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# Syntheses, structures and fluorescent properties of two silver(I) complexes with 5-sulfo-salicylic acid as ligand templated by alkaline-earth metals

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## Abstract

Two silver(I) complexes, $[Mg(H_2O)_6][Ag_2(HL)_2]$ (**1**) and $Sr_2Ag_4(HL)(H_2O)_{14} \cdot 2H_2O$ (**2**) ($H_3L$ = 5-sulfo-salicylic acid), have been synthesized by use of alkaline-earth metals ($Mg^{2+}$ and $Sr^{2+}$, respectively) as templates. Single-crystal X-ray diffractions reveal that compound **1** is a 1-D chain polymer built from $[Ag_2(HL)_2]$ dimers and compound **2** is a 2-D framework constructed from unusual tetramer units of $[Ag_2(HL)_2]$ dimers. The two complexes are both further linked into 3-D networks by the extensive intermolecular hydrogen bonding interactions.

*Keywords:* Alkaline-earth metals; Silver complexes; Template synthesis; Tetramer

In recent years, much efforts have been made for controlling the assembly of molecules and designing the crystal structures of coordination polymers [1] for their potential applications as functional materials on catalysis, nonlinear optics, microelectronics, sensors, and molecular recognition [2]. Numerous studies on this challenge have reveled that many factors affect the assembly of molecules, and little change of the synthetic conditions can often result in the different ultimate structure. Recently self-assembly syntheses with alkali or alkaline earth metals as template are of great interest due to their abilities in the controlling of molecules assembly and the crystal structures of coordination polymers [3]. There is a need for much work to be done in understanding the nature of the reactions, which plays a crucial role in the design of novel functional materials.

On the other hand, the selection of suitable ligand is important in the design of novel coordination polymers [4]. 5-Sulfosalicylic acid ($H_3L$), which contains –OH, –COOH, and $–SO_3H$ groups, can offer versatile coordination modes, and was selected as ligand in the present work due to its potential multi-coordinating ability. Although the ligand has been known for a long time and some metal complexes bridged with it have been reported so far [5,6], the silver coordination polymers based on $H_3L$ ligand have been reported to be very limited [6]. When synthesizing these $Ag^+$ complexes, the different synthetic conditions always result in very different structure motif [6]. Great efforts have been made on the pH value of the solutions have great effects on the resulting complexes. In this contribution, after $AgNO_3$ and $H_3Ssal$ were dissolved in water, the pH value of the solution was adjusted with $[N(CH_2CH_3)_4](OH)$ to about 5. Then different alkali earth ions ($Mg^{2+}$ and $Sr^{2+}$) are introduced as templates into the reactions, respectively [7], and result in two silver coordination polymers, $[Mg(H_2O)_6][Ag_2(HL)_2]$ (**1**) with 1-D chain polymer built from the $[Ag_2(HL)_2]$ building block, and $[Sr_2Ag_4(HL)(H_2O)_{14}] \cdot 2H_2O$ (**2**) with 2-D framework constructed from unusual tetramer units of $[Ag_2(HL)_2]$ building block [8].

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Single-crystal X-ray analysis reveals that complex **1** is a 1-D chain polymer with hydrated $Mg^{2+}$ as counter ions and lattice water stacking besides the chains, as shown in Fig. 1. The asymmetric unit of **1** contains one $Ag^+$ ion, half occupied $Mg^{2+}$ ion, one $HL^{2-}$ ligand, four coordinated water molecules and two lattice water molecules. Four-coordinated Ag1 was coordinated by two carboxylic O atoms, one sulfonate O atom and one coordinated water molecule with the Ag–O bond distances being in the range of 2.225(2)–2.591(2) Å. Mg1 cation adopts six-coordinated mode and displays octahedral coordination geometry completed by six water molecules. The $HL^{2-}$ ligand adopts a $\mu_3$ coordination mode with sulfonate group coordinating to one metal and carboxylate group connecting two metals in a *trans–trans* mode. Two carboxylate groups of $HL^{2-}$ double-bridge two symmetry-related Ag1 atoms to form a $[Ag_2(HL)_2]$ building block with the Ag atoms and carboxylate groups being coplanar, which is further linked by the O14 atoms of sulfonate groups from adjacent dimers with the Ag1–O14 bonds approximately perpendicular to the plane of dimer to form a chain extending along the *b*-axis.

The existence of abundant coordinated water, lattice water, the ionized sulfonate group and carboxylate group in **1** yield seven kinds of hydrogen bonding interactions (Table S1): (a) between coordinated water molecules and sulfonate oxygen atoms; (b) between coordinated water molecules and phenolic oxygen atoms; (c) between coordinated water molecules and lattice water molecules; (d) between coordinated water molecules and carboxylate oxygen atoms; (e) between lattice water molecules and sulfonate oxygen atoms; (f) between phenolic oxygen and carboxylate oxygen atoms; (g) among the lattice water molecules. The chains, hydrated $Mg^{2+}$ ions and the lattice water molecules are linked to each other by these hydrogen bonding interactions to form a 3-D supramolecular structure (Fig. S1).

Single-crystal X-ray analysis reveals that complex **2** is 2-D network constructed from the unusual tetramers of $[Ag_2(HL)_2]$ building block connected by $Sr^{2+}$ ions. Four $Ag^+$ ions, two $Sr^{2+}$, four $HL^{2-}$ ligand, fourteen coordinated water and two lattice water molecules are found in the asymmetric unit, as shown in Fig. S2. The coordination polyhedra of the crystallographically independent Ag1, Ag2 and Ag4 atoms can be described as distorted trigonal geometries, which were completed by the O12, O32 and O12W atoms for Ag1; the O13, O33 and O13W atoms for Ag2; and O23, O43 and O14 atoms for Ag4. While the Ag3 atom adopts four-coordinated mode and displays a distorted tetrahedron geometry completed by the O42, O46, O22 and O14W atoms. The Sr1 and Sr2 atoms are both eight-coordinated with one phenolic oxygen atom, two sulfonate oxygen atoms from two different $HL^{2-}$ ligand and five-coordinated water molecules for Sr1 and one sulfonate oxygen atom, one phenolic oxygen atom and six coordinated water molecules for Sr2. The four asymmetric $HL^{2-}$ ligands exhibit three types of coordination modes: $\mu_3$-$\kappa^1O(2):\kappa^1O(3):\kappa^1O(4)$; $\mu_4$-$\kappa^1O(1):\kappa^1O(2):\kappa^1O(3):\kappa^1O(4)$; $\mu_5$-$\kappa^1O(1):\kappa^1O(2):\kappa^1O(3):\kappa^1O(4)\kappa^1O(5)$, which are reported for the first time (Fig. S3).

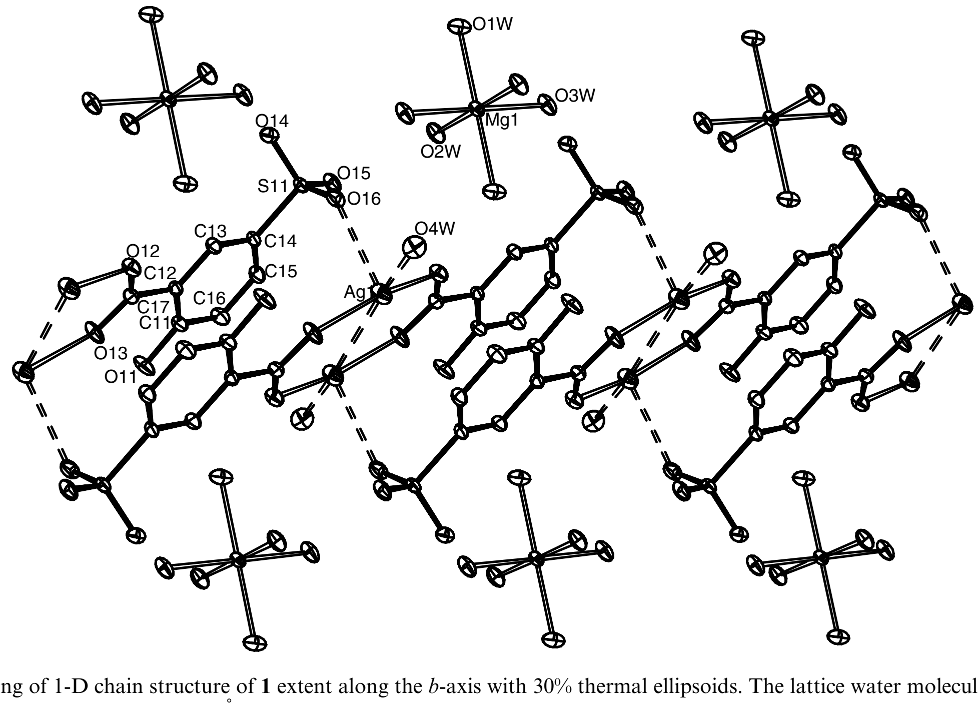

Fig. 1. ORTEP drawing of 1-D chain structure of **1** extent along the *b*-axis with 30% thermal ellipsoids. The lattice water molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag(1)–O(13)B 2.2245(19); Ag(1)–O(12)A 2.2292(18); Ag(1)–O(16) 2.578(2); Ag(1)–O(4W) 2.591(2); Ag(1)–Ag(1)C 2.9143(12); Mg(1)–O(1W) 2.0780(19); Mg(1)–O(2W) 2.0393(18); Mg(1)–O(3W) 2.073(2); O(13)B–Ag(1)–O(12)A 161.81(7); O(13)B–Ag(1)–O(16) 95.15(7); O(12)A–Ag(1)–O(16) 91.72(6); O(13)B–Ag(1)–O(4W) 87.91(7); O(12)A–Ag(1)–O(4W) 110.03(7). Symmetry code: A $x$, $y+1$, $z$; B $-x+1$, $-y$, $-z+1$; C $-x+1$, $-y+1$, $-z+1$.

Each of the Ag1 and Ag2 pair, and Ag3 and Ag4 pair is double-bridged by two $HL^{2-}$ ligands in a *trans–trans* mode to form two kinds of $[Ag_2(HL)_2]$ dimers, which link to each other through the Ag4–O14 bond to form bi-dimer. The bi-dimer further connects to its centrosymmetry-related unit by Ag3–O46 bond to yield a novel tetramer of $[Ag_2(HL)_2]$ dimers (Fig. 2). Although the $[Ag_2L'_2]$ ($L'$ = carboxylic ligand) dimers have been found to be either isolated [9] or linked to each other to form bi-dimer [10], 1-D [11], 2-D [12] and 3-D [13] structures, to our best knowledge, prior to the present work no tetramer of $[Ag_2L'_2]$ dimers has been reported. The adjacent tetramer units in **2** link to each other by the bonding interactions of Sr1–O34, Sr1–O41, Sr2–O31 and Sr2–O44 to form a chain extending along the [1 1 0] direction, which are further connected to each other by Sr1–O26 bonds to form 2-D network along the [1 −1 0] direction (Fig. 3). Abundant hydrogen bonds are also found in **2**, which link the layers to form 3-D supramolecular structure (Table S2).

It is interesting that the two complexes were synthesized in the similar conditions with different alkaline earth ions added to the synthetic system, while compound **1** is a

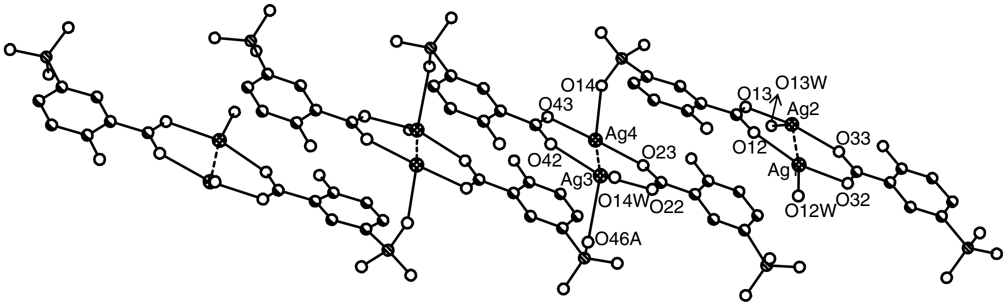

Fig. 2. The diagram of unusual tetramer of $[Ag_2(HL)_2]$ dimers with hydrogen atoms being omitted for clarity. Ag(1)–O(12) 2.218(4); Ag(1)–O(32) 2.226(4); Ag(1)–O(12W) 2.489(4); Ag(1)–Ag(2) 2.8403(8); Ag(2)–O(13) 2.179(4); Ag(2)–O(33) 2.196(4); Ag(2)–O(13W) 2.497(4); Ag(3)–O(22) 2.246(4); Ag(3)–O(42) 2.260(4); Ag(3)–O(14W) 2.426(4); Ag(3)–O(46)A 2.589(4); Ag(3)–Ag(4) 2.8499(7); Ag(4)–O(23) 2.171(4); Ag(4)–O(43) 2.188(4); Ag(4)–O(14) 2.563(4). Symmetry code: A $-x-1$, $-y$, $-z+1$.

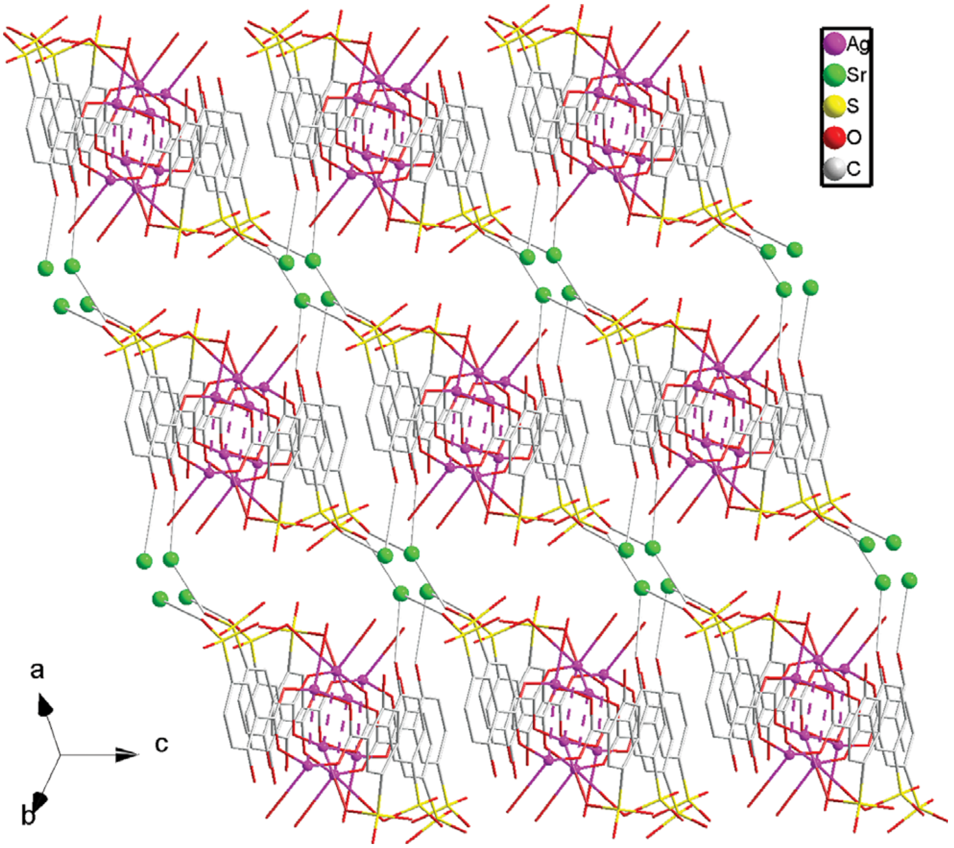

Fig. 3. The 2-D layer of **2** constructed from the unusual tetramer of $[Ag_2(HL)_2]$ dimers connected by $Sr^{2+}$ ions with the lattice water molecules and coordinating water molecules of $Sr^{2+}$ being omitted for clarity.

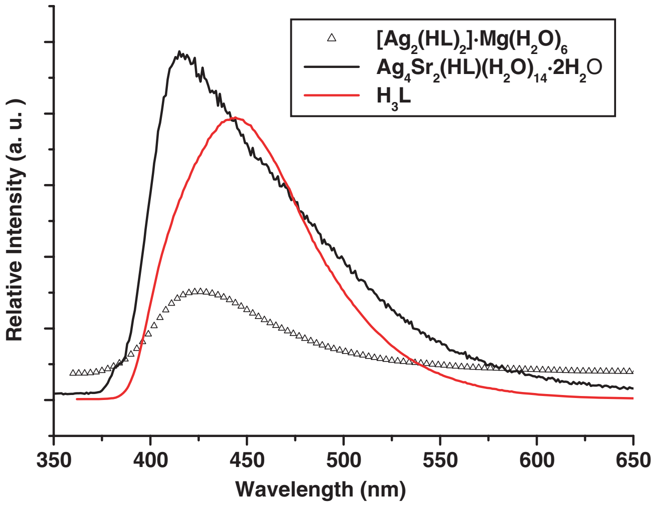

Fig. 4. The emission spectra of title complexes and pure ligand in the solid state at room temperature.

1-D chain polymer and compound **2** is a 2-D framework. The alkaline-earth metal ions play the roles as templates in the construction of the two complexes. In **1**, the Mg$^{2+}$ ion is fully coordinated by six water molecules and the hydrated Mg$^{2+}$ ions arrange around the chains of [Ag$_2$(HL)$_2$] dimers and prevent the chains linking to each other; in **2**, Sr atoms are coordinated by not only water molecules but also the sulfonate groups to form the 2-D network, as shown in Fig. 3. The different coordination numbers between Mg$^{2+}$ ion and Sr$^{2+}$ due to the different radius of both metal cations, may account for the different dimensions of both complexes.

Three kinds of [Ag$_2$(HL)$_2$] dimers were found in two complexes with obvious difference of the Ag···Ag separations of 2.9143(12) Å in **1** and 2.8403(8), 2.8499(7) in **2**, which are much shorter than the sum of the van der Waals radii of two silver atoms, 3.44 Å [14], suggesting the existence of *argentophilic* interactions.

The fluorescent emission spectra of the two complexes and the pure ligand in the solid state are shown in Fig. 4. All the experiments were done under the same condition. The emission peaks are centered at 416 nm ($\lambda_{ex} = 320$ nm) for **1**, 423 nm ($\lambda_{ex} = 338$ nm) for **2** and 447 nm ($\lambda_{ex} = 350$ nm) for the pure ligand. The emission of the pure ligand may be attributable to $\pi \rightarrow \pi^*$ transition [15], while the emissions of title complexes show obviously blue shift compared to that of the pure ligand, which may be ascribed to ligand-to-metal charge transfer (LMCT) modified by Ag…Ag interactions [16]. The luminescence lifetimes are 0.86 and 1.20 ns for **1** and **2**, respectively, (Figure S4) which are shorter than the lifetimes of the reported Ag$^+$ complexes [6c].

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.04.021.

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[7] Syntheses: For **1**: AgNO$_3$ (0.170 g, 0.1 mmol) and H$_3$Ssal (0.380 g, 0.15 mmol) were dissolved in 15 mL water. After adjusting the pH value with [N(CH$_2$CH$_3$)$_4$](OH) to about 5, the Mg(NO$_3$)$_2$ was added to the mixture and stirred for 12 h at room temperature, the resulted solution was filtered and colorless crystals of 1 were obtained after a week. (Yield: 62%, based on Ag$^+$). Anal. **1**: Calcd. (%): C, 18.69; H, 1.34. Found: C, 18.60; H, 1.15. IR (cm$^{-1}$, KBr): 3406 s, 1595 m, 1557 s, 1485 s, 1435 s, 1353 m, 1298 s, 1265 m, 1177 m, 1121 m, 1083 m, 1038 m, 893 m, 809 m, 733 m, 672 m, 579 m, 439 m. For **2**: The synthetic procedure for **2** is similar to that for **1** by replacing the Mg(NO$_3$)$_2$ with Sr(NO$_3$)$_2$ (yield, 57%, based on Ag$^+$). Anal. **2**: Calcd. (%): C, 18.69; H, 1.34. Found: C, 18.60; H, 1.15. IR (cm$^{-1}$, KBr): 3406 s, 1595 m, 1557 s, 1485 s, 1435 s, 1353 m, 1298 s, 1265 m, 1177 m, 1121 m, 1083 m, 1038 m, 893 m, 809 m, 733 m, 672 m, 579 m, 439 m.

[8] Crystal data: **1**: $C_{14}H_{32}Ag_2MgO_{24}S_2$, triclinic, space group $P\bar{1}$, $M = 888.57$, $a = 7.896(4)$, $b = 8.048(4)$, $c = 11.884(6)$ Å, $\alpha = 105.423(4)$ $\beta = 102.466(4)$, $\gamma = 93.548(4)°$, $V = 705.1(6)$ Å$^3$, $Z = 1$, $D_c = 2.093$ g/cm$^3$, $F(000) = 446$, and $\mu(\text{Mo K}_\alpha) = 1.661$ mm$^{-1}$, 4453 reflections measured ($3.58 \leqslant \theta \leqslant 25.02°$), 2442 unique ($R_{\text{int}} = 0.0129$) and 2225 observed reflections [$I > 2\sigma(I)$], final $R = 0.0228$, $wR_2 = 0.0602$ and $S = 1.052$; **2**: $C_{28}H_{48}Ag_4O_{40}S_4Sr_2$, triclinic, space group $P\bar{1}$, $M = 1759.62$, $a = 13.6122(19)$, $b = 14.567(2)$, $c = 15.716(3)$ Å, $\alpha = 112.253(3)$ $\beta = 105.561(3)$, $\gamma = 102.386(3)°$, $V = 2598.1(7)$ Å$^3$, $Z = 2$, $D_c = 2.249$ g/cm$^3$, $F(000) = 1728$, and $\mu(\text{Mo K}_\alpha) = 3.789$ mm$^{-1}$, 16943 reflections measured ($3.02 \leqslant \theta \leqslant 25.03°$), 9064 unique ($R_{\text{int}} = 0.0374$) and 7159 observed reflections [$I > 2\sigma(\text{I})$], final $R = 0.0445$, $wR_2 = 0.0999$ and $S = 1.039$. Crystal structure measurement for both complexes were performed on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo $K_\alpha$ radiation ($\lambda = 0.71073$ Å, rotating-anode, 50 kV, 150 mA) at 293 K. The structures were solved by the direct methods and subsequent difference Fourier syntheses. The hydrogen atoms of aromatic rings were added according to theoretical models, while the hydrogen atoms of coordinating water and lattice water molecules were added based from difference Fourier maps.

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