

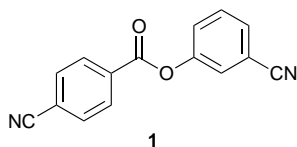
Crystallization of 3-cyanophenyl 4-cyanobenzoate with AgSbF_6 : a polar coordination network based on the crisscrossing of intertwined helices

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Crystallization of 3-cyanophenyl 4-cyanobenzoate **1** with AgSbF_6 yields the non-centrosymmetric, fourfold interpenetrated grid structure $[\text{Ag}(\mathbf{1})_2]\text{SbF}_6$ **2** through the crisscrossing of two-dimensional sheets.

The construction of self-assembled materials through metal coordination is an area of research that has grown tremendously in recent years.¹ The challenge that faces chemists working in this field is to identify packing trends that may allow for the rational design of functional materials. In this vein, we developed a packing model for interpenetrated diamondoid networks that was applied with success to our structures and those in the literature.² Also, many interesting structural studies on other coordination networks have been put forth,³ and some have yielded materials exhibiting novel properties.⁴ In order to observe packing trends such that coordination network topology may be better anticipated, systematic structural studies should continue to elucidate the role of variables such as counterion and ligand structure. In time, such studies may allow for the rational construction of materials exhibiting catalytic or non-linear optical activity. In continuing towards this goal, we report a novel, non-centrosymmetric coordination network based on 3-cyanophenyl 4-cyanobenzoate **1**. Included here is a description of this structure that accounts for its packing in a polar space group.



3-Cyanophenyl 4-cyanobenzoate **1** was prepared in 92% yield by reaction of 3-cyanophenol (1.0 equiv.) and 4-cyanobenzoyl chloride (1.0 equiv.) in CH_2Cl_2 at room temperature in the presence of DMAP (0.1 equiv.) and NEt_3 (2.4 equiv.). Crystallization of ligand **1** (1.0 equiv.) with AgSbF_6 (1.1 equiv.) was achieved by heating and slow cooling from toluene in a programmable oven. The temperature program involved heating from room temperature to 100 °C at a rate of 20 °C h^{-1} , holding at 100 °C for 2 h, and cooling to ambient temperature at a rate of 1.2 °C h^{-1} . Colorless columnar crystals of the complex $[\text{Ag}(\mathbf{1})_2]\text{SbF}_6$ **2** were obtained and one was selected for X-ray analysis.† The resulting structure crystallizes in the non-centrosymmetric, orthorhombic space group $Ccc2$ and is composed of crisscrossing sheets that form an infinite grid.

In complex **2**, silver(I) adopts a distorted tetrahedral geometry coordinated by four nitrile nitrogen atoms of ligand **1**. The metal ion bonds to nitrile nitrogens of two cyanobenzoyl rings and two cyanophenyl rings. N–Ag–N bond angles about silver(I) range from 100.4(3) to 130.1(4)°. The SbF_6^- ions do not coordinate to silver(I) and are disordered over two sites, each of which is half-occupied. The shortest $\text{Ag}\cdots\text{F}$ separation is 5.30 Å.

The sheet topology of complex **2** is shown in Fig. 1. Within a sheet, the Ag–Ag distance is 16.11 Å. Twofold interpenetration is observed to partially fill void space created

by a single sheet. This interpenetration may be viewed as the intertwining of two 2/1 helices (Fig. 1). Closest-packing in complex **2** is not achieved by twofold interpenetration. Rather, it results from further interpenetration of twofold interpenetrated sheets that propagate orthogonal to one another. Crisscrossing of orthogonal twofold sheets yields a fourfold interpenetrated grid structure overall (see Fig. 2). π – π Stacking is observed between molecules of ligand **1** that originate from orthogonal sheets [Fig. 2(b)]. Specifically, stacking occurs between cyanobenzoyl rings at a plane-to-plane distance of 3.35 Å and between cyanophenyl rings at a plane-to-plane distance of 3.44 Å.

Fourfold interpenetration in complex **2** can be viewed as arising from the crisscrossing of orthogonal pairs of 2/1 helices (see Fig. 3). Orthogonal sheets are mirror images of one another and, therefore, orthogonal helices are of opposite handedness [Fig. 3(b)]. The reason that this structure is polar is that helices of opposite handedness propagate orthogonal to one another. Therefore, the opposite twist sense associated with these helices does not cancel. Had helices of opposite handedness propagated

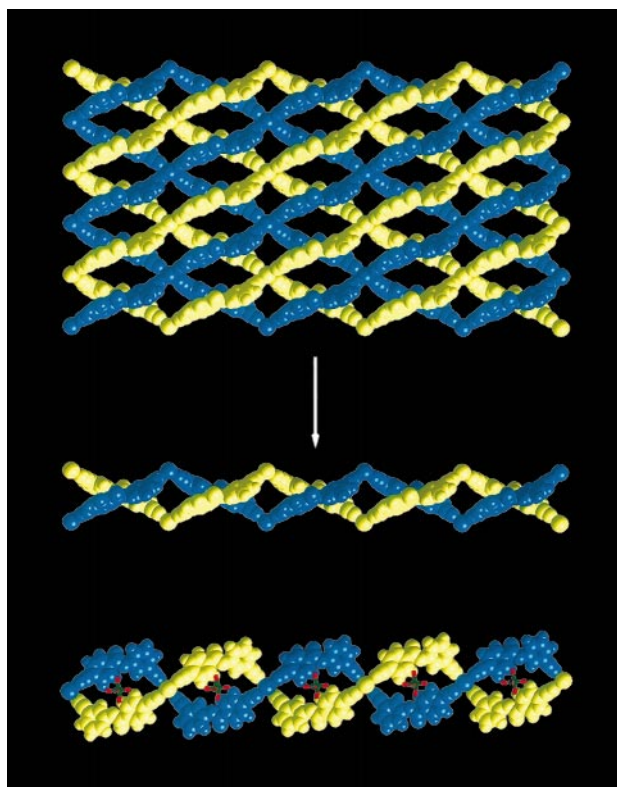


Fig. 1 Twofold interpenetrated sheets as a means to partially fill void space in the grid structure $[\text{Ag}(\mathbf{1})_2]\text{SbF}_6$ **2**. Interpenetration may be viewed as the intertwining of two 2/1 helices that are derived from the sheets as shown. The projection at the bottom is obtained by rotation of the middle figure by ca. 90° about the horizontal axis. The inclusion of counterions is shown in this projection (antimony is green and fluorine is red).

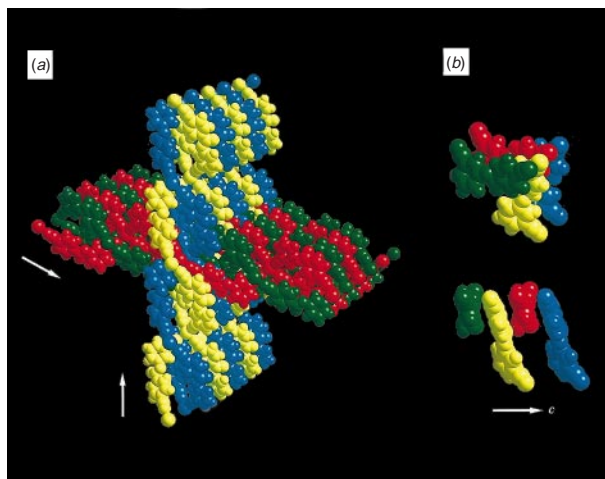


Fig. 2 (a) Fourfold interpenetration in $[\text{Ag}(\mathbf{1})_2]\text{SbF}_6$ **2** resulting from the crisscrossing of an orthogonal pair of twofold interpenetrated sheets. The blue and yellow networks constitute one set of twofold sheets and the red and green networks constitute the other. The arrows indicate the directions of propagation for the orthogonal sheets. Fourfold interpenetration is shown from left to right in a blue–green–yellow–red sequence where the orthogonal sheets cross. (b) Two views of π – π stacking of cyanobenzoyl rings of compound **1** as a result of fourfold interpenetration. Stacking occurs between ligands of orthogonal sheets along the polar c -axis. The direction of the c -axis is indicated for the bottom projection. The plane-to-plane distance for this stacking interaction is 3.35 Å.

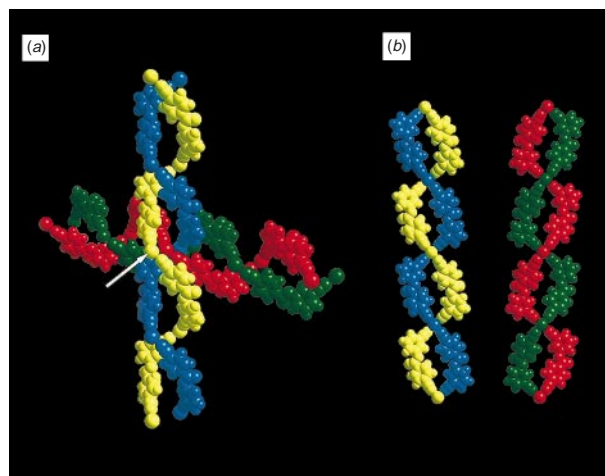


Fig. 3 The crisscrossing of orthogonal pairs of 2/1 helices in $[\text{Ag}(\mathbf{1})_2]\text{SbF}_6$ **2**. (a) Pairs of intertwined helices crisscross to afford fourfold interpenetration. Fourfold interpenetration is indicated by the arrow, which highlights a yellow–red–blue–green sequence of silver(I) ions (balls). Orthogonal helices are of opposite handedness. This point is clarified on the right. (b) Two orthogonal pairs of helices separated to reveal mirror symmetry. The blue and yellow helices are left-handed and the red and green helices are right-handed.

along the same direction, a non-polar structure could have formed. Such a packing of helices was observed in the sheet

structures $[\text{Ag}(3,3'\text{-dicyanodiphenylacetylene})_2]\text{XF}_6$ ($X = \text{P, As, Sb}$), which we reported recently.^{3a} These structures crystallized in space group $P\bar{1}$ and the topology is twofold interpenetrated sheets that are very similar to those shown in Fig. 1. However, for the 3,3'-dicyanodiphenylacetylene structures, closest-packing arises from the interdigitation of helices of opposite handedness^{3a} rather than the crisscrossing of such helices. As a result, left- and right-handed helices propagate along the same axis such that the opposite twist sense associated with these helices cancel out, and the structures are non-polar ($P\bar{1}$). The difference in the packing between the structure presented here and those of 3,3'-dicyanodiphenylacetylene may be a result of the *para*-nitrile group of ligand **1**, which changes the conformation of the 2/1 helix. This comparison demonstrates the value of viewing solid-state packing in terms of helices in order to better understand gross structure. An increased understanding of solid-state packing is essential if self-assembled materials possessing novel properties are to be designed.

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Footnotes and References

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† *Crystal data* for **2**: orthorhombic, space group $Ccc2$ (no. 37), $a = 18.9697(5)$, $b = 21.25190(10)$, $c = 7.5365(2)$ Å, $U = 3038.21(11)$ Å³, $D_c = 1.837$ g cm⁻³, $Z = 4$, $M = 840.09$, Mo-K α , L_p corrected, 9596 reflections collected at -75 °C, 3589 unique reflections. The structure was solved using SHELXS and was refined using SHELXTL. 3586 Reflections refined based on F_o^2 by full-matrix least squares; number of parameters = 237; $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.0570$ (for $F_o > 4\sigma$) and 0.1086 (for all data); $wR_2 = [\Sigma(w|F_o^2 - F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2} = 0.0804$ (for $F_o > 4\sigma$) and 0.1042 (for all data); GOF = 1.171. The space group choice was confirmed using the CALC MISSYM option of PLATON (A. L. Spek, *J. Appl. Crystallogr.*, 1988, **21**, 578) as no extra crystallographic symmetry was detected. CCDC 182/684.

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