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Synthesis, Structure, and Reactivity of the Nickel(II) Complex of 7-Aza-1,4-dithiacyclononane

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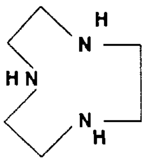
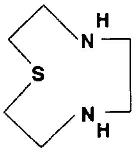
The "missing" member of the series of ligands, L_1–L_4, based on cyclononane [9]aneN_xS_y ($x + y = 3$), namely 7-aza-1,4-dithiacyclononane, L_3, [9]aneNS_2, has been synthesized and characterized. A key step in the synthesis is the final detosylation, upon which comments are made. The Ni(II) complex has been prepared as a perchlorate salt and investigated by X-ray diffraction. Octahedral symmetry is observed, with each nitrogen in an axial position. The species $[Ni(L_3)_2](ClO_4)_2$ crystallizes in the monoclinic space group $P2_1/a$ (No. 14) with $a = 16.607$ (3) Å, $b = 8.837$ (1) Å, $c = 7.465$ (1) Å, $\beta = 93.3$ (2)°, $V = 1093.7$ Å^3, and $Z = 2$. Of 1929 reflections, 1645 were used ($F > 3\sigma(F)$), and the structure was refined to $R(F_o) = 0.0517$ and $R_w = 0.0591$. Stepwise replacement of N by S has a pronounced effect on the geometry of the nickel(II) complexes. Electrochemical oxidation in dry CH_3CN yields $[Ni(L_3)_2]^{3+}$ (ESR active, axial spectrum, $g_\perp = 2.121$, $g_\parallel = 2.019$), which is stable for several hours. However, the Ni(III) species is very sensitive to moisture. Cyclic voltammetry in acetonitrile shows two features. The oxidation to Ni(III) occurs at $E_{1/2} = 1.044$ V (vs $Ag^{+/0}$). An irreversible reduction wave at −1.52 V is associated with an oxidation wave at −0.122 V. Reduction of $[Ni(L_3)_2]^{3+}$ in deoxygenated water using sodium borohydride yields a brownish yellow species, ESR inactive, that is unstable and deposited Ni(0) on standing. On immediate aeration, this species is reoxidized to the starting Ni(II) complex. Chemical reduction of $[Ni(L_3)_2]^{2+}$ in acetonitrile media produces an ESR-active Ni(I) species that differed in the presence of triphenylphosphine. On the basis of electronic and ESR spectroscopy, it is concluded that such species adopt a tetrahedral geometry but may be involved in equilibria with other 5-coordinate complexes. Although the NiS_4 chromophore is analogous with some hydrogenases based on that metal center, it appears that the completely saturated macrocycles and 6-coordinated Ni(II) centers do not represent models for such activity.

Introduction

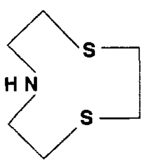
Of the tridentate ligands L_1–L_4, L_1 ([9]aneN_3 or 1,4,7-triazacyclononane) has been extensively used in recent years to study 3d transition-metal ions.[1] Two such ligands can coordinate to transition-metal ions occupying the trigonal faces to form octahedral complexes. This stereorestrictive mode of coordination renders remarkable stability toward ligand dissociation.[2] Many such complexes involving L_1 with transition-metal ions have been characterized in more than one oxidation state. For example, crystal structures of the complexes of the Fe(II),[3] Fe(III),[3] Co(II),[4] Co(III),[5] Ni(II),[6] Ni(III),[7] and Pd(II),[8] Pd(III)[9] pairs have been determined. On the basis of the structural differences observed in the two oxidation states, self-exchange electron-transfer rates have been calculated[4,10] by use of the Marcus–Sutin theory of electron transfer that have been shown to agree well with the experimentally measured rates. Thus, the bis complexes of these ligands are known to behave as pure outer-sphere oxidants or reductants.



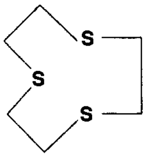
L_1



L_2



L_3



L_4

The trithia analogue, L_4 (1,4,7-trithiacyclonane), has been used to complex 3d, 4d, and 5d transition-metal ions.[11] Owing to its soft donor atoms, this ligand forms complexes with noble metal ions and stabilizes uncommon oxidation states such as Pd(III), Pt(III), and Ag(II).[12-14]

The two other members, ligands L_2 and L_3 ([9]aneN_2S, 1-thia-4,7-diazacyclononane, and [9]aneNS_2, 7-aza-1,4-dithiacyclononane) are interesting, since they contain both the hard N-donor and soft S-donor atoms. Hancock and co-workers have reported the synthesis and properties of complexes prepared from ligand L_2.[15,16] These workers have also carried out[17] molecular mechanics calculations in several related systems, in which a specific ring conformation is proposed for the nickel(II) complex of L_3. Interest in such mixed donor ligands stems not only from metal ion selectivity but also from the possible presence of such coordination environments around metal centers in methanogenic bacterial enzymes.[18,19]

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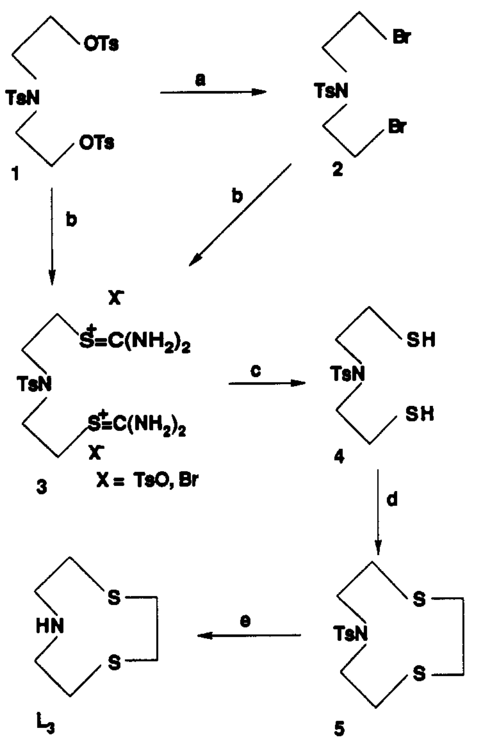
Scheme I. Synthesis of Ligand L_3[a]



[a] Conditions: (a) sodium bromide/DMF, 140 °C, 3 h; (b) thiourea/ethanol or THF under reflux, 8 h; (c) approximately 10% KOH/120 °C, 30 min; (d) Cs_2CO_3/DMF, dibromoethane, 60 °C, rate of addition 12 mL/h; (e) anhydrous phosphoric acid, 140 °C, 30–40 min.

No reports are available on [9]aneNS$_2$ (L_3). Therefore, it is of interest to investigate the complexing properties of this ligand and compare them with other members of this series. With this in view, we report here the synthesis of [9]aneNS$_2$ and the chemistry of its Ni(II) complex.

Experimental Section

All chemicals used were of reagent grade and used without further purification. Organic intermediates were characterized by common spectroscopic methods. Infrared spectra were obtained on KBr disks by using a Perkin-Elmer 283 grating spectrometer. ^1H NMR spectra were recorded on a Perkin-Elmer R-32 instrument, and ^{13}C NMR spectra were obtained on a Bruker WM 250 instrument. NMR spectra were run with $CDCl_3$ as solvent, and chemical shifts are reported in ppm relative to TMS. Mass spectra of all organic intermediates and the ligand were obtained from a Finnegan GC 360 mass spectrograph by electron impact or chemical ionization methods.

ESR spectra were obtained with a frozen matrix at liquid-N_2 temperatures by using a Varian E-6S spectrometer. DPPH (diphenylpicrylhydrazide, $g = 2.0037$) was used as an external standard. UV-visible spectra were recorded by using either a Perkin-Elmer Lambda 4 or a Cary 17 spectrophotometer.

Elemental analysis were performed by Canadian Microanalytical Services, Vancouver, BC, Canada.

Electrochemical data were obtained by use of a Princeton Applied Research Model 273 potentiostat/galvanostat. All measurements were made in freshly distilled, deaerated acetonitrile containing 0.1 M Et_4NBF_4. The electrolyte solutions were saturated with argon prior to any measurements being made, and an argon atmosphere was maintained as data were collected. Pt electrodes were used as working electrodes, and the Ag/Ag^+ electrode was used as the reference electrode.[20] Potentials are reported against this reference electrode. The ferrocene/ferrocenium ($E_{1/2} = 0.157$ V; $\Delta E_p = 90$ mV) couple was used as an external standard.

Synthesis. The synthetic route for the ligand L_3 is outlined in Scheme I. The tritosylate of diethanolamine, **1**, was prepared according to published procedures.[21] The intermediate dithiol was obtained by usual methods,[22] and cyclization was carried out by using Cs_2CO_3 as base according to methods similar to that of Blower and Cooper.[23] The *N*-tosyl cyclic ligand was detosylated with anhydrous phosphoric acid.

***N*-Tosylbis(2-bromoethyl)amine (2).** Tritosylate of diethanolamine (125 g, 0.22 mol) and sodium bromide (54 g, 0.5 mol) were dissolved in 250 mL of DMF, and the mixture was heated under stirring in an oil bath maintained at 140 °C. As the reaction proceeded, crystalline, silky voluminous sodium tosylate was formed. After 3 h the reaction mixture was cooled to room temperature and poured into 1–1.5 L of water kept under vigorous stirring in a 3-L beaker. The dibromo compound separated as a viscous oil and solidified, on standing, to a yellow solid. This material was crushed and filtered under suction in a Büchner funnel, washed with water, and dried in air under suction. The dry solid thus obtained weighed about 70 g. This solid was redissolved in 300 mL of boiling ethanol, and the mixture was decolorized with charcoal and filtered while hot. The pale yellow ethanolic solution deposited colorless crystals of the pure dibromo compound (62 g, yield 74%). A further 2–5 g of the compound could be recovered on allowing the mother liquor to stand in a freezer. The dry crystals melted at 63 °C without decomposition. Anal. Calcd for $C_{11}H_{15}NSO_2Br_2$: C, 34.28; H, 3.89; N, 3.6; Br, 42.07. Found: C, 33.98; H, 3.77; N, 3.44; Br, 41.64. ^1H NMR ($CDCl_3$): 7.36–7.73 (m, 4 H), aromatic protons; 3.51 (s, br, 8 H), CH_2–; 2.44 (s, 3 H), aromatic CH_3. ^{13}C NMR ($CDCl_3$): 144.1, 135.7, 130.0, 127.2, aromatic carbons; 51.4, CH_2–NTs; 29.5, CH_2–Br; 21.5, aromatic CH_3. Mass spectral data: $m/e = 385$ (M^+) (electron impact).

***N*-Tosylbis(2-mercaptoethyl)amine (4). Formation of Thiouronium Salt 3.** The dibromo compound **2** (35 g, 0.095 mol) and thiourea (16 g, 0.21 mol) were refluxed in 250 mL of dry THF under a nitrogen atmosphere for 5 h. The substrates were not soluble, and the reaction mixture boiled with occasional bumping. The reagents slowly disintegrated to form a fine crystalline mass (or a viscous yellow oil on prolonged heating, which solidified on standing or on adding a small amount of ethanol). The resulting solid was filtered out under suction, washed with ether, and dried in air. The crude thiouronium salt thus obtained weighed 40 g (yield 78%) and was used as such without further purification.

Ethanol can be used as a solvent in place of THF. Also the tritosylate of diethanolamine, **1**, can be used in place of the dibromo compound **2**. However, the reaction takes a longer time and also the yields of the dithiol were found to be 30% or lower.

Hydrolysis of Thiouronium Salt 3. Potassium hydroxide (15 g, 0.27 mol) was dissolved in 250 mL of water, and the solution was saturated with nitrogen for at least 30 min in a 500-mL 3-necked round-bottomed flask equipped with a reflux condensor. A 20-g amount of the solid thiouronium salt was added in lots of 4 g over a period of 20 min. Stirring was maintained by vigorously bubbling nitrogen through the reaction mixture, which was refluxed at 120 °C for about 30 min. The thiouronium salt dissolved immediately to form a clear solution. The reaction mixture was cooled to room temperature and if necessary filtered through glass wool (to remove any *N*-tosylthiomopholine formed as a byproduct). The resulting clear filtrate was again diluted with deaerated water to 500 mL and maintained under a nitrogen atmosphere with stirring. The temperature of this diluted solution was maintained at 0 °C and concentrated HCl saturated with nitrogen was added dropwise to make the solution distinctly acidic. The solution turned cloudy owing to liberation of the dithiol, **4**, which separated as a clear, very pale yellow oil. After 100 mL of dichloromethane was added to this mixture to dissolve the viscous oil, the dichloromethane layer was removed in a separating funnel. The aqueous layer was extracted with further 2 × 50 mL portions of dichloromethane, and the combined dichloromethane extracts were washed with deaerated water to remove any free hydrochloric acid, dried over anhydrous sodium sulfate, and concentrated under vacuum to give a pale greenish yellow viscous oil, which slowly solidified to a waxy solid (8.0 g, yield 58%). This waxy solid was characterized by ^1H and ^{13}C NMR and mass spectroscopy and used as such without further purification. ^1H NMR ($CDCl_3$): 7.3–7.55 (m, 4 H), aromatic protons; 3.27 (t, 7.5 Hz, 4 H), –CH_2–N; 2.72 (m), –CH_2–S; 2.42 (s), aromatic CH_3; 1.42 (t, 8.5 Hz, 2 H), –SH. ^{13}C NMR ($CDCl_3$): 143.9, 136.3, 130.0, 127.2, aromatic carbons; 52.85, –CH_2–NTs; 24.0, –CH_2–SH; 21.5, aromatic CH_3. Mass spectral data: $m/e = 291$ (M^+) (electron impact; loss of hydrogen sulfide observed).

1-Tosyl-1-aza-4,7-dithiacyclononane (5). Cesium carbonate (25 g, 0.077 mol) was dried in an oven at 75 °C for 10 h and then transferred to a 5-L three-necked flask equipped with a mechanical stirrer and a heating mantle. This reaction vessel was kept under a continuous flow of dry nitrogen. A 1.5-L volume of DMF (from a freshly opened bottle

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of reagent quality) was deaerated under suction and then transferred to the 5-L reaction vessel and saturated with nitrogen. The reaction mixture was stirred vigorously to keep the cesium carbonate as a fine suspension. The temperature was maintained at 40 °C, and a blanket of nitrogen was maintained. A mixture of *N*-tosyl dithiol **4** (9 g, 0.03 mol) and 1,2-dibromoethane (5.8 g, 0.03 mol) dissolved in 1 L of deaerated DMF saturated with nitrogen was added at a rate of 10–12 mL/h from a dropping funnel equipped with a needle valve. Throughout the addition, the reaction mixture was kept under a blanket of nitrogen and kept vigorously stirred at 40 °C. After completion of addition of reagents, the reaction mixture was reacted for another 4 h.

At the end of reaction, DMF was distilled off in a rotary evacuator to dryness. The resulting mass was suspended in 250 mL of water and extracted with 3 × 50 mL of dichloromethane. The combined extracts were dried over anhydrous sodium sulfate and concentrated to dryness to a brown viscous oil. Traces of solvents were removed under vacuum, and the viscous oil subsequently solidified to a brown crystalline solid. This crude material weighed about 7 g and was not pure. It was dissolved in 75 mL of hot ethanol, and 3 g of activated charcoal was added. The solution was maintained at 70 °C for 5–10 min and filtered while hot. The pale yellow filtrate was allowed to cool slowly. Any viscous insoluble oil was separated by decanting the supernatant. The supernatant on standing yielded a fine white crystalline solid of 1-tosyl-1-aza-4,7-dithiacyclononane, (**5**) (5.6 g) in 59% yield. MP: 132–133 °C. Anal. Calcd for $C_{13}H_{19}NS_3O_3$: C, 49.21; H, 5.99; N, 4.41; S, 30.28. Found: C, 48.82; H, 5.98; N, 4.40; S, 30.40. ^1H NMR ($CDCl_3$): 7.5 (m), aromatic protons; 3.4 (m, br, 4 H), CH_2–N; 3.13 (m, br, 8 H), CH_2–S; 2.40 (s, 3 H) aromatic CH_3. ^{13}C NMR ($CDCl_3$): 143.85, 129.8, 127.6, 127.9, aromatic carbons; 21.5, aromatic CH_3; 53.6, CH_2–N; 34.3, 32.5, CH_2–S. Mass spectral data: *m*/*e* = 317 (M^+).

Detosylation of 5 to [9]aneNS$_2$, L$_3$. A 25-mL volume of orthophosphoric acid (80%) was taken in a two-necked flask equipped with a magnetic stirrer and a reflux condenser. A 30-g amount of phosphorus pentoxide was added while the orthophosphoric acid was stirred under a blanket of N_2 gas. This mixture was stirred until all the phosphorus pentoxide dissolved to form a clear solution. After it was heated in an oil bath to 140 °C under a slow stream of N_2 gas, 2 g (6.3 mmol) of **5** was added. Compound **5** dissolved immediately to form a clear light brown solution. The reaction mixture was maintained at 140 °C for about 45 min. When it was removed from the oil bath, cooled to 100 °C, and poured slowly into N_2-saturated ice cold water (400 mL), it gave a clear brown solution. This acidic solution was made strongly basic (pH = 13) by dropwise addition of 10% NaOH. Any insoluble residues were filtered off through glass wool. The light brown clear filtrate was extracted with five 50-mL portions of dichloromethane. The dichloromethane extracts were collected, dried over anhydrous sodium sulfate, and concentrated to give the crude ligand as a viscous brown liquid. This material was dissolved in 75 mL of ethanol, and the mixture was treated with decolorizing charcoal (2 g) for 10 min in a water bath at 50 °C. Filtration yielded a pale yellow solution, which was concentrated on a rotary evaporator and dried under vacuum. The light brown oil solidified to form nearly colorless long rods (0.5 g, 50% yield) of the pure ligand.[24] Mp: 73 °C. ^1H NMR ($CDCl_3$): 3.05 (t, 5.5 Hz, 4 H), CH_2–N; 3.0 (s, br, 4 H), –SCH_2CH_2S–; 2.82 (t, 5.5 Hz, 4 H), –CH_2S–; 3.5 (br), N–*H*. ^{13}C NMR ($CDCl_3$): 47.9, CH_2–NH; 33.2, –S–CH_2–CH_2–NH; 32.8, (CH_2–S)$_2$. Mass spectral data: *m*/*e* = 163 (M^+).

$Ni^{II}(L_3)_2(ClO_4)_2$. Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

To a solution of 0.1 g (0.6 mmol) of the ligand in 15 mL of dichloromethane was added a solution of 90 mg (0.3 mmol) of nickel perchlorate hydrate in 10 mL acetonitrile and the reaction mixture refluxed for 10 min. A dark brown precipitate was formed, leaving a very pale yellow supernatant. The dark brown precipitate was filtered under suction and dried. The solid formed was dissolved in acetonitrile or water containing sodium perchlorate, and pink crystals of the complex were obtained by slow evaporation of the solvent. Yield: 80%. Anal. Calcd for $C_{12}H_{26}N_2S_4NiCl_2O_8$: C, 24.67; H, 4.45; N, 4.79; S, 21.93. Found: C, 24.93; H, 4.65; N, 4.62; S, 22.08.

Crystallography. The experimental parameters for the complex are presented in Table I. Supplementary information is provided in supplementary material Table S1. Single crystals suitable for crystallography were obtained by slow diffusion of dichloromethane into a solution of the perchlorate salt of the complex in nitromethane.[25] Crystals were mounted in glass Lindemann tubes and the unit cells and space groups determined by use of Weissenberg and precession photography, after which the crystals were transferred to a Picker four-circle diffractometer automated with a PDP 11/10 computer.

Table I. Experimental Crystallographic Data

formula	$C_{12}H_{26}N_2S_4NiCl_2O_8$
fw	583.6
space group	$P2_1/a$ (No. 14)
cell params	a = 16.607 (3) Å
	b = 8.837 (1) Å
	c = 7.465 (1) Å
	α = 90°
	β = 93.3 (2)°
V	1093.6 (2) Å^3
T	23°
Z	2 molec/cell
D_{calcd}	1.78 g/cm^3
radiation	0.710 69 Å
μ	15.5 cm^{-1}
transm factors	0.674–0.731
abs corr	by numerical integration of 8 × 8 × 16 Gaussian grid
R	0.0517
R_w	0.0591

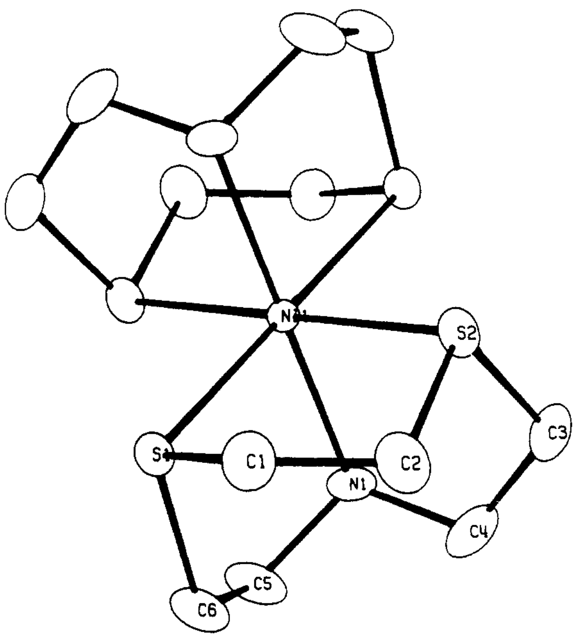

Figure 1. ORTEP diagram of the complex cation $[Ni^{II}(L_3)_2]^{2+}$ with atomic labeling for non-hydrogen atoms showing 25% thermal ellipsoids.

The unit cell was refined by using 22 pairs of reflections in the 2θ range 24–44°. The intensity measurements were obtained by scanning the $\theta/2\theta$ mode using 200 steps of 0.01° in 2θ counting for 0.25 s per step. Background counting was introduced for 25 s at the end of each scan. A set of three internal standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity observed during the collection.

The solution of the phase problem was achieved with MULTAN[26] and refined by direct methods with SHELX76.[27] The atomic scattering factors were those included in the SHELX76 program together with the Ni *f*-curve from ref 28. The program used for absorption correction was a local

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(24) Some of these crystals were found suitable for crystallography: space group *R*3 (rhomohedral, noncentrosymmetric); unit cell dimensions a = 7.758 (2) Å, b = 7.763 (1) Å, c = 7.765 (2) Å, α = 104.85 (2)°, β = 104.83 (2)°, δ = 104.78 (2)°, V_{cell} = 410.4 Å^3. However, owing to scrambling of the N and S sites, the data could not be refined to provide any meaningful structural parameters.

(25) Crystals of $[Ni^{II}(L_3)](ClO_4)_2$ obtained from acetonitrile/water media gave the following parameters: space group $P2_1/n$ (monoclinic); unit cell dimensions a = 17.607 (4) Å, b = 8.549 (2) Å, c = 7.658 (2) Å, β = 90.59 (2)°, V_{cell} = 1152.7 Å^3, D_{measd} = 1.660 g cm^{-3}, D_{calcd} = 1.658 g cm^{-3}. However, these were found to be different from and inferior in quality to those obtained from nitromethane that were used for analysis.

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Table II. Fractional Atomic Coordinates and Temperature Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ni(1)	0 (0)	50000 (0)	50000 (0)	246 (3)
Cl(1)	34729 (9)	34458 (16)	1608 (22)	573 (5)
S(1)	8698 (7)	44309 (14)	26169 (15)	381 (4)
S(2)	1682 (8)	24008 (14)	59499 (17)	429 (4)
O(1)	2767 (3)	2647 (8)	557 (10)	105 (3)
O(2)	4111 (4)	2470 (10)	298 (11)	131 (3)
O(3)	3426 (5)	4013 (14)	−1545 (15)	216 (7)
O(4)	3533 (13)	4503 (19)	1350 (32)	441 (16)
N(1)	1084 (2)	5407 (5)	6520 (6)	41 (1)
C(1)	920 (4)	2381 (7)	2715 (8)	50 (2)
C(2)	935 (4)	1657 (7)	4537 (8)	56 (2)
C(3)	776 (4)	2958 (8)	7973 (8)	62 (2)
C(4)	1386 (4)	4119 (9)	7648 (8)	61 (2)
C(5)	1700 (4)	5982 (9)	5357 (10)	61 (2)
C(6)	1823 (4)	5008 (8)	3756 (9)	59 (2)
H(1)	1047 (35)	6040 (68)	7468 (80)	49 (16)′
H(11)	1401 (36)	2120 (65)	2218 (78)	44 (14)′
H(12)	387 (38)	1896 (74)	2066 (79)	54 (16)′
H(21)	838 (4)	456 (7)	4367 (8)	66 (19)′
H(22)	1521 (4)	1849 (7)	5203 (8)	154 (42)′
H(31)	269 (82)	3472 (125)	8856 (155)	168 (46)′
H(32)	1024 (35)	2060 (74)	8632 (79)	52 (16)′
H(41)	1844 (60)	3461 (101)	7073 (132)	113 (30)′
H(42)	1769 (35)	4649 (70)	8673 (88)	54 (17)′
H(51)	2133 (45)	5736 (83)	6231 (92)	67 (19)′
H(52)	1504 (36)	6931 (77)	4835 (80)	52 (17)′
H(61)	2169 (4)	5635 (8)	2824 (9)	54 (16)′
H(62)	2153 (4)	4007 (8)	4188 (9)	271 (91)′

[a] Estimated standard deviations are given in parentheses. Coordinates × 10^n, where n = 5, 5, 4, 4, 4, 4, and 5 for Cl, S, O, N, C, H, and Ni. Temperature parameters × 10^n, where n = 4, 4, 3, 3, 3, 3, and 4 for Cl, S, O, N, C, H, and Ni. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(a_i{\cdot}a_j)$. Primed values indicate that U_{iso} is given. $T = \exp-(8\pi^2 U_{iso}(\sin^2\theta)/\lambda^2)$.

Table III. Interatomic Distances (Å)[a]

S(1)–Ni(1)	2.408 (1)	C(6)–S(1)	1.826 (6)
S(2)–Ni(1)	2.415 (1)	C(2)–S(2)	1.822 (5)
N(1)–Ni(1)	2.104 (4)	C(3)–S(2)	1.835 (7)
O(1)–Cl(1)	1.414 (5)	C(4)–N(1)	1.485 (8)
O(2)–Cl(1)	1.366 (6)	C(5)–N(1)	1.470 (8)
O(3)–Cl(1)	1.367 (8)	C(2)–C(1)	1.502 (9)
O(4)–Cl(1)	1.289 (11)	C(4)–C(3)	1.472 (11)
C(1)–S(1)	1.815 (6)	C(6)–C(5)	1.497 (9)

[a] Estimated standard deviations are given in parentheses.

modification of an existing procedure.[29] Completion and refinement of the structure was carried out by using difference electron density maps and least-squares techniques. All atoms were refined anisotropically except for hydrogen atoms, which were observed and refined isotropically. Four hydrogen atoms were eventually calculated at 1.08 Å (H_{21}, H_{22}, H_{61}, H_{62}). The refinement converged with a maximum shift/esd of 0.047 (H_{31}, 0.127) and a maximum peak of 0.80 e Å^{-3}.

Results

Synthesis of the ligand was achieved according to the reactions outlined in Scheme I. The structure (Figure 1) of the complex $[Ni^{II}([9aneNS_2]_2](ClO_4)_2$ was determined. Relevant data are provided in Tables II–IV. An analysis of the electronic spectrum of the nickel(II) complex was compared with that of similar complexes in the N_xS_y ($x + y = 3$) series (Tables V and VI). Electrochemical and chemical (BH_4^- reduction) studies provide access to Ni(III) and Ni(I) states. ESR measurements confirm these observations. Details are introduced at appropriate places in the sections that follow.

Discussion

Synthesis. The sequence of reactions involved in the synthesis of 1-aza-4,7-dithiacyclononane is shown in Scheme I. The tritosylate of diethanolamine was prepared according to the literature methods[20] and characterized by ^1H NMR spectroscopy and melting point determination. The dibromo compound **2** was prepared by nucleophilic displacement of the tosyl oxy groups from compound **1**.

Table IV. Bond Angles (deg)[a]

S(2)–Ni(1)–S(1)	87.4 (0)	C(2)–S(2)–Ni(1)	104.2 (2)
N(1)–Ni(1)–S(1)	84.4 (1)	C(3)–S(2)–Ni(1)	92.0 (2)
N(1)–Ni(1)–S(2)	85.6 (1)	C(3)–S(2)–C(2)	101.7 (3)
O(2)–Cl(1)–O(1)	108.6 (4)	C(4)–N(1)–Ni(1)	115.1 (4)
O(3)–Cl(1)–O(1)	112.0 (5)	C(5)–N(1)–Ni(1)	110.1 (4)
O(3)–Cl(1)–O(2)	107.7 (6)	C(5)–N(1)–C(4)	112.1 (5)
O(4)–Cl(1)–O(1)	104.5 (6)	C(2)–C(1)–S(1)	117.4 (4)
O(4)–Cl(1)–O(2)	112.1 (13)	C(1)–C(2)–S(2)	113.2 (4)
O(4)–Cl(1)–O(3)	112.0 (13)	C(4)–C(3)–S(2)	113.7 (4)
C(1)–S(1)–Ni(1)	101.9 (2)	C(3)–C(4)–N(1)	114.5 (5)
C(6)–S(1)–Ni(1)	98.0 (2)	C(6)–C(5)–N(1)	113.9 (5)
C(6)–S(1)–C(1)	102.9 (3)	C(5)–C(6)–S(1)	112.2 (4)

[a] Estimated standard deviations are given in parentheses.

Table V. Structural Parameters of Ni(II) Bis Complexes of Ligands L_1–L_4[a]

	L_1	L_2	L_3	L_4
Ni–N	2.102	2.108	2.104	
Ni–S		2.418	2.412	2.386
X_1–Ni–X_1				
eq–Ni–eq	82.5	80.5	87.4	88.0
ax–Ni–eq	83.1	84.8	85.0	88.7
X_1–Ni–X_2				
eq–Ni–eq	99.5	99.7	92.1	91.9
ax–Ni–eq	95.3	95.0	92.0	91.3

[a] X_1–Ni–X_1 represent angles between donors within the same ligand. X_1–Ni–X_2 represent angles between donors from the different ligands. eq–Ni–eq and ax–Ni–eq represent angles between equatorial donors and equatorial and axial donors, respectively. Bond distances are in Å units, and angles are in degrees.

Table VI. UV–Visible Data for the Ni(II) Complexes of Ligands L_1–L_4[a]

	L_1	L_2	L_3	L_4
10*Dq*	12 500 (9)	11 770	11 904 (22.5)	12 760 (27)
	20 000 (9)	19 230	19 083 (15)	18 975 (26)
	32 300 (12)		33 670 (680)	30 769 (14 000)
	11 500	10 500	9661 (12.2)	
Dq	1 235	1 177	1 193	1 276
B	993	820		680

[a] Absorption maxima, *Dq*, and *B* values are in cm^{-1}, and absorption coefficients are in mol^{-1} cm^{-1}.

The dithiol **4**, required for the cyclization reaction, was prepared by the reaction of thiourea with compound **1** or **2** to form the dithiouronium salt. Excess thiourea (3 mol equiv) and a reaction time of at least 8 h in THF or ethanol were required to obtain the thiouronium salt. Both ethanol or THF as solvents gave the same results. In ethanol, the reactants and products were highly soluble and the reaction mixture had to be concentrated. In THF, the reactants were only sparingly soluble and the product was insoluble. Hence, the product was recovered quantitatively by a simple filtration.

The dithiol **4** was obtained by hydrolyzing the thiouronium salt under basic conditions. It was found necessary to use a large excess of base under strictly anaerobic conditions during hydrolysis. Under nonideal conditions the predominant product obtained was found to be *N*-tosylthiomorpholine.[30] This, being insoluble in aqueous basic media, usually separated out as an oil under the experimental conditions (at 120 °C) and could be separated as a solid on cooling. For this reason, the reaction mixture was

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(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(29) Coppens, P.; Lieserowitz, L.; Rabinovich, D. Modified by G. W. Bushnell, University of Victoria.

(30) *N*-Tosylthiomorpholine was characterized by NMR and mass spectroscopy. Mp: 116 °C. ^1H NMR: 7.27–7.64, aromatic protons; 3.73 (t, J = 5 Hz), –CH_2–N-tosyl; 2.98 (t, J = 5 Hz), –CH_2–S; 2.44 (s), aromatic CH_3 MS: m/e = 257 (M^+).

filtered through glass wool to remove any *N*-tosylthiomorpholine before acidification of the dithiolate salt to liberate free dithiol.

Cyclization of the dithiol to the *N*-tosyl derivative of 1-aza-4,7-dithiacyclononane was carried out according to the method that Blower and Cooper[23] used in the preparation of 1,4,7-trithiacyclononane, L_4, using cesium carbonate as the base. With 1,2-dibromoethane as the substrate, the yields of the cyclized tosylate were about 60%.

The major difficulty was encountered in the deprotection of the cyclized amine. Conventional methods[31] with acid and base hydrolysis did not prove successful. With sulfuric or hydrobromic acid the cyclic tosylate was degraded completely. Reductive hydrolysis in alkaline media such as with sodium/1-butanol or transamidation with ethylenediamine-like bases also did not prove useful.

A number of methods are available for detosylation of tosylamides. However, only a few of these have been investigated in detail for the detosylation process in the presence of other sensitive functional groups.[32,33] The reductive elimination with sodium naphthalenide in DME has been utilized successfully.[32] Substrates with thiol functional groups have been found to be insensitive to sodium naphthalenide. Detosylation experiments carried out with this and the milder sodium anthracenide under a variety of conditions gave only very poor yields of L_3 in the range 0–5%.

Considering the sensitivity of C–S bonds to reducing and oxidizing reagents, phosphoric acid was used to remove the tosyl group. Reactions carried out with the commercially available (85%) phosphoric acid were ineffective. However, phosphoric acid made anhydrous by addition of appropriate amounts of phosphorus pentoxide proved to be an effective reagent, providing L_3 in about 50% yields.

Crystal Structure of $[Ni^{II}([9]aneNS_2)_2](ClO_4)_2$. The ORTEP diagram of the complex cation $[Ni(L_3)_2]^{2+}$ with atomic labeling for the non-hydrogen atoms is shown in Figure 1. The atomic coordinates are presented in Table II, bond lengths are in Table III, and bond angles are in Table IV.

The complex is overall octahedral, with the cation located on a crystallographic inversion center. Although there are several possible configurations, the expected and presumably most stable form is that observed with the secondary nitrogen ligators occupying the trans positions. The four sulfur donors and the nickel ion lie in a plane as dictated by symmetry. The Ni–N distance of 2.104 (4) Å is very similar to that in the corresponding $([9]aneN_3)_2$ complex[6] (2.10 Å) and is only slightly shorter than those in the N_2S complex[15] (2.12 Å). Such values are typical of Ni–N bonds in an octahedral complex. The Ni–S bonds are also quite similar in length to those found previously. The values (2.408 (1) and 2.415 (1) Å) are close to that (2.42 Å) found in the $[Ni(L_2)_2]^{2+}$ ion[15] but distinctly longer than in the symmetric $[Ni(L_4)_2]^{2+}$ ion (2.39 Å).[34] In the latter case, the greater distance apart of the two rings permits efficient packing around the metal center, thus providing a relatively strain free coordination.[15] However, in some ways the ligand system does show similarities intermediate between the N_3 and S_3 donors. In L_2 (N_2S) the axial donor gives rise to an ion elongated in that direction and the two nitrogen atoms with their smaller radii show an N_2–Ni–N_1 angle of 80.5°. In L_3 (NS_2) where the larger sulfur atoms are now planar, the corresponding angle, S_2–Ni–S_1, is 87.4° much closer to the 88.4° observed in the $[9]aneN_3$ system. In both cases, however, the N–Ni–S angles are remarkably similar at 84.4 and 85.6° (L_3) and 85.1° (L_2) and considerably distorted from octahedral symmetry. The distortions are of interest in that whereas it has been shown that interweaving of the N–H bonds in $[Ni(L_1)_2]^{2+}$ is sufficient to cause repulsion,[1] there are no secondary hydrogens present in the Ni plane in L_3. The essential structural parameters for the series are presented in Table V.

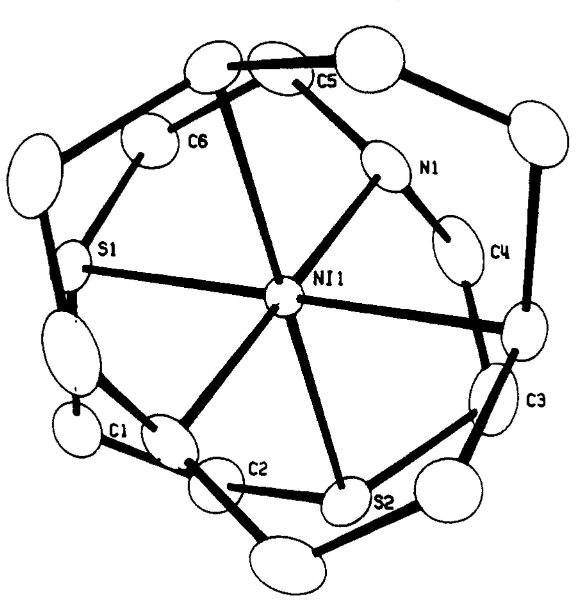

Figure 2. ORTEP diagram of the $[Ni^{II}(L_3)_2]^{2+}$ cation viewed through the trigonal axis, showing the [3,3,3] conformation adopted by the ligands.

Another important aspect of the structure is the conformation of the macrocyclic ligand in this series of complexes. Hancock et al.[17] have carried out detailed molecular mechanics calculations on these and related ions and have justified the existence of a [3,3,3] conformer in the case of the complexes of L_1 and L_4 on the basis of strain energies. (In the [3,3,3] conformation the ligand is considered to be a triangle with three sides each comprising three bonds, as indicated in Figure 2. Whereas in the Ni(II) complex of L_2 the [3,3,3] conformer arrangement is observed, the more unstable [2,3,4] system has been identified in the copper(II) complex.[16] For a complete discussion of this nomenclature, see ref 35.) The calculations predicted should L_3 be prepared, its nickel(II) complex would adopt the [3,3,3] conformation. The present work confirms this to be the case. Strain energy calculations are important in that whereas in the L_1 and L_4 systems all Ni–X bonds are of equal length, in the case of L_2 and L_3 the differences in Ni–X bond lengths causes strain in the metal to ligand bonds. In this regard L_2 and L_3 are quite similar. These features have an impact on the ligand field strength.

Although, all the bis Ni(II) complexes of ligands L_1–L_4 adopt approximately octahedral geometry, subtle variations arising from the gradual replacement of N-donors by S-donors are reflected in the gradual disappearance of the trigonal distortion observed in the case of $[Ni^{II}(L_1)_2]^{2+}$ ion. As the N-donors are replaced successively by S-donors in L_2, L_3, and L_4, the X–Ni–X bond angles (where X represents donors) vary, gradually reaching the ideal octahedral angle of 90° in the $[Ni^{II}(L_4)_2]^{2+}$ ion. This is reflected in both the internal (X_1–Ni–X_1 angle, where X_1 represent donors from only one of the two ligands in the bis complexes) and the external angles (X_1–Ni–X_2 angle, where X_1 and X_2 represent adjacent donors from the two different ligands or the interring angles) observed for the complexes of L_1–L_4. These angles are presented for comparison in Table V.

Electronic Spectroscopy. The spectrum of the complex ion $[Ni^{II}(L_3)_2]^{2+}$ shows four features as summarized in Table VI. The data for the other members of the series are also presented. Four bands are observed in the case of the complex based on L_3. Although single-crystal spectroscopic data[36] are available for the complex $[Ni^{II}(L_1)_2]^{2+}$, it is only recently that attempts have proved successful in determining accurate ligand field parameters.[37] Part of the problem lies in the fact that the spin-forbidden $^3A_{2g} \leftarrow {}^1E_g$

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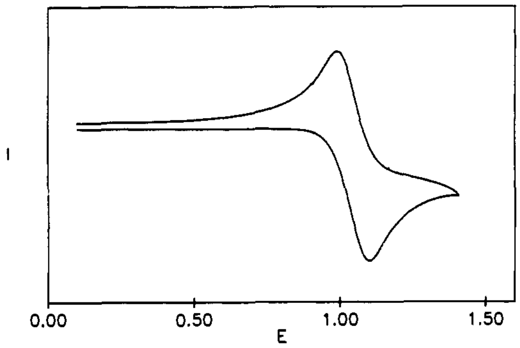

Figure 3. Cyclic voltammogram for the $Ni^{2+/3+}$ couple of the cation $[Ni^{II}(L_3)]^{2+}$ in acetonitrile containing 0.1 M TEAB. The current is in arbitrary units.

transition is observed (at $\approx$1035 nm for L_3) owing to the close approach of that transition to the anticipated $^3A_{2g} \leftarrow {}^3T_{2g}$ feature from which the ligand field parameter $10Dq$ would be determined. The situation has been resolved for the complexes where N and O are the ligating donors in the NiX_6^{2+} inner sphere. However, when second-row elements including sulfur are involved, the point of crossing of the $^3T_{2g}$ and ^1E_g levels is different. A modified equation suggested by Hancock[37] for the $[Ni^{II}(L_2)_2]^{2+}$ complex ion makes use of the equation $\nu_1 = \nu_m + 1.142\delta_m(\epsilon_1/\epsilon_2 - 1)$, where ν_1 is the "true" position of the $^3A_{2g} \leftarrow {}^3T_{2g}$ band and ν_m is the midpoint in energy of the two bands. δ_m is the separation in energy of the transitions to $^1E_g \leftarrow {}^3T_{2g}$ as observed, ϵ_1 and ϵ_2 are the extinction coefficients of the high and lower energy bands, and the factor 1.142 is derived from an analysis of Ni(II) spectra with first-row donors. As seen in Table VI, the value for Dq lies intermediate between those of the symmetrical N_3 and S_3 donor systems.

A similar approach in the case of L_3 yields a field strength parameter $10Dq = 12950$ cm^{-1}, which is considerably higher and probably unreasonable. The origin is the very large separation of energies of the two low-energy bands (2243 cm^{-1}). However, if we assume that the extent of interaction is sufficiently weak that the feature at 840 nm is in fact the true $^3A_{2g} \leftarrow {}^3T_{2g}$ absorption, then $10Dq = 11930$ cm^{-1}. The Racah parameter values, B, for the Ni(II) complexes of L_1, L_2, and L_4 have been evaluated to be 993, 820, and 680 cm^{-1}, respectively. This decrease in the interelectronic repulsion parameters is consistent with the gradual replacement of the harder secondary nitrogen donors by the softer thioether donors and the covalent nature of the Ni–S bond in these complexes. The trend indicates the B value for the complex $[Ni^{II}(L_3)_2$ should lie in between those of L_2 and L_4.

Electrochemistry. The behavior of the Ni(II) complex of L_3 was studied in acetonitrile for the $Ni^{2+/3+}$ and $Ni^{+/2+}$ couples. Cyclic voltammograms show a reversible wave (see Figure 3) for the $Ni^{2+/3+}$ couple at a potential of 1.044 V with a peak current ratio $(i_{p,a}/i_{p,c}) = 1$. A peak to peak separation (ΔE_p) of 110 mV observed for the $Ni^{2+/3+}$ couple is much higher than that expected for a reversible system. Some reorganization in the oxidized product would account for such a finding. The Ni(III) ion (d^7) is expected to exhibit Jahn–Teller distortion, and hence, the observed ΔE_p might be possibly due to axial compression of the N-donors. The one-electron oxidation process was confirmed by ESR spectroscopy of the $[Ni^{III}(L_3)_2]^{3+}$ species generated electrochemically in dry acetonitrile. The observed ESR spectrum was comparable to that of the species generated by Co^{3+} in 3 M $HClO_4$ at 10 °C, which showed features characteristic of an axial spectrum (see Figure 4) with $g_\perp = 2.121 > g_\parallel = 2.019$ and $A_\parallel = 20$ G. In dry acetonitrile, the orange-brown $[Ni^{III}(L_3)_2]^{3+}$ species generated by electrolysis was stable for several hours. However, the solution was very sensitive to moisture and the Ni(III) species decomposed to form the $[Ni^{II}(L_3)_2]^{2+}$ species. The UV–vis spectrum of the electrochemically generated $[Ni^{III}(L_3)_2]^{3+}$ shows absorption bands at 205 (1250), 222 (850), 248 (315), 297 (275), and 371 (115) nm and broad overlapping features at 435 (80) and 480 (75) nm.

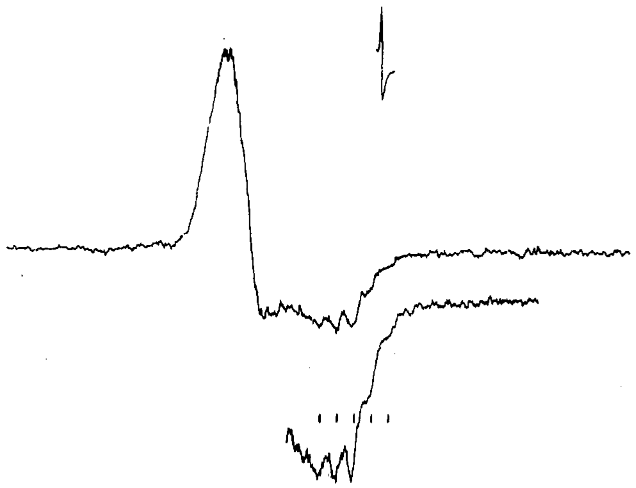

Figure 4. ESR spectrum (at 77 K) of the $[Ni^{III}(L_3)_2]^{3+}$ cation generated by Co^{3+} oxidation in 1.0 M $HClO_4$.

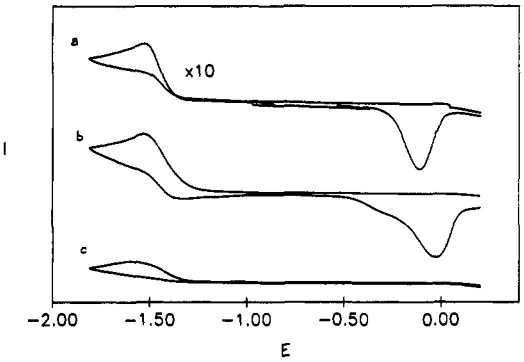

Figure 5. Cyclic voltammograms for the $Ni^{+/2+}$ couple in acetonitrile containing 0.1 M TEAB: (a) first scan; (b) after eight scans; (c) in the presence of triphenylphosphine. The current is in arbitrary units.

Cyclic voltammetric studies in acetonitrile media showed an irreversible reduction wave at a peak potential ($E_{p,c}$) of −1.52 V and an irreversible oxidation wave ($E_{p,a}$) at −0.122 V (Figure 5a) for scan rates of 5–500 mV/s. The reduced species produced at −1.52 V was found to be strongly adsorbed on the working electrode, which is evident from the shape of the oxidation peak. However, this adsorbed species was reoxidized only partially during the reverse scan. As a result of this quasi-reversibility, the surface characteristics of the electrode changed with successive scans, resulting in the growth of a shoulder peak (see Figure 5b) at slightly more negative potential. The characteristics of the reduction peak did not change significantly. However, it was shifted to more negative potentials by about 20 mV. Thus, the reduced species generated at −1.52 V was not expected to be sufficiently stable for coulometric evaluation of the number of electrons involved in the process. However, in a constant-potential electrolysis experiment, a solution of the complex cation $[Ni^{II}(L_3)_2]^{2+}$ in 0.1 M TEAB in acetonitrile was electrolyzed at −1.52 V to identify the formation of any ESR-active Ni(I) species. Well before the plateau current was reached, the light brown solution species formed initially and deposited a black material on the working electrode, and as a result, no plateau current was generated. Samples drawn at any stage during the electrolysis showed no evidence of an ESR-active species. On the time scale of this experiment, the black material deposited initially on the platinum working electrode appeared similar to that observed in the cyclic voltammetric experiment. However, eventually this material was found to be converted into metallic nickel. Thus, in the absence of coulometric data it is not possible to predict the number of electrons involved in the reduction process.

However, the large separation between the reduction and oxidation peak suggests a distinct rearrangement in the structure of the complex. One possible explanation considered initially was the octahedral to tetrahedral rearrangement of the ligands in which the four sulfurs in the NiS_4 plane rearrange to occupy the vertices of a tetrahedron with the N-donors dissociating from the coordination sphere. The absence of any ESR-active Ni(I) species ruled out such a possibility. The other possible process could involve dimerization of a species of type $[Ni^I(L_3)]^+$ formed by removal of one of the ligands. Under such circumstances, the dimeric $[Ni^I(L_3)]_2$ species would be ESR inactive.[38,39] Hence, the absence of a Ni(I) species cannot be ruled out.

The possibilities of trapping any of the species, based on $[Ni^I(L_3)]^+$, were investigated. Addition of triphenylphosphine to the electrolyte solution caused the oxidation wave at 0.122 V to disappear (see Figure 5c), and the reduction wave was shifted further to −1.60 V. Also, in the presence of triphenylphosphine no black material was deposited on the working electrode during the reduction scan. Instead, an electrochemically nonoxidizable yellow material was deposited on the electrode that gradually retarded the observation of any electrochemical process. However, this material may be oxidized by air.

Cyclic voltammetric studies of electrochemically generated nickel(II) perchlorate in the presence of various ligands has been investigated extensively.[40,41] In these studies, the relative stabilization of the various oxidation states of nickel was shown to be dependent upon the nature of the coordination environment around nickel. Comparison of these studies with the behavior observed in the case of the $[Ni^{II}(L_3)_2]^{2+}$ system suggests that the black material initially observed on the working Pt electrode (in absence of triphenylphosphine) during the reduction scan could not be metallic nickel.

Reduction with Sodium Borohydride. Both electrochemically and chemically generated Ni(I) species are known to function as catalysts in many organic synthesis[42,43] and in the study of processes such as reduction of carbon dioxide.[44] The most widely used and well-documented reducing agents for the in situ generation of Ni(I) species are the borohydrides. Holah et al.[39,45,46] have investigated the redox process involving both octahedral nickel(II) amine complexes and nickel(II) phosphine complexes. The nature of the product isolated was shown to be dependent upon the ligand to metal ratio, amount and type of borohydride used, and the nature of the amine or phosphine ligands. Sodium borohydride (solid or aqueous solution) was used to reduce the $[Ni^{II}(L_3)_2]^{2+}$ ion, both in the presence and absence of triphenylphosphine.

Reduction in Aqueous Solutions. Reduction of $[Ni(L_3)_2]^{2+}$ in deoxygenated water with sodium borohydride yielded brownish yellow solutions similar to that obtained during bulk electrolysis. These solutions were found to be stable for short periods of time but, on prolonged standing, deposited black nickel powder. However, if purged with oxygen immediately, the brown reduced species was reoxidized to the starting nickel(II) complex. These reduced species did not show any ESR activity and hence was presumed to be dimeric Ni(I) species of the type described by Holah et al.[39] These authors also have shown that octahedral Ni(II) complexes such as $[Ni^{II}(phen)_3]^{2+}$ and $[Ni^{II}(bpy)_3]^{2+}$ are reduced by borohydrides with the dissociation of a bidentate ligand to form square-pyramidal and square-planar complexes of Ni(I). Analogous processes can be visualized in the case of $[Ni^{II}(L_3)_2]^{2+}$ forming species of the type $[Ni^I(L_3)]$ which yielded a diamagnetic dimeric species.

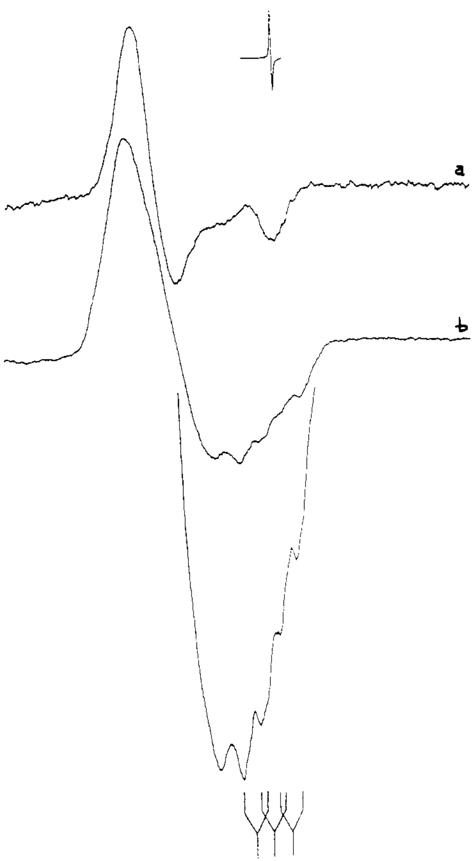

Figure 6. ESR spectrum of the Ni(I) cation generated by sodium borohydride reduction of $[Ni^{II}(L_3)_2]^{2+}$ (a) in acetonitrile and (b) in acetonitrile in the presence of phosphine.

Reduction in Acetonitrile. Mixed coordination environments can effectively stabilize Ni(I) species against disproportionation, and under such circumstances monomeric Ni(I) species have been isolated.[41] Reduction of $[Ni(L_3)_2]^{2+}$ by solid sodium borohydride in acetonitrile under an inert atmosphere yielded yellow solutions that were ESR active and stable in absence of oxygen. In presence of oxygen, such solutions decolorized, with the resulting species not the original complex, $[Ni(L_3)_2]^{2+}$. However, the colorless oxidized species (ESR inactive) was rereducible to the ESR-active yellow species. The ESR spectrum of the yellow species showed three broad components at $g = 2.230$, 2.080, and 2.006, consistent with an anisotropic environment around the Ni(I) center (see Figure 6a). This clearly suggests the formation of Ni(I) species during the reduction process.

Even though the ESR spectrum (in Figure 6a) of the Ni(I) species prepared in acetonitrile showed more resemblance to an axial type spectrum, no hyperfine coupling was observed. However, addition of triphenylphosphine (solid or a solution in acetonitrile) caused a change in the ESR spectrum (see Figure 6b). This spectrum (in Figure 6b) showed a broad unsymmetrical g component at 2.227 with another feature at $g = 2.025$ displaying hyperfine coupling. These features can be attributed to the g_{xx}, g_{yy}, and g_{zz} components of an anisotropic Ni(I) center. The observed hyperfine coupling pattern shows dissymmetries consistent with the coupling of a single nitrogen and a phosphorus donor. The nitrogen nucleus ($I = 1$) gives rise to a triplet pattern that is further split by a phosphorus ($I = {}^1/_2$) to form triplets of doublets. The hyperfine coupling constants were estimated to be 63.5 and 47.5 G, respectively. Considering the π-bonding and soft nature of phosphorus, the larger value of 63.5 G can be assigned to coupling to that center, with the 47.5 G constant assigned to nitrogen coupling. The geometry around the Ni(I) center, is probably tetrahedral with two sulfurs and one nitrogen from the ligand L_3 and one phosphorus from a triphenylphosphine.

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This species can be prepared directly by addition of solid (or a solution of) sodium borohydride to a solution of $[Ni^{II}(L_3)_2]^{2+}$ and excess triphenylphosphine in acetonitrile.

The formation of Ni(I) species in acetonitrile media was enhanced by the presence of moisture by which the solubility of sodium borohydride was promoted. However, it decreased the solubility of triphenylphosphine and also the stability of the Ni(I) species. In order to enhance both the solubility of reagents and stability of the Ni(I) species, a mixture of acetonitrile and water (9:1) was used.

The necessity of triphenylphosphine or an acetonitrile-like solvent for the isolation of a monomeric Ni(I) species and the formation of a different Ni(II) species on aerial oxidation of the Ni(I) species is consistent with the possible displacement of one of the L_3 ligands from $[Ni(L_3)_2]^{2+}$ cation with the substitution of a monodentate ligand like triphenylphosphine or acetonitrile. Formulation of such a species is consistent with the formation of a $[Ni^{I}(L_3)]^{+}$ species during electrochemical reduction.

The UV-visible and near-IR spectrum of the Ni(I) species obtained both in the absence and in the presence of triphenylphosphine showed similar characteristics. In the presence of triphenylphosphine, two bands at 400 (ϵ = 2500 mol^{-1} cm^{-1}) and 370 nm (ϵ = 2700 mol^{-1} cm^{-1}) and a broad weak band around 1380 nm (ϵ = 30 mol^{-1} cm^{-1}) were observed. The two bands observed in the UV-visible region can be assigned to the charge-transfer transitions. Similar bands were observed in square-pyramidal Ni(I) species, as in the case of carbonyl-substituted Ni(I) cyclam.[44] The weak band observed in the near-IR region is typical of tetrahedral Ni(I) species.[41,46] These observations do not provide any definite conclusion about the geometry of the solution species. However, they suggest that the tetrahedral species predominantly observed at 77 K in the ESR experiments could undergo further substitution by phosphine ligands at high temperatures leading to either a trigonal-pyramidal or square-pyramidal Ni(I) species of type $[Ni^{I}(NS_2)(P)_2]$. Stabilization of such five-coordinate species might be possible with smaller phosphines like trimethylphosphine. Further studies with various phosphines (of different steric hindrance or cone angle) and variable-temperature UV-visible or ESR spectroscopy will provide information on the structural aspects of these solution species. On the basis of electrochemical studies,[41] proper balance of σ- and π-donors has been proposed as essential for the stabilization of Ni(I) against disproportionation to Ni(II) and Ni(0). The electrochemical and chemical behavior combined with the spectroscopic properties of the species described here provide strong evidence for the presence of a Ni(I) species in mixed coordination environment.

The data presented relate to neutral (thioether) donors. There is evidence[19] that anionic sulfur centers are more feasible in decreasing the redox potential of the $Ni^{2+/3+}$ couple to values close to those found in hydrogenases. Current work underway is directed toward studies involving the open chain analogue of L_3 (detosylated form of compound **4** in Scheme I).

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Supplementary Material Available: Tables S1-S4, containing anisotropic temperature parameters, interatomic distances for hydrogen atoms, hydrogen atom bond angles, and selected interatomic distances (5 pages); Table S5, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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Novel Cu_6O_{15} "Bowls" in Seven New Barium Copper Oxides: $M_6Ba_{46}Cu_{24}O_{84}$ (M = Al, Si, Ti, Fe, Ga, Ge, Zr)

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Large single crystals of a nonstoichiometric oxide with nominal formula $Al_6Ba_{46}Cu_{24}O_{84}$ (per unit cell) were grown by slow cooling of a mixture of alumina and cupric oxide in a barium hydroxide-barium chloride flux. Single-crystal X-ray methods revealed hexagonal Laue symmetry with unit cell dimensions a = 13.1524 (11) Å and c = 17.3122 (15) Å. The structure was refined in the space group $P6_3mc$ to an R value of 1.8%. This compound has a novel layered structure, and all the copper atoms are in unique bowl-shaped rings of composition Cu_6O_{15}. The crystals are shiny, black, hexagonal plates, and resistance measurements show that the compound is semiconducting. Magnetic measurements indicate that the bowls exhibit a spin $^3/_2$ ground state. $Si_6Ba_{46}Cu_{24}O_{84}$, $Ti_6Ba_{46}Cu_{24}O_{84}$, $Fe_6Ba_{46}Cu_{24}O_{84}$, $Ga_6Ba_{46}Cu_{24}O_{84}$, $Ge_6Ba_{46}Cu_{24}O_{84}$, and $Zr_6Ba_{46}Cu_{24}O_{84}$ were prepared by similar methods and found to be isomorphous.

Introduction

The recent discovery of superconductivity in copper oxide based materials[1] has stimulated interest in the synthesis and characterization of new cuprates. In particular, the barium-copper-oxide system is extremely interesting and has a very rich and complex chemistry. Several barium copper oxide phases have been known for some time,[2] but the traditional synthetic method of mixing, grinding, and firing the component oxides yields only a limited number of compounds. We have found that reacting the oxides in a flux consisting of molten barium hydroxide can lead to new barium copper oxides.[3,4] In this paper, we present the synthesis, crystal structure, and properties of one of these new compounds, $Al_6Ba_{46}Cu_{24}O_{84}$. This formula reflects the nominal composition, given 100% occupation of all atomic sites. However, the compound is nonstoichiometric, with many sites showing significant deviations from full occupancy.

Previous work in this laboratory has shown that molten alkali-metal and alkaline-earth-metal hydroxides are superior fluxes for the synthesis of copper oxides.[3-5] In particular, barium hydroxide can be used to synthesize barium copper oxides by using the flux as the source of barium. Cupric oxide dissolves readily

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