Assembly of Silver(I) Polymers with Helical and Lamellar Structures

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Abstract: The new versatile multidentate nonchelating ligand 1,2-bis[(2-pyrimidinyl)-sulfanylmethyl]benzene (bpsb) was designed and prepared for supramolecular syntheses. Self-assembly between silver nitrate and the bpsb ligand resulted in the polymer $[Ag_4(bpsb)_2(NO_3)_4]_n$ (**1**) with a single-stranded helical chain structure. Each bpsb ligand in **1** acts as a tetradentate ligand, in which two sulfur atoms and two nitrogen atoms from different pyrimidine groups coordinate to four Ag atoms in four different directions. The nitrate anions serve as a template for the formation of the helix and are either embedded in the interior of the helix or located in the flank of the helix. Self-assembly between silver perchlorate and the bpsb ligand under the same conditions gave rise to the polymer $[Ag_2(bpsb)_3(ClO_4)_2]_n$ (**2**) comprising a two-dimensional lamellar network containing crownlike cavities. The silver atoms in two adjacent layers are arranged staggered in **2**. The two-dimensional lamellar network comprising isolated cavities of $[Ag_6(bpsb)_6]$ is very different from that of usual honeycomb structures.

Keywords: helical structures · polymers · silver · supramolecular chemistry

Introduction

The self-assembly process between metal ions and ligands may be considered as resulting from the operation of a programmed system, in which the steric and interactive information stored in the ligands is read by the metal ions through the algorithm defined by their coordination geometry.[1] Accordingly, the design of ligands is crucial to the construction of specific supramolecular architectures. This concept has been demonstrated by a great variety of structural topologies of discrete supramolecular complexes or infinite supramolecular arrays, such as molecular racks and grids as well as helicates. For instance, molecular racks and grids can be prepared by self-assembly of metal ions with linear rigid polytopic ligands containing bi- or terpyridyl groups,[2] and helicates may be obtained from the combination of metal ions with the flexible chain of bidentate subunits such as 2,2′-bipyridine groups connected by short covalent bridges[3] or 2,2′:6′,2 -terpyridine and its derivatives with conformational freedom.[4] In a sense, the formation of molecular racks and grids results from the rigidity of the ligands, while that of helicates results from the flexibility of the ligands. If achiral ligands are used, inherently chiral helicates are generally formed as a racemic mixture.[5b, 5d] However, enantiopure helicates can be obtained upon incorporation of a chiral element or substituent into helicating ligands,[5, 6] which comes apparently from the information in the chiral group in the ligand. For *exo*-bis-bidentate ligands, their combination with metal ions that adopt tetrahedral coordination geometry can lead to several kinds of structures, such as discrete cycles, infinite linear chains, or helices. When bulky substituents are introduced into *exo*-bis-bidentate ligands, only the helical polymer is favored,[7] indicating that the information regarding steric hindrance in the ligands is exhibited by the resulting structure which minimizes steric repulsion between bulky groups.

The potential use of both discrete molecular cages[8] and two- and three-dimensional synthetic receptors and extended porous frameworks[9] largely depends on their cavity size and type. Similarly, the information with regard to ligands controls the cavity size and type through appropriate metal ions.[10] For example, treatment of $[Pd(NO_3)_2(en)]$ (en = ethylenediamine) with 2,4,6-tris(4-pyridyl)-1,3,5-triazine resulted in a molecular cage, while the similar reaction with 2,4,6-tris(3-pyridyl)-1,3,5-triazine led to a bowllike macrotricycle.[10h, 10i]

In previous studies, we used some simple ligands, such as pyridine-2-thiolate, pyrimidine-2-thiolate, pyridine-2-thione, and 2-mercaptoethylamine, which contain both sulfur and

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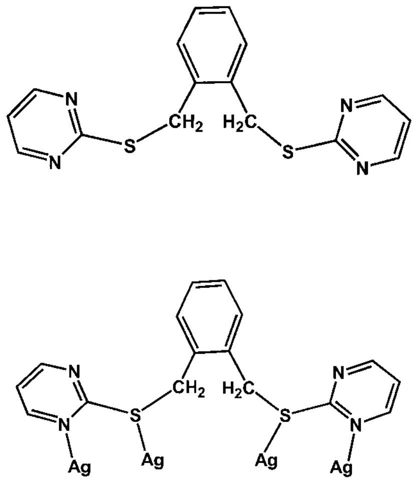
nitrogen donors for supramolecular syntheses, and obtained the complex polymers with linear chain or three-dimensional (3D) network structures.[11] As little information was contained in the ligands used in this earlier work, we began to design ligands containing more information, for example, ligands with several different donor atoms, with the aim of obtaining polymers with novel structures. Herein, we report a new ligand 1,2-bis[(2-pyrimidinyl)sulfanylmethyl]-benzene (bpsb), which contains two 2-thiopyrimidine groups separated by an *o*-xylyl spacer, and two polymeric silver(I) complexes, $[Ag_4(bpsb)_2(NO_3)_4]_n$ (**1**) and $[Ag_2(bpsb)_3(ClO_4)_2]_n$ (**2**) prepared from anion-controlled self-assembly reactions of a silver salt with the ligand bpsb.

Results and Discussion

The ligand bpsb was prepared from the reaction of 1,2-bis(bromomethyl)benzene and sodium pyrimidine-2-thiolate in MeCN. It possesses six possible bonding sites, that is, two sulfur and four nitrogen atoms (Scheme 1 top). Owing to the fact that the pyrimidine group[12] behaves as an *exo*-bidentate ligand, together with the *o*-xylyl spacer group, the N atoms of the two 2-thiopyrimidine groups can only bond to different metal atoms. Thioether ligands have relatively poor metal-complexing ability and bond to relatively soft metal ions,[13] such as Ag^I. Moreover, each sulfur atom of the thioether group in bpsb hardly adopts a chelating coordination mode by incorporation with adjacent nitrogen atoms because of the instability of the four-membered chelating ring. Therefore, the ligand bpsb is a multidentate but nonchelating ligand, capable of bridging different metal atoms in specific directions. In other words, the ligand bpsb stores rich information, which can be interpreted by the steric arrangement of metal atoms bound to it.



Scheme 1. Top: bpsb ligand; Bottom: coordination mode of bpsb in **1**.

The reaction of $AgNO_3$ with bspb was carried out in a metal-to-ligand ratio of 2:1 in DMF/MeCN. Slow diffusion of acetone into the reaction solution produced crystals suitable for single-crystal X-ray diffraction. The crystallographic analysis of complex **1** reveals that its structure is a one-dimensional polymeric helix consisting of $[Ag_4(bpsb)_2(NO_3)_4]$ units (Figure 1). Each bpsb ligand in **1** acts as a tetradentate ligand, in which two sulfur atoms and two nitrogen atoms from different pyrimidine groups coordinate to four Ag atoms in four different directions, respectively (see Scheme 1 bottom). Thus, the array of ligands linked by Ag atoms forms a single-stranded helix with the period of 8.5 Å (Figure 2). As shown in Figure 3, two kinds of coordination modes of the nitrate anions are present in **1**: one is embedded in the interior of the helix, while the other is located in the flank of the helix. In this sense, nitrate anions serve as a template for formation of the helix.[14] Each silver atom is tetracoordinated in a highly distorted tetrahedral fashion ($AgSNO_2$).

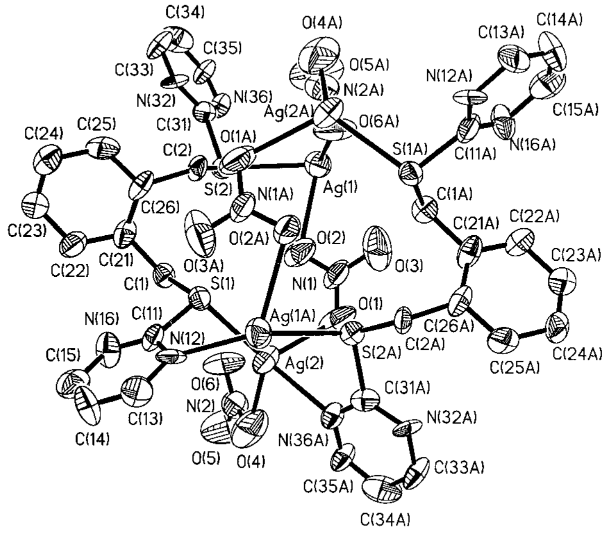


Figure 1. View of the basic tetrameric unit $[Ag_4(bpsb)_2(NO_3)_4]$ in the polymeric chain of **1**.

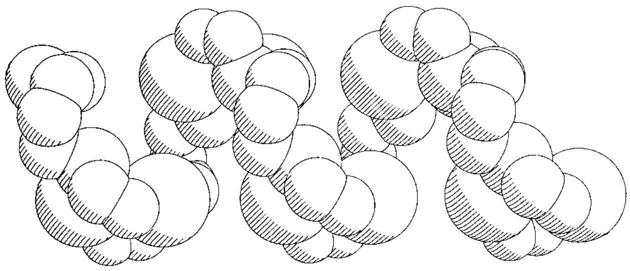


Figure 2. Space-filling representation of the helix in **1** with unrelated carbon atom omitted, down the direction normal to helix.

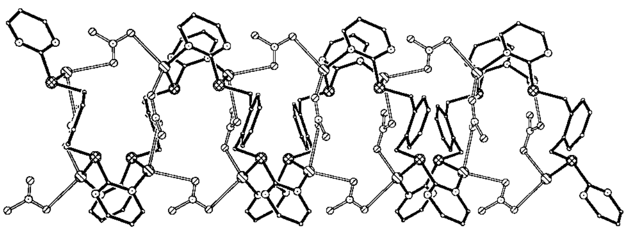


Figure 3. View of the helical chain polymer with $[NO_3]^-$ ions in **1**, running along *b* axis.

Table 1 lists the bond lengths and angles of **1**. The Ag–S bond lengths range between 2.493(2) and 2.567(3) Å, while the Ag–N and Ag–O bonds range between 2.260(8) and 2.315(8) Å and between 2.501(2) and 2.567(2) Å, respectively. The average S-Ag-N, S-Ag-O, N-Ag-O, and O-Ag-O bond angles are 135.6(2), 99.5(4), 100.3(4), and 96.7(4)°, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Ag(1)–O(2)	2.501(14)	Ag(2)–O(1)	2.505(8)
Ag(1)–S(2)	2.493(2)	Ag(2)–O(4)	2.514(13)
Ag(1)–O(6A)	2.479(10)	Ag(2)–S(1)	2.567(3)
Ag(1A)–N(12)	2.315(8)	Ag(2)–N(36A)	2.260(8)
O(2)-Ag(1)-S(2)	127.5(4)	O(2)-Ag(1)-O(6A)	98.7(6)
O(6A)-Ag(1)-S(2)	113.6(2)	N(12)-Ag(1A)-O(2A)	84.8(3)
N(12)-Ag(1A)-S(2A)	137.4(2)	O(2A)-Ag(1A)-S(2A)	127.5(4)
O(1)-Ag(2)-O(4)	94.7(4)	O(1)-Ag(2)-S(1)	78.3(2)
O(4)-Ag(2)-S(1)	106.9(4)	N(36A)-Ag(2)-O(1)	121.2(3)
N(36A)-Ag(2)-O(4)	112.0(4)	N(36A)-Ag(2)-S(1)	133.8(2)

Symmetry transformations used to generate equivalent atoms: A: $x,y,z+1$

Considering the influence of anions on self-assembly of supramolecular entities, $AgClO_4$, a silver salt with the poorly coordinating perchlorate anion, was used instead of $AgNO_3$. Similar to the preparation of complex **1**, the reaction of $AgClO_4$ with the ligand bpsb in a metal-to-ligand ratio of 2:1 gave rise to the 2D lamellar polymer **2**, which was confirmed by X-ray structure analysis. As shown in Figure 4, Each silver atom in **2** is trigonally coordinated by three nitrogen atoms from different but symmetry-equivalent bpsb ligands that are related by a threefold axis passing through the Ag atom.

The ligand bpsb bridges two silver atoms with two nitrogen atoms from different pyrimidine groups. Continual symmetry operations about threefold axes passing through two silver atoms lead to a 2D lamellar network (Figure 5), which is made up of the repeating unit $[Ag_6(bpsb)_6]$ with a crownlike conformation. The $[Ag_6(bpsb)_6]$ unit possesses a crystallographic C_3 symmetry axis passing through its center; three of the Ag atoms related by a threefold axis are located on one plane perpendicular to the *c* axis (three Ag atoms on one plane, the other three Ag atoms on another plane) (Figure 6).

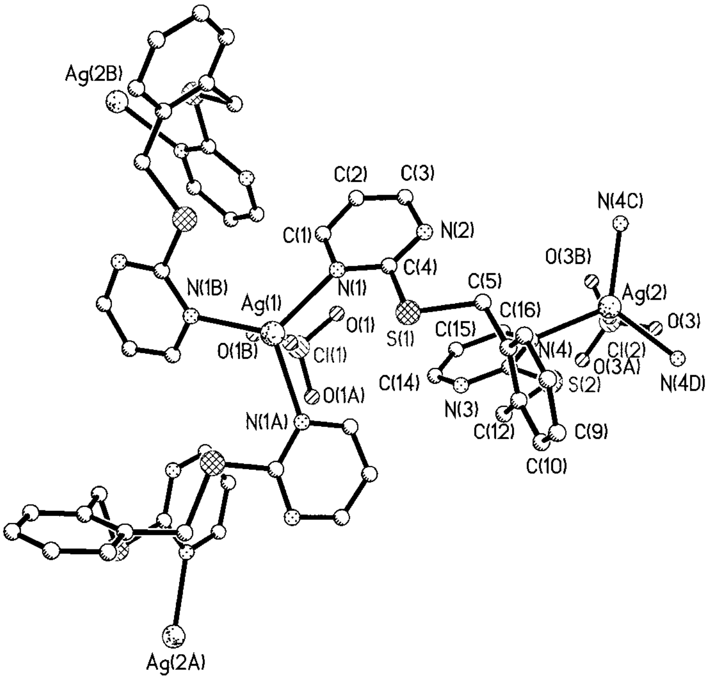


Figure 4. View of the basic unit $[Ag_2(bpsb)_3(ClO_4)_2]$ in **2**.

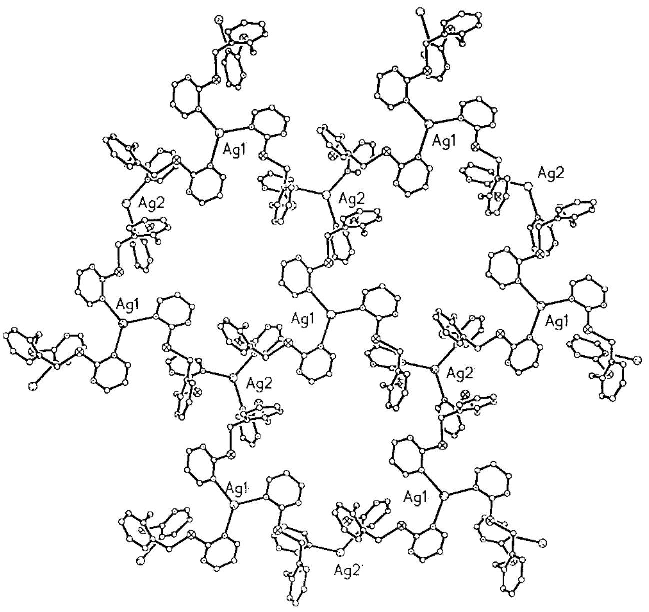


Figure 5. View of the lamellar structure of **2** with $[ClO_4]^-$ ion omitted, running along *ab* plan.

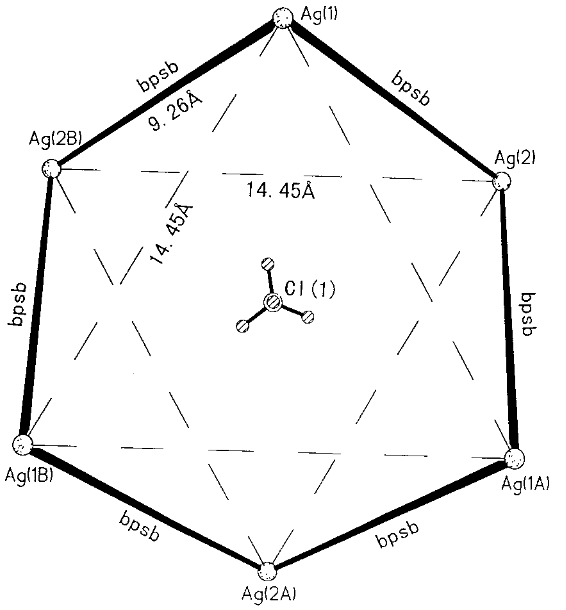
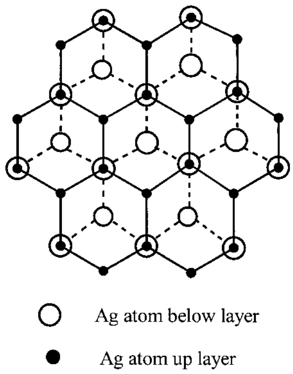


Figure 6. View of $[Ag_6(bpsb)_6]$ nanocavity with $[ClO_4]^-$ in it.

The distance between the two triangular planes is 3.96 Å, and that between two Ag atoms on the same plane is 14.45 Å; thus, the repeating unit forms a crownlike nanocavity. The silver atoms in two adjacent layers are arranged staggered, as shown in Scheme 2. Such a network comprising isolated cavities of $[Ag_6(bpsb)_6]$ is very different from the usual honeycomb structure.[10a, 10b] Each of the $[ClO_4]^-$ ions is partly encapsu-



Scheme 2. Silver atom arrangement in two adjacent layers.

lated inside the cavity of [$Ag_6(bpsb)_6$] and weakly bound to the Ag^I center of another layer (Ag–O 2.801 Å, typical for the ion interaction between Ag^I and ClO_4^-). To the best of our knowledge, the structure of **2** is a unique lamellar structural motif in supramolecular coordination chemistry. Both Ag(1) and Ag(2) are coordinated by three nitrogen atoms from bpsb; the coordination geometry of the Ag(1) atom is highly distorted trigonal planar, while that of the Ag(2) atom is near trigonal planar. Table 2 lists the bond lengths and bond angles of **2**. The Ag–N bond lengths range between 2.231(9) and 2.327(8) Å. The average N-Ag-N bond angles for the Ag(1) and Ag(2) centers are 113.2(2)° and 119.62(5)°, respectively.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.

Ag(1)–N(1)	2.327(8)	Ag(1)–N(1A)	2.327(8)
Ag(1)–N(1B)	2.327(8)	Ag(2)–N(4)	2.231(9)
Ag(2)–N(4C)	2.231(9)	Ag(2)–N(4D)	2.231(9)
S(1)–C(4)	1.749(10)	S(1)–C(5)	1.827(11)
S(2)–C(13)	1.728(10)	S(2)–C(12)	1.833(11)
N(1)-Ag(1)-N(1A)	113.2(2)	N(1)-Ag(1)-N(1B)	113.2(2)
N(1A)-Ag(1)-N(1B)	113.2(2)	N(4)-Ag(2)-N(4C)	119.62(5)
N(4)-Ag(2)-N(4D)	119.62(5)	N(4C)-Ag(2)-N(4D)	119.62(5)
C(4)-S(1)-C(5)	101.4(5)	C(13)-S(2)-C(12)	101.5(5)

Symmetry transformations used to generate equivalent atoms: A: $-y+1, x-y-1, z$; B: $-x+y+2, -x+1, z$; C: $-y, x-y-1, z$; D: $-x+y+1, -x, z$

Experimental Section

The IR spectra as KBr disk were recorded on a Magna 750 FT-IR spectrophotometer. ^1H NMR spectra were measured on a Varian Unit-500 spectrometer with TMS as standard. Elemental analyses were carried out by elemental analysis group in this Institute. The chemicals in this research work were used as purchased without further purification. White powder sodium pyrimidine-2-thiolate was obtained through the reaction of pyrimidine-2-thiol with sodium metal in THF.

Synthesis of the ligand bpsb: A solution of 1,2-bis(bromomethyl)benzene (2.63 g, 10 mmol) and sodium pyrimidine-2-thiolate (2.68 g, 20 mmol) in MeCN (50 mL) was heated to 50°C for 5 h with vigorous stirring. After cooling the mixture, the pale yellow solution was filtered. Removal of the solvent gave an oil, which afforded a light yellow powder (bpsb) on recrystallization from CH_2Cl_2/Et_2O/hexane (yield: 2.6 g, 80%). ^1H NMR (500 MHz, DMSO, 25°C): $\delta = 8.526, 7.286, 7.232, 7.221, 4.510$; IR (KBr pellet): $\tilde{\nu} = 3091$(w), 2996(w), 2939(w), 1724 (s), 1581.3(s), 1454.1(m), 1380.8(s), 1205.3(m), 771.4(m) cm^{-1}; $C_{16}H_{14}N_4S_2$ (326.32): calcd C 58.9, H 4.29, N 17.2; found C 58.6, H 4.21, N 17.4.

Synthesis of [$Ag_4(bpsb)_2(NO_3)$]$_n$ (1): A solution of the ligand bpsb (0.32 g, 1 mmol) in acetonitrile (10 mL) was added to a solution of $AgNO_3$ (0.085 g, 0.5 mmol) in DMF (10 mL). The reaction mixture was stirred for 15 min to give a colorless solution, which was filtered. Slow diffusion of acetone into the resulting solution yielded colorless needlelike crystals of **1**·Me_2CO. IR (KBr pellet): $\tilde{\nu} = 3064$ (w), 3029 (w), 2981.4 (w), 2933.2 (w), 1668.1 (m), 1564.0 (s), 1533.1 (s), 1382.7 (s), 1182.2 (m), 825 (m), 764.5 (m), 748.2 (m), 680.7 (m) cm^{-1}; $C_{35}H_{34}N_{12}O_{13}Ag_4S_4$ (1390.49): calcd C 30.2, H 2.45, N 12.1; found C 29.8, H 2.36, N 12.2.

Synthesis of [$Ag_2(bpsb)_3(ClO_4)_2$]$_n$ (2): A solution of the ligand bpsb (0.32 g, 1 mmol) in acetonitrile (10 mL) was added to a solution of $AgClO_4$ (0.11 g 0.5 mmol) in DMF, and the reaction mixture was stirred for 1 h and then filtered. Slow diffusion of acetone into the resulting solution gave colorless block crystals of **2**. IR (KBr pellet): $\tilde{\nu} = 3066.3$ (w), 3029 (w), 2983 (w), 2939 (w), 1640.4 (w), 1567.8 (s), 1550.5 (s), 1380.8 (s), 1187.9 (m), 1087.7 (s), 769 (m), 622.9 (m) cm^{-1}; $C_{48}H_{42}N_{12}O_8Ag_2S_6Cl_2$ (1393.94): calcd C 41.3, H 3.03, N 12.1; found C 41.5, H 2.98, N 12.0.

Crystallography: A summary of the crystal data for **1** and **2** is given in Table 3. Only special features of the analysis are noted here. The intensity data of both **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation at room temperature. All of the calculations were performed by using the SHELXTL-PL version 5.5 package on an HP 5/75 computer. The positions of all hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement. For **1**·Me_2CO: The coordinates of Ag and S atoms were obtained from an E-map. Successive difference Fourier syntheses gave all the coordinates of the non-hydrogen atoms. The structure was refined by full-matrix least-squares minimization of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the atoms of solvent acetone. For **2**: the coordinates of Ag, Cl, and S atoms were obtained from an E-map. Successive difference Fourier syntheses gave all the coordinates of the non-hydrogen atoms. The structure was refined by full-matrix least-squares minimization of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the oxygen atoms of the perchlorate anion. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124958 (**1**·Me_2CO) and CCDC-124957 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Crystal data for **1** and **2**.

Compound	**1**·Me_2CO	**2**
formula	$C_{35}H_{34}N_{12}O_{13}Ag_4S_4$	$C_{48}H_{42}N_{12}O_8Ag_2S_6Cl_2$
Fw	1390.49	1393.94
crystal size [mm]	0.22 × 0.28 × 0.35	0.15 × 0.20 × 0.26
crystal system	orthorhombic	rhombic
space group	*Fdd2*	*P3c*
a [Å]	29.059(6)	14.454(2)
b [Å]	37.326(7)	14.454(2)
c [Å]	8.606(2)	15.300(3)
U [Å^3]	9334.6(32)	2768.2(8)
Z	8	2
ρ_{calcd} [g cm^{-3}]	1.981	1.672
μ [mm^{-1}]	1.907	1.004
T [K]	293	293
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073
reflections collected	9527	10898
unique reflections	2432	1892
observed reflections ($F = 2.0\sigma(F)$)	2424	1404
parameters	297	223
S on F^2	1.006	1.026
R_1[a]	0.046	0.047
R_w[b]	0.057	0.059
$\Delta\rho_{\text{min and max}}$ [e Å^{-3}]	045 and −1.036	0.639 and −0.667

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

Acknowledgments

This work was supported by the National Nature Science Foundation of China and Nature Science Foundation of Fujian Province.

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Received: August 11, 1999 [F 1972]