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Syntheses and Reactivity of Nickel Complexes of 8-Aza-1,5-dithiacyclodecane and the Macrobicyclic Ligand 1,2-Bis(8-aza-1,5-dithia-8-cyclodecanyl)ethane

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The syntheses of the mixed donor macrocycle 8-aza-1,5-dithiacyclodecane ([10]-aneS$_2$N = **4**) and the macrobicycle 1,2-bis(8-aza-1,5-dithia-8-cyclodecanyl)ethane ("ear-muff" = **5**) are discussed. Perchlorate salts of [Ni(**4**)$_2$]$^{2+}$ and [Ni(**5**)]$^{2+}$ have been isolated and examined using X-ray crystallography. Refinement for the monoclinic complex [Ni(**4**)$_2$](ClO$_4$)$_2$·2CH$_3$CN, (space group $P2_1/n$, No. 14) (a = 9.566 (1), b = 22.037 (2), c = 14.603 (2) Å; β = 106.90 (1)°) converged at R = 0.0668 (R_w = 0.0783) for 334 parameters using 3132 reflections with $I > 3\sigma(I)$. The complex ion is a tetragonally compressed octahedron with Ni–S = 2.407 (2) Å and Ni–N = 2.125 (5) Å. For the complex [Ni(**5**)](ClO$_4$)$_2$·2CH$_3$CN, (space group $C2/c$, No. 15) (a = 18.483 (2), b = 11.395 (2), c = 15.505 (3) Å; β = 111.65 (1)°) refinement converged at R = 0.0583 (R_w = 0.0666) for 174 parameters using 2042 reflections with $I > 3\sigma(I)$. Although the ion is octahedral, there is distortion induced by the bridge linking the two macrocycles. Both chemical and electrochemical oxidation of the complex ions result in the formation of the corresponding Ni(III) complex ions. It is of interest that electron spin resonance observations are consistent with low-spin d^7 Ni(III) centers in a tetragonally compressed state for both the [Ni(**4**)$_2$]$^{3+}$ ion and the [Ni(**5**)]$^{3+}$ species with $g_\parallel > g_\perp$. Electrochemical features of the two ions are also discussed.

Introduction

Recently there have been extensive investigations made on the transition-metal complexes of homoleptic macrocycles containing N donor atoms.[1-3] Bis complexes of 1,4,7-triazacyclononane ([9]-aneN$_3$, **1**) have been obtained with Fe,[4] Co,[5] Ni,[6] Pd,[7] Ru,[8] and Pt[9] ions in various oxidation states. The steric demands of the ligand render it stable toward ligand dissociation and facilitate oxidation of the metal center. Thus stable [M([9]-aneN$_3$)$_2$]$^{3+}$ octahedral complexes have been obtained, e.g., M = Ni,[6] Pd,[10] and Ru.[8] These complexes serve as one-electron outer-sphere reagents in electron transfer reactions and the rates of self-exchange have been obtained for a variety of [M([9]-aneN$_3$)$_2$]$^{3+/2+}$ couples.
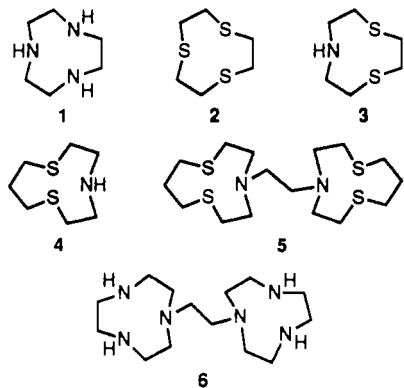
Thioether ligands can serve as π-donors via donation of the available lone pair or as π-acceptors using empty d-orbitals on sulfur. The π-donor capability of the S atoms is manifested in the stabilization of the Pd(III)[11] and Pt(III)[12] complexes of 1,4,7-trithiacyclononane ([9]-aneS$_3$, **2**)[12] the Nb(V) complex of

[14]-aneS$_4$,[13] and the Mo(IV) ion of [16]-aneS$_4$.[14] By incorporation of both hard and soft donor atoms in the macrocycle, the stabilization of both low and high oxidation states in the transition-metal complex ions might be achieved. However, such a mixed donor environment may induce distortion of the geometry at the metal centers. Nickel enzymes have been identified in certain methanogenic bacteria where mixed donor coordination environments around the central metal atom are thought to be present.[15]

The synthesis and reactivity of the nine-membered ligand 7-aza-1,4-dithiacyclononane ([9]-aneS$_2$N, **3**) and its nickel complex have been studied recently.[16a] An independent report on this ligand has also been made,[16b] and complexes of the related bis-(1-thia-4,7-diazacyclononane) species[16c] have been prepared. There has been no investigation to date on the mixed donor ten-membered macrocycles. The lower symmetry of these ten-membered ligands offers new stereochemical characteristics that are not present in the more symmetrical analogues. Hence the synthesis and study of the reactivity of the hitherto unknown ligand, 1-aza-4,8-dithiacyclodecane ([10]-aneS$_2$N, **4**) and its Ni(II) complex were undertaken. In addition, coupling of the nitrogen centers by use of an ethane bridge has permitted the synthesis of the hexadentate macrobicyclic "ear-muff" ligand, 1,2-bis(8-aza-1,5-dithia-8-cyclodecanyl)ethane (**5**). The synthesis and characterization of this ligand and its Ni(II) complex are reported. Wieghardt et al.[17] have synthesised Cr, Mn, Fe, Co, and Ni complexes of the ligand 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (**6**, dtne). Only recently was crystallographic evidence obtained for the formation of a mononuclear Fe octahedral complex, [Fe(dtne)]Br$_3$·4H$_2$O.[18]

Experimental Section

Materials and Methods. All chemicals were of reagent grade except where otherwise indicated. Infrared spectra were obtained as KBr disks or as neat samples on NaCl plates with a Perkin-Elmer 283 grating spectrometer. ^{1}H NMR spectra were measured on a 90-MHz Perkin-Elmer R32 spectrometer. High-field ^{1}H NMR and ^{13}C NMR spectra were obtained with a Brüker WM250 instrument or a Brüker 360 in-

(1) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.
(2) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *25*, 329.
(3) Bhula, R.; Osvath, P.; Weatherburn, D. C. *Coord. Chem. Rev.* **1988**, *91*, 89.
(4) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953.
(5) Küppers, H.-J.; Neves, A.; Pomp, C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.
(6) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1938.
(7) Hunter, G.; McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 2634.
(8) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 2582.
(9) Wieghardt, K.; Köppen, M.; Swirdoff, W.; Weiss, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1869.
(10) McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 3090.
(11) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 987.

(12) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Lavery, A. J.; Odulate, M. O.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 118.
(13) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 942.
(14) Cragel, J.; Petts, V. B.; Glick, M. D.; DeSimone, R. E. *Inorg. Chem.* **1978**, *17*, 2885.
(15) Cammack, R. *Nickel in Metalloproteins*; Advances in Inorganic Chemistry; Sykes, A. G., Ed.; Academic Press, Inc.: New York, Vol. 32, 1988.
(16) (a) McAuley, A.; Subramanian, S. *Inorg. Chem.* **1990**, *29*, 2830. (b) Parker, D.; Craig, A. S.; Ferguson, G.; Lough, A. *Polyhedron* **1989**, *8*, 2951. (c) Heinzel, U.; Mattes, R. *Polyhedron* **1991**, *10*, 19.
(17) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.
(18) Geilenkirchen, A.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1989**, *44B*, 1333.

Scheme I. Synthetic Route to Ligands 4 and 5
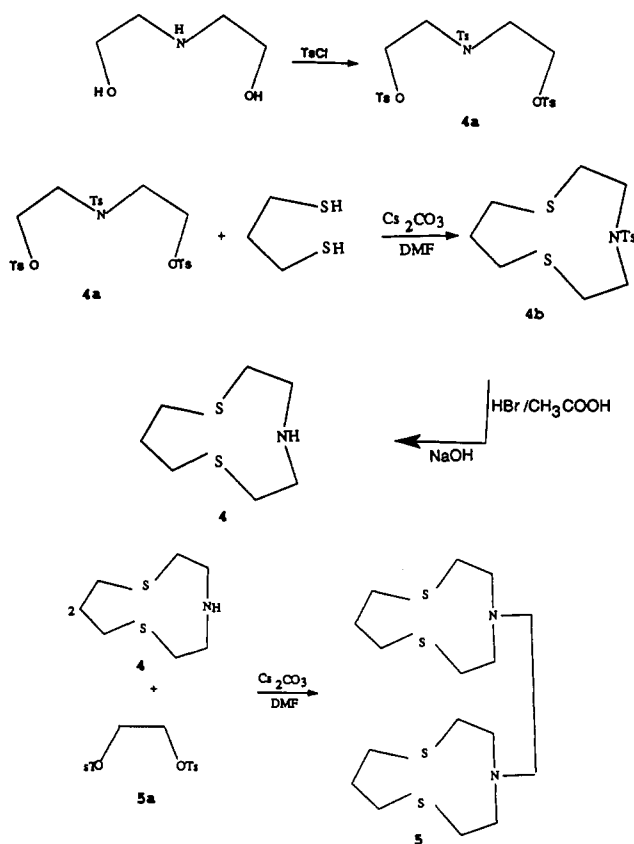
strument. All chemical shifts are reported relative to tetramethylsilane. Electronic spectra were recorded on a Philips PU 8740 or a Cary-5 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were obtained with a Varian E6S spectrometer. Diphenylpicrylhydrazyl radical (dpph) was used as a field marker (g = 2.0037). Mass spectra were recorded in a Finnegan 330GC-MS instrument by electron impact or methane or isobutane chemical ionization. Elemental analyses were performed by Microanalytical Services, Vancouver, BC, Canada. Electrochemical measurements were recorded with a Princeton Applied Research Model 273 potentiostat–galvanostat, interfaced with an IBM/PC. Cyclic voltammograms were run using the Headstart program (Princeton). The electrochemical cell employed the standard three-electrode configuration with a Pt working electrode, a Pt auxiliary electrode, and the reference electrode. A Ag/AgNO₃ (0.1 M) electrode was used as the reference in nonaqueous systems containing 0.1 M NEt₄BF₄. Blank electrolyte solutions were scanned before each experiment and in each instance the ferrocenium/ferrocene couple (Fc⁺/Fc) was used as an external standard to calibrate the reference electrode, $E_{1/2}$(Fc⁺/Fc) = 0.15 V vs Ag⁺/Ag. Acetonitrile was distilled over CaH₂ prior to use for electrochemical purposes.

Synthesis. The ligands **4** and **5** were synthesized according to the routes outlined in Scheme I. The compounds β,β'-[(p-tolylsulfonyl)imino]bis(ethyl p-toluenesulfonate) (NTs(CH₂CH₂OTs)₂, **4a**) and the ditosylate of 1,2-ethanediol (**5a**) were synthesized as described previously.[19,20]

8-(p-Tolylsulfonyl)-8-aza-1,5-dithiacyclodecane A dry, 5-L, three-necked, round-bottom flask was equipped with a 500-mL addition funnel, a reflux condenser, and a mechanical stirrer with a 7-cm Teflon blade. The entire system was kept under a positive pressure of dry nitrogen. The flask was charged with 2.2 L of DMF and 13.04 g (40 mmol) of cesium carbonate (oven-dried at 150 °C overnight). The mixture was stirred vigorously and heated to 55–60 °C. A solution was prepared containing a mixture of 1,3-propanedithiol (4.32 g, 40 mmol) and **4a** (22.7 g, 40 mmol) in 600 mL of DMF. Half of this mixture was added through the addition funnel over an 8-h period. The reaction mixture was then charged with a second portion of 13.04 g (40 mmol) of cesium carbonate and the second half of the solution mixture was added (8 h). The solution was stirred at 60 °C for a further 6 h and then filtered. The filtrate was reduced to a small volume (100 mL), after which the resultant solution

(19) Searle, G. H.; Geue, R. J. *Aust. J. Chem.* **1984**, *37*, 959.
(20) Atkins, T. J. *Org. Synth.* **1978**, *58*, 86.

was added dropwise to a vigorously stirred mixture (2 L) of ice/water. The colorless solid obtained was filtered off and dried under vacuum. The solid was recrystallized from boiling ethanol to give colorless crystals of the monotosylate. Yield: 8.6 g, 65%. Mp: 138 °C. ¹H NMR: δ 1.88 (p, 2 H, C–CH₂–C), 2.40 (s, 3 H, –CH₃), 3.06 (m, 4 H, –CH₂–N), 3.15 (m, 8 H, –CH₂–S), 7.24–7.67 (m, 4 Ar). ¹³C NMR: δ 21.5 (1 C, CH₃), 29.5 (1 C, C–C–C), 31.3 (2 C, C–C–C), 33.8 (2 C, CH₂–S), 53.2 (2 C, CH₂–N), 127.7 and 129.7 (2 C + 2 C, Ar), 133.8 and 143.7 (1 C + 1 C, Ar). MS(CI): 332 (M + 1), 360 (M + 29), 372 (M + 44).

8-Aza-1,5-dithiacyclodecane (4). The cyclized tosylate **4b** (2.6 g, (7.9 mmol) was added to a solution of 30% HBr in acetic acid (30 mL) containing phenol (3.0 g) and the mixture was stirred at 70 °C for 30 h. The solution was cooled to room temperature and added dropwise to a stirred mixture of ether/ethanol (300 mL, 5:1 (v/v)) cooled in an ice bath. A colorless solid (the ligand hydrobromide salt, **4c**) was obtained which was filtered off and washed with ether and dried under vacuum. Yield: 1.2 g, 59%. ¹H NMR: δ 1.73 (m, 2 H, C–CH₂–C), 2.85–2.95 (m, 8 H, CH₂–S), 3.42–3.47 (m, 4 H, CH₂–N). ¹³C NMR: δ 25.6 (1 C, C–C–C), 29.8 (2 C, C–C–C), 30.7 (2 C, CH₂–S), 46.0 (2 C, CH₂–N). Anal. Calcd for C₇H₁₅S₂N·HBr·H₂O: C, 30.41; H, 5.84; N, 5.07. Found: C, 30.15; H, 5.81; N, 5.04.

The hydrobromide salt **4c** (1.1 g, 4.3 mmol) was dissolved in water and made basic (pH ~13) with concentrated NaOH solution. This was continuously extracted with CHCl₃ overnight. The CHCl₃ layer was dried over anhydrous Na₂SO₄ and evaporated to dryness, leaving behind the free ligand, **4**, as a colorless sticky solid. Yield: 0.7 g, 93%. ¹H NMR: δ 1.63 (p 2 H, C–CH₂–C), 2.55 (t, 4 H, CH₂–N), 2.83 (t, 8 H, CH₂–S–CH₂), 3.68 (s, 1 H, –NH). ¹³C NMR: δ 28.4 (1 C, C–C–C), 29.7 (2 C, C–C–C), 33.6 (2 C, CH₂–S), 48.7 (2 C, CH₂–N). MS(CI): 178 (M + 1), 206 (M + 1), 218 (M + 41).

CAUTION. Complexes involving perchlorates are potentially hazardous and subject to explosion. Extreme caution must be exercised in using these compounds.

[Ni(4)₂](ClO₄)₂. An ethanolic solution (20 mL) of Ni(ClO₄)₂·6H₂O (280 mg, 0.77 mmol) was added dropwise to an ethanolic solution (50 mL) of the ligand **4** (300 mg, 1.7 mmol). The solution was refluxed for 1 h. The red-purple solid obtained was dried under vacuum. Yield: 0.312 g, 51%. Anal. Calcd for NiC₁₄H₃₀S₄N₂Cl₂O₈: C, 27.46; H, 4.93; N, 4.57. Found: C, 27.49; H, 4.69; N, 4.66%.

Diffusion of ether into acetonitrile solutions of the solid yielded violet crystals (suitable for X-ray diffraction studies) which were filtered, washed with small amounts of ethanol and ether, and dried under vacuum.

1,2-Bis(8-aza-1,5-dithia-4-cyclodecanyl)ethane (5). To a mechanically stirred suspension of Cs₂CO₃ (4.89 g, 15 mmol) in fresh N,N'-dimethylformamide (75 mL) was added a solution of the ligand **4** (1.77 g, 0.01 mol) in 25 mL of DMF. The mixture was stirred vigorously at 80 °C for 4 h, after which a solution of 1,2-ethanediol ditosylate (**5a**) (2.96 g, 8 mmol) in 50 mL of DMF was added over a period of 1 h. The mixture was stirred for another 24 h at 100 °C. The DMF solution was filtered and the mixture taken to dryness on a rotary evaporator. The residue was dissolved in distilled dichloromethane (100 mL) and the CH₂Cl₂ layer was washed with saturated Na₂CO₃ solution and then thrice with water (200 mL). The CH₂Cl₂ layer was dried over anhydrous Na₂SO₄ and then taken to dryness leaving behind the free ligand **5** as a pale yellow oil. Crude yield: 1 g, 53%.

Additional resonances were obtained in the ¹H and ¹³C NMR and were attributed to the presence of 8-10% of the starting material. The crude ligand (1 g, 2.6 mmol) was dissolved in ethanol (50 mL) and its Ni(II) complex prepared. An aqueous solution of the crude Ni(II) complex was loaded on to a C-25 Sephadex column. The violet band that was eluted with 0.05 M NaClO₄ was evaporated to dryness and dissolved in 25 mL of ethanol. After the sodium perchlorate residue was filtered, the ethanolic solution was taken to dryness yielding the Ni complex of **5** as a purple solid. Yield, 0.77 g, 51%.

This Ni(II) complex of **5** (500 mg) was dissolved in water (200 mL) and heated to reflux, and a solution of NaCN (1 g, 20 mmol) in water (200 mL) was added slowly. The solution became turbid and a colorless solid separated out. The solution was refluxed for 4 h at which point it turned to a pale yellow color. The colorless solid obtained after filtration was washed with water (20 mL) and dissolved in dichloromethane. The CH₂Cl₂ layer was dried with anhydrous Na₂SO₄ and then evaporated to dryness yielding the pure ligand as a colorless solid which was further dried under vacuum. Yield: 0.13 g, 40%. Anal. Calcd for C₁₆H₃₂S₄N₂·CH₂Cl₂: C, 46.38; H, 7.36; N, 6.01. Found: C, 46.16; H, 7.37; N, 6.35. ¹H NMR: δ 1.86 (p, 4 H, C–CH₂–C), 2.63 (s, 4 H, N–CH₂–CH₂–N), 2.67 (m, 8 H, S–CH₂–C–CH₂–S), 2.74 (m, 8 H, S–CH₂–CH₂–N), 3.14 (t, 8 H, S–CH₂–CH₂–N). ¹³C NMR: δ 30.3 (2 C, C–C–C), 30.8 (4 C, S–C–C–C–S), 33.2 (4 C, S–C–C–N), 52.0 (2 C, N–C–C–N), 57.1 (4 C, S–C–C–N).

Table I. Experimental Crystallographic Data

formula	$NiS_4N_2C_{18}H_{36}Cl_2O_8$	$NiS_4N_4C_{20}H_{38}Cl_2O_8$
mol wt	693.9	719.9
space group	$P2_1/n$	$C2/c$
cell dimensions		
a, Å	9.566 (1)	18.483 (2)
b, Å	22.037 (2)	11.395 (2)
c, Å	14.603 (2)	15.505 (3)
$\alpha = \gamma$, deg	90	90
β, deg	106.90 (1)	111.65 (1)
V, Å^3	2945.45	3035.1
Z	4	8
T, K	296	296
D_{calcd}, g/cm^3	1.566	1.566 (measd 1.576)
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ, cm^{-1}	10.87	10.56
R^a	0.0668	0.0583
R_w^b	0.0783	0.0666
w	$6.94/(\sigma^2 F + 0.001F^2)$	$0.75/(\sigma^2 F + 0.001F^2)$

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

[Ni(5)](ClO$_4$)$_2$·2CH$_3$CN. The ligand 5 (500 mg, 1.3 mmol) was dissolved in 50 mL of ethanol and the solution was heated to 40 °C. A solution of Ni(ClO$_4$)$_2$·6H$_2$O (293 mg, 2.7 mmol) in 20 mL of EtOH was added dropwise to the ethanolic solution of the ligand and the mixture was refluxed for 1 h. The purple crystals which formed were filtered, dissolved in a minimum quantity of water, and loaded on to a C-25 Sephadex column. A violet and a green band separated upon using 0.05 M NaClO$_4$. The violet band was taken to dryness and dissolved in a minimum quantity of ethanol. Sodium perchlorate crystals were filtered off and purple crystals of [Ni(5)](ClO$_4$)$_2$·2CH$_3$CN were obtained by slow evaporation of the ethanolic solution of the complex. These were filtered off and washed with small amounts of ethanol and ether and dried under vacuum. Diffraction quality crystals were grown by diffusion of ether into acetonitrile solutions of the complex. Yield: 0.57 g, 60%. IR: −NH band at 3280 cm^{-1} absent. Anal. Calcd for NiC$_{20}$H$_{38}$S$_4$N$_4$Cl$_2$O$_8$: C, 32.87; H, 5.25; N, 7.67. Found: C, 32.74; H, 5.17; N, 7.40.

Crystallography. Experimental parameters for both complexes are listed in Table I. Supplementary data are provided in Tables S1 and S2. The purple crystals were mounted in a glass Lindemann tubes and the unit cells and space groups determined using Weissenberg and precession photography, after which the crystals were mounted and centered on a Nonius CAD4 diffractometer. Intensity measurements were carried out with Zr-filtered Mo radiation, λ = 0.71069 Å. Background counting was introduced at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity observed during the collection for both the complexes.

[Ni(4)$_2$](ClO$_4$)$_2$·2CH$_3$CN. The cell was refined using 25 centered reflections in the range θ = 22–43°. The solution of the phase problem was achieved using MULTAN[21] which revealed the position of the Ni atom. Subsequent Fourier syntheses revealed the positions of the carbon and nitrogen atoms. Hydrogen atoms were not included in the calculations. The atomic scattering factors used were those included in the SHELX76 program together with the Ni f curves from the international tables.[22,23] Absorption corrections were made using the EMPABS (Nonius) program. The completion of the structure and the refinement were carried out by difference electron density maps and the method of least squares. In the final cycles of full-matrix least-squares refinement all non-hydrogen atoms were refined with anisotropic thermal parameters. The asymmetric unit consisted of the complex cation, two perchlorate anions, and two molecules of acetonitrile as solvent of crystallization. Data reduction yielded 3132 reflections with $I > 3\sigma(I)$, which were used for solution and refinement of the structure. Refinement converged with a maximum shift/estimated standard deviation of 0.050 on the final cycle, R = 0.0668 and R_w = 0.0783, and a maximum peak of 0.18 e Å^{-3}.

Ni(5)(ClO$_4$)$_2$·2CH$_3$CN. A deep purple crystal of the Ni complex obtained by slow evaporation of acetonitrile solutions was sealed in a Lindemann tube to prevent loss of acetonitrile. This was mounted and centered on a Nonius CAD4 diffractometer. Intensity measurements were made with Mo radiation, λ = 0.71069 Å. The cell was refined by using 25 centered reflections in the range 2θ = 30–49°. The total number of reflections measured was 2540, but this reduced to 2042 independent

measurements after suppression, $I > 3\sigma(I)$.

The solution of the phase problem was solved by direct methods using SHELX76.[24] The atomic scattering factors, together with the Ni f curves were taken from ref 25. Absorption corrections were made as indicated previously. Completion and refinement of the structure were achieved by difference electron density maps and by least-squares minimization. The asymmetric unit consisted of half a molecule, one perchlorate anion and one acetonitrile molecule, as solvent of crystallization. Hydrogen atoms were not included in the calculations. All non-hydrogen atoms were refined using anisotropic thermal vibration parameters. The refinement converged to R = 0.0583 and R_w = 0.0666 with a maximum shift/estimated standard deviation of 0.010 on the final cycle. A final difference map had a maximum peak of 0.1 e Å^{-3}.

Results and Discussion

Syntheses. The ligands 4 and 5 were synthesized in good yields. During the preparation of 4, care was taken to ensure that both the diol groups were tosylated in the tritosylate of diethanolamine, **4a.** The cyclization with 1,3-propanedithiol (Scheme I) was carried out using Cs$_2$CO$_3$ as a base according to the method of Buter and Kellogg.[24] Several methods were attempted for the detosylation of the cyclized aminetosylate (**4b**). When sulfuric acid was used, the cyclized tosylate degraded completely. Reductive elimination with sodium naphthalenide in DME[25] was not successful and yields were extremely poor (0–5%). Detosylation of the corresponding nine-membered tosylate ([9]-aneS$_2$NTs) was carried out using anhydrous phosphoric acid.[16] In the present case, overall yields of about 25% of the free ligand, 4, were obtained with this reagent. Reduction with lithium aluminum hydride in THF[26] proved to be mild, but the detosylation was not complete even after a 4-day reaction period. One of the most frequently used reagents for the cleavage of sufonamides is hydrobromic acid in a mildly acidic organic solvent containing phenol.[27,28] Detosylation was carried out using 30% HBr in CH$_3$COOH containing phenol where yields of 55–60% of the free ligand were obtained. The end point of the detosylation was confirmed by periodically testing the solubilities of the reaction mixture in 1 M NaOH.

Reaction of the ligand 4 with TsOCH$_2$CH$_2$OTs in 2:1 ratio yielded the macrobicyclic species 5. The purity of the ligand and the yield depended on the quality of the starting ligand, [10]-aneS$_2$NH. The coupling reaction was carried out in the presence of cesium carbonate as base in DMF solution, with slow addition of the ditosylate of 1,2-ethanediol. Vigorous mechanical stirring proved vital to the formation of the product and completion of the reaction. The crude product was used as produced for complexation with Ni(ClO$_4$)$_2$. The resulting impure Ni(II) complex was purified on a Sephadex (C-25) column. Decomplexation of this Ni(II) complex with NaCN in aqueous solutions precipitated the pure ligand 5. This material was used for subsequent preparations of the Ni(II) complex.

The five-line ^{13}C NMR spectrum (supplementary material) is characteristic of the ligand with five inequivalent carbon atoms. In the ^{1}H NMR spectrum, the C–CH$_2$–C quintet of the propylene linkage is seen at 1.86 ppm (4 H). The singlet at 2.63 ppm (4 H) is due to the N–CH$_2$ protons of the ethylene linkage. The S–CH$_2$ protons are coupled and appear as a complicated multiplet centered at 2.71 ppm (16 H). A triplet further downfield at 3.14 ppm (8 H) is attributed to the protons of the macrocyclic ring attached to the electronegative N atom.

Crystal Structure of [Ni(4)$_2$](ClO$_4$)$_2$·2CH$_3$CN. The ORTEP diagram of the complex cation [Ni([10]-aneS$_2$NH)$_2$]$^{2+}$ with atomic labeling is shown in Figure 1. Fractional atomic coordinates and isotropic temperature parameters are shown in Table II. The interatomic bond lengths and bond angles around the metal ion are shown in Table III. Complete bond lengths and bond angles are provided in Supplementary Tables S3 and S4, respectively.

(21) Main, P. *MULTAN*; University of York: York, U.K., 1978.
(22) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Refinement*; University of Cambridge: Cambridge, U.K., 1974.
(23) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
(24) Buter, J.; Kellogg, M. *Org. Synth.* **1987**, *65*, 150.
(25) Ji, S.; Gortler, L. B.; Waring, A.; Battisti, A.; Bank, S.; Closson, W. D.; Wriede, P. *J. Am. Chem. Soc.* **1967**, *89*, 5371.
(26) Searles, S.; Nukina, S. *Chem. Rev.* **1959**, *59*, 1077.
(27) Snyder, H. R.; Heckert, R. E. *J. Am. Chem. Soc.* **1952**, *74*, 2006.
(28) Haskell, B. E.; Bowlus, S. B. *J. Org. Chem.* **1976**, *41*, 159.

Table II. Fractional Atomic Coordinates and Temperature Parameters for $[Ni(4)_2](ClO_4)_2 \cdot 2CH_3CN$

atom	x/a	y/b	z/c	U_{eq}, $\mathring{A}^2$
Ni(1)	19 600 (9)	25 949 (4)	51 507 (6)	372 (4)
Cl(1)	24 422 (23)	40 127 (10)	-3 660 (17)	590 (9)
Cl(2)	15 403 (23)	8 896 (10)	8 070 (16)	587 (9)
S(1)	12 215 (21)	34 714 (9)	41 403 (13)	454 (7)
S(2)	25 016 (24)	31 447 (10)	66 374 (14)	539 (8)
S(3)	26 667 (22)	17 115 (10)	61 514 (14)	481 (8)
S(4)	13 830 (22)	20 582 (10)	36 480 (14)	503 (8)
O(1)	3 317 (10)	4 471 (4)	-524 (11)	161 (7)
O(2)	1 192 (13)	4 191 (5)	-233 (12)	200 (9)
O(3)	2 018 (31)	3 729 (11)	-1 188 (15)	395 (22)
O(4)	3 033 (16)	3 563 (7)	136 (20)	297 (16)
O(5)	2 660 (9)	679 (4)	496 (8)	125 (5)
O(6)	838 (10)	407 (4)	1 082 (8)	129 (5)
O(7)	570 (15)	1 223 (6)	60 (11)	188 (8)
O(8)	2 025 (21)	1 284 (7)	1 532 (10)	258 (12)
N(1)	-237 (7)	2 585 (3)	5 201 (5)	48 (2)
N(2)	4 158 (7)	2 585 (3)	5 103 (5)	50 (3)
N(3)	-908 (11)	4 706 (5)	2 654 (7)	93 (4)
N(4)	-208 (28)	1 679 (9)	7 712 (20)	263 (18)
C(1)	1 837 (11)	4 190 (4)	4 731 (7)	70 (4)
C(2)	1 618 (11)	4 298 (4)	5 722 (7)	75 (4)
C(3)	2 679 (10)	3 975 (4)	6 555 (7)	69 (4)
C(4)	782 (13)	3 008 (7)	6 853 (9)	111 (6)
C(5)	-452 (11)	2 863 (8)	6 047 (7)	111 (6)
C(6)	-1 229 (9)	2 868 (5)	4 342 (7)	72 (4)
C(7)	-726 (8)	3 464 (4)	4 047 (7)	61 (4)
C(8)	1 931 (10)	1 016 (4)	5 539 (7)	66 (4)
C(9)	2 135 (11)	890 (4)	4 546 (7)	69 (4)
C(10)	1 145 (10)	1 241 (4)	3 714 (6)	65 (4)
C(11)	3 108 (12)	2 181 (6)	3 432 (8)	100 (6)
C(12)	4 333 (11)	2 278 (7)	4 242 (7)	98 (6)
C(13)	4 150 (9)	2 310 (4)	5 977 (6)	58 (3)
C(14)	4 597 (9)	1 693 (4)	6 224 (7)	64 (4)
C(15)	40 (12)	4 823 (5)	2 340 (7)	69 (4)
C(16)	1 189 (15)	4 959 (7)	1 918 (11)	120 (7)
C(17)	-8 (20)	1 140 (11)	7 658 (12)	144 (10)
C(18)	417 (15)	535 (6)	7 666 (11)	108 (6)

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

Table III. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[Ni(4)_2]^{2+}$ Ion

S(1)–Ni	2.408 (2)	S(3)–Ni	2.410 (2)
S(2)–Ni	2.407 (2)	S(4)–Ni	2.411 (2)
N(1)–Ni	2.125 (5)	N(2)–Ni	2.124 (6)
S(2)–Ni–S(1)	95.6 (1)	S(3)–Ni–S(1)	179.2 (1)
S(3)–Ni–S(2)	84.9 (1)	S(4)–Ni–S(1)	83.5 (1)
S(4)–Ni–S(2)	178.9 (1)	S(4)–Ni–S(3)	96.0 (1)

The complex consists of four S donor and two N atoms from the two ten-membered ligands coordinated to the central Ni atom in an octahedral fashion. The two trimethylene bridges are trans to one another as are the N atoms. The bond lengths and the bond angles for various ten-membered macrocyclic complexes are compared in Table IV. The Ni–N distance (2.125 (6) Å) is comparable to the corresponding $[Ni(7)_2]^{2+}$ ion (7 = 1,4,7-triazacyclodecane) (2.12 (2) Å)[29] and slightly shorter than the $[Ni(8)_2]^{2+}$ complex (2.142 (5) Å)[30,31] (8 = 1,5-diaza-8-thiacyclodecane). The Ni–S bonds (2.408 (2) Å) are also similar to those observed in the Ni(II) complexes of 8 (2.395 (1) Å) and 9 (2.395 (9) Å) (9 = 1,4,7-trithiacyclodecane).[30,31] Thus the $[Ni(4)_2]^{2+}$ ion exhibits characteristics intermediate between those
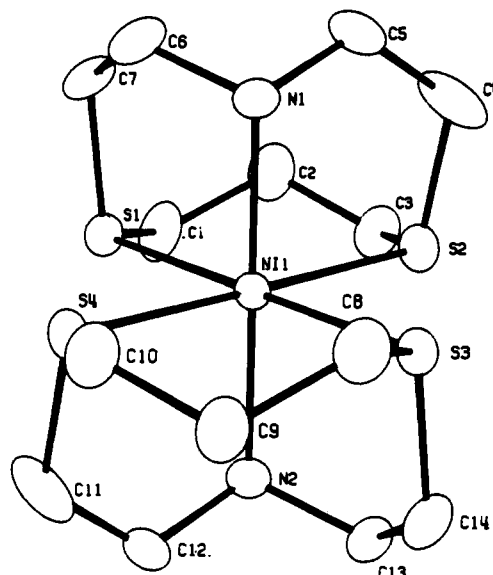
Figure 1. ORTEP diagram of $[Ni(4)_2]^{2+}$ cation with 25% thermal ellipsoids.

Table IV. Comparison of Bond Lengths (Å) and Bond Angles (Deg) in Ni(II) Complexes of Ten-Membered Macrocycles[f]

	7^a	8^b	4^c	9^b
Ni–N	2.123	2.142	2.125	
Ni–S		2.395	2.408	2.395
N–Ni–N[d]	86.6	87.1		
S–Ni–S[d]			95.8	94.1
S–Ni–N[e]		85.5	85.4	
N–Ni–N[e]	82.4			
S–Ni–S[e]				89.1

^a Reference 29. ^b Reference 31. ^c Present work. ^d Six-membered chelate bite angle. ^e Five-membered chelate bite angle. ^f Key: 7 = [10]-aneN$_3$, 8 = [10]-aneN$_2$S, 4 = [10]-aneS$_2$N, 9 = [10]-aneS$_3$.

of $[Ni(7)_2]^{2+}$ and $[Ni(9)_2]^{2+}$ ions. As the N atoms are replaced by the S donor atoms, the bite angle for the five-membered chelate ring increases toward the ideal octahedral angle of 90° in the $[Ni(9)_2]^{2+}$ ion. In the Ni complex of 4, the angle in the six-membered chelate ring S_1–Ni–S_2 (95.8 (2)°) is significantly larger than for N_1–Ni–N_2 angle of the $[Ni(8)_2]^{2+}$ complex (87.1 (2)°), consistent with the larger S atoms. In the $[Ni(9)_2]^{2+}$ ion the six-membered chelate bite angle, S_1–Ni–S_2 has been shown to be 94.1 (1)°,[31] smaller than that in the complex $[Ni(4)_2]^{2+}$ under study. In the present case the axially-compressed nitrogen atoms force the equatorial sulfur atoms further apart giving rise to a larger equatorial S_1–Ni–S_2 six-membered chelate bite angle. The S–Ni–N intraligand angles for both the Ni complexes of 4 and 8 compare well at 85.5 (1)° and 85.4 (8)°, respectively. The Ni complex of the corresponding nine-membered ligand [9]-aneS$_2$N (3) shows an S–Ni–S equatorial angle of 87.4 (0)° which is closer to that observed in the [9]-aneS$_3$ system, 88.0°. The larger ten-membered ring in the present case allows for the axial N atoms to reach over and better occupy the apical position. However, for the $[Ni(3)_2]^{2+}$ complex ion the N donor atoms in the smaller ring are unable to occupy this site completely.

There are four conformational possibilities for the ten-membered ligand in which all the ligating atoms are endodentate, facilitating facial coordination of the ligand. The various conformations have been discussed previously.[32,33] The conformation of the ten-membered ring, 4, in its nickel complex is the [2233] conformation with the six-membered chelate ring in the chair form.

Crystal Structure of $[Ni(5)](ClO_4)_2 \cdot 2CH_3CN$. The Ni complex was found to be monoclinic and crystallized in the space group

(29) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263.
(30) Chandrasekhar, S.; McAuley, A. Presented at the 72nd Canadian Chemical Conference and Exhibition, Victoria, B.C., June 1989.
(31) Chandrasekhar, S. Ph.D. Dissertation, University of Victoria, Victoria, BC, Canada, 1991.

(32) Hancock, R. D.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1987**, *133*, 221.
(33) Setzer, W. N.; Cacioppo, E. L.; Guo, Q.; Grant, G. J.; Kim, D. D.; Hubbard, J. L.; VanDerveer, D. G. *Inorg. Chem.* **1990**, *29*, 2672.

Table V. Fractional Atomic Coordinates and Temperature Parameters for $[Ni(5)](ClO_4)_2 \cdot CH_3CN^a$

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ni(1)	0 (0)	12 478 (8)	25 000 (0)	249 (4)
Cl(1)	38 655 (9)	12 068 (15)	38 116 (12)	447 (6)
S(1)	9 970 (9)	−310 (14)	34 593 (11)	364 (6)
S(2)	3 776 (8)	12 175 (14)	11 658 (10)	363 (6)
O(1)	3 494 (6)	127 (7)	3 868 (9)	156 (7)
O(2)	3 308 (4)	2 081 (6)	3 665 (6)	102 (4)
O(3)	4 138 (5)	1 103 (10)	3 099 (6)	143 (5)
O(4)	4 485 (4)	1 362 (9)	4 640 (6)	145 (5)
N(1)	838 (3)	2 595 (4)	2 987 (3)	32 (2)
C(1)	1 548 (4)	−850 (7)	2 883 (5)	54 (3)
C(2)	1 725 (4)	−230 (7)	2 113 (5)	49 (3)
C(3)	1 018 (4)	−45 (7)	1 226 (5)	49 (3)
C(4)	1 012 (4)	2 489 (6)	1 427 (4)	44 (2)
C(5)	1 377 (4)	2 745 (6)	2 471 (4)	41 (2)
C(6)	1 335 (3)	2 329 (6)	3 984 (4)	41 (2)
C(7)	1 689 (4)	1 125 (6)	4 108 (4)	42 (2)
C(8)	372 (4)	3 685 (5)	2 944 (5)	43 (3)
C(9)	3 127 (5)	1 312 (7)	745 (6)	62 (4)
C(10)	3 913 (4)	1 600 (7)	850 (6)	59 (3)
N(2)	2 504 (5)	1 094 (9)	658 (7)	106 (5)

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

**Table VI.** Selected Bond Lengths (Å) and Bond Angles (Deg) for $[Ni(5)](ClO_4)_2 \cdot 2CH_3CN$

Ni–S(1)	2.389 (2)	Ni–S(2)	2.415 (2)
Ni–N(1)	2.112 (5)		
S(2)–Ni–S(1)	97.1 (1)	N(1)–Ni–S(2)	84.9 (1)
N(1)–Ni–S(1)	85.7 (1)	S(1)–Ni–S(1)	104.8 (1)
N(1)–Ni–N(1)	86.8 (3)		

$C2/c$. In this centrosymmetric space group the Ni atom is in a special position (Wyckoff type e) of multiplicity 4 and site symmetry 2. The asymmetric unit is made up of half a molecule and is repeated by a 2-fold symmetry axis to form the molecule. The molecule lacks an inversion center (no $\bar{1}$ symmetry) and the coordinates of the second half of the molecule are obtained not by $\bar{1}$ symmetry but by transposing x, y, z to $-x$, y, $0.5 - z$.

Details are provided in Table I and the fractional atomic coordinates of the complex are given in Table V. The ORTEP diagram of the complex together with the atomic labeling scheme is shown in Figure 2, where only the atoms of the asymmetric unit are labeled. Selected bond lengths and angles for the complex are shown in Table VI with additional material in supplementary tables. The Ni–N bond length of 2.112 Å is comparable to the normal Ni–N bond length (2.12 Å) expected for high-spin Ni(II).[34] The mean Ni–S bond length is also as expected (2.40 (2) Å). The constraint imposed by the ligand requires the N atoms to be cis to each other. In the centrosymmetric space group related by the "c" glide plane, the crystals obtained are racemic, so that both the Λ and Δ configurations are present in equal numbers. The two six-membered chelate rings are cis to each other and adopt a Λ configuration in the crystal structure obtained.

The bond angle subtended at the Ni(II) ion by the two S atoms linked by a propyl group is 97.1°, whereas the five-membered chelate bite angles of the macrocyclic rings are 84.9° and 85.7°. Although the Ni(II) ion is octahedral in geometry there is a severe distortion induced by the bridge linking the two macrocycles. This strain is reflected in the trans S–Ni–N angles which average to 164°. However, the presence of the six-membered chelate ring allows the ten-membered ring to expand and the S atoms encapsulate the metal ion making the trans S–Ni–S angles 178°. Thus the twist between the two ten-membered macrocyclic rings
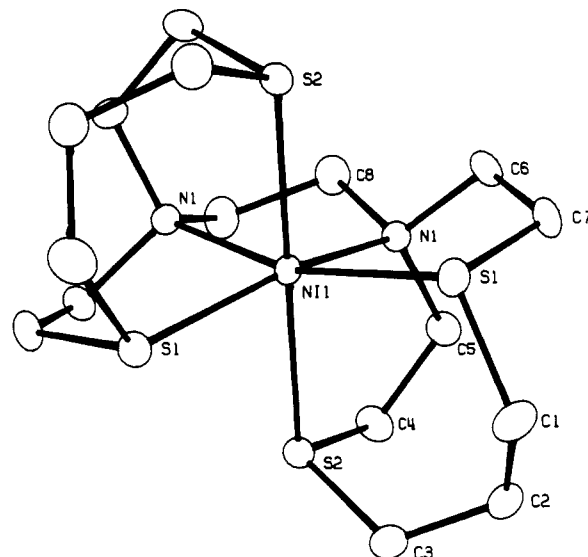
Figure 2. ORTEP diagram of $[Ni(5)]^{2+}$ cation with 25% thermal ellipsoids.
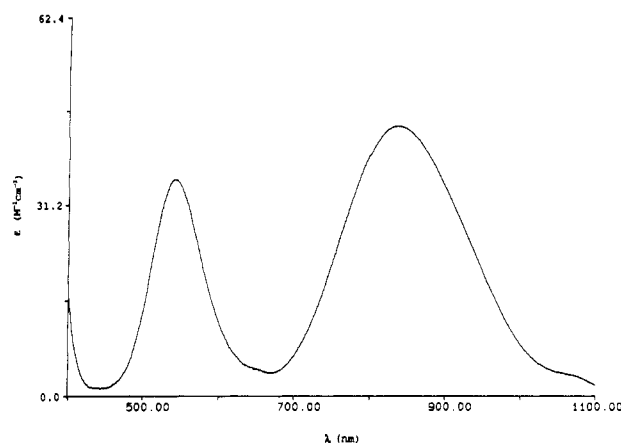
Figure 3. UV–vis spectrum of the $[Ni(5)]^{2+}$ ion.

imposed by the ethylene bridge was found to be 20°. The conformation of the ligand in the complex is [1324].[33] Since the Ni(II) ion is d^8 high spin, one cannot distinguish between the axial and the equatorial ligating atoms based on the Ni(II) crystal structure.

Electronic Spectra. Details of the electronic spectra of the Ni complexes are provided in Table VII. The absorption spectra for the other members of the ten-membered series and similar examples are also shown in this table. For the complex [Ni-$(4)_2](ClO_4)_2$ three bands are observed in the region 400–900 nm. The complex absorbs strongly below 400 nm which is attributed to charge transfer bands. The band at 843 nm reflects the d–d transition $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1). The ligand field strength, $10Dq$, obtained from this transition is 11 844 cm^{-1}. The absorption at 526 nm is due to the $^3T_{1g} \leftarrow {}^3A_{2g}$ transition (ν_2). The absorption spectrum of Ni(5)$^{2+}$ complex shows two spin-allowed transitions at 836 nm ($\epsilon = 43$ M^{-1} cm^{-1}) and 540 nm ($\epsilon = 37$ M^{-1} cm^{-1}) due to $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transitions respectively, Figure 3. The occurrence and similarity of these transitions with analogous complexes are consistent with the presence of an octahedral NiS$_4$N$_2$ core. The ligand field strength $10Dq$ has been evaluated from the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition to be 11 962 cm^{-1}. The Racah parameter, B, for the Ni(II) complex of **4** has been found to be 784 cm^{-1} from the following equation:[35]

$$B = \frac{(2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)}{15\nu_2 - 27\nu_1} = 784 \text{ cm}^{-1} \qquad (1)$$

(34) Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum Press: New York, 1979; p 228.

(35) Cooper, S. R.; Rawle, S. C.; Hartman, J. R.; Hintsa, E. J.; Adams, G. A. *Inorg. Chem.* **1988**, 27, 1209.

Table VII. Electronic Spectra and Ligand Field Parameters

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$10Dq$, cm^{-1}	B,^{a} cm^{-1}	β, cm^{-1}	ref
$[Ni(4)_2]^{2+}$	843 (10), 526 (14), 418 (25)	11 844	778	0.75	PW^b
$[Ni(5)]^{2+}$	836 (44), 540 (37), 318 (4412)	11 962	784	0.76	PW
	270 (3145), 191 (5356)				
$[Ni(7)_2]^{2+}$	870 (sh), 800, 513, 327	12 500	937	0.90	29
$[Ni(8)_2]^{2+}$	960 (sh), 863 (14), 529 (14), 343 (27)	11 588	882	0.85	31
$[Ni(9)_2]^{2+}$	850 (sh), 800 (37), 530 (66)	12 500	717	0.69	31
$[Ni(3)_2]^{2+}$	840 (23), 524 (15), 297 (680)	11 930			16
$[Ni(6)_2]^{2+}$	917 (31), 848 (31), 516 (18), 363 (16)				17
$[Ni(4)_2]^{3+}$	558 (44), 393 (49), 336 (57), 228, 192 (995)				PW
$[Ni(5)]^{3+}$	548 (2011), 394 (3369), 323 (2987)				PW
	274 (2118), 204				
$[Ni(6)_2]^{3+}$	1020 (12), 623 (62), 311 (9000)				17

$^a B_{\text{free ion}} = 1038$ cm^{-1}.^{43} ^{b}PW = present work.

The values of $10Dq$ and the Racah parameter B (784 cm^{-1}) are intermediate between the homoleptic N_3 ligands and homoleptic S_3 ligands.

Replacing the harder donors with softer S donor atoms allows for delocalization of the t_{2g} electron density into the empty low lying ligand orbitals. Such delocalization reduces electron–electron repulsions. Thus, the thioethers exhibit a greater nephelauxetic effect compared to the aza donor atoms. This is manifested in the values of the Racah parameter, B, for the Ni complexes of 9, 8, and 7 (Table VII). In the case of $[Ni(4)_2]^{2+}$ ion, the $^3\Pi(P) \leftarrow {}^3A_2$ transition is obscured by charge transfer bands. Since B is very sensitive to the $^3\Pi(F) \leftarrow {}^3A_2$ transition,^{36} it has been assumed that the B value for $[Ni(4)_2]^{2+}$ ion is similar to that of $[Ni(5)]^{2+}$ ion with the same NiS_4N_2 core (784 cm^{-1}). This fits in the order of B values [10]-aneN$_3$ > [10]-aneSN$_2$ > [10]-aneS$_2$N > [10]-aneS$_3$.

The ligand field strengths for the Ni complexes of ten-membered series first decrease upon replacing one N atom with an S and then increases as more N atoms are replaced. This is in keeping with the lack of strain in the homoleptic S_3 and N_3 ligand systems (larger ligand field strength) which is present in the mixed donor complexes (smaller ligand field strength). The molar absorption coefficients of the $^3T_{2g} \leftarrow {}^3A_{2g}$ bands are significantly larger than the corresponding Ni([10]-aneS$_2$NH)$_2^{2+}$ and Ni([9]-aneS$_2$NH)$_2^{2+}$ ions and are comparable to that of the Ni([10]-aneS$_3$)$_2^{2+}$ ion, Table VII. This can be attributed to both the presence of tertiary amine donor atoms and a severe distortion of the NiS_4N_2 core. The ethylene bridge linking the two macrocyclic units enforces a twist of the two rings with respect to each other. Large molar absorption coefficients have been noted for the homoleptic macrobicyclic ligand, dtne (6),^{17} compared to the $[Ni(1)]^{2+}$ ion consistent with the twist of the two nine-membered rings. Unusually high extinction coefficients have also been noted for Co(daptacn)$^{3+}$ where the trigonal twist angle calculated from its structural parameters was found to be 11.1°.^{37}

Redox Studies. Oxidation of $[Ni(4)_2]^{2+}$ complex in aqueous medium (with Co^{3+} or $S_2O_8^{2-}$) or in nonaqueous medium (NO$^+$/CH$_3$CN) yielded a red species of $[Ni(4)_2]^{3+}$ complex cation. In dry deaerated CH$_3$CN, the Ni(III) complex cation is stable for about 2 h. The solution is extremely sensitive to moisture and decomposes to the Ni(II) complex cation. The $[Ni(4)_2]^{3+}$ complex cation shows an interesting electron spin resonance (ESR) spectrum characteristic of a tetragonally compressed octahedral geometry, with $g_\parallel = 2.127$ and $g_\perp = 2.061$, Figure 4a. For this low-spin d^7 metal ion, the unpaired electron is located primarily in the $d_{x^2-y^2}$ orbital as illustrated by the spectrum, the reverse of that normally observed for Ni(III) (i.e., $g_\parallel < g_\perp$). Coupling to the axial N atoms ($I = 1$) through the metal orbital is not discernible. This may be due to a smaller coupling constant. In contrast, the $[Ni([9]-aneS_2N)_2]^{3+}$ complex cation shows an axially elongated spectrum with $g_\parallel$ (2.019) < $g_\perp$ (2.121).^{16} Also in that
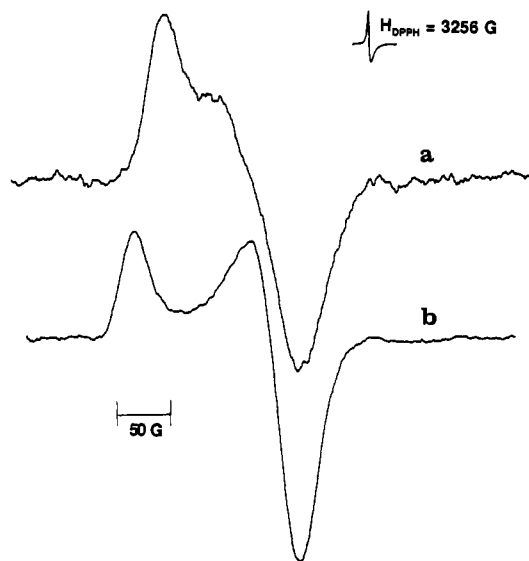
Figure 4. (a) ESR spectrum of $[Ni(4)_2]^{3+}$ ion in CH$_3$CN at 77 K. (b) ESR spectrum of $[Ni(5)]^{3+}$ ion in CH$_3$CN at 77 K.

case the $g_\parallel$ feature shows hyperfine interaction with the N atoms ($I = 1$). Static or dynamic disorder in the equatorial bonds may lead to an elongated coordination. This phenomenon of a "planar dynamics" of "antiferrodistortive order of elongated octahedra" is known to occur in low-spin d^7 cations with an E_g ground state.^{38} Another example of an octahedral complex exhibiting this behavior is $[Ni(bpy)_3](ClO_4)_3 \cdot 2CH_3CN \cdot 0.5CH_2Cl_2$ with two short axial Ni–N bond lengths of 1.92 Å and four long Ni–N bond lengths of 2.01 Å. On the basis of this structure it was concluded that the single unpaired electron was in the $d_{x^2-y^2}$ orbital, consistent with axial compression.^{39} However, EPR spectra of its frozen solutions at 77 K showed $g_\parallel$ (2.02) < $g_\perp$ (2.13), indicative of a d_{z^2} ground state. The present study shows that for the nine- and ten-membered rings with the same ligating atoms, the axial distortion is significantly different. Since no hyperfine interaction with the N atoms was observed, the possibility of two axial S atoms in a compressed octahedral coordination cannot be ruled out.

Oxidation of $[Ni(5)]^{2+}$ in aqueous medium using Co^{3+}, $S_2O_8^{2-}$, or NO$^+$ in CH$_3$CN solutions yielded a red ESR-active species due to the formation of a low-spin d^7 octahedral $[Ni(5)]^{3+}$ complex cation. Frozen solutions of the red Ni(III) complex species at 77 K showed an anisotropic EPR spectrum with $g_\parallel = 2.148$ and $g_\perp = 2.063$, Figure 4b. This spectrum with $g_\parallel > g_\perp > g_e$ is again consistent with a compressed octahedron having a $d_{x^2-y^2}$ ground state. The ethylene bridge linking the two N atoms forces a cis geometry. Such an inverted spectrum characteristic of a compressed octahedral species is found among other cis complexes

(36) Hart, S. M.; Boeyens, J. C. A.; Michael, J. P.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1601.

(37) Taylor, S. G.; Snow, M. R.; Hambley, T. W. *Aust. J. Chem.* **1983**, *36*, 2359.

(38) Wieghardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650.

(39) Brodovitch, J.-C.; Haines, R. I.; McAuley, A. *Can. J. Chem.* **1981**, *59*, 1610.

Table VIII. Formal Redox Potentials (V) for Ni Complexes

complex	$E_{1/2}$, V (vs Fc$^+$/Fc)	ΔE, mV	$E_{1/2}$, V (vs NHE)	ref
[Ni(5)]$^{3+/2+\,a}$	0.90	90	1.30	PW^b
[Ni(4)$_2$]$^{3+/2+\,a}$	0.86	114	1.26	PW
[Ni(1)$_2$]$^{3+/2+}$		75	0.95	4
[Ni(6)]$^{3+/2+}$		85	1.10	17
[Ni(3)$_2$]$^{3+/2+}$	0.88	110	1.28	16

^{a} In CH$_3$CN (0.1 M NEt$_4$BF$_4$), ref electrode Ag/AgNO$_3$ (0.1 M). ^{b} PW = present work.

viz., [Ni([12]-aneN$_4$)(CH$_3$CN)$_2$]$^{3+}$ cation.[40] A similar spectrum has been obtained for frozen solutions of the ion [Ni$_2$^{III}(maptacn)$_2$(μ-oxalato)]$^{4+}$ in acetonitrile[41] (maptacn = 1-(aminopropyl)-1,4,7-triazacyclononane).

The g value is a function of the spin–orbit coupling constant ζ and the ligand-field splitting 10Dq. For a compressed octahedron with a d$_{x^2-y^2}$ ground state, the g tensor is given by[42]

$$g_\parallel = g_e + 8\mu + 2\mu' \tag{2}$$

$$g_\perp = g_e + 2\mu + 2\mu' \tag{3}$$

where $\mu = (1/2)\zeta[1.38/E_3 + 0.62/E_4]$ and $\mu' = \zeta^2/\delta^2$ and δ is the energy separation between the low-spin ground state ($^2A_{1g}$) and the first excited high-spin state (split level of the octahedral $^4T_{1g}$ parent state) and E_3 and E_4 are the transitions from $^2A_{1g}$ to the octahedral $_a^2T_{2g}$ and $_b^2T_{2g}$ parent states. For the species [Ni(5)$^{3+}$], substituting the g values in eqs 2 and 3, μ and μ' were calculated to be 0.0142 and 0.0162, respectively. From the above equations, a high-spin to low-spin separation of 3001 cm^{-1} and ζ = 382 cm^{-1} were obtained, taking E_3 = 25 381 cm^{-1} and E_4 = 36 497 cm^{-1}. The covalency parameter, K, was determined from[43]

$$\zeta = K^2\zeta_c \quad (\zeta_c = 705 \text{ cm}^{-1} \text{ for the free ion})$$

to be 0.7. For the [Ni(4)$_2$]$^{3+}$ ion, using the values of $g_\parallel$ = 2.127, $g_\perp$ = 2.061, E_3 = 25 445 cm^{-1}, and E_4 = 29 761 cm^{-1}, the values of δ and ζ were found to be 2202 and 293 cm^{-1} respectively. A value of 0.7 was obtained for the covalency parameter (K). The covalency parameters obtained for both the Ni(III) complexes under study are lower than that of the [Ni(1)$_2$]$^{3+}$ ion (K = 0.8)[38] consistent with the greater degree of covalency in the M–S bond (greater delocalization in the present mixed donor complexes) compared to the M–N bond in the homoleptic aza complex.

Electrochemistry. Formal redox potentials for the Ni(II) complexes of **4**, **5**, and related complexes are summarized in Table VIII. Cyclic voltammograms of complex [Ni(4)$_2$](ClO$_4$)$_2$ in acetonitrile showed an oxidation wave at $E_{1/2}$ = 1.01 V vs Ag$^+$/Ag^0 due to the [Ni(4)]$_2$$^{3+/2+}$ couple. (ΔE = 114 mV.) At lower potentials an irreversible reduction wave due to Ni(I)

complex cation formation is seen at E_{pc} = 0.306 V (E_{pc} = cathodic peak) which is related to an irreversible oxidation wave at E_{pa} = –0.188 V (E_{pa} = anodic peak) observable at scan rates of 100 mV/s. The reduced species is not sufficiently stable for coulometric evaluation of the number of electrons in the process. The large separation between the reduction and the oxidation peaks is suggestive of a rearrangement in the structure of the complex. Ni(I) being d^9 probably prefers a tetrahedral geometry.

The $E_{1/2}$ value for the [Ni(5)]$^{3+/2+}$ couple was found to be 1.05 V vs Ag$^+$/Ag electrode (1.30 V vs NHE) and is only marginally larger than the corresponding value for the [Ni(6)]$^{3+/2+}$ couple. The π-acceptor properties of the S atoms destabilize Ni(III) with respect to Ni(II), which results in the higher redox potential for the former complex. Although the replacement of a secondary amine with a tertiary amine donor is expected to destabilize the Ni(III) state, the redox potential for the [Ni(5)]$^{3+/2+}$ couple is comparable to that of the Ni–bis complex of **4**, indicating the ligand constraint imposed by the ethylene bridge in the macrobicyclic ligand **5** appears not to affect too greatly the thermodynamic stability of the former.

Conclusions

The hitherto unknown mixed donor macrocyclic ligand [10]-aneS$_2$NH, **4**, was successfully synthesized and its Ni(II) complex was structurally characterized. Two ligands coordinate to the Ni(II) metal ion occupying the trigonal faces to form octahedral complexes with the two N atoms in trans positions. Oxidation to the low-spin d^7 Ni(III) complex ion reveals a compressed octahedral geometry as opposed to an elongated octahedral complex obtained for the Ni(III) complex of the nine-membered [9]-aneS$_2$N, **3**. Both the spectroscopic and the redox properties of the Ni complexes were intermediate between that of the trithia and triaza ligands.

The macrobicyclic ligand **5** was also synthesized. The ligand forms distorted octahedral complexes with Ni(II) with the N atoms cis to each other in comparison with the complexes of [10]-aneS$_2$NH, **4**. The constraint imposed by the ethylene bridge is reflected on the large twist angle of the macrocyclic rings with respect to each other and on the large molar absorption coefficients observed for the Ni(II) complex. The Ni(III) complex ion is in a compressed octahedral geometry with the unpaired electron in the d$_{x^2-y^2}$ orbital.

(40) Bencini, A.; Fabbrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544.
(41) Fortier, D. G.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1991**, 101.
(42) Lacroix, R.; Hoechli, V.; Müller, K. A. *Helv. Phys. Acta* **1964**, *37*, 627.
(43) Lever, A. B. P. *Inorganic electronic spectroscopy*; Elsevier Publishing Co.: New York, 1968.