Self-Assembly of A Novel Sulphonate Silver(I) Complex

Daofeng Sun, Rong Cao,* Yucang Liang, and Maochun Hong*
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou, 350002, P. R. China

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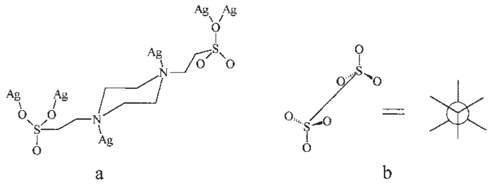
Self-assembly of dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp) with $AgNO_3$ in H_2O/DMF gave rise to a novel three-dimensional sulphonate silver(I) complex, $[Ag_2(\mu_2\text{-}OH_2)(\text{pesp})]_n$ (**1**). Each silver(I) ion is coordinated by one nitrogen and two oxygen atoms from three pesp ligands and one oxygen atom from coordinated water molecule in a distorted tetrahedral geometry.

In the past ten years, studies on polymeric complexes containing ligands that were regarded as poorly coordinated anions have been increased rapidly, due to the important roles of such ligands in inorganic synthons.[1] For instance, sulphonate complexes possess high value as inorganic synthons or as precursors to a range of derivatives.[2] In previous reports on sulphonate complexes,[3] most sulphonates are aromatic, e.g., $-SO_3$ is connected with benzene ring directly; and the studies on non-aromatic sulphonates are rare owing to their poor coordination ability. In our work, dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp) and silver(I) are selected as starting materials, we hope the additional coordination from piperzazine nitrogen along with the high affinity of Ag(I) for nitrogen and oxygen atoms[4] will result in the successful isolation of complex with non-aromatic sulphonate ligands. Herein, we report the self-assembly reaction of K_2pesp and $AgNO_3$ in H_2O/DMF at room temperature, and we will show that the coordination of nitrogen and oxygen atoms of pesp to Ag(I) results in a novel three-dimensional silver(I) complex, $[Ag_2(\mu_2\text{-}OH_2)(\text{pesp})]_n$ (**1**), constructed by tetra-coordinate silver(I) centers.



Scheme 1.

Complex **1** was obtained by self-assembly reaction of dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp) and $AgNO_3$ in H_2O/DMF.[5] Crystallographic analysis[6] reveals that the complex is a novel three-dimensional polymer constructed by tetra-coordinate silver(I) centers.

As shown in Figure 1, each Ag(I) ion is coordinated by two oxygen atoms from two different pesp, a nitrogen atom from another pesp and an oxygen atom from water molecule, in a distorted tetrahedral geometry. The water molecule (O(7)) acts as μ_2-bridge linking two Ag ions (Ag(1) and Ag(2)) with average Ag(1,2)-O(7) distance being 2.490(6) Å and the Ag(1)-O(7)-Ag(2) angle being 88.21(19)°, respectively. The Ag(1)-Ag(2) distance is 3.466(6) Å which is slightly longer than the Van der Waals contact distance for Ag-Ag (3.40 Å),[8] illustrating the lack of direct metal-metal interaction. Although all the two $-SO_3$ groups of pesp act as μ_2-bridges, one links two silver ions through two oxygen atoms (O(1), O(2)) while the other links two silver ions only through one oxygen atom (O(4)) (Scheme 1a). The piperazine ring of pesp adopts the most stable "chair" configuration, and the six sulphonate oxygen atoms are in a staggered arrangement, structurally similar to that of the hydrogen atoms of ethane molecule (Scheme 1b).

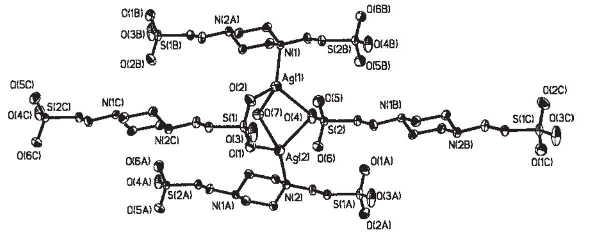


Figure 1. Coordination environment of metal ions in **1**. Selected bond lengths(Å) and angles(°): Ag(1)-N(1), 2.305(5); Ag(1)-O(2), 2.309(5); Ag(1)-O(7), 2.467(6); Ag(1)-O(4), 2.526(6); Ag(2)-N(2), 2.312(5); Ag(2)-O(1), 2.358(5); Ag(2)-O(7), 2.513(6); Ag(2)-O(4), 2.549(6); N(1)-Ag(1)-O(2), 125.15(1); N(1)-Ag(1)-O(7), 115.9(2); O(2)-Ag(1)-O(7), 94.6(2); N(1)-Ag(1)-O(4), 117.87(18); O(2)-Ag(1)-O(4), 111.86(19); O(7)-Ag(1)-O(4), 78.73(19); N(2)-Ag(2)-O(1), 127.90(18); N(2)-Ag(2)-O(7), 118.0(2); O(1)-Ag(2)-O(7), 87.1(2); N(2)-Ag(2)-O(4), 120.49(18); O(1)-Ag(2)-O(4), 108.69(18); O(7)-Ag(2)-O(4), 77.47(18); Ag(1)-O(7)-Ag(2), 88.21(19)°.

In **1**, the binuclear $[Ag_2(\mu_2\text{-}OH_2)(\text{pesp})]$ species may be viewed as the building unit of the whole structure. Each two Ag_2 units are linked head-to-tail through Ag-O_{pesp} bonding to form a one-dimensional chain structure (Figure 2), with the Ag-O_{pesp} distances falling in the range from 2.309(5) to 2.549(6) Å. The one-dimensional chains are further linked by Ag-N_{pesp} bonding from different directions to complete the tetrahedral coordination environments of Ag(I) ions and result in the formation of the final three-dimensional structure (Figure 3), with the Ag-N_{pesp} distances ranging from 2.305(5) to 2.312(5) Å.

To prepare other silver-pesp complexes with different structures, other silver salts (such as $AgClO_4$ and $AgBF_4$) and mixed solvents (such as H_2O/MeOH and H_2O/CH_3CN) as well as different metal/ligand ratios were employed in our experiments, however, the same products were obtained although the yields were different. This result illustrates that the formation of **1** may

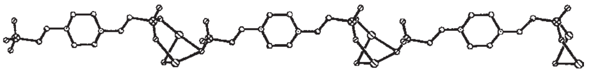


Figure 2. The one-dimensional chain structure in **1**.

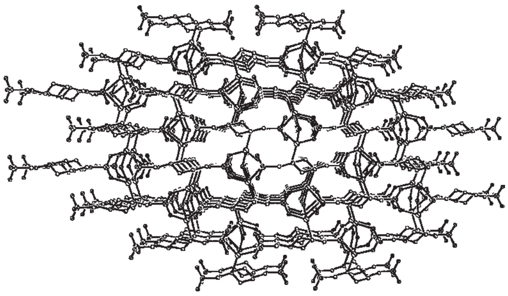


Figure 3. The three-dimensional structure of **1**.

not be influenced by organic solvent and anion.

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References and Notes

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5 Synthesis of compound **1**: K_2pesp (0.045 g, 0.125 mmol) was dissolved in 10 ml water and placed on the bottom of a glass tube. Then, a solution of $AgNO_3$ (0.043 g, 0.25 mmol) in DMF (5 ml) was carefully layered on it. After standing the tube in darkness for about one week, colorless prism-like crystals were obtained. Yield: 55%. Anal. Calcd for $C_8H_{18}Ag_2N_2O_7S_2$: C, 17.99; H, 3.40; N, 5.25%. Found: C, 18.05; H, 3.25; N, 5.26%. IR(KBr, cm^{-1}): 3450(vs), 2949(m), 2825(s), 1655(m), 1315(s), 1250(s), 1213(vs), 1167(vs), 1039(vs), 783(m), 588(vs).

6 Crystallographic data for **1**: Crystal dimensions $0.20 \times 0.14 \times 0.12$ mm, Formula: $C_8H_{18}Ag_2N_2O_7S_2$, $F_w = 534.10$, monoclinic, space group $P2_1/c$, $a = 6.5597(6)$, $b = 16.6357(15)$, $c = 13.2576(12)$ Å, $\beta = 90.51(7)^\circ$, $V = 1446.7(2)$ Å^3, $Z = 4$, $T = 293$ K, $\rho = 2.452$ g/cm^3, $R = 0.0451$ and $Rw = 0.0932$ for 2557 independent reflections with $F \geq 2.0\,\sigma(Fo)$. The intensity data of **1** was collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature. The structure was solved by directed methods and the positions of H atoms were generated from difference Fourier maps. All of the calculations were performed on a Legand computer by using the SHELXTL-93 program package. Detail crystallographic data of **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC-171424).

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