

Group 1 Coordination Chains and Hexagonal Networks of Host Cyclotrimeratrylene with Halogenated Monocarbaborane Anions

Ruksanna Ahmad, Andreas Franken, John D. Kennedy, and Michaele J. Hardie*^[a]

Abstract: Halogenated carbaborane ions $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ in which $\text{X} = \text{Cl}$ or Br have been combined with the host molecule cyclotrimeratrylene (CTV) and Group 1 metal cations to give crystalline materials. The complexes $[\text{Na}(\text{ctv})(\text{H}_2\text{O})(\text{CB}_{11}\text{H}_6\text{X}_6)](\text{CF}_3\text{CH}_2\text{OH})$ feature chiral Na–CTV coordination chains with complexation of the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion by the Na^+ ion, together with the CTV molecular cavity. The coordination chains are hydrogen

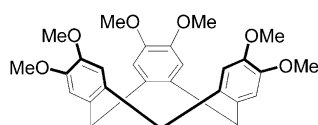
bonded together to give a puckered two-dimensional hexagonal grid structure. $[\text{K}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CF}_3\text{CH}_2\text{OH})_{0.5}]$ is essentially isostructural. Complexes $[\text{Rb}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Br}_6)(\text{H}_2\text{O})]$ and $[\text{Cs}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{X}_6)(\text{CH}_3\text{CN})]$ are coor-

dination polymers with related distorted hexagonal grid structures. Use of *N,N'*-dimethylformamide (DMF) as a solvent results in an entirely different type of assembly, with $[\text{Na}_2(\text{dmf})_4(\text{H}_2\text{O})_2(\text{ctv})][(\text{dmf})_{0.5}(\text{ctv})][\text{CB}_{11}\text{H}_6\text{Br}_6]_2$ showing unusual $\{\text{Na}-\mu-(\text{dmf})-\text{Na}\}$ bridges, and once again forming a distorted hexagonal coordination polymer.

Keywords: alkali metals • carbaboranes • coordination polymers • cyclotrimeratrylene • halogens • host–guest chemistry

Introduction

The host molecule cyclotrimeratrylene (CTV) has a relatively rigid bowl shape, with its molecular cavity capable of complexing guest molecules. Unsubstituted, or native, CTV



CTV

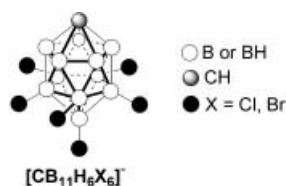
forms ball-and-socket type supermolecules with large neutral and cationic guest molecules such as *closo*-1,2-dicarbododecarborane,^[1,2] fullerene- C_{60} ,^[3] $[\text{Fe}(\text{Cp})(\text{C}_6\text{H}_5\text{R})]^+_{[4]}$ and $[\text{Na}[2.2.2]\text{cryptate}]^+_{[5]}$. With small guest molecules CTV tends to form clathrate crystalline materials in which the CTV molecules stack on top of one another and the guest molecules are contained in channels created by the packing of pillars of CTV molecules. There are two types of stacking motif, designated the α - and β -phases.^[6] There is also one

example of a γ -phase in which an acetone guest molecule is complexed between two CTV molecules to form a capsule-like dimer,^[7] but in general native CTV does not complex small molecules within its molecular cavity. In contrast to native CTV itself, coordination polymers and hydrogen-bonded network structures involving CTV have been shown to feature intracavity complexation of small organic solvent molecules.^[2,8–11] CTV may form coordination complexes with Ag^+ and Group 1 metals with the 1,2-dimethoxy groups acting as chelating ligands.^[2,9–12] CTV has also proved to be a valuable building block for the covalent synthesis of more sophisticated host molecules such as cryptophanes and extended arm cavitands, for which intracavity complexation of small and large guest molecules is commonplace,^[13] and CTV derivatives find applications as liquid crystals^[14] and in anion extraction.^[15] A number of reported examples of crystalline CTV assemblies have included carbaboranes as either neutral guest or templating molecules, or as counterions.^[1,2,5,8–11] The carbaboranes appear to have an important role in stabilising the overall crystalline assemblies. They have a number of features that lend themselves to the formation of such species, including good solubilities, the spherical shape of neutral compounds, hydrogen-bonding donor ability^[16] and the “weakly coordinating” nature of the anions.^[17] To date, investigations have been restricted to the neutral icosahedral *closo*-1,2-dicarbododecarborane $\text{C}_2\text{B}_{10}\text{H}_{12}$, the anionic icosahedral $[\text{CB}_{11}\text{H}_{12}]^-$, and the anionic sandwich complex $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$. The anionic carbaboranes may be halogenated at boron vertices *para* and *meta* to

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the C–H group to give species such as $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ $\text{X} = \text{Cl}, \text{Br}$.^[17]

We report herein a series of crystalline complexes formed by the combination of CTV, an M^+ ion, whereby M is a Group 1 metal, and the halogenated monocarbaborane



$[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ions. The structures of the complexes that were isolated were determined by single-crystal X-ray diffraction techniques. All such complexes feature M –CTV coordination polymers in chain or grid assemblies. When the molecular components are initially mixed in CH_3CN , followed by recrystallisation from $\text{CF}_3\text{CH}_2\text{OH}$, two structural types are formed depending on the metal cation and the nature of the halogen on the carbaborane unit. The isostructural complexes $[\text{Na}(\text{ctv})(\text{H}_2\text{O})(\text{CB}_{11}\text{H}_6\text{X}_6)](\text{CF}_3\text{CH}_2\text{OH})$ ($\text{X} = \text{Cl}$: **1**; $\text{X} = \text{Br}$: **2**) have chiral coordination chains with complexation of the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion by the CTV molecular cavity and the Na^+ ion. The poorly defined $[\text{K}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CF}_3\text{CH}_2\text{OH})_{0.5}]$ (**3**) has a structure closely related to those of **1** and **2** although with purely coordinate interactions to form a grid structure. Identical two-dimensional grid structures are found for complexes $[\text{Rb}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Br}_6)(\text{H}_2\text{O})]$ (**4**) and $[\text{Cs}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{X}_6)(\text{CH}_3\text{CN})]$ ($\text{X} = \text{Cl}$: **5**; $\text{X} = \text{Br}$: **6**). When the molecular components are mixed in N,N' -dimethylformamide (DMF) rather than $\text{CH}_3\text{CN}/\text{CF}_3\text{CH}_2\text{OH}$ an entirely different type of assembly is generated, that of $[\text{Na}_2(\text{dmf})_4(\text{H}_2\text{O})_2(\text{ctv})][(\text{dmf})_{0.5}(\text{ctv})][\text{CB}_{11}\text{H}_6\text{Br}_6]_2$ (**7**), which forms a hexagonal grid structure with unusual $\{\text{Na}-\mu(\text{dmf})-\text{Na}\}$ bridges.

Experimental Section

Cyclotrimeratrylene (CTV) was prepared by literature methods.^[18] Caesium salts of the halogenated monocarbaborane anions were prepared by an adaptation of literature methods^[19] for the synthesis of NEt_4^+ salts, but using CsCl to effect precipitation rather than NEt_4Cl . AR grade solvents were used without further purification. Infrared spectra were run as KBr discs using a Midac FTIR. ^1H NMR spectra were run on a Bruker ARX250 instrument in CD_3CN .

Synthesis

[Na(ctv)(H₂O)(CB₁₁H₆Cl₆)](CF₃CH₂OH) (1): CTV (27 mg, 6.0 μmol) and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]$ (30 mg, 4.6 μmol) were dissolved separately in CH_3CN (3 cm^3), the solutions were mixed, and an excess of 0.1 M aqueous NaOH (0.1 cm^3) was added. After complete evaporation of acetonitrile, $\text{CF}_3\text{CH}_2\text{OH}$ was added to make a new solution mixture, which was left to stand to give colourless prismatic crystals of **1** in ~10% yield after several days. Selected IR data: $\tilde{\nu} = 3507, 3044$ (C–H), 2923, 2851, 2616, 1611, 1514, 1447, 1264, 1144, 1084, 1021, 941, 866, 826, 662, 619 cm^{-1} .

[Na(ctv)(H₂O)(CB₁₁H₆Br₆)](CF₃CH₂OH) (2): CTV (50.5 mg, 0.112 mmol), $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]$ (84 mg 0.112 mmol) and 0.1 M aqueous NaOH were treated as for **1**. Colourless prismatic crystals of **2** formed after several days in 9% yield. Selected IR data: $\tilde{\nu} = 3543, 3054, 2940,$

2848, 2605, 1610, 1513, 1445, 1263, 1219, 1194, 1142, 1083, 990, 858, 741, 635, 619 cm^{-1} ; ^1H NMR: $\delta = 7.03$ (aryl C–H), 4.80 (d, CH_2), 3.82 (OCH_3), 3.60 (d, CH_2), 2.92 (br, carborane CH), 2.2 ppm (H_2O).

[K(ctv)(CB₁₁H₆Cl₆)(CF₃CH₂OH)_{0.5}] (3): CTV (51 mg, 0.106 mmol), $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]$ (47 mg, 0.106 mmol) and an excess of 0.1 M aqueous KOH (0.1 cm^3) were treated as for **1**. Colourless prismatic crystals of **3** appeared in 8% yield after several days. EDX studies of the crystal confirmed that potassium was within the crystal structure and not caesium. Selected IR data: $\tilde{\nu} = 3524, 3044, 2923, 2851, 2614, 2340, 1611, 1514, 1445, 1264, 1144, 1086, 1021, 990, 941, 866, 853, 619 \text{ cm}^{-1}$; ^1H NMR: $\delta = 7.01$ (aryl C–H), 4.78 (d, CH_2), 3.91 (q, $\text{CF}_3\text{CH}_2\text{OH}$), 3.80 (OCH_3), 3.62 (d, CH_2), 2.3 ppm (br, carborane CH).

[Rb(ctv)(CB₁₁H₆Br₆)(H₂O)] (4): $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]$ (98 mg 0.131 mmol), CTV (59 mg, 0.131 mmol) and RbOH were treated as for **1**. After a few days, colourless prismatic crystals of **4** formed in 12% yield. Selected IR data: $\tilde{\nu} = 3573, 3052, 2832, 2606, 2026, 1611, 1447, 1399, 1086, 1034, 858, 810, 619 \text{ cm}^{-1}$; ^1H NMR: $\delta = 7.04$ (aryl C–H), 4.80 (d, CH_2), 3.83 (OCH_3), 3.60 (d, CH_2), 2.90 (br, carborane CH), 2.2 ppm (H_2O).

[Cs(ctv)(CB₁₁H₆Cl₆)(CH₃CN)] (5): CTV (52 mg, 0.108 mmol) and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]$ (50 mg, 0.108 mmol) were dissolved separately in CH_3CN (2 cm^3) and then mixed together. Following a complete evaporation of acetonitrile, the mixture was redissolved in $\text{CF}_3\text{CH}_2\text{OH}$ and gave colourless prismatic crystals of **5** in 9% yield after standing for several days. Selected IR data: $\tilde{\nu} = 3632, 3058, 2938, 2847, 2597, 2255, 1611, 1466, 1260, 1221, 1086, 1019, 741, 619 \text{ cm}^{-1}$.

[Cs(ctv)(CB₁₁H₆Br₆)(CH₃CN)] (6): $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]$ (102 mg 0.136 mmol) and CTV (61 mg, 0.136 mmol) were treated as for **5**, colourless prismatic crystals of **6** formed in 11% yield after several days standing. IR data: $\tilde{\nu} = 3440, 3054, 2936, 2847, 2606, 1611, 1514, 1466, 1395, 1264, 1219, 1196, 1144, 1086, 936, 860, 741, 619 \text{ cm}^{-1}$; ^1H NMR: $\delta = 7.01$ (aryl C–H), 4.78 (d, CH_2), 3.80 (OCH_3), 3.58 (d, CH_2), 2.92 ppm (br, carborane CH).

[Na₂(dmf)₄(H₂O)₂(ctv)][(dmf)_{0.5}(ctv)][CB₁₁H₆Br₆]₂ (7): $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]$ (32 mg, 4.3 μmol) and CTV (19 mg, 4.2 μmol) were dissolved separately in hot DMF and mixed; an excess of 0.1 M aqueous NaOH was then added. The solution mixture was cooled and left to stand, after several weeks prismatic colourless crystals of **7** were formed in low yield. Crystals lost solvent on exposure to the atmosphere.

X-ray data collections and structure determinations: Details of data collection and structure refinement for complexes **1**, **3–5** and **7** are given in Table 1. Single crystals of **1–7** were mounted on a glass fibre under oil, and the X-ray data collected on a Nonius KappaCCD diffractometer at low temperatures with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were corrected for Lorentzian and polarization effects and absorption corrections were applied by using multiscan methods. The structures were solved by direct methods by using SHELXS-97 and refined by full matrix least-squares on F^2 by using SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometrically estimated positions with a riding refinement unless otherwise indicated. Additional details for some structures are given below.

CCDC-218400–218404 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[Na(ctv)(H₂O)(CB₁₁H₆Cl₆)](CF₃CH₂OH) (1): The $\text{CF}_3\text{CH}_2\text{OH}$ molecule was disordered, with each F atom of the CF_3 group modelled as disordered over two positions at 50% occupancy, with common displacement factors. C–F bond lengths were restrained. Only B–H and C–H hydrogen positions were included in the refinement (CCDC-218400).

[Na(ctv)(H₂O)(CB₁₁H₆Br₆)](CF₃CH₂OH) (2): Complex **2** is isostructural with complex **1**, with orthorhombic unit cell parameters $a = 14.1176(4)$, $b = 15.6014(2)$, $c = 20.7727(3) \text{ \AA}$.

[K(ctv)(CB₁₁H₆Cl₆)(CF₃CH₂OH)_{0.5}] (3): Crystals of complex **3** were small and poorly diffracting and only gave significant observed data to 2θ values of around 40° . Higher angle data were very weak and were excluded. The structure showed significant disorder that could not be fully modelled; this led to high final R factors and residual electron density around the disordered carbaborane cage. The $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion appears

Table 1. Details of data collection and structure refinement for complexes **1**, **3–5**, **7**.

| | 1 | 3 | 4 | 5 | 7 |
|---|--|--|---|--|--|
| formula | C ₃₀ H ₄₁ B ₁₁ Cl ₆ F ₃ O ₈ Na | C ₂₉ H _{37.5} B ₁₁ Cl ₆ F _{1.5} KO _{6.5} | C ₂₈ H ₃₈ B ₁₁ Br ₆ O ₇ Rb | C ₃₀ H ₃₉ B ₁₁ Cl ₆ NO ₆ Cs | C ₇₀ H ₁₀₉ B ₂₂ Br ₁₂ N _{4.5} Na ₂ O _{18.5} |
| M_r | 941.23 | 889.30 | 1170.42 | 974.14 | 2552.34 |
| crystal colour/shape | colourless, prismatic | colourless, prismatic | colourless, prismatic | colourless, prismatic | colourless, prismatic |
| crystal size [mm] | 0.14 × 0.09 × 0.07 | 0.20 × 0.14 × 0.11 | 0.37 × 0.10 × 0.07 | 0.25 × 0.16 × 0.13 | 0.24 × 0.20 × 0.16 |
| crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| T [K] | 150(2) | 173(2) | 173(2) | 173(2) | 150(2) |
| space group | $P2_12_12_1$ | $P2_12_12_1$ | $Pbca$ | $Pbca$ | $Pnma$ |
| a [Å] | 14.0296(4) | 20.5892(4) | 21.2870(2) | 21.0380(2) | 28.8316(4) |
| b [Å] | 15.1755(4) | 14.0580(2) | 15.6950(2) | 15.6644(1) | 14.6725(2) |
| c [Å] | 20.6310(7) | 15.4536(2) | 25.8840(4) | 26.2472(2) | 25.7030(3) |
| V [Å ³] | 4392.5(2) | 4472.94(12) | 8647.83(19) | 8649.70(12) | 10873.2(2) |
| Z | 4 | 4 | 8 | 8 | 4 |
| ρ_{calcd} [g cm ⁻³] | 1.423 | 1.321 | 1.798 | 1.496 | 1.559 |
| $F(000)$ | 1920 | 1812 | 4512 | 3888 | 5042 |
| μ [cm ⁻¹] | 0.459 | 0.522 | 6.730 | 1.268 | 4.486 |
| θ range [°] | 1.76–28.00 | 2.45–20.00 | 3.18–28.28 | 1.55–28.27 | 2.13–25.00 |
| data collected | 24659 | 11047 | 61046 | 78509 | 48976 |
| unique data | 10084 | 4148 | 10616 | 10625 | 9952 |
| R_{int} | 0.0621 | 0.0604 | 0.0850 | 0.0650 | 0.0957 |
| observed data [$I > 2\sigma(I)$] | 7197 | 3226 | 7475 | 7778 | 7342 |
| parameters | 542 | 315 | 484 | 506 | 656 |
| restraints | 6 | 6 | 0 | 0 | 0 |
| R_1 [$I > 2\sigma(I)$] | 0.0576 | 0.1653 | 0.0478 | 0.0383 | 0.0847 |
| wR_2 (all data) | 0.1428 | 0.4096 | 0.1160 | 0.1161 | 0.2378 |
| S | 1.029 | 2.865 | 1.035 | 1.097 | 1.096 |
| max/min residual e density [e Å ⁻³] | 1.779, -0.465 | 2.507, -0.706 | 1.148, -1.320 | 2.007, -1.161 | 2.108, -1.738 |

to be disordered over two sites, by rotation around the vector defined by the C1 and B12 vertices of the icosahedral cage. Only the chlorine atom positions could be adequately modelled in this way, with the five Cl atoms each disordered over two positions at 50% occupancy. The boron atom cage positions were each refined at a single position, as satisfactory disordered positions could not be modelled. The CF₃CH₂OH ligand was poorly defined and refined at 50% occupancy with restraints on the bond lengths. Only the chlorine positions were refined anisotropically and hydrogen atoms were not included for the poorly defined CF₃CH₂OH (CCDC-218401).

[Rb(ctv)(CB₁₁H₆Br₆)(H₂O)] (4): Hydrogen atoms on the coordinated water were not included in the refinement (CCDC-218402).

[Cs(ctv)(CB₁₁H₆Cl₆)(CH₃CN)] (5): CCDC-218403.

[Cs(ctv)(CB₁₁H₆Br₆)(CH₃CN)] (6): Complex **6** is isostructural with **5** with orthorhombic unit cell parameters $a = 21.4197(2)$, $b = 15.7195(3)$, $c = 26.5060(4)$ Å.

[Na₂(dmf)₄(H₂O)₂(ctv)]{(dmf)_{0.5}(ctv)}[CB₁₁H₆Br₆]₂ (7): The structure showed significant disorder of the Na₂ core, in which one Na atom was disordered across a mirror plane; this Na position therefore had 50% occupancy in the asymmetric unit. One aquo ligand coordinating to this Na also had 50% occupancy, while another showed further dynamic disorder with two sites in the asymmetric unit at occupancies 30% and 20%. Some DMF molecules were disordered. One had an oxygen atom disordered over two symmetry related sites at 50% occupancy per site; another showed disorder of the NCH₃ and NCHO groups, with the O atom refined at 50% occupancy with two symmetry related sites. The guest DMF was refined with an overall occupancy of 50% and was also disordered by symmetry across two positions. The disordered guest DMF was refined isotropically. Hydrogen atoms of water were excluded from refinement (CCDC-218404).

Results and Discussion

The crystalline complex [Na(ctv)(H₂O)(CB₁₁H₆Cl₆)](CF₃-CH₂OH) (**1**) was isolated from a mixture of CTV, NaOH

and Cs[CB₁₁H₆Cl₆] that had been initially mixed in CH₃CN, evaporated to dryness, and recrystallised from CF₃CH₂OH. The complex crystallises with an orthorhombic cell and the structure was solved in the chiral space group $P2_12_12_1$. The asymmetric unit comprises an Na⁺ ion, a coordinated water molecule, and a molecule each of CTV, [CB₁₁H₆Cl₆]⁻ and CF₃CH₂OH, all on general positions.

The Na⁺ ion is complexed by two symmetry equivalent chelating CTV host molecules, which act as ligands with Na–O distances in the range 2.314(3)–2.526(3) Å, one aquo ligand, with an Na–O bond length of 2.259(4) Å, and the [CB₁₁H₆Cl₆]⁻ ion, through a single Na–Cl interaction at 2.855(2) Å (Figure 1). The Na–Cl distance is effectively the same as the Na–Cl separation of 2.81 Å observed for NaCl. The coordination geometry is highly irregular octahedral. The five-membered chelate rings formed by the dimethoxy groups of CTV show sharp O–Na–O angles at around 65°, accounting for the irregular geometry. The [CB₁₁H₆Cl₆]⁻ ion

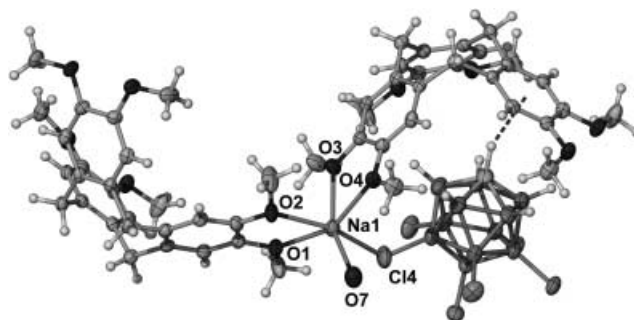


Figure 1. Na coordination sphere in [Na(ctv)(H₂O)(CB₁₁H₆Cl₆)](CF₃-CH₂OH) (**1**). Ellipsoids are shown at 50% probability level, and the dotted line indicates a C–H... π hydrogen bond.

is bound to the Na^+ ion through one chloro group, and the carbaborane cage is directed into the molecular cavity of the CTV host molecule. Binding of this $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion within the CTV cavity is augmented by the formation of a $\text{C}-\text{H}\cdots\pi$ hydrogen bond between the acidic $\text{C}-\text{H}$ of the anion and an aromatic face of the CTV at a $\text{C}-\text{H}\cdots\text{ring}$ centroid distance of 2.51 Å with a $\text{C}-\text{H}\cdots\pi$ angle 155.5° (corresponding $\text{C}\cdots\pi$ centroid distance 3.56 Å). The effects of this hydrogen bond are observable in the infrared spectra of **1**, in which the carbaborane $\text{C}-\text{H}$ stretching frequency is shifted from 3065 cm^{-1} in $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]$ to 3044 cm^{-1} in complex **1**. The formation of $\text{C}-\text{H}\cdots\pi$ hydrogen bonds in host-guest complexes of carbaboranes has been previously observed with neutral 1,2-dicarbadoecaborane guest molecules with the hosts CTV^[1a] and calix[5]arene,^[20] with typical $\text{C}\cdots\pi$ distances in the range 3.4–3.6 Å.

Although neutral carbaboranes are known to form host-guest complexes with CTV,^[1,2] calix[5]arene^[20] and other host molecules such as cyclodextrins,^[21] this is one of the first examples of an anionic carbaborane forming a complex with a neutral molecular host. A cationic metallo-host has been reported to complex $[\text{Ph}-\text{CB}_9\text{H}_9]^-$ ^[22] and a saddle-shaped Ni macrocycle is known to complex the sandwich complex $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$.^[23] Other examples of CTV acting as a host for anionic guests involve considerably more electropositive CTV–metal complexes, typically multinuclear sandwich complexes with iridium, ruthenium and rhodium.^[15,24] Similar experiments to those reported here, but using the non-halogenated $[\text{CB}_{11}\text{H}_{12}]^-$ ion, do show Na^+ complexation by the CTV; however, it does not lead to the anion being contained within the molecular cavity of CTV.^[10] Hence, in complex **1**, CTV effectively binds an ion pair, at least in the solid state. Some more general examples of ditopic receptors that are capable of binding an ion pair are also able to do so in solution.^[25]

The interaction between the $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ and Na^+ ions is itself an unusual feature of the $[\text{Na}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{H}_2\text{O})]$ coordination complex of **1**. Halogenated carbaboranes are weakly coordinating and there are few examples of them coordinating to metal centres, with most examples involving $\text{B}-\text{Br}\cdots\text{Ag}$ interactions,^[26,27] as well as a $\text{B}-\text{Br}\cdots\text{Fe}^{\text{II}}$ porphyrin complex^[28] and a $\text{B}-\text{Br}\cdots\text{Mo}$ organometallic complex.^[29] There are also a handful of examples of chlorinated carbaborane anions in which coordinate interactions through chloro groups to Ag^{I} and Si centres^[30] have been investigated. However, any interactions with an Na^+ ion have not been previously reported, and the only reported investigations into interactions between Group 1 metals and halogenated carbaborane anions have involved caesium salts of brominated carbaboranes, in which there is a high ionic character to the interactions.^[26,31]

Each CTV molecule in **1** binds two symmetry equivalent Na^+ centres and a chiral coordinate chain is hence propagated in the crystallographic *b* direction (Figure 2a). Notably, the chiral assembly is composed of achiral components. The chirality of the chain is due to the bowl-shape of the CTV ligand: a topologically identical chain with a flat ligand would not be chiral. Chiral self-assembled chain structures with CTV have also been reported for a hydrogen-bonded

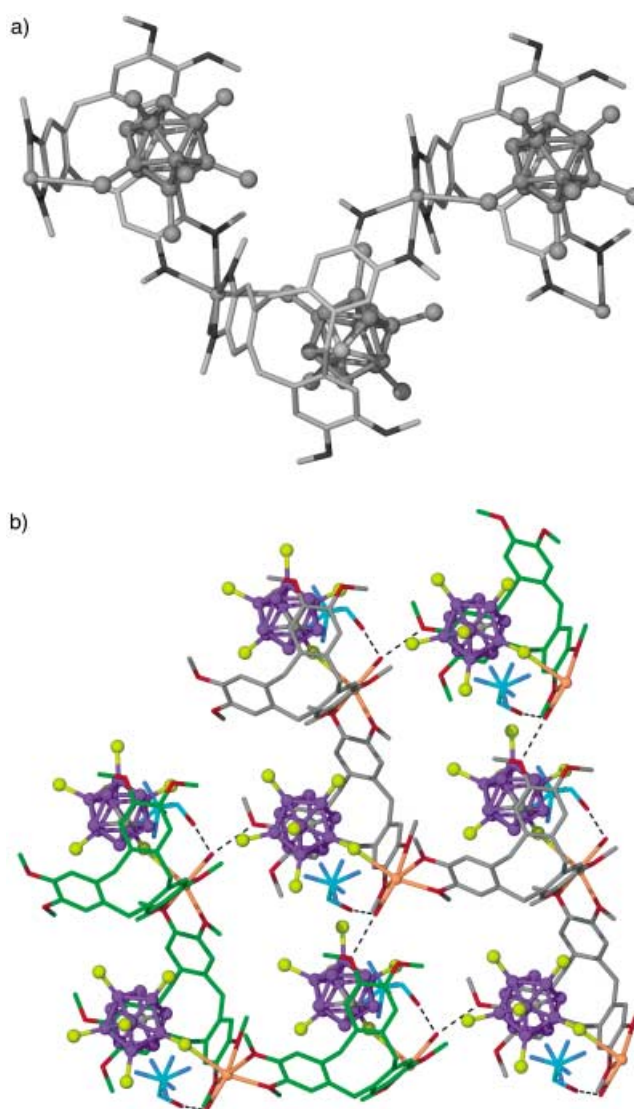


Figure 2. Details from the crystal structure of complex **1**: a) chiral coordination chain; b) two-dimensional network formed by adjacent coordinate chains hydrogen-bonding together. Different coordinate chains are distinguished by grey or green carbon atoms of CTV, disordered $\text{CF}_3\text{CH}_2\text{OH}$ shown in light blue. Hydrogen atoms are excluded for clarity.

structure with neutral 1,2-dicarbadoecaborane.^[1b] Adjacent coordinate chains in **1** are linked together into a two-dimensional grid structure by $\text{OH}\cdots\text{O}$ hydrogen bonding (Figure 2b). Each metal centre connects to three CTV ligands, while each CTV ligand connects to three metal centres; hence the grid has a three-connected hexagonal topology. The terminal aquo ligand that completes the Na^+ coordination sphere is the hydrogen-bond donor with an $\text{O}\cdots\text{O}$ separation of 2.91 Å to a methoxy O atom of a CTV molecule from an adjacent coordinate chain. The aquo ligand also forms a hydrogen bond with the disordered $\text{CF}_3\text{CH}_2\text{OH}$ solvent molecule, at an $\text{O}\cdots\text{O}$ separation of 2.81 Å. The two-dimensional grid structures are not coplanar, but form two-tiers in the *ab* plane with the orientation of the CTV molecular bowl alternating in the *a* and *b* directions. The hexagonal grids stack in an offset arrangement in the *c* direction, with each CTV molecule forming back-to-back π stacking

interactions with two CTV molecules from the next two-dimensional grid with ring-to-ring centroid separations of 3.92 Å. The closest interactions to the uncoordinated chloro groups of the $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion are $\text{Cl}\cdots\text{H}-\text{C}$ contacts with neighbouring CTV molecules at around 2.9 Å.

Use of the brominated $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ ion in place of $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ results in the isolation of a crystalline complex $[\text{Na}(\text{ctv})(\text{H}_2\text{O})(\text{CB}_{11}\text{H}_6\text{Br}_6)](\text{CF}_3\text{CH}_2\text{OH})$ **2** that is isostructural with **1**. Once again the anionic halogenated carbaborane anion coordinates to the Na^+ ion.

Changing the cation from Na^+ to the larger K^+ also leads to a crystalline product that has essentially similar structural features as **1** and **2**, although there are some important differences. The complex $[\text{K}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CF}_3\text{CH}_2\text{OH})_{0.5}]$ (**3**) was isolated from a $\text{CF}_3\text{CH}_2\text{OH}$ containing an excess of aq. KOH, CTV and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]$. Electron diffraction X-ray measurements confirm that the metal present in the crystals is potassium and not caesium. Similar use of the brominated ion $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ with an excess of K^+ did not result in the isolation of a potassium-containing species. The crystals of **3** that were obtained were of poor quality and the refined structure showed significant disorder that has not been fully resolved. Despite these problems, however, the main structural features of **3** can be elucidated, although because the structure is of poor quality the positional parameters are not reliable. Complex **3** crystallises in an orthorhombic unit cell, with parameters similar to those of **1** and **2**, and was similarly solved in the chiral space group $P2_12_12_1$. The asymmetric unit comprises a K^+ centre, a CTV molecule, together with a $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion and a $\text{CF}_3\text{CH}_2\text{OH}$ molecule refined at half occupancy. The K^+ centre shows weakly coordinating interactions to three CTV molecules, to the $\text{CF}_3\text{CH}_2\text{OH}$ molecule and to the $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion through a chloro group (Figure 3). Given the long inter-

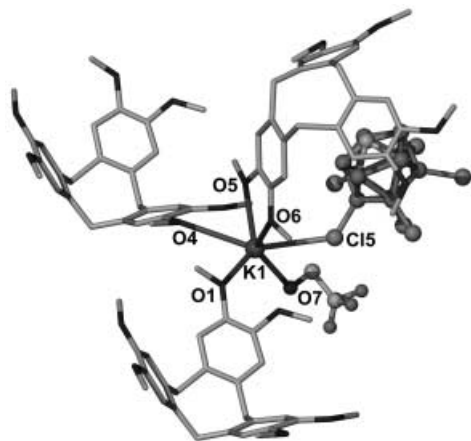


Figure 3. Potassium coordination sphere from the partially resolved crystal structure of $[\text{K}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CF}_3\text{CH}_2\text{OH})_{0.5}]$ (**3**). Only one position of the disordered $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion is shown.

atomic distances and disorder of the $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ ion, it is difficult to define a stereochemistry for the K^+ centre, although these six closest contacts form a distorted trigonal prism with one $\text{CF}_3\text{CH}_2\text{OH}$ ligand at a $\text{K}-\text{O}$ distance of

3.12(4) Å, a $\text{K}-\text{Cl}$ distance of 3.356(11) Å and four $\text{K}-\text{O}$ distances ranging from 2.940(19) to 3.121(17) Å. These interactions are long, but are similar to other recently reported $\text{K}-\text{O}$ links in crown ether and 1,2-dimethoxyethane complexes with potassium.^[32] Whereas in complexes **1** and **2** a two-dimensional grid structure is formed by coordinate chains linking together through hydrogen bonds, in complex **3** a topologically identical and structurally very similar grid structure is formed only from coordinate interactions to the metal centre. The terminal aquo ligand evident in **1** and **2** that acts as a hydrogen-bond donor forming a link between the coordination chains is not evident in **3**. The same linkage is effectively established through the $\text{K}-\text{O}$ bond shown between K1 and O1 in Figure 3. Coordination polymers with hexagonal structure are not uncommon,^[33] but the only previously reported trischelate $\text{Na}-\text{CTV}$ two-dimensional coordination polymer has a three-connected 4:8 topology.^[9]

The structure of **3** suggests that the introduction of an even larger cation may give a two-dimensional coordination polymer with a more ordered structure. We find that this is indeed the case, with the use of either Rb^+ or Cs^+ resulting in materials **4**, **5** and **6** that have two-dimensional coordination polymeric structures topologically the same as the network structures of **1-3**, but now with quite distinct geometrical arrangements of the molecular components. Thus, the essentially isostructural crystalline complexes $[\text{Rb}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Br}_6)(\text{H}_2\text{O})]$ (**4**), $[\text{Cs}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CH}_3\text{CN})]$ (**5**) and $[\text{Cs}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Br}_6)(\text{CH}_3\text{CN})]$ (**6**) were isolated from solutions of RbOH , CTV and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$,^[34] CTV and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$; and CTV and $\text{Cs}[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, respectively, in $\text{CH}_3\text{CN}/\text{CF}_3\text{CH}_2\text{OH}$. All complexes had similar orthorhombic unit cells, and the structures were solved in the centrosymmetric space group $Pbca$. The major difference between the structures of **4-6** is the identity of a terminally coordinated solvent molecule; H_2O for the Rb^+ complex **4**, and CH_3CN for the Cs^+ complexes **5** and **6**.

The Rb^+ coordination sphere of **4** and the Cs^+ coordination sphere of **5** are shown in Figure 4. In each case the metal centre is nine coordinate with a distorted capped square antiprismatic geometry. Interatomic distances around the metal centre are given in Table 2. In all cases, three symmetry equivalent CTV molecules coordinate to the metal as chelating ligands, the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion coordinates to the metal in a chelating fashion through two halogen atoms arranged *ortho* to each other within the carbaborane cage; the

Table 2. Interatomic distances around the metal for complexes **4** and **5**; $\text{M} = \text{Rb}$ or Cs , $\text{X} = \text{Cl}$ or Br .^[a]

| | 4 | 5 |
|----------------------------------|-----------|-----------|
| $\text{M}-\text{O1}^{\text{I}}$ | 3.029(4) | 3.106(2) |
| $\text{M}-\text{O2}^{\text{I}}$ | 2.903(4) | 3.184(2) |
| $\text{M}-\text{O3}$ | 2.898(3) | 3.084(2) |
| $\text{M}-\text{O4}$ | 2.964(3) | 3.208(2) |
| $\text{M}-\text{O5}^{\text{II}}$ | 2.942(3) | 3.177(2) |
| $\text{M}-\text{O6}^{\text{II}}$ | 3.016(3) | 3.128(2) |
| $\text{M}-\text{X2}$ | 3.7753(7) | 3.7932(8) |
| $\text{M}-\text{X6}$ | 3.6572(7) | 3.5161(8) |
| $\text{M}-\text{O7}$ | 3.058(5) | – |
| $\text{M}-\text{N1}$ | – | 3.141(4) |

[a] Symmetry operations: I: $0.5+x, y, 0.5-z$; II: $-x-1, 0.5+y, 0.5-z$.

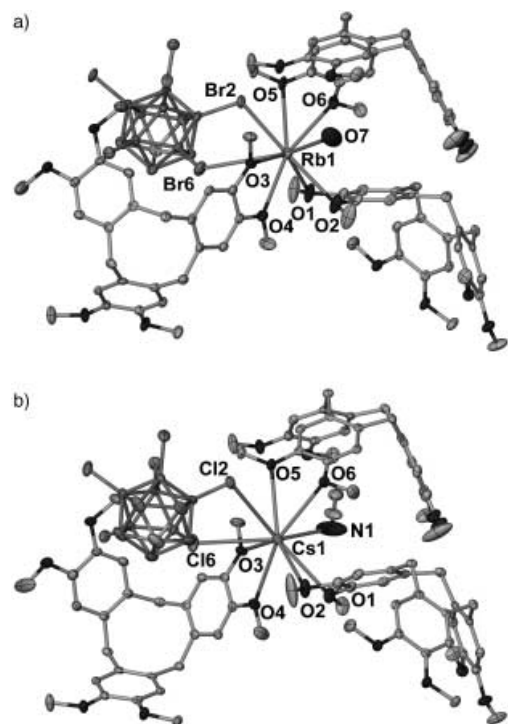


Figure 4. a) Rb^+ coordination sphere of $[\text{Rb}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Br}_6)(\text{H}_2\text{O})]$ (**4**). b) Cs^+ coordination sphere of $[\text{Cs}(\text{ctv})(\text{CB}_{11}\text{H}_6\text{Cl}_6)(\text{CH}_3\text{CN})]$ (**5**). Ellipsoids are drawn at 50% probability levels, hydrogen atoms are omitted for clarity.

coordination sphere is completed by the coordinated solvent molecule: H_2O for **4** and CH_3CN for **5** and **6**.

Each metal centre interacts with three molecules of CTV, and each CTV molecule complexes three metal centres, one through each dimethoxy moiety. This leads to a two-dimensional coordination polymer as shown for **5** in Figure 5a. The network is not coplanar, but is two-tiered in the *ab* plane. The CTV molecules within the network are arranged in a skewed, triangular grid arrangement. The orientation of the CTV molecular bowls alternate in the *b* direction similar to the observed pattern in complexes **1–3**, but now they have a repeating ...up, up, down, down, up, up... pattern in the *a* direction. The two-dimensional coordination polymers stack together through a single π - π stacking interaction per CTV molecule at a ring-to-ring centroid separation of 3.79 Å.

In contrast to the structures of complexes **1–3**, the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion is not directed into the cavity of the CTV molecular host. Instead, a coordinated solvent molecule occupies the CTV molecular cavity, shown for the CH_3CN molecule of **5** in Figure 5b. In the case of complexes **5** and **6** this coordinated acetonitrile has the carbon atom of its methyl group pointed directed over the centre of the CTV host, at a distance of around 3.9 Å to the centre of the plane of three $-(\text{CH}_2)-$ groups of the CTV. The $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion is positioned directly above the coordinated solvent. The acidic C-H group of the anion is directed away from the CTV molecular cavity and towards the external face of an adjacent CTV aromatic ring. The C-H vector points towards the side rather than the centre of the aromatic ring, with a

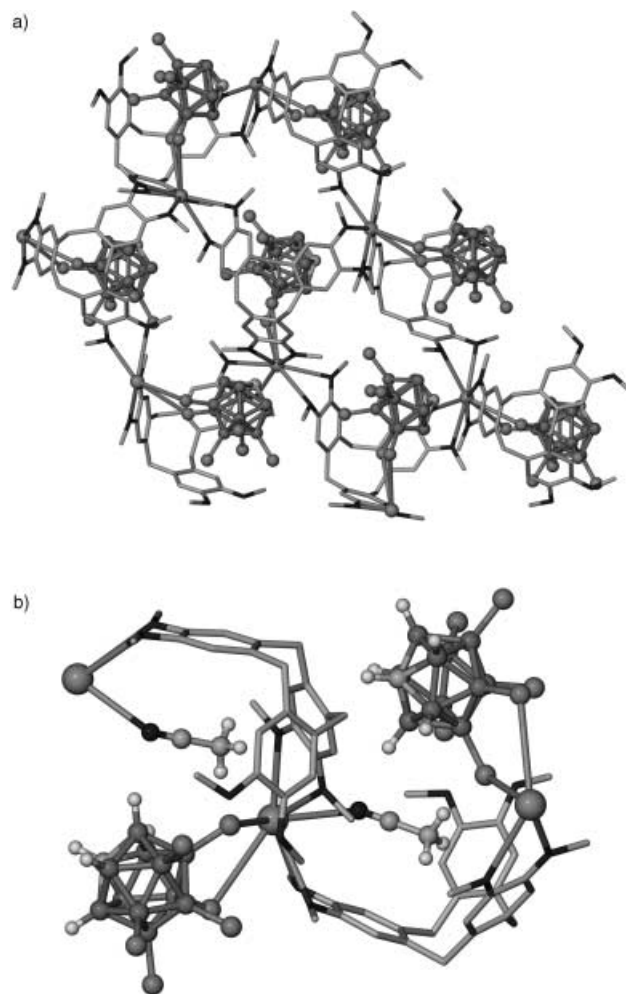


Figure 5. Details from the crystal structure of **5** showing a) the extended two-dimensional coordination network; coordinated CH_3CN and hydrogen atoms have been omitted for clarity. b) The host-guest associations of the CTV host; hydrogen atoms of CTV omitted.

$\text{C-H}\cdots\text{ring}$ centroid distance of 2.59 Å and $\text{C-H}\cdots\pi$ centroid angle of 142.1°. This is a considerably less direct interaction than the $\text{C-H}\cdots\pi$ hydrogen bond seen for complexes **1–3** and this is reflected in the infrared data in that the carbaborane $\nu(\text{C-H})$ value for **5** is shifted by only around 8 cm^{-1} , compared with the 21 cm^{-1} shift observed for **2**.

The possibility of solution-phase complex formation between M^+ , $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ and CTV was investigated by means of ^1H NMR spectroscopy. As representative Na^+ , K^+ , Rb^+ and Cs^+ complexes single crystals of complexes **2**, **3**, **4**, and **6** were each dissolved in CD_3CN and their ^1H NMR spectra recorded. Compared to the chemical shift values of the principal components in simple one-component solutions, significant ^1H chemical shift changes were not observed, nor were any changes to the symmetry of the CTV molecule indicated. This suggests that fragments of the coordination polymers do not exist in solution to any significant extent.

The structures of complexes **1** to **6** have features in common. The extended network structure in each is a dis-

torted two-dimensional hexagonal grid. In complexes **1** and **2** with the small Na^+ ion this is achieved through the formation of chiral coordination chains which hydrogen bond together. When the larger K^+ ion is introduced to the system in complex **3** the terminal aquo ligand involved in hydrogen bonding in **1** and **2** is not evident and the same network structure occurs through long coordinate interactions between each K^+ centre and three CTV molecules. This structure shows significant disorder of the carbaborane anion. The long $\text{K}\cdots\text{O}$ separations suggest that a larger cation is required to stabilise this structural motif through purely coordinate interactions and not a mixture of coordinate and hydrogen-bonding interactions. Use of the larger Rb^+ or Cs^+ ions in complexes **4** to **6** does indeed give stable two-dimensional hexagonal network structures with coordinate interactions between each M^+ centre and three CTV molecules, and three M^+ centres for each CTV molecule. The host-guest chemistry is subtly changed. In complexes **1–3** the carbaborane anion is the primary guest molecule perched above the CTV molecular cavity and shows $\text{C–H}\cdots\pi$ hydrogen bonding, whereas in complexes **4–6** the primary guest is a complexed solvent molecule and the carbaborane anion is positioned above this guest. This change may occur due to the significant increase in M–X distance from 2.85 Å in the Na^+ complex **1** to around 3.5–3.8 Å in the Rb^+ and Cs^+ complexes. This increase in bond length effectively pushes the carbaborane anion away from the molecular cavity of the CTV and the space is instead occupied by coordinated solvent guest molecules.

The structures or topologies adopted by coordination polymers or discrete coordination assemblies are frequently influenced by the solvent used for crystallisation, even though the crystallising solvent is not necessarily incorporated in the matrix of the crystalline product. This is especially true for potentially coordinating solvents. There was therefore merit in the examination for such effects in the present system. By using a similar procedure for the synthesis of complex **2**, but with *N,N'*-dimethylformamide (DMF) as the solvent rather than $\text{CH}_3\text{CN}/\text{CF}_2\text{CH}_2\text{OH}$, an entirely different crystalline complex is yielded, namely $[\text{Na}_2(\text{dmf})_4(\text{H}_2\text{O})_2(\text{ctv})][(\text{dmf})_{0.5}(\text{ctv})][\text{CB}_{11}\text{H}_6\text{Br}_6]_2$ (**7**). The $\text{Na}:\text{Br}$ ratio of this formulation was confirmed by electron diffraction X-ray measurements. Complex **7** crystallises in an orthorhombic unit cell and the structure was solved in space group *Pnma*. The asymmetric unit comprises half the stoichiometry given above, and most molecular components are sited across mirror planes.

The basic coordination complex of **7** is based on $[\text{Na}_2(\text{dmf})_4(\text{H}_2\text{O})_2(\text{ctv})]^{2+}$ units with two distinct Na^+ positions. These Na^+ positions are bridged by chelating CTV ligands and μ -DMF ligands. The μ -DMF-bridged Na_2 core exhibits disorder across a mirror plane such that a symmetry-expanded representation appears as a trimeric unit (Figure 6). It is not, however, a trimeric unit as the two symmetry related Na_2 positions evident in Figure 6 each have 50% occupancy, that is, each Na_2 position is only occupied one half of the time. One position of the disordered Na_2 core can be seen by ignoring the Na_2^1 atom and related ligand positions shown in white in Figure 6. Na_1 is sited on

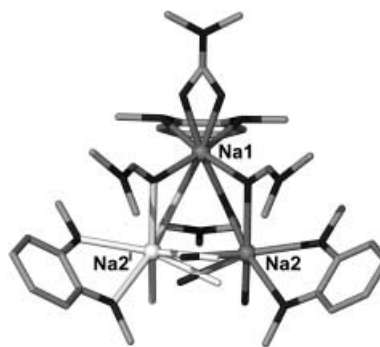


Figure 6. Sodium coordination from the crystal structure of complex **7**. Only the coordinating 1,2-dimethoxybenzene moiety of each CTV ligand is shown for clarity. Note that Na_2 and the symmetry related Na_2^1 each have an occupancy of 50%, hence the Na core is $[\text{Na}_2(\text{H}_2\text{O})_2(\text{dmf})_2-\mu(\text{dmf})_2]^{2+}$ cluster and not an $\{\text{Na}_3\}$ trimer. One of the two disordered positions of the Na_2 core can be visualised by ignoring Na_2^1 and related positions all shown in white. One aquo ligand and a DMF molecule show further disorder and coordinating O atoms are split into two positions. Symmetry operation I: $x, 0.5-y, z$.

a mirror plane and is coordinated by a chelating CTV molecule and four DMF molecules in an irregular octahedral configuration. The $\text{Na}_1\text{–O–Me}$ separation is 2.442(7) Å, and $\text{Na}_1\text{–O=C}$ bond lengths range from 2.305(16)–2.423(14) Å. Two of the DMF molecules are disordered. Bearing in mind the symmetry imposed disorder discussed above, two of the DMF ligands bridge to an Na_2 position. The coordination sphere of Na_2 is likewise irregular octahedral with a chelating CTV ligand ($\text{Na}_2\text{–O–Me}$ bond lengths 2.478(9) and 2.526(9) Å), two bridging DMF ligands ($\text{Na}_2\text{–O=C}$ bond lengths 2.324(15) and 2.630(13) Å) and two terminal aquo ligands, one of which is disordered over two sites ($\text{Na}_2\text{–OH}_2$ bond lengths 2.179(15) to 2.37(4) Å). The $\text{Na}_1\cdots\text{Na}_2$ separation is 3.648(8) Å. DMF-bridged Na clusters are rare, with only a handful having been previously reported.^[35] Intermolecular separations reported here are consistent with these previous studies.

Each $[\text{Na}_2(\text{H}_2\text{O})_2(\text{dmf})_4]^{2+}$ subunit in **7** effectively bridges between three CTV ligands and each CTV ligand bridges between three $[\text{Na}_2(\text{H}_2\text{O})_2(\text{dmf})_4]^{2+}$ subunits, thus giving a two-dimensional coordination network of hexagonal topology in the *bc* plane (Figure 7). The coordination networks stack in such a way as to create hexagonal channels running through the structure that are occupied by hydrogen-bonded chains of $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ ions. Within the chains there are two crystallographically distinct $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ ions that are each bound to a neighbouring anion through a bifurcated $\text{C–H}\cdots(\text{Br})_2$ hydrogen-bonding interaction. The chain is zig-zagged and shows a short interaction at a $\text{C–H}\cdots\text{Br}$ distance of 2.88 Å (corresponding $\text{C}\cdots\text{Br}$ distance 3.71 Å), and a long interaction at a $\text{C–H}\cdots\text{Br}$ distance of 3.40 Å (corresponding $\text{C}\cdots\text{Br}$ distance 4.13 Å).

The orientation of CTV molecules within the hexagonal network of **7** is the same in the *b* direction (all bowl-up, or bowl-down) and alternates in the *c* direction. Each CTV ligand within a network is effectively a host molecule with another crystallographically independent molecule of CTV perched above its molecular cavity. The simple crystalline

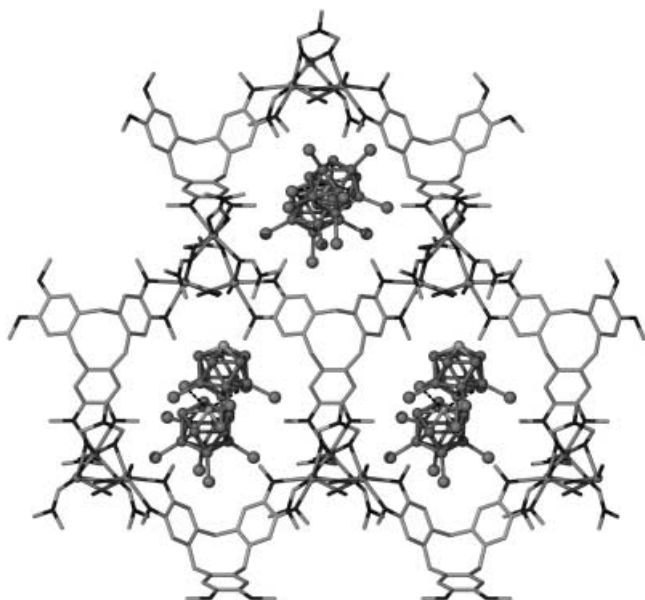


Figure 7. Hexagonal two-dimensional coordination net of complex **7**. $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ ions form hydrogen-bonded chains that run through the middle of the hexagonal windows of the coordination polymer.

clathrate complexes of CTV, α -CTV and β -CTV, also feature a similar self-stacking motif of CTV host molecules, although the orientation of the “guest” CTV here in **7** is quite distinct from either of those packing motifs. Rather in **7** the two CTV molecules have mutually similar orientations, although with one aromatic face of the “guest” CTV tilted by about 50° from the equivalent face of the “host” CTV. The closest C...C distance is 3.54 \AA . The “guest” CTV molecules are not involved in any coordinate interactions and complex a molecule of disordered DMF as a guest. The coordination networks stack as shown in Figure 8 which creates channels

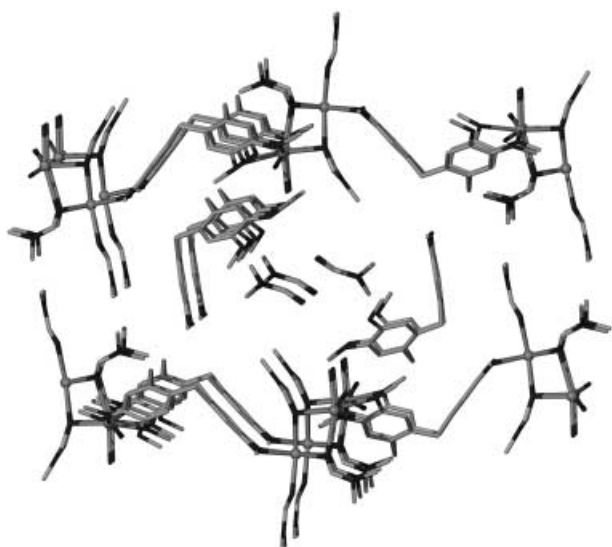


Figure 8. Side view of the hexagonal coordination networks and the additional CTV host molecules in complex **7**. Each CTV within a coordination net hosts an additional CTV unit, which itself is a host for DMF. Anions are not shown for clarity.

which run in the b direction. These channels are filled by the “guest” $[(\text{DMF})_n\text{CTV}]$ host–guest complexes.

Conclusion

Mixtures of CTV, halogenated carbaborane ions $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ and Group 1 metals in $\text{CH}_3\text{CN}/\text{CF}_2\text{CH}_2\text{OH}$ yield crystalline materials with one of two types of structures. The smaller Na^+ ion gives a chiral structure in which the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion coordinates through one halogen atom to the six coordinate metal centre, and is furthermore contained within the molecular bowl of the CTV. Chiral coordinate chains are linked into a two-dimensional hexagonal network through hydrogen-bonding interactions. The larger ions Rb^+ and Cs^+ give essentially isostructural structures in which the $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ion coordinates through two halogen atoms to the nine-coordinate metal centre and in which the anion is displaced from within the CTV molecular cavity by coordinated solvent guest molecules. These coordination polymers also have a two-dimensional hexagonal network. The high coordination numbers and longer interatomic distances to the metal centre that are seen in the second type of structure presumably exclude its formation with Na^+ and K^+ . A metal cation of intermediate size, K^+ , gives a poorly defined and highly disordered intermediate structure, essentially isostructural to the first type of structure, but with long coordinate interactions replacing the combination of coordinate and hydrogen-bonding interactions. Crystallisation from the strongly coordinating solvent DMF rather than $\text{CH}_3\text{CN}/\text{CF}_3\text{CH}_2\text{OH}$ leads to a third type of structure. Despite differences in composition and coordination number and geometry at the metal, all three types of network structure are similar in that all have three-connected hexagonal networks with an identical formal topology, although there are differences in geometries and relative orientations of the bowl-like CTV molecules.

Acknowledgments

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