SYNTHESIS AND STRUCTURE OF A METAL-ORGANIC SOLID HAVING THE CADMIUM(II) SULFATE NET

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ABSTRACT

Reaction of silver(I) nitrate and hexamethylenetetramine (HMTA) gives crystals of $Ag_2(HMTA)(NO_3)_2$, which was formulated by elemental microanalysis and a single crystal x-ray study. Its $Ag_2(HMTA)$ open-framework is the first example of a decorated $CdSO_4$ net. The relative orientation of the tetrahedral HMTA building blocks in this structure point to numerous opportunities toward constructing novel chiral and polar porous frameworks.

INTRODUCTION

Soluble organic,[1] metal-organic,[2] organometallic,[3] and inorganic[4] molecular building blocks have been linked using addition copolymerization and condensation polymerization reactions to yield open-framework solids. Generally, these structures are held together by attractive and directional forces such as hydrogen bonding and metal-ligand coordination. The demonstrated ability to manipulate and exploit these forces toward the design of porous solids, coupled to the vast number of molecular building units that are available as starting materials have yielded framework structures of diverse topology and architecture. For example, structures that adopt topologies related to the archetypes diamond,[4,5] rutile,[6] α-$ThSi_2$,[2d,e] PtS,[7] and quartz[8] have been reported. The structures of these solids are conceptually related to the assembled analogues by simply replacing their constituent atoms and/or bonds with metal ions and large molecular entities such as clusters, metal complexes or organic ligands to yield less dense frameworks. This report shows how silver(I) ions combined with the *tetra*-monodentate ligand, hexamethylenetetramine (HMTA), produce the first example of a three-dimensional, four-connected (3-D, 4-C) open-framework solid that is topologically related to $CdSO_4$.[9]

EXPERIMENTAL

A 70 mL aqueous solution of silver nitrate (0.280 g, 1.65 mmol) was combined at room-temperature with another 10 mL aqueous solution of hexamethylenetetramine (0.100 g, 0.71 mmol). The resulting clear colorless mixture was stirred for 1 min. and allowed to stand in an uncovered container for 2 days. The large colorless crystals that appeared at the bottom of the container were isolated from the small amount of needle-like crystals at the surface of the solution and washed with 1:1 solution mixture of water and ethanol to give 0.061 g (18 % yield) of $Ag_2(HMTA)(NO_3)_2$. This compound is stable in air, and insoluble in ethanol, chloroform and tetrahydrofuran, however, it slowly dissolves in water, acetonitrile and *N, N*-dimethylformamide. Anal. Calcd for $C_6H_{12}N_6O_6Ag_2$: C, 15.01; H, 2.52; N, 17.51; Ag, 44.95. Found: C, 14.96; H, 2.51; N, 17.26; Ag, 44.97. The

homogeniety of the bulk product was confirmed by comparison of the observed and calculated x-ray powder diffraction patterns. The calculated pattern was produced using (SHELXTL-XPOW) program with the single crystal data. Single crystals of $Ag_2(HMTA)(NO_3)_2$ were analyzed at 20 ± 1 °C, tetragonal, space group $P4_122$ (no. 142) with $a = 6.751$ (1) Å, $c = 26.240$ (5) Å, $V = 1195.9$ (4) Å^3, $Z = 4$, $\rho_{calcd} = 2.666$ g. cm^{-3}, $\mu_a(MoK\alpha) = 3.31$ mm^{-1} and R_1 (unweighted, based on F) = 0.027. Atomic coordinates for nonhydrogen atoms in crystalline $Ag_2(HMTA)(NO_3)_2$ are listed below.

Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Ag_2(N_4C_6H_{12})(NO_3)_2$

Atom	Fractional Coordinates			Equivalent Isotropic Thermal Parameter,
Type	10^4x	10^4y	10^4z	B, Å^2 x 10
Ag_1	5000	5263(1)	0	21(1)
Ag_2	567(1)	9433(1)	1250	26(1)
N_1	1830(6)	3668(5)	-38(1)	14(1)
N_2	142(6)	1120(5)	464(1)	14(1)
N_3	4858(7)	8269(7)	855(1)	22(1)
O_1	3449(9)	7472(8)	631(2)	43(1)
O_2	4493(7)	9677(7)	1151(1)	31(1)
O_3	6576(8)	7710(9)	786(2)	43(1)
C_1	1923(7)	2389(7)	418(1)	15(1)
C_2	1634(7)	2395(7)	-496(1)	15(1)
C_3	0	4899(9)	0	14(1)
C_4	0	-111(8)	0	15(1)

RESULTS AND DISCUSSION

Reacting aqueous solutions of silver(I) nitrate and HMTA in approximately 2 : 1 mole ratio yields large grey rectangular crystals of $Ag_2(HMTA)(NO_3)_2$, which was formulated by elemental microanalysis and structurally characterized by an x-ray single crystal study. This compound was found to have an extended network composed of the building units shown in Figure 1.

The asymmetric unit consists of two crystallographically distinct silver atoms (Ag1 and Ag2) with each lying on a 2-fold-axis, one adamantane-like HMTA unit (N1 and N2), and one nitrate anion (N3). Each silver (I) is bound to two symmetry equivalent HMTA units (Ag1-N1, N1a = 2.462 (5) Å and Ag2-N2b, N2d = 2.373 (3) Å) and two nitrate anions with each being shared by two symmetry inequivalent silver atoms. Here, Ag1
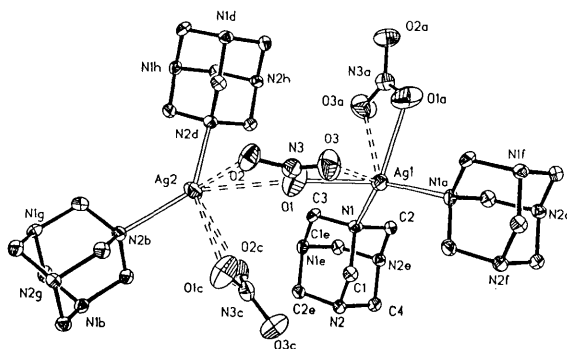
Figure 1. Perspective drawing of the coordination environment for the silver atoms in the solid-state structure of $Ag_2(HMTA)(NO_3)_2$ with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50 % of their electron density. Hydrogen atoms have been omitted for purpose of clarity. Atoms labelled with an additional letters *a-h* are related to atoms without such labels by the following symmetry operations: *a*, 1-x, y, -z; *b*, -y, 1-x, _-z; *c*, 1-y, 1-x, _-z; *d*, x, 1+y,z; *e*, -x, y, -z; *f*, 1+x, y, z; *g*, -y,1+x, _-z; and *h*, -x, 1+y, -z.

forms two strong (Ag1-O1, O1a = 2.462 (5) Å) and two weak (Ag1-O3, O3a = 2.849 (5) Å) bonding interactions to the nitrate anions N3 and N3a.[10] The anion N3 is shared with Ag2, through intermediate (Ag2-O2 = 2.668 (5) Å) and weak (Ag2-O1 = 2.859 (5) Å) bonds, which also form between Ag2 and a second anion (N3c) that is shared with a different Ag1. Excluding consideration of weak Ag-O interactions, each silver atom has a distorted tetrahedral coordination (N1-Ag1-O1 = 85.5 (2)°, N1-Ag1-O1a = 105.4 (2)°, N1-Ag1-N1a = 126.6 (2)°, and N2d-Ag2-O2 = 90.3 (1)°, O2-Ag2-N2b = 123.6 (2)°, N2b-Ag2-N2d = 129.7 (2)°) due to the steric demands of the HMTA units. The bond length and angle values of HMTA in this structure remain unchanged upon its coordination to the metal center as they are coincident with those observed for pure HMTA.[11] In the present structure, each HMTA is bridged by a silver(I) center to form a 3-D, 4-C network shown in Figure 2a.

It is worth noting that the nitrate anions point to the center of a 2-D channel system having rectangular pores with aperture dimension of nearly 9 × 18 Å, that is constricted at the center to 4 × 18 Å as shown in Figure 2b.

Attempts to exchange the nitrates by immersing solid samples of $Ag_2(HMTA)(NO_3)_2$ in alcoholic solutions containing excess potential guest anions such as BF_4^-, PF_6^-, and $CF_3SO_3^-$ at room-temperature were unsuccessful. Simple anions such as Cl⁻ and Br⁻ gave new crystalline phases as observed by x-ray powder diffraction data obtained on the products. It appears that the integrity of the framework is compromised upon mobilizing the nitrates due to their close and multiple bonding interactions to the silver ions. This is in contrast to the anion exchange behavior of the Ag(4,4'-bpy)⁻NO₃ solid,[2a] where the process occurs reversibly and without destruction of its framework. Here, each nitrate ion bonds weakly to silver (Ag-O = 2.78 (1) and 2.83 (2) Å) using one oxygen to give loosely bound anions that can be mobilized without affecting the structural organization of the host framework.

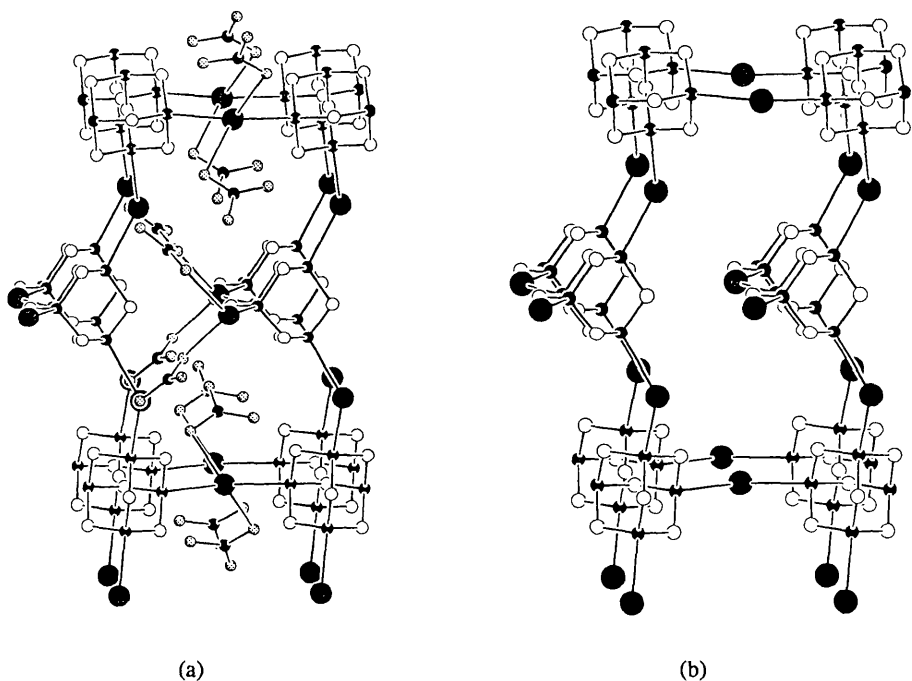(a)   (b)

Figure 2. Perspective view for the solid-state structure of $Ag_2(HMTA)(NO_3)_2$ (a) The nitrogen atoms (small dark spheres) of HMTA are bound to silver atoms (large dark spheres) which are coordinated to two nitrate ligands (small dark spheres for nitrogen and shaded spheres for oxygen). (b) The same view is shown without the nitrate ions.

       The novelty of the $Ag_2(HMTA)$ framework structure lies in its relationship to the 4-C net of $CdSO_4$, which is revealed upon comparison of Figure 2b and 3. The $CdSO_4$ structure and the derived net are shown in Figure 3a and b, respectively. Replacing every vertex in the net of $CdSO_4$ (Fig. 3b) by a tetrahedron of vertices (4 N of HMTA) gives the $Ag_2(HMTA)$ framework, in which the tetrahedra are linked by silver atoms—shown as lines in Figure 3c. This process has been referred to as *decorating*. [9a,12] The two simplest 4-C nets (only two vertices in the topological repeat unit) are those of C in diamond, and Cd and S in $CdSO_4$. Numerous[5] decorated diamond networks exist such as the porous Mn-Ge-S framework of the $MnGe_4S_{10} \cdot 2TMA$,[4] where Ge_4S_6 and MnS_4 tetrahedra alternately replace the carbon vertices in diamond. On the other hand, the $Ag_2(HMTA)$ network is the first example of a decorated $CdSO_4$ net which is interesting because, unlike other decorated nets reported in the literature where the derived nets are unique, for this structure an infinite series of nets related as polytypes can be derived. The simplest of such possibilities have chiral $P4_122$ (Figure 3c) (or the enantiomorphic form) and polar $Ama2$ (Figure 3d) symmetries. The $Ag_2(HMTA)$ structure has the first symmetry and the HMTA groups are arranged in helices around the 4_1 axes.
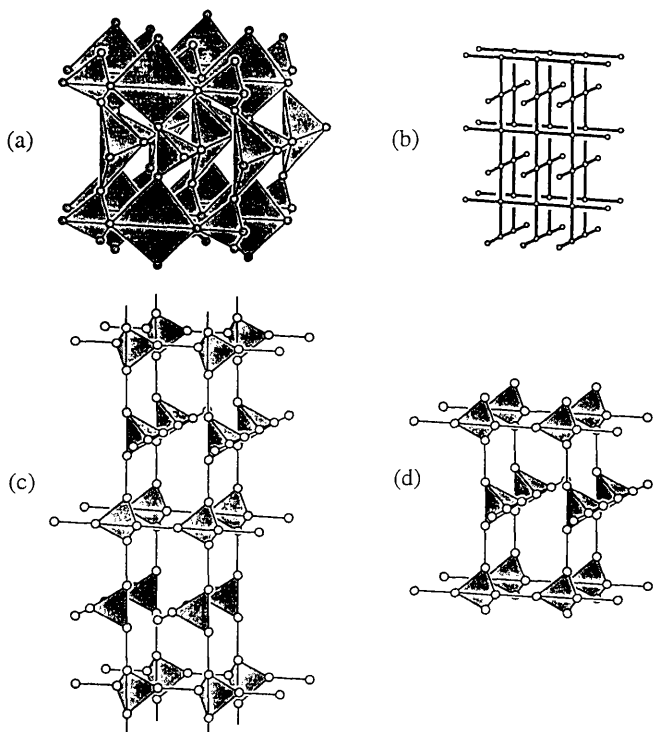
Figure 3. A schematic illustration of the structure of $CdSO_4$ represented as CdO_4 and SO_4 tetrahedra (a) and its net represented having vertices (open spheres) corresponding to Cd and S atoms and edges (solid lines) corresponding to —O— links (b), including its two simplest decorated nets having chiral (c) and polar (d) symmetries with the tetrahedra of vertices and the lines connecting them representing the HMTA building blocks and Ag(I) ions, respectively.

The importance of the anion in the formations of metal-organic networks is shown by the fact that in the presence of PF_6^-, the silver ions and HMTA building units assemble to give crystalline $Ag(HMTA)^{\cdot}PF_6(H_2O)$. This framework is based on the $SrSi_2$ net, in which the vertices are alternately occupied by Ag and HMTA.[13] A 3-D, 3-C network in crystalline $Ag(HMTA)NO_3$[14] is produced by the combination of Ag(I) and HMTA (unreported quantities) in the presence of NO_3^- at room-temperature yields. To our knowledge the extended 3-D, 4-C network present in $Ag_2(HMTA)(NO_3)_2$ is the first of its kind in the metal coordination chemistry of HMTA. Given the simplicity of the building units used in the assembly of this solid, it is our current objective to examine in detail and elaborate on the anion-framework interactions and their connection to the resulting structure.

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