A Novel 3-D Open Coordination Polymeric Network Assembled from Silver(I) and 4,5-Bis(cyanoethylsulfanyl)-1,3-dithiole-2-thione with S···S Contacts

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A novel 3-D silver(I) cationic coordination polymeric network, $[Ag_4(bcdt)_4(CF_3SO_3)_2]\cdot(CF_3SO_3)_2\cdot$acetone (bcdt = 4,5-bis(cyanoethylsulfanyl)-1,3-dithiole-2-thione) with double (3,4)-connected nodes and extensive face-to-face and side-by-side S···S contacts, was synthesized and crystallographically characterized.

The synthesis and design of supramolecular coordination polymeric networks has been drawing a great deal of attention not only for their beautiful architectures but also some potential properties.[1,2] Some sulfur-rich molecules, such as TTF (tetrathiafulvalene) and dmit (4,5-dimercapto-1,3-dithiole-2-thione) derivatives, are very attractive compounds due to their excellent donor properties. Some notable donor–acceptor complexes or charge-transfer salts of TTF derivatives having intermolecular S···S contacts exhibit metallic conductivity or even superconductivity at low temperature.[3,4] Metal dithiolene complexes also afford a new system of molecular superconductors.[5] However, the building of metal coordination polymeric networks with potential properties is rare from half of neutral TTF derivatives with coordination bonds and S···S contacts. We have reported a few Cu(I) and Ag(I) complexes and coordination polymers of 4,5-ethylenedithio-1,3-dithiole-2-thione.[6] Recently, two Cu(I) supramolecular complexes of 4,5-bis(methylthio)-1,3-dithiole-2-thione were reported.[7] Here, we report a novel 3-D coordination polymeric network of silver(I) and 4,5-bis(cyanoethylsulfanyl)-1,3-dithiole-2-thione with extensive face-to-face and side-by-side S···S contacts.

The treatment of bcdt with $AgCF_3SO_3$ in acetone gave rise to the formation of the polymer $[Ag_4(bcdt)_4CF_3SO_3)_2]\cdot(CF_3SO_3)_2\cdot$acetone **1**.[8] X-ray structural determination reveals that a 3-D open framework was constructed from the coordination of silver(I) to bcdt. It is noteworthy that there are two crystallographically independent silver(I) atoms [Ag(1) and Ag(2)] in this network. The ligand also involves two different coordination modes: ligand L_1 acts as a tri-connected node and L_2 features a tetra-connected center. As shown in Figure 1, Ag(1) adopts a distorted tetrahedral coordination sphere. Two Ag(1) atoms and two thioketone sulfur atoms result in a Ag_2S_2 rhombohedron plane in which the Ag···Ag distance is 3.456 Å, slightly longer than the sum of van der Waals radii of two silver atoms (3.44 Å), indicating the absence of Ag···Ag interactions. Ag(2) also exhibits a distorted tetrahedral coordination geometry, it bridges four different L_1 and L_2 ligands through the nitrogen atoms (Figure 2). In this complex, the ligand L_2 behaves as tetra-connected centers to bridge Ag(1) and Ag(2) forming a 1-D wavy chain, while ligand L_1 acts as tri-connected centers to connect three different 1-D wavy chains, which leads to a 3-D polymeric network. Four different bcdt molecules coordinate to two Ag(1) cations to form a tetramer unit $[Ag_4(bcdt)_4]$ in which there is an inversion center located at the center of the Ag_2S_2 rhombohedron. Viewed along the *b* axis, four different kind of irregular channels were found and free acetone molecules are included in the largest one (Figure 2, acetone omitted for clarity).

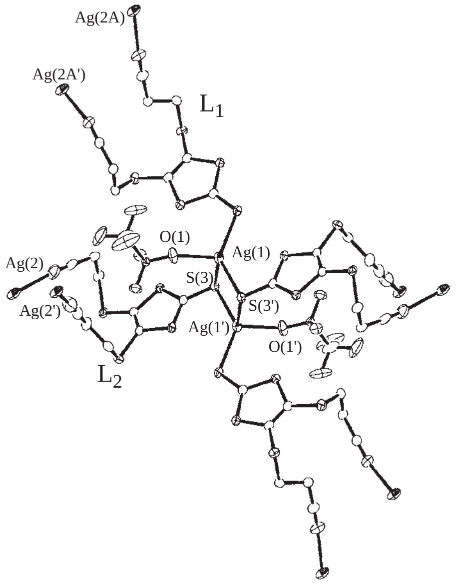

Figure 1. Coordination geometry of Ag(1) and tetramer unit of bcdt.

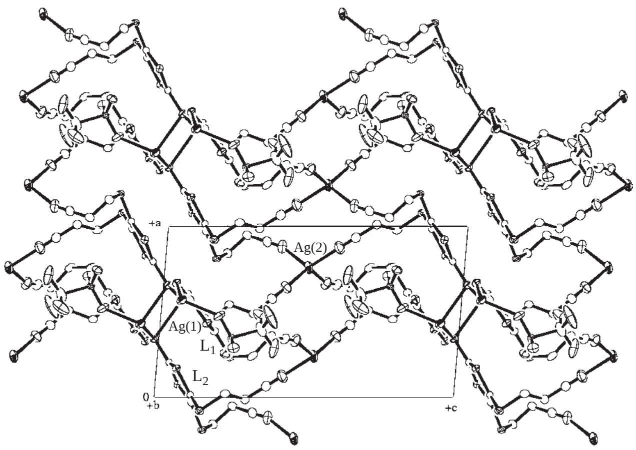

Figure 2. Perspective view of the 3-D polymer running along the *b* axis.

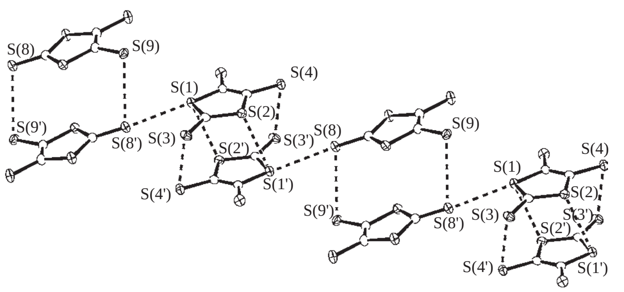

Figure 3. Face-to-face and side-by-side S···S contacts in the polymer.

The tetramer units extend in the direction of *b* and pack in the direction of *a*, such an arrangement results in extensive intramolecular face-to-face and side-by-side S···S contacts. The planes of C_3S_5 moieties for L_1 or L_2 molecules are coplanar in the tetramer. However, the dihedral angle between the planes of C_3S_5 moieties of two crystallographically independent ligands is 10.96(2)°. The short intratetramer S···S contacts is 3.5005(7) Å of S(1)···S(8), and the short intertetramer S···S contacts are 3.6143(7) Å of S(1)···S(2), 3.5829(7) Å of S(3)···S(4) and 3.6198(7) Å of S(8)···S(9), respectively (Figure 3).

Commpared with other metal complexes containing neutral C_3S_5 moieties (metal complexes of silver(I) and 4,5-ethylenedithio-1,3-dithiole-2-thione,[6] copper(I) and 4,5-bis(methylthio)-1,3-dithiole-2-thione[7]), complex **1** is the first 3-D metal coordination polymer only constructed from coordination bonds, therefore its stability is higher. In addition, polymer **1** is also the first example for single component metal complexes of neutral C_3S_5 analogs with semiconductive behavior. The semiconducting behavior of the polymer can be ascribed to the extensive short S···S contacts existing in the 2-D tetramer sheets.

3-D (3,4)-connected open networks are common for silver(I) coordination polymers, such as some polymers of silver(I) and hmt (hexamethylenetetramine).[9] A few 3-D interpenetrating networks with (3,4)-connected centers also have been reported previously, such as $[Ag_2(bdmi)_2]$ [bdmi = 1,3-bis(dicyanomethylidene)indan] and $[Ag_2Si(p\text{-}C_6H_4CN)_4]\cdot CF_3SO_3\cdot 2$benzene.[10] In addition, a coordination polymer $[Ag_2(\mu_2\text{-hmt})(\mu_3\text{-hmt})(H_2O)(SbF_6)]$ which features a 1-D ribbon with two kinds of (2,3)-connected centers in which hmt molecules adopt a mixed μ_2-/μ_3-bridging mode and Ag(I) atoms act as bi-connected and tri-connected centers was also reported.[11] However, the construction of 3-D open networks with two kinds of (3,4)-connected centers are rare by means of identical metals and ligands. From the viewpoint of topology, $[Ag_4(\mu_3\text{-bcdt})_2(\mu_4\text{-bcdt})_2(CF_3SO_3)_2]\cdot(CF_3SO_3)_2\cdot$acetone, the network presented here, is an unprecedented 3-D open net with twofold (3,4)-connected centers. On the other hand, compared with the known 3-D (3,4)-connected open networks,[9] polymer **1** exhibits semiconductivity because of existing extensive S···S contacts, while the known 3-D open frameworks only give new topologies and no interesting properties were observed due to the absence of molecular interactions, such as S···S contacts and $\pi\cdots\pi$ interactions.

Polymer **1** is stable in ambient daylight. UV–vis absorption spectrum of complex **1** give two intense absorption bands at 365 and 398 nm which are ascribed to $\pi \rightarrow \pi^*$ transition of bcdt ligand. The room temperature conductivities of complex **1** and free bcdt ligand were measured by conventional two-probe technique, respectively. Complex **1** displays semiconductive behavior with a σ value of 6.46×10^{-8} S·cm^{-1}, while the free bcdt ligand is an insulator.

In summary, a novel 3-D open coordination polymer with double (3,4)-centers was constructed from silver(I) and the tritopic ligand bcdt. The coordination polymeric network exhibits semiconductive behavior because of extensive intramolecular S···S contacts, and includes some uncoordinated solvent molecules.

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8 Complex **1** was synthesized by adding an acetone solution (5 mL) of $AgCF_3SO_3$ (23.4 mg, 0.09 mmol) into an acetone solution (5 mL) containing bcdt (27.4 mg, 0.09 mmol). The mixture was stirred and filtered, the filtrate was introduced into a glass tube and layed with *n*-hexane as a diffusion solvent. The glass tube was sealed, after standing at room temperature for a week, orange block crystals of **1** were obtained. Selected spectroscopic and analytical data for **1**: IR: $\nu = 1034$ cm^{-1} (C=S), $\nu = 2248$ cm^{-1} (C≡N), $\nu = 644$, 1176, 1259 cm^{-1} (CF_3SO_3); UV: $\lambda_{max} = 365$ nm; Anal. Calcd for $C_{43}H_{38}Ag_4F_{12}N_8O_{13}S_{24}$: C, 22.42; H, 1.66; N, 4.86%. Found: C, 22.15; H, 1.66; N, 4.67%. *Crystal data for* **1**: $[Ag_4(bcdt)_4(CF_3SO_3)_2]\cdot(CF_3SO_3)_2\cdot$acetone: $C_{43}H_{38}Ag_4F_{12}N_8O_{13}S_{24}$, MW = 2303.71, orange block, triclinic, space group $P\bar{1}$ (#2), $a = 9.8618(5)$, $b = 11.7050(5)$, $c = 17.5577(5)$ Å, $\alpha = 78.366(8)$, $\beta = 84.120(9)$, $\gamma = 84.769(10)$°, $V = 1969.5(2)$ Å^3, $Z = 1$, $D_{calcd} = 1.942$ g·cm^{-3}, $\mu(\text{Mo K}\alpha) = 16.99$ cm^{-1}. Data collection ($6.0 < 2\theta < 55.0$°) was performed at 175 K on a Rigaku/MSC Mercury CCD diffractometer ($\lambda = 0.71070$ Å). 29871 reflections were collected, 8887 were unique ($R_{int} = 0.022$), $R1 = 0.028$, final $wR2$ was 0.062 (all data). The structure was solved using direct methods and refined with full-matrix least-squares (SHELX-97).

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