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New Framework Iodoargentates: $M(en)_3Ag_2I_4$ (M = Zn, Ni) with Tridymite Topology

Yan-Si Jiang,[†] Hua-Gang Yao,[†] Shou-Hua Ji,[‡] Min Ji,[†] and Yong-Lin An*[,†]

Departments of Chemistry and of Materials, Dalian University of Technology, Dalian 116024, China

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Two novel framework compounds, $Zn(en)_3Ag_2I_4$ (**1**) and $Ni(en)_3Ag_2I_4$ (**2**), have been synthesized by a self-assembly reaction. Both of them contain an unexpected framework, $Ag_2I_4^{2-}$ with tridymite topolopy, and the discrete $M(en)_3^{2+}$ cations are located in the channels. Their thermal properties and circular dichroism spectra were investigated.

Microporous materials are of great interest because of their chemical diversity and immense practical importance for commercial applications such as gas storage, ion exchange, and catalysis.[1] In the past decades, nature's geological examples have been followed by transforming commom silicate, aluminate, and phosphate building blocks into zeolite-type materials with microporous frameworks.[2] There are many elements that can be incorporated into the frameworks to manipulate the chemical properties of the materials. In spite of extensive substitution for the framework composition, the known classes of microporous materials are overwhelmingly dominated by oxide, mixed oxide/fluoride matrices, or sulfides.[3,4] The refractory nature of the metal oxides provides remarkable stability to the microporous frameworks at the expense of reactivity and tractability. For this reason, there is considerable interest in the synthesis of microporous solids from inorganic and organic building blocks to obtain greater control of the framework design.[5]

In 1997, Martin and Zubieta independently introduced a new type of microporous compound, which utilized halide ions as replacements for the oxygen or chalcogenide anions.[6] These materials were formed by transition-metal halides such as zinc dichloride and cuprous chloride; zinc and copper are both known to exhibit tetrahedral geometries with chlorine atoms. 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 microporous halozeotype materials have been reported so far.

To achieve a rational design of halozeotype materials, a promising route is the choice of suitable inorganic compositions as building units and flexible organic molecules as templates. Recently, the reaction between silver iodide and iodide ions attracted our attention because the solubility of AgI increases in appropriate solvents upon the addition of excess KI and the active intermediate AgI_2^- anion is a good precursor to construct higher dimension compounds. Significantly, the introduction of the metal complexes as templates instead of organic amines has proven to be an

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* To whom correspondence should be addressed. E-mail: ylan@dlut.edu.cn.

[†] Department of Chemistry.

[‡] Department of Materials.

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effective route to generating open-framework architectures.[7] Here we report two new framework complexes, **1** and **2**, which represent the first framework iodoargentates.

Both compounds **1** and **2** were prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (0.089 g) or $Ni(NO_3)_2 \cdot 6H_2O$ (0.058 g) in 2 mL of *N*,*N*-dimethylformamide (DMF). To the resulting solution were added 1 mL of ethylenediamine and 3.8 g of a 0.1 M AgI_2^-/DMF solution. The 0.1 M AgI_2^-/DMF solution was prepared as follows: $AgNO_3$ (0.865 g) was dissolved in 10 mL of DMF; the resulting solution was added to 20 mL of the saturated KI/DMF solution and stirred until the mixture became a clear solution; last, the solution was diluted to 50 mL by the addition of DMF. The reactive solution was kept at room temperature for 5 days, colorless single crystals of **1** with 90% yield based on zinc and purple single crystals of **2** with 93% yield based on nickel were formed, and the products were washed with ethanol and water, respectively. This synthetic route allowed us to obtain a pure phase. The composition analyses of **1** and **2** by energy-dispersive spectrometry indicate molar ratios of Zn:Ag:I = 1.0:2.1:4.1 and Ni:Ag:I = 1.0:2.0:3.9, respectively, which are in agreement with the results by X-ray diffraction analyses below.

Single-crystal X-ray diffraction analyses of compounds **1** and **2** revealed that they are isomorphous and possess a three-dimensional framework of AgI_4 tetrahedra with tridymite topology.[8] The Ag−I distances within the tetrahedral AgI_4 geometry range from 2.8529(10) to 2.890(3) Å, the I−Ag−I angles vary between 104.93(6) and 113.88(5)°, and the tetrahedral AgI_4 is slightly distorted as compared with those in other silver iodides.[9]

The structures of compounds **1** and **2** can be viewed as built from the alternative stacking of two layers of AgI_4 tetrahedra along the *c* axis. In each layer, the tetrahedra share three corners to form six-membered rings with alternating tetrahedral aprices pointing up and down in the *c* direction, as shown in Figure 1. The relationship between the two layers is that all tetrahedra in one layer rotated by 37.59° about the *c* axis with respect to one another. Corner sharing between adjacent layers creates a three-dimensional framework of all corner-shared AgI_4 tetrahedra with tridymite topology depicted in Figure 2. The discrete $M(en)_3^{2+}$ cations are located in the six-membered channels.

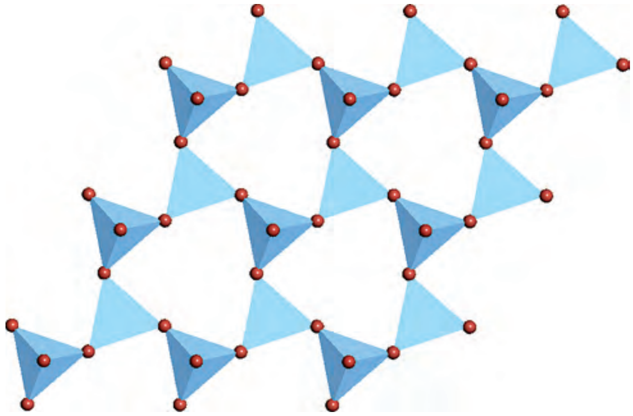

Figure 1. Sheet of tetrahedra AgI_4 viewed along the *c* axis showing a sharing of the tetrahedra with alternating tetrahedral aprices pointing in the opposite direction.

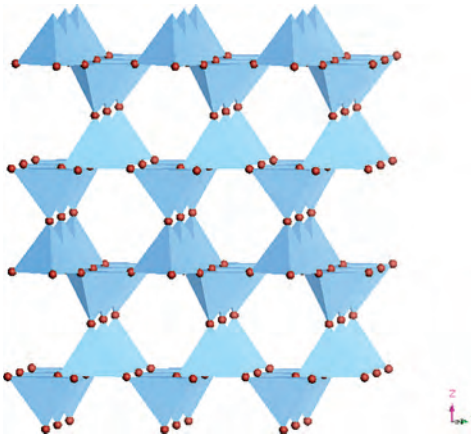

Figure 2. Structure of compound **1**. Corner sharing of adjacent tetrahedra sheets creates a three-dimensional framework with tridymite topology. $Zn(en)_3^{2+}$ cations have been omitted for clarity.

Thermogravimetric analyses (TGA) of compounds **1** and **2** were carried out under a flow of nitrogen (40 mL/min) from 25 to 600 °C with a heating rate of 10 °C/min. The curve for **1** shows multistep losses. The mass loss before 218 °C can be attributed to liberation of one organic ligand (weight loss: theoretical 6.2%; obsd 6.0%). In the following step, **1** loses gradually the remaining organic ligands, and this process overlaps with sublimation of ZnI_2; therefore, it is difficult to make out these two thermal processes. The total loss of 30.8% between 232 and 471 °C corresponds to the loss of two organic amines and half of ZnI_2 (calcd: 12.4% for 2 en and 16.5% for 0.5 ZnI_2). The thermal decomposition behavior of compound **2** is in a similiar pattern. It releases organic ligands roughly in three steps with corresponding mass losses of 2.6%, 3.1%, and 13.9%, respectively. The total mass loss of 19.6% is in accordance with the theoretical value of the complete loss of three organic ligands (calcd 18.6% for a loss of 3 en). The fourth loss of 19.9% from 430 to 525 °C is ascribed to the release of AgI.

The circular dichroism (CD) spectra of $M(en)_3^{2+}$ (M = Zn^{2+}, Ni^{2+}) of compounds **1** and **2** in the visible region

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(8) Crystal data for **1**: $C_6H_{24}Ag_2I_4N_6Zn$, fw = 969.02, monoclinic, *P*6(3), $a = 9.0550(6)$ Å, $b = 9.0550(6)$ Å, $c = 14.4468(19)$ Å, $\gamma = 120.00°$, $V = 1025.84(17)$ Å^3, $Z = 2$, $D_{calc} = 3.137$ g cm^{-3}, $R = 0.0422$, $R_w = 0.1027$, reflections used 5740 with $I > 2\sigma(I)$. Crystal data for **2**: $C_6H_{24}Ag_2I_4N_6Ni$, fw = 962.36, monoclinic, *P*6(3), $a = 8.9969(2)$ Å, $b = 8.9969(2)$ Å, $c = 14.4374(7)$ Å, $\gamma = 120.00°$, $V = 1012.06(6)$ Å^3, $Z = 2$, $D_{calc} = 3.158$ g cm^{-3}, $R = 0.0360$, $R_w = 0.0776$, reflections used 7767 with $I > 2\sigma(I)$. Data collection was performed on a Bruker Smart APEX II diffractometer equipped with graphite-monochromitized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K.

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consist of two overlapping components of opposite sign. These two CD spectra indicate D_3 symmetry of the complex ions of zinc or nickel with chelating ethylenediamine.[10]

In conclusion, two novel frameworks with tridymite topology were successfully synthesized by a self-assembly reaction of AgI_2^- and the corresponding metal complex ions in a solution. The use of the metal complexes as templates instead of organic amines causes condensation of AgI_2^- to three-dimensional open-framework $Ag_2I_4^{2-}$. These results provide a new avenue for the design and generation of new solid-state materials based on the concept of using simple clusters as building blocks to construct open-framework structures.

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Supporting Information Available: X-ray crystallographic data for compounds **1** and **2**. The TGA data and CD spectra are shown in Figures S1 and S2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 662863 and 6662864 contain supplementary crystallographic data for **1** and **2**, respectively. The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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