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Solid state supramolecular assemblies of charged supermolecules (Na[2.2.2]cryptate)$^+$ and anionic carboranes with host cyclotriveratrylene†

Michaele J. Hardie‡ and Colin L. Raston*‡

School of Chemistry, Monash University, Clayton, Melbourne, Victoria 3800, Australia

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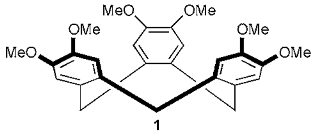
The complex {(Na[2.2.2]cryptate)[CTV][Co($C_2B_9H_{11}$)$_2$]}$_2$(MeCN) (CTV = cyclotriveratrylene) features (Na[2.2.2]cryptate)$^+$∩CTV interplay as well as a closely packed chain of [Co($C_2B_9H_{11}$)$_2$]$^-$ counter-anions exhibiting dihydrogen bonding, and a similar cation–CTV assembly is found in (Na[2.2.2]cryptate)[CTV]($CHCl_3$)$_3$[$CB_{11}H_{12}$].

Cyclotriveratrylene (= CTV) **1** is a curved host molecule which forms ball-and-socket supermolecules with a number of large guest molecules such as fullerenes,[1,2] carborane,[2,3] and organometallic sandwich complexes;[4] and lattice inclusion structures with smaller organic guest molecules.[5] CTV can also be a π type donor ligand[6] or a chelating ligand for group 1 metals.[7] Chelating M(CTV) complexes feature polymeric or extended hydrogen bonded structures with solvent as intracavity CTV guest molecules and carborane $C_2B_{10}H_{12}$ or the anionic carboranes [Co($C_2B_9H_{11}$)$_2$]$^-$ **2** or [$CB_{11}H_{12}$]$^-$ **3** as lattice type guests.[7] The carboranes appear to play an important steric role in the stabilisation of the crystalline species. Entirely different host–guest and overall supramolecular behaviour between CTV and M$^+$(carborane)$^-$ is expected if M$^+$ is completely encapsulated by another host molecule such as [2.2.2]cryptand **4**, thus preventing the formation of M(CTV) chelate rings. This also introduces a large supercation (M[2.2.2]cryptate)$^+$ as a potential guest molecule for CTV, noting that the confinement of such species in container molecules is limited,[8] along with the large carborane anion. The crystalline complexes formed by (Na[2.2.2]cryptate)[Co($C_2B_9H_{11}$)$_2$] and (Na[2.2.2]cryptate)[$CB_{11}H_{12}$] with CTV are reported herein.



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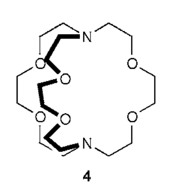

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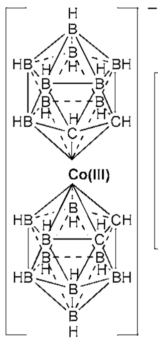

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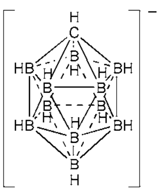

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A yellow powder of (Na[2.2.2]cryptate)[Co($C_2B_9H_{11}$)$_2$] is obtained in high yields by mixing Na.**2** with **4** in aqueous solution. Combining this powder with 1 equivalent of CTV yields yellow–orange crystals of {(Na[2.2.2]cryptate)[CTV][Co($C_2B_9H_{11}$)$_2$]}$_2$(MeCN) **5** from MeCN–H_2O solution.† The structure was determined by single crystal X-ray diffraction techniques,§ and is shown in Fig. 1. Two cations, two **3** anions, two CTV hosts and one molecule of CH_3CN comprise the asymmetric unit. Each CTV molecule acts as a host for one molecule of (Na[2.2.2]cryptate)$^+$. There are two such (Na[2.2.2]cryptate)$^+$∩CTV supermolecules, each with a different orientation of the (Na[2.2.2]cryptate)$^+$ within the molecular cavity of the CTV, although both with hydrophobic ethylene groups within the CTV bowl. In one (Na[2.2.2]cryptate)$^+$∩CTV assembly the N–Na–N axis of the [2.2.2]cryptate is close to parallel with the plane formed by the three methylene carbons of the CTV. The distance between the Na and the centre of this plane is 7.66 Å and N–Na···plane centroid angles of 95.9 and 87.7° are observed. The other (Na[2.2.2]cryptate)$^+$∩CTV assembly is more skewed Na–N···centroid angles 64.9 and 114.9°. CTV molecules within the extended crystal lattice do not feature any π···π interactions, instead showing close contacts between the methylene groups of one CTV and methoxy oxygens of an adjacent molecule (C–H···O distances 2.3–2.4 Å).

The cobalticarborane anions stack in columns along the *b* axis, and are remarkably close given their electrostatic repulsion, with C–H···H–B separations under 2 Å, and closest C···B distance 3.65 Å. These distances are consistent with the formation of nonclassical H···H hydrogen bonds or dihydrogen bonds. Dihydrogen bonds have been previously reported for X–H···H–B (X = N, O) systems with similar H···H separations.[9] The C–H groups of carboranes are acidic and are known to form both classical hydrogen bonds,[10] and nonclassical C–H···π hydrogen bonds.[3,11] The anions are in one of two alternating orientations (Fig. 1) approximately perpendicular relative to one another. The torsion angle between the cobalticarborane vectors (vector defined as that between the two apical B positions *para* to the Co) is −65.9°. The anions are situated close to the methyl groups of the CTV, at closest B···C_{methyl} separation 3.71 Å. The siting of a carborane or anionic carborane near methyl groups or within methyl-lined cavities within a crystal lattice has also been observed in a number of other materials containing both carboranes and CTV[7] and is emerging as a structural trend.

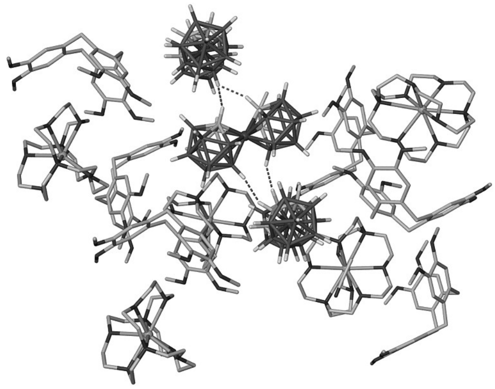

Fig. 1 Partial packing diagram from the crystal structure of {(Na[2.2.2]cryptate)[CTV][Co($C_2B_9H_{11}$)$_2$]}$_2$(MeCN) **5**. All C–H···B-H contacts < 2.3 Å between [Co($C_2B_9H_{11}$)$_2$]$^-$ anions consistent with dihydrogen bonds are shown as dashed lines.

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† Electronic supplementary information (ESI) available: Synthesis of complexes **5** and **6** and discussion of structure solution and refinement for **5**. See http://www.rsc.org/suppdata/cc/b0/b009581h/

‡ Present address: School of Chemistry, University of Leeds, UK LS2 9JT. E-mail: c.l.raston@chem.leeds.ac.uk

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Colourless crystals of (Na[2.2.2]cryptate)[CTV](CHCl$_3$)$_3$[CB$_{11}$H$_{12}$] **6** grew from diffusion of hexane into a mixture of (Cs[2.2.2]cryptate)[CB$_{11}$H$_{12}$], CTV and NaOH in CHCl$_3$–MeOH.† The structure was determined by single crystal X-ray diffraction techniques,§ and, as for complex **5**, features (Na[2.2.2]cryptate)$^+$$\cap$CTV supermolecules as the primary host–guest species, [Fig. 2(a)]. The (Na[2.2.2]cryptate)$^+$ guest molecule is positioned in a more end-on fashion than was seen in **5**, with a longer Na-to-host centroid distance at 7.85 Å, and N–Na$\cdots$centroid angles 55.0 and 134.8°. The CTV molecules also show secondary inclusion behaviour, with a molecule of CHCl$_3$ at distances consistent with the formation of bifurcated hydrogen bonds to each CTV dimethoxy group [Fig. 2(a)] at Cl$_3$C–H$\cdots$OMe distances ranging from 2.23 to 2.52 Å (corresponding C$\cdots$O separations 3.09 to 3.24 Å). Similar hydrogen bonding of CHCl$_3$ to two dimethoxy groups is observed in crystalline CTV(CHCl$_3$)$_2$.[5] Two of the CHCl$_3$ molecules have their donating C–H group in-plane with their respective acceptor dimethoxy groups, while the third binds in a different mode, with the C–H out-of-plane with the dimethoxy groups and the CHCl$_3$ molecule tilted in towards the molecular cavity of the CTV. One of the chlorines of this CHCl$_3$ is directed into the cleft of the (Na[2.2.2]cryptate)$^+$ guest molecule, shown in space filling representation in Fig. 2(b), hence both the CTV and the (Na[2.2.2]cryptate)$^+$ can be regarded as acting as host molecules for this CHCl$_3$.

As with complex **5**, the carborane anion is involved in hydrogen bonds *via* the acidic C–H. In **6** the [CB$_{11}$H$_{12}$]$^-$ anion forms a bifurcated hydrogen bond to two chlorine atoms of the out-of-plane CHCl$_3$ (Fig. 2). Notably, an identical reaction mixture with CH$_2$Cl$_2$, which is less likely to form hydrogen bonding interactions than CHCl$_3$, failed to produce crystalline products, indicating that these interactions are important in stabilising the crystalline product. The CTV molecules within the extended crystal lattice associate in pairs *via* a single, long $\pi\cdots\pi$ interaction, with coplanar aromatic rings at a centroid$\cdots$centroid separation of 3.79 Å.

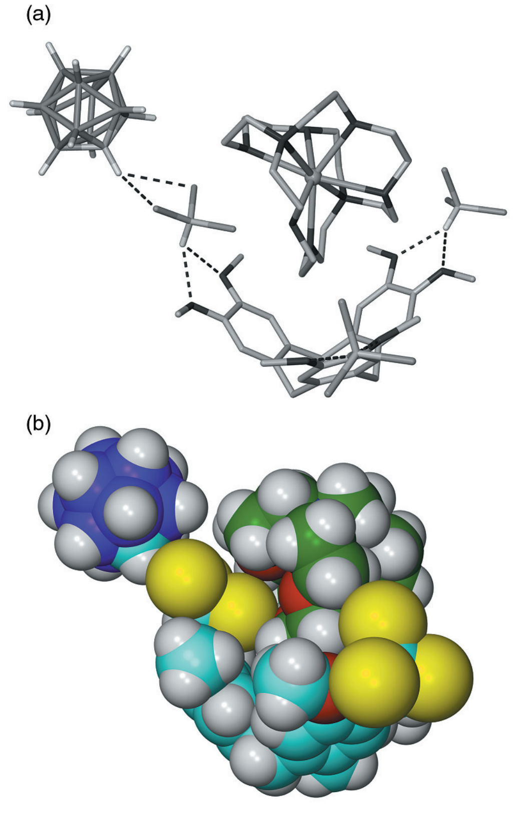

Fig. 2 Crystal structure of (Na[2.2.2]cryptate)[CTV](CHCl$_3$)$_3$[CB$_{11}$H$_{12}$] **6**. (a) Hydrogen bonding interactions between the molecular components (see text), only hydrogen positions on the CHCl$_3$ molecules and **3** anions are shown for clarity; (b) space filling representation, highlighting how a Cl from one CHCl$_3$ molecule is directed into the cleft of the (Na-[2.2.2]cryptate)$^+$. Carbon atoms of [2.2.2]cryptate shown in green, others in blue.

The cation (Na[2.2.2]cryptate)$^+$, itself a host–guest complex, behaves as an intracavity guest for the host molecule CTV, while the bulky counter-anions [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ and [CB$_{11}$H$_{12}$]$^-$ are lattice counter-ions within the crystal packing. These and other carborane anions may be used to build up complicated supramolecular assemblies and generate new types of materials.

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Notes and references

§ *Crystal data*: X-ray data were collected at 123(1) K on an Enraf-Nonius KappaCCD single crystal diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. Carbon positions within carborane cages were assigned by an analysis of displacement parameters and bond lengths. All non-hydrogen atoms were refined anisotropically and hydrogens included at geometrically estimated positions, unless otherwise indicated. {(Na[2.2.2]cryptate)[CTV]-[Co(C$_2$B$_9$H$_{11}$)$_2$]}$_2$(CH$_3$CN) **5**: C$_{100}$H$_{179}$B$_{36}$Co$_2$N$_5$Na$_2$O$_{24}$, M_r = 2388.48, monoclinic, space group $P2_1$, a = 16.5391(7), b = 12.7151(3), c = 29.6858(12) Å, β = 92.349(1), U = 6237.6(4) Å^3, Z = 2, D_c = 1.272 g cm^{-1}, μ = 0.341 mm^{-1} (no correction), yellow–orange needle, 0.33 × 0.12 × 0.05 mm, $2\theta_{max}$ = 50°, 36186 reflections measured, 19710 unique reflections (R_{int} = 0.107), 711 parameters, R_1 = 0.1270 (on 14445 observed data [$I > \sigma(I)$]), wR_2 = 0.2787 (all data), S = 1.061. The crystal was weakly diffracting, and the structure showed pseudosymmetry (see ESI†), with only the Na and Co refined anisotropically. (Na[2.2.2]cryptate)-[CTV](CHCl$_3$)$_3$[CB$_{11}$H$_{12}$] **6**: C$_{49}$H$_{81}$B$_{11}$Cl$_9$N$_2$NaO$_{12}$, M_r = 1351.11, monoclinic, space group $P2_1/n$, a = 13.5449(2), b = 25.3840(4), c = 19.4565(4) Å, β = 94.084(1), U = 6672.6(2) Å^3, Z = 4, D_c = 1.345 g cm^{-1}, μ = 0.440 mm^{-1} (no correction), colourless block, 0.30 × 0.28 × 0.23 mm, $2\theta_{max}$ = 52.0°, 38224 reflections measured, 13085 unique reflections (R_{int} = 0.076), 763 parameters, R_1 = 0.0603 (on 6971 observed data [$I > 2\sigma(I)$]), wR_2 = 0.1514 (all data), S = 1.031. CCDC 154067 and 154068. See http://www.rsc.org/suppdata/cc/b0/b009581h/ for crystallographic data in .cif or other electronic format.

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