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Crystal-packing motifs of $[Ag_4L_4]^{4+}$ star-burst tetrahedra

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Received (in Montpellier, France) 3rd July 2006, Accepted 3rd August 2006
First published as an Advance Article on the web 24th August 2006
DOI: 10.1039/b609356f

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Published on 24 August 2006 on http://pubs.rsc.org | doi:10.1039/B609356F

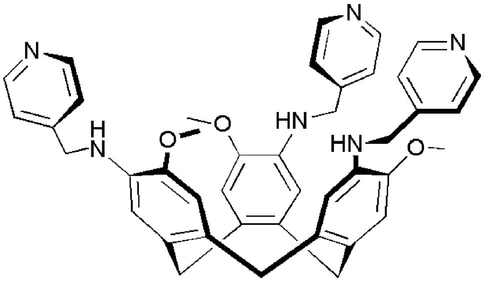
Further examples of a metallo-supramolecular ‘star-burst’ tetrahedron are reported from reaction of the ligand tris(4-pyridylmethylamino)cyclotriguaiacylene, **1**, and $AgPF_6$ in the presence of dinitrile species, or from reaction of **1** with Ag[1-Ph-*closo*-1-CB_9H_8-6-I]. Complex $[Ag_4(\mathbf{1})_4(CH_3CN)_3]\cdot4(PF_6)\cdot5(CH_3CN)\cdot(H_2O)$ has a hexagonal structure where packing of the $[Ag_4(\mathbf{1})_4]^{4+}$ tetrahedra mimics the close-packing of spheres. In complex $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}\cdot2[PhCB_9H_8I]\cdot11(CH_3CN)$ the [1-Ph-*closo*-1-CB_9H_8-6-I]$^-$ anion coordinates to the $[Ag_4(\mathbf{1})_4]^{4+}$ tetrahedron through Ag–I and Ag···H–B interactions, and a less symmetric packing motif is found. The synthesis and crystal structure of the novel monocarbaborane species (NEt_4)[1-Ph-*closo*-1-CB_9H_8-6-I] are also reported.

Introduction

The self-assembly of metallo-supramolecular assemblies with three-dimensional polyhedral structures has advanced significantly in the past decade,[1] and their use as nano-scale reaction vessels is beginning to be explored.[2] Most examples involve planar or angular ligands, but we are interested in forming such species using cavitand ligands which themselves have intrinsic properties as molecular hosts. There have been several of examples of capsule-type metallo-supramolecular structures with cavitand ligands,[3,4] but examples of higher-order assemblies remain rare. Known examples include an assembly with calixresorcinarene ligands on the vertices of a metallo-supramolecular tetrahedron,[5] and hexameric spheroidal assemblies with the formula $Ga_{12}L_6$.[6] Higher assemblies involving cavitand ligands that self-assemble through hydrogen bonding, host–guest associations and/or π–π stacking are also known.[7] Our work has focussed on ligand functionalised cavitands based on the cyclotriveratrylene host, and a number of such cavitands have been reported by ourselves and others.[4,8–10]

We have recently reported examples of the cavitand ligand tris(4-pyridylmethylamino)cyclotriguaiacylene, **1**, forming discrete $[Ag_4(\mathbf{1})_4]^{4+}$ tetrahedral metallo-supramolecular assemblies.[8,9] Each assembly consists of four Ag(I) centres at the corners of a tetrahedron, with each ligand **1** forming a face of the tetrahedron. The cavitand ligands have their molecular cavities facing into the centre of the assembly giving the tetrahedron a spiked or ‘star-burst’ appearance. A number of M_4L_4 metallo-supramolecular tetrahedral assemblies have been previously reported,[11] mainly utilising relatively flat ligands. The use of a cavitand ligand instead of an analogous planar ligand significantly increases the internal space of the star-burst tetrahedron, which then contains up to five CH_3CN guest molecules, with four forming specific host–guest interactions with the ligands, while the fifth forms (sometimes long) interactions with one of the Ag(I) centres. Either two or three of the four Ag(I) centres have externally coordinated CH_3CN ligands.

The tetrameric $[Ag_4(\mathbf{1})_4]^{4+}$ star-burst prism crystallises by vapour diffusion of ether into acetonitrile solutions of **1** and the silver salts of a number of anions, namely BF_4^-,[8] PF_6^-, and SbF_6^-, and NMR and MS studies demonstrate that it is present in solution.[9] Further to these findings, we report here a new highly symmetric $[Ag_4(\mathbf{1})_4]^{4+}$ prism structure with PF_6^- counter-anions, and also a structure with the novel monocarbaborane anion [1-Ph-*closo*-1-CB_9H_8-6-I]$^-$ **2**, and compare the crystal packing of these with known structures.



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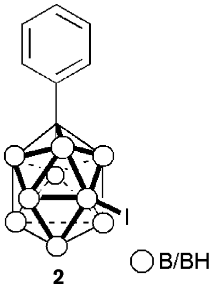

2

Closo-monocarbaborane anions possess chemical, electrochemical and thermal stability, and the anionic charge is highly delocalised, so that they have use in ‘least-coordinating-anion’ chemistry.[12] Although regarded as weakly

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coordinating, they are nevertheless known to exhibit coordinate interactions with transition metal cations, with most examples involving B–X–M interactions where X is a halogen,[13,14] or 3c–2e B–H···Ag interactions.[15,16] There are currently few examples of their use as counter-anions for metallo-supramolecular assemblies,[8,17] although more examples are known in the field of coordination networks where they can act as templating counter-anions or anionic ligands.[16,18] Examples of structurally authenticated *closo*-$[PhCB_9]^-$ iodinated cages such as **2** are rare, with only the structures of $[PhCB_9H_4I(C_6H_4Me)_4]^-$,[19] $[PhCB_9H_4I_5]^-$ and the 10-halogenated isomer of **2** having been previously reported.[20] As anions such as **2** are considerably bulkier than traditionally used anions, and also could in principle bind to Ag(I) *via* the iodo group, through Ag···phenyl interactions, or through B–H···Ag interactions, we are interested in whether their use has a significant impact on the formation of the $[Ag_4(\mathbf{1})_4]^{4+}$ tetrahedral prism and/or on the crystal-packing motifs formed. In this context we have found that a change of guest molecule does indeed have a significant impact on the formation of the $[Ag_4(\mathbf{1})_4]^{4+}$ tetrahedral prism,[9] with a coordination network being formed in the presence of glutaronitrile guest molecules as described in more detail below.

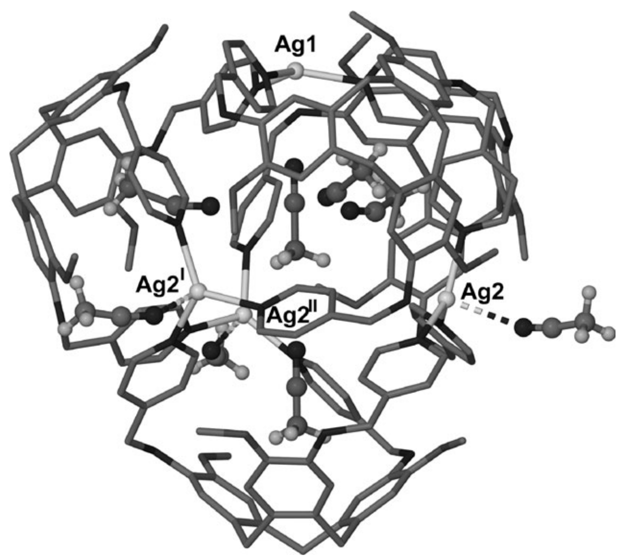

Fig. 1 Star-burst $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}\cap(CH_3CN)_5$ tetrahedron of complex **3**. Long Ag···N interaction is indicated by dashed line. Guest CH_3CN molecules are shown in ball-and-stick. Symmetry codes: I − *Y*, *X* − *Y*, *Z*; II −*X* + *Y*, −*X*, *Z*.

Results and discussion

Addition of glutaronitrile to solutions of AgX and **1** in CH_3CN, where X = PF_6^- or $[Co(C_2B_9H_{11})_2]^-$, leads to the formation of two-dimensional $[Ag\mathbf{1}]^+$ coordination networks of 4.8^2 topology rather than the discrete $[Ag_4(\mathbf{1})_4]^{4+}$ species.[9] In the $[Ag\mathbf{1}]^+$ coordination networks the glutaronitrile guest molecules occupy the molecular cavities of the cavitand ligands, which is a host–guest association that is not sterically possible within a discrete star-burst tetrahedron. These complexes form from the slow evaporation of solutions, but we report here that similar mixtures of $AgPF_6$, ligand **1** and glutaronitrile in CH_3CN that are precipitated more rapidly give the $[Ag_4(\mathbf{1})_4]^{4+}$ star-burst tetrahedra, as shown here for complex $[Ag_4(\mathbf{1})_4(CH_3CN)_3]\cdot 4(PF_6)\cdot 5(CH_3CN)\cdot(H_2O)$ **3**. Crystals of **3** were precipitated by diffusion of ether vapour into an acetonitrile solution. If left in their mother liquor the precipitated crystals of **3** eventually redissolve. This, along with ^1H NMR spectra of the initial mixture in CD_3CN being identical (plus glutaronitrile peaks) to that of the $[Ag_4(\mathbf{1})_4]^{4+}$ species in solution, supports the idea that the star-burst tetrahedron is the kinetic product of this system.

Crystals that we were able to obtain of **3** diffracted X-rays very poorly but the data collected were sufficient to establish the main features of the structure. Unlike all other known structures of $[Ag_4(\mathbf{1})_4]^{4+}$, including the previously reported PF_6^- salt, complex **3** has high symmetry, crystallising in a hexagonal space group with the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra lying on a crystallographic three-fold axis. There are two crystallographically distinct Ag(I) centres, Ag1 which lies on the three-fold axis and Ag2 which is on a general position. The $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedron is similar to those previously reported. It has Ag centres on the vertices of a tetrahedron with Ag···Ag separations 8.591 and 9.034 Å. Each ligand **1** coordinates to three Ag(I) positions and forms a face of the tetrahedron, Fig. 1. Three of the four Ag(I) positions have an externally coordinated acetonitrile ligand. This is a relatively weak interaction, with an Ag2···N distance of around 2.68 Å. This is a longer interatomic distance than seen for other reported examples where the externally coordinated CH_3CN ligands have Ag···N distances ranging from 2.390 to 2.574 Å.[8,9] There are five molecules of CH_3CN bound inside the cavity, four with hydrophobic host–guest associations to the ligands and one in a central position with the CN group directed towards Ag1 with an Ag···N distance of 3.16 Å.

Complex **3** is the most symmetrical structure containing the star-burst tetrahedron. The packing of the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra approximates to the close-packing of spheres. Each tetrahedron is closely surrounded by twelve others with distances between the centres of the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra of 19.53 within the plane viewed down the *c* axis as shown in Fig. 2a, or 19.27 and 19.32 Å to tetrahedra above and below this plane. Despite this efficient packing there is no evidence of any π–π stacking interactions between aromatic rings of the tetrahedra, and the closest ring-centroid separation between them is 4.462 Å. In the close-packing of spheres, *n* spheres create 2*n* tetrahedral interstitial sites and *n* octahedral interstitial sites. Packing of the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra in **3** are sufficiently similar to true close-packing to be able to clearly identify such sites. There are two types of tetrahedral interstitial site, of which one contains a disordered PF_6^- anion while the other contains an ordered PF_6^- anion, Fig. 2b. The octahedral sites are occupied by two PF_6^- anions that are disordered across three positions, Fig. 2c. The packing of 'close-packed' layers of $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra does not follow a simple repeat pattern, as indicated by the very long *c* unit-cell length. Instead there are six layers within the unit cell giving an ABCDEFABCDEF... stacking pattern. Notably, the

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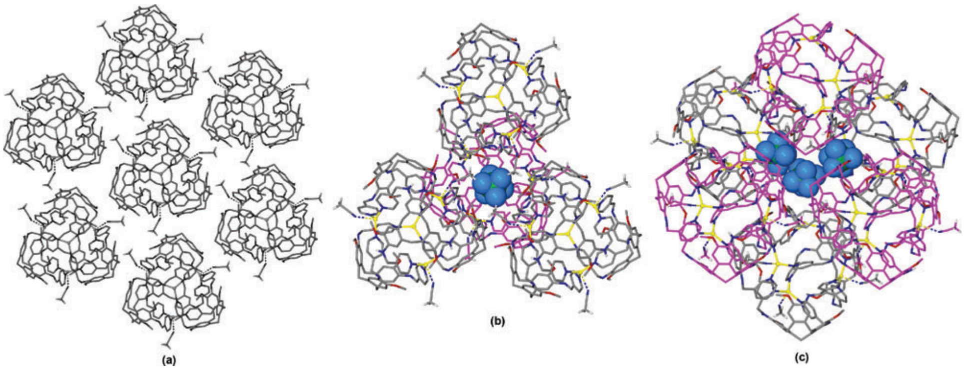

Fig. 2 Packing of $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra in complex **3**. Guest CH_3CN and water molecules are excluded for clarity and anions are shown in space filling mode. (a) Layer of 'close-packed' tetrahedra viewed down the *c* axis and three-fold symmetry axis of the tetrahedra. Packing between layers creates interstitial sites (different layers are shown in different colours); (b) one type of tetrahedral site with an ordered PF_6^- anion; (c) an octahedral site with two PF_6^- anions disordered across three positions.

$[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra pack in a polar fashion with the same orientation throughout the structure. For all $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra the vector along the three-fold axis that runs from Ag1 to the base of the tetrahedron is parallel to *c*, running in the positive *c* direction.

When $[Ag_4(\mathbf{1})_4]^{4+}$ star-burst tetrahedra were crystallised from similarly prepared solutions containing **1**, $AgPF_6$, and now the smaller dinitrile succinonitrile, an isomorphous and isostructural hexagonal structure was obtained that once again does not incorporate the dinitrile.† The crystals obtained in such crystallisations were of poor quality and rapidly lost solvent, preventing the collection of a useful full data-set. Isomorphous, but not isostructural, hexagonal structures were also obtained by vapour diffusion of ether into acetonitrile solutions of **1**, $AgBF_4$, and either glutaronitrile or succinonitrile.† No evidence for coordination networks of 4.8^2 topology incorporating the dinitriles were observed in these crystallisations.

The crystalline complex $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}\cdot 2[PhCB_9H_8I]\cdot 11(CH_3CN)$ **4** was isolated from an acetonitrile solution of $Ag[PhCB_9H_8I]$ and **1**. The anionic 6-iodinated species $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_8\text{-}6\text{-}I]^-$ **2** was obtained *via* the direct iodination of the parent anion $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_9]^-$ species using a stoichiometric amount of *N*-iodosuccinimide in CH_3CN at room temperature. It was isolated as its $[NEt_4]^+$ salt in a yield of 88%. Monitoring by NMR spectroscopy of the process suggested that a small quantity of the 10-halogenated isomer $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_8\text{-}10\text{-}I]^-$ was also present in the crude product mixture. The crystal structure of $[NEt_4]^+\cdot\mathbf{2}$ was determined in the monoclinic space group $P2_1/c$ with a pair of ions in the asymmetric unit. The asymmetric unit of the structure is shown in Fig. 3. The geometry of the CB_9 cage is unremarkable with B–B and C–B interatomic distances ranging from 1.695(4) to 1.856(4) and 1.609(4) to 1.618(4) Å respectively. The B–I distance is 2.205(3) Å. $[NEt_4]^+\cdot\mathbf{2}$ was converted to its Ag(I) salt by metathesis reaction with $AgNO_3$ *via* its conjugate acid $H\cdot\mathbf{2}$.

Complex **4** crystallises in the triclinic space group $P\bar{1}$ and the formula given above represents the asymmetric unit. Unlike other reported examples of the $[Ag_4(\mathbf{1})_4]^{4+}$ prism with two or three externally coordinated CH_3CN molecules, in **4** there is only one externally coordinated CH_3CN ligand. The mono-carbaborane counter-anions coordinate to two external vertices of the tetrahedron, giving a $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}^{2+}$ prism. Otherwise, the prism is similar to other reported examples. Each of the four Ag(I) centres in the tetrahedron has a slightly different coordination environment.

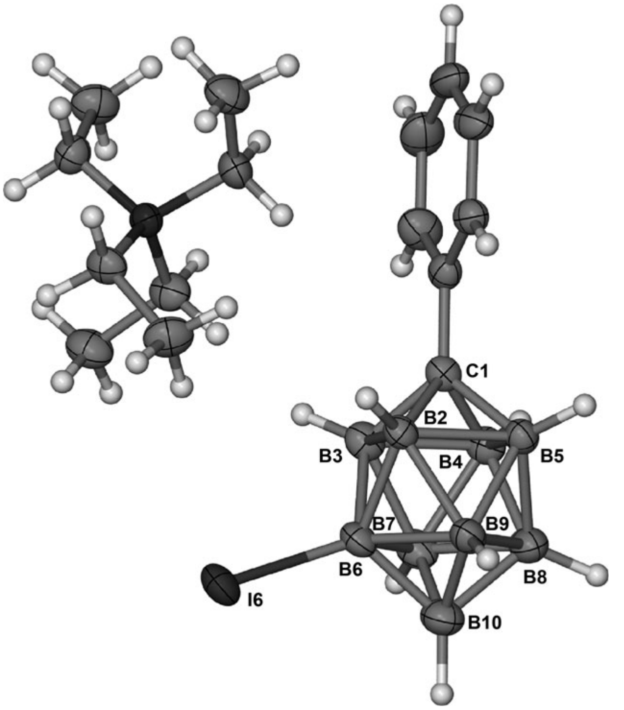

Fig. 3 Asymmetric unit of the crystal structure of $[NEt_4]^+\cdot\mathbf{2}$. Ellipsoids are shown at 50% probability levels.

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† Hexagonal unit-cell parameters from crystals obtained from the following reaction mixtures in acetonitrile with the diffusion of ether: ligand **1**, $AgPF_6$, succinonitrile: a = 19.34, c = 93.52 Å; ligand **1**, $AgBF_4$, succinonitrile: a = 18.98, c = 94.59 Å; ligand **1**, $AgBF_4$, glutaronitrile: a = 19.32, c = 77.32 Å. Crystals were not of sufficient quality to be able to obtain full data-sets.

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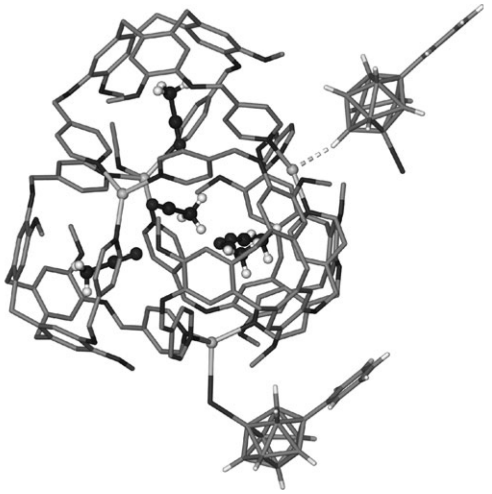

Fig. 4 $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}^{2+} \cap (CH_3CN)_4$ tetrahedra of complex **4**. Weak 3c–2e Ag···H–B interaction indicated by dashed line.

All are coordinated by three pyridyl arms from three different ligands. Two Ag(I) centres are irregular tetrahedral with terminal ligands external to the prism: either a CH_3CN ligand, or a $[PhCB_9H_8I]^-$ anion that coordinates through its iodo position at an Ag–I interatomic distance of 2.9305(9) Å. This is consistent with previously reported examples of Ag–I distances for Ag(I) complexes of iodated carbaborane anions, which range from around 2.84 to 3.34 Å.[14] The coordinated $[PhCB_9H_8I]^-$ anion is oriented such that its phenyl ring accepts an edge-to-face π-stacking interaction with a pyridyl ring of one of the ligands with a CH···$\pi_{centroid}$ distance of 2.60 Å. One of the other Ag(I) centres forms a weak Ag···H–B 3c–2e interaction to another $[PhCB_9H_8I]^-$ anion, again external to the prism, at an Ag···H–B distance of 2.332 Å, Fig. 4. This is slightly longer than other reported examples of Ag···H–B interactions with carbaborane anions that tend to be in the range of 2.0–2.2 Å.[15,16] The final Ag(I) has an irregular trigonal-planar geometry but with an additional weak coordination to a guest CH_3CN molecule located inside the prism, at Ag···N distance 2.656 Å. Outside the prism, a further $[PhCB_9H_8I]^-$ anion is located above this Ag centre but the Ag···H–B distance of 2.78 Å is too long to indicate a substantial interaction between them. As for **3** there are five full-occupancy molecules of CH_3CN inside the prism, of which one coordinates to a Ag(I) centre, while the other four form host–guest interactions with the ligands. The solution ^1H NMR spectrum of **4** in CD_3CN is consistent with previously reported examples of the ^1H NMR spectrum of the $[Ag_4(\mathbf{1})_4]^{4+}$ cation with other counter-anions, along with one set of signals from the $[PhCB_9H_8I]^-$ anion. This suggests that, under these conditions, the anions do not show a strong coordination to the tetrahedral prism in solution.

The packing of the $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}^{2+}$ tetrahedra in **4** is quite distinct from the highly symmetrical packing observed in complex **3**. As for **3**, layers can be identified where a central prism is surrounded by six others in an approximation to a close-packing layer. This layer is shown in Fig. 5a, where the distances between the centres of the tetrahedra (taken as the centre of four Ag cations) range from 18.616 to 20.148 Å. All tetrahedra within this layer are approximately coplanar. Unlike **3**, however, this close-packing motif is not maintained into a third dimension, and the three closest tetrahedra above and below the central tetrahedral prism shown in Fig. 5a are at centroid–centroid distances

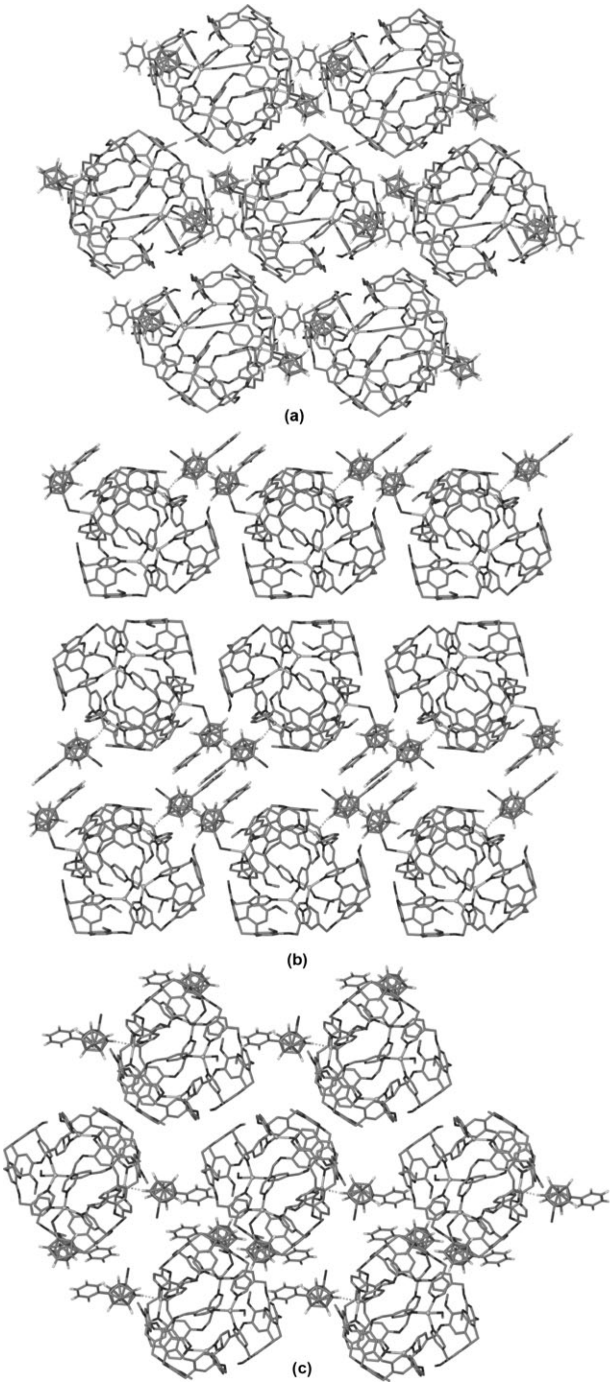

Fig. 5 Three orthogonal views of the crystal packing of $\{Ag_4(\mathbf{1})_4(CH_3CN)_2[PhCB_9H_8I]_2\}^{2+}$ prisms in complex **4**: (a) layer with a 'close-packing' arrangement of prisms; (b) open packed layer; (c) close-packed motif pushed apart by bulky anions. Hydrogen atoms are only shown on anions, and uncomplexed anions and CH_3CN molecules have been excluded for clarity.

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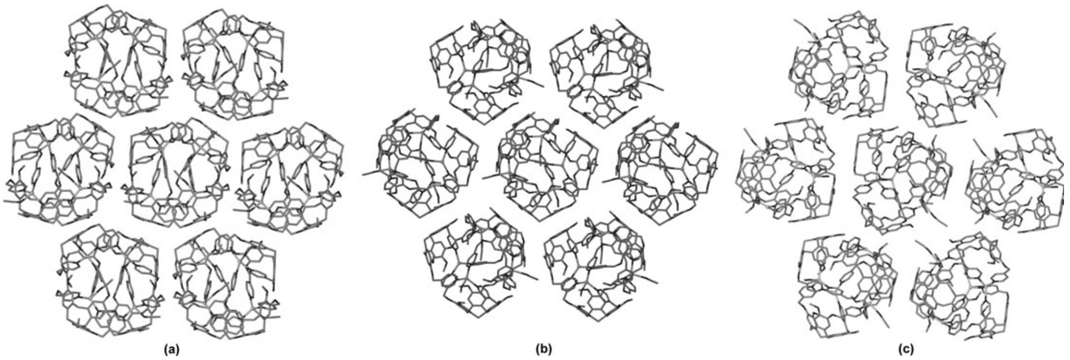

Fig. 6 Approximate close-packing motifs found in other known examples of the $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedra. (a) The BF_4^- containing complex **5** where only five of the six tetrahedral surrounding the central tetrahedral are in-plane with it. (b) A layer of the PF_6^- containing complex **6** that again is not coplanar. (c) A 'close-packed' layer of the SbF_6^- containing complex **7** that is coplanar. In this case the approximation to close-packing is found in three dimensions.

ranging from 19.116 to 31.588 Å. Orthogonal, non-close-packed layers of coplanar tetrahedral prisms can be identified, shown in Fig. 5b and 5c, where either the packing of the prisms occurs in a open fashion that creates square interstitial spaces between them (Fig. 5b) or where the tetrahedra are positioned a long way apart due to the presence of the bulky $[PhCB_9H_8I]^-$ anion (Fig. 5c). The uncoordinated $[PhCB_9H_8I]^-$ anions and additional acetonitrile molecules occupy spaces between the tetrahedral prisms, the spaces being of a type that approximates either to a three-dimensional tetrahedral interstitial site, or to a more extended cavity. One $[PhCB_9H_8I]^-$ anion shows a π–π stacking interaction through its phenyl ring with a C6 ring of the ligand **1**, at an aromatic centroid separation of 3.95 Å.

In addition to the isomorphous hexagonal structures described above with $AgPF_6$ and $AgBF_4$, three other structures of the $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedra have been previously reported, specifically complexes $[Ag_4(\mathbf{1})_4(CH_3CN)_4]\cdot4(BF_4)\cdot3(CH_3CN)\cdot2.8(H_2O)$ **5**,[8] $[Ag_4(\mathbf{1})_4(CH_3CN)_3]\cdot4(PF_6)\cdot13.5(CH_3CN)\cdot0.5(H_2O)$ **6** and $[Ag_4(\mathbf{1})_4(CH_3CN)_3]\cdot4(SbF_6)\cdot9(CH_3CN)$ **7**.[9] All three examples have an internally coordinated CH_3CN ligand, but only complex **5** has three externally coordinated CH_3CN ligands. All three complexes have layers where one $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedron is surrounded by six others in an approximation to a close-packing layer, as shown in Fig. 6. However, for both complexes **5** and **6** all the tetrahedra within these layers are not coplanar, and, as for **4**, the close-packing motif does not extend into the third dimension. Of the two complexes, **3** and **6**, that have PF_6^- counter-anions, complex **6** shows a distinct reduction in crystallographic and molecular symmetry: the three-fold axis of the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra of **3**, with three externally coordinated CH_3CN ligands, is not found in the $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedra of **6**, where there are only two externally coordinated CH_3CN ligands (and one CH_3CN internally coordinated). This reduction in symmetry of the cationic species may partially account for the less symmetric overall packing motif. Note also, that, unlike in **3**, the crystal-packing in **6** allows for multiple π–π stacking interactions between the tetrahedral prisms. The packing of $[Ag_4(\mathbf{1})_4(CH_3CN)_3]^{4+}$ tetrahedral prisms in complex **7**, on the other hand, does now approximate to the close-packing of spheres. The layer shown in Fig. 6c has all tetrahedral prisms coplanar with distances between their centres ranging from 18.69 to 20.74, and there are π–π stacking interactions at aromatic centroid separations of 3.59 Å. Tetrahedral prisms above and below this layer have similar separations, and tetrahedral and octahedral interstitial sites that contain the SbF_6^- counter-anions and solvent CH_3CN molecules can be identified between the layers.

Conclusions

Analysis of the packing modes of known $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedra shows that the tetrahedra can pack together like spheres, with good approximations to close-packing occurring for the complexes with hexagonal symmetry, and also for the SbF_6^- complex of lower symmetry. In these cases, anions occupy tetrahedral and octahedral interstitial sites typical of close-packed spheres. In other examples, a layer of close-packing of $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedra can be identified, but this does not extend into the third dimension. In the case of complex **4** with [1-Ph-*closo*-1-CB_9H_8-6-I]$^-$ counter-anions, the coordination of the bulky anions to the $[Ag_4(\mathbf{1})_4(CH_3CN)_n]^{4+}$ tetrahedra sterically hinders close-packing of the tetrahedra. Otherwise, the packing motif adopted does not appear to be related to the counter-anion, but rather to the method of crystallisation, with the highly symmetric structures crystallising from solutions that (a) also contain a dinitrile, and that (b) are precipitated by vapour diffusion of ether. That the same reaction mixture in the case of $AgPF_6$ and glutaronitrile gives the previously reported 4.8^2 coordination network under slow evaporation conditions indicates that the tetrahedra may be a kinetic product in this case, and that the tetrahedra are slowly broken up in solution by the alternative glutaronitrile guest.

Experimental

Ligand **1**[9] and Cs[1-Ph-*closo*-1-CB_9H_9][21] were prepared by previously reported methods. Infrared spectra were measured as solid-state samples on a Perkin-Elmer FTIR spectrometer. The microanalytical laboratory at the University of Leeds performed elemental analyses, typically on samples that were

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dried *in vacuo* for several hours (crystals of the 'star-burst' tetrahedra rapidly lose solvent on removal from their mother liquors and thus analyses were carried out on dried samples). ^{1}H NMR spectra were recorded on a Bruker DPX 500 spectrometer using a 5 mm probe. ^{1}H NMR spectra recorded were referenced relative to the internal standard Me_4Si, or to the residual solvent peak: acetonitrile, 2.0 ppm; acetone, 2.17 ppm. ^{11}B and ^{13}C NMR spectra were recorded on a Bruker ARX 250 MHz spectrometer, with chemical shifts $\delta(^{11}B)$ quoted ±0.5 ppm relative to $[BF_3(OEt_2)]$ and $\delta(^{13}C)$ quoted to ±0.05 ppm relative to Me_4Si.

Syntheses

$[NEt_4][PhCB_9H_8I]$ and $Ag[PhCB_9H_8I]$. Cs[1-Ph-*closo*-1-CB_9H_9] (330 mg; 1 mmol) was dissolved in CH_3CN (10 mL), and *N*-iodosuccinimide (490 mg, 1.1 mmol) was then added. The reaction mixture was stirred for 18 h at ambient temperature, and then H_2O (50 mL) and Na_2SO_3 (600 mg, 9 mmol) were added. Following removal of the CH_3CN *in vacuo*, the resulting pale yellow aqueous solution was extracted with Et_2O (3 × 50 mL), and the combined ether layers were evaporated *in vacuo* to yield a colourless oil. This oily residue was dissolved in H_2O (50 mL) and stirred. After slow addition of $[NEt_4]^+Cl^-$ (500 mg, 3 mmol) under continuous stirring, a colourless precipitate developed. This white precipitate was filtered off, and dried *in vacuo* to yield colourless $[NEt_4]^+$ [1-Ph-*closo*-1-CB_9H_8-6-I]$^{-1}$ ($[NEt_4]^+\cdot$**2**) as a white solid (400 mg, 880 μmol, 88%). NMR data in $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$(ppm) [$\delta(^{1}H)$(ppm)] are as follows: BH(10) +28.3 [+5.50], BH(4,5) −13.7 [+2.15], BH(2,3) −13.7 [+1.65], BH(7,9) −21.4 [+1.44], BH(8) −24.2 [+0.83], BI(6) −27.2; additionally $\delta(^{1}H)$(Ph) *ca.* +7.92 to +7.29 (5H, compact overlapping multiplet), and $\delta(^{1}H)$(Et) at 3.49 (8H, quartet), +1.40 (12H, triplet), also $\delta(^{13}C)$(Ph) +126.2 (1C), +127.9 (2C), +130.5 (2C) and +143.0 (1C), with $\delta(^{13}C)$ (cluster) +31.6 and $\delta(^{13}C)$(Et) +7.10 and 52.5 ppm.

Crystals of $[NEt_4]^+\cdot$**2** suitable for a single-crystal X-ray diffraction analysis were obtained from a concentrated solution in $(CH_3)_2CO$ that was overlayered with a *ca.* five-fold excess of Et_2O.

$[NEt_4]$[1-Ph-*closo*-1-CB_9H_8I] (167 mg, 510 μmol) was dissolved in a mixture of aqueous HNO_3 (5% v/v; 65 mL) and Et_2O (35 mL). After vigorous shaking the ethereal layer was separated. Two more extractions with Et_2O were performed (2 × 30 mL) and the ethereal extracts were combined. Deionised H_2O (50 mL) was added to the combined extracts, and the Et_2O was then removed *in vacuo*. The resulting aqueous solution was filtered and cooled to 0 °C. A solution of $AgNO_3$ (117 mg, 690 μmol) in distilled H_2O (5 mL) was then added to the cooled solution in the absence of light. A white precipitate formed and was immediately filtered off under reduced pressure. The resulting Ag[1-Ph-*closo*-1-CB_9H_8I] was then dried *in vacuo*, as a white powder (207 mg, 440 μmol, 86%).

$[Ag_4(1)_4(CH_3CN)_3]\cdot4(PF_6)\cdot5(CH_3CN)(H_2O)$ 3. A solution of silver hexafluorophosphate (4.1 mg, 0.016 mmol) dissolved in acetonitrile (1.5 mL) and a solution of **1** (10.0 mg, 0.015 mmol) dissolved in acetonitrile (1.5 mL) were mixed together. An excess of glutaronitrile was added to the crystallisation solution and slow vapour diffusion of ether into this solution gave colourless crystals suitable for X-ray diffraction studies. Yield 6.5 mg: 43%. ^{1}H NMR (CD_3CN, 300 K) δ 8.45 (d, 6H, pyH2/H6), 7.03 (bs, 6H, pyH3/H5), 6.28 (bs, 3H, aryl H), 6.23 (bs, 3H, aryl H), 4.52 (d, 3H, CH_2NH), 4.43 (d, 3H, Ph–CH_2–Ph), 4.31 (d, 3H, CH_2NH), 3.16 (d with broad shoulder, 12H, Ph–CH_2–Ph, OCH_3), 2.51 (t, $CH_2(CH_2CN)_2$), 1.96 (q, $CH_2(CH_2CN)_2$). Analysis (on sample dried at 80 °C *in vacuo*): calc. for $C_{168}H_{176}N_{24}O_{16}F_{24}P_4Ag_4$ (with 4 waters) C 53.11, H 4.68, N 8.85; found C 53.0, H 4.6, N 8.55%. IR (solid state, cm^{-1}) 3636, 3438, 2924, 2861, 2289 (C≡N), 2248 (C≡N), 1607, 1561, 1518, 1460, 1422, 1408, 1360, 1311, 1267, 1222, 1199, 1148, 1092, 1065, 1014, 984, 939, 925, 875, 837, 796, 741, 719, 618, 557, 477.

$\{Ag_4(1)_4(CH_3CN)[PhCB_9H_8I]_2\}\cdot2[PhCB_9H_8I]\cdot12(CH_3CN)$ 4. Solutions of $Ag[PhCB_9H_8I]$ (3.4 mg, 10.6 μmol), dissolved in acetonitrile (1 mL), and of **1** (5.4 mg, 7.95 μmol) dissolved in acetone (1 mL), were mixed together and concentrated by slow evaporation in the dark to give very small colourless crystals. Yield 4.7 mg: 53%. ^{1}H NMR (CD_3CN, 300K) δ 8.45 (d, 6H, pyH2/H6), 7.88 (d, 2H, carborane phenyl H2/H6), 7.40 (t, 2H, carborane phenyl H3/H5), 7.33 (t, 1H, carborane phenyl H4), 7.05 (bs, 6H, pyH3/H5), 6.31 (bs, 3H, aryl H), 6.24 (bs, 3H, aryl H), 4.50 (d, 3H, CH_2NH), 4.44 (d, 3H, Ph–CH_2–Ph), 4.30 (d, 3H, CH_2NH), 3.25 (bs, 9H, OCH_3), 3.18 (d, 3H, Ph–CH_2–Ph). Analysis (on sample dried at 80 °C *in vacuo*): calc. for $C_{196}H_{220}B_{36}N_{24}O_{12}Ag_4I_4$ C 53.11, H 5.01, N 7.59; found C 52.85, H 4.90, N 7.40%. IR (solid state, cm^{-1}) 3638, 3433, 2934, 2858, 2556 (B–H stretch), 1710, 1607, 1561, 1516, 1456, 1422, 1359, 1311, 1268, 1221, 1198, 1147, 1066, 1020, 984, 939, 924, 877, 849, 794, 758, 741, 716, 697, 618, 592, 519, 479.

X-Ray crystallography

Crystals were mounted on a glass fibre under oil. Data were collected at 150(1) K with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer, or on a Bruker-Nonius X8 Apex-II diffractometer with a Mo rotating anode. Data were corrected for Lorentz, polarisation and absorption effects. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97. Hydrogen atoms were included at geometrically estimated positions and refined with a riding model. All non-hydrogen atoms were refined anisotropically for $[NEt_4]^+\cdot$**2** and complex **4**.

$[NEt_4]^+\cdot$2. $C_{15}H_{33}B_9IN$, M_r = 451.61, monoclinic, $P2_1/c$, crystal size = 0.43 × 0.30 × 0.22 mm, a = 9.1510(2), b = 14.8907(3), c = 17.1566(4) Å, β = 104.5760(8)°, V = 2262.60(9) Å^3, Z = 4, ρ_{calc} = 1.326 g cm^{-3}, μ = 1.415 mm^{-1}, θ_{min} = 2.74°, θ_{max} = 26.00°, 18685 reflections collected, 4419 unique reflections, R_{int} = 0.0422, 4017 observed reflections ($I > 2\sigma(I)$), 235 parameters, 0 restraints, R_1 = 0.0313 (observed data), wR_2 = 0.0839 (all data), S = 1.058.

Complex 3. This complex was very weakly diffracting with data observed to a maximum of 38° in 2θ. Hence only Ag and P centres were refined anisotropically. A disordered PF_6^- sited on a three-fold axis was refined with its equatorial F atoms

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disordered across multiple positions, and a further PF_6^- on a general position was refined at 2/3rd occupancy. Some P–F distances and C–C, C≡N distances of CH_3CN were restrained to be chemically reasonable and a guest CH_3CN was refined with a group U_{iso} value. The structure was refined as a merohedral twin. $C_{184}H_{194}Ag_4F_{24}N_{32}O_{13}P_4$, M_r = 4073.07, hexagonal, $R3c$, crystal size = 0.10 × 0.10 × 0.03 mm, a = 19.5276(12), c = 93.940(2) Å, V = 31023(3) $Å^3$, Z = 6, ρ_{calc} = 1.308 g cm^{-3}, μ = 0.487 mm^{-1}, θ_{min} = 1.48°, θ_{max} = 18.41°, 55985 reflections collected, 5055 unique reflections, R_{int} = 0.0797, 4212 observed reflections ($I > 2\sigma(I)$, Flack parameter = 0.45(9), 336 parameters, 9 restraints, R_1 = 0.1089 (observed data), wR_2 = 0.2934 (all data), S = 1.111.

Complex 4. $C_{222}H_{259}Ag_4B_{36}I_4N_{37}O_{12}$, M_r = 4965.90, triclinic, $P\bar{1}$, crystal size = 0.35 × 0.20 × 0.18 mm, a = 20.1481(19), b = 23.478(3), c = 30.814(3) Å, α = 68.529(5), β = 73.259(4), γ = 65.528(4)°, V = 12185(2) $Å^3$, Z = 2, ρ = 1.353 g cm^{-3}, μ = 0.887 mm^{-1}, θ_{min} = 0.72°, θ_{max} = 27.39°, 248516 reflections collected, 54070 unique reflections, R_{int} = 0.0990, 30362 observed reflections ($I > 2\sigma(I)$, 2862 parameters, R_1 = 0.0944 (observed data), wR_2 = 0.3040 (all data), S = 1.088. Residual electron density peaks in the structure are located close to iodine and silver atoms (highest peak 4.120 e $Å^3$).

CCDC reference numbers CCDC 616830–616832.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609356f

Acknowledgements

We thank the EPSRC and the DTI for financial support. Additionally, we would like to thank Mr Martin Huscroft for microanalysis.

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