A Novel Three-Dimensional Framework: Self-Assembly of $AgNO_3$ and Pyrimidine

Hu Cai, Huai-Ming Hu,† Wan-Zhi Chen, Hao-Guo Zhu, and Xiao-Zeng You*
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Department of Chemistry,
Nanjing University, Nanjing 210093, P.R. China
†*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,*
Chinese Academy of Science, Fuzhou 350002, P.R. China

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The uncharged complex $\{Ag(pyrimidine)_{0.5}NO_3\}_\infty$ is prepared and characterized by X-ray diffraction studies which reveal a novel non-centrosymmetric three-dimensional (3-D) framework based both on the metal ions bound to ligands and anion bonding mode.

The crystal engineering of low and 3-D metal coordination molecules and supramolecules is one of the most active research topics of current chemistry and molecular material science,[1] which is not only for their novel structures and geometries,[2] but also for their interesting properties such as optical, electronic and magnetic functions,[3] as well as ion- or molecule-exchange and catalytic properties.[4] One of the simplest and most widely employed strategies to fabricate low and 3-D systems is based upon linear bridging ligands bound to metal ions. Different metal ions with various coordination geometry (such as octahedral, tetrahedral, or square planar etc.) connected with numerous ligands provide a wide range of possibilities for constructing metal-organic frameworks.[5] However, the majority of the studies of the supramolecular architectures put forth were based upon this way, while the coordination chemistry depend upon both anions and ligands was not well studied.[6] We report herein a new crystal engineering strategy for constructing a novel 3-D supramolecular architecture through self-assembly of $AgNO_3$ and pyrimidine.

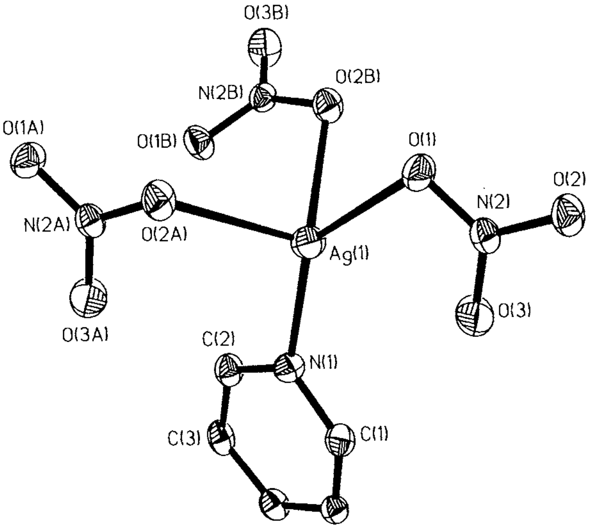

Figure 1. Section of the crystal structure of $\{Ag(pym)_{0.5}NO_3\}_\infty$ (30% probability thermal ellipsoids, hydrogen atoms have been omitted for clarity). Selected bond lengths(Å) and angles(°): Ag(1)-N(1) 2.2322(14), Ag(1)-O(1) 2.409(2), Ag(1)-O(2A) 2.4052(14), Ag(1)-O(2B) 2.530(2), N(1)-Ag(1)-O(1) 140.23(5), N(1)-Ag(1)-O(2A) 121.17(5), N(1)-Ag(1)-O(2B) 110.59(5), O(1)-Ag(1)-O(2B) 93.18(4), O(2A)-Ag(1)-O(1) 83.47(4), O(2A)-Ag(1)-O(2B) 99.55(4). (generated by symmetry: (A) -x+0.5, y, z+0.5; (B) x, y+0.5, z+0.5).

Although pyrimidine as a bidentate N,N'-donor linking ligand with angular geometry is of interest in constructing multi-

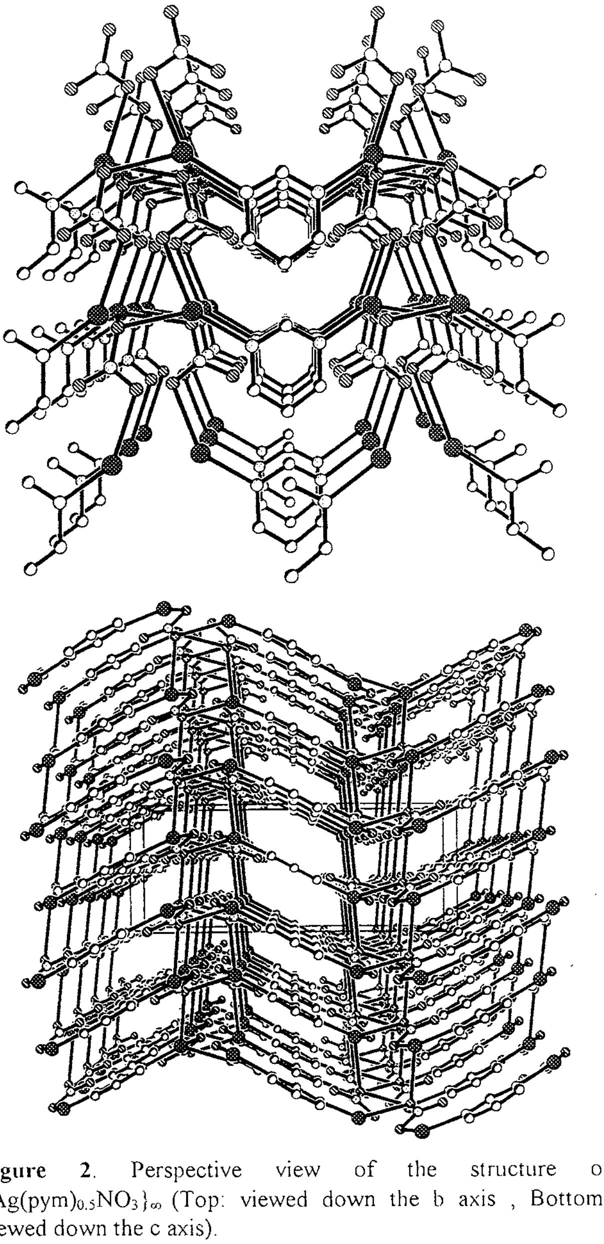

Figure 2. Perspective view of the structure of $\{Ag(pym)_{0.5}NO_3\}_\infty$ (Top: viewed down the b axis , Bottom: viewed down the c axis).

dimensional architectures, only a few reports have appeared describing coordination networks based on pyrimidine and metal ions.[7] In this vein, we synthesized the complex $\{Ag(pym)_{0.5}NO_3\}_\infty$ (pym = pyrimidine) aimed at yielding zeolite materials exhibiting potential novel properties. Colorless crystals of $\{Ag(pym)_{0.5}NO_3\}_\infty$ suitable for single-crystal X-ray diffraction[8] were obtained when a CH_3OH solution of $AgNO_3$ was reacted with a aqueous solution of pyrimidine (molar ratio 1:1) through careful layering in a test tube at room temperature.[9] X-ray structure determination of the complex reveals that the formation of this 3-D framework rests on both the anion NO_3^- and the bent bridging ligand pyrimidine. The building units are shown in Figure 1. Each silver atom is four-coordinated in a distorted tetrahedral geometry by the one nitrogen atom of pyrimidine and three oxygen atoms from three different nitrates. Each of the pyrimidine ligands bridges two silver ions. In the meanwhile,the nitrate NO_3^- acts as a tri-dentate ligand which connects with three silver ions by two of the oxygen atoms, one of which is a μ_2-oxygen bridge linked two silver ions (O(2)-Ag(1d) 2.530(2), O(2)-Ag(1c) 2.4052(14) Å, Ag(1c)-O(2)-Ag(1d) 109.15(5)°) (generated by symmetry: (c) –x+0.5, y, z–0.5, (d) x, y–0.5, z–0.5), the other is a mono-dentate oxygen linked another silver ion (Ag(1)-O(1) 2.409(2) Å). So, by this way, a uncharged novel non-centrosymmetric 3-D framework structure was built up (Figure 2.). The NO_3^- anions played a significant role in building this 3-D supramolecular architecture.

In fact, the NO_3^- anions as tri-dentate bridges formed what is to our knowledge the first example of infinite three-dimensional structure. This gives a completely different structural motif from those of the corresponding complexes of pyrimidine and metal ions.[7] The structure determination of this complex confirms, at least in part , that nitrate is a potential template to construct supramolecular architectures from identical building blocks with diverse structures and unusual topology simply by connecting them in different ways. It provide a convenient way and will be widely applied to the rational design of functional materials.

Further investigation on the reactivities of other metal nitrates with ligands is in progress.

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References and Notes

1 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, and J. Liu, "Supramolecular Architecture", ACS publications, (1992), Ch. 19; J. -M. Lehn, "Supramolecular Chemistry", VCH, Weinhein, (1995), Ch. 9; T. Iwamoto, "Comprehensive Supramolecular Chemistry", ed by D. D. MacNicol, F. Toda and R. Bishop, Oxford, (1996), Vol. 6, Chap. 19, pp. 643-690.

2 B. J. Hathaway, "Comprehensive Coordination Chemistry", ed by G. Wilkinson, Pergamon, London, (1988), Vol. 15, pp. 533.

3 C. T. Chen and K. Sulick, *Coord. Chem. Rev.*, **128**, 293 (1993); H.-Y. Shen, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, B.-W. Sun, G.-L. Wang, X.-K. Yao, and H.-G. Wang, *Chem. Lett.*, **1998**, 469.

4 M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **118**, 9096 (1996); H. Yuge, Y. Noda, and T. Iwamoto, *Inorg. Chem.*, **35**, 1842 (1996); P. Schwarz, E. Siebel, R. D. Fischer, D. C. Apperley, N. A. Davies, and R. K. Harris, *Angew. Chem., Int. Ed. Engl.*, **34**, 1197 (1995).

5 B. F. Hoskin, and R. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990); B. Olenyuk, A. Fechtenkötter, and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, **1998**, 1707.

6 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W. -S. Li, and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, **36**, 2327 (1997); M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and K. Sugimoto, *Inorg. Chem.*, **36**, 4903 (1997); M. Moutalti, and L. Prodi, *Chem. Commun.*, **1998**, 1461.

7 S. W. Keller, *Angew. Chem., Int. Ed. Engl.*, **36**, 247 (1997); C. V. K. Sharma, S. T. Griffin, and R. D. Rogers, *Chem. Commun.*, **1998**, 215; F.Lloret, G. De Munno, M. Julve, J. Cano, R. Ruiz, and A. Caneschi, *Angew. Chem., Int. Engl.*, **37**, 135 (1998).

8 Crystal data for $\{Ag(pym)_{0.5}NO_3\}_\infty$ are: $C_2H_2AgN_2O_3$ Mr = 209.93, orthorhombic, space group Aba2(no.41), a = 15.969(3), b = 6.332(1), c = 9.116(2) Å, U = 926.8(3) $Å^3$, Z = 8, D_c = 3.009 gcm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 4.248 mm^{-1}, $F(000)$ = 792, Crystal dimensions 0.9 × 0.2 × 0.2 mm, Enraf-Nonius CAD4 diffractometer, graphite-monochroated $Mo\text{-}K_\alpha$ radiation, ω-2θ scans, T = 293 K, 537 independent reflections measured ($5.10 < 2\theta < 54.06°$), of which 537 were considered to be observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 to give R_1 = 0.0274 and wR_2 = 0.0670. Computations were carried out with the SHELXTL5.03 package.

9 Anal. Calcd for $C_2H_2AgN_2O_3$: C 11.44; H 0.96; N 13.34%. Found: C 11.58; H 1.03; N 13.38%.