Design and structural analysis of interpenetrated 3-D co-ordination networks formed by self-assembly using tetrapyridinocyclophane and silver cations

Letter

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A [1,1,1,1]metacyclophane blocked in the 1,3-alternate conformation and bearing four pyridine units leads, under self-assembly conditions in the crystalline phase, to the formation of a fourfold interpenetrated 3-D co-ordination network in the presence of silver cations; the 3-D net is generated through the bridging by linearly co-ordinated silver cations of consecutive tectons presenting a pseudo-tetrahedral arrangement of four co-ordination sites.

The increased interest in the design and characterisation of molecular networks may be justified by the promise that this type of architecture offers for the design of "smart materials". However, at the present moment, researchers active in this area have not yet acquired the knowledge and understanding necessary to design such materials with predicted properties. Therefore, the exploration of design principles, so far structural in nature, is still needed and justified. Molecular networks, which may be considered as hypermolecules, are chemical architectures composed of molecular or atomic entities interconnected in a defined topology (1-, 2- or 3-D nets) through interaction patterns that define the structural nodes or assembling cores of the network. The dimensionality of the network thus results from the connectivity scheme of the assembling nodes. 3-D molecular networks are infinite assemblies presenting three translations of identical or different structural nodes in three spatial directions. Although examples of 3-D networks based on co-ordination[1,2] or hydrogen[3] bonds have been reported, the design of 3-D networks is nevertheless still a challenge.

A possible strategy for the design of 3-D co-ordination networks may be based on the use of organic tectons adopting a pseudo-tetrahedral geometry and bearing four co-ordination sites occupying the apices of the pseudo-tetrahedron and metal cations adopting a linear co-ordination geometry. The formation of infinite networks, which can only be achieved under self-assembly conditions, requires reversible co-ordination events between the metal centres and the binding sites located on the organic partner. In this respect the, silver cation appears to be a possible candidate since it forms labile complexes with pyridine-containing ligands and may adopt a linear co-ordination geometry (Fig. 1). Using a single organic tecton of the type mentioned above and a metal cation with linear co-ordination geometry as the connector, 3-D networks based on three translations of a unique structural node of the type X–M–X may be generated (the co-ordination pattern is defined by linear co-ordination of the metal centre M by co-ordination sites X belonging to consecutive tectons).

Continuing our effort to design co-ordination networks,[4,5] in the present contribution we report the design and structural characterisation of a 3-D fourfold interpenetrated co-ordination network based on the use of tecton **1** and silver cation.

The backbone for compound **1** (Scheme 1) is a [1,1,1,1] metacyclophane blocked in the 1,3-alternate conformation, thus possessing an S_4 axis of symmetry and offering the possibility of anchoring four pyridine units in an alternating fashion (two above and two below the main plane of the

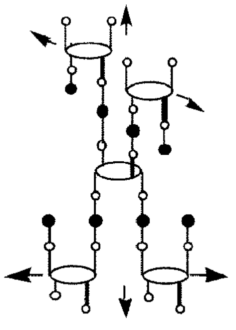
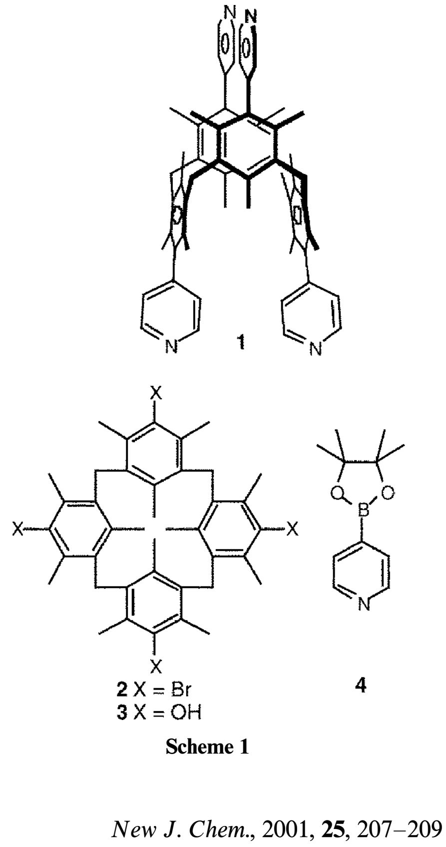


Fig. 1 Schematic representation of the 3-D network resulting from the interconnection of ligands **1** by Ag^+ cations (●) having a linear co-ordination geometry.



1

2 X = Br
3 X = OH

4

Scheme 1

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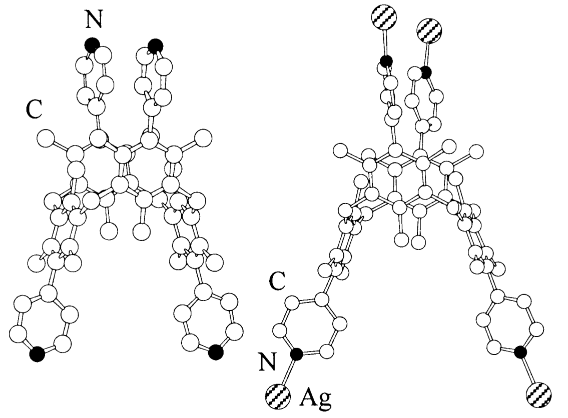

Fig. 2 X-Ray structure of the free ligand **1** (left) and a portion of the X-ray structure of the 3-D network formed between **1** and Ag^+, showing the co-ordination mode of **1** (right). H atoms, solvent molecules and anions are not represented for clarity.

cyclophane). In order to ensure the divergent orientation of the co-ordination sites, the connection of the pyridine units at the *para* position was chosen, based on CPK models. The 1,3-alternate conformation of the metacyclophane has been established in the solid state for its tetrahydoxyl **3**,[6] tetracyano[5] and tetramercapto,[7] bisbipyridine and bisquinoline[8] derivatives. A vast majority of co-ordination networks reported to date are based on 4,4′-bipyridine derivatives as bis monodentate ligands. In this respect, compound **1**, a tetrakis monodentate ligand, may also be regarded as two interconnected bis-4,4′-bipyridine units.

The synthesis of **1** was based on a Suzuki coupling reaction under basic conditions (Cs_2CO_3) in a 1 : 1 toluene–DMF mixture using $Pd(PPh)_3$ as the catalyst. Upon reaction of the cyclic tetrabromo cyclophane **2** with the boronic derivative of pyridine **4**, compound **1** was obtained in 80% yield as a white solid. Compounds **2**[5] and **4**[9] were prepared according to previously reported procedures. The 1,3-alternate conformation for both the bromo derivative **2** (structure not reported here) and the desired tetrapyridine compound **1** (Fig. 2, left) was established in the solid state by X-ray diffraction methods. The four pyridine ($d_{CN} = 1.31$–1.33 Å) units, tilted (dihedral angles of -88.0 and $-94.5°$) with respect to the aromatic rings of the cyclophane, are slightly offset with respect to the perpendicular to the main plane of the cyclophane.

Upon slow diffusion, in the dark and at room temperature, of a 2 : 1 1,2-dichlorobenzene–CH_2Cl_2 mixture containing the ligand **1** into a MeOH solution containing $AgPF_6$ in excess, a colourless crystalline material was obtained after one week. X-Ray diffraction on single crystals (tetragonal, space group $I4/c$) revealed, in addition to **1**, Ag^+ and PF_6^- anions, the presence of 10 disordered H_2O and 2 1,2-dichlorobenzene solvent molecules in the lattice. Due to the disorder of the solvent molecules, the quality of refinement was rather poor ($R = 0.134$). As predicted (Fig. 1), the cationic part of the structure composed of **1** and Ag^+ cations forms a 3-D co-ordination network of the diamond-net type through the bridging of consecutive cyclic units by Ag^+ cations. The ligand **1** adopts, as expected, the imposed 1,3-alternate conformation (Fig. 2, right). As in the case of the free ligand **1** mentioned above (Fig. 2, left), the pyridine groups ($d_{CN} = 1.31$–1.33 Å), tilted with respect to the aromatic rings of the cyclophane (dihedral angles of -74.6 and $-102.5°$), are slightly offset with respect to the perpendicular to the main plane of the backbone. The Ag^+ cation is almost linearly coordinated (N–Ag–N angle of 178.4°) to the nitrogen atoms of pyridine units ($d_{NAg} \approx 2.14$–2.17 Å) belonging to consecutive ligands. The 3-D network results from the fact that for ligand **1**, the two sets of pyridine units are located above and below the main plane of the cyclophane with a 90° angle between them, leading to an S_4 axis of symmetry. Thus, two translations in two perpendicular directions operate on the assembling nodes resulting from interconnection of ligands **1** by cationic centres with a linear co-ordination geometry. Rather interestingly, although not predicted, the cationic 3-D networks interpenetrate each other with a fourfold interpenetration pattern (Fig. 3). Furthermore, a rather short $Ag^+\cdots Ag^+$ distance of 3.08 Å between silver cations belonging to two independent and adjacent 3-D networks is observed. Thus, it appears that in the present case, the interpenetration may not only take place in order to occupy the empty space generated by individual 3-D networks,[1] but the metal-metal interactions may also play a stabilising role.

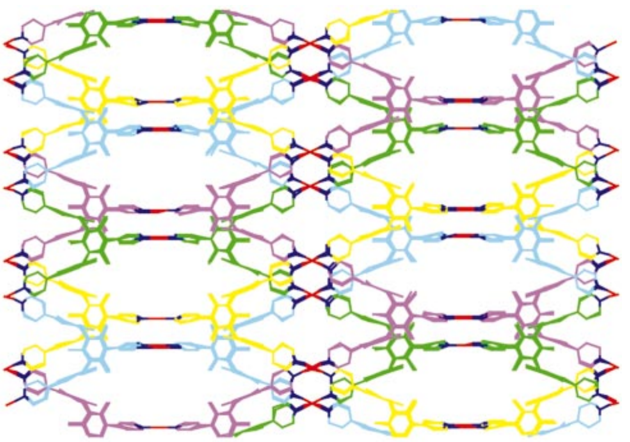

Fig. 3 A portion of the structure showing the fourfold interpenetration of the 3-D networks. and the $Ag^+\cdots Ag^+$ interaction. The four independent 3-D networks are presented in different colours for clarity. H atoms, PF_6^- anions and solvent molecules (1,2-dichlorobenzene and H_2O) are not represented for clarity.

For the PF_6^- anions, although no specific interactions can be observed with the cationic 3-D networks, some interactions of the hydrogen-bonding type between the F atoms and water molecules with one short (2.23 Å) and one rather long (2.92 Å) F–O distance are found. For the 1,2-dichlorobenzene and water molecules present in the lattice and occupying the empty space, again no specific interactions with the 3-D network are present. The presence of 1,2-dichlorobenzene, a toxic chlorinated solvent, in the lattice is of interest. Work is currently under progress to explore the possibility of using the present system for the removal of such toxic liquids.

In conclusion, employing the self-assembly strategy, the formation of a silver 3-D fourfold interpenetrated co-ordination network was observed in the solid state using the [1,1,1,1] metacyclophane backbone blocked in the 1,3-alternate conformation and bearing four pyridine units. The 3-D diamond-type net is generated through the bridging of consecutive tectons presenting a pseudo-tetrahedral arrangement by linearly co-ordinated metal centres.

Experimental

Syntheses

Ligand 1. Compound **2** (300 mg, 0.355 mmol), $Pd(PPh_3)_4$ (73 mg, 0.063 mmol) and Cs_2CO_3 (700 mg, 2.14 mmol) were added to dry and argon-degassed toluene–DMF (60 ml, 1 : 1 v/v) and the mixture was heated under argon to 100 °C. To this mixture, compound **4** (437 mg, 2.14 mmol) was added and the mixture was further heated at 130 °C for 48 h under argon. It was then allowed to cool to room temperature before it was filtered and the filtrate evaporated to dryness. The solid residue thus obtained was purified by chromatography (SiO_2, 92 : 8 CH_2Cl_2–MeOH), affording the pure compound **1** (236 mg) as colourless needles in 80% yield after crystallisation from CH_2Cl_2–Et_2O. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ 1.35 (s, 12H, *para*-CH_3), 2.07 (s, 24H, *ortho*-CH_3), 4.07 (s, 8H, Ar–CH_2–Ar), 7.09 (d, $J = 8.8$, 8H, H–Py), 8.69 (d, $J = 8.8$, 4H, H–Py), 8.72 (d, $J = 8.8$ Hz, 4H, H–Py); ^{13}C-NMR ($CDCl_3$, 50 MHz, 25 °C): δ 18.10, 19.29, 32.86, 124.99, 125.28, 130.67, 135.55, 137.90, 138.43, 150.08, 150.20, 152.08. Anal. calc. for $C_{60}H_{60}N_4 \cdot 2H_2O$: C 82.53, H 7.39, N 6.42; found: C 82.40, H 7.33, N 6.69%.

$(1 \cdot AgPF_6)_n$. In a crystallisation tube (15 cm long, 0.4 cm diameter) a mixture of 1,2-dichlorobenzene (0.5 ml) and CH_2Cl_2 (0.25 ml) containing the ligand **1** (3.0 mg, 3.6×10^{-6} mol) was slowly diffused, in the dark and at room temperature, into a MeOH (1.25 ml) solution containing excess $AgPF_6$ (3.3 mg, 1.3×10^{-5} mol) to afford a colourless crystalline material after one week.

X-Ray crystallography

Data were collected on a Nonius Kappa CCD diffractometer using Mo-Kα graphite-monochromated radiation. Absorption corrections were partially integrated in the data reduction procedure. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions. For all computations the Nonius OpenMoleN package[10] was used.

CCDC reference number 440/238. See http://www.rsc.org/suppdata/nj/b0/b008259g/ for crystallographic files in .cif format.

Crystal data for **1** (colourless, 294 K). $C_{60}H_{60}N_4$, $M = 837.17$, tetragonal, space group $P\bar{4}/c$, $a = b = 15.669(1)$, $c = 11.4392(4)$ Å, $U = 2808.6(5)$ Å^3, $Z = 2$, μ(Mo-Kα) = 0.057 mm^{-1}, 6066 reflections measured, 890 reflections having $I > 3\sigma(I)$, $R = 0.084$, $wR = 0.119$.

Crystal data for (**1**, AgPF6)$_n$ (colourless, 173 K): $C_{60}H_{60}Ag_2N_4 \cdot 2PF_6 \cdot 2C_6H_4Cl_2 \cdot 10H_2O$, $M = 908.50$, tetragonal, space group $I4/c$, $a = b = 24.4478(4)$, $c = 68.740(1)$ Å, $U = 41\,085(2)$ Å^3, $Z = 32$, μ(Mo-Kα) = 0.710 73 mm^{-1}, 23000 reflections measured, 3533 reflections having $I > 3\sigma(I)$, $R = 0.134$, $wR = 0.173$.

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