COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Synthesis and structure of a new macrotricyclic ligand that encapsulates lithium and transition metal ions

Tosha M. Barclay,[a] **Alex McAuley***[b] **and S. Subramanian**[c]
[a] *Dept. of Chemistry, North Harris College, Houston, TX 77073, USA*
[b] *Dept. of Chemistry, PO Box 3065, University of Victoria, Victoria, BC, Canada V8W 3V6. E-mail: amcauley@uvic.ca*
[c] *Dept. of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, B.C, Canada V6T 1Z1*

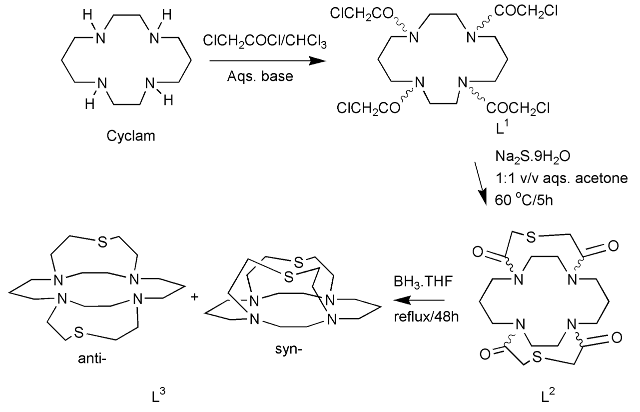
Received (in Cambridge, UK) 26th October 2001, Accepted 5th December 2001
First published as an Advance Article on the web 4th January 2002

A new macrotricyclic ligand, L^3 with an N_4S_2 donor set that encapsulates lithium and transition metal ions has been synthesized from the tetraazamacrocycle cyclam.

Macrocyclic ligands capable of complexing a variety of metal ions are of considerable interest because of their exceptional inertness to kinetic substitution, thermodynamic stability and photo-physical and electron transfer properties of their complexes.[1,2] Syntheses of cryptates with O_6, N_6, S_6 and N_3S_3 donor sets that posses S_3 or C_3 symmetry have been achieved either by transition metal ion templated reactions[3] or by a purely organic synthesis approach.[2,4–6] However, macrotricycles with C_2 or C_4 symmetry that can encapsulate metal ions are relatively rare. Other macrotricycles based on cyclam have been prepared, but they tend to form binuclear complexes by accommodating metal ions in their outer-rings rather than in the middle cyclam ring.[7,8] This is due to the large size of the external rings which reduces the role of the cyclam frame to a mere bridging structure. Whereas, structures in which two [9]ane rings are singly bridged by short carbon chains, encapsulation of metal ions by both [9]ane rings is enhanced.[9] In our laboratory, efforts have been directed towards the synthesis of ligands of the type L^3 in which two [9]aneN_2X (X = O, NH and S) macrocycles are doubly bridged by propylene chains to incorporate a cyclam ring that can accommodate a metal ion while the donors of the smaller [9]ane rings can enforce encapsulation by occupying either the axial or the equatorial sites. Here, we describe the synthesis of L^3 and the structures of [Li(HL^3)](ClO$_4$)$_2$ and [H$_2$L^3](ClO$_4$)$_2$.

The synthetic route to L^3 is shown in Scheme 1. 1,4,8,11-Tetrakis(chloroacetyl)-1,4,8,11-tetraazacyclotetradecane (L^1), was prepared (85% yield based on cyclam) by reacting an excess of chloroacetyl chloride (5:1 mol/mol) with a $CHCl_3$ solution of cyclam in the presence of an aqueous base such as M_2CO_3 (M = Li, Na or K) or [Me_4N]OH·5H_2O at 5 °C. The tetraamide, L^1 was reacted with $Na_2S·9H_2O$ in aqueous acetone and in the presence of excess K^+, Na^+ or Li^+ ion. Due to complexation of alkali metal ions, it was difficult to purify L^2. FAB-MS always showed a 1:1 mixture of L^2 and [ML^2]$^+$ (M = Na, K, Li). However, reduction of this mixture with BH_3·THF provided pure L^3. The overall yield of the ligand was 30–35% based on cyclam. However, when Li^+ ion was present in the reduction mixture, the Li^+ complex, Li[HL^3](ClO$_4$)$_2$, rather than the free ligand was obtained. Acidification of this complex yielded the salt, H_2L^3(ClO$_4$)$_2$.

The crystal structures of these compounds have been determined. ORTEP views of the cations [Li(HL^3)]$^{2+}$ and [H$_2$L^3]$^{2+}$ are shown in Fig. 1.† In the Li complex, the Li sits on a special position (the inversion center) and only one set of the *trans*-nitrogens is coordinated (Li–N 2.080(3) Å and N(2)′–Li–N(2) 180.0°) to the cation. Also, only one half of an N–H bond is present on each of the other nitrogens. For the sake of clarity a full bond is shown on one of the nitrogens and there are two perchlorates per cation. In [H$_2$L^3]$^{2+}$ cation, again only the *trans*-nitrogens are protonated thereby minimizing the electrostatic interaction. The cyclam rings adopt essentially the same conformation in both these ions as was observed in the structure of [H$_2$(cyclam)]$^{2+}$ [10] and the [9]ane rings are oriented in an *anti*- or the *trans*-fashion. L^3 can exist in both the *syn*- and *anti*-conformation. However, in these structures only the *trans*-form was observed. By contrast, in the *cis*-[Ni(L^3)]$^{2+}$ and *trans*-[Ni(L^3)]$^{2+}$ cations, the *syn*- and the *anti*-form, respectively, were observed with the former being the dominant product.[11]



Scheme 1

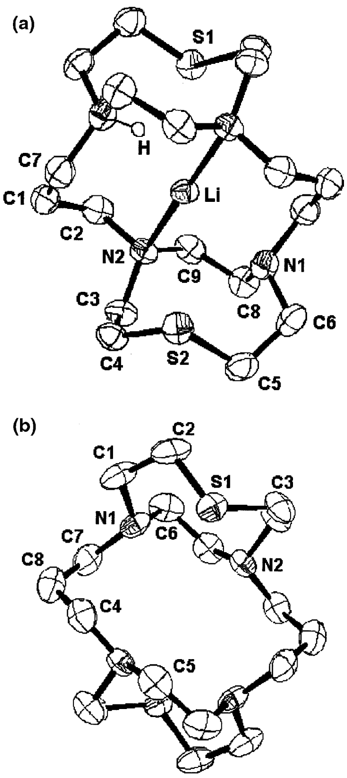


Fig. 1 ORTEP views of the cations: (a) [Li(HL^3)]$^{2+}$ and (b) [H$_2$L^3]$^{2+}$.

DOI: 10.1039/b109793h

According to NMR measurements, the free ligand, the Li complex and the protonated form all showed five carbons signals as expected. Most tetrakis-N-substituted cyclam derivatives prefer to adopt the *trans*-I conformation[12] in which all the N-substituents orient on the same side of the cyclam ring as in the *syn*-conformation of L^3. Only recently, the Ni(II) complex of tetramethylcyclam in the *trans*-III conformation has been reported.[13] Thus, the *trans*-IV conformation observed in our structures is rather unusual.

Extensive literature is available on the coordination chemistry of the Li^+ ion.[14] Coordination numbers of 4–8 are not uncommon in macrocyclic complexes and also a wide variety of coordination geometries other than linear coordination have been observed for Li^+.[14] Though in most Li^+ complexes, the *cis*-positions are occupied by the adjacent donors of a multidentate ligand, in $[Li(HL^3)]^+$, only the *trans*-nitrogens are coordinated. Replacing one of the protons in $[H_2L^3]^{2+}$ by Li^+ does not appear to perturb the structure. Thus, the protonation of one of the nitrogens may not be a factor for this coordination mode. The Li–N distances are very similar to those found in other complexes (2.01–2.08 Å).[15] To our knowledge, linear coordination of Li^+ by a multidentate macrocyclic ligand is unknown. Also, the *in situ* formation of this complex during macrocyclisation substantiates its role as a template in the exclusive formation of L^3. Although there is evidence of complexation of Na^+ and K^+ by L^2, so far, neither the Na^+ nor the K^+ complex of L^3 could be isolated.

A. McA. and S. S. thank the NSERC for funding.

Notes and references

† *Crystal data*: $[Li(HL^3)](ClO_4)_2$, $C_{18}H_{37}N_4S_2LiCl_2O_8$, M = 579.48, triclinic, space group $P\bar{1}$, a = 7.3867(16), b = 9.057(2), c = 10.269(2) Å, α = 72.895(4), β = 80.625(4), γ = 85.607(4)°, V = 647.6(2) Å^3, T = 293 K, Z = 1, μ = 0.46 mm^{-1}. No. of reflections: total = 4921; unique = 2280, refined ($I > 2\sigma(I)$) = 1408 (R_{int} = 0.033). The final $wR(F^2)$ = 0.046. $[H_2L^3](ClO_4)_2$, $C_{18}H_{38}N_4S_2Cl_2O_8$, M = 573.54, monoclinic, space group $P2_1/c$, a = 7.408(2), b = 16.534(5), c = 10.412(3) Å, β = 97.364(6)°, V = 1264.8(7) Å^3, T = 293 K, Z = 2, μ = 0.47 mm^{-1}. No. of reflections: total = 6459, unique = 2230, refined ($I > 2\sigma(I)$) = 1284 (R_{int} = 0.049). The final $wR(F^2)$ = 0.048. CCDC reference numbers 173092 and 173093. See http://www.rsc.org/suppdata/cc/b1/b109793h/ for crystallographic data in CIF or other electonic format.

1 V. Balzani, *Gazz. Chim. Ital.*, 1991, **119**, 311.

2 J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.

3 P. A. Lay, J. Lyndon, A. W.-H. Mau, P. Osvath, A. M. Sargeson and W. H. F. Sasse, *Aust. J. Chem.*, 1993, **46**, 641.

4 M. Cesario, J. Guilhem, C. Pascard, E. Anklam, R. Deschenaux and J.-M. Lehn, *Helv. Chem. Acta.*, 1991, **74**, 179.

5 X. X. Zhang, R. M. Izatt, J. S. Bradshaw and K. E. Krakowiak, *Coord. Chem. Rev.*, 1998, **174**, 179.

6 F. Rabiet, F. Denat and R. Guilard, *Synth. Commun.*, 1997, **27**, 979.

7 I. Murase, G. Vuckovic, M. Hodera, H. Harada, N. Matsumoto and S. Kida, *Inorg. Chem.*, 1991, **30**, 728.

8 A. Damsyik, P. J. Davies, C. I. Keeble, M. R. Taylor and K. P. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1998, 703.

9 A. S. Craig, R. Kataky, R. C. Matthews, D. Parker, G. Ferguson, A. Lough, H. Adams, N. Bailey and H. Schneider, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1523.

10 C. Nave and M. Truter, *J. Chem. Soc., Dalton Trans.*, 1974, 2351.

11 T. M. Barclay, A. McAuley and S. Subramanian, unpublished results.

12 N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1979, 441; and references therein.

13 C. Bucher, E. Duval, E. Espinosa, J. M. Barbe, J. N. Verpeaux, C. Amatore and R. Guilard, *Eur. J. Inorg. Chem.*, 2001, 1077.

14 U. Olsher, R. M. Izatt, J. S. Bradshaw and N. K. Dalley, *Chem. Rev.*, 1991, **91**, 137.

15 A. Bencini, A. Bianchi, A. Borselli, M. Ciampolini, M. Micheloni, N. Nardi, P. Paoli, B. Valtancoli, S. Chimichi and P. Dapporto, *J. Chem. Soc., Chem. Commun.*, 1990, 174.