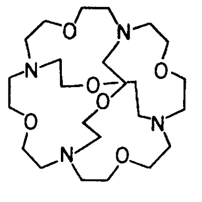
[3] Cryptates: *X*-Ray Crystal Structures of the Chloride and Ammonium Ion Complexes of a Spheroidal Macrotricyclic Ligand

By BERNARD METZ, JONATHAN M. ROSALKY, and RAYMOND WEISS*
(*Institut de Chimie, Université Louis Pasteur*, B.P. 296/R8, 67008 *Strasbourg-Cedex, France*)

Summary The *X*-ray structures of the two complexes $[NH_4L]^+I^-.H_2O$ and $[ClLH_4]^{3+}3Cl^-.7H_2O$, where $L = C_{24}H_{48}N_4O_6$, show that the ammonium ion and the chloride ion are each encapsulated in the macrotricyclic ligand.

Recently the synthesis of the macrotricyclic ligand L = $C_{24}H_{48}N_4O_6$ and the formation of various of its alkali metal complexes were reported.[1] The conformation of L with all four nitrogen bridgeheads in the *endo* form was noted as being particularly favourable for the formation of complexes with spherically symmetric metal cations. It also has been shown recently by ^{13}C n.m.r. potentiometric measurements that the tetraprotonated species LH_4^{4+} is able to form anion inclusion complexes, for instance with chlorine atoms, $[ClLH_4]^{3+}$.[2]



L = $C_{24}H_{48}N_4O_6$

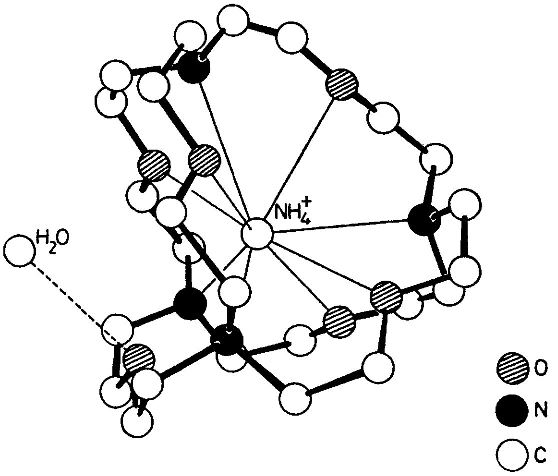


Figure 1. The *X*-ray structure of the complex cation $[NH_4L]^+$ (A).

We report the *X*-ray crystal structures of: (i) the ammonium cation complex $[NH_4L]^+I^-.H_2O$ (A) and (ii) the chloride anion complex $[ClLH_4]^{3+}3Cl^-.7H_2O$ (B).

Crystal data: (A) $C_{24}H_{48}N_4O_6.NH_4I.H_2O$, monoclinic, space group $P2_1/c$, $a = 13{\cdot}949$, $b = 11{\cdot}130$, $c = 20{\cdot}431$ Å, $\beta = 95{\cdot}63°$, $Z = 4$, $D_c = 1{\cdot}37$. (B) $C_{24}H_{48}N_4O_6.4HCl.7H_2O$, monoclinic, space group $P2_1/c$, $a = 11{\cdot}565$, $b = 12{\cdot}694$, $c = 26{\cdot}401$ Å, $\beta = 95{\cdot}08°$, $Z = 4$, $D_c = 1{\cdot}31$.

The intensity data were measured on a Philips PW 1100 four-circle automatic diffractometer, using Mo-K_α radiation. The number of reflections with $I > 3\sigma(I)$ was 1688 for (A) and 1133 for (B). The structure of (A) was solved by heavy atom methods, the current value of the *R* factor being 0·063. The structure of (B) was solved by conventional direct methods, and the present value of the *R* factor is 0·097. An appreciable amount of disorder in one of the six macrotricyclic chains considerably hampered the refinement of (B) and is also almost certainly the reason for the low number of 'observable' data.

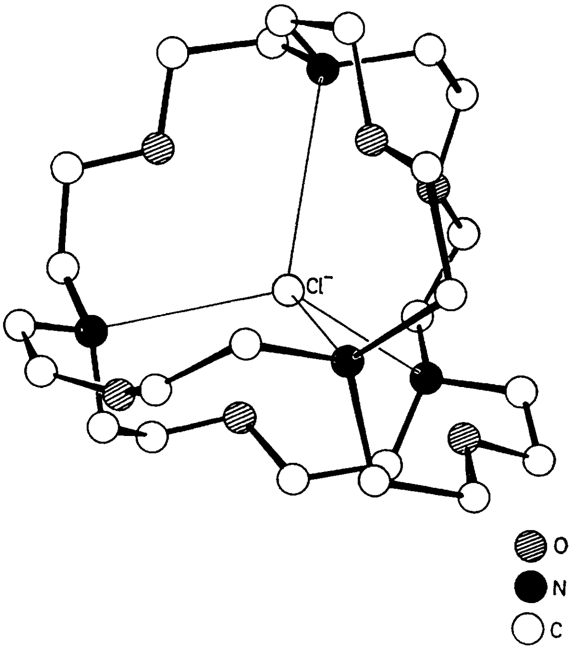


Figure 2. The *X*-ray structure of the complex cation $[ClLH_4]^{3+}$ (B).

The structures of the two cations $[NH_4L]^+$ and $|ClLH_4|^{3+}$ are shown in Figures 1 and 2. In both, the ligand L has the expected i_4 conformation[1] with the nitrogen atoms pointing into the cavity. The ammonium ion and the chloride ion lie in this intramolecular cavity. These central ions are probably held in place by four hydrogen bonds as is shown by the $NH_4^+ \cdots N$ and $Cl^- \cdots N$ bond distances. In (B) the average $Cl \cdots N$ distance, 3·09(2) Å, is less than the sum of the van der Waals' radii and similar to that in the cage compound $[(C_9H_{18})_3(NH)_2Cl]^+$,[3] **while the** mean $Cl \cdots O$ distance is 3·25(3) Å. For (A) the evidence is less clear: the average $NH_4^+ \cdots N$ and $NH_4^+ \cdots O$ distances are 3·13(1) and 3·11(2) Å, respectively.

The water molecule in (A) is hydrogen bonded to O(16) and most probably to the iodine ion at distances of 2·92(1) and 3·61(1) Å, respectively. The value of the angle I-(H_2O)-O(16) is *ca.* 114°.

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[1] E. Graf and J. M. Lehn, *J. Amer. Chem. Soc.*, 1975, **97**, 5022.

[2] E. Graf and J. M. Lehn, personal communication; to be published.

[3] R. A. Bell, G. C. Christoph, F. R. Fronczek, and R. E. Marsh, *Science*, 1975, **190**, 151.