

S...S Contact-assembled tetrathiafulvalene derivatives of copper(I) and silver(I) co-ordination polymers and organic radical cation salt

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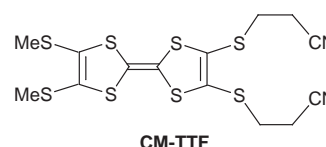
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The reactions of 2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (CM-TTF) with copper(II) and silver(I) salts resulted in the isolation and structural characterization of S...S contact assembled co-ordination polymers, $[\text{Cu}(\text{CM-TTF})][\text{ClO}_4] \cdot \text{thf}$ **1** and $[\text{Ag}(\text{CM-TTF})(\text{CF}_3\text{SO}_3)]$ **2**, and radical cation salt, $[\text{CM-TTF}][\text{CuCl}_2]$ **3**. Both **1** and **2** are 1 : 1 metal-ligand complexes in which the metal ions and CM-TTF molecules are alternately linked forming two-dimensional networks and infinite linear chain structures, respectively, which are further reinforced by close intermolecular S...S interactions. The structure of **3** consists of segregated stacks of $\text{CM-TTF}^{\cdot+}$ donors and CuCl_2^- acceptors associated *via* short S...Cl contacts leading to an alternate donor-acceptor-donor columnar arrangement. The complexes were additionally characterized by IR, UV/VIS and ESR spectra as well as electrical resistivity measurements. All the complexes and their corresponding air-oxidized species are poor electrical conductors, but they show typical charge-transfer ESR signals and electronic absorptions. Complex **3** was found to exhibit transition from antiferro- to ferro-magnetic coupling upon air oxidation.

Coupled with suitable electron acceptors, tetrathiafulvalene (TTF) and its derivatives can give rise to conductive or superconductive molecular stacks through S...S molecular interactions.¹ Over the last two decades there has been an unabated interest in chemical modifications of the TTF framework by introducing additional sulfur atoms at the periphery of the TTF skeleton.^{1,2} Efforts in synthesis and characterization have revealed a wide range of such compounds as bis(ethylenedithio)-TTF (BEDT-TTF) and tetrakis(alkylthio)-substituted TTFs ($\text{TTC}_n\text{-TTF}$). These strong π -molecular donors often react with acceptor molecules to form ion-radical salts and charge-transfer compounds in which the prominent role of the outer sulfur atoms has been recognized for their highly conducting or superconducting behaviours.³⁻⁸

We therefore focused our attention on the peripherally modified TTF derivatives such as $\text{TTC}_n\text{-TTF}$ ^{5,7,8} and 4,5-ethylenedithio-1,3-dithiole-2-thione⁹ which has a similar structure to half of BEDT-TTF, as building blocks to generate conductive supramolecular and macromolecular systems. Our general synthetic strategy is based on (1) formation of extended polymeric structure by the co-ordination of the outer sulfur atoms of the derived TTF moiety to metal ions and (2) bridge formation between the segregated columns of the co-ordination polymeric chains by selective, intermolecular S...S contacts. These two measures effectively enhanced dimensionality and conductivity of the resulted organic charge-transfer complexes.¹⁰ Recently Becher¹¹ and Underhill¹² and co-workers have developed routes for synthesis of a variety of unsymmetrical TTF derivatives. These sulfur-rich ligands have the ability to act as a bridge between different metal centres to give polynuclear complexes with an increased potential for intermolecular stacking and orbital overlap which could lead to enhanced conduction properties. In this regard, we present our results with one of such ligands, 2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (CM-TTF). Its synthesis, structures and conductive properties with copper(I) and silver(I) ions are described.



Results and discussion

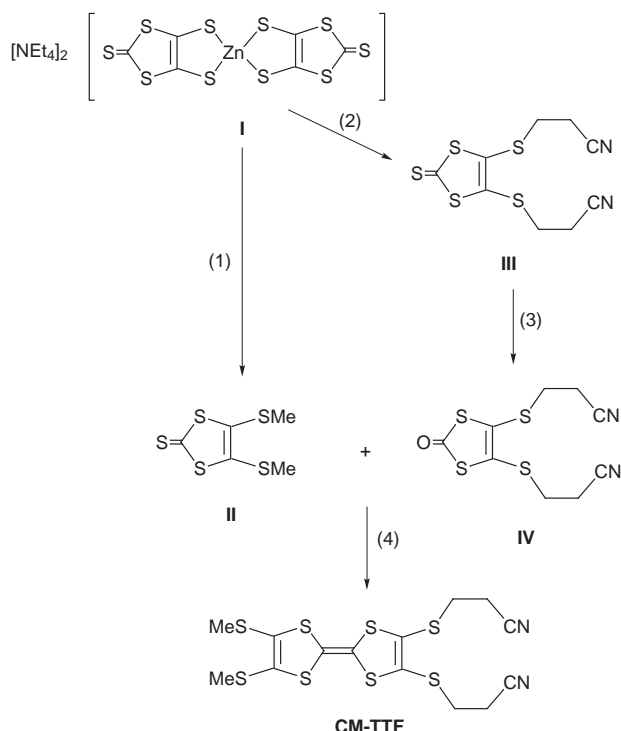
Synthesis

The tetrathiafulvalene derivative CM-TTF was prepared from $[\text{NEt}_4]_2[\text{Zn}(\text{C}_3\text{S}_5)_2]$, where $\text{C}_3\text{S}_5 = 4,5\text{-disulfanyl-1,3-dithiole-2-thione}$, following the methods of Becher and Underhill (Scheme 1).¹¹⁻¹³ Alkylation of the zinc complex **I** in acetonitrile produced 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione **II**. The reaction of **II** and 4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiol-2-one **IV** in neat triethyl phosphite at 110 °C afforded CM-TTF as a deep red precipitate in 58% yield.

The reaction of equimolar CM-TTF and silver(I) triflate in thf proceeded readily to yield $[\text{Ag}(\text{CM-TTF})(\text{CF}_3\text{SO}_3)]$ **2**. Similar reactions of copper(II) salts $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with CM-TTF in 1 : 2 and 1 : 1 ratios, respectively, afforded copper(I) complexes $[\text{Cu}(\text{CM-TTF})][\text{ClO}_4] \cdot \text{thf}$ **1** and $[\text{CM-TTF}][\text{CuCl}_2]$ **3**. It is well known that TTF can easily be oxidized by copper(II) salts forming charge-transfer or radical cation species.^{6e,7a,14-17} The results of elemental analysis, electronic and infrared spectroscopy, and structural analysis (see below) of **1** and **3** are consistent with the suggested stoichiometries and confirm formation of the radical cation $\text{CM-TTF}^{\cdot+}$ in the systems. While the one electron oxidation of CM-TTF by CuCl_2 resulted in formation of $\text{CM-TTF}^{\cdot+}$ cation and CuCl_2^- ion in **3** is clear-cut, the formation of copper(I) species in **1** may be represented by eqn. (1).



Compounds **2** and **3** are reasonably stable at room temperature for several days. However, great care is needed to obtain



Scheme 1 (1) MeCN, MeI, reflux; (2) MeCN, BrCH₂CH₂CN, reflux; (3) thf, Hg(MeCO₂)₂, CHCl₃-MeCO₂H; (4) P(OEt)₃, reflux.

satisfactory structural analysis for **1**. The product cannot be dried *in vacuo* and even trying to remove the excess of thf with a slow stream of dry argon resulted in loss of the crystallized solvent molecules. Therefore, the crystal used for structure determination was enclosed in a glass capillary with mother-liquor. Even in the solid state the red crystals of **1** gradually changed to black copper(II) species upon exposure to air.

Description of structures

2-D co-ordination polymer [Cu(CM-TTF)][ClO₄]-thf **1.** Complex **1** comprises discrete perchlorate anions and two-dimensional infinite undulated nets of cationic meshes as shown in Fig. 1. These meshes are formed by alternate four-coordinate copper ions and tridentate CM-TTF molecules. The distorted tetrahedral co-ordination sphere around the copper atom is comprised of two methylsulfanyl sulfur atoms and two cyano nitrogen atoms of three separate CM-TTF molecules. Each ligand group in turn bridges three copper(i) ions in a head-to-tail mode forming a coupled [Cu₂(CM-TTF)₂] core which is linked to its adjacent counterpart through the span of the two CN groups between two separate metal centres. This gives a 2-D co-ordination polymeric structure spreading on the *bc* plane. The bond distances of Cu-S [2.335(5) and 2.327(4) Å] and Cu-N [1.96(1) and 1.97(1) Å] are normal,¹⁰ Table 1, and the bond angles around the metal centre range from 90.6(2) [S(5)-Cu-S(6)] to 123.5(4)° [S(6)-Cu-N(2)]. The shortest S...S distance between two CM-TTF groups in the dimeric unit is 4.08 Å, significantly longer than the van der Waals radius sum (3.7 Å). Thus, the S...S interaction within the dimeric unit is negligible. On the other hand, the shortest S...S distance of 3.72 Å between the neighboring dimeric units indicates the presence of S...S interacting networks in the 2-D sheets.

1-D linear co-ordination polymer [Ag(CM-TTF)(CF₃SO₃)] **2.** Complex **2** crystallizes in the triclinic space group *P*1 with one molecule in the unit cell, the structure of which is depicted in Fig. 2(a) together with the atom numbering scheme. The complex consists of an infinite linear chain arrangement of silver(I) ions bridged by CM-TTF molecules. Each Ag ion adopts a

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

1			
Cu-S(5)	2.335(5)	Cu-S(6)	2.327(4)
Cu-N(1)	1.96(1)	Cu-N(2)	1.97(1)
C(1)-C(2)	1.34(1)	C(5)-C(6)	1.34(1)
S(5)-Cu-S(6)	90.6(2)	S(5)-Cu-N(1)	121.6(5)
S(5)-Cu-N(2)	103.7(4)	S(6)-Cu-N(1)	105.8(4)
S(6)-Cu-N(2)	123.5(4)	N(1)-Cu-N(2)	111.4(5)
2			
Ag-S(1)	2.618(1)	Ag-N(1)	2.410(5)
Ag-N(2)	2.277(5)	Ag-S(2)	2.879(2)
Ag-O(1)	2.537(6)	C(5)-C(6)	1.334(6)
S(1)-Ag-S(2)	74.11(4)	S(1)-Ag-O(1)	118.7(2)
S(1)-Ag-N(1)	94.9(1)	S(1)-Ag-N(2)	154.8(1)
S(2)-Ag-O(1)	96.1(2)	S(2)-Ag-N(1)	162.7(2)
S(2)-Ag-N(2)	93.6(2)	O(1)-Ag-N(1)	101.0(2)
N(1)-Ag-N(2)	91.1(2)	O(1)-Ag-N(2)	83.8(2)
3			
Cu-Cl(1)	2.087(2)	Cu-Cl(2)	2.078(2)
C(5)-C(6)	1.382(8)		
Cl(1)-Cu-Cl(1')	180	Cl(2)-Cu-Cl(2')	180

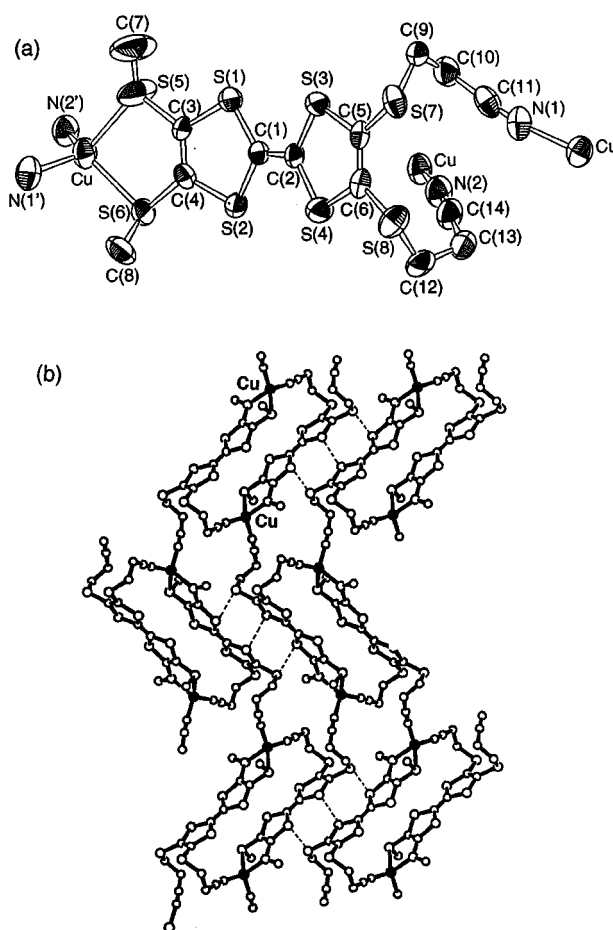


Fig. 1 Crystal structure of [Cu(CM-TTF)][ClO₄]-thf **1**: (a) labeling scheme and (b) molecular packing showing 2-D network reinforced by intermolecular S...S contacts of 3.692 Å (dashed lines).

five-co-ordinate square-pyramidal geometry comprising two S, Ag-S 2.618(1) and 2.879(2) Å, and two N atoms, Ag-N 2.277(5) and 2.410(5) Å, from two separate CM-TTF molecules forming the basal plane with the furthest oxygen atom of the triflate located at the apex. The stereochemistry of silver(I)

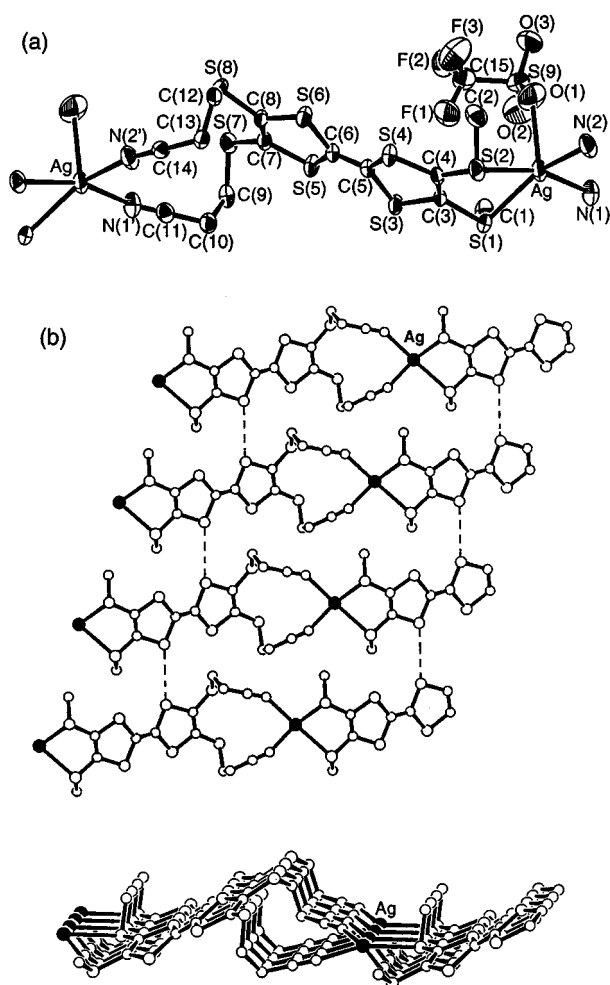


Fig. 2 Crystal structure of $[\text{Ag}(\text{CM-TTF})(\text{CF}_3\text{SO}_3)]$ **2**: (a) labeling scheme and (b) top and side views of the molecular packing showing linear chains associated by intermolecular $\text{S} \cdots \text{S}$ contacts of 3.686 Å (dashed lines).

complexes is dominated by four- and three-co-ordination. In contrast five-co-ordinate silver(i) compounds are unusual.^{9a} The apical $\text{Ag}-\text{O}$ bond distance of 2.537(6) is about 0.25–0.3 Å longer than the normal $\text{Ag}-\text{O}$ distance, consistent with the fifth-ligand elongation of a square-based pyramidal stereochemistry. The Ag atom is lifted out of the basal plane by a distance of 0.24 Å in a direction towards the terminal oxygen atom. Each CM-TTF molecule bridges two metal centres, rather than three as observed in **1**, with two terminal methylsulfanyl and two cyano-groups, each chelating one Ag atom forming six-membered and thirteen-membered rings, respectively. This gives an infinite linear chain structure. The adjacent chains approach each other through $\text{S} \cdots \text{S}$ contacts of 3.686 Å, forming a two-dimensional network, Fig. 2(b). The structure is reminiscent of a series of copper(i) complexes ($\text{TTC}_n\text{-TTF}$)- CuX ($n = 2$ or 3 and $\text{X} = \text{Cl}$, Br or I) where each ligand group bridges two metal centres with its four alkylsulfanyl sulfur atoms in a chain fashion.⁸

Organic radical cation salt $[\text{CM-TTF}][\text{CuCl}_2]$ **3.** Oxidation of CM-TTF with CuCl_2 in thf yielded the organic radical cation salt **3**. The atom numbering scheme is given in Fig. 3(a) while a projection of the crystal structure is shown in Fig. 3(b). There are two crystallographically independent linear CuCl_2^- acceptors in the structure. The cationic donors CM-TTF^{•+} are paired in a head-to-tail mode to assume a dimeric structure, with close intradimeric $\text{S} \cdots \text{S}$ contacts of 3.439 Å between the central TTF sulfur atoms S(3) and S(6') and 3.467 Å between S(4) and S(5'). Coupled with two dimeric units is one CuCl_2^- anion, i.e.,

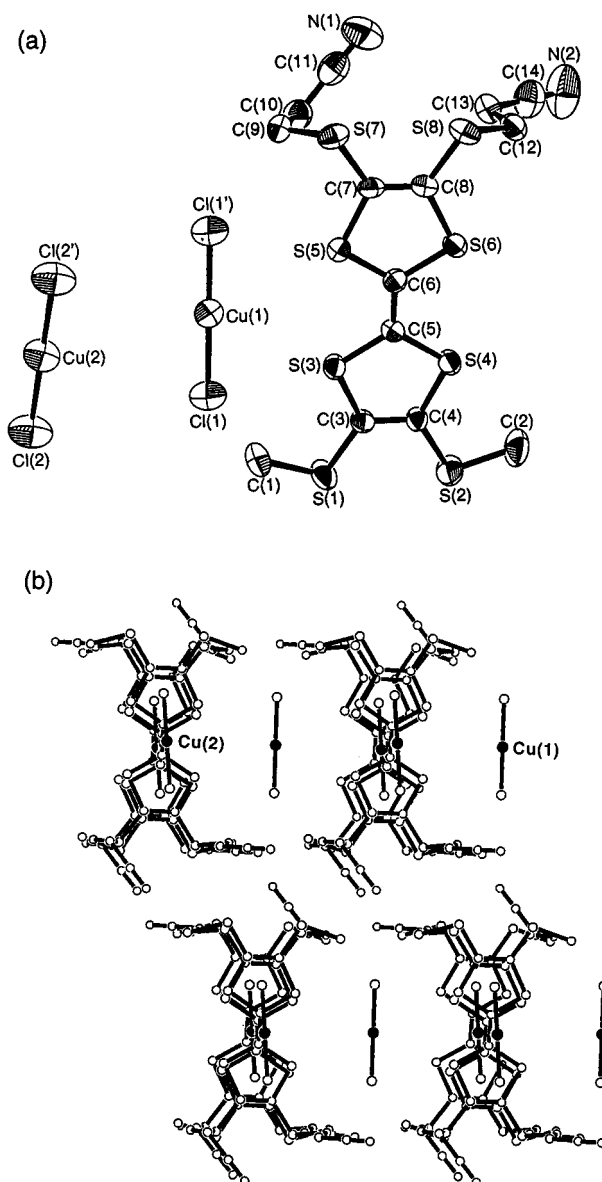


Fig. 3 Crystal structure of $[\text{CM-TTF}][\text{CuCl}_2]$ **3**: (a) labeling scheme and (b) molecular packing viewed on the bc plane showing segregated stacks of donors and acceptors.

$\text{Cl}(2)-\text{Cu}(2)-\text{Cl}(2')$, and the association between them occurs via a short $\text{S} \cdots \text{Cl}$ contact of 3.709 Å between S(6) and Cl(2), leading to an alternating DDA stacking along the a axis, Fig. 4. The donor–acceptor molecular separation is 3.44 Å defined by the copper atom to the least-squares plane of the TTF moiety. This distance is well within the optimum donor–acceptor range suggested by Bent¹⁸ (2.3–3.6) and slightly longer than the range suggested by Slifkin¹⁹ (3.00–3.4 Å). Furthermore, the adjacent columns of donors approach each other through the terminal sulfur–sulfur interactions with $\text{S}(1) \cdots \text{S}(1')$ separation of 3.526 Å. Such connection gives rise to two-dimensional networks connected by both $\text{S} \cdots \text{S}$ and $\text{S} \cdots \text{Cl}$ contacts and leaves a void volume where the second type of CuCl_2^- anions, i.e. $\text{Cl}(1)-\text{Cu}(1)-\text{Cl}(1')$, is located in a segregated column and weakly interact with the donor having $\text{S} \cdots \text{Cl}$ contacts of 3.79 Å, Fig. 3(b).

Previously, similar direct redox reactions of copper(ii) halides with TTF or its analogues have yielded a variety of charge-transfer or radical cation complexes that incorporate copper halide as acceptors.^{6e,7a,14–17} Among 1:1 charge-transfer complexes such as $[\text{TTC}_1\text{-TTF}][\text{CuCl}_2]$,^{6e} $[\text{TTC}_2\text{-TTF}][\text{Cu}_2\text{X}_6]$ ($\text{X} = \text{Cl}$ or Br),^{7a} $(\text{TTF})_n\text{CuX}_2$ ($\text{X} = \text{Cl}$, Br or I),¹⁵ $(\text{TTF})\text{-Cu}(\text{SCN})_2$ ¹⁶ and $(\text{BEDT-TTF})\text{CuCl}_2$,¹⁷ the molecular packing

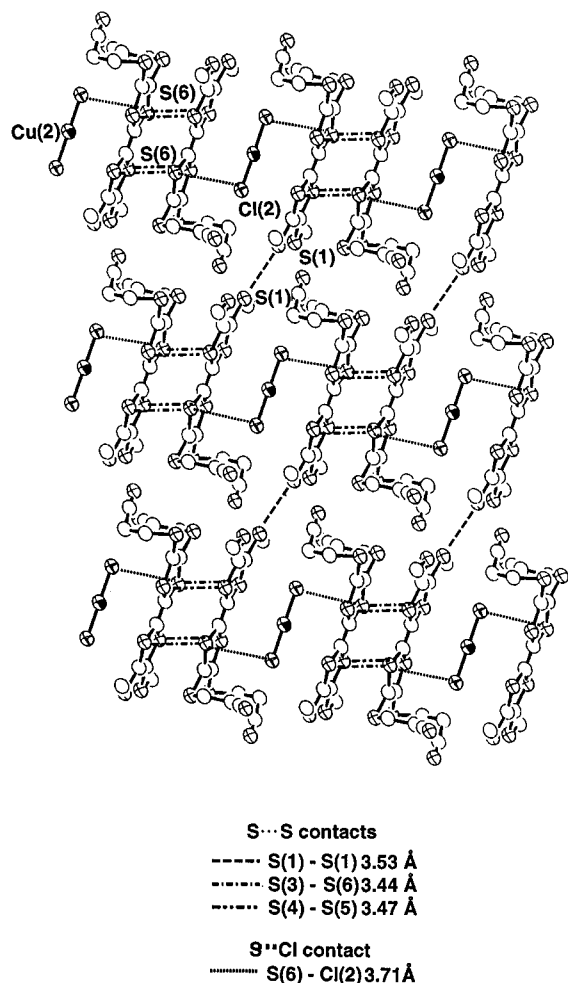


Fig. 4 Unit cell packing diagram of $[\text{CM-TTF}][\text{CuCl}_2]$ **3** viewed on the ac plane [$\text{Cl}(1)\text{--Cu}(1)\text{--Cl}(1')$ ions omitted for clarity] showing column of coupled $\text{CM-TTF}^{+\bullet}$ dimers incorporating $\text{Cl}(2)\text{--Cu}(2)\text{--Cl}(2')$ ions.

usually involves two segregated stacks of donors and acceptors. The most striking structural aspect of complex **3** is the donor–acceptor stacking sequence, incorporating half the acceptor molecules into the columnar donor dimeric units, Fig. 4. To our knowledge, this is the first reported instance of such a sequence for this type of complexes. Apart from this, the structures of the individual radical cations or anions in **3** provided no surprises: the structural parameters for CuCl_2^- were within experimental error of those found for the same ion in the TTF complexes.^{6e}

The central $\text{C}=\text{C}$ bond distance of the TTF unit is the charge-sensitive parameter for all the TTF-type molecules, which is expected to increase with decreasing electron density in the highest occupied (bonding) molecular orbitals.^{6c,20} For example, in a series of $\text{TTC}_n\text{--TTF}^0$, $\text{TTC}_n\text{--TTF}^{+\bullet}$ and $\text{TTC}_n\text{--TTF}^{2+}$ complexes the $\text{C}=\text{C}$ bond distances have been reported as 1.33–1.35, 1.38–1.40 and 1.42–1.43 Å, respectively.^{5–7} This distance for the $\text{CM-TTF}^{+\bullet}$ entity in **3** is found to be 1.382(8) Å. By comparison, the corresponding distances for **1** and **2** are 1.34(1) and 1.334(6) Å, respectively. It leaves little doubt that the $\text{C}=\text{C}$ bond distance observed in **3** corresponds to the monovalent cation $\text{CM-TTF}^{+\bullet}$ species.

Physicochemical properties

Both the IR and electronic spectra provide important information about the oxidation state of CM-TTF in the complexes. The infrared spectra were recorded in the region 4000–400 cm^{-1} on KBr discs. It is known that the central $\text{C}=\text{C}$ stretching of TTF undergoes a large frequency shift on oxidation,^{20–22} for

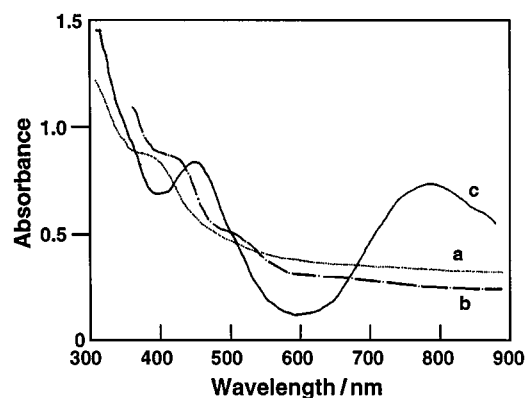


Fig. 5 Electronic spectra of CM-TTF (**a**), $[\text{Cu}(\text{CM-TTF})][\text{ClO}_4]\cdot\text{thf}$ **1** (**b**) and $[\text{CM-TTF}][\text{CuCl}_2]$ **3** (**c**).

example from 1512 cm^{-1} in neutral TTF²³ to 1413 cm^{-1} in $[\text{TTF}]\text{Br}$.²² The unco-ordinated CM-TTF molecule has several very distinctive signals, including $\nu_{\text{C-H}}$ (2922), $\nu_{\text{C=N}}$ (2253) and $\nu_{\text{C=C}}$ (1420 cm^{-1}). While the $\text{C}=\text{C}$ stretching bands for the coordination polymers **1** and **2** were observed at 1416 and 1419 cm^{-1} , respectively, the IR spectrum of the donor–acceptor complex **3** revealed two sharp bands at 1387 and 1339 cm^{-1} , Table 2. This finding indicates that CM-TTF exists as a neutral ligand in **1** and **2**, but as a cation in **3**. In the UV/VIS electronic spectra of CM-TTF and all its complexes a strong absorption band at ca. 400–470 nm was detected which is ascribable to local excitation of the organic molecules, Fig. 5. In addition, **1** and **2** also exhibit a weak shoulder at ca. 530 nm. By contrast, complex **3** does not show such a shoulder, instead it exhibits a strong broad band at 790 nm, which may be assigned as CM-TTF/CM-TTF⁺⁺ charge-transfer transitions.^{6e} Similar broad bands were detected at 775 and 793 nm, respectively, for our recently reported I_2 -doped polymeric copper(i) complexes $[\text{Cu}(\text{TTC}_2\text{--TTF})][\text{BF}_4][\text{I}_3]_{0.33}$ and $[\text{Cu}(\text{TTC}_3\text{--TTF})][\text{BF}_4][\text{I}_3]_{0.33}$.^{7d}

An X-band ESR spectrum of a microcrystalline sample of complex **1** observed at room temperature consists of a broad ($\Delta H = 2.0$ mT) symmetric line at $g = 2.008$. On the basis of a comparison of g values reported for $\text{TTF}^{+\bullet}$ radicals in the solid state,^{15a} the observed signal is reasonably assigned to CM-TTF⁺⁺ radicals broadened by anisotropy. However, the spin density estimated from comparison with dpph (diphenylpicrylhydrazyl) standard was less than 1%. It is considered that a part of the radicals formed in reaction (1) might be incorporated in the crystals. Consequently, the compound is an insulator at room temperature. On deliberate exposure to air red crystals of **1** gradually changed to black and the ESR line broadening persists until finally the line splits into a doublet and a second signal attributable to copper(ii) ions was detected at $g = 2.187$. It is interesting that 1 month later the black sample showed increased spin density of 15.9% and became semi-conductive with $\sigma_{25^\circ\text{C}} = 10^{-7} \text{ S cm}^{-1}$.

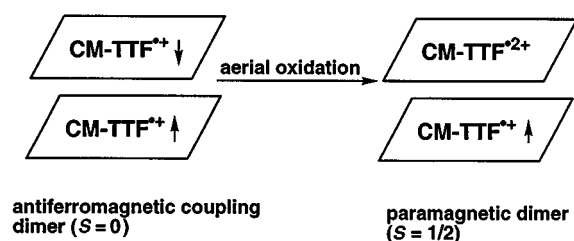
The ESR spectrum of complex **2** consists of a broad asymmetric line at $g = 2.007$. Upon exposure to air the intensity of the signal decreases and the linewidth increases while the g value remains virtually constant. The fact that both the linewidth and doublet splitting are sensitive to oxidation by air is interpreted as arising from spin exchange between mobile excitons. That the excitations must be largely confined to a single chain is clear from Fig. 2(b). In contrast to **1**, the complex is found to be an insulator even after long exposure to air. The conductivity dependence on metal ions in CM-TTF complexes suggests that copper(i) ion is a better candidate in the design of conductive materials in the system.

The spectrum obtained for complex **3** is isotropic with $g = 2.009$. The thermal variation of the molar susceptibility is not shown since it exhibits practically a Curie-law behaviour. Since magnetic susceptibility measured by SQUID does not

Table 2 Physical properties of CM-TTF and its derived compounds 1–3

Compound	$\tilde{\nu}_{\text{C-C}}/\text{cm}^{-1}$	UV/VIS (λ/nm)	ESR		Conductivity, $\sigma_{25^\circ\text{C}}/\text{S cm}^{-1}$
			g	Spin density (%)	
CM-TTF	1420	400			
1	1416	440, 530	2.008	0.64	Non-conductive
*			2.006	15.9	10^{-7}
			2.187		
2	1419	430, 520	2.007	0.5	Non-conductive
*			2.007	0.5	Non-conductive
3	1387, 1339	470, 790	2.009	0.42	Non-conductive
*			2.010	10.1	10^{-7}

* Air oxidized sample.

**Scheme 2**

show temperature dependence except for Curie-like behaviour at low temperature, the observed ESR signal is not due to thermally activated spins but intrinsic radical species with low concentration. This implies the spin-pair formation occurs through $S \cdots S$ contacts between adjacent CM-TTF $^{\bullet+}$ radicals, not through the CuCl_2^- anion. The spin density was found to be significantly small (0.42%), indicating antiferromagnetic coupling between two cation radicals CM-TTF $^{\bullet+}$ in the dimeric unit. The spin density increased to 10.1% on exposure to air for 3 d, but both the intensity and the linewidth remain essentially unchanged and the g value is almost constant (2.010). This finding shows that part of the antiferromagnetic coupling dimer is oxidized to the dication CM-TTF $^{\bullet2+}$ as shown in Scheme 2. Although **3** is essentially insulating, its oxidized species exhibits conductivity with $\sigma_{25^\circ\text{C}} = 10^{-7} \text{ S cm}^{-1}$.

Conclusion

So far most of the TTF-containing conductive compounds are composed of organic radical ions. Although some of them contain metal atoms in an anion part, these metal ions are not co-ordinated to the organic molecules.^{1e} Complexes **1** and **2** presented here add new examples to the limited number of known metallotetrathiafulvalene co-ordination polymers.^{5,7} It has been shown that, due to the attachments of the methylsulfanyl group at one end of TTF and the cyanoethylsulfanyl group at the other, the unsymmetrical TTF derivative CM-TTF indeed displays unique co-ordination flexibility which has never been described in previously reported co-ordination complexes containing symmetrical TTF analogues. Apart from being able to chelate two metal ions with the terminal MeS and CN groups forming a linear chain structure, it can also bridge three metal ions because the two cyanoethylsulfanyl groups are flexible enough to bite two metal centres forming a 2-D network structure. Nevertheless, the basic feature of the TTF moiety for formation of the fully oxidized or completely charge transferred complex is retained as we observed here in **3**. Although all the complexes and their corresponding air-oxidized species are poorly conductive, they show typical charge-transfer ESR signals and electronic absorptions. The intrinsic transition from antiferro- to ferro-magnetic coupling observed in complex **3**, in particular, certainly deserves further investigation.

Experimental

General

All chemicals were reagent grade. Reactions and manipulations were carried out under an argon atmosphere by using the standard Schlenk vacuum line techniques. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use. High-purity argon was used to deoxygenate solvents. Copper(II) perchlorate hexahydrate purchased from Tokyo, Kasei Kogyo Co. Ltd. was dried at 60°C under reduced pressure for 5 h before use. Silver triflate was from Aldrich. All other chemicals were from Wako Pure Chemical, Inc. and used without further purification. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. The IR spectra were recorded as KBr discs on a JASCO 8000 FT-IR spectrometer, UV/VIS spectra on a Hitachi 150-20 spectrophotometer and ESR spectra on a JEOL JES-TE200 ESR spectrometer. The electrical conductivity of a compacted disc of the complexes was measured by conventional four-probe methods at room temperature. Silical-gel TLC and column chromatography were carried out on a Merck precoated TLC no. 5715 and Merck Kieselgel 60 no. 7734 or 9385, respectively. **CAUTION:** although no problems were encountered during the preparation of the perchlorate salt described below, suitable care and precautions should be taken when handling such potentially hazardous compounds.

Syntheses

2-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (CM-TTF). The compound was synthesized by the improved literature methods (Scheme 1).^{11–13} Coupling of compounds 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione **II** (4 g, 0.17 mol) and 4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiol-2-one **IV** (5 g, 0.17 mol) in neat $\text{P}(\text{OEt})_3$ (100 cm^3) at reflux for 1 h produced a deep green precipitate which was filtered off, washed with water and dried in air. The residue was purified by silica gel chromatography using dichloromethane as eluent to give the product as a deep red solid (58%), mp $83\text{--}85^\circ\text{C}$ (Found: C, 36.32; H, 2.98; N, 6.12. $\text{C}_7\text{H}_7\text{NS}_4$ requires C, 36.05; H, 3.00; N, 6.01%). $\tilde{\nu}_{\text{max}}$ (KBr)/ cm^{-1} 2922, 2253, 1420, 1305, 1277, 1248, 966, 893, 797 and 779.

[Cu(CM-TTF)][ClO₄] \cdot thf **1.** A thf solution (10 cm^3) containing CM-TTF (23.3 mg, 0.05 mmol) was mixed with an acetone solution (10 cm^3) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (9.3 mg, 0.025 mmol). After stirring for 10 min the mixture was filtered. The filtrate was introduced into a 7 mm diameter glass tube which was sealed under an argon atmosphere. After standing at room temperature for 2 weeks red brick crystals of complex **1** were obtained (Found: C, 29.84; H, 2.86; N, 4.10. $\text{C}_{18}\text{H}_{22}\text{ClCuN}_2\text{O}_5\text{S}_8$ requires C, 30.77; H, 3.13; N, 3.99%).

[Ag(CM-TTF)(CF₃SO₃)] **2.** A thf solution (3 cm^3) containing CM-TTF (18.7 mg, 0.04 mmol) was mixed with an

Table 3 Crystal and refinement data for complexes 1–3

	1	2	3
Molecular formula	C ₁₈ H ₂₂ ClCuN ₂ O ₅ S ₈	C ₁₅ H ₁₄ AgF ₃ N ₂ O ₃ S ₉	C ₁₄ H ₁₄ Cl ₂ CuN ₂ S ₈
<i>M</i>	701.86	723.69	601.21
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.979(3)	7.946(3)	10.487(2)
<i>b</i> /Å	25.785(4)	11.202(4)	13.620(6)
<i>c</i> /Å	11.086(4)	7.707(3)	9.908(8)
<i>a</i> °		92.95(3)	107.95(5)
<i>β</i> °	92.51(3)	109.25(2)	90.54(5)
<i>γ</i> °		93.28(3)	74.99(3)
<i>U</i> /Å ³	2849(1)	644.8(4)	1296(1)
<i>Z</i>	4	1	2
<i>D</i> _c /g cm ^{−3}	1.636	1.864	1.540
Crystal size/mm	0.20 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.15
<i>F</i> (000)	1432.0	360.0	606.0
<i>μ</i> (Mo-Kα)/cm ^{−1}	14.79	15.52	16.96
No. reflections measured	7070	3181	6278
No. observations	2963	2710	2733
	[<i>I</i> > 2.50σ(<i>I</i>)]	[<i>I</i> > 3.00σ(<i>I</i>)]	[<i>I</i> > 3.00σ(<i>I</i>)]
No. parameters	291	298	247
<i>R</i> ^a	0.092	0.027	0.053
<i>R</i> ' ^b	0.101	0.034	0.062
Goodness of fit	2.54	1.52	1.39

$$^a R = \Sigma(|F_o - F_c|)/\Sigma|F_o|. \quad ^b R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}}.$$

acetonitrile solution (1 cm³) of Ag(CF₃SO₃) (10.3 mg, 0.04 mmol). The mixture was stirred and filtered, and the filtrate introduced into a glass tube and layered with 2 cm³ of diethyl ether. After standing at room temperature for 1 d red plate crystals of complex **2** were obtained (Found: C, 24.90; H, 1.91; N, 3.91. C₁₅H₁₄AgF₃N₂O₃S₉ requires C, 24.87; H, 1.93; N, 3.87%).

[CM-TTF)][CuCl₂] 3. This compound was synthesized in a similar manner to that for **2**. The compound CM-TTF (18.7 mg, 0.04 mmol) in 4 cm³ of thf was added to an acetone solution (4 cm³) containing CuCl₂·2H₂O (6.8 mg, 0.04 mmol). The mixture was treated as that for **2** and gave the final product as black plate crystals (Found: C, 28.21; H, 2.65; N, 4.39. C₇H₁₄Cl₂CuN₂S₈ requires C, 27.95; H, 2.33; N, 4.65%).

Crystallography

All measurements were carried out at room temperature on a Rigaku AFC-5R diffractometer for complex **2**, and on a Rigaku AFC-7R diffractometer for **1** and **3**. Crystallographic data are summarized in Table 3. For **2** and **3** a suitable single crystal was mounted on a glass fiber while that for **1** was enclosed in a glass capillary. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections in which the appropriate cell angles were constrained to their ideal values. Intensity data were collected by using standard scan techniques (ω – 2θ). Space groups were selected on the basis of systematic absences and intensity statistics which in all cases led to satisfactory refinements. For **2** and **3** the intensities of 3 standard reflections, monitored at 150 reflection intervals throughout data collection, remained constant within experimental error, indicating crystal and electronic stability. Thus, no decay correction was applied. Over the course of data collection for **1** the standards increased by 0.6%. A linear correction factor was applied to the data to account for this phenomenon.

For complexes **1** and **3** an empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.80 to 0.99 and 0.77 to 0.99, respectively. For **2** azimuthal scans of several reflections indicated no need for an absorption correction. All intensity data were corrected for Lorentz-polarization effects.

The structures were solved by a direct method²⁵ and expanded using Fourier techniques.²⁶ All the full-occupancy non-H atoms were refined anisotropically. The crystal of **1** included one thf molecule per complex as solvent of crystallization. It was disordered heavily and was refined isotropically. The highest residual peak for **1** resulted from this disorder. Hydrogen atoms of the three structures were introduced in their calculated positions, except for those of the disordered thf molecule in **1**. The positions of all the hydrogen atoms were included, but not refined. Computations were carried out using TEXSAN program systems.²⁷

CCDC reference number 186/1125.

See <http://www.rsc.org/suppdata/dt/1998/3255/> for crystallographic files in .cif format.

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