Three-Dimensional Interpenetrating Network of $[Ag_2(hmt)(NO_3)_2]_n$

Wei-Ming Bu, Ling Ye, and Yu-Guo Fan*
Key Lab of Supramolecular Structure and Spectroscopy, Jilin University, Changchun 130023, P.R.China

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The neutral network of $[Ag_2(hmt)(NO_3)_2]_n$ was prepared and characterized by X-ray diffraction studies which reveal a novel interpenetrating three-dimensional framework based both on the metal ions bound to μ4-hmt ligands and anions bonding mode. The anion bridges give a unique helical cylinder structure motif.

In recent years, there has been increasing interest in the areas of crystal engineering and the design of solid-state architectures.[1] Assembling extended supramolecular architectures by selecting the chemical structure of organic ligands and the coordination geometry of metal ions may yield a series of novel networks with potential utility as novel materials.[2] It has been proven that the counterions may play an important role in the framework construction.[3] Anion control has been reported for the two-dimensional coordination polymers of Ag(I) with 4,4'-pytz, in which the NO_3^- anions form a templated helical staircase motif.[4] In addition, due to its donor ability, the NO_3^- anion can be chosen to construct T-shaped building blocks.[5] In contrast, in the presence of the other anions, such as BF_4^- and ClO_4^-, the silver coordination polymers with diverse conformation can be achieved.[3,4,6] Self-assembly is currently the most efficient approach toward the design of one-, two- and three-dimensional organic/inorganic hybrid frameworks. Using a 'building block' methodology, combination of hexamethylenetetramine (hmt) as a potential tetradentate ligands and silver ions has produced a wide variety of supramolecular architectures.[7] For these reported silver complexes, it was not well studied that the coordination chemistry depends on both anions and ligands.[8] We report herein a new crystal engineering strategy for constructing a novel supramolecular architecture through self-assembly of $AgNO_3$ and hmt. Furthermore, the structure of $[Ag_2(hmt)(NO_3)_2]_n$ is both anion-controlled for NO_3^- and dependent upon ligand functionality, in which the NO_3^- gives rise to a unique helical structural motif. To our knowledge, it is first three-dimensional anion-controlled silver-hmt network.

The title compound obtained by the following method: An aqueous solution (5 cm^3) of hmt (0.070 g, 0.5 mmol) was added dropwise to a stirred MeCN solution (5 ml) of $AgNO_3$ (0.170 g, 1 mmol) at 50 °C. The resulting colorless solution was left to stand undisturbed at room temperature for several days. X-Ray qualified colorless single crystals were obtained, which were filtered, washed with water and dried under vacuum: yield: 75%.[9,10]

The X-ray structure analysis shows the molecular structure consists of a three-dimensional interpenetrating network, in which Ag is linked by μ_4-hmt ligand and NO_3^- anion. There are two kinds of hmt ligand geometries (A and B) present in the structure. The Ag(1) atom is coordinated by two hmt molecules (A) in a parallel plane and two oxygen atoms of two nitrate anions, while the Ag(2) ion is coordinated by two hmt molecules (B) in a perpendicular fashion (Figure 1). As illustrated in Figure 1, the potential tetradentate nature of the hmt ligand allows the silver ions to be bridged into a corrugated square-grid layer structure along bc or ac plane. Each square unit consists of six silver ions (two Ag(1) ions and four Ag(2) ions) and six hmt molecules (four hmt molecules (A) and two hmt molecules (B)). The two hmt molecules (B) link the Ag (1) ions in the direction of a or b axis, resulting in the novel three-dimensional interpenetrating neutral network (Figure 2).

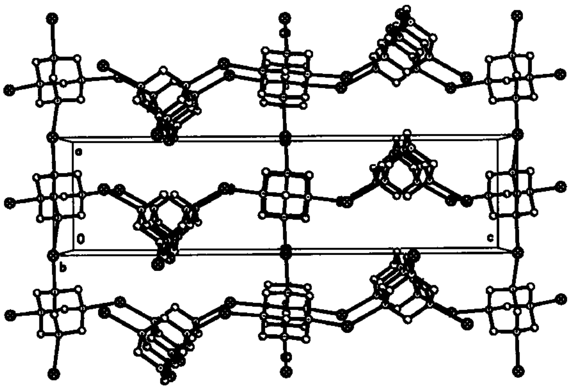


Figure 1. ORTEP view showing the layers in $[Ag_2(hmt)(NO_3)_2]_n$ along b axis. The NO_3^- ions are omitted for clarity. Cross-hatched circles represent silver atoms.

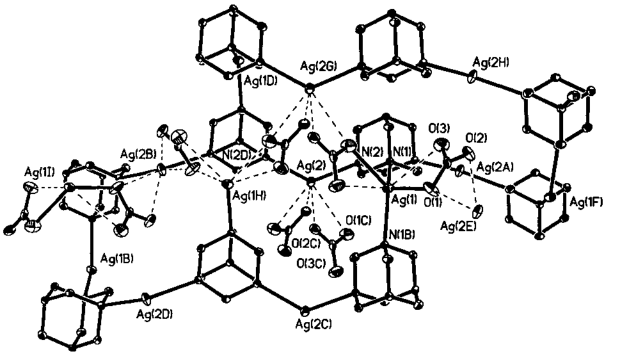
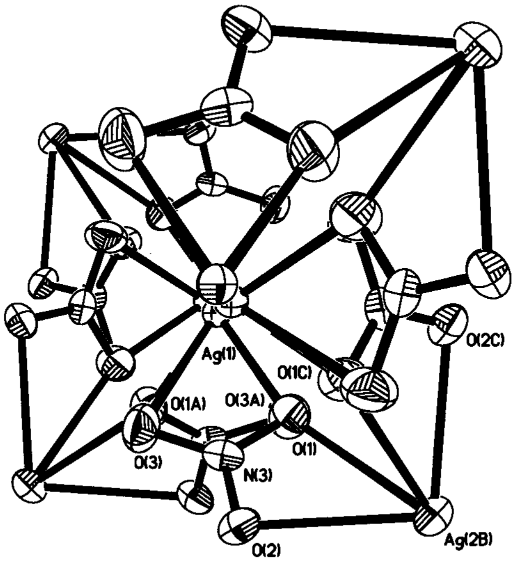


Figure 2.ORTEP diagram with labeling schems.Selected bond lengths (Å) and angles(°): Ag(1)-N(1)#1: 2.399(5), Ag(1)-N(1): 2.399(5), Ag(1)-O(1): 2.456(6), Ag(1)-O(1)#1: 2.456(6), Ag(2)-O(2): 2.369(5), Ag(2)-N(2)#2: 2.369(5). Ag1-O3: 2.850, Ag1-O3#1: 2.850, Ag2-O1#4: 2.861, Ag2-O2#4: 2.682, Ag2-O1#5: 2.861, Ag2-2#5: 2.682. N(1)#1-Ag(1)-N(1): 126.7(3), N(1)#1-Ag(1)-O(1): 85.5(2), N(1)-Ag(1)-O(1): 128.5(2), N(1)#1-Ag(1)-(1)#1: 128.5(2), N(1)-Ag(1)-O(1)#1:85.5(2), O(1)-Ag(1)-O(1)#1: 105.2(3), N(2)-Ag(2)-N(2)#2: 129.8(2). (generated by symmetry : #1: -x,y,-z, #2: y+1,x-1,-z-1/4, #3: -x+1,y,-z, #4:y,-x-1,z-1/4, #5: -x,y-1,-z)



Figures 3. View of the helical chain along c axis. Selected bond lengths (Å): Ag(1)-O(1): 2.456(6), Ag(1)-O(1)A: 2.456(6), Ag(1)-O(3): 2.850, Ag(1)-O(3)A: 2.850, Ag(2)B-O(1): 2.861, Ag(2)B-O(2): 2.682, Ag(2)B-O(1)C: 2.861, Ag(2)B-O(2)C: 2.682. (generated by symmetry : A: -x, +y, -z, B: -y-1, +x, z+1/4, C: -y, -x,1/4-z).

In fact, each silver center interacts weakly two NO_3^- ions. The Ag···O distances vary from 2.682 Å to 2.861 Å, which consistent with those in other nitrate salts of silver complexes.[11] The dihedral angle between two NO_3 around Ag (1) or Ag (2) is 88.0° or 40.9°. The nitrate NO_3 acts as bidentate ligand by three of the oxygen atoms, one of which is μ_2-oxygen bridge linked Ag (1) and Ag (2) ions, the other is two monodentate oxygen linked Ag(1) or Ag(2) ion, respectively. So, by this way, the NO_3^- ions bridge two silver ions resulting in a unique helical chain along the c axis. Chirality arises from a 4_1 screw axis along the chain in the c-direction. Seen along c axis (Figure 3), each helical chain may illustrate the cylinder arrangement. All Ag (1) ions point to the center, while all Ag (2) ions are disposed around the cylinder. The chirality results from the adoption of one of enatiomorphic space group pairs (e.g., $P4_122$, $P4_322$). A similar nickel chiral network which crystallizes in the space group $P4_232$ has been described recently.[12] We believe this helical motif to be unique in inorganic supramolecular architectures, and, significantly, it contrasts markedly with the structure observed for $\{Ag(pytz)(NO_3)\}$.[4] This confirms the importance of ligand functionality in determining the structure of these types of inorganic supramolecular arrays.

The result not only represents the first examples of a helical cyclinder structural motif by anions but also a remarkable case of anion control of three-dimensional supramolecular architecture construction. In addition, the structure of this complex suggests that nitrate may serve as structure-directing template in constructing supramolecular architectures. It provides a convenient way in the rational design of functional materials. Further investigations on this system are in progress.

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References and Notes

1 D. Braga, F.Grepioni, and G. R. Desiraju, *Chem. Rev.*, **98,** 1375(1998); K. A. Hirsch, S.R.Wilson, and J.S. Moore, *Inorg. Chem.*, **36**, 2960(1997); K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, **1998**, 595; S. W. Keller, *Angew. Chem., Int. Ed. Engl.*, **36**, 247(1997).

2 C. L. Bowes and G. A. Ogin, *Adv. Mater.*, **8**, 13(1996); F. Lloret, G. D. Munno, M. Julve, J. Cano, R. Ruiz A., and Caneschi, *Angew. Chem., Int. Ed. Engl.*, **37,** 135 (1998); B. F. Hoskins and R. J. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990).

3 M. L. Tong, X. M. Chen, B. H. Ye, and S. W. Ng, *Inorg. Chem.*, **37**, 5278 (1998); Hu. Cai, H. M. Hu, W. Z. Chen, H. G. Zhu, and X. Z. You, *Chem. Lett.*, **1999,** 221;

4 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, and M. Schroder, *Angem. Chem., Int. Ed. Engl.*, **36**, 2327 (1997).

5 L. Carlucci, C. Ciani, P. Macchi, and D. M. Proserpio, *Chem. Commun.*, **1998**, 1837; P. Losier and M. L. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, **35**, 2779 (1996); M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, and K. Ogura, *J. Am. Chem. Soc.*, **117**, 7287 (1995).

6 D. Whang and K. Kim, *J. Am. Chem. Soc.*, 119, 451 (1997).

7 M. L. Tong, S. L. Zheng, and X. C. Chen, *Chem. Commun.*, **1999**, 561; L. Carlucci, G. Giani, D. M. Proserpio, and A. Sironi, *J. Am. Chem. Soc.*, **117**, 12861 (1995); *Chem. Commun.*, **1997**, 631; *Inorg. Chem.*, **36,** 1736 (1997).

8 M. Moutalti and L. Prodi, *Chem. Commun.*, **1998**, 1461; M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and K. Sugimoto, *Inorg. Chem.*, **36**, 4903 (1997).

9 Anal. Calcd for $C_6H_{12}Ag_2N_6O_6$: C, 15.01; H, 2.52; N, 17.51%. Found: C, 15.05; H, 2.65; N, 17.58%.

10 Crystal data for $[Ag_2(hmt)(NO_3)_2]_n$ are: $C_6H_{12}Ag_2N_6O_6$: Mr=479.96, tetragonal, space group $P4_122$(No.91), a=b=6.7497(4), c=26.713(4) Å, V=1193.2(2) Å^3, Z=2, Dc=1.336 g cm^{-1}, μ(MoKα)=1.661 mm^{-1}, F(000)=464, Crystal dimensions 0.26 x 0.24 x 0.2 mm, Siemens P4 diffractometer, graphite-monochroated MoKα radiation, ω scans, T=293 K, 1029 independent reflections measured($3^\circ<2\theta<50^\circ$), of which 940 were considered to be observed[$I>4\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 to give R1=0.0342 and wR2=0.0792. Computations were carried out with the SHELXTL5.03 package.

11 F. Robinson and M. J. Zaworotko, *Chem. Commun.*, **1995**, 2413.

12 C. J. Kepert and M. J. Rosseinsky, *Chem. Commun*, **1998,** 31.