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Design of 3-D coordination networks: topology and metrics

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Using 4,4′,4″-tricyanotriphenylmethanol 1 as a hetero-tetradentate tecton with C_{3v} symmetry bearing three CN and one OH group, under self-assembly conditions a 3-D coordination network was obtained in the presence of Ag^+ cations acting as a tetrahedral metallic tecton; due to the metrics of 1 (three long and one short distance between the central C atom and N and O coordination sites, respectively), the 3-D network is of pseudo-diamondoid type with different cavity sizes; although a two-fold homo-interpenetration is observed for the 3-D networks, the remaining space is occupied by $CHCl_3$, MeOH solvent molecules and SbF_6^- anions.

The design of coordination networks is a subject of current interest.[1] The rational design of such molecular architectures may be achieved using the molecular tectonics approach[2a] which is based on the use of metal cations and organic ligands acting as tectons[2b] or building blocks.

Whereas the design of 1-D coordination networks is rather trivial, in particular when using bis-monodentate tectons and metal cations adopting a linear coordination geometry, this is not the case for 2- and 3-D coordination networks. In the latter case, considering a connectivity pattern centred on the metal cation, 3-D networks of diamondoid or cubic type may be formed between metal cations adopting T_d or O_h coordination geometries, respectively. In the case of diamondoid type networks, the most widely used strategy is based on linear bis-monodentate tectons connecting metal cations adopting a T_d coordination geometry (Fig. 1a). Another strategy consisting in the interconnection of tetradentate tectons with pseudo-tetrahedral disposition of the coordination sites and a metal cation adopting a linear coordination geometry has been also explored (Fig. 1b).[3] Finally, the use of organic tectons bearing four coordination sites occupying the apices of a tetrahedron and metal cations adopting T_d coordination geometry has been recently reported (Fig. 1c).[4] It is of note that for all the cases reported so far, the organic tectons contain identical coordination sites (homosite ligands) and furthermore, in terms of metrics, all sites are equidistant from the centroid of the organic backbone thus leading to identical cavities. With the perspective of using diamondoid structures as porous materials for separation or catalytic purposes, it is of interest to generate 3-D structures possessing cavities of different shape and size.

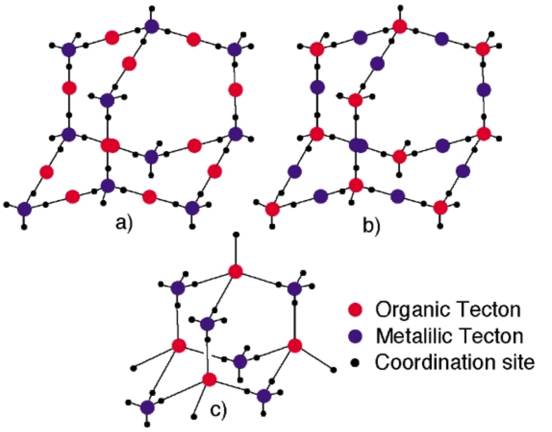

Fig. 1 Schematic representation of diamondoid 3-D coordination networks formed by: (a) linear bismonodentate tectons and metal cations adopting a T_d coordination geometry, (b) tetradentate tectons with pseudo-tetrahedral geometry and metal cations adopting a linear coordination geometry, (c) tectons bearing four coordination sites occupying the apices of a tetrahedron and metal cations adopting T_d coordination geometry.

In the context of our systematic effort to understand factors governing the formation of coordination networks,[3,5] we report here an investigation dealing with the role played by metric and topological factors in the formation of 3-D diamondoid type coordination networks.

Compound **1**, bearing three CN and one OH group as coordination sites, is an interesting hetero tetradentate tecton with C_{3v} symmetry. Furthermore, whereas a regular tetrahedral tecton leads, in the presence of a metal centre adopting T_d coordination geometry, to regular diamondoid type 3-D networks with identical cavities, tecton **1**, owing the presence of the phenylene moiety connecting the CN coordination sites to the central sp^3 carbon atom, possesses three long and one short distance and thus should lead to the formation of pseudo-diamondoid 3-D networks with different cavity sizes. Compound **1** has been used in the formation of 2-D networks using Ag^+ and coordinating anions.[6]

Tecton **1** was prepared according to published procedures[7] and its structure in the solid state was investigated by X-ray diffraction on a single-crystal† obtained from a $CHCl_3$–hexane mixture. Compound **1** crystallises in the monoclinic system, with $C2/c$ space group. The crystal is composed only of **1**. Interestingly, because of the presence of intermolecular H-bonds ($d_{O\cdots N}$ = 3.007 Å) between the OH (d_{CO} = 1.431 Å) and CN (average d_{CN} = 1.143 Å) groups, compound **1** is present as centrosymmetric H-bonded dimers (Fig. 2). Within the dimers, due to the disposition of two phenylene groups, π stacking with an aromatic–aromatic distance of *ca.* 3.57 Å is observed. Furthermore, the dimers are interconnected by π stacking with a distance of *ca.* 3.43 Å thus leading to a 1-D π stacked network.

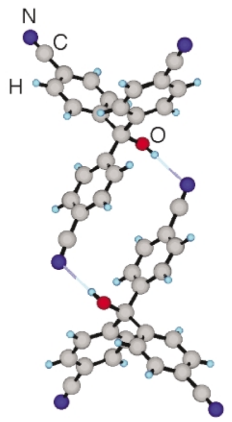

Fig. 2 A portion of the X-ray structure of the free tecton **1** showing the formation of H-bonded dimers. Selected bond distances and angles for the central sp^3 carbon atom: CCC angles 106.4–113.0°; CCO angles 105.7 and 110.8° with d_{CC} and d_{CO} distances of 1.53 and 1.43 Å, respectively.

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Fig. 3 A portion of the X-ray structure of the 3-D network formed between **1** and Ag$^+$ cation: along *b* (top) and along *a* (bottom). H atoms, anions and solvent molecules are omitted for clarity.

Upon slow diffusion of a $CHCl_3$ solution (0.75 ml) of compound **1** (4 mg) into a MeOH solution (1 ml) of $AgSbF_6$ (4 mg), colourless crystals were obtained. The X-ray diffraction† revealed the following relevant features: the crystal (monoclinic system, *C*2/*c* space group) is composed of **1**, Ag$^+$ cations, SbF_6^- anions 1 $CHCl_3$ and 4 MeOH solvent molecules. The $CHCl_3$ molecule is disordered. Upon coordination of Ag$^+$ by **1** an infinite polycationic 3-D coordination network is formed. The latter is obtained by translation of an assembling node composed of a Ag$^+$ cation bridging four consecutive tectons **1**. No specific interactions between the polycationic network and the SbF_6^- anions are observed. The coordination sphere around the Ag$^+$ cation is composed of three N atoms belonging to three CN groups of three tectons **1** ($d_{Ag–N}$ = 2.196, 2.222, 2.257 Å) and one O atom belonging to the fourth unit **1** ($d_{Ag–O}$ = 2.610 Å). The coordination geometry around the Ag$^+$ cation is a distorted T_d (NAgN angles of 107.8, 120.8, 123.7° and NAgO angles of 84.4, 96.0, 117.6°). The topology of the 3-D network is of the diamondoid type and may be described as interconnected corrugated sheets composed of Ag$^+$ cations connecting consecutive tectons **1** through Ag$^+$–N interactions (Fig. 3). The OH groups are located alternately below and above the mean plane of the sheet leading thus through coordination to Ag$^+$ cations belonging to adjacent sheets to the 3-D network. Because of the different metrics of the coordination sites, *i.e.* three long distances for the CN groups and one short distance for the OH moiety with respect to the central carbon atom of **1**, the inter-sheet interconnection distance is considerably shorter, thus affording different cavity dimensions (Fig. 3).

Although, probably in order to achieve better packing, a two-fold homo-interpenetration is observed (Fig. 4), nevertheless, the cavities generated are still large enough to include 1 $CHCl_3$ and 4 MeOH molecules.

In conclusion, we have demonstrated that by controlling the metrics of an organic tecton bearing four coordination sites, a pseudo-diamondoid type 3-D coordination network with different cavity sizes may be generated when using Ag$^+$ cation adopting T_d coordination geometry as the metallic tecton. The porous nature of the above network as well as the design along the same principles of other 3-D coordination networks are under investigation.

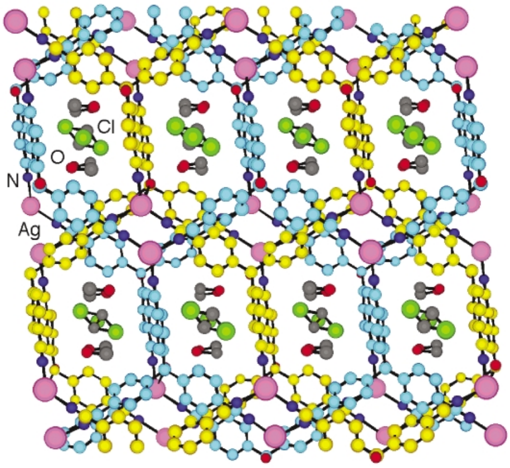

Fig. 4 A portion of the X-ray structure of two interpenetrated 3-D networks showing the inclusion of 1 $CHCl_3$ and 4 MeOH solvent molecules. The carbon atoms of the two networks are differentiated by colour. H atoms and SbF_6^- anions which are not in specific interactions with the network are omitted for clarity.

Notes and references

† *Crystal data*: for **1**: (colourless, 173 K), $C_{22}H_{13}N_3O$, M = 335.37, monoclinic, space group *C*2/*c*, a = 25.1606(7), b = 9.3019(3), c = 15.4356(7) Å, β = 91.112(5), U = 3611.9(2) Å^3, Z = 8, D_c = 1.23 g cm^{-3}, Mo-Kα, μ = 0.078 mm^{-1}, 1835 data with $I > 3\sigma(I)$, R = 0.038, R_w = 0.049. For **1**·$2AgSbF_6$: (colourless, 173 K), $C_{44}H_{26}Ag_2N_6O_2 \cdot 2SBF_6 \cdot 4CH_3OH \cdot CHCl_3$, M = 1605.51, monoclinic, space group *C*2/*c*, a = 15.2905(2) b = 15.2386(2), c = 25.6472(4) Å, β = 94.269(5), U = 5959.4(1) Å^3, Z = 4, D_c = 1.79 g cm^{-3}, μ(Mo-Kα) = 1.766 mm^{-1}, 4642 data with $I > 3\sigma(I)$, R = 0.033, R_w = 0.065; Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMolenN package.[8] CCDC reference numbers 172695 and 172696. See http://www.rsc.org/suppdata/cc/b1/b109444k/ for crystallographic data in CIF or other electronic format.

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