Molecular Structure of Inclusion Complex with Chloride Anion Eccentrically Bound into the Cavity of a Tetraazamacrotricyclic Receptor Having Asymmetrically Charged Nitrogen Centers

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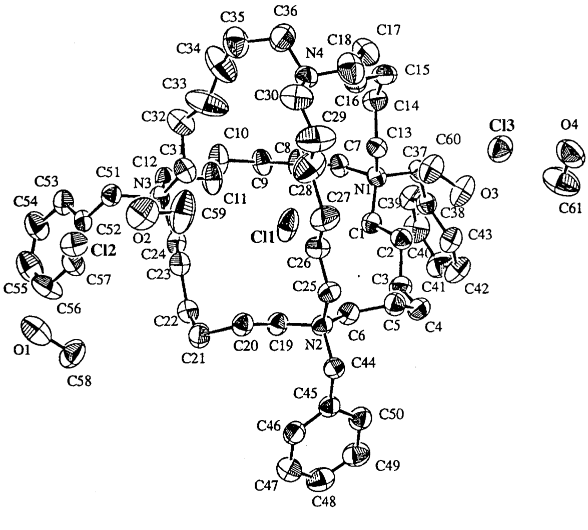
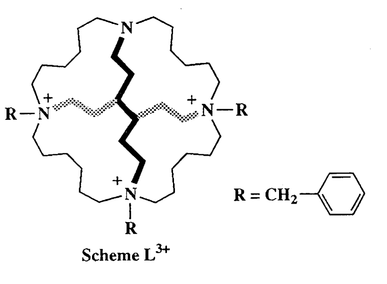
The crystal structure of $[ClL]^{2+}\cdot 2Cl^{-}\cdot 3CH_3OH$, where $L=(C_6H_5CH_2)_3N_4((CH_2)_6)_6$, shows the complete encapsulation of a chloride anion into the intramolecular cavity of the macrotricyclic cage L^{3+}. The included anion is held eccentrically into the cavity with a distance of about 4.1 Å from the three charged nitrogen cations and 5.7 Å from the uncharged nitrogen atom.

The study on non-covalent interactions that occur in synthetic host-guest complexes has been demonstrated to be one effective way to gain insight into the origins of natural binding process as well as a guide to design novel supramolecular structures.[1] Despite the significant progresses in the field of cation complexation by artificial hosts, the corresponding area of anion complexation is in a more preliminary state. Moreover, and perhaps of greater significance, there are even fewer accounts of research describing the solid state structures of anion inclusion complexes.[2] The macrotricyclic ammonium ions are capable of recognizing halide ions in a distance and binding them in solution by the predominant forces of electrostatic interactions.[3] We have previously reported that the chloride ion can be encapsulated into the cavity of quaternized form of macrotricyclic amine $N_4((CH_2)_6)_6$, **MA 666,** even the guest is relatively smaller compared with the size of the cage.[4] In this paper we report the crystal structure of $[ClL]^{2+}\cdot 2Cl^{-}\cdot 3CH_3OH$ where one chloride ion is encapsulated eccentrically by L^{3+} with asymmetric binding sites.

A portion of **MA 666**[3b] and benzyl chloride at the molar ratio of 1:8 was refluxed in presence of Na_2CO_3 for 72 h. After cooling down to room temperature, the pale yellow solution was separated by filtration, and concentrated in vacuo. The resulting residue after dissolving in methanol was kept at room temperature. Its single crystals $[ClL]^{2+}\cdot 2Cl^{-}\cdot 3CH_3OH$ suitable for X-ray study was grown on slow vapor diffusion of THF after 4 days.[5]

As viewed in Figure 1, the structure of $[ClL]^{2+}\cdot 2Cl^{-}\cdot 3CH_3OH$[6] shows that one chloride ion has been encapsulated within the cavity. Even one of nitrogen atoms is uncharged, however the triangular interactions of the three positively charged nitrogen centers provide the essential binding force for the inclusion of the anionic guest. The chloride ion is held at a distance of 4.08 - 4.20 Å from the nitrogen ions which are comparable to those[7] as observed in the case of $Cl^{-}\subset[(C_6H_5CH_2)_4N_4(C_5H_{10})_3(C_6H_{12})_3]^{4+}$ and shorter than the (I-N) of 4.50 - 4.59 Å distances in the case of $[Me_4N_4(C_6H_{12})_6]^{4+}(I^{-})$.[8] The other two chloride ions are located





Scheme L^{3+}

Figure 1. ORTEP representation of $[ClL]^{2+}\cdot 2Cl^{-}\cdot 3CH_3OH$ with thermal ellipsoids drawn at the 50% probability level, where L^{3+} is shown in scheme. The hydrogen atoms are omitted for clarity. Selected geometric parameters (Å, °): Cl(1)-N(1) 4.201; Cl(1)-N(2) 4.079; Cl(1)-N(3) 4.126; Cl(1)-N(4) 5.710; Cl(2)-N(3) 4.704; Cl(3)-N(1) 4.315; Cl(2)-O(1) 3.127; Cl(2)-O(2) 3.128; Cl(3)-O(3) 3.011; Cl(3)-O(4) 3.041; N(1)-N(2) 7.109; N(1)-N(3) 7.321; N(1)-N(4) 7.126; N(2)-N(3) 6.990; N(2)-N(4) 7.841; N(3)-N(4) 6.927; N(1)-Cl(1)-N(2) 118.295; N(1)-Cl(1)-N(3) 123.086; N(1)-Cl(1)-N(4) 90.630; N(2)-Cl(1)-N(3) 116.833; N(2)-Cl(1)-N(4) 105.215; N(3)-Cl(1)-N(4) 88.001.

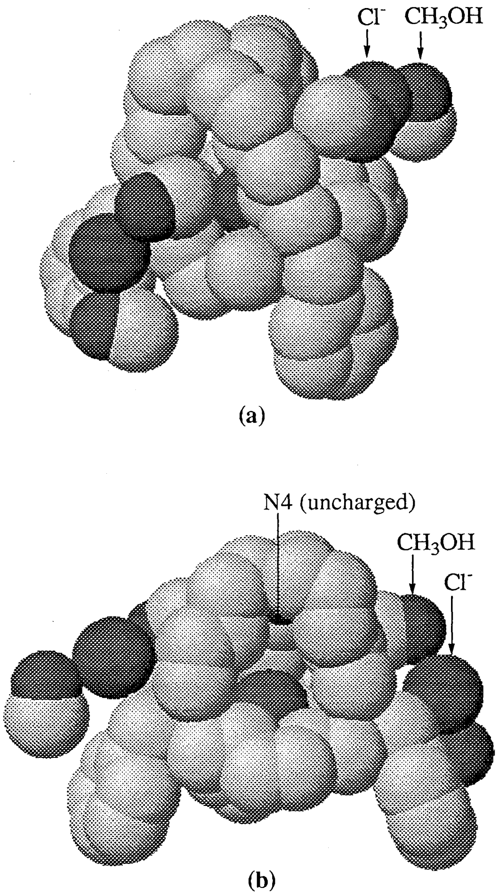


Figure 2. Space filling molecular structures of $[ClL]^{2+}\cdot 2Cl^- \cdot 3CH_3OH$. a) side view of figure 1 and b) back view of figure 1 of the inclusion complex: encapsulated chloride guest is visible in the cavity near the three charged nitrogen ions.

outside the cavity and centered towards N(1) and N(3) having the distances of 4.3 and 4.7 Å, respectively. These distances are slightly longer than those of the encapsulated chloride ion to the ammonium centers. A considerable longer distance (5.71 Å) is attained for Cl(1) - N(4) since the electrically neutral nitrogen atom does not interact with the anion.

There is no fractional population of the anions, however, three crystalline methanol molecules are disordered at four locations with an equal occupancy of 0.75. The space filling models of the molecular structure as shown in Figure 2 indicate that each of the outside chloride ions is coupled with two methanol molecules possibly by hydrogen bonding of $OH\text{--}Cl^-$ as predicted from the Cl - O distances of 3.0 to 3.1Å. The hydrophobic interactions make the alkyl parts of methanol molecules directed towards the hydrocarbon units of the host (Figure 2a). The three benzyl groups are spaced at the same direction like a tripod. Figure 2b shows that the encapsulated chloride ion holds a position closest to charged nitrogen ions. Although all the endocyclic hydrocarbon chains consist of equal number of methylene groups, nevertheless the cavity is distorted from its tetrahedral structure as inferred from N-N distance of 7.99 to 7.84 Å.

Indeed, the cavity consisting of all $-(CH_2)_6-$ bridge is large enough compared with the ionic radius of chloride ion and can easily be displaced by iodide ion in solution,[4] nevertheless the coulumbic forces exerted by nitrogen centers lead the formation of inclusion complex with chloride guest.

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References and Notes

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5 The final compound gives the data of elemental analysis and NMR in accordance with its structure.
6 Crystal data of $[ClL]^{2+}\cdot 2Cl^-\cdot 3CH_3OH$: $C_{60}H_{105}N_4Cl_3O_3$, M = 1036.87, colorless prism, dimension 0.35x0.20x0.10 mm, monoclinic, a = 21.002 (4), b = 13.551 (6), c = 24.601(8) Å, β = 112.47 (2) °, V = 6469 (2) °Å^3, space group $P2_1/a$, Z = 4, D_c = 1.064 g/cm^3, F_{000} = 2272.00, μ(MoKα) = 1.83 cm^{-1}. Data were collected at room temp. on a Rigaku RAXIS II imaging plate and were corrected for Lorentz and polarization effects. The structure was solved by direct methods[9], and expanded using Fourier techniques[10]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinements was based on 4098 observed reflections ($I > 5.00\ \sigma(I)$) and 650 variable parameters and converged to R = 0.076 and R_W = 0.113. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.40 and -0.25 e/ Å^3, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[11]
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