

Anion Inclusion without Auxiliary Hydrogen Bonds: X-Ray Structure of the Iodide Cryptate of a Macrotricyclic Tetra-quaternary Ammonium Receptor

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The X-ray crystal and molecular structure of $[L-L^{4+}]^{3+} 3I^{-} \cdot 3MeCN \cdot H_2O$, $L = N_4Me_4(C_6H_{12})_6$, shows one iodide anion to be encapsulated symmetrically into the spherical intramolecular cavity of the macrotricyclic L^{4+} and held in place by the electrostatic potential of the four quaternary ammonium sites arranged at the corners of an almost perfect tetrahedron; the $N^+ \cdots I^-$ distances average to 4.54(2) Å whereas the distances between iodide and the carbon atoms of the $[CH_2]_6$ chains are of van der Waals type or longer.

Artificial host-guest systems owe much of their relevance to the analogy which can be drawn to natural enzymes and receptors.¹ The rapidly increasing availability of precise structural data of enzyme-substrate complexes, obtained to a large extent by X-ray crystallographic methods, set the stage for a basic understanding of the principles governing selectivity in enzymic reactions.²

Approaches to adapt these principles for gaining selectivity in nonenzymic reactions depend on the availability of abiotic receptor molecules, capable of binding their respective guests in a functionally and geometrically well defined fashion. Whereas a variety of receptor groups for hydrophobic and cationic substructures of guest molecules are known,³ which fulfil these requirements, candidates for binding anionic substrate moieties are very rare.⁴ Still fewer are examples in which the topological and geometrical relationship between the artificial host and anionic guest has unambiguously been proven. The vast majority (*ca.* 70%) of natural enzymes bind anionic species, yet X-ray structures of anion complexes involving only three different artificial receptors have been published for comparison.⁵⁻⁷

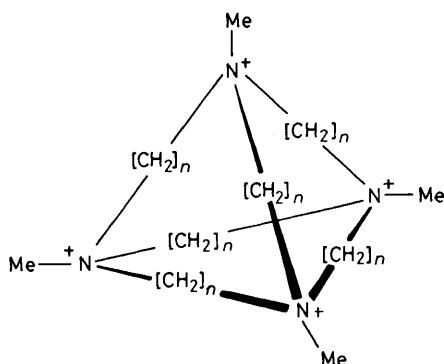
Here we present the structure of a host-guest complex of iodide anion and the totally synthetic macrotricyclic receptor L^{4+} which has been shown to bind anions in aqueous solution.⁸ This complex does not rely on the formation of multiple hydrogen bonds as in the structures known so far,⁵⁻⁷ but rather owes its existence to the strong positive electrostatic potential residing in the molecular cavity of the host. By virtue of this the location of the anion relative to the host is clearly defined.

Crystal data: $C_{40}H_{84}I_4N_4 \cdot 3MeCN \cdot H_2O$, $M_r = 1269.93$, monoclinic, space group Cc , $a = 19.084(5)$, $b = 18.601(4)$, $c = 16.226(4)$ Å, $\beta = 95.94(2)^\circ$, $U = 5729.00$ Å³, $D_x = 1.472$ g/cm³ for $Z = 4$, $F(000) = 2560$, $\mu(Mo-K\alpha) = 21.87$ cm⁻¹. 4650 Unique reflections were measured on a Syntex P2₁ automated four-circle diffractometer equipped with a graphite mono-

chromator (Mo- $K\alpha$ radiation, $\lambda = 0.71069$ Å, ω -scans, $1 \leq \theta \leq 24^\circ$, $T = -40^\circ C$).

After Lorentz polarisation and absorption corrections (empirical) 221 reflections with $F_o \leq 4.0 \sigma(F_o)$ were deemed unobserved and excluded from all further calculations. The structure was solved by direct methods (MULTAN 80) and completed by Fourier syntheses. Refinement, first by full-matrix least-squares (2 large blocks), then by block-diagonal least-squares converged at $R = 0.037$, $R_w = 0.052$, $w = 1/\sigma^2(F_o)$ for 471 parameters. (Non-hydrogen atoms anisotropic, except those of two disordered CH_2 groups and of the solvate molecules which were refined isotropically; hydrogen atoms included as fixed atom contributions with the omission of those in solvate molecules.) A final difference-Fourier synthesis was qualitatively featureless, $\Delta\rho_{max} = 0.77$ e/Å³.†

As Figure 1 shows, one of the four iodide anions is situated approximately in the centre of the intramolecular cavity of the macrotricyclic receptor cation. A tetrahedral co-ordination geometry of I(1) may be inferred from nearly equal I-N distances [av. 4.54(2) Å] and from N-I-N angles coming close to the tetrahedral standard (see caption to Figure 1). Likewise, from the pattern of the N-N distances [av. 7.42(7) Å] it follows that the four tetra-alkylammonium centres are arranged at the vertices of an almost perfect tetrahedron whose edges are spanned by $[CH_2]_6$ bridges. The distances from the iodide guest to the carbon atoms of these $[CH_2]_6$ chains range between 3.83(1) and 5.55(1) Å, the former value coming close to the sum of the ionic radius of I^- (2.16 Å⁹) and the van der Waals radius of carbon (1.65–1.70 Å⁹). These close contacts imply that the large spherical I^- fits very snugly in the tetrahedral cage of the host cation, thus forcing the $[CH_2]_6$ bridges to bend 'outwards' and leading to an approximate spherical shape of the host-guest complex as a whole. This idea is also borne out by the rather short distances of I(1) to the N,N,N planes (*i.e.* the faces) of the N_4 tetrahedron [av. 1.51(5) Å] and from the conformations of the chains themselves. As may be seen in Figure 1, most N-C-C and C-C-C fragments approach *anti* conformations (torsion angles $\geq 160^\circ$), indicating a rather relaxed conformational state of the bridges. However, in order to achieve an overall spherical shape of the anion cryptate, at least one C-C-C fragment per bridge has to be in a *gauche* conformation which is usually realized in the middle of the bridges. [Exceptions are the chains N(2)-N(3) and N(1)-N(4) which contain two *gauche* fragments.] It is interesting to note that most N-C-C and C-C-C angles are



The macrotricyclic receptor L^{4+} ($C_{40}H_{84}N_4$), $n = 6$.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

noticeably greater than 109° , thus implying again a certain stretch of the N—N bridges.

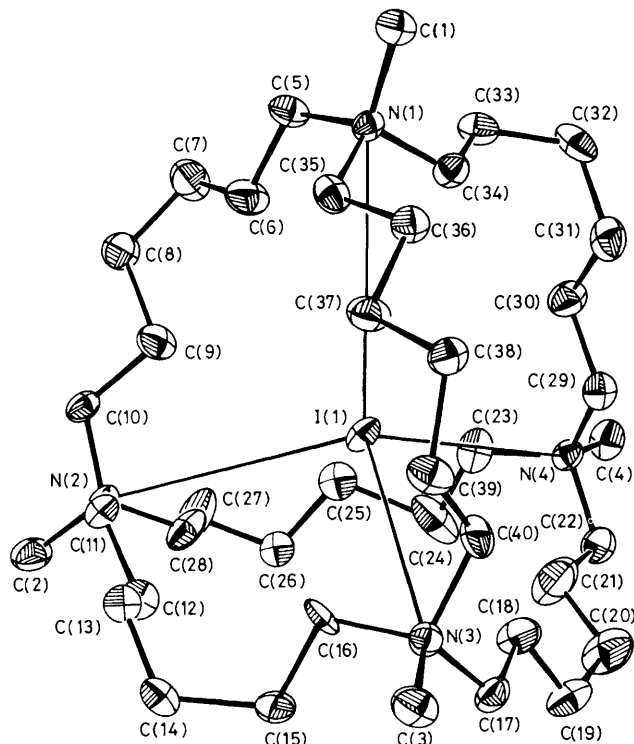


Figure 1. Molecular structure of the complex cation $[I-L^{4+}]^{3+}$ with thermal ellipsoids at the 50% probability level (ORTEP). Hydrogen atoms are omitted for clarity. A twofold positional disorder of atoms C(24) to C(27) could be resolved for C(25)/(26). Only the alternative with major weight is shown. Principle distances (Å) and angles ($^\circ$) of the cage geometry are: I(1)—N(1) 4.504(7), I(1)—N(2) 4.541(7), I(1)—N(3) 4.591(7), I(1)—N(4) 4.540(7), N(1)—N(2) 7.36(1), N(1)—N(3) 7.52(1), N(1)—N(4) 7.10(1), N(2)—N(3) 7.50(1), N(2)—N(4) 7.45(1), N(3)—N(4) 7.57(1); N(1)—I(1)—N(2) 108.9(5), N(1)—I(1)—N(3) 111.5(5), N(1)—I(1)—N(4) 103.5(5), N(2)—I(1)—N(3) 110.5(5), N(2)—I(1)—N(4) 110.2(5), N(3)—I(1)—N(4) 112.0(5).

The molecular geometry found for $[I-L^{4+}]^{3+}$ implies that the anionic guest is held in the cavity of the host cation by predominantly coulombic interactions exercised by the positive charges of the four ammonium centres arranged with optimum possible symmetry around the negative charge of the guest ion. This may also be inferred from the arrangement of the three I^- ions which are located outside the L^{4+} cage. Their distances from the ammonium centres [range of closest contacts: 4.455(7)—5.228(7) Å] are in most cases somewhat longer than those of the encapsulated I^- , but nevertheless directly comparable with them. Even the number of closest $I^- \cdots N^+$ distances for the anions outside the cage is in two cases [I(2), I(3)] equal to that for the cryptated I(1), whereas for I(4) there are only three such close contacts. The high symmetry and the optimum charge separations of the coulombic potential inside the cage explain the much higher binding force for the guest anion, however. Ion-induced dipole and London forces between I^- and the CH_2 groups should only play a minor but nevertheless synergistic role.

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