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Propeller-shaped chain and 2D grid coordination polymers with the host molecule cyclotriveratrylene and $(CB_9H_5Br_5)^-$

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The host molecule cyclotriveratrylene (CTV) forms coordination polymers with the Group 1 metals K^+ and Rb^+ and with the carbaborane $(CB_9H_5Br_5)^-$ as the counter-anion. $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ has a chain structure with an unusual propeller-shaped cross-section, while $[Rb(CTV)(CB_9H_5Br_5)(CH_3CN)]$ has a two-dimensional grid structure of distorted hexagonal topology and is one of the few examples of a rubidium acetonitrile complex.

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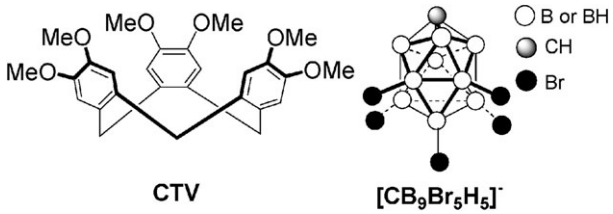
Introduction

The generation of coordination polymers has become a popular undertaking in recent years due to their potential applications including their use as solid framework hosts and as magnetic materials.[1] The role of the counter-anion in determining the topology and geometry of coordination polymers is often very important.[2] Carbaboranes, often referred to as carboranes, are cage cluster molecules with B and C vertices. The weakly coordinating nature of anionic *closo*-carbaboranes and their large size make them interesting counterions for coordination polymers and several such systems have been reported,[3–5] including those where halogenated carbaboranes form part of the coordination sphere.[6] Other supramolecular applications of carbaboranes include their use as neutral[7,8] or anionic guest molecules,[9] hydrogen bonding interactions through their acidic C–H groups,[10] and carbaborane-based macrocyclic host molecules.[11]

The host molecule cyclotriveratrylene (CTV) has a relatively rigid bowl shape, creating a molecular cavity that can complex large neutral and cationic guest molecules[12] including *closo*-1,2-dicarbadodecarborane.[8] Derivatives of CTV, including covalently extended hosts,[13] Ag–CTV metal complexes,[14] coordination polymers [3–5] and hydrogen bonded network structures,[15] may show intracavity complexation of small organic solvent molecules. Other metallated CTV derivatives have applications in anion extraction.[16] CTV forms coordination polymers with the Group 1 metals Na, K, Rb and Cs.[3–4,6,17] These coordination polymers bind metal centres at the CTV 1,2-dimethoxy groups which act as chelating sites. For instance, the complex $[Na(CTV)(H_2O)(CB_{11}H_6Cl_6)](CF_3CH_2OH)$ has a chiral coordinate chain structure with each Na^+ centre coordinated by two chelating CTV ligands; the $(CB_{11}H_6Cl_6)^-$ anion also coordinates to the Na^+ centre and is also complexed within the CTV molecular cavity.[6]

The steric influence of the anion is an important factor in determining the structure of cationic coordination polymers. $[M(CTV)]_n$ (M = Na to Cs) coordination polymers have been synthesised with the carbaborane anions $[Co(C_2B_9H_{11})_2]^-$,[3] $(CB_{11}H_{12})^{-4}$ and $(CB_{11}H_6X_6)^-$ (X = Cl, Br)[6] and these show distinct structural types. Each of the latter two anions produce isostructural or related structures with different Group 1 metals. In order to investigate further the steric influence of the anion on the overall crystalline assembly we have investigated the assembly of CTV with Group 1 metal cations and the smaller halogenated carbaborane *closo*-$(CB_9H_5Br_5)^-$. $(CB_9H_5Br_5)^-$ is a carbaborane anion with a bicapped square antiprismatic $\{CB_9\}$ cage with all boron positions *meta* and *para* to the C–H unit being halogenated. Unlike CTV assemblies involving $(CB_{11}H_{12})^-$ and $(CB_{11}H_6X_6)^-$, the structures reported herein with different metals are not simply related: complex $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ **1** has a propeller-shaped chain structure whereas $[Rb(CTV)(CB_9H_5Br_5)(CH_3CN)]$ **2** has a 2D grid structure of distorted hexagonal topology.



Experimental

Synthesis

CTV was synthesised according to published procedures.[18] The synthesis of $Cs[CB_9H_5Br_5]$[19] has also been previously reported. Other chemicals were used as supplied from commercial sources. Infrared spectra were run as KBr discs, and microanalyses performed by the School of Chemistry's microanalytical service.

$[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ 1. CTV (21 mg, 4.6 μmol) and $Cs(CB_9H_5Br_5)$ (30 mg, 4.6 μmol) and an excess of aq. KOH were dissolved and mixed in CH_3CN and the solution evaporated to dryness. The residue was recrystallised from CF_3CH_2OH to give colourless crystals of **1** in 49% yield. Main IR ν (cm^{-1}): 3439, 3256, 2934, 2826, 2604, 2345, 1609, 1514, 1466, 1394, 1261, 1196, 1088, 995, 738 and 619. Concordance of unit cell parameters of crystals from several different reaction attempts indicate that the synthesis of the major product **1** is repeatable, however satisfactory microanalytical data could not be obtained. This may be due to crystals losing solvent on exposure to the atmosphere, and/or contamination with Cs^+ product (see Results and discussion).

Calculated for desolvated **1**: C 45.43, H 4.50%; found C 48.85, H 5.1% or (Cs^+ contaminated product) C 36.1, H 6.7%.

[Rb(CTV)($CB_9H_5Br_5$)(CH_3CN)] 2. CTV (70 mg, 0.15 mmol) and $Cs(CB_9H_5Br_5)$ (100 mg, 0.15 mmol) and an excess of aq. RbOH were dissolved and mixed in CH_3CN and the solution evaporated to dryness. The residue was recrystallised from CF_3CH_2OH to give colourless crystals of **2** in 68% yield. Main IR ν (cm^{-1}): 3106, 2917, 2847, 2587, 2257, 1611, 1514, 1441, 1397, 1346, 1261, 1221, 1034, 991, 879, 740 and 619. Microanalysis, calculated C 33.03, H 3.52, N 1.28%; found C 32.3, H 3.45, N 1.20%.

X-Ray crystallography

Crystals were mounted on a glass fibre under oil. Data were collected on a Nonius KappaCCD diffractometer with graphite-filtered MoKα radiation (λ = 0.71073 Å). Data were corrected for Lortentz, polarisation and absorption effects. Structures were solved by direct methods using SHELXS-97[20] and refined with full-matrix least-squares on F^2 using SHELXL-97[21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically estimated positions and refined with a riding model.†

Complex 1. $C_{59}H_{71}B_9Br_5F_6O_{14}K$, M_r = 1654.10, triclinic, $P\bar{1}$, crystal size = 0.46 × 0.36 × 0.10 mm, a = 12.1110(2), b = 15.9535(3), c = 19.4105(4) Å, α = 91.725(1), β = 93.531(1), γ = 110.335(1)°, V = 3504.63(11) Å^3, Z = 2, ρ_{calc} = 1.567 g cm^{-3}, μ = 3.002 mm^{-1}, T = 150(2) K, θ_{min} = 2.44°, θ_{max} = 27.88°, 69031 reflections collected, 16612 unique reflections, R_{int} = 0.0913, 12734 observed reflections ($I > 2\sigma(I)$), 861 parameters, no restraints, R_1 = 0.0625 (observed data), wR_2 = 0.1672 (all data), S = 1.028.

Complex 2. $C_{60}H_{76}B_{18}Br_{10}N_2O_{12}Rb_2$, M_r = 2181.85, monoclinic, $P2_1/c$, crystal size = 0.23 × 0.16 × 0.12 mm, a = 15.9580(2), b = 27.3290(4), c = 19.3860(3) Å, β = 90.226(1)°, V = 8454.5(2) Å^3, Z = 4, ρ_{calc} = 1.714 g cm^{-3}, μ = 5.937 mm^{-1}, T = 173(2) K, θ_{min} = 2.58°, θ_{max} = 27.48°, 28884 reflections collected, 12936 unique reflections, R_{int} = 0.0629, 8970 observed reflections ($I > 2\sigma(I)$), 951 parameters, no restraints, R_1 = 0.0510 (observed data), wR_2 = 0.1355 (all data), S = 1.020.

Results and discussion

$[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ 1

Slow evaporation of a 1 : 1 mixture of $Cs(CB_9H_5Br_5)$, CTV and an excess of aq. KOH mixed in CH_3CN then recrystallised from CF_3CH_2OH gave crystals of $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ **1**. Notably some crystallisations produced a sample that was contaminated with crystals of the Cs^+ analogue of complex **2**,[22] but which also contained **1**.

The K^+ centre of **1** is coordinated by four CTV molecules in a chelating fashion and its coordination sphere has a distorted triangular dodecahedral geometry with K–O bond lengths ranging from 2.717(3) to 2.824(3) Å (Fig. 1). Each CTV ligand bridges between two K^+ centres to form an infinite {K–μ–$(CTV)_2$} coordinate chain, Fig. 1. The only other previously reported K–CTV coordinate chain is six-coordinate, also with bridging μ–CTV ligands, but these bridge between K–μ–$(OH)_2$–K units.[4] There are two crystallographically distinct CTV ligands within the coordinate chain, with two of each type

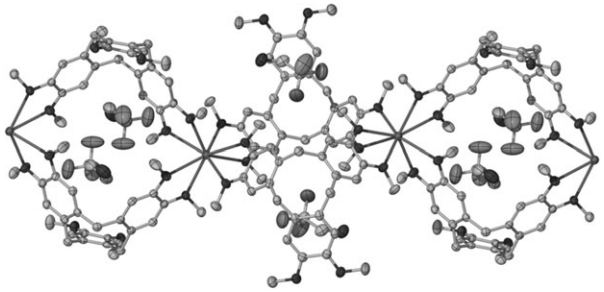


Fig. 1 $\{K(CTV)_2\}_\infty$ coordination chain and host–guest interactions from the crystal structure of $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ **1**. Ellipsoids shown at 50% probability levels, hydrogen atoms excluded for clarity.

coordinating to each K^+ cation with identical CTV ligands in a *cis* arrangement. The identical *cis* CTV ligands about each K^+ centre have opposite orientations in terms of their molecular cavities pointing up or down. Each CTV ligand acts as a host, with a molecule of CF_3CH_2OH perched above its molecular cavity. The anisotropic displacement parameters of the CF_3CH_2OH guest molecules indicate some thermal motion of the CF_3 groups as would be expected, and it is notable that the orientation of the CF_3CH_2OH guests is quite different for each type of CTV host.

The two crystallographically independent CTV ligands are structurally quite different. For all CTV ligands the 1,2-dimethoxybenzene moieties involved in chelating ligand interactions are essentially planar with torsion angles between the O–Me bond and C1–C2 bond ranging from around 2 to 10°. Each CTV ligand has one 1,2-dimethoxybenzene moiety that does not coordinate—for one type of CTV this group is also essentially flat (the "planar" CTV), however the other CTV has an OMe group bent in an *exo* fashion out-of-plane with a torsion angle of around 62° between the OMe bond and the C1–C2 bond of the benzene (the "bent" CTV). Out-of-plane bending of one OMe group within CTV has also been observed for β-phase CTV.[23] In complex **1** the bending of the OMe group can be accounted for by considering the packing of adjacent $\{K(CTV)_2\}$ coordination chains within the crystal lattice. Adjacent coordination chains show a coplanar and slipped π–π stacking interaction between two "planar" CTV molecules at an aromatic centroid separation of 3.62 Å, with the closest plane–plane distance 3.45 Å and a slip angle of 22.76 °; this is consistent with other reported π stacking interactions.[24] As can be seen in Fig. 2(a), this positioning of the coordinate chains leads to "planar" and "bent" CTV ligands from different coordinate chains approaching very closely, and an OMe group of the "bent" CTV is bent away from the 1,2-dimethoxybenzene plane in order to avoid steric conflict. Had this OMe been in-plane, the C···C distance between the methoxy carbon atom and C3 of the neighbouring phenyl is estimated to be less than 2.3 Å—a physical impossibility—hence the OMe bends away so that the methoxy oxygen atom is 3.59 Å from the C3 phenyl carbon atom, and the methoxy carbon atom is 3.3–3.4 Å from adjacent methoxy carbon atoms.

The host–guest interactions formed between the CTV and CF_3CH_2OH guest molecules are different for the two types of CTV host. The molecular cavity of CTV is hydrophobic. According to the hydrophobic effect, it would be expected that the hydrophobic region of a guest molecule would be contained within, or perch above, the molecular cavity. This is the case for the host–guest assembly of the "planar" CTV where the –CH_2– group of the guest is directed into the CTV cavity, and is similar to a previously reported CTV–CF_3CH_2OH species.[4] The guest molecule is not perched over the centre of the CTV host but is displaced to one side. This is likely to be due to strong hydrogen bonding interactions between the CF_3CH_2OH

† CCDC reference numbers 235719 and 235720. See http://www.rsc.org/suppdata/nj/b4/b405031b/ for crystallographic data in .cif format.

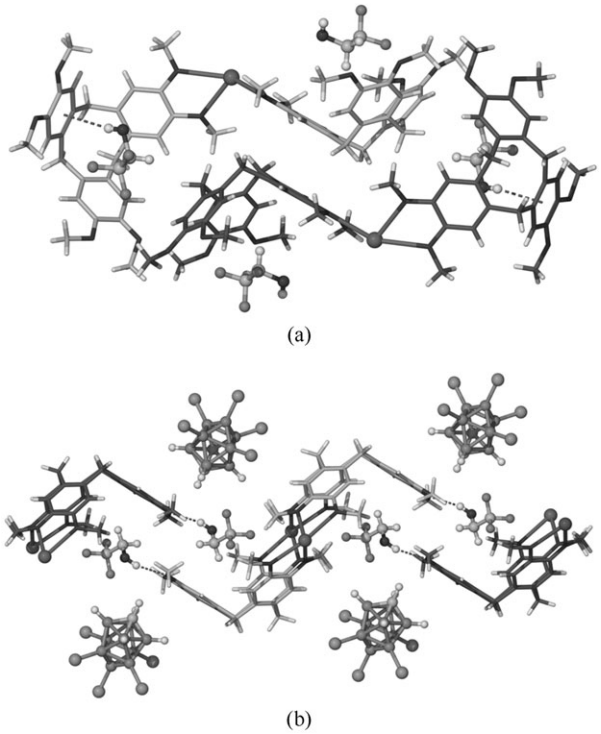


Fig. 2 Packing modes of coordination chains in two directions and host–guest interactions in **1**, different coordination chains have different shading of C atoms, (a) detail showing bent OMe group, $CF_3CH_2OH\cdots\pi$ hydrogen bonds (dashed lines) and π stacking interaction; (b) detail at 90° to (a) showing hydrogen bonding interactions (dashed lines) between guest CF_3CH_2OH and OMe groups of adjacent coordinate chains. Note that the full K^+ coordination sphere is not shown.

guest molecule and an OMe group of a "planar" CTV from an adjacent coordinate chain (Fig. 2(b)) where the O–H···OMe distance is 2.16 Å (corresponding O···O distance 2.91 Å). The "bent" CTV, however, has the alcohol group of the CF_3CH_2OH guest molecule directed into the cavity, Fig. 2(a). The alcoholic hydrogen atom is directed at a CTV phenyl group with an O–H···π separation of 2.61 Å (corresponding O···π distance 3.43 Å), consistent with a weak hydrogen bonding interaction. Similar O–H···π hydrogen bonding interactions have been reported for water and calixarene host molecules.[25]

The overall packing of $\{K(CTV)_2\}$ coordination polymers in complex **1** is shown in Fig. 3. When viewed down the K···K axis, the coordination chains have a bent propeller-shaped cross-section, and pack together to form a grid-like pattern. The $\{K(CTV)_2\}$ coordination polymers pack around $(CB_9H_5Br_5)^-$ anions. The anions are isolated from one another, in contrast to related complexes involving the larger $(CB_{11}H_6X_6)^-$ anions, [6] and in contrast to complex **2**, do not show distinct hydrogen bonding or coordinate interactions.

[Rb(CTV)($CB_9H_5Br_5$)(CH_3CN)] 2

Slow evaporation of a mixture of $Cs(CB_9H_5Br_5)$, CTV and an excess of aq. RbOH in CH_3CN, followed by recrystallisation from CF_3CH_2OH, gave crystals of $[Rb(CTV)(CB_9H_5Br_5)(CH_3CN)]$ **2**. In contrast to **1**, this is a 1 : 1 metal–CTV complex.

The two Rb^+ centres in **2** have different coordination spheres (Fig. 4). Rb(1) is ten-coordinate with an irregular geometry formed by chelating interactions from three CTV molecules at Rb–O distances ranging from 2.856(5) to 3.078(5) Å, a coordinated acetonitrile at a Rb–N bond length of 3.107(7) Å, and a η^3–$(CB_9H_5Br_5)^-$ anion at Rb–Br distances of 3.695(1), 3.7581(9) and 3.9793(9) Å. The three coordinating bromine atoms originate from the same triangular face of the $(CB_9H_5Br_5)^-$ anion. Rb(2) is nine-coordinate with a distorted tri-capped trigonal prismatic geometry. It also forms chelating interactions with three CTV molecules at Rb–O distances ranging from 2.836(5) to 3.060(5) Å, and has a coordinated acetonitrile at a Rb–N distance of 3.070(7) Å, and a η^2–$(CB_9H_5Br_5)^-$ anion at Rb–Br distances of 3.583(1) and 3.745(1) Å. Most previously reported examples of brominated carbaborane anions coordinating to Group 1 cations *via* B–Br–M interactions have been restricted to Cs^+ complexes.[26]

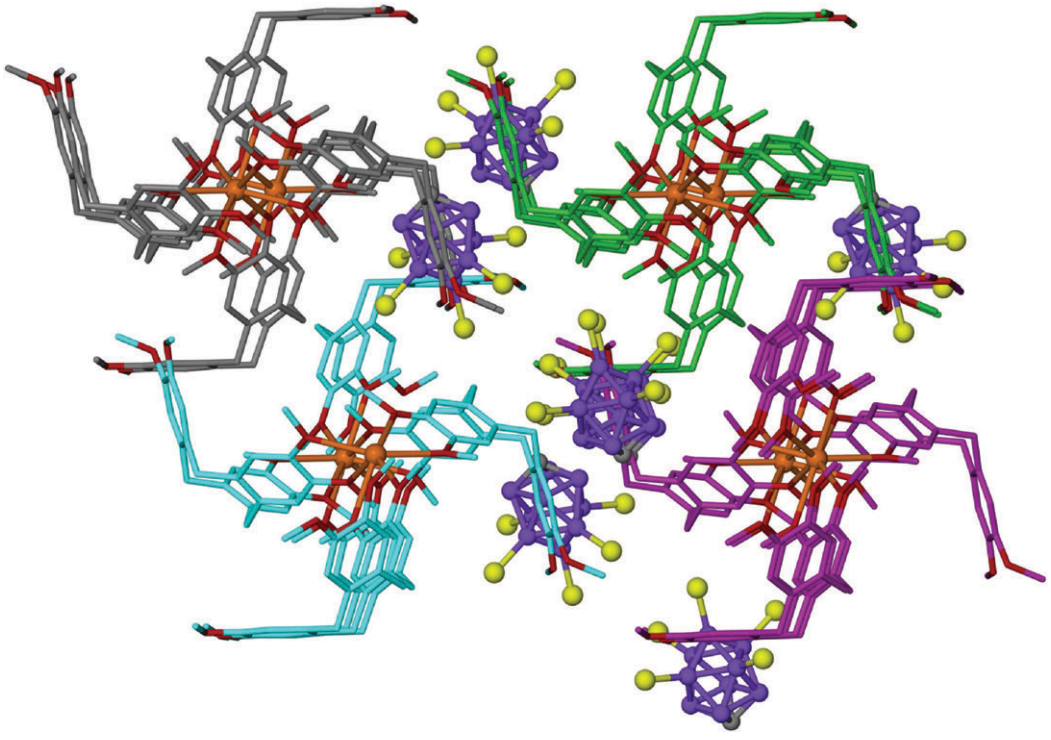


Fig. 3 Overall packing in complex **1** with coordination chains viewed along K···K axes. Different coordination chains are distinguished by different colours of C atoms, CF_3CH_2OH molecules and hydrogen atoms have been excluded for clarity.

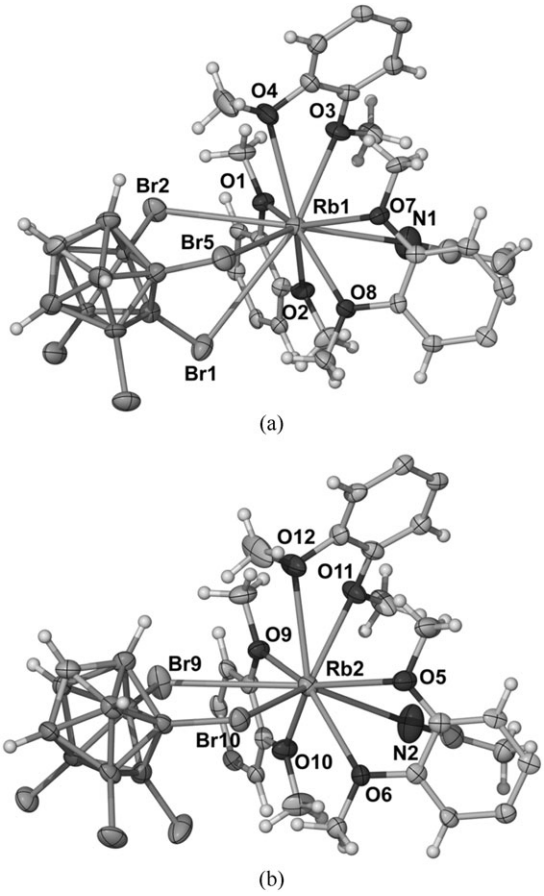


Fig. 4 Rb^+ coordination spheres of $[Rb(CTV)(CB_9H_5Br_5)(CH_3CN)]$ **2**; (a) ten-coordinate Rb(1); (b) nine-coordinate Rb(2). Only dimethoxy groups of CTV ligands are shown for clarity. Ellipsoids are shown at 50% probability levels.

The larger halogenated carbaborane anions $(CB_{11}H_6X_6)^-$ where X = Cl, Br, are known to coordinate to Group 1 metals Na^+, K^+, Rb^+ and Cs^+ in related CTV complexes. The Na^+ and K^+ complexes show a single B–X–M interaction while the larger Rb^+ and Cs^+ cations show η^2 interactions.[6]

The host–guest behaviour of CTV is illustrated in Fig. 5. The primary guest molecule for each crystallographically distinct CTV molecule is a CH_3CN ligand which is coordinated to a Rb^+ cation that is also bound by a dimethoxy group of that host. The hydrophobic methyl end of each CH_3CN molecule points in towards the cavity of the CTV unit at a distance of

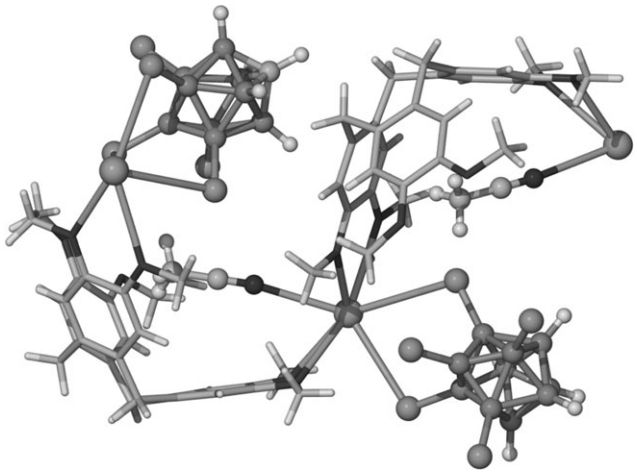


Fig. 5 Detail of host–guest behaviour of CTV hosts from the crystal structure of complex **2**. Note that full Rb^+ coordination spheres are not shown.

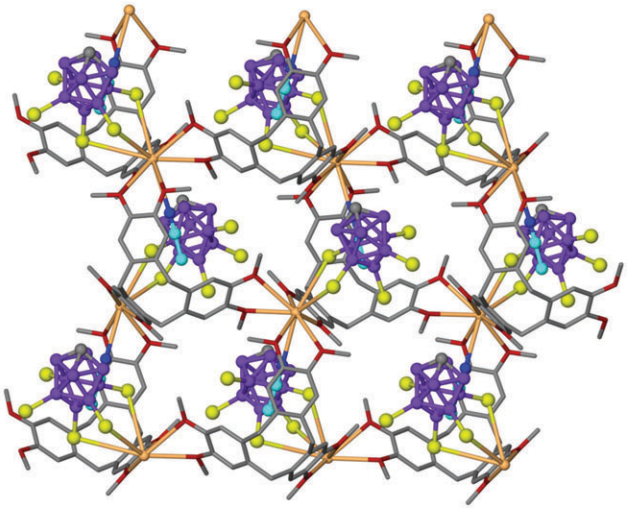


Fig. 6 The (6,3) distorted hexagonal coordination polymer of complex **2**.

around 4 Å from the methyl carbon atom to the centre of the CTV–$(CH_2)_3$ plane. It is notable that there are very few examples of structurally authenticated rubidium acetonitrile complexes in the literature, with most involving [18]-crown-6 complexes.[27] The coordinated $(CB_9H_5Br_5)^-$ anions perch above the guest CH_3CN with the closest $Br\cdots C_{methyl}$ contacts 3.83 and 3.70 Å. This host–guest behaviour is similar to that shown by Rb^+ and Cs^+ CTV complexes with the larger $(CB_{11}H_6X_6)^-$ anions, where X = Cl, Br, of composition $[M(CTV)(CB_{11}H_6X_6)(solvent)]$.[6] In those complexes the acidic C–H group of the anion is directed towards an arene ring of a neighbouring CTV to form a weak C–H$\cdots\pi$ hydrogen bond.[6] This is not the case for **2**, where there are no hydrogen bonding interactions involving the carbaborane C–H.

Each CTV molecule within **2** binds three Rb^+ centres, while each Rb^+ centre is bound by three CTV molecules creating an extended network structure, shown in Fig. 6. The network has (6,3) topology, meaning that each connecting centre connects to three others, and the shortest continuous circuit is a 6-gon. The network is not flat, but is substantially puckered with CTV molecules falling into roughly two tiers. The geometry of the network is a distorted hexagonal net, which is remarkably similar to that found for the previously mentioned $[M(CTV)(CB_{11}H_6X_6)(solvent)]$ series of complexes.[6] Furthermore, the coordination polymers pack together within the crystal lattice in a similar manner, hence the two can be described as isomorphic. Despite this, complex **2** and the $[M(CTV)(CB_{11}H_6X_6)(solvent)]$ complexes are not isostructural with the latter having orthorhombic symmetry.

In contrast to the behaviour of the larger $(CB_{11}H_6X_6)^-$ anions where grossly related structures were obtained for Na^+, K^+, Rb^+ and Cs^+, crystalline assemblies of $(CB_9H_5Br_5)^-$, CTV and Group 1 metals were only obtained for K^+ and Rb^+, with a minor Cs^+ contaminant observed. Solutions containing Na^+ or Cs^+ with $(CB_9H_5Br_5)^-$ and CTV did not produce crystalline products that include all components. The Rb^+-containing complex **2** is isomorphic with similar $(CB_{11}H_6X_6)^-$ complexes whereas the K^+ containing complex **1** has different stoichiometry and a distinctly different chain structure with a bent propeller-shaped cross-section.

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