

2-D silver(I) coordination polymer with *octakis*(benzylsulfanyl)naphthalene and twisted naphthalene structure

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Abstract

The silver(I) complexes of *octakis*(benzylsulfanyl)naphthalene (obsn), $[\text{Ag}_4(\text{obsn})(\text{C}_2\text{F}_3\text{COO})_4]_2 \cdot 0.7(\text{CH}_2\text{Cl}_2)$ **1** and *octakis*(phenylsulfanyl)naphthalene (ophn), $[\text{Ag}_6(\text{ophn})(\text{C}_2\text{F}_3\text{COO})_6(\text{H}_2\text{O})_2]$ **2** have been prepared and these molecular structure were determined by X-ray crystallography. In **1**, the silver ion prefers tetrahedral coordination geometry comprised of two S atoms from the obsn molecules and the two O atoms from the counter anion then producing two-dimensional sheet structure. Interestingly, the naphthalene ring in the complex has large deviations from planarity and end-to-end twists on the order of 32°. On the other hand six sulfur atom of ophn coordinate with silver(I) ion and naphthalene ring of complex **2** has almost planar structure.

Keywords: silver(I) complex; *octakis*(benzylsulfanyl)naphthalene; *octakis*(phenylsulfanyl)naphthalene; two-dimensional sheet structure; twisted naphthalene ring

1. Introduction

Whereas simple alternant polyarenes are usually planar, intramolecular crowding in more complex polyarenes may result in considerable distortion of their molecular geometry [1]. Recently, a variety of polycyclic aromatic hydrocarbons (PAH) have been prepared and these twisted structures were determined by X-ray crystallography. In 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a,c*]naphthacene [2], the central naphthacene moiety is a smoothly twisted aromatic ribbon in which the terminal bonds are rotated by 105.4(8)°. Also, the central ring of the naphthalene with bulky

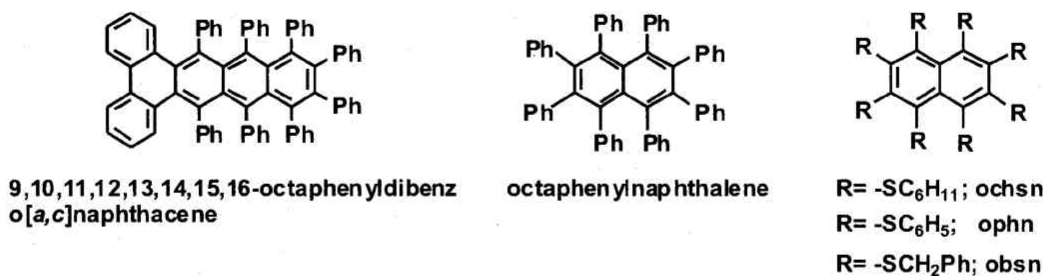
substituents shows 20-30° deviation angles from planarity in the solid state. Such examples are the octapheny- [3], octachloro- [4], octabromo- [5], and octamethyl-naphthalene [6]. On the other hand, *octakis*(alkylsulfanyl)naphthalene [7] adopted an undulating structure. Any electronic effects due to steric distortion of these PAHs may be more important in the field of material science. Up to now in inorganic molecules, the multinuclear Ru complex by multiple substitution of Cp*Ru⁺ on 5,6,11,12-tetraphenylnaphthacene (rubrene) [8], and $[\text{Ag}_4(\text{rubrene})(\text{ClO}_4)_4(\text{H}_2\text{O})_4]$ [9] have been

reported. However, unfortunately, the number of such metal complexes with a highly strained ligand is quite low.

We have been studied the silver(I) coordination polymer with polysulfanyl substituted aromatic compounds, which are well known for their host-guest chemistry in the solid state [10]. One of these

octakis(phenylsulfanyl)naphthalene (*ophn*), was identified by D. D. MacNicol *et al.* [7(c)], and had a central naphthalene ring with an undulating structure as already mentioned.

In this paper, we report the silver(I) coordination polymer with a two-dimensional sheet structure, in which the central naphthalene ring has a large twisted structure on the order of 32(1)°.



Scheme 1

2. Experimental

General

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-8000 spectrometer. The ¹H NMR spectra were obtained with a Varian MERCURY-300 FT spectrometer at 23 °C. Tetramethylsilane was used as the internal reference.

Syntheses

obsn

obsn was synthesized essentially according to a literature method [7(c)]. Recrystallization from acetone-pentane yielded yellow columns (6.1 g, 55%), mp 142-145 °C. IR (KBr disc): ν/cm^{-1} 3059m, 2926w, 1494m, 1453m, 766m, 697s. ¹H NMR (300 MHz, CDCl₃): $\delta_{\text{H}}/\text{ppm}$ 3.729 (8H, s), 4.193(8H, s), 6.974-7.000(8H, m), 7.128-7.232(32H, m). EI Mass spectrum: m/z 1105 (M). (Found: C, 71.82; H, 5.17. Calc. for C₆₆H₅₆S₈: C, 71.69; H, 5.10 %).

ophn

ophn was synthesized essentially according to a literature method [7(c)]. Recrystallization from THF-pentane yielded red columns (18.2 g, 80 %), mp 200-203 °C. IR (KBr disc): ν/cm^{-1} 3067m, 1578s, 1474m, 1438m, 1068m, 733s, 686s. ¹H NMR (300 MHz, CDCl₃): $\delta_{\text{H}}/\text{ppm}$ 6.55-6.59 (8 H, m), 6.98-7.02 (H, m), 7.04-7.06(16H, m), 7.17-7.20 (16 H, m). EI Mass spectrum: m/z 992 (M). (Found: C, 70.18; H, 4.26. Calc. for C₅₈H₄₀S₈: C, 70.12; H, 4.06 %).

[Ag₄(obsn)(C₂F₅COO)₄]₂ · 0.7(CH₂Cl₂) 1

Single crystals suitable for X-ray analysis were obtained by the reaction of AgC₂F₅COO (6.7 mg, 5.0 mM) dissolved in 5 cm³ of dichloromethane and a dichloromethane solution (5 cm³) containing *obsn* (55 mg, 10 mM). The mixture was stirred for 1 h and the yellow filtrate transferred to a glass tube and layered with 2 cm³ of *n*-pentane as the diffusion solvent. After standing for 5 d at ambient temperature, the orange brick crystals of complex **1** were isolated. Yield: 34 % based on silver.

[Ag₆(ophn)(C₂F₅COO)₆(H₂O)₂] **2**

Single crystals suitable for X-ray analysis were obtained by the reaction of $\text{AgC}_2\text{F}_5\text{COO}$ (6.7 mg, 5.0 mM) dissolved in 5 cm^3 of acetone and a acetone solution (5 cm^3) containing ophn (50 mg, 10 mM). 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 8 d at ambient temperature, the orange brick crystals of complex **2** were isolated. Yield: 48 % based on silver.

Crystallography

Crystal data for obsn, complex **1** and complex **2** are given in Table 1. The single crystal structure were solved by a direct method [11] and refined by a

full-matrix least-square analysis on F^2 [12]. Data collection for these complexes were performed on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation. All the full-occupancy non-hydrogen atoms were anisotropically refined. The positions of all the hydrogen atoms were determined from the difference electron density maps and included, but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources. Computations were carried out using TEXSAN [13]. The selected bond lengths and bond angles for obsn, complex **1** and complex **2** are listed in Table 2.

3. Result and Discussion

The ORTEP view of the obsn with selected atom labeling is shown in Figure 1. The descriptions **a** and **b** denote the side-chain benzyl moieties projecting above or below, respectively, the mean plane of the naphthalene core. The side-benzyl groups are perpendicular to the naphthalene ring plane, and the conformation is **baababba**. The core naphthalene ring has almost a planar structure. It is noteworthy that *octakis*(phenylsulfanyl)naphthalene (ophn) exists in two crystal forms (either polymorphs or different solvates) with both C_2 and C_i symmetric naphthalenes represented, suggesting that the two geometries are very close in energy. However we have not observed a second crystal form of obsn. On the other hand, the silver complex structure together with the atomic numbering scheme is given in Figure 2. A single-crystal structure determination reveals that the coordination compound **1** contains a two-dimensional structure. In the cation, all the obsn units are attached to the four silver centers on the S atoms. The Ag-S distances are in the range of 2.469(2)-2.638(2) Å. Each of silver ion is coordinated by two S atoms of the obsn donors and two O atoms of the counter anion in a tetrahedral coordination sphere (Figure 3). The two counter anions act as a bridge between the pairs of Ag atoms. The cavity structure within a sheet of the two-dimensional network comprises

large rings with four $\text{Ag}_4(\text{obsn})$ units at each corner (a)

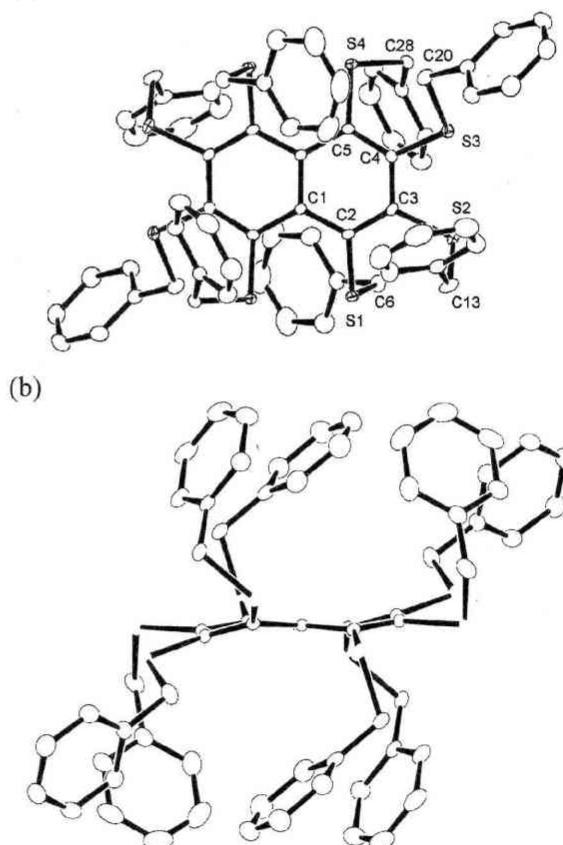


Figure 1. ORTEP view of obsn. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. (a) Top view (b) Side view.

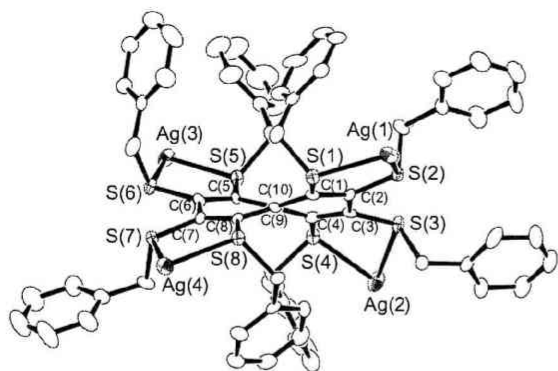


Figure 2. ORTEP view of surrounding obsn in complex **1**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

connected by two counter anions. Each of these large rings is comprised of 30 linked atoms, i.e., O-Ag-S-C-C-S moieties, as shown in Figure 4. This cavity occupied by CH_2Cl_2 molecules.

Eight benzyl groups are perpendicular to the core naphthalene ring plane in complex **1**, with **baabbaa** as shown in the yellow form of ophn [14]. This conformation is different from obsn. Interestingly, the core naphthalene ring is twisted by $32(1)^\circ$ end to end to produce the coordination structure (Figure 5). In the yellow form of ophn, its end-to-end twist angle is 31° . A significant bond alternation is observed, where the long bonds average $1.450(8) \text{ \AA}$ and the short bonds $1.391(8) \text{ \AA}$. As might be expected from the twist, the external angles of the type C(1)-C(9)-C(8) are significantly greater than the usual 120° ($126.7(5)^\circ$) while the internal angles of the types C(1)-C(2)-C(3)-C(4)-C(10)-C(9) ($118.5(5)^\circ$) and C(5)-C(6)-C(7)-C(8)-C(9)-C(10) ($118.6(4)^\circ$) are almost the same. The distances S...S of the 1-position and 8-position into the naphthalene ring are 3.09 \AA . This is considerably shorter than twice the van der Waals radii of 3.70 \AA . The range of the sulfur angles ($99.6(3)$ - $106.4(3)^\circ$) is almost same as that (102 - 107°) found in the solid structure of the silver(I) coordination polymer with polysulfanyl substituted aromatic compounds.

ophn was crystallized from chloroform-pentane to give red crystals and from DMI-diethylether to give yellow crystals. As their X-ray crystal structures have already been reported by D. D.

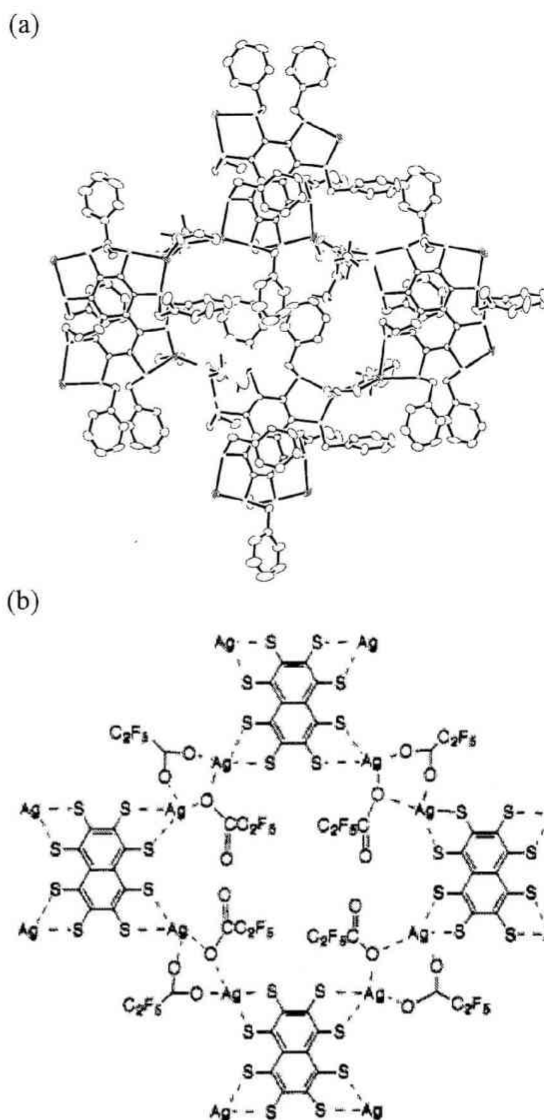


Figure 3. (a) Cavity structure of complex **1**. (b) Schematic view.

MacNicol *et al.* in 1983 [3], we present a summary of their molecular structures. An ORTEP view of the red and yellow forms with selected atom labeling is shown in Figure 6(a) and (b), respectively. The side-phenyl groups are perpendicular to the naphthalene ring plane, however, the conformation of the red form is **aababbab**. The core naphthalene ring has almost a planar structure. In contrast, the conformation of the yellow form is **aabbaabb**, and it is interesting to note that the two benzene rings in the core naphthalene ring have a torsion angle of 31° at the 9, 10-position carbon. We are interested in the structure as the silver(I) complex are conform.

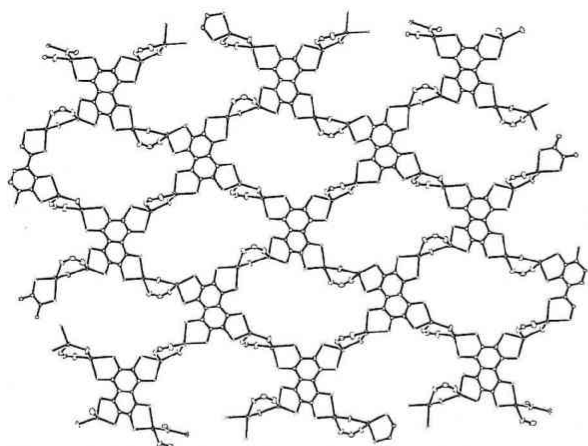


Figure 4. 2-D sheet structure of complex 1. H atoms and CH_2Cl_2 , side-benzyl group have been omitted for clarity.

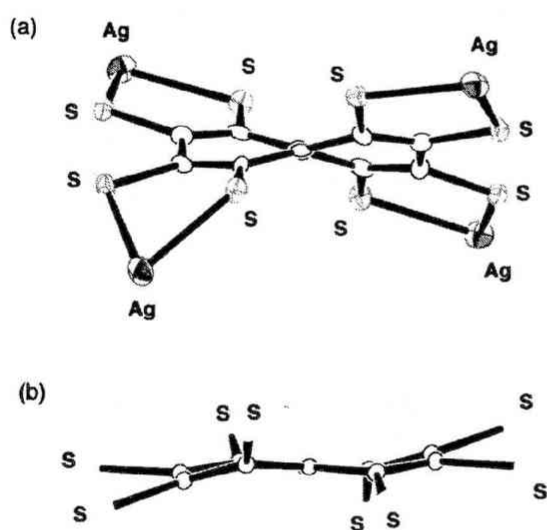
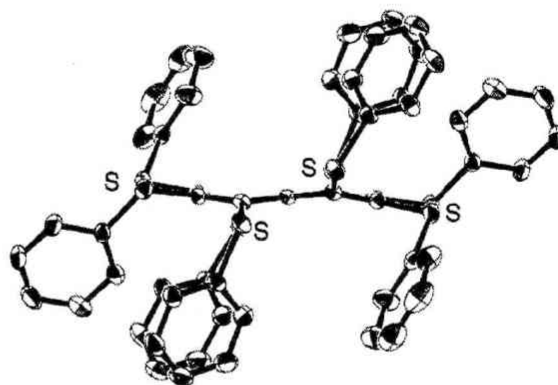


Figure 5. (a) Structure of complex 1 with twisted conformation of the naphthalene skeleton (b) Undulating structure of obsn.

The silver complex structure together with the atomic numbering scheme is given in Figure 7. A single-crystal structure determination reveals that the coordination compound 2 contains a two-dimensional structure. In the cation, all the o-phn units are attached to the six silver centers on the eight S atoms. The Ag-S distances are in the range of 2.537(1)-2.767(1) Å. Ag(1) ion is coordinated by one S atom of the o-phn donors and two O atoms of the counter anion and also, one O atom of the water molecule in a tetrahedral coordination sphere. Ag(2) and Ag(3) ions are coordinated by one S atom of the o-phn donors and

two O atoms of the counter anion in a trigonal coordination sphere (Figure 8). The two counter anions act as a bridge between the pairs of Ag atoms. The cavity structure within a sheet of the two-dimensional network comprises large rings with four $\text{Ag}_6(\text{o-phn})$ units at each corner connected by two counter anions.

(a)



(b)

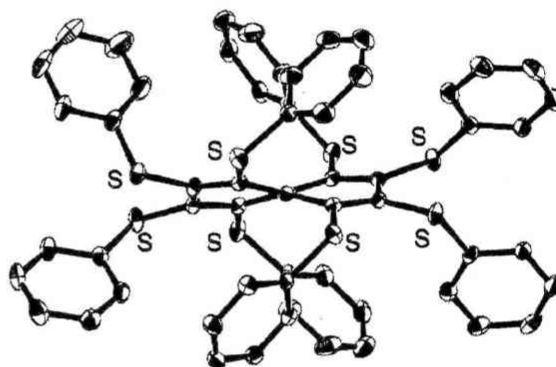
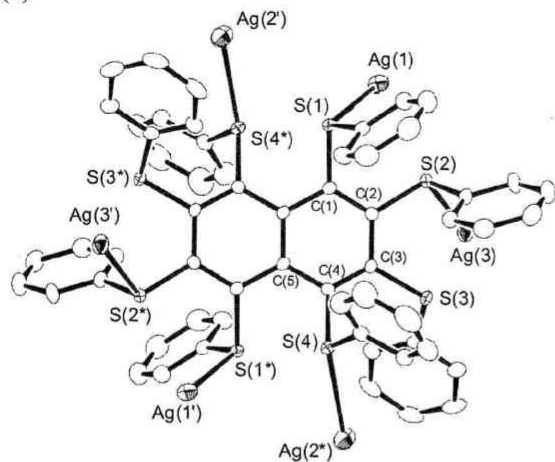


Figure 6. ORTEP view of o-phn. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. (a) red form (b) yellow form.

The co-ordination types of the Ag(I) complexes with multi-S substituted ligands are shown in Figure 9. Using *hexakis*(methylsulfanyl)benzene, *hexakis*(phenylsulfanyl)benzene (hphb) and *octakis*(cyclohexylsulfanyl)naphthalene as ligands, the crystal structures formed is a linear chain of the coordination type shown in Figure 9(b)(f) with alternating silver ions and ligands [15, 16]. In $[\text{Ag}_2(\text{hphb})](\text{PF}_6)_2$ all the hphb units attached to the four silver centers by the S atoms (Figure 9(e)) form a three-dimensional structure [17]. In complex 2, all

the ophn units attached to the six silver centers on the S atoms (Figure 9(c)) interestingly form a two-dimensional structure with a cavity.

(a)



(b)

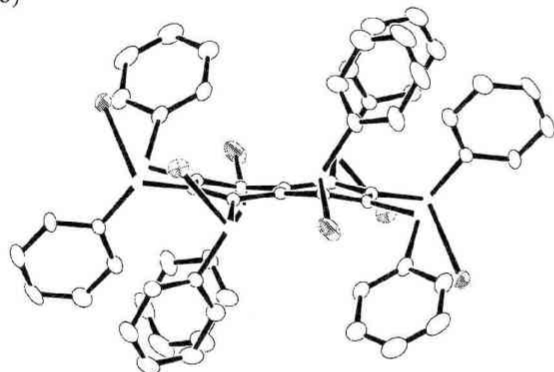


Figure 7. ORTEP view of complex 2. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. (a) Top view (b) Side view.

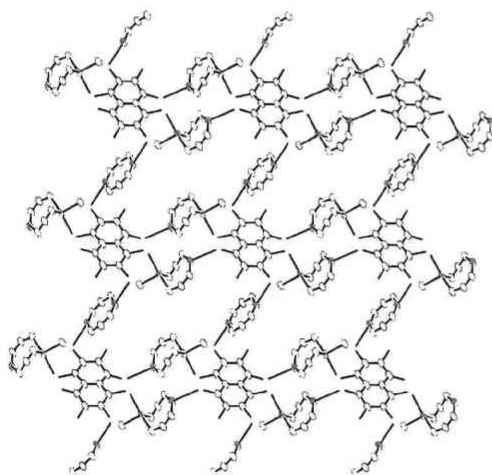


Figure 8. 2-D sheet structure of complex 2. H atoms side-phenyl group have been omitted for clarity.

The difference in the complexation mode of

complexes 1 and 2 are related to the conformation of the ligand side-substituent groups when recrystallised from solution. These ligands have many possible crystal form, i.e., in the regular mode (**abababab** or **aababbab**), and form a metal co-ordination polymer with a linear chain structure. On the other hand, in the irregular mode (**bbaabbaa**), it may form a strange structure as shown in Figure 9(a) [16].

In conclusion, the obsn ligand reacts with silver(I) to form a 1:4 metal-ligand complex. All the S atoms in the obsn ligand are coordinated to the silver atom to consist of two-dimensional sheet structure, thus the central naphthalene ring of the complex shows deviations from planarity and its end-to-end twist angle is $32(1)^\circ$.

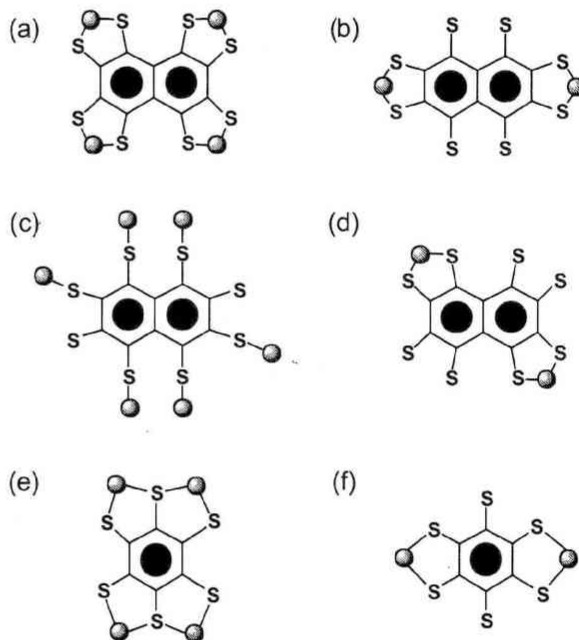


Figure 9. Schematic view of metal co-ordination type with poly-thioether substituted aromatic ligand.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 290855 ($[\text{Ag}_4(\text{obsn})(\text{C}_2\text{F}_5\text{COO})_4]_2 \cdot 0.7(\text{CH}_2\text{Cl}_2)$), CCDC No. 290856 ($[\text{Ag}_6(\text{ophn})(\text{C}_2\text{F}_5\text{COO})_6(\text{H}_2\text{O})_2]$) and CCDC No. 290857 (obsn). Copies of this information may be obtained free of charge from:

The Director, CCDC, 12 Union Road, Cambridge,
 CB21 EZ, UK (fax: +44-1223-336-033; e-mail:
deposit@ccdc.cam.ac.uk or [www:](http://www.ccdc.cam.ac.uk)
<http://www.ccdc.cam.ac.uk>).

5. Acknowledgements

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 assistance with analysis of X-ray crystallography.

Table 1 Crystallographic data for obsn, complex 1 and complex 2

	obsn	complex 1	complex 2
Chemical formula	$C_{66}H_{56}S_8$	$C_{156.7}H_{113.4}Ag_8F_{40}O_{16}S_{16}Cl_{1.4}$	$C_{76}H_{44}Ag_6F_{30}O_{14}S_8$
Formula weight	1105.65	4437.88	2654.82
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)
Lattice Parameters			
$a/\text{\AA}$	10.769(1)	16.463(5)	12.5647(1)
$b/\text{\AA}$	14.176(2)	19.834(7)	12.7198(2)
$c/\text{\AA}$	9.956(1)	25.288(8)	15.5350(5)
$\alpha/^\circ$	101.382(2)		66.984(9)
$\beta/^\circ$	110.230(3)	91.981(4)	69.019(10)
$\gamma/^\circ$	91.775(2)		82.32(1)
Unit Cell Volume			
$V/\text{\AA}^3$	1390.0(3)	8252(4)	2133.6(2)
Z	1	2	1
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	3.63	12.57	16.70
No. reflections measured	22130	64989	24780
No. observed reflections	5660	26585	7565
$[I > 2\sigma(I)]$			
R	0.034	0.056	0.048
Rw	0.086	0.097	0.127
T/K	150.0	150.0	150.0

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad R_w = \left[\frac{\sum \omega(F_o^2 - F_c^2)^2}{\sum \omega(F_o^2)^2} \right]^{1/2}$$

Table 2 Selected bond lengths(Å) and bond angles(°) for obsn, complex 1 and complex 2

obsn			
S(1)-C(2)	1.779(1)	S(2)-C(3)	1.776(1)
S(3)-C(4)	1.763(2)	S(4)-C(5)	1.781(1)
C(1)-C(2)-C(3)	119.9(1)	C(2)-C(3)-C(4)	120.7(1)
C(3)-C(4)-C(5)	118.4(1)		
Complex 1			
Ag(1)-S(1)	2.626(2)	Ag(1)-S(2)	2.487(1)
Ag(2)-S(3)	2.638(2)	Ag(2)-S(4)	2.514(2)
Ag(3)-S(5)	2.470 (2)	Ag(3)-S(6)	2.590(2)
Ag(4)-S(7)	2.469(2)	Ag(4)-S(8)	2.589(2)
C(2)-C(1)-C(9)	120.5(5)	C(1)-C(2)-C(3)	118.2(5)
C(2)-C(3)-C(4)	119.3(5)	C(3)-C(4)-C(10)	119.0(5)
C(6)-C(5)-C(10)	119.7(5)	C(5)-C(6)-C(7)	118.4(5)
C(6)-C(7)-C(8)	119.1(5)	C(7)-C(8)-C(9)	119.9(5)
C(1)-C(9)-C(8)	126.7(5)	C(1)-C(9)-C(10)	115.9(5)
C(8)-C(9)-C(10)	117.4(5)	C(4)-C(10)-C(5)	124.8(5)
C(4)-C(10)-C(9)	118.3(5)	C(5)-C(10)-C(9)	116.8(5)
Complex 2			
Ag(1)-S(1)	2.537(1)	Ag(2)-S(4)	2.767(1)
Ag(3)-S(2)	2.674(1)		
C(1)-C(2)-C(3)	119.9(4)	C(2)-C(3)-C(4)	118.6(5)
C(3)-C(4)-C(5)	120.1(4)	C(4)-C(5)-C(5')	119.8(5)
C(2)-C(1)-C(5')	119.9(4)		

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