

An Unusual Three-Dimensional Coordination Network Formed by Parallel Polycatenation of Two-Fold Interpenetrated (6,3) Layers Based on a Novel Three-Connecting Ligand

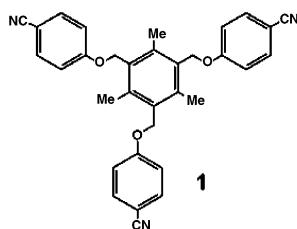
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ABSTRACT: The novel tridentate ligand 1,3,5-tris(4-cyano-phenoxy)methyl)-2,4,6-trimethylbenzene (**1**) together with silver(I) triflate has afforded the interesting coordination polymer $[\text{Ag}(\mathbf{1})(\text{CF}_3\text{SO}_3)] \cdot 0.5\text{H}_2\text{O}$, containing undulated (6,3) layers of hexagonal meshes, with alternating Ag and **1** triconnected centers, entangled into 2-fold parallelly interpenetrated sheets, which, furthermore, are polycatenated to generate an unique three-dimensional array.

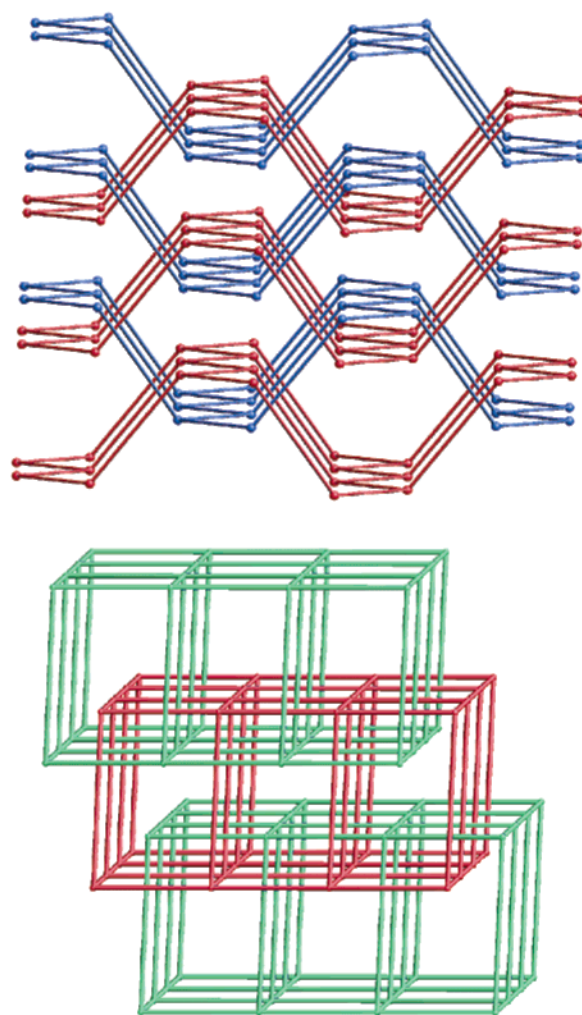
In recent years, the use of crystal engineering concepts has produced a variety of coordination networks,¹ many of which exhibit unusual and fascinating modes of entanglement of individual motifs.² There is an increasing interest in these species not only for their potential properties as functional solid materials,³ in host–guest chemistry, ion exchange, catalysis, and for the development of optical, magnetic, and electronic devices, but also for their intriguing architectures and topologies. In these investigations, a large number of molecular building blocks have been employed, suitable, at least in principle, for the assembly of desired structures. Among them, different types of tritopic ligands, with rigid or flexible backbones and variated donor functionalities, have been used together with metal centers, resulting in the formation of interesting structural motifs that include finite architectures (cages, polyhedra, etc.),⁴ extended 2D layers,⁵ and 3D networks.⁶ These ligands are useful for introducing three-connected nodes in an extended array, giving often honeycomb layers with large six-membered rings.^{4g,5a–d} For this purpose, we have prepared the novel tritopic ligand 1,3,5-tris(4-cyano-phenoxy)methyl)-2,4,6-trimethylbenzene (**1**) containing flexible sidearms with three nitriles as donor groups.



The aim of our investigation was to obtain 2D coordination polymers with (6,3) topology, possibly showing new modes of entanglements. Many layers of this type are, in fact, interlocked into *n*-fold interpenetrating sheets,² or in polycatenated (2D → 3D) systems,^{2c,7,8} or even interwoven via unusual Borromean links, as we have recently observed.⁹

The reaction of **1** with silver(I) triflate has, indeed, afforded a new 3D polymeric species, *namely*, $[\text{Ag}(\mathbf{1})(\text{CF}_3\text{SO}_3)] \cdot 0.5\text{H}_2\text{O}$ (**2**), containing (6,3) interlocked layers. It belongs to the class of “polycatenated networks”, i.e., nets having the peculiarity that the whole array has a higher

Scheme 1. Two Examples of Polycatenated Layers



dimensionality than that of each of the component motifs.^{2c,7,8} Examples of polycatenated (2D → 3D) arrays are illustrated in Scheme 1. Compound **2** shows a higher topological complexity than the species in Scheme 1 that will be described here.

The ligand **1** was obtained with standard methods¹⁰ by reacting 4-cyanophenol with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene.¹¹ The ligand flexibility allows different

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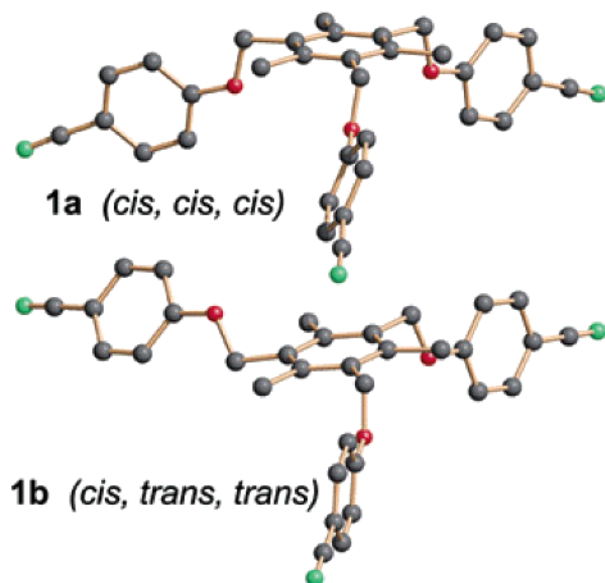


Figure 1. Molecular structures of **1a** and **1b** showing different conformations of the ligand **1** in the solid state.

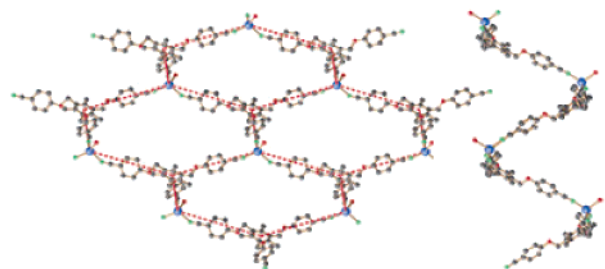


Figure 2. Front and side views of a single layer in compound **2**.

conformations that have been observed in the solid-state structures¹² of two *pseudo*-polymorphs of **1**, the free ligand (**1a**) and an ethanol solvated form **1**·0.5EtOH (**1b**), illustrated in Figure 1.

The coordination polymer **2** was obtained by reacting **1** in acetonitrile/chloroform solution with silver triflate dissolved in acetone.¹⁰ The product is obtained after many days by slow evaporation, and its formation was evidenced by the shift upon coordination of the $\nu(\text{CN})$ signal in the IR spectra.

The structure¹² of complex **2** is comprised of (6,3) layers of hexagonal meshes, with alternating three-connected Ag(I) centers and tridentate ligands in the (cis, trans, trans) conformation (like **1b** in Figure 1). The layers, with a structure of the black-P type, are highly undulated, with a thickness of ca. 13 Å, as illustrated in Figure 2.

The size of the windows can be estimated from the distances of the silver atoms from the baricenters of the benzene rings of the ligands that fall in the range 11.98–12.51 Å. The coordination around the silver centers is distorted tetrahedral with three nitrile groups of three different ligands [Ag–N 2.238(8)–2.256(8) Å] and an oxygen atom of a triflate counteranion [Ag–O 2.440(5) Å]. The bond angles around Ag are in the range 91.2(2)–117.4(3)°.

The undulated layers are associated in pairs, sharing the same average plane, to give (2D → 2D) 2-fold parallelly interpenetrated sheets of the usual type,^{2a} as shown in Figure 3. Highly undulated (6,3) layers were also obtained with similar tritopic ligands possessing flexible side-arms;^{4g,5a–c} in all previous cases, however, the layers simply exhibited deep interdigitation but were never catenated.

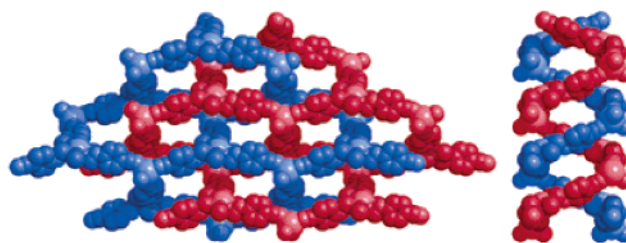


Figure 3. Two views of the parallel interpenetration of pairs of layers in **2**.

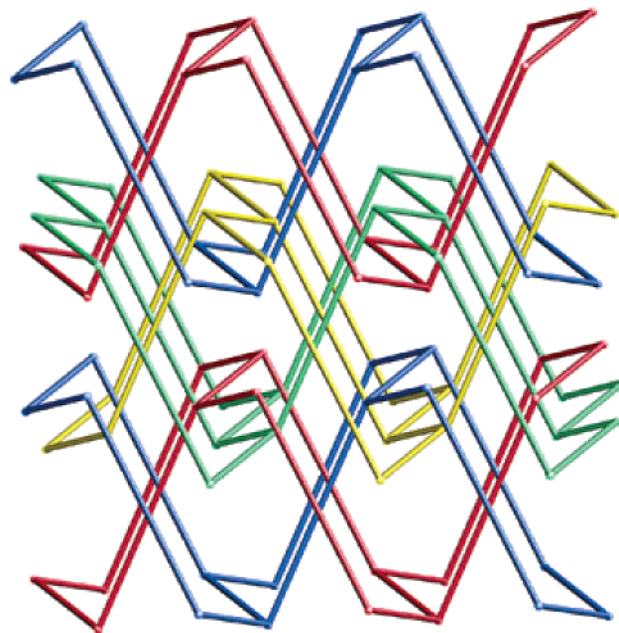


Figure 4. Schematic view of the parallel polycatenation of the 2-fold interpenetrated layers in **2**.

The unusual topological feature of complex **2** consists of the fact that the 2-fold interpenetrated sheets are further catenated to the two adjacent (“upper” and “lower”) sheets in a parallel fashion (average planes displaced by $1/2 b$, 8.5 Å in the normal direction) to give an overall unique (2D → 3D) polycatenated network. In the resulting array (schematically illustrated in Figure 4) each layer is interlocked with three others, i.e., one on the same average plane, *plus* one of the two interpenetrated “above” and one of the two interpenetrated “below” layers. An analysis of the packing does not show particular interlayer interactions that could explain the unusual polycatenation.

The type of entanglement of 2D motifs observed in complex **2** is completely unprecedented in the area of coordination polymers. The *phenomenon* of (2D → 3D) parallel polycatenation has been discovered only recently (the first example was reported in 1997).¹³ Few examples of parallelly polycatenated simple layers, both of (4,4)¹⁴ and (6,3)¹⁵ topology, are now known. We have recently shown that a species erroneously ascribed to this class, *namely*, $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$ [$\text{H}_2\text{L} = N,N$ -bis(salicylidene)-1,4-diaminobutane],¹⁶ contains, in fact, undulated (6,3) layers that are not catenated but interlocked via Borromean links.⁹ In the “normal” cases of parallel polycatenation the characterizing feature is that *all* the entangled layers show different average planes that are displaced in the perpendicular direction. The presence of interpenetrated layers (as in **2**), i.e., interlocked layers sharing the same average plane, was never observed before in these systems, but only in an exceptional organic array sustained by hydrogen

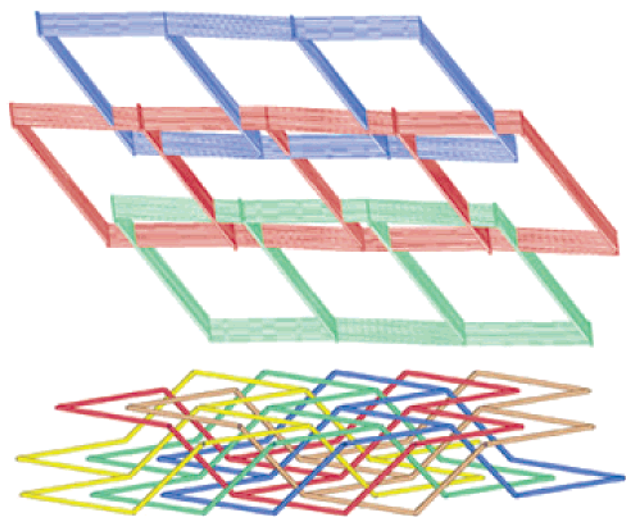


Figure 5. Schematic views of the 5-fold interpenetrated sheet (bottom) and its polycatenation (top) in the hydrogen bonded organic network reported in ref 17.

bonds and derived by the self-assembly of 1,1,1-tris(4-hydroxyphenyl)ethane and 4,4'-bipyridyl,¹⁷ forming a 2:3 adduct. This is comprised of puckered 2D nets of very large hexagonal meshes that give parallel (2D \rightarrow 2D) 5-fold interpenetrated sheets (see Figure 5, bottom). The sheets are (2D \rightarrow 3D) polycatenated into an unique 3D array (schematized in Figure 5, top). Each layer results interlinked with 10 others, i.e., four sharing the same average plane, *plus* three out of the five "above" and three out of the five "below".

The novelty represented by the simultaneous occurrence of layer interpenetration and (2D \rightarrow 3D) polycatenation phenomena can be also considered in comparison with another noteworthy species, i.e., [AgL₂](SbF₆) (L = 3-cyanophenyl 4-cyanobenzoate),¹⁸ containing (4,4) layers. These layers show 2-fold parallel interpenetration of the common type, and, furthermore, the double layers give (2D \rightarrow 3D) polycatenation in the inclined mode, rather than in the parallel one, as in **2**.

Despite the large dimensions of the windows in a single layer of **2**, the entanglement with other layers fills almost all the free voids. Only about 6.5% of the cell volume remains available inside the networks that actually is occupied by solvated water molecules.

Further investigations on the use of ligand **1** and related ligands are in progress.

Supporting Information Available: Crystallographic information files (CIF) are available free of charge on the Internet at <http://pubs.acs.org>.

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- (10) Synthesis of ligand **1**: Potassium *tert*-butoxide (1.15 g; 9.9 mmol) was added to 4-cyanophenol (1.18 g; 9.9 mmol) dissolved in *N,N*-dimethylformamide (10 mL). The resultant mixture was left to stir under nitrogen for 20 min at room temperature and the 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1.20 g; 3 mmol), prepared according to the literature method,¹¹ was added. A condenser was mounted and the mixture was heated at 120 °C for 2 h; then, it was allowed to cool to room temperature and filtered to remove the formed KBr. The mixture was diluted with ethyl acetate (150 mL) and washed with water (3 \times 80 mL). The organic layer was dried over sodium sulphate, and the solvent was removed on a rotary evaporator. The residue was chromatographed on silica with dichloromethane/methanol (9:1) as eluent, and the product was obtained as a white powder on evaporating the solvent under vacuum. Yield: 62% (0.9550 g). Recrystallization in chloroform/ethanol afforded samples containing different forms of the ligand (crystals of **1a** and **1b** were characterized by X-ray diffraction, see text). IR (Nujol mull): ν (CN) 2223 cm⁻¹. ¹H NMR (CDCl₃): δ 7.65 (d, 6H; *J* = 7.63 Hz); 7.09 (d, 6H, *J* = 7.64); 5.18 (s, 6H); 2.45 (s, 9H). ¹³C NMR (CDCl₃): δ 162.55, 140.19, 134.54, 131.53, 119.46, 115.70, 104.96, 65.63, 16.41. Anal. Calcd. for (1·CH₂CH₃OH) C₃₅H₃₃N₃O₄: C, 75.11; H, 5.94; N, 7.51. Found: C, 74.88; H, 5.70; N, 7.86. Synthesis of complex **2**: To a stirred solution of ligand **1** (0.0244 g; 0.0511 mmol) dissolved in acetonitrile/chloroform (6 mL) a solution of silver triflate (0.0206 g; 0.0766 mmol) in acetone (6 mL) was added dropwise. The mixture was stirred at room temperature for 1 h and then it was left to stand in the dark. The solvent evaporated very slowly to dryness and a powdered material was recovered, which was washed with small

portions of ethanol and dried under vacuum. Yield: 63% (0.025 g). The XRPD analysis on this bulk material confirmed its nature as almost pure complex **2**. Single crystals of **2** were obtained from layered solutions of the silver salt dissolved in ethanol over chloroform solutions of the ligand leading, on concentration to dryness, to mixtures containing also many crystals of unreacted ligand. IR (Nujol mull): $\nu(\text{CN})$ 2241 cm^{-1} . Anal. Calcd. for $\text{C}_{34}\text{H}_{27}\text{AgF}_3\text{N}_3\text{O}_6\text{S}$: C, 52.99; H, 3.53; N, 5.45. Found: C, 52.65; H, 3.70; N, 5.28.

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- (12) Crystal data for **1a**, $\text{C}_{33}\text{H}_{27}\text{N}_3\text{O}_3$: monoclinic, space group $P2_1/n$ (No. 14), $a = 16.632(4)$, $b = 10.470(2)$, $c = 17.549(4)$ Å, $\beta = 114.53(1)^\circ$, $V = 2780(1)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.227$ Mg m^{-3} , final $R1$ value 0.0906 for 1591 independent reflections [$I > 2\sigma(I)$]. Crystal data for **1b**, $\text{C}_{34}\text{H}_{30}\text{N}_3\text{O}_{3.5}$: monoclinic, space group $C2/c$ (no. 15), $a = 30.762(2)$, $b = 8.6307(5)$, $c = 25.003(1)$ Å, $\beta = 118.669(2)^\circ$, $V = 5824.5(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.224$ Mg m^{-3} , final $R1$ value 0.0600 for 3295 independent reflections [$I > 2\sigma(I)$]. Crystal data for **2**, $\text{C}_{34}\text{H}_{28}\text{AgF}_3\text{N}_3\text{O}_{6.5}\text{S}$: monoclinic, space group $P2_1/n$ (No. 14), $a = 8.739(3)$, $b = 17.023(6)$, $c = 23.119(8)$ Å, $\beta = 94.077(9)^\circ$, $V = 3431(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.5097$ Mg m^{-3} , final $R1$ value 0.0592 for 2710 independent reflections [$I > 2\sigma(I)$]. The data collections were performed at room temperature for **1a** and **2**, and at 200 K for **1b** on a Bruker SMART CCD area-detector diffractometer, using Mo-K α radiation ($\lambda = 0.71073$

Å), by the ω -scan method, within the limits $2 < \theta < 25^\circ$ for **1b**, **2** and $2 < \theta < 22^\circ$ for **1a**. Empirical absorption corrections (SADABS) were applied. The structure was solved by direct methods (SIR97) and refined by full-matrix least-squares on F^2 (SHELX-97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms but to the water molecule with half occupancy in **2** and to the disordered ethanol solvate molecule in **1b**. Due to the poor diffraction of crystals of **1a** significant data were collected only up to 22° resulting in high agreement factors. All the diagrams were generated using the SCHAKAL 97 program.

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