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The First Two-Dimensional Polycatenane: A New Type of Robust Network Obtained by Ag-Connected One-Dimensional Polycatenanes

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ABSTRACT: The two-dimensional structure described here is the first example of a coordination polymer structure consisting of one-dimensional polycatenanes fused via silver ions. It can be derived from simple rings consisting of two silver ions and two ligand molecules.

In the past decade, metal−organic frameworks (MOFs) have turned out to be a fascinating pool for structure design, synthesis, and applications in numerous fields such as catalysis, magnetism, luminescence, or gas storage.[1] By judicious choice of the building units, (i) the ligand concerning rigidity, form, and donor functions and (ii) the metal ion with its capacity to accept coordination by a given number of ligands, low-dimensional frameworks can be designed and constructed.[2] However, polymorphism and supramolecular isomerism occur more frequently the more flexible both building blocks are.[3] Porous frameworks with large empty spaces are a big challenge as interpenetration can occur.[4]

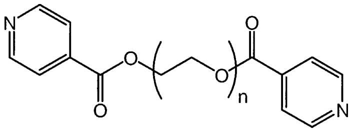
We are interested in using a flexible system with a metal ion such as Ag$^+$ and a multitopic ligand L*n* ($n = 1, 2$ ...) (Scheme 1) with N- and O-donor atoms to synthesize adaptable MOFs, which are able to link a second metal ion type. With the shorter ligand L1, $n = 1$, a number of one-dimensional (1D) structural motifs could be characterized,[5−7] whereas with L2, a zero-dimensional metallacycle with two Ag$^+$ ions and two L2 molecules, as well as a 1D helix, could be reported.[8] Whereas with this ligand type L*n* and Ag$^+$, only coordination numbers of two for Ag$^+$ with respect to the nitrogen atoms of L*n* were reported so far;[6−9] we now report a new type of network derived from the polycatenation of a 1D chain of fused metallacycles in which Ag$^+$ has a coordination number of four with respect to L2. The obtained structure is an unprecedented example of linked polycatenane chains to give a very robust two-dimensional (2D) network of high density.

Results and Discussion. The reaction of L2 with $AgClO_4$ in the ratio 1:1 yields the 2:2 metallacycle or a 1D helix as a supramolecular isomer.[8] With $AgPF_6$, exo-linked 2:2 metallacycles of the composition $[Ag(L2)]_2(PF_6)_2$·THF (**1**) (THF = tetrahydrofuran) are obtained. The ratio L2/Ag$^+$ of 2:1 yields, after a long reaction time of over two months, a very dense and highly catenated structure of composition $[Ag(L2)_2](PF_6)$ (**2**) representing a missing link in polycatenation motifs.

1 crystallizes in the triclinic space group $P\bar{1}$ (No. 2),[15] with one molecule per unit cell. Two ligands L2 adopt a U-shape and coordinate to two metal ions to yield a cyclic structure, with Ag−N distances of 2.136(4) and 2.143(4) Å, and an N1−Ag−N2 angle of 169.31(19)° (Figure 1). The two PF_6^- anions bridge two silver ions belonging to the same ring; the Ag−F bonds are weak with distances of 2.960(7) and 3.092(5) Å. Because of this arrangement, the Ag−Ag distance within the ring is rather long at 5.213(13) Å, and π-stacking within the ring is thus excluded with pyridine rings offset from each other by 5.1218 Å.

The rings in **1** are arranged parallel to each other so that weak π-stacking between adjacent pyridine rings are possible (C5−C15′ 3.511(11) Å, N1−N2′ 3.529(11) Å. The Ag−Ag contact is the shortest between two rings with a distance of 3.4591(10) Å. Taking into account the positions of the Ag atoms, they form a zigzag line with Ag−Ag−Ag angles of 124.4(1)°. The chains of rings are arranged in parallel to form sheets, between which the THF molecules are found, not coordinating to the rings in any way. Thermogravimetric and differential thermal analysis measurements show a quantitative loss of THF between 160 and 230 °C. **1** differs from the literature known ClO_4 analogue insofar as the ring in **1** has no intraring Ag−Ag contact, but an inter-ring one, the opposite of which is true in the perchlorate compound.[8] Solvent-containing structures such as **1** are usually not the thermodynamically most stable compounds, but so far the THF-free ring compound could only be generated by heating of **1** and not by crystallization from solvent. Qualitative powder spectra following the elimination of THF show peaks different from **1** and **2**, indicating a new structure (ESI[17]). However, if the mother liquor of **1** is allowed to stand for two months, new crystals can be observed, corresponding to the compound $[Ag(L2)_2](PF_6)$ (**2**).

Scheme 1. Ligand Series L*n*, *n* = 1, 2, ...



The basic motif of **2** consists of a chain of silver cations,[16] which are coordinated in a distorted tetrahedral fashion by four nitrogen atoms of four different ligand molecules (Figure 2). The Ag1−N distances are longer than in **1** and range from 2.287(3) to 2.381(3) Å, as expected for a coordination number of four for Ag$^+$.[10] The

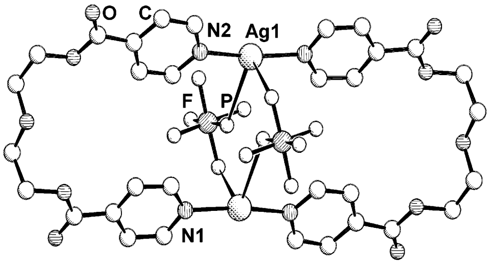


Figure 1. Molecular structure of **1**; hydrogen atoms and THF are not shown for clarity.

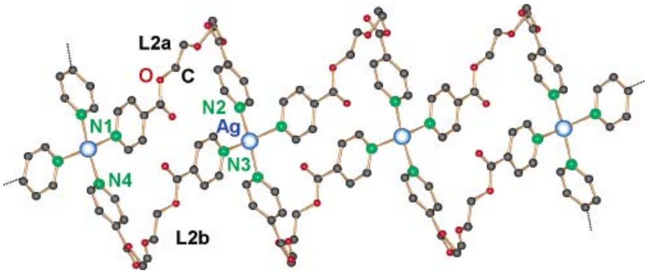


Figure 2. Simple chain motif of **2** showing the 1D structure of Ag-fused metalla-cycles; hydrogen atoms and anions are omitted for clarity.

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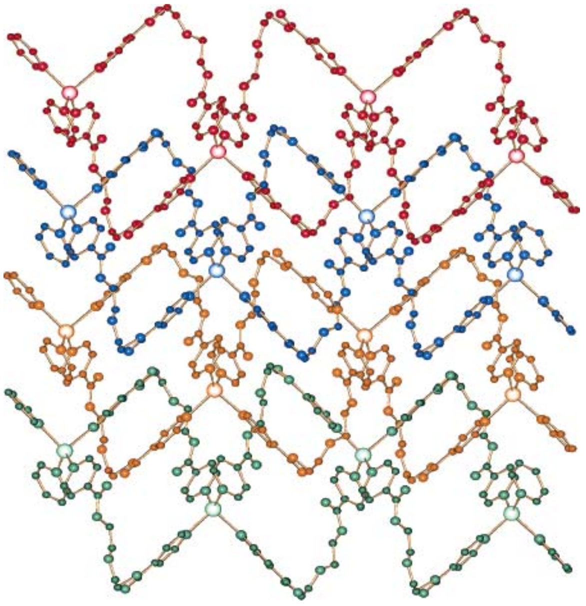

Figure 3. Interpenetration of 1D chains to yield 2D polycatenanes **2**; hydrogen atoms and anions are omitted for clarity.

N−Ag−N angles at the silver ion range from 103.53(8) to 118.2(1)°, the two larger angles being found within a metallacycle. Thus, within the chain, two silver ions are linked to each other by two ligands, L2a (labeled from N1 to N2) and L2b (from N3 to N4), forming such a ring (Figure 2). Whereas L2a possesses an all-gauche conformation with torsion angles at the ethyl groups of ca. 60°, L2b has one gauche arrangement and one ethyl group almost perfectly eclipsed with a torsion angle of only ca. 6.8° about the O8−C25−C26−O9 bonds. The so-formed $[L2Ag]_2$-metallacycle forms a cavity of the dimension of ca. 9.2 × 17.2 Å. This cavity is large enough to allow the insertion of two other ligand molecules, one from a neighbor chain below and the other from above (Figure 3). Another way to describe the topology can be to consider the structure as parallel chains of 1D polycatenates, fused via the silver cations to yield the 2D overall motif. The so-formed entangled structure yields an unprecedented structure that is vaguely reminiscent of a chain mail motif, but with linked rings instead of separated ones, extending in a 2D array.

Organic- and metal-mediated synthesis of organic and metal-containing catenanes and more complicated knots has been well-established now;[11] however, coordination catenanes are rarer. Quantitative self-assembly of a coordination [2]catenane has been described by Fujita with Pd^{2+} and Pt^{2+},[12] showing that simple rings and [2]catenane are in equilibrium, which can be influenced by the concentration of the participating species. The mechanism to obtain such a [2]catenane is proposed as a reversible ring formation and reopening processes during which interpenetration can occur. Whereas this process was shown to be rapid, the formation of the polycatenane **2** seems to be a more complicated, slower process since the only product first observed is **1**, while **2** forms only after a long period with L2 in excess. Indeed, entropically, a high order has to be established in **2**, leading to a very dense structure with only 0.8% of free space, as compared to 10% in **1** (without THF). Fujita showed also that one or the other species of his compounds can be obtained in high yield depending on the polarity of solvent. This can also be applied to our system, since crystals of **1** were obtained in more aqueous medium, while **2** crystallized from the compartment containing a high concentration of THF or ethanol. Another example to be mentioned in this context is the system observed by Puddephatt et al. where a U-shaped diacetylide (L) forms rings with two gold ions of the type $[LAu_2(dppe)]$ (dppe = diphenylphosphine ethane), which can entangle or not. Au−Au contacts can lead to a 1D chain of the simple rings without catenation.[13]

Polycatenation has been observed in coordination polymer networks, however, not with the topology observed in **2**, and usually involving larger ring species, such as (4,4) or (6,3) nets.[14] Here, **2** is the parallel catenation of ribbons of rings.

In summary, we have synthesized the first chain mail topology of a coordination compound via polycatenation of 1D chains of $[Ag_2(L2)_2]$-rings connected by Ag^+-nodes.

Experimental Section. Synthesis of 1. In an H-tube, 4 mg (0.015 mmol) of $AgPF_6$ dissolved in 4 mL of water were allowed to diffuse through 25 mL of THF to an organic solution of 4 mL of THF or EtOH containing 5 mg (0.015 mmol) of L2. Single crystals of **1** suitable for single-crystal X-ray analysis were obtained growing on the wall of the glass recipient in a yield of 46% with respect to Ag^+. Higher concentrations of reactants cause precipitation instead of crystallization.

Elemental Analysis. Calculated for **1**, $[AgC_{16}H_{16}N_2O_5]PF_6{\cdot}THF$: C 37.5, H 3.8, N 4.4; found: C 37.1, H 3.7, N 4.3%.

IR (KBr, cm^{-1}). ν(Ar−H) 3061.8 s, ν(−HC−H) 2947.9 s, ν(C=O) 1733.4 s, ν (C=C) 1602.7 m, ν (ArC−C, C=N) 1411.8 m, ν (CO−O) 1272.7 s, ν (−C−O) 1108.6 m, δ(ArC−H) 1056.6 m, ν (PF_6) 822.1 s, broad

Melting Point. 242 °C (decomposition)

Synthesis of 2. Following the same procedure as for **1**, but using ethanol as linking solvent between the two solutions containing the ligand and the silver salt, afforded rodlike crystals of **2** in the bottom of the salt-containing part of the H-tube and crystals of **1** growing on the walls. Another way to crystallize **2** purely was achieved after 2 days of slow evaporation from a solution in which the ligand and the silver salt were mixed together in acetone. Yield: 20% with respect to Ag^+.

Elemental Analysis. Calculated: C 43.4, H 3.6, N 6.3%; found: C 43.6, H 3.8, N 6.2%.

IR (cm^{-1}). ν(Ar−H) 3105.4 s, ν(−HC−H) 2922.8 s, ν(C=O) 1733.4 s, ν (C=C) 1602.7 m, ν (ArC−C, C=N) 1411.8 m, ν (C−O) 1282.8 s, δ(ArC−H) 1056.6 m, ν (PF_6) 822.1 s, broad.

Melting Point. 130 °C (decomposition).

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(15) Crystallographic data for **1**: AgC$_{20}$H$_{24}$N$_2$O$_6$PF$_6$, $M = 641.25$ g mol^{-1}, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.701(1)$, $b = 12.961(3)$, $c = 13.021(3)$ Å, $\alpha = 94.55(3)$, $\beta = 95.85(3)$, $\gamma = 107.23(3)°$, $V = 1226.7(4)$ Å^3, $Z = 2$, $T = 240(2)$ K, $\rho = 1.736$ Mg m^{-3}, μ(Mo Kα) $= 0.971$ mm^{-1}, $F(000) = 644$, 4984 reflections of which 4984 unique and 4984 observed, 325 parameters refined, GOF $= 0.931$, R1 $= 0.0602$, wR2 $= 0.1342$ for $I > 2\sigma(I)$ and R1 $= 0.1157$, wR2 $= 0.1584$ for all data.

(16) Crystallographic data for **2**: AgC$_{32}$H$_{32}$N$_4$O$_{10}$PF$_6$, $M = 885.46$ g mol^{-1}, orthorhombic, space group *Pbcn* (No. 60), $a = 28.388(8)$, $b = 15.020(1)$, $c = 17.059(6)$ Å, $V = 7274(3)$ Å^3, $Z = 8$, $T = 153(2)$ K, $\rho = 1.617$ Mg m^{-3}, μ(Mo Kα) $= 0.690$ mm^{-1}, $F(000) = 3584$, 56 024 reflections of which 21 906 unique and 4391 observed, 488 parameters refined, GOF $= 1.032$, R1 $= 0.0698$, wR2 $= 0.1840$ for $I > 2\sigma(I)$ and R1 $= 0.0971$, wR2 $= 0.2075$ for all data.

(17) The single crystals of **1** and **2** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoKα radiation, at 240 K (1) and 153 K (2). The structures were solved with direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-295448 (1) and CCDC-295449 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).