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Note

Chiral Noninterpenetrated (10,3)-a Net in the Crystal Structure of Ag(I) and Bisthioether

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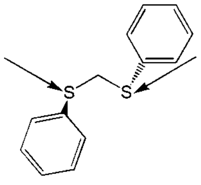
Introduction

The rational design of polymeric complexes with network structures has been an interesting area of research in recent years as the geometry of the network profoundly influences the final bulk physical and chemical properties and functions of that solid.[1] The chiral coordination polymers are specially attractive for their potential applications in enantioselective separations and syntheses.[2] In this context, the most symmetrical 3-connected (10,3)-a net, which is formulated by Wells, is one of the promising networks due to the presence of inherent chirality in the net.[3] Accordingly several coordination polymers containing (10,3)-a net topology were reported recently.[4−7]However in most cases the resultant crystals are racemic as the nets of opposite handedness interpenetrate with each other and also the coordination bonds involved in network formation are between either metal and nitrogen or between metal and carboxylate. Here we present an interesting structure that provides a noninterpenetrated (10,3)-a net in a coordination polymer of Ag(I) and a simple bisthioether ligand, bis(phenylthio)methane (L) (see Chart 1). Such a chiral crystal was achieved by eschewing interpenetration of (10,3)-a nets using smaller spacers and Ph-groups as space filling moieties. The anion effect has also been studied.

Chart 1



L

Experimental Section

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used as received. The ligand L was synthesized as previously described.[6]

Physical Methods. A Perkin-Elmer 240 elemental analyzer was used to collect microanalytical data (CHN), and IR spectra were recorded on a Nicolet 170 SX FT-IR spectrometer. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 800 °C.

CAUTION! Although we have experienced no problems in handling perchlorate compounds, these should be handled with great caution due to the potential for explosion.

Synthesis of Complex 1. The slow diffusion of ether into the mixture of acetone solution (5 mL) of $AgClO_4 \cdot 6H_2O$ (315 mg, 1 mmol) and $CHCl_3$ solution (5 mL) of L (464 mg, 2 mmol) resulted in the formation of the single crystals of $[Ag_2(L)_3(ClO_4)_2]_n$ (**1**) in 50% yield. Anal. Calcd for $C_{39}H_{36}Ag_2Cl_2O_8S_6$: C, 42.14; H, 3.26. Found: C, 42.00; H, 3.09%. IR (KBr pellets): 1582s, 1479vs, 1438s, 1400m, 1143vs, 1111vs, 1090vs, and 625s cm^{-1}. DTA data (peak position): 166 and 454 °C.

Synthesis of Complex 2. The colorless needles of $[Ag(L)(NO_3)]_n$ (**2**) were obtained when a methanol solution (5 mL) of $AgNO_3$ (170 mg, 1 mmol) and $CHCl_3$ solution (5 mL) of L (464 mg, 2 mmol) were stirred at 50 °C for ca. 1 h. Single crystals suitable for X-ray analysis were obtained by recrystallization from DMF (yield 36%). Anal. Calcd for $C_{13}H_{12}AgNO_3S_2$: C, 38.82; H, 2.98; N, 3.48. Found: C, 38.64; H, 2.92; N, 3.41%. IR (KBr pellets): 1582m,

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Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
empirical formula	$C_{39}H_{36}Cl_2Ag_2O_8S_6$	$C_{13}H_{12}AgNO_3S_2$
fw	1111.68	402.23
space group	$P4_332$ (cubic)	$P2_1/c$ (monoclinic)
a, Å	17.350(3)	5.2688(16)
b, Å	17.350(3)	17.831(6)
c, Å	17.350(3)	15.226(5)
β, deg	90	93.106(6)
V, Å^3	5222.6(14)	1428.4(8)
Z	4	4
T, K	298(2)	298(2)
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.414	1.870
μ, mm^{-1}	1.133	1.708
R^a	0.0473	0.0417
$R_w{}^b$	0.1132	0.0578

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2]^{1/2}$.

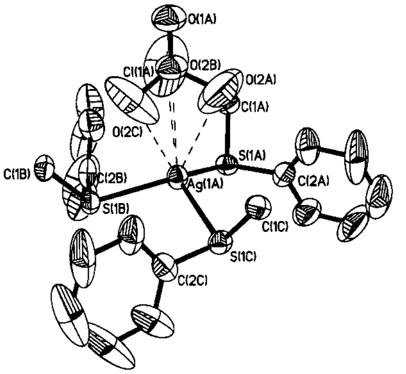

Figure 1. ORTEP view of complex **1** showing 30% thermal probability ellipsoids.

1479s, 1436s, 1383vs, 735s, and 687s cm^{-1}. DTA data (peak position): 168, 281, and 430 °C.

X-ray Crystallography. Single-crystal X-ray diffraction measurements of complexes **1** (0.25 × 0.35 × 0.40 mm) and **2** (0.20 × 0.20 × 0.25 mm) were carried out with a Bruker Smart 1000 diffractometer at room temperature. Intensities of reflections were measured at room temperature by use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) with ω scan mode in the range of 1.66° ≤ θ ≤ 25.01° (for **1**) and 1.76° ≤ θ ≤ 25.02° (for **2**). Unit cell dimensions were obtained with least-squares refinements. The structures were solved by direct methods (SHELXS-97),[8] and the Ag(I) atoms were located from *E*-maps. The other non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods on F^2 by the SHELXL-97 program package. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. Refinement of the flack parameter[9] of **1** converged at 0.05(11), and in the inverse structure and enantiomer space group $P4_132$ converged at 1.00(13). Crystallographic data and experimental details for structural analyses are summarized in Table 1 and in Supporting Information.

Table 2. Selected Bond Lengths and Angles for Complexes **1** and **2**[a]

Complex **1**			
Ag(1A)−S(1B)	2.5487(18)	Ag(1A)−S(1A)	2.5487(18)
Ag(1A)−S(1C)	2.5487(18)	Ag(1A)−O(2A)	3.0121(16)
S(1B)−Ag(1A)−S(1A)	111.78(4)	S(1B)−Ag(1A)−S(1C)	111.78(4)
S(1A)−Ag(1A)−S(1C)	111.78(4)		
Complex **2**			
Ag(1A)−O(2A)	2.539(6)	Ag(1A)−S(2B)	2.5700(18)
Ag(1A)−S(1A)	2.6085(17)		
O(2A)−Ag(1A)−S(2B)	151.82(13)	O(2A)−Ag(1A)−S(1A)	103.95(13)
S(2B)−Ag(1A)−S(1A)	104.23(6)		

[a] Bond lengths are given in angstroms; bond angles are given in degrees.

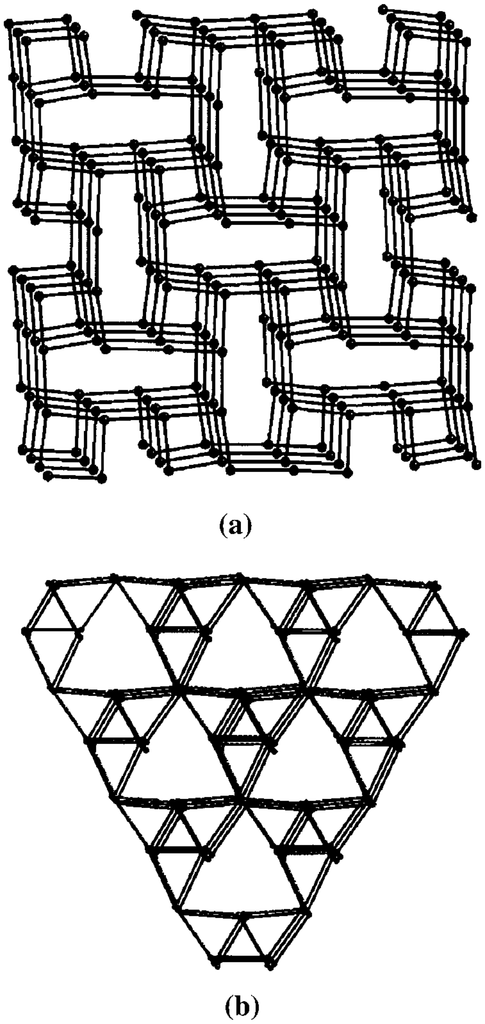

Figure 2. The (10,3)-a network exhibited by complex **1**: (a) View along the 4_3 axis; (b) view along the 3-fold axis. The ligands are shown as linear connectors and Ag atoms as nodes. Counterions and hydrogen atoms are omitted for clarity.

Results and Discussion

An ORTEP view of complex **1** is given in Figure 1. In complex **1**, every Ag^I is bounded to three S-donors of three distinct L ligands with similar bond lengths and adopts trigonal pyramidal geometry with an S−Ag−S angle of 111.8° (very near to 120°) (Table 2). The distances between three O-atoms of the perchlorate anion and the Ag^I center are in the range of 3.0−3.2 Å, suggesting the existence of weak coordination,[10] and the Ag^I ion is elevated from the S_3 plane by 0.75 Å.

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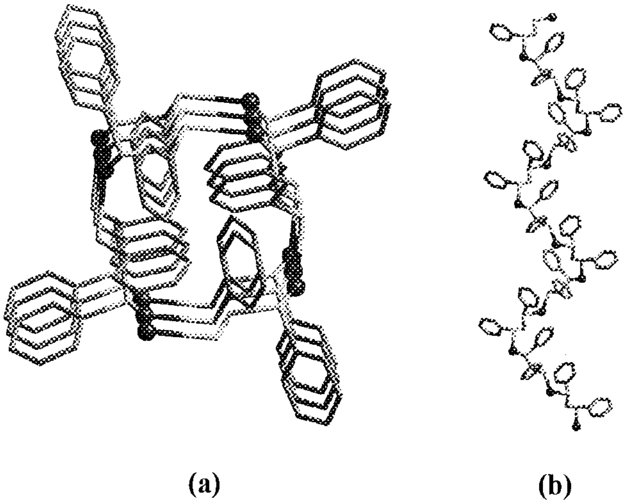
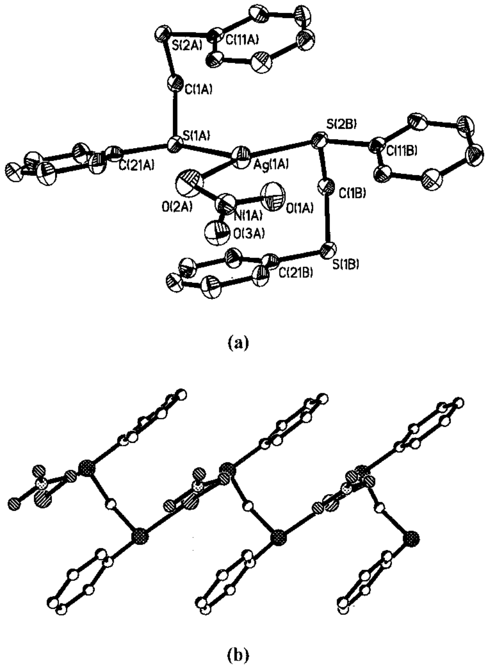

(a) (b)

Figure 3. The 4_3-helices exhibited in complex **1**: (a) top view; (b) side view.

The crystal structure of **1** reveals the formation of a noninterpenetrated 3D network in which Ag^I is connected to three S-donors of three distinct L ligands. The asymmetric unit of **1** contains $^1/_3$ unit of Ag atom and ClO_4^- and $^1/_2$ unit of the ligand L. Furthermore, the C_6 rings of L are almost perpendicular to the $S-CH_2-S$ plane with an interplanar angle of 80°, while the $Ag-S-CH_2-S-CH_2$ are in near planar geometry. The 3D network formed here can be classified as (10,3)-a network when the ligands are considered as spacers of length 5 Å and Ag atoms as nodes (Figure 2). Two types of channels can be seen in the network when it is viewed along either the 4-fold or 3-fold axis. These channels are perfectly filled by the phenyl groups and anions, leaving no space for the inclusion of solvent molecules.

The shortest closed circuits contain 10 Ag atoms and 10 moieties of L and have nonplanar geometry. Each turn of the 4-fold helix in the (10,3)-a net contains four ligands and four Ag atoms with a pitch length of 17.35 Å (Figure 3). Interestingly, two of the O atoms of the ClO_4^- ion and H atoms of the methylene group of L form a $C-H\cdots O$ hydrogen-bonded 4-fold helix that runs along with the coordination helix [$C\cdots O$, 3.27(1) Å; $C-H\cdots O$, 122°].

Here it is noteworthy that the mere presence of a dithioether as a spacer and Ag atom as a 3-connected node does not automatically lead to the formation of (10,3)-a net. For example the formation of a 1D coordination polymer was reported when thioether, $MeS-(CH_2)_3-SMe$, was used as a spacer for a 3-connecting Ag node.[10] In the present contribution the shorter length of the spacer and the effective space filling of the network voids/channels by phenyl groups and ClO_4^- ions lead to the formation of a noninterpenetrated (10,3)-a net instead of other possible 1D and 2D polymers.



(a)

(b)

Figure 4. (a) ORTEP view of complex **2** showing 30% thermal probability ellipsoids; (b) part of the one-dimensional chain structure in **2**.

To examine the role of counterions in the formation of a noninterpenetrated (10,3)-a net,[11] the reaction has been carried out with $AgNO_3$ instead of $AgClO_4$.

The single-crystal X-ray analysis of complex **2** (Figure 4) reveals the formation of a 1D coordination polymer but not the anticipated (10,3)-a net. Here Ag(I) coordinates to only two distinct S donors of L, as one of the coordination sites of Ag was occupied by the nitrate ion. The Ag atom adopts a trigonal coordination arrangement in which the sum of three angles around the Ag atom is 360° and L connects the Ag centers in pseudo-4-helical fashion with Ag−Ag separation of 5.27 Å.

In conclusion, this work suggests that in the current system the formation of a noninterpenetrated (10,3)-a net depends on factors such as the length of the spacer unit and the presence of anions. Further studies to understand the effect of changing the phenyl groups in L are underway in our laboratory.

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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