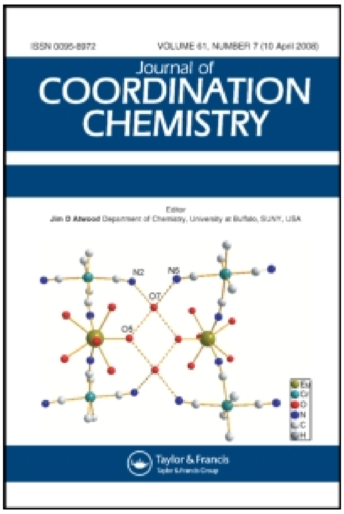

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# A 3-D open network constructed from metallamacrocycle chains with a simple 'corner' ligand of 2,4-diamino-6-methyl-1,3,5-triazine(dmt) via cross-linked hydrogen bonds

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# A 3-D open network constructed from metallamacrocycle chains with a simple 'corner' ligand of 2,4-diamino-6-methyl-1,3,5-triazine(dmt) via cross-linked hydrogen bonds

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The title polymer Ag(I) complex was synthesized through the reaction of 2,4-diamino-6-methyl-1,3,5-triazine(dmt) and $Ag_2SO_4$. X-ray structure analysis shows that the crystal structure of title complex consists a infinite 1-D polymer chains with novel metallamacrocycles, which are cross-linked to each other by four types of hydrogen bonds, resulting in the formation of a new 3-D open network with large channels.

*Keywords*: 2,4-Diamino-6-methyl-1,3,5-triazine; Metallamacrocycle; Hydrogen bonds; Crystal structure

## 1. Introduction

Macrocycle complexes and 2, 3-D extended porous frameworks based on inorganic–organic molecular systems have become the focus of interest because of their intrinsic aesthetic appeal and potentially exploitable properties [1, 2]. There are two types of ligands utilized in this field. One is anionic polydentate ligands, such as 1,3-benzenedicarboxylate with a 120 or 90° angle between two functional groups, used by Yaghi and coworkers [3] and Zaworotko *et al.* [4] to form nanometersized polygons. Using 7-oxadibenzofluorene-3,11-dicarboxylic acid(L) as ligand, Lin W.B. *et al.* reported the syntheses of $[Cu_4(L)_4{-}(Py)_8]\cdot 2DMF\cdot 10H_2O$ and $[Co_2(L)_2(Py)_4]\cdot 2DMF\cdot 2H_2O$ [5]. Other neutral ligands [6], such as $N,N'$-bipyridine-type ligands [7], pyrimidine [8], hexamethylenetetramine (hmt) [9], pyrazine and their derivatives were also untilized [10]. Based on the above ligands containing special angles between different functional groups, a large number of porous polymers have been reported recently, such as $Ag_4(hmta)_3(H_2O)\cdot(PF_6)_4\cdot 3EtOH$, $[Cu\text{-}(pyrd)_2]\cdot BF_4$ and $[Ag_2(2,3\text{-}Me_2pz)_3]\cdot SbF_6$ (Venkataraman *et al.* [11]).

Triazine and its derivatives with a 120° angle among the three functional groups are potential polydentate ligands. By the self-assembly of proper metal salts with those

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ligands, a great number of polymers have been prepared, which show 1-D chain, 2-D planar sheet and 3-D network structures [11, 12]. However, there are few complexes reported with a 3-D network structure assembled from 1-D polymeric chains containing metallamacrocycles. Here we have investigated the reactions of 2,4-diamino-6-methyl-1,3,5-triazine (dmt) with different silver salts, and the products were structurally characterized by single crystal X-ray diffraction analysis. However, only one compound prepared by the reaction of $Ag_2SO_4$ with dmt shows 1-D coordination polymer with metallamacrocycles based on the $Ag_2L_2SO_4$ building unit, cross-linked by hydrogen bonding to form a 3-D open network with large channels filled with water molecules.

## 2. Experimental

### 2.1. *Materials*

All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted.

### 2.2. *Physical measurements*

Elemental analysis for C, H, and N was performed on a Perkin-Elmer 240C elemental analyser, and IR spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the 5000–400 $cm^{-1}$ regions.

**$[Ag_2(dmt)_2(SO_4)] \cdot 2H_2O$ (1)** was prepared as block crystals, from the reaction of $Ag_2SO_4$ (0.1 mmol, 31.6 mg) and 2,4-diamino-6-methyltriazine (0.2 mmol, 25 mg) in a mixed solvent of ethanol-water at 90°C for 0.5 h. By cooling to room temperature and filtering, white solid of **1** was obtained in 46% total yield. Colorless single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of reaction mixture over several weeks. Yield 26.5%. Calcd (%) for **1**: C, 16.05; N, 23.46; H, 3.01. Found: C, 15.86; N, 23.29; H, 2.82. IR(KBr) ($cm^{-1}$): 3429.64s, 3371.82s, 3330.15s, 3125.24s, 1665.00s 1614.31s, 1582.92s, 1527.20s, 1473.66s, 1412.03s, 1269.99m, 1111.96s, 1015.64m, 801.88s, 618.66s.

### 2.3. *X-ray structure determination*

Parameters for data collection and refinement of **1** are summarized in table 1, and selected bond lengths and angles are listed in table 2. The intensities of **1** were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatic Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Data were reduced using the Bruker SAINT program, empirical absorption was done by using the SADABS program. The crystal structure was solved by direct methods. All non-H atoms were refined anisotropically by means of full-matrix least-squares on $F^2_{obs}$ using the SHELXTL-PC software package. The hydrogen atom positions were fixed geometrically and allowed to ride on the attached atom.

Table 1. Crystal data and structure refinement parameters for complexes.

| | |
|---|---|
| Empirical formula | $C_8H_{18}N_{10}O_6SAg_2$ |
| Formula weight | 598.12 |
| Crystal system | Monoclinic |
| Space group | $C2/c$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 17.144(4) |
| $b$ | 26.188(5) |
| $c$ | 8.600(2) |
| $\alpha$ | 90.00 |
| $\beta$ | 108.730(10) |
| $\gamma$ | 90.00 |
| $V$ (Å$^3$) | 3656.6(14) |
| $Z$ | 8 |
| $Dc$ (g cm$^{-3}$) | 2.173 |
| $\mu$(Mo-K$\alpha$) (mm$^{-1}$) | 2.307 |
| $F$(000) | 2352 |
| $\theta$ range (°) | 2.51–25.99 |
| Goodness-of-fit on $F^2$ | 1.033 |
| $R_1$, $wR_2$ $[I>2\sigma(I)]^a$ | 0.0541, 0.1092 |
| $R_1$, $wR_2$ (all data) | 0.0551, 0.120 |

$w=1/2[(F_o^2)+(0.0460P)^2+19.9091P]$; $P=(F_o^2+2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and bond angles (°) for complex 1.

| | | | |
|---|---|---|---|
| Ag1–N6 | 2.221(5) | Ag1–N1 | 2.238(6) |
| Ag1–O1 | 2.375(5) | Ag1–O1 | 2.530(5) |
| Ag2–N3 | 2.204(6) | Ag2–N4 | 2.217(6) |
| N6–Ag1–N1 | 141.1(2) | N6–Ag1–O1 | 110.9(2) |
| N1–Ag1–O1 | 106.93(19) | N1–Ag1–O1 | 88.32(18) |
| O1–Ag1–O1 | 75.23(19) | N3–Ag2–N4 | 145.2(2) |
| S1–O1–Ag1 | 136.6(3) | S1–O–Ag1 | 125.5(3) |
| Ag1–O1–Ag1 | 91.22(16) | C3–N1–Ag1 | 119.5(5) |
| C1–N1–Ag1 | 123.2(5) | C3–N3–C2 | 111.5(7) |
| C3–N3–Ag2 | 122.5(5) | C2–N3–Ag2 | 125.8(5) |
| C4–N4–Ag2 | 123.3(5) | C6–N4–Ag2 | 122.3(5) |
| O1$_W$···O12 | 3.062(13) | N4···N7 | 2.970(6) |
| N4···O13 | 3.055(7) | N5···O13 | 3.159(6) |
| N5···O14 | 3.093(7) | N5···N2 | 3.080(6) |
| N9···O1W | 3.187(12) | N9···O12 | 2.954(7) |
| N9···O14 | 3.142(8) | N10···O12 | 2.987(6) |
| N10···N3 | 3.092(6) | C4···O13 | 3.251(8) |
| C4···O1W | 3.154(13) | C8···O14 | 3.404(8) |

Symmetry codes for: **1** (a) $1-x$, $2-y$, $1-z$; (b) $-x$, $1-y$, $2-z$; (c) $x$, $1+y$, $z$; (d) $1-x$, $1-y$, $1-z$; (e) $1-x$, $2-y$, $1-z$; (f) $1-x$, $1-y$, $2-z$; (h) $1+x$, $y$, $z$; (i) $1-x$, $2-y$, $2-z$; (k) $-1+x$, $y$, $z$; (l) $-x$, $1-y$, $2-z$; (m) $-x$, $2-y$, $1-z$; (o) $-x$, $2-y$, $2-z$; (p) $-x$, $1-y$, $1-z$; (q) $x$, $y$, $1+z$; (r) $x$, $-1+y$, $z$; (s) $x$, $y$, $-1+z$.

## 3. Results and discussion

### 3.1. *Characterization of the complex*

The silver compound $[Ag_2(L)_2(SO_4)]\cdot 2H_2O$ was obtained in 36% yield, by reaction of the corresponding metal sulfate with L in a mixed solvent of ethanol-water at 90°C. The IR spectrum $[Ag_2(L)_2(SO_4)]\cdot 2H_2O$ displays characteristic bands of $NH_2$ groups of triazine at 3027–3117 cm$^{-1}$. Thermogravimetric analyses (TGA) shows that $[Ag_2(L)_2(SO_4)]\cdot 2H_2O$ loses 6.83% of total weight in the 70–160°C temperature

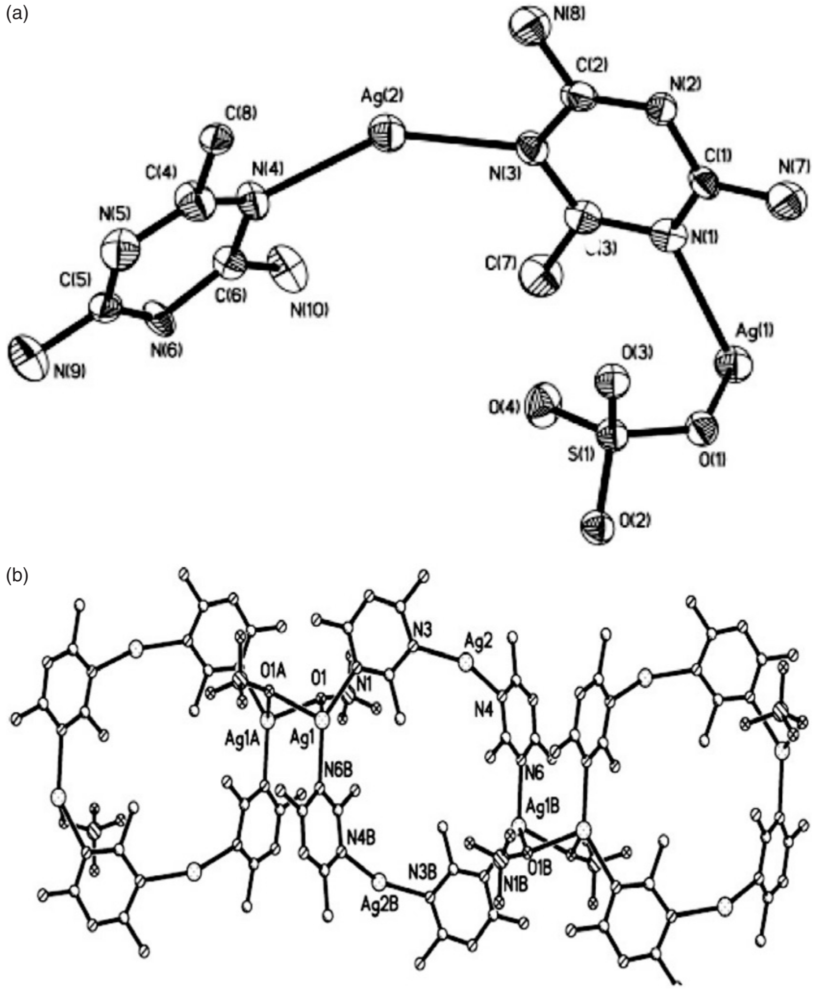

Figure 1. (a) The asymmetric unit shown in ellipsoids at 30% probability. (b) 1-D polymeric chain based on the $Ag_2L_2SO_4 \cdot 2H_2O$ building unit with macrocycles. All hydrogen atoms and water molecules are omitted for clarity. Key bond distances and bond angular: N(4)-Ag(2) 2.217(6), N(3)-Ag(2) 2.204(6), N(1)-Ag(1) 2.238(6), O(1)-Ag(1) 2.530(5)Å, N4-Ag2-N3 145.2(2), N1-Ag1-N6A 141.1(2)°.

range, which corresponds to the loss of two water molecules per formula unit (expected 6.02%). Furthermore, XRD of the remnant after TGA analysis shows that the composition of the product is consistent with $[Ag_2(L)_2(SO_4)] \cdot 2H_2O$, which was further confirmed by elemental analysis.

## 3.2. *Crystal structure*

The structure of the complex is shown in figure 1. Selected bond distances and angles are shown in table 2. Single crystal X-ray analysis of $[Ag_2(L)_2(SO_4)] \cdot 2H_2O$ revealed a 1-D polymeric structure with the $Ag_2L_2SO_4$ macrocycle building block, with a center of symmetry lying halfway along the $Ag(1) \cdots Ag(1A)$ separation figure 1(b).

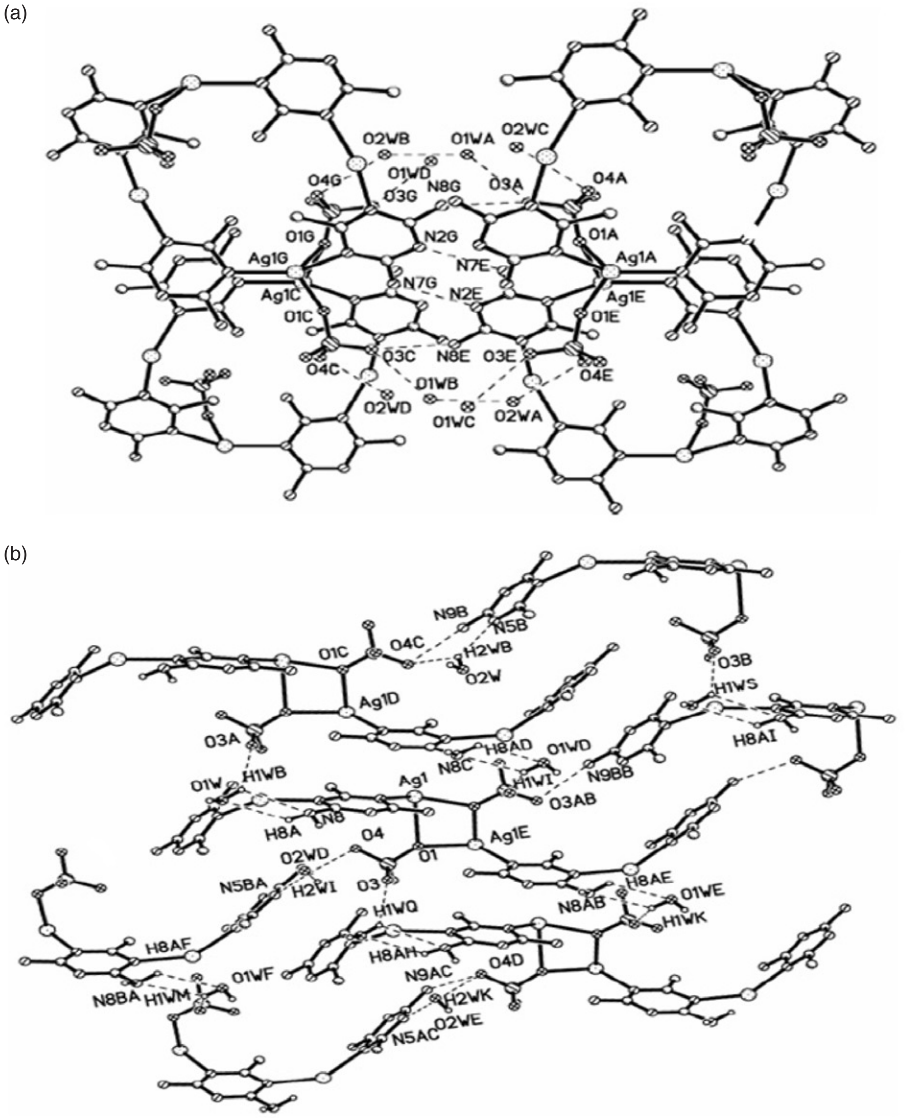

Figure 2. (a) 2-D sheet formed by spider web hydrogen bonding linkages in the *ab* plan. (b) 1-D polymeric chains stacked along the c-axis yielding adjacent 1-D polymeric chains through hydrogen bonding linkages. All hydrogen atoms are omitted for clarity.

The asymmetric unit comprises two Ag(I) centers, two dmt ligands, one sulfate and two $H_2O$ molecules. However, two silver centers exhibit different coordination environments, as shown in figure 1(a). One silver atom is joined by two N atoms from two different dmt ligands. However, the other silver atom is coordinated with two bridging O atoms from different sulfate anions and two N atoms from two dmt ligands forming a distorted trigonal-pyramidal coordination geometry. The coordination of one dmt ligand to two different silver atoms via two nitrogen atoms led to the formation of a big metallamacrocycle with four silver cations and four dmt molecules, in which four silver atoms (Ag(1), Ag(1b), Ag(2) and Ag(2b)) lie in one plane. A dihedral angle of 40.1° was

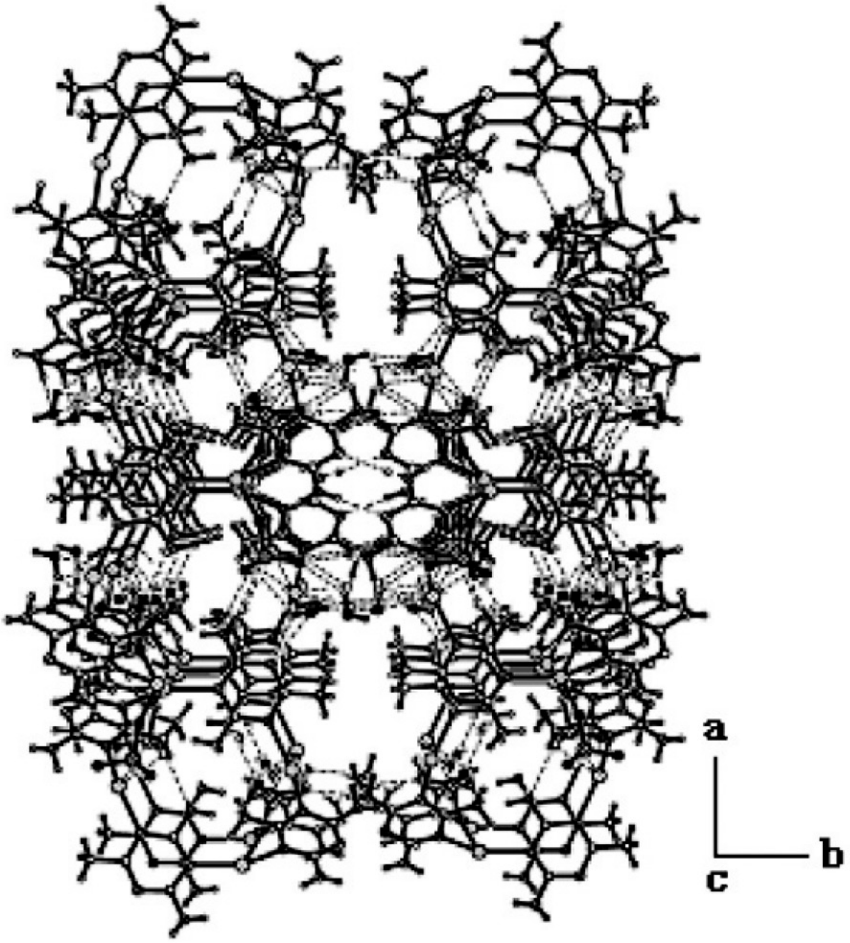

Figure 3. Crystal packing of $[Ag_2(dmt)_2OSO_3]\cdot 2H_2O$ viewed down the crystallographic *c* axis showing the 3-D open network with large channels produced by cross-linked hydrogen bonds. All hydrogen atoms are omitted for clarity.

found for the two adjacent metallamacrocycles, which were connected by two $\mu$-oxygen atoms from two sulfate ions via coordination to two silver cations from two different metallamacrocycles. Thus 1-D polymeric chains along the *a*-axis were established. Furthermore, hydrogen bonds and weak face-to-face $\pi$–$\pi$ interactions from two triazine rings of adjacent macrocycles play crucial roles in the formation and stabilization of the chains. The Ag $\cdots$ Ag distances from neighboring metallamacrocycles are 3.507 Å, while the distances of Ag(1b) $\cdots$ Ag(1) and Ag(2) $\cdots$ Ag(2b) in one metallamacrocycle are 9.374 Å and 8.376 Å, respectively.

A three-dimensional open network with large channels was constructed from 1-D polymeric chains joined by various hydrogen bonds, as shown in figure 3. From figure 2(a), one can see 1-D polymeric chains are held together by the hydrogen bonds of N(7)–H $\cdots$ N, N–H $\cdots$ O(3)–S and S–O(3) $\cdots$ O(1W) $\cdots$ O(2W) $\cdots$ O(4)–S to form spider web like planar sheets in the *ab* plane. And along the *c*-axis, the 1-D polymeric chains are connected via the formation of N(8) $\cdots$ O(1W) $\cdots$ O(3) and

N(5) $\cdots$ O(2W) $\cdots$ O(4) hydrogen bonds, leading to the construction of open channels (see figure 2b). There are two types of N(8) $\cdots$ O(1W) hydrogen bonds (N(8)–H(8A) $\cdots$ O(1W) 2.539(3) Å $(x, y, z+1)$ and O(1W)–H(1WB) $\cdots$ N(8) 2.325(5) Å $(x, y, z-1)$) existing in the network. Thus the 2-D spider web like sheets, which are formed from the 1-D infinite metallamacrocycle chains utilizing the N–H $\cdots$ N and N–H $\cdots$ O(3)–S hydrogen bonds along the *b*-axis, stack along the *c*-axis to build a three dimensional open network with large channels containing uncoordinated water molecules as guest molecules via the formation of cross-linked hydrogen bonds. In the construction of the 3-D network, uncoordinated water molecules play vital roles. At least, four novel hydrogen bonding linkages as shown in figure 3 were found for water molecules in the network, formulated as S–(3) $\cdots$ O(1) $\cdots$ O(2W) $\cdots$ O(4)–S, S–O(3) $\cdots$ O(1W) $\cdots$ O(2W) $\cdots$ N(5), N(8) $\cdots$ O(1W) $\cdots$ O(2W) $\cdots$ O(4)–S, and N(8) $\cdots$ O(W) $\cdots$ O(2W) $\cdots$ N(5).

In conclusion, we have demonstrated the self-assembly of the dmt and $Ag^+$ into a 1-D coordination polymer comprising metallamacrocycles. Furthermore, a three-dimensional network with large channels was constructed from 1-D polymer chains cross-linked to each other by various types of hydrogen bond linkages.

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