Supramolecular Cages

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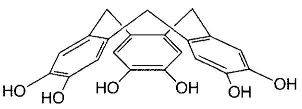
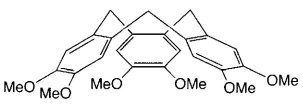
Cages with Tetrahedron-Like Topology Formed from the Combination of Cyclotricatechylene Ligands with Metal Cations**

Brendan F. Abrahams, Nicholas J. FitzGerald, and Richard Robson**

Cyclotricatechylene, **1a**, ($ctcH_6$) is readily obtained[1] from the hexaether cyclotriveratrylene **1b**. As such, it is surprising that such little investigation of its metal complexes has been undertaken; indeed, to the best of our knowledge, there are no previously recorded examples of coordination compounds of the ctc^{6-} ligand. Cage compounds, constructed from multiple metal–ligand coordinate bonds, have been reported in which the ligands, such as the ctc^{6-} ligand in the examples described below, act as building blocks with threefold symmetry; the ligands in question are structurally similar to **1b**: three methoxy groups were replaced by nitrogen-containing functional groups and the ligands terminated in metal-binding pyridyl donors.[2] Recently, we indicated that ctc-derived anions appear to have a marked affinity for Cs^+ and Rb^+ ions, generating "clamlike" structures in which the cation is trapped between two hydrogen-bonded ctc-derived units that act as the shells of the clam.[3] The immediate environment around the alkali metal cation is provided entirely by the internal carbon π surface of the ctc, and this despite the fact the compounds are generated in mixtures that contain a substantial proportion of water. The preliminary results presented herein indicate the vast potential of the easily generated $ctcH_6$ for providing a wide range of interesting metal derivatives.



1a



1b

The compounds described herein were usually obtained by adding base to a mixture of $ctcH_6$ in either dioxane or acetone and the transition-metal salt in water (together in some cases with a water-soluble source of co-cations, such as Cs^+, Rb^+, or Ca^{2+}). When a combination of VO^{2+} and Ca^{2+} was used, crystals were formed, the X-ray diffraction analysis of which revealed well defined $[(VO)_6(ctc)_4]^{12-}$ clusters (Figure 1 a).[4] The clusters have the same topology as that of a tetrahedron: the four ctc^{6-} ligands provide the three-connecting corners and the six VO^{2+} centers act as two connecting links between them. The Ca^{2+} counterions, of which there are two types, associate with the oxygen centers of the catechol units to give an overall electrically neutral cluster with a metal/ctc composition of $[Ca_6(VO)_6(ctc)_4]$ (Figure 1 b). A twofold axis (indicated by a black arrow) passes through two of the vanadyl centers (V1). The other four vanadyl centers (V2) are symmetry related to each other around this axis. The six vanadium centers are located at the corners of an octahedron that is somewhat elongated along the V1···V1 twofold axis (V1···V1, 14.998 Å, V2···V2, 14.035 Å). Associated with each V2 atom, through four-

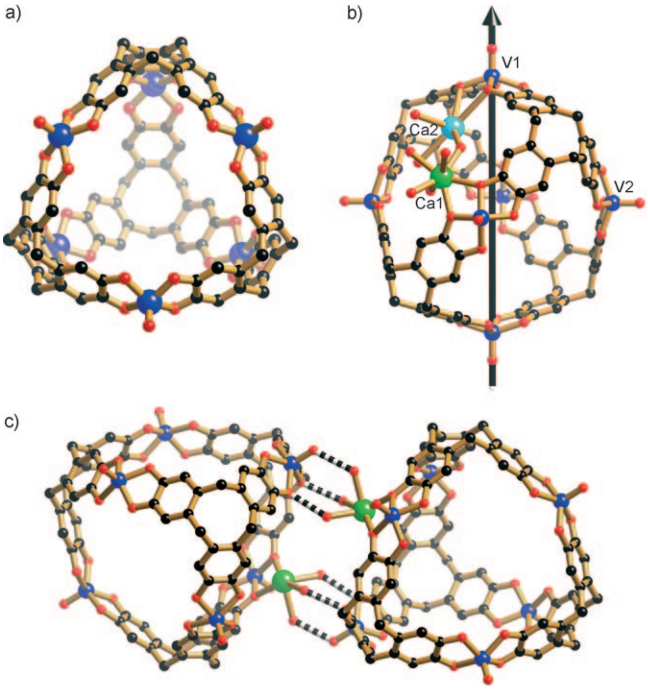


Figure 1. a) A view of the $[(VO)_6(ctc)_4]^{12-}$ cluster. The centers of the four ctc^{6-} ligands are almost (but not quite) at the corners of a regular tetrahedron and the six vanadium centers are close to the corners of a regular octahedron. b) A view of $[Ca_6(H_2O)_{18}(VO)_6(ctc)_4]$ with the twofold axis (indicated by a black arrow) close to vertical. For simplicity, only one Ca1 and only one Ca2, together with their attached water molecules, are shown. There are four Ca1 centers. Two Ca2 centers are disordered over four equivalent sites. c) A view of two cages held together by a pair of triple hydrogen bonds involving the water molecules on Ca1 (dotted lines).

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[*] Assoc. Prof. B. F. Abrahams, N. J. FitzGerald, Prof. R. Robson
School of Chemistry, University of Melbourne
Victoria 3010 (Australia)
Fax: (+61) 3-9437-5180
E-mail: bfa@unimelb.edu.au
r.robson@unimelb.edu.au

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membered V2–O–Ca1–O rings, is a Ca1 center, only one example of which is shown for simplicity in Figure 1 b. A second Ca^{2+} ion (Ca2) is associated with V1, somewhat more weakly, by similar four-membered rings, only one example of which is shown for simplicity in Figure 1 b. A total of two Ca2 centers per cage are disordered over four equivalent sites. Four water molecules are attached to Ca1, one of which bridges to Ca2, which in turn has two other bound water molecules. Enclosed within the $[Ca_6(VO)_6(ctc)_4]$ cage are four dioxane molecules, each disordered over two positions; in one of these two orientations, a dioxane oxygen atom is located 2.48(1) Å from Ca2. Each cluster is attached to four neighbors by two triple hydrogen bonds, an example of which is shown in Figure 1 c. The extended three-dimensional arrangement of clusters is closely related to the arrangement of carbon atoms in a diamond but is slightly distorted from cubic symmetry (in fact, the structure is tetragonal). The formation of this diamond-like network leads to the generation of very large adamantane-type cavities that are filled with highly disordered solvent (see the Supporting Information).

A Mg/VO analogue of the above Ca/VO compound, which contains the closely related tetrahedral $[(VO)_6(ctc)_4]^{12-}$ clusters, was obtained in a similar fashion (see the Supporting Information). A number of metal–ligand cages that have a tetrahedron-like topology have been previously reported, including early examples by Saalfrank et al.[5] and Raymond and co-workers,[6] in which the metal centers provide the 3-connecting nodes in cages that have a composition of M_4L_6; in contrast, the examples reported herein have a composition of M_6L_4 and the 3-connecting nodes are provided by the ligand L.

As mentioned above, anions that are derived from the ctc ligand appear to have a high affinity for Rb^+ and Cs^+ ions, associating with these cations through the π system of their C_6 rings, even in the presence of water.[3] Therefore, it was of interest to see if we could obtain $[M_6(ctc)_4]$ clusters that have Rb^+ or Cs^+ ions trapped in all four corners of the tetrahedral cage. The usual preparative procedure, by using VO^{2+} in the presence of Cs^+ ions, afforded crystals suitable for X-ray analysis that again contained $[(VO)_6(ctc)_4]^{12-}$ clusters.[4] As expected, a Cs^+ ion is snugly embedded in each corner of the tetrahedral cluster; the cations make multiple contacts with ctc-derived carbon atoms, as indicated in Figure 2. A $[Na(H_2O)_6]^+$ ion is found at the center of the cluster, which was unexpected, but with hindsight is not too surprising because sodium hydroxide was the base used in the reaction. A twofold axis passes through two vanadyl centers (V1) and through the Na^+ ion. The four vanadyl centers in the "equatorial" plane, perpendicular to the twofold axis, are labeled as V2. The four water molecules, attached to the Na^+ ion in this equatorial plane, bridge to the Cs^+ centers (Figure 2). As well as the six well-defined water molecules that are associated with Na^+, there are other molecules inside the cage that are very disordered. A second type of Cs^+ center, which is external to the clusters (see the Supporting Information), is also clearly defined, and interacts directly with the oxo and catechol oxygen atoms associated with V1 in one cluster and with catechol oxygen centers associated with V2 in an adjacent cluster.

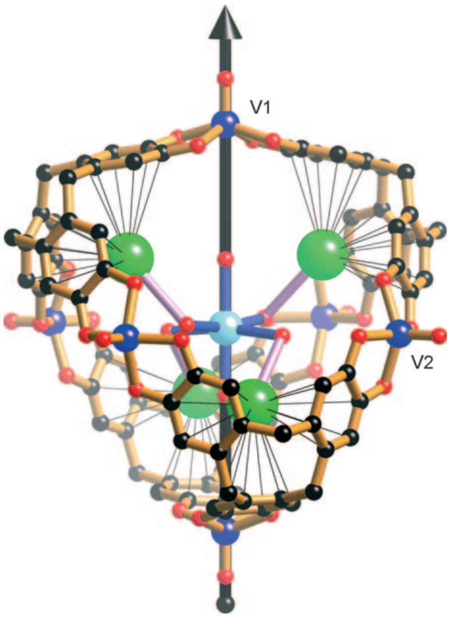

Figure 2. A view of a $[(VO)_6(ctc)_4]^{12-}$ cage with four Cs^+ ions (green) embedded in the tetrahedron corners and a $[Na(H_2O)_6]^+$ ion at the center (light blue). The twofold axis shown here is close to vertical. Fine black lines indicate Cs–C interactions.

When the combination of Mn^{2+} and Cs^+ ions is used in the general procedure with sodium hydroxide as the base, cubic crystals are obtained that contain clusters similar to the VO/Cs clusters described above.[4] In this case, the $[Mn_6(ctc)_4]^{12-}$ cluster is highly symmetrical, with a Cs^+ ion embedded in each corner of the tetrahedral cage and a $Na(H_2O)_6^+$ ion at the center (Figure 3 a); four threefold axes pass through the sodium center. Each of the six water molecules that are associated with the Na^+ ion also bridge to two equivalent Cs^+ ions. The six equivalent Mn^{2+} centers, located at the corners of a regular octahedron, are in a roughly square pyramidal coordination environment that consists of two chelating catechol ligands and an "axial" hydroxo ligand that bridges to a manganese center in an adjacent cluster; the bridging hydroxo ligand is disordered over four positions. A bond valence sum analysis of the manganese–ligand bond distances indicated a valence state for the manganese of 1.9.[7] Every cluster is connected by Mn–OH–Mn bridges to six others whose centers lie at the corners of a regular octahedron. The coordination polymer so formed has a simple cubic α-polonium topology (Figure 3 b). A second type of Cs^+ ion (Cs2), located outside the cages, is found close to the bridging hydroxo groups, in contact with the π systems of the catechol components of two flanking clusters (Figure 3 c). These Cs2 centers, as well as making contact with the π systems of the catechol components on opposite sides, associate with disordered water molecules. A similar α-polonium-related hydroxo-bridged network has also been synthesized in which Mn^{2+} and Cs^+ ions are replaced by Co^{2+} and Rb^+, respectively (see the Supporting Information).[4]

In conclusion, the preliminary work reported herein describes the first characterized examples of coordination complexes that are derived from the readily accessible $ctcH_6$.

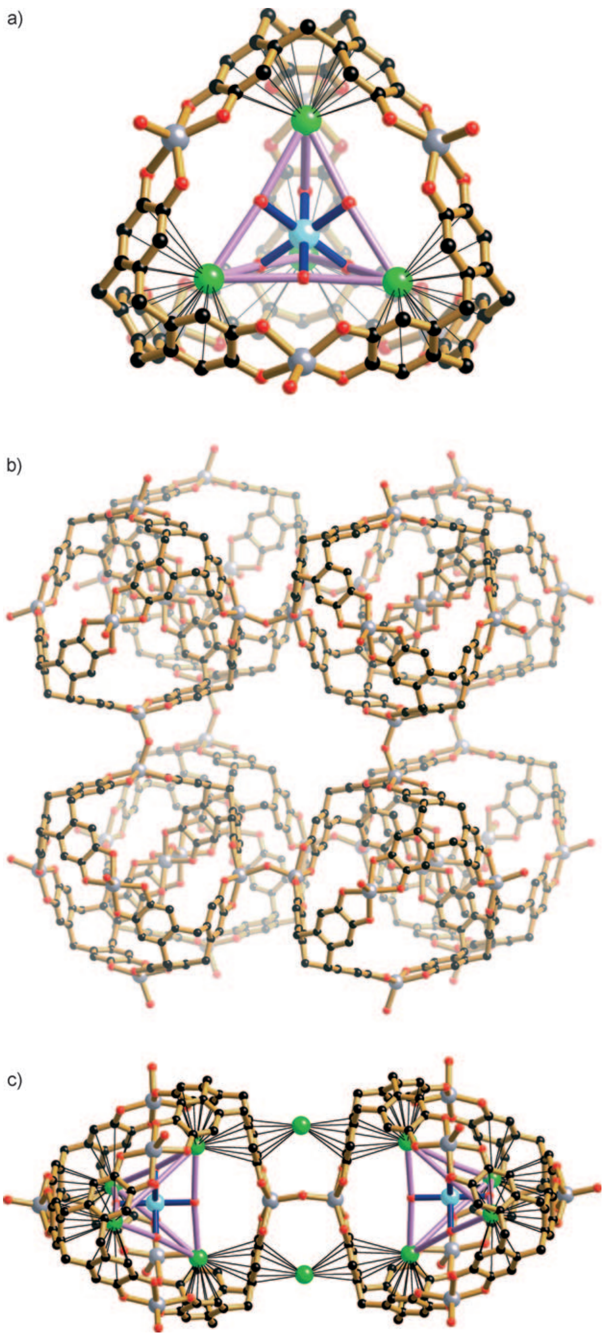

Figure 3. a) A view of a $[Mn_6(OH)_3(ctc)_4]^{12-}$ cage with four Cs^+ ions (green) embedded in the tetrahedron corners and a $[Na(H_2O)_6]^+$ ion (light blue) in the center. The "axial" hydroxo ligands on the manganese atoms (O red, Mn silver) are disordered over four sites, only one orientation being shown here. b) The α-polonium-like three-dimensional coordination polymer in which every cage is attached to six others by Mn–OH–Mn bridges. c) "External" Cs^+ ions (Cs2) sandwiched between C_6 aromatic rings of ctc units in adjacent cages. Disordered water molecules bound to the Cs^+ ions have been omitted.

On the basis of the results presented above, we confidently expect ctc^{6-} ligands to be used to afford a wide range of structurally interesting new metal derivatives, since many combinations of catechol-binding metals and countercations are readily envisaged. Indeed, in addition to the above examples, we have isolated a number of crystalline transition metal compounds containing the ctc^{6-} ligand, the X-ray diffraction analyses of which very clearly reveal $[M_6(ctc)_4]$ tetrahedral cage structures that are closely related to those described herein; however, disorder in the large regions of space left between the cages leads to crystallographic problems that require further work. The binding of a variety of cationic or electrically neutral species into either the corners of the tetrahedra or into the central regions may be anticipated and may be of considerable interest. Cyclotriveratrylene, the hexaether from which $ctcH_6$ is generated, has been very widely studied as a host for a wide range of guests;[8] the cages reported herein contain not one but four receptor sites related to that found in cyclotriveratrylene, thus providing many possibilities for new chemistry. The promotion of chemical reactions within cages of various types has been the subject of recent research.[9] On the basis of the large size of the $[M_6(ctc)_4]$ cages, large enough, as indicated above, to include four molecules of dioxane or four cesium cations and a sodium cation together with on the order of a dozen water molecules, these cages would appear particularly well suited to this sort of application. Available, inward-pointing coordination sites on the six metals that form the cage may be used to promote unusual reactions inside the cage. Extended coordination arrays, such as the one seen in Figure 3b, with large channels between cages, raise intriguing possibilities of catalytic solids whose active sites are the cage interiors.

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[4] Crystal data for $[Ca_6(VO)_6(ctc)_4]\cdot 4C_4H_8O_2\cdot 110H_2O$, $M_r = 4417.5$, tetragonal, $I4_1/a$, $a = 21.1696(7)$, $c = 47.577(2)$ Å, $V = 21321.8(15)$ Å^3, $Z = 4$, $\theta_{max} = 68.0°$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 4.371$ mm^{-1}, 21208 reflections measured, 9286 unique which were used in all calculations, 433 parameters, $wR2 = 0.2737$ (all data) and $R1 = 0.0910(I > 2\sigma(I))$. Crystal data for $[Mg_6(VO)_6(ctc)_4]\cdot 76H_2O$, $M_r = 3357.9$, cubic, $P\bar{4}3n$, $a = 31.6182(2)$ Å, $V = 31609.0(3)$ Å^3, $Z = 8$, $\theta_{max} = 68.0°$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 4.371$ mm^{-1}, 27808 reflections measured, 8166 unique which were used in all calculations, 367 parameters, $wR2 = 0.1895$ (all data) and $R1 = 0.0700$ $(I > 2\sigma(I))$. Crystal data for $[Cs_8Na_4(VO)_6(ctc)_4]\cdot 75H_2O$, $M_r = 4349.3$, cubic, $I\bar{4}3d$, $a = 37.9956(4)$ Å, $V = 54852.9(10)$ Å^3, $Z = 12$, $\theta_{max} = 68.0°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 15.645$ mm^{-1}, 17908 reflections measured, 6291 unique which were used in all calculations, 278 parameters, $wR2 = 0.2577$ (all data) and $R1 = 0.1188$ $(I > 2\sigma(I))$. Crystal data for $[Cs_{10}Na_5Mn_6(OH)_3(ctc)_4]\cdot 105H_2O$, $M_r = 5157.6$, cubic, $Fm\bar{3}m$, $a = 36.5356(8)$ Å, $V = 48770(2)$ Å^3, $Z = 8$, $\theta_{max} = 67.9°$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 14.782$ mm^{-1}, 8267 reflections measured, 2203 unique which

were used in all calculations, 99 parameters, $wR2 = 0.2652$ (all data) and $R1 = 0.0882$ ($I > 2\sigma(I)$). Crystal data for $[Rb_{11}Na_4Co_6(OH)_3(ctc)_4]\cdot 111\,H_2O$, $M_r = 4877.7$, cubic, $Fm\bar{3}m$, $a = 35.5734(10)$ Å, $V = 45\,017(2)$ Å^3, $Z = 8$, $\theta_{max} = 67.9°$, $Cu_{K\alpha}$ radiation $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 7.205$ mm^{-1}, 7684 reflections measured, 2014 unique which were used in all calculations, 113 parameters, $wR2 = 0.3279$ (all data) and $R1 = 0.1050$ ($I > 2\sigma(I)$). All structures were solved by direct methods and refined using a full-matrix least-squares procedure (SHELX97).[10] Crystallographic analyses were performed using the winGX system of programs.[11] Comments regarding the treatment of disordered solvent within the structure refinements are presented in the Supporting Information. CCDC 760922 ($[Ca_6(VO)_6(ctc)_4]\cdot 4C_4H_8O_2\cdot 110\,H_2O$), CCDC 760924 $[Mg_6(VO)_6(ctc)_4]\cdot 76\,H_2O$, CCDC 760923 $[Cs_8Na_4(VO)_6(ctc)_4]\cdot 75\,H_2O$, CCDC 760921 $[Cs_{10}Na_5Mn_6(OH)_3(ctc)_4]\cdot 105\,H_2O$, and CCDC 760925 $[Rb_{11}Na_4Co_6(OH)_3(ctc)_4]\cdot 111\,H_2O$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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