

Syntheses and Crystal Structure of a New 3D Ag(I)-Fumaric Acid Framework, $[\text{Ag}(\text{hmt})(\text{fma})_{1/2} \cdot 2\text{H}_2\text{O}]_n$

BI, Wen-Hua(毕文华) SUN, Dao-Feng(孙道峰) CAO, Rong*(曹荣) LI, Xing(李星)
SHI, Qian(时茜) HONG, Mao-Chun(洪茂椿)

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A new silver (I) coordination polymer, $[\text{Ag}(\text{hmt})(\text{fma})_{1/2} \cdot 2\text{H}_2\text{O}]_n$ (1), (hmt = hexamethylenetetramine, fma = fumaric acid), was obtained by self-assembly of hmt, fma and AgNO_3 in the mixed solvent of methanol, dichloromethane and water ($\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2:\text{H}_2\text{O} = 5:5:1$), and characterized by X-ray diffraction analysis. Complex 1 belongs to orthorhombic space group *Pbcn* with cell parameters $a = 1.72043(5)$ nm, $b = 1.19704(2)$ nm, $c = 1.11685(3)$ nm, $V = 2.30007(10)$ nm³, $Z = 8$, CCDC number: 194381. In complex 1, each hmt ligand acts as a μ_3 -bridge to link three Ag(I) atoms and in turn every Ag(I) ion attaches to three hmt ligands to produce a 2D honeycomb network, which is further linked by the bidentate fma ligands to form a 3D noninterpenetrating open framework with one-dimensional channels being filled by guest molecules.

Keywords fumaric acid, silver polymer, honeycomb layer, crystal structure

Introduction

In recent several decades, the design and syntheses of novel structure material have become an active research field.¹⁻³ However, the deliberate design of new functional materials based on polymer is still an arduous challenge to inorganic chemists because the assembly of those structures is heavily influenced by many factors such as the pH value, the solvent and counterion.⁴ Much effort has been devoted to explore useful synthetic strategies in order to obtain the anticipatory framework. Fortunately, a lot of intriguing structures have been synthesized by carefully selecting different synthons and controlling the condition of growth,⁵ which will attribute great to extend our knowledge of the designs and syntheses strategies. As well known, Ag(I) ion is a favorable and fashionable building block for coordination polymers because of its various coordination models, for example, Ag(I) ion can exhibit linear,^{6,7} trigonal^{8,9} and tetrahedral coordination and has high affinity for hard donor atoms such as nitrogen or oxygen atoms. Hexamethylenetetramine (hmt) is a rigid polydentate ligand and suitable for assembly to generate extended framework,

which has been documented by Chen and his co-workers.^{4,5} In the realm of Ag(I)-hmt complexes,^{4,5,10-14} a great number of bi-functional co-ligand is used (such as 4-hydroxybenzoic acid, 4,4'-biphenyldicarboxylic acid and 1,4-butanedioic acid), but fumaric acid acts as a bridged ligand is not documented yet. In this paper we report a new three-dimensional Ag polymer based on mixed ligands, namely hmt and fumaric acid. It is shown that the fma ligand links the cationic honeycomb layers of $[\text{Ag}(\mu_3\text{-hmt})]_n^+$ to generate a new three-dimensional non-interpenetrating open framework with one-dimensional channels, in which water molecules reside.

Experimental

Materials

The reagents and solvents employed were commercially available and used as received without further purification.

Preparation of $[\text{Ag}(\text{hmt})(\text{fma})_{1/2} \cdot 2\text{H}_2\text{O}]_n$

Fma (0.035 g, 0.30 mmol) was solved in the mixture of 10 mL of CH_2Cl_2 and 4 mL of H_2O . The solution was poured into a test tube and a solution of AgNO_3 (0.051 g, 0.30 mmol) and hmt (0.042 g, 0.30 mmol) in 10 mL of CH_3OH was carefully layered on it. The tube was sealed and kept in the dark, after about three weeks, colorless prism-like crystals were collected in 58% yield.

Elemental analysis

Elementary analyses were carried out in the elementary analysis group of this institute. Anal. calad for $\text{AgC}_8\text{H}_{17}\text{O}_4\text{N}_4$: C 28.17, N 16.42, H 5.02; found C 28.20, N 16.46, H 4.98.

* E-mail: rcao@ms.fjirsm.ac.cn

Received October 8, 2002; revised January 6, 2003; accepted February 10, 2003.

Project supported by the National Natural Science Foundation of China (No. 29901005).

Infrared spectrum

Infrared spectrum of the title complex was recorded with a Nicolet AVATAAR FT-IR Model 950 spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) in KBr pellets. IR ν : 3383 (s), 3026 (s), 2955 (m), 2928 (m), 2870 (s), 1668 (m), 1572 (vs), 1456 (s), 1426 (m), 1392 (s), 1286 (br, m), 1231 (s), 1016 (s), 968 (s), 917 (m), 815 (s), 728 (m).

Crystal structure determination

A prism crystal of dimensions $0.40\text{ mm} \times 0.18\text{ mm} \times 0.10\text{ mm}$ of the title compound was mounted on a glass fiber in a random orientation. Diffraction data were collected at room temperature (293 K) on a Siemens SMART-CCD area detector equipped with graphite monochromated Mo K α radiation ($\lambda = 0.071073\text{ nm}$). A total of 6791 reflections were collected in the range of $2.07^\circ < \theta < 25.05^\circ$ using ω - 2θ scan mode of which 2041 independent reflections with $I > 2.50\sigma(I)$ were used in the succeeding refinement. The structure was solved by direct methods and refined by full-matrix least-squares method. The positions of H atoms were generated geometrically (C—H bond fixed at 0.096 nm), assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms before the final cycle of refinement. The final cycle of refinement included 175 variable parameters and converged to $R = 0.0318$ and $wR = 0.1104$. All calculations were performed on a Legend Pentium III computer with SHELXTL 97 program package. Crystal parameters and refinement results are summarized in Table 1.

Results and discussion

The selected bond distances and angles are listed in Table 2, the atomic coordinates and equivalent displacement parameter are listed in Table 3. In complex **1**, the molar ratio of $\text{Ag}:\text{hmt} = 1$, as shown in Fig. 1, each Ag ion is coordinated by three nitrogen atoms from different hmt and a oxygen atom from fma ligand in a greatly distorted tetrahedral geometry [N(1)-Ag-O(2) $134.67(12)$, N(4)-Ag-O(2) $82.08(13)$, N(2)-Ag-O(2) $88.99(12)^\circ$]. The Ag—N bond lengths range from $0.2378(3)$ to $0.2428(3)\text{ nm}$ which is agreement with those observed in other reported Ag-hmt complexes.^{4,5} Every hmt ligand links three Ag ions and each Ag ion attaches to three hmt to form a 2D honeycomb-like layer (Fig. 2), in which three hmt and three Ag ions constitute a hexagonal unit and each hmt and Ag ion occupies a corner. This layer is much similar to the 2D wavy networks namely $[\text{Ag}(\mu_3\text{-hmt})(\text{NO}_2)]$ and $[\text{Ag}_2(\mu_3\text{-hmt})_2](\text{S}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$,⁴ in which no higher dimensional frameworks are formed owing to NO_2^- and $\text{S}_2\text{O}_6^{2-}$ only acting as monodentate ligand in those networks. The 2D layer is further linked by the fma ligand in a bis-monodentate bridging mode to generate a 3D channel-like framework with the distance of adjacent

layers being 0.86021 nm (Fig. 3). The structure is quite different from that observed in $[\text{Ag}_2(\mu_2\text{-hmt})_2(\text{bda})] \cdot 4\text{H}_2\text{O}$ ($\text{bda} = 1,4\text{-butanedioate}$),⁵ although the ligand used in the two compounds are very similar. In $[\text{Ag}_2(\mu_2\text{-hmt})_2(\text{bda})] \cdot 4\text{H}_2\text{O}$, the hmt ligands coordinated with two Ag(I) atoms via its two nitrogen atoms to form a zigzag $[\text{Ag}(\mu_2\text{-hmt})]_\infty$ chain which is further linked each other by the weak interaction between the adjacent Ag(I) atoms to generate a double chain, and then the double chain is connected by the bda ligand to result in the final 2D neutral rectangular layer structure. It has been indicated that self-assembly reaction is highly influenced by many factors, such as pH value, solvent system and the metal-ligand.

Table 1 Crystal data for $\text{AgC}_8\text{H}_{17}\text{O}_4\text{N}_4$ ra-tio

Chemical Formula	$\text{AgC}_8\text{H}_{17}\text{O}_4\text{N}_4$
Formula weight	341.13
Temperature	293(2) K
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
<i>a</i>	1.72043(5) nm
<i>b</i>	1.19704(2) nm
<i>c</i>	1.11685(3) nm
<i>V</i>	2.30007(10) nm ³
<i>D_c</i>	1.970 g/cm ³
<i>Z</i>	8
Absorption coefficient	1.764 mm ⁻¹
Wavelength	0.071073 nm
Absorption coefficient	3.929 mm ⁻¹
<i>F</i> (000)	1376
Crystal size	0.40 nm × 0.18 nm × 0.10 mm
θ Range for data collection	2.07° to 25.05°
Limiting indices	$-15 \leq h \leq 20$, $-14 \leq k \leq 11$, $-13 \leq l \leq 9$
Reflections collected/unique	6791/2041 [$R_{\text{int}} = 0.0273$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2041/0/175
Goodness-of-fit on F^2	1.056
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0318$, $wR_2 = 0.1104$
<i>R</i> Indices (all data)	$R_1 = 0.0451$, $wR_2 = 0.1314$

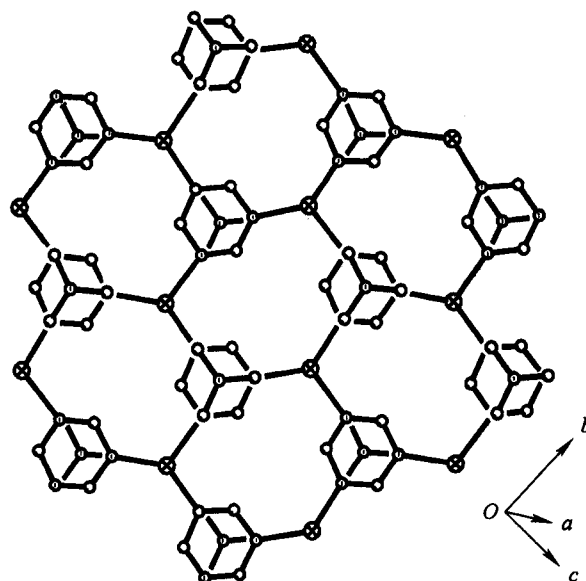
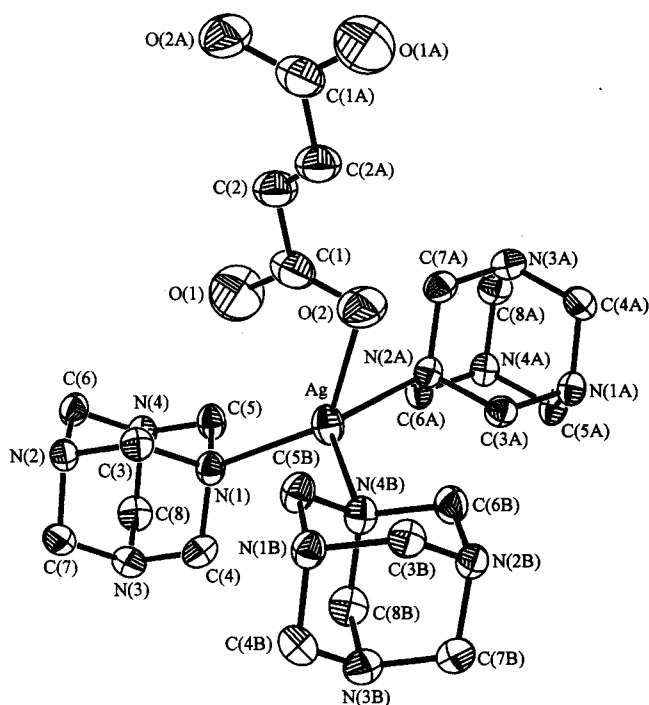
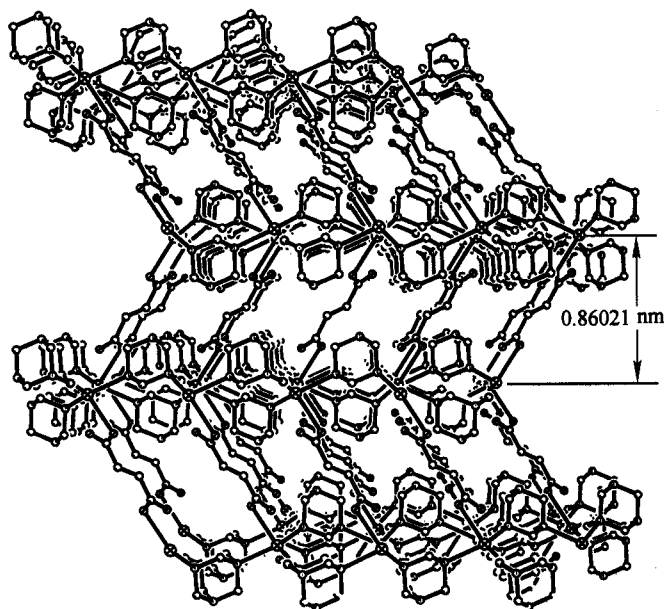
Table 2 Bond lengths (nm) and angles (°) for complex **1**

Ag—N(1)	0.2378(3)	Ag—O(2)	0.2557(4)
Ag—N(4)	0.2422(3)	C(1)—C(2)	0.1504(7)
Ag—N(2)	0.2428(3)	C(2)—C(2)	0.1291(10)
N(1)-Ag-N(4)	111.06(11)	N(1)-Ag-O(2)	134.67(12)
N(1)-Ag-N(2)	114.41(11)	N(4)-Ag-N(2)	123.27(11)
N(4)-Ag-O(2)	82.08(13)	N(2)-Ag-O(2)	88.99(12)

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameter ($\text{nm}^2 \times 10$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ag	7407(1)	8983(1)	2024(1)	34(1)
N(1)	8058(2)	10424(3)	3092(3)	28(1)
N(2)	8073(2)	12471(3)	3270(3)	27(1)
N(3)	9194(2)	11382(3)	3908(3)	32(1)
N(4)	7993(2)	11311(3)	5077(3)	30(1)
O(1)	6207(3)	10432(4)	1789(5)	100(2)
O(01)	5759(2)	6739(4)	189(4)	63(1)
O(2)	6154(2)	8873(3)	797(4)	56(1)
O(02)	5912(5)	12535(5)	2657(5)	110(2)
C(1)	5886(3)	9798(4)	1066(5)	46(1)
C(2)	5147(3)	10197(4)	488(5)	42(1)
C(3)	7817(3)	11509(3)	2560(4)	29(1)
C(4)	8917(3)	10439(4)	3181(4)	34(1)
C(5)	7732(3)	10369(4)	4318(4)	31(1)
C(6)	7751(3)	12360(4)	4496(4)	32(1)
C(7)	8934(2)	12429(4)	3354(4)	31(1)
C(8)	8857(3)	11296(4)	5112(4)	35(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

**Fig. 2** View of the layer with honeycomb-like network along *a*-axis. All hydrogen atoms are omitted for clarity.**Fig. 1** Coordination environment of Ag(1) in the title complex.**Fig. 3** Wave-like crystal packing structure for the title complex along *b*-axis. The free water molecules and all hydrogen atoms are omitted for clarity.**Table 4** Hydrogen bond (nm and $^\circ$) in the title complex

D—H \cdots A	Symm	D—H	H \cdots A	D \cdots A	D—H \cdots A
O ₀₁ —H ₀₁ \cdots O ₂	<i>x</i> , <i>y</i> , <i>z</i>	0.0888	0.1850	0.2972	170
O ₀₂ —H ₀₃ \cdots O ₁	<i>x</i> , <i>y</i> , <i>z</i>	0.1065	0.1701	0.2744	165
O ₀₁ —H ₀₂ \cdots N ₃	<i>x</i> - 0.5, <i>y</i> - 0.5, 0.5 - <i>z</i>	0.0984	0.1933	0.2907	170.1
O ₀₂ —H ₀₄ \cdots O ₀₁	<i>x</i> , 2 - <i>y</i> , <i>z</i> + 0.5	0.0798	0.2177	0.2972	174

Various structures can be constructed through deliberately controlling reaction conditions

The absorption peaks in 3026 and 968 cm^{-1} in **1** indicate the existence of hydrogen atoms of C = C double bonds ($\nu_{\text{C-H}} = 3062 \text{ cm}^{-1}$, $\gamma_{\text{C-H}} = 968 \text{ cm}^{-1}$). The free water molecules reside in the channels and form hydrogen bonds [O...O 0.2744—0.2972 nm; O...N 0.2907 nm] with uncoordinated carboxylate oxygen and hmt nitrogen atoms, the hydrogen bonds in **1** are listed in Table 4.

References

- 1 Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.
- 2 Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
- 3 Munakata, M.; Wu, L.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173.
- 4 Tong, M. L.; Zheng, S. L.; Chen, X. M. *Chem.-Eur. J.* **2000**, *6*, 3729.
- 5 Zheng, S. L.; Tong, M. L.; Yu, X. L.; Chen, X. M. *J. Chem. Soc., Dalton Trans.* **2001**, 586.
- 6 Mak, T. C. W. *Inorg. Chim. Acta* **1984**, *84*, 19.
- 7 Bi, W. H.; Sun, D. F.; Cao, R.; Hong, M. C. *Acta Crystallographica, Section E: Structure Reports Online*, **2002**, *58*, m324.
- 8 Carlucci, L.; Ciani, G.; Prosperio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562.
- 9 Fei, B. L.; Sun, W. Y.; Okamura, T.; Tang, W. X.; Uegama, N. *New J. Chem.* **2001**, *25*, 210.
- 10 Carlucci, L.; Ciani, G.; Prosperio, D. M.; Sironi, A. *Chem. Commun.* **1997**, 631.
- 11 Bertelli, M.; Carlucci, L.; Ciani, G.; Prosperio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271.
- 12 Liu, Q.; Sun, X. Q.; Zhu, Y. Q.; Li, B. L.; Xu, Z.; Liu, H. B.; Yu, K. B. *Transition Met. Chem. (Dordrecht, Neth.)* **2001**, *26*, 369.
- 13 Tong, M. L.; Zheng, S. L.; Chen, X. M. *Chem. Commun.* **1999**, 561.
- 14 Carlucci, L.; Ciani, G.; Prosperio, D. M.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 1736.

(E0210083 LU, Y. J.; DONG, L. J.)