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SYNTHESES AND STRUCTURES OF ONE- AND TWO-DIMENSIONAL COPPER(I) COORDINATION POLYMERS WITH TETRAKIS(ETHYLTHIO)TETRATHIAFULVALENE (TTC_2-TTF) AND THE PROPERTIES OF THEIR IODINE-DOPED COMPOUNDS

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Abstract—Two copper(I) complexes with tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF), [$(CuCl)_2TTC_2$-TTF] (**1**) and [$(CuBr)_2TTC_2$-TTF] (**2**), have been synthesized and characterized by spectroscopic and X-ray crystallographic methods. Both **1** and **2** are neutral 2 : 1 (metal/ligand) complexes in which each metal ion is coordinated in a distorted tetrahedral geometry to two bridging halide ions and two sulphur atoms from TTC_2-TTF. The crystal of **1** has a two-dimensional structure in which TTC_2-TTF molecules are connected between novel helical CuCl frames, while the crystal of **2** has a one-dimensional polymeric chain structure. The average Cu—Cl and Cu—S bond lengths are 2.282(2) and 2.405(2) Å in **1** and Cu—Br and Cu—S bond lengths are 2.445(2) and 2.349(1) Å in **2**, respectively. Compounds **1** and **2** were doped with iodine to afford [$(CuCl)_2TTC_2$-TTF]I (**3**) and [$(CuBr)_2TTC_2$-TTF]I (**4**) which exhibit electrical conductivities of 6×10^{-7} and 3×10^{-7} S cm^{-1}, respectively, at 25°C for compacted pellets.

Considerable attention in recent years has been focused on the chemistry and physics of materials which exhibit highly anistropic electrical, optical and magnetic properties.[1] Of particular interest has been organic and metal–organic solids which exhibit metal-like charge transport properties. Tetrathiafulvalene (TTF) and some of its derivatives are excellent electron donors and have been found to form a class of electroconductive substances termed "organic metals" or "synthetic metals".[2–5] The electrical conductivities of these substances can be varied over a wide range, from semiconductor to superconductor, by changing the nature of the component species. Most of these compounds are composed of organic radical ions. Although some of them contain metal atoms in the anion, these metal ions are not coordinated to the organic molecules.[4] In an effort to develop a new type of conductive compound, we are currently studying the metallotetrathiafulvalene polymers in which TTF or its derivatives directly coordinate to the metal ions. Tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF), which has a central tetrathio-TTF (C_6S_4) π system and a side ethylthio chain system, is a single-component organic semiconductor with low conductivity ($\sigma_{RT} \approx 10^{-10}$ S cm^{-1})[6] and its physical properties have been widely investigated.[7,8] The only compound of TTC_2-TTF reported so far is the charge-transfer complex [TTC_2-TTF]·[TCNQ].[9] In this paper we report the syntheses and structural characterization of one- and two-dimensional copper(I) halide (X = Cl and Br) coordination polymers with TTC_2-TTF, [$(CuCl)_2TTC_2$-TTF] and [$(CuBr)_2TTC_2$-TTF], and the properties of their iodine-doped compounds.

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EXPERIMENTAL

General

The preparation of the complexes was performed under argon using usual Schlenk techniques. The reagent TTC$_2$-TTF (m.p. 70°C) was prepared according to the literature method.[10] Copper(I) chloride and copper(I) bromide (Wako) were used as purchased. Acetonitrile, tetrahydrofuran and acetone were dried and distilled by a standard method before use. IR spectra and electronic spectra as KBr discs were recorded with a Jasco 8000 FT-IR spectrometer and Hitachi 150-20 spectrophotometer, respectively. Electrical resistivity was measured by a conventional two-probe method at 25°C with compacted pellet.

Preparation of [(CuCl)$_2$TTC$_2$-TTF] (**1**)

A solution of copper(I) chloride (19.8 mg, 0.2 mmol) in acetonitrile (1 cm^3) was added to a TTC$_2$-TTF (44.4 mg, 0.1 mmol) solution in acetone (10 cm^3) under argon. After stirring for 30 min at room temperature, the resultant orange solution was filtered and the filtrate was sealed in four 7-mm-diameter glass tubes, which were allowed to stand at −5°C. After 1 week, orange crystals of [(CuCl)$_2$TTC$_2$-TTF] (**1**) were obtained, yield 45%. Found: C, 25.9; H, 2.9. Calc. for $C_{14}H_{20}Cl_2Cu_2S_8$: C, 26.2; H, 3.1%. IR (cm^{-1}): 2959 (m), 2922 (m), 2866 (w), 2822 (w), 1446 (s), 1409 (s), 1373 (s), 1255 (s), 1057 (m), 966 (m), 897 (s), 767 (s). Electronic spectrum (λ_{max}, nm): 420 (s).

Preparation of [(CuBr)$_2$TTC$_2$-TTF] (**2**)

A solution of copper(I) bromide (28.6 mg, 0.2 mmol) in acetonitrile (2 cm^3) was added to a TTC$_2$-TTF (44.4 mg, 0.1 mmol) solution in tetrahydrofuran (10 cm^3) under argon. After stirring for 5 min at 50°C, the resultant orange solution was filtered and the filtrate was sealed in four 7-mm-diameter glass tubes, which were allowed to stand in a Dewar vessel filled with 50°C water. After 1 week, orange crystals of [(CuBr)$_2$TTC$_2$-TTF] (**2**) were obtained, yield 50%. Found: C, 23.2; H, 2.9. Calc. for $C_{14}H_{20}Cu_2Br_2S_8$: C, 23.0; H, 2.8%. IR (cm^{-1}): 2976 (w), 2957 (w),2926 (w), 2864 (w), 1446 (s), 1410 (s), 1375 (s), 1273 (s), 1055 (m), 966 (m), 897 (s), 754 (s), 497 (w). Electronic spectrum (λ_{max}, nm): 420 (s).

Preparation of [(CuCl)$_2$TTC$_2$-TTF]I (**3**)

Crystals of complex [(CuCl)$_2$TTC$_2$-TTF] (**1**) (20 mg, 0.031 mmol) were placed in one arm of an h-shaped glass tube which contained iodine (20 mg, 0.079 mmol) in another arm. The h-shaped tube was sealed under argon and was allowed to stand at ambient temperature. After 5 days, a black solid (23.5 mg) with the composition [(CuCl)$_2$TTC$_2$-TTF]I (**3**) was obtained. Found: C, 21.7; H, 2.7. Calc. for $C_{14}H_{20}Cl_2Cu_2IS_8$: C, 21.9; H, 2.6%. IR (cm^{-1}): 2964 (w), 2920 (w), 2862 (w), 2820 (w), 1444 (s), 1400 (s), 1377 (sh), 1331 (s), 1257 (s), 1055 (m), 964 (m), 893 (m), 761 (m). Electronic spectrum (λ_{max}, nm): 422 (s), 783 (br).

Preparation of [(CuBr)$_2$TTC$_2$-TTF]I (**4**)

Crystals of complex [(CuBr)$_2$TTC$_2$-TTF] (**2**) (20 mg, 0.027 mmol) was placed in one arm of an h-shaped glass tube which contained iodine (20 mg, 0.079 mmol) in another arm. The h-shaped tube was sealed under argon and was allowed to stand at ambient temperature. After 5 days, a black solid (23.3 mg) with the composition [(CuBr)$_2$TTC$_2$-TTF]I (**4**) was obtained. Found: C, 19.5; H, 2.2. Calc. for $C_{14}H_{20}Cu_2\,Br_2IS_8$: C, 19.6; H, 2.3%. IR (cm^{-1}): 2957 (w), 2926 (w), 2866 (w), 2814 (w), 1466 (s), 1406 (s), 1375 (s), 1331 (s), 1271 (s), 1055 (m), 966 (m), 897 (s), 754 (s), 493 (m). Electronic spectrum (λ_{max}, nm): 423 (s), 780 (br).

X-ray structure determination

Orange crystals of **1** and **2** suitable for X-ray diffraction study were mounted on the diffractometer with graphite-monochromated Mo-K_α radiation. The conditions for data collection and crystal data are listed in Table 1. The structures were solved by a direct method (MITHRIL)[11] and refined by full-matrix least with anisotropic thermal parameters for non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier difference synthesis, using the program system TEXSAN.[12] Reliability factors are defined as $R = \Sigma||F_0|-|F_c|/\Sigma|F_0||$ and $R_w = [\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2]^{1/2}$, where $w = 4F_0^2/\Sigma\sigma^2(F_0^2)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 13. The final R and R_w values were 0.037 and 0.042 for **1** and 0.033 and 0.038 for **2**, respectively. The atomic coordinates, full set of bond lengths and angles, thermal parameters, and F_c and F_0 tables have been deposited with the Editor as supplementary materials.

Table 1. Crystal data and measurement conditions for complexes **1** and **2**

Complex	1	2
Molecular formula	$C_{14}H_{20}Cl_2Cu_2S_8$	$C_{14}H_{20}Cu_2Br_2S_8$
Formula weight	642.78	731.75
Crystal dimension (mm)	0.20 × 0.10 × 0.05	0.50 × 0.50 × 0.60
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/m$
a (Å)	27.833(5)	9.805(4)
b (Å)	5.045(5)	12.585(4)
c (Å)	17.072(3)	10.132(4)
β (°)	102.12(1)	99.53(4)
V (Å^3)	2344(2)	1233(2)
Z	4	2
D_c (g cm^{-3})	1.821	1.971
Diffractometer type	Rigaku AFC-5R	Rigaku AFC-6S
λ/(Mo-K_α) (Å)	0.71069	0.71069
μ(Mo-K_α) (cm^{-1})	27.38	55.95
Scan type	ω–2θ	ω–2θ
Scan rate (° min^{-1})	8.0	2.0
Scan width (°)	(1.47+0.30 tan θ)	(1.15+0.30 tan θ)
$2\theta_{max}$ (°)	55.0	55.0
No. of reflections measured	3076	3133
No. of reflections observed [$I \geqslant 3\sigma(I)$]	1755	2206
R	0.037	0.033
R_w	0.042	0.038

RESULTS AND DISCUSSION

Structure of $[(CuCl)_2TTC_2\text{-}TTF]$ (1)

The molecular structure of **1** is illustrated in Fig. 1. Figure 2 shows the perspective views in the crystal. Selected bond lengths and angles are summarized in Table 2.

In compound **1**, each copper atom is coordinated in a distorted tetrahedral geometry to two bridging chloride ions and two sulphur atoms from the ligand, with bond angles around copper ranging from 86.9 to 116.1°. The average Cu—Cl and Cu—S bond lengths are 2.282(2) and 2.405(2) Å, respectively. The TTC_2-TTF molecular structure in the present complex contains an inversion centre between the two central carbon atoms and the molecule is a chair-like form (Fig. 1b), with a tilt angle of 6.6°. Two of the four ethyl groups lie on one side of the C_6S_8 plane, while the other two lie on the opposite side. This conformation is different from that of the free TTC_2-TTF molecule, which is a boat-like form with four ethyl groups orientated in the same direction.[14]

Table 2. Selected bond lengths (Å) and angles (°) of complex **1**

Cu—Cl	2.268(2)	S(3)—C(1)	1.761(5)
Cu—Cl′	2.295(2)	S(3)—C(2)	1.757(4)
Cu—S(1)	2.418(2)	S(4)—C(1)	1.761(4)
Cu—S(2)	2.392(1)	S(4)—C(3)	1.754(4)
S(1)—C(2)	1.755(4)	C(1)—C(1′)	1.339(7)
S(1)—C(4)	1.828(5)	C(2)—C(3)	1.333(6)
S(2)—C(3)	1.756(4)	C(4)—C(5)	1.495(7)
S(2)—C(6)	1.870(6)	C(6)—C(7)	1.384(9)
Cl—Cu—Cl′	116.10(4)	Cl′—Cu—S(1)	114.66(8)
Cl—Cu—S(1)	115.06(5)	Cl′—Cu—S(2)	104.20(5)
Cl—Cu—S(2)	115.97(8)	S(1)—Cu—S(2)	86.87(5)

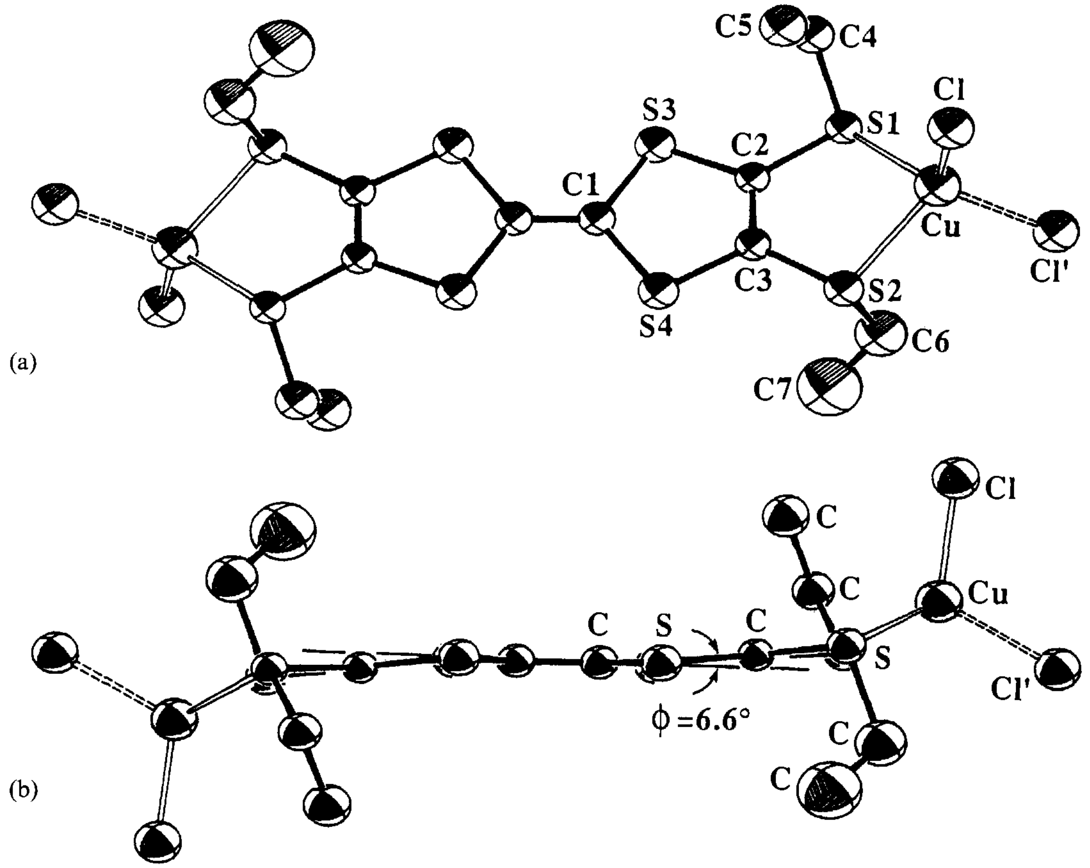

Fig. 1. Molecular structure and atomic numbering schemes of **1**. (a) Top view. (b) Side view.

Figure 2 shows a segment of the two-dimensional structure of **1** in which TTC$_2$-TTF molecules are connected between copper chloride frames. It is noteworthy that the CuCl frame in **1** is a novel helical structure and the neighbouring helices rotate alternatively in the reverse direction. The shortest distance between the heterocyclic sulphur atoms in the neighbouring TTC$_2$-TTF molecules is 3.74 Å (Fig. 2). This value is longer than the sum of van der Waals radii (3.60 Å) of two sulphur atoms.[15] Therefore, the S $\cdots$ S interaction between the TTC$_2$-TTF molecules is weak in the present complex.

Structure of [(CuBr)$_2$TTC$_2$-TTF] (**2**)

The molecular structure of **2** is illustrated in Fig. 3. Figure 4 shows the packing arrangement in the crystal. Selected bond lengths and angles are summarized in Table 3.

Each copper atom in compound **2** is tetrahedrally coordinated by two bridging bromide ions and two sulphur atoms from the ligand, with an average Cu—Br bond length of 2.445(2) Å and Cu—S bond length of 2.349(1) Å. The TTC$_2$-TTF molecular structure in the present complex is a boat-like form (Fig. 3b). The four ethyl groups elongate nearly perpendicular to the central C$_6$S$_8$ group. The central skeleton is appreciably non-planar, and the tilt angles are 10.4° and 11.4°, respectively. This conformation is analogous to that of the neutral TTC$_2$-TTF molecule.[14] It can be seen from Fig. 3 that the TTC$_2$-TTF molecules and bromide ions behave as bridging groups in the complex and the metal ions are linked by TTC$_2$-TTF molecules and bromide ions to form coordination polymeric chains. In the crystal phase it is observed that to decrease the repulsion between the ethyl groups in neighbouring chains all the ethyl groups in a polymeric chain take the same orientation, while the ethyl groups in its two neighbouring chains orientate to the opposite direction so that these polymeric chains can pack more closely to each other. The shortest S $\cdots$ S distance between the neighbouring polymeric chains is S(3) $\cdots$ S(3) [3.577(2) Å] and S(2) $\cdots$ S(4) [3.610(2) Å (Fig. 4). The S $\cdots$ S interaction between the linear chains is not strong in the complex.

Spectroscopic and electrical property studies

Both the IR spectra and electronic spectra provide important information about the oxidation

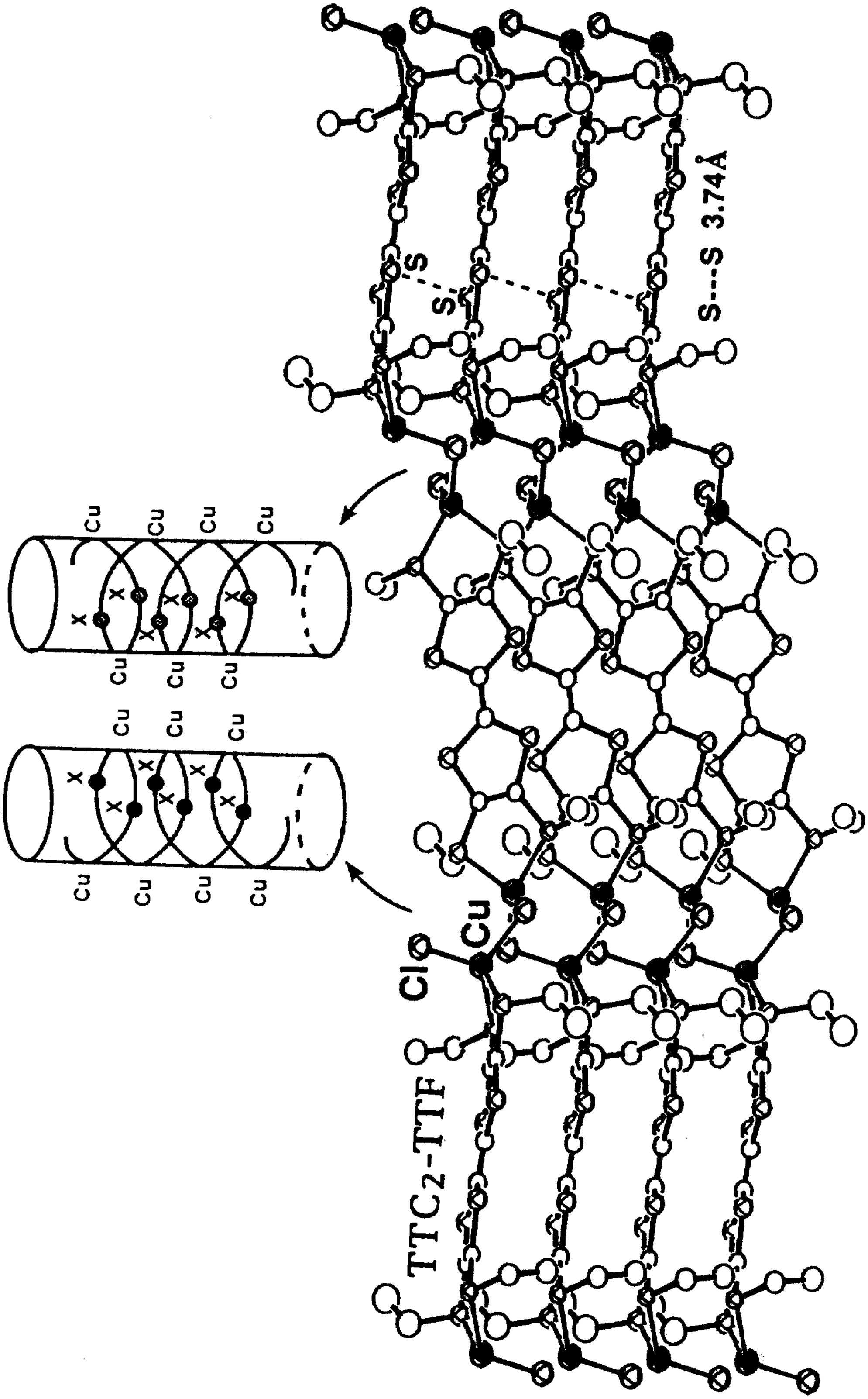

Fig. 2. Perspective views of 1.

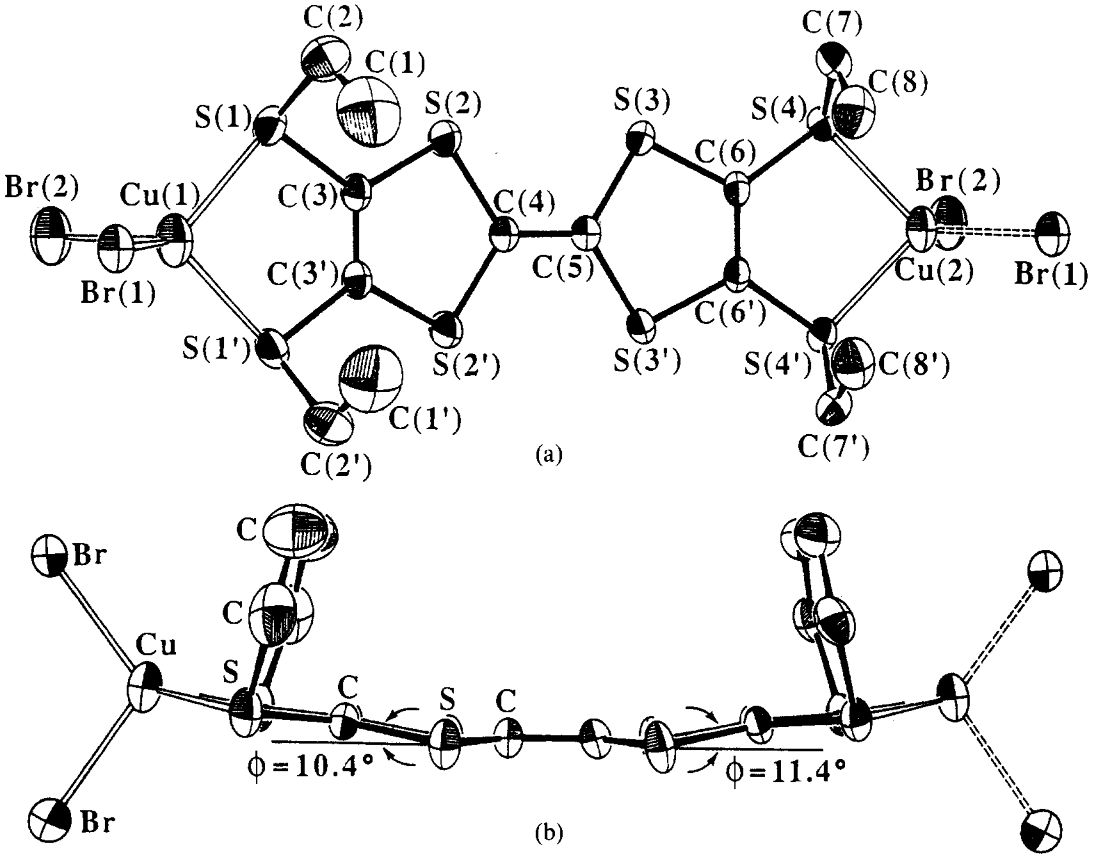

Fig. 3. Molecular structure and atomic numbering schemes of **2**. (a) Top view. (b) Side view.

state of TTC$_2$-TTF in the coordination polymers [(CuCl)$_2$TTC$_2$-TTF] (**1**) and [(CuBr)$_2$TTC$_2$-TTF] (**2**) and in their iodine-doped compounds [(CuCl)$_2$TTC$_2$-TTF]I (**3**) and [(CuBr)$_2$TTC$_2$-TTF]I (**4**). It is well known[16–18] that the central C=C stretch of TTF undergoes a large frequency shift on oxidation, for example, from 1512 cm^{-1} in neutral TTF[16] to 1413 cm^{-1} in (TTF)Br.[17] Similarly, the central C=C stretching frequency of TTC$_2$-TTF is also sensitive to its oxidation state. In the IR spectra of free TTC$_2$-TTF and the coordination polymers (**1** and **2**), the central C=C stretching band of TTC$_2$-TTF occurs at 1448 and 1146 cm^{-1}, respectively, which indicates the presence of neutral TTC$_2$-TTF in the coordination polymers. The IR spectra of the iodine-doped compounds reveal two sharp bands (one band at 1444 cm^{-1} for **3** and 1446 cm^{-1} for **4**, and another band at 1331 cm^{-1} for both **3** and **4**), which arise from the neutral TTC$_2$-TTF and TTC$_2$-TTF$^{+\cdot}$ radical cation, respectively. In the electronic spectra, both of the coordination polymers and their iodine-doped compounds show a strong absorption band near 420 nm. These bands near 420 nm may be ascribed to local excitation of the TTC$_2$-TTF molecule, since the free TTC$_2$-TTF ligand also exhibits an absorption band at 419 nm. The other broad absorption band around 780 nm in the spectra of the iodine-doped compounds may arise from the TTC$_2$-TTF–TTC$_2$-TTF$^{+\cdot}$ charge-transfer transition.[18]

One of the common features of a conducting complex is that the constituent molecules are in a mixed-valence (or partial oxidation) state.[19,20] Although **1** and **2** are insulators ($\sigma_{25^\circ C} < 10^{-12}$ S cm^{-1}), **3** and **4** behave as semiconductors: $\sigma_{25^\circ C} = 6 \times 10^{-7}$ S cm^{-1} for **3** and $\sigma_{25^\circ C} = 3 \times 10^{-7}$ S cm^{-1} for **4**. This may be due to the (TTC$_2$-TTF)$^{+\cdot}$–(TTC$_2$-TTF)$^{+\cdot}$ and/or (TTC$_2$-TTF)–(TTC$_2$-TTF)$^{+\cdot}$ interaction in the crystal.[18]

In conclusion, copper(I) chloride and copper(I) bromide can react with the sulphur-rich ligand TTC$_2$-TTF to form neutral 2 : 1 (metal/ligand) complexes. All the copper atoms in the complexes are coordinated by the bridging halide and the organic ligand to form a two-dimensional sheet coordination polymer in **1** and a one-dimensional linear coordination polymer in **2**, respectively. Their iodine-doped products behave as semiconductors.

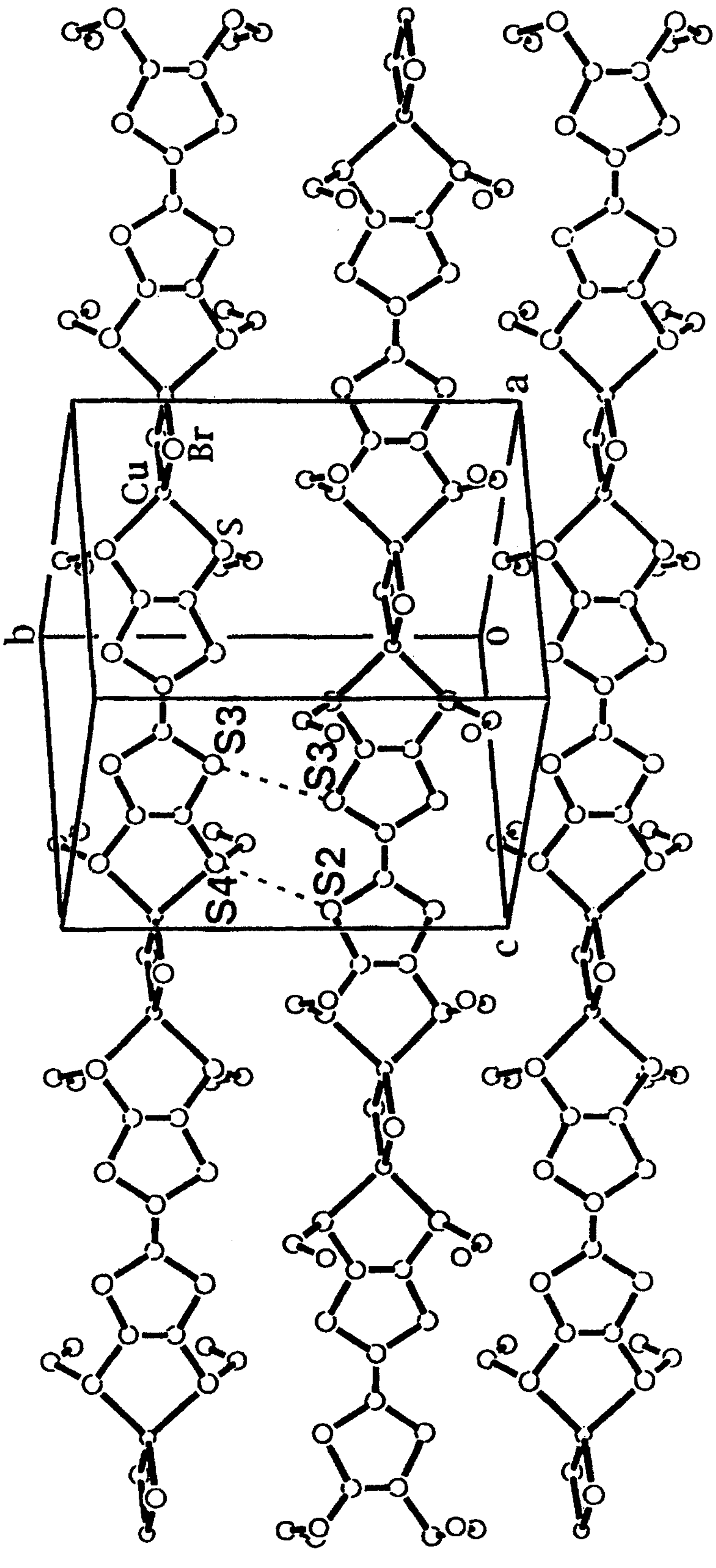

Fig. 4. The polymeric chain arrangement in the crystal of 2.

Table 3. Selected bond lengths (Å) and angles (°) of complex **2**

Cu(1)—Br(1)	2.419(1)	C(3)—C(3′)	1.337(7)
Cu(1)—Br(2)	2.479(2)	C(4)—S(2)	1.754(3)
Cu(1)—S(1)	2.349(1)	C(4)—C(5)	1.345(6)
Cu(2)—Br(1)	2.413(1)	C(5)—S(3)	1.754(3)
Cu(2)—Br(2)	2.470(2)	C(6)—S(3)	1.753(3)
Cu(2)—S(4)	2.349(1)	C(6)—C(6′)	1.349(6)
C(1)—C(2)	1.472(8)	C(6)—S(4)	1.746(3)
C(2)—S(1)	1.832(5)	C(7)—S(4)	1.823(4)
C(3)—S(1)	1.752(3)	C(7)—C(8)	1.494(6)
C(3)—S(2)	1.757(3)		
Br(1)—Cu(1)—Br(2)	108.86(5)	Br(1)—Cu(2)—Br(2)	109.34(5)
Br(1)—Cu(1)—S(1)	120.94(4)	Br(1)—Cu(2)—S(4)	121.07(4)
Br(2)—Cu(1)—S(1)	106.34(4)	Br(2)—Cu(2)—S(4)	106.19(4)
S(1)—Cu(1)—S(1′)	91.39(6)	S(4)—Cu(2)—S(4′)	90.74(6)

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