

Synthesis and Structural Study of Copper(I) or Silver(I) Complexes of 2,11-Dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophanes

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The complexes of 2,11-dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane (dthhpcp) with Cu(I), i.e. $[\text{Cu}_2\text{I}_2(\text{dthhpcp})_2] \cdot 2\text{H}_2\text{O}$ **1**, or with Ag(I), i.e. $[\text{Ag}(\text{dthhpcp})(\text{NO}_3)] \cdot \text{thf}$ **2** and $[\text{Ag}(\text{dthhpcp})(\text{CF}_3\text{COO})]$ **3**, were prepared for structural study by single-crystal X-ray diffraction analysis. For these three complexes, dthhpcp serves as a bridging group in the polymeric structure through bridging sulfur atoms *via* metal, while the bonding of anion with the second metal atom forms the multi-diminished structures. Complex **1** is a novel two-dimensional coordination polymer composed of Cu_6 motifs, in which Cu_2I_2 formed a square planar unit to link the dthhpcp molecule. The two oxygen atoms of the nitrate anion as a bridge for two Ag atoms in complex **2** provides a three-dimensional channel framework of silver(I) with a tetrahydrofuran molecule as a guest inside the open cavities. In contrast, the analogous reaction with silver trifluoroacetate gave a complex **3**, which is composed of infinite linear chains of $-\text{Ag}-\text{dthhpcp}-\text{Ag}-\text{dthhpcp}-$ along the *a* axis. Unit cell data: complex **1**, orthorhombic system, space group $P2(1)2(1)2(1)$, $a = 19.2982(11)$ Å $b = 16.5661(10)$ Å, $c = 25.3006(15)$ Å, $\beta = 90^\circ$, $Z = 8$; complex **2**, orthorhombic system, space group $Pna2(1)$, $a = 8.8595(6)$ Å, $b = 12.6901(9)$ Å, $c = 19.8449(14)$ Å, $\beta = 90^\circ$, $Z = 4$; complex **3**, monoclinic system, space group $P2(1)/n$, $a = 8.845(3)$ Å, $b = 20.841(6)$ Å, $c = 11.061(3)$ Å, $\beta = 107.832(6)^\circ$, $Z = 4$.

Keywords: Hexahydrocyclophane; Multi-diminished structures; Polymeric complexes; X-ray analysis; Diffusion technique.

INTRODUCTION

Transition metal complexes of cyclophane have been studied because of much interest in their properties such as structure, in spectroscopic analysis, catalytic function, conductivity, electrochemical and in supramolecular chemistry as functional materials.¹ The majority of pure hydrocarbon cyclophanes contain two face to face arene rings bridged by a methylene bridge.² In the past few years, we have prepared a series of strain dithia[3.3]- and [2.2]-hexahydroparacyclophanes bearing a benzene ring and a *cis*- or *trans*-cyclohexane ring bridged with two carbons, i.e. 3*e*,4,5,6*e*,7,8-hexahydro[2.2]paracyclophane,³ and 3*a*,4,5,6*e*,7,8-hexahydro[2.2]paracyclophane.⁴ In our previous studies, we have also prepared the [2.2]*meta*-, *ortho*- and *para*-cyclophanes containing either 1,4-cyclohexane or 1,3-cyclohexanes.⁵ On the other hand, [2.2]- and [3.3]-paracyclophanes have attracted attention in organometallic chemistry as the interaction of the two aromatic decks.⁶

Very recently, several copper(I) and silver(I) coordinated with the sulfur atoms of dithiaparacyclophane (dthhpcp) to form the polymeric style crystals for X-ray crystallographic analysis.^{7,8} However, little information is available concerning the coordination chemistry of the structurally related thia-bridged paracyclophanes containing a cyclohexane ring.⁹ Previously the crystal structure of dthhpcp, a dithia-bridged cyclophane containing both a benzene ring and a cyclohexane ring, has been analyzed.¹⁰ It is a potential candidate for formation of multi-dimensional networks *via* linking the transition metal cation through two sulfur atoms. Herein we report the study on the structural characterization of three new complexes of polymeric species obtained from the reaction of the soft metal ions, either copper(I) or silver(I) ion, with dthhpcp. The spherical d^{10} electronic configuration of Cu(I) and Ag(I) does not impose a preferred coordination geometry or number in its interaction with anionic ligands.¹¹ The complexes with different bonding fashions upon the counter anion were obtained in

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Table 1. Experimental crystallographic data collection for complexes **1-3**

Compound	1	2	3
Empirical formula	C ₃₂ H ₄₄ Cu ₂ I ₂ S ₄ ·2H ₂ O	C ₁₆ H ₂₂ AgNO ₃ S ₂ ·C ₄ H ₈ O	C ₁₈ H ₂₂ AgF ₃ O ₂ S ₂
Formula weight	973.79	520.44	499.35
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	P2(1)2(1)2(1)	Pna2(1)	P2(1)/n
<i>a</i> (Å)	19.2982(11)	8.8595(6)	8.845(3)
<i>b</i> (Å)	16.5661(10)	12.6901(9)	20.841(6)
<i>c</i> (Å)	25.3006(15)	19.8449(14)	11.061(3)
α (°)	90	90	90
β (°)	90	90	107.832(6)
γ (°)	90	90	90
<i>V</i> (Å ³)	8088.5(8)	2231.1(3)	1941.0(9)
<i>D</i> _{calc} (Mg m ⁻³)	1.593	1.549	1.709
<i>Z</i>	8	4	4
Crystal size (mm ³)	0.36 × 0.22 × 0.11	0.25 × 0.21 × 0.18	0.49 × 0.31 × 0.24
<i>F</i> (000)	3840	1072	1008
Absorption coefficient (mm ⁻¹)	1.593	1.116	1.291
θ Range (°)	1.61-26.04	1.90-26.00	1.95-26.22
Reflection collections	44375	11837	10980
Independent reflections	7991 [<i>R</i> _{int} = 0.0850]	3345 [<i>R</i> _{int} = 0.0293]	3840 [<i>R</i> _{int} = .0650]
Completeness to θ %	26.04° 99.9%	26.00° 100%	26.22° 98.6%
Absorption correction	SADABS	SADABS	SADABS
Max/min transmission	1.00, 0.509	1.00, 0.506	1.00, 0.185
Data/restraints/parameters	7991/0/370	3345/1/253	3840/0/289
Goodness-of-fit on <i>F</i> ²	0.917	1.028	1.155
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.443, <i>wR</i> ₂ = 0.1152	<i>R</i> ₁ = 0.0272, <i>wR</i> ₂ = 0.0709	<i>R</i> ₁ = 0.0399, <i>wR</i> ₂ = 0.0743
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1149, <i>wR</i> ₂ = 0.1687	<i>R</i> ₁ = 0.314, <i>wR</i> ₂ = 0.743	<i>R</i> ₁ = 0.0617, <i>wR</i> ₂ = 0.0798

this study.

RESULTS AND DISCUSSION

Synthesis and properties of the complexes

The compound dthhpcp was obtained *via* the coupling reaction of the corresponding 1,4-bis(halomethyl)benzenes with *cis*-1,4-bis(mercaptomethyl)cyclohexane under a high dilution condition in 10% ethanolic NaOH solution in good yields.^{12,13} The compound dthhpcp formed the air-stable complexes with each of the metal ions Cu(I) and Ag(I). Since direct reaction of a dilute solution of dthhpcp and a coinage metal salt at room temperature leads to either a microcrystalline or powder precipitates, which are insoluble in most of the solvents for crystallization. Therefore, single crystals of all three complexes **1**, **2**, and **3** must be prepared by the slow diffusion technique in a sealed-tube. Due to the substantial difference in polarity

between the metal salts and dthhpcp, the solvents for the two reactants were carefully chosen. We found that the adducts contained the molar ratios between dthhpcp to metal ion are 1:1 regardless of the molar ratio of the two reactants being used. Therefore, equivalent molarities of metal salt in acetonitrile and dthhpcp in THF were used for the preparation of the complexes.

All of the complexes **1-3** are insoluble in common organic solvents for determining ¹H NMR spectra. Attempts to determine the FAB mass spectra also failed due to the solubility and the high molecular weight. The IR spectra of the bound state of dthhpcp are almost identical to its free state. All complexes exhibit strong CS absorption at 671-674 cm⁻¹.¹⁴ However, the asymmetric stretching and symmetric stretching of N-O bonds appear at 1378, 830 cm⁻¹, respectively, as inorganic salts in complex **2**. Complex **3** displays the characteristic absorption at 1684 cm⁻¹ ($\nu_{\text{CO}_2, \text{asym.}}$), 1426 cm⁻¹ ($\nu_{\text{CO}_2, \text{sym.}}$), 1205 cm⁻¹ ($\nu_{\text{CF}_3, \text{asym.}}$) and 1130 cm⁻¹ ($\nu_{\text{CF}_3, \text{sym.}}$) for trifluoroacetate. The absorption of

the carboxylate group appears at the up-bound region (the typical absorption at 1650-1420 cm^{-1}), which suggests that the Ag tie bound with oxygen of carboxylate group leading to less ionic character, i.e. $\text{—}\overset{\ominus}{\text{O}}\text{—}$. Crystal data and details of measurements for the Cu(I) **1** and Ag(I) **2**, **3** complexes are summarized in Table 1.

Crystal structure of two-dimensional polymeric $[\text{Cu}_2\text{I}_2(\text{dthhpcp})_2] \cdot 2\text{H}_2\text{O}$ **1**

The yellow-green color complex **1** was prepared from the reaction of a THF solution of dthhpcp with one molar equivalent of Cu_2I_2 in acetonitrile solution *via* a diffusion

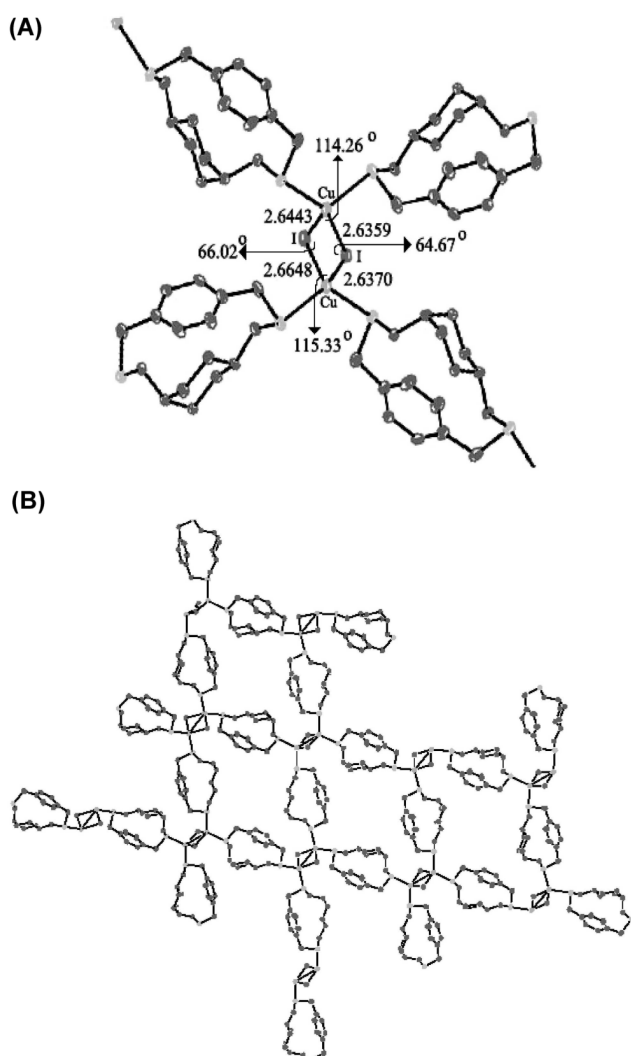


Fig. 1. An ORTEP view of the dinuclear unit $[\text{Cu}_2\text{I}_2(\text{dthhpcp})]$ in complex **1** (a) and a perspective view of the infinite chains in complex **1** (b).

Table 2. Selected bond distances (\AA) and angles ($^\circ$) for complexes **1-3**

Complex 1			
Bond lengths			
Cu(1)-I(1)	2.6370(11)	Cu(1)-I(2)	2.6648(12)
Cu(2)-I(1)	2.6359(9)	Cu(2)-I(2)	2.6443(9)
Cu(1)-S(1)	2.376(2)	Cu(1)-S(2)	2.315(2)
Cu(2)-S(4)	2.320(2)	Cu(3)-S(3)	2.303(2)
Bond angles			
Cu(1)-I(1)-Cu(2)	64.67(4)	I(1)-Cu(1)-I(2)	115.33(4)
Cu(2)-I(2)-Cu(1)	66.02(4)	I(1)-Cu(2)-I(2)	114.26(5)
S(2)-Cu(1)-S(1)	115.47(8)	S(2)-Cu(1)-I(1)	105.71(6)
S(1)-Cu(1)-I(1)	107.67(7)	S(2)-Cu(1)-I(2)	106.93(7)
S(1)-Cu(1)-I(2)	106.06(7)		
Complex 2			
Bond lengths			
Ag-S(1)	2.5256(11)	Ag-S(2)	2.4981(11)
Ag-O(1)	2.421(3)	Ag-O(2)	2.585(3)
Bond angles			
S(1)-Ag-S(2)	125.36(4)	S(1)-Ag-O(1)	97.84(8)
S(2)-Ag-O(1)	127.73(8)	O(1)-Ag-O(2)	81.96(10)
Complex 3			
Bond lengths			
Ag-O(1)	2.475(13)	Ag-S(1)	2.529(4)
Ag-S(2)	2.459(3)		
Bond angles			
S(1)-Ag-S(2)	127.56(16)	S(1)-Ag-O(1)	122.2(4)
S(2)-Ag-O(1)	109.7(4)		

technique. The crystal structure of **1** determined from X-ray analysis is depicted in Fig. 1A. The selected geometric parameters are shown in Table 2. Complex of $[\text{Cu}_2\text{I}_2(\text{dthhpcp})_2]$ consists of Cu_2I_2 as a bridged unit, which is quite common in copper(I) halide complexes.¹⁵ The repeating Cu_2I_2 frameworks make a two-dimensional coordination polymeric sheet, which are built by the alternating arrangement of the two different Cu atoms of a Cu_6 unit, as shown in Fig. 1B. The coppers of the two-dimensional sheet arrangement laying in the same plan have been also reported in $[\text{Cu}_2\text{I}_2(\text{dtpcp})_2] \cdot \text{thf}$ **4**.⁷ The $\text{Cu} \cdots \text{Cu}'$ distances for complex **1**, between 2.836(2) and 2.877(2) \AA , are 0.3 \AA shorter than a $\text{Cu} \cdots \text{Cu}'$ separation distance in the iodide-bridged complex **4**.⁷ The shorter intermetallic distance in the dthhpcp complex means more $\text{Cu} \cdots \text{Cu}$ interactions. But it is longer than the complexes of $[\text{Cu}_4(\text{L})_2\text{I}_4]$ (2.551(1), 2.528(1) \AA)¹⁶, $[\text{Cu}_2\text{I}_2(\text{Py})_4]$ (2.699(5) \AA)¹⁷, $[\text{Cu}_2\text{I}_2(\text{Me}_4\text{en})_2]$ (2.57(4) \AA)¹⁸ and $[\text{Cu}_4(4,6\text{-bis}(\text{methylsulfanylmethyl})\text{dibenzofuran})_2\text{I}_4]$ (2.464(2) \AA)¹⁹ with four-coordinate copper(I) atoms. The central $\text{Cu}_2\text{I}_2\text{Cu}$ molecu-

lar core, the bond angles of [64.67(4)°, 66.02(4)°] for Cu-I-Cu' and [114.26(2)°, 113.70(5)°] for I-Cu-I' with the four relatively short Cu-I bond distances (2.6359(9) ~ 2.6648(12) Å) form as a symmetrical and coplanar rhombic CuICuI ring. However, the bond lengths fall within the range of 2.632(4) ~ 2.785(4) Å in the iodine-bridge complex **4**.⁷ The moiety dthhpcp connected by rhomboid frame of Cu₂I₂ in **1** is not coplanar.

The structure of **1** consists of two water molecules; the bond angles around Cu(1) are within the range of 105.71(6)° to 115.46(8)°. Each copper(I) is coordinated in distorted tetrahedral geometry to two iodide ions and one sulfur atom from two distinct dthhpcp molecules. The average Cu-S bond distances of 2.322 Å are almost the same as the Cu-S (thioether) bond distances reported for 3,6,10,13-tetrathiapentadecane (2.31(3) Å average),²⁰ [14]janeS4 (2.317(4) Å average),²⁰ and longer than the Cu-S bond for [Cu₂Br₂(dtpcp)(MeCN)₂] (2.309(1) Å) and [Cu₂I₂(dtpcp)₂].thf (2.300(4) Å and (2.283(5) Å),⁷ respectively. This is consistent with the shorter Cu-Cu separation distance found to increase the interaction between two copper atoms due to a weaker interaction between Cu-S compared with complex **4**.

Crystal structure of three-dimensional polymeric [Ag(dthhpcp)(NO₃)]·thf **2**

The colorless Ag(I) complex **2** was obtained by the reaction of dthhpcp and AgNO₃ with an equal molar ratio in THF solution. The crystallographic analysis of [Ag(dthhpcp)(NO₃)]·thf is shown in Fig. 2. The local coordination environment about each silver(I) is coordinated to a sulfur atom of two different dthhpcp molecules and two oxygen atoms of different nitrate groups. This bonding fashion is different from that in Ag(dthhpcp)(NO₃) (**5**), in which two silver atoms bound with two oxygen atoms of the same nitrate group.⁷ In the complex **2**, the bond distances of Ag-S being [2.4981(11) Å] and Ag(1)-S(2) [2.5256(11) Å] are shorter than the mean Ag-S bond length from fifty-one complexes (i.e., 2.675 Å, with a standard deviation of 0.015 Å).²¹ The coordination geometry of Ag(I) in complex **2** can be considered as a highly distorted tetrahedral geometry as shown in Table 1, the bond angles S(1)-Ag-S(2), O(1)-Ag-S(2), O(1)-Ag-S(1) and O(1)-Ag-O(2), being 125.36(4)°, 127.73(8)°, 97.84(8)° and 81.96(10)°, respectively. Among the oxygen atoms of a nitrate group, two oxygen atoms are bound with two silver atoms, i.e., adjacent chains are bridged

by the NO₃⁻ with an Ag-ON(O)O-Ag made through two oxygen atoms.^{22,23,24} The bond distances of Ag-O being 2.421(3) and 2.585(3) Å, fall in the range of 2.367-2.689 Å for silver(I) complexes with nitrate.^{22,25} The difference between the bond distance of Ag(1)-O(1) [2.421(3) Å] and Ag(2)-O(2) [2.585(4) Å] suggests that a different bonding fashion between the two N-O bonds.²⁴ This is due to the oxygen atoms of unhybrid N-O bonds (i.e., N-O and N=O) bound with silver atoms.

The packing arrangement of [Ag(dthhpcp)(NO₃)]·thf in Fig. 2B shows a polynuclear complex as a sheet with a zigzag three-dimensional framework of silvers interconnected by dthhpcp molecules.²⁶ The two oxygens bridging two metals give an infinite network, which lead to an interchain Ag...Ag separation of 5.037 Å. The Ag-O-N-O-Ag bonding fashion will result in a much longer distance between Ag-Ag, as well as cyclophane units, than that in Ag(dtpcp)NO₃. **5**,⁷ and results in a large ring containing six silver atoms and one THF solvent molecule in the open cavity. In contrast, the solvent molecule is absent

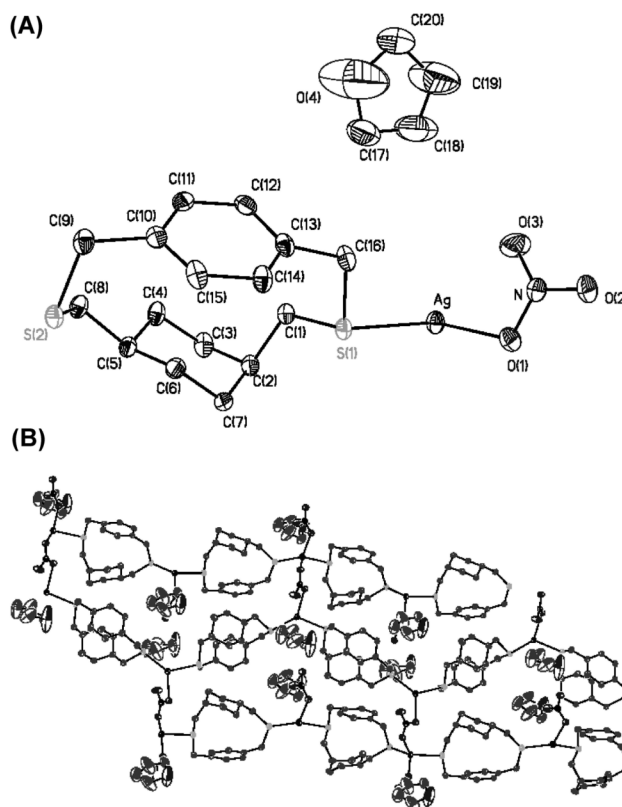


Fig. 2. An ORTEP view of the [Ag(dthhpcp)].thf complex **2** (a) and a perspective view of the infinite chains in complex **2** (b).

in its analogue **5**. All dthhpcp molecules are at some intermediate angle between parallel and perpendicular angles to the sheet plan.

Crystal structure of one-dimensional polymeric [Ag(dthhpcp)(CF₃COO)] **3**

Reaction of silver(I) trifluoroacetate in MeCN with one molar equivalent of dthhpcp in THF yielded the pink colored complex **3**. The crystallographic analysis of **3** reveals that its structure is also a polymeric structure consisting of a [Ag(dthhpcp)(CF₃COO)] unit. The ORTEP drawings are shown in Fig. 3A. Some of selected bond lengths and bond angles are listed in Table 2. The coordination sites of the Ag(I) atom are occupied by two sulfur atoms from different dthhpcp ligands, and an oxygen donor from the trifluoroacetate counter anion results in a distorted trigonal structure. The bond angles of S(1)-Ag-S(2), S(1)-Ag-O(1) and S(2)-Ag-O(1) are 127.56(16)°, 122.2(4)° and 109.7(4)°, respectively. The silver-sulfur bond distances are 2.495(3) Å and 2.529(4) Å, which are similar to the Ag-S bond distances of complex **2**, and a Ag-O bond distance of 2.475(13) Å is close to complex **2** (2.421(3) Å and 2.585(4) Å). The dthhpcp of **3** does not form a six-silver

atom ring unit 3D network structure but interconnects a one-dimensional polymer of silvers as in Fig. 3B. This might be due to the preference of the Ag(I) ion to form a two-coordinated linear geometry rather than three and four-coordinate geometries in the presence of CF₃COO⁻ as a counter ion. Also, this indicates that geometrical effect and electronic effect influence the counter anion in controlling the formation of these structures.

CONCLUSIONS

Despite the strong affinity of sulfur of thioether or crown thioether for silver(I)²⁷ and copper(I),²⁸ little information is available concerning the metal complexes or coordination chemistry of the polymeric structure of the thia-bridged paracyclophane. This work shows that two sulfur atoms of dthhpcp functioning as a bidentate linkage can form coordination one-, two-, or three-dimensional polymeric complexes with the soft metals, i.e. copper(I) and silver(I) metal ions, depending on the nature of anion. The dthhpcp is known to possess a high strain character resulting in a bent benzene ring,¹¹ which incorporates a rigid cyclohexane unit introduced conformational strain into the macrocycle backbone that limits the conformation flexibility of the macrocycle ring. This rigid nature of dthhpcp creates a cavity to adapted two molecules in complex **1** and a THF molecule in complex **2**. However, our attempts to prepare the corresponding polymeric copper(II) complexes by using a borderline hard acid of CuCl₂·2H₂O in place of CuI failed.²⁹ Ag(I) is a fashionable building block for sulfur-containing ligands to form the coordination polymers. In the Ag(I) of complex **2**, the adjacent chains are bridged by nitrate ions through two oxygen atoms, which lead to a long distance of Ag–Ag and a long distance of dthhpcp allowing the formation of the cavity which adopts a THF molecule as a guest. Complex **3** is formed as a complex with an infinite chain interconnected by Ag(I) and the sulfur of dthhpcp. This might be rationalized that the CF₃COO⁻ counter ion is bulkier than the halide and nitrate anions and this allows it to form the second coordination with Ag(I) atom. The structural differences for complexes **1-3** might be considered as the bonding nature of anions in arranging to form different coordination frameworks. The benzene ring doesn't display the tendency to interact with Cu(I) and

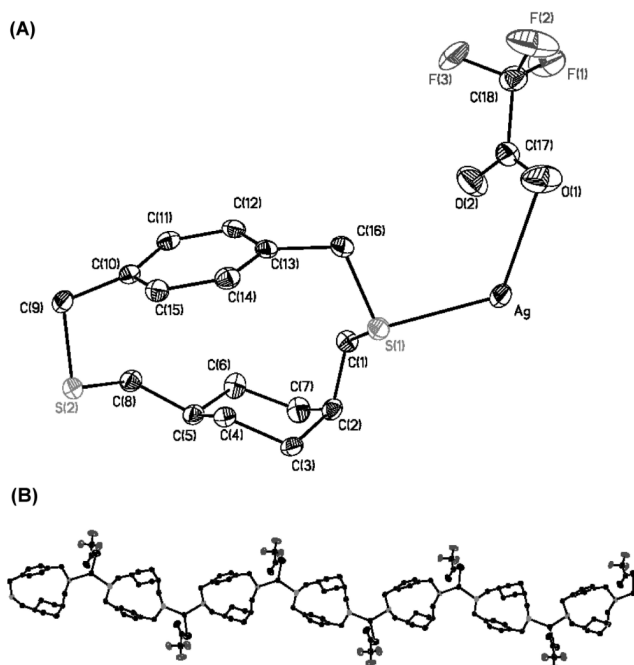


Fig. 3. An ORTEP view of the [Ag(dthhpcp)(CF₃CO₂)] complex **3** (a) and a perspective view of the infinite chains in complex **3** (b).

Ag(I), although both ions could be classified as soft metals.

EXPERIMENTAL

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

Preparation of 2,11-dithia-4,5,6,7,8,9-hexahydro[3.3]-paracyclophane (dthhpcp)

A solution of α,α' -dichloroxylylene (1.23 g, 6.8 mmol) and *cis*-1,4-bis(mercaptomethyl)cyclohexane (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 \times 20 mL), dried over MgSO_4 , filtered, and evaporated to give a waxy residue. The residue was separated chromatographically on silica gel with $\text{CH}_2\text{Cl}_2/n$ -hexane (2/3: v/v) as an eluent to afford the product 2,11-dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane, (3.72 g, 68% yield), colorless crystals, mp 142 °C (from hexane- CH_2Cl_2 , lit.¹⁰ 140~141.5 °C); ¹H NMR (CDCl_3) δ 0.45 (br., 2H, s), 0.95~1.65 (br., 8H, s), 2.33 (d, 4H, *J* = 20 Hz), 3.58 (s, 4H), 6.96 (s, 4H).

Preparation of $[\text{Cu}_2\text{I}_2(\text{dthhpcp})]\cdot 2\text{H}_2\text{O}$ 1

An acetonitrile solution (2.0 mL) of copper(I) iodide (4 mg, 0.02 mmol) was introduced slowly *via* a syringe through a septa to a 6 mm diameter glass tube containing a THF solution (2 mL) of dthhpcp (5.4 mg, 0.02 mmol). After standing at room temperature for 1 week, the green-yellow brick crystals were produced in the buffer zone and were harvested by removal of the solution to yield complex **1** (8 mg, 40% yield), mp 194-197 °C (decomp); IR (KBr): 3441 ($\nu_{\text{O-H}}$), 2852-2914 ($\nu_{\text{C-H}}$), 1451 (ν_{CH_2}), 672 cm^{-1} ($\nu_{\text{C-S}}$); Anal. Calcd. for $\text{C}_{32}\text{H}_{44}\text{Cu}_2\text{I}_2\text{S}_4\cdot 2\text{H}_2\text{O}$: C, 39.43; H, 4.52. Found: C, 40.06; H, 4.76.

Preparation $[\text{Ag}(\text{dthhpcp})(\text{NO}_3)]\cdot \text{THF}$ 2

An acetonitrile solution (2.0 mL) of silver nitrate (17

mg, 0.1 mmol) was introduced slowly *via* a syringe through a septa into a 6 mm diameter glass tube containing a THF solution (2.0 mL) of dthhpcp (27 mg, 0.1 mmol) in THF (2.0 mL). The glass tube was wrapped with tin foil to avoid the decomposition of silver salt by light. After standing at room temperature for 1 week, the colorless brick crystals of complex **2** were produced in the buffer zone and were harvested by removal of the solution to yield complex **2** (29.3 mg, yield 56%), mp 183-185 °C (decomp); IR (KBr): 2869-2917 ($\nu_{\text{C-H}}$), 1459 (ν_{CH_2}), 1384 ($\nu_{\text{N-O}}$), 674 cm^{-1} ($\nu_{\text{C-S}}$); Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{AgNO}_3\text{S}_2\cdot \text{THF}$: C, 46.11; H, 5.76; N, 2.69. Found: C, 45.82; H, 5.96; N, 2.50.

Preparation $[\text{Ag}(\text{dthhpcp})(\text{CF}_3\text{COO})]$ 3

Complex **3** was obtained in the same procedure for preparation of **2** by using silver nitrate instead of silver trifluoroacetate (22 mg, 0.1 mmol). The light pink prismatic crystals of **3** (33.2 mg, 66% yield) were obtained, mp 214-216 °C (decomp.). IR (KBr): 2873-2906 ($\nu_{\text{C-H}}$), 1684 ($\nu_{\text{C=O}}$), 1454 (ν_{CH_2}), 1426 (ν_{CH_2}), 1130-1205 (ν_{CF_3}), 671 cm^{-1} ($\nu_{\text{C-S}}$); Anal. Calcd. For $\text{C}_{18}\text{H}_{22}\text{AgF}_3\text{O}_2\text{S}_2$: C, 43.29; H, 4.44. Found: C, 42.98; H, 4.29.

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 graphite monochromated Mo K radiation ($\mu = 0.7107 \text{ \AA}$). 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 variations 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. 273267 for Complex

1, No. 273268 for complex **2**, No. 273269 for complex **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, e-mail: deposit@ccdc.cam.ac.uk. or http://www.ccdc.cam.ac.uk.

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