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Synthesis and characterization of polymacrocyclic ligands and protonated ions

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Contents

Abstract

The synthesis of a novel macrotricyclic ligand (L**3**) containing a N_4S_2 donor set and characterization of a protonated macrobicyclic ion with N_4S donors ($[H_2(L\mathbf{2})]^{2+}$) is reported. The approach to the tricyclic system differs from that used previously for the bicyclic N_4S ligand, employing the formation of a tetraamide that reacts with sodium sulfide to effect ring closure of two nine-membered rings. Alkali ions present in the reaction mixture were found to be incorporated into the tricyclic tetraamide framework suggesting an equilibrium between Group(I) metal ions and the product L**5**. The reduced ligand, (L**3**), can maintain two configurations, *syn*- or *anti*- depending on whether the nine-membered rings are on the same or opposite sides of the cyclam ring. A detailed crystallographic analysis is presented of the ions ($[H_2(L\mathbf{2})]^{2+}$), ($[H_2(L\mathbf{3})]^{2+}$) and a mono-protonated lithium complex ($[Li(HL\mathbf{3})]^{2+}$). In the case of the tricyclic ions, the N-substituents on the cyclam ring adopt the *anti*-orientation providing examples of the unusual *trans*-IV cyclam ring conformation (*trans-R*,*R*,*S*,*S*) that is extremely rare.

Keywords: Macrobicyclic; Macrotricyclic; Ligand; Protonation; Ring configuration

1. Introduction

The significant thermodynamic stability and kinetic inertness associated with polymacrocyclic complexes is well known and continues to be of interest [1–5] especially where variation of donors leads to selectivity of metal ions into the ligand cavity. Features that influence significantly the chemistry of metal complexes are the electronic nature of the donors and the structural aspects of the ligand. Variation of the donor provides insight into the electronic consequences of coordination. However, it is also of interest to vary the ligand structure systematically (while keeping the nature of the donors constant) in order to gain insight into such properties as ligand field strength and ligand rigidity among others.

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1.1. Previous studies

The syntheses of macrobicyclic pentacoordinate ligands 14-X-1,4,8,11-tetraazabicyclo[10.5.2]nonadecane (L**1**) have been reported [6–10] in which a 9-membered cyclononane ring ([9]aneN_2X where X = NH, O, S) is constructed over an ethylene segment of the 14-membered tetraaza cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) ring. Each of the metal-complexed cations adopts the *trans*-I conformation [11] in the solid state. A detailed analysis has been presented recently of all nickel 14-membered macrocycles in the Cambridge data base [12], where it is seen that the majority of *trans*-I species are square planar or square pyramidal, and the *trans*-III conformation is associated with octahedral symmetry. Also, N-alkylation appears to confer additional thermodynamic stability to the *trans*-I configuration [13].

Although there have been many studies published of metal complexes incorporating a variety of transition metal ions into macrobicyclic frameworks, (e.g., [6–10,14–17]) the available data on protonated or lithiated ions is much less documented. This is also true of the macrotricyclic analogues.

Variations have been identified in protonated complexes of several ligand types. In the case of the macrobicycle derived from the ‘fusion of a nine-membered ring onto a cyclam residue, (L**1**, X = O), [8], Fig. 1, $[H_4(L\mathbf{1})]^{4+}$, both the tertiary and the secondary nitrogens are protonated, and there is considerable puckering shown in the rings, particularly around the tertiary centers, N1 and N2. Owing to the disorder of the perchlorate counter ions, the precise locations of the protons were not discernable, but it is noteworthy that the ether O donor lies *exo* to the tetraazamacrocyclic ring, in contrast to the comparable metal complexes of Cu(II) and Ni(II) [8], each of which exhibits a N_4O donor set in the solid state.

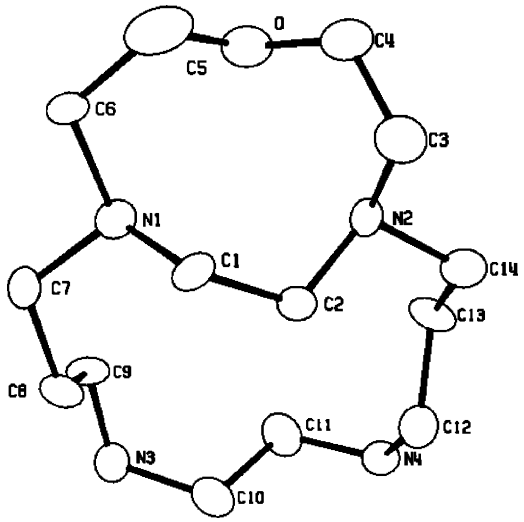
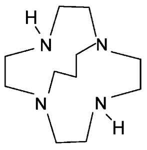


Fig. 1. ORTEP diagram of $[H_4(\mathbf{L1})]^{4+}$ (X = O).

The smaller ringed tetraazamacrocycles 1 and 2 have been bridged across the *trans* nitrogens, and reveal differing protonation reactions [14–21].



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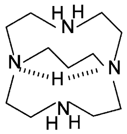
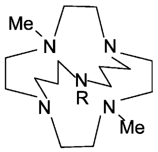


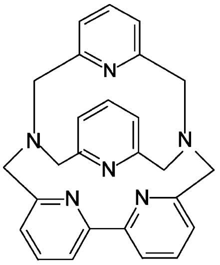
$[H_3(1)]^{3+}$



2: R = Me **3**: R = H

In the case of ligand **1**, the ion $[H_3(1)]^{3+}$ is formed, where both secondary nitrogens are full protonated and a third proton is ‘shared’ between the tertiary centers. However, a mono-protonated precursor has also been identified [20] in which only the bridgehead proton is present. Interestingly, upon reaction with the ditosylate of propylene glycol, a tricyclic ion is formed with the same proton arrangement as the bicyclic species. In contrast, ligand **2**, which can be regarded as an iso-cyclam ring bridged across the *trans* nitrogens in the 14-membered ring, only the tertiary nitrogen in the bridge is protonated, the proton being positioned close towards the center of the bicyclic cavity (Fig. 2).

Details on the lithiated analogues of these ions are rare. Ligand **2** has been shown to act selectively in the encapsulation of Li^+ ions. In the structure, the metal ion sits within a distorted square pyramid at 0.85 Å above the basal plane. The Li–N distances are between 2.14 and 2.45 Å in length, slightly longer than the 2.08 Å observed in the current work (vide infra) (Fig. 3).



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The structure of $[Li(4)]^+$ has been determined [22], where although there is an environment of six N donors around the metal center, there is no encapsulation by the macrobicycle.

1.2. Present investigation

In this paper, we describe the preparation and characterization of a protonated form of the macrobicyclic form of (L**1**), (X = S, L**2**) that may be regarded as a ‘half-way’ precursor to the fully developed macrotricyclic ligand (L**3**) the synthesis of which is also presented. A preliminary report on some of this work has been published [23]. The ligand (L**3**) can potentially adopt either *syn*- or *anti*- configurations (vide infra) depending upon the disposition of the thioether or the nine-membered rings relative to the N_4 plane. Details

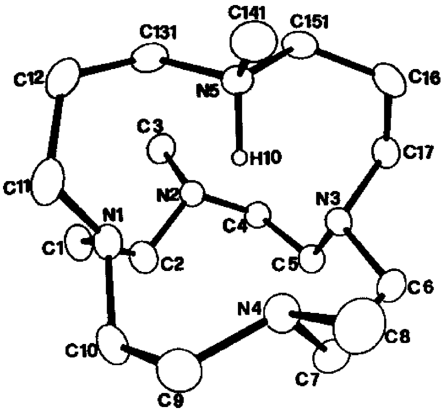


Fig. 2. ORTEP diagram of $[H(2)]^+$.

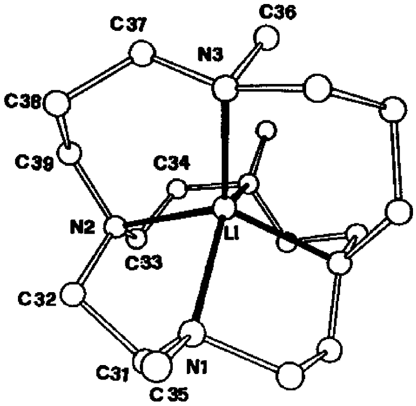
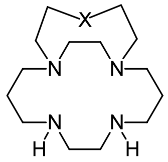
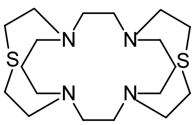


Fig. 3. ORTEP diagram of Ion $[Li(\mathbf{3})]^+$.

of the diprotonated and a mono protonated lithium complex of (L**3**) are presented in which the *anti*-form of the ligand is observed with the extremely unusual *trans*-IV configuration in the cyclam ring.



L1
L2 X = S



(L**3**)

2. Experimental

NMR spectra, both ^1H and ^{13}C, were recorded on Bruker AMX360 or Bruker AC300 high field spectrometers with either D_2O (MeOH or CH_3CN as external standard) or $CDCl_3$ as solvent. Mass spectra of the free ligands were recorded on a Finnegan 330 GC–MS instrument by methane chemical ionization and electron impact techniques. Mass spectra of acidified ligand perchlorate salts and metal complexes were recorded on a Kratos Concept spectrometer either by FAB or electrospray ionization techniques. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada.

2.1. Structure determinations

Crystal data and details of data collection are presented in Table 1. In all cases, crystals were mounted on glass fibre with silicone glue. Data were collected on a Smart 1000 Diffractometer (Mo–Kα, graphite monochromated radiation, $\lambda = 0.71073$ Å). Data were collected over the 2θ range 4–50°. An empirical absorption correction (SADABS) was applied. Structures were solved by direct methods (SHELX-97) and H atoms were placed at idealised positions and refined according to the riding model. Structures were refined according to the full-matrix least-squares method on F^2 (SHELXL-97). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre reference numbers are 197082, 173092 and 173093 for $[H_2(L\mathbf{2})](ClO_4)_2$, $[Li(HL\mathbf{3})](ClO_4)_2$ and $[H_2(L\mathbf{3})](ClO_4)_2$ respectively.

2.2. Synthesis

The ligand (L**2**) was prepared as described previously [6]. The salt $[H_2(L\mathbf{2})](ClO_4)_2$ was prepared by the addition of about 5 mg of the free ligand to 0.5 ml water to which 2 drops of 70% perchloric acid were added. The salt that precipitated instantaneously and in near quantitative yield was redissolved by warming the solution and allowed to crystallize slowly. Faintly yellow crystals of X-ray quality were obtained. (Found: C, 34.42; H, 6.40; N 11.55. Calc. for $C_{14}H_{32}N_4SCl_2O_8$: C, 34.50; H, 6.62; N 11.50%) MS ($(L\mathbf{2})+1 = 287$). ^{13}C-NMR (D_2O, ppm) 21.9 (C–**C**H_2–C); 27.1 (**C**H_2–S); 39.5, 43.2, 48.9, 49.8, 52.3 (**C**H_2–N). *Caution: perchlorate salts are potentially explosive and should be handled in small quantities with great care.*

The synthetic route to L**3** is shown in Scheme 1.

2.2.1. 1,4,8,11-tetrakis-(chloroacetyl)-1,4,8,11-tetraazacyclotetradecane (L4)

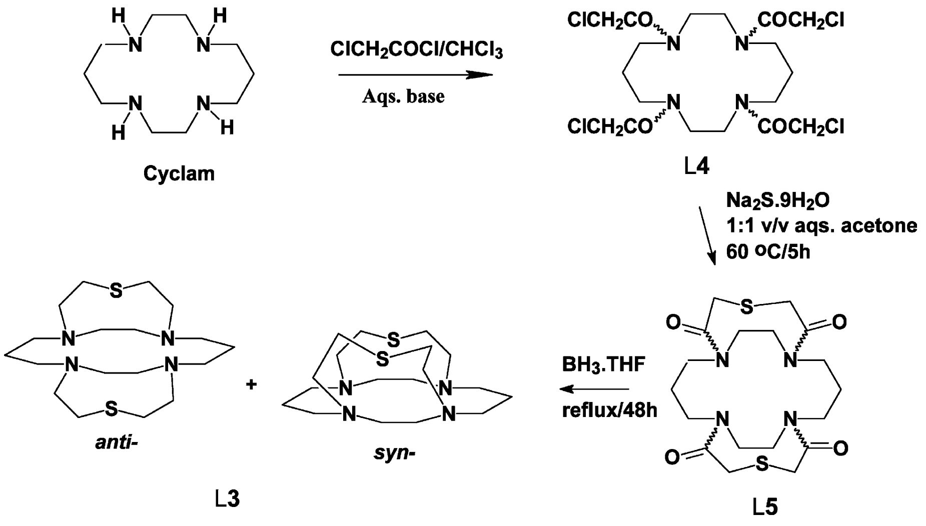
A solution of cyclam (2.5 g, 12.48 mmol) in 400 ml of ethanol free $CHCl_3$ was prepared in a 3 necked 1.0 l round bottomed flask and cooled to −5 °C in an ice–salt bath and stirred vigorously using a magnetic or overhead stirrer. To this, a solution of chloroacetyl chloride (9.67 g, 85.6 mmol) in 200 ml of ethanol free $CHCl_3$ was added drop-wise while maintaining the temperature well below 0 °C. After the addition of a quarter of the acid chloride, 5 ml of a solution of $Me_4NOH{\cdot}5H_2O$ (9.0 g, 49.7 mmol) in 20 ml of water was added in one portion. In a similar manner, after the drop-wise addition of the second quarter of the acid chloride, the second 5 ml of the base solution was added. After the addition of the third quarter of the acid chloride, the final 10 ml of the base was added. The final quarter of the acid chlo-

Table 1
Crystal, data collection and refinement parameters

	$[H_2(L\mathbf{2})](ClO_4)_2$	$[HLi(L\mathbf{3})](ClO_4)_2$	$[H_2(L\mathbf{2})](ClO_4)_2$
Formula	$SCl_2O_8N_4C_{14}H_{32}$	$S_2Cl_2O_8N_4C_{18}H_{37}Li$	$S_2Cl_2O_8N_4C_{18}H_{38}$
Formula weight	487.40	579.48	573.54
Crystal size (mm)	0.32×0.35×0.38	0.08×0.15×0.18	0.14×0.15×0.47
Crystal color	Cream	colorless	colorless
a (Å)	14.354(2)	7.3867(16)	7.408(2)
b (Å)	14.592(2)	9.057(2)	16.534(5)
c (Å)	20.898(3)	10.269(2)	10.412(3)
α (°)		72.895(4)	
β (°)		80.625(4)	97.364(6)
γ (°)		85.607(4)	
V (Å^3)	4377.3(10)	647.6(2)	1264.8(7)
Cell detn, refls	775	248	486
D_{calc} (g cm^{-3})	1.48	1.49	1.51
Space group	$Pbca$	$P\bar{1}$	$P2_1/c$
Z	8	1	2
$F(0\,0\,0)$	2064	306	608
Lin abs coefficient (mm^{-1})	0.44	0.46	0.47
h, k, l ranges	−17, 16; −17, 17; −24, 15	−8, 8; −10, 10; −11, 12	−8, 8; −19, 19; −7, 12
Crystal decay (%)	0.11	0.15	0.03
Absorption range	0.86–1.00	0.84–1.00	0.79–1.00
Refl meas	22 141	4921	6459
Unique refls	3874	2280	2230
R for merge	0.042	0.033	0.049
Refls in reft $I > 2.0\sigma(I)$	2139	1408	1284
Parameters refined	327	160	154
R_1, wR_2	0.050, 0.140	0.046, 0.115	0.048, 0.114
R_1 for $I > 0.0\sigma(I)$	0.101	0.086	0.100
Goodness-of-fit on F^2	1.01	0.98	0.96
Largest Δ/σ	0.00	0.00	0.00
Final diff map, (e Å^{-3})	−0.38, +0.40	−0.28, +0.45	−0.28, +0.30
H atom treatment	riding		
Scattering factors	International tables for crystallography, vol C		

$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ for all reflections with $F > 2\sigma(F)$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections.

ride was the added. The whole reaction was conducted with the exclusion of light since chloroacetyl chloride undergoes photo-hydrolysis in the presence of aqueous base. The reaction mixture was allowed to rise slowly to room temperature and the aqueous layer was separated. The $CHCl_3$ layer was dried over anhydrous Na_2SO_4 and diluted with hexane until the solution turned completely cloudy. Upon standing, 3.9 g of a white crystalline solid were deposited. Upon concentra-



Scheme 1.

tion to about 25 ml, the mother liquor yielded an additional ~0.7 g of pure material. A small amount, ~0.2 g was also deposited from the aqueous layer. Total yield: 4.8 g (77%, 9.48 mmol). ^{1}H-NMR: 1.92 (4H, m, C–CH_2–C); 3.38 (8H, m, CH_2–N in propylene); 3.52 (8H, s, CH_2–N in ethylene) and 4.43 (8H, m, CO–CH_2–Cl). ^{13}C-NMR: 166.2 (**C**=O), 46.12 (**C**H_2Cl), 42.1 (CO–NH**C**H_2), 41.7 (N–CH_2–**C**H_2). Minor peaks in both the carbonyl (e.g., 166.0,166.6, 166.8) and methylene carbon regions were consistent with the existence of various conformation isomers. MS FAB: $m/e = 507$ (M+1).

It is interesting to note that during the preparation of the tetraamide, L**4**, the isolated product always indicated a tendency to complex Group I ions derived from the base used to neutralize the HCl liberated during the acylation reaction. This significantly increased the water solubility of this tetraamide and reduced the yield. Only when the base [Me_4N]OH was used, was the tetraamide, L**4** isolated in excess of 85% yield.

The tetraamide, L**4,** was reacted with 2 mole equivalents of $Na_2S\cdot 9H_2O$ in aqueous acetone or acetonitrile (1:1 v/v). Owing to complexation of alkali metal ions, it was difficult to purify L**5**. Since $Na_2S\cdot 9H_2O$ was the only accessible reagent that could be used successfully as a source for the thioether, some complexation of sodium ions was inevitable. However, by carrying out the cyclisation in the presence of a large excess K^+ or Li^+ ions, other alkali metal ion complexes were obtained. As a result of the use of the electrospray technique (LSIMS–MS) to characterize the reduced products, the mass spectra always showed a mixture of L**5** and [ML**5**]$^+$ (M=Na, K, Li). For example, when the cyclisation was carried out with only sodium present, principal signals were observed at 429.1 [HL**5**]$^+$ (60%) and 451.5 [NaL**5**]$^+$ (50%). The product obtained in the presence of large excess of potassium ion showed peaks at 429.1 [HL**5**]$^+$ (45%) and 467.1 [KL**5**]$^+$ (90%). Clearly, there exists an equilibrium between free L**5** and [ML**5**]$^+$ in solution. However, in the latter case, when FAB–MS was used, only the peak corresponding to [KL**5**]$^+$ was observed. Reduction of the reaction product with $BH_3\cdot$THF formed with only minimal Na^+ present provided pure L**3**. The overall yield of the ligand was 30–35% based on cyclam. However, when excess Li^+ ion was used during cyclisation or was present in the reduction mixture, the Li^+ complex, Li[HL**3**]$(ClO_4)_2$, rather than the free ligand was obtained. ^{1}H-NMR: ($CDCl_3$, ppm) 1.48 (quintet, C–CH_2–C); 2.62 (m, CH_2–S–CH_2); 2.75 and 2.90 (m, CH_2–NH^+–C) ^{13}C-NMR: 27.6 (C–**C**–C); 34.3 (S–**C**–C); 54.7 (N–**C**–C–S); 55.5 (N–**C**–C–**C**–N) and 58.5 (N–**C–C**–N). MS: 380.6 [Li(L**3**)]$^+$.

Acidification of this complex yielded the salt, H_2L**3** $(ClO_4)_2$. ^{1}H-NMR (D_2O; D_2SO_4, ppm) 1.87 (quintet, C–CH_2–C); 2.73 (m, CH_2–S–CH_2); 2.90 and 3.02 (m, CH_2–NH^+–C), ^{13}C-NMR: 22.7 (C–**C**–C); 28.0 (S–**C**–C); 48.8 (N–**C**–C–S); 51.2 (N–**C**–C–**C**–N) and 52.5 (N–**C–C**–N).

3. Discussion

The crystal structures of several of these compounds have been determined. In the bis-protonated macrobicycle, the thioether adopts an *endo* configuration as is shown in Fig. 4. In this ion, one tertiary and a secondary nitrogen atom located diagonally across the cyclam ring are protonated, the hydrogen atoms on nitrogens being determined from difference map positions. Interestingly, both N1 and N2 each have one hydrogen atom attached and N3 has two. The observation is of interest in view of the relative basicities of secondary and tertiary nitrogen atoms. In general, tertiary nitrogens are more basic than secondary. In this case instead of two tertiary nitrogens, one tertiary and one secondary nitrogen is protonated for reasons of electrostatic repulsion and steric and strain control within the ring. The relevant bond distances are: S1–HN1 = 2.734, S1–HN2 = 2.985, S1–HN3a = 2.544, and S1–HN3b = 3.16 Å, respectively.

The relatively short distances between the sulfur and the protons on N1 and N3 distances are probably responsible for the configuration adopted (the angles C(11)–C(12)–S1 and C(14)–C(13)–S1 being 119.4(3) and 114.4(3)°, respectively. The ion adopts a *trans*-I configuration similar to that observed in metal complexes of this type [6,7,24].

The ORTEP view of cation, [Li(HL**3**)]$^{2+}$ is shown in Fig. 5. In this Li(I) complex, the metal ion sits on a special position (the inversion center) and only one set of the *trans*-nitrogens is coordinated to the cation (Li–N, 2.080(3) Å and N(2)–Li–N(2), 180.0°). Also, the proton is distributed equally between the two tertiary amines N(1) and N(1)′ so that effectively only one half of an N–H bond is present on each nitrogen. For the sake of clarity a full bond is shown on N(1). In each thioether ring, the config-

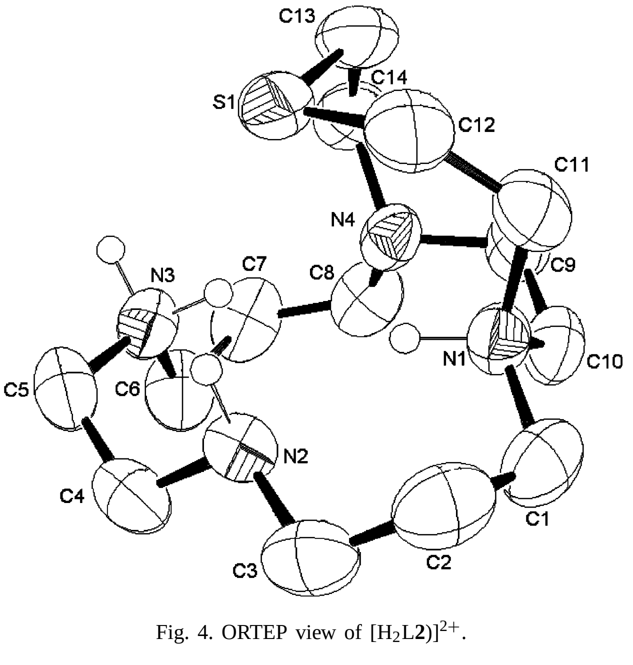


Fig. 4. ORTEP view of [H_2L**2**)]$^{2+}$.

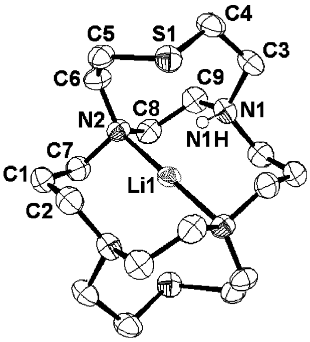


Fig. 5. ORTEP view of $[Li(HL\mathbf{3})]^{2+}$.

uration adopted is similar to that in the macrobicycle L**2,** (C6–C5–S1 = 117.8(3) and C3–C4–S1 = 111.4(2)°.

The coordination chemistry of lithium is very rich, with the element now known in 20 coordination geometries with coordination numbers ranging from 1 to 12, [25,26]. There appear to be very few instances of two-coordinate Li^+, one example being the dialkyllithiate ion $[Li\{C(SiMe_3)_3\}_2]^-$ prepared by the reaction of tris(trimethylsilyl)methane with methyl lithium in thf [27]. In this case, the anion is linear and the Li–C bonds (2.16 Å) may be compared to the current values, again in a linear configuration, of 2.08 Å. The fact that the current complex is made in relatively mild conditions reflects the strength of the binding inside the cyclam cavity in the tricyclic species.

In the $[H_2L_3]^{2+}$ cation (Fig. 6), again only the *trans*-nitrogens are protonated thereby minimizing electrostatic interaction. Also, the angles subtending the thioether are remarkably similar to those observed in the other cations (C4–C3–S1 = 117.5(3) and C1–C2–S1 = 111.8°, respectively). The lack of identity of these angles is attributable to the presence of both a protonated and neutral tertiary amine in each ring as is also seen in the $[H_2(L\mathbf{2})]^{2+}$ ion. In each of the ions investigated, this asymmetry in the nine-membered ring is exhibited not only in the angles identified above, but also in the carbon–sulfur lengths, and distances and angles around the nitrogen centers. In each ion, the bond lengths and angles around the uncharged nitrogen atom are perceptibly larger than those around the charged center (Table 2).

In each ion investigated, the cyclam ring adopts essentially the same conformation as has been observed in the structure of $[H_2(cyclam)]^{2+}$ [28] and, where appropriate, the [9]-ane rings may be oriented in an *anti*- or the *trans*-fashion. The ligand, L**3,** can exist in both the *syn*- and *anti*- conformation. However, in the latter two protonated ionic structures, only the *trans*-form was observed.

The results of this study indicate that use of a base with a large cation such as Me_4N^+ results almost exclusively in the formation of the *syn* form of the ligand, whereas the incorporation of the alkali metal ion into the ligand framework prior to the final reduction leads to an *anti* form. Preliminary experiments on the corresponding Ni(II) and Cu(II) complexes reveal that in the *cis*-$[Ni(L\mathbf{3})]^{2+}$ and *trans*-$[Ni(L\mathbf{3})]^{2+}$

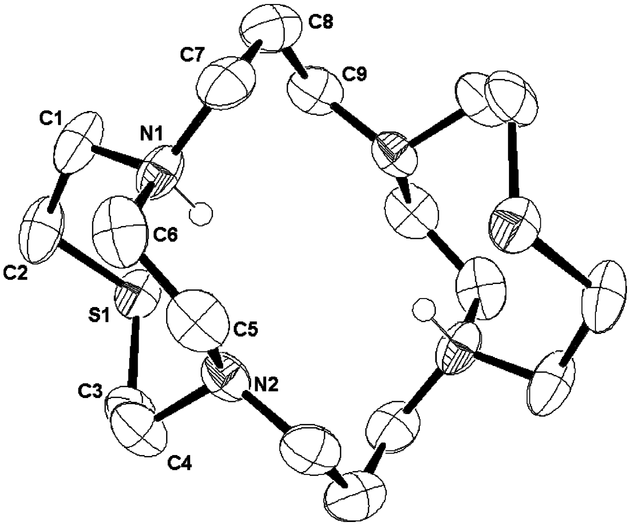


Fig. 6. ORTEP view of $[(H_2L\mathbf{3})]^{2+}$.

Table 2
Significant bond lengths (Å) and angles [°]

Ion $[L\mathbf{2}]^{2+}$			
S(1)–C(12)	1.800(4)		
S(1)–C(13)	1.811(4)		
N(1)–C(10)	1.497(4)	C(12)–S(1)–C(13)	104.07(18)
N(1)–C(11)	1.508(4)	C(10)–N(1)–C(11)	113.5(3)
N(1)–C(1)	1.509(4)	C(10)–N(1)–C(1)	108.4(3)
N(4)–C(9)	1.463(4)	C(11)–N(1)–C(1)	112.5(2)
N(4)–C(14)	1.469(4)	C(9)–N(4)–C(14)	111.4(3)
N(4)–C(8)	1.481(4)	C(9)–N(4)–C(8)	109.4(3)
C(9)–C(10)	1.492(5)	C(14)–N(4)–C(8)	110.6(3)
C(11)–C(12)	1.519(5)	C(11)–C(12)–S(1)	119.6(2)
C(13)–C(14)	1.509(5)	C(14)–C(13)–S(1)	114.0(2)
Ion $[Li(HL\mathbf{3})]^{2+}$			
		C(5)–S(1)–C(4)	104.70(18)
S(1)–C(5)	1.807(4)	$N(2)^1$–Li(1)–N(2)	180.0
S(1)–C(4)	1.817(4)	C(3)–N(1)–C(2)	114.5(3)
Li(1)–N(2)	2.080(3)	C(3)–N(1)–C(9)	111.7(3)
N(1)–C(3)	1.501(4)	C(2)–N(1)–C(9)	110.4(3)
N(1)–C(2)	1.503(4)	C(8)–N(2)–C(7)	107.7(3)
N(1)–C(9)	1.510(4)	C(8)–N(2)–C(6)	112.3(3)
N(2)–C(8)	1.467(4)	C(7)–N(2)–C(6)	112.1(3)
N(2)–C(7)	1.472(4)	C(3)–C(4)–S(1)	111.4(2)
N(2)–C(6)	1.473(4)	C(6)–C(5)–S(1)	117.8(3)
Ion $[H_2L\mathbf{3}]^{2+}$			
S(1)–C(3)	1.804(4)	C(3)–S(1)–C(2)	104.0(2)
S(1)–C(2)	1.814(4)	C(6)–N(1)–C(7)	109.6(3)
N(1)–C(6)	1.495(5)	C(6)–N(1)–C(1)	112.7(3)
N(1)–C(7)	1.508(5)	C(7)–N(1)–C(1)	114.2(3)
N(1)–C(1)	1.508(5)	C(5)–N(2)–C(4)	112.6(3)
N(2)–C(5)	1.473(5)	C(5)–N(2)–C(9)	107.0(3)
N(2)–C(4)	1.476(5)	C(4)–N(2)–C(9)	111.7(3)
N(2)–C(9)	1.478(5)	N(1)–C(1)–C(2)	111.4(3)
		C(1)–C(2)–S(1)	111.8(3)
		C(4)–C(3)–S(1)	117.5(3)

Symmetry code: 1 = −x, −y+1, −z+1.

cations, both species are octahedral, and the *syn*- and the *anti*-form respectively were observed, the former being the dominant product. However, in the corresponding copper(II) ion, it appears that the metal ion remains five-coordinate, with one N donor unbound, despite its proximity to the metal center [29].

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