

One-, two- and three-dimensional copper(I) and silver(I) complexes of 2,11-dithia[3.3]paracyclophane

Megumu Munakata,^{*a,b} Liang Ping Wu,^a Takayoshi Kuroda-Sowa,^a Masahiko Maekawa,^a Yusaku Suenaga^a and Sohei Nakagawa^a

^a Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan

^b Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Two copper(I) and one silver(I) complex of 2,11-dithia[3.3]paracyclophane (dtpcp), $[\text{Cu}_2\text{Br}_2(\text{dtpcp})(\text{MeCN})_2]$ **1**, $[\text{Cu}_2\text{I}_2(\text{dtpcp})_2]\cdot\text{thf}$ **2** and $[\text{Ag}(\text{dtpcp})(\text{NO}_3)]$ **3**, have been synthesized and their molecular structures determined by X-ray crystallography. All three structures contain an infinite network comprising metal cations linked *via* dithia-bridged paracyclophane and the counter anions. Complexes **1** and **2** are not isostructural. The repeating dinuclear units $[\text{Cu}_2\text{Br}_2(\text{dtpcp})(\text{MeCN})_2]$ joined by dtpcp in **1** generate a one-dimensional polymeric chain running parallel to a diagonal axis of the triclinic cell. Complex **2** is a two-dimensional sheet structure in which a large ring containing six copper atoms includes a tetrahydrofuran molecule as guest inside the open cavity. The one-nitrate oxygen bridging two metal centres in complex **3** yields a unique three-dimensional channel framework of silver(I) ions. The iodine-doped black products of compounds **1–3** at room temperature exhibited conductivities of $10^{-5.9}$, $10^{-5.1}$ and $10^{-4.7}$ S cm^{-1} , respectively.

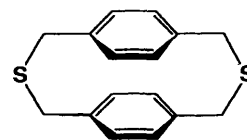
The chemistry of cyclophane has been the subject of detailed experimental and theoretical studies for half a century.^{1,2} Initial studies were concerned primarily with the presence of transannular electronic effects and high molecular strain,³ but particular attention has been devoted recently to the rational synthesis of polymeric transition-metal cyclophane complexes with potentially interesting electrical properties and possible conductivity.^{4,5} Among them [2.2]- and [3.3]-paracyclophanes have attracted much attention in organometallic chemistry as the interaction of the two aromatic decks can give one overall π -electron system and co-ordination of these molecules is almost exclusively through delocalized π electrons.^{4–7} Conversely, relatively little is known about the co-ordination chemistry of the structurally related thia-bridged paracyclophanes,^{8,9} and in particular polymeric metal complexes of this type of compound remain unknown. Previously the crystal structure of 2,11-dithia[3.3]paracyclophane has been documented.¹⁰ Although this compound is commercially available, its potential for bridging metal atoms through two sulfur groups and the formation of an infinite network has not so far been reported.

With the principal aim of isolating and structurally characterizing co-ordination polymers exhibiting novel frameworks, we have recently undertaken a systematic investigation on one-, two- and three-dimensional polymeric copper(I) and silver(I) complexes of sulfur- or nitrogen-containing aromatic compounds.^{11–14} Here we report the synthesis and structural characterization of a new type of polymeric species obtained from the reaction of a copper(I) or silver(I) salt with 2,11-dithia[3.3]paracyclophane.

Results and Discussion

Synthesis of the complexes and properties

The compound dtpcp forms air-stable complexes with each of the metal ions Cu^{I} and Ag^{I} . Since direct reaction of a dilute solution of dtpcp and a coinage metal salt at room temperature often leads to a microcrystalline precipitate, single crystals of all three complexes $[\text{Cu}_2\text{Br}_2(\text{dtpcp})(\text{MeCN})_2]$ **1**, $[\text{Cu}_2\text{I}_2(\text{dtpcp})_2]\cdot\text{thf}$ and $[\text{Ag}(\text{dtpcp})(\text{NO}_3)]$ **3** were grown by slow diffusion of dtpcp in tetrahydrofuran (thf) (or toluene) and a MeCN solution of metal salt using a 1:1 molar ratio in a sealed glass



2,11-dithia[3.3]paracyclophane (dtpcp)

tube. A number of experiments have also been conducted at metal:dtpcp ratio 1:2 or 2:1, but the products obtained were the same as those from the reactions with a 1:1 molar ratio. Increasing the metal:dtpcp ratio to 3:1 resulted in rapid deposition of the complex as a white precipitate. Similar reactions to that described in the Experimental section but performed in other solvents led to a mixture of a white precipitate and tiny single crystals unsuitable for X-ray analysis.

Compounds **1–3** decompose at 251.6–252.5, 258.3–259.3 and 212.9–214.0 °C, respectively. The infrared spectra were recorded in the region 4000–400 cm^{-1} on KBr discs. All three complexes exhibit strong $\nu(\text{CS})$ absorption at 721–856 cm^{-1} , as expected for co-ordination of dtpcp.¹⁵ The strong interactions between the silver cation and the nitrate group in **3** are reflected in the large magnitude of the splitting of the asymmetric N–O stretching mode ν_1 at 1294, 1358 and 1426 cm^{-1} , consistent with a bridging mode for NO_3^- .¹⁵

Crystal structure of one-dimensional polymeric complex **1**

X-Ray-quality single crystals of complex **1** were obtained by liquid diffusion of a toluene solution of dtpcp with 1 molar equivalent of CuBr in MeCN. The structure consists of a neutral dinuclear unit $[\text{Cu}_2\text{Br}_2(\text{dtpcp})(\text{MeCN})_2]$ in which each copper(I) ion has distorted-tetrahedral geometry comprising one nitrogen atom of acetonitrile, two symmetry-related bromide ions and one sulfur atom from dtpcp, Fig. 1(a). A crystallographic inversion centre is located at the centre of the cyclophane. Table 1 lists important bond distances and angles involving the metal co-ordination. The Cu–S distance of 2.309(1) Å is comparable with those of Cu–S (thiolate) bonds for Me_3PS^- [2.259(6) Å]¹⁷ and PhS^- [2.295(4), 2.29(1) Å],¹⁸ and

Table 1 Selected bond lengths (Å) and angles (°) for complexes 1–3

Complex 1			
Cu–Br	2.5116(8)	Cu–Br'	2.4764(8)
Cu–S	2.309(1)	Cu–N	1.995(2)
Cu–Br–Cu'	77.68(3)	Br–Cu–Br'	102.32(3)
Br–Cu–S	112.31(3)	Br–Cu–N	110.69(8)
Br'–Cu–S	109.01(3)	Br'–Cu–N	114.6(1)
S–Cu–N	107.90(9)		
Complex 2			
Cu(1)–I(1)	2.785(4)	Cu(1)–I(2)	2.619(4)
Cu(2)–I(1)	2.632(4)	Cu(2)–I(2)	2.664(5)
Cu(1)–S(1)	2.300(4)	Cu(2)–S(2)	2.283(5)
Cu(1)–I(1)–Cu(2)	71.8(1)	Cu(1)–I(2)–Cu(2)	74.0(1)
I(1)–Cu(1)–I(2)	105.5(1)	I(1)–Cu(1)–S(1)	100.0(2)
I(2)–Cu(1)–S(1)	110.3(2)	S(1)–Cu(1)–S(1')	127.4(3)
I(1)–Cu(2)–I(2)	108.7(1)	I(2)–Cu(2)–S(2)	107.3(2)
I(1)–Cu(2)–S(2)	106.7(2)	S(2)–Cu(2)–S(2')	119.8(3)
Complex 3			
Ag–S(1)	2.510(2)	Ag–S(2)	2.534(2)
Ag–O(1)	2.374(6)	Ag–O(1')	2.664(6)
S(1)–Ag–S(2)	112.73(9)	S(1)–Ag–O(1)	122.3(2)
S(2)–Ag–O(1)	116.5(2)		

the average Cu–S bond distance of 2.358(3) Å in a copper(I) complex of tetrakis(methylthio)tetrathiofulvalene.¹⁴ The distorted geometry about the copper atom is indicated by the six bond angles around the metal which are in the range 102.32–112.31°. Each dtpcp acts as a linking ligand bound on each side to two separate metal cations through two sulfur atoms, resulting in a one-dimensional polymeric chain running parallel to a diagonal axis of the triclinic cell as shown in Fig. 1(b).

The two bromide ions in the dinuclear unit bridge pairs of copper atoms to form a rhombic CuBrCuBr ring, which leads to a Cu...Cu separation of 3.13 Å and Br...Br 3.89 Å. This type of dinuclear structure bridged by halide ions is quite common in copper(I) complexes.¹⁹ The two Cu–Br bond distances of 2.5116(8) and 2.4764(8) Å are within the range 2.370(2)–2.610(2) Å in the bromide-bridged complex [Cu₂(PPh₃)₃Br₂]²⁰ and 2.376(2)–2.664(2) Å in the tetranuclear stepped cubane structure [Cu(PPh₃)Br]₄·2CHCl₃.²¹ In contrast with the linear coordination of MeCN in [Cu(MeCN)₄]⁺ ion,²² the acetonitrile in **1** is not linearly co-ordinated to the copper atom, instead it has a bent angle of 170.3°. Such bent co-ordination has been observed in a copper(I)–pyrazine system,¹¹ and causes the Cu–N bond to incline toward the Cu–S bond. In spite of this, the Cu–N distance of 1.995(2) Å is normal.^{11,12}

Crystal structure of two-dimensional polymeric complex 2

Reaction of dtpcp with 1 molar equivalent of CuI affords colourless brick crystals of complex **2**. The single-crystal structure determination reveals that this complex and the above bromide are not isostructural. It consists of a dinuclear [Cu₂I₂(dtpcp)₂] unit in which each copper(I) ion is tetrahedrally co-ordinated to two iodide ions and one sulfur donor of two distinct dtpcp molecules as shown in Fig. 2. As in the bromide, the rhombic CuICuI ring formed by bridging of the two iodide ions between pairs of copper atoms leads to a Cu(1)...Cu(2) distance of 3.18 Å and I(1)...I(2) of 4.30 Å. The two symmetry-related dtpcp molecules bound to the same copper atom are well separated to minimize steric interaction, with S–Cu–S' bond angles of 127.4(3) and 119.8(3)° for Cu(1) and Cu(2), respectively, which causes a significant distortion of the metal geometry from idealized tetrahedral. It can be seen from Table 1 that the detailed bond parameters for the two crystallographically independent copper(I) ions are appreciably different. The bond angles around Cu(2) ranging from 106.2

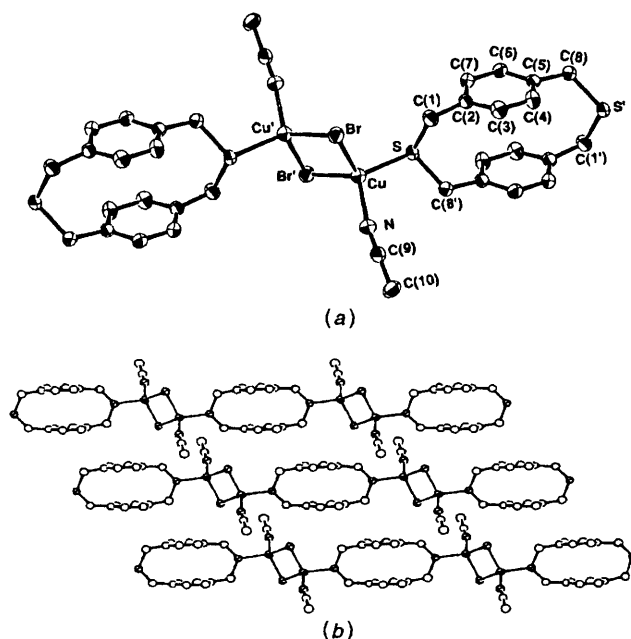


Fig. 1 An ORTEP¹⁶ view of the dinuclear unit [Cu₂Br₂(dtpcp)-(MeCN)₂] in complex **1** (a) and a perspective view of the infinite chains in **1** with an interchain Cu...Cu separation of 10.34 Å (b)

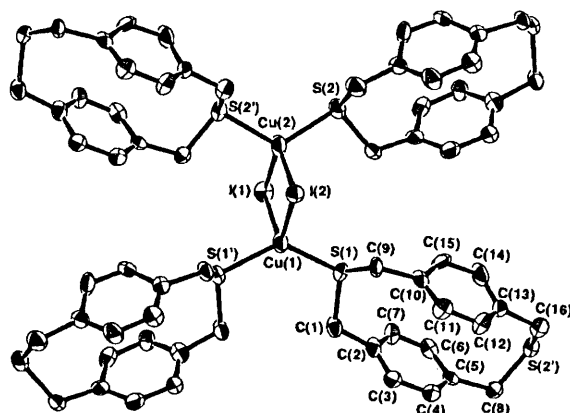


Fig. 2 An ORTEP view of the dinuclear unit [Cu₂I₂(dtpcp)₂]·thf in complex **2**

to 119.8(3)° are markedly less varied compared with the corresponding angles of 100.0(2) to 127.4(3)° for Cu(1), indicative of a less-distorted geometry for Cu(2). It is surprising that the bond length Cu(1)–I(1) 2.785(4) Å is as much as 0.153 Å longer than that of Cu(2)–I(1), 2.632(4) Å, while the rest of the bond distances for the two copper atoms are comparable.

As in complex **1**, each dtpcp fragment bridges two separate metal cations through two sulfur donors, and this results in a two-dimensional sheet arrangement of copper(I) ions spreading out along the *ab* plane to form an infinite network, Fig. 3(a). A large ring containing six copper atoms incorporates one thf molecule in the open cavity. However, this guest molecule is not firmly fixed by hydrogen bonds or other interactions, but weakly included. Fig. 3(b) shows a schematic drawing of Cu₆ motifs as planar hexagons constructed by the alternating arrangement of the two different copper ions. This two-dimensional sheet network is similar to that observed in our previously reported copper(I)–pyrazine complex,¹¹ where the cavity of the Cu₆ hexagon is occupied by an acetone molecule and the counter anion PF₆[−] is placed over the side of the cavity. These inclusion compounds might have properties such as microporosity and catalytic activity, in the area of host–guest chemistry.²³

Crystal structure of three-dimensional polymeric complex 3

Colourless brick crystals of complex 3 were obtained by slow reaction of dtpcp with 1 molar equivalent of AgNO_3 . In this polymeric complex each silver(I) ion is co-ordinated to one sulfur donor of two separate dtpcp molecules and one O atom from each of the two nitrate ligands. Fig. 4 shows a portion of the polymer and the atom numbering scheme. The co-ordination geometry is a rather distorted trigonal pyramid in which the Ag atom is lifted out of the plane defined by S(1), S(2) and O(1) at a distance of 0.4189 Å in the direction towards the terminal O(1') atom. A zigzag polymeric chain formed *via* dtpcp linking two metal centres extends along the *b* axis, Fig. 5(a). The NO_3^- ion acts as a one-oxygen-atom bridge connecting two Ag atoms belonging to two different chains with Ag–O distances of 2.374(6) and 2.664(6) Å, respectively, which fall in the range 2.367–2.689 Å for silver(I) complexes with nitrate.^{12,24} This leads to a close interchain $\text{Ag} \cdots \text{Ag}$ separation of 4.78 Å. The total crystal structure is built up from these infinite chains to give a three-dimensional channel framework of silver atoms as illustrated in Fig. 5(b).

The one nitrate oxygen bridging two metal atoms which gives a Ag_2O core in complex 3 is interesting. Similar bridges have been reported in $[\{\text{Ag}(\mu\text{-NO}_3)(\text{PR}_3)\}_2]$ ($\text{R} = \text{Ph}$ ²⁵ or OMe ²⁶).

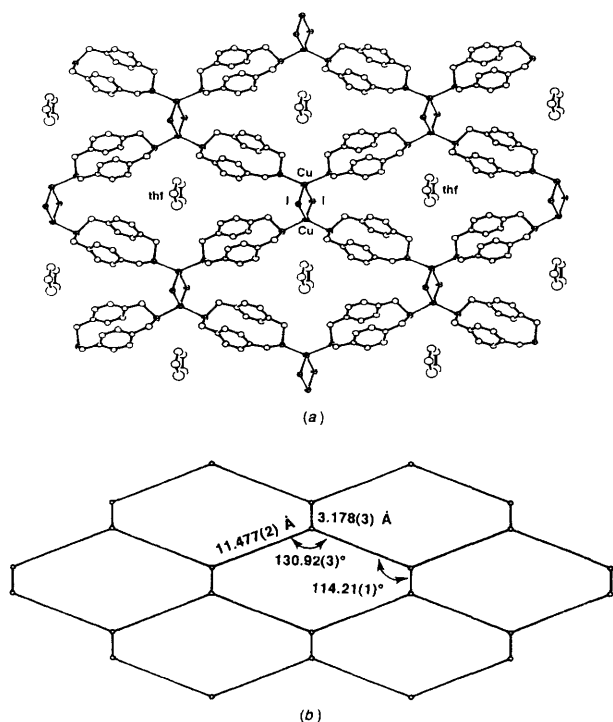


Fig. 3 Molecular packing diagram of complex 2 in the *ab* plane (a) and a view of the two-dimensional sheet consisting of Cu_6 hexagons (b) where only the metal centres are presented as open circles

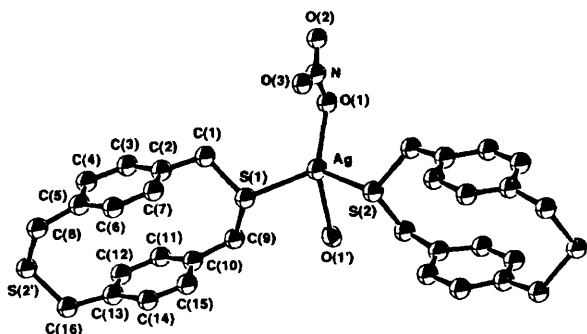


Fig. 4 An ORTEP diagram of the partial molecular structure of complex 3

Crystal structures of co-ordinated nitrate complexes have shown that NO_3^- can bond to a metal as a unidentate, chelating bidentate, and bridging ligand with various structures.²⁷ The most frequent co-ordination mode for bridging nitrate involves two oxygens, one bound to each metal;¹³ the cases in which one nitrate oxygen is co-ordinated to more than one metal are rather limited.^{25,26}

Electrical conductivity

Although all three complexes are insulators ($\sigma_{25^\circ\text{C}} < 10^{-12} \text{ S cm}^{-1}$), their iodine-doped black products in powder form behave as semiconductors with conductivities of $10^{-5.9}$, $10^{-5.1}$ and $10^{-4.7} \text{ S cm}^{-1}$ for 1–3, respectively. A similar phenomenon has been reported for a polymeric copper(I) complex of [3.3]paracyclophane,⁵ which is electrically non-conducting but becomes slightly coloured and conducting in air. A common feature of conducting complexes is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.²⁸ A partial oxidation can be assumed to have occurred in 1–3, and metal–metal, metal–ligand and ligand–ligand interactions might result in electrical conduction pathways. A detailed understanding of the conductivity observed in these partially oxidized polymers will only be possible when sufficient structural data are available.

Co-ordination of the thia-bridged paracyclophane

Previous investigations of the co-ordination chemistry of cyclophane have been primarily focused on [2_n]-paracyclophanes.^{4–7} Although a number of sulfur analogues of cyclophane have been reported,^{10,29} the investigation of their co-ordination behaviour with transition-metal ions is far less extensive. There is only one report on the structure of a mononuclear tungsten complex of 2,6,15,19-tetra-thia[7.7]paracyclophane.⁸ The three complexes reported here represent the first examples of a thia-bridged cyclophane

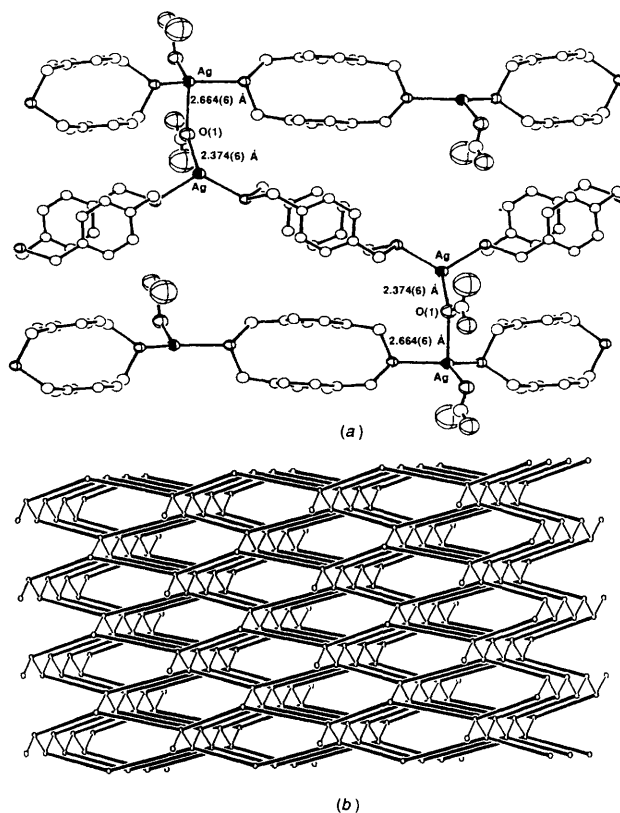


Fig. 5 A perspective view of the infinite zigzag chains running along the *b* axis for complex 3 (a) and a view of the three-dimensional channel framework of silver(I) ions interconnected by dtpcp (bold lines) and NO_3^- (thin lines) where only metal atoms are shown as open circles (b)

complex having a polymeric structure. In contrast to the metallocyclophane system, the co-ordination of the dithia-bridged paracyclophane involves exclusively the two sulfur atoms rather than the delocalized π electrons of the benzene rings. If a second bridging ligand is present, a wide range of co-ordination polymers appear to be possible for dtpcp, ranging from one-dimensional infinite chains to two-dimensional sheets or three-dimensional frameworks with various metal ions and counter anions. Thus the choice of the other linking ligand is important. Halide ions have been chosen in this study because they have been known for decades to play a bridging role in many complexes.¹⁹ The corresponding polymeric copper(II) compound³⁰ was isolated by using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in place of CuBr or CuI . As in **1** and **2**, the dinuclear unit $[\text{Cu}_2\text{Cl}_2(\text{dtpcp})_2]^{2+}$ is still maintained in this complex in which each Cl^- ion bridges two copper(II) ions. Nitrate is known to be a strong interconnecting ligand in many co-ordination compounds.^{13,25-27} In **3** the one-nitrate-oxygen bridging plays a key role in the formation of the three-dimensional array of metal ions. On the other hand, however, our attempts to isolate single crystals of the corresponding polymeric copper and silver complexes with non-bridging counter anions PF_6^- , BF_4^- and ClO_4^- have so far been unsuccessful.

In conclusion, the dithia-bridged paracyclophane, dtpcp, is a unique versatile organic ligand for the formation of polymeric chains in the presence of bridging anions. The arrangement of such chains in the lattice is controlled and modified by co-ordination of a suitable counter anion. This conclusion is in line with the results of our previous investigations.¹¹⁻¹⁴

Experiment

General methods

Preparations were performed under an argon atmosphere using the usual Schlenk techniques. All solvents were dried and deoxygenated by standard methods prior to use. The standard chemicals and reagent-grade 2,11-dithia[3.3]paracyclophane were obtained from Wako Chemical Co., Japan, and used without further purification. Infrared spectra were measured as KBr discs on a JASCO FT/IR-8000 spectrometer. Electrical resistivities of compacted pellets were measured by the conventional two-probe technique.

Syntheses

[Cu₂Br₂(dtpcp)(MeCN)₂] 1. A solution of toluene (10.0 cm³) containing 2,11-dithia[3.3]paracyclophane (14.0 mg, 0.05 mmol) was poured into a 6 mm diameter glass tube and then layered with a MeCN (10.0 cm³) solution of CuBr (7.0 mg, 0.05 mmol). The glass tube was sealed under argon. After standing at room temperature for 1 week colourless brick crystals of complex **1** were isolated at the interface between the two solutions (Found: C, 38.70; H, 3.70; N, 3.10. Calc. for $\text{C}_{10}\text{H}_{11}\text{BrCuNS}$: C, 37.45; H, 3.45; N, 4.35%).

[Cu₂I₂(dtpcp)₂·thf 2. A solution (10.0 cm³) of thf containing 2,11-dithia[3.3]paracyclophane (27.0 mg, 0.1 mmol) was introduced into a glass tube and layered with MeCN (2.0 cm³) as a buffer zone. Then a dilute solution of CuI (19.0 mg, 0.1 mmol) in MeCN (10.0 cm³) was added gently to avoid possible mixing. After standing at room temperature for 1 week colourless brick crystals of complex **2** were isolated in the buffer zone (Found: C, 42.85; H, 3.90. Calc. for $\text{C}_{36}\text{H}_{40}\text{Cu}_2\text{I}_2\text{OS}_4$: C, 43.30; H, 4.00%).

[Ag(dtpcp)(NO₃)] 3. Colourless brick crystals of complex **3** were obtained in the same way as for **2** using AgNO_3 (17.0 mg, 0.1 mmol) instead of CuI (Found: C, 44.70; H, 3.80; N, 4.00. Calc. for $\text{C}_{16}\text{H}_{16}\text{AgNO}_3\text{S}_2$: C, 43.45; H, 3.65; N, 3.15%).

Crystallography

Single crystals of complexes **1-3** were coated with paraffin to avoid possible decomposition in the air. Details of the crystal data collection and processing, structure analysis and refinement are given in Table 2. The unit-cell data and intensities were collected on a Rigaku AFC-6S four-circle diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71069 \text{ \AA}$) radiation. The standard reflections were monitored every 25 measurements, and the decay in their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

All three structures were solved by a direct method (MITHRIL)³¹ and refined on F by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$. Anisotropic thermal para-

Table 2 Crystal and refinement data for complexes **1-3***

Compound	1	2	3
Formula	$\text{C}_{10}\text{H}_{11}\text{BrCuNS}$	$\text{C}_{36}\text{H}_{40}\text{Cu}_2\text{I}_2\text{OS}_4$	$\text{C}_{16}\text{H}_{16}\text{AgNO}_3\text{S}_2$
M	320.71	997.86	442.30
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$Cmc2_1$	$P2_12_12_1$
$a/\text{\AA}$	7.907(2)	20.883(3)	11.071(5)
$b/\text{\AA}$	10.435(3)	15.842(8)	21.824(2)
$c/\text{\AA}$	7.731(3)	11.352(5)	7.953(2)
$\alpha/^\circ$	77.68(3)		
$\beta/^\circ$	65.83(3)		
$\gamma/^\circ$	71.87(2)		
$U/\text{\AA}^3$	550.3(7)	3755(3)	1921.4(10)
$D_c/\text{g cm}^{-3}$	1.935	1.765	1.639
Z	2	4	4
Crystal size/mm	0.17 × 0.18 × 0.26	0.50 × 0.50 × 0.20	0.30 × 0.30 × 0.20
$F(000)$	316	1968	952
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	57.27	30.05	12.70
No. reflections measured	2704	2401	2556
No. observations [$I > 3.00\sigma(I)$]	1992	1785	1766
No. parameters	128	201	221
R	0.024	0.039	0.039
R'	0.029	0.043	0.047
Goodness of fit	1.16	1.63	1.74

* Details in common: ω -2 θ scans; scan rate 4° min⁻¹.

Table 3 Atomic coordinates for complex 1

Atom	x	y	z
Cu	0.291 99(5)	0.574 41(4)	0.509 11(5)
Br	0.490 38(4)	0.343 66(3)	0.408 97(4)
S	0.220 3(1)	0.718 86(7)	0.263 4(1)
N	0.045 7(4)	0.561 7(3)	0.723 3(4)
C(1)	0.284 5(5)	0.876 8(3)	0.246 7(5)
C(2)	0.241 4(4)	0.979 1(3)	0.091 5(4)
C(3)	0.092 6(5)	1.093 6(3)	0.136 9(4)
C(4)	-0.029 7(5)	0.821 3(3)	0.002 9(5)
C(5)	-0.117 0(4)	0.850 7(3)	0.190 4(4)
C(6)	-0.275 3(4)	0.960 3(3)	0.237 6(4)
C(7)	0.336 1(4)	0.956 3(3)	-0.098 0(5)
C(8)	-0.039 8(4)	0.769 9(3)	0.341 6(4)
C(9)	-0.103 6(4)	0.572 8(3)	0.836 4(4)
C(10)	-0.293 4(5)	0.589 3(4)	0.982 7(5)

Table 4 Atomic coordinates for complex 2

Atom	x	y	z
Cu(1)	0.5	0.0541(2)	0.2969(4)
Cu(2)	0.5	0.2538(2)	0.2696(4)
I(1)	0.5	0.1487(1)	0.0901
I(2)	0.5	0.1646(1)	0.4685(2)
S(1)	0.4013(2)	-0.0094(3)	0.2821(6)
S(2)	0.0946(2)	-0.1741(3)	0.2621(6)
O	1.0	0.0237	0.3304
C(1)	0.4090(7)	-0.123(1)	0.265(2)
C(2)	0.3446(8)	-0.167(1)	0.256(2)
C(3)	0.3259(9)	-0.228(1)	0.339(2)
C(4)	0.2638(9)	-0.259(1)	0.337(2)
C(5)	0.2204(8)	-0.235(1)	0.248(2)
C(6)	0.2427(9)	-0.179(1)	0.162(2)
C(7)	0.3032(9)	-0.146(1)	0.166(2)
C(8)	0.1523(8)	-0.262(1)	0.257(2)
C(9)	0.3643(8)	0.007(1)	0.421(2)
C(10)	0.2943(8)	-0.019(1)	0.428(2)
C(11)	0.2717(9)	-0.074(1)	0.514(2)
C(12)	0.2097(10)	-0.106(1)	0.511(2)
C(13)	0.1689(8)	-0.082(1)	0.425(2)
C(14)	0.1888(9)	-0.017(1)	0.347(2)
C(15)	0.2507(9)	0.010(1)	0.348(2)
C(16)	0.1041(9)	-0.124(1)	0.410(2)
C(17)	1.0	0.0380	0.2211
C(18)	1.0	0.1365	0.2054
C(19)	1.0	0.1562	0.3107
C(20)	1.0	0.1001	0.3872

meters were refined for all non-hydrogen atoms. Hydrogen atoms were included as a fixed contribution in the last cycle; their thermal parameters were assumed to be isotropic. All calculations were performed using the TEXSAN crystallographic software package³² on a micro VAX computer. Reliability factors are defined as $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$, where $w = 4F_o^2 / \sigma^2(F_o^2)$. Atomic scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from ref. 33. The final atomic coordinates for non-hydrogen atoms are given in Tables 3–5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Science Research [Nos. 07232226 and 07241260 (priority areas)] from the Ministry of Education, Science and Culture in Japan. The authors are also grateful to Kinki University for financial support (GG 1100).

Table 5 Atomic coordinates for complex 3

Atom	x	y	z
Ag	0.130 41(6)	0.002 73(3)	0.026 60(7)
S(1)	0.050 9(2)	0.098 98(9)	-0.106 1(4)
S(2)	0.041 7(2)	-0.093 40(9)	-0.102 6(4)
O(1)	0.182 6(5)	-0.002 7(5)	0.315 8(7)
O(2)	0.104 0(8)	0.004 1(6)	0.554 6(7)
O(3)	0.001 0(8)	0.011 1(9)	0.328 5(10)
N	0.094 1(7)	0.003 7(7)	0.402 3(9)
C(1)	0.015 3(9)	0.156 3(3)	0.054(1)
C(2)	-0.041 9(8)	0.213 7(3)	-0.016(2)
C(3)	0.003 2(9)	0.271 0(3)	0.027(2)
C(4)	-0.042 3(9)	0.323 5(3)	-0.049(2)
C(5)	-0.132(1)	0.319 7(4)	-0.174(1)
C(6)	-0.180 0(8)	0.263 2(4)	-0.207(2)
C(7)	-0.138(1)	0.210 7(4)	-0.130(2)
C(8)	0.165 5(10)	-0.125 1(4)	-0.224(2)
C(9)	0.174 5(9)	0.130 5(4)	-0.229(2)
C(10)	-0.137(1)	-0.313 3(1)	-0.171(1)
C(11)	-0.186 0(10)	-0.254 1(4)	-0.209(1)
C(12)	-0.143(1)	-0.205 2(4)	-0.128(2)
C(13)	-0.050 4(9)	-0.208 2(4)	-0.012(2)
C(14)	-0.008 6(9)	-0.265 6(4)	0.028(2)
C(15)	-0.051 6(9)	-0.317 4(4)	-0.045(2)
C(16)	0.012 0(10)	-0.151 1(3)	0.055(2)

References

- 1 C. J. Brown and A. C. Farthing, *Nature (London)*, 1949, **164**, 915.
- 2 F. Diederich, in *Cyclophanes*, Monographs in Supramolecular Chemistry 2, ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1991.
- 3 D. J. Cram and R. H. Bauer, *J. Am. Chem. Soc.*, 1959, **81**, 5971.
- 4 T. Swann, A. W. Hanson and V. Boekelheide, *J. Am. Chem. Soc.*, 1986, **108**, 3324.
- 5 H. Schmidbaur, W. Bublak, B. Huber, G. Reber and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1089.
- 6 H. Schmidbaur, W. Bublak, B. Huber, G. Reber and G. Müller, *Helv. Chim. Acta*, 1986, **69**, 1742.
- 7 H. Schmidbaur, W. Bublak, B. Huber, J. Hofmann and G. Müller, *Chem. Ber.*, 1989, **122**, 265.
- 8 B. K. Balbach, A. R. Koray, A. Okur, P. Wulknitz and M. L. Ziegler, *J. Organomet. Chem.*, 1981, **212**, 77.
- 9 C. Cohen-Addad, M. Consigny, G. D'Assenza and P. Baret, *Acta Crystallogr., Sect. C*, 1988, **44**, 1924.
- 10 T. L. Chan, C. D. Poon and T. C. W. Mak, *Acta Crystallogr., Sect. C*, 1986, **42**, 897.
- 11 S. Kitagawa, M. Munakata and T. Tanimura, *Inorg. Chem.*, 1992, **31**, 1714; S. Kitagawa, S. Kawata, M. Kondo, Y. Nozaka and M. Munakata, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3387.
- 12 M. Munakata, S. Kitakawa, N. Ujimar, M. Nakamura, M. Maekawa and H. Matsuda, *Inorg. Chem.*, 1993, **32**, 826.
- 13 M. Munakata, T. Kuroda-Sowa, M. Maekawa, M. Nakamura, S. Akiyama and S. Kitagawa, *Inorg. Chem.*, 1994, **33**, 1284.
- 14 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.*, 1995, **34**, 2705.
- 15 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1970.
- 16 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 17 P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 1971, 105.
- 18 D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem.*, 1980, **19**, 2993.
- 19 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 533–774.
- 20 H. Negita, M. Hiura, Y. Kushi, M. Kuramoto and T. Okuda, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1247.
- 21 M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1427.
- 22 I. Csöreg, P. Kierkegaard and R. Norrestam, *Acta Crystallogr., Sect. B*, 1975, **31**, 314.
- 23 J. D. Wright, *Molecular Crystals*, 2nd edn., Cambridge University Press, Cambridge, 1994; R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, New York, 1978.
- 24 F. Guay and A. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 6260; D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4073.

- 25 P. G. Jones, *Acta Crystallogr., Sect. C*, 1993, **49**, 1148.
- 26 J. H. Meiners, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, 1975, **14**, 632.
- 27 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Barner, *Q. Rev. Chem. Soc.*, 1971, **25**, 289.
- 28 J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79; M. B. Inoue, M. Inoue, Q. Fernando and K. W. Nebesny, *Inorg. Chem.*, 1986, **25**, 3976.
- 29 W. Anker, G. W. Bushnell and R. H. Mitchell, *Can. J. Chem.*, 1979, **57**, 3080; G. J. Bodwell, L. Ernst, H. Hopf, P. G. Jones, J. P. McNally and D. Schomburg, *Chem. Ber.*, 1990, **123**, 2381.
- 30 M. Munakata and S. Nakagawa, unpublished work.
- 31 MITHRIL, an integrated direct method computer program, University of Glasgow, C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.
- 32 TEXSAN-TEXRAY, Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.
- 33 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 1st November 1995; Paper 5/07204B