

Building of 2D Sheet of Tetrakis(methylthio)tetrathiafulvalenes Coordinating to Copper(I) Halides with Zigzag and Helical Frames and the 3D Network through the S··S Contacts

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Three copper (I) complexes with tetrakis(methylthio)tetrathiafulvalene (TMT-TTF), $[(\text{Cu}_2(\mu\text{-X})_2(\mu\text{-TMT-TTF}))_\infty]$ (X = Cl, **1**; X = Br, **2**; and X = I, **3**) were synthesized and their molecular structures and packing were determined by using single crystal X-ray diffraction methods. **1** is 2D sheet composed of TMT-TTF molecules arranged between new zigzag frames of CuCl and 3D structure is formed through S··S contacts of 3.53 and 3.63 Å between the 2D sheets. **2** has a 2D structure in which TMT-TTF molecules are connected between novel helical frames of CuBr and the S··S contacts of 3.68 Å exist between the neighboring molecules. The methyl thioether groups of TMT-TTF in **3** are coordinated to the coppers of rhomboid Cu_2I_2 to give linear chains. The black I₂-doped compounds **1–3** show a new broad band at ca 880 nm indicative of the oxidation of TMT-TTF molecules and gave electric conductivities of $10^{-3.6}$, $10^{-2.1}$, and $10^{-1.7}$ S cm⁻¹, respectively. Crystal data: **1**, monoclinic $P2_1/n$, $a = 6.657(8)$ Å, $b = 6.23(1)$ Å, $c = 24.067(8)$ Å, $\beta = 91.77(7)^\circ$, $V = 998(2)$ Å³, $Z = 4$, 1913 reflections, $R = 0.028$; **2**, monoclinic $C2/c$, $a = 15.443(3)$ Å, $b = 4.906(4)$ Å, $c = 26.686(1)$ Å, $\beta = 96.36(1)^\circ$, $V = 2009(2)$ Å³, $Z = 8$, 1304 reflections, $R = 0.037$; **3**, monoclinic $C2/m$, $a = 7.921(3)$ Å, $b = 13.266(6)$ Å, $c = 10.498(6)$ Å, $\beta = 107.79(4)^\circ$, $V = 1052(2)$ Å³, $Z = 8$, 1072 reflections, $R = 0.027$.

Introduction

Recently, a large numbers of organic conductors of one-component materials and CT complexes have been synthesized and studied progressively, because metallic conductivity and superconductivity are the most fascinating phenomena to have been discovered in these materials.^{1–4} Perylene-bromide complex with high conductivity was reported in 1954.⁵ It was found that TCNQ salts are organic semiconductors in 1962,⁶ and 1:1 CT complex of (TTF)(TCNQ) exhibits metallic behavior.⁷ Organic superconductivity was first reported for (TMTSF)₂X (TMTSF = tetramethylselenafulvalene; X = ClO₄⁻, PF₆⁻).^{8,9} The two-dimensionally superconducting compound κ -(BEDT-TTF)₂[Cu(NCS)₂] has Tc of about 10 K, where BEDT-TTF is the organic electron donor bis(ethylenedithio)-tetrathiafulvalene.¹⁰ BEDT-TTF layers connected through only

the S··S contacts are separated by an insulating layer of the polymer anions of Cu(NCS)₂.

The global challenge for chemists working on a conducting CT complex is the preparation of new molecular systems which meet the stringent requirements at the intermolecular level for high conductivity or superconductivity. Since our abilities to introduce molecules to pack within a crystal lattice in a prescribed fashion is still very limited, the rational design of new conducting compounds is essentially restricted to controlling the key properties of the individual molecules which can be deduced, e.g. planarity, ionization potential/electron affinity, extent of conjugation, etc.² On the other hand, copper ions play an most important role in superconducting copper oxide ceramics with high Tc.⁴ The ions have been however used only a electron acceptor or a counter ion in synthesizing organic CT complexes.^{10–15} If copper ion can be coordinated to TTF derivative to give the coordination polymer it would be expected to be as a new molecule system of which the derivatives are connected by the coordination bonds as well as S··S contact and the properties are changed by copper coordination. In this paper we report the synthesis, crystal structure, and properties of two- and three-dimensional copper halide complexes with TMT-TTF (tetrakis(methylthio)tetrathiafulvalene), and discuss the role of copper halide on the construction of coordination polymer with TMT-TTF.

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- (1) Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whanbo, M.-H. Rational Design of Synthetic Metal Superconductors. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1987; Vol. 35, pp 1–50.
- (2) Bryce, M. R. *Chem. Soc. Rev.* **1991**, 20, 355.
- (3) Cassoux, P.; Valade, L. Molecular Inorganic Superconductors. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; John Wiley & Sons: Chichester, England, 1992; pp 1–58.
- (4) Adrian, F. K.; Cowan, D. O. *Chem. Eng.* **1992**, 24.
- (5) Akamatsu, H.; Inokuchi, H.; Matsunaga, Y. *Nature* **1954**, 173, 168.
- (6) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, 84, 3374.
- (7) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, 95, 948.
- (8) Jerome, D.; Mazand, A.; Ribault, M.; Bechgaard, K. J. *Phys. Lett.* **1980**, 41, L95.
- (9) Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* **1980**, 33, 1119.
- (10) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55.

- (11) Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, 50, 270.
- (12) Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saitou, K.; Ishiguro, T.; Kobayashi, K.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, 55, 3435.
- (13) Papavassiliou, G. C.; Mousdis, G. A.; Zambounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Met.* **1988**, B27, 379.
- (14) Beno, M. A.; Wang, H. H.; Kini, A. M.; Carlson, K. D.; Geiser, U.; Kwok, W. K.; Thompson, J. E.; Williams, J. M.; Ren, J.; Whangbo, M.-H. *Inorg. Chem.* **1990**, 29, 1599.
- (15) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, 29, 2555.

Experimental Section

General Data. All operations were carried out under argon and ethylene by using the standard Schlenk or vacuum line technique. Acetonitrile was purified according to literature.¹⁶ The reagent grade of copper(I) chloride was purified according to literature.¹⁷ Both copper(I) bromide and copper(I) iodide were used without further purification. Reagent grade TMT-TTF was obtained from Tokyo Chemical, Industry Co., Ltd. All other chemicals of reagent grade were used without further purification. Electronic spectra were recorded on a Hitachi spectrometer. Electrical resistivities of compacted pellets were measured by the conventional two-probe technique.

Syntheses. $[(\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-TMT-TTF}))_\infty]$ (**1**). An acetonitrile solution (5 mL) of copper(I) chloride (19.7 mg, 0.2 mM) was added to a THF solution (5 mL) of TMT-TTF (38.9 mg, 0.1 mM) and was stirred for 0.5 h at 25 °C under argon atmosphere. The orange solution was sealed in a glass tube under an argon atmosphere. After this solution was allowed to stand for 3 days in a thermos bottle at 25 °C, orange brick crystals were obtained (yield 46%). Anal. Calcd for $\text{C}_5\text{H}_6\text{S}_4\text{-ClCu}$: C, 19.93; H, 2.06. Found: C, 20.46; H, 2.04.

$[(\text{Cu}_2(\mu\text{-Br})_2(\mu\text{-TMT-TTF}))_\infty]$ (**2**). An acetonitrile solution (2.5 mL) of copper(I) bromide (14.3 mg, 0.1 mM) was added to a THF solution (2.5 mL) of TMT-TTF (19.4 mg, 0.05 mM) and was stirred for 1 h at 50 °C under an argon atmosphere. The orange solution was sealed in a glass tube under an argon atmosphere. After this solution was allowed to stand for 7 days in thermos bottle at 50 °C at the beginning, orange crystals were obtained (yield 49%). Anal. Calcd for $\text{C}_5\text{H}_6\text{S}_4\text{BrCu}$: C, 17.93; H, 1.74. Found: C, 17.77; H, 1.79.

$[(\text{Cu}_2(\mu\text{-I})_2(\mu\text{-TMT-TTF}))_\infty]$ (**3**). Copper(I) iodide (19.1 mg, 0.1 mM) and TMT-TTF (19.4 mg, 0.05 mM) were stirred in acetonitrile (10 mL) for 1 h at 70 °C under an argon atmosphere. The orange solution was sealed in a glass tube under argon atmosphere. After this solution was allowed to stand for 7 days in thermos bottle at 70 °C at the beginning, orange brick crystals were obtained (yield 56.7%). Anal. Calcd for $\text{C}_5\text{H}_6\text{S}_4\text{ICu}$: C, 15.60; H, 1.57. Found: C, 15.70; H, 1.45.

Iodine-Doped Compounds. The orange compounds **1–3** and solid I_2 were separately placed in the sealed Y shape glass tube for 1 month to oxidize partially the compounds of insulator by I_2 vapor, respectively. The black I_2 -doped compounds $\{[(\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-TMT-TTF}))\text{I}_x]_\infty\}$ (**4**), $\{[(\text{Cu}_2(\mu\text{-Br})_2(\mu\text{-TMT-TTF}))\text{I}_x]_\infty\}$ (**5**) and $\{[(\text{Cu}_2(\mu\text{-I})_2(\mu\text{-TMT-TTF}))\text{I}_x]_\infty\}$ (**6**) obtained show a new broad band at ca. 870 nm.

X-ray Data Collections, Structure Solution, and Refinement. Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer at ambient temperature. Crystal data and details of measurements for the copper(I) complexes with TMT-TTF, **1–3** are summarized in Table 1. Standard reflections were monitored every 25 measurements, and no decay in their intensities was observed. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by a direct method¹⁸ and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.¹⁹ Hydrogen atoms were included as a fixed contribution in the last cycle; their temperature factors were assumed to be isotropic. The calculations were performed on the VAX computer by using the TEXAN program

Table 1. Crystal Data for $[(\text{Cu}_2(\mu\text{-X})_2(\mu\text{-TMT-TTF}))_\infty]$

X	Cl (1)	Br (2)	I (3)
chem formula	$\text{Cu}_5\text{H}_6\text{S}_4\text{Cl}$	$\text{Cu}_5\text{H}_6\text{S}_4\text{Br}$	$\text{Cu}_5\text{C}_2.5\text{H}_3\text{S}_2\text{I}_{0.5}$
fw	293.34	337.79	192.40
space group	$P2_1/n$	$C2/c$	$C2/m$
<i>a</i> , Å	6.657(8)	15.443(3)	7.921(3) [7.928(2)] ^c
<i>b</i> , Å	6.23(1)	4.906(4)	13.266(6) [13.272(1)]
<i>c</i> , Å	24.067(8)	26.686(3)	10.498(6) [10.523(2)]
β , deg	91.77(7)	96.36(1)	107.79(4) [107.82(2)]
<i>V</i> , Å ³	998(2)	2009(2)	1050(2) [1054]
<i>Z</i>	4	8	8 [8]
ρ_{calcd} , g·cm ⁻³	1.953	2.233	2.433
<i>T</i> , °C	23	23	23
λ , Å	0.710 69	0.710 69	0.710 69
μ , cm ⁻¹	32.06	68.56	57.00 [56.8]
2θ , deg	55.1	55.0	55.0 [60]
<i>R</i> ^a	0.028	0.037	0.027 [0.027]
<i>R</i> _w ^b	0.044	0.040	0.036 [0.031]

^a $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^b $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2\}^{1/2}$. ^c Reference 36.

Table 2. Positional Parameters and *B*(eq) for $[(\text{CuX})_2(\text{TMT-TTF})_\infty]$ ^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq) ^b
[[CuCl] ₂ (TMT-TTF)] _∞ (1)				
Cu(1)	0.29817(7)	0.05192(7)	0.70788(2)	2.86(2)
Cl(1)	0.29817(2)	-0.0845(1)	0.79488(3)	3.12(4)
S(1)	0.1112(1)	-0.0920(1)	0.63262(3)	2.32(3)
S(2)	0.6024(1)	-0.0630(1)	0.66867(3)	2.33(3)
S(3)	0.2370(1)	-0.3422(2)	0.53436(4)	3.13(4)
S(4)	0.6689(1)	-0.3411(2)	0.56823(4)	3.62(4)
C(1)	0.4802(5)	-0.4351(6)	0.5212(1)	2.8(1)
C(2)	0.5025(5)	-0.2040(5)	0.6111(1)	2.2(1)
C(3)	0.3074(5)	-0.2059(5)	0.5956(1)	2.1(1)
C(4)	0.7003(6)	-0.2794(7)	0.7109(2)	3.3(2)
C(5)	0.0491(7)	0.1332(7)	0.5887(2)	4.3(2)
[[CuBr] ₂ (TMT-TTF)] _∞ (2)				
Cu(1)	0.72177(6)	0.2588(2)	0.70370(3)	4.03(4)
Br(1)	0.85137(5)	0.4840(2)	0.73893(2)	3.52(3)
S(1)	0.6057(1)	0.5063(4)	0.65362(5)	2.90(7)
S(2)	0.7554(1)	0.0567(4)	0.62628(6)	2.84(7)
S(3)	0.4968(1)	0.3008(4)	0.56044(6)	3.45(8)
S(4)	0.6348(1)	-0.0731(4)	0.53341(6)	3.26(7)
C(1)	0.5280(4)	0.044(1)	0.5194(1)	2.8(3)
C(2)	0.6550(4)	0.112(1)	0.5898(2)	2.5(3)
C(3)	0.5930(4)	0.280(1)	0.6021(2)	2.4(2)
C(4)	0.8224(4)	0.306(2)	0.5989(3)	4.1(4)
C(5)	0.5063(5)	0.442(2)	0.6820(2)	4.6(4)
[(CuI) ₂ (TMT-TTF)] _∞ (3)				
Cu(1)	1.0419(1)	0	0.37711(8)	3.88(3)
I(1)	0.71948(5)	0	0.38773(4)	3.52(2)
S(1)	1.1014(1)	0.12573(8)	0.2343(1)	3.54(4)
S(2)	1.3230(2)	0.11089(8)	0.0484(1)	3.99(4)
C(1)	1.4279(8)	0	0.0200(5)	3.2(2)
C(2)	1.2115(5)	0.0504(3)	0.1481(4)	2.9(1)
C(3)	1.2798(8)	0.2052(4)	0.3283(6)	5.3(2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

system.²⁰ The final *R* and *R*_w values were 0.028 and 0.044 for **1**, 0.037 and 0.040, for **2**, 0.027 and 0.036 for **3**, respectively. The final positional coordinates for non-hydrogen atoms of complexes **1–3** are given in Table 2. Selected bond distances and angles for **1–3** are given in Table 3.

Results

Structure of 1. The copper atom in **1** is coordinated to two chlorides and two sulfur atoms of methyl thioethers in a TMT-

- (16) Biddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents II*, 4th ed.; John Wiley: New York, pp 1048, 1986.
- (17) Andrieth, L. F.; Bailar, J. C.; Fernelius, W. C.; Johnson, W. C.; Kirk, R. E. *Inorg. Synth.* **1946**, 2, 1.
- (18) (a) MITHRIL—an integrated direct methods computer program. C. J. Gilmore, *J. Appl. Crystallogr.* **1984**, 17, 42. (b) DIRDIF—Direct methods for difference structures—an automatic procedure for phase extension and refinement of difference structure factors: P. T. Beurskens, *Technical Report 1984/1*; Crystallography Laboratory: Toenhooiveld, 6525 Nijmegen, The Netherlands.
- (19) Keller, H. J.; Noethe, D.; Pritzkow, H.; Wehe, D.; Werner, M. *Mol. Cryst. Liq.* **1980**, 62, 181.

- (20) TEXRAY Structure Analysis Package. Molecular Structure Corp., 1985.

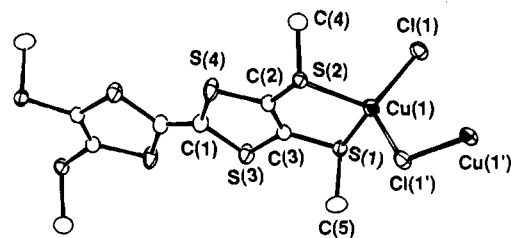
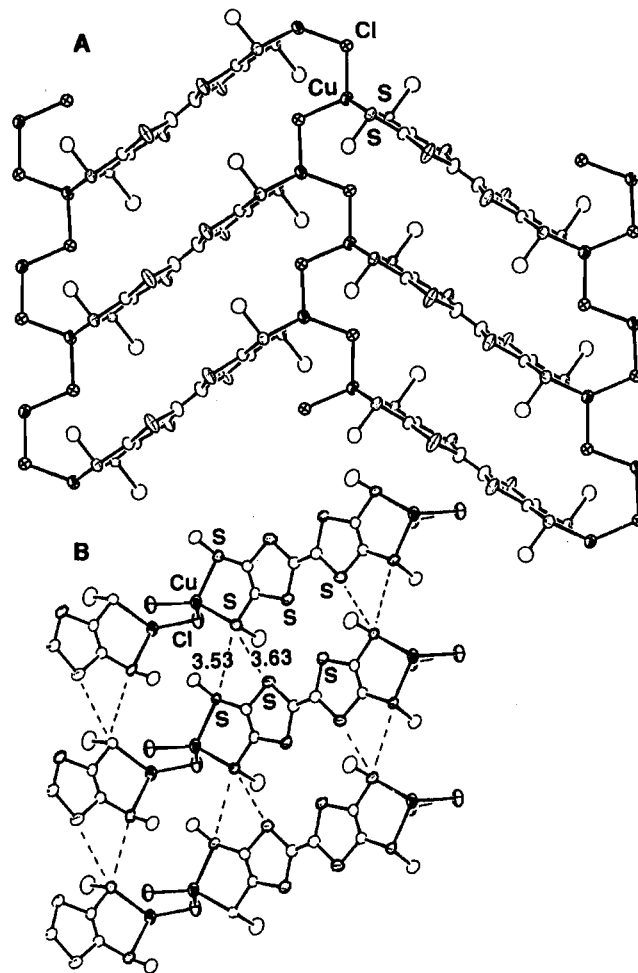
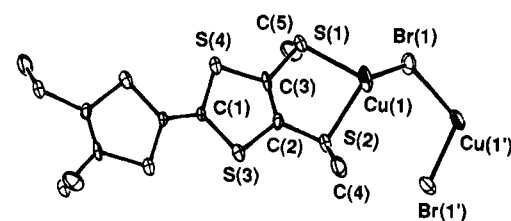
Table 3. Selected Bond Distances (Å) and Angles (deg) for 1-3

	1 (X = Cl)	2 (X = Br)	3 (X = I)
Cu(1)-S(1)	2.344(2)	2.438(2)	2.384(1)
Cu(1)-S(2)	2.371(3)	2.400(2)	
Cu(1)-S(1')			2.384(1)
Cu(1)-X(1)	2.277(1)	2.386(1)	2.590(1)
Cu(1)-X(1')	2.304(4)	2.412(1)	2.611(2)
C(1)-C(1')	1.336(7)	1.35(1)	1.33(1)
C(2)-C(3)	1.340(5)	1.334(9)	
C(2)-C(2')			1.337(8)
S(1)-Cu(1)-S(2)	90.94(8)	87.13(6)	
S(1)-Cu(1)-S(1')			88.80(7)
S(1)-Cu(1)-X(1)	120.21(7)	121.27(8)	114.46(4)
S(2)-Cu(1)-X(1)	111.24(7)	106.17(6)	
S(1)-Cu(1)-X(1')	105.20(6)	121.27(8)	111.69(5)
S(2)-Cu(1)-X(1')	116.24(4)	118.48(8)	
X(1)-Cu(1)-X(1')	111.75(5)	116.10(4)	113.43(4)
Cu(1)-X(1)-Cu(1')	111.31(5)	94.45(4)	66.57(5)

TTF molecule in distorted tetrahedral geometry as shown in Figure 1, the bond angles Cl(1)-Cu(1)-Cl(1'), S(1)-Cu(1)-S(2) and Cl(1 or 1')-Cu(1)-S(1 or 2) being 111.75(5), 90.94(8), and 105.20(6)-120.21(7)°, respectively. The Cu^I-S distance of 2.358(3) Å (average) is almost the same as Cu^I-S(thioether) bond distances reported for 3,6,10,13-tetrathiapentadecane (2.31(3) Å (average)),²¹ [14]janeS₄ (2.317(4) Å (average)),²¹ and [18]janeS₆ (2.33 Å (average))²², and longer than Cu^I-S(thiolate) bonds for Me₃PS⁻ (2.259(6) Å (average))²³ and C₆H₅S⁻ (2.295(4) (average) and 2.29(1) Å (average)).²⁴ There is only a report on the copper(I) complexes with single chloride bridging, [Cu₂(tmen)₂(CO)₂Cl]BPh₄.²⁵ The Cu-Cl distance of 2.328(2) Å (average) and Cu-Cl-Cu angle of 103.0(1)° are not very different from 2.291(4) Å and 111.31(5)° for 1, respectively.

The most remarkable feature of 1 is 2D sheet composed of TMT-TTF molecules arranged between novel zigzag frames of {CuCl}_n, as shown in Figure 2. This is the first 2D metal complex with TTF and the derivatives. The TTF moiety is almost same plane, the dihedral angle being only 2.95° between the planes defined by C(1), S(3) and S(4), and C(2), C(3), S(3) and S(4). Furthermore, the TTF skeleton and four S atoms of TMT-TTF molecule in 1 lie on almost coplanar whereas the methyl groups are sited up and down to the plane. It is noteworthy that 3D network is formed through S(1)···S(2) and S(2)···S(4) contacts of 3.53 and 3.63 Å between the 2D sheets, respectively; Two values of 3.74²⁶ and 3.60 Å²⁷ have been used as the van der Waals radius sum of two sulfur atoms. On the other hand, there are no S···S contacts within the 2D sheet, the interplanar spacing being 4.9 Å between neighboring TMT-TTF molecules.

Structure of 2. The copper(I) complex with TMT-TTF, 2, was synthesized using bromide in order to regulate the molecular and packing structures. Figure 3 shows the structure of 2. The

**Figure 1.** Molecular structure of [(Cu₂(μ-Cl)₂(μ-TMT-TTF))_n], 1.**Figure 2.** Side (A) and top views (B) of the packing arrangement of 1.**Figure 3.** Molecular structure of [(Cu₂(μ-Br)₂(μ-TMT-TTF))_n], 2.

Cu(1) is coordinated in a distorted tetrahedral geometry to two S atoms of a TMT-TTF and two bromide ions, the bond angles around Cu being 94-121°. The Cu-S distances of 2.419(2) Å (average) are longer than those in 1 and slightly shorter than 2.439(2) Å in [Cu₂Br₃(BEDT-TTF)].³⁰ Generally, the Cu^I-ligand distance of [CuX(ligand)] complexes become long in the order X = Cl < Br < I. For example, the Cu-P distances of Cu(I) complexes [Cu(X)PPh₃]₄ are 2.19 Å for X = Cl, 2.21 Å

- (21) Diaddario, L. L.; Dockal, E. R.; Glick, M. D.; Ochrymowicz, L. A.; Rorabacker, D. B., *Inorg. Chem.* **1985**, *24*, 356.
 (22) Gould, R. Q.; Lavery, A. L.; Schroeder, M., *J. Chem. Soc., Chem. Commun.* **1985**, 1492.
 (23) Eller, P. G.; Corfield, P. W. R., *J. Chem. Soc., Chem. Commun.* **1971**, 105.
 (24) Coucouvanis, D.; Murphy, C. N.; Kanodia, *Inorg. Chem.* **1980**, *19*, 2993.
 (25) Pasquali, M.; Marini, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1979**, 937.
 (26) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.
 (27) Parkin, S. S. P.; Engler, E. M.; Lee, V. Y.; Schumaker, R. R. *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 375.
 (28) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.
 (29) Bousseau, M.; Valade, L.; Bruniquel, M.-F.; Cassoux, P.; Garbaskas, M.; Interrante, L. V.; Kasper, K. *Nouv. J. Chim.* **1984**, *8*, 653.

- (30) Inoue, M. B.; Inoue, M.; Bruck, M. A.; Fernando, Q. *J. Chem. Soc. Chem. Commun.* **1992**, 515.

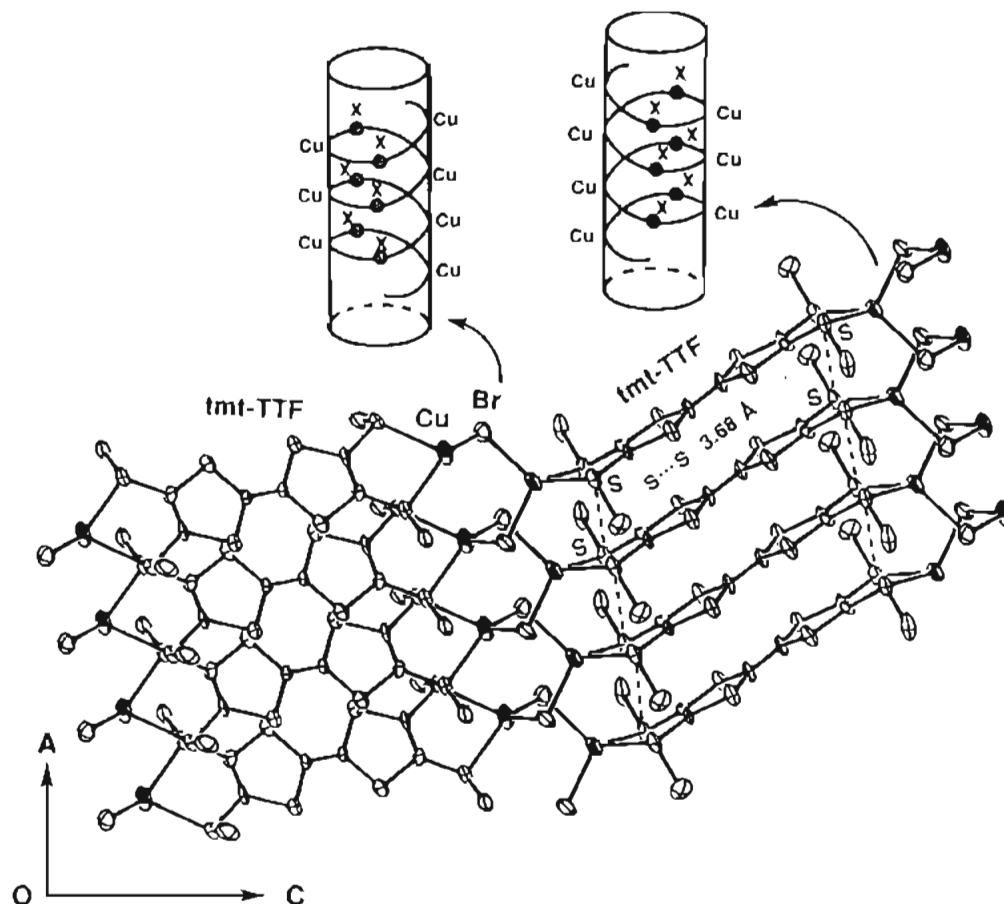


Figure 4. Perspective views of **2**.

for Br, and 2.26 Å for I.³¹ The Cu–N distances of 2.005 Å for X = Cl are shorter than 2.030 Å for Br in the Cu(I) complexes [Cu₂X₂(phenazine)] with polymeric stair frames.³² The same tendency has been found for the Cu–S distances of [(CuX)₂-(TMT-TTF)], as described above.

Figure 4 depicts a segment of 2D structure of **2** in which TMT-TTF molecules are connected between copper bromide frameworks. Copper(I) halide complexes with unidentate ligands are notable for the variety of stoichiometries and structural formats. Stoichiometries of Cu:X:ligand of 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2, and 1:1:3 have been observed.³³ These complexes give the variety of structures, dimmer,³⁴ tetramers³⁵ of cubane and stepped cubane, rhombs,³⁶ chairs,³⁷ and polymers³⁴ of stair, split, and displaced stairs. It is noteworthy that

the CuBr frame in **2** is a novel helical structure and the neighboring helices rotate alternatively in the reverse direction. The dihedral angle between the neighboring TMT-TTF molecules is essentially zero degree on the stacking axis, whereas it is 90.9° on the perpendicular to the axis.

The S(1)···S(2) distance of 3.68 Å between TMT-TTF molecules along the *a* axis indicates S···S contact. The TTF moiety of TMT-TTF is slightly bent, the dihedral angle being only 5.18° between the planes defined by C(1), S(3), and S(4), and C(2), C(3), S(3), and S(4).

Structure of 3. The methyl thioether groups of TMT-TTF are coordinated to the coppers of rhomboid Cu₂I₂ to give linear chains (Figure 5).³⁸ The TTF moiety of TMT-TTF is bent ca 22.5° at S(2) to S(2') position to give a chair form as shown in Figure 5B. The plane of Cu₂I₂ is perpendicular to the plane of TMT-TTF. The chair forms avoid favorably steric hindrance of I atoms of Cu₂I₂ rhomboid between the linear chains and give a S···S distance of 3.75 Å indicative of weak S···S contact along the stacking axis. On the other hand the methyl groups of TMT-TTF prevent the linear chains approaching each other on the side direction of the TMT-TTF plane.

Discussion

CuI and both CuBr and CuCl in the coordination polymers with phenazine (phz), [(CuX)₂phz]_n, form rhomboid, infinite stair frames, respectively.³² In the case of the coordination polymers with TMT-TTF, the copper halogen frameworks are also dramatically changed by the halogen and give rhomboid structure, novel helical and zigzag structures for I, Br and Cl, respectively (Figure 6). Thus, copper halide frameworks are

(31) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 831.

(32) Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Honda, A.; Kitagawa, S. *J. Chem. Soc., Dalton Trans.* **1994**, 2771.

(33) Hathaway, B. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987, Vol. 5; p 535.

(34) Campbell, J. A.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 1937.

(35) (a) Healy, P. C.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1917. (b) Schramm, V. *Cryst. Struct. Commun.* **1980**, *9*, 1231. (c) Schramm, V. *Cryst. Struct. Commun.* **1982**, *11*, 1549. (d) Raston, C. L.; White, A. A. *J. Chem. Soc., Dalton Trans.* **1976**, 2153. (e) Healy, P. C.; Kildea, J. D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 79.

(36) (a) Dyason, P. C.; Engelhardt, L. M.; Healy, P. C.; Pakawatchai, C.; White, A. H. *Inorg. Chem.*, **1985**, *24*, 1950. (b) Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 2201.

(37) Strähle, J.; Hiller, H.; Eitel, E.; Oelkrug, D. *Z. Kristallogr.* **1980**, *153*, 277.

(38) Brunn, K.; Endres, H.; Weiss, J. *Z. Naturforsch.* **1988**, *43b*, 224.

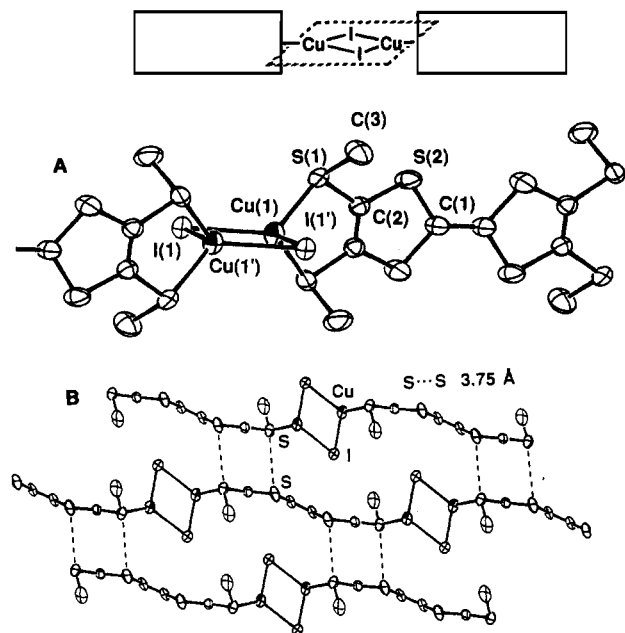


Figure 5. Molecular structure (A) and side views (B) of the packing arrangement of $[(\text{Cu}_2(\mu\text{-I})_2(\mu\text{-TMT-TTF}))_n]_n$, **3**.

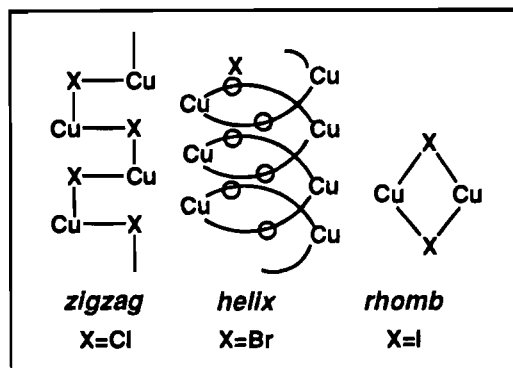


Figure 6. Copper halide frames of $[(\text{Cu}_2(\mu\text{-X})_2(\mu\text{-TMT-TTF}))_n]_n$.

extensively changed by the coordination atoms and stereofactors of the ligand. The diversity of copper halide frameworks make it of interest to construct two- and three-dimensional coordination polymers using frameworks (Figure 7). Compound **1** forms novel 2D sheets of TMT-TTF molecules arranged by zigzag frames of CuCl and furthermore give a 3D network through $\text{S}\cdots\text{S}$ contacts between the 2D sheets since TMT-TTF molecules are arranged in parallel in the sheets between the zigzag frame. The long $\text{Cu}\cdots\text{Cu}$ distance of 5.78 Å on the same side of the zigzag frame gives a long interplanar spacing (4.90 Å) of TMT-TTF, and accordingly, there are no $\text{S}\cdots\text{S}$ contacts within the 2D sheet. On the contrary the compound **2** give $\text{S}\cdots\text{S}$ contact of 3.67 Å within the 2D sheet, because the helical frames of copper bromide give a short $\text{Cu}\cdots\text{Cu}$ distance (3.49 Å) compared with the zigzag structure. On the other hand TMT-TTF molecules of **2** are alternatively arranged in a perpendicular manner along the *c* axis to interfere with the $\text{S}\cdots\text{S}$ contact between the 2D sheets. The TTF moiety of TMT-TTF connected by rhomboid frame of Cu_2I_2 in **3** is not coplanar, but bent. The $\text{S}\cdots\text{S}$ distance of 3.75 Å is nevertheless near the $\text{S}\cdots\text{S}$ contact on top and bottom sides of the TMT-TTF plane. The $\text{C}(1)\text{-C}(1')$ double bond distances of 1.33(1)–1.35(1) Å, and $\text{C}(2)\text{-C}(3)$ or $\text{C}(2)\text{-C}(2')$ double bond distances of 1.334(9)–1.340(5) Å indicate that TMT-TTF molecules are essentially neutral in the TMT-TTF-containing molecules of **1–3**.

Both of the IR spectra and electronic spectra provide important information about the oxidation state of TMT-TTF

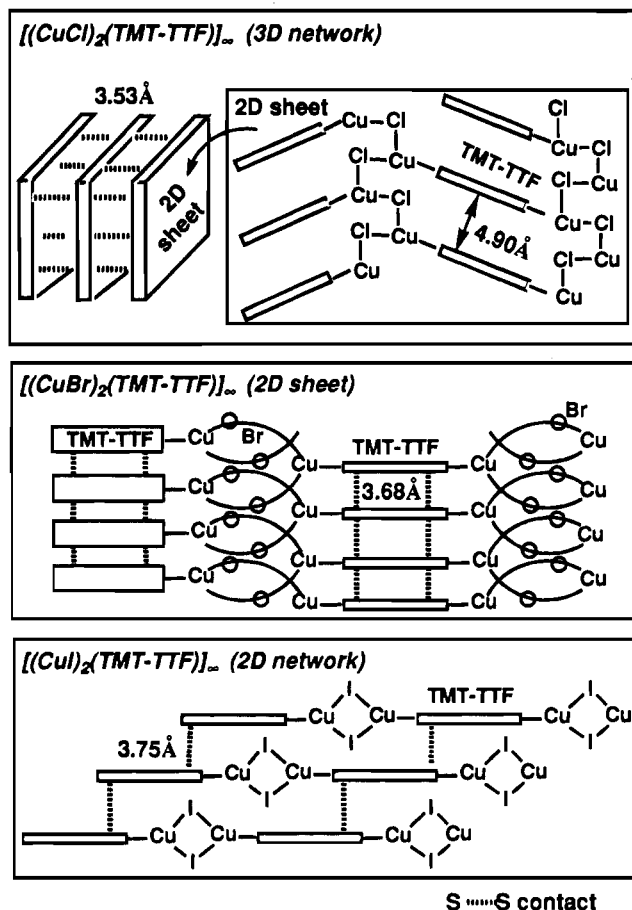


Figure 7. Schematic diagrams of molecular packing of $[(\text{Cu}_2(\mu\text{-X})_2(\mu\text{-TMT-TTF}))_n]_n$.

in the coordination polymers **1–3** and in their iodine-doped compounds $\{[(\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-TMT-TTF}))_n]_x\}_n$ (**4**), $\{[(\text{Cu}_2(\mu\text{-Br})_2(\mu\text{-TMT-TTF}))_n]_x\}_n$ (**5**), and $\{[(\text{Cu}_2(\mu\text{-I})_2(\mu\text{-TMT-TTF}))_n]_x\}_n$ (**6**). It is well-known^{39–41} that the central $\text{C}=\text{C}$ stretch of TTF undergoes a large frequency shift on oxidation, for example, from 1512 cm^{-1} in neutral TTF³⁹ to 1413 cm^{-1} in $(\text{TTF})\text{Br}$.⁴⁰ Similarly the central $\text{C}=\text{C}$ stretching frequency of TMT-TTF is also sensitive to its oxidation state. In the IR spectra of free TMT-TTF and the coordination polymers (**1–3**), the central $\text{C}=\text{C}$ stretching band of TMT-TTF occurs at 1410 cm^{-1} and 1310 cm^{-1} , respectively, which indicates the presence of neutral TMT-TTF in the coordination polymers. While the IR spectra of the iodine-doped compounds reveal two pair bands (one pair near 1400 and 1310 cm^{-1} , and another pair near 1350 and 1270 cm^{-1}), which arise from the neutral TMT-TTF and TMT-TTF⁺ radical cation, respectively. In the electronic spectra, all of the coordination polymers and their iodine-doped compounds show a strong absorption band near 505 nm. These bands near 510 nm may be ascribed to local excitation of the TMT-TTF molecule, since the free TMT-TTF ligand also exhibits the absorption band at 500 nm. While the another broad absorption band around 870 nm in the spectra of the iodine-doped compounds may be arisen from TMT-TTF/TMT-TTF⁺ charge-transfer transition.⁴¹

(39) Siedle, A. R.; Candela, G. A.; Finnegan, T. F.; Duyne, R. P. V.; Cape, T.; Kokoszka, G. F.; Woyciejes, P. M.; Hashmall, J. A. *Inorg. Chem.* **1981**, *20*, 2635.

(40) Siedle, A. R.; Kistenmacher, T. J.; Metzger, R. M.; Kuo, C.-S.; Duyne, R. P. V.; Cape, T. *Inorg. Chem.*, **1980**, *19*, 2048.

(41) Matsubayashi, G.; Yokoyama, K.; Tanaka, T. *J. Chem. Soc. Dalton Trans.* **1988**, 3059.

One of the common features of the conducting complex is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.^{42,43} Although **1–3** are insulator ($\sigma_{25^\circ\text{C}} < 10^{-12}$ S cm⁻¹) **4–6** behave as semiconductor: $\sigma_{25^\circ\text{C}} = 10^{-3.6}$ S cm⁻¹ for **4**, $\sigma_{25^\circ\text{C}} = 10^{-2.1}$ S cm⁻¹ for **5** and $10^{-1.7}$ S cm⁻¹ for **6**, respectively. This may be due to the (TMT-TTF)^{•+}/(TMT-TTF)^{•+} and/or (TMT-TTF)/(TMT-TTF)^{•+} interaction in the crystal.⁴¹ They must give a greater electrical conductivity in their single crystals than those values in the powder. However the single crystals were not obtained, since all single crystals of **1–3** were broken in the process of iodine-doping.

The control of dimensionality in the solid state is a fascinating challenge for synthetic chemists. Only where two-dimensional interstack interactions become predominant is superconductivity observed. It is essential that new donor and acceptor systems are synthesized so that the subtle factors which govern the structural, electrical, magnetic properties of CT compounds can

be better understood. As we have described here, metal coordination polymers with organic donor molecules can be expected to be as a new molecular system because the dimensionality, S••S contact, and key properties of the polymer can be controlled by metal ions. Thus, the future for the synthesis of new conductors and superconductors of metal coordination polymers with organic donor appears bright.

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Supplementary Material Available: Text describing the details of the experimental procedure for the X-ray data collection and Tables S1–S15, giving complete positional parameters including H atoms, bond angles, bond distances, and anisotropic thermal parameters (33 pages). Ordering information is given on any current masthead page.

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(42) Torrance, J. B. *Acc. Chem. Res.*, **1979**, *12*, 79.

(43) Inoue, M. B.; Inoue, M.; Fernando, Q.; Nebesny, K. W. *Inorg. Chem.* **1986**, *25*, 3976.