DALTON
COMMUNICATION

Extraordinary bromide anion templated self-assembly of the $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ trication

Nicolette S. Fender,[a] Ishenkumba A. Kahwa,*[,a] Andrew J. P. White[b] and David J. Williams[b]

[a] *Chemistry Department, University of the West Indies, Mona Campus, Kingston 7, Jamaica*
[b] *Chemical Crystallography Laboratory, Chemistry Department, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*

An elegant self-assembled cation, $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$, templated by the bromide anion has been prepared and structurally characterized.

Anion recognition is a well established phenomenon.[1] Many substrate cavities with appropriate shape and size complementarity have been used to encapsulate a variety of anionic species ranging from simple halides (X^-)[2] and oxide (O^{2-})[3] to the more complex dihydrogen phosphate $(H_2PO_4^-)$,[4] hexafluorophosphate (PF_6^-)[5] and hydrogen isophthalate.[6] However, rarely have anions served as organizational templates for discrete cations in the same way as metal ions have proved to be effective facilitators for anion assemblies.[7] To our knowledge, examples of self-assembled cations in which anions exhibit an unambiguous organizational role are limited to T_d $[\{A(18\text{-crown-}6)\}_4MX]^{2+}$ (A = monocation; M = 3d element)[8] and, the recently reported, very unusual discrete tetrahedral $[A_4Br]^{3+}$ (A = K or Cs) cations trapped in tetrahedral sites of the $[Zr_6(B)Br_{18}]^{6-}$ and $[Zr_6(B)Br_{16}]^{3-}$ clusters synthesized at high temperatures,[9a] and circular iron polypyridyl helicates.[9b]

Herein we report an extraordinary Br^- templated self-assembly of $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ and the structure of the compound $[\{Na(15\text{-crown-}5)\}_4Br][TlBr_4]_3$ **1**.

Good yields† of crystalline **1** (*ca.* 75%) and the ethanol solvate of $[\{K(15\text{-crown-}5)\}_4Br][TlBr_4]_3$ **2** (*ca.* 60%) are obtained from alcoholic solutions of stoichiometric amounts of 15-crown-5, alkali-metal bromides and thallium(III) bromides. Complex **1** was first isolated serendipitously, the unsuccessful preparation being that of $[\{Na(15\text{-crown-}5)\}_4MnBr_4][TlBr_4]_2$ **3**. The hot stoichiometric mixtures designed[8] for **3** gave the sandwich $[A(15\text{-crown-}5)_2][TlBr_4]$ (A = Na, K or Rb)[8b,c] whilst room-temperature crystallization, again, yielded **1** and **2**.

The X-ray analysis ‡ of **1** (Fig. 1) shows the Na^+ cations to be bound in the 'sunrise' geometry by the 15-crown-5 macrocycle, the oxygens being arranged in a 'four up one down' conformation. Four of these 1 : 1 Na^+ : 15-crown-5 complex cations are then arranged approximately tetrahedrally (the crystallographic symmetry is D_{2d}) around a central Br^- anion. The Na–Br distance [2.889(6) Å] is significantly less than that in crystalline NaBr [2.983(3) Å][10] though comparable with the terminal Na–Br distance [2.883(3) Å] in the sodium bromide complex of a carbon-pivot lariat 16-crown-5 ether.[11] It is, however, slightly longer than that observed (2.762 Å) for a mono-substituted benzo-15-crown-5 complex.[12] The $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ trications have an approximately spherical hydrophobic exterior and are positioned like 'eggs in an egg-box' within a folded network of $TlBr_4^-$ anions [Fig. 2(a)]. There are two crystallographically independent types of $TlBr_4^-$ anions in the crystal. Both of these have approximate T_d symmetry, though the crystallographic site symmetry differs: one has D_{2d} symmetry whereas the other has C_{2v}, in a 1 : 2 ratio. Those with D_{2d} symmetry [Tl(1)] have each of their four Br atoms in van der Waals contact (Br · · · Br = 4.04 Å) with a Br atom on a neighbouring $TlBr_4^-$ anion with C_{2v} symmetry [Tl(2)], thereby producing the box-like array depicted in Fig. 2(b). Adjacent layers are offset such that the corner $TlBr_4^-$ anions in one layer are positioned over the center of the next, thus completely encapsulating the cation [Fig. 2(a)].

There are many examples in the literature of 'four-coordinate' halides. In the majority of cases however, these involve either soft Lewis acids with the halogen atom at the apex of a square pyramid or a few severely distorted non-discrete four-co-ordinate arrangements such as those of a Li_6Br_4 core.[13]

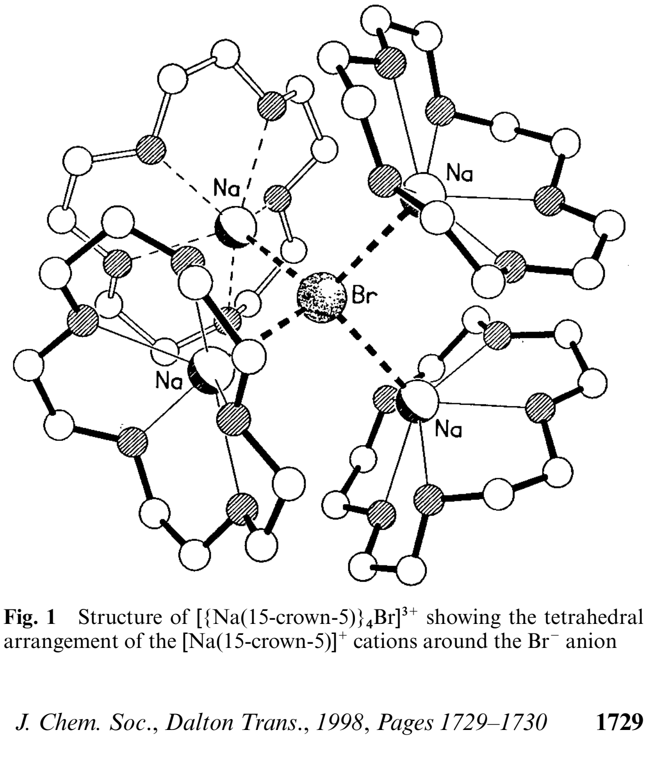

Fig. 1 Structure of $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ showing the tetrahedral arrangement of the $[Na(15\text{-crown-}5)]^+$ cations around the Br^- anion

---

† Complexes **1** and **2** were prepared by addition of the alkali-metal bromide (1 mmol) to 15-crown-5 (1 mmol) dissolved in 20 cm³ of ethanol in a 50 cm³ conical flask. Thallium(III) bromide (0.75 mmol) was added to the solution formed on warming, and the mixture then reduced to *ca.* 10 cm³ on a hot plate. Butanol (1 cm³) was added and the mixture left to evaporate slowly at room temperature (*ca.* 24 °C). Rod-shaped crystals obtained over 4–7 d were harvested and dried with tissue paper (Found: C, 17.74; H, 2.97. $C_{40}H_{80}Br_{13}Na_4O_{20}Tl_3$ **1** requires: C, 18.3; H, 3.1%).

‡ Crystal data for **1**: $C_{40}H_{80}Br_{13}Na_4O_{20}Tl_3$, $M = 2624.9$, tetragonal, space group $P4_2/nmc$ (no. 137), $a = b = 14.186(2)$, $c = 19.253(2)$ Å, $U = 3874.6(7)$ Å³, $Z = 2$, $\rho_c = 2.250$ g cm^{-3}, μ(Cu-Kα) = 203 cm^{-1}, $F(000) = 2444$, $T = 183$ K. A yellow octahedron of dimensions 0.20 × 0.17 × 0.17 mm was used. 1575 Independent reflections were measured giving $R1 = 0.049$, $wR2 = 0.117$ for 1140 independent observed absorption corrected reflections $[|F_o| > 4\delta(|F_o|), 2\theta \leq 120°]$ and 169 parameters. The 15-crown-5 macrocycle was found to be disordered about a crystallographic mirror plane. Crystals of **2** have similar lattice parameters as those of **1**, but two structures are not perfectly isomorphous due to solvent effects. Elemental analyses can not distinguish between butanol and ethanol solvent molecules. CCDC reference number 186/988.

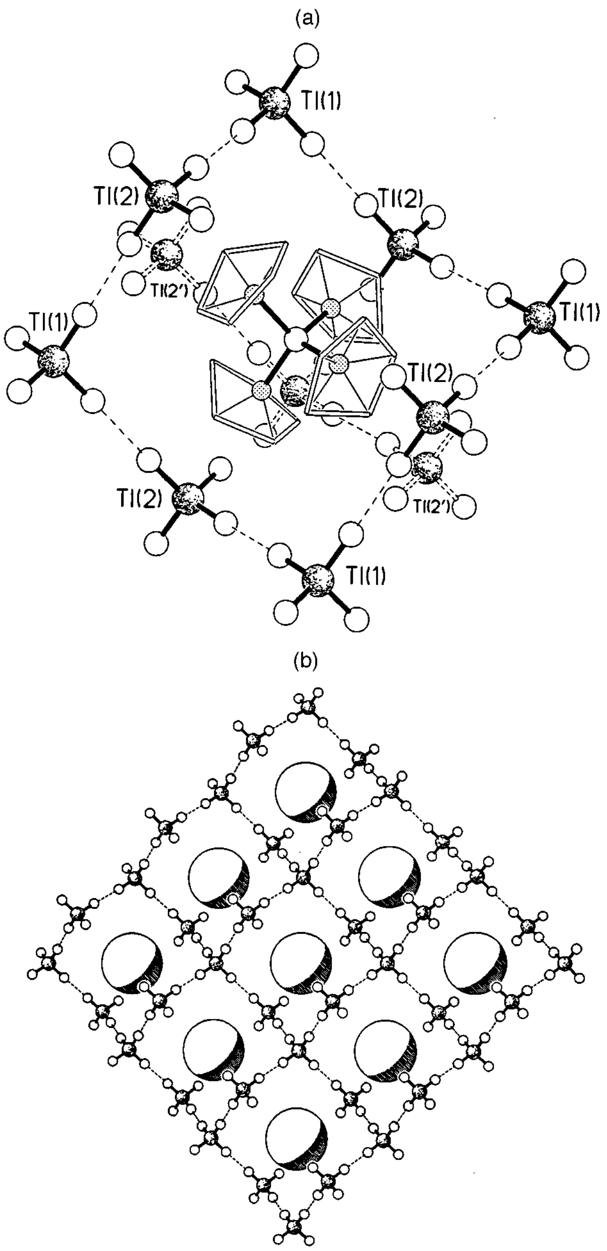

Fig. 2 (a) The $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ trication trapped in an 'egg-box' network of $TlBr_4^-$ anions with interanion Br···Br contacts. (b) The extended structure showing part of one layer of the 'eggs in an egg-box' array of $[\{Na(15\text{-crown-}5)\}_4Br][TlBr_4]_3$; $[\{Na(15\text{-crown-}5)\}_4Br]^{3+}$ trications are shown as partially shaded circles for clarity

Strong anion-substrate binding generally occurs in receptor cavities featuring sites suitably disposed[1–6] for hydrogen bonding, π–π stacking and/or electrostatic interactions with coordinatively unsaturated metal ions or quaternary nitrogens.

Thus the formation and stabilization of $[\{A(15\text{-crown-}5)\}_4Br]^{3+}$ supramolecular species and the nature of the corresponding A–Br bonding are extraordinary in view of the low charge density on Br^-, the extremely weak covalence in alkali metal–bromide bonds and the lack of similar behavior in other anions such as SO_4^{2-}, PO_4^{3-}, MX_4^- and ClO_4^-.[8] The hydrophobic nature of $[\{A(15\text{-crown-}5)\}_4Br]^{3+}$ may be a decisive factor here. The potential generality of these results with respect to other anions and cations is being explored.

Acknowledgements

This work was supported by the Inter-American Development Bank-UWI Development Program, project no. 29.

References

1 P. D. Beer and D. K. Smith, *Prog. Inorg. Chem.*, 1997, **46**, 1.
2 G. B. Karet, Z. Sun, D. D. Heinrich, J. K. McCusker, K. Folting, W. E. Streib, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1996, **35**, 6450; W. J. Evans and M. S. Sollberger, *ibid.*, 1988, **27**, 4417; W. J. Evans, M. S. Sollberger and T. P. Hanusa, *J. Am. Chem. Soc.*, 1988, **110**, 1841.
3 J. Ribas, B. Albela, H. Stoeckli-Evans and G. Christou, *Inorg. Chem.*, 1997, **36**, 2353; C. E. Anson, J. P. Bourke, R. D. Cannon, U. A. Jayasooriya, M. Molinier and A. K. Powell, *ibid.*, 1997, **36**, 1265; C. G. Pernin and J. A. Ibers, *ibid.*, 1997, **36**, 3802.
4 P. D. Beer, M. G. B. Drew, D. Hesek, M. Shode and F. Szemes, *Chem. Commun.*, 1996, 2161.
5 M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2068; *Angew. Chem.*, 1997, **109**, 2158.
6 D. M. Y. Barrett, I. A. Kahwa, B. Radüchel, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, in the press.
7 S. P. Sinha, *Struct. Bonding* (*Berlin*), 1974, **25**, 69; M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.
8 (*a*) N. S. Fender, F. R. Fronczek, V. John, I. A. Kahwa and G. L. McPherson, *Inorg. Chem.*, 1997, **36**, 5539 and refs. therein; (*b*) N. S. Fender, S. S. Finegan, D. Miller, M. Mitchell, I. A. Kahwa and F. R. Fronczek, *ibid.*, 1994, **33**, 4002; (*c*) N. S. Fender, Ph.D. Thesis, University of the West Indies, Mona, 1998.
9 (*a*) R.-Y. Qi and J. D. Corbett, *Inorg. Chem.*, 1997, **36**, 6039; (*b*) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. van Dorsselaer, B. Kneisel and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10 956; B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum and D. Fenske, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1838.
10 J. R. Rusk and W. Gordy, *J. Chem. Phys.*, 1964, **40**, 456; *Phys. Rev.*, 1962, **127**, 817.
11 L. K. Liu, C.-S. Lin, D.-S. Young, W.-J. Shyu and C.-H. Ueng, *Chem. Commun.*, 1996, 1255.
12 R. Hanson, D. G. Parsons and M. R. Truter, *Acta. Crystallogr.*, *Sect. B*, 1982, **38**, 448.
13 M. Y. Chiang, E. Böhlen and R. Bau, *J. Am. Chem. Soc.*, 1985, **107**, 1679.

Received 10*th March* 1998; *Communication* 8/01947I