Caged Anions: Perchlorate and Perfluoroanion Cryptates

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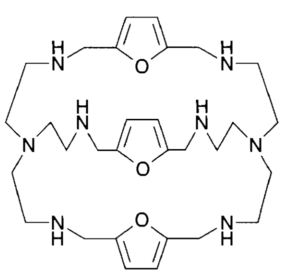
The structure of a perchlorate cryptate shows complete encapsulation of the anion within the crypt: in a mixed BF_4^--SiF_6^{2-} cryptate the SiF_6^{2-} anion is preferentially encapsulated.

Despite the significance of anion complexation in biology[1] and the chemical and environmental benefits[2] which await the development of reliable procedures for its abiological achievement, this chemistry is still in its infancy compared to the coordination chemistry of cations. Metal ion complexation owes its dominance to the many obvious (in some cases even visible) manifestations which attend the alteration of cation ligation, and the range of spectroscopic techniques which are capable of probing it. On the other hand, relatively few techniques yield information about structural relationships in anion complexes. Dominant among these, however, are X-ray crystallography and NMR spectroscopy, techniques whose current rapid development augurs well for progress in this potentially important field.

Structural studies are particularly important in establishing the nature of the host–guest interactions involved, leading to definition of factors which determine stability of the complexes and in turn guide the design of improved anion receptors. The first artificial anion complexes to be structurally characterised were halide and azide complexes synthesised in the laboratories of Fronzcek,[3] Weiss[4] and Lehn,[5] who also investigated the stability of these and other (including oxoanion) adducts by electrochemical techniques.[6] Other groups have since contributed structural,[7–11] electrochemical[8–12] and modelling[13] studies of chelate, podand and macrocyclic receptors using protonated amine, calixarene or guanidinium functions as anion ligating sites.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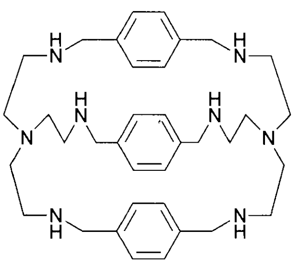
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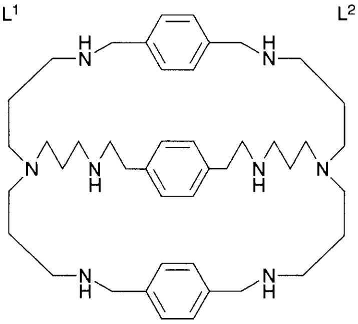
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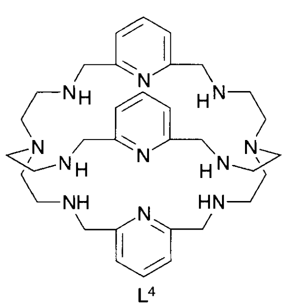
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Apart from the linear triatomic azide, however, no polyatomic inorganic (*e.g.* oxo or perhalo) anion cryptate has been structurally characterised to date. We now report the first structures of such polyatomic anion cryptates.

The host $[L^1H_6]^{6+}$, with two sets of trigonally disposed protonated amine functions, is well-suited to the encapsulation of six- or four-coordinate anionic guests. The flexibility inherent in the saturated cryptand skeleton allows the furan rings to adopt a trigonal disposition around the bridgehead-N axis, allowing sufficient space in the cavity to accommodate a relatively bulky guest. The crystal structure of $[L^1H_6][ClO_4]_6 \cdot 9H_2O$ **1** shows unambiguous encapsulation of one perchlorate oxoanion within the cryptand (Fig. 1). Both

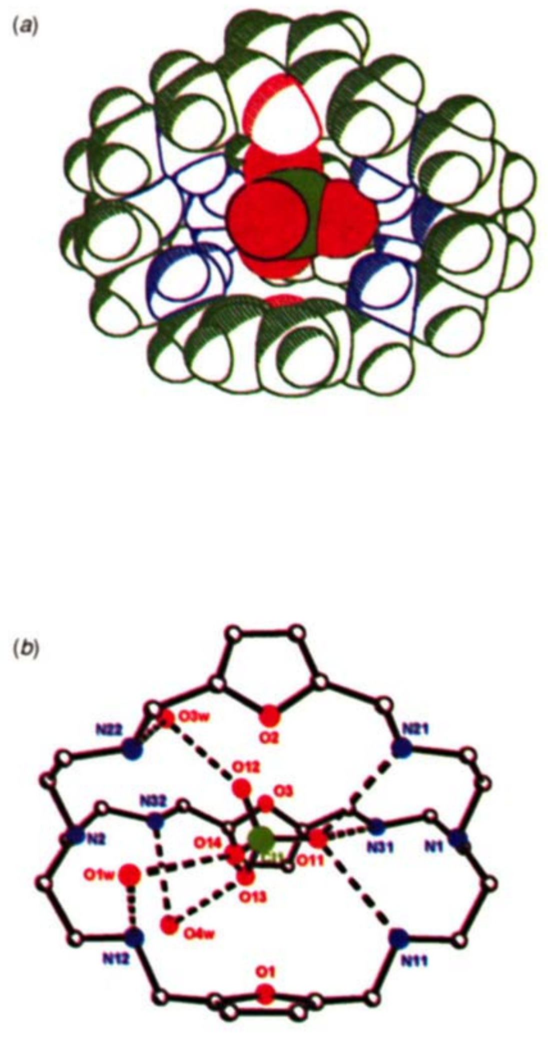

Fig. 1 (*a*) Space-filling model, and (*b*) perspective view of the $[(L^1H_6)(ClO_4)]^{5+}$ cation **1**.† The perchlorate is shown in one of the disordered sites only; dotted lines represent hydrogen bonds. Colour coding: red = O, blue = N (and H on N), solid green = Cl.

electrostatic and hydrogen-bonding effects contribute to the stability of the complex.

The encapsulated perchlorate anion is disordered between two positions with occupancies of 60% for the major orientation [Cl(1), O(11), O(12), O(13), O(14)] and 40% for the minor site [Cl(1′), O(15), O(16), O(17), O(18)]. The two sites are very similar and are related by a non-crystallographic mirror plane passing between Cl(1) and Cl(1′) perpendicular to the N(1)–N(2) vector (Fig. 1). Cl(1) and Cl(1′) are close to the centre of the cage and are almost coincident [C(1)–Cl(1′) 0.2 Å]. The Cl(1)–O(11) and Cl(1′)–O(15) bonds lie along the approximate threefold axis of the cryptate, directed towards the bridgehead atoms N(1) and N(2), respectively. This orientation allows O(11) [or O(15)] to form hydrogen bonds to the three protonated nitrogen donors N(11), N(21) and N(31) [or N(12), N(22) and N(32)]. These bonds are rather long (mean N–O 3.11 Å, Table 1), probably as a consequence of geometric constraints within the cryptand. The three remaining oxygen atoms in each perchlorate orientation form normal hydrogen bonds to water molecules O(1w)–O(6w), located in the clefts between the arms of the ligand (Fig. 2; Table 1). Each of these six water molecules is also hydrogen-bonded to one protonated amine of the cryptand, an arrangement which has been seen previously in the fully protonated cryptands L^2 [14] and L^3 [15]. Extensive further hydrogen bonding links these water molecules with the five uncoordinated perchlorate anions and three additional water molecules [O(7w), O(8w) and O(9w)] in the lattice, every water molecule making either three or four hydrogen bonds. These interactions are listed in Table 1.

Comparison of the structures of $[(L^1H_6)(ClO_4)]^{5+}$ and $[Cu_2L^1(OH)]^{3+}$ **2** illustrates the geometric flexibility of the cryptand ligand. The most significant difference is in the overall length of the cavity, 9.33 Å in **1** and 8.05 Å in **2**.[16] This difference in length is not matched by any significant corresponding change in the width of the cavity. Rather, the shorter cavity in the dicopper complex is a result of the helical conformation adopted by the cryptand. In the binuclear cryptates we have structurally characterised to date,[16,17] the strands twist about the N_{br}–N_{br} axis, resulting in a shorter cavity with a helical structure. Metal-free cryptand ligands may adopt either a helical conformation or one, as here, in which the ligand arms at one bridgehead nitrogen atom are approximately eclipsed with respect to the second bridgehead.[14,18]

In order to discover whether encapsulation could be recognised *via* NMR spectroscopy of the anion, we synthesised the BF_4^- salt of protonated L^1 and examined its ^{11}B NMR spectrum. A signal at δ −0.25 with *ca.* 1/5 of the intensity of the free BF_4^- resonance at δ −0.55 was seen which is a possible candidate for the cryptated anion resonance. Although the ^{11}B signals were broadened on reducing temperature there was no sign of coalescence of signals at any temperature within the solvent (MeCN) fluid range. This observation is at least consistent with anion incorporation within the cryptand host. However, we were unable to grow crystals of this salt suitable for crystallographic study, so direct confirmation of encryptation is lacking.

In an attempt at structural characterisation of a fluoborate cryptate using other cryptand hosts, we grew crystals of X-ray diffraction quality of the product, **3**, of reaction of HBF_4 with L^4. Unexpectedly, in this structure the encryptated anion turns out not to be fluoroborate, but an octahedral anion, later shown (by ES-MS and ^{19}F NMR) to be SiF_6^{2-} [this anion apparently derives from action of (technical grade) HBF_4 on the glass reaction vessel]. A preliminary structural analysis has been carried out on this material which shows an SiF_6^{2-} ion encapsulated within the cryptand ligand (Fig. 3). The anion

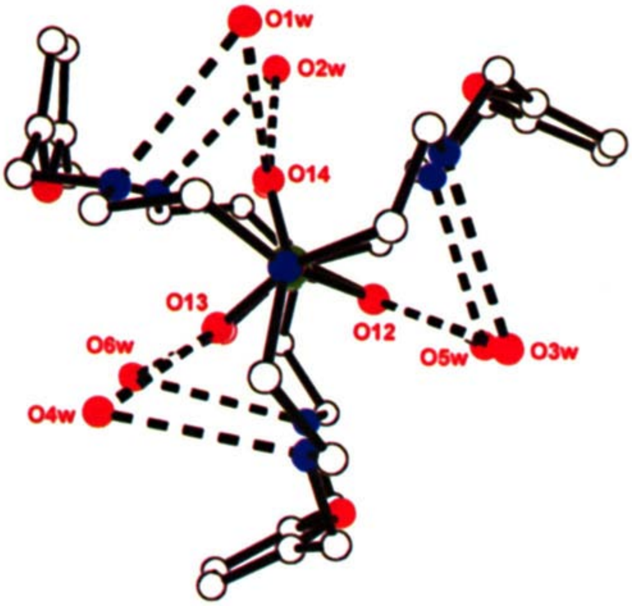

Fig. 2 Perspective view of **1** along the N(1)–N(2) axis illustrating hydrogen-bonding to water. Colour code: red = O, blue = N, uncoloured = C. Dotted lines show hydrogen bonds; for all H-bond distances see Table 1.

Table 1 Hydrogen-bonding distances in **1**[a]

	d/Å		d/Å
O(11)–N(11)	3.064 (0.019)	O(15)–N(12)	3.095 (0.028)
O(11)–N(21)	3.088 (0.016)	O(15)–N(22)	3.110 (0.025)
O(11)–N(31)	3.194 (0.022)	O(15)–N(32)	3.099 (0.030)
O(12)–O(3w)	2.736 (0.017)	O(16)–O(6w)	2.596 (0.030)
O(13)–O(4w)	2.758 (0.018)	O(17)–O(5w)	2.806 (0.022)
O(14)–O(1w)	2.909 (0.015)	O(18)–O(2w)	2.775 (0.024)
O(1w)–N(12)	2.792 (0.009)	O(2w)–N(11)	2.777 (0.009)
O(1w)–O(62)_$1	2.864 (0.009)	O(2w)–O(62)_$1	2.883 (0.009)
O(1w)–O(7w)	2.853 (0.011)	O(2w)–O(8w)	2.725 (0.011)
O(3w)–N(22)	2.830 (0.010)	O(4w)–N(32)	2.926 (0.010)
O(3w)–O(63)	2.896 (0.009)	O(4w)–N(12)	3.125 (0.011)
O(3w)–O(8w)_$2	2.853 (0.011)	O(4w)–O(41)	2.826 (0.015)
O(5w)–N(21)	2.850 (0.010)	O(6w)–N(31)	2.888 (0.010)
O(5w)–O(63)	2.883 (0.009)	O(6w)–O(33)_$4	2.935 (0.016)
O(5w)–O(7w)_$2	2.920 (0.011)	O(6w)–O(53)	2.848 (0.019)
O(7w)–O(44)_$3	3.058 (0.013)	O(9w)–O(23)_$4	2.951 (0.017)
O(8w)–O(9w)	2.679 (0.014)	O(9w)–O(32)	2.957 (0.018)

[a] Symmetry transformations used to generate equivalent positions: $1 = 0.5 − x, 0.5 + y, 1.5 − z $2 = 0.5 − x, −0.5 + y, 1.5 − z $3 = 0.5 + x, 1.5 − y, 0.5 + z $4 = 1 − x, 2 − y, 1 − z.

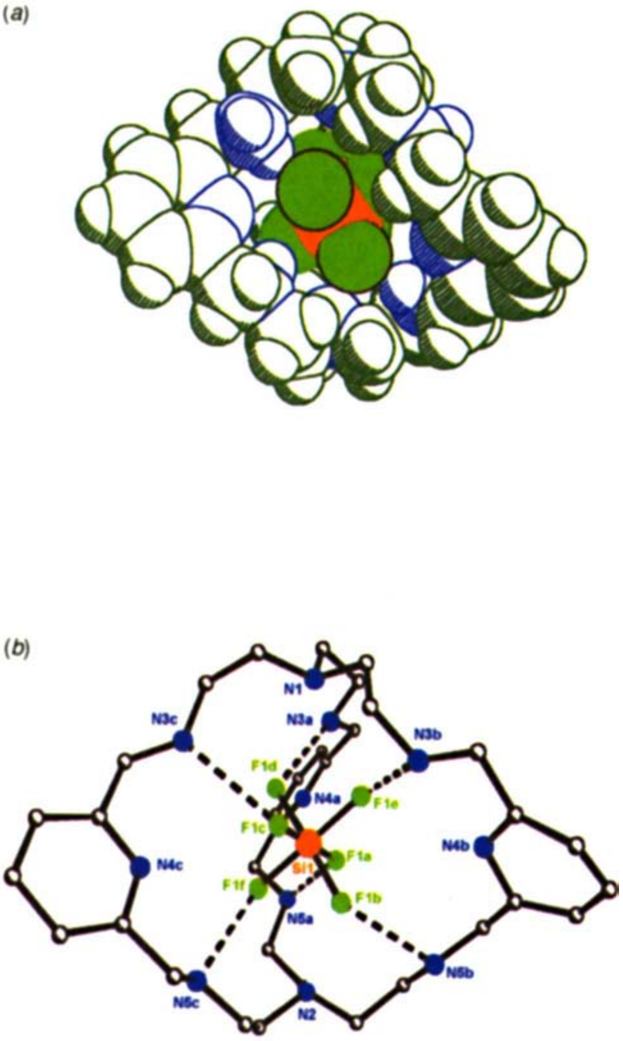

Fig. 3 (*a*) Space-filling model, and (*b*) perspective view of the mixed SiF_6^{2-}–BF_4^- cryptate **3**.‡ Dotted lines represent hydrogen bonds; range of F···N distances 2.69–2.83 Å. Colour code: solid green = F, gold = Si, blue = N (or H on N).

shows regular octahedral geometry with each fluorine atom hydrogen-bonded to one protonated secondary amine (2.69–2.82 Å); the amines are also hydrogen-bonded to either water molecules [N(3a), N(3b), N(3c) and N(5a)] or to BF_4^- anions [N(5b) and N(5c)] lying outside the cavity. The cation, five BF_4^- counter-ions and four lattice water molecules are well defined but the presence of disordered water and $B/Si(O/F)_n$ species, combined with weak diffraction data, prevented a full refinement. For the same reason, the extent of ligand protonation cannot be determined with certainty. The preferential complexation of SiF_6^{2-} over BF_4^- suggests stronger interaction with the cryptand host arising from complementarity of hydrogen-bond donor and acceptor dispositions, together with electrostatic considerations. This implies that by judicious choice of host geometry, we may eventually be able to ensure selectivity for a particular anionic guest.

We hope to extend our structural investigations to other anionic geometries, such as trigonal or linear, and independently to vary anionic charges, to ascertain the importance of directional effects such as hydrogen-bonding as against electrostatic effects which are non-directional. We would also wish to attempt the encapsulation of organic-solvent insoluble oxoanions such as sulfate to see if they can be solubilized upon cryptation. Finally, the study of selectivity for particular environmentally significant anions such as nitrate, chromate, arsenate or phosphate is an important priority.

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Footnotes

† *Crystal data*: $[(L^1H_6)(ClO_4)]\cdot 5ClO_4\cdot 9H_2O$, $C_{30}H_{72}Cl_6N_8O_{36}$, pale yellow block, dimensions 0.34 × 0.30 × 0.24 mm, monoclinic, a = 14.228(2), b = 19.241(3), c = 21.797 Å, β = 107.32(1)°, U = 5697(1) Å^3, μ = 0.406 mm^{-1}, space group $P2_1/n$, Z = 4, $F(000)$ = 2792. Data were collected at room temp. on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Using 1.4° ω-scans at 5° min^{-1}, 7707 reflections were collected in the range $4 < 2\theta < 45°$ and all 7356 unique reflections (R_{int} = 0.031) were used in the refinement. The data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods,[19] which revealed the positions of most of the non-H atoms, the remainder were located from difference fourier maps. H atoms were inserted at calculated positions and all the non-H atoms were assigned anisotropic displacement parameters. The data set was quite weak and there was evidence of disorder in some of the perchlorate anions. The alternative positions used to model the encapsulated perchlorate anion are described above; in addition, two sets of oxygen positions centred on C(5) were inserted. Similarity restraints (SAME)[20] were applied to all the lattice perchlorate anions and, separately, to the encapsulated perchlorate. Refinement on F^2 converged with $wR2$ = 0.166, GOF = 0.768 and conventional $R1$ = 0.063 [$I > 2\sigma(I)$] for 799 parameters with 680 restraints. The final difference map showed no significant residual electron density. All programs used in the structure refinement are contained in the SHELXL-93[20] package.

‡ *Crystal data*: modelled as $[H_nL^4(SiF_6)]\cdot 5BF_4\cdot B/Si(F/O)_6\cdot 5.5H_2O$, $C_{33}H_{68}B_5F_{34}N_{11}O_{5.5}Si_2$, crystal dimensions 0.62 × 0.44 × 0.16 mm, monoclinic, a = 16.446(2), b = 13.829(2), c = 25.616(2) Å, β = 91.487(8)°, U = 5801(1) Å^3, space group $P2_1/c$, Z = 4. Data were collected at 123 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Using 1.4° ω-scans at 5° min^{-1}, 8922 reflections were collected in the range $4 < 2\theta < 45°$, 7561 unique reflections (R_{int} = 0.028) were used in the refinement [only 41% had $I > 3\sigma(I)$]. The structure was solved by Patterson methods.[19] Non-hydrogen atoms of the cation and of the five well-defined BF_4^- ions were refined with anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions on the cation. One of the pyridine rings of the cation is disordered and was modelled with 50% occupation of each of two conformations. The lattice also contains four water molecules hydrogen-bonded to the cation and some unidentified fragments modelled as either partial-occupancy water molecules or $Si/B(F/O)_n$ species. All the data were used for refinement on F^2 giving a current conventional $R1$ = 0.097 [for $I > 2\sigma(I)$]. All programs used in the structure refinement are contained in the SHELX-93[20] package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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