

A novel polymeric Ag^I complex consisting of two three-dimensional networks which are enantiomeric and interpenetrating†

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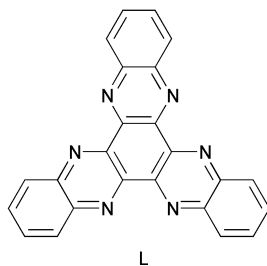
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One-pot reaction of AgNO₃ and a large aromatic bridging ligand, diquinoxalino[2,3-a:2',3'-c]phenazine, which has three bidentate coordination sites, afforded a Ag^I complex consisting of two independent three-dimensional (3D) networks which are enantiomeric and interpenetrating.

A major goal of the polymer-based approach to crystal engineering is to develop new robust materials with useful electronic, magnetic, electrochemical, optical or catalytic properties. Among various types of molecular-based frameworks, interpenetrating networks are of particular interest with regard to the topological types of 3D nets postulated by Wells.¹ Since the groups of Robson² and Ciani³ reported their first pioneering works on '3D racemates' using suitable metal ions and polydentate ligands, in which two enantiomeric interpenetrating networks are included, compounds bearing two or more metal chelating sites have often been used as connecting units for the generation of interpenetrating 3D networks.^{4–6}

In our effort to construct novel 3D coordination polymer networks, diquinoxalino[2,3-a:2',3'-c]phenazine (L) has at-



tracted our attention. This ligand is a nitrogenous aromatic compound with three bidentate sites, which was expected to provide a coordination network characterized by a delocalized π -electron system. We report here, the synthesis and X-ray crystal structure of a novel Ag^I complex⁷ **1** with L, consisting of an interpenetrating enantiomeric pair of nets.

Complex **1** was prepared in the dark by carefully layering a solution of AgNO₃ in MeCN on top of a solution of L in CH₂Cl₂. After *ca.* two weeks, yellow–orange crystals of **1** {(Ag₃L₂)(NO₃)₃·solvent} were isolated in *ca.* 90% yield. The structure of **1** was established by single-crystal X-ray diffraction.‡

Each Ag^I center in **1** acts as a two-connecting node by connecting two ligands of L. Interestingly, **1** exhibits twofold interpenetrating networks with the two-connected (Ag^I) and three-connected (L) nodes. A single cationic network of the

doubly interpenetrating networks is shown Fig. 1(a). The basic building block of the network contains distorted tetrahedral Ag^I atoms and two types of ligand L with B ligands parallel to the *xy*-plane [Fig. 1(a)]. The coordination geometry around each Ag^I center is not perfectly tetrahedral. A ligands in the building block make an interplanar angle of 100° with B ligands and arranged in a propeller fashion around them. These basic building blocks are linked by Ag^I atoms to form a 3D network. A ligands along the *z*-axis are connected by Ag^I atoms to form a one-dimensional threefold helical network [see the bold lines in Fig. 1(b)]. A crystallographic C₃ axis exists perpendicular to ligand B. Interestingly, these helices are interlinked with ligands

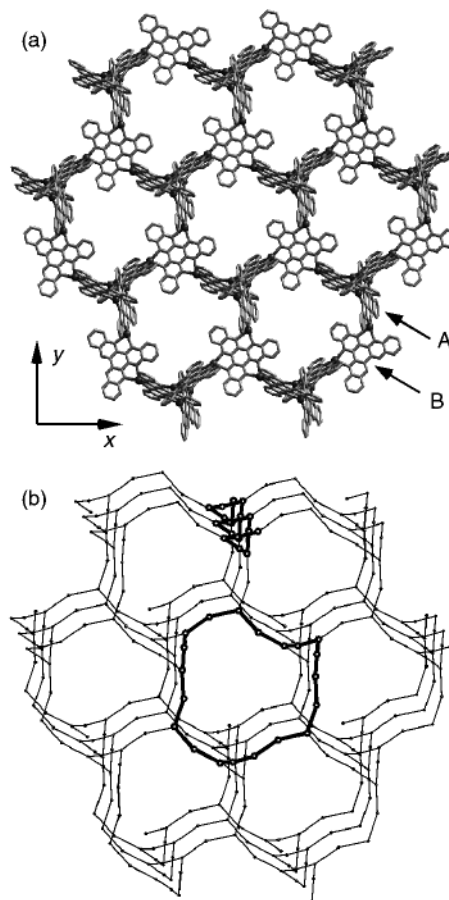


Fig. 1 Representations of (a) a single 3D network in complex **1**, where metal atoms are shown as spheres and (b) a schematic view of a single network with the ligands replaced by trigonal nodes; one of the 20-gons and a helix are highlighted by bold lines.

† Electronic supplementary information (ESI) available: experimental procedure for complex **1**. See <http://www.rsc.org/suppdata/cc/b0/b003183f/>

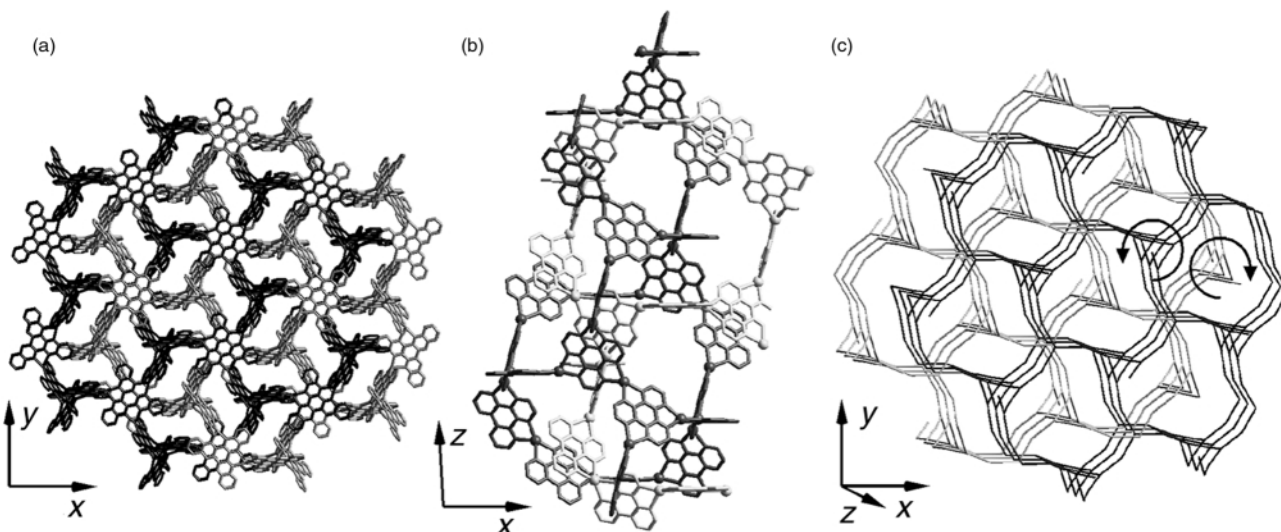


Fig. 2 Representations of (a) a top view of the doubly interpenetrating networks of **1**, where the two networks are colored black and gray, (b) a side view of the two interpenetrating networks of **1**, where the outer phenyl rings of the ligands are omitted for clarity and (c) a schematic view of the 3D nets in which the ligands are replaced by trigonal nodes. Note the difference in the handedness of the helical networks in each 3D net.

B *via* Ag^I atoms to form a 3D network with large channels. The shortest loop in the network is a 20-gon that is constituted of 10 Ag^I-atoms and 10 ligands [see the bold lines in Fig. 1(b)]. The structure can be regarded as a 3D network in which half of the nodes are replaced by three-fold helices, and is quite different from that of the Ag^I complex with Hat (1,4,5,8,9,12-hexaaza-triphenylene) which similarly has three bidentate sites but differs in the size of the π -plane. In the Hat complex, all the Ag^I centers are chelated by three Hat ligands to form an octahedral coordination environment.^{5a}

The extended structure of **1** reveals interesting twofold interpenetrating networks as shown in Fig. 2(a) and (b). These two interpenetrating networks are topologically equivalent but differ in the handedness of the threefold helices [see Fig. 2(c)], where the two arrows show the handedness of helices. Thus complex **1** contains an interpenetrating enantiomorphic pair of nets with a (10,3)-a type topology^{1a} consisting of Ag^I ions coordinated by nitrogenous aromatic ligands in a tetrahedral fashion. This type of interpenetration of 3D nets was referred to by Wells as 'a 3D racemate'.^{1a} The interactions observed between the two interpenetrating networks are aromatic edge-to-face interactions between A ligands in one network and adjacent B' ligands in the other, with no face-to-face interactions between B and B' ligands observed in the structure. Although the channels in one network are occupied by another network, there are still large vacant spaces between the two, corresponding to the 53% of crystal volume, which is filled by solvent molecules and the counter anions. However, some of the solvent molecules and counter ions were found to be disordered owing to the high symmetry of the network.

This study has revealed a one-pot, high-yield synthesis of a Ag^I complex consisting of doubly interpenetrating 3D networks with nitrogenous heterocyclic bridging ligands L. Furthermore, L has a large delocalized π -electron system which may allow facile d- π interactions between ligands and remote metal centers throughout extended 3D networks.

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Notes and references

‡ Reflection data were collected on a Bruker CCD SMART system with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $193 \pm 2 \text{ K}$. The structure was solved by direct methods using the SHELXTL program.⁸ Non-hydrogen atoms of the complex were refined with anisotropic thermal parameters. Refinement was done by full-matrix least squares on F^2 .

Crystal data for 1: $M = 1580.04$, crystal size $0.20 \times 0.15 \times 0.15 \text{ mm}$, trigonal, space group $R\bar{3}$, $a = b = 32.223(2)$, $c = 20.827(2) \text{ \AA}$, $V = 18728(2) \text{ \AA}^3$, $Z = 12$, $\mu = 1.258 \text{ mm}^{-1}$, $D_c = 1.681 \text{ g cm}^{-3}$, min./max. transmission = $0.8031/0.8468$, $1.22 < \theta < 27.93^\circ$, $R(R_w) = 0.0790(0.2077)$ for 9985 ($R_{\text{int}} = 0.1083$) independent reflections out of a total of 47197 reflections with $I > 2\sigma(I)$ and 506 parameters, and $R(R_w) = 0.1711(0.2417)$ for all the data. The goodness-of-fit on F^2 is 1.241, and the residual electron density (min./max.) is $-1.041/1.646e \text{ \AA}^{-3}$.

Yellow-orange crystals of Ag₃L₂(PF₆)₃·0.75CHCl₃·2.25CH₃CN were obtained using AgPF₆ in place of AgNO₃. This compound has the same 3D interpenetrating networks as compound **1**. Crystal data (at 223 K): trigonal, space group $R\bar{3}$, $a = b = 33.936(2)$, $c = 20.462(2) \text{ \AA}$, $V = 20407(1) \text{ \AA}^3$, $Z = 12$.

CCDC 182/1773. See <http://www.rsc.org/suppdata/cc/b0/b003183f/> for crystallographic files in .cif format.

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