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Synthesis of a Novel Macrobicyclic Ligand, 15-Thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane, and Its Nickel(II) and Copper(II) Complexes. X-ray Crystal Structures of $[Cu(L1)](ClO_4)_2$ and $[Ni(L1)(ClO_4)]ClO_4$

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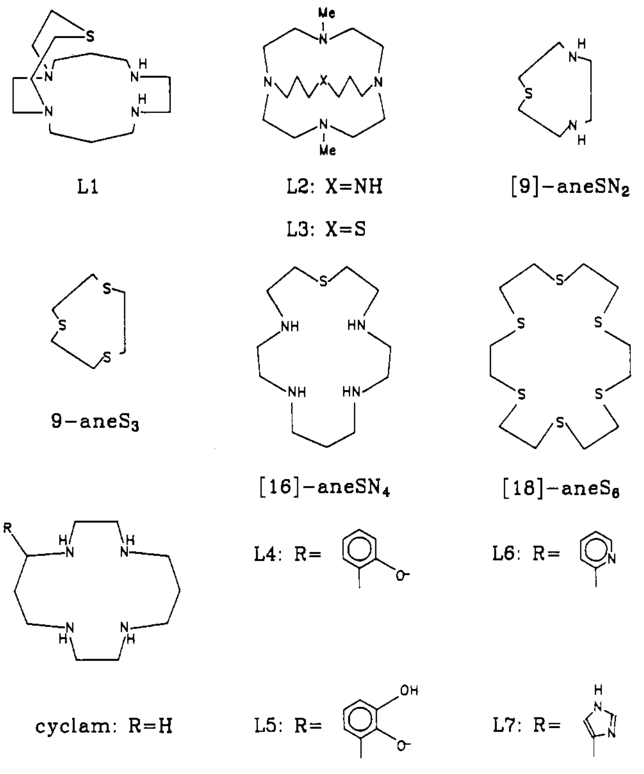
The syntheses of the novel macrobicyclic ligand 15-thia-1,5,8,11-tetraazabicyclo[10.5.2]nonadecane (L1) and its copper(II) and nickel(II) complexes are described. The method provides the first example of a successful reduction of a copper-promoted glyoxal cyclization and is a rare instance of cyclization of a functionalized tetraazadodecane. Perchlorate salts of $[Cu^{II}(L1)]^{2+}$ and $[Ni^{II}(L1)(ClO_4)]^+$ have been isolated and examined by using X-ray crystallography. Both complexes crystallize in the orthorhombic space group *Pbca*. Refinement for the copper(II) complex ($a = 20.373$ (7), $b = 14.205$ (3), $c = 15.242$ (3) Å) converged at $R = 0.0652$ ($R_w = 0.0789$) for 391 parameters using 2333 reflections with $I > 2\sigma(I)$. The complex is square pyramidal, with a Cu–S bond length of 2.549 (2) Å. Refinement for the nickel(II) complex ($a = 20.347$ (8), $b = 13.854$ (4), $c = 15.614$ (4) Å) converged at $R = 0.0608$ ($R_w = 0.788$) for 391 parameters using 2866 reflections with $I > 2\sigma(I)$. The complex is pseudooctahedral, the Ni–S bond length is 2.385 (2) Å, and the Ni–$OClO_3$ distance is 2.563 Å. In aqueous media, the copper(II) complex remains five-coordinate and exhibits remarkable kinetic stability. Cyclic voltammetry of the nickel(II) complex in CH_3CN shows two reversible redox waves corresponding to the $Ni^{2+/+}$ couple (−1.675 V vs $Fc^{+/0}$) and the $Ni^{3+/2+}$ couple (0.775 V). In aqueous media, the nickel(III) complex can be generated chemically. Both the nickel(II) and nickel(III) complexes are six-coordinate in solution. The $[Ni^{III}(L1)(X)]^{n+}$ complexes are ESR active, and frozen solutions give rise to axial spectra with features dependent upon the sixth ligand present ($X = H_2O$, $g_\parallel = 2.025$, $g_\perp = 2.169$; $X = F^-$, $g_\parallel = 2.028$ ($A^F{}_\parallel = 210$ G), $g_\perp = 2.163$ ($A^F{}_\perp = 48$ G)). In solution, a value of $(3.0 \pm 0.5) \times 10^4$ M^{-1} was obtained for the equilibrium constant of the anation reaction of $[Ni^{III}(L1)(H_2O)]^{3+}$ with fluoride ions, confirming that the Ni(III) complex is six-coordinate in solution.

Introduction

The ligand cyclam (1,4,8,11-tetraazacyclotetradecane) is well recognized as exemplary among cyclic polyamines in its ability to impart thermodynamic and kinetic stability to a variety of oxidation states of metal ions.[1-4] This is particularly true of nickel(I), nickel(II), and nickel(III) complexes that have been the subject of study.[5] More recently, a number of ligands have been synthesized[6-9] in which a pendant arm donor is attached to the cyclam unit. These impose pseudooctahedral geometry on the Ni(II) complexes formed such that upon electron transfer between the nickel(II/III) oxidation states there is no change in coordination number. However, such systems exhibit acid lability owing to facile protonation of the pendant arm ligand. Other pentacoordinate macrocyclic complexes have been reported previously involving both S and N donor groups in a variety of ligands ([15]-aneN_5, [16]-aneN_5, [17]-aneN_5[10] and [16]-aneSN_4[11]), but these are also unstable in acidic conditions,[12] presumably because the ring is too large to accommodate the metal effectively and protonation of a secondary amine is possible.

Chart I



Parallel with such developments we have seen the emergence of the small macrocyclic ligand systems [9]-aneN_3 and [9]-aneSN_2, which coordinate facially to a metal ion.[13] In the case of nickel with the former, both the +2[14] and +3 ions[15] exhibit octahedral geometry, and the latter reagent has found extensive use as an outer-sphere-electron-transfer reagent with a moderately high driving force ($E° = 0.947$ V vs NHE).[16] An X-ray study of the bis(ligand) complex $[Ni([9]\text{-}aneSN_2)_2]^{2+}$ shows the sulfur donors to be axially disposed.[17] Oxidation to Ni(III) yields an ESR spectrum in CH_3CN that is consistent with a similar geometry.

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(1) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979.

(2) Busch, D. H. *Adv. Chem. Ser.* **1971**, *No. 100*, 44; *Acc. Chem. Res.* **1978**, *11*, 392.

(3) Fabbrizzi, L. *Comments Inorg. Chem.* **1985**, *4*, 33.

(4) Che, C. M.; Wong, K. Y.; Poon, C. K. *Inorg. Chem.* **1986**, *25*, 1809.

(5) Lappin, A. G.; McAuley, A. The Redox Chemistry of Nickel. *Adv. Inorg. Chem.* **1988**, *32*, 241.

(6) Kimura, E. *Pure Appl. Chem.* **1986**, *58*, 1461.

(7) Kimura, E.; Shionoya, M.; Mika, T.; Iitaka, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1712.

(8) Barefield, E. K.; Foster, K. A.; Freeman, G. M.; Hodges, K. D. *Inorg. Chem.* **1986**, *25*, 4663.

(9) Pallavicini, P. S.; Perotti, A.; Poggi, A.; Seghi, B.; Fabbrizzi, L. *J. Am. Chem. Soc.* **1987**, *109*, 5139.

(10) Benecini, A.; Fabbrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544. Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 104. Fabbrizzi, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1063.

(11) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497.

(12) Hay, R. W.; Bembi, R.; Moodie, W. T.; Norman, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2131.

(13) For a review, see: Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

(14) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157.

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

(16) McAuley, A.; Norman, P. R.; Olubuyide, O. *J. Chem. Soc., Dalton Trans.* **1984**, 1501.

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

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In the present paper we describe a synthetic route to the preparation of a pentacoordinate ligand system that incorporates both the tetraaza macrocycle and the [9]-aneSN$_2$ moiety. Cu(II) and Ni(II) complexes have been characterized that show differing coordination number. Redox reactions of nickel are consistent with retention of an octahedral ion that has only one axial site solvated.

Experimental Section

All materials were of reagent grade, except where otherwise indicated.

Infrared spectra were obtained on KBr disks by using a Perkin-Elmer 283 grating spectrometer. High-field ^{1}H and ^{13}C spectra were obtained on a Bruker WM 250 instrument. All chemical shifts are reported relative to tetramethylsilane (TMS).

ESR spectra were obtained by a Varian E6S spectrometer or a Bruker ER200tt instrument with an IBM-PC attachment. Diphenylpicrylhydrazyl (dpph, g = 2.0037) was used as a reference standard. For equilibrium studies, the ESR spectra obtained on the Bruker instrument were integrated twice by using the program EPRDAS (Schultz, R. O. "EPR Data Acquisition System", Version 1.22B; Adaptable Laboratory Software Inc.: Rochester, NY, 1987).

UV–visible spectra were run on either a Cary 17 or a Perkin-Elmer Lambda 4B dual beam spectrophotometer.

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

Electrochemical measurements were made by using a Princeton Applied Research Model 273 potentiostat/galvanostat. Background electrolyte (0.5 M Li_2SO_4 or 0.1 M $(n\text{-Bu})_4NPF_6$) was always present in water or acetonitrile, respectively. The acetonitrile was freshly distilled over calcium hydride under inert atmosphere immediately before use, and all electrochemical solutions were deaerated with Ar. Pt working and counter electrodes were used, while the reference electrode was a saturated calomel electrode linked to the cell via a bridge containing a saturated aqueous solution of KCl or a CH_3CN solution containing 0.1 M $(n\text{-Bu})_4NPF_6$ for nonaqueous measurements. The $E_{1/2}$ values (in nonaqueous systems are reported with reference to ferrocene ($Fc^{+/0}$) as an external standard.

Syntheses. The synthetic route is outlined in Scheme I. The dihydrobromide salt of 1-thia-4,7-diazacyclononane ([9]-aneSN$_2$·2HBr) was prepared by using a literature method.[18] The free ligand was obtained by extraction with CH_2Cl_2 from a 3 M NaOH solution containing the ligand. The CH_2Cl_2 fractions were dried over Na_2SO_4 and evacuated to dryness.

4,7-Bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (1). To a solution of the free ligand [9]-aneSN$_2$ (650 mg, 4.4 mmol) in CH_2Cl_2 (50 mL) was added K_2CO_3 (0.5 g) and acrylonitrile (5 mL, about a 10-fold excess) before refluxing overnight. The K_2CO_3 was filtered off and the solvent removed under reduced pressure. The resulting oil contained the desired bis adduct, although traces of the mono adduct were also present. The product was used without further purification in the next step.

^{13}C NMR ($CDCl_3$): δ 16.7 (CH_2CN); 31.1 (CH_2–S) 53.7, 56.0, 58.9 (CH_2–N); 119.1 (CN). Mass spectral data: m/e 253 (M + 1), 281 (M + 29), 293 (M + 41).

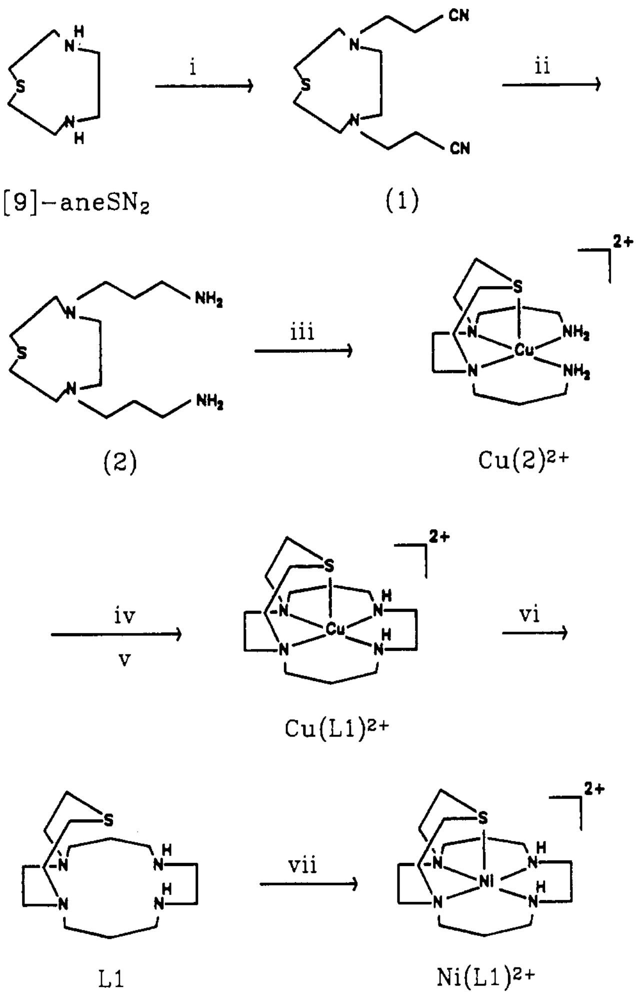
4,7-Bis(3-aminopropyl)-1-thia-4,7-diazacyclononane (2). The crude product containing **1** was dissolved in BH_3·THF (1 M in THF, 25 mL) and brought to reflux for 4 h. Ethanol (15 mL) was added carefully to the cooled solution in order to destroy the excess BH_3. The mixture was taken to dryness under reduced pressure and subsequently dissolved in a methanolic solution of HCl (4 M, 20 mL) and refluxed for 1 h. The solvent was again removed under reduced pressure, and the resulting oil was dissolved in 3 M NaOH (10 mL) and extracted into CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4 and taken to dryness. The oil contained the desired product as well as some 4-(3-aminopropyl)-1-thia-4,7-diazacyclononane.

^{13}C NMR ($CDCl_3$): δ 28.0 (C–CH_2–C); 31.9 (CH_2S); 39.8 (CH_2–NH_2); 54.0, 55.0, 56.0 (CH_2–N). Mass spectral data: m/e 251 (M + 1), 289 (M + 29), 301 (M + 41). The desired product was isolated as its Cu(II) complex in the following manner.

Cu(2)(ClO_4)$_2$. To a solution of the crude oil containing **2** in water (50 mL) was added $Cu(H_2O)_6(ClO_4)_2$ (1.33 g, 4.3 mmol). The solution turned blue immediately, but was heated to 60 °C for 30 min to ensure complete complexation. The solution was taken to dryness. The desired Cu(II) complex crystallized out preferentially upon recrystallization from hot H_2O (25 mL).

Yield: 1.15 g, 2.2 mmol (50% from [9]-aneSN$_2$). IR: NH_2 stretch, 3260, 3290 cm^{-1}; NH_2 scissor: 1600 cm^{-1}; ClO_4 stretch: 620, 1100 cm^{-1}.

Scheme I



Anal. Calcd for $[Cu(C_{12}H_{28}N_4S)](Cl_2O_8)$: C, 27.56; H 5.39; N, 10.71; S, 6.13. Found: C, 28.56; H, 5.50; N, 10.36; S, 6.39.

(15-Thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane)copper Diperchlorate {[Cu(L1)](ClO_4)$_2$}. To a solution of $[Cu(2)](ClO_4)_2$ (600 mg, 1.1 mmol) in methanol/water (9:1, 500 mL) was added glyoxal (40% solution in H_2O, 225 μL, 1.5 mmol). The mixture was refluxed overnight, after which the cooled solution was treated with $NaBH_4$ (120 mg, 3.2 mmol) and heated to reflux for 2 h. The reaction mixture was taken to dryness under reduced pressure. The product was recrystallized from hot water (10 mL) and acidified with 4 M $HClO_4$ (0.5 mL), providing X-ray quality crystals, which were filtered off, rinsed with 2-propanol and air-dried.

Yield: 450 mg (72%).

Anal. Calcd for $[Cu(C_{14}H_{30}N_4S)](Cl_2O_8)$: C, 30.63; H, 5.50; N, 10.20; S, 5.84; Cl, 12.91. Found: C, 30.63; H, 5.40;, N, 9.94; S, 5.53; Cl, 12.23.

IR: NH, 3200, 3250 cm^{-1}; ClO_4, 620, 1100 cm^{-1}.

15-Thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane (L1). To a solution of Cu(L1)(ClO_4)$_2$ (500 mg, 0.91 mmol) in water (100 mL) was added a solution of Na_2S (0.12 M, 30 mL, 3.6 mmol), and the mixture was refluxed overnight, at which point the characteristic reddish blue color of the complex had disappeared. The CuS precipitate was filtered off through a fine glass frit, and the supernatant was reduced to one-fourth of its original volume under reduced pressure. NaOH (3 g) was added to give [NaOH] ≈ 3 M, and the free ligand was extracted into CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, and taken to dryness, yielding L1 as a hydroscopic colorless oil (200 mg) in 77% yield.

^{13}C NMR ($CDCl_3$): δ 26.7 (C–CH_2–C); 36.4 (CH_2–S); 47.4, 48.4, 54.4, 56.8, 58.1 (CH_2–N). Mass spectral data: m/e 287 (M + 1), 315 (M + 29), 327 (M + 41).

[Ni(L1)](ClO_4)$_2$. To a solution of L1 in ethanol was added $Ni(H_2O)_6(ClO_4)_2$ (190 mg, 0.52 mmol) and the mixture refluxed for 1 h to ensure complete coordination. The solution was then taken to dryness, and the resulting solid dissolved in a 2-propanol/water (1:1, 20 mL) solvent mixture and filtered to remove a small amount of excess $Ni^{II}(ClO_4)_2$. The volume was then reduced to 10 mL and 4 M $HClO_4$ (0.5

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[18] Boyens, J. C. A.; Dobson, S. M.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3073.

Table I. Crystallographic Data

(a) $[Cu(L1)](ClO_4)_2$

chemical formula: $CuCl_2SO_8N_4C_{14}H_{30}$
fw: 548.92
space group: *Pbca* (No. 61)
$a = 20.373\ (7)$ Å
$b = 14.205\ (3)$ Å
$c = 15.242\ (3)$ Å
$V = 4411.1$ Å^3
$Z = 8$ molecules

$T = 22 \pm 2$ °C
$\lambda = 0.71069$ Å
$\rho_{obs} = 1.634$ g cm^{-3}
$\rho_{calc} = 1.653$ g cm^{-3}
$\mu = 14.64$ cm^{-1}
transmissn coeff = 0.5536–0.5911
$R(F_o) = 0.0652$
$R_w = 0.0789$

(b) $[Ni(L1)(ClO_4)](ClO_4)$

chemical formula: $NiCl_2SO_8N_4C_{14}H_{30}$
fw: 544.09
space group: *Pbca* (No. 61)
$a = 20.378\ (8)$ Å
$b = 13.854\ (4)$ Å
$c = 15.614\ (4)$ Å
$V = 4401.4$ Å^3
$Z = 8$ molecules

$T = 20 \pm 2$ °C
$\lambda = 0.71069$ Å
$\rho_{obs} = 1.632$ g cm^{-3}
$\rho_{calc} = 1.642$ g cm^{-3}
$\mu = 12.60$ cm^{-1}
transmissn coeff = 0.545 - 0.671
$R(F_o) = 0.0608$
$R_w = 0.0788$

mL) added. When this mixture was allowed to stand for a few days, X-ray quality crystals formed. These were filtered off, rinsed with 2-propanol, and air-dried.

Yield: 162 mg (0.3 mmol, 60%).

Anal. Calcd for $[Ni(C_{14}H_{30}N_4S)](Cl_2O_8)$: C, 30.90; H, 5.55; N, 10.29; S, 5.89; Cl, 13.03. Found: C, 31.04; H, 5.47; N, 10.17; S, 5.87; Cl, 12.66.

$[Ni(L1)]^{3+}$. Solutions of the $[Ni^{III}L1]^{3+}$ complex were prepared in situ electrochemically or by oxidation with Co^{III}(aq) or 3.5 M HNO_3 in aqueous media, by use of NO^+ as the oxidant under nonaqueous conditions. In general, a stoichiometric deficiency of the oxidant was used in the solvent under consideration. The reaction to yield the tervalent nickel ion was rapid and solutions were of sufficient stability ($t_{1/2} > 30$ min) that spectroscopic measurements could be made. Attempts at isolating a solid form of the nickel(III) complex using either concentrated HNO_3 or acidic chloride media have been unsuccessful. However, solutions of the nickel(III) species are remarkably stable under such conditions.

Caution! Transition-metal complex perchlorates are known to be hazardous and must be treated with care, especially in the presence of organic solvents.

Crystallography. The experimental parameters for both complexes are listed in Table I. Crystals were mounted in glass Lindemann tubes and the unit cells and space groups determined by using Weissenberg and precession photography, after which the crystals were transferred to a Picker four-circle diffractometer automated with a PDP11/10 computer.

$[Cu(L1)](ClO_4)_2$. The unit cell was refined by using 20 pairs of reflections in the 2θ range 17–45°. The intensity measurements were obtained by scanning in the $\theta/2\theta$ mode using 200 steps of 0.01° in 2θ counting for 0.25 s/step. Background counting was introduced for 25 s 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.

Solution of the phase problem was achieved by direct methods using SHELX76.[19] The atomic scattering factors used were those included in the SHELX76 program together with the Cu *f*-curve from ref 20. The programme used for absorption correction was a local modification of an existing procedure.[21] Completion and refinement of the structure were carried out by different electron density maps and least-squares techniques. All atoms were refined anisotropically except for the hydrogen atoms, which were observed and refined isotropically. In addition, a blocked matrix was used in the final stages because of the large number of parameters used. The refinement converged with a maximum shift/esd of 0.163 on the final cycle and a maximum peak of 0.24 e Å^{-3}.

$[Ni(L1)](ClO_4)_2$. The unit cell was refined by using 17 pairs of reflections in 2θ from 17 to 47°. The intensity measurements were obtained by scanning in the $\theta/2\theta$ mode using 160 steps of 0.01° in 2θ counting for 0.25 s/step. Background counting was introduced for 20 s 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. The crystal was found to be isomorphous with the Cu complex, so the phase problem was solved by using the same heavy-atom coordinates. The structure was then refined in a similar manner. The refinement converged with a maximum shift/esd of 0.104 on the final cycle and a maximum peak of 0.19 eÅ^{-3}.

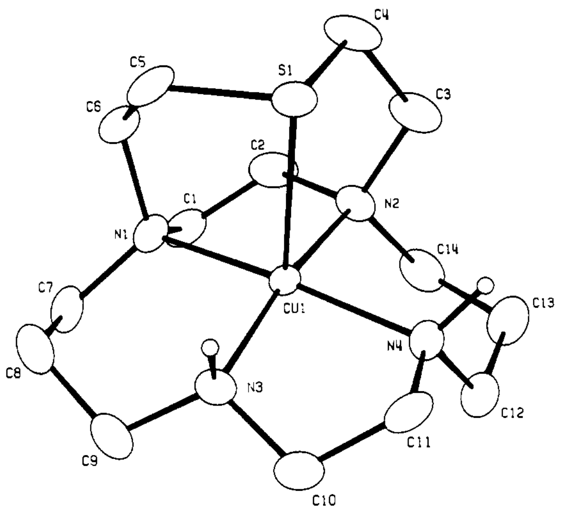

Figure 1. ORTEP diagram of the $[Cu(L1)]^{2+}$ cation showing 20% thermal ellipsoids. Only the amine H atoms are shown for clarity.

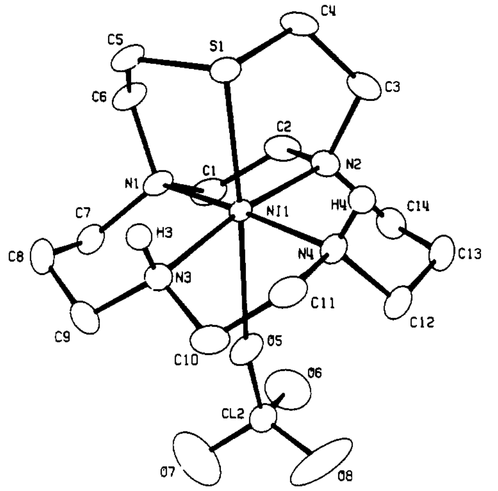

Figure 2. ORTEP diagram of the $[Ni(L1)(ClO_4)]^+$ cation showing 20% thermal ellipsoids. Only the amine H atoms are shown for clarity.

Results and Discussion

The preparation of the complexes is as shown in Scheme I. Upon reduction of 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (**1**), reaction with Cu(II) yielded blue crystals of a copper complex. After the reaction mixture was refluxed, a cyclized diene product was obtained, which was not isolated. Further reduction (borohydride) yielded the desired saturated ligand complex. This procedure is of interest, in that it represents the first example of a successful glyoxal cyclization promoted by Cu(II). Barefield et al.[22] were unable to prepare the copper cyclam complex by glyoxal condensation because of copper metal precipitation in the BH_4^- reduction step. There is to our knowledge only one other example of cyclization of a functionalized tetraazadodecane. In this instance[23] the nickel(II) complex of 5-(3-aminopropyl)-8-methyl-1,5,8,12-tetraazadodecane was reacted with glyoxal with further reduction using $NaBH_4$, to yield an *N*-methylcyclam derivative with a 3-aminopropyl arm. Perhaps noteworthy is the fact that, in both cases, five-coordinate metal centers are involved,

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(19) Sheldrick, G. M. "SHELX76, Program for Crystal Structure Refinement", University of Cambridge, Cambridge, U.K., 1976.

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

(21) Coppens, P.; Lieserowitz, L.; Rabinovich, D.: modified by G. W. Bushnell, University of Victoria.

(22) Barefield, E. K.; Wagner, F.; Hodges, K. D. *Inorg. Chem.* **1976**, *15*, 1370.

(23) Franz, J.; Freeman, G. M.; Barefield, E. K.; Volkent, W. A.; Ehrhardt, G. J.; Holmes, R. A. *Nucl. Med. Biol.* **1987**, *14*, 479.

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

atom	*x/a*	*y/b*	*z/c*	U_{eq}
		(a) $[Cu(L1)](ClO_4)_2$		
Cu(1)	11173 (5)	58077 (6)	25518 (6)	465 (3)
S(1)	12246 (13)	41145 (14)	20110 (17)	707 (9)
Cl(1)	−10069 (12)	38372 (16)	18740 (17)	758 (9)
Cl(2)	14652 (11)	32705 (14)	48658 (15)	732 (8)
O(1)	−1135 (7)	4058 (7)	2711 (7)	195 (7)
O(2)	−375 (5)	3852 (7)	1812 (12)	286 (10)
O(3)	−1205 (5)	2914 (7)	1826 (8)	185 (6)
O(4)	−1282 (6)	4498 (10)	1365 (7)	211 (7)
O(5)	1558 (5)	4061 (5)	5399 (6)	145 (4)
O(6)	1541 (9)	3432 (8)	4028 (8)	253 (9)
O(7)	825 (6)	3124 (13)	4866 (12)	312 (11)
O(8)	1795 (6)	2505 (6)	5111 (7)	194 (6)
N(1)	2077 (4)	6057 (4)	2213 (5)	70 (3)
N(2)	873 (4)	6162 (5)	1279 (4)	67 (3)
N(3)	1298 (4)	5687 (6)	3860 (5)	67 (3)
N(4)	159 (4)	5719 (5)	2885 (5)	67 (3)
C(1)	1988 (6)	6795 (7)	1509 (8)	89 (5)
C(2)	1510 (7)	6488 (7)	849 (7)	88 (5)
C(3)	610 (8)	5324 (8)	804 (8)	93 (5)
C(4)	1055 (8)	4450 (8)	870 (7)	100 (5)
C(5)	2105 (6)	4242 (8)	2108 (10)	95 (5)
C(6)	2383 (6)	5190 (8)	1798 (11)	92 (5)
C(7)	2488 (6)	6481 (8)	2912 (11)	89 (5)
C(8)	2482 (8)	5957 (10)	3735 (13)	120 (7)
C(9)	1865 (7)	6144 (9)	4274 (9)	93 (5)
C(10)	682 (6)	5927 (8)	4295 (7)	84 (4)
C(11)	129 (6)	5437 (7)	3819 (7)	80 (4)
C(12)	−214 (6)	6581 (8)	2699 (10)	85 (5)
C(13)	−266 (7)	6727 (10)	1745 (10)	94 (6)
C(14)	378 (7)	6928 (8)	1258 (8)	92 (5)
H(3)	1327 (45)	5082 (72)	3911 (59)	82 (33)′
H(4)	−111 (39)	5330 (54)	2490 (50)	58 (22)′
		(b) $[Ni(L1)(ClO_4)](ClO_4)$		
Ni(1)	10960 (3)	58354 (4)	25389 (4)	384 (2)
Cl(1)	14696 (8)	32242 (11)	48861 (9)	645 (5)
Cl(2)	10156 (8)	86328 (12)	31430 (11)	694 (6)
S(1)	12114 (9)	42153 (10)	20453 (11)	591 (5)
O(1)	1585 (3)	4050 (4)	5388 (4)	120 (3)
O(2)	1794 (4)	2406 (4)	5178 (4)	145 (3)
O(3)	1540 (4)	3381 (4)	4018 (4)	156 (4)
O(4)	788 (4)	3016 (7)	4973 (6)	195 (5)
O(5)	1088 (2)	7605 (3)	3018 (3)	86 (2)
O(6)	1133 (4)	9079 (5)	2364 (4)	151 (4)
O(7)	1486 (5)	8975 (7)	3685 (5)	200 (5)
O(8)	403 (4)	8818 (5)	3376 (8)	257 (7)
N(1)	2064 (2)	6118 (3)	2176 (4)	63 (2)
N(2)	845 (3)	6210 (3)	1297 (3)	58 (2)
N(3)	1291 (3)	5643 (4)	3819 (3)	59 (2)
N(4)	123 (2)	5687 (4)	2890 (4)	55 (2)
C(1)	1953 (4)	6871 (5)	1517 (5)	75 (3)
C(2)	1450 (4)	6585 (6)	873 (5)	76 (3)
C(3)	571 (4)	5349 (5)	831 (4)	76 (3)
C(4)	1016 (5)	4465 (5)	930 (4)	78 (3)
C(5)	2101 (4)	4282 (5)	2082 (7)	77 (3)
C(6)	2377 (4)	5236 (5)	1766 (7)	83 (3)
C(7)	2490 (4)	6521 (6)	2862 (6)	79 (3)
C(8)	2494 (4)	5966 (7)	3677 (7)	96 (4)
C(9)	1873 (5)	6123 (6)	4212 (6)	82 (3)
C(10)	679 (4)	5871 (5)	4269 (4)	77 (3)
C(11)	130 (5)	5388 (6)	3810 (5)	73 (3)
C(12)	−277 (4)	6553 (5)	2706 (5)	73 (3)
C(13)	−314 (4)	6740 (6)	1759 (5)	80 (3)
C(14)	321 (4)	6986 (5)	1296 (5)	75 (3)
H(3)	1393 (29)	5100 (46)	3787 (36)	50 (18)′
H(4)	−42 (33)	5220 (44)	2548 (34)	56 (17)′

[a] Estimated standard deviations are given in parentheses. Coordinates are $\times 10^n$ where $n = 5$ for Cu or Ni, S, and Cl and 4 otherwise. Temperature parameters are $\times 10^n$ where $n = 4$ for Cu or Ni, S, and Cl and 3 otherwise. U_{eq} = the equivalent isotropic temperature parameter. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_u^*a_j^*(a_i\cdot a_j)$. Primed values indicate that U_{iso} is given: $T = \exp[-8\pi^2 U_{iso}(\sin^2\theta)/\lambda_2]$.

leading possibly to stabilization of intermediates formed in the condensation process.

Table III. Interatomic Distances (Å)[a]

	(a) $[Cu(L1)](ClO_4)_2$		
S(1)–Cu(1)	2.549 (2)	C(7)–N(1)	1.482 (16)
N(1)–Cu(1)	2.053 (7)	C(2)–N(2)	1.526 (15)
N(2)–Cu(1)	2.064 (7)	C(3)–N(2)	1.492 (14)
N(3)–Cu(1)	2.035 (7)	C(14)–N(2)	1.485 (14)
N(4)–Cu(1)	2.021 (7)	C(9)–N(3)	1.468 (16)
C(4)–S(1)	1.836 (11)	C(10)–N(3)	1.458 (15)
C(5)–S(1)	1.808 (13)	C(11)–N(4)	1.481 (13)
O(1)–Cl(1)	1.339 (11)	C(12)–N(4)	1.467 (13)
O(2)–Cl(1)	1.291 (10)	C(2)–C(1)	1.466 (17)
O(3)–Cl(1)	1.373 (10)	C(4)–C(3)	1.539 (18)
O(4)–Cl(1)	1.340 (13)	C(6)–C(5)	1.535 (17)
O(5)–Cl(2)	1.398 (8)	C(8)–C(7)	1.459 (24)
O(6)–Cl(2)	1.307 (12)	C(9)–C(8)	1.525 (21)
O(7)–Cl(2)	1.320 (13)	C(11)–C(10)	1.510 (16)
O(8)–Cl(2)	1.331 (10)	C(13)–C(12)	1.471 (21)
C(1)–N(1)	1.509 (14)	C(14)–C(13)	1.535 (20)
C(6)–N(1)	1.517 (14)		
	(b) $[Ni(L1)(ClO_4)](ClO_4)$		
S(1)–Ni(1)	2.385 (2)	C(6)–N(1)	1.519 (10)
N(1)–Ni(1)	2.087 (5)	C(7)–N(1)	1.487 (10)
N(2)–Ni(1)	2.072 (5)	C(2)–N(2)	1.491 (10)
N(3)–Ni(1)	2.055 (5)	C(3)–N(2)	1.504 (8)
N(4)–Ni(1)	2.065 (5)	C(14)–N(2)	1.517 (9)
O(5)–Ni(1)	2.563 (6)	C(9)–N(3)	1.490 (11)
O(1)–Cl(1)	1.407 (6)	C(10)–N(3)	1.465 (10)
O(2)–Cl(1)	1.388 (7)	C(11)–N(4)	1.494 (10)
O(3)–Cl(1)	1.381 (6)	C(12)–N(4)	1.478 (9)
O(4)–Cl(1)	1.422 (8)	C(2)–C(1)	1.488 (12)
O(5)–Cl(2)	1.445 (5)	C(4)–C(3)	1.532 (12)
O(6)–Cl(2)	1.386 (7)	C(6)–C(5)	1.518 (11)
O(7)–Cl(2)	1.363 (9)	C(8)–C(7)	1.486 (14)
O(8)–Cl(2)	1.324 (8)	C(9)–C(8)	1.531 (14)
C(4)–S(1)	1.819 (7)	C(11)–C(10)	1.487 (12)
C(5)–S(1)	1.813 (8)	C(13)–C(12)	1.503 (12)
C(1)–N(1)	1.484 (10)	C(14)–C(13)	1.519 (12)

[a] Estimated standard deviations are given in parentheses.

Molecular Structures. The structures of the $[Cu(L1)]^{2+}$ and $[Ni(L1)(ClO_4)]^+$ ions are shown in Figures 1 and 2 respectively. The atomic coordinates are listed in Table II. In both structures, the ligand arrangement is very much the same, the cyclam ring adopting a trans-I configuration (see below), and the sulfur atom coordinating axially, with the S–M vector showing a slight deviation from perpendicularity with the N_4 plane (the angles between the S–M vector and the N_4 plane are 81.8 and 83.5° for the Cu(II) and Ni(II) complexes, respectively). This may reflect the inability of the nonane ring to reach over fully and encapsulate the axial site. The main difference in structure between the two systems is seen to be the result of the preferred coordination number of the metal. The Cu(II) complex is best described as square pyramidal with the metal center lying out of the N_4 plane, 0.141 Å toward the S donor. The trans-basal angles (N(1)–Cu–N(4) = 173.6° and N(2)–Cu–N(3) = 170.0°) are typical of that expected for square-pyramidal d^9 Cu(II) complexes.[24] A weak copper to perchlorate interaction is observed (Cu···O = 3.140 Å), which is best described as an electrostatic rather than a bonding interaction. On the other hand, in the Ni(II) complex, the metal to perchlorate interaction is much stronger (Ni–O = 2.563 Å) leading to a pseudooctahedral geometry at the nickel center. The stronger Ni–O bond results in a smaller displacement (0.111 Å) of the nickel atom out of the N_4 plane. According to molecular mechanics calculations performed by Hancock and co-workers,[25] the ideal position for a metal ion coordinated to the cyclam trans-I configuration is 0.06 Å out of the N_4 plane.

In Table III the bond lengths are shown for both complexes, and in Table IV the corresponding bond angles. The Cu–N bond lengths (average 2.04 Å) are typical of N_4 ligands coordinated in planar fashion around copper(II),[26] while the Cu–S bond is at

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(24) Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.
(25) Thom, V. J.; Fox, C. C.; Boyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.

Table IV. Bond Angles (deg)[a]

(a) $[Cu(L1)](ClO_4)_2$			
N(1)–Cu(1)–S(1)	90.0 (2)	C(7)–N(1)–C(1)	107.3 (8)
N(2)–Cu(1)–S(1)	86.9 (2)	C(7)–N(1)–C(6)	113.4 (8)
N(2)–Cu(1)–N(1)	87.2 (3)	C(3)–N(2)–Cu(1)	105.8 (6)
N(3)–Cu(1)–S(1)	102.8 (3)	C(3)–N(2)–Cu(1)	110.4 (6)
N(3)–Cu(1)–N(1)	95.1 (3)	C(3)–N(2)–C(2)	109.8 (8)
N(3)–Cu(1)–N(2)	170.0 (3)	C(14)–N(2)–Cu(1)	111.3 (6)
N(4)–Cu(1)–S(1)	96.0 (2)	C(14)–N(2)–C(2)	110.2 (8)
N(4)–Cu(1)–N(1)	173.6 (3)	C(14)–N(2)–C(3)	109.3 (9)
N(4)–Cu(1)–N(2)	91.0 (3)	C(9)–N(3)–Cu(1)	121.7 (7)
N(4)–Cu(1)–N(3)	85.6 (3)	C(10)–N(3)–Cu(1)	105.7 (6)
C(4)–S(1)–Cu(1)	92.6 (4)	C(10)–N(3)–C(9)	112.3 (9)
C(5)–S(1)–Cu(1)	88.0 (4)	C(11)–N(4)–Cu(1)	107.3 (6)
C(5)–S(1)–C(4)	103.8 (7)	C(12)–N(4)–Cu(1)	113.6 (6)
O(2)–Cl(1)–O(1)	105.0 (10)	Cu(12)–N(4)–C(11)	113.0 (9)
O(3)–Cl(1)–O(1)	102.6 (7)	C(2)–C(1)–N(1)	111.2 (9)
O(3)–Cl(1)–O(2)	107.8 (6)	C(1)–C(2)–N(2)	111.1 (9)
O(4)–Cl(1)–O(1)	107.9 (7)	C(4)–C(3)–N(2)	113.5 (11)
O(4)–Cl(1)–O(2)	111.3 (8)	C(3)–C(4)–S(1)	112.5 (8)
O(4)–Cl(1)–O(3)	120.9 (8)	C(6)–C(5)–S(1)	115.4 (9)
O(6)–Cl(2)–O(5)	114.3 (6)	C(5)–C(6)–N(1)	115.5 (11)
O(7)–Cl(2)–O(5)	105.0 (9)	C(8)–C(7)–N(1)	114.0 (10)
O(7)–Cl(2)–O(6)	98.3 (11)	C(9)–C(8)–C(7)	112.4 (12)
O(8)–Cl(2)–O(5)	115.1 (6)	C(8)–C(9)–N(3)	110.0 (11)
O(8)–Cl(2)–O(6)	111.0 (8)	C(11)–C(10)–N(3)	108.4 (9)
O(8)–Cl(2)–O(7)	111.7 (9)	C(10)–C(11)–N(4)	107.9 (9)
C(1)–N(1)–Cu(1)	100.6 (6)	C(13)–C(12)–N(4)	110.2 (11)
C(6)–N(1)–Cu(1)	110.9 (6)	C(14)–C(13)–C(12)	116.3 (12)
C(6)–N(1)–C(1)	108.4 (9)	C(13)–C(14)–N(2)	115.6 (10)
C(7)–N(1)–Cu(1)	115.2 (7)		
(b) $[Ni(L1)(ClO_4)](ClO_4)$			
N(1)–Ni(1)–S(1)	89.7 (1)	C(6)–N(1)–Ni(1)	111.0 (4)
N(2)–Ni(1)–S(1)	87.6 (1)	C(6)–N(1)–C(1)	109.7 (6)
N(2)–Ni(1)–N(1)	86.1 (2)	C(7)–N(1)–Ni(1)	115.2 (5)
N(3)–Ni(1)–S(1)	100.0 (2)	C(7)–N(1)–C(1)	108.9 (5)
N(3)–Ni(1)–N(1)	96.1 (2)	C(7)–N(1)–C(6)	111.2 (6)
N(3)–Ni(1)–N(2)	172.2 (2)	C(2)–N(2)–Ni(1)	107.4 (4)
N(4)–Ni(1)–S(1)	95.0 (1)	C(3)–N(2)–Ni(1)	110.2 (4)
N(4)–Ni(1)–N(1)	174.9 (2)	C(3)–N(2)–C(2)	111.6 (5)
N(4)–Ni(1)–N(2)	92.1 (2)	C(14)–N(2)–Ni(1)	110.6 (4)
N(4)–Ni(1)–N(3)	85.1 (2)	C(14)–N(2)–C(2)	109.5 (5)
O(5)–Ni(1)–S(1)	174.4 (2)	C(14)–N(2)–C(3)	107.5 (5)
O(5)–Ni(1)–N(1)	84.6 (2)	C(9)–N(3)–Ni(1)	119.8 (5)
O(5)–Ni(1)–N(2)	91.8 (2)	C(10)–N(3)–Ni(1)	105.9 (4)
O(5)–Ni(1)–N(3)	80.9 (2)	C(10)–N(3)–C(9)	112.4 (6)
O(5)–Ni(1)–N(4)	90.7 (2)	C(11)–N(4)–Ni(1)	105.9 (5)
O(2)–Cl(1)–O(1)	113.7 (4)	C(12)–N(4)–Ni(1)	113.2 (4)
O(3)–Cl(1)–O(1)	113.7 (4)	C(12)–N(4)–C(11)	114.7 (6)
O(3)–Cl(1)–O(2)	113.6 (4)	C(2)–C(1)–N(1)	112.7 (6)
O(4)–Cl(1)–O(1)	105.9 (5)	C(1)–C(2)–N(2)	111.2 (6)
O(4)–Cl(1)–O(2)	105.4 (5)	C(4)–C(3)–N(2)	111.5 (7)
O(4)–Cl(1)–O(3)	103.2 (5)	C(3)–C(4)–S(1)	112.2 (5)
O(6)–Cl(2)–O(5)	107.7 (4)	C(6)–C(5)–S(1)	113.8 (5)
O(7)–Cl(2)–O(5)	110.8 (5)	C(5)–C(6)–N(1)	114.1 (7)
O(7)–Cl(2)–O(6)	105.5 (5)	C(8)–C(7)–N(1)	115.2 (7)
O(8)–Cl(2)–O(5)	109.0 (4)	C(9)–C(8)–C(7)	112.9 (7)
O(8)–Cl(2)–O(6)	108.5 (6)	C(8)–C(9)–N(3)	111.6 (7)
O(8)–Cl(2)–O(7)	115.1 (6)	C(11)–C(10)–N(3)	108.1 (6)
C(4)–S(1)–Ni(1)	96.3 (2)	C(10)–C(11)–N(4)	110.3 (7)
C(5)–S(1)–Ni(1)	92.3 (2)	C(13)–C(12)–N(4)	111.1 (6)
C(5)–S(1)–C(4)	103.8 (5)	C(14)–C(13)–C(12)	117.7 (7)
Ni(1)–O(5)–Cl(2)	169.3 (3)	C(13)–C(14)–N(2)	116.1 (6)
C(1)–N(1)–Ni(1)	115.2 (5)		

[a] Estimated standard deviations are given in parentheses.

Table V. Electronic Spectral Data for $[M(L1)]^{n+}$ Complexes

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[Ni^{II}(L1)H_2O]^{2+}$	261 (1900), 330 (sh), 504 (14), 845 (sh), 1020 (16)
$[Ni^{III}(L1)H_2O]^{3+}$	320 (8400), 360 (6500), 715 (31)
$[Ni^{III}(L1)F]^{2+}$	245 (sh), 310 (sh), 346 (3700), 678 (30)
$[Cu^{II}(L1)]^{2+}$	281 (5400), 532 (143), 728 (37)

the short end of the range (2.56–2.82 Å) expected for axial Cu–S bonds.[18] Structural data on CuN_4S systems are, to our knowledge, unavailable; therefore, a direct comparison cannot be made readily. However a small number of five- and six-coordinate structures containing a mixtures of nitrogen and sulfur donors have been published. For example, the Cu–S bonds in the octahedral $[Cu([9]\text{-}aneSN_2)_2]^{2+}$ are considerably longer (2.707 Å)[18] due to a coordination number of 6, resulting in greater elongation of both axial bonds. In contrast, in $[Cu([9]\text{-}aneSN_2)Br_2]$ and in $[Cu(peas)NO_3]^+$, both square-pyramidal five-coordinate complexes, the apical Cu–S bond lengths are 2.567[27] and 2.564 Å,[28] respectively (peas = $N(CH_2CH_2SEt)_2(CH_2CH_2py)$). Another Cu(II) complex, with a S_3N_2Br chromophore, has been reported.[29] It has a weak Cu–Br bond (3.13 Å) and can be considered almost five-coordinate. In this case, the Cu–S(axial) bond is 2.576 Å. All three of these complexes have Cu–S(apical) bond lengths closely resembling the distance found in the present system. Thus Cu–S values of ≈2.56 Å appear appropriate for axial bonds in square-pyramidal Cu(II) complexes.

For the Ni(II) complex, the Ni–N bond lengths (average 2.07 Å) may represent a compromise between the calculated ideal M–N distance for cyclam in the trans-I configuration (2.01 Å),[2,30] and the ideal Ni(high-spin)–N bond length (2.10 Å).[31] The Ni–S bond (2.385 Å) is shorter than in octahedral $[Ni([9]\text{-}aneSN_2)_2]^{2+}$ (2.418 Å),[17] but is comparable to those in the less strained homoleptic thioether complexes $[Ni([9]\text{-}aneS_3)_2]^{2+}$ (Ni–S(av) = 2.386 Å)[32] and $[Ni([18]\text{-}aneS_6)]^{2+}$ (2.388 Å).[33] The structures of a variety of $[Ni^{II}(L)X]^{n+}$ complexes (L = L3, L5, L6), where X is a solvent molecule or counterion, have been reported by Kimura and co-workers. In such systems, there is a pendant arm R attached to a cyclam ring (R = phenolate,[7] pyridine,[34] or imidazole[35]). In all three complexes, the observed Ni–N bond lengths are 2.07 Å, consistent with the present complex.

The conformation of the cyclam ring warrants discussion. The chirality of the coordinated nitrogen centers gives rise to five possible conformations, which are trans-I (++++), trans-II (+−++), trans-III (+−−+), trans-IV (++−−), and trans-V (+−+−), where + indicates that the hydrogen or substituent on the N atom is above the plane of the macrocycle and − indicates that it is below. The terminology is that of Bosnich et al.[36] Various studies[25,30,36] have shown for *trans* complexes, trans-III is of the lowest energy, whereas for cis complexes, conformation V is preferred. For the ligand system under discussion, the presence of the fused nine-membered ring forces both substituents on one of the five-membered chelate rings to be on the same side of the macrocycle, thus conformers trans-III, and trans-V are not possible. A molecular mechanics study by Connolly and Billo[30] on cyclam itself has shown that, of the remaining three possible conformers, the trans-I form has the lowest relative strain energy for both planar and octahedral geometries at the metal center. In fact, they report ^1H NMR evidence for the presence of ≈15% of the trans-I form in aqueous solutions of $[Ni(cyclam)]^{2+}$, indicating that the trans-I conformer is of only slightly higher energy than the preferred trans-III form. It is not surprising, therefore, that the complexes reported here both adopt the trans-I configuration.

A closer look at the structures indicates that the five-membered chelate rings adopt the gauche configuration (the torsion angles

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(26) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1581.

(27) Hancock, R. D.; Dobson, S. M.; Boyens, J. C. A. *Inorg. Chim. Acta* **1987**, *133*, 221.

(28) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In *Copper Coordination Chemistry*: Biochemical *and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; p 97.

(29) Drew, M. G. B.; Rice, D. A.; Richards, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2503.

(30) Connolly, P. J.; Billo, E. J. *Inorg. Chem.* **1987**, *26*, 3224.

(31) Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1857.

(32) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(33) Hintsa, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738.

(34) Kimura, E.; Koike, T.; Nada, H.; Iitaka, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1322.

(35) Iitaka, Y.; Koike, T.; Kimura, E. *Inorg. Chem.* **1986**, *25*, 402.

(36) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *8*, 1102.

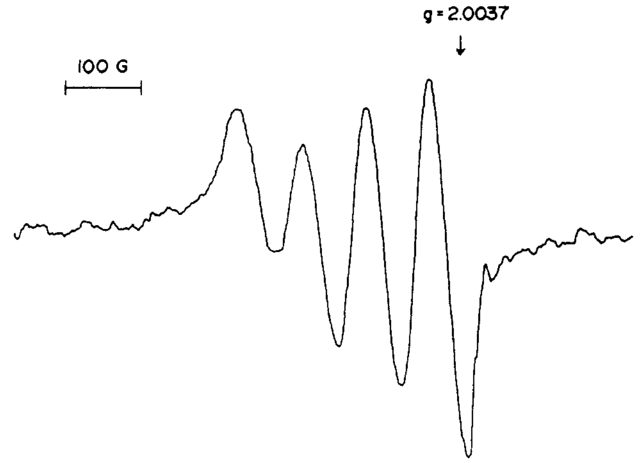

Figure 3. Room-temperature solution ESR spectrum of $[Cu(L1)]^{2+}$ in aqueous media.

around the central C–C bonds range between 48 and 55° in both complexes) while the six-membered rings are in the chair form. Thus the ligand is in a relatively low-energy arrangement. Furthermore, in both complexes, the metal to tertiary amine bonds are somewhat longer than the metal to secondary amine as expected due to the increased steric repulsion at the tertiary amines.

Solution Studies. The UV–visible spectral data are listed in Table V. The spectrum of the $Cu^{II}(L1)^{2+}$ complex is indictive of five-coordinate geometry around the metal center,[37] whereas that for $Ni^{II}(L1)^{2+}$ corresponds to that expected for a six-coordinate complex, where presumably a molecule of water is coordinated to the Ni(II) center. The bicyclic ligand system exerts a strong ligand field on the metal center, and the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition (504 nm) of the Ni(II) complex is at fairly high energy for a high-spin Ni(II) system (for comparison, $[Ni^{II}([9]\text{-aneSN}_2)_2]^{2+}$ displays λ_{max} at 520 nm[17]); similarly, the d–d transition of the Cu(II) complex (532 nm or 18 800 cm^{-1}) is at much higher energy than expected for a five-coordinate Cu complex.[38] This blue shift is indicative of an increase in the in-plane field strength.

In aqueous solution, both the $[Ni^{II}(L1)(H_2O)]^{2+}$ and $[Cu^{II}(L1)]^{2+}$ complexes are exceptionally acid-stable. Both complexes may be recrystallized from hot 1 M $HClO_4$, and their respective UV–vis spectra are identical in both H_2O and in 4 M $HClO_4$. Furthermore, the latter spectra show no decomposition after 14 days at room temperature.

The complexes also exhibit remarkable resistance to protonation of the pendant donor as attested by their behavior in acidic media. In the case of the Cu(II) complex, the only satisfactory means of removal of the metal ion is by refluxing with Na_2S overnight, the driving force being formation of the insoluble copper(II) sulfide.

To our knowledge, only two other pentacoordinate macrocyclic ligands have been synthesized that form acid-stable complexes with Ni^{2+} and Cu^{2+}. These are bicyclic systems based on 12-aneN_4—L2[39] and L3[40]—that form square-pyramidal complexes. However, the size of the 12-membered ring forces the metal ion well out of the ring, thus preventing the formation of six-coordinate complexes with these ligands, since octahedral geometry requires the metal atom to be accommodated in the N_4 plane. The displacement of the metal atom out of the plane results in a much weaker ligand field. For example for the $[Cu(L3)]^{2+}$ complex (L3 = 12,17-dimethyl-5-thia-1,9,12,17-tetraazabicyclo[7.5.5]nonadecane) the d–d transition is observed at 15 100 cm^{-1},[40] i.e. at 3700 cm^{-1} lower energy when compared to the present complex.

The dominant features of the UV–visible spectrum of $[Ni^{III}(L1)H_2O]^{3+}$ are the charge-transfer bands at 320 and 360 nm.

Figure 4. Frozen solution ESR spectra at 77 K in aqueous media: (a) $[Ni^{III}(L1)(H_2O)]^{3+}$; (b) $[Ni^{III}(L1)(F)]^{2+}$.

These are typical of Ni(III) complexes with tetraazamacrocyclic ligands.[41] Upon coordination of F^-, these features are shifted to slightly higher energy and their intensities are greatly diminished. This system is the first in which there is only one labile ligand in a Ni(III) complex, permitting the study of substitution reaction kinetics at a single site on Ni(III). This will be the focus of a future communication.

ESR Spectroscopy. Room-temperature solution ESR spectra of the $[Cu(L1)]^{2+}$ complex show four hyperfine lines (g_{iso} = 2.092, $A_{iso}{}^{Cu}$ = 86 G) (see Figure 3), due to the interaction of the unpaired electron of the copper(II) ion with the nuclear spin of the copper nucleus ($^{63,65}Cu$; $I = {}^3/_2$). Upon addition of a 250–500-fold excess of fluoride or thiocyanate anions, no change in the ESR spectrum was observed. Coordination of F^- would have resulted in further splitting of the signal as is observed for the Ni(III) complex (see below). Thus the Cu(II) complex remains five-coordinate even in the presence of large amounts of potentially strongly coordinating monodentate ligands. In contrast with the $Cu^{II}(L1)^{2+}$ complex, Cu(II) complexes of [15]-aneN_5[12] form six-coordinate complexes with thiocyanate.

The $[Ni^{III}(L1)(H_2O)]^{3+}$ complex ion exhibits an ESR spectrum (see Figure 4a) characteristic of a low-spin d^7 ion in a distorted octahedral environment with $g_\perp$ = 2.169 and $g_\parallel$ = 2.025 in frozen solutions (77 K). At room temperature, an isotropic signal (g_{iso} = 2.121) is observed, which in the presence of F^- in the inner coordination sphere results in the splitting of the signal into a doublet ($A_{iso}{}^F$ = 93.5 G) (see Figure 5). When aqueous solutions of the $[Ni^{III}(L1)(F)]^{2+}$ complex are frozen, an axial ESR spectrum (see Figure 4b) is obtained with $g_\perp$ = 2.163 ($A_\perp{}^F$ = 48 G) and $g_\parallel$ = 2.028 ($A_\parallel{}^F$ = 210 G), consistent with a coordinated fluoride anion. It is of interest that, unlike that for other axially coordinated ligands, the splitting in $g_\perp$ is sufficient that a value for $A_\perp$ may be derived.

The ESR behavior of the Ni(III) complex permits closer examination of the anation reaction of $[Ni^{III}(L1)(H_2O)]^{3+}$ with fluoride ions. The ESR signal due to the fluoride complex is well enough resolved from that of the aqua complex (Figure 5) that integration of the signals gives relative concentrations of the two species in solution, namely $[Ni^{III}(L1)(H_2O)]^{3+}$ and $[Ni^{III}(L1)(F)]^{2+}$. The equilibrium was found to be dependent on the hydrogen ion concentration, as expected, in view of the weak acid

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(37) Ciampolini, M. *Struct. Bonding (Berlin)* **1969**, *6*, 52.

(38) Hathaway, B. J.; Tomlinson, A. A. G. *Coord. Chem. Rev.* **1970**, *5*, 1.

(39) Ciampolini, M.; Micheloni, M.; Vizza, F.; Zanobini, F.; Chimichi, S.; Dapporto, P. *J. Chem. Soc., Dalton Trans.* **1986**, 505.

(40) Bianchi, A.; Garcia-España, E.; Micheloni, M.; Vizza, F. *Inorg. Chem.* **1986**, *25*, 4379.

(41) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

Table VI. Determination of the Equilibrium Constant for the Anation Reaction of $[\mathrm{Ni^{III}(L1)H_2O}]^{3+}$ with Fluoride Ions[a]

$[\mathrm{H^+}]$, M	$[\mathrm{Ni^{III}}]_{\mathrm{tot}}$, mM	$[\mathrm{F}]_{\mathrm{tot}}$, mM	$[\mathrm{Ni^{III}(L1)F}]$, mM	$[\mathrm{Ni^{III}(L1)H_2O}]$, mM	$10^{-4}K_1$, $\mathrm{M^{-1}}$	K_2
1.0	0.5	50.5	0.23	0.27	2.7	17
0.5	0.5	25.5	0.33	0.17	3.1	20
0.10	0.5	12.5	0.34	0.16	2.8	18
0.05	0.5	5.0	0.34	0.16	3.6	23

mean $K_1 = (3.1 \pm 0.3) \times 10^4\ \mathrm{M^{-1}}$
mean $K_2 = 20 \pm 3$

[a] Conditions: room temperature; 1.0 M ionic strength ($\mathrm{LiClO_4}$).

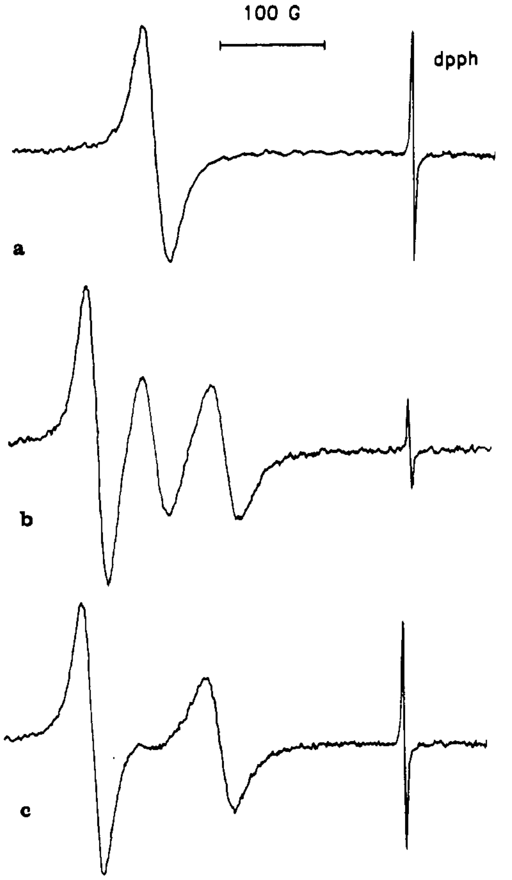

Figure 5. Room-temperature solution ESR spectra of $[\mathrm{Ni^{III}(L1)(X)}]^{n+}$ in various concentrations of added fluoride ion in aqueous media. Conditions: 1.0 M ionic strength ($\mathrm{LiClO_4}$); (a) $[\mathrm{Ni}]_{\mathrm{tot}} = 2.60$ mM, $[\mathrm{F}]_{\mathrm{tot}} = 0$, and $[\mathrm{H^+}] = 0.1$ M; (b) $[\mathrm{Ni}]_{\mathrm{tot}} = 2.56$ mM, $[\mathrm{F}]_{\mathrm{tot}} = 25.6$ mM, and $[\mathrm{H^+}] = 0.1$ M; (c) $[\mathrm{Ni}]_{\mathrm{tot}} = 0.80$ mM, $[\mathrm{F}]_{\mathrm{tot}} = 80.0$ mM, and $[\mathrm{H^+}] = 0.1$ M.

behavior of HF. The anation reaction can thus be described in terms of eq 1–3. The equilibrium constants K_1 and K_2 may be

$$[\mathrm{Ni^{III}(L1)(H_2O)}]^{3+} + \mathrm{F^-} \overset{K_1}{\rightleftharpoons} [\mathrm{Ni^{III}(L1)(F)}]^{2+} + \mathrm{H_2O} \tag{1}$$

$$[\mathrm{Ni^{III}(L1)(H_2O)}]^{3+} + \mathrm{HF} \overset{K_2}{\rightleftharpoons} [\mathrm{Ni^{III}(L1)(F)}]^{2+} + \mathrm{H_3O^+} \tag{2}$$

$$\mathrm{HF} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{F^-} \tag{3}$$

$$K_1 = \frac{[\mathrm{Ni^{III}(L1)(F)}]}{[\mathrm{Ni^{III}(L1)(H_2O)}][\mathrm{F^-}]} \qquad K_2 = \frac{[\mathrm{Ni^{III}(L1)(F)}][\mathrm{H^+}]}{[\mathrm{Ni^{III}(L1)(H_2O)}][\mathrm{F^-}]}$$

determined from the relative concentrations of $[\mathrm{Ni^{III}(L1)(H_2O)}]^{3+}$ and $[\mathrm{Ni^{III}(L1)(F)}]^{2+}$ obtained from the ESR spectra of solutions containing variable amounts of added fluoride ions, at different hydrogen ion concentrations. Solving K_1 for known parameters, we obtain eq 4. From K_1, we can determine K_2 since $K_2 = K_1K_a$.

$$K = \frac{K_a + [\mathrm{H^+}]}{K_a[\mathrm{F}]_{\mathrm{tot}}\left\{\dfrac{[\mathrm{Ni^{III}(L1)(H_2O)}]}{[\mathrm{Ni^{III}(L1)(F)}]} - \dfrac{[\mathrm{Ni^{III}(L1)(H_2O)}]}{[\mathrm{F}]_{\mathrm{tot}}}\right\}} \tag{4}$$

Data used in the determination of the equilibrium constants are listed in Table VI. All values were measured in solutions with hydrogen ion concentrations greater than or equal to 0.05 M in order to eliminate the contribution of reaction 5, in which the

$$[\mathrm{Ni^{III}(L1)(H_2O)}]^{3+} \overset{K_H}{\rightleftharpoons} [\mathrm{Ni^{III}(L1)(OH)}]^{2+} + \mathrm{H^+} \tag{5}$$

hydroxy complex is formed. The $\mathrm{p}K_\mathrm{H}$ for reaction 5 is estimated to be ca. 3.5, based on the results of Meyerstein and co-workers[42] for $\mathrm{Ni^{III}}$(cyclam).

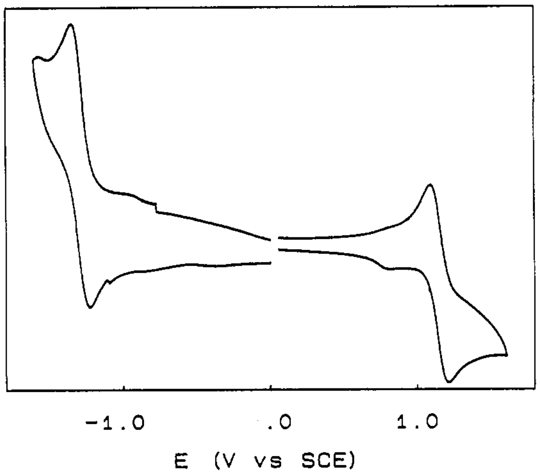

Figure 6. CV of [Ni(L1)] in $\mathrm{CH_3CN}$ containing 0.1 M $(n\text{-Bu})_4\mathrm{NPF_6}$. On this scale, the $\mathrm{Fc^{+/0}}$ couple is seen at +0.375 V.

The value for K_1 was found to be $(3.1 \pm 0.3) \times 10^4\ \mathrm{M^{-1}}$, indicating a very strong complex. For comparison, $\mathrm{Ni^{III}(cyclam)(H_2O)_2}^{3+}$, which could undergo two consecutive anation reactions, had equilibrium constants for the first anation of 210 $\mathrm{M^{-1}}$ and 34 $\mathrm{M^{-1}}$ with chloride and bromide ions, respectively.[43] Instead of a second anation step subsquent to the formation of the monohalide complex, a rearrangement to a five-coordinate $[\mathrm{Ni(cyclam)X}]^{2+}$ has been postulated.[44] The Ni(III) complex of [16]-ane$\mathrm{N_5}$ is also believed to be a five-coordinate species.[45] However the present results provide strong evidence for a six-coordinate Ni(III) species.

Electrochemistry. Cyclic voltammetry of the $\mathrm{Cu^{II}L1^{2+}}$ complex in $\mathrm{CH_3CN}$ shows a reversible wave at −0.935 V vs $\mathrm{Fc^{+/0}}$ corresponding to the $\mathrm{Cu^{2+/+}}$ couple. The $\mathrm{Cu^{I}(L1)^+}$ complex is therefore a strong reductant, but it is still approximately 400–500 mV less reducing than $\mathrm{Cu^{I}(cyclam)^+}$,[46] as a result of the π-acceptor properties of the sulfur ligand. The $E_{1/2}$ value found here is in sharp contrast with that of crown thioether complexes of copper. For example, the $E°$ values for $[\mathrm{Cu([9]\text{-}aneS_3)_2}]^{2+/+}$ and $[\mathrm{Cu([18]\text{-}aneS_6)}]^{2+/+}$ are +0.854 and 0.964 V vs NHE,[47] respectively. Thus the cyclam ring predominates over the π-acceptor ability of the sulfur donor in the redox properties of the $[\mathrm{Cu(L1)}]^{n+}$ complex.

Studies of the Ni(II) complex show a reversible wave for the $\mathrm{Ni^{3+/2+}}$ couple at 0.765 V vs SCE in aqueous medium (0.5 M

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(42) Jaacobi, M.; Meyerstein, D.; Lilie, J. *Inorg. Chem.* **1979**, *18*, 429.
(43) Haines, R. I.; McAuley, A. *Inorg. Chem.* **1980**, *19*, 719.
(44) Fairbank, M. G.; McAuley, A. *Inorg. Chem.* **1986**, *25*, 1233.
(45) Fabbrizzi, L.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2125.
(46) Fabbrizzi, L.; Poggi, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2191.
(47) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202.

Table VII. Electrochemical Data for $Ni^{3+/2+}$ Couples in an 0.5 M Sulfate Medium, vs SCE

complex	$E_{1/2}$, V	ref	complex	$E_{1/2}$, V	ref
[Ni(L1)]	0.76	this work	[Ni(L5)]	0.10	6
[Ni(cyclam)]	0.50	11	[Ni(L6)]	0.61	31
[Ni(L4)]	0.35	32	[Ni(L7)]	0.54	7

Li_2SO_4), and two reversible waves in CH_3CN (0.1 M (*n*-Bu)$_4$NPF$_6$), corresponding to the $Ni^{2+/+}$ couple (−1.675 V vs $Fc^{+/0}$) and the $Ni^{3+/2+}$ couple (0.775 V vs $Fc^{+/0}$) (see Figure 6). The difference between these waves (2.45 V) is in good agreement with that observed by other workers for a variety of nickel macrocyclic complexes.[48,49]

Direct comparisons can be made between [16]-aneSN$_4$ and L1 to determine the effect of the additional chelate ring on the stability of the complex. The $E_{1/2}$ of the $[Ni([16]\text{-aneSN}_4)]^{3+/2+}$ couple has been reported as 0.77 V vs SCE in 0.5 M Na_2SO_4,[11] which is identical with the value obtained in this work; thus, no effect is apparent. However, it is well documented that replacement of a secondary with a tertiary amine donor in a tetraaza ring destabilizes the Ni(III) state by approximately 100 mV.[49] Therefore the additional six-membered chelate ring imparts an extra stabilization of ≈200 mV on the Ni(III) complex over that expected for a di-*N*-alkyl derivative of [16]-aneSN$_4$. The extra stability for the Ni(III) state can be attributed to two factors.

(1) The additional chelate ring, creating a macrobicycle, leads to the cryptate effect.

(2) The formation of the 14-membered N_4 ring results in stronger in-plane interactions, thereby raising the energy of the e_g orbitals and making it easier to remove an electron from the metal center.

Both of these effects result in a greater ligand field being exerted on the metal center as observed in the UV-vis spectrum of the M(II)L1 complexes.

It is also of interest to compare the $E_{1/2}$ value for the $[Ni(L1)(X)]^{3+/2+}$ couple with that of other Ni^{II}(cyclam) derivatives with a single pendant arm. These are presented in Table VII. The series can be divided into two classes, those with negatively charged pendant arm donors (Ni(L4) and Ni(L5)) that have $E_{1/2}$ values lower than that of $Ni(cyclam)^{2+}$ due to their σ-donation ability and those with neutral donors that have $E_{1/2}$ values greater than that of $Ni(cyclam)^{2+}$. The order of the latter series reflects the π-donor ability of the axial ligand, stabilizing the Ni(III) center in the order imidazole > pyridine > thioether.

Acknowledgment. We thank, the NSERC (Canada) and the University of Victoria for support. D.G.F. was the recipient of a NSERC Post Graduate Fellowship.

Registry No. **1**, 118459-51-1; **2**, 118459-52-2; L1, 118459-53-3; [9]-aneSN$_2$, 88194-17-6; BH_3·THF, 14044-65-6; Cu(**2**)$(ClO_4)_2$, 118459-55-5; $[Cu(L1)](ClO_4)_2$, 118459-57-7; $[Ni(L1)](ClO_4)_2$, 118459-59-9; $[Ni(L1)]^{3+}$, 118459-60-2; Co^{3+}, 22541-63-5; NO^+, 14452-93-8; $[Ni^{II}(L1)H_2O]^{2+}$, 118459-63-5; $[Ni^{III}(L1)H_2O]^{3+}$, 118459-61-3; $[Ni^{III}(L1)F]^{2+}$, 118459-62-4; acrylonitrile, 107-13-1; glyoxal, 107-22-2.

Supplementary Material Available: Tables S1–S6, containing anisotropic temperature parameters, selected intermolecular distances, hydrogen atom fractional atomic coordinates and isotropic temperature parameters, interatomic distances and bond angles involving the hydrogen atoms, and mean planes calculations, and Table S9, containing experimental crystallographic data for both complexes (11 pages); Tables S7 and S8, listing calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

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[48] Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438.

[49] Barefield, E. K.; Freeman, G. M.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 552.

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Silver(II) Complexes of Hindered N-Heterocyclic Ligands. Electron Spin Resonance of Nitrato(6,6′-dimethyl-2,2′-bipyridine)silver(II) and Nitrato(2,9-dimethyl-1,10-phenanthroline)silver(II) Ions

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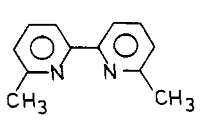
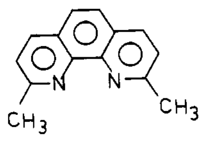
$AgLNO_3$ complexes, with L = 6,6′-dimethyl-2,2′-bipyridine (dmbp) and 2,9-dimethyl-1,10-phenanthroline (dmp), have been prepared and oxidized by peroxodisulfate to give silver(II) complex ions that have been isolated as the magnetically dilute salts $[AgLNO_3]PF_6{\cdot}NH_4PF_6$. The small *g* anisotropy combined with the relatively small ^{14}N hyperfine splittings in $AgLNO_3^+$ indicate extensive delocalization involving the nitrate ion. The ESR parameters and electronic transition energies are used to evaluate the bonding parameters in these and other silver(II) complexes of N-heterocyclic ligands. The redox stabilities of silver and copper complexes of hindered N-heterocycles are compared.

Introduction

It is well-known that the +2 oxidation state of silver is stabilized by N-heterocyclic ligands.[1] There have been several ESR studies on $Ag(py)_4^{2+}$,[2] $Ag(bpy)_2^{2+}$,[2c,3] and $Ag(phen)_2^{2+}$[2a,c] (py = pyridine, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline). Most of these studies have been confined to undiluted polycrystalline samples and frozen aqueous solutions. With the exception of those of $Ag(py)_4^{2+}$ doped into $Cd(py)_4(ClO_4)_2$,[2a,b] silver and nitrogen hyperfine splittings are (partially) resolved only in frozen solutions. It has been recently pointed out that dissociation of one of the ligands occurs in solution, which complicates the analysis of such spectra.[2a] There has been no report on the isolation and characterization of silver(II) complexes of the sterically hindered ligands 6,6′-dimethyl-2,2′-bipyridine and 2,9-dimethyl-1,10-phenanthroline, abbreviated as dmbp and dmp, respectively. These



dmbp



dmp

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[1] (a) Levason, W.; Spicer, M. D. *Coord. Chem. Rev.* **1987**, *76*, 45. (b) Po, H. N. *Ibid.* **1976**, *20*, 171. (c) McMillan, J. A. *Chem. Rev.* **1962**, *62*, 65.

[2] (a) Evans, J. C.; Gillard, R. D.; Lancashire, R. J.; Morgan, P. H. *J. Chem. Soc., Dalton Trans* **1980**, 1277. (b) Buch, T. *J. Chem. Phys.* **1965**, *43*, 761. (c) McMillan, J. A.; Smaller, B. *Ibid.* **1961**, *35*, 1698. (d) Hecht, H. G.; Frazier, J. B., III. *J. Inorg. Nucl. Chem.* **1967**, *29*, 613.

[3] (a) Halpern, T.; McKoskey, S. M.; McMillan, J. A. *J. Chem. Phys.* **1970**, *52*, 3526. (b) Thorpe, W. G.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3962.

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