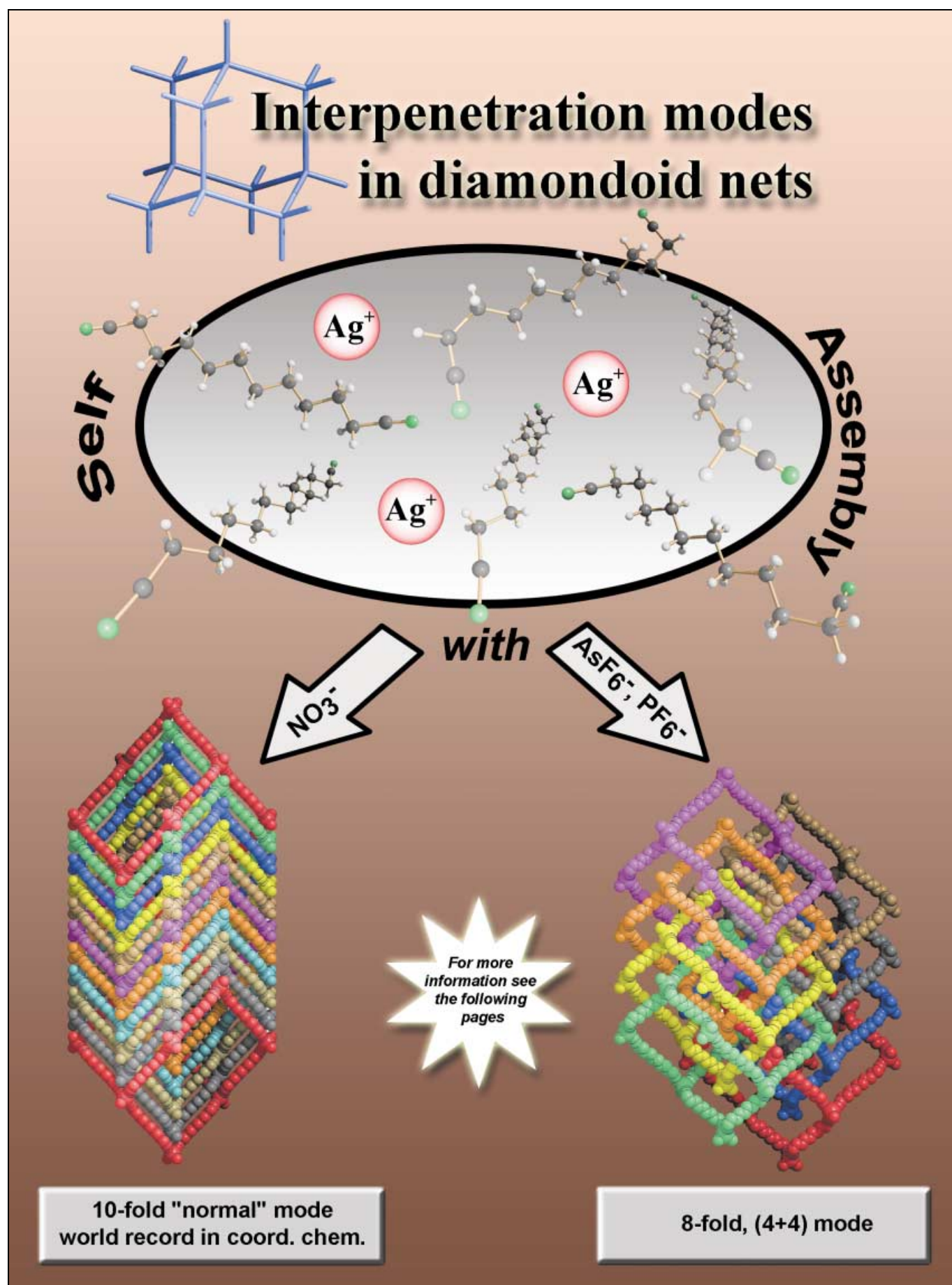




# Three Novel Interpenetrating Diamondoid Networks from Self-Assembly of 1,12-Dodecanedinitrile with Silver(I) Salts

Lucia Carlucci,<sup>[b]</sup> Gianfranco Ciani,<sup>\*,[a]</sup> Davide M. Proserpio,<sup>[a]</sup> and Silvia Rizzato<sup>[a]</sup>

**Abstract:** The self-assembly of 1,12-dodecanedinitrile (ddn) with various silver salts ( $\text{NO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$ ) afforded new polymeric coordination networks with the general formula  $[\text{Ag}(\text{ddn})_2]\text{X}$ . All these species contain interpenetrating diamondoid nets showing interesting features: with  $\text{X} = \text{NO}_3^-$  the cationic  $[\text{Ag}(\text{ddn})_2]^+$  network exhibits the highest interpenetration (tenfold)

ever found within diamondoid nets exclusively based on coordinative bonds. When  $\text{X} = \text{PF}_6^-$  or  $\text{AsF}_6^-$  an eightfold diamondoid network is obtained that shows an unusual [4+4] mode of inter-

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penetration, instead of the “normal” set of eight nets equally translated along a principal axis of the adamantanoid cages. The polymeric species that forms with  $\text{X} = \text{ClO}_4^-$  is a fourfold interpenetrating diamondoid network; the lower degree of interpenetration in this case is related to the conformation assumed by the flexible ddn ligands.

## Introduction

The crystal engineering of networked coordination polymers<sup>[1]</sup> is of great current interest due to their potential properties as novel zeolite-like materials,<sup>[2]</sup> for molecular sieving, ion exchange, gas storage, molecular sensing, and catalysis. Many efforts have been devoted to the investigation of new synthetic strategies, with the use of novel rigid or flexible spacer ligands. Though a rich variety of topologies is evident in the polymeric networks with hydrogen bonds or coordinative bonds obtained recently, doubtless the most common and important type of topology is related to the structure of diamond (or sphalerite). The synthetic routes to diamondoid networks, their structures, and degrees of interpenetration have been discussed and reviewed.<sup>[1, 3–6]</sup> It is noteworthy that one of the first examples of coordination networks, reported many years ago, was a sixfold diamondoid net based on  $\text{Cu}^{\text{I}}$  ions and the flexible bidentate adiponitrile.<sup>[7]</sup>

We are currently performing a systematic study on the reactions of long-chain dinitriles with silver salts, in order to

obtain information at the basic structural level, of interest for the crystal engineering of novel coordination networks and devices. With these ligands we have obtained many examples of interpenetrating diamondoids<sup>[8]</sup> and other interesting polymers with 1,10-dodecanedinitrile (sebaconitrile).<sup>[9]</sup> We report here on our investigations of the self-assembly of silver(I) salts with the longer 1,12-dodecanedinitrile (ddn). We obtained three novel cases of  $[\text{Ag}(\text{ddn})_2]\text{X}$  super-diamond networks with different types of interpenetration: fourfold with  $\text{AgClO}_4$ , eightfold [4+4] with  $\text{AgPF}_6$  and  $\text{AgAsF}_6$ , and tenfold with  $\text{AgNO}_3$ . The last-mentioned is the highest degree of interpenetration ever found within diamondoid nets exclusively based on coordinative bonds. The different modes of interpenetration in the known frameworks of this fundamental topology are also discussed and compared.

## Results

The new coordination polymers were obtained in good yields by the method used for previously reported  $\text{Ag}^{\text{I}}$ -dinitrile polymers,<sup>[9]</sup> that is, by slow evaporation of solutions of ddn and an  $\text{Ag}^{\text{I}}$  salt in molar ratio 2:1. The mixtures, left to concentrate in the dark for several days, gave colourless crystals of the adducts, which were characterized by single-crystal X-ray analyses. The reactions led in each case to a single product of composition  $[\text{Ag}(\text{ddn})_2]\text{X}$ , namely,  $[\text{Ag}(\text{ddn})_2]\text{NO}_3$  (**1**),  $[\text{Ag}(\text{ddn})_2]\text{PF}_6$  (**2a**),  $[\text{Ag}(\text{ddn})_2]\text{AsF}_6$  (**2b**), and  $[\text{Ag}(\text{ddn})_2]\text{ClO}_4$  (**3**).  $\text{AgBF}_4$  gives crystals that are isomorphous with those of compound **3** but always of insufficient quality for single-crystal X-ray analysis.

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All products are air-stable for long times at 4 °C. They dissolve in common organic solvents and are poorly thermally resistant because of their low melting points, similar to those observed within the family of sebaconitrile–silver adducts.<sup>[9]</sup> Nevertheless, they are useful model compounds in coordination polymer chemistry due to their novel structural motifs and interpenetration modes.

The topology of all these polymers can be related to that of diamond, but different degrees and modes of interpenetration are observed, depending on the anions. Crystal data are reported in Table 1, and selected bond lengths and angles are listed in Table 2.

**The tenfold interpenetrated diamondoid network of 1:** The structure of **1** consists of cationic diamondoid frameworks, containing large identical adamantanoid cages. A single cage is illustrated in Figure 1 (left); it exhibits equal Ag⋯Ag edges that are 19.80 Å long; these are the longest M⋯M separations in all known diamondoid coordination networks.<sup>[1e]</sup> Ten independent equivalent networks are interpenetrated within the crystals, related by a translation vector corresponding to the crystallographic *c* axis (5.837(2) Å), as schematically shown in Figure 1 (right). The adamantanoid cages are strongly compressed in one direction and exhibit maximum dimensions (corresponding to the longest intracage Ag⋯Ag distances) of  $2a \times 2b \times 10c$  (i.e.,  $19.02 \times 50.03 \times 58.37$  Å). This is clearly visible in the view down the *c* axis (Figure 2), which also shows the compressed channels occupied by the anions.

Distortions of the cages from an ideal geometry can arise in these polymers from factors such as the different ligand conformations, the possibility of bent Ag–N–C interactions ( $172.1(6)^\circ$  in **1**) and the versatility of the coordination geometry at the silver centers.

Table 2. Selected distances [Å] and angles [°] in **1–3**.

| Compound <b>1</b>  |                      |        |                                        |
|--------------------|----------------------|--------|----------------------------------------|
| Ag–N               | 2.241(5)             | N–Ag–N | 103.0(3), 107.6(3), 118.2(3)           |
| N–C                | 1.136(7)             | Ag–N–C | 172.1(6)                               |
| Compound <b>2a</b> |                      |        |                                        |
| Ag–N               | 2.255(14), 2.261(11) | N–Ag–N | 100.0(8), 108.2(6), 111.3(5), 113.0(5) |
| N–C                | 1.125(9), 1.120(9)   | Ag–N–C | 160.5(16), 164.6(13)                   |
| Compound <b>2b</b> |                      |        |                                        |
| Ag–N               | 2.253(10), 2.267(9)  | N–Ag–N | 101.3(7), 109.8(4), 110.5(5), 112.6(4) |
| N–C                | 1.110(8), 1.116(8)   | Ag–N–C | 157.6(13), 168.8(10)                   |
| Compound <b>3</b>  |                      |        |                                        |
| Ag–N               | 2.251(13), 2.259(11) | N–Ag–N | 103.2(7), 106.1(6), 111.6(5), 112.3(5) |
| N–C                | 1.139(9), 1.139(8)   | Ag–N–C | 154.0(14), 170.3(12)                   |

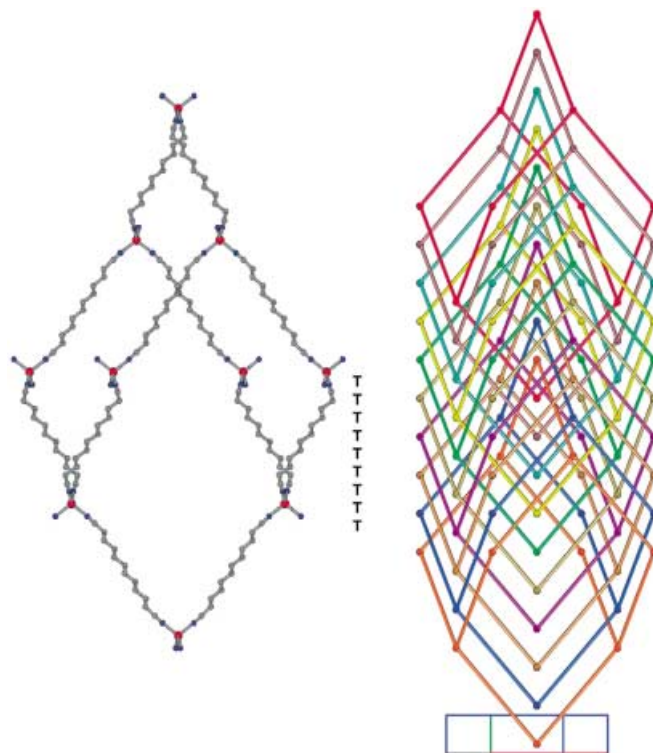


Figure 1. A single adamantanoid cage (left) and a schematic view of the tenfold interpenetration (right) in **1**.

Table 1. Crystal data and structure refinement parameters for compounds **1–3**.

| Formula                                                                                             | C <sub>24</sub> H <sub>40</sub> AgN <sub>3</sub> O <sub>3</sub> ( <b>1</b> ) | C <sub>24</sub> H <sub>40</sub> AgF <sub>6</sub> N <sub>4</sub> P ( <b>2a</b> ) | C <sub>24</sub> H <sub>40</sub> AgAsF <sub>6</sub> N <sub>4</sub> ( <b>2b</b> ) | C <sub>24</sub> H <sub>40</sub> AgClN <sub>4</sub> O <sub>4</sub> ( <b>3</b> ) |
|-----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| <i>M</i> <sub>r</sub>                                                                               | 554.48                                                                       | 637.44                                                                          | 681.39                                                                          | 591.92                                                                         |
| crystal system                                                                                      | orthorhombic                                                                 | monoclinic                                                                      | monoclinic                                                                      | monoclinic                                                                     |
| space group (no.)                                                                                   | <i>Pnnm</i> (48)                                                             | <i>C2/c</i> (15)                                                                | <i>C2/c</i> (15)                                                                | <i>P2/c</i> (13)                                                               |
| <i>a</i> [Å]                                                                                        | 9.512(2)                                                                     | 24.220(8)                                                                       | 24.046(8)                                                                       | 10.993(2)                                                                      |
| <i>b</i> [Å]                                                                                        | 25.013(5)                                                                    | 12.214(3)                                                                       | 12.278(4)                                                                       | 5.654(1)                                                                       |
| <i>c</i> [Å]                                                                                        | 5.837(2)                                                                     | 11.062(7)                                                                       | 11.193(3)                                                                       | 23.724(3)                                                                      |
| $\beta$ [°]                                                                                         | 90                                                                           | 109.76(4)                                                                       | 109.78(2)                                                                       | 90.98(2)                                                                       |
| <i>V</i> [Å <sup>3</sup> ]                                                                          | 1388.8(6)                                                                    | 3080(2)                                                                         | 3109.6(17)                                                                      | 1474.3(4)                                                                      |
| <i>Z</i>                                                                                            | 2                                                                            | 4                                                                               | 4                                                                               | 2                                                                              |
| $\rho_{\text{calcd}}$ [g cm <sup>−3</sup> ]                                                         | 1.326                                                                        | 1.375                                                                           | 1.455                                                                           | 1.333                                                                          |
| $\mu$ [mm <sup>−1</sup> ]                                                                           | 0.757                                                                        | 0.761                                                                           | 1.758                                                                           | 0.807                                                                          |
| reflections collected                                                                               | 20944                                                                        | 2539                                                                            | 2866                                                                            | 17148                                                                          |
| unique reflections, <i>R</i> <sub>int</sub>                                                         | 2139, 0.039                                                                  | 2408, 0.032                                                                     | 2723, 0.025                                                                     | 3296, 0.171                                                                    |
| observed reflections [ <i>I</i> > 2σ( <i>I</i> )]                                                   | 1683                                                                         | 889                                                                             | 1155                                                                            | 1010                                                                           |
| final <i>R</i> 1, <i>wR</i> 2 [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )] <sup>[a]</sup> | 0.0675, 0.1979                                                               | 0.0773, 0.2099                                                                  | 0.0712, 0.2189                                                                  | 0.1263, 0.3225                                                                 |

[a] Weights during refinement were:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ;  $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $wR2 = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$ .

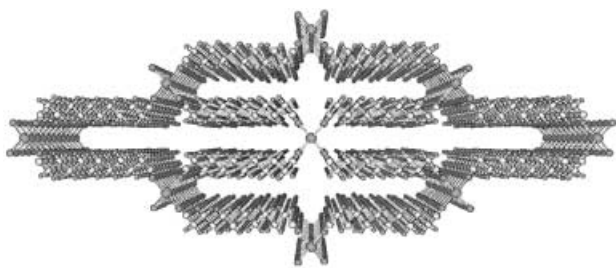


Figure 2. A perspective view down  $c$  of the anionic channels in compound **1**.

All the *ddn* ligands assume the TTTTTTTTTT conformation, which results in the longest possible N–N distance for this ligand (15.7 Å in **1**). The Ag<sup>I</sup> cations have a somewhat distorted tetrahedral coordination geometry (Ag–N 2.241(5) Å, N–Ag–N 103.0(3)–118.2(3)°).

The interpenetration mode of the ten independent nets in **1** is of the so-called normal type<sup>[5, 6]</sup> for diamondoid frames. However, the degree of interpenetration is exceptional and particularly surprising in the presence of a flexible ligand like *ddn* (cf. the structure of **3**). For many years the highest degree of interpenetration for diamondoid networks was the ninefold interpenetration in [Ag(BPCN)<sub>2</sub>]*X* (BPCN = 4,4'-biphenyldicarbonitrile; *X* = PF<sub>6</sub><sup>−</sup>, AsF<sub>6</sub><sup>−</sup>, SbF<sub>6</sub><sup>−</sup>).<sup>[4, 10]</sup> Only recently, 11-fold interpenetration of diamondoid frames has been reported for a hydrogen-bonded structure, with molecules of a tetraphenol as tetrahedral centres and benzoquinone units as rods, giving adamantane cages with edges of about 23 Å.<sup>[11]</sup> Compound **1**, however, contains the maximum number presently known of such interpenetrating nets in coordination polymers.

**The eightfold interpenetrated diamondoid networks of 2a and 2b:** Compounds **2a** and **2b** are isomorphous and their structure again consists of diamondoid cationic frameworks

containing large adamantanoid cages (Ag⋯Ag edges of 19.7 and 16.3 Å in **2a**, and 19.8 and 16.2 Å in **2b**). A single cage is illustrated in Figure 3a for **2b**. The cages exhibit maximum dimensions (i.e., longest intracage distances) of  $2a \times 4b \times 2c$  (i.e., 48.44 × 48.86 × 22.12 Å in **2a**, 48.09 × 49.11 × 22.39 Å in **2b**).

Eight such independent equivalent networks interpenetrate in the crystal (eightfold diamondoids), as shown in Figure 3b. This interpenetration mode differs from the normal mode in **1** and can be described as two sets of normal fourfold nets (gray and black in Figure 3, interpenetration vector in each set is the  $b$  axis) with a relative displacement vector of  $a/2 + b/2 = 13.49$  Å. We call this a [4+4] interpenetrated diamondoid system.

The view down the common direction of interpenetration for both sets (the  $b$  axis) reveals that the metal centres of one set of four networks are located in the midpoints of the anionic channels of the other set, and vice versa (Figure 3c). Thus, in contrast to the normal mode of interpenetration, which exhibits continuous rows of anions along the channels, here the anions are located between metal atoms (Figure 3d).

To the best of our knowledge, there are only three previous examples of eightfold interpenetrated diamondoid coordination networks, namely, [Ag(*sbn*)<sub>2</sub>]*ClO*<sub>4</sub> and [Ag(*sbn*)<sub>2</sub>]*BF*<sub>4</sub> (*sbn* = sebaconitrile, Ag⋯Ag 17.78, 15.30 Å and 17.79, 15.17 Å, respectively),<sup>[9]</sup> and [Ag(3,3'-*dcpa*)<sub>2</sub>]*ClO*<sub>4</sub> · H<sub>2</sub>O (3,3'-*dcpa* = 3,3'-dicyanodiphenylacetylene, with the ligand in a *transoid* conformation, Ag⋯Ag edges of 17.02 Å).<sup>[12]</sup> While the first two species show the normal mode of interpenetration, we observed that the third is another example of a [4+4] interpenetration as in **2a** and **2b**, an aspect that was previously neglected.<sup>[13]</sup>

The *ddn* ligands in **2a** and **2b** have two different conformations: half of them are of the TTTTTTTTTT type, with a N–N distance of about 15.2 Å, and the other half of the GTTTTTTTG' type, with a significantly shorter N–N distance

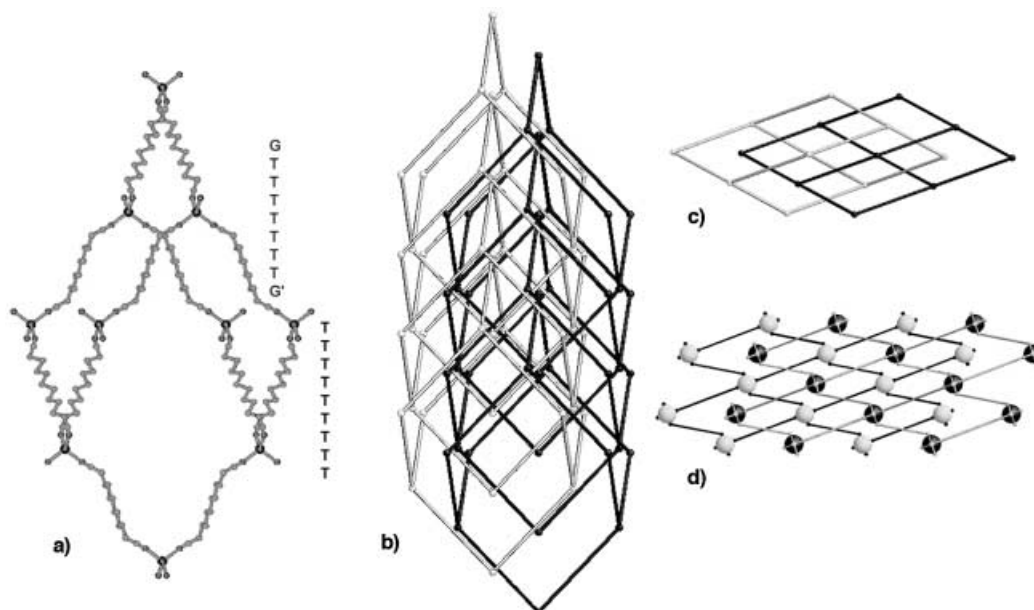


Figure 3. A single adamantanoid cage (a), two schematic views of the [4+4] interpenetration (b, c) and a view showing the positions of the anions, represented as spheres (d) in **2b**.

of about 12.8 Å. The presence of ligands with the second type of conformation is consistent with the observed decrease in the cage dimensions relative to that of **1**, especially in the direction of interpenetration, and can explain the lower degree of interpenetration in **2a** and **2b**.

In both compounds the coordination of the silver ions is slightly distorted tetrahedral (see Table 2).

**The fourfold interpenetrated diamondoid network of 3:** The structure of compound **3** consists of diamondoid frameworks containing strongly distorted adamantanoid cages (Ag...Ag edges of 16.32 and 16.08 Å). A single cage is shown in Figure 4a. Four independent equivalent networks are interpenetrated (fourfold diamondoid), with a translation vector corresponding to the crystallographic *b* axis (5.654(1) Å), as shown schematically in Figure 4b.

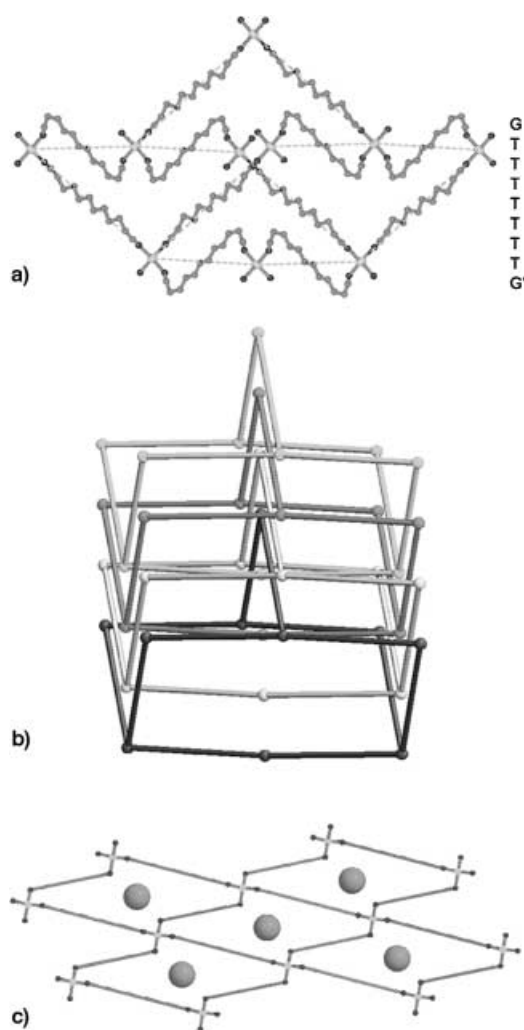


Figure 4. A single adamantanoid cage (a), a schematic view of the fourfold interpenetration (b) and a view showing the anion positions in the channels (c) in compound **3**.

The highly distorted adamantanoid cages exhibit maximum dimensions of  $2a \times 4b \times 2(c-a)$ , that is,  $21.99 \times 22.62 \times 52.63$  Å. The interpenetration mode is of the normal type, and the structure exhibits the usual anionic channels (see

Figure 4c). The most peculiar structural feature of this species is the relatively low degree of interpenetration compared to the other members of this family. This could be related to the fact that all the ddn ligands assume the GTTTTGTG' conformation, with N–N distances of 12.9 and 13.0 Å.

## Discussion

Interpenetrated diamondoid networks are much more common than noninterpenetrated ones in coordination polymer chemistry; only a very limited number of single diamondoid nets is presently known in this area.<sup>[1a, 14]</sup> The study of these systems in general implies the analysis and rationalization of two main aspects: 1) the degree of interpenetration, together with the factors that are responsible for the presence of a specific number of independent nets, and 2) the topology of interpenetration, together with the enumeration of the possible different types.

The degree of interpenetration remains difficult to predict and fully explain.<sup>[15]</sup> It is strongly related to the length of the spacer ligands, which dictates the M...M separations, that is, the length of the edges of the adamantanoid cages, and hence influences the number *n* of interpenetrating nets. However, even in the presence of rigid ligands, a precise *n*/M...M correlation does not exist. For example, the Ag...Ag separation in the ninefold diamondoids [Ag(bpcn)<sub>2</sub>]*X*<sup>[4, 10]</sup> is about 16.4 Å, while the corresponding separation in the eightfold interpenetrated network [Ag(3,3'-dcpa)<sub>2</sub>]*ClO*<sub>4</sub>·H<sub>2</sub>O is 17.02 Å.<sup>[12]</sup> Many factors can influence the degree of interpenetration, such as the bulkiness of the ligands and of the counterions, the number and type of solvated molecules, the presence of  $\pi$ – $\pi$  interactions between aromatic bridging ligands, the coordination geometry at the pseudotetrahedral centers and other more subtle effects. With flexible ligands the specific conformation drives the distance and orientation of the donor groups and thus modifies the degree of interpenetration, as shown by the rather regular trend observed for **1**–**3**. However, the reasons for such different conformations of the ddn ligands are not clear.

The second point of interest is the topology of interpenetration. As previously outlined,<sup>[5, 6]</sup> there is a dominant mode of interpenetration for *n* identical diamondoid nets. This is shown in Figure 5 (left) for a twofold interpenetrated diamondoid net. The typical feature that characterizes this interpenetration mode is that the nodes of all the independent nets are equally spaced along one of the "ideal" twofold axes of the adamantanoid units.<sup>[5]</sup> Each individual net is translated along this direction by  $1/n$  of the cage height. One can also observe that any pseudopolyhedral adamantanoid cage, delimited by four cyclohexane-like windows (in chair conformation), contains just one node for each of the other independent networks, and that each of the four rods starting from this node threads one of the four windows of the host cage.<sup>[16]</sup> Other frequently observed features can also be listed: a) this mode generates large channels of "ideal" square section that run parallel to the direction of interpenetration and usually contain the anions (anionic channels, see Figure 5, right); b) the adamantanoid cages are stretched in the

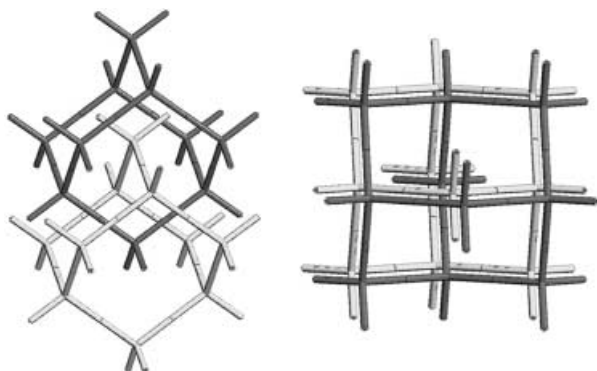


Figure 5. Schematic views of two normally interpenetrated diamondoid nets (left) and of the anionic channels (right).

direction of interpenetration and, moreover, c) this direction corresponds to the shortest crystallographic axis.

Almost all known  $n$ -fold interpenetrated diamondoid networks display this topology, though not all the normally interpenetrated diamondoid nets also show all the above-mentioned minor features. For instance, compound **1** conforms to all the above points, while in compound **3** the adamantanoid cages are stretched in a direction that is not coincident with that of interpenetration.

Exceptions to this normal topological type are limited, to the best of our knowledge, to only six cases, which include, besides the [4+4] mode of compounds **2a**, **2b**, and  $[\text{Ag}(3,3'\text{-dcpa})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ , the three examples shown schematically in Figure 6.

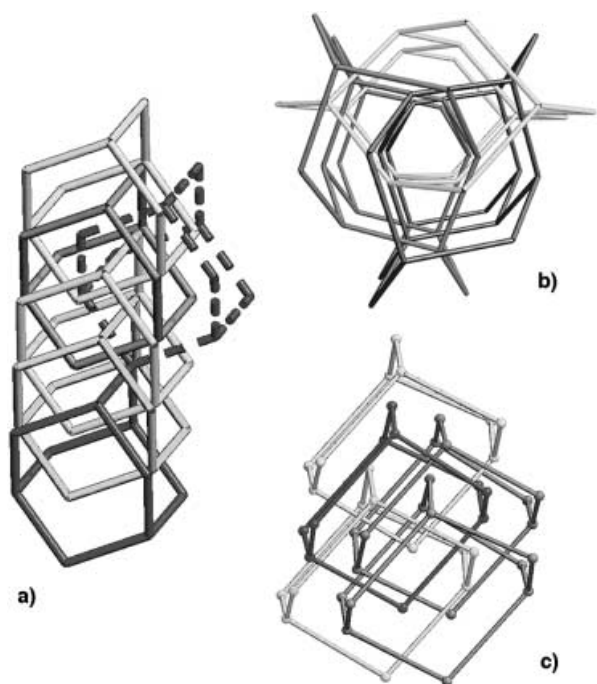


Figure 6. Schematic representations of three cases of unusual interpenetration in diamondoid networks. a) Fivefold interpenetrated adamantane-1,3,5,7-tetracarboxylic acid.<sup>[17]</sup> The dashed cage shows catenation with all the other nets. b) Threefold interpenetrated  $[\text{Cu}(2,7\text{-diazapyrene})_2]\text{PF}_6$ .<sup>[18]</sup> The view is approximately down the threefold cubic axis. c) Fivefold interpenetrated  $\beta\text{-}[\text{Cu}(\text{dca})(\text{bpe})]$ .<sup>[20]</sup> The view shows a possible way in which the other four cages can catenate the central cage.

To achieve a certain degree of rationalization we can consider a set of  $n$  identical diamondoid nets with identical cages and nodes. These independent nets can be related by a translation, by a rotation or by a roto-translation. Translationally equivalent diamondoid nets are related by an interpenetration vector  $T_i$ . This is the shortest crystallographic vector that when applied  $n$  times to one net generates the whole interpenetrated array. The vector  $T_i$  can span different crystallographic directions, but when its orientation coincides with one of the “ideal” twofold axes of the adamantanoid cage, the normal interpenetration mode results as a particular case of translational equivalence.

Unusual modes of interpenetration within translationally equivalent diamondoid nets are present in the fivefold interpenetrated adamantane-1,3,5,7-tetracarboxylic acid (Figure 6a), well described by Ermer,<sup>[17]</sup> but also in the eightfold [4+4] interpenetrated **2a**, **2b** and  $[\text{Ag}(3,3'\text{-dcpa})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ . Figure 7 shows two alternative ways of representing the

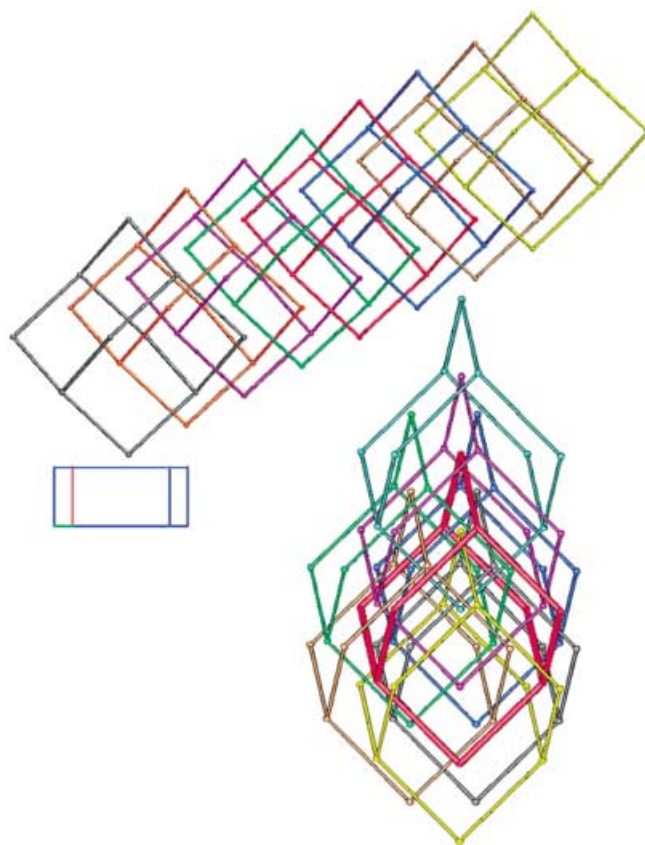


Figure 7. Two alternative representations of the eightfold interpenetration in **2b**: eight translationally equivalent cages, generated by repeated application of the interpenetration vector  $T_i = a/2 + b/2$  (top); a possible way in which the other seven cages can catenate the central cage (bottom).

interpenetration in these species to that illustrated in Figure 3b: the top diagram shows (for **2b**) that the 8 nets are translationally equivalent and are generated by a unique interpenetration vector  $T_i (= a/2 + b/2)$ . Moreover, the bottom diagram of the same figure illustrates a possible way to catenate to a single cage of a net one cage for each of the other seven nets.

We are aware of a single example of rotationally equivalent interpenetrated diamondoid nets, namely, the threefold interpenetrated  $[\text{Cu}(2,7\text{-diazapyrene})_2]\text{PF}_6$ ,<sup>[18]</sup> in which the three nets are related by rotation about the threefold axis of the cubic lattice, as shown schematically in Figure 6b. No example of roto-translational equivalence has been reported.<sup>[19]</sup>

The last case of unusual interpenetration (Figure 6c) is a fivefold interpenetrated structure recently described by Batten et al.<sup>[20, 6]</sup> This is a different situation that arises essentially from the fact that the individual networks contain nonidentical adjacent adamantanoid cages that show rather different geometry and orientation. Although the five independent nets are translationally equivalent ( $T_i = c = 14.64 \text{ \AA}$ ), the presence of different cages that cannot have a common normal interpenetration axis results in this unusual interpenetration mode.

The discussion here presented can be considered a rather naive attempt to classify the different modes of interpenetration for diamondoid nets, but surely the topology of these interpenetration phenomena should be based on a more rigorous mathematical background.<sup>[21]</sup> First, a correct definition of what makes two interpenetration modes really different (especially for 3D networks) and criteria for recognizing the difference are needed. For instance, one can suggest that: “two interpenetration modes of  $n$  networks of identical topology are different when the mutual transformation requires the breaking and reforming of links”. Assessment of the correctness of this statement and its application to real or hypothetical cases is left to discussions within the scientific community and to future work.

## Experimental Section

**Materials:** All reagents and solvents employed were commercially available high-purity materials (Aldrich Chemicals) and were 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 at room temperature by treating solutions of the silver salts in ethanol ( $\text{AgClO}_4$ ,  $\text{AgPF}_6$ ,  $\text{AgAsF}_6$ ) or water ( $\text{AgNO}_3$ ) with ethanolic solutions of ddn in the molar ratio 1:2. For example,  $[\text{Ag}(\text{ddn})_2]\text{PF}_6$  was obtained by layering an ethanolic solution (4 mL) of ddn (0.024 mL, 0.182 mmol) on a solution of  $\text{AgPF}_6$  (0.023 g, 0.091 mmol) in ethanol (4 mL). The mixtures were left for 10–15 d in the dark and then allowed to concentrate by slow evaporation in air. In the case of  $\text{AgNO}_3$  the mixture was kept at  $4^\circ\text{C}$  because the crystals melt at room temperature. The crystals of all products were recovered in good yield by filtration and washed with EtOH. All the products are low-melting solids, air- and light-stable for long times when kept at low temperature. Elemental analyses:  $[\text{Ag}(\text{ddn})_2]\text{NO}_3$  (**1**): calcd (%) for  $\text{C}_{24}\text{H}_{40}\text{AgN}_3\text{O}_3$  (554.48): C 51.99, H 7.27, N 12.63; found: C 52.01, H 7.25, N 12.53.  $[\text{Ag}(\text{ddn})_2]\text{PF}_6$  (**2a**): calcd (%) for  $\text{C}_{24}\text{H}_{40}\text{AgF}_6\text{N}_4\text{P}$  (637.44): C 45.22, H 6.32, N 8.79; found: C 45.35, H 6.23, N 8.68.  $[\text{Ag}(\text{ddn})_2]\text{AsF}_6$  (**2b**): calcd (%) for  $\text{C}_{24}\text{H}_{40}\text{AgAsF}_6\text{N}_4$  (681.39): C 42.31, H 5.92, N 8.22; found: C 42.27, H 5.82, N 8.15.  $[\text{Ag}(\text{ddn})_2]\text{ClO}_4$  (**3**): calcd (%) for  $\text{C}_{24}\text{H}_{40}\text{AgClN}_4\text{O}_4$  (591.92): C 48.70, H 6.81, N 9.47; found: C 48.82, H 6.75, N 9.33.

**Crystallography:** Crystal data are reported in Table 1. Data were collected on a Bruker SMART-CCD diffractometer at 233 K for **1** and at 293 K for **3** by the  $\omega$ -scan method within the ranges  $2 < \theta < 30^\circ$  (**1**) and  $2 < \theta < 28^\circ$  (**3**). Data for **2a** and **2b** were collected at 293 K on an Enraf-Nonius CAD4 by the  $\omega$ -scan method within the ranges  $3 < \theta < 24^\circ$  (**2a**) and  $3 < \theta < 25^\circ$  (**2b**). Empirical absorption corrections (SADABS)<sup>[22]</sup> were applied for **1** and **3**, and  $\psi$  scans for **2a** and **2b**. The structures were solved by direct methods (SIR97)<sup>[23]</sup> and refined by full-matrix least-squares on  $F^2$  (SHELX-97).<sup>[24]</sup>

Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Disordered nitrate anion was found in **1**, and a suitable 50/50 model was refined. The low-quality data for compound **3** due to weak diffraction of small needle-like crystals required the use of constraints on the geometry of the ligands, and this resulted in relatively high agreement factors. All the diagrams were plotted the SCHAKAL99 program.<sup>[25]</sup> CCDC-169567 (**1**), CCDC-169568 (**2a**), CCDC-169569 (**2b**), and CCDC-169570 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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