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FULL PAPER

Three-dimensional silver(I) co-ordination polymer with pocket structures

Yusaku Suenaga,*[a] Takayoshi Kuroda-Sowa,[a] Masahiko Maekawa[b] and Megumu Munakata[a]

[a] *Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*
[b] *Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*

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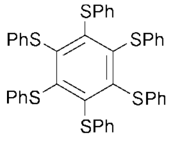
Silver(I) complexes of hexakis(phenylsulfanyl)benzene (hphb), $[Ag_2(hphb)][PF_6]_2$ **1** and $[Ag(hphb)(NO_3)]$ **2**, have been prepared and their molecular structures determined by X-ray crystallography. In **1** the silver ion adopts a tetrahedral co-ordination geometry comprising four S atoms from two different hphb molecules and giving an eight-membered Ag–S ring structure in a co-ordination polymer. This ring (6.46 × 6.79 Å) forms a three-dimensional framework with pockets. On the other hand, for **2**, the silver(I) ion has a square pyramidal environment with four S atoms and one O atom of a NO_3^- anion. The complex forms a linear-chain structure with an alternating arrangement of silver ions and hphb.

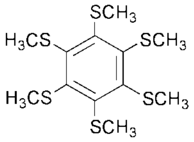
The self-assembling process of metal complexes continues to be of considerable interest in the context of developing new solid-state polymeric materials with specific architectural and functional features.[1] Silver(I) ions are regarded as extremely soft acids favouring co-ordination to soft bases, such as ligands containing S and unsaturated N. Complexes with these soft ligands give rise to an interesting array of stereochemistries and geometric configurations, with co-ordination numbers of two to six all occurring. Therefore silver(I) is often used to construct network structures.[2] However co-ordination complexes of thioether ligands with the d^{10} silver(I) ion have mainly been restricted to macrocyclic thioethers.[3] We are exploring ways to modify the substituents to tailor the silver(I)/SR ligand polymer structures as to the mode of polymerization, dimensionality and the framework. In its complex with hexakis(methylsulfanyl)benzene (hmb), silver(I) has a tetrahedral co-ordination by four S atoms and two S atoms in *para* position are not co-ordinated. The nearest distances between interchain unco-ordinated S atoms is 3.57 Å. Therefore, the molecular packing of the complex forms a two-dimensional network structure through $S\cdots S$ contacts.[4] Using ligands with multi-thioether groups we have successfully obtained a silver(I) and copper(I) co-ordination polymer.[5]

As one such ligand, hexakis(phenylsulfanyl)benzene (hphb) is known to form host–guest compounds with $CHCl_3$, $CBrCl_3$, $C(CH_3)Cl_3$, $C(NO_2)Cl_3$, $C(CN)Cl_3$, CCl_4, *etc.* MacNicol and co-workers[6] have reported that the hphb host shows remarkable guest selectivity properties when recrystallized from solvent mixtures. Also, Pang *et al.*[7] have studied the orientation of the guest molecules in host–guest compounds using hphb as the host. Michalski *et al.*[8] have discussed the crystal structure and thermal expansion of a hphb–CBr_4 clathrate. Recently, the redox properties of polythiaarene derivatives and the crystal structure of a diacetylene-linked polythiaarene have been reported by Tucker *et al.*[9] and Mayor *et al.*,[10] respectively.

In this study hphb was used in place of hmb to synthesize and characterize crystallographically the silver(I) co-ordination polymer, and explore the effect of the substituent group on the structure.



hphb



hmb

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 disks on a JASCO FT/IR-8000 spectrometer, ^{1}H NMR with a Varian Marcury 300 FT-NMR spectrometer at 23 °C. Tetramethylsilane was used as the internal reference. Thermal gravimetry (TG) analyses were obtained with a TG/DTA-200 and DSC-200 instrument from the SEIKO Instrument Co. under nitrogen at rates of 20 and 10 °C min^{-1}, respectively. The curves for complex **1** show a one-step decomposition behavior (366 °C), corresponding to elimination of the hphb ligand. The melting point (T_m) of the complex is 222 °C. After the complex had been heated at 180 °C for 3 h under vacuum, DSC showed one sharp T_m at 221 °C. This result indicates that the structure is maintained during this heat treatment. On the other hand, TG for complex **2** shows a two-step decomposition (254 and 401 °C), corresponding to the elimination of NO_3^- and the hphb ligand. The T_m and decomposition temperature (T_d) of hphb are 189 and 417 °C, respectively.

Syntheses

Hexakis(phenylsulfanyl)benzene (hphb).[11] In a three-necked flask equipped with a magnetic stirring bar, septum cap and argon gas inlet tube were placed 3.3 g (25.6 mmol) of sodium benzenethiol (Aldrich Chemical Co., Inc.) and 25 cm^3 of dry 1,3-dimethyl-2-imidazolidinone (Tokyo Chemical Industry Co., Ltd.). To this suspension was added with stirring

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0.50 g (0.3 cm^3, 3.2 mmol) of hexafluorobenzene *via* a syringe through the septum cap. The addition was at a relatively fast rate, resulting in a mildly exothermic reaction. After 6 d at 60 °C, TLC (silica gel, 3 : 1 hexane–diethyl ether) showed only one spot. At this point the reaction mixture was added to 100 cm^3 of water and a yellow precipitate was filtered off and copiously washed with water and sparingly with cold methanol to yield 2.02 g (87%) of a yellow powder. Recrystallization from chloroform–*n*-pentane yielded yellow brick crystals (0.91 g, 39%), mp 185–190 °C. IR (KBr disc): ν/cm^{-1} 3067w, 3015w, 2936w, 1578s, 1476s, 1439m, 1267m, 1076m, 1024m, 997w, 901w, 741s, 700m and 689m. ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.9–6.95 (12 H, d) and 7.07–7.18 (18 H, m). EI Mass spectrum: *m*/*z* 726 (100%, M).

$[Ag_2(hphb)][PF_6]_2$ 1. Single crystals suitable for X-ray analysis were obtained by the reaction of $AgPF_6$ (4.1 mg, 6 mmol) dissolved in 5 cm^3 of 2-butanone and a 2-butanone solution (5 cm^3) containing hphb (5.1 mg, 3 mmol). The mixture was stirred for 1 h and the yellow filtrate transferred to a glass tube and layered with 2 cm^3 of *n*-pentane as the diffusion solvent. After standing for 7 d at ambient temperature, yellow plate crystals of complex **1** were isolated. Yield: 34% based on silver. IR (KBr disc): ν/cm^{-1} 3059w, 2926m, 2855w, 1580m, 1478m, 1441m, 1296, 1269, 1071w, 1024w, 999w, 849s, 741s, 687s and 559s (Found: C, 40.7; H, 2.7; S, 15.3. Calc. for $C_{21}H_{15}AgF_6PS_3$: C, 40.9; H, 2.5; S, 15.6%).

$[Ag(hphb)(NO_3)]$ 2. Crystals suitable for X-ray analysis were obtained by procedures similar to those for complex **1**. $AgNO_3$ (6.4 mg, 5 mmol) was dissolved in 5 cm^3 of THF and to this solution was added a THF solution (5 cm^3) containing hphb (18.2 mg, 5 mmol) and layered with 2 cm^3 of *n*-pentane as the diffusion solvent. After standing for 3 d at ambient temperature yellow prismatic crystals of complex **2** were isolated. Yield: 54% based on silver. IR (KBr disc): ν/cm^{-1} 3054m, 2973w, 2859w, 1580s, 1476s, 1439s, 1416s, 1372s, 1285s, 1180m, 1157w, 1071s, 1022s, 999m, 901w, 853w, 743s, 687s and 502m (Found: C, 56.3; H, 3.1; S, 21.2. Calc. for $C_{42}H_{30}AgNO_3S_6$: C, 56.2; H, 3.4; S, 21.4%).

Crystallography

Crystal data for complexes **1** and **2** are given in Table 1. The structures were solved by a direct method[12] and refined by full-matrix least-squares analysis on F^2. Data collection was performed on a Quantum CCD area detector coupled with a Rigaku AFC-7R diffractometer. 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.[13] Computations were carried out using TEXSAN.[14] Selected bond lengths and bond angles for **1** and **2** are listed in Table 2.

CCDC reference number 186/2158.

See http://www.rsc.org/suppdata/dt/b0/b003944f/ for crystallographic files in .cif format.

Results and discussion

Three-dimensional structure of complex 1

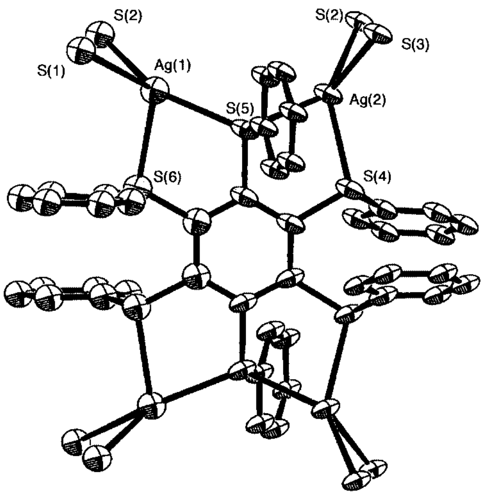

Fig. 1 An ORTEP view of complex **1**. Thermal ellipsoids are at the 50% probability level.

An ORTEP[15] view of the complex, with selected atom labelling is shown in Fig. 1. All hphb molecules are attached to the four silver centers by the S atoms, and the silver ion has a tetrahedral geometry. The Ag–S distances are in the range 2.557–2.606 Å, which is comparable to that in the complexes of hmb with silver(I) hexafluorophosphate [2.565(2) Å]. Four ligands are arranged around the Ag–S eight-membered ring as shown in Fig. 2(a). The two ligands on opposite sides are projected above the planar Ag–S eight-membered ring, with another two molecules below (Fig. 2(b)). Thus, complex **1** forms a pocket structure. The Ag···Ag distances in the Ag–S eight-membered ring are 6.46 Å and the S···S distances are 6.79 Å. The crystal packing of complex **1** is shown in Fig. 3 (the PF_6^- anions, which do not co-ordinate, are omitted for clarity). It was found that the pocket structure has a regular arrangement and forms a three-dimensional framework. Two PF_6^- anions occupy each pocket. The side-phenyl groups of hphb are positioned so as to avoid the pocket (Fig. 2(a)). We use descriptors **a** and **b** to denote side-chain phenyl moieties projecting above or below, respectively, the mean plane of the benzene core. The conformation of hexakis(phenoxy)benzene and hphb have regular alternating pairs of legs, **ababab**. The side-phenyl groups are perpendicular to the benzene ring plane, however the conformation of hphb is **abaabb** (Fig. 1).

Linear chain of complex 2

The molecular structure together with the atomic numbering scheme is given in Fig. 4. A single-crystal structure determination reveals that the co-ordination compound **2** contains an infinite linear chain structure. In the cation all hphb units are attached to the two silver centers by the S atoms except for the *para*-positioned S atoms. The Ag–S distances are in the range of 2.689–2.831 Å. Each silver ion is co-ordinated by two hphb donors and one oxygen atom from a NO_3^- anion in a distorted square pyramidal arrangement. The ligand acts as a bridge between pairs of Ag atoms to produce a linear chain polymer. The Ag(1)–O(1) distances are 2.395 Å. Six phenyl groups are perpendicular to the core benzene ring plane in complex **2**, with regular alternating, **ababab**. Both the linear chain structure and conformation of the ligand are the same as in the Ag–hmb complex except for the co-ordination number of Ag.

Comparison between complex 1 and 2

The co-ordination types of the silver(I) complexes with multi-S substituted ligands are shown in Fig. 5. Using tetrakis(methylsulfanyl)benzene, tetrakis(isopropylsulfanyl)-*p*-benzoquinone,[16] hexakis(methylsulfanyl)benzene[4] and hexakis(phenylsulfanyl)benzene (complex **2**) as ligands, the crystal structures formed is a linear chain of the co-ordination type shown in Fig. 5(a) with alternating silver ions and ligands. In complex **1** all the hphb units attached to the four silver centers by the S atoms (Fig. 5(c)) interestingly form a three-dimensional structure with pockets. The difference in complexation modes in complexes **1**

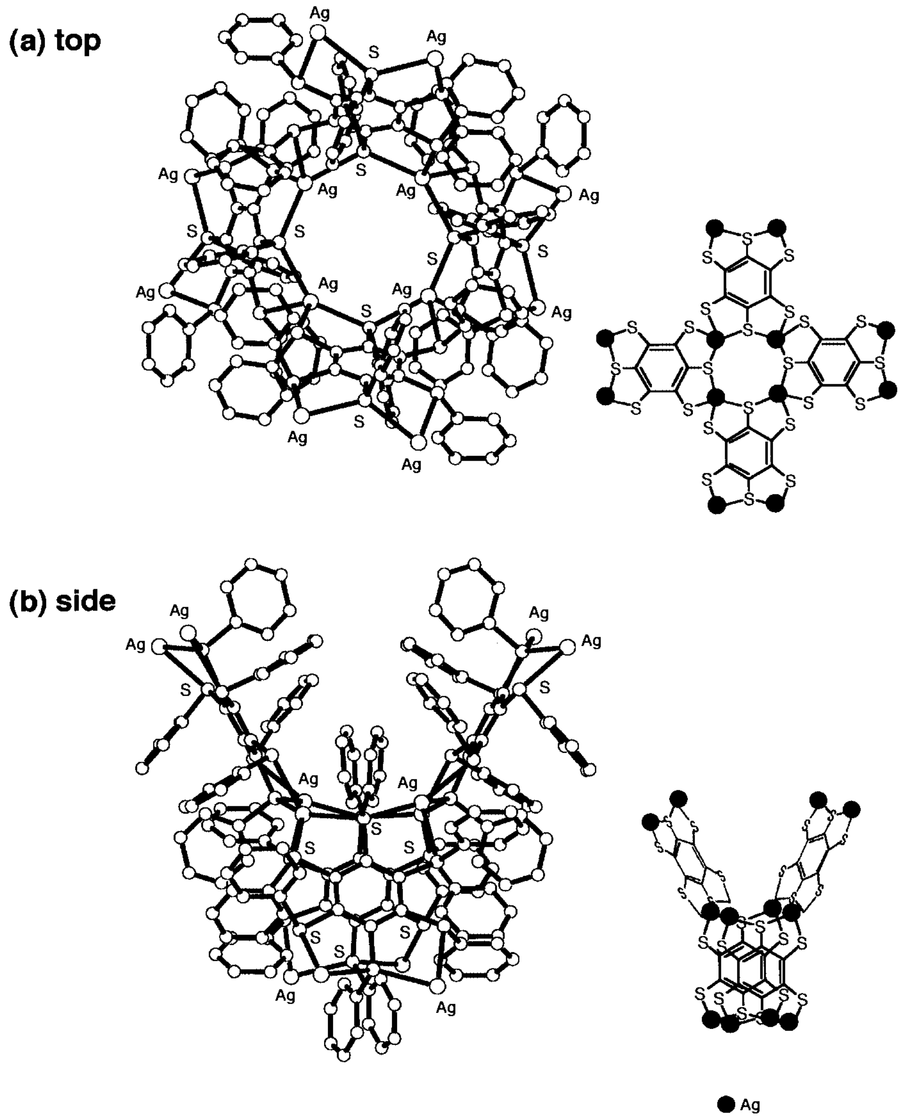

Fig. 2 Crystal structure of complex **1**: (a) top view, (b) side view.

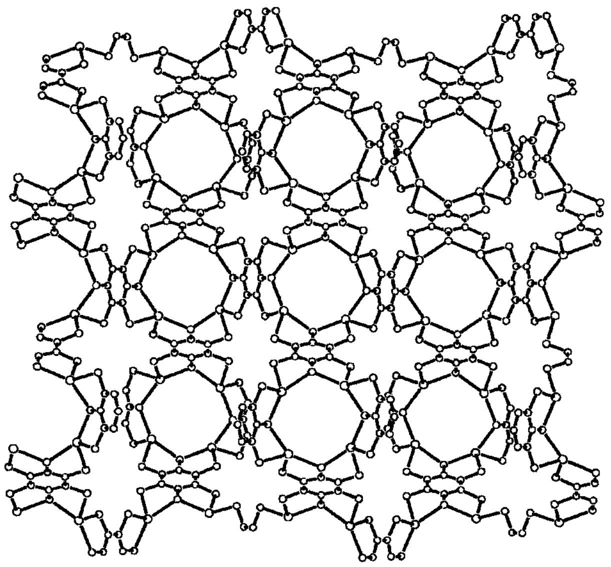

Fig. 3 Crystal packing of complex **1** (the PF_6^- anions, which do not co-ordinate, are omitted for clarity).

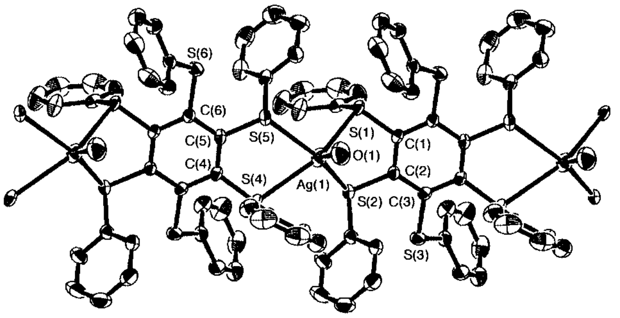

Fig. 4 An ORTEP view of complex **2** Thermal ellipsoids are at the 50% probability level.

and **2** relates to the conformations of the hphb side-phenyl groups when recrystallized from solution. hphb has many possible crystal forms. In regular mode (**ababab**), it gives a metal co-ordination polymer with linear structure. On the other hand, in irregular mode (**abaabb**), it forms the strange structure of Fig. 5(c). The $Au(PPh_3)$ complex with benzenehexathiol has been reported by Schmidbaur and co-workers.[17] The $[AuCS(PPh_3)]_6$ complex forms a wheel-like structure (Fig. 5(d)), however, the complex is not a co-ordination polymer.[18] As far as we are aware, there are a few examples of metal carbonyl complexes with structures of the type shown in Fig. 5(b).[19]

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

	1	**2**
Chemical formula	$C_{42}H_{30}Ag_2F_{12}P_2S_6$	$C_{42}H_{30}AgNO_3S_6$
Formula weight	1232.72	896.93
Crystal system	Orthorhombic	Triclinic
Space group	$I2_12_12_1$ (no. 24)	$P\bar{1}$ (no. 2)
a/Å	19.086(8)	9.302(1)
b/Å	19.060(1)	10.639(2)
c/Å	25.9042(7)	21.118(6)
α/°		93.514(6)
β/°		92.144(3)
γ/°		115.429(1)
V/Å^3	9423(3)	1879.1(5)
Z	8	2
μ(Mo-Kα)/cm^{-1}	12.41	9.11
No. reflections measured	5721	8072
No. observed reflections [$I > 10.00\sigma(I)$]	5648	8067
$R1$	0.069	0.043
$wR2$	0.119	0.113
T/K	200.0	296.2

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

1			
Ag(1)–S(1)	2.599(2)	Ag(1)–S(2)	2.596(2)
Ag(1)–S(5)	2.561(3)	Ag(1)–S(6)	2.606(2)
Ag(2)–S(2)	2.557(2)	Ag(2)–S(3)	2.606(2)
Ag(2)–S(4)	2.600(2)	Ag(2)–S(5)	2.600(2)
S(1)–Ag(1)–S(2)	75.31(5)	S(1)–Ag(1)–S(5)	139.57(6)
S(1)–Ag(1)–S(6)	108.81(6)	S(2)–Ag(1)–S(5)	140.97(6)
S(2)–Ag(1)–S(6)	111.28(6)	S(5)–Ag(1)–S(6)	78.04(5)
S(2)–Ag(2)–S(3)	77.98(5)	S(2)–Ag(2)–S(4)	139.59(6)
S(2)–Ag(2)–S(5)	140.92(6)	S(3)–Ag(2)–S(4)	108.83(6)
S(3)–Ag(2)–S(5)	111.29(6)	S(4)–Ag(2)–S(5)	75.37(5)
2			
Ag(1)–S(1)	2.8313(7)	Ag(1)–S(2)	2.6924(6)
Ag(1)–S(4)	2.6892(6)	Ag(1)–S(5)	2.7453(6)
Ag(1)–O(1)	2.395(3)		
S(1)–Ag(1)–S(2)	71.53(2)	S(1)–Ag(1)–S(4)	149.05(2)
S(1)–Ag(1)–S(5)	97.00(2)	S(1)–Ag(1)–O(1)	103.31(6)
S(2)–Ag(1)–S(4)	104.46(2)	S(2)–Ag(1)–S(5)	150.36(2)
S(2)–Ag(1)–O(1)	78.75(6)	S(4)–Ag(1)–S(5)	71.08(2)
S(4)–Ag(1)–O(1)	105.93(6)	S(5)–Ag(1)–O(1)	130.88(6)

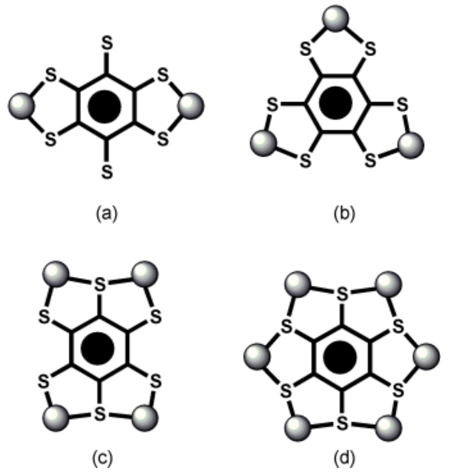

Fig. 5 Schematic view of metal co-ordination types with poly-thioether substituted benzene.

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