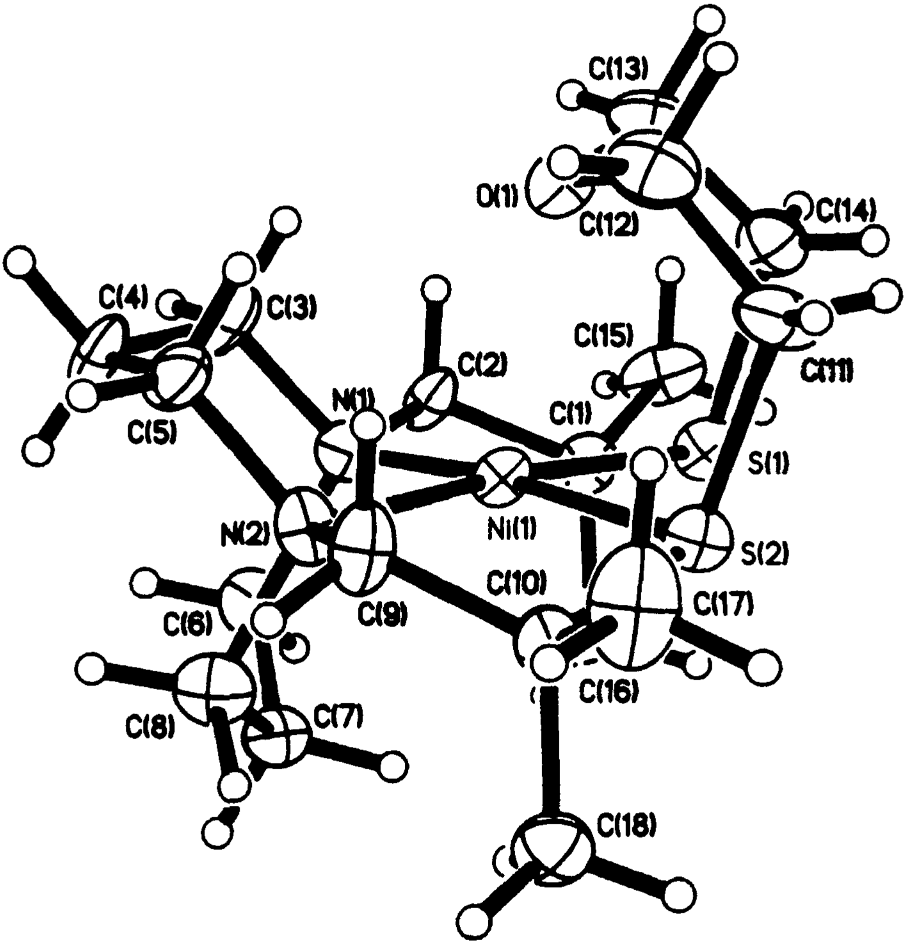
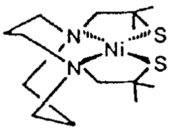
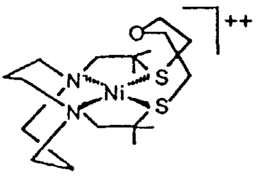


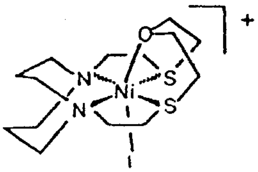
Figure 2 Molecular structure (thermal ellipsoid plot at 50% probability) of the [Ni(bmmp-ether)]$^{2+}$ cation with the atom-labeling scheme.

complexes.[18] The most convincing evidence that there is no O-Ni bonding in **2*** is in the Ni-S$_{av}$ and Ni-N$_{av}$ bond distances. At 2.195Å and 1.975Å, respectively, they are almost identical with those in other N_2S_2 tetracoordinate complexes derived from bme-daco.[7,8,18,19] As can be seen in Table 2, the hexacoordination in the non-methylated analogue [(Ni(ether)I][BPh$_4$] elicits major increases in the Ni-N (> 0.2Å) and Ni-S (*ca.* 0.1 Å) bond distances. Should the ether position of **2*** form a long-range interaction with Ni^{2+}, one would expect at least some lengthening of the Ni-N and Ni-S bonds distances. *Hence we conclude that nickel in complex* [**2***]I$_2$ *is tetracoordinate and the inward folding of the ether bridge is the result of efficient packing rather than a drive towards pentacoordination about Ni.*

Table 2 Selected bond lengths (Å)[a] and bond angles (deg)[a] for [(bmmp-daco)Ni] (**1***), $[Ni(bmmp\text{-}ether)]I_2 \cdot CH_3OH$ (**2*I_2CH_3OH**) and $[Ni(ether)I]BPh_4$ (**2BPh_4**).







Bond lengths	**[(bmmp-daco)Ni]**	**$[Ni(bmmp\text{-}ether)]I_2$**	**$[Ni(ether)I]BPh_4$**[b]
Ni(1)-S(1)	2.152(1)	2.200(2)	2.405(2)
Ni(1)-S(2)	2.152(1)	2.191(2)	2.362(2)
Ni(1)-N(1)	1.995(3)	1.970(6)	2.101(5)
Ni(1)-N(2)	1.995(3)	1.981(6)	2.116(5)
Ni(1)-X[c]	-	*2.534*	2.814(1)
Ni(1)-O	-	*2.431(5)*	2.387(5)
Bond angles			
N(1)-Ni(1)-N(2)[d]	90.4(1)	91.1(2)	85.5(2)
S(1)-Ni(1)-S(2)[d]	88.8(1)	87.7(1)	97.4(1)
S(1)-Ni(1)-N(1)	90.4(2)	90.4(2)	87.7(1)
S(1)-Ni(1)-N(2)[d]	178.6(1)	175.1(2)	165.6(1)
S(2)-Ni(1)-N(1)[d]	178.7(1)	173.6(2)	174.8(1)
S(2)-Ni(1)-N(2)[d]	90.4(1)	90.4(2)	89.8(1)
O-Ni(1)-S(1)	-	84.5(1)	79.3(1)
O-Ni(1)-S(2)	-	84.8(1)	78.5(1)
O-Ni(1)-N(1)	-	101.1(2)	103.7(2)
O-Ni(1)-N(2)	-	99.9(2)	90.0(2)
O-Ni(1)-X[c]	-	170.9	155.8(1)

[a] Estimated standard deviations are given in parentheses. [b] Ref. 6. [c] X = H(7a) in complex **2*I_2**; X = I in complex $2BF_4$. [d] In **1*** label (2) corresponds to (1A).

Electrochemistry

The [(bmmp-daco)Ni] complex **1*** undergoes a reversible reduction in acetonitrile at $E_{1/2} = -2.41$ V (Table 3), *i.e.*, at a potential *ca.* 190 mV more negative than its

Table 3 Physical, spectroscopic, and electrochemical data for [(bmmp-daco)Ni] and $[Ni(bmmp\text{-}ether)]X_2$ complexes.

	[(bmmp-daco)Ni]	**$[Ni(bmmp\text{-}ether)]I_2$**	**$[Ni(bmmp\text{-}ether)[BF_4]_2$**
Color (in solid state)	purple	orange brown	red
μ_{eff}, BM[a](20°C)	0	diam.	diam.
Λ_M,[b]Scm^2mol^{-1}	-	339	294
m.p.(°C)	298-300	165(dec.)	145(dec.)
VS-vis λ, nm(ε)			
acetonitrile	353sh(143) 498(91)	298 (8,320) 470(135)	298 (8,090) 428(638)
water	330sh (192) 530(70)	298(10,890) 486(250)	298 (6,635) 486(289)
Cyclic Voltammetry[c]			
$E_{1/2}$	-2408 mV	-747 mV	-729 mV
ΔE	85 mV	80 mV	86 mV
I_{pa}/I_{pc}	0.95	0.90	0.83

[a] Solid state measurements. [b] Molar conductance values for ca. 10^{-3} M solutions of the compounds in acetonitrile. [c] In acetonitrile for ca. 10^{-3} M solutions of analyte, with glassy carbon as working electrode *vs.* $Ag/AgNO_3$ and $TBAPF_6$ as supporting electrolyte.

non-methylated analogue, **1**.[20] Such a shift is expected upon addition of four methyl groups, electron donating relative to H, to the ligand's framework. The (bme-daco)Ni^{II} complex shows an irreversible oxidation at + 85 mV, assumed to be S-based and resulting in disulfide formation. This was substantiated by chemical oxidation. A similar feature is observed in **1*** at *ca.* O V *i.e.*, also at more negative potential than in **1**. This attests to the change of electron density in the complex as compared to its non-methylated analogue **1**, a change that makes electron removal easier. In addition, there is a quasi-reversible wave observed at + 882 mV ($\Delta E = 184$ mV) in the voltammogram of **1***.

Both [Ni(bmmp-ether)]$^{2+}$ salts, I^- and BF_4^-, exhibit reversible Ni$^{II/I}$ redox behavior at the same potentials, Table 3. This indicates that both complexes are similarly ligated, *i.e.*, tetracoordinate, in acetonitrile solution. Comparison with the non-methylated congeners is complicated by the difference in coordination numbers in [**2***]X_2 and [**2**]X_2. However, for the same coordination, both **2***[**I**]$_2$ and **2***[BF_4]$_2$ are more easily reduced than their non-methylated counterparts.[8] This may be explained in the following way. Even though the [**2**]X_2 complexes with noncoordinating counterions are four coordinate, the metal center is more efficiently solvated than in sterically encumbered [**2***]X_2, where solvation may be completely precluded by steric effects. This makes Ni^{2+} less receptive to the addition of an electron in the former. No Ni^{II} to Ni^{III} oxidation is observed within the solvent window (up to + 1.6 V) for either of the **2*** complexes.

CONCLUSION

An attempt to produce pentacoordinate Ni(II) in a square pyramidal N_2S_2O environment by providing a fifth donor site on the more open side of a macrocyclic ligand, while impeding hexacoordination by increasing steric encumbrance on the opposite side of the macrocyclic ligand was unsuccessful. Spectral as well as crystallographic studies indicate that [Ni(bmmp-ether)]X_2 salts are tetracoordinate, both in solid state and in solution. The presence of four methyl groups in positions α to the sulfur atoms efficiently prevents halide ions and also donor solvent molecules from coordinating to the metal center. The above results further emphasize the conclusions from studies of the non-methylated analogue [**2**]X_2;[8] *i.e.*, the presence of a sixth ligand in the coordination sphere is a requirement for binding of the ethereal oxygen donor site of the macrocyclic ligand. If the second axial ligand is not available, we suggest that the energy required for rearrangement of the N_2S_2 donor set (*i.e.*, as a minimum, bond lengthening as the coordination number is increased) is not balanced by the energy gained from the single, and in this case relatively weak, additional metal-ligand bond. The tetracoordinate complex is favored.

Acknowledgement

The National Institutes of Health is acknowledged for funding of this work (RO1 GM44865-01) and the National Science Foundation for the X-ray diffractometer and crystallographic computing system (CHE-8513273).

Supplementary material

Tables of crystallographic data collection parameters, atomic coordinates and equivalent isotropic displacement parameters, complete listings of bond lengths and bond angles, anisotropic displacement parameters, H atom coordinates and isotropic displacement parameters, molecular structure of the [Ni(bmme-ether)]$I_2 \cdot CH_3OH$ molecule, and packing diagrams (13 pages); listing of final observed and calculated structure factors (22 pages) are available from the authors on request.

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