Self-Assembly of a One-Dimensional Silver Complex Containing Two Kinds of Helical Chains

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Keywords: Self-assembly / S ligands / N ligands / Silver / Helical structures

Self-assembly of the potassium sulfonate salt K_2pesp [H_2pesp = piperazine-1,4-bis(2-ethanesulfonic acid] with piperazine (PIP) and a silver(I) salt in solution allows the preparation of a novel one-dimensional helical polymer $[Ag(PIP)]_n\cdot[Ag(pesd)]_n\cdot 2nH_2O$ (**1**), which is made up of two independent silver-containing helical chains, namely $[Ag(PIP)]_n$ and $[Ag(pesd)]_n$. There is no direct bonding interaction between the two chains, and the hydrogen bonds between the chains give **1** a two-dimensional layer supramolecular architecture.

Inorganic supramolecular chemistry, in particular the construction of specific structural networks, is a particularly active field of chemistry.[1] In the past few decades, helical structures have received much attention from chemists due to their fundamental role in biology, and their potential applications in asymmetric catalysis and nonlinear optical materials.[2,3] Although the most effective method to construct helical polymers is to carefully design helical ligands,[4] the use of oligopyridines and other optically active ligands has resulted in a large number of helical structures, such as di- and oligonuclear, infinite single or double helical chains.[5] However, no helical structures constructed from sulfonic ligands have been reported, probably due to the weak coordinating ability of sulfonate ligands.[6,7] Recently, we began to study the reactions of the flexible sulfonate ligand[8] piperazine-1,4-bis(2-ethanesulfonic acid) (H_2pesp) with silver salts, with the aim of obtaining information on the coordination ability of sulfonic ligands, which have previously been regarded as poorly coordinating anions,[7] and for constructing novel coordination architectures. In this paper, we describe a novel silver polymer containing two independent silver helical chains $[Ag(PIP)]_n\cdot[Ag(pesp)]_n\cdot 2nH_2O$ (**1**).

Complex **1** was obtained as colorless crystals by the self-assembly reaction of dipotassium salt of piperazine-1,4-bis(2-ethanesulfonic acid) (K_2pesp), piperazine hexahydrate (PIP) and $AgNO_3$ in H_2O/MeOH at room temperature. X-ray diffraction analysis shows **1** to be a one-dimensional polymer containing two independent silver-containing helical chains, namely $[Ag(pesp)]_n$ and $[Ag(PIP)]_n$. The crystal structure consists of two independent subunits, $[Ag(pesp)]^-$ and $[Ag(PIP)]^+$. In $[Ag(pesp)]^-$, the central silver is coordinated by two oxygen atoms and two nitrogen atoms from different ligands in a distorted tetrahedral geometry similar to that found in $[Ag_2(\mu_2\text{-}OH_2)(pesp)]_n$,[8] with an average Ag−O bond length of 2.433(10) Å and an average Ag−N bond length of 2.334(9) Å. Due to the presence of a flexible ethyl group, one oxygen atom of the sulfonate group and one nitrogen atom of the piperazine unit of $pesp^{2-}$ chelate the silver ion and the whole ligand acts as a μ_2-bridge. The coordination mode of the $pesp^{2-}$ ligand in **1** is quite different from that found in $[Ag_2(\mu_2\text{-}OH_2)(pesp)]_n$,[8] in which $pesp^{2-}$ is almost linear and acts as a μ_6-bridge to link six silver ions. This result illustrates that the flexible $pesp^{2-}$ ligand can adopt diverse coordination modes according to the different geometric requirements of the metal ions.[9] Thus, each $pesp^{2-}$ ligand links two silver ions and to form a one-dimensional anionic 2_1 helical chain, as shown in Figure 1. To the best of our knowledge, this is the first example of a silver(I) helical structure constructed by sulfonate ligands. The charge balance comes from another one-dimensional cationic helical chain, $[Ag(PIP)]_n$. In this $[Ag(PIP)]^+$ unit, the silver ion is coordinated by two nitrogen atoms from two PIP ligands in a linear geometry with the average Ag−N distance being 2.200(10) Å, shorter than that in the $[Ag(pesp)]^-$ unit. Each PIP links two silver ions to form a one-dimensional cationic helical chain (Figure 2). The piperazine rings in both $pesp^{2-}$ and PIP ligands adopt the most stable "chair" configuration as found in other Ag-PIP complexes.[10]

Considering that the most volatile component of the structure should be the piperazine units, thermogravimetric analyses (TGA) were performed to determine the thermal

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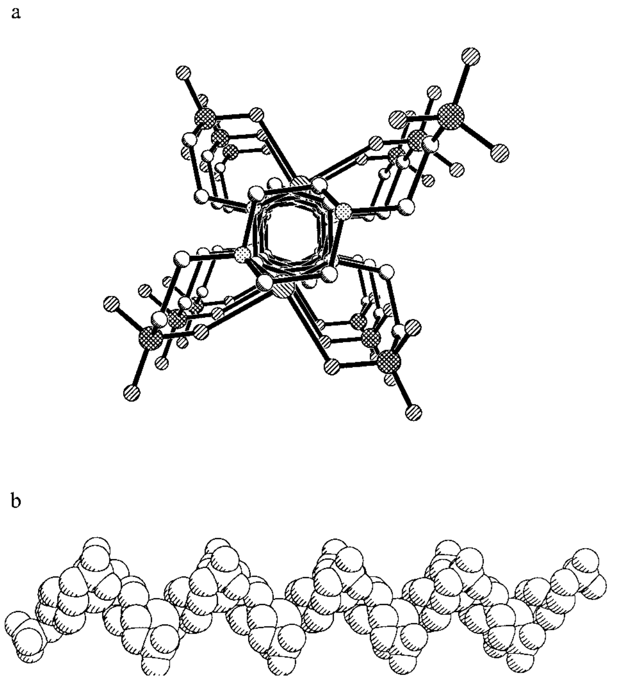

Figure 1. The $[\mathrm{Ag(pesp)}]_n^{n-}$ anion helical chain in **1**: a) along the helical axis; b) space filling representation; selected bond lengths (Å) and angles (°): Ag(1)−N(1) 2.308(9), Ag(1)−N(2) 2.359(9), Ag(1)−O(4) 2.388(8), Ag(1)−O(1) 2.477(10); N(1)−Ag(1)−N(2) 143.1(3), N(1)−Ag(1)−O(4) 119.2(3), N(2)−Ag(1)−O(4) 88.5(3), N(1)−Ag(1)−O(1) 91.1(3), N(2)−Ag(1)−O(1), 113.2(3), O(4)−Ag(1)−O(1), 92.2(3)

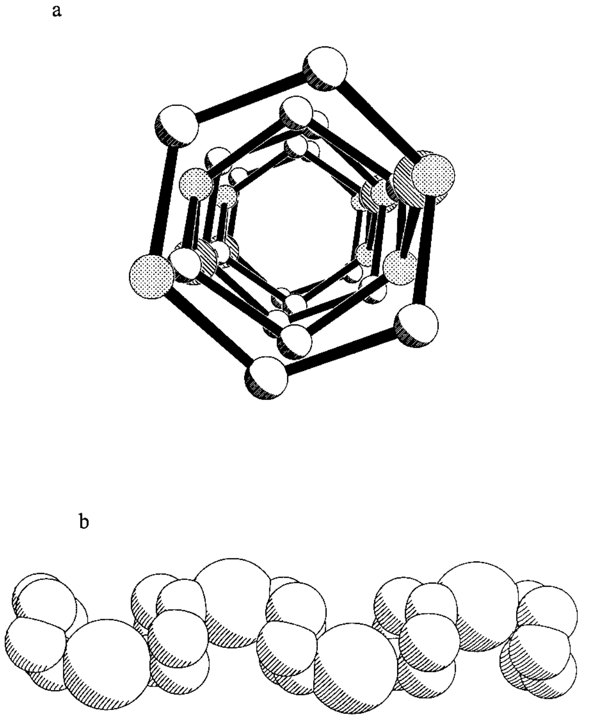

Figure 2. The $[\mathrm{Ag(PIP)}]_n^{n+}$ cation helical chain in **1**: a) along the helical axis; b) space filling representation; selected bond lengths (Å) and angles (°): Ag(2)−N(3) 2.197(10), Ag(2)−N(4) 2.203(10); N(3)−Ag(2)−N(4) 153.9(4)

stability of complex **1**. After a total weight loss of 5.50% is achieved at 250 °C, which corresponds to the loss of two uncoordinated water molecules per formula unit, complex **1** starts to decompose gradually and the decomposition ends above 700 °C.

The most intriguing feature of **1** is the independence of the cationic and anionic helical chains. Although some polymeric complexes containing two kinds of helical chains have been reported, the chains are usually not independent and are connected by coordination bonds.[11,12] In **1**, there is no direct bonding interaction between the two chains, only hydrogen bonding interactions between some nitrogen atoms of the PIP ligands and the oxygen atoms of pesp^{2-} are observed — the shortest N−O distance is 2.876(9) Å — and a two-dimensional wave-like layer structure is formed by such weak interactions (Figure 3). Aside from the hydrogen bonds between the chains, there are also weak Ag−O interactions between the layers: the sulfonate oxygen atom [O(3)] coordinates weakly to the silver ion [Ag(2)] of another layer with an Ag−O distance of 2.793 Å. This weak interaction makes the inter-layer distance much shorter (6.667 Å; Figure 4); the free water molecules are found between the layers.

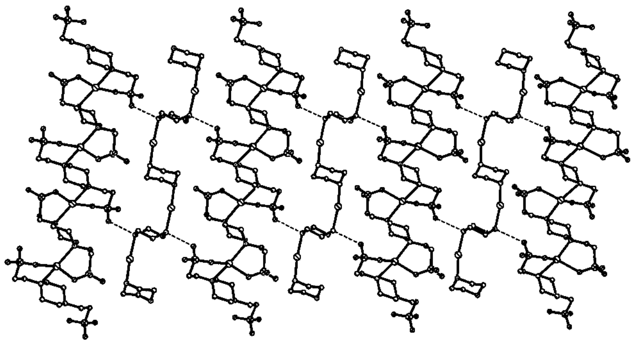

Figure 3. The 2D layer structure of **1** constructed by hydrogen bond between chains

As is well known, the self-assembly reaction is strongly influenced by many factors such as the pH value, the solvent and the metal:ligand ratio. We therefore changed the reaction conditions in order to attempt the preparation of different structures. However, when we adjusted the pH value to 7 or 8 by addition of $\mathrm{HClO_4}$, we obtained the polymer $[\mathrm{Ag_2(\mu_2\text{-}OH_2)(pesp)}]_n$,[8] which presumably arises from partial protonation of the piperazine moiety this pH value and subsequent loss of its coordination ability. When we attempted the reaction in different solvents and metal:ligand ratios, only an unknown precipitate was obtained, which indicates that the pH value, the solvent and the metal:ligand ratio do indeed influence the formation of **1**. Further study of this reaction is underway and will be reported shortly.

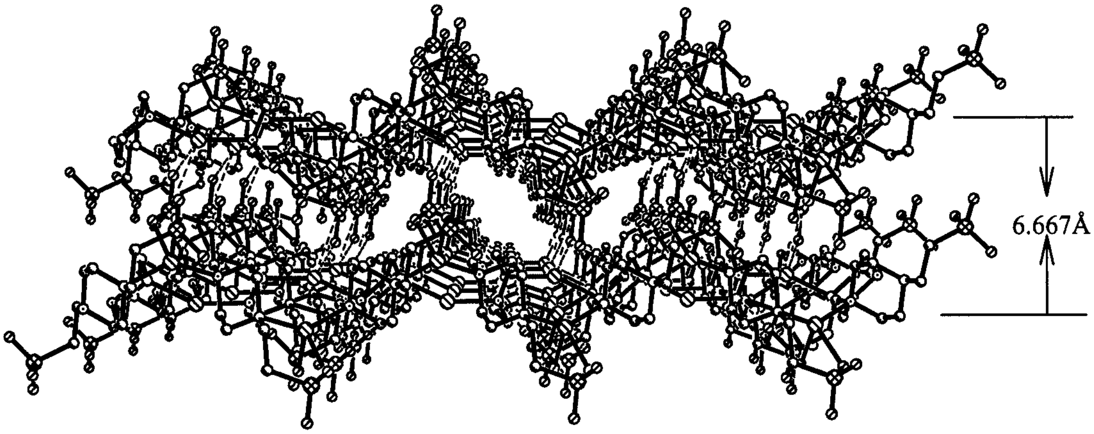

Figure 4. Structure of **1** showing the interlayer network

Experimental Section

Synthesis of 1: K_2pesp (0.045 g, 0.125 mmol) and PIP (0.021 g, 0.25 mmol) were dissolved in 10 mL of water. Then, a solution of $AgNO_3$ (0.043 g, 0.25 mmol) in MeOH (5 mL) was carefully layered on it. After standing in the dark for about two weeks, colorless prism-like crystals were obtained. Yield: 35%. $C_{12}H_{30}Ag_2N_4O_8S_2$ (638.2): calcd. C 22.58, H 4.74, N 8.78; found C 22.60, H 4.65, N 8.80. IR (KBr): $\tilde{\nu}$ = 3450(vs), 3261(m), 2827(m), 1655(m), 1552(m), 1460(m), 1358(m), 1315(s), 1250(s), 1200(vs), 1215(vs), 1167(vs), 1039(vs), 866(s), 588(vs) cm^{-1}.

X-ray Crystallography: $C_8H_{18}Ag_2N_2O_7S_2$, (**1**), M_r = 638.26, triclinic, $P\bar{1}$, a = 6.7657(8), b = 10.5093(13), c = 14.8207(18) Å, α = 101.281(2)°, β = 97.091(2)°, γ = 90.516(2)°, V = 1024.9(2) Å^3, Z = 2, D_c = 2.068 g/cm^3, μ(Mo-K_α) = 2.162 mm^{-1}, T = 293(2) K, R $[I < 2\sigma(I)]$ = 0.0738, wR = 0.1636 for 3604 independent reflections with $F \geq 2.0\sigma(F_o)$.

Table 1. Crystallographic data for complex **1**

	1
Empirical formula	$C_8H_{18}Ag_2N_2O_7S_2$
Fw	638.26
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	6.7657(8)
b, Å	10.5093(13)
c, Å	14.8207(18)
α, deg	101.281(2)
β, deg	97.091(2)
γ, deg	90.516(2)
V, Å^3	1024.9(2)
Z	2
D_c, g·cm^{-3}	2.068
μ, mm^{-1}	2.162
R_1 $[I < 2\sigma(I)]$[a]	0.0738
wR_2 (all data)[b]	0.1636

[a] $R_1 = \|F_0| - |F_c\|/|F_0|$. [b] $wR_2 = [w(F_0^2 - F_c^2)^2/w(F_0^2)^2]^{1/2}$.

The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at room temperature with the ω-2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated in idealized positions. All calculations were performed using the SHELXTL program. Crystallographic data for the complex **1** are given in Table 1.
CCDC-188274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors acknowledge financial support from the NSFC and a key project from CAS. We also thank Prof. Guoyu Yang for the thermogravimetric analysis.

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Received July 24, 2002
[I02412]