PERSPECTIVE

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Network structures of cyclotriveratrylene and its derivatives

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The host molecule cyclotriveratrylene can be incorporated into network structures by acting as a hydrogen bond acceptor or as a chelating ligand for Group 1 metals. New CTV-based ligands with pyridyl functional groups have been synthesised for use as multifunctional ligands in coordination networks. Resultant hydrogen bonded network structures and coordination networks show a range of chain, 2-D and 3-D structures with hexagonal 6^3 nets predominating. Recent results are discussed including highly complex 3-D networks where the molecular hosts pack in a tetrameric back-to-back fashion.

Introduction

Network structures are crystalline materials where molecular components are arranged into infinite 1-D chain or ladder, 2-D grid or 3-D structural motifs constructed using the principles of crystal engineering. Crystal engineering involves controlling and understanding the way molecules are oriented in crystal lattices.[1] The molecular components of network structures are termed tectons, and are usually organised through directional intermolecular associations such as hydrogen bonds, or through coordinate interactions.[2] Coordination materials have been dubbed coordination polymers, metal-organic frameworks (MOF) or coordination networks, the final terminology being adopted here. Network structures show both fascinating structural chemistry and offer great scope for a range of potential applications. The structural analysis of network structures usually focuses on the topology of the network, which requires reducing the structure to a series of connecting points or nodes. Network, or framework, structures often feature significant cavities or channels and many of their potential applications rely on these materials acting as host assemblies, capable of containing lattice-type guest molecules within these channels and cavities. Such materials can be envisaged for use in zeolitic applications, and there have been notable advances in the field of gas storage.[3] The ability to act as a host is not intrinsic to the molecular components but rather a function of the overall network assembly, unlike for molecular hosts.

Molecular host molecules generally feature a molecular cavity or cleft into which other molecules may be non-cova-

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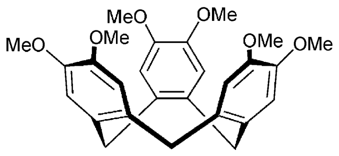
lently bound. Cyclotriveratrylene (CTV, **1**) is a cyclic trimer that usually adopts a bowl-shaped conformation, seemingly ideal for a molecular host.[1] Simple host–guest complexes of CTV with small organic guest molecules tend to form crystalline clathrate materials, which are known in two phases α- and β-CTV, where the CTV molecules stack on top of one another and guests occupy channels created by packing of the CTV molecules.[4] Exceptions to such lattice-inclusion behaviour include crystalline complexes with guests acetone[5] and some chlorinated organic species[6] where complexation of the guest occurs within the molecular cavity of CTV. On the other hand large guest molecules, such as *o*-carborane,[7,8] fullerenes,[8–10] organometallic complexes,[11] and [Na-2.2.2.cryptate]$^+$,[12] normally form ball-and-socket type supermolecules with CTV through intracavity complexation. The basic CTV framework can be built upon by covalently synthesising extended-arm derivatives or cavitands, or by indirectly linking two CTV fragments together in a head-to-head fashion to form cryptophanes.[13–18] Some of the recent advances in CTV chemistry have led to compounds with potential applications as liquid crystals,[14] in biological systems,[15] in ion-pair recognition,[16] in optical resolution,[17] and as selective anion sensors.[18]



CTV

We are interested in incorporating CTV, or its derivatives, into network structures, as this will produce materials with the potential to show both lattice-inclusion chemistry and site-specific molecular recognition chemistry. The dimethoxy groups of CTV can be hydrogen bond acceptors or chelating ligand groups for hard metals such as Group 1 cations, and such interactions allow for its use as a tecton for network structures. CTV is potentially a 3-connecting node, which species tend to form 2-D hexagonal nets of 6^3 topology, Fig. 1a. An alternative 2-D net from 3-connecting centres has 4.8^2 topology (Fig. 1b). The topology is described using a Schläfli symbol which describes the size of the shortest circuit that can be formed, and the number of such circuits as the superscripted number.[19] For instance, 6^3 means that 6-gons are the shortest circuit of connecting nodes that can be formed, and that there are three such circuits in different directions from each node, while 4.8^2 indicates that the shortest circuit in each direction is either a 4-gon or one of two 8-gons. Earlier work with Raston and others established that CTV will form hydrogen bonded network structures with water or *o*-carborane as the hydrogen bond donor.[8,20,21] Carboranes have acidic C–H groups and hence are good hydrogen bond donors.[22] The types of hydrogen bonded structures found include chiral chain and grid structures, including hexagonal 6^3 nets. The intracavity guest molecules for the CTV hosts range from large *o*-carborane and fullerene-C_{70} molecules[8] to small dimethylformamide (DMF).[20] Coordination chain and network structures have also been established.[20,21,23] In general, discrete coordination complexes and coordination chains form additional hydrogen bonding interactions to give overall 2-D networks, and complexes with metal centres ranging from Na^+ to Cs^+ have closely related structures, best described as centred hexagonal nets.[20,21] There is also one example of a $[Na(CTV)]^+$ coordination network with 4.8^2 topology.[23] In all of these examples the intracavity guest is a small organic molecule such as DMF or 2,2,2-trifluoroethanol. A complicated 2-D coordination network has also been reported for the complex $Cs_2(C_{70}^-)_2 \cdot CTV \cdot (DMF)_7(C_6H_6)_{0.75}$ where dimeric $(C_{70}^-)_2$ anions form host–guest interactions with the CTV hosts,[10] which is discussed in more detail below.

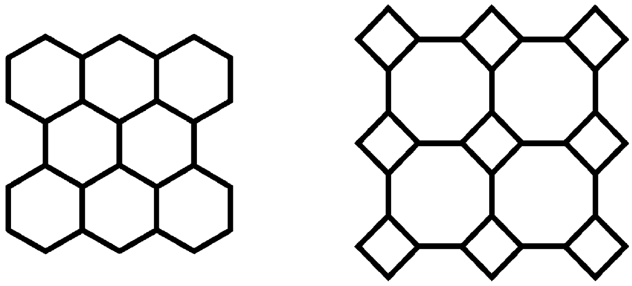
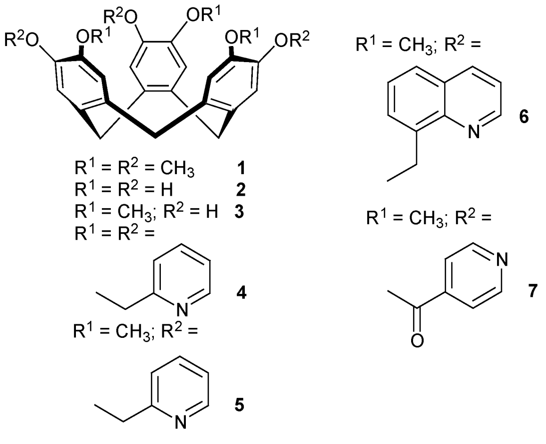

(a) (b)

Fig. 1 2-D nets from 3-connecting nodes: (a) 6^3 topology; (b) 4.8^2 topology.

Other host molecules are also known to form network structures with a range of co-tectons. Hydrogen bonded networks and coordination chains and/or networks are known for crown ether,[24] calixarene,[25–27] calixresorcinarene,[28,29] and cucurbituril[30] host molecules, while cyclodextrins[31] can be involved in hydrogen bonded networks. Network structures have also been built-up through host–guest interactions between calixarene hosts and guest molecules, as well as self-inclusion motifs.[32] Notably, work by Atwood and Barbour has shown that the simple crystalline phases of some calixarene host molecules can themselves bind gaseous guest molecules.[33]

New pyridyl functionalised CTV derivatives

In order to access transition metal chemistry, a series of pyridyl functionalised CTV analogues have been synthesised.[34,35] CTV itself may act as a π-type ligand,[36] and a handful of CTV-derived ligands have been previously reported.[37–44] Examples of known CTV-based ligands are shown in Fig. 2 and include thiols, catechols, N-donor ligands and more. It is intended that new molecular hosts will be used as ligands for a variety of transition metal cations, although our initial work has focused on Ag(I) complexes. Both hexa- and tri-substituted ligands can be synthesised. Hexa-substituted ligands can be accessed *via* the demethylated CTV analogue cyclotricatechylene **2**, while tri-substituted derivatives can be accessed from the mixed methoxy, hydroxy derivative cyclotriguaiacylene **3**. A range of new host molecules have been synthesised but only the 2-pyridylmethyl derivatives **4** and **5**, 8-quinolinylmethyl derivative **6** and isonicotinoyl derivative **7** will be discussed in detail in this perspective article. Synthesis of the pyridyl functionalised hosts follows standard methodologies and typical synthetic pathways are shown for ligands **4** and **7** in Scheme 1.[34,35]



Thus far we have characterised three types of crystalline inclusion behaviour for the pyridyl functionalised CTV derivatives. The hexa-substituted ligand hexakis(2-pyridylmethyl)-cyclotriveratrylene **4** forms a clathrate inclusion complex with water in the complex $\mathbf{4} \cdot 4.5H_2O$.[34] Within this complex the host

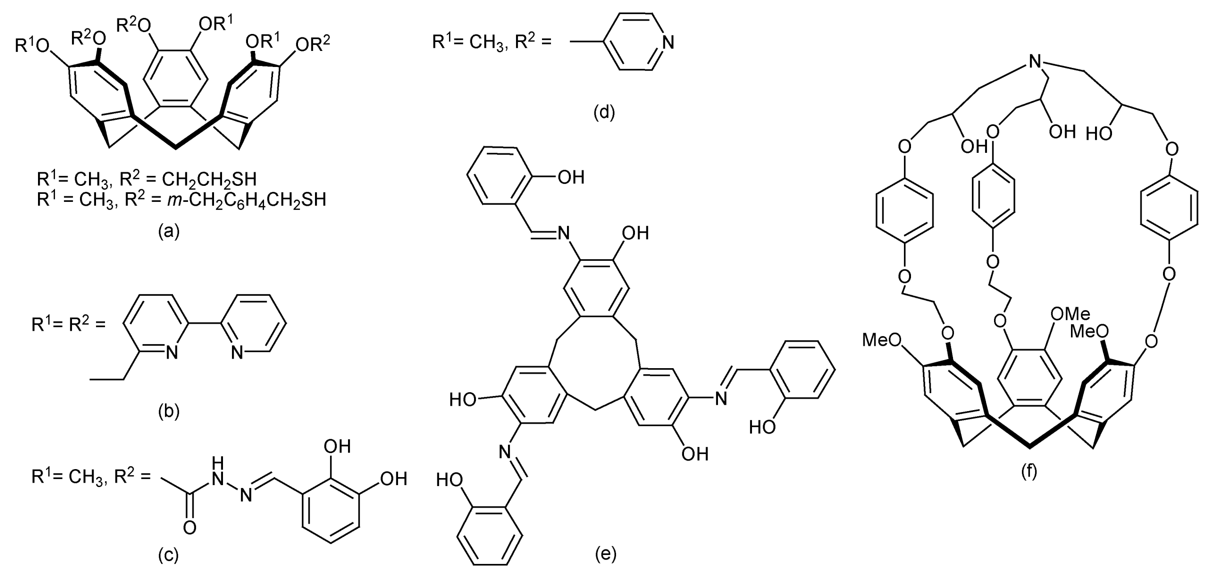


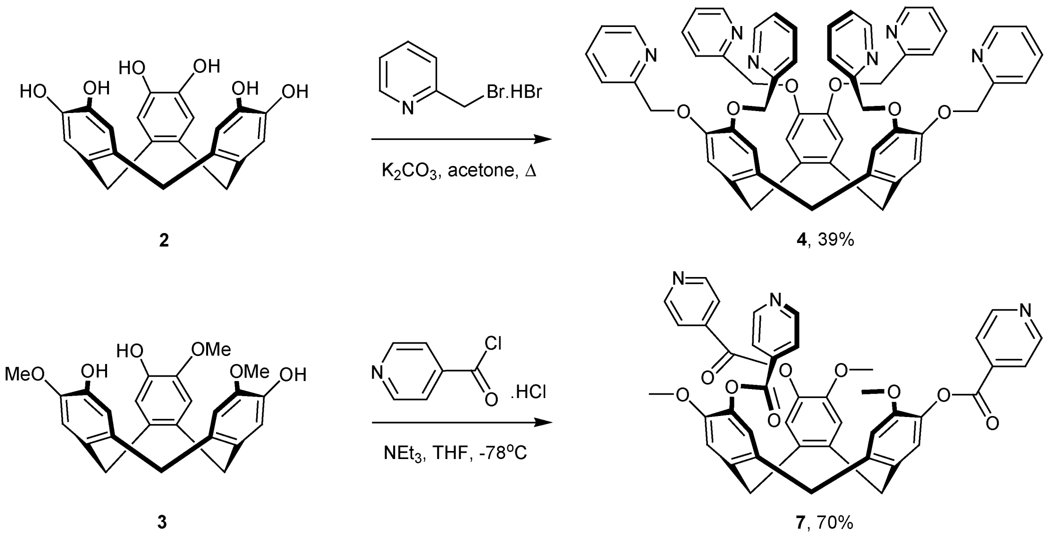
Fig. 2 Examples of ligand functionalised CTV-analogues, (a) thiol,[37] (b) 2,2′-bipyridine,[38] (c) catechol,[39] (d) pyridyl,[40] and (e) salicylaldiminato[41] derivatives and (f) a hemicryptophane with an internal metal binding site.[42]

molecules **4** form an aligned self-stacking motif with one host fitting into the bowl of the next host to form an infinite pillar of host molecules. This is in contrast to the misaligned self-stacking seen in α-phase CTV clathrates.[4] All such pillars throughout the crystal lattice have the same orientation, hence this is a polar arrangement of molecules. Disordered water molecules are lattice-type guests, Fig. 3a. The tri-substituted ligand tris(8-quinolinylmethyl)cyclotriguaiacylene **6** also crystallises with a self-inclusion motif but one that occurs in a dimeric, rather than an infinite, fashion.[34] In the crystalline complex **6**·2CH_3CN, a quinoline arm of one molecule of **6** is directed into the molecular cavity of a second molecules of **6** and *vice versa* to form a skewed dimeric capsule-like arrangement, Fig. 3b. The positioning of the quinoline arm precludes the possibility of further guest binding by the host molecular cavity and the CH_3CN is a lattice-type guest, positioned at the periphery of the host dimer. Intracavity guest encapsulation is seen in the host–guest complex of tris(isonicotinoyl)cyclotriguaiacylene **7**, although guest positions were too disordered to be modelled in the crystal structure.[35] This ligand forms an aligned head-to-head dimeric capsule with the pyridyl arms forming long π-stacking interactions, Fig. 3c. Isostructural complexes can be generated with acetonitrile or acetone as the intracavity guest. Curiously, despite a range of known derivatives, there are very few examples in the literature of crystal structures of extended arm CTV hosts with which to compare these structures. Known examples fall into two structural categories: a misaligned self-stacking quite different to that of complex **4**·4.5H_2O which occurs where $R^1 = CH_3$ and $R^2 = CH_2CH_2Br$[45] or CH_2CHCH_2;[46] and the self-clasping dimer motif seen in complex **6**·2CH_3CN which is also known for molecules where $R^1 = CH_3$ and $R^2 = (CH_2)_4Br$[47] and where $R^1 = CH_2CH_3$ and $R^2 = CH(CH_3)COOCH_3$.[48]

Chain and 2-D network structures

CTV has been shown to coordinate to Group 1 metal ions, usually in the presence of large polyhedral anions such as reduced fullerenes or carborane anions.[10,21,23] We investigated forming network structures with CTV, Group 1 cations and a range of halogenated carboranes. Although there are few reports of such interactions, the halogenated carboranes are capable of coordinating to metal cations through their halo groups.[49] The anions $(CB_{11}H_6X_6)^-$ where X = Cl, Br and $(CB_9H_5Br_5)^-$ form chain and 2-D network structures with CTV and a Group 1 cation.

The complexes $[Na(CTV)(H_2O)(CB_{11}H_6X_6)](CF_3CH_2OH)$, where X = Cl, Br, are isostructural and feature a chiral



Scheme 1 Examples of synthetic methodologies for hexa- and tri-substituted CTV ligands.

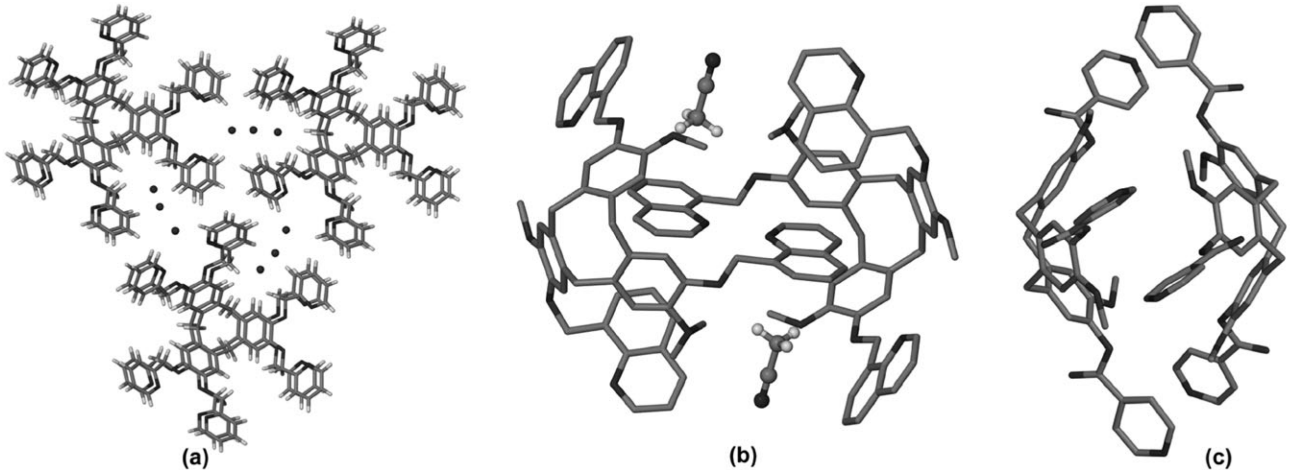


Fig. 3 Inclusion behaviour of pyridyl functionalised host molecules. (a) Aligned self-stacking of **4** with disordered water lattice-type guest molecules, (b) dimeric self-inclusion of **6** with CH_3CN guest molecules at the periphery of the dimer, (c) head-to-head dimerisation of **7** forming a molecular capsule where included guest molecules were too disordered to model.

coordination chain.[50] In $[Na(CTV)(H_2O)(CB_{11}H_6Cl_6)]$ (CF_3CH_2OH) **8** the Na(I) centre is coordinated by two chelating CTV ligands, one aquo ligand and the $(CB_{11}H_6Cl_6)^-$ anion through a single B–Cl–Na interaction. The $(CB_{11}H_6Cl_6)^-$ anion is directed into the cavity of the CTV host, with the interaction stabilised by a C–H$\cdots\pi$ hydrogen bond, Fig. 4a. Such C–H$\cdots\pi$ interactions have been previously observed for neutral $C_2B_{10}H_{12}$ with both CTV[7] and calix[5]arene.[51] The CTV ligands bind Na^+ centres through two of three dimethoxy groups, leading to a chiral coordination chain. These chains hydrogen bond together through Na–$OH_2\cdots$OMe interactions between the aquo ligands of one chain and the non-coordinating CTV methoxy groups of adjacent chains, Fig. 4b. Overall the network structure is 2-D and has distorted hexagonal 6^3 topology with both CTV and Na^+ centres acting as 3-connecting nodes.

The larger cation K^+, gives a disordered structure in complex $[K(CTV)(CB_{11}H_6Cl_6)(CF_3CH_2OH)_{0.5}]$ **9**, which has similar unit cell parameters to complex **8** and is largely isostructural with it.[50] The significant differences between complexes **8** and **9** occur in the metal coordination sphere. In **9** the K^+ cation is bound by three CTV ligands, the $(CB_{11}H_6Cl_6)^-$ anion *via* a chloro group and solvent CF_3CH_2OH, Fig. 5. While in the Na^+ complex **8** the 2-D network structure is generated by coordinate interactions and hydrogen bonding between the aquo ligand and CTV, in complex **9** an identical network structure is obtained from only coordinate interactions. The K–O interatomic distances are very long, and the structure is rather disordered, indicating that K^+ is a poor fit, and that larger cations may be better suited to forming the network structure. Indeed in the complexes $[Rb(CTV)(CB_{11}H_6Br_6)$ $(H_2O)]$ and $[Cs(CTV)(CB_{11}H_6X_6)(CH_3CN)]$ where X = Cl, Br, isostructural 2-D coordination networks are formed that are very similar to the 2-D network of **9**.[50] In $[Cs(CTV)(CB_{11}H_6Cl_6)(CH_3CN)]$ **10**, for instance, each CTV ligand bridges between three Cs^+ centres, and each Cs^+ is complexed by three chelating CTV ligands, forming a 6^3 hexagonal network, Fig. 6. The Cs^+ coordination sphere is completed by a coordinated acetonitrile ligand, and the $(CB_{11}H_6Cl_6)^-$ anion which coordinates through two chloro groups. Notably, the host–guest associations within these complexes are different to those seen with complexes **8** and **9**. Here the primary molecular guest is coordinated acetonitrile, or aquo ligand in the case of the Rb^+ complex, and the $(CB_{11}H_6Cl_6)^-$ anion is oriented out of the CTV molecular cavity. This difference in host–guest behaviour can be easily accounted for by considering the M–X bond lengths involved in the $(CB_{11}H_6Cl_6)^-$-to-metal interaction. The longer Cs–X and Rb–Br interatomic distances would mean that the $(CB_{11}H_6X_6)^-$ anion would be pushed too far out of the molecular cavity to be able to form the C–H$\cdots\pi$ interaction as was seen for the Na^+ complexes.

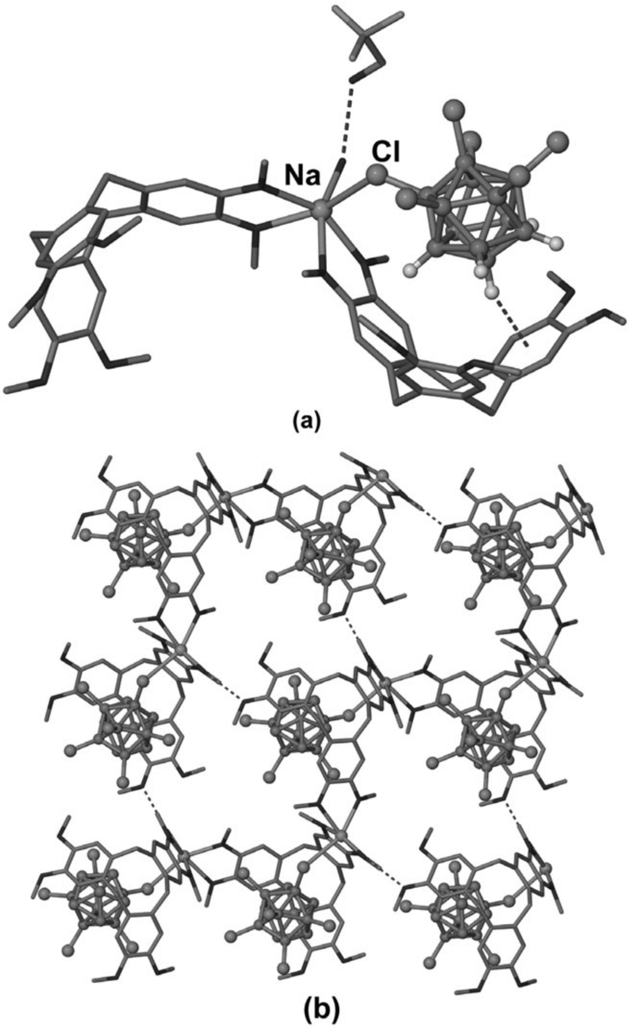


Fig. 4 Crystal structure of complex $[Na(CTV)(H_2O)(CB_{11}H_6Cl_6)]$ (CF_3CH_2OH) **8**. (a) Na coordination environment and host–guest interactions, (b) 2-D network formed by coordination chains hydrogen bonding together. Dashed lines indicate hydrogen bonds.

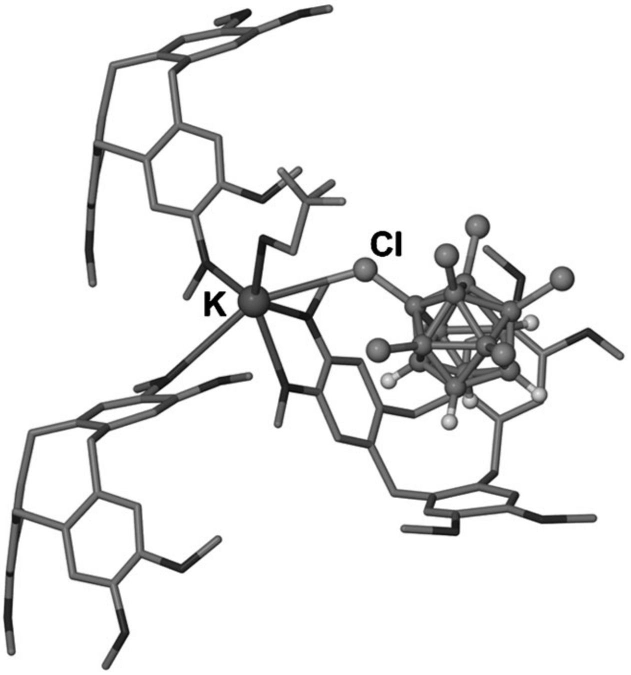


Fig. 5 Coordination sphere of K^+ in complex $[K(CTV)(CB_{11}H_6Cl_6)(CF_3CH_2OH)_{0.5}]$ **9**.

In contrast to the behaviour with the anions $(CB_{11}H_6X_6)^-$, where all the complexes isolated showed related 6^3 topology 2-D network structures, when the smaller $(CB_9H_5Br_5)^-$ anion is utilised, different structural types are isolated.[52] Complex $[Rb(CTV)(CB_9H_5Br_5)(CH_3CN)]$ **11** has a structure isomorphic with those of complex **10** and its isostructural Cs^+ and Rb^+ complexes. In **11** a 2-D coordination network with 6^3 topology is formed with both Rb^+ and CTV acting as 3-connecting nodes. The network structure is essentially the same as that of complex **10**; minor differences occur with the metal coordination sphere, where there are two crystallographically independent Rb^+ centres, one with a $(CB_9H_5Br_5)^-$ anion coordinating in a η^2 fashion and the other with η^3 coordination. Again the primary guest molecule is the coordinated CH_3CN.

The K^+ complex, $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ **12**, however, shows an unrelated $[K(CTV)_2]^+$ coordination chain structure that does not show further associations into a 2-D network.[52] The $[K(CTV)_2]^+$ coordination chain is shown in Fig. 7 and comprises eight coordinate K^+ centres, each coordinated by four chelating CTV ligands. The CTV ligands only coordinate through two of their three dimethoxy groups, leading to a chain structure. The CTV ligands also act as molecular host for trifluoroethanol guest molecules. There are two crystallographically distinct CTV ligands and they show subtly different host–guest associations. The first has the hydrophobic $–CH_2–$ group of the CF_3CH_2OH guest directed into the hydrophobic cavity of the host, as would be anticipated from the hydrophobic effect. The second has the OH group of the CF_3CH_2OH directed into the cavity forming an $O–H\cdots\pi$ hydrogen bond. This CTV also shows a rotation of one methoxy group, with a $–CH_3$ group bent out of plane, rather like the conformation found for β-phase CTV clathrates. The formation of $O–H\cdots\pi$ hydrogen bonds within a hydrophobic cavity have been reported for water guests and calixarene host molecules.[53] It is notable, however, that a recent neutron diffraction study of a water cluster within a metallo-supramolecular prism concludes that water$\cdots\pi$ interactions are through the lone pair on the O rather than the OH.[54] The coordination chains in complex **12** have a propeller-shaped cross-section and pack around the $(CB_9H_5Br_5)^-$ anions.

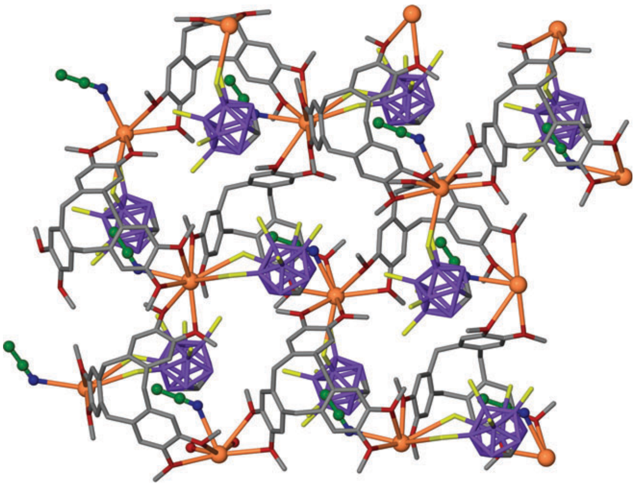


Fig. 6 The 2-D coordination network of complex $[Cs(CTV)(CB_{11}H_6Cl_6)(CH_3CN)]$ **10** with guest acetonitrile shown in green.

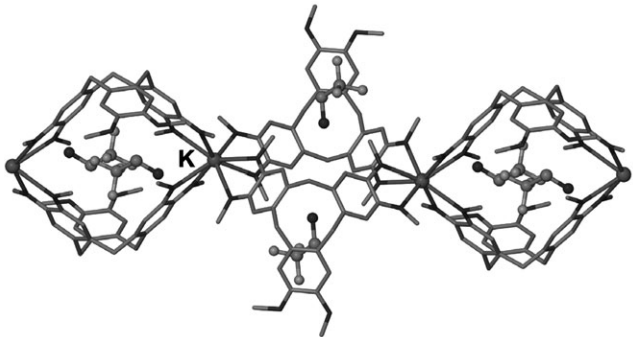


Fig. 7 1-D coordination chain and host–guest interactions in complex $[K(CTV)_2](CB_9H_5Br_5)(CF_3CH_2OH)_2$ **12**.

Solvent effects can also be important in determining the overall structure of network materials, particularly if potentially coordinating solvents are used. An example of this is $[Na_2(DMF)_4(H_2O)_2(CTV)]\{(DMF)_{0.5}(CTV)\}(CB_{11}H_6Br_6)_2$ **13** which shows unusual {Na–μ-(DMF)–Na} bridges.[50] In $[Na(CTV)(H_2O)(CB_{11}H_6Br_6)](CF_3CH_2OH)$—synthesised from the same primary molecular components as **13**—an hexagonal 2-D network structure is formed from hydrogen bonding coordination chains, as described for the $(CB_{11}H_6Cl_6)^-$ complex **8**. The change of solvent for complex **13** has a large effect on the overall structure, but the coordination network formed is again an hexagonal 6^3 network. The coordination network of **13** is based on a 2-D $[Na_2(DMF)_4(H_2O)_2(CTV)]^{2+}$ network with CTV molecules as 3-connecting nodes and a disordered $\{Na_2(DMF)_4(H_2O)_2\}^{2+}$ cluster that is an averaged 3-connecting node, Fig 8a. The $\{Na_2(DMF)_4(H_2O)_2\}^{2+}$ cluster has bridging DMF ligands, and is disordered across a mirror plane giving three Na^+ positions, each of which has one chelating CTV ligand. Each CTV chelates to three $\{Na_2(DMF)_4(H_2O)_2\}^{2+}$ clusters, forming the 2-D network, Fig. 8b. The host–guest associations in **13** are quite different to those seen in other CTV network structures. Here the molecular bowl of each CTV within the coordination network is occupied by another CTV molecule that does not participate in network formation. This CTV is a molecular host for uncomplexed DMF guest molecules, Fig. 8c. The self-stacking of CTV molecules within **13** is reminiscent of the types of self-stacking behaviour seen in simple CTV clathrates.[4]

Interestingly, the $Cs_2(C_{70}^-)_2\cdot CTV\cdot (DMF)_7(C_6H_6)_{0.75}$ complex reported by Konarev and Saito *et al.* also features DMF ligands bridging between the Group 1 metal centres, in this case within an ordered {Cs–μ-(DMF)$_3$–Cs} dimer.[10] In that structure a rather complicated arrangement is formed, with CTV and the {Cs–μ-(DMF)$_3$–Cs} acting as connecting centres.

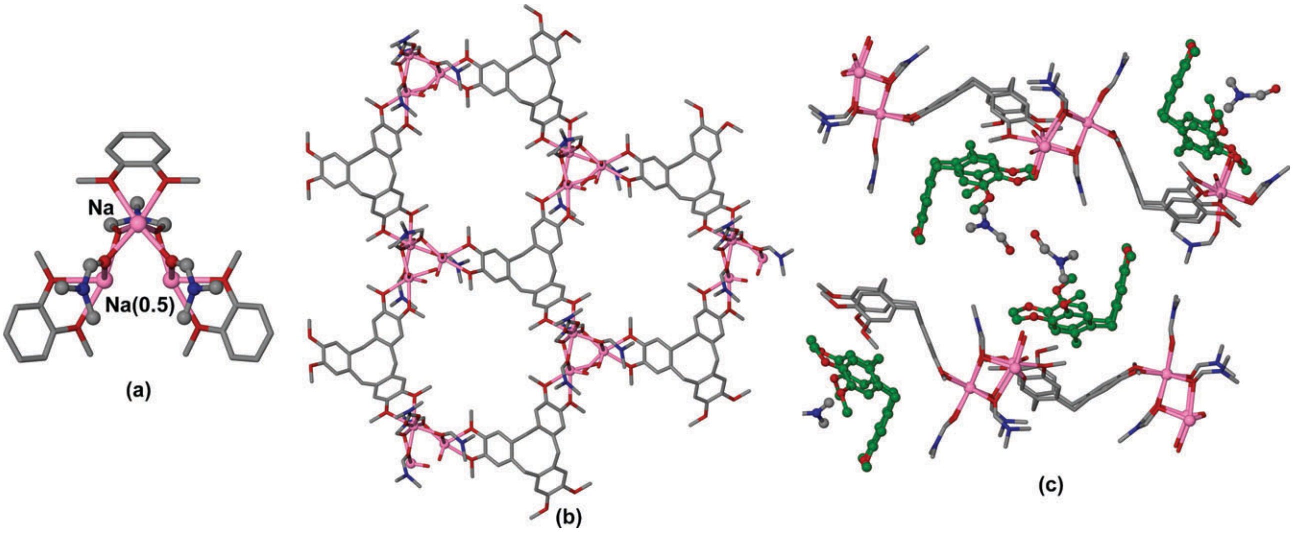


Fig. 8 Structure of complex $[Na_2(DMF)_4(H_2O)_2(CTV)]\{(DMF)_{0.5}(CTV)\}(CB_{11}H_6Br_6)_2$ **13**. (a) Disordered Na_2 core (only bridging ligands shown for clarity) with two Na positions at 0.5 occupancy. (b) Hexagonal 2-D coordination network. (c) Host–guest associations with CTV molecules not involved in the coordination networks shown in ball-and-stick representation.

There are two crystallographically independent CTV molecules, one of which binds to three {Cs–μ-$(DMF)_3$–Cs} dimers *via* the dimethoxy groups, and one which binds to only two {Cs–μ-$(DMF)_3$–Cs} dimers. Likewise there are two crystallographically unique {Cs–μ-$(DMF)_3$–Cs} dimers, with one coordinated by two CTV ligands, and the other by three CTV ligands. When analysing network topology, 2-connecting nodes are regarded as trivial, hence this structure reduces to a 3-connected network, in particular a 2-D net of highly distorted 6^3 topology.

The isonicotinoyl derived molecular host **7** also forms a coordination chain structure with metal centres, in the complex $[Ag(\mathbf{7})_2][Co(C_2B_9H_{11})_2]\cdot 9CH_3CN$ **14**.[35] Complex **14** is a further example of a 1-D coordination chain forming an overall 2-D network through additional interactions. Each ligand within **14** coordinates to a Ag(I) centre through two of its three isonicotinoyl nitrogens. The Ag(I) centres have approximately tetrahedral geometry and each is coordinated by a isonicotinoyl nitrogen from four separate ligands. A doubly bridged chain structure is formed. There are two parallel strands of ligands within this chain and, in each strand, the orientation (up or down) of the molecular cavity of the ligands alternates along the strand. This alternation is important as it allows the $[Ag(\mathbf{7})_2]^+$ coordination chains to interweave into a 2-D network through a combination host–guest associations and π-stacking, Fig. 9. Each ligand forms a head-to-head dimeric capsule with a ligand from an adjacent coordination chain. This capsule motif forms through host–guest associations with acetonitrile guest molecules, and is remarkably similar to the dimeric capsule arrangement that unmetallated ligand **7** forms with guest solvent, Fig. 3c. Furthermore, the isonicotinoyl arm of **7** that does not complex to Ag(I) in complex **14** forms π-stacking interactions with symmetry-equivalent isonicotinoyl groups from other coordination chains. These π-stacking associations do not form between adjacent $[Ag(\mathbf{7})_2]^+$ chains, but rather between every second chain within the interwoven 2-D network.

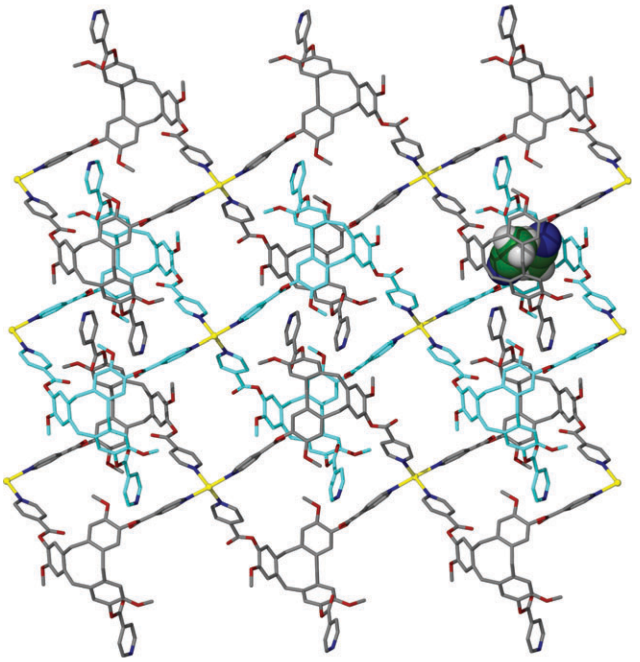


Fig. 9 Interwoven 2-D network of $[Ag(\mathbf{7})_2][Co(C_2B_9H_{11})_2]\cdot 9CH_3CN$ **14**. Three coordination chains are shown, with the host–guest associations with two CH_3CN guest molecules shown for one pair of ligands.

3-D network structures

Three-connecting tectons generally form 2-D network structures, unless combined with additional nodes of higher connectivity. The most common exception to this is the 10^3-a net which is known for a number of 3-connecting tectons.[55] Thus far, CTV and its derivatives have largely formed chain and 2-D grid structures, however three examples of 3-D network structures are also known. These 3-D structures have unusual or unique topologies based around a common structural feature: the back-to-back packing of CTV or derivatives into tetrameric clusters.

The series of complexes $[M(H_2O)_8][(CH_3CN)(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ where M = Ca, Sr, Ba are isostructural with tetragonal symmetry, and feature a complicated hydrogen bonding network.[56,57] CTV acts as a hydrogen bond acceptor and 3-connecting tecton, while the hydrogen bond donors are aquo ligands along with uncomplexed water molecules. The Sr complex $[Sr(H_2O)_8][(CH_3CN)(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **15** will be used for detailed discussion.[56] Complex **15** has an octaaquostrontium cation with triangular dodecahedral geometry. Four of the aquo ligands are hydrogen bond donors to uncomplexed water molecules, creating an expanded coordination assembly $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$. All of the O–H groups within this assembly are involved in hydrogen bonding interactions, donating to acetonitrile or to CTV molecules. The

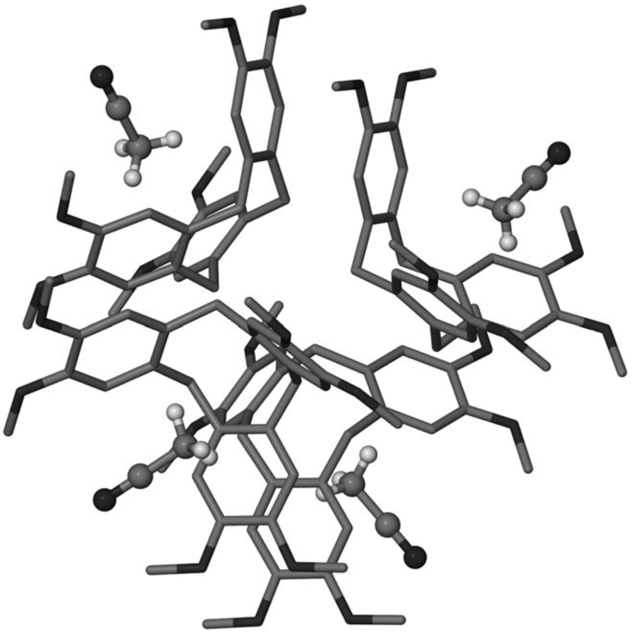


Fig. 10 Back-to-back stacking of CTV molecules found in complex $[Sr(H_2O)_8][(CH_3CN)(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ **15**. Host–guest associations with CH_3CN are also shown.

acetonitrile molecules also act as intracavity guests for the CTV hosts. Overall, the $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$ assembly hydrogen bonds to twelve CTV host molecules.

The CTV molecules exhibit back-to-back packing with four CTV molecules arranged in an approximately tetrahedral cluster with their molecular cavities oriented outwards, Fig. 10. Within this $[CTV]_4$ cluster the dimethoxy groups of each CTV pair-up in a rough alignment with those of neighbouring CTV hosts. A $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$ assembly hydrogen bonds to the dimethoxy groups of two CTV molecules at these points. The pairs of aligned dimethoxy groups occur at six positions within the $[CTV]_4$ cluster, hence each $[CTV]_4$ cluster hydrogen bonds to six $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$ assemblies, such that the Sr centres form an octahedron around the $[CTV]_4$ tetrahedron. This gives an adamantoid assembly as shown in Fig. 11a.

Each CTV molecule is a three-connecting tecton, and each $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$ assembly hydrogen bonds to twelve CTV molecules, hence a 3,12-connected 3-D network structure is generated. The network is a vertice-sharing adamantoid network with six adamantoid cages emanating from each 12-connecting node (the Sr centre), Fig. 11b. This is a unique, and rather complicated, network structure. A previous report of a coordination network with a vertice-sharing adamantoid structure had only two adamantoid cages engaged in vertice sharing.[58] A simplified view is to consider each $[CTV]_4$ tetrahedral cluster as a single octahedral connecting centre, in which case the network can be described as an α-Po type network with alternating $[CTV]_4$ cluster and Sr connecting nodes.

Isostructural complexes can also be formed with octahedral 2+ transition metal aquo complexes in place of $[Sr(H_2O)_8]^{2+}$. In these cases, the $[M(H_2O)_6]^{2+}$ (M = Fe, Ni) cations are disordered across a four-fold inversion axis, which results in eight disordered ligand positions, effectively mimicking the eight coordinate $[Sr(H_2O)_8]^{2+}$ cation, Fig. 12.[57,59]

The tri-substituted CTV derivative tris(2-pyridylmethyl) cyclotriguaiacylene forms a 3-D coordination network with Ag^+. The structure of $\{Ag_3[tris(2\text{-}pyridylmethyl)cyclotriguaiacylene]_2\}(PF_6)_3$ **16** has some marked similarities, as well as important differences, to that of **15**.[60] The structure of complex **16** is cubic and is extremely disordered with pyridyl groups disordered over two positions and Ag centres also disordered at 50% occupancy. Nevertheless, a meaningful structural analysis can be performed. The tris(2-pyridylmethyl)cyclotri-

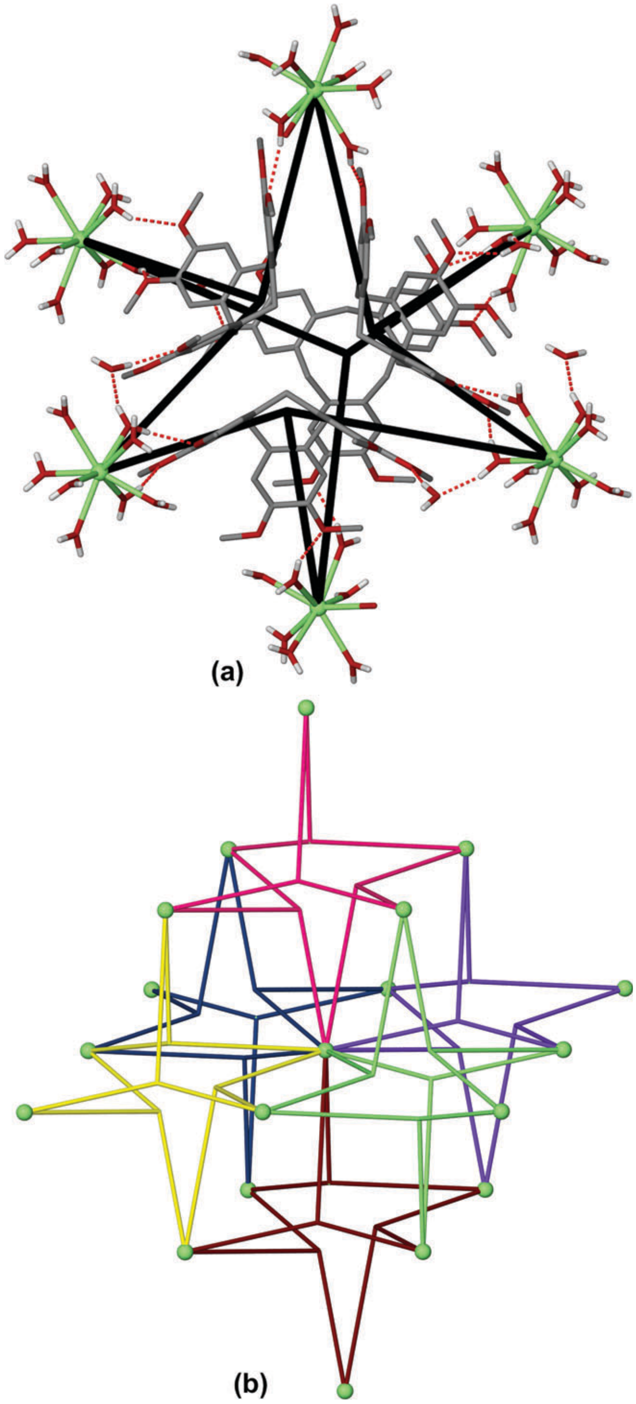


Fig. 11 3-D hydrogen bonded network of complex **15**. (a) Adamantoid unit formed by hydrogen bonding interactions between Sr and CTV centres with heavy lines indicating overall connections between these nodes. (b) Extended connectivity diagram showing six vertice-sharing adamantoid units (each shown in different colour).

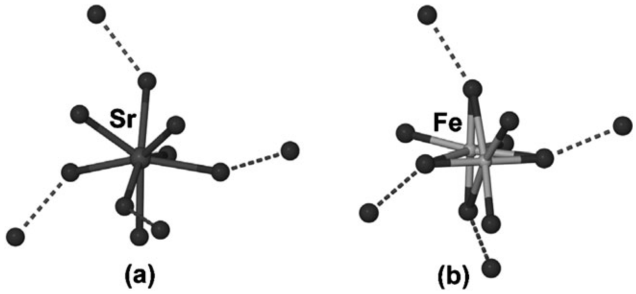


Fig. 12 (a) $\{[Sr(H_2O)_8](H_2O)_4\}^{2+}$ assembly from complex **15** compared with (b) disordered $\{[Fe(H_2O)_6](H_2O)_4\}^{2+}$ assembly from Fe-containing analogue.

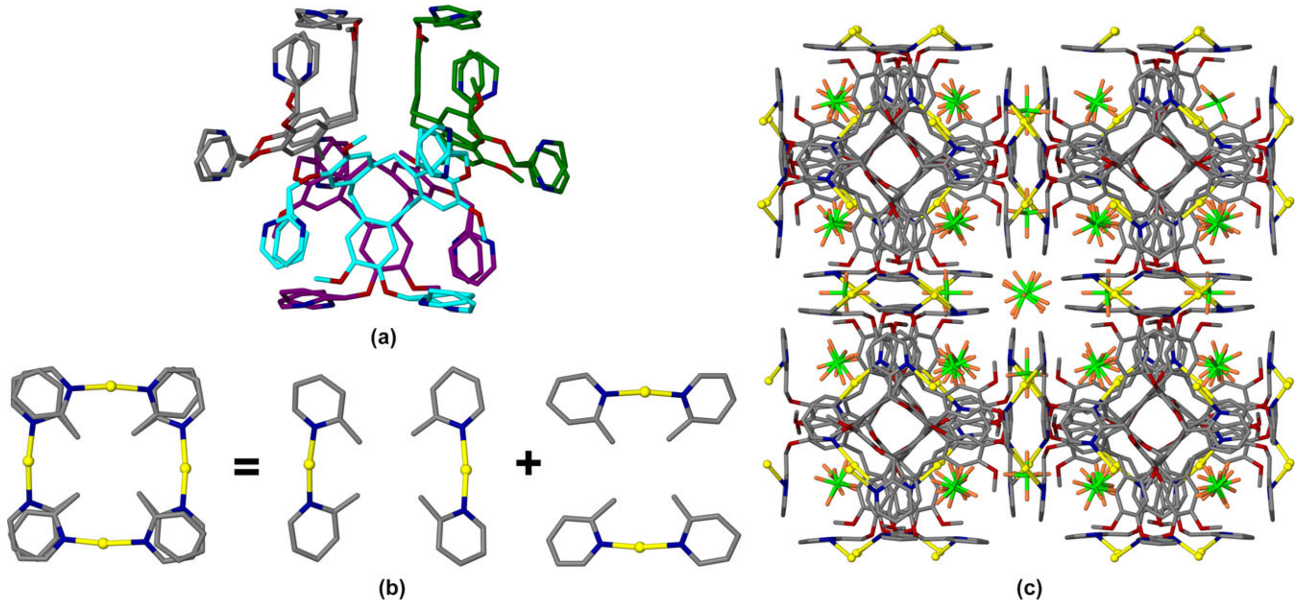

(a)
(b)
(c)

Fig. 13 Disordered structure of complex {Ag_3[tris(2-pyridylmethyl)cyclotriguaiacylene]$_2$}(PF_6)$_3$ **16**. (a) Back-to-back [**5**]$_4$ cluster with each pyridyl group disordered over two positions. (b) Ag^+ coordination environment and disorder model. The disordered "square" shown on the left is a superposition of the two ordered linear arrangements shown on the right-hand side. (c) Partial packing diagram (disordered pyridyl groups shown in single averaged position for clarity) showing 3-D coordination network and positions of disordered PF_6^- anions.

guaiacylene **5** ligands within complex **16** are arranged in a back-to-back fashion entirely analogous to the back-to-back stacking of CTV within the hydrogen bonded complex **15**. The [**5**]$_4$ clusters form a perfect tetrahedron and show π-stacking interactions between arene rings, Fig. 13a. The [**5**]$_4$ clusters are linked together by the silver cations.

Silver centres have a roughly linear coordination from pyridyl groups of different ligands. A disordered "square" of Ag and pyridyl sites is formed, though it is important to realise that disorder of the structure is such that, while there are always four pyridyl groups within this "square", only two of the four Ag positions exist in any one unit cell. The disorder model is shown in Fig. 13b. Each "square" of Ag sites links between two [**5**]$_4$ clusters, and this occurs at six positions around each [**5**]$_4$ cluster to give the disordered 3-D coordination network shown in Fig. 13c. In a distinct echo of the structure of complex **15**, if the centres of the Ag "squares" are taken, they form a perfect octahedron around the tetrahedral [**5**]$_4$ back-to-back cluster.

Complex **16** is a very disordered structure, and initial examination of it does not give an easily recognisable framework structure. The simple disorder model shown in Fig. 13b, however, allows us to disentangle the disorder provided that an assumption of genuine C_3 symmetry in the ligand is made. Then choosing one initial pyridyl position and its coordinated Ag site allows the disorder to be pulled apart, and gives a four-fold interpenetrating 10^3-a net. One such net is shown in Fig. 14. Each ligand **5** within the [**5**]$_4$ clusters is from a different interpenetrating net.

The third known 3-D network structure involving CTV or a derivative is considerably more complicated than the previous examples. The complex $[Eu(H_2O)_9]_{1.5}(CTV)_6(CH_3CN)_{5.5}(H_2O)_{7.5}[Co(C_2B_9H_{11})_2]_{4.5}$ **17** has a 3-D hydrogen bonded structure, and again features back-to-back tetrameric clusters of the molecular host.[61] As in complex **15**, a hydrogen bonded network is formed between the CTV molecules, water and complex aquo cations. The complexity of the hydrogen bonding network in complex **17** is such that considering individual CTV molecules as connecting centres gives an incomprehensible (at least to us) series of connections. Considering the tetrameric CTV clusters as a single connecting node reduces the complexity to a level which is much more easily understood.

In complex **17** there are two types of [CTV]$_4$ back-to-back clusters; one entirely analogous to that of complex **15**, and the

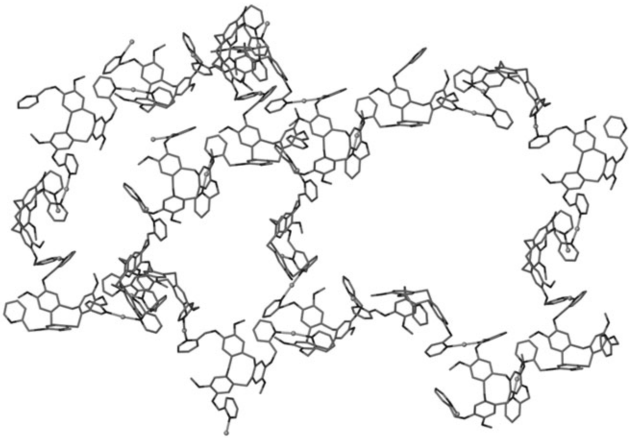


Fig. 14 Section of a disentangled 10^3-a net of complex **16**.

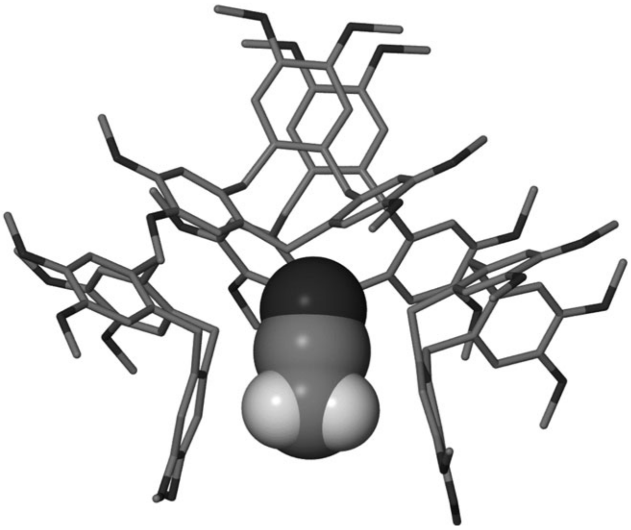


Fig. 15 Splayed $[CTV]_4 \cdot CH_3CN$ tetramer of complex $[Eu(H_2O)_9]_{1.5}(CTV)_6(CH_3CN)_{5.5}(H_2O)_{7.5}[Co(C_2B_9H_{11})_2]_{4.5}$ **17**.

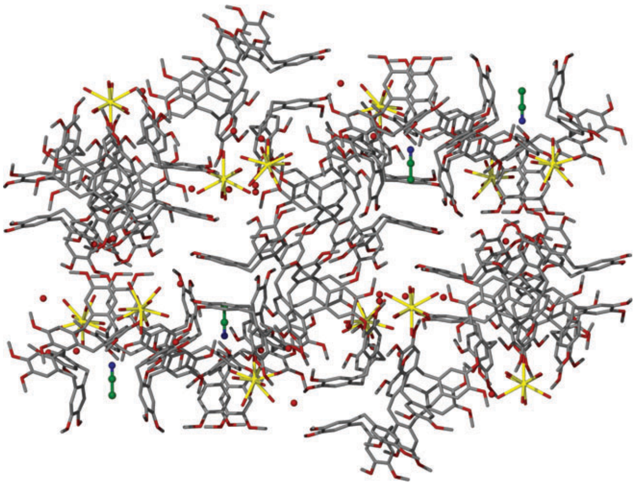


Fig. 16 Section of the 3-D hydrogen bonded network structure of complex **17** illustrating the cage-like structure.

second a $[CTV]_4 \cdot CH_3CN$ cluster that has been splayed apart by the insertion of a molecule of acetonitrile between two of the CTV molecules, Fig. 15. In the regular $[CTV]_4$ tetrahedral cluster, dimethoxy functional groups are aligned at six positions around the cluster as was seen for **15**, and this $[CTV]_4$ cluster hydrogen bonds to $[Eu(H_2O)_9]^{2+}$ and water molecules to act as a 6-connecting node. In the splayed $[CTV]_4 \cdot CH_3CN$ cluster such alignment of functional groups only occurs at five positions, and the cluster acts as a 5-connecting node, again hydrogen bonding to $[Eu(H_2O)_9]^{2+}$ and water molecules. There are two types of $[Eu(H_2O)_9]^{2+}$ complex cation, both of which hydrogen bond to four water molecules, though with different geometric arrangements. The two types of $\{[Eu(H_2O)_9](H_2O)_4\}^{3+}$ assemblies act as 5-connecting or 4-connecting nodes, hydrogen bonding to the CTV tetramers. The final type of connecting node is a disordered cluster of uncomplexed water molecules that hydrogen bonds to three CTV tetramers.

The various connecting nodes link together to form a cage-like structure shown in Fig. 16. These cages show a staggered tessellation in 3-D to form the overall network structure. Each CTV molecular cavity is occupied by an acetonitrile guest molecule, and the anions occupy spaces within the cage-like structure.

The back-to-back packing of the host molecules is a function of the rigid bowl shape of the host and has the effect of creating a pseudo-six-connecting centre. This occurs due to the aligned functional groups, which are arranged in an octahedron. Back-to-back packing of these molecular hosts gives a divergent arrangement of functional groups, ideal for infinite structures. Back-to-back packing of host molecules has also been observed for sulfonated calix[4]arenes[62,63] and a calix[4]resorcinarene.[64] In these cases infinite tubular[62,64] or large icosahedral[62] and cuboctahedral[63] assemblies have resulted.

Conclusions and outlook

The molecular host CTV can be incorporated into hydrogen bonded and coordination networks as either a 2-connecting or 3-connecting tecton. Coordination chain structures show a marked tendency to form secondary associations to give 2-D networks overall. For 2-D networks, the predominant structural type is the hexagonal 6^3 net, though other nets including centred hexagonal nets[20,21] and the 4.8^2 net[23] are also known. All known examples of CTV or derivatives that organise into 3-D network structures show a tetrameric back-to-back clustering of hosts.

Crystalline complexes tend to show both guest inclusion within the CTV molecular cavity and within the overall crystal lattice. Intracavity host–guest associations shown by these materials have included small organic guests such as acetonitrile, small anions such as PF_6^- and larger globular anions such as $(CB_{11}H_6Cl_6)^-$.

Expanding this chemistry into transition metal chemistry through use of pyridyl functionalised CTV ligands offers considerable scope for generating coordination networks with interesting structural and host–guest properties. Indeed, in the $\{Ag[tris(isonicotinoyl)cyclotriguaiacylene]_2\}^+$ coordination complex, the double stranded coordination chains interlink into a 2-D network through the host–guest associations themselves. Potential also exists with this early example of a CTV-based coordination network to probe the differences between lattice and specific intracavity association of guest molecules. If the extensive range of network structures observed with CTV can be in some way replicated with the new pyridyl derivatives and transition metals, then this area may represent a considerable source of materials with potentially useful properties such as selective guest sorption/desorption behaviour.

A recent literature report of a coordination chain based on a pyridyl-derived calix[4]resorcinarene host molecule[28] illustrates that this approach can be applied to a variety of molecular hosts, and should result in numerous novel network structures and inclusion materials in the future. It is also interesting to note that tri-substituted CTV-based cavitands are chiral. Although racemic mixtures of ligands were used in the structures described here, resolution of the chiral ligands offers scope to create chiral network materials where the bulk material, and not just individual crystals, exhibits chirality.

While the majority of the coordination networks described in the literature are formed from simple flat organic bridging ligands, we believe that a greater diversity of structure (and thereby function) can be obtained by utilising a 3-D molecule with latent host–guest behaviour. Having established that CTV and derivatives form networks displaying our required characteristics we are now in the process of manipulating the parameters of crystal engineering to achieve materials with robust characteristics and desirable and readily utilisable properties.

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