JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

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An Exceptional 54-Fold Interpenetrated Coordination Polymer with 10^3-srs Network Topology

Hua Wu,[†,§] Jin Yang,[*,†] Zhong-Min Su,[†] Stuart R. Batten,[*,‡] and Jian-Fang Ma[*,†]

[†]Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

[‡]School of Chemistry, Monash University, Victorian 3800, Australia

[§]Heilongjiang Agricultural College of Vocational Technology, Jiamusi 154007, People's Republic of China

Supporting Information

ABSTRACT: Entanglement is one of the most important features of coordination polymer frameworks and has attracted considerable attention due to its aesthetic and topological interest. Among entangled systems, interpenetrating frameworks represent an intriguing subset; however, there are few examples of materials containing very high levels of interpenetration. In this work a coordination polymer with 10^3-**srs** topology, constructed from a star-like tridentate ligand, tri(4-imidazolylphenyl)amine, and Ag^I ions, has been hydrothermally synthesized. It contains a record 54 interpenetrating networks.

Metal ions linked by ligands into infinite arrays are generally referred to as coordination polymers.[1] This term was first used in the early 1960s,[2] but now remarkable potential applications such as gas storage, ion-exchange and catalysis have been shown for these materials.[3] Besides their functions, coordination polymer frameworks can also have great aesthetic appeal. Thus far, many structural types and entangled topological features unprecedented in the world of inorganic compounds and minerals have been observed in coordination polymer frameworks.[4]

Entangled arrays, as defined by Ciani et al., are one of the most important features of the coordination polymers and have attracted considerable attention due to their aesthetic and topological interest.[4a] Of particular interest are interpenetrating frameworks. These species can be regarded as infinite ordered polycatenanes and are characterized by the presence of two or more independent networks that cannot be separated in a topological sense without breaking of bonds.[4b] In the past decade, considerable effort has been invested in interpenetrating coordination polymer frameworks because of their unique advantages in enhancing stability, specific surface area, gas sorption, and molecular dynamics, as well as their general structural aesthetics.[5] However, although there are now an enormous number of reported cases of interpenetration, there are surprisingly few examples of very high degrees of interpenetration.[1d]

Usually the origin of interpenetration can be ascribed to the presence of large free voids in a single network.[6] As we know, long ligands will lead to larger voids that may result in high-fold interpenetrating structures. Thus, one effective way to increase the number of interpenetrating folds is to extend the length of the ligand sustaining the framework.[7] However, extending the length of the ligand may lead to difficulty in crystallization of the complex. Thus, the increase of ring size of the coordination frameworks to synthesize high-fold interpenetrating coordination polymer frameworks becomes a significant challenge.

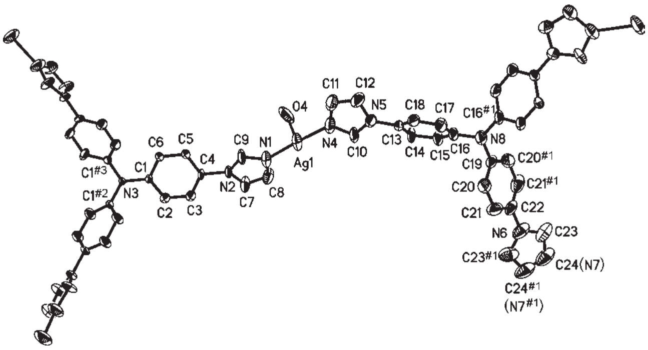


Figure 1. Coordination modes of Ag atoms and Tipa ligands. Symmetry codes: #1 = x, $1 - y$, $0.5 - z$; #2 = z, $x + 1$, $y - 1$; and #3 = $y - 1$, $z + 1$, x.

One strategy is to use metal ions which coordinate to only two polydentate ligands. The metal ion therefore acts only as a part of the spacer (rather than a node), leading to longer links between nodes and thus greater ring sizes. Based on this hypothesis, it would be possible to construct high-fold interpenetrating coordination polymer frameworks, in which each metal ion bridges only two polydentate ligands. Another strategy would be to target networks with 3-connecting nodes; all being equal (e.g., linker lengths), lower connectivity nets give more open frameworks. In this work we report the hydrothermal synthesis of the coordination polymer $[Ag_3(OH)(H_2O)_2(Tipa)_{2.5}][Mo_2O_7]\cdot 4.5H_2O$ (**1**; Tipa = tri(4-imidazolylphenyl)amine), which contains 3-connecting ligands and 2-connecting metal ions. Topologically it is composed of 54 interpenetrating 3D frameworks with the 10^3-**srs** topology.[8,9] This is the highest level of interpenetration reported to date.

The structure of **1** has one kind of Ag atom and two kinds of Tipa ligands (Figure 1). The silver is three-coordinated by two N atoms from two Tipa ligands and one O atom (this position is shared by H_2O and OH, with occupancies of 0.666 and 0.333, respectively). For one Tipa there is a 3-fold axis at the central N atom, and it coordinates to three Ag atoms through the three imidazole groups. For the other Tipa there is a 2-fold axis through the central N atom and one C atom (C19) bonded to the central N

Received: March 14, 2011
Published: July 05, 2011

dx.doi.org/10.1021/ja202303b | J. Am. Chem. Soc. 2011, 133, 11406–11409

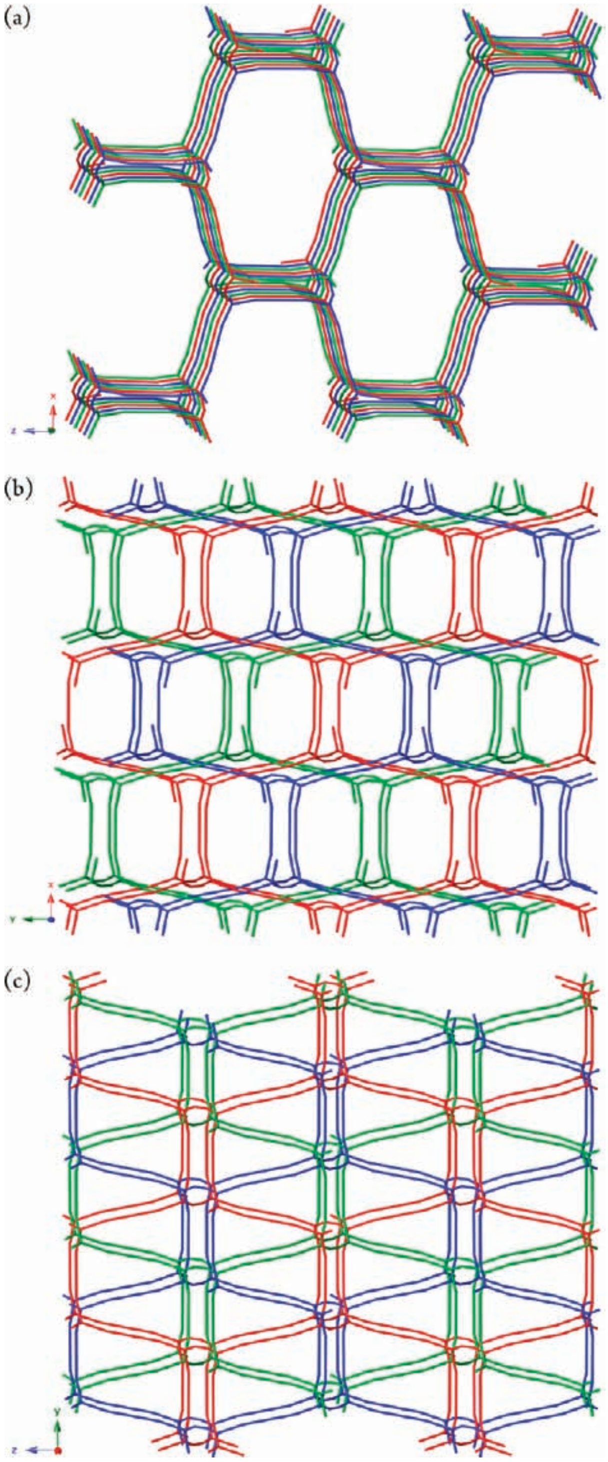


Figure 2. Three interpenetrating 10^3-**srs** nets viewed slightly offset from the three unit cell axes. Note the identical chirality of all the distorted 4-fold helices.

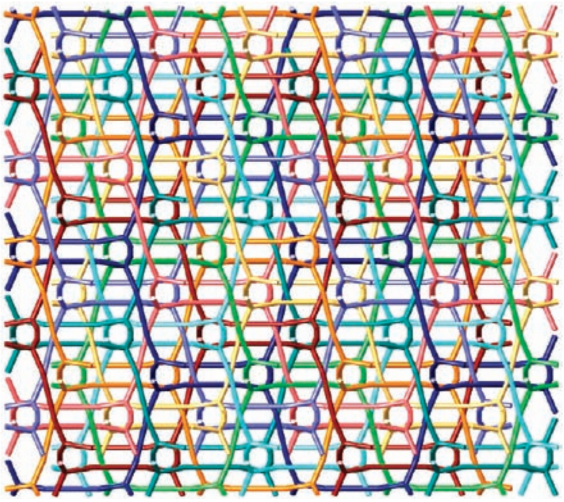


Figure 3. Interpenetration of 27 nets (or nine trios) of the same chirality.

atom, and the ligand coordinates to only two Ag atoms through two imidazole groups (the 4-imidazolylphenyl arm lying across the 2-fold axis does not coordinate).

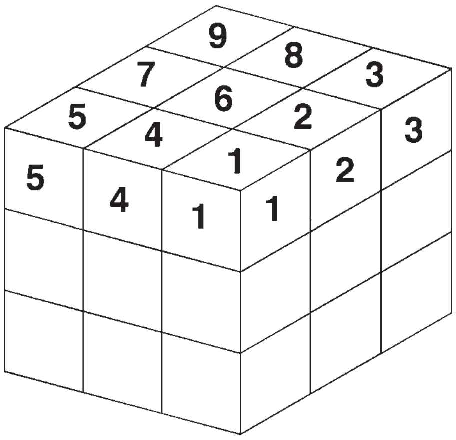
The frameworks of **1** thus contain one unique Ag atom, and the Ag atoms are interconnected by two different ligand bridges, one 2-connecting and one 3-connecting. As each Ag only coordinates to two ligands, the network can be simplified as a 3-connected net, with the nodes being assigned as the central N atoms of the 3-connecting ligands and the Ag atoms and 2-connecting ligands acting simply as links. This gives a network in which the links between the nodes are N3-R-Ag-R-N8-R-Ag-R-N3 (R = 4-imidazolylphenyl); this link is 36.85 Å in length.

Using this simplification, the structure consists of 54 interpenetrating nets with the 3-connected 10^3-**srs** topology.[10] All nets are crystallographically identical. Three of the interpenetrating nets are shown in Figure 2. Note the presence of (distorted) 4-fold helices: in the 10^3-**srs** net there are three sets of helices which run in three mutually perpendicular directions. In the most symmetrical form of the net, and indeed in the structure discussed here, these helices run along the directions of the three unit cell axes. Furthermore, all helices are of the same handedness, and thus the net is chiral. As clearly evident in the diagrams, the 4-fold helices in this structure are quite distorted: rather than having a square cross-section, as found in the ideal net, the helices are distinctly rectangular.

The three interpenetrating 10^3-**srs** nets in Figure 2 all have the same chirality, and they interpenetrate such that the 4-fold helices share a common axis along one direction (Figure 2a) but are offset in the other two directions (Figure 2b,c). Thus, each net is just a translation of another of the nets along the direction of that first 4-fold helix. To simplify our understanding of the interpenetration, we shall view the structure end-on to the helices, such that the nets occur in sets of three eclipsed nets (trios), as show in Figure 2a, and appear to be a single net from this angle. The channels and open spaces apparent in Figure 2a are large enough to accommodate eight other network trios of the same chirality (Figure 3). Thus, there are nine interpenetrating trios, or 27 nets in total.

Of course the three nets in a trio which appear to be eclipsed in one direction are offset when viewed along the directions of the other 4-fold helices (as shown in Figure 2); each of these nets is then eclipsed with nets from other trios, resulting in the same arrangement as before, but with individual nets swapping roles. One way to understand this arrangement is to consider a 3×3×3 cube (Scheme 1), with each of the 27 cells in the cube representing one of the interpenetrating networks. When the cube is viewed along an axis (i.e., perpendicular to a face), there appear to only be nine cells, with each cell eclipsing two others (like the nine apparent nets in Figure 3). For example, cell 1 eclipses cells 2 and 3 when viewed from the left of the scheme. When viewed along a different axis (e.g.,

Scheme 1. Schematic Drawing of the 3×3×3 Cube



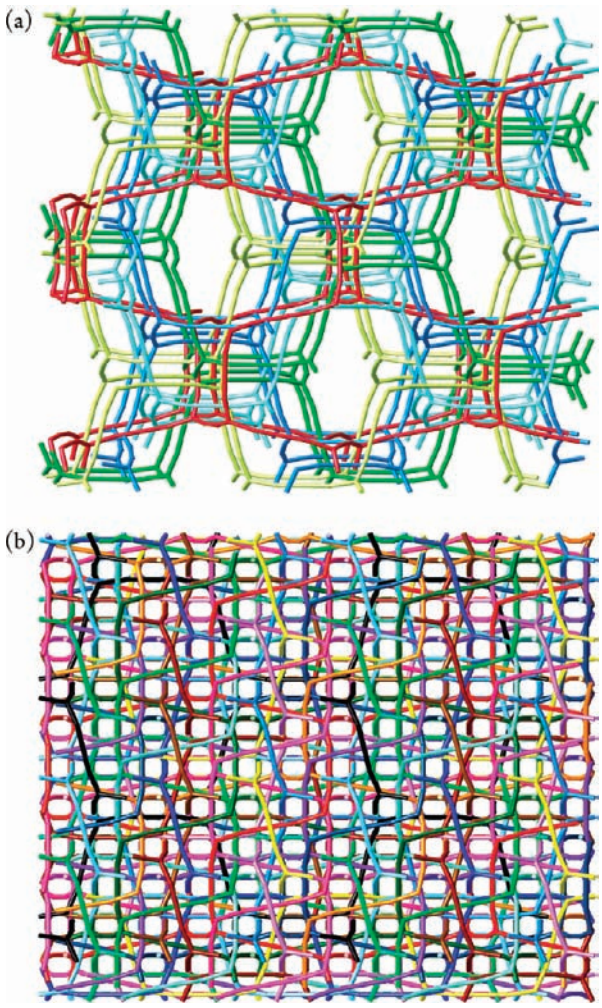


Figure 4. (a) Interpenetration of four nets of one handedness (green/blue nets) with one of the opposite handedness (red). (b) Interpenetration of all 54 networks.

from the right of the scheme), there again appears to be only nine cells, but in this instance the identity of the eclipsed cells is different: cell 1 now eclipses cells 4 and 5, cell 2 eclipses cells 6 and 7, and so forth. Thus, the translation of one net along the three different directions of the 4-fold helices (or combinations of translations in different directions) generates the 27 interpenetrating networks (just as translation of an individual cell in the 3×3×3 (=27) cube generates 27 cells in total).

The other 27 interpenetrating networks show the same relationship between the individual nets, but the two sets of nets are related by a *d*-glide (the space group is $I\bar{4}3d$), and thus they have the opposite chirality (Figure S4). Three nets of one chirality and one of the opposite chirality are shown in Figure 4a. Note that not only does the chirality change but also the direction of the long axis of the rectangular cross-section of the distorted 4-fold helices. The two sets of 27 interpenetrating nets generate the overall 54-fold interpenetration (Figure 4b). The interpenetration belongs to the rare class IIIb.[11] To date, only three examples of this class have been reported.[12,13]

This level of interpenetration of **1** is remarkable, and indeed unprecedented. The highest number of interpenetrating nets previously reported is the 18 interpenetrating nets in the hydrogen-bonded structure of polymorph I of the 2:3 co-crystal of trimesic acid and 1,2-bis(4-pyridyl)ethane.[13] Notably, the networks in this structure also display the 10^3-**srs** topology. In fact, the interpenetration topology is similar: two sets of nine nets of opposite chirality, with each set generated by the translation of one net along two of the three 4-fold helix axes but not along the third (giving a 3×3×1 = 9 “cube” analogy rather than a 3×3×3 = 27 one).

It is worth noting that the compounds contains long, weak Mo—O···Ag interactions of 2.87 Å. If these internetwork interactions are taken into account, the topological description becomes one of 2-fold interpenetration of a self-penetrated trinodal 3-connected net with 10^3 topology (vertex symbol [10.10.10][10.10.10][10.10.10]).

In conclusion, a coordination polymer network has been synthesized which contains an unprecedented 54 interpenetrating networks, providing a possible template for future very highly interpenetrated structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data, experimental details, XRPD patterns, TG analysis, TOPOS analysis, and an extra figure of the interpenetration. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

yangjinnenu@yahoo.com.cn; stuart.batten@monash.edu; jianfangma@yahoo.com.cn

■ ACKNOWLEDGMENT

We thank Program for Changjiang Scholars and Innovative Research Teams in Chinese Universities, the National Natural Science Foundation of China (Grant No. 21071028, 21001023), the Science Foundation of Jilin Province (20090137, 20100109), the Fundamental Research Funds for the Central Universities, the Specialized Research Fund for the Doctoral Program of Higher Education, the Training Fund of NENU's Scientific Innovation Project, and the China Postdoctoral Science Foundation (20080431050 and 200801352) for support.

■ REFERENCES

(1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (c) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.(d) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; Royal Society of Chemistry: Cambridge, 2009. (e) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1991**, 445–447.

(2) Bailar, J. C., Jr. *Prep. Inorg. React.* **1964**, *1*, 1.

(3) (a) Shimomura, S.; Higuchi, M.; Matsuda, R; Yoneda, K.; Hijikata, Y.; Kubota, Y.; Mita, Y.; Kim, J.; Takata, M.; Kitagawa, S. *Nat. Chem.* **2010**, *2*, 633–637. (b) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466–1496. (c) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schroeder, M. *Coord. Chem. Rev.* **2001**, *222*, 155–192. (d) Wang, B.; Côté, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2008**, *453*, 207–211.

(4) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247–289.(b) Batten, S. R.; Robson, R. In *Molecular Catenanes, Rotaxanes and Knots: A Journey Through the World of Molecular Topology*; Sauvage, J. P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999; pp 77—105.

(5) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490–2509.

(6) (a) Yang, J.; Ma, J.-F.; Batten, S. R.; Su, Z.-M. *Chem. Commun.* **2008**, 2233–2235. (b) Wu, H.; Liu, H.-Y.; Liu, Y.-Y.; Yang, J.; Liu, B.; Ma, J.-F. *Chem. Commun.* **2011**, *47*, 1818–1820.

(7) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494.

(8) Pale yellow crystals of $[Ag_3(OH)(H_2O)_2(Tipa)_{2.5}][Mo_2O_7]\cdot 4.5H_2O$ (**1**) were obtained by heating a mixture of Tipa (0.044 g, 0.1 mmol), $AgNO_3$ (0.051 g, 0.3 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.0618 g, 0.05 mmol), and H_2O (10 mL) under hydrothermal conditions at 170 °C for 72 h (yield 15% based on Tipa). Anal. Calcd for $C_{67.5}H_{65.5}Ag_3Mo_2N_{17.5}O_{14.5}$: C, 43.37; H, 3.53; N, 13.11. Found: C, 43.18; H, 3.46; N, 13.30. IR (KBr, cm^{-1}): 3441 (m), 3126 (w), 2926 (w), 1631 (w), 1516 (s), 1286 (m), 1245 (m), 1123 (m), 1060 (s), 961 (w), 876 (m), 826 (m), 788 (m), 651 (m), 536 (m).

(9) Crystal data for **1**: cubic, space group $I\bar{4}3d$, $M_r = 1869.36$, $a = 30.5678(1)$ Å, $V = 28562.3(2)$ Å^3, $Z = 16$, $\mu = 9.935$ mm^{-1}, $D_c = 1.739$ Mg m^{-3}, $F(000) = 14\,944$, $T = 293(2)$ K, 35 133 reflections collected, 4152 unique with $R_{int} = 0.0965$ after SQUEEZE, $R1 = 0.0695$, $wR2 = 0.1830$ ($I > 2\sigma(I)$), and GOF = 1.021.

(10) (a) Hyde, S. T.; O'Keeffe, M.; Proserpio, D. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7996–8000. (b) Blatov, V. A.; O'Keeffe, M.; Proserpio, D. M. *CrystEngComm* **2009**, *12*, 44–48.

(11) (a) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377–395. (b) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Solid State Chem.* **2005**, *178*, 2452–2474.

(12) (a) Murphy, D. L.; Malachowski, M. R.; Campana, C. F.; Cohen, S. M. *Chem. Commun.* **2005**, 5506–5508. (b) Lysenko, A. B.; Govor, E. V.; Krautscheid, H.; Domasevitch, K. V. *Dalton Trans.* **2006**, 3772–3776.

(13) Shattock, T. R.; Vishweshwar, P.; Wang, Z.; Zaworotko, M. J. *Cryst. Growth Des.* **2005**, *5*, 2046–2049.