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Two-dimensional supramolecular co-ordination compounds of silver(I) with box structures

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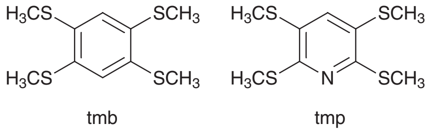
Silver(I) complexes of 2,3,5,6-tetrakis(methylsulfanyl)pyridine (tmp), $[Ag_3(tmp)_4][ClO_4]_3\cdot C_3H_6O$ **1** and $[Ag_2(tmp)_2][C_2F_5CO_2]_2$ **2**, have been prepared and their molecular structures determined by X-ray crystallography. In both complexes two tmp ligands are positioned face to face by two Ag atoms and form a box structure. In **1** three types of silver(I) ion are present depending on the co-ordination numbers. One tmp molecule acts as a bridge between box structures leading to a tape arrangement. The π–π stackings between pyridine rings give a two-dimensional network. In **2**, by contrast, the silver(I) ion has a trigonal planar environment with three thioether S atoms; each tmp acts as a ligand bridging metal centres resulting in a two-dimensional sheet.

Unique network structures of metal complex polymers are often designed by a combination of co-ordination bonds and some weaker intermolecular interactions such as hydrogen bonds, π–π stacking[1] and S···S contacts.[2] The study of the self-assembling process of metal complexes continues to be a theme of considerable current interest in the context of developing new solid-state polymeric materials with specific architectural and functional features.[3] Silver(I) is often used to construct network structures.[4] Co-ordination complexes of thioether ligands with d^{10} silver(I) ions are mainly restricted to macrocyclic thioethers. The structure of $[Ag_n([15]aneS_5)_n][PF_6]_n$ ($[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane) shows two independent and antiparallel, infinite polymeric chains of $[Ag([15]aneS_5)]^+$ cations. Variation of counter anions has been shown to alter the structure of the cation. Interestingly, this complex exhibits reversible electrochemical interconversion of silver-(I) and -(II) species at low temperature.[5] Hannon *et al.*[6] studied the crystal structure of a polymeric assembly of silver(I) cage units of 4-methylsulfanyl-6-(4-pyridyl)-2,2′-bipyridine. Each silver(I) centre is bound to a bipyridyl unit from one ligand and a pyridyl from the other, resulting in the formation of a dimeric M_2L_2 box species. Thus silver is co-ordinated with three N atoms and one SCH_3 group, forming a tetrahedral geometry. We are exploring ways to modify the substituents to tailor the silver/SR ligand polymer structures as to mode of polymerization, dimensionality and the framework. A silver(I) complex with 1,2,4,5-tetrakis(methylsulfanyl)benzene (tmb) forms a linear chain structure in which silver(I) has a tetrahedral co-ordination by four S atoms. In case of the complex with hexakis(methylsulfanyl)benzene (hmb), the silver(I) again has tetrahedral co-ordination by four S atoms and the two S atoms in *para* position are not co-ordinated. The nearest distances between intrachain unco-ordinated S atoms is 3.57 Å. Therefore the molecular packing of the complex forms a two-dimensional network structure through S···S contacts. This silver(I) hmb complex shows an electrical conductivity, $\sigma = 10^{-6}$ S cm^{-1} at 25 °C. Using ligands with multi-thioether groups, we have successfully obtained silver(I) and copper(I) co-ordination polymers.[7]

In this study 2,3,5,6-tetrakis(methylsulfanyl)pyridine (tmp) was used in place of tmb to synthesize and characterize crystallographically a silver(I) co-ordination polymer, and explore the effect of anions and of the nitrogen atom in the pyridine ring on the structure.



Experimental

Preparations were performed using the usual Schlenk techniques. All solvents were dried and distilled by standard methods before use. The standard chemicals were obtained from Wako Chemical Co., Japan and used without further purification. The IR spectra were measured as KBr discs on a JASCO FT/IR-8000 spectrometer, ^{1}H NMR with a JEOL GSX-270 FT-NMR spectrometer at 23 °C. Tetramethylsilane was used as an internal reference. **CAUTION**: perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

Syntheses

2,3,5,6-Tetrakis(methylsulfanyl)pyridine (tmp).[8] In a three-necked flask equipped with a magnetic stirring bar, septum cap and argon gas inlet tube were placed 2.0 g (28.5 mmol) of sodium methanethiolate (Aldrich Chemical Co., Inc.) and 16 cm^3 of dry 1,3-dimethyl-2-imidazolidinone (Tokyo Chemical Industry Co., Ltd.). To this suspension was added with stirring 0.81 g (0.5 cm^3, 4.4 mmol) of 1,2,4,5-tetrafluoropyridine *via* a syringe through the septum cap. The addition was at a relatively fast rate, resulting in a mildly exothermic reaction. After 3 d at room temperature, TLC (silica gel, 3:1 hexane–diethyl ether) showed only one spot. At this point the reaction mixture was added to 50 ml of water and a white precipitate was filtered off and washed copiously with water and sparingly with cold methanol to yield 1.5 g (98%) of white powder. Recrystallization from chloroform–*n*-pentane yielded light yellow needles (1.1 g, 81%), mp 125–126 °C. IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2913s, 1489m, 1431s, 1368s, 1329m, 1292s, 1233m, 1219m, 1167s, 1073s, 963m, 864m and 639m. δ_H(270 MHz, CDCl$_3$) 2.43 (6 H, s), 2.59 (6 H, s) and 7.42 (1 H, s). EI Mass spectrum: *m*/*z* 263 (100%, M).

[Ag$_3$(tmp)$_4$][ClO$_4$]$_3$·C$_3$H$_6$O 1. Single crystals suitable for X-ray analysis were obtained by reaction of AgClO$_4$ (4.1 mg, 2 mM) dissolved in 10 cm^3 of acetone and an acetone solution (10 cm^3) containing tmp (5.1 mg, 2 mM). The mixture was stirred for 1 h and the colourless filtrate transferred to a glass tube and layered with 2 cm^3 of *n*-pentane as a diffusion solvent. After standing for two days at ambient temperature colourless plate crystals of complex **1** were isolated. Yield: 43% based on silver. The crystals are unstable. They lose their clarity and decompose upon drying, probably due to loss of the acetone molecule incorporated in the crystals. IR (KBr disc): $\tilde{\nu}$/cm^{-1} 3020w, 2934w, 1701m, 1528w, 1493w, 1427m, 1369s, 1231m, 1169s, 1094s and 619s (Found: C, 26.6; H, 3.3; Ag, 18.8; N, 3.4. Calc. for $C_{39}H_{58}Ag_3Cl_3N_4O_{13}S_{16}$: C, 27.0; H, 3.4; Ag, 18.7; N, 3.2%).

[Ag$_2$(tmp)$_2$][C$_2$F$_5$CO$_2$]$_2$ 2. Crystals suitable for X-ray analysis were obtained by similar procedures as for complex **1**. The salt Ag(C$_2$F$_5$CO$_2$) (40.6 mg, 15 mM) was dissolved in 10 cm^3 of acetone and an acetone solution (10 cm^3) containing tmp (39.5 mg, 15 mM) was added. After standing for one week at ambient temperature colourless prismatic crystals of **2** were isolated. Yield: 37% based on silver. They were air-stable and light sensitive. IR (KBr disc): $\tilde{\nu}$/cm^{-1} 3443m, 2914m, 1678s, 1491w, 1433m, 1366s, 1327m, 1292m, 1219s, 1165s, 1073m, 1030m, 963m, 864m, 818m, 733m and 637m (Found: C, 26.4; H, 2.5; Ag, 19.5; N, 2.9. Calc. for $C_{12}H_{13}AgF_5NO_2S_4$: C, 27.0; H, 2.4; Ag, 20.2; N, 2.6%).

Crystallography

Crystal data for complexes **1** and **2** are given in Table 1. Diffraction data were collected on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation in the ω–2θ scanning mode and a Quantum CCD area detector, respectively. The structures were solved by a direct method[9] and refined by full-matrix least-squares analysis on F^2. The counter anion ClO$_4^-$ and solvent C$_3$H$_6$O in complex **1** were found to have high thermal motions. Data collection for **2** was performed on a Quantum CCD area detector. All the full-occupancy non-hydrogen atoms were refined anisotropically. The positions of all the hydrogen atoms were determined from difference electron density maps and included, but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[10] Computations were carried out using TEXSAN.[11] The selected bond lengths and bond angles for **1** and **2** are listed in Table 2.

CCDC reference number 186/1531.

See http://www.rsc.org/suppdata/dt/1999/2737/ for crystallographic files in .cif format.

Results and discussion

Two-dimensional structure of complex 1 through π–π interactions

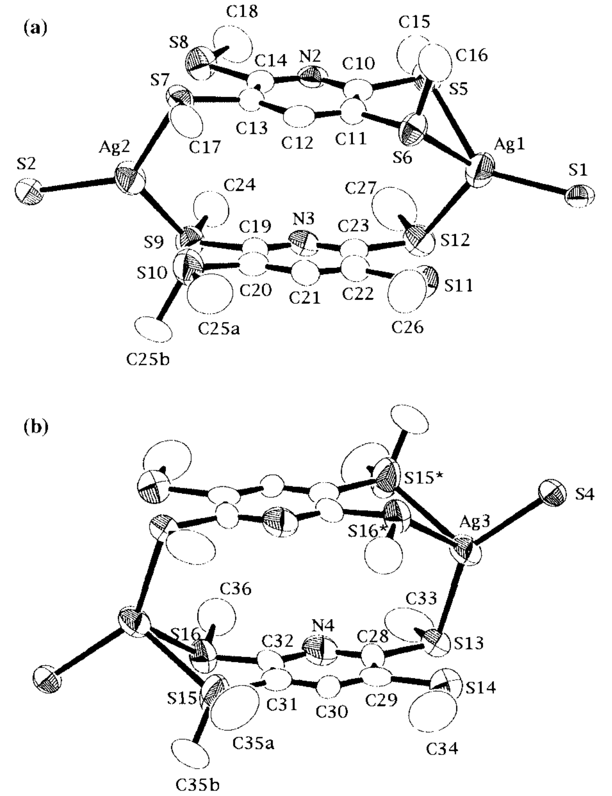
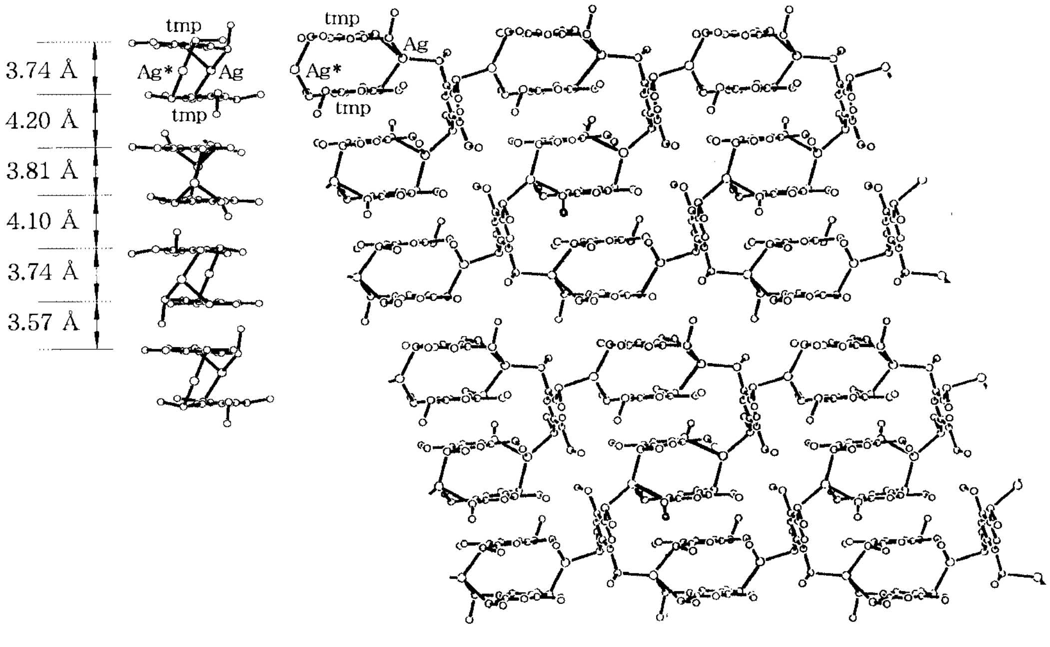


Fig. 1 The ORTEP views of two types of box structure in complex **1**.

Two ORTEP[12] views of the complex **1**, with selected atom labelling are shown in Fig. 1 (unco-ordinated perchlorate anion and acetone molecule are omitted for clarity). The structure consists of dimeric M$_2$L$_2$ box species co-ordinated with only SCH$_3$ groups. This box has two types of structures which differ in silver co-ordination geometries as shown in Fig. 1(a), (b). Both Ag(1) and Ag(3) are 4-co-ordinated with Ag–S distances in the range 2.546–2.787 Å. Atom Ag(2) has a 3-co-ordination geometry and the Ag–S distances in the range 2.533–2.638 Å. Atoms C(25) and C(35) of the methyl groups are disordered. Two tmp ligands are positioned face to face by two Ag atoms and form a box structure. The nitrogen atom in the pyridine ring is either on the same side (Fig. 1(a)), or the opposite side (Fig. 1(b)). The molecular packing of this compound is shown in Fig. 2(b). Another tmp molecule acts as a bridge between box structures leading to a tape arrangement. The face to face distance of tmp in the box is 3.74, 3.81 Å, respectively, indicative of negligible π–π interactions due to the long separations. However, the shortest inter-tape tmp distance is 3.57 Å, indicative of weak π–π stacking interactions as shown in Fig. 2(a). Thus the complex forms a two-dimensional network structure. The structure of a silver(I) complex of tmb molecules without nitrogen atoms has been reported.[7] The silver atoms are co-ordinated by four S atoms from two different tmb ligands in a distorted tetrahedral geometry. The ligand acts as a bridge between pairs of Ag atoms to give a linear chain polymer. The difference may be caused by the counter anion and the ligand dipole moment. The solvated acetone molecules are incorporated in the network, and the perchlorate anions are located adjacent between the sheets. The incorporated acetone molecules are not strongly bound in the lattice but are easily removed by drying the crystals in argon or air, resulting in the destruction of the crystal structure. This causes instability of the compound in the solid. Nevertheless, this is the first example of a silver(I) polymeric co-ordination compound that consists of dimeric M$_2$L$_2$ box species co-ordinated with only SCH$_3$ groups. On the other hand, in the case of the tmb complex the Ag atom is co-ordinated by four S atoms from two tmb ligands in a tetrahedral geometry. Its molecular structure is a linear chain polymer (see Fig. 5).

Two-dimensional sheet structure of complex 2

The molecular structure together with the atomic numbering scheme is given in Fig. 3. A single-crystal structure determination reveals that the co-ordination compound **2** contains an infinite two-dimensional cation and interacting C$_2$F$_5$CO$_2^-$ anion. In the cation all tmp units are attached to three silver centres by the SCH$_3$ groups. Each silver ion is co-ordinated by three tmp donors in a distorted trigonal planar arrangement.



(a) side view (b) molecular structure

Fig. 2 Molecular structure of complex **1**: (a) side view, (b) molecular packing.

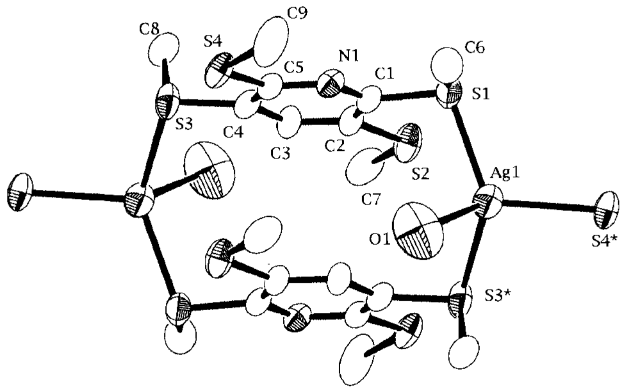


Fig. 3 An ORTEP view of complex **2**.

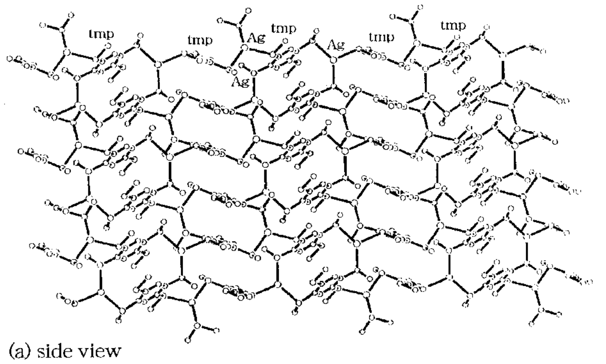
The axial co-ordination sites of the silver ion are occupied by one oxygen atom from the $C_2F_5CO_2^-$ anion. The Ag(1)–O(1) distance is 2.538 Å, suggesting at least a weak co-ordinative interaction between Ag and O. Two tmp ligands are positioned face to face by two Ag atoms forming a box structure similar to that of **1**. The molecular packing of this compound is shown in Fig. 4. The face to face distance of tmp in the box is 3.73 Å, indicative of negligible π–π interactions due to the long separations.

Effect of counter anions ClO_4^- and $C_2F_5CO_2^-$

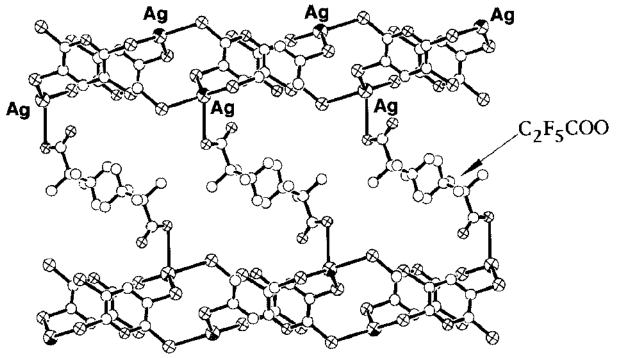
Silver(I) is a soft metal centre with a high affinity for soft sulfur ligands. Many of its salts with counter ions such as tetrafluoroborate, hexafluorophosphate, perchlorate, triflate ($CF_3SO_3^-$) and pentafluoropropionate ($C_2F_5CO_2^-$) are known to be soluble in organic solvents. As the perchlorate anion is non-co-ordinating in complex **1**, it would be possible to pinpoint the specific co-ordination network of tmp from materials in which the metal ions are bonded only to bridging ligands. In **2** the pentafluoropropionate anion is weakly co-ordinated to silver(I); the anions are present between the sheet structure as shown in Fig. 4(b).

Spectroscopic studies and properties of the iodine doped complex

Although the C–S stretch at 570–705 cm^{-1} doesn't give rise to a strong band in the infrared spectra of tmp and its complexes,[13] complex **1** exhibits a band at 1094 cm^{-1} that can readily be assigned to the ClO_4^- anions and complex **2** exhibits a band at 1678 cm^{-1} assigned to the $C_2F_5CO_2^-$ anions. The ^1H NMR spectra of d_6-DMSO solutions of the complexes showed the expected one resonance in the aromatic region and the presence of single CH_3S resonances. The latter appear at a similar chemical shift for both the complex and the "free" ligand, indicating that the aggregation process is not occurring in DMSO



(a) side view



(b) top view

Fig. 4 Molecular structure of complex **2**: (a) side view, (b) top view.

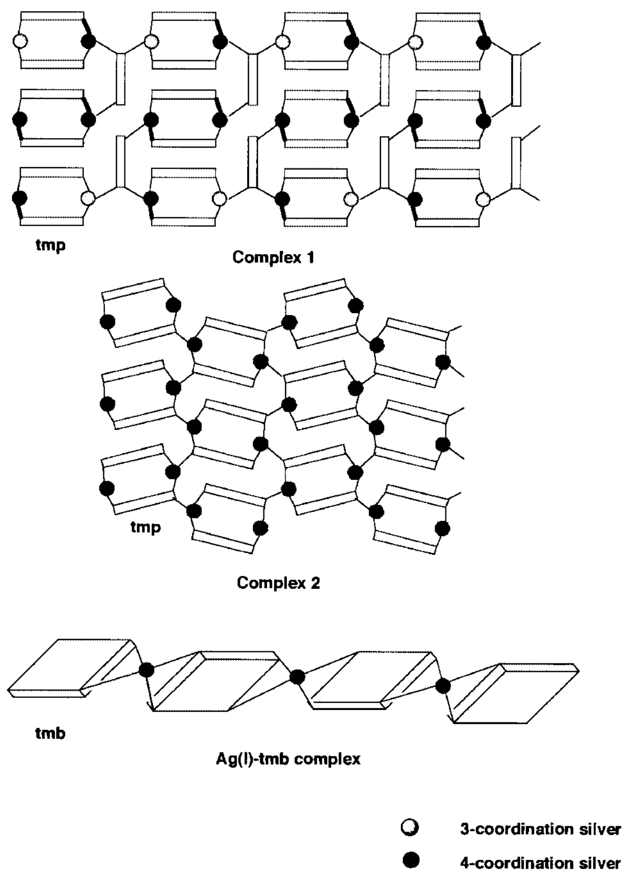


Fig. 5 Schematic co-ordination modes of complexes **1**, **2** and the tmb complex.

Table 1 Crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{39}H_{58}Ag_3Cl_3N_4O_{13}S_{16}$	$C_{12}H_{13}AgF_5NO_2S_4$
Formula weight	1733.83	534.34
Colour, habit	Colourless, plate	Colourless, plate
Crystal size/mm	0.20 × 0.15 × 0.10	0.18 × 0.20 × 0.03
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	15.743(4)	15.894(5)
b/Å	15.694(3)	8.523(2)
c/Å	13.584(2)	16.078(5)
α/°	73.46(2)	
β/°	79.01(1)	110.779(2)
γ/°	84.68(2)	
V/Å^3	3155(1)	15702.2(5)
Z	2	4
D_c/g cm^{-3}	1.824	1.743
F(000)	1744.00	1056.00
λ/Å	0.71069	0.71069
μ(Mo-Kα)/cm^{-1}	16.33	14.46
No. reflections measured (total, unique)	15045, 14514	4633 4593
No. observed reflections [$I > 2\sigma(I)$]	6690	3270
$R1$	0.084	0.069
$wR2$	0.208	0.173
T/K	296.2	296.2

solution. This is expected to compete effectively with the weakly co-ordinating CH_3S group. The two complexes were partially oxidized by iodine doping by the gaseous diffusion method at room temperature. In 3 weeks they gave dark brown compounds. The electrical resistivity of compacted pellets of the compounds was measured by the conventional two-probe technique. Although complex **1** is an insulator at 25 °C, $\sigma < 10^{-12}$ S cm^{-1}, its iodine-doped product behaves as a semiconductor with conductivity of 7.1×10^{-4} S cm^{-1}.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1			
Ag(1)–S(1)	2.546(2)	Ag(1)–S(5)	2.734(3)
Ag(1)–S(6)	2.687(3)	Ag(1)–S(12)	2.684(3)
Ag(2)–S(2)	2.582(2)	Ag(2)–S(7)	2.533(2)
Ag(2)–S(9)	2.638(3)	Ag(3)–S(4)	2.583(2)
Ag(3)–S(13)	2.542(3)	Ag(3)–S(15)	2.687(3)
Ag(3)–S(16)	2.787(3)		
S(1)–Ag(1)–S(5)	136.61(8)	S(1)–Ag(1)–S(6)	114.48(8)
S(1)–Ag(1)–S(12)	120.58(8)	S(5)–Ag(1)–S(6)	71.82(8)
S(5)–Ag(1)–S(12)	93.98(9)	S(6)–Ag(1)–S(12)	108.90(9)
S(2)–Ag(2)–S(7)	134.04(8)	S(2)–Ag(2)–S(9)	99.91(7)
S(7)–Ag(2)–S(9)	119.37(8)	S(4)–Ag(3)–S(13)	143.38(8)
S(4)–Ag(3)–S(15)	108.0(1)	S(4)–Ag(3)–S(16)	93.77(8)
S(13)–Ag(3)–S(15)	103.3(1)	S(13)–Ag(3)–S(16)	114.74(8)
S(15)–Ag(3)–S(16)	69.8(1)		
2			
Ag(1)–S(1)	2.567(2)	Ag(1)–S(3)	2.558(2)
Ag(1)–S(4)	2.650(2)	Ag(1)–O(1)	2.538(7)
S(1)–Ag(1)–S(3)	133.14(5)	S(1)–Ag(1)–S(4)	113.77(5)
S(3)–Ag(1)–S(4)	104.51(4)		

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