Conclusions

By employing relatively small variations in the size and substituents of macrocyclic, equatorial ligands, we have shown that stereochemical influences result in substantial alterations of the Pt(IV)/Pt(II) reduction potential and that these influences correlate with inhibitions of axial binding in the Pt(IV) complex. These observations suggest that related stereochemical alterations could be used to decrease the tendency of metastable Pt(III) species to disproportionate, since axial bonding is expected to be relatively weak in the low-spin d^7 electronic configuration.

Acknowledgment. The diffractometer used herein was purchased by an NSF equipment grant to Wayne State University. The Cambridge Structural Database[38] assisted in the literature searches. We are grateful to Professor D. B. Rorabacher for useful discussions, for providing access to some of the ligands, and for providing us with the report of some of his unpublished work. We also thank Mr. Michael J. Mayer for help with ligand syntheses.

Supplementary Material Available: Tables A and B, giving thermal parameters and hydrogen atomic positions for $[trans\text{-}Pt([14]aneN_4)Cl_2]Cl_2{\cdot}HCl{\cdot}H_2O$, Tables D and E, giving thermal parameters and hydrogen atomic positions for $[Pt(ms\text{-}(5,12)\text{-}Me_6[14]aneN_4)](ClO_4)_2{\cdot}2H_2O$, and Tables G and H, giving thermal parameters and hydrogen atomic positions for $[Pt([14]aneS_4)](ClO_4)_2$ (5 pages); Tables C, F, and I, listing observed and calculated structure factors for the three complexes (47 pages). Ordering information is given on any current masthead page.

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Nickel Template Syntheses of Pentadentate and Macrocyclic Nitrogen–Sulfur Ligands: Single-Crystal X-ray Structure of (1,10-Diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane)nickel(II) Bis(tetraphenylborate)–Acetonitrile(1/3)

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Complexes of nickel with macrocyclic and pentadentate nitrogen–sulfur donor ligands have been prepared via the reaction of $[Ni(bdt)_2]^-$ with bis(2-chloroethyl)amine and 2,6-bis(chloromethyl)pyridine, respectively. The coordination sphere of the pentacoordinate compound (2,6-bis(((2-mercaptophenyl)thio)methyl)pyridinato)nickel(II) (**2**) consists of an aromatic amine, two thioether, and two thiolate donors. It is thermochromic, being yellow-orange at low temperatures and red-violet upon heating, and there is no major change in the vis–near-IR spectrum, which simply show a shift of λ_{max} from 480 to 520 nm. Magnetic measurements indicate that the compound contains high-spin Ni(II) (μ_{eff} 3.05 μ_B). A rather low quasi-reversible oxidation potential is observed at +0.144 V (all potentials are reported vs SCE), a second is observed at +0.546 V, and two irreversible reduction potentials are observed at −0.754 and −1.228 V. The hexadentate, macrocyclic complex (1,10-diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane)nickel(II) bis(tetraphenylborate) (**3**) was characterized by X-ray crystallography, which showed the complex to be a distorted octahedron with the four thioether donors (Ni–S = 2.398 (2), 2.440 (2) Å) in the equatorial plane and the nitrogen atoms (Ni–N = 2.082 (4) Å) in the axial positions. Crystal data are a = 18.213 (4) Å, b = 18.213 (12) Å, c = 20.115 (8) Å, and β = 103.51° with space group $C2/c$, Z = 4, R = 0.0434, and R_w = 0.0434. This complex has a high, irreversible oxidation potential at +0.964 V and a quasi-reversible reduction wave at −0.864 V. No hydrogen bonding is observed in the solid state but the N–H stretch of the amine is lowered to 3200 cm^{-1} upon coordination to the nickel ion.

Since the relatively recent discovery that a number of hydrogenases contain nickel, many studies have been carried out[1,2] in attempts to elucidate the role of nickel in catalyzing the reaction $H_2 \rightleftharpoons 2H^+ + 2e^-$. The EPR spectrum of these enzymes changes upon exposure to molecular hydrogen, giving rise to signals that can be attributed to Ni(I).[3-5] ESEEM evidence suggests that there is nitrogen in the coordination sphere,[6] and EXAFS studies indicate that sulfurs (probably three or four) are the predominant donors.[7,8] The salient feature of these nickel centers are the very low Ni(II)/Ni(III) oxidation potentials of −0.390 to −0.640 V (vs SCE),[1,9,10] which is striking when compared to the values reported for classical coordination compounds of nickel (+0.50 to +1.50 vs SCE).[11-13] An exception is $[Ni(S_2\text{-norbornane})_2]^{2-}$, reported by Millar, which contains nickel coordinated by four thiolates and has an oxidation potential at −0.76 V (vs SCE).[14] Since no hydrogenase has yet been subjected to an X-ray crystallographic structure determination, there is still considerable speculation as to the nature of the nickel site.

Recently a number of model compounds have been synthesized in hopes of mimicking the properties of the nickel site in hydrogenases.[15-21] In search for complexes of nickel with novel

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coordination spheres, we have synthesized multidentate ligands that contain amine, thioether, and thiolate donors. One ligand, a flexible macrocycle, provides classical, octahedral coordination, while the backbone of the second, a pentacoordinate ligand, is made rigid by the introduction of an aromatic amine. The convenient template synthesis of these novel ligands and the characterization of their nickel complexes are described herein.

Experimental Section

Caution! The amines bis(2-chloroethyl)amine and 2,6-bis(chloromethyl)pyridine are both mustard analogues and should be handled with care.

Physical Measurements. Infrared spectra were recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 330 spectrometer, and vis–near-IR spectra, from 300 to 2000 nm on a Perkin-Elmer 330 instrument. EPR measurements were conducted at 77 K on a Jeol JES-RE2X spectrometer. Mass spectra were measured on a Finnigan MAR SQ-70 triple quadrupole mass spectrometer, and differential pulse polarograms, on an EG&G Par C Model 303 potentiostat with an EG&G Par 384B polarographic analyzer. Microanalyses were performed by the Microanalytical Laboratory, University College, Dublin, Ireland. Magnetic measurements were performed by means of an automatized Faraday balance, described in detail by Arbouw.[22]

Abbreviations used: H_2bdt = 1,2-benzenedithiol; H_2tdt = 3,4-toluenedithiol (S_2Ar = bdt or tdt); Hacac = 2,4-pentanedione; TEA = tetraethylammonium; TBAP = tetrabutylammonium perchlorate; N2S4 = 1,10-diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane; NS4 = a bis(thiolate) bis(thioether) amine ligand.

Syntheses. Reagents and solvents were used as received. Ni(acac)$_2$ was prepared by the method of Bullen et al.,[23] and 2,6-bis(chloromethyl)pyridine was prepared as described in the literature.[24]

(Et$_4$N)[Ni(bdt)$_2$] (1) (bdt = Benzenedithiolate). Ni(acac)$_2$ (908 mg) was dissolved in warm MeCN (100 mL), and 4 mL of Et$_3$N was added. To this solution H_2bdt (1.0 mL), dissolved in 10 mL MeCN, was added, and the color immediately deepened to a dark olive green. The mixture was allowed to reflux for 10 min and was filtered, and (Et$_4$N)Br (8 g), dissolved in 30 mL of MeOH, was added. Cooling to 0 °C produced a crop of flaky dark green crystals, which were collected and washed with cold MeOH. Yield: 1.37 g (83%).

Anal. Calcd for $C_{20}H_{28}NNiS_4$: C, 51.17; H, 6.01; N, 2.98. Found: C, 50.83; H, 5.89; N, 2.91.

(2,6-Bis(((2-mercaptophenyl)thio)methyl)pyridinato)nickel(II) (2). Compound **1** (80 mg) was dissolved in MeCN (40 mL), and MeOH (20 mL) was added. To the resulting solution was added Et$_3$N (0.3 mL), $Na_2S_2O_4$ (240 mg) in 3 mL of H_2O, and 2,6-bis(chloromethyl)pyridine. The resulting mixture was allowed to stand, and orange crystals grew overnight. They were collected by filtration, washed thoroughly with water to remove dithionite and NaCl, and recrystallized from DMF/MeOH to yield pure samples of **2**. Yield: 57 mg (76%).

Anal. Calcd for $C_{19}H_{15}NNiS_4$: C, 51.37; H, 3.40; N, 3.15; S, 28.86. Found: C, 51.10; H, 3.42; N, 2.81; S, 27.68. Vis–near-IR: λ_{max} 480 nm (diffuse reflectance spectrum); λ_{max} 520 nm (DMF, DMSO). FABMS(+) (*m/z* (%), assignment): 888 (10), $[M_2]^+$; 444 (100), $[M]^+$; 413 (15), $[MH - S]^+$; 334 (15), $[MH_2 - C_6H_4S]^+$; 304 (17), $[M - C_6H_4S_2]^+$; 231 (15), $[pyCH_2SC_6H_4S - H]^+$. $E_{1/2}$ (DMF, TBAP, V vs SCE): oxidation, 0.144 (quasi-reversible, $E_a - E_c$ = 140 mV); 0.546 (irreversible); reduction, −0.754 (irreversible); −1.228 (irreversible). A plot of the magnetic data is shown in Figure S1 (supplementary material). μ_{eff} = 3.05 μ_B (304 K).

(1,10-Diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane)nickel(II) Bis(tetraphenylborate) (3). Compound **1** (80 mg) and bis(2-chloroethyl)amine (80 mg, Aldrich) were dissolved in warm 2:1 MeCN/MeOH (45 mL). To this was added Et$_3$N (0.3 mL), $Na_2S_2O_4$ (240 mg) in 3 mL of H_2O, and Na(Ph$_4$B) (400 mg), dissolved in 5 mL of MeOH. Upon standing at room temperature for 3 days, the solution deposited a crop of pale pink, microcrystalline material, which was collected, washed with MeOH, and dried in the air. Yield: 168 mg (62%) as **3**·MeOH.

Anal. Calcd for $C_{69}H_{70}B_2N_2NiOS_4$: C, 72.01; H, 6.04; N, 2.43; S, 11.14. Found: C, 71.97; H, 6.07; N, 2.40; S, 11.34. IR (KBr): 3200 cm^{-1} (NH). Vis–near-IR (diffuse reflectance spectrum): λ_{max} 530, 820, 1145, 1380 nm. FABMS(+) (*m/z* (%), assignment): 481 (100), $[M]^+$; 411 (55), $[MH - CH_2CH_2NHCH_2CH_2]^+$. $E_{1/2}$ (DMF, TBAP, V vs

Table I. X-ray Data for the Structure Determination of **3**·3MeCN

$C_{74}H_{75}B_2N_5NiS_4$
fw = 1243.0
a = 18.213 (4) Å
b = 18.213 (12) Å
c = 20.115 (8) Å
β = 103.51 (3)°
V = 6487.6 (55) Å^3
Z = 4

space group = *C*2/*c*
T = 22 °C
λ = 0.71069 Å
σ_{calcd} = 1.27 g/cm^3
R = 0.0434
R_w = 0.0434
goodness of fit = 1.53

Table II. Non-Hydrogen Atomic Positional Parameters for **3**·3MeCN

	x/z	*y/b*	*z/c*
Ni1	0.5000	0.2234 (1)	0.7500
S1	0.4124 (1)	0.3197 (1)	0.7571 (1)
S2	0.4102 (1)	0.1401 (1)	0.7838 (1)
N1	0.4458 (2)	0.2170 (3)	0.6468 (2)
C11	0.1580 (3)	0.2229 (3)	0.2079 (3)
C12	0.2123 (3)	0.1780 (4)	0.1903 (3)
C13	0.2685 (3)	0.2087 (4)	0.1640 (3)
C14	0.2713 (4)	0.2835 (4)	0.1559 (3)
C15	0.2171 (3)	0.3285 (4)	0.1723 (3)
C16	0.1591 (3)	0.2983 (3)	0.1978 (3)
C1	0.3670 (3)	0.3198 (3)	0.6658 (3)
C2	0.3671 (3)	0.2443 (3)	0.6340 (3)
C3	0.4499 (3)	0.1430 (3)	0.6204 (3)
C4	0.4641 (3)	0.1202 (3)	0.8706 (3)
B1	0.2588 (4)	0.0007 (3)	−0.0216 (3)
C21	0.3267 (3)	0.0621 (3)	−0.0003 (2)
C22	0.3145 (3)	0.1379 (3)	−0.0007 (3)
C23	0.3728 (3)	0.1872 (3)	0.0202 (3)
C24	0.4457 (3)	0.1634 (4)	0.0443 (3)
C25	0.4597 (3)	0.0900 (4)	0.0459 (3)
C26	0.4018 (3)	0.0404 (3)	0.0239 (3)
C31	0.2346 (3)	−0.0297 (3)	0.0474 (3)
C32	0.1735 (3)	−0.0785 (3)	0.0409 (3)
C33	0.1504 (4)	−0.1079 (3)	0.0962 (4)
C34	0.1888 (4)	−0.0886 (4)	0.1619 (4)
C35	0.2491 (4)	−0.0408 (4)	0.1711 (3)
C36	0.2717 (3)	−0.0118 (3)	0.1145 (3)
C41	0.2915 (3)	−0.0672 (3)	−0.0602 (3)
C42	0.2952 (3)	−0.1404 (3)	−0.0391 (3)
C43	0.3217 (3)	−0.1965 (3)	−0.0733 (3)
C44	0.3452 (3)	−0.1821 (4)	−0.1315 (3)
C45	0.3433 (3)	−0.1105 (4)	−0.1555 (3)
C46	0.3183 (3)	−0.0541 (3)	−0.1194 (3)
C51	0.1824 (3)	0.0364 (3)	−0.0715 (3)
C52	0.1554 (3)	0.0212 (3)	−0.1414 (3)
C53	0.0921 (3)	0.0539 (3)	−0.1814 (3)
C54	0.0518 (3)	0.1044 (3)	−0.1540 (3)
C55	0.0755 (3)	0.1220 (3)	−0.0853 (3)
C56	0.1386 (3)	0.0879 (3)	−0.0458 (3)
N2	−0.0068 (4)	−0.1756 (4)	−0.0610 (3)
C5	−0.0222 (4)	−0.1165 (4)	−0.0740 (4)
C6	−0.0422 (4)	−0.0413 (4)	−0.0925 (4)
N3	0.5000	0.0101 (7)	0.2500
C7	0.5000	0.0684 (9)	0.2500
C8	0.5000	0.1527 (8)	0.2500

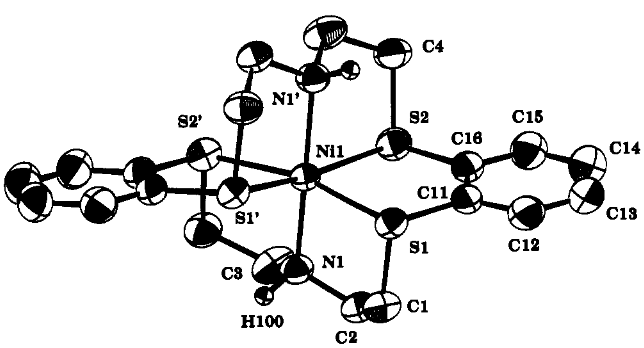

Figure 1. ORTEP representation of the structure of **3**·3MeCN, showing the atom-labeling scheme and 50% probability ellipsoids.

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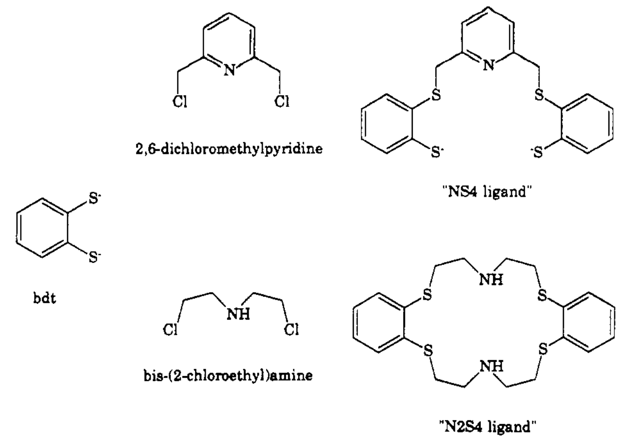

Figure 2. Chart of relevant structures.

SCE): oxidation, 0.964 (irreversible); reduction, −0.864 (quasi-reversible, $E_a - E_c$ = 130 mV).

Single-Crystal X-ray Structure Determination of 3·3MeCN. Pink plates were grown from a solution of 3 in acetonitrile/methanol. Rapid solvent loss precluded any density measurements. Crystal data are presented in Table I, non-hydrogen atomic positional parameters are in Table II, and an ORTEP-drawn diagram is shown in Figure 1. A single monoclinic crystal of approximate dimensions 0.3 mm × 0.3 mm × 0.1 mm was chosen and mounted in a capillary with Nujol, and the space group was determined to be *C*2/*c*. A total of 4333 reflections (of which 4128 were unique, R_{int} = 0.0306) were collected on an Enraf-Nonius CAD-4 diffractometer ($2\theta_{max}$ = 44; octants collected $\pm h,+k,+l$; scan mode = zigzag). Solution and refinement of the structure were carried out by using SHELX-76. Neutral atomic scattering factors[25] were used throughout, and no extinction effects were observed. The structure was solved by using direct methods, and all non-hydrogen atoms were refined anisotropically. The amine hydrogen atom, H100, was found in the difference map, and all other hydrogen atoms were refined from their calculated positions.

Results and Discussion

Syntheses. Syntheses of macrocyclic ligands are often involved, multistep processes, and the products are generally obtained in poor yields. The use of metal templates in the preparation of macrocyclic ligands has been well established as a simple method by which high yields of target compounds can be obtained. Furthermore, when working with sulfur ligands, this method has the added advantage that the metal also acts as a protecting group against thiol oxidation.

Prolonged reflux of (TEA)[Ni(bdt)$_2$] (**1**) (bdt = 1,2-benzenedithiolate) with 2,6-bis(chloromethyl)pyridine affords no reaction. However, reduction of the complex with dithionite increases the nucleophilicity of the sulfurs, and the reaction then proceeds to yield a five-coordinate species **2**, in which the nickel is coordinated by the pyridine nitrogen, two thioethers, and two thiolates (Figure 2). The addition of a large excess of the amine does not cause further reaction to give a doubly bridged species. On the other hand, the analogous reaction with the more flexible, aliphatic amine bis(2-chloroethyl)amine causes all four sulfurs to be alkylated. The resulting complex **3** thus contains nickel surrounded by an N2S4 macrocycle. Attempts to stop the reaction at the monobridged complex by adding only 1 equiv of amine produced undefined mixtures of products. This is in direct contrast to the related reaction of $[Fe(CO)_2(S_2C_6H_4)_2]^{2+}$ reported by Sellmann.[26,27] In this system only singly bridged species are isolated. A possible explanation is that the singly bridged nickel intermediate should contain an open coordination site which allows the coordination of a second amine, inducing further alkylation. The iron system,[26] on the other hand, contains bound carbon monoxide, and this ligand would have to be lost before an amine can coordinate.

In the process of work on the above syntheses, we found that (TEA)[Ni(S$_2$Ar)$_2$] (S$_2$Ar = bdt and 3,4-toluenedithiolate) can be conveniently prepared by the addition of the appropriate dithiol to an aprotic solution of Ni(acac)$_2$ and Et$_3$N. Oxidation of Ni(II) occurs smoothly in the presence of air to give the olive green Ni(III) complexes, which can then be isolated by the addition of (TEA)Br. The advantage of this synthesis over the method of Baker-Hawkes et al.[28] is that less of the insoluble material, which probably consists of thiolate-bridged polymers, is formed and pure material is obtained directly from the reaction mixture. It has been shown that protic solvents induce thiolate bridging.[21,29] Furthermore, the monoanionic complex is more easily crystallized than the reduced, dianionic species and, therefore, the complex is isolated in the oxidized form.

Spectral and Magnetic Characterization. As do many nickel complexes, **2** exhibits thermochromism.[30] In the solid state and in solution at room temperature, the complex is orange with a band maximum in the visible spectrum of 480 nm. At higher temperatures (>50 °C) the λ_{max} shifts reversibly to 520 nm, and the compound appears dark pink. Since the shapes of vis–near-IR spectra of the compound at both temperatures appear similar, showing only a shift in the λ_{max} of the major band, it is likely that the thermochromism is due to a conformational change and not to monomer–dimer equilibrium. The coordination geometry of this compound is as yet unclear, but the vis–near-IR spectrum is consistent with high-spin, trigonal-bipyramidal coordination.[31] An analogous complex that has a ligand with a similar structure, albeit different donors, has a distorted pentagonal-planar geometry.[32] This cannot be the case for **2**, however, since such a complex could not be paramagnetic (vide infra) and the elemental analysis of **2** precludes the presence of any axially coordinated solvent molecules. Without the help of crystallographic characterization, it is difficult to assign the geometry of this complex, and unfortunately, numerous attempts at crystal growth produced only thin platelets. The macrocyclic complex **3**·MeOH, on the other hand, exhibits a classical octahedral ligand field spectrum with no noteworthy features.

Since the origin of the thermochroism of compound **2** is not clear and five-coordinate complexes can be either high-spin or low-spin, magnetic measurements were carried out. A plot of $1/\chi$ versus temperature from 87 to 304 K is linear, and μ, with a value of 3.05 μ_B at room temperature, remains nearly constant as the temperature is lowered (3.29 μ_B at 87 K). Additional measurements on a pendulum Faraday instrument between 6 and 77 K also showed a Curie–Weiss type behavior, with a small positive zero-field splitting (to be published), typical for mononuclear Ni(II). Unfortunately, magnetic moments cannot be used to distinguish between trigonal-bipyramidal and square-pyramidal geometries.

In the infrared spectrum of **3**, there is a sharp band at 3200 cm^{-1}, which is assigned as the NH stretch. The band is present in all IR spectra of this compound regardless of the morphology of the sample, and the assignment was confirmed by deuterium exchange resulting in an isotopic shift to 2380 cm^{-1}. Powdered samples that analyzed for **3**·MeOH exhibit the same NH stretch as samples prepared from X-ray crystals, which have the composition **3**·MeCN, and as desolvated single crystals. In fact, the infrared spectra of all three samples were identical with the exception of a band at 2250 cm^{-1}, which occurs in the spectrum of the X-ray-quality crystals and is assigned to the CN stretch of

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Table III. Bond Lengths and Angles around Nickel(II) for 3·3MeCN

Bond Lengths (Å)			
Ni1–S1	2.398 (2)	S2–C4	1.829 (5)
Ni1–S2	2.440 (2)	S2–C16	1.790 (5)
Ni1–N1	2.082 (4)	N1–C2	1.481 (6)
S1–C1	1.830 (5)	N1–C3	1.458 (7)
S1–C11	1.778 (5)		
Bond Angles (deg)			
S1–Ni1–S2	86.5 (1)	Ni1–S1–C1	95.2 (2)
S1–Ni1–N1	86.2 (1)	Ni1–S2–C4	98.3 (2)
S2–Ni1–N1	92.1 (1)	Ni1–N1–C2	111.7 (3)
S1–Ni1–S1′	86.0 (1)	Ni1–N1–C3	111.2 (3)
S2–Ni1–S2′	103.2 (1)	C2–N1–C3	112.1 (4)

acetonitrile. Thus, despite an N–NCMe distance of 2.988 Å (vide infra), which just falls within the generally accepted upper limit of 3.00 Å for hydrogen bonding, the low NH stretching frequency cannot be attributed to such an interaction and must be due to electronic effects. Indeed, coordination of amines is known to lower the NH stretching frequency.[33]

The positive mode fast-atom-bombardment mass spectrum (FABMS(+)) of compound **2** contains peaks corresponding to the molecular ion, its dimer, and a number of logical fragments. Dimer formation is often observed under mass spectral conditions and does not necessarily indicate the presence of dimeric units in the sample. The FABMS(+) of complex **3** reaffirms the assignment of the molecular formula, containing peaks that can be assigned as the molecular ion and loss one of the amine bridges.

The electrochemistry of the macrocyclic compound **3** is typical for octahedral nickel(II) complexes. The nickel(II/III) couple occurs at +0.964 V (vs SCE), which compares poorly with the range observed for the native enzyme (−0.390 to −0.640 V).[1,9,10] The strong preference of this system for an oxidation state of 2+ is further substantiated by the low, but reversible, nickel(II/I) potential at −0.864 V. Compound **2**, on the other hand, shows irreversible reduction waves at −0.754 V and −1.228 V, while the first of the two oxidation potentials (+1.44 and +0.546 V) is uncharacteristically low and also quasi-reversible. It is not clear where the oxidation is centered, and it may be a ligand process. In attempts to clarify this situation, the complex was chemically oxidized with iodine, whose redox potential lies cleanly between the two oxidation waves, and an EPR spectrum was sought. As is the case for the Ni(II) complex **2**, no spectrum was observed down to 77 K, suggesting that Ni(III) is not present and that the first oxidation wave of **2** is probably due to a ligand-centered process.

X-ray Crystal Structure of 3·3MeCN. As can be seen in Figure 1 and Table III, complex **3**·3MeCN contains nickel in a distorted octahedral environment with the four thioether sulfur atoms coordinated in the equatorial plane and the amine nitrogens sitting in the axial sites. The bridges lie along the diagonal axes as does the amine bridge in $[Fe(CO)(NS_4)]$, reported by Sellmann.[26,27] The octahedron is distorted so that the sulfurs which are bound to each amine bridge are pulled toward that bridge. A factor influencing this geometry may be that the ethylene chelate rings are slightly too short to comfortably accommodate the nickel ion. The amine hydrogens were found in the electron density map, confirming the oxidation state as +2. Cell diagrams show that these hydrogens are barely within hydrogen-bonding distance of four of the six acetonitrile molecules in the unit cell (N1–N2 = 2.988 (2) Å). However, infrared spectra do not show any indication of hydrogen bonding (vide supra). Although the metal-nitrogen distances are almost the same for both, the M–thioether bond lengths in **3** (2.440 (2), 2.398 (2) Å) are considerably longer than in the above-mentioned, related iron structure (2.251 (3), 2.225 (3) Å). This may be due simply to a difference in charge or may be a manifestation of the changing ligand requirements upon going from an open, pentadentate ligand to a hexadentate macrocycle.

Final Remarks

We have shown that, upon reduction, the sulfurs of $[Ni(S_2Ar)_2]$ are activated toward alkylation and that this method can be utilized to prepare macrocyclic and pentadentate complexes in high yields. The template approach is useful both in reducing the entropy of the reaction and in preventing oxidation of the thiolates. Through the use of different amines, we can control the number of amines added to the complex and obtain either singly or doubly bridged products, which have contrasting physical properties. In the future, this method could be used to synthesize a range of sulfur-containing ligands as models for the active site of hydrogenase.

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Supplementary Material Available: Figure S1, showing a plot of the magnetic data, and Tables SI–SIII, listing anisotropic thermal parameters, hydrogen atom positions, and complete bond distances and angles (14 pages); Table SIV, listing calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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[33] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1978, p 206.