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A 3,12-connected vertice sharing adamantoid hydrogen bonded network featuring tetrameric clusters of cyclotriveratrylene

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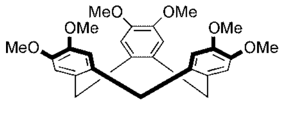
Received (in Cambridge, UK) 22nd June 2001, Accepted 3rd August 2001
First published as an Advance Article on the web 5th September 2001

The crystalline supramolecular complex $[Sr(H_2O)_8][(CH_3CN)\cap(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ features $[(CH_3CN)\cap(CTV)]$ host–guest interactions, back-to-back tetrameric clusters of CTV host molecules and an extensive hydrogen bonding giving a 3,12-connected net.

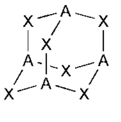
The bowl-shaped molecular host cyclotriveratrylene (= CTV) forms host–guest complexes with large neutral and cationic guest molecules including fullerenes[1] and metal complexes[2] where the guest sits within the molecular cavity. In contrast, smaller organic guest molecules tend to form lattice inclusion complexes with CTV,[3] although covalent derivatives[4] show different host–guest behaviour. It has recently been shown that CTV can act as a crystal engineering tecton, chelating ligand to group 1 metals, and as a hydrogen bond acceptor to form 1D chain or 2D grid structures.[5] As with covalent derivatisation, the inclusion behaviour of CTV is altered, and the complexation of small organic molecules within the CTV bowl is observed. We report herein crystalline complexes of CTV and aquated metal salts of the weakly coordinating anion $[Co(C_2B_9H_{11})_2]^-$,[6] where a complicated hydrogen bonded network is formed between CTV and free and ligated water molecules that can be conceptualised as a 3,12-connected or a more simple α-Po net. The creation of infinite hydrogen bonding network structures is an aspect of crystal engineering that has attracted much attention in the past decade.[7]

Yellow–orange crystals with a uniform highly faceted habit of $[Sr(H_2O)_8][(CH_3CN)\cap(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **1** were obtained in 75% yield from a mixture of CTV (3.9 mg in 1.5 ml acetonitrile) and $Sr[Co(C_2B_9H_{11})_2]_2$ (9.7 mg in 0.5 ml water) in 4:1 proportions. The structure was determined by single crystal X-ray diffraction techniques.†

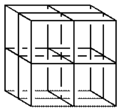
Acetonitrile forms $(CH_3CN)\cap(CTV)$ host–guest interactions within the structure. As would be anticipated from the hydrophobic effect, the methyl points into the hydrophobic cavity of the CTV molecule at a distance of 3.76 Å to the CTV methylene plane, Fig. 1. The nitrile forms a hydrogen bond with the uncoordinated water molecule with an OH···N distance of 2.22 Å (corresponding O···N distance 3.08 Å). This water molecule also forms a hydrogen bond to a methoxy O of the CTV (OH···O 2.08, O···O 2.89 Å) and is a hydrogen bond acceptor from an aquo ligand of the $[Sr(H_2O)_8]^{2+}$ complex ion (Sr–OH···O 1.87, O···O 2.74 Å), Fig. 1. The same aquo ligand hydrogen bonds to a neighbouring CTV at an Sr–OH···O distance of 2.04 Å (O···O separation 2.89 Å). The crystallographically distinct aquo ligand forms hydrogen bonds to the same CTV dimethoxy group (OH···O 2.18, O···O 3.01 Å) and to an O of an adjacent CTV (OH···O 2.09, O···O 2.94 Å). Each $[Sr(H_2O)_8]^{2+}$ complex ion hydrogen bonds to twelve CTV molecules directly or indirectly *via* the uncoordinated water.



CTV



X_6A_4 adamantoid



α-Po net

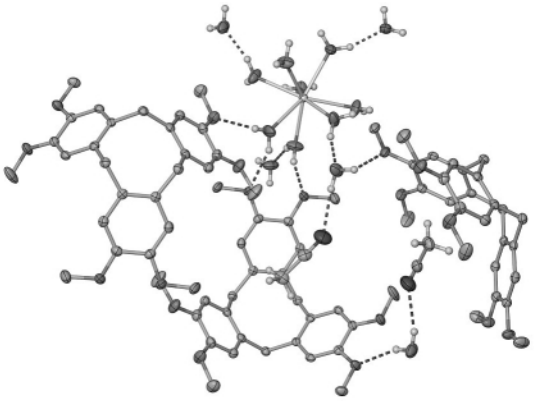


Fig. 1 Detail of the hydrogen bonding interactions between $[Sr(H_2O)_8]^{2+}$, H_2O, CH_3CN and CTV from the crystal structure of **1**.

The CTV molecules stack in a back-to-back tetrameric cluster of approximately tetrahedral geometry such that each dimethoxy group is roughly aligned with those of an adjacent CTV, Fig. 2. This packing arrangement of CTV hosts has not been previously reported, and it is notable that another host molecule, *p*-sulfonatocalix[4]arene, can pack in a back-to-back fashion to produce a considerably larger polyhedral cluster.[8] Whilst the aryl groups of the CTV tetrahedron are coplanar there is no evidence that π–π interactions play a significant role as the aryl centroid separations are long at 3.88 and 4.32 Å. Instead the complex metal ions act as clamps, holding each cluster together at the aligned dimethoxy groups. For each $[CTV]_4$ cluster there are six such $[Sr(H_2O)_8]^{2+}/(H_2O)_4$ species arranged in a near perfect octahedron. The overall arrangement of the $Sr_6[CTV]_4$ assembly is a deformed adamantoid cage, Fig. 2. Adamantoid M_6L_4 supramolecular cages formed with

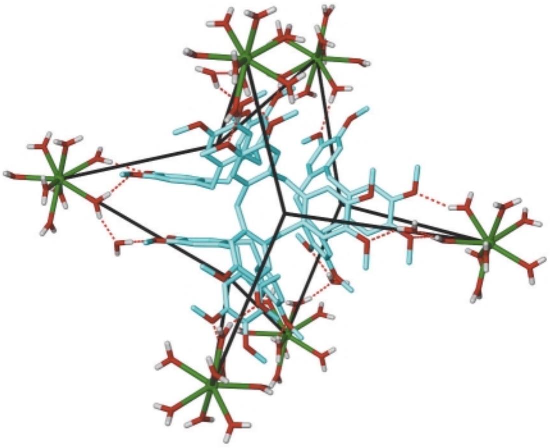


Fig. 2 Crystal structure of **1** showing back-to-back packing of CTV molecules to form a tetrahedral $[CTV]_4$ cluster, surrounded by six $[Sr(H_2O)_8]^{2+}$ in an adamantoid assembly (adamantoid connectivity indicated with black lines between the Sr and CTV centres). Sr centres are sited on four-fold inversion axes.

trigonal connecting ligands have been previously reported as discrete clusters[9] and within a vertice sharing 3D coordination polymer.[10]

The hydrogen bonding network of **1** extends in three dimensions, and in terms of its topology, there are two types of connecting centre, the 3-connecting CTV, and the 12-connecting $[Sr(H_2O)_8]^{2+}/(H_2O)_4$. Each Sr centre is a shared vertex for six $Sr_6[CTV]_4$ adamantoid cages and the 3,12-connected network is shown schematically in Fig. 3(a). To the best of our knowledge this is the first example of a network with this topology, and is notable for its extremely high connectivity. Related examples of vertice-sharing adamantoid network structures involve sharing between only two adamantoid cages.[10] A considerably simpler network structure can be conceptualised by considering the tetrameric cluster of back-to-back CTV molecules as a single six-connecting centre. As each $[Sr(H_2O)_8]^{2+}/(H_2O)_4$ hydrogen bonds to six $[CTV]_4$ clusters, they are also six-connecting centres. Hence the simplified view of the network is of α-Po topology with alternating $[CTV]_4$ and Sr centres, which can be readily appreciated from the packing diagram in Fig. 3(b). The rectangular channels expected for an α-Po type structure are filled by $[Co(C_2B_9H_{11})_2]^-$ anions.

Crystalline supramolecular complexes isostructural with **1** can be obtained in low yield, with CTV needles as the major crystalline product, by reacting CTV with $Ln[Co(C_2B_9H_{11})_2]_3$ (Ln = Y, La, Ce; from metathesis reactions of $Ag[Co(C_2B_9H_{11})_2]$ with $LnCl_3$) in aqueous acetonitrile. The rare earth cations all have a 3+ oxidation state, however there are only two 1− counter-anions per metal centre, and the $[M(H_2O)_8]$ complex ion appears to achieve the required 2+ charge through a 1:1 Ln:Na disorder at the metal centre. The source of the Na^+ is likely to be glassware, and crystal growth is promoted by addition of $Na[Co(C_2B_9H_{11})_2]$, but not by addition of a source of K^+. A Ln/Na disorder is also consistent with the X-ray diffraction data obtained, reported here for the La complex $[Ln_{0.5}Na_{0.5}(H_2O)_8][(CH_3CN)\cap(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **2**.† The ability of the system to adjust to an unfavourable charge on the proffered metal is extraordinary and reflects the stability of this hitherto unknown packing mode of CTV.

Support of this research from the Australian Research Council and the University of Leeds is gratefully acknowledged.

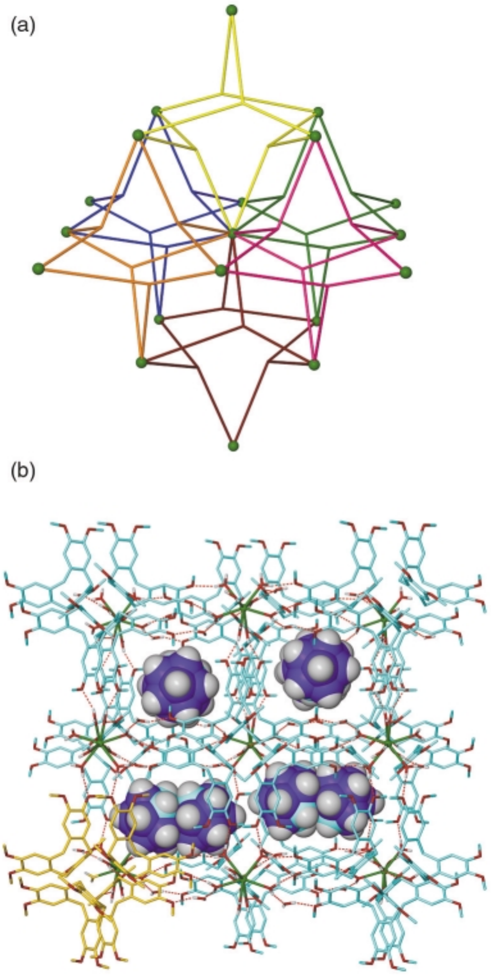


Fig. 3 Two views of the network topology of complex **1**. (a) 3,12-connected network of vertice sharing adamantoid units. Green circles represent Sr^{2+} centres, 3-connected centres are CTV molecules. The six adamantoid assemblies that share a single Sr centre are shown in different colours; (b) packing diagram of **1** with $[Co(C_2B_9H_{11})_2]^-$ anions shown as in space-filling mode. If the $[CTV]_4$ clusters (one highlighted in yellow) are considered as a single 6-connecting centre, the network is related to the 6-connected α-Po structure. Co centres are sited on two-fold rotation axes.

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. All non-hydrogen atoms were refined anisotropically. $[Sr(H_2O)_8][(CH_3CN)\cap(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **1**: $C_{31}H_{50}B_9Co_{0.5}NO_9Sr_{0.25}$, M_r = 729.38, tetragonal, $P4_2/n$, $a = b = 17.7771(1)$, $c = 23.6753(3)$ Å, U = 7482.0(2) Å^3, Z = 8, D_c = 1.295 g cm^{-3}, μ = 0.648 mm^{-1}, yellow–orange prism, 0.13 × 0.11 × 0.10 mm, θ_{max} = 27.48°, 46587 reflections measured, 8567 unique reflections (R_{int} = 0.0796), 658 parameters, R_1 = 0.0437 (on 6202 observed data [$I > 2\sigma(I)$]), wR_2 = 0.1023 (all data), S = 1.013. Hydrogens were fully refined with O–H bond lengths restrained to be chemically reasonable. $[La_{0.5}Na_{0.5}(H_2O)_8][(CH_3CN)\cap(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **2**: $C_{31}H_{50}B_9Co_{0.5}La_{0.125}NNa_{0.125}O_9$, M_r = 727.71, tetragonal, $P4_2/n$, $a = b = 17.6914(3)$, c = 23.6592(3) Å, U = 7405.0(2) Å^3, Z = 8, D_c = 1.305 g cm^{-3}, μ = 0.441 mm^{-1}, yellow–orange prism, 0.32 × 0.32 × 0.18 mm, θ_{max} = 26°, 45683 reflections measured, 7271 unique reflections (R_{int} = 0.068), 459 parameters, R_1 = 0.0776 (on 5082 observed data [$I > 2\sigma(I)$]), wR_2 = 0.2324 (all data), S = 1.038. Hydrogens were included at calculated positions. Anisotropic displacement parameters and overall scale factor were unreasonable for the M = La model for the $[M(H_2O)_8]$ moiety, but were acceptable for a M = La/Na disorder. Displacement parameters indicate disorder within the aquo ligands. Given the extensive hydrogen bonding dynamic disorder is unlikely, and a static disorder of $[La(H_2O)_8]^{3+}$ and $[Na(H_2O)_n]^+$, which would not have identical geometries, was the chosen model. Unit cell parameters for the Y complex: tetragonal, $a = b$ = 17.6918(3), c = 23.7339(3) Å (full details in supplementary data), for the Ce complex: tetragonal, $a = b$ = 17.505(7), c = 23.997(7) Å. CCDC reference numbers 166360–166362. See http://www.rsc.org/suppdata/cc/b1/b105517h/ for crystallographic data in CIF or other electronic format.

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