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Research Article

SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTY OF A NEW TRIDYMITE-TYPE IODOARGENTATE

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ABSTRACT

A new compound, $Cd(en)_3Ag_2I_4$ (**1**), has been synthesized by self-assembly reaction, and characterized by elemental analysis, IR spectra, PXRD, and single-crystal X-ray diffraction. The compound contains a three-dimensional framework built by AgI_4 tetrahedra with tridymite topology, and the discrete $Cd(en)_3^{2+}$ cations are located in the channels. The thermal property of the compound has also been investigated.

Keywords: *Iodoargentate; Tridymite Topology; Three-Dimensional Framework; AgI$_4$ Tetrahedron; Self-Assembly*

INTRODUCTION

In a broad solid-state field, the known classes of nature' s geological examples are overwhelmingly dominated by oxides, such as silicates (Villaescusa *et al*., 1999), aluminosilicates, phosphates (Freyhardt *et al*., 1996), and aluminophosphates (Wilson *et al*., 1982). These oxides exhibit widely diverse applications in gas storage, ion exchange, and catalysis because they contain infinite framework structures with ordered pores exclusively by TO_4 tetrahedra (T = tetrahedrally coordinated Al or Si or P atom). In addition to traditional oxide-containing systems, open frameworks are now being found in the realm of sulfides (Cahill *et al*., 1998), chlorides (Zones *et al*., 1982), and nitrides (Schnick *et al*., 1994), as well as in coordination compounds (Chae *et al*., 2004). And the new generation of porous materials offers a wider range of chemical and physical properties that are beginning to be explored.

Interest in open-framework metal halides was stimulated by the discovery of the $[H_2NEt_2][CuZn_5Cl_{12}]$ and $[H_2NMe_2]_n[Cu_nZn_{6-n}Cl_{12}]$ (n =1 or 2) (Martin *et al*., 1997), consistent with aluminosilicate analogy, are also constructed from corner sharing tetrahedral primary building units, which utilized halide ions as replacements for the oxygen or chalcogenide anions. These novel halozeotype materials represent non-oxide analogues of microporous aluminosilicates and provide the foundation for new developments in host-guest chemistry through crystal engineering of chemical framework building units. However, few halozeotype materials have been reported in the past decades (Debord *et al*., 1998).

The design of open-framework materials remains a significant challenge both in terms of the syntheses as well as in the understanding of the principles of structure and bonding that direct the formation of extended structures. Recently, we have initiated syntheses of silver-iodide framework materials in order to exploit the reactivity of AgI_4^{3-} building blocks, and found transition metal coordination complexes as structure-directing agents in the synthesis of the iodoargentate compounds offer a range of unique conformations that are not found with organic amine molecules (Jiang *et al*., 2008). In an attempt to extend this work, we obtained a new framework iodoargentate, $Cd(en)_3Ag_2I_4$.

MATERIALS AND METHODS

Materials and Physical Measurements

All reagents were of analytical grade and were used as obtained by commercial sources without further purification. The elemental analysis was carried out on an Elemental Vario EL III microanalyzer. EDS analysis of compound **1** was performed using JSM-5600LV (Japan). The Ag: I molar ratio in **1** is 1: 2.07. IR spectra of the sample was recorded on Nicolet Avatar 360 FTIR spectrometer in the spectral region from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} using the KBr technique. The thermal behavior (TGA) of the compound **1** was carried out by Metter Toledo Star under a flow of nitrogen (40 mL/min) from 50 to 550 °C at heating rate of 10 °C /min.

Synthesis of the Title Compound

The compound **1** was prepared by dissolving $Cd(NO)_3{\cdot}4H_2O$ (0.064 g) in 2 mL DMF, and the AgI_2^- solution(3.779 g), which was prepared by $AgNO_3$(0.865 g) dissolved in DMF solution, then added the excessive KI/DMF solution and stirred until the solvent clear, dropping the DMF solution until 50ml. And then the mixed solution was added 1mL en. The solution was kept in room temperature for six days, and the products were washed with ethanol and water, respectively. Well-formed colorless block single **1** with 91% yield based on cadmium. C, N, H analysis: calcd C 7.09, N 8.27, H 2.36%; found C 7.26, N 8.11, H 2.50%. IR (KBr): v = 3428 (vs), 2920 (m), 2857 (m), 1635 (m), 1560 (m), 1468 (w), 1406 (vw), 1387 (vw), 1328 (w), 1130 (w), 1110 (w), 1086 (m), 965 (m), 679 (m), 608 (m), 469 (m) cm^{-1}.

Table 1: Crystal data and structure refinement for compound 1

Compound	**1**
Formula	$C_6N_6H_{24}CdAg_2I_4$
Formula weight	1016.06
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	*P6322*
a/Å	9.0461(14)
b/ Å	9.0461(14)
c/ Å	14.438(2)
γ/°	120.00
Volume	1023.2(3) $Å^3$
Z	2
Calculated density	3.298 $Mg{\cdot}m^{-3}$
F(000)	912
θ range for data collection	2.60 to 24.99
Limiting indices	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-17 \leq l \leq 14$
	615/ 601
Reflections collected/unique	99.5%
Completeness	1.019
GOF on F^2	$R_1 = 0.0499$, $wR_2 = 0.1595$
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0506$, $wR_2 = 0.1601$
R indices (all data)	- 1.219/ 1.052 $e{\cdot}Å^{-3}$
Largest diff. peak and hole	

Crystal Structure Determination

A suitable single crystal of the compound **1** with the dimensions of 0.25 × 0.20 × 0.10 mm^3 was carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. The intensities of the crystal data were collected on a Bruker SMART APEX CCD diffractometer with graphite–monochromated Mo–$K\alpha$ (λ = 0.71073 Å) using the SMART and SAINT programs. The structure solution was performed with direct methods using SHELXS-97. Structure refinement was done against F^2 using SHELXL-97 (Sheldrick *et al*., 2008). All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealised geometry and were refined with isotropic displacement parameters using the riding model. The details of the crystal parameters, data collection, and refinements for the complexes are listed in Table 1, and selected bond lengths and angles are summarized in Table 2.

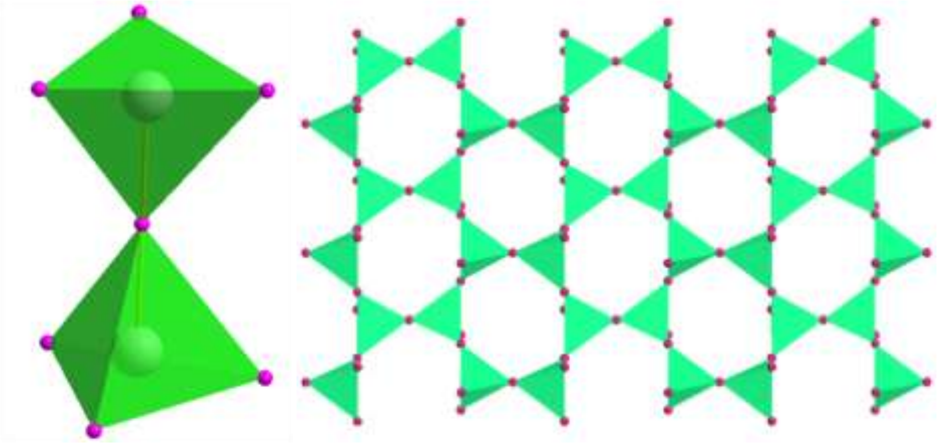
Table 2: Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Angle	**(°)**	Angle	**(°)**
Ag1-I1	2.879(2)	I2- Ag1- I2	113.68(3)	Ag1-I1-Ag1	180.0
Ag1-I2	2.8541(8)	I2 -Ag1 -I1	104.83(4)	Ag1-I2-Ag1	143.65(5)

RESULTS AND DISCUSSION

Crystal Structure of the Complex

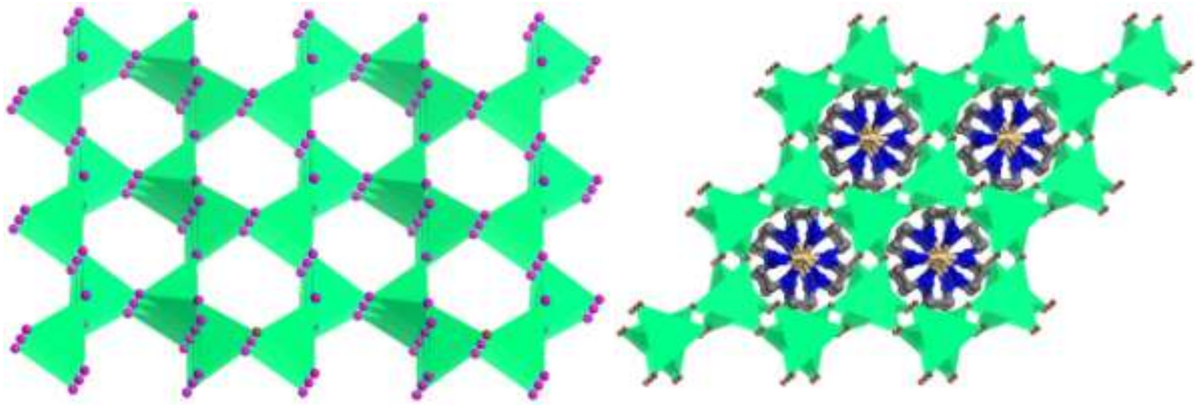
Single-crystal X-ray diffraction analysis reveals that compound 1 belongs to the stuffed tridymite structure with a hexagonal unit cell and space group $P6_322$. In this stuffed tridymite structure, each AgI_4 tetrahedron is connected with four other AgI_4 tetrahedron by corner sharing to build up the tridymite skeleton. The Ag-I distances within the tetrahedral AgI_4 geometry range from 2.8541(8) to 2.879(2) Å, the I-Ag-I angles vary between 104.83(4) and 113.68(3)°, and the tetrahedral AgI_4 is slightly distorted as compared with those in other silver iodides(Sheldrick *et al*., 2010).



(a) **(b)**

Figure 1a: Ag_2I_7 unit on which 6^3 layers are based, with silver atoms at the tetrahedral centers and iodine atoms at the vertices; 1b: The 6^3 layer formed by connecting four of the units shown on panel a

The structure of compound **1** can be viewed as built from the alternative stacking of parallel 6^3 layers along *c* axis. The basic unit in each layer is two AgI_4 tetrahedra sharing a single vertex with a Ag-I-Ag angle of 180° (Figure 1a). The two another vertices bridge to other units to form six-membered rings with 6^3 net, as shown in Figure 1b. The remaining vertex sharing of AgI_4 tetrahedra between adjacent layers creates a three-dimensional framework with tridymite topology depicted in Figure 2a. The discrete $Cd(en)_3^{2+}$ cations are located in the six-membered channels (Figure 2b).



(a) **(b)**

Figure 2a: **Structure of the title compound. Corner sharing of adjacent tetrahedra sheets creates a three-dimensional framework with tridymite topology; 2b: The discrete $Cd(en)_3^{2+}$ cations are located in the six-membered channels**

The similar structure found in $BaAl_2O_4$ and $SrAl_2O_4$, the barium or strontium ions are in the channels, which are formed by $[A1O_4]^{5-}$ tetrahedral (Poort *et al*., 1995). The structure of $LiBaPO_4$ is closely related to $BaAl_2O_4$ with tridymite topology. The most important difference between the structures of $LiBaPO_4$ and $BaAl_2O_4$ is the difference in size of the two kinds of tetrahedra in $LiBaPO_4$ ($[LiO_4]^{7-}$ and $[PO_4]^{3-}$) (Zhang *et al*., 2011), whereas there is only one kind of tetrahedron in $BaAl_2O_4$ ($[A1O_4]^{5-}$).

Powder XRD and Thermogravimetric Analysis

The XRD experimental and computer-simulated patterns of compound 1 are presented in Figure 5, where the main diffraction peaks of the experimental and simulated patterns match well in the key positions, confirming the purity of compound **1**. To examine the thermal stability of compound **1**, thermal gravimetric (TG) analyses were carried out for **1** between 50 and 600 °C (Figure. 5). The samples were heated up under a flow of nitrogen (40 mL/min) at a heating rate of 10 °C/min. The curve for **1** shows three steps losses. The first loss before 312 °C can be attributed to liberation of one organic ligand (weight loss: theoretical 5.9%; obsd 5.7%). In the following steps, **1** loses gradually the remaining organic ligands, and this process overlaps with sublimation of CdI_2; therefore, it is difficult to make out these two thermal processes. The total loss of 30.1% between 330 and 504 °C corresponds to the loss of two remaining organic amines and half of CdI_2 (calcd: 11.8% for 2 en and 18.0% for 0.5 CdI_2).

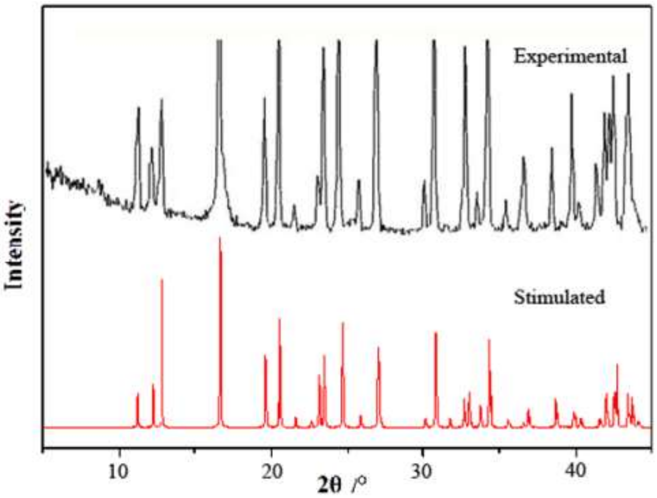


Figure 3: Experimental and simulated XRD spectra of the title compound

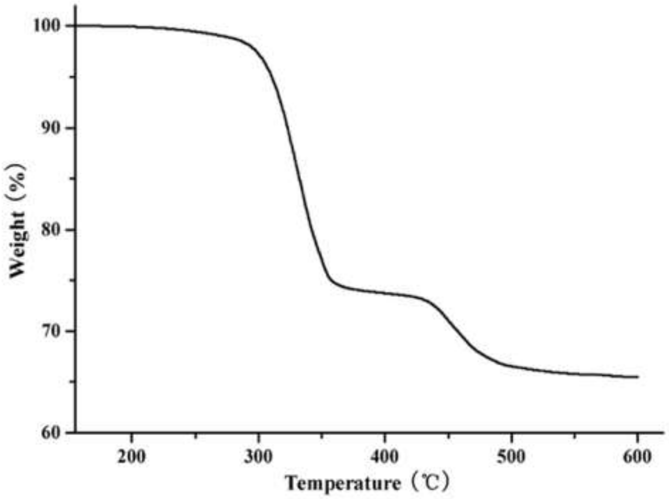


Figure 4: TG curves of the title compound

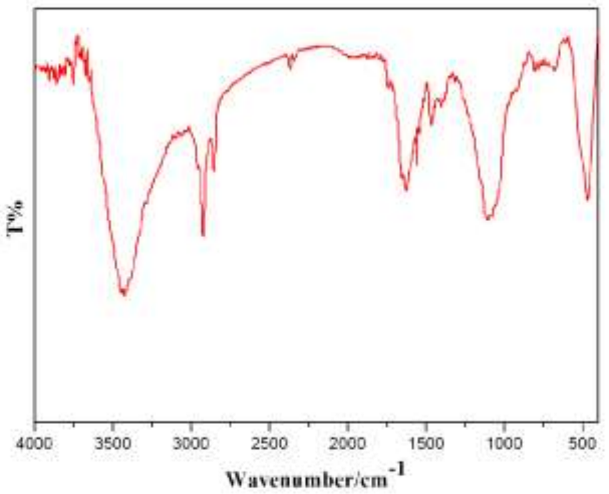


Figure 5: IR spectrum of the title compound

IR spectra

The bands in the region of 3420-2857 cm-1 correspond to the N-H and C-H stretching vibrations from organic amines, 1384-956 cm-1 are attributed to the NH_2 twisting and C-N stretching vibrations, the bands at 1635, 1560 cm-1 is assigned to vs (-NH_2), which indicate the presence of organic amine (Iwamoto *et al*., 2011). These IR results are corresponding to the crystallographic structural analyses. Some important assignments of the infrared spectrum for the title compound are shown in the experimental section.

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