

# Structure and Reactivity of the Nickel(II) Complex of a New Open-Chain Amine 6,6-Bis(4-amino-2-azabutyl)-1,4-diazacycloheptane and of the Nickel(III) Complex of Its Macrocyclic Analogue: Effects on the Reduction of Perchlorate Ion

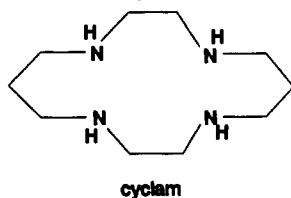
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Received March 22, 1990

The syntheses of the Ni(II) complex of the protonated form ( $\text{HL}_1^+$ ) of a new open-chain hexaaza ligand  $L_1$  ( $L_1 = 6,6\text{-bis(4-amino-2-azabutyl)-1,4-diazacycloheptane}$ ) and of the corresponding macrocyclic analogue ( $\text{H}_2\text{L}_3^{2+}$ ;  $L_3 = 2,5,9,12,16,19\text{-hexaaza-7-spiro[6.13]icosane}$ ) are described. In the presence of perchlorate and iodide, the Ni(II) complex of  $\text{HL}_1^+$  crystallizes with either one triiodide and two iodide ions or two triiodides and one iodide as counterions. The structure of  $[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_7\cdot\text{H}_2\text{O}$  ( $P\bar{1}$ , triclinic,  $a = 9.317$  (3) Å,  $b = 18.276$  (5) Å,  $c = 9.132$  (3) Å,  $\alpha = 99.43$  (3)°,  $\beta = 72.89$  (2)°,  $\gamma = 87.54$  (3)°,  $V = 1459$  Å<sup>3</sup>) has been refined to an  $R$  value of 0.0595 ( $R_w = 0.0624$ ) by using 2751 ( $I > 5\sigma(I)$ ) of the 3807 reflections collected. The nickel ion adopts a square-planar geometry with an average Ni-N distance of 1.935 (14) Å. Iodine donors on each triiodide ion lie about 3.5 Å on each side of the Ni(II) center. In acidic perchlorate media containing chloride, the Ni(II) complex of  $\text{H}_2\text{L}_3^{2+}$  crystallized as the *trans*-dichloronickel(III) complex. The structure of this Ni(III) species,  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$  (orthorhombic, noncentrosymmetric, space group  $P2_12_12_1$  (No. 19),  $a = 10.996$  (3) Å,  $b = 31.535$  (8) Å,  $c = 7.808$  (2) Å, has been refined to an  $R$  value of 0.0614 ( $R_w = 0.0628$ ) for 325 parameters by using 1249 reflections ( $I > 4\sigma(I)$ ) of the 1500 collected. The complex is pseudooctahedral with an average Ni-N distance of 1.983 (14) Å and a Ni-Cl distance of 2.415 (6) Å. The Ni(III) species shows an axial ESR spectrum with  $g_{\perp} = 2.17$  and  $g_{\parallel} = 2.02$ ;  $A_{\parallel} = 30$  G. The  $\text{Ni}^{2+/3+}$  couple is only quasi-reversible in 0.1 M lithium perchlorate or triflate media. However, in 1.0 M LiCl ( $[\text{H}^+] = 0.1$  M) a reversible wave at 0.57 V vs SCE was observed. Similar behavior is noted for the Ni(II) complex of the open-chain ligand  $\text{HL}_1^+$ . The two nitrogens of the 1,4-diazacycloheptane rings in the ligands  $L_1$  and  $L_3$  are not accessible to coordination. However, these nitrogens can be protonated and the presence of such secondary ammonium centers in the Ni(II) complexes of  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  enhances a redox process between perchlorate ion and the Ni(II) centers. The formation of both the triiodide anions in the preparation of the Ni(II) complexes of  $\text{HL}_1^+$  and of the oxidized center in *trans*-dichloronickel(III) species is also explained in terms of such a redox reaction.

## Introduction

During the past three decades complexes of transition-metal ions with the tetraaza ligand cyclam (cyclam = 1,4,8,11-tetraa-

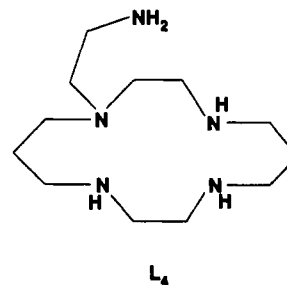


zacyclotetradecane) have been studied extensively.<sup>1-4</sup> The kinetic and thermodynamic stability imparted by this ligand has led to the study of metal ions in oxidation states not previously accessible.<sup>5,6</sup> However, in solution, Ni(II) complexes of cyclam-like ligands display predominantly square-planar geometry but do form 5- and 6-coordinate species in the presence of coordinating counterions or solvent molecules. Such extraneous ligands often show kinetic lability and facilitate redox processes that require a change in the coordination geometry as in the formation of octahedral Ni(III) ( $d^7$ ) species from square-planar Ni(II) ( $d^8$ ).<sup>5</sup>

In order to circumvent the need for additional ligands in the stabilization of Ni(III) species, a number of pendant-arm macrocyclic ligands bearing potentially coordinating groups have been prepared and studied. Several carbon- and nitrogen-substituted macrocycles bearing O, N, and S donors have been prepared and their complexes investigated for coordination geometry changes that accompany protonation of the donors and redox reactions involving metal centers.<sup>7-9</sup> Although the presence of an additional coordinating group in the pendant arm may enhance the metal-based redox processes thermodynamically, the competing reactions of the pendant arm between protonation and axial liga-

tion<sup>7,9,10</sup> have a pronounced effect on the electron-transfer reactions.<sup>7,8</sup>

Apart from functioning as an additional coordinating group, the donor atom on the pendant arm can also play the role of a binding site for substrates, which again may be competitive with the ligation process. There have been only a few cases identified in which the metal ion catalyzes the transformation of functional groups in the pendant arm.<sup>10</sup> Recently Fabbri et al.<sup>7</sup> have studied a redox reaction involving the Ni(II) center in the scorpion ligand  $L_4$  and perchlorate ion. This reaction is thought



to be mediated via binding and positioning of the perchlorate ion in the vicinity of the metal center as a result of the protonated amino group in the pendant arm.

In our recent studies of reactions of ethylenediamine with pentaerythritol derivatives, ligand  $L_1$  was isolated in 30-40% yield.<sup>11</sup> This report describes the cyclization of  $L_1$  to form  $L_3$  and the chemistry of the Ni(II) complexes of protonated forms of these ligands. Also reported is the reduction of perchlorate owing to the presence of protonated amines adjacent to the  $\text{NiN}_4$  plane of the Ni(II) complex ion.

## Experimental Section

Lithium perchlorate and triflate were prepared from commercially available lithium carbonate and perchloric and triflic acids, respectively, and crystallized twice from distilled water. Sodium perchlorate (BDH chemicals) was crystallized twice from water to remove salts of lower oxyacids of chlorine. All other chemicals used were of reagent grade and were used as received.

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UV-visible spectra were obtained in a quartz cell by using a Perkin-Elmer Lambda 4 instrument equipped with a Haake D8 thermostat. Temperature dependences of UV-visible spectra were obtained in 0.1 M sodium perchlorate solution over the temperature range of 10 to 50 °C ( $\pm 0.2$  °C). Cyclic voltammograms were recorded by using a PAR Model 273 potentiostat/galvanostat instrument. A three-electrode configuration was employed with Pt-bead electrodes as working and counter electrodes, and potentials were measured and reported with respect to the SCE. Chloride dependence of the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  couple for the macrocyclic complex was carried out by adding 20- $\mu\text{L}$  aliquots of 8 M LiCl to  $6 \times 10^{-5}$  mol of complex in 1 M lithium triflate ( $[\text{H}^+] = 0.1$  M) to produce chloride concentrations in the range of 0.01 to 0.1 M. From a plot of  $\log [\text{Cl}^-]$  vs  $E_{1/2}$ , the number of chloride ions complexing with the nickel centers were calculated.<sup>12</sup>

NMR spectra were obtained on a Bruker WM 250 instrument on  $\text{D}_2\text{O}$  solutions.  $\text{CH}_3\text{CN}$  was used as an internal standard, and chemical shifts are reported in parts per million relative to the nitrile carbon of  $\text{CH}_3\text{CN}$  (118.2 ppm relative to TMS). Microanalyses were performed by Canadian Microanalytical Services, Vancouver, BC, Canada.

**Synthesis.** The ligand  $\text{L}_1$  was obtained as a byproduct in the reaction of ethylenediamine with pentaerythryl derivatives. The preparation, isolation, and characterization of the chloride salts of the cations  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  and  $[\text{H}_6\text{L}_1]^{6+}$  have been described recently.<sup>11</sup> Cyclization of the ligand  $\text{L}_1$  to form the macrocyclic ligand  $\text{L}_3$  was carried out by a method similar to that of Tabushi et al.<sup>17</sup>

**6,6-Bis(4-amino-2-azabutyl)-1,4-diazacycloheptane ( $\text{L}_1$ ).** In a typical experiment, 5.35 g (10 mmol) of  $[\text{H}_6\text{L}_1]\text{Cl}_6 \cdot 4\text{H}_2\text{O}$  (see ref 11) was dissolved in 20 mL of water, and the solution was added to 100 mL of 35–40% NaOH solution. The free amine liberated as an oil was extracted into three 50-mL portions of pyridine. The pyridine extracts were dried over KOH pellets and decanted. This solution was concentrated under reduced pressure, and traces of pyridine were removed under vacuum to obtain the anhydrous amine (2.3 g) in near-quantitative yields.

**13,15-Dioxo-2,5,9,12,16,19-hexaaza-7-spiro[6.13]jicosane ( $\text{L}_2$ ).**  $\text{L}_1$  (2.0 g (8 mmol)) was dissolved in 800 mL of deaerated absolute ethanol in a 2-L Erlenmeyer flask, and 1.1 g (8.3 mmol) of dimethyl malonate in 100 mL of deaerated absolute ethanol was added. The reaction mixture was stirred magnetically at room temperature for 15 days under an atmosphere of nitrogen. The outlet of the vessel was connected to a trap filled with KOH pellets. After reaction the mixture was taken to dryness under reduced pressure, and traces of excess ester present in the viscous oily product were removed under vacuum. The resulting solid was digested in THF under reflux and filtered out under suction. The solid was further washed with a 1:1 mixture of THF and ethanol and dried under vacuum to yield 2.8 g of the crude product. The cyclic lactam  $\text{L}_2$  thus obtained was characterized by  $^{13}\text{C}$  NMR and mass spectroscopy and used for reduction without any further purification.  $^{13}\text{C}$  NMR (in  $\text{D}_2\text{O}$ ): 37.1 (s) (quaternary carbon); 168.6 (C=O); 53.5 (t), 52.8 (t), 52.2 (t), 50.7 (t), 47.6 (t), 41.6 (t) ( $-\text{CH}_2-$  carbons). MS:  $m/e = 313$  ( $\text{M} + 1$ , 90%).

**2,5,9,12,16,19-Hexaaza-7-spiro[6.13]jicosane ( $\text{L}_3$ ).** Reduction of the cyclic lactam  $\text{L}_2$  was carried out with  $\text{BH}_3 \cdot \text{THF}$ . A 2.8-g amount of the crude lactam was suspended in 100 mL of 1.0 M  $\text{BH}_3 \cdot \text{THF}$  solution in THF and the mixture kept stirred under an inert, moisture-free atmosphere at 40–50 °C for 12 h. The reaction mixture was cooled and excess reductant decomposed by slow addition of 10% NaOH solution. The solution was rotoevaporated to dryness. The resulting solid was digested with 100 mL of 1 M HCl, and the moisture was filtered to remove insoluble boric acid. The filtrate was adsorbed onto a Dowex-50X8 cation-exchange resin (column dimension 5  $\times$  35 cm). The column was washed with 2 L of water to remove any nonadsorbable material (in some instances there was evidence for a noncoordinating material as a byproduct) and then with 2 M HCl to remove any traces of lower amines. Further elutions with 2 L of 5 M HCl provided chloride solutions of cation  $[\text{H}_6\text{L}_3]^{6+}$ . The 5 M HCl elutions were concentrated to 20 mL, and 10 mL of ethanol was added. On standing, the solution yielded white crystals of the monohydrate of the hexahydrochloride salt of ligand  $\text{L}_3$  (1.5 g, yield of 32% based on the amine  $\text{L}_1$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{44}\text{N}_6\text{Cl}_6\text{O}$ : C, 30.16; H, 7.89; N, 15.08; Cl, 38.24. Found: C, 30.38;

**Table I.** Crystallographic Data

$[\text{Ni}(\text{HL}_1)](\text{I}_3)_2(\text{I}) \cdot \text{H}_2\text{O}$	
chem formula: $\text{NiN}_6\text{C}_{11}\text{H}_{31}\text{I}_7\text{O}$	fw: 1210.4
$a = 9.317$ (3) Å	space group $P\bar{1}$ (No. 2)
$b = 18.276$ (5) Å	$T = 22 \pm 2$ °C
$c = 9.132$ (3) Å	$\lambda = 0.71069$ Å
$\alpha = 99.43$ (3)°	$\rho_{\text{obs}} = 2.714$ g cm $^{-3}$
$\beta = 72.89$ (2)°	$\rho_{\text{calc}} = 2.748$ g cm $^{-3}$
$\gamma = 87.54$ (3)°	$\mu = 75.06$ cm $^{-1}$
$V = 1459.1$ Å $^3$	transm coeff = 0.153–0.270
$Z = 2$	$R(F_o) = 0.0595$ ; $R_w = 0.0624$
$[\text{NiCl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	
chem formula: $\text{NiC}_{14}\text{N}_6\text{H}_{34}\text{Cl}_5\text{O}_{10}$	fw: 682
$a = 10.996$ (3) Å	space group $P2_12_12_1$ (No. 19)
$b = 31.535$ (8) Å	$T = 22 \pm 2$ °C
$c = 7.808$ (2) Å	$\lambda = 0.71069$ Å
$\alpha = 90.0^\circ$	$\rho_{\text{obs}} = 1.685$ g cm $^{-3}$
$\beta = 90.0^\circ$	$\rho_{\text{calc}} = 1.673$ g cm $^{-3}$
$\gamma = 90.0^\circ$	$\mu = 12.77$ cm $^{-1}$
$V = 2707.34$ Å $^3$	transm coeff = 0.860–0.965
$Z = 4$	$R(F_o) = 0.0615$ ; $R_w = 0.0628$

H, 7.73; N, 14.94; Cl, 38.29.  $^{13}\text{C}$  NMR (in  $\text{D}_2\text{O}$ ): 37.9 (s) (quaternary carbon); 20.4 (t) ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ); 49.9 (t), 48.4 (t), 43.3 (t), 43.2 (t), 42.6 (t), 41.6 (t) ( $-\text{CH}_2\text{NH}-$  carbons).

$[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_5$ .  $[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{Cl}_5 \cdot 1/2\text{H}_2\text{O}$  (0.66 g (1.58 mmol)) was dissolved in 50 mL of water to form a pale violet solution. No satisfactory crystalline solids were produced in chloride media. However, a mixture of sodium perchlorate (>2 M) and sodium iodide (>3 M) yielded a bright golden yellow solution, which, on standing, slowly turned acidic and also dark brown owing to the liberation of iodine. Over a period of 2 weeks dark brown lustrous needles of  $\text{Ni}(\text{HL}_1)\text{I}_5$ , 1.58 g (yield  $\approx 35\%$ ), were formed. The crystals were filtered off under suction, washed in sequence with 50% aqueous ethanol and ether, and dried in air. The crystals thus obtained were found to be suitable for crystallography. Anal. Calcd for  $\text{C}_{11}\text{H}_{29}\text{N}_6\text{NiI}_5$ : C, 14.06; H, 3.09; N, 8.95; Ni, 6.25; I, 67.65. Found: C, 14.03; H, 3.12; N, 8.80; Ni, 6.42; I, 67.66.

$[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_7$ . A reaction mixture similar to that above was prepared and was acidified with sufficient HCl to produce a hydrogen ion concentration of about 0.1–0.2 M. The bright golden yellow solution of the square-planar Ni(II) complex described above turned greenish owing to some decomposition of the complex cation,  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$ . On standing, this solution formed dark brown lustrous rhombic crystals of  $\text{Ni}(\text{HL}_1)\text{I}_7$  in about 25% yield. These crystals were used in the structure determination. Anal. Calcd for  $\text{C}_{11}\text{H}_{29}\text{N}_6\text{NiI}_7$ : C, 12.82; H, 2.38; N, 6.9; I, 73.00. Found: C, 12.79; H, 2.40; N, 6.79; I, 72.53.

$[\text{Ni}^{\text{II}}(\text{HL}_3)]\text{Cl}_3 \cdot \text{H}_2\text{O}$ .  $[\text{H}_6\text{L}_3]\text{Cl}_6 \cdot 3\text{H}_2\text{O}$  (0.56 g, 1 mmol) was dissolved in 15 mL of water in a 100-mL beaker, and a solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.24 g, 1 mmol) in 10 mL of water was added. This solution was maintained at 60 °C on a hot plate, and solid sodium carbonate was added in small amounts to neutralize the liberated acid. The final pH of the solution was adjusted to 7, and the resulting complex solution was evaporated to dryness to remove excess sodium chloride. Final traces of sodium chloride were removed by repeated extraction with 90% ethanol, and the chloro complex was obtained as a pale violet crystalline powder. Yields were nearly quantitative. Anal. Calcd for  $\text{C}_{13}\text{H}_{35}\text{N}_6\text{NiCl}_3\text{O}$ : C, 35.95; H, 7.47; N, 17.97. Found: C, 35.82; H, 7.31; N, 17.94.

As an alternative procedure, the sodium chloride can be removed by selectively extracting the chloro complex with chloroform in a Soxhlet apparatus. Attempts to precipitate the complex as the perchlorate salt were unsuccessful.

**trans- $[\text{Ni}^{\text{II}}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .** The Ni(II) complex  $[\text{Ni}^{\text{II}}(\text{HL}_3)]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (0.3 g, 1.06 mmol) was dissolved in 50 mL of water in a 250-mL beaker, and the solution was saturated with sodium perchlorate. To this solution were added 25 mL of absolute ethanol and 25 mL of concentrated hydrochloric acid, and the mixture was allowed to stand for 2–3 days. The solution gradually turned greenish yellow, and straw brown crystals of the *trans*-dichloronickel(III) complex (0.3 g) precipitated out. Yield: 68%. The recovery of the complex from the mother liquor was not efficient owing to continuous decomposition of the complex and the presence of a large excess of salt. Anal. Calcd for  $\text{C}_{14}\text{H}_{38}\text{N}_6\text{NiCl}_5\text{O}_{10}$ : C, 24.48; H, 5.53; N, 12.24. Found: C, 24.48; H, 5.53; N, 12.00.

**Caution!** Transition-metal perchlorates are hazardous and may explode. Only small quantities should be prepared and great care taken.

**Crystallography.** Experimental parameters for the two crystal structures are listed in Table I. Crystals of the complex  $[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_7$  were prepared as described. The *trans*-dichloronickel(III) complex of  $\text{H}_2\text{L}_3^{2+}$  was recrystallized from 1.0 M  $\text{HClO}_4$  saturated with NaCl. Crystals

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**Table II.** Fractional Atomic Coordinates and Temperature Parameters for  $[\text{Ni}(\text{HL}_1)](\text{I}_3)_2(\text{I})\cdot\text{H}_2\text{O}^a$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> , Å <sup>2</sup>
I(1)	9445 (14)	29550 (8)	20658 (13)	640 (5)
I(2)	-18913 (13)	28314 (6)	14115 (11)	473 (4)
I(3)	-49297 (14)	28039 (7)	10887 (13)	617 (5)
I(4)	54520 (13)	9560 (6)	38313 (12)	512 (5)
I(5)	24614 (12)	7804 (6)	34109 (11)	461 (4)
I(6)	-4010 (14)	5596 (8)	28466 (16)	711 (6)
I(7)	26587 (25)	54468 (9)	21187 (16)	1084 (9)
Ni(1)	53066 (23)	18826 (10)	-25444 (20)	408 (8)
O(1)	7477 (19)	877 (7)	-339 (15)	91 (7)
N(1)	7420 (17)	1588 (8)	-3015 (16)	58 (6)
N(2)	5921 (14)	2789 (6)	-3319 (13)	41 (5)
N(3)	3174 (14)	2159 (6)	-1982 (13)	39 (5)
N(4)	4781 (18)	975 (7)	-1739 (16)	63 (6)
N(5)	3284 (27)	4616 (9)	-1698 (20)	99 (10)
N(6)	3050 (22)	4328 (8)	-4687 (18)	82 (8)
C(1)	8330 (20)	2182 (11)	-3423 (21)	62 (8)
C(2)	7532 (20)	2621 (10)	-4329 (19)	58 (7)
C(3)	4963 (17)	3144 (8)	-4144 (16)	42 (6)
C(4)	3280 (19)	3296 (8)	-3233 (16)	45 (6)
C(5)	2521 (18)	2580 (9)	-2974 (18)	48 (6)
C(6)	2320 (20)	1462 (9)	-1806 (20)	59 (7)
C(7)	3153 (22)	1043 (9)	-894 (19)	62 (8)
C(8)	2969 (20)	3814 (7)	-1607 (17)	50 (7)
C(9)	2053 (65)	5041 (17)	-2064 (33)	267 (37)
C(10)	2162 (38)	5010 (13)	-3672 (26)	129 (16)
C(11)	2475 (23)	3625 (10)	-4289 (19)	63 (8)

<sup>a</sup> Estimated standard deviations are given in parentheses. Coordinates  $\times 10^4$ , where  $n = 5, 5, 4, 4,$  and  $4$  for I, Ni, O, N, and C. Temperature parameters  $\times 10^4$ , where  $n = 4, 4, 3, 3,$  and  $3$  for I, Ni, O, N, and C.  $U_{\text{eq}}$  = the equivalent isotropic temperature parameter.  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j)$ .  $T = \exp(-8\pi^2 U_{\text{iso}} (\sin^2 \theta) / \lambda^2)$ .

**Table III.** Interatomic Distances (Å) for  $[\text{Ni}(\text{HL}_1)](\text{I}_3)_2(\text{I})\cdot\text{H}_2\text{O}^a$ 

I(2)–I(1)	2.885 (2)	N(1)–Ni(1)	1.920 (15)
I(3)–I(2)	2.933 (2)	N(2)–Ni(1)	1.949 (12)
I(5)–I(4)	2.946 (1)	N(3)–Ni(1)	1.923 (12)
I(6)–I(5)	2.894 (2)	N(4)–Ni(1)	1.946 (13)

<sup>a</sup> Estimated standard deviations are given in parentheses.

were mounted inside a Lindemann tube by using epoxy resin and the unit cell dimensions and space group determined by use of Weissenberg and precession photography, after which the crystals were transferred to a Picker 4-circle diffractometer automated with a PDP11/10 computer.

**$[\text{Ni}(\text{HL}_1)]\text{I}_3$ .** The unit cell was refined by using 24 pairs of reflections in the  $2\theta$  range  $17$ – $39^\circ$ . The intensity measurements were obtained by scanning in the  $\theta/2\theta$  mode using 200 steps of  $0.01^\circ$  in  $2\theta$  counting for 0.25 s per step. Background counting was introduced for 25 s at the end of each scan. A set of three standard reflections preceded each batch of 50 measurements. No decay of the standards was observed.

The phase problem was solved by use of MULTAN.<sup>13</sup> The atomic scattering factors used were those included in the compilation of the Cromer and Mann<sup>14</sup> together with the Ni  $f$ -curve from ref 15. The program used for absorption correction was a local modification of an existing procedure.<sup>16</sup> Completion and refinement of the structure were carried out by using difference electron density maps and least-squares techniques. Of the 3807 observed reflections, 2751 ( $I > 5\sigma(I)$ ) were used. The refinement was converged to a final  $R(F_o)$  value of 0.0595 ( $R_w = 0.0624$ ). The Fourier difference map had a maximum peak height of  $1.88 \text{ e}/\text{\AA}^3$ . All non-hydrogen atoms were refined anisotropically.

**$[\text{Ni}^{III}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ .** The unit cell was refined with 18 pairs of reflections in the  $2\theta$  range  $17$ – $37^\circ$ . The intensity measurements were obtained by scanning in the  $\theta/2\theta$  mode using 128 steps of  $0.01^\circ$  in  $2\theta$  counting for 0.5 s per step. Background counting was introduced for 34 s at the end of each scan. A set of three standard reflections preceded each batch of 50 measurements, and no significant decay of these standards was observed. The structure was refined with 1249 ( $I > 4\sigma(I)$ ) of the 1500 reflection collected by using least-squares techniques, and the solution of the phase problem was achieved by using MULTAN.<sup>13</sup> The refinement was converged to a final  $R(F_o)$  value of 0.0615 ( $R_w = 0.0628$ ) with a maximum shift/csd of 0.027. The residual electron density was  $0.5 \text{ e}/\text{\AA}^3$ .

## Results

Synthesis and characterization of ligands  $\text{L}_1$  and  $\text{L}_3$  and of complexes involving nickel and (noncoordinating) protonated forms

**Table IV.** Bond Angles (deg) for  $[\text{Ni}(\text{HL}_1)](\text{I}_3)_2(\text{I})\cdot\text{H}_2\text{O}^a$ 

I(3)–I(2)–I(1)	173.7 (0)	C(1)–N(1)–Ni(1)	112.1 (11)
I(6)–I(5)–I(4)	177.1 (0)	C(2)–N(2)–Ni(1)	106.8 (9)
N(2)–Ni(1)–N(1)	86.4 (6)	C(3)–N(2)–Ni(1)	118.1 (9)
N(3)–Ni(1)–N(1)	177.3 (5)	C(3)–N(2)–C(2)	111.2 (12)
N(3)–Ni(1)–N(2)	95.7 (5)	C(5)–N(3)–Ni(1)	121.1 (9)
N(4)–Ni(1)–N(1)	91.2 (6)	C(6)–N(3)–Ni(1)	109.6 (9)
N(4)–Ni(1)–N(2)	177.2 (6)	C(6)–N(3)–C(5)	106.5 (12)
N(4)–Ni(1)–N(3)	86.7 (6)	C(7)–N(4)–Ni(1)	109.7 (10)

<sup>a</sup> Estimated standard deviations are given in parentheses.

**Table V.** Fractional Atomic Coordinates and Temperature Parameters for  $[\text{Ni}^{III}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}^a$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> , Å <sup>2</sup>
Ni(1)	33404 (22)	32838 (7)	68409 (32)	243 (8)
Cl(1)	45782 (47)	31091 (16)	44080 (68)	351 (19)
Cl(2)	20597 (49)	34425 (16)	92951 (65)	384 (20)
Cl(3)	24039 (47)	46974 (14)	86632 (65)	356 (18)
Cl(4)	32937 (51)	17115 (18)	33286 (82)	484 (20)
Cl(5)	13480 (67)	5479 (24)	77437 (103)	715 (29)
O(1)	2404 (14)	1986 (5)	2650 (26)	86 (8)
O(2)	4316 (17)	1683 (7)	2336 (31)	111 (10)
O(3)	2793 (16)	1306 (5)	3575 (30)	103 (9)
O(4)	3665 (19)	1851 (7)	4973 (26)	117 (10)
O(5)	1480 (23)	1005 (6)	7433 (31)	153 (13)
O(6)	1599 (28)	356 (10)	6175 (41)	199 (17)
O(7)	153 (15)	459 (6)	8286 (30)	107 (10)
O(8)	2109 (23)	414 (11)	8942 (50)	231 (21)
O(9)	4119 (15)	551 (5)	1897 (24)	80 (7)
O(10)	3983 (17)	1327 (5)	8350 (33)	112 (10)
N(1)	1838 (13)	3280 (5)	5447 (18)	27 (5)
N(2)	3127 (14)	2669 (4)	7170 (20)	31 (6)
N(3)	4845 (13)	3309 (5)	8220 (20)	30 (5)
N(4)	3560 (13)	3911 (4)	6528 (20)	27 (5)
N(5)	659 (14)	4627 (4)	5201 (19)	30 (6)
N(6)	796 (14)	4288 (5)	1550 (21)	32 (6)
C(1)	1964 (17)	4010 (5)	4139 (26)	25 (7)
C(2)	1796 (17)	3523 (5)	3783 (23)	21 (6)
C(3)	1571 (19)	2811 (5)	4995 (28)	38 (8)
C(4)	1868 (18)	2570 (5)	6631 (27)	35 (7)
C(5)	3396 (20)	2479 (6)	8889 (26)	43 (8)
C(6)	4708 (23)	2558 (7)	9284 (34)	66 (11)
C(7)	4917 (22)	3046 (7)	9751 (27)	49 (9)
C(8)	5062 (17)	3754 (6)	8638 (26)	35 (8)
C(9)	4870 (18)	4014 (6)	7007 (28)	40 (8)
C(10)	3273 (18)	4092 (5)	4852 (27)	33 (8)
C(11)	956 (19)	4164 (5)	5335 (27)	34 (8)
C(12)	-310 (17)	4705 (6)	3855 (28)	33 (8)
C(13)	130 (18)	4690 (6)	2006 (27)	33 (8)
C(14)	2027 (18)	4220 (5)	2376 (25)	29 (7)

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

**Table VI.** Selected Interatomic Distances (Å) for  $[\text{Ni}^{III}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}^a$ 

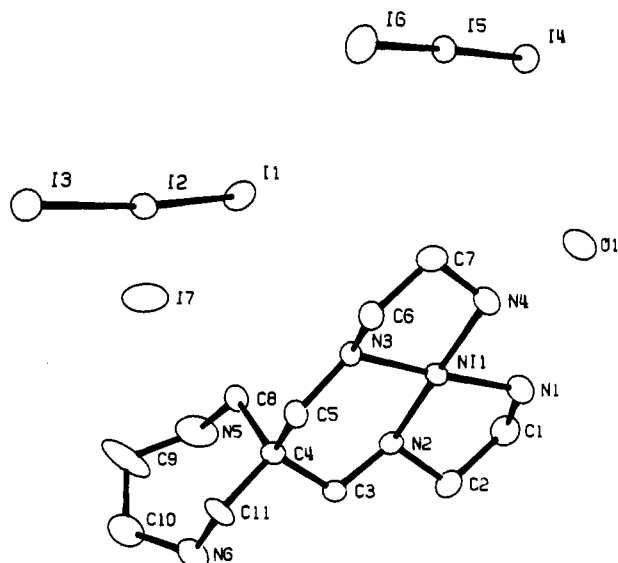
Cl(1)–Ni(1)	2.401 (6)	N(2)–Ni(1)	1.970 (14)
Cl(2)–Ni(1)	2.430 (6)	N(3)–Ni(1)	1.976 (14)
N(1)–Ni(1)	1.978 (14)	N(4)–Ni(1)	2.007 (14)

<sup>a</sup> Estimated standard deviations are given in parentheses.

**Table VII.** Bond Angles (deg) for  $[\text{Ni}^{III}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}^a$ 

Cl(2)–Ni(1)–Cl(1)	178.5 (2)	N(3)–Ni(1)–N(1)	178.1 (7)
N(1)–Ni(1)–Cl(1)	92.1 (4)	N(3)–Ni(1)–N(2)	93.9 (6)
N(1)–Ni(1)–Cl(2)	87.2 (4)	N(4)–Ni(1)–Cl(1)	93.5 (5)
N(2)–Ni(1)–Cl(1)	86.8 (5)	N(4)–Ni(1)–Cl(2)	87.9 (4)
N(2)–Ni(1)–Cl(2)	91.8 (5)	N(4)–Ni(1)–N(1)	92.3 (6)
N(2)–Ni(1)–N(1)	88.1 (6)	N(4)–Ni(1)–N(2)	179.5 (6)
N(3)–Ni(1)–Cl(1)	88.0 (5)	N(4)–Ni(1)–N(3)	85.8 (6)
N(3)–Ni(1)–Cl(2)	92.7 (5)		

<sup>a</sup> Estimated standard deviations are given in parentheses.



**Figure 1.** ORTEP diagram of  $[\text{Ni}^{\text{II}}(\text{HL}_1)](\text{I})_3$  complex, showing 25% thermal ellipsoids and atomic labeling for the non-hydrogen atoms.

**Table VIII.** UV-Visible Spectroscopic Data for Ni(II) and Ni(III) Complexes of  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  in Various Media at 25 °C

complex	solvent	abs max, nm ( $\epsilon$ , $\text{mol}^{-1} \text{cm}^{-1}$ )
$[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{Cl}_3 \cdot 1/2\text{H}_2\text{O}$	0.1 M $\text{NaClO}_4$	790 (3), 747 (35), 538 (4), 448 (3), 348 (7)
	80% ethanol	740 (3), 714 (3), 548 (5), 351 (10)
$[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_5$	6 M $\text{NaClO}_4$	448 (44)
	100% ethanol	360 (2600), 290 (5000), 245 (2500), 216 (2300)
$[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_7$	100% ethanol	360 (4000), 290 (7300), 245 (1200), 216 (1500)
	1.0 M $\text{Cl}^-$	228, 276, 310 (sh)
$[\text{Ni}^{\text{II}}(\text{HL}_3)]\text{Cl}_3$	0.1 M $\text{NaClO}_4$	450 (38)
	5.0 M $\text{NaClO}_4$	450 (82)
$[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)](\text{Cl})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	1.0 M $\text{HClO}_4$	358 (sh) (3200), 303 (6700), 219 (8000)

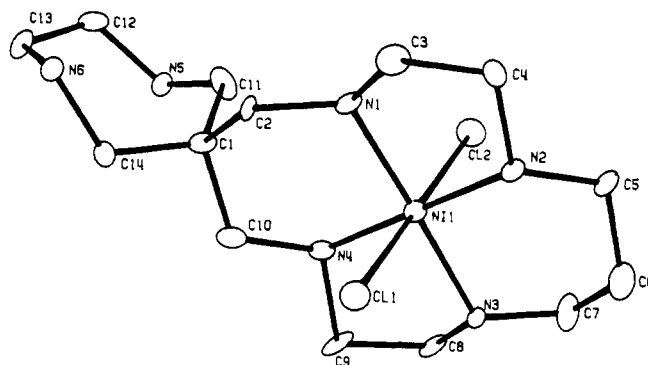
**Table IX.** Thermodynamic Parameters for the Square-Planar  $\rightleftharpoons$  Octahedral Equilibrium of Various Ni(II) Complexes in 0.1 M  $\text{NaClO}_4$

ligand	% square planar	$\Delta G$ , $\pm 0.3$ kcal/mol	$\Delta H$ , $\pm 0.3$ kcal/mol	$\Delta S$ , $\pm 0.6$ eu	ref
2,3,2-tet	22.0	2.21	3.4	9.0	31
cyclam	71.0	-0.50	5.4	20.0	31
$\text{HL}_1$	7.0	1.51	4.4	9.7	this work
$\text{HL}_3$	58.0	-0.10	1.3	4.6	this work

of these amines have been achieved. The structures (Figures 1 and 2) of  $[\text{Ni}^{\text{II}}(\text{HL}_1)]\text{I}_7$  and  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$  have been determined. Relevant data are presented in Tables II–VII. Temperature dependences of the UV-visible spectra of the nickel(II) complexes were monitored to provide information on square-planar–octahedral equilibria (Tables VIII and IX). ESR and electrochemical studies have also been made. Of interest is the observation that, in the presence of chloride, both in air and in the rigorous absence of oxygen, the counterion  $\text{ClO}_4^-$  is reduced, probably via a Ni(III) intermediate. If  $\text{I}^-$  is present in solution, oxidation of this ion leads to the formation of  $\text{I}_3^-$  observed in the crystalline products formed.

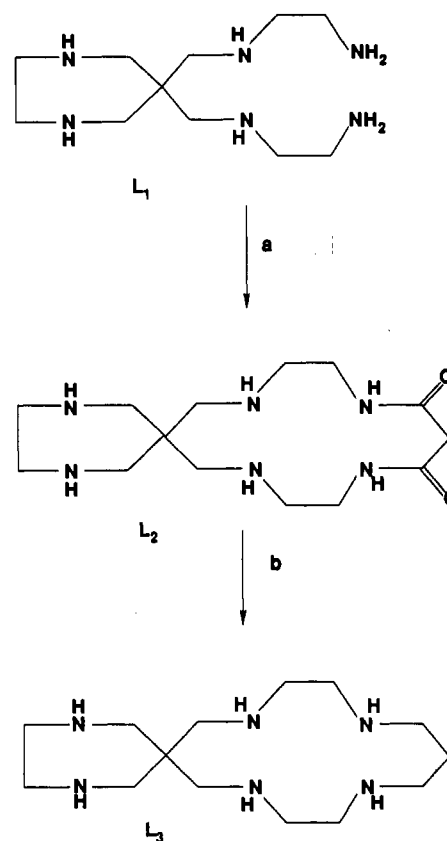
### Discussion

**Synthesis.** The macrocyclic ligand  $\text{L}_3$  was prepared by reaction of diethyl malonate with the amine  $\text{L}_1$  by a method similar to that of Tabushi et al.<sup>17</sup> to obtain the cyclic lactam  $\text{L}_2$ , which was subsequently reduced with  $\text{BH}_3 \cdot \text{THF}$  to obtain  $\text{L}_3$  (see Scheme I). The low yield (15%) of the cyclized product was due to instability of the free amine  $\text{L}_1$  under the conditions used (reflux



**Figure 2.** ORTEP diagram of the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$ , showing 25% thermal ellipsoids with atomic labeling for the non-hydrogen atoms.

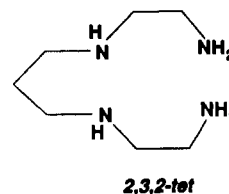
**Scheme I.** Synthesis of Macrocyclic Ligand  $\text{L}_3^a$



<sup>a</sup>Conditions: (a) diethyl malonate, ethanol/25 °C/15 days; (b)  $\text{BH}_3 \cdot \text{THF}/\text{THF}$ , reflux for 20 h.

in ethanol for periods of greater than 24 h). Cyclization reactions of  $\text{L}_1$  under these conditions often led to a spiro azetidine derivative (see ref 11) and rarely was the desired cyclized product isolated. However, if cyclization of  $\text{L}_1$  with diethyl malonate was allowed to proceed at room temperature over a period of 15 days, the cyclic lactam  $\text{L}_2$  was obtained in about 50–60% yield. This white powder was characterized by  $^{13}\text{C}$  NMR spectroscopy and reduced to  $\text{L}_3$  without further purification. A polymeric noncoordinating material was the only byproduct.

Ligands  $\text{L}_1$  and  $\text{L}_3$  are related structurally to 2,3,2-tet and cyclam, whose metal complexes have been well documented.<sup>6,18</sup>



The presence of a 1,4-diazacycloheptane ring in  $L_1$  and  $L_3$  has a significant impact on the stability and reactivity of the corresponding Ni(II) and Ni(III) complexes. Differences observed between the Ni(II) complexes of  $L_1$  and 2,3,2-tet and that of  $L_3$  and cyclam can be attributed to two factors. The 1,4-diazacycloheptane ring is formed on the central methylene carbon of the propylene bridge to form a spiro (quaternary) carbon. As a result, the carbon frame bearing the four donor nitrogens experiences the effect of a *gem*-dialkyl lock (Thorpe-Ingold effect),<sup>19,20</sup> which reduces significantly the flexibility of the propylene chain. This, in turn, also influences the flexibility of the ethylene chains. As a result, the N-donors may be predisposed at appropriate sites to bind the metal ion. This kind of conformational rigidity imposed by a ring substituent is more prominent in the open-chain amine  $L_1$  than in the macrocyclic ligand  $L_3$ . The other important aspect is related to the presence of the two secondary nitrogens in the 1,4-diazacycloheptane ring. These nitrogens are not accessible to coordination. However, they may be protonated to form secondary ammonium ions, which might result in possible electrostatic repulsion with the metal ion. Also, such protonation can play the role of enhancing anion binding either through ion-pairing or hydrogen-bonding interactions. This latter effect is discussed in detail in the context of a redox reaction between perchlorate and Ni(II) ion in the complexes of  $HL_1^+$  and  $H_2L_3^{2+}$ .

Although both the open-chain amine ligands  $L_1$  and 2,3,2-tet form the sequence of 5,6,5-membered chelate rings favored thermodynamically<sup>21-23</sup> in their nickel complexes,  $NiHL_1^{3+}$  is kinetically more stable than the complex with 2,3,2-tet. There is significantly greater acid stability of both the Ni(II) and Ni(III) complexes of  $HL_1^+$ . Oxidation of the Ni(II) complex of 2,3,2-tet, even with neutral reagents such as sodium peroxydisulfate, does not produce a Ni(III) complex that may be characterized. This can be attributed to the lability of terminal primary amines. However, the complex cation  $[Ni^{III}(HL_1)]^{3+}$  on oxidation with the peroxydisulfate anion or Co(III) ion in acidic media provides a Ni(III) cation that is sufficiently stable ( $t_{1/2} \approx$  several minutes) to identify the species by common spectroscopic techniques (vide infra). The increased stability is probably the result of the kinetic inertness to substitution of the in-plane primary nitrogens. The presence of the 1,4-diazacycloheptane ring, which controls the flexibility of the five- and six-membered chelate rings, is thus a factor.

**Structures of Complexes.** The ORTEP diagrams of the complex  $[Ni^{II}HL_1](I_3)_2(I)$  and of the cation  $[Ni^{III}Cl_2(H_2L_3)]^{3+}$  are shown in Figures 1 and 2 with the atomic-labeling scheme for the non-hydrogen atoms. The fractional atomic coordinates, bond lengths, and bond angles are included in Tables II-IV and V-VII, respectively. All other Tables S1-S7 are available as supplementary material.

**Structure of  $[Ni^{II}(HL_1)](I_3)_2(I) \cdot H_2O$ .** In this complex, the nickel atom and the four nitrogens are coplanar and the ligand adopts the most stable *trans*-III configuration, as suggested by Bosnich et al.<sup>24</sup> In the cation, the six-membered chelate rings adopt a chair conformation and the five-membered chelate rings adopt a *gauche* conformation, which implies a minimum strain in the carbon skeleton. The nitrogens in the 1,4-diazacycloheptane ring are not directly involved in coordination.

Each cation is associated with three anions, but the complex is not ESR active. This suggests that one of the nitrogens in the 1,4-diazacycloheptane ring must be protonated in order to satisfy electroneutrality. Both triiodide ions are located in the unit cell on one side of the  $NiN_4$  plane. The unique iodide ion is also

positioned on the same side of the cation. Neither triiodide ion is bonded directly to the nickel. The shortest distances are those between the metal center and I(3') and I(4') of the triiodide ions (which are related by symmetry to I(3) and I(4)) at 3.406 and 3.424 Å, respectively. Each of these donors occupies a near-octahedral site (angles  $N1-Ni-I(3)' = 92.25^\circ$  and  $N1-Ni-I(4)' = 89.07^\circ$ ). The  $I(3)'-Ni-I(3)'$  angle is  $178.6^\circ$ . The distances are considered too long for formal bonding, but the situation resembles that in the structure of  $Ni(\text{cyclam})(I)_2$ , where long Ni-I distances were observed.<sup>25</sup> Although the deviation from axial symmetry found in the present structure is slight, the significant Ni-I distances are a good indication that the Ni(II) center adopts a (low-spin  $d^8$ ) square-planar geometry. This is further confirmed by the average Ni-N bond distances (1.935 (14) Å), which are comparable to those found in many square-planar complexes.<sup>26</sup>

The water molecule in the lattice is hydrogen-bonded to the primary amine N(1) (2.962 Å). The remaining iodide, I(7), is positioned near one of the two nitrogens, N(5), of the 1,4-diazacycloheptane ring at 3.434 Å. Any interaction with N(6) appears to be much weaker. If the criterion for hydrogen bonding is based on the sum of the Van der Waals radii<sup>27</sup> (3.65 Å), then only the interaction between N(5) and I(7) constitutes a moderate hydrogen bond, consistent with only one of the two nitrogens, N(5), in the 1,4-diazacycloheptane ring being protonated. The distance between N(5) and N(6) is 2.77 Å. However, since the hydrogen atoms were not found from structural analysis, the position of the hydrogen and the linearity of the N-H...I interaction are not known.

**Structure of  $[Ni^{III}Cl_2(H_2L_3)](Cl)(ClO_4)_2 \cdot 2H_2O$ .** In this complex cation, the Ni(III) center adopts a tetragonally elongated octahedral geometry. The nickel and the four nitrogen atoms are in a square-planar geometry with two chloride ions occupying the *trans* axial positions. The average Ni-N distance is 1.983 (14) Å typical of similar bonds in octahedral Ni(III) complexes.<sup>28,29</sup> The Ni-Cl bond distances are 2.415 (6) Å, somewhat shorter than the Ni-Cl distance (2.451 (1) Å) in the *trans*-dichloronickel(III) cyclam complex.<sup>28</sup> As indicated earlier, from the conformations of the chelate rings it is concluded that the coordinated nitrogens adopt a *trans*-III configuration. In the 1,4-diazacycloheptane ring both nitrogens, N(5) and N(6), are protonated, which accounts for the three anions per complex cation found in the crystal lattice. The distance between these two nitrogens (N(5) and N(6)) is 3.048 Å and considerably longer than that in the Ni(II) complex of  $HL_1^+$  (2.77 Å).

In the three cations  $[H_6L_1]^{6+}$ ,  $[Ni^{II}(HL_1)]^{3+}$ , and  $[Ni^{III}Cl_2(H_2L_3)]^{3+}$ , the common structural feature is the presence of a 1,4-diazacycloheptane ring. On the basis of simple electrostatic considerations and in the absence of any other influences, the distance between the nitrogens in the 1,4-diazacycloheptane ring should depend on only the extent of protonation. This is observed in the series. In the ligand hydrochloride  $[H_6L_1]^{6+}Cl_6^{11-}$  and in the  $[Ni^{III}Cl_2(H_2L_3)]^{3+}$  cation both nitrogens in the seven-membered rings are protonated with distances between these centers of 3.20 and 3.048 Å, respectively. However, in the  $[Ni^{II}(HL_1)]^{3+}$  cation, where only one of the ring nitrogens in the ring is protonated, there is a marked decrease to a distance of 2.77 Å.

Two other factors that may play a role in reactivity are the nature of the nitrogens forming the tetraaza unit and the extent of ion pairing or hydrogen bonding involving solvents and anions. In the cation  $[H_6L_1]^{6+}$  all six nitrogens are protonated and hence the electrostatic repulsion between the nitrogens in the open-chain arm tends to widen the angle subtended by these two arms at the spiro carbon. As a result, the value of  $116.7 (1.3)^\circ$  is observed

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compared to an ideal tetrahedral angle of  $109.4^\circ$ . However, widening of this exterior angle does not influence significantly the interior angle within the ring. This angle at the spiro carbon is  $110.2 (1.2)^\circ$ , which is typical of the value expected for a cyclic compound. In the cations  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  and  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$ , where all four nitrogens in the tetraaza unit are coordinated to the nickel centers, the exterior angles,  $112.7 (1.2)$  and  $109.4 (1.4)^\circ$ , respectively, are closer to the tetrahedral value. However, the interior angles are  $112.2 (1.2)$  and  $116.5 (1.5)^\circ$ .

In the cation  $[\text{H}_6\text{L}_3]^{6+}$ , the two protonated amines in the 1,4-diazacycloheptane ring are bridged to similar nitrogens of the adjacent cations through waters of crystallization present in the lattice.<sup>11</sup> Hence, the overall reduction of charge, if any occurs, is through interaction with the dipole of the water molecules. In the cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  an iodide ion (I(7)) shows a weak interaction with one of the nitrogens (N(5)) and there is a hydrogen bond to the water of crystallization via N(1). However, in the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$ , the nitrogen N(5) in the 1,4-diazacycloheptane ring is interacting with a perchlorate and a chloride ion and also with a water molecule at distances of 3.012, 3.243, and 2.884 Å, respectively. The nitrogen N(6) is hydrogen-bonded only to O(10) of a water molecule, the N(6)⋯O(10) distance being 2.784 Å. Also, in the Ni(III) cation, two chloride ions are strongly bound to the nickel center and hence the net charge on the tetraaza unit is only +1 compared to a +2 charge in the square-planar Ni(II) complex. Thus, any charge on the seven-membered ring nitrogens may be dissipated in the lattice structure, permitting a closer approach. It will be interesting to obtain structural data on the Ni(II) complex of  $\text{L}_3$  (preferably both of the square-planar and octahedral forms) in order to conclude on the effect of both geometry and d-electron configuration. Since the hydrogen atoms were not refined during structural analysis, it is also not possible to conclude that a hydrogen atom might be bridging the nitrogens in the seven-membered ring in the Ni(III) complex cation. However, such a possibility cannot be ruled out.

**UV-Visible Spectroscopic Studies.** UV-visible spectra of both the Ni(II) and Ni(III) complexes of  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  were obtained in various media, and spectroscopic data are presented in Table VIII.

The  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  cation in aqueous media shows two bands around 450 and 540 nm, which may be assigned to the square-planar and octahedral forms, respectively. The behavior of the cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  is similar. However, in this case, the two bands corresponding to the square-planar and octahedral forms are overlapping and hence the less intense band corresponding to the octahedral form is not seen clearly.

The square-planar and octahedral forms of the Ni(II) species are interconvertible, which is a characteristic behavior observed in many tetraaza Ni(II) complexes.<sup>30</sup> This square-planar  $\rightleftharpoons$  octahedral equilibrium is dependent on temperature, ionic strength, and also on the nature of solvent. The temperature dependence of the square-planar  $\rightleftharpoons$  octahedral equilibrium for the Ni(II) complexes of both  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  were studied in 0.1 M sodium perchlorate media, and the thermodynamic parameters derived were compared with those of 2,3,2-tet and cyclam complexes (see Table IX). These data indicate that under identical conditions, when compared with the Ni(II) complexes of 2,3,2-tet and cyclam, the positions of equilibria for the cations  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  and  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  are shifted more toward the octahedral side. For  $\text{NiN}_4$  square-planar species the molar extinction coefficient is expected to be in the range  $50\text{--}80 \text{ M}^{-1} \text{ cm}^{-1}$  (see Table VIII for complexes of  $\text{HL}_1$  and  $\text{H}_2\text{L}_3$ ). The observed values for  $\text{Ni}(\text{HL}_1)^{3+}$  and  $\text{Ni}(\text{H}_2\text{L}_3)^{4+}$  in 0.1 M perchlorate media are approximately 3 and  $38 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, indicating the presence of large amounts of octahedral species.

In comparison with 2,3,2-tet and cyclam, the ligands  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  differ only in the presence of the rigidly held 1,4-diazacycloheptane ring. The positive charge on the protonated nitrogens of this ring may influence the orientation of solvent molecules

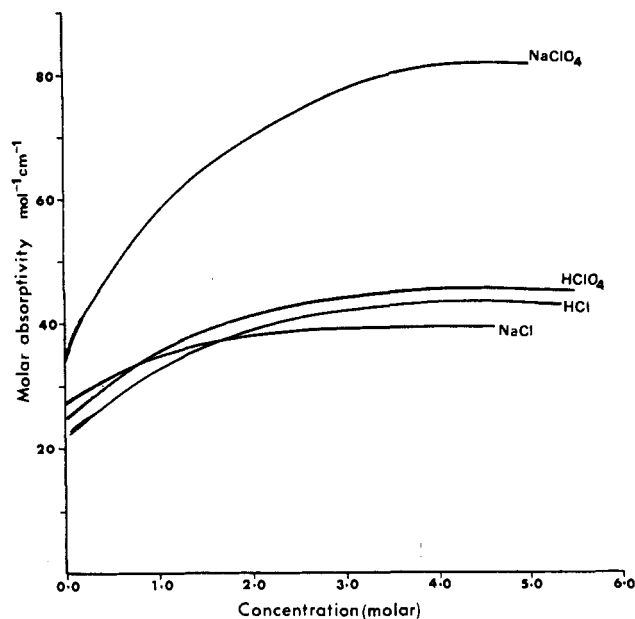


Figure 3. Behavior of the  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  cation in various media.

around the nickel center and thus hold a solvent ( $\text{H}_2\text{O}$ ) molecule close to the axial site of the metal center. This location of a coordinated water molecule would also diminish electrostatic repulsion between the positive charges on the 1,4-diazacycloheptane rings and on the metal ions. This is reflected especially in the  $\Delta S$  value for the cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$ . An identical situation might prevail also for the cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$ . However, the open-chain nature of the ligand could permit elongation of the Ni-N distances during formation of octahedral species, which partly compensate the entropy lost through solvent binding. Similar behavior is observed in many binuclear complexes<sup>31-33</sup> and has been explained in terms of electrostatic repulsion between metal centers.

In Figure 3 is shown the behavior of the cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  in various media. With increasing  $[\text{NaClO}_4]$ , the content of the square-planar form increased sharply and in 5.0 M sodium perchlorate it is the only species present. No temperature dependence is observed under this condition. Similarly, only the square-planar form of  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  is present in 6 M  $\text{NaClO}_4$  and the octahedral form is present exclusively in 85% ethanol (see Table VIII). The equilibrium is shifted only to a very small extent with increasing concentrations of sodium chloride.

The two secondary amines in the 1,4-diazacycloheptane rings can undergo stepwise protonation to form a mono- or diprotonated species. With increasing acid concentration, the extent of protonation increases, leading to higher electrostatic repulsion, which might be expected to favor formation of the octahedral species. However, in the case of the  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  cation in both hydrochloric and perchloric acid, there is an equilibrium shifted toward the square-planar side but to different extents (Figure 3). Even in the maximum attainable concentrations of  $\text{Cl}^-$  and  $\text{H}^+$ , the limiting value corresponding to 100% square-planar form is not reached. At very high concentrations of acid ( $\approx 9.0 \text{ M}$ ), although the diprotonated cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  is the predominant species, there is still a significant amount of the octahedral form. Under such conditions, in the presence of  $\text{ClO}_4^-$  and  $\text{Cl}^-$  oxidation of the Ni(II) center to the *trans*-dichloronickel(III) complex is promoted. Owing to acid instability, the acid-dependent behavior of the cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  was not studied.

The Ni(III) species of  $\text{HL}_1^+$  in neutral aqueous media showed two overlapping bands at 303 and 350 nm. The molar extinction

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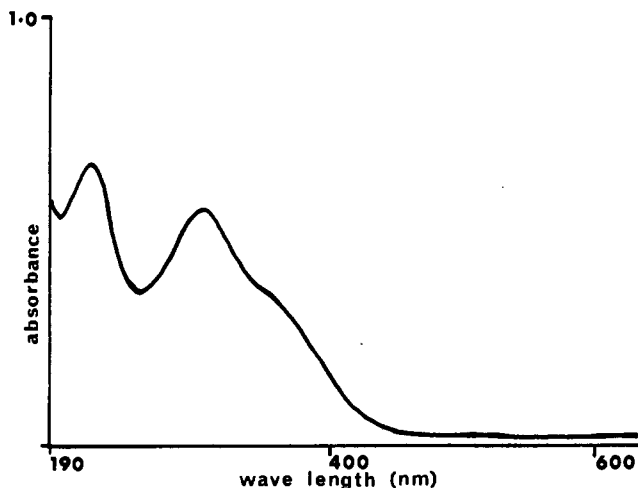


Figure 4. UV-visible spectrum of the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$  in 1.0 M  $\text{HClO}_4$ .

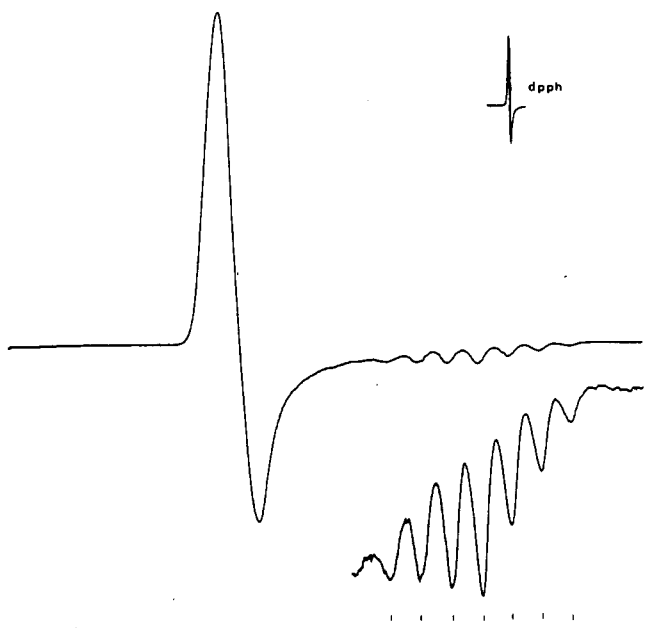


Figure 5. ESR spectrum of the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$  in acidic aqueous media.

coefficients were not determined owing to continuous decomposition of the species. However, the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$  is stable in acidic media and showed two distinct bands at 219 and 303 nm with a shoulder peak at 358 nm (see Figure 4). This is characteristic of many Ni(III) species in tetraaza ligands.<sup>34</sup>

**ESR Spectroscopy.** ESR spectra of Ni(III) species derived from oxidation of both the complex cations  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  and  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  were recorded at 77 K. Owing to the instability of the cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  in acidic media, the Ni(III) species was prepared in neutral aqueous conditions by using sodium peroxydisulfate as the oxidizing agent. The ESR spectrum shows an axial spectrum characteristic of Ni(III) complexes of many tetraaza ligands.<sup>34</sup> In the presence of chloride as axial ligands hyperfine splitting is observed. The observed  $g$  components with values  $g_{\perp} = 2.167 > g_{\parallel} = 2.017$  and  $A_{\parallel} = 30$  G are consistent with a *trans*-dichloro octahedral geometry. A solution prepared from the isolated *trans*-dichloronickel(III) complex of  $\text{H}_2\text{L}_3^{2+}$  in acidic aqueous media showed (see Figure 5) a similar spectrum at 77 K and is identical with the Ni(III) species obtained by oxidation of the  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  cation with chemical oxidants such as aqueous Co(III) or sodium peroxydisulfate in chloride media (see discussion below). The  $g$  components with  $g_{\perp} = 2.170 >$

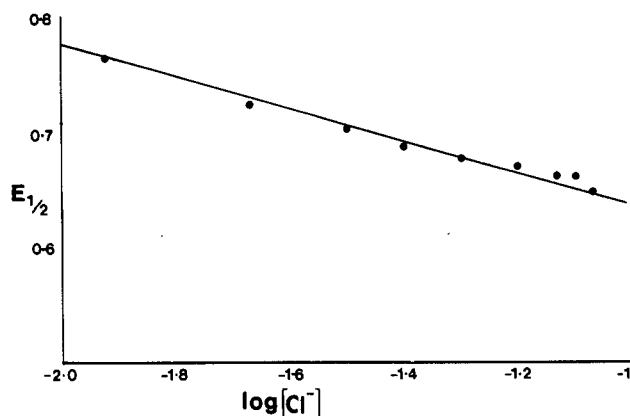


Figure 6. Chloride dependence of redox potential for the  $\text{Ni}^{2+/3+}$  couple in the cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  in aqueous media ( $[\text{H}^+] = 0.1$  M).

$g_{\parallel} = 2.020$  and  $A_{\parallel} = 30$  G again confirm axial symmetry. Thus, both these species adopt the same *trans*-dichloro octahedral geometry with the unpaired electron residing in the  $d_{z^2}$  orbital.

**Electrochemical Studies.** Cyclic voltammetry of the  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  and  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  cations was studied in aqueous media for the  $\text{Ni}^{2+/3+}$  couple. The cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  showed no wave in lithium perchlorate or triflate media, and only in 0.3 M lithium chloride was a well-defined reversible wave observed at  $E_{1/2} = 0.75$  V vs SCE. At a scan rate of 100 mV/s, the cyclic voltammogram showed values of  $\Delta E_p = 63$  mV and  $i_{p,a}/i_{p,c} = 1.0$ , consistent with the reversibility of the process. In the case of the  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  cation, a quasi-reversible wave close to the solvent limits was observed in 1.0 M lithium triflate.  $E_{1/2}$  is estimated to be 0.85 V vs SCE. The reversibility of the couple improved dramatically with increasing concentrations of chloride ions with  $E_{1/2}$  shifting to 0.57 V in  $[\text{Cl}^-] = 1.0$  M. In 1.0 M lithium chloride a  $\Delta E_p$  value of 63 mV and a current ratio of 1.0 are observed. A plot of  $E_{1/2}$  vs  $\log [\text{Cl}^-]$  (see Figure 6) was found to be linear, and the number of axial ligands<sup>12</sup> was determined to be  $2 \pm 0.2$ , consistent with the formation of a *trans*-dichloronickel(III) species.<sup>35</sup>

**Reduction of Perchlorate by Ni(II) Complexes.** For most Ni(II) complexes, oxidation to the higher valent Ni(III) or Ni(IV) state occurs only at very positive potentials and, in general, they are not good reducing agents. However, some macrocyclic<sup>36</sup> and thiolate Ni(II) complexes<sup>37</sup> exhibit low redox potentials and aerial oxidation of a Ni(II) center in a pentadentate macrocyclic ligand has been reported.<sup>38</sup> In contrast, there is no kinetic route for perchlorate ion to oxidize Ni(II) centers in these complexes.

Recently, Fabbrizzi et al.<sup>7</sup> have described the transient formation of a Ni(III) species from the Ni(II) complex of the ligand  $\text{L}_4$  ( $\text{L}_4 = N$ -(2-aminoethyl)cyclam). This process was proposed to involve a redox reaction between perchlorate and Ni(II) centers in the complex. The enhancement of this unusual redox reaction was attributed to binding and positioning of perchlorate ion by the protonated primary amino group in the side chain of the ligand  $\text{L}_4$ . A similar process is also envisioned in the complexes described in this report. The secondary amines in the 1,4-diazacycloheptane rings of the Ni(II) complexes  $\text{HL}_1^+$  and  $\text{H}_2\text{L}_3^{2+}$  are in a plane approximately orthogonal to the  $\text{NiN}_4$  plane and are not accessible to coordination. However, when these nitrogens are protonated to form secondary ammonium ions, they can act as binding sites for perchlorate ion, leading to the enhancement of the redox process.<sup>39</sup>

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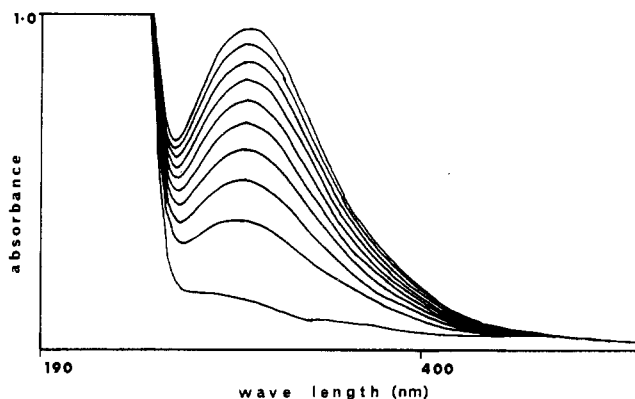
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**Figure 7.** Formation of Ni(III) species from the cation  $[\text{Ni}^{\text{II}}(\text{HL}_3)]^{3+}$  in 9.0 M  $\text{HClO}_4$  at 25 °C ( $[\text{Cl}^-] = 1.0 \text{ M}$ ). Each spectrum is taken at a 1-h interval.

**Formation of Triiodide Ions in the Ni(II) Complexes of  $\text{HL}_1^+$ .** Aqueous solutions of  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$  saturated with perchlorate and iodide yielded species containing triiodide as counterions. When neutral solutions of the complex cation  $[\text{Ni}^{\text{II}}(\text{HL}_1)]^{3+}$ , saturated with sodium perchlorate and sodium chloride, were left to stand, they turned acidic, decomposing most of the complex. However, in the presence of iodide, triiodide was formed as one of the counterions. The formation and decomposition of a transient Ni(III) species can account both for the generation of acid in the absence of iodide and for the formation of triiodide. Ni(III) species of this type are, in general, unstable in neutral media and tend to oxidize water with the generation of protons and dioxygen gas.<sup>40</sup> The open-chain amine complexes of Ni(II) are acid unstable and hence decompose to  $\text{Ni}^{2+}(\text{aq})$  ion. However, in presence of a reducing agent such as iodide, Ni(III) macrocycles have been shown to be reduced<sup>41</sup> rapidly with the formation of iodine, which can combine with the excess iodide to form triiodide ions.

In absence of acid the formation of triiodide ion is very slow. Addition of even a trace amount acid tends to accelerate the formation of triiodide ion, and the Ni(II) complex crystallized with two triiodide ions. However, in either case the yields of these complexes are not more than 30–40% due to partial decomposition of the complex.

**Formation of *trans*-Dichloronickel(III) Complex.** In the case of the macrocyclic ligand  $\text{H}_2\text{L}_3^{2+}$ , the Ni(II) complex is very stable in strong mineral and organic acids and hence can be isolated under suitable conditions. In the presence of an acid and chloride ion, the complex cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$  is oxidized by perchlorate ion ( $[\text{ClO}_4^-] = 3.0\text{--}9.0 \text{ M}$ ) to the corresponding *trans*-dichloronickel(III) species. The gradual development of a Ni(III) species in perchloric acid ( $[\text{HClO}_4] = 9 \text{ M}$ ) in the presence of 1.0 M sodium chloride (1 M) is shown in Figure 7. The broad feature around 300 nm is characteristic of a Ni(III) ion in a tetraaza ligand.<sup>34</sup>

The Ni(III) species is *not* formed in absence of perchlorate anion. The presence of a coordinating anion such as chloride and also hydrogen ion is essential for the enhancement of this redox process, which takes place in both the presence and absence of dioxygen.

For the macrocyclic ligand, the nickel(II) species generated upon decomposition of the Ni(III) ion differs from the original square-planar species. The former, exhibiting a strong absorption band at 540 nm, rearranges slowly to the square-planar ion. Various authors<sup>42–44</sup> have detected transient Ni(III) complex ions

with absorbances at 540 nm. Meyerstein<sup>43</sup> has attributed this to the formation of a Ni(III)–hydroxo complex. However, in the present system under acidic conditions it is likely that the absorbance is due to an octahedral form of the Ni(II) complex ion.

**Mechanism of Perchlorate Reduction.** In absence of kinetic data, only qualitative details of the mechanism can be provided.<sup>39</sup> The structure of the ligand plays an important role in this redox process, and hence the discussion is addressed mainly to this aspect.

Thermodynamically, perchlorate ion is a powerful oxidizing agent ( $E_{1/2} = 1.39 \text{ V vs NHE}$ ). However, for kinetic reasons it is inert toward most reducing agents under normal conditions. While a number of transition-metal ions<sup>45</sup> reduce perchlorate at a measurable rate, it is relatively unknown for Ni(II) to reduce this anion.<sup>7</sup> Ni(II) complexes of many tetraaza ligands including that of cyclam do not show this tendency. Thus, the presence of a 1,4-diazacycloheptane ring in the ligands described here is an essential factor. Protonation of the two secondary amines in this ring leads to a configuration where the  $\text{ClO}_4^-$  ion may be held in a position for ion pairing and interaction of one of the oxygens with the Ni(II) center. Upon oxygen atom transfer (there is some preliminary ESR evidence for the formation of  $\text{ClO}_2^0$ ), the route is open to formation of Ni(III). Perchlorate ion is known to function as a weak ligand in various coordination modes.<sup>46</sup> The presence of chloride promotes the formation of octahedral Ni(III) species as demanded by the  $d^7$  configuration. There is current interest in the mechanism of molecular recognition. The present system provides an inorganic model for assembly configuration through ion pairing.

The probability that a strong ion-pairing effect plays a crucial role is confirmed from the UV–visible and ESR spectroscopy of a freshly formed Ni(III) species from the cation  $[\text{Ni}^{\text{II}}(\text{H}_2\text{L}_3)]^{4+}$ . Immediately on formation in solution, these species showed UV–visible and ESR spectra that are distinctly different from those obtained from the cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$  prepared by dissolution of the crystalline complex. The UV–visible spectra of a freshly formed Ni(III) species did not show clearly the two features observed at 310 and 350 nm for the isolated cation  $[\text{Ni}^{\text{III}}\text{Cl}_2(\text{H}_2\text{L}_3)]^{3+}$ . Instead, only a broad band is observed (Figure 7). This can be ascribed to distortions arising from strong ion pairs. Also, the distortion observed in the hyperfine coupling of the  $g_{\parallel}$  component is an indication of a deviation from the  $D_{4h}$  symmetry of the *trans*-dichloronickel(III) species. However, the presence of a mixture of different species cannot be ruled out. The fate of the perchlorate ion undergoing reduction is not known with certainty. However, preliminary experiments suggest that it is converted into lower oxyanions of chlorine ( $\text{ClO}_2^0$  has been identified to be one of the products by ESR spectroscopy). The final product is probably a chloride ion. Control experiments indicate that oxygen and light are not contributing factors to the redox processes described here.

**Acknowledgment.** We thank the NSERC and University of Victoria for financial support. The assistance of Mrs. K. Beveridge and T. W. Whitcombe in the crystal structure determination is appreciated.

**Supplementary Material Available:** Tables S1–S7, containing crystallographic data, anisotropic temperature parameters, selected bond lengths and angles, and intermolecular distances for both complexes (12 pages); Tables S8 and S9, listing calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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