

Extraordinary bromide anion templated self-assembly of the $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}^{3+}$ trication

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An elegant self-assembled cation, $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}^{3+}$, 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 $[\{\text{A}(\text{18-crown-6})\}_4\text{MX}\}^{2+}$ (A = monocation; M = 3d element)⁸ and, the recently reported, very unusual discrete tetrahedral $[\text{A}_4\text{Br}\}^{3+}$ (A = K or Cs) cations trapped in tetrahedral sites of the $[\text{Zr}_6(\text{B})\text{Br}_{18}]^{6-}$ and $[\text{Zr}_6(\text{B})\text{Br}_{16}]^{3-}$ clusters synthesized at high temperatures,^{9a} and circular iron polypyridyl helicates.^{9b}

Herein we report an extraordinary Br^- templated self-assembly of $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}^{3+}$ and the structure of the compound $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}[\text{TlBr}_4]_3$ **1**.

Good yields† of crystalline **1** (ca. 75%) and the ethanol solvate of $[\{\text{K}(\text{15-crown-5})\}_4\text{Br}\}[\text{TlBr}_4]_3$ **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 $[\{\text{Na}(\text{15-crown-5})\}_4\text{MnBr}_4][\text{TlBr}_4]_2$ **3**. The hot stoichiometric mixtures designed⁸ for **3** gave the sandwich $[\text{A}(\text{15-crown-5})_2][\text{TlBr}_4]$ (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

† 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. $\text{C}_{40}\text{H}_{80}\text{Br}_{13}\text{Na}_4\text{O}_{20}\text{Tl}_3$ **1** requires: C, 18.3; H, 3.1%).

‡ Crystal data for **1**: $\text{C}_{40}\text{H}_{80}\text{Br}_{13}\text{Na}_4\text{O}_{20}\text{Tl}_3$, $M = 2624.9$, 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, $\mu(\text{Cu-K}\alpha) = 203$ cm⁻¹, $F(000) = 2444$, $T = 183$ K. A yellow octahedron of dimensions $0.20 \times 0.17 \times 0.17$ mm was used. 1575 Independent reflections were measured giving $R1 = 0.049$, $wR2 = 0.117$ for 1140 independent observed absorption corrected reflections $[|F_o| > 4\sigma(|F_o|)]$, $2\theta \leq 120^\circ$ 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.

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 $\text{Na}^+:\text{15-crown-5}$ 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 $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}^{3+}$ 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 ($\text{Br} \cdots \text{Br} = 4.04$ 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

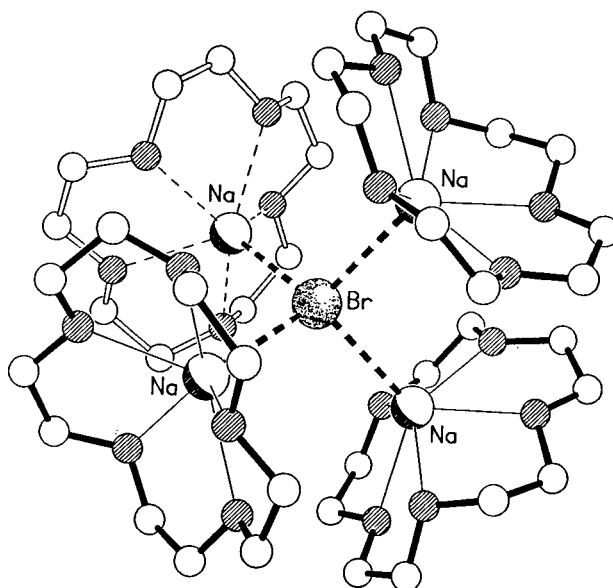


Fig. 1 Structure of $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}\}^{3+}$ showing the tetrahedral arrangement of the $[\text{Na}(\text{15-crown-5})]^+$ cations around the Br^- anion

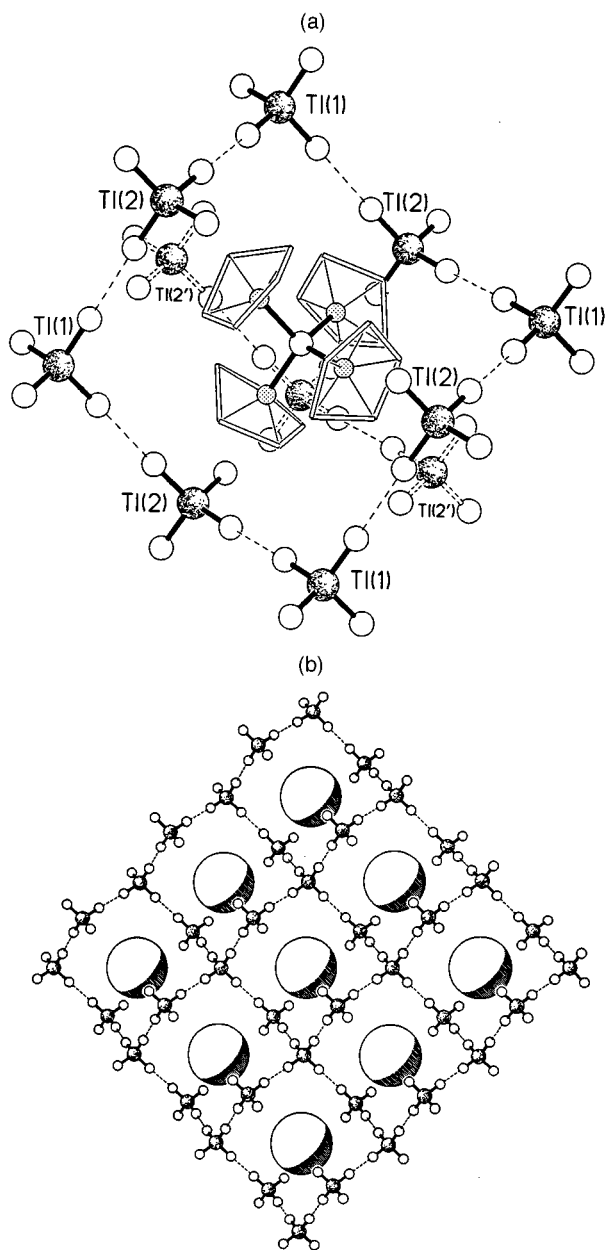


Fig. 2 (a) The $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}]^{3+}$ trication trapped in an 'egg-box' network of TlBr_4^- anions with interanion $\text{Br}\cdots\text{Br}$ contacts. (b) The extended structure showing part of one layer of the 'eggs in an egg-box' array of $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}][\text{TlBr}_4]^-$; $[\{\text{Na}(\text{15-crown-5})\}_4\text{Br}]^{3+}$ trications are shown as partially shaded circles for clarity

Strong anion-substrate binding generally occurs in receptor cavities featuring sites suitably disposed¹⁻⁶ for hydrogen bonding, π - π stacking and/or electrostatic interactions with coordinatively unsaturated metal ions or quaternary nitrogens.

Thus the formation and stabilization of $[\{\text{A}(\text{15-crown-5})\}_4\text{Br}]^{3+}$ 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 $[\{\text{A}(\text{15-crown-5})\}_4\text{Br}]^{3+}$ may be a decisive factor here. The potential generality of these results with respect to other anions and cations is being explored.

Acknowledgements

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