Entanglement of individual coordination polymers having helicates as building intermediates†

Qiaozhen Sun,a Meilin Wei,a Yan Bai,a Cheng He,a,b Qingjin Menga and Chunying Duana,b*

Received 24th April 2007, Accepted 6th July 2007
First published as an Advance Article on the web 31st July 2007
DOI: 10.1039/b706183h

A series of Ag(i) coordination compounds, from one-dimensional chains to 3D porous frameworks, were achieved from N,N′-bis[1-(2-pyrazinyl)ethylidene]benzil dihydrazone, L, via self-assembly, using helicates as effective secondary building units. Compound 2 [{(Ag2.75L)(NO3)2.75}] was comprised of two opposite-handed 3D frameworks formed by connecting the 4, helical chains into (103-b) nets. The pairs of the racemic 3D frameworks were connected through additional silver(i) centers and entangled each other forming a racemic 3D net. Compound 3 [{(Ag13L2)(BF4)10(H2O)12}] was comprised of a 3D framework that was constructed from double-helical building intermediates Ag2L2 with one-dimensional infinite chains being threaded into the large voids of a 3D framework to form a weave structure. The ladder-like chains in compound 4 [{(Ag5L)(ClO4)3(CH3OH)2(CH3CN)}] were formed by the addition of excess NaClO4 into the methanol solution containing AgNO3 and the ligand L, and the zigzag chains in compound 5 [{(Ag2L)(ClO4)3(CH3CN)2}] were constructed by the addition of excess NaClO4 into an acetonitrile solution containing AgNO3 and the ligand L.

Introduction

Metal–organic frameworks, which are often accessible by self-assembly under exceedingly mild conditions, are particularly attractive not only for their interesting properties and potential applications as functional solid materials, but also for their intriguing, often complicated architectures and topologies. Great effort has been expended to explore the structural diversity and fascinating topologies of these materials which sometimes are analogues of naturally occurring structures and other times represent entirely new structural architectures. Particular attention has recently been turning to a burgeoning family described as polythreaded coordination networks, which can be considered as periodic analogues of the molecular rotaxanes or pseudo-rotaxanes.

On the other hand, assemblies of Ag(i) coordination polymers have attracted attention for a long time due to their interesting structure and potential physical and chemical functions. The variable coordination number of Ag(i) and various supramolecular forces in the Ag(i) compounds such as metal–ligand, metal–metal and metal–anion interactions, increase the possibility of the compounds forming complicated geometries, which also stimulate the study of polythreaded coordination networks. Taking inspiration from our previous works on Ag(i) coordination polymers, herein we report a new three-dimensional racemate framework that was constructed from double-helical building intermediates Ag2L2 with the two opposite-handed 3D frameworks being connected argentophilically, and another new entangled net containing one 3D framework and one 1D infinite chain. Both of the compounds were assembled from the ligand L, N,N′-bis[1-(2-pyrazinyl)ethylidene]benzil dihydrazone (Scheme 1). As can be expected, the special conformation of the ligand provided an opportunity to form helical structures, and the additional coordination donors of the pyrazine moieties could link the helical species into the three-dimensional framework to complete the special entanglement.

Experimental

Materials and measurements

All chemicals used were of reagent grade, or better, obtained from commercial sources and used without further purification except that the solvents used for physical measurements were purified by classical methods. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 analyzer. The ligand L was prepared according to literature methods.

Compound 2 [{(Ag2.75L)(NO3)2.75}]. The ligand L (0.1 mmol, 0.046 g) and AgNO3 (0.5 mmol, 0.085 g) were mixed in methanol and acetonitrile (20 ml : 1 : 1). After refluxing for 1 h, the yellow solution was filtered and evaporated in air at room temperature. One month later orange block crystals were obtained. Yield: 50%.
Compound 3 [(Ag₈L₈)(BF₄)₁₃(H₂O)₁₂]. The ligand L (0.2 mmol, 0.089 g) and AgNO₃ (0.3 mmol, 0.051 g) were mixed in methanol (40 mL). After refluxing for 2 h the yellow solution obtained was then added to a CH₃CN solution (5 mL) of NaBF₄ (0.3 mmol); yellow crystalline solids were filtered out and dried under vacuum. Yield: 76%. IR (KBr, cm⁻¹): 3552 m, 3062 m, 1617 m, 1565 m, 1467 m, 1445 m, 1403 s, 1370 s, 1305 m, 1255 m, 1168 s, 1057 vs, 851 s, 777 s, 755 s, 693 s, 604 m, 521 m, 3062 m, 1617 m, 1565 m, 1467 m, 1445 m, 1403 s, 1370 s, 1305 m, 1255 m, 1168 s, 1057 vs, 851 s, 777 s, 755 s, 693 s, 604 m, 521 m, 421 m. Anal. calcd (%) for Ag₁₃C₂₀₈H₂₀Oₙ₆N₄O₁₂B₁₃F₅₂: C, 39.5; H, 12.55 m, 1168 s, 1057 vs, 851 s, 777 s, 755 s, 693 s, 604 m, 521 m, 421 m. Crystals suitable for X-ray diffraction determination were obtained by evaporating a CH₃CN–MeOH (1 : 1) solution in air at room temperature.

Compound 4 [(Ag₃L₂)(ClO₃)₃(CH₃OH)₂(CH₃CN)]. Analogously to the method for the preparation of complex 3, NaClO₃·H₂O was used in place of NaBF₄ and solids were obtained in 76% yield. IR (KBr, cm⁻¹): 3456 m, 3060 m, 1608 s, 1564 m, 1469 m, 1406 s, 1384 vs, 1287 m, 1252 m, 1175 s, 1111 m, 1024 s, 849 m, 762 m, 693 s, 605 m. Anal. calcd (%) for Ag₃C₅₆H₅₅N₁₇O₧₁Cl₃: C, 42.8; H, 3.5; N, 15.1. Found: C, 42.7; H, 3.3; N, 15.2.

Compound 5 [(Ag₂L₅)(ClO₃)₃(CH₃CN)]. Analogously to the method for the preparation of complex 3, NaClO₃·H₂O was used in place of NaBF₄ and solids were obtained in 76% yield. IR (KBr, cm⁻¹): 3552 m, 3063 m, 1597 m, 1569 m, 1473 m, 1445 m, 1402 m, 1370 m, 1320 m, 1243 m, 1176 s, 1090 vs, 1030 s, 852 m, 777 m, 755 m, 692 m, 623 s, 603 m, 483 s, 423 m. Anal. calcd (%) for Ag₃C₅₆H₅₅N₁₇O₧₁Cl₃: C, 42.8; H, 3.5; N, 15.1. Found: C, 42.7; H, 3.3; N, 15.2.

Crystallography

X-Ray intensity data were measured at 300 K on a Bruker SMART APEX CCD-based diffractometer (Mo-Kα radiation, λ = 0.71073 Å) using the SMART and SAINT programs. Raw data frame integration and Lp corrections were performed with SAINT.* Final unit cell parameters were determined by least-squares refinement of strong reflections for the respective compounds 2–5. The structures were solved by direct methods and refined on F² by full-matrix least-squares methods with SHELXTL version 5.1. All of the non-hydrogen atoms except the disordered solvent molecules were refined with anisotropic thermal displacement coefficients. Hydrogen atoms were located geometrically, whereas those of solvent molecules were found on Fourier difference maps, and all of the hydrogen atoms were refined in a riding model. The methyl H atoms at C6 in compound 2, at C6, C22, C32, C48, C58, C74, C84, C100 in compound 3, at C21, C36, C49 in compound 4, and at C6 in compound 5, were generated using HFIX 33 and that their orientation may not be totally accurate. To assist the refinement of compounds 2, 4 and 5, several restraints were applied: (1) the geometrical constraints of idealized regular polygons and polyhedrons for the anions were used; (2) thermal parameters on adjacent atoms in solvents and disordered moieties were restrained to be similar.

For compound 2, the additional silver ions Ag(3) and Ag(4) were refined as disordered with the site occupancy factors (s.o.f.) being fixed at suitable values for consistency with the elemental analysis data as well as giving suitable thermal parameters. The nitrate anions were also refined as disordered with the s.o.f. of the two pairs of oxygen atoms attached to nitrogen atom N(5) being fixed at 0.5, and these atoms in the other two dependent anions being fixed at 0.25. For compound 3, the lattice water molecules were refined as disordered with the s.o.f. being fixed at 0.5. For compound 4, two of the three dependent chlorate anions and the methanol solvents were refined as disordered with the factor of the oxygen atoms in the anions being refined as a free variable and the atoms in the solvent being fixed. For compound 5, the perchlorate anions were refined as disordered with the s.o.f. of these oxygen atoms being refined as free variables. Parameters for data collection and refinement of these compounds are summarized in Table 1.

Results and discussion

Reaction of the ligand L with excess AgNO₃ in a methanol–acetonitrile mixed solution afforded compound 2. Compound 2 exhibited space group I4₁/acd and had a quite similar but more complicated structure to that of compound 1. As shown in Fig. 1, each silver atom Ag(1) was bound to two bidentate chelators from different ligands in a distorted tetrahedral geometry. Each ligand adopted a twist chiral conformation and spanned two silver Ag(1) ions to transmit the chirality from one silver center to the other, thus a chiral infinite 4₁ monohelical chain along the c direction was achieved. The metal centers with the same chirality were coordinated by the coupled ligands leading to the replication of the conformational chirality from one ligand to others. The helical pitch, given by one full rotation around the 4₁ axis, was 23.33 Å (the unit cell length along the crystallographic c axis), and the axis of the helix was at (½, 0, z) with the Ag···Ag separation being 6.43 Å.

For compound 3, the coordination geometry of the ligand L in compound 2 showing the 4₁ screw chain along the c axis. Selected bond distances (Å): Ag₁–N(3) 2.322(6), Ag₁–N(1) 2.362(6), Ag₁–N(2) 2.362(6), Ag₁–N(2) 2.322(6). Symmetry code A: x, 2 − y, −z + 0.5.

Two exo-positions of the pyrazine rings from different helical chains coordinated to one silver atom Ag(2) and connected the helical chains together featuring a three-dimensional chiral network. The fourfold helices in the same network were all of the same handedness running parallel to the c axis. The Schiff base ligand then could be pre-designed as a three-connecting node in

4090 | Dalton Trans., 2007, 4089–4094 This journal is © The Royal Society of Chemistry 2007

Fig. 1 The coordination mode of the ligand L in compound 2 showing the 4₁ screw chain along the c axis. Selected bond distances (Å): Ag₁–N(3) 2.322(6), Ag₁–N(1) 2.362(6), Ag₁–N(2) 2.362(6), Ag₁–N(2) 2.322(6). Symmetry code A: x, 2 − y, −z + 0.5.

Two exo-positions of the pyrazine rings from different helical chains coordinated to one silver atom Ag(2) and connected the helical chains together featuring a three-dimensional chiral network. The fourfold helices in the same network were all of the same handedness running parallel to the c axis. The Schiff base ligand then could be pre-designed as a three-connecting node in

which two of the directional connectors were single silver atoms and the third directional connector was the double silver bridge. A schematic view of the 103-b nets presented in the structure is shown in Fig. 2. The windows (between the four 4 axes) of the channels were about 24 × 24 Å2.

The anions and the solvent molecules were not sufficient to fill the whole free space and a second network of the same type, but opposite chirality, interpenetrated the former one. Being positioned on the crystallographic inversion center, the Ag(3) atom connected the two opposite-handed enantiomers through the argentophilic Ag(2)···Ag(3) interactions with an Ag(2)···Ag(3) separation of 3.06 Å (Fig. 3). The three-dimensional enmeshed “racemate”, whose potential existence and definition had been anticipated by Wells,17 was further stabilized by the static interactions of the positively charged frameworks and the negatively charged Ag(NO3)43− anion. Thus the presence of excess Ag(NO3)43− coordination anions made the structure rather more of an entanglement than an interpenetrating network.

Treatment of ligand L and AgNO3 in the presence of NaBF4 afforded compound 3. Single-crystal X-ray diffraction revealed that compound 3 was comprised of two distinct and crystallographically independent polymeric motifs packed together. The asymmetric unit contained two slightly different double helicates and three additional silver centers (Fig. 4). Each silver(I) atom in the helicates was coordinated to two imine and two pyrazine nitrogen atoms (2-position) forming a distorted tetrahedral geometry. The two silver centers in each helicate with the same chirality were coordinated by two coupled ligands with Ag···Ag separations of 3.40 and 3.06 Å for helicates I (comprising an Ag(1)···Ag(2) helical axis) and II (comprising a Ag(3)···Ag(4) helical axis), respectively, leading to the replication of the conformational chirality of each pair of ligands.
The 5-position nitrogen atoms of the pyrazine rings coordinated to the additional silver(I) centers Ag(5), Ag(6) and Ag(7), linking these helicates together into three-dimensional polymers. Each silver atom Ag(5) coordinated to pyrazine nitrogen atoms from four different helicates, which were N(8A) and N(16) and their symmetry-related ones, in a tetrahedral geometry. The helicates of type I were then linked into a one-dimensional polymer with dimeric double-helicates acting as building intermediates. Each silver atom Ag(6) was also coordinated to two pyrazine nitrogen atoms N(2D) and N(10) from different helicates of type I, along with one water molecule and one pyrazine nitrogen atom N(28) from the helicate of type II, in a tetrahedral geometry; the two coordinating bonds connected the one-dimensional chains, formed by Ag(7) and helicate I, in two different directions, constructing a three-dimensional framework (Fig. 5). Without solvent, anions, hydrogen atoms and helicates of type II, the framework exhibited large voids possessing approximate dimensions of 19 × 25 Å along the c direction and an analysis of the void showed that ca. 72% of the space was empty. Thus, the presence of a very large porous window within the 3D motif could be envisaged to play an important role in the generation of mutual polythreading in compound 3.

The helicates of type II were captured within the voids and connected to the three-dimensional framework through the Ag(6)–N(28) bond forming a stable host–guest structure. In addition to the pyrazine nitrogen atom N(28) coordinating to silver Ag(6), two of the other three pyrazine nitrogen atoms N(30) and N(22) coordinated to the additional silver Ag(7) making a one-dimensional chain with the silver atom Ag(7) being coordinated in a linear fashion. Since the one-dimensional chains were threaded into the large voids of the three-dimensional framework, the whole structure was considered as an entanglement of the (1D + 3D) type. If we regarded each large void as a wheel and the one-dimensional helical chain as a single rod, the nature of the entanglement in 3 could be described as poly-pseudo-rotaxane. The ample space of the voids was filled with the BF$_4^-$ anions and water molecules.

The above results of compounds 2 and 3 suggested that with the multidentate ligand L, different crystal structures could be obtained by changing the anions. To provide further examples, compounds 4 and 5 were synthesized. Compound 4 was obtained as yellow crystals by the self-assembly reaction of AgNO$_3$, ligand L and NaClO$_3$ in CH$_3$OH–CH$_3$CN. X-Ray diffraction analysis showed that compound 4 contained three different coordinated silver atoms, two ligands L, three ClO$_3^-$ anions and solvent molecules in the asymmetric unit (Fig. 6a). In this structure, Ag(1) coordinated with two nitrogen atoms of pyrazine, one CH$_3$CN molecule, and one nitrogen atom of imine. Ag(2) was five-coordinated with two nitrogen atoms of pyrazine, one nitrogen of imine and two oxygen atoms of chlorate, while Ag(3) was three-coordinated with two nitrogen atoms of pyrazine and one oxygen of chlorate. Each ligand L acted as a tetradentate ligand by using one nitrogen atom from imine and three nitrogen atoms from pyrazine rings. Viewed along the c direction, compound 4 exhibited ladder-like chains (Fig. 6b). Each chain was constituted of rectangular six-silver rings. In each ring, two Ag(1) and two Ag(2) atoms occupied the vertices of the rectangle with the angles of N(3)–Ag(1)–N(7A) being 92.8° and N(16A)–Ag(2)–N(12) being 87.8°. Ag(3) bridged two nitrogen atoms of pyrazine rings constituting the long side of the rectangle. The angle of N(13)–Ag(3)–N(8) was 151.1°. Chlorate anions and methanol molecules filled in the ring. The infinite one-dimensional chains were further connected through hydrogen bonding of chlorate anions.

X-Ray analysis of compound 5 revealed a single helix consisting of one silver atom, one perchlorate and one coordinated CH$_3$CN molecule in the asymmetric unit (Fig. 7). The ligand adopted a distorted helical conformation with a torsion angle of 78.9°.

![Fig. 4](image4.png) Structure of two cationic helical units in a unique unit of compound 3 with the H-atoms, anions and water molecules omitted for clarity. Selected bond distances (Å): Ag(1)–N(11) 2.280(4), Ag(1)–N(6) 2.294(3), Ag(1)–N(7) 2.347(4), Ag(1)–N(9) 2.372(4), Ag(2)–N(3) 2.308(4), Ag(2)–N(14) 2.322(4), Ag(2)–N(15) 2.369(3), Ag(2)–N(1) 2.380(4), Ag(3)–N(27) 2.285(4), Ag(3)–N(34) 2.297(4), Ag(3)–N(35) 2.335(4), Ag(3)–N(26) 2.377(4), Ag(4)–N(29) 2.242(4), Ag(4)–N(21) 2.287(5), Ag(4)–N(23) 2.445(4), Ag(4)–N(31) 2.485(4), Ag(7)–N(22) 2.267(4), N(30)–Ag(7) 2.180(4), N(10)–Ag(6) 2.316(4), N(28)–Ag(6) 2.233(3), Ag(6)–O(1) 2.521(3), N(16)–Ag(5) 2.399(4).

![Fig. 5](image5.png) A view of the three-dimensional framework formed by helicate I at the (1,1,0) plane (top); and the weave structure with the one-dimensional chains formed from helicates of type II threaded into the 3D framework formed by helicates of type I (bottom) in compound 3.
between N(4)–C(7)–C(14)–N(5). The Ag(I) ion coordinated with two nitrogen atoms from pyrazine rings, two nitrogen atoms of imine and one nitrogen atom of the neighboring ligand, allowing the discrete helices to interlink into a zigzag chain (Fig. 7). A close inspection of the packing of the chains revealed that each chain interacted with neighboring chains via π–π and C–H···π interactions to form a two dimensional layer. The interacting pyrazine rings, related by π–π interactions, were parallel with a center to center separation of 3.60 Å. With respect to C–H···π interactions between pyrazine rings and benzene rings, the distance of C···M (M is the center of the pyrazine ring) was 3.62 Å on average, and the angle of C–H···M was 123.1° (symmetry code: 1 − x, −y, 1 − z).

Conclusions
In conclusion, we have successfully constructed a series of Ag(I) coordination compounds from one-dimensional chains to 3D porous frameworks by using helicates as effective secondary building units in the self-assembly. The structures of these Ag compounds could be influenced by the argentophilic interactions and coordination ability of counterions and solvents. With the change of anions, the Ag(I) atoms showed variable coordination modes, providing various complicated compounds, of which two kinds of entangled structures were formed.

Fig. 6 (a) Molecular structure of compound 4. Selected bond distances (Å): Ag(1)–N(3) 2.339(4), Ag(1)–N(6A) 2.334(4), Ag(1)–N(7A) 2.410(4), Ag(1)–N(9) 2.195(5), Ag(1)–N(11) 2.353(4), Ag(1)–N(12) 2.449(4), Ag(1)–N(16A) 2.342(5), Ag(2)–O(1) 2.593(5), Ag(2)–O(3) 2.413(5), Ag(3)–N(8) 2.262(4), Ag(3)–N(13) 2.268(5), Ag(3)–O(4) 2.544(7). Symmetry code A: x + 1, y, z. (b) Perspective of ladder-like chain along the c direction. Anions and solvent molecules are omitted for clarity.

Fig. 7 Molecular structure of compound 5 from single crystal X-ray analysis. Selected bond distances (Å): Ag(1)–N(1) 2.388(4), Ag(1)–N(3) 2.524(4), Ag(1)–N(6) 2.491(4), Ag(1)–N(7) 2.423(4), Ag(1)–N(8A) 2.418(4) (top) and one-dimensional zigzag chains linked through C–H···π and π–π interactions (bottom).

Acknowledgements
We are grateful for financial support from the National Natural Science Foundation and the Natural Science Foundation of Jiangsu Proviance.

Notes and references

This journal is © The Royal Society of Chemistry 2007
2006, 45, 2972; (d) X. Guo, G. Zhu, F. Sun, Z. Li, X. Zhao, X. Li, 
H. Wang and S. Qiu, Inorg. Chem., 2006, 45, 2581; (e) X. Li, X.-Y. 
Wang, S. Gao and R. Cao, Inorg. Chem., 2006, 45, 1508; (f) J. He, 

5 (a) H. Li, M. Eddaoudi, M. O’ Keeffe and O. M. Yaghi, Nature, 1999, 
Xu, Inorg. Chem., 2005, 44, 5978; (c) S. K. Ghosh and P. K. Bhargava, 

17153; (b) S. R. Halper, L. Do, J. R. Stork and S. M. Cohen, J. Am. 
Chem. Soc., 2006, 128, 15255; (c) M.-L. Wei, C. He, W.-J. Hua, C.-Y. 
(d) S. Xiang, X. Wu, J. Zhang, R. Fu, S. Hu and X. Zhang, J. Am. 

7 (a) A. C. Sudik, A. P. Côté, A. G. Wong-Fry, M. O’ Keeffe and O. M. 
Yaghi, Angew. Chem., Int. Ed., 2006, 45, 2528; (b) C.-D. Wu and W. Lin, 
Angew. Chem., Int. Ed., 2005, 44, 1958; (c) B. Kesanli, Y. Cui, M. R. 
Ed., 2005, 44, 72; (d) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, 
Angew. Chem., Int. Ed., 2004, 43, 971; (e) J. Sun, L. Weng, Y. Zhou, J. 
4471; (f) G. S. Papaefstathiou and L. R. MacGillivray, Angew. Chem., 

8 (a) Y.-Q. Huang, B. Ding, H.-B. Song, B. Zhao, P. Ren, P. Cheng, 
(b) J. Wang, Y.-H. Zhang and M.-L. Tong, Chem. Commun., 2006, 
3106; (c) Y. Liu, V. C. Kravtsov, R. Larsen and M. Eddaoudi, Chem. 
Commun., 2006, 1488; (d) D. L. Murphy, M. R. Malachowsky, C. F. 
Campana and S. M. Cohen, Chem. Commun., 2005, 5506; (e) C.-D. Wu 
Zhang, C. Sun, D. Li and Z. Su, Chem. Commun., 2005, 2402; (g) D. N. 

9 (a) Y. H. Li, C. Y. Su, A. M. Go forth, K. D. Shimizu, K. D. Gray, 
M. D. Smith and H. C. zur Loye, Chem. Commun., 2003, 1630; (b) M. J. 
Zaworotko, Chem. Commun., 2001, 1; (c) M. Eddaoudi, D. B. Moler, 
H.-L. Li, B.-L. Chen, T. M. Reineke, M. O’ Keeffe and O. M. Yaghi, 

10 (a) X.-L. Wang, C. Qin and E.-B. Wang, Cryst. Growth Des., 2006, 6, 
2196; (c) S. R. Batten, CrystEngComm, 2001, 3, 67.

Kang and C.-Y. Su, Aust. J. Chem., 2006, 59, 3; (c) C. M. Fitchett and 
P. J. Steel, Aust. J. Chem., 2006, 59, 19; (d) T. Dorn, K. M. Fromm and 
30.

Dalton Trans., 1999, 183; (b) C. Janiak, L. Uehlin, H.-P. Wu, P. Klufers, 
1999, 3121.

2005, 2678.

14 SMART and SAINT, Area Detector Control and Integration Software, 

15 G. M. Sheldrick, SHELXTL V5.1, Software Reference Manual, Bruker, 

16 M. A. Romero, J. M. Salas, M. Quiros, M. P. Sánchez, J. Molina, J. E. 

17 (a) A. F. Wells, 3D Nets and Polyhedra, Wiley-Interscience, New York, 
1977; (b) A. F. Wells, Further Studies of Three-dimensional Nets, ACA 
Monograph No. 8, American Crystallographic Association, Buffalo, 

18 M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. 

19 F. Tuna, J. Hamblin, G. Clarkson, W. Errington, N. W. Alcock and 

20 (a) C. Janiak, J. Chem. Soc., Dalton Trans., 2000, 3885; (b) M. Nishio, 
CrystEngComm, 2004, 6, 130.