Structural analyses of tetrathiadodecahydro[3.3.3.3]paracyclophane complexes with copper(I) and silver(I)

Ya-Chen Yang[a], **Shaw-Tao Lin**[b*], **Wen-Shing Chen**[b]

[a]*Department of Applied Life Science, Asia University, Wufeng, Taichung Hsien, Taiwan, 413*

[b]*Department of Applied Chemistry, Providence University, Sha-Lu, Taichung Hsien, Taiwan, 433*

The preparation and X-ray structures of complexes of 2,11,20,29-tetrathia-4*e*,5,6,7*e*,8,9,22*e*,23,24,25*e*,26,27-dodecahydro[3.3.3.3]cyclophane (**2**) (*t*TTDHPCP) with Cu(I), *i.e.* $[Cu_2I_2(t\text{TTDHPCP})]\cdot\text{thf}$ **3**, and with Ag(I), *i.e.* $[Ag_2(\text{tTTDHPCP})(CF_3COO)_2]$ **4**, are reported. The sulfur atoms of compound **2** bind with metals to serve as the bridge in the polymeric structures, while anions interact with other metal atoms forming multi-dimensional structures. Complex **3** is a novel three-dimensional coordination polymer composed of Cu_4 motifs, in which $(CuI)_2$ forms a square planar unit to link the compound **2** molecules with a THF molecule situated outside the open cavities. In contrast, the Ag atom in complex **4** serves as a bridge for two compound **2** molecules, providing a two-dimensional channel framework. Unit cell data: complex **3**, monoclinic system, space group *P2(1)/n*, a = 14.1935(19) Å, b = 13.7879(19) Å, c = 22.222(3) Å, β = 107.888(3)°, Z = 4.; complex **4**, triclinic system, space group *P-1*, a = 9.4736(7) Å, b = 12.0619(8) Å, c = 18.0914(10) Å, β = 80.1260(10)°, Z = 2.

Keywords: tetrathiacyclophane, multi-dimensional structures, polymeric complexes, diffusion technique, structural analysis

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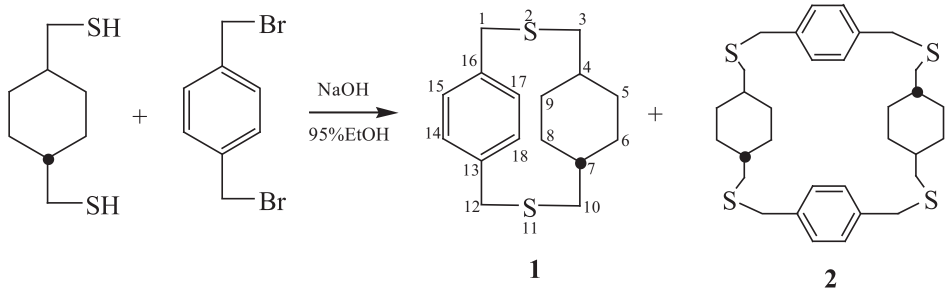
Cyclophane has attracted much attention because of its unusual high molecular strain geometry and interesting interaction between two benzene rings observed in chemical reactions and by ^1H NMR spectroscopic analysis. More recently transition metal complexes of cyclophane have been studied because of their distinct character, such as structural strain, catalytic function, conductivity, electrochemistry and supramolecular chemistry in functional materials.[1-9] The majority of pure hydrocarbon cyclophanes contain two face to face arene rings bridged by methylene units.[10,11] Among them [2.2]- and [3.3]-paracyclophanes are charge transfer compounds through the π-electron interaction of the two aromatic decks in organometallic chemistry.[12-15] In the past few years, we have prepared other high strain cyclophane series, such as 3*e*,4,5,6*e*,7,8-hexahydro[2.2]paracyclophane,[16,17] 3*a*,4,5,6*e*,7,8-hexahydro[2.2]paracyclophane,[18] hexahydro-[2.2]metaparacyclophane and hexahydro[2.2]orthoparacyclophane,[19] containing a benzene ring and either a 1,4-*cis*- or a 1,4-*trans*-cyclohexane ring bridged with two ethylene units from pyrolysis of their dithia-precursors. Those dithia-precursors, containing two sulfur atoms and a benzene ring with a cavity between a benzene ring and a cyclohexane ring, are potential hosts to adopt a small molecule or metal ion as a guest. In the previously work, our attempts to use Cu(I) and Ag(I) ions as guests in preparing host–guest compounds resulted in polymeric complexes *via* sulfur–metal–sulfur linkages.[25] The structures display a different dimensional fashion depending on the nature of the anion. The failure to form a host-guest compound can be attributed to the small volume of the cavity between the two rings. Recently, we carried out the coupling reaction between substituted 1,4-bis(bromomethyl)benzene and *trans*-1,4-bis(mercaptomethyl)-cyclohexane to give a mixture of 2,11-dithia-4e,5,6,7e,8,9-hexa[3.3]-paracyclophanes (**1**) (*t*-DTHHPCP, monomers) and 2,11,20,29-tetrathia-4*e*,5,6,7*e*,8,9,22*e*,23,24,25*e*,26,27-dodecahydro[3.3.3.3]paracyclophanes (**2**) (*t*-TTDHPCP, dimers). The formation of a dimer is not observed in their *cis*-counterparts. The formation of the dimer is attributed to the larger ring strain in the *trans* cyclohexane ring for the formation of small cyclophane compounds. The macro dimer ring has both a large cavity, and the potential Lewis base sites, to host a Lewis acid. The spherical d^{10} electronic configuration of Cu(I) and Ag(I) does not impose a preferred coordination geometry and number in its interaction with a Lewis base.[20-21] The complexes of the dimeric cyclophane **2** with Cu(I) and Ag(I) were prepared for the structural analysis in this study. Endohedral silver complexes with cyclophanes have been studied to some extent.[22] Amongst these studies, the most used cyclophanes contain no sulfur atom at the methylene bridge, and the silver ion tends to be a guest present in the cavity of the cyclophane by forming a coordination link with the π-bond of the benzene rings. In this study, our cyclophane contains four sulfur atoms and two cyclohexane units, thus the bonding fashion is different from those in the literature.

Results and discussion

Preparation of tTTDHPCP complexes

The macro molecule of compound **2** was isolated from the coupling reaction of 1,4-bis(bromomethyl)benzene and *trans*-1,4-bis(mercaptomethyl)cyclohexane (Scheme 1).



Scheme 1

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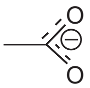
* Correspondent. E-mail: sdlin@pu.edu.tw

Single crystals of [Cu_2I_2(*t*TTDHPCP)]·thf **3** and [Ag_2(tTTDHPCP)($CF_3COO)_2$] **4** complexes were prepared by means of a slow diffusion technique in a sealed-tube.[25] Compound **2** formed air-stable complexes with the metal ions Cu(I) and Ag(I). We found that these adducts contain compound **2** to metal ion with the mole ratio of 1 : 1 regardless of the molar ratio of the two reactants being employed. Direct reaction of a dilute solution of compound **2** and a coinage metal salt at room temperature lead to either microcrystalline or powdery precipitates, which are insoluble in most of the common solvents for further crystallisation. Therefore, an equivalent amount of metal salt in acetonitrile and compound **2** in THF were used for the preparation the complexes. The two complexes are insoluble in the deuterated solvents thus preventing determination of ^{1}H NMR spectra. Attempts to obtain FAB mass spectra also failed due to too low solubility and the high molecular weight.

The IR spectra of the bound state of compound **2** are almost identical to thse of its free state. All complexes exhibit a strong CS absorption at 671–672 cm^{-1}.[23] Complex **4** displays characteristic absorptions at 1684 cm^{-1}(νCO_2, asym.), 1454 cm^{-1}(νCO_2, sym.), 1205 cm^{-1}(νCF_3, asym.) and 1130 cm^{-1}(νCF_3, sym.) contributed by the trifluoroacetate ion. The absorption of the carboxylate group appears in the up-bound region (the typical absorption at 1650–1420 cm^{-1}), which suggests that the Ag bind to oxygen of the carboxylate group leading to less ionic character, *i.e.*



Crystal data and details of measurements for the Cu(I) **3** and Ag(I) **4** complexes are summarised in Table 1 and the characteristics of the coordination modes of Cu(I) and Ag(I) are discussed below.

Crystal structure of three-dimensional polymeric complex [Cu_2I_2(tTTDHPCP)]·thf **3**

The red-brown three-dimensional polymeric complex [Cu_2I_2(tTTDHPCP)]·thf was harvested from the interface zone between Cu_2I_2 in CH_3CN solution and compound **2** in THF solution. The selected geometric parameters are shown in Table 2. [Cu_2I_2(tTTDHPCP)$_2$]·thf **3** contains $(CuI)_2$ as a bridgng unit,[10] and each copper(I) ion is bound in a distorted tetrahedral geometry to two iodide ions and one sulfur of two different compounds **2**. The repeating $(CuI)_2$ frameworks makes a three-dimensional coordination polymeric sheet. Similarly, the coppers of a two-dimensional sheet arrangement lying in the same plane have been reported in [Cu_2I_2(DTPCP)$_2$]·thf **5**,[25] and in our previous work on a small cyclophane containing a cis-cyclohexane ring in complex [Cu_2I_2(cDTHHPCP)$_2$]·$2H_2O$ **6**.[12] The symmetry and coplanar rhombic CuICuI ring formed in **3** has the bond angles [66.45(3)°, 66.30(3)°] for Cu–I–Cu' and [113.52(3)°, 113.69(3)°] for I–Cu–I' with the four short Cu–I bond distances (2.6288(10)–2.6366(10) Å). These bond lengths resemble the observed values of 2.6359(9)–2.6648(12) Å for **6**[12] and 2.632(4)~2.785(4) Å for **5**[10] in the iodine-bridged complexes. This type of dinuclear structure has a rhombic CuICuI ring, which leads to a Cu…Cu' separation of 2.8830 Å and I…I' of 4.4072Å as in complex **6** [2.836(2)–2.877(2) Å]. The shorter intermetallic distance in the complex **3** means a greater Cu…Cu interaction. It is about 0.3 Å shorter than the Cu…Cu' separation distance in the iodide-bridged complex **5** (3.18 Å).[25] But it is longer than that in the complexes [$Cu_4I_4(L)_2$] (2.551(1), 2.528(1) Å),[27] [$Cu_2I_2(Py)_4$] (2.699(5) Å),[28] [$Cu_2I_2(Me_4en)_2$] (2.57(4) Å)[29] and [Cu_4(4,6-bis(methylsulfanylmethyl)dibenzofuran)$_2I_4$] (2.464(2) Å)[30] with the four-coordinate copper(I) unit.

The two large compound **2** molecules bound to the same copper atom are well separated to minimise steric interaction. The two moieties of compound **2** connected by the rhomboid frame of Cu_2I_2 in **3** are not coplanar. The bond angles around the two Cu metal cations are within the range from 101.60(6)° to 113.69(3)°, respectively, the two large compound **2** molecules cause a distortion of the metal geometry from idealised tetrahedral. The S–Cu–S' bond angles are 103.20(7)° and 107.93(7)° for Cu(1) and Cu(2). The average Cu–S bond distances of 2.3487 Å is almost the same as the Cu-S (thioether) bond distances reported for [Cu_2I_2(DTHHPCP)$_2$]·$2H_2O$

Table 1 Experimental crystallographic data collected from complexes **3** and **4**

Compound	**3**	**4**
Empirical formula	$C_{32}H_{44}Cu_2I_2S_4 \cdot C_4H_8O$	$C_{36}H_{44}S_4Ag_2F_6O_4S_4$
Formula weight	1009.90	998.69
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
a(Å)	14.1935(19)	9.4736(7)
b(Å)	13.7879(19)	12.0619(8)
c(Å)	22.222(3)	18.0914(13)
α(°)	90	88.4650(10)
β(°)	107.888(3)	80.1260(10)
γ(°)	90	77.1700(10)
V (Å^3)	4138.6(10)	1985.7(2)
D_{cala} (Mg m^{-3})	1.621	1.670
Z	4	2
Crystal size (mm^3)	0.32 x 0.24 x 0.18	0.52 x 0.35 x 0.24
F(000)	2016	1008
Absorption coefficient (mm^{-1})	2.747	1.291
θ Range (°)	1.76 to 26.09	2.09 to 26.02
Reflection collections	23276	11303
Independent reflections	8161 [R(int) = 0.0776]	7701 [R(int) = 0.0242]
Completeness to θ	26.04 °_99.3%	26.02°_98.4%
Absorption correction	SADABS	SADABS
Max/min transmission	1.00, 0.752	1.000, 0.524
Data/restrains/parameters	8161/0/406	7701/0/514
Goodness-of-fit on F^2	0.997	1.074
Final *R* indices [$I\ 2\sigma(I)$]	R_1 = 0.0446, wR_2 = 0.0946	R_1 = 0.0622, wR_2 = 0.2142
R indices (all data)	R_1 = 0.1088, wR_2 = 0.1228	R_1 = 0.0837 wR_2 = 0.2468

Table 2 Selected bond distance (Å) and angles (°) for complexes **3** and **4**

Complex **3**			
Bond lengths			
Cu(1)–I(1)	2.6328(10)	Cu(2)–I(1)	2.6288(10)
Cu(1)–I(2)	2.6366(10)	Cu(2)–I(2)	2.6354(10)
Cu(1)–S(4)#2	2.3459(19)	Cu(1)–S(2)#1	2.3751(19)
Cu(2)–S(1)	2.303(2)	Cu(2)–S(3)#3	2.3482(19)
Cu(1)–Cu(2)	2.8830(12)		
Bond angles			
Cu(1)–I(1)–Cu(2)	66.45(3)	I(1)–Cu(1)–I(2)	113.52(3)
Cu(1)–I(2)–Cu(2)	66.30(3)	I(1)–Cu(2)–I(2)	113.69(3)
S(2)#1–Cu(1)–S(4)#2	103.20(7)	S(2)#1–Cu(1)–I(1)	112.59(6)
S(4)#2–Cu(1)–I(1)	107.10(6)	S(2)#1–Cu(1)–I(2)	111.29(6)
S(4)#2–Cu(1)–I(2)	108.43(5)		
S(1)#1–Cu(2)–S(3)#3	103.20(7)		
	106.67(7)	I(1)#1–Cu(1)–S(1)	106.06(7)
Complex **4**			
Bond lengths			
Ag(1)–O(1)	2.570(6)	Ag(2)–O(3)	2.252(6)
Ag(1)–S(4)#1	2.4787(14)	Ag(1)–S(1)	2.5137(15)
Ag(2)–S(2)	2.4678(16)	Ag–S(3′)#2	2.477(4)
Ag(2)–S(3)#2	2.537(3)	Ag(2)#2–S(3)	2.537(3)
Ag(2)#2–S(3′)	2.477(4)	Ag(1)–S(4)	2.4787(14)
Bond angles			
S(4)#1–Ag(1)–S(1)	142.77(6)	S(4)#1–Ag(1)–O(1)	133.76(15)
S(1)–Ag(1)–O(1)	80.93(15)	S(2)–Ag(2)–S(3′)#2	139.73(9)
O(3)–Ag(2)– S(3′)#2	116.2(2)	O(3)–Ag(2)–S(2)	103.9(2)

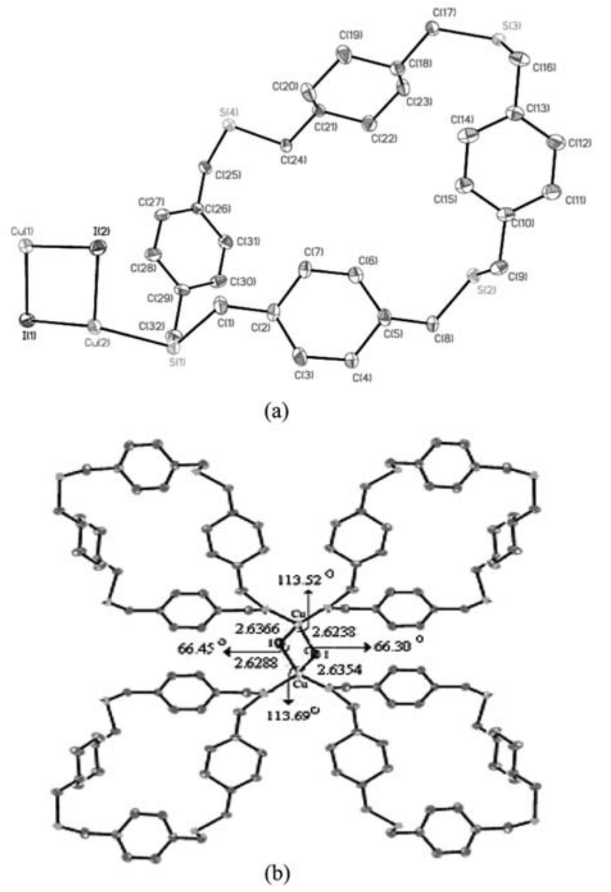


Fig. 1 An ORTEP view of the dinuclear unit [Cu_2I_2(*t*TTDHPCP)]·thf in complex **3** (a) a perspective view of the infinite chains in **3** with an interchain Cu…Cu′ separation of 2.8830 Å (b).

6 (2.322 Å),[26] 3,6,10,13-tetrathiapentadecane (2.31(3) Å average),[31] [14]aneS4 (2.317(4) Å (average)),[31] and longer than the Cu–S bond for [Cu_2Br_2(DTPCP)$(MeCN)_2$] (2.309(1) Å) and [$Cu_2I_2$$(DTPCP)_2$].thf (2.300(4) Å and (2.283(5) Å)),[26] respectively. This is consistent with that the shorter Cu…Cu separation distance increasing the interaction between two copper atoms due to a weaker interaction between Cu…S in comparison with complex **5**. The THF molecule is situated outside the cyclophane cavity. A distance (7.756Å) between Cu and oxygen of THF is far more than of the sum of the van der Waals radii of the two atoms, which indicates the absence of a coordinated bond. By inspection the ORTEP view of structure **3** (Fig. 2), the THF molecules are located on the surface of the cyclohexane rings with the oxygen atom toward to them.

Crystal structure of two-dimensional polymeric [Ag_2(tTTDHPCP)$(CF_3COO)_2$] 4

The pink two-dimensional polymeric complex [Ag_2(tTTDHPCP)$(CF_3COO)_2$] **4** was obtained from the interface zone by diffusion. The crystallographic analysis of **4** reveals that it has a two-dimensional polymeric structure. The ORTEP drawings are shown in Fig. 3(a). Some selected bond lengths and bond angles were listed in Table 2. Each compound **2** molecule in turn coordinates to four separate Ag(I) ions to yield a polymeric network structure. The coordination sites of Ag(I) atom are occupied by two sulfur atoms from different compound **2** fragments and an oxygen donor from the trifluoroacetate counter anion, resulting in a distorted trigonal structure. The chelating S–Ag–S' bond angles are 142.77(6)°, and 139.73(9)°, while the S'–Ag–O and S–Ag–O bond angles are 133.76(15)°, 116.2(2)° and 80.93(15)°, and 103.9(2)°, respectively. Bond angles at silver reflect a distortion from trigonal geometry. The distortion results from the large size of two compound **2** molecules, which cannot simultaneously afford optimal S–Ag–S' trigonal bond angles as in the monomer [Ag(cDTHHPCP)(CF_3COO)] **7** [127.56(16)°, 122.2(4)° and 109.7(4)°]. The average Ag–S bond distances in complex **4** is 2.496 Å, which is similar to the Ag–S bond distances of complex **7** (2.494 Å) and [Ag(12S3)](CF_3SO_3)·MeCN (2.463–2.621 Å)[32-34]. Furthermore, the two Ag–O and Ag'–O' bond distances are 2.570(6) Å and 2.252(6) Å, comparable to those of complex **7** (2.34–2.57 Å) and (2.483 Å).[35] Each compound **2** molecule in complex **4** coordinates to four different Ag(I) ions, yielding a polymeric structure that is similar to the one-dimensional polymer of the three-coordinated silvers in complex **7** (2S-cDTHHPCP)**.** This might be due to the preference of Ag(I) ion to form a three-

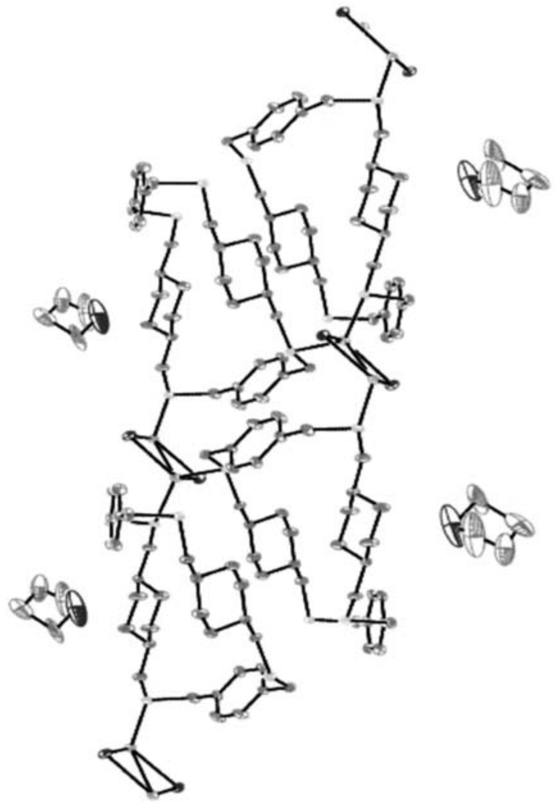


Fig. 2 A perspective view of the infinite chains in [Cu_2I_2(*t*TTDHPCP)]·thf in complex **3**.

coordinated geometry with this class of dithia[3.3]PCPs (monomer or dimer) including the cyclohexane unit, rather than four-coordinate geometry ($AgNO_3$) in the presence of CF_3COO^- as a counter ion. Also, this illustrates the geometrical effect and electronic effect of the counter anion in controlling the formation of these structures. The total crystal structure is built up from these four Ag–S chains to give an infinite two dimensional network structure as shown in Fig. 3(b). The benzene ring shows no tendency to interact with Cu(I) and Ag(I), although both Cu(I) and Ag(I) ions could be classified as soft metals.

Conclusions

The strong affinity of the sulfur atom of thioether or crown thioether towards silver(I)[32-34] and copper(I)[35] are well established. Therefore, the coordination of the dithia-bridge PCP involves the two or four sulfur atoms rather than the delocalised π-electrons of the benzene rings. This work shows that four sulfur atoms of compound **2** connect to different Ag(I) or Cu(I) metal ions to form either two- or three-dimensional polymeric complexes. The dinuclear unit Cu_2I_2 is still maintained in complex **3** in which each I^- ion serves as a bridge between two copper ions. Ag(I) is a fashionable building block for sulfur-containing ligands to form coordination polymers. Complex **4** is an infinite chain interconnected by four Ag(I) cations with the four sulfur atoms of a compound **2** molecule. The resulting Ag coordination is a four-coordination sphere consisting of a trifluoroacetate anion and two thioether groups from two separated cyclophanes. These results highlight the profound influence of steric effects, not only of the compound **2** ligand conformation on the rigid structure of the 1,4-cyclohexane ring, but also the bulk of the CF_3COO^- counter ion to allow it to form four-coordination with the Ag(I) atom.

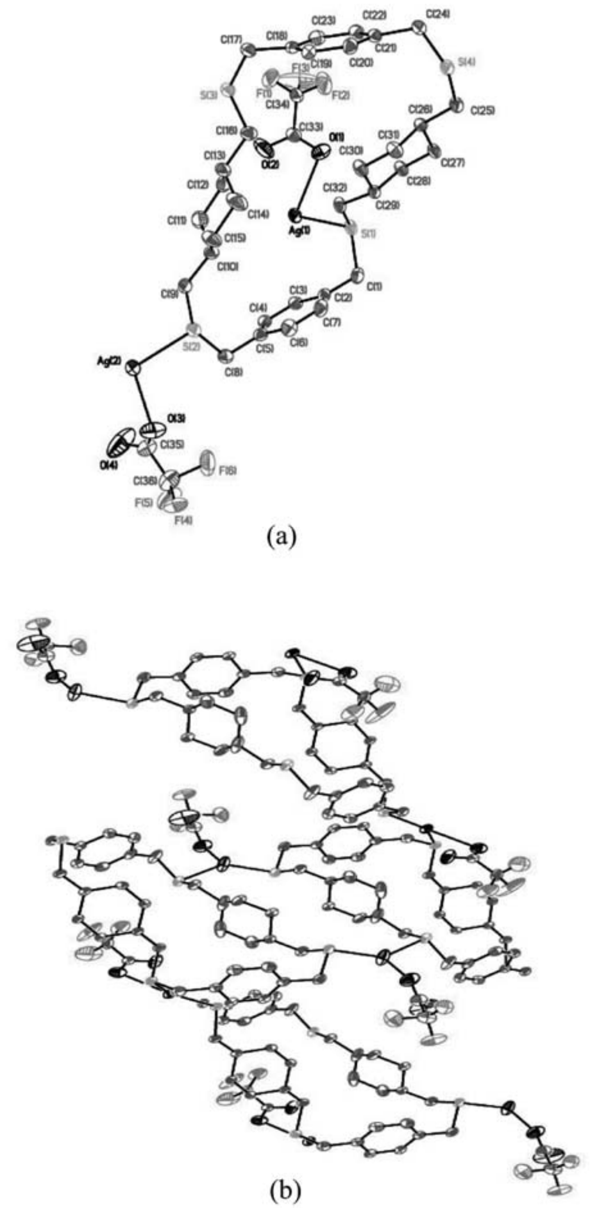


Fig. 3 An ORTEP diagram of the partial molecular structure of complex **4** (a), and a view of the two-dimensional polymeric channel framework in complex **4** (b).

The structural differences for complexes **3** and **4** might be considered as due to the nature of the anions in arranging to form different coordination frameworks. The failure to form a complex containing a metal inside the cyclophane might be rationalised on the basis that the combination of two sulfur atoms and two benzene rings is unable to coordinate a metal ion to form a complex.[22]

Experimental

All operations were carried out under dinitrogen by using the Schlenk technique. All solvents were dried and distilled under a nitrogen stream. IR spectra were measured as KBr discs on a JASCO-320 spectrometer. Microanalyses were carried out on a Heraceus CHN–O analyser at National Chung-Hsin University, Taichung, Taiwan.

Procedure for the coupling reaction: A solution of 1,4-bis(bromomethyl)benzene (1.80 g, 6.8 mmol) and *trans*-1,4-bis (mercaptomethyl)cyclohexane[35] (1.21 g, 6.8 mmol) was added over a period of 70 h to a solution of NaOH (0.6 g, 1.5 mmol) in 95%

ethanol (200 ml), using a high dilution technique. The solution was refluxed for an additional 2 h and then concentrated *in vacuo* to give a viscous residue. The residue was extracted with CH_2Cl_2 (3×20 ml), dried over $MgSO_4$, filtered, and evaporated to give a waxy residue. The residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexane (2/3: v/v) as an eluent to afford 2,11-dithia-4e,5,6,7e,8,9- hexahydro[3.3]paracyclophane **1** and 2,11,20,29-tetrathia-4e,5,6,7e,8,9,22e, 23,24,25e,26,27-dodecahydro[3.3.3.3] cyclophane **2** (*t*TTDHPCP). Compound **1**: yield 0.27 g (14%), colourless crystals, m.p. 114–115°C (lit.[36] 141.5°C); Compound **2**: yield 1.10 g (58%), colourless crystals, m.p. 185–186°C; ^1H NMR ($CDCl_3$) δ0.53–0.61 (m, 8H), 0.96 (m, 7H), 1.57–1.60 (m, 5H, $J = 7.5$ Hz), 2.17 (d, 8H, $J = 8.8$ Hz), 3.60 (s, 8H), 7.19 (s, 8H); ^{13}C NMRδ32.2, 36.7, 37.8, 38.5, 128.8, 137.9; EIMS *m/z* (rel. int) 556 (M^+, 45), 414 (49), 278 (12), 141 (60), 104 (100); Anal. Calcd. for $C_{32}H_{44}S_4$: C, 69.0; H, 8.0. Found: C, 70.0; H, 8.0%.

Preparation of [Cu_2I_2(tTTDHPCP)] • thf **3**

Under a dinitrogen atmosphere, an acetonitrile solution (2.0 ml) of copper(I) iodide (4.0 mg, 0.02 mmol) was introduced slowly *via* a syringe through a septa to a 6 mm diameter glass tube contained compound **2** (10.8 mg, 0.02 mmol) in THF (2 ml) solution. After standing at room temperature for 1 week, red-brown crystals were produced at the interface zone and were harvested by removal of the solution to yield complex **3** (3.6 mg, 10% yield), m.p. 254–255°C (decomp); IR(KBr): 2852-2914($\nu_{C\text{-}H}$), 1413 (ν_{CH2}), 672 cm^{-1}($\nu_{C\text{-}S}$); Anal. Calcd. for $C_{36}H_{52}OCu_2I_2S_4$: C, 42.8; H, 5.2.. Found: C, 42.6; H, 5.2%.

Preparation [Ag_2(tTTDHPCP)($CF_3COO)_2$] **4**

Complex **4** was obtained in the same procedure for preparation of **3** by using silver trifluoroacetate instead of copper(I) iodide. Light pink prismatic crystals of **4** (16.1 mg, 33% yield) were obtained, m.p. 269–270°C (decomp.); IR(KBr) 2873–2906($\nu_{C\text{-}H}$), 1684($\nu_{C=O}$, asym.), 1454(νCO_2, sym.), 1413 (ν_{CH2}), 1205 (νCF_3, asym.), 1130 (νCF_3, sym.), 671 cm^{-1}($\nu_{C\text{-}S}$); Anal. Calcd. For $C_{36}H_{44}Ag_2F_6O_4S_4$: C, 43.3; H, 4.4. Found: C, 43.2; H, 4.3%.

X-ray data collections, structure solution, and refinement

Crystals were mounted on a glass fiber for X-ray structural analysis. Cell constants were derived from least-squares refinement of 25 high-angle reflections. Intensity data were collected using a μ scan mode on an graphite monochromated Mo K radiation ($\mu = 0.7107$Å). An empirical absorption correction based on a series of ψ scans was applied to the data. The standard reflections were measured at every 100 reflections and only small (<0.4%) random variation were obtained. Lp corrections were applied. The ellipsoids on the ORTEP figures are drawn with 30% probabilities.

The positions of the metal atom were determined from analysis of the Patterson map. All other atoms were located from subsequent Fourier differential syntheses. The structures were refined by the full-matrix least-squares method using the NRCVAX software package.

Supplementary material

Full crystallographic data for the X-ray crystal structural analysis have been deposited with the Cambridge crystallographic Centre, CCDC No. 635118 for Complex **3**, No. 635119 for complex **4**. Copies of this information may be obtained free of charge the Director, CCDC, 12 Union Road, e-mail:deposit@ccdc.cam.ac.uk. or http://www.ccdc.cam.ac.uk.

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