

Complex Interwoven Polymeric Frames from the Self-Assembly of Silver(I) Cations and Sebaconitrile

Lucia Carlucci, Gianfranco Ciani,* Piero Macchi, Davide M. Proserpio, and Silvia Rizzato^[a]

Abstract: Interesting interwoven polymeric frames have been obtained from the self-assembly of the flexible long-chain bidentate sebaconitrile (sebn, 1,10-decanedinitrile) and different silver salts. Out of the eight products isolated and characterized, six present a metal-to-ligand ratio of 1:2 and contain interpenetrated three-dimensional (3D) or two-dimensional (2D) structural motifs, that is [Ag(sebn)₂](BF₄) (**1**), [Ag(sebn)₂](ClO₄) (**2**), [Ag(sebn)₂](PF₆) (**3**), [Ag-

(sebn)₂](SbF₆) (**4**), [Ag(sebn)₂](AsF₆) (**5b**) and [Ag(sebn)₂](CF₃SO₃) (**6b**). The remaining two derivatives, [Ag(sebn)](AsF₆) (**5a**) and [Ag(sebn)](CF₃SO₃) (**6a**), present one-dimensional (1D) polymeric chains. Depending on the counterions and on the conforma-

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tion of the ligands, different frameworks are obtained. These include the eightfold interpenetrated diamondoid frame of **1** and **2**, the fourfold interwoven 3D four-connected frame topologically related to the prototypical SrAl₂ of **3** and **5b**, and the first example of an infinitely catenated 2D multiple layer in **4** and **6b**. A unique example of self-organization of 1D chains, propagating in three directions to form a 3D entangled array, is observed in **5a**.

Introduction

Metal-based supramolecular self-assembly^[1] has produced in recent times both fascinating molecular devices, such as rotaxanes, catenanes, knots, and helicates,^[2,3] and interesting 2D and 3D networks.^[4,5] Flexible ligands are typical building elements of the former species, while in the second class of compounds essentially rigid rodlike organic units are usually employed to connect the metal center. However, long flexible-chain bidentate ligands have shown the ability to produce unique interwoven extended structural motifs, such as polycatenanes,^[6] polyrotaxanes,^[7] double helices,^[8] and other uncommon species.^[9]

One of the first examples of diamondoid coordination networks (sixfold interpenetrated), reported many years ago, was based on Cu^I ions and the flexible bidentate adiponitrile ligand.^[10] Since then few studies on polymeric coordination compounds assembled with aliphatic dinitriles have been described, all containing NC(CH₂)_nCN ligands with $n \leq 4$ but one, the 2D polymer [Cu{NC(CH₂)₁₀CN}₃](SbCl₆)₂.^[11] In the

course of a systematic investigation on the reactions of long-chain dinitriles with silver cations we have obtained particularly interesting polymers with 1,10-decanedinitrile (sebaconitrile, sebn). The aim of these studies was essentially to ascertain the networking ability of the flexible sebaconitrile, which can assume a variety of conformations, and the preferred topologies of the self-assembled frames on changing the counterions, in order to obtain information at the basic structural level, which should be of interest for the crystal engineering of novel coordination networks and devices.

We describe here the products obtained on reacting sebaconitrile with the salts AgBF₄, AgClO₄, AgPF₆, AgAsF₆, AgSbF₆, and Ag(CF₃SO₃), which include remarkable polymeric motifs and unprecedented examples of interwoven networks.

Results and Discussion

All the derivatives were obtained by slow evaporation of ethanolic solutions of sebn and the appropriate Ag^I salt in molar ratios of 1:1 or 2:1. The solutions, left to concentrate in the dark for some days, gave in all cases colorless crystals of the adducts, which were characterized by single-crystal X-ray analyses. The reactions with AgBF₄, AgClO₄, AgPF₆, and AgSbF₆ led in each case to one product, of stoichiometry [Ag(sebn)₂]X, also using a 1:1 reagent ratio, that is

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[Ag(sebn)₂](BF₄) (**1**), [Ag(sebn)₂](ClO₄) (**2**), [Ag(sebn)₂](PF₆) (**3**), and [Ag(sebn)₂](SbF₆) (**4**).

On the other hand, with AgAsF₆ and Ag(CF₃SO₃) the equimolar reactions gave the [Ag(sebn)](AsF₆) (**5a**) and [Ag(sebn)](CF₃SO₃) (**6a**) derivatives, respectively, and only on using a twofold excess of the sebn ligand the [Ag(sebn)₂]X species were isolated, that is [Ag(sebn)₂](AsF₆) (**5b**) and [Ag(sebn)₂](CF₃SO₃) (**6b**).

All the products are air stable for long times. They dissolve in the common organic solvents and are poorly thermal resistant because of their low melting points. Nevertheless they are interesting model compounds in coordination polymer chemistry, due to the variety and novelty of their structural motifs.

The [Ag(sebn)₂]X derivatives belong to three classes: interpenetrated diamondoids (compounds **1** and **2**), interpenetrated four-connected 3D networks topologically related to SrAl₂ (compounds **3** and **5b**), and infinitely catenated 2D layered frames (compounds **4** and **6b**). The [Ag(sebn)]X species form 1D polymeric chains with different spatial self-organization (compounds **5a** and **6a**).

Interpenetrated diamondoid nets: Compounds **1** and **2** are isomorphous and their structures consist of diamondoid cationic frameworks, containing large adamantanoid cages (Ag...Ag separations of 17.79 and 15.17 Å in **1** and 17.78 and 15.30 Å in **2**). A single cage is illustrated in Figure 1 (left) for **1**. Eight independent equivalent networks are interpenetrated within the crystals (eightfold diamondoids), and are related by a translation vector corresponding to the crystallographic *b* axis (5.703(1) Å in **1** and 5.780(2) Å in **2**) (Figure 1 right). The

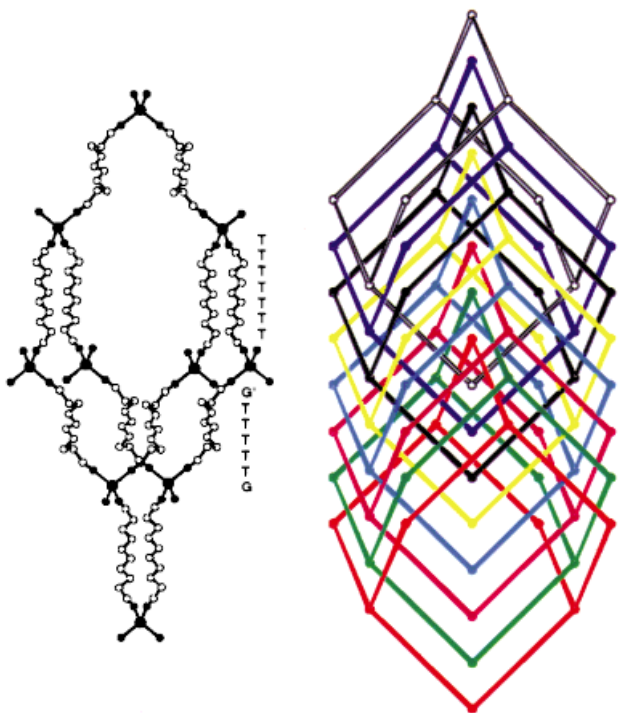


Figure 1. A view of the single diamondoid frame of **1** (left), showing the ligand conformations (only one of the two models for the GTTTTTG' chains is reported), and a schematic drawing of the eightfold interpenetrated net (right).

adamantanoid cages are very compressed in one direction, and exhibit maximum dimensions (corresponding to the longest intracage Ag–Ag distances) of $2a \times 8b \times 2c$ (that is 21.03 × 45.62 × 42.71 Å in **1**, 21.15 × 46.24 × 42.48 Å in **2**). This is clearly illustrated by the sphere packing diagram down *b* given in Figure 2, which shows also the compressed channels

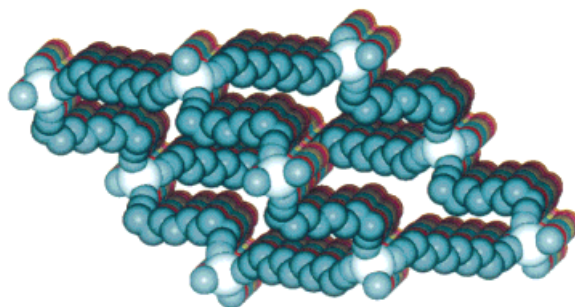


Figure 2. A packing view of the eight interpenetrated diamondoid cages down vector *b*.

occupied by the anions. Distortions of the cages can arise from different factors, including the varied ligand conformations, the bent Ag–N–C interactions (161–163° in **1** and **2**) and the versatility of the coordination geometry of the silver cations. The two independent sebn ligands assume in both compounds a TTTTTT conformation (N-to-N mean distance of 13.29 Å) and a GTTTTTG' one (N-to-N mean distance of 11.15 Å). The Ag^I cations display a somewhat distorted tetrahedral geometry (mean Ag–N 2.26 Å (**1**) and 2.28 Å (**2**); N–Ag–N 102.3(6)–113.8(5)° (**1**) and 102.5(4)–114.5(3)° (**2**)). Though many diamondoid coordination networks are presently known, almost all exhibiting interpenetration, up to a maximum of nine nets in [Ag(bpcn)₂]X (bpcn = 4,4'-biphenyldicarbonitrile; X = PF₆⁻, AsF₆⁻, SbF₆⁻),^[12] the eightfold interpenetration of **1** and **2** is rather surprising in the presence of the flexible sebn ligands (see below). To our knowledge, within coordination polymers only one other example of an eightfold diamondoid has been previously reported, that is [Ag(3,3'-dcpa)₂]ClO₄·H₂O (3,3'-dcpa = 3,3'-dicyanodiphenylacetylene); the ligand is in a *transoid* conformation (Ag...Ag separation of 17.02 Å).^[13]

Interpenetrated 3D nets with the SrAl₂ topology: The structure of [Ag(sebn)₂](PF₆) (**3**), as well as that of the isomorphous [Ag(sebn)₂](AsF₆) (**5b**),^[14] represents a possible alternative to the diamond topology for a M(ligand)₂ frame. It consists of four interpenetrated 3D networks of four-connected metal centers linked by sebn ligands, which display three distinct conformations (TTTTTTT, N-to-N 13.42 Å, Ag...Ag 17.95 Å; GTTTTTG', N-to-N 10.44 Å, Ag...Ag 11.96 Å; GTTGTTG, N-to-N 8.24 Å, Ag...Ag 10.72 Å). The metal atoms present a distorted tetrahedral geometry [Ag–N 2.253(4)–2.299(4) Å; N–Ag–N 106.1(1)–116.4(1)°]. The Ag–N–C angles are scattered in the range 150.7(3)–175.2(4)°. The topology of a single frame can be rationalized by considering that the shortest circuits starting and ending at each silver ion are tetragons, hexagons, and octagons (Figure 3) in the ratio 2:3:1, that is this is a 4²6³8 net (the 4²6³8-a net described by

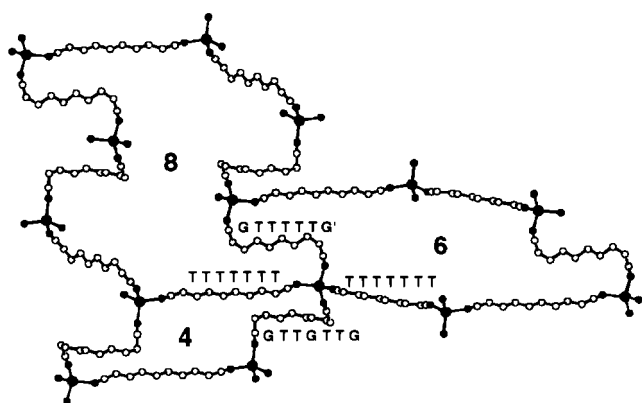


Figure 3. The three types of circuits and the ligand conformations in **3**.

Wells^[15]). More specifically, this topological type is related to the prototypical structure of SrAl_2 (or of other binary inorganic phases like CeCu_2 and KHg_2),^[16] and, according to Smith,^[17] it is the same as that observed in $(\text{NH}_4)\text{LiSO}_4$, RbAlSiO_4 , and in the synthetic zeolite $\text{Li}-\text{A}(\text{BW})$. We have previously observed the same topology in a framework assembled from Cu^{I} ions and an anionic acetonyl derivative of tetracyanoethylene.^[18] A schematized view of a single frame of **3** and of the fourfold interpenetration is shown in Figure 4. The single network can be described in the monoclinic space group $C2/c$ with cell vectors $\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = 2\mathbf{b}$, $\mathbf{c}' = \mathbf{a} + \mathbf{c}$ ($a' = 42.119$, $b' = 20.985$, $c' = 30.422$ Å, $\beta' = 129.4^\circ$). The interpenetration law produces from a single net three identical ones generated by the translation vectors $[0\ 1\ 0]$, $[1/2\ 1/2\ 0]$ and $[1/2\ -1/2\ 0]$. This is, to our knowledge, the first example of interpenetration for this type of network.

Though a single net contains large channels, these are mainly filled by the other interpenetrated nets, leaving only isolated cavities to host the anions, in contrast to the diamondoid nets where the parallel interpenetration leaves large empty channels.

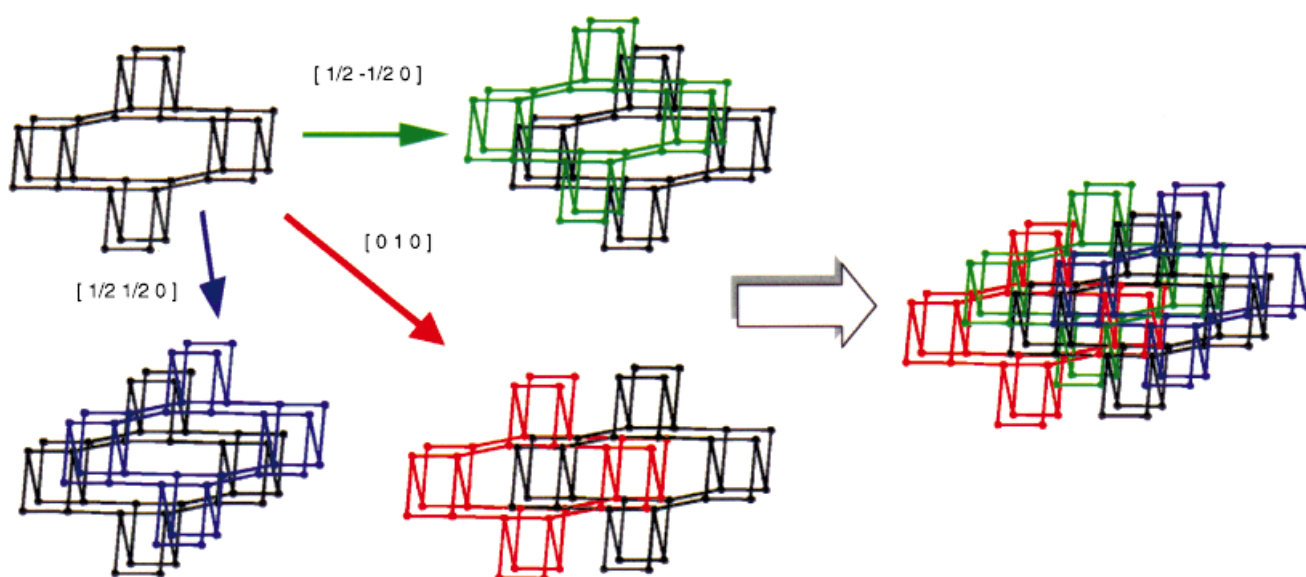


Figure 4. A schematic view of a single frame in **3** (top left) and the interpenetration process leading to the fourfold interwoven SrAl_2 type nets.

Infinitely catenated 2D multiple layers: Another completely different structural motif is that found for the two species $[\text{Ag}(\text{sebn})_2](\text{SbF}_6)$ (**4**) and $[\text{Ag}(\text{sebn})_2](\text{CF}_3\text{SO}_3)$ (**6b**), which are isomorphous in spite of the different shape of the anions. Their structure contains 2D complex layers based on distorted tetrahedral silver(I) centers disposed on four different levels (Ag–N mean 2.28 Å in **4** and 2.27 Å in **6b**, N–Ag–N and Ag–N–C range 102.1(5)–118.0(10) and 165(5)–174(2)° in **4**, 101.4(5)–118.1(5) and 162(2)–174(1)° in **6b**). A single layer, of thickness 31.5 Å for **4** and 32.1 Å for **6b** (measured as the distance between the two limiting planes passing through the outmost carbon atoms of the GTTGTTG chains) is illustrated in Figure 5. All the shortest circuits at each metal center are hexagons, and the short topological symbol of the net is 6^6 . It is surprising that, in spite of the presence of two different types of silver ions in these layers (the *internal* ones and the *surface* ones), all the centers exhibit an identical topology.^[19] Incomplete open adamantanoid-like units can be envisaged (Figure 5, bottom), but the layers contain channels rather than finite cages. The sebn ligands present three different conformations: TTTTTTT (N-to-N 13.18, Ag⋯Ag 17.60 Å in **4**, N-to-N 13.20, Ag⋯Ag 17.64 Å in **6b**), GTTTTTG' (N-to-N 10.69, Ag⋯Ag 14.18 Å in **4**, N-to-N 10.66, Ag⋯Ag 13.97 Å in **6b**) and GTTGTTG (N-to-N 9.01, Ag⋯Ag 11.53 Å in **4**, N-to-N 8.94 Å in **6b**).

These layers are intertwined by translation (translation vector corresponding to the b axis) in such a manner that each one is interpenetrated by the two adjacent (the upper and the lower ones) identical motifs. The resulting 3D array is, therefore, an infinite catenane of 2D architectures (Figure 6), an intertwining type never observed before. While polycatenated ladderlike 1D polymers are known, producing infinite 2D^[6c] or 3D^[6b] arrays, no example of an infinite catenane of 2D motifs has been previously described, to our knowledge, neither in inorganic nor in coordination polymer chemistry.

Besides the interpenetration with the two nearest layers (translated by $\pm \mathbf{b}$) on the two opposite sides of the polymeric plane, each layer exhibits also *interdigitation* with the second

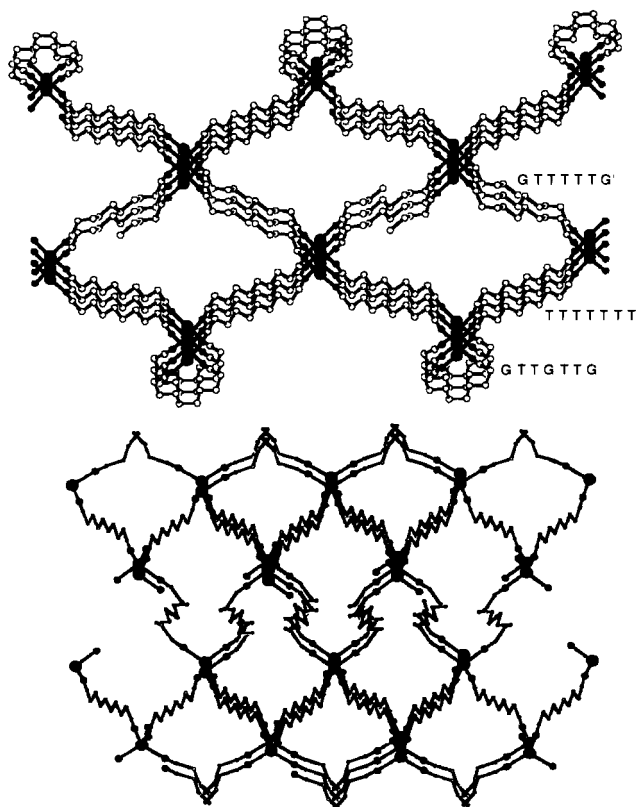


Figure 5. Two side views of a single 2D layer in **4**, with the ligands conformations. Top, down [1 0 0], bottom, down [1 0 1].

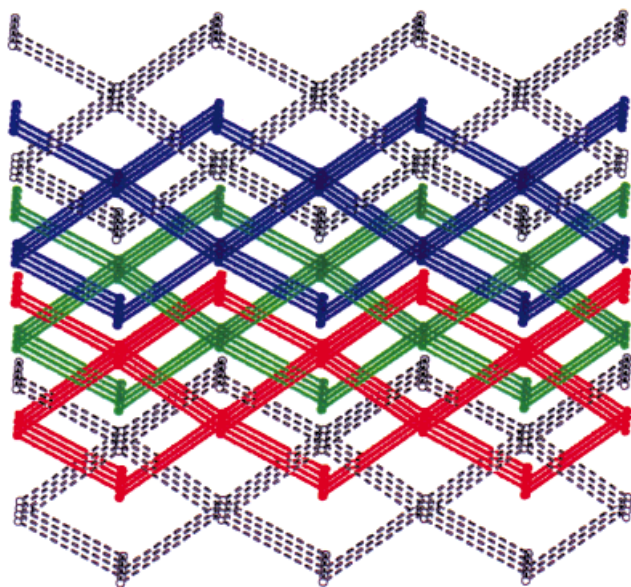


Figure 6. A schematic view of the infinite interpenetration of the 2D catenane **4**, the green layer is interwoven with the two nearest neighboring blue and red layers, and *interdigitated* with the two dashed layers.

nearest neighboring layers (translated by $\pm 2b$). The anions are hosted in parallel channels extending along *a* and, alternately, along *c*.

It is noteworthy that this species contains sebn ligands with the same conformations as those in the SrAl_2 type frames. The structural difference is related to the number of independent silver centers: only one in the SrAl_2 nets (with $2 \times \text{TTTTTTT}$,

GTTGTG and $\text{GTTTTTGT}'$ ligands); two in **4** and **6b** (the first with $2 \times \text{TTTTTTT}$ and $2 \times \text{GTTGTG}$, and the second with $2 \times \text{TTTTTTT}$ and $2 \times \text{GTTTTTGT}'$ ligands).

One-dimensional polymers: Compounds $[\text{Ag}(\text{sebn})](\text{AsF}_6)$ (**5a**) and $[\text{Ag}(\text{sebn})](\text{CF}_3\text{SO}_3)$ (**6a**) contain 1D polymeric -sebn-Ag-sebn-Ag- chains, which, however, display a quite different spatial arrangement. In compound **6a** the chains are disposed in pairs, connected at the silver ions through triflate bridges (Ag-O-S-O-Ag), all running in the *c* direction with a period equal to two successive Ag-sebn-Ag steps (24.21 Å; Figure 7). The sebn ligands display a GTTTTTT conformation. (N-to-N 10.87 Å, Ag...Ag 12.34 Å). The silver ions show a quite distorted tetrahedral coordination with two sebn N atoms and two O atoms of the triflates.

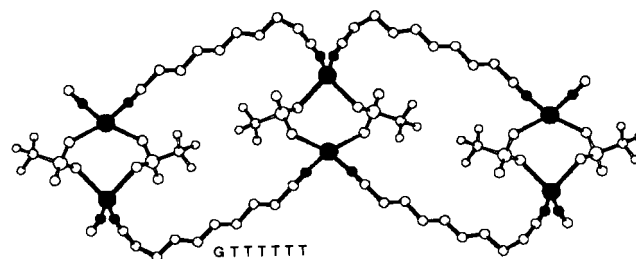


Figure 7. A part of the double 1D chain in **6a**, showing the bridging at the silver ions.

In **5a** the sebn ligands display a TGTTTG'T conformation (N-to-N 12.33 Å, Ag...Ag 16.43 Å) and a period of the polymer corresponding again to a couple of successive Ag-sebn-Ag steps (32.84 Å). Due to two weak interactions of each silver ions with anionic F atoms (Ag-F 2.56(1) Å) the metal coordination shows a certain deviation from linearity (Ag-N 2.085(7) Å, N-Ag-N 165.3(4)°). The peculiar structural feature of this compound consists in the unique self-organization of the polymeric chains which extend in three non coplanar directions (generated by the threefold crystallographic axes), as schematized by the rod-packings of Figure 8. Two views of the resulting 3D array are given in Figure 9. The

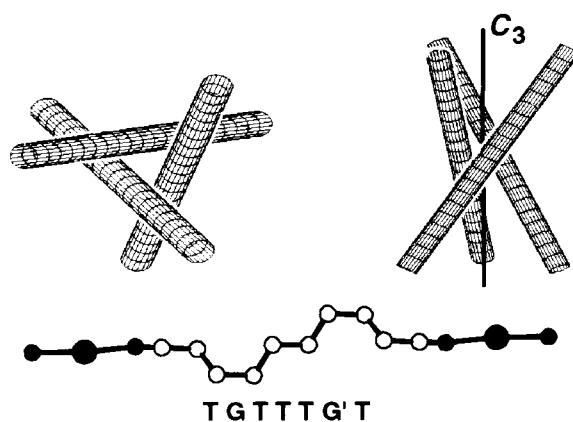


Figure 8. Two rod-packing pictures of the three entangled 1D polymers for **5a** (top). The directions of the three rods are $[-1 -2 1]$, $[2 1 1]$, and $[-1 1 1]$, with angles between each others of 53.75° and with the threefold axis of 31.47° . A view of the ligand conformation is shown at the bottom.

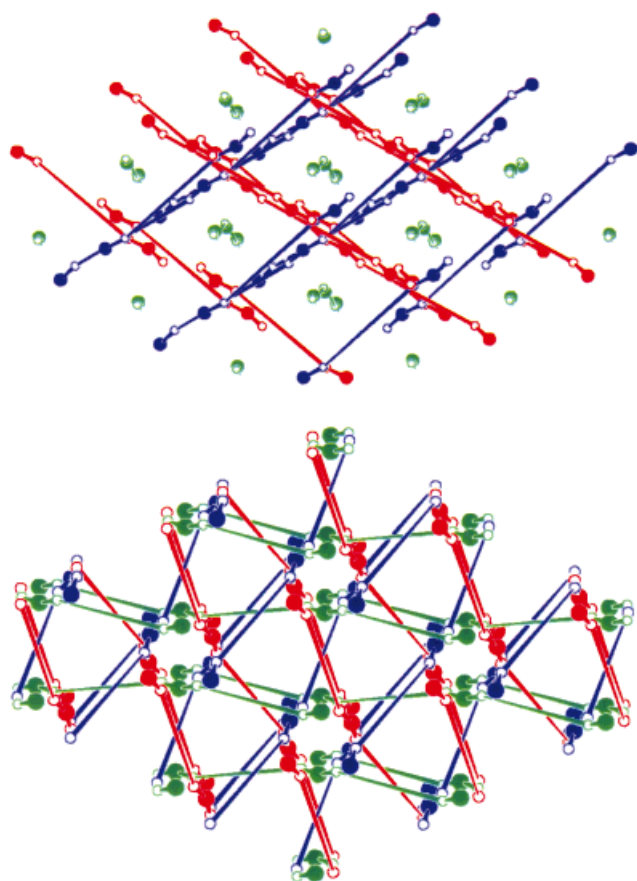


Figure 9. Two schematic views of the entangled 1D polymers in **5a**, approximately down $[-1\ 1\ 1]$ (top) and $[0\ 0\ 1]$ (bottom), with silver atoms represented by full circles and nitrogen atoms by small empty circles.

packing of 1D polymers usually occurs with parallel orientation of all chains (as in **6a**); less commonly they can span two different directions on alternate layers. The recently reported complex $[\text{Ag}(\text{pytz})](\text{NO}_3)$ [pytz = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine]^[20] consists of linear polymers (presenting weak interactions among the chains through the NO_3^- ions) arranged on parallel layers, rotated by 60° on passing from one to any successive layer. However, compound **3** differs from all other 1D species in that there is no plane that can separate the whole array into two halves without breaking bonds, and only on slipping the chains the 3D arrangement can be disentangled.

Conclusion

The reactions of sebaconitrile with different silver salts have shown that the use of such long-chain flexible ligands can afford a variety of fascinating self-assembled polymeric architectures. New topologies and interpenetration phenomena have been observed that are of interest at the basic structural level. Four-connected frames for $\text{M}(\text{ligand})_2$ polymers alternative to the more common diamondoid nets can be achieved thanks to the conformational nonrigidity of the ligands. Indeed, a number of different conformations for the versatile sebn ligands, giving quite different metal–metal

separations, have been observed. The role of the counterions of the silver cations in orienting the self-assembly processes has been investigated. A variation of the structural type of the networks is observed with the progressive increase of the dimensions of the anions (smaller = interpenetrated diamond, intermediate = interpenetrated SrAl_2 , larger = catenated 2D multilayer), but it is still difficult to rationalize this trend further. While isomorphism was to be expected for pairs of anions of the same shape and similar dimensions (as BF_4^- and ClO_4^- for the diamond eightfold, and PF_6^- and AsF_6^- for the SrAl_2 fourfold), more surprising was finding the same structure (2D catenane) for the pair SbF_6^- and CF_3SO_3^- , the two largest, but different in shape, anions.

The structural types here reported can serve as models for other more robust polymeric systems. Attempts are in progress to test the possibility of introducing suitable guest molecules, instead of having interpenetration, in the large cavities and channels of these frames and to clarify, by using other dinitriles, the relationship between topological type and length of the aliphatic chains.

Experimental Section

Materials: All reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University.

Synthesis of the polymers: All the compounds were prepared by treating at room temperature the silver salts [AgBF_4 , AgClO_4 , AgPF_6 , AgAsF_6 , AgSbF_6 and $\text{Ag}(\text{CF}_3\text{SO}_3)$] dissolved in ethanol with ethanolic solutions of the sebn ligand in molar ratios of 1:1 or 1:2. For example, $[\text{Ag}(\text{sebn})_2](\text{SbF}_6)$ (**4**) was obtained on layering an ethanolic solution (4 mL) of sebn (0.023 mL, 0.134 mmol) on a solution of AgSbF_6 (0.023 g, 0.067 mmol) in ethanol (4 mL). The mixtures were left for 10–15 days in the dark and then allowed to concentrate by slow evaporation in the air. The crystals were recovered in good yield except for **5a**; they were filtered and washed with hexane. All the products are air and light stable for long periods. **1**: M.p. $75-77^\circ\text{C}$; elemental analysis calcd for $\text{C}_{20}\text{H}_{32}\text{AgBF}_4\text{N}_4$: C 45.91, H 6.16, N 10.71; found C 45.50, H 6.00, N 10.55. **2**: M.p. $71-74^\circ\text{C}$; elemental analysis calcd for $\text{C}_{20}\text{H}_{32}\text{AgClN}_4\text{O}_4$: C 44.83, H 6.02, N 10.46; found C 45.01, H 6.00, N 10.40. **3**: M.p. $91-92^\circ\text{C}$; elemental analysis calcd for $\text{C}_{20}\text{H}_{32}\text{AgF}_6\text{N}_4\text{P}$: C 41.32, H 5.55, N 9.64; found C 41.02, H 5.51, N 9.72. **4**: M.p. $99-104^\circ\text{C}$, elemental analysis calcd for $\text{C}_{20}\text{H}_{32}\text{AgF}_6\text{N}_4\text{Sb}$: C 35.74, H 4.80, N 8.34; found C 36.02, H 4.95, N 8.28. Compound **5a** was obtained in very low yield and its nature was established only on the basis of the single-crystal X-ray analysis. **5b**: M.p. $96-99^\circ\text{C}$; elemental analysis calcd for $\text{C}_{20}\text{H}_{32}\text{AgAsF}_6\text{N}_4$: C 38.42, H 6.16, N 8.96; found C 38.58, H 5.01, N 9.05. Compounds **6a** and **6b** were always affected by some impurities that were difficult to completely eliminate; this gave rise to particularly low melting points (ca. 30°C for **6a** and ca. 40°C for **6b**). **6a**: elemental analysis calcd for $\text{C}_{11}\text{H}_{16}\text{AgF}_3\text{N}_2\text{O}_3\text{S}$: C 31.37, H 3.83, N 6.65; found C 31.93, H 4.08, N 6.91. **6b**: elemental analysis calcd for $\text{C}_{21}\text{H}_{32}\text{AgF}_3\text{N}_4\text{O}_3\text{S}$: C 43.08, H 5.51, N 9.57; found C 42.68, H 5.35, N 9.78.

Crystallography: The crystal data for all the compounds are listed in Table 1. The data collections were performed at 293 K ($\text{MoK}\alpha$, $\lambda = 0.71073\text{ \AA}$) on a Siemens SMART CCD area-detector diffractometer for **3** and **5a**, and an Enraf-Nonius CAD4 for **1**, **2**, **4**, **5b**, **6a**, **6b**, by the ω -scan method, within the limits $3 < \theta < 20^\circ$ (**5b**), $3 < \theta < 25^\circ$ (**2**, **4**, **6a**), $3 < \theta < 26^\circ$ (**1**, **6b**), $2 < \theta < 28^\circ$ (**3**, **5a**). An empirical absorption correction was applied (SADABS^[21] for **3** and **5a**, ψ scan for the others). The structures were solved by direct methods (SIR97)^[22] and refined by full-matrix least-squares (SHELX97).^[23] Anisotropic thermal parameters were assigned to all the non-hydrogen atoms but to the disordered ones that were refined isotropically (for **5b**, only Ag and As were treated anisotropically). Disordered anions were found in all compounds but in **4**, **5b**, and **6a** and

Table 1. Crystallographic data for compounds **1–6**.

	Diamond eightfold	Diamond eightfold	SrAl ₂ fourfold	SrAl ₂ fourfold
chemical formula	[Ag(sebn) ₂](BF ₄) (1)	[Ag(sebn) ₂](ClO ₄) (2)	[Ag(sebn) ₂](PF ₆) (3)	[Ag(sebn) ₂](AsF ₆) (5b)
formula weight	C ₂₀ H ₃₂ AgBF ₄ N ₄	C ₂₀ H ₃₂ AgClN ₄ O ₄	C ₂₀ H ₃₂ AgF ₆ N ₄ P	C ₂₀ H ₃₂ AgAsF ₆ N ₄
crystal system	523.18	535.82	581.34	625.28
space group	monoclinic	monoclinic	monoclinic	monoclinic
<i>a</i> [Å]	<i>P2/n</i> (no. 13)	<i>P2/n</i> (no. 13)	<i>C2/c</i> (no. 15)	<i>C2/c</i> (no. 15)
<i>b</i> [Å]	10.515(3)	10.574(3)	21.126(3)	21.225(7)
<i>c</i> [Å]	5.703(1)	5.780(2)	10.511(2)	10.467(7)
β [°]	21.356(4)	21.239(5)	23.643(3)	23.555(7)
<i>V</i> [Å ³]	101.75(2)	101.25(2)	94.21(2)	94.36(2)
<i>Z</i>	1253.8(5)	1273.1(6)	5235.9(14)	5218(4)
ρ_{calcd} [g cm ⁻³]	2	2	8	8
μ [mm ⁻¹]	1.386	1.398	1.475	1.592
obs. refl. criterion	0.846	0.926	0.887	2.088
<i>R</i> indices ^[a,b]	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 1 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
	<i>R</i> 1 0.0851, <i>wR</i> 2 0.2583	<i>R</i> 1 0.0578, <i>wR</i> 2 0.1496	<i>R</i> 1 0.0471, <i>wR</i> 2 0.1061	<i>R</i> 1 0.0722, <i>wR</i> 2 0.1821
	2D Catenane	2D Catenane	1D Entangled	1D Coupled
chemical formula	[Ag(sebn) ₂](SbF ₆) (4)	[Ag(sebn) ₂](SO ₃ CF ₃) (6b)	[Ag(sebn)](AsF ₆) (5a)	[Ag(sebn)](SO ₃ CF ₃) (6a)
formula weight	C ₂₀ H ₃₂ AgF ₆ N ₄ Sb	C ₂₁ H ₃₂ AgF ₃ N ₄ O ₃ S	C ₁₀ H ₁₆ AgAsF ₆ N ₂	C ₁₁ H ₁₆ AgF ₃ N ₂ O ₃ S
crystal system	672.12	585.44	461.04	421.19
space group	monoclinic	monoclinic	trigonal	monoclinic
<i>a</i> [Å]	<i>P2/c</i> (no. 13)	<i>P2/c</i> (no. 13)	<i>P3c1</i> (no. 165)	<i>C2/c</i> (no.15)
<i>b</i> [Å]	11.533(6)	11.481(3)	9.900(1)	14.240(5)
<i>c</i> [Å]	10.134(6)	10.262(6)	9.900(1)	9.554(3)
β [°]	23.185(5)	23.184(5)	28.019(2)	24.209(10)
<i>V</i> [Å ³]	92.51(2)	93.66(2) ^o	–	93.76(3)
<i>Z</i>	2707(2)	2725.9(18)	2378.2(4)	3287(2)
ρ_{calcd} [g cm ⁻³]	4	4	6	8
μ [mm ⁻¹]	1.649	1.427	1.931	1.702
obs. refl. criterion	1.776	0.863	3.394	1.392
<i>R</i> indices ^[a,b]	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
	<i>R</i> 1 0.0702, <i>wR</i> 2 0.1706	<i>R</i> 1 0.0792, <i>wR</i> 2 0.2261	<i>R</i> 1 0.0523, <i>wR</i> 2 0.1389	<i>R</i> 1 0.0858, <i>wR</i> 2 0.2142

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$; weighting: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$

suitable disorder models were refined in those cases, as well as for a few C atoms of some aliphatic chains in **1**, **2**, **4**, and **6b**. All the diagrams were obtained by using SCHAKAL97 program.^[24] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-101892 to CCDC-101899. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

- [1] *Comprehensive Supramolecular Chemistry* (Ed.: J.-M. Lehn), Pergamon, Oxford, **1995**.
- [2] See for example: C. Dietrich-Buchecker, J.-P. Sauvage, *Bull. Soc. Chem. Fr.* **1992**, 129, 113; R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, 90, 5394.
- [3] For a recent review article see: M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn.* **1996**, 69, 1471, and references therein.
- [4] a) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, 112, 1546; b) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, J. Liu, *Supramolecular Architecture*, ACS publications, **1992**, ch. 19; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, 110, 1558; *Angew. Chem. Int. Ed.* **1998**, 37, 1460.
- [5] See for example a) T. Soma, H. Yuge, T. Iwamoto, *Angew. Chem.* **1994**, 106, 1746; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1665; b) L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1994**, 1325; c) G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, 374, 792; d) O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, 378, 703; e) A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li, M. Schröder, *Chem. Commun.* **1997**, 1005; f) K. A. Hirsch, S. R. Wilson, J. S. Moore *Chem. Commun.* **1998**, 13; g) K. N. Power, T. L. Hennigar,

- M. J. Zaworotko, *Chem. Commun.*, **1998**, 595; h) L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio, *Chem. Commun.* **1998**, 1837.
- [6] a) D. M. L. Goodgame, S. Menzer, A. M. Smith, D. J. Williams, *Angew. Chem.* **1995**, 107, 605; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 574; b) M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Amer. Chem. Soc.*, **1995**, 117, 7287; M. Fujita, O. Sasaki, K. Watanabe, K. Ogura, K. Yamaguchi, *New J. Chem.*, **1998**, 189; c) A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovkii, W.-S. Li, M. Schröder, *Chem. Commun.* **1997**, 2027.
- [7] a) D. Whang, K. Kim, *J. Am. Chem. Soc.* **1997**, 119, 451; b) B. F. Hoskins, R. Robson, D. A. Slizys, *J. Am. Chem. Soc.* **1997**, 119, 2952.
- [8] L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, 36, 3812.
- [9] D. M. L. Goodgame, S. Menzer, A. M. Smith, D. J. Williams, *Chem. Commun.* **1997**, 339.
- [10] Y. Kinoshita, I. Matsubara, T. Higuchi, Y. Saito, *Bull. Chem. Soc. Jpn.* **1959**, 32, 1221.
- [11] S. Gorter, G. C. Verschoor, *Acta Cryst. B* **1976**, 32, 1704.
- [12] a) K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore, S. Lee, *J. Chem. Soc. Chem. Commun.* **1995**, 2199; b) K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore, *Chem. Eur. J.* **1997**, 3, 765.
- [13] K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore, *Inorg. Chem.* **1997**, 36, 2960.
- [14] Because of the poor quality of the structural data for **5b** the detailed discussion concerns only the results for compound **3**.
- [15] A. F. Wells, *Further studies of Three-dimensional Nets*, ACA Monograph No.8, 1979; this array is Net 8 in: A. F. Wells, *Three-dimensional Nets and Polyhedra*, Wiley, New York, **1977**.
- [16] a) M. O'Keeffe, B. G. Hyde, *Crystal Structures I. Patterns and Symmetry*, Mineralogical Society of America, **1996**; b) G. Nussli, K. Polborn, J. Evers, G. A. Landrum, R. Hoffmann, *Inorg. Chem.* **1996**, 35, 6922.

- [17] J. V. Smith, *Am. Mineral.* **1977**, *62*, 703.
- [18] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Angew. Chem.* **1996**, *108*, 1170; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1088.
- [19] The topological classifications (see ref. [16a]) of all the silver centers is represented by the long Schläfli symbol: $6666_26_26_2$. Both the independent silver ions present the same coordination sequence (with the values up to the 10th neighbors of 4, 12, 27, 40, 50, 62, 74, 86, 98, 110). Under these conditions a 3D net is called uninodal; we prefer to call this 2D net *pseudo-uninodal*.
- [20] M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder, *Angew. Chem.* **1997**, *109*, 2430; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2337.
- [21] G. M. Sheldrick, SADABS, Siemens Area Detector Absorption Correction Software, Universität Göttingen, Germany, **1996**.
- [22] A. Altomare, G. Casciarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli *J. Appl. Crystallogr.* **1994**, *27*, 435.
- [23] G. M. Sheldrick, SHELX-97, program for structure refinement, Universität Göttingen, Germany, **1997**.
- [24] E. Keller, SCHAKAL97, a computer program for the graphical representation of crystallographic models, Universität Freiburg, Germany, **1997**.

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