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Four New ET- and TTM-TTF-Based CT Salts with Cu-Containing Binuclear Polyhalide Complex Anions: Synthesis, Properties, and Structure

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Four new CT salts with Cu-containing binuclear polyhalide complex anions $ET_3Cu_2Br_x(x \sim 5)$ (A), $ET_3Cu_2Cl_4$ (B), (TTM-TTF) $Cu_2Br_{4.72}$ (C), and $(TTM\text{-}TTF)_2\ Cu_2Cl_6$ (D) [ET = BEDT-TTF = bisethylenedithio-tetrathiafulvalene, TTM-TTF = tetrathiomethyl-tetrathiafulvalene] are prepared and the degree of charge transfer as well as the valence states of the Cu atom in the four CT salts are discussed based on the analysis of X-ray photoelectron spectroscopy. The conductivity of the four charge-transfer salts A, B, C, and D at room temperature and their temperature dependence from room temperature down to 77 K along the crystal growth direction are reported. A behaves metallic down to about 250 K, then turns to a semi-conductor; B is an organic metal down to liquid nitrogen temperature; C shows a semi-conducting behavior down to about 230 K, then turns to an insulator and D is an insulator. The crystal structures of C and D are determined. In crystal C, both donors and acceptors occupy symmetry centers in the cell and are stacked in segregated columns. We have observed short intracolumnar and intercolumnar S. . .S contacts of 3.214(10), 3.417(12) Å, respectively in the donor columns; the binuclear polybromide metal complex acceptor anions are planar and stacked forming complicated polymeric columns along the b axis, the Cu atom of each of the polymeric columns is five-coordinate. In crystal D, the donor molecules TTM-TTF form dimers and the plane is almost perpendicular to that of the metal complex anion $(Cu_2Cl_6)^{2-}$.

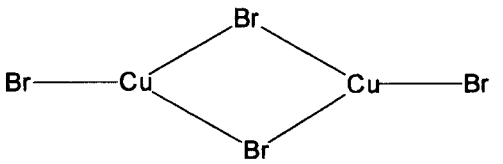
Keywords: BEDT-TTF (ET), TTM-TTF, binuclear Cu polyhalide anion, mixed valency, synthetic metal

INTRODUCTION

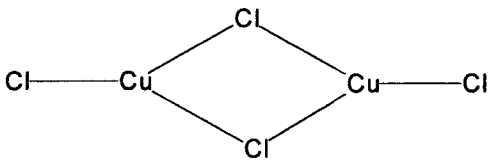
Since the discovery of the TTF-TCNQ charge-transfer (CT) complex as a conductor in 1973, intensive work has been done in order to understand the physical properties of related compounds. Dozens of new donors, mostly with an heterocyclic nature and containing chalcogen atoms, and a number of acceptors have been synthesized and co-crystallized in order to tune and improve the conductivity, transition temperatures and also to get superconducting states. Recently, scientists have been interested in introducing localized spins into CT salts in order to investigate the magnetic interactions between the localized spins and the organic pi radicals or conduction electrons, namely pi-d interactions. In order to develop the pi-d interaction, many trials have been made for transition metal halides to be introduced into ET-based CT salts.[1–6] On the other hand, in the past few years, great progress in the field of organic metals and

superconductors based on ET was made through the design and use of polymeric metal-containing anions.[7] In the first organic superconductors with polymeric metal-containing anions $ET_4(Hg_{3-\delta}X_8)$ (X = Cl, Br),[8-10] organic sheets composed of ET dimers ($\mathscr{K}$-phase) alternated with anionic sheets constructed of Hg-containing polymeric chains. Later on, a lot of superconductors with metal-containing anions $[Cu(NCS)_2]^-$,[11] $\{Cu[N(CN)_2]X\}^-$ (X = Cl,Br),[12,13] $[NH_4Hg(SCN)_4]^-$,[14] $[Ag(CN)_2H_2O]^-$,[15] Cu(CN) $[N(CN)_2]$ and $Cu_2(CN)_3$[16] were shown to have mainly a $\mathscr{K}$-phase structure of the cation sheet and complicated polymeric anions. Organic superconductors $ET_2[Cu\mathscr{K}(NCS)_2]$,[11] $ET_2Cu(CN)[N(CN)_2]$[16] and $ET_2\{Cu[N(CN)_2]X\}$ (X = Br, Cl)[12,13] with the highest temperatures of superconducting transition (10.4, 11.2, 11.6, and 12.8 K (at 0.3 Kbar), respectively) have just these polymeric metal-containing anion layers and furthermore, the layers having the same 3d transition metal atoms.

In order to get new organic conductors or even superconducting states with long chain metal-containing anions and, if possible, to investigate the magnetic interactions between the localized spins from magnetic metal ions and the organic pi radicals or conduction electrons, i.e, pi-d interactions, we have designed and synthesized two novel Cu-containing binuclear polyhalide complex anions $(Cu_2Cl_4)^{2-}$ and $(Cu_2Br_4)^{2-}$ (see Figure 1) and complexed the acceptor anions with the donor molecules ET and TTM-TTF, respectively. As the first part of the work, in this paper, we report the preparation, electrical properties, and structure determination of four new organic CT



$(Cu_2Br_4)^{2-}$



$(Cu_2Cl_4)^{2-}$

FIGURE 1 Chemical structure of metal complex dianions $(Cu_2Br_4)^{2-}$ and $(Cu_2Cl_4)^{2-}$

salts $ET_3Cu_2Br_x(x \sim 5)$ (A), $ET_3Cu_2Cl_4$ (B), (TTM-TTF) $Cu_2Br_{4.72}$ (C) and (TTM-TTF)$_2Cu_2Cl_6$ (D).

EXPERIMENTAL

Single crystals of the four CT salts were prepared by electrocrystallizatioin using ET or TTM-TTF as donor molecules and the TBA (tetrabutylammonium) salt of the Cu-containing binuclear polyhalide complex anions as supporting electrolyte under galvanostatic conditions in 9:1 CH_2Cl_2/ethanol, 12:1 CH_2Cl_2/ethanol, CH_2Cl_2, CH_2Cl_2, respectively at room temperature. Crystal A was crystallized in both very thin needles and bad-quality plates; crystal B in thin needles; crystal C in needles whose longer direction corresponds to the crystallographic *b*-axis; crystal D in blocks whose growth direction corresponds to the crystallographic c-axis; ascertained by X-ray oscillation photographs. The stoichiometry for compounds A and B was deduced only from the elemental analysis, and the stoichiometry for compounds C and D was not only determined by elemental analysis but also by crystal structure analysis. The structure determination for compounds A and B is under way.

Preparation of bis (tetrabutylammonium)-di-μ-bromo-dibromodicuprate

$$2CuBr_2 + 3TBAI \longrightarrow (TBA)_2Cu_2Br_4.H_2O + TBAI_3$$

A solution of absolute methanol (50 mL) containing $CuBr_2$ (3.4 g, 14.5 mmol) and TBAI (5.6 g, 15.2 mmol) was refluxed for 2 h. After removal of the heating bath, stirring for further 2 h at room temperature and initial filtration, the resulting dark brown solution was concentrated under reduced pressure. The residual crude products were recrystallized twice from ethyl acetate and dried in vacuum at 50°C for 7 h, yielded 1.6 g (66.7%) as yellow crystals, m.p 82. 5–84. 5°C. Anal. Found: C% 40.48, H% 7.60, N% 2.95; calc. for $C_{32}H_{74}N_2Cu_2Br_4O$: C% 40.47, H% 7.85, N% 2.95. FT-IR (KBr, cm^{-1}) spectra: 2956 (vs), 2930(s), 2870(vs), 1484(m), 1465(m), 1376(s), 1107(m), 1027(m), 879(s), 801(m), 742(vs). ^{1}H-NMR (200MHz, $CDCl_3$, TMS): 1.12 ppm(CH_3), 1.59 ppm(CH_2), 1.78 ppm(CH_2), 3.33 ppm(CH_2). Negative ion FAB mass spectra showed 445(6%) [$(Cu_2Br_4)^{2-}$] and 689 (1.2%) [$(TBACu_2Br_4)^-$] peaks, no higher negative ion was detected in the spectra indicating the absence of the species of TBA · $Cu_2Br_{(4-x)}I_x$. The byproducts $TBAI_3$ were validated by elemental analyses and melting point measurements.

Preparation of bis(tetrabutylammonium)-di-μ-chloro-dichlorodicuprate

$$2CuCl_2.2H_2O + 3TBAI \longrightarrow (TBA)_2Cu_2Cl_4.3H_2O + TBAI_3$$

A mixture of 3.14 g $CuCl_2.2H_2O$, 3.7 g TBAI and 50 mL methanol was strirred for 3 h at room temperature. After initial filtration, the resulting dark brown solution was concentrated under reduced pressure. The crude products were recrystallized twice from ethyl acetate and dried in vacum at 50°C for 10 h forming 2.9 g yellow crystals, m.p 115–117°C. Anal. Found: C% 47.36, H% 9.49, N% 3.44; calc. for

$C_{32}H_{78}N_2Cu_2Cl_4O_3$: C% 47.57, H% 9.73, N% 3.46. Negative ion FAB mass spectra showed 269 (7%) $[(Cu_2Cl_4)^{2-}]$ and 511 (1.5%) $[(TBACu_2Cl_4)^-]$ peaks, no higher negative ion was detected in the spectra indicating the absence of the species of $TBA.Cu_2Cl_{(4-x)}I_x$. The byproducts $TBAI_3$ were validated by elemental analyses and melting point measurements.

Preparation of $ET_3Cu_2Br_x(x \sim 5)$ (A) single crystals

Single crystals of the title complex were grown by electrocrystallization (1 mm diameter Pt wire electrodes) of ET (10 mg, 0.026 mmol) in a 35 mL mixed solvent of CH_2Cl_2(30 mL) and absolute ethanol (5 mL) in the anode compartment and $(TBA)_2Cu_2Br_4.H_2O$ (100 mg, 0.1 mmol) in 15 mL of CH_2Cl_2 in the cathode compartment with galvanostatic conditions (2 μA) at room temperature (ca. 298 K). The solvent was redistilled, dried and degassed before use and the cell was set on a stable place. After 2 days, black shiny, thin needlelike and few bad-quality platelike crystals were cautiously harvested from the anode. Elemental analyses performed on the needles showed: C% 21.42, H% 1.21, S% 45.64, Cu% 7.49, Br% 23.59; calc. for $C_{30}H_{24}S_{24}Cu_2Br_x(x \sim 5)$: C% 21.43, H% 1.43, S% 45.77, Cu% 7.55, Br% 23.77. It must be pointed out that the accurate bromine content in the crystal would be deduced from structure determination, considering the complexity of the analogous compound of crystal C.

Preparation of $ET_3Cu_2Cl_4$ (B) single crystals

Single crystals of $ET_3Cu_2Cl_4$ were grown by electrochemical oxidation of ET (10 mg, 0.026 mmol) in a mixture solvent of CH_2Cl_2 (60 mL) and ethanol (5 mL) using $(TBA)_2Cu_2Cl_4.3H_2O$ (81 mg, 0.1 mmol) as supporting electrolyte under constant currents of 1 μA at room temperature (22°C). After two days, black shiny needlelike crystals were obtained. Anal. Found: C% 25.27, H% 1.65, S% 54.20, Cu% 8.87, Cl% 9.86; calc. for $C_{30}H_{24}S_{24}Cu_2Cl_4$: C% 25.32, H% 1.68, S% 54.07, Cu% 8.92, Cl% 9.97.

Preparation of (TTM-TTF)$Cu_2Br_{4.72}$ (C) single crystals

Single cyrstals of the title complex were also grown by electrocrystallization (1 mm diameter Pt wire electrodes) of TTM-TTF (15 mg, 0.038 mmol) in 35 mL of CH_2Cl_2 in the anode compartment and $(TBA)_2Cu_2.Br_4.H_2O$ (90 mg, 0.095 mmol) in 15 mL of CH_2Cl_2 in the cathode compartment with galvanostatic conditions (1 μA) at room temperature (ca. 298 K). The solvent was redistilled, dried and degassed before use and the cell was set on a stable place. After 29 days, black shiny needelike crystals were cautiously harvested from the anode. Anal. Found: C% 13.40, H% 1.32, S% 28.58, Cu% 14.07, Br% 42.20; calc. for $C_{10}H_{12}S_8Cu_2Br_{4.72}$: C% 13.45, H% 1.34, S% 28.72, Cu% 14.23, Br% 42.23.

Preparation of $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D) single crystals

Single crystals of the title complex were grown by electrocrystallization using TTM-TTF (15 mg, 0.038 mmol) and $(TBA)_2Cu_2Cl_4.3H_2O$ (90 mg, 0.11 mmol) in CH_2Cl_2

(50 mL) under constant currents of 1 μA at room temperature. After 15 days, black shiny blocks were formed. Anal. Found: C% 21.51, H% 2.11, S% 45.78, Cu% 11.20, Cl% 18.93; calc. for $C_{20}H_{24}S_{16}Cu_2Cl_6$: C% 21.52, H% 2.15, S% 45.96, Cu% 11.37, Cl% 19.08.

Measurements of spectra and physical parameters

Infrared spectra were recorded on a Bruker IFS-113V Fourier Transform Infrared spectrophotometer in the region of 4000-400 cm^{-1} as KBr pellets at room temperature.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a ES-300 (KRATOS) photoelectron spectrophotometer using an AlK_α (1486.6 eV) X-ray source under vacuum of $2 \sim 6 \times 10^{-6}$ Pa. The X-ray source was operated at 15 KV and 10 mA. All compounds were used in powder form, which was ground from needlelike crystals for compounds A, B, and C or from blocklike crystals for compound D, and were dusted on a double side adhesive tape, mounted on a sample holder. C(1s) [B. E. = 285 eV] (B. E. = binding energy) from pump oil contamination was used as standard for charge correction. Multiscan data were collected and analysed on an IBM-386 computer, interfacing the spectrometer.

Electrical conductivity measurements

D.c. resistance temperature dependence measurements along the crystal growth direction were performed by the usual four-probe technique with a 148 NANOVOLTMETER (KEITHLEY INSTRUMENTS) and a locally built computer-controlled instrument [for crystals A and B] or data recorded on a SOLARTRON SCHLUMBERGER 7081 PRECISION VOLTMETER [for crystal C] from room temperature down to liquid nitrogen temperature (77.9 K) using a selected black shiny needlelike crystal along the crystal longer direction. Four gold contact wires (7 μm diameter) were glued to the crystal by gold paste.

X-ray data collection and structure determination

Intensity measurements were collected on a RASA-IIS RIGAKU four-circle diffractometer with ω-2θ scans. Structure solutions and refinements were performed using the direct methods and conventional least- squares and Fourier techniques.

RESULTS AND DISCUSSION

XPS analysis

X-ray photoelectron spectroscopy (XPS) which measures the binding energy (B. E.) of core electrons in atoms and molecules has been successfully applied to the study of the oxidation states in mixed valence compounds.[17,18] The XPS spectra of the compounds studied here have been used to determine the binding energies of Cu ($2p_{3/2}$), Cl (2p), Br (3d), or S (2p). The interest in these studies has sprung mainly from hoping to deduce the

degree of charge transfer in the CT salts, which is vital to their electrical conductivity, and the difficulty to assign formal oxidation states to the transition metal according to the traditional rules of valence, especially for those of non-stoichiometric compounds. The B.E. data of Cu ($2p_{3/2}$), Cl (2p), Br (3d), and S (2p) in the CT salts of $ET_3Cu_2Br_x(x \sim 5)$ (A), $ET_3Cu_2Cl_4$ (B), (TTM-TTF)$Cu_2Br_{4.72}$ (C), and (TTM-TTF)$_2Cu_2Cl_6$ (D) and some reference B. E. data of Cu ($2p_{3/2}$), Br (3d), Cl (2p) and S (2p) in $(TBA)_2Cu_2Br_4.H_2O$, $(TBA)_2Cu_2Cl_4.3H_2O$, ET, TTM-TTF, $CuBr_2$ and $CuCl_2$ are tabulated in Table I. All B. E.'s were reproducible to within $\pm$ 0.1 eV. It is noted that the S (2p) binding energy in the donor molecule ET and TTM-TTF is 163.9 and 164.0 eV, respectively, but in $ET_3Cu_2Br_x(x \sim 5)$ (A) and (TTM-TTF) $Cu_2Br_{4.72}$(C), it increases to 164.4 and 164.5 eV. On the other hand, the Cu ($2p_{3/2}$) binding energy in $(TBA)_2Cu_2Br_4 \cdot H_2O$ is 934.1 eV, but in $ET_3Cu_2Br_x(x \sim 5)$ (A) and $(TBA_2Cu_2Br_{4.72}$ (C), it decreases to 933.5 eV and 933.3 eV, respectively. The Br (3d) binding energy in the TBA salt is 68.9 eV; however, in $ET_3Cu_2Br_x(x \sim 5)$ (A) and (TTM-TTF)$Cu_2Br_{4.72}$ (C), it decreases to 68.7 eV and 68.5 eV, respectively. The XPS analyses show that the charge transfer may occur between the donor molecule ET, TTM-TTF and the Cu-containing binuclear polybromide complex anions. Similarly, charge transfer may also happen between the donor molecule ET, TTM-TTF and the Cu-containing binuclear polychloride complex anions in the salts of $ET_3Cu_2Cl_4$ (B) and (TTM-TTF)$_2Cu_2Cl_6$ (D).

It is our feeling that the CT salt $ET_3Cu_2Br_x(x \sim 5)$ (A) may contain mixed valence states of Cu(II) and Cu(I). The reasons for this assignment are as follows. Although the main peak of Cu ($2p_{3/2}$) of compound A centered at 933.5 eV is lower than that of $CuBr_2$, the existence of a minimum amount of Cu(II) cannot be ruled out because there are rather higher B. E. satellite features in the spectra of Cu ($2p_{3/2}$) of the CT salt examined (see Figure 2). If only Cu (I) existed in the compound, the satellite features could not be observed in the spectra of Cu ($2p_{3/2}$). However, it is hard to determine the exact ratio of Cu(II): Cu(I) in the compound, so it is difficult to deduce the degree of charge transfer between the donor molecules and the acceptor anions. But, partial charge transfer might happen between ET and the anion $(Cu_2Br_x)^{m-}(x \sim 5)$ based on its stoichiometry, XPS data, and high conductivity (vide infra). For compound B, there are no high B. E. satellite features in the Cu ($2p_{3/2}$) spectra; this may indicate the existence of

TABLE I

Cu ($2p_{3\,2}$), Cl (2p), Br (3d) and S (2p) binding energies (eV) in $ET_3Cu_2Br_x(x \sim 5)$, $ET_3Cu_2Cl_4$, (TTM-TTF) $Cu_2Br_{4.72}$, and (TTM-TTF)$_2Cu_2Cl_6$ and some reference compounds

Compounds	Cu ($2p_{3\,2}$)	Cl (2p)	Br (3d)	S (2p)
$ET_3Cu_2Br_x(x \sim 5)$	933.5		68.7	164.4
$ET_3Cu_2Cl_4$	932.4	196.4		164.6
(TTM-TTF)$Cu_2Br_{4.72}$	933.3		68.5	164.5
(TTM-TTF)$_2Cu_2Cl_6$	935.0	198.1		164.6
$(TBA)_2Cu_2Br_4.H_2O$	934.1		68.9	
$(TBA_2Cu_2Cl_4.3H_2O$	933.8	198.5		
$CuBr_2$	934.2		70.2	
$CuCl_2$	934.3	199.5		
ET				163.9
TTM-TTF				164.0

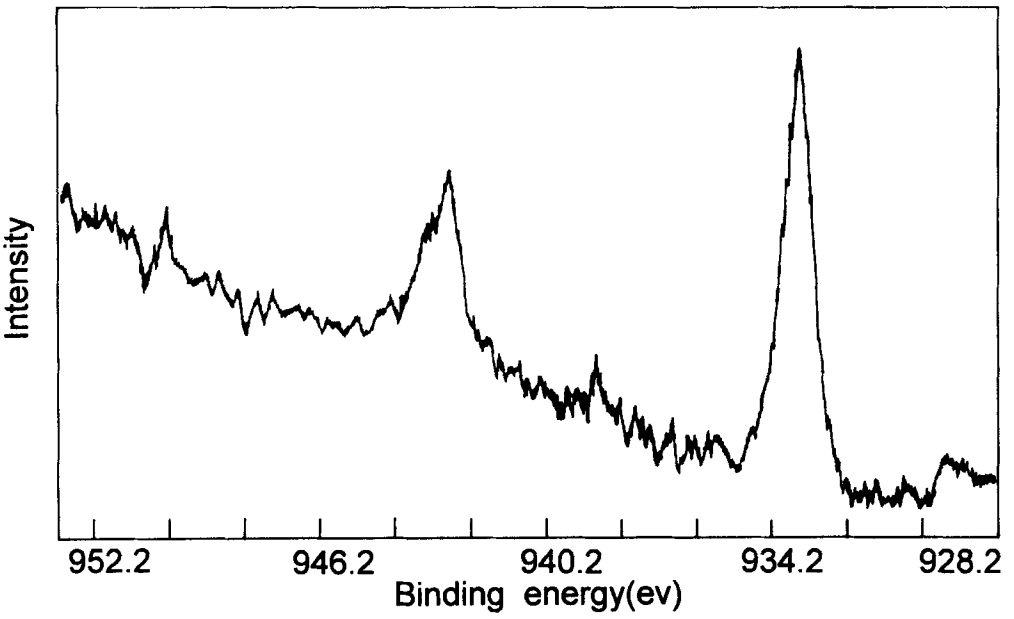


FIGURE 2 XPS spectra of Cu ($2p_{3/2}$) core region in compound $ET_3Cu_2Br_x(X \sim 5)$ (A).

only Cu(I) in the CT salt of $ET_3Cu_2Cl_4$. Hence, the donor molecule ET could be considered to have the formal valence of $+2/3$ in the CT salt $ET_3Cu_2Cl_4$. For compound C, although no intense satellite features were observed in the spectra of Cu ($2p_{3/2}$) in the compound examined, formally indicating the absence of Cu(II), the formal oxidation states of Cu atom in the compound are not clear because the anion forms complicated polymeric columns and the Cu atom of each of the polymeric columns is five-coordinate (see Figure 6). Hence, the degree of charge transfer between donors and acceptor anions and the formal valence of the donor TTM-TTF is hard to be determined as well. For compound D, both of the line position and behavior of the spectrum of Cu($2p_{3/2}$) indicate the presence of Cu(II) only. Therefore, the formal valence of TTM-TTF is $+1$. Total charge transfer happened and thus resulted in the donor cation $TTM\text{-}TTF^{+1}$ and the acceptor dianion $(Cu_2Cl_6)^{2-}$. So, the conductivity is very low resulting in an insulator.

Since the Cu(II) ion has localized 3d electrons, this might anticipate the possibility of the existence of localized spins in the anion layers in the compound $ET_3Cu_2Br_x(x \sim 5)$ (A) or $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D).

Electrical conductivity

Room temperature (ca. 295 K) conductivity and resistance temperature dependence were measured by the usual four-probe technique along the crystal longer direction. Reproducibility was ascertained for three samples. The conductivity of the three CT salts of A-C is about 10, 4 and 7×10^{-4} $S.cm^{-1}$ at room temperature, respectively. The

CT salt of $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D) is an insulator. If the anion $Cu_2Br_x(x \sim 5)$ in the compound A consists of Cu(I) and Br^-, an almost completely ionized state of ET molecules would be deduced based on its stoichiometry. That will lead an insulating behavior to this compound. However, compound A behaves a very weak metallic temperature dependence between 295 K and 250 K, then turns to semiconductivity, as is plotted in Figure 3. The metallic character of this compound is in good accordance with the mixed valence state of Cu ions estimated by the XPS measurements.

Figure 4 shows the temperature dependence of the relative electrical resistance of $ET_3Cu_2Cl_4$ (B). It presents a metallic behavior from room temperature down to 77 K. When lower temperature measurements were going on, the crystal was breaking down. Temperature dependence of the resistance of $(TTM\text{-}TTF)_2Cu_2Br_{4.72}$ (C) is plotted in Figure 5, which presents a very weak semiconductive temperature dependence between 295 K and 230 K, then turns to an insulator below 230 K. The reasons for the different behavior ($220 \sim 250$ K) between cooling and heating (Figure 5) are not clear and further work is under way.

Crystal structure

Single crystal X-ray structure of compounds C and D is determined at room temperature. Key crystallographic parameters are summarized in Table II. We have previously reported the structure of compound C.[19] In the crystal, the TTM-TTF donor cations and the $Cu_2Br_{4.72}$ binuclear polyhalide complex acceptor anions are segregated

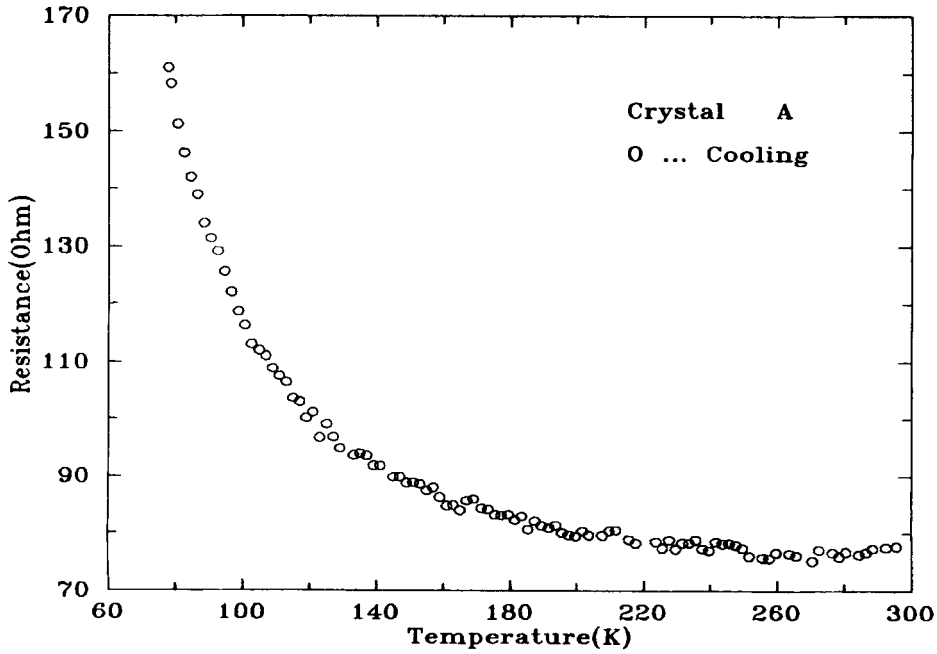


FIGURE 3 D.c. resistance temperature dependence of $ET_3Cu_2Br_x(x \sim 5)$.

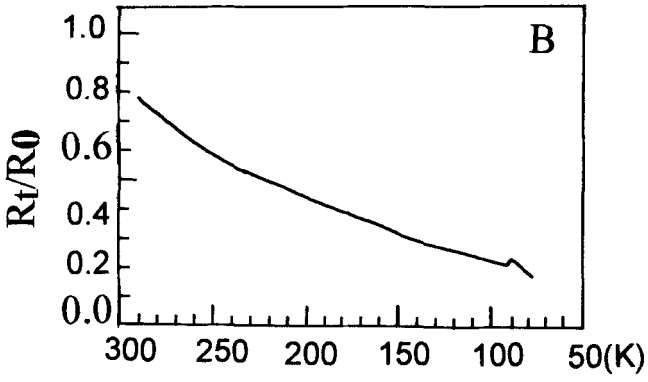


FIGURE 4 Temperature dependence of relative resistance of $ET_3Cu_2Cl_4$ (B).

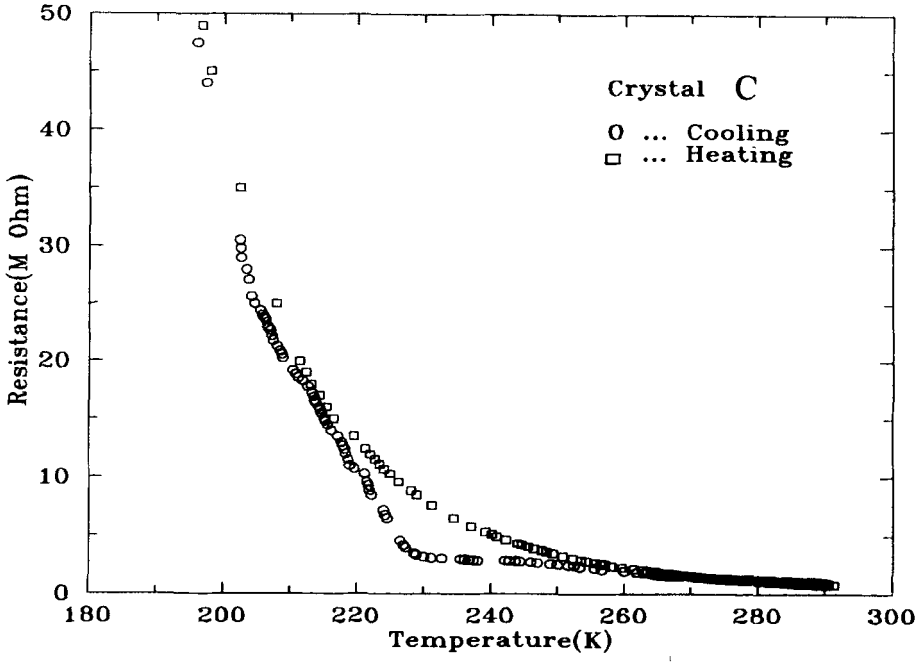


FIGURE 5 D.c. resistance temperature dependence of $(TTM\text{-}TTF)Cu_2Br_{4.72}$ (C).

columns. The acceptor anions form complicated polymeric columns along the b axis: 1,1'-di-μ-bromo-2,2'-dibromodicuprate moieties of the binuclear polybromide acceptor are planar, the shortest distances from Br (3) atoms to the anion planes are 1.201 (13) Å and the Cu atom of each of the polymeric columns is five-coordinate (see Figure 6).

Accordingly, the TTM-TTF cations form columns along the *b* axis. The shortest S...S contacts between the adjacent cations in a column and the shortest intercolumn S...S

TABLE II

Crystal parameters for compounds $(TTM\text{-}TTF)_2Cu_2Br_{4.72}$ (C) and $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D)

Parameter	Compound C[19]	Compound D
a (Å)	27.817 (9)	11.295 (6)
b (Å)	4.0295 (6)	11.841 (5)
c (Å)	22.814 (7)	8.598 (4)
α (°)		88.10 (5)
β (°)	117.98 (4)	74.20 (5)
γ (°)		63.37 (4)
V (Å^3)	2258.3 (11)	983.8 (1)
Z	4	1
Sp.	C2/c	P1
Dc (mg. mm^{-3})	2.626	1.885

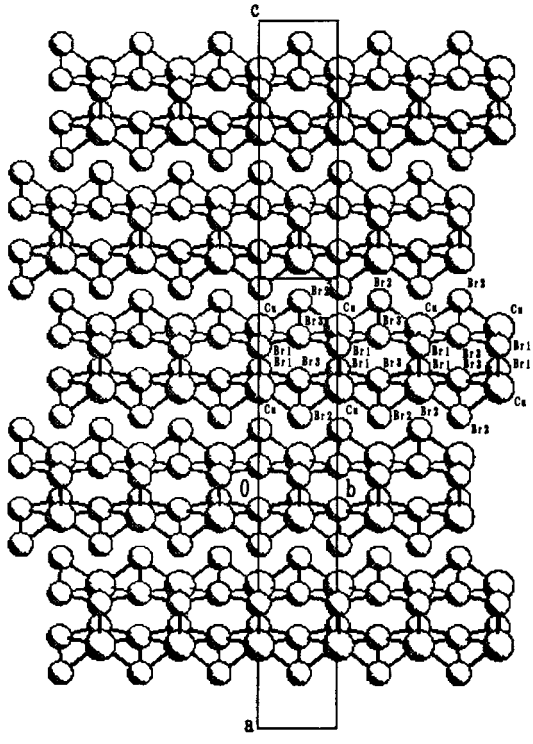


FIGURE 6 Complicated polymeric anions with removal of the cations in $(TTM\text{-}TTF)Cu_2Br_{4.72}$ (C).

contacts are found with a distance of 3.214 (10), 3.147 (12) Å, respectively. Both of them are shorter than the sum of the van der Waals radii (3.6 Å); these results suggest 2-dimensional interactions of the TTM-TTF cations in the crystal. This arrangement is in good accordance with its high conductivity.

The numbering scheme of the crystal structure of compound D is shown in Figure 7. The atomic parameters and bond distances and angles are listed in Table III and Table IV, respectively. In the crystal, TTM-TTF are stacked to form columns along the *c*-axis in face-to-face mode. In the column, TTM-TTF donor molecules are dimeric in bond-over-bond mode (see Figure 8). In the dimer, two TTM-TTF molecules are almost parallel to each other with dihedral angles of 0.451°. The shortest contacts in the dimer are found between S(2) and S(10) atoms with a distance of 3.366 Å and the shortest contacts between two adjacent dimers are found between S (7) and S (9) atoms with a distance of 3.696 Å. In TTM-TTF, C(1), C(2), C(3), C(4), C(5), C(6), S(1), S(2), S(3), S(4), S(5), S(6), S(7) and S(8) are nearly coplanar forming a least-square plane with a mean difference of 0.049 Å and the longest distances are from S(5) atom to the plane with a distance of 0.087 Å. Among the four carbon atoms in the methyl group, the perpendicular distances from C(7), C(8), C(9) and C(10) to the plane are 0, 0.175, 1.481 and 0.646 Å, respectively. Similarly, C(11), C(12), C(13), C(14), C(15), C(16), S(9), S(10), S(11), S(12), S(13), S(14), S(15) and S(16) are nearly coplanar forming a least-square plane with a mean difference of 0.047 Å and the longest distances are from C(11) atom to the plane with a distance of 0.098 Å. From C(17), C(18), C(19) and C(20) to the plane, the perpendicular distances are 0, 1.483, 1.683 and 1.567 Å, respectively. In the metal complex anion, Cu and Cl atoms share worse planarity forming a least-square plane with a mean difference of 0.148 Å. The longest distances are from the Cl(2) atom to the plane with a distance of 0.329 Å. The dihedral angles between the $(Cu_2Cl_6)^{2-}$ anion plane and the two TTM-TTF planes are 96.13 and 96.51°, respectively. Investigation of the structure-property correlations will be submitted soon in an extended form.

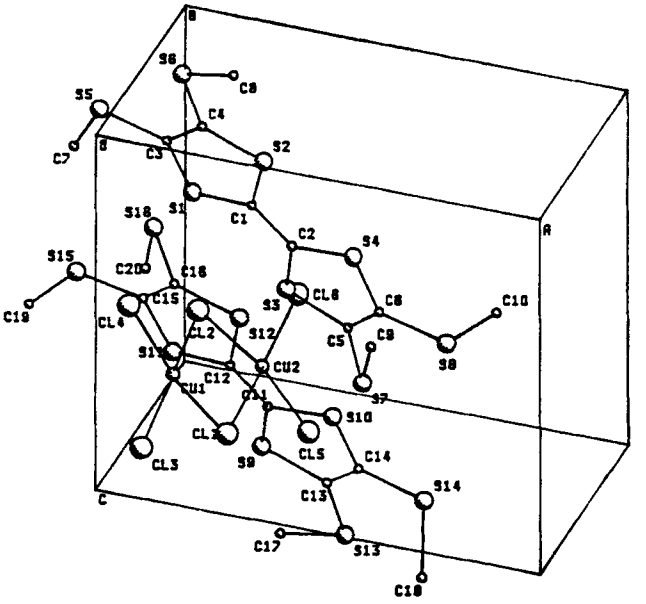


FIGURE 7 Structure of (TTM-TTF)Cu_2Cl_6 (D) with atoms numbering.

TABLE III

Fractional atomic coordinates and equivalent isotropic thermal parameters ($Å^2$) with e.s.d.'s in parentheses in an independent unit

atom	X	Y	Z	Ueq
S1	0.0709 (9)	0.7321 (9)	0.4129 (11)	0.039 (2)
S2	0.1979 (8)	0.9024 (8)	0.3575 (10)	0.036 (2)
S3	0.3232 (8)	0.5354 (5)	0.5501 (7)	0.040 (2)
S4	0.4398 (9)	0.7127 (8)	0.4969 (10)	0.041 (2)
S5	−0.1742 (6)	0.9123 (6)	0.3033 (8)	0.048 (2)
S6	−0.0257 (6)	1.0963 (6)	0.2348 (8)	0.048 (2)
S7	0.5329 (6)	0.3527 (6)	0.6981 (7)	0.047 (2)
S8	0.6787 (6)	0.5570 (6)	0.6256 (8)	0.050 (2)
S9	0.2561 (9)	0.5889 (8)	1.0325 (11)	0.042 (2)
S10	0.3842 (8)	0.7584 (8)	0.9794 (10)	0.034 (2)
S11	0.0174 (8)	0.7729 (8)	0.8862 (10)	0.034 (2)
S12	0.1346 (5)	0.9504 (5)	0.8275 (6)	0.035 (2)
S13	0.4848 (6)	0.3919 (6)	1.1558 (7)	0.049 (2)
S14	0.6257 (6)	0.5788 (6)	1.0931 (8)	0.049 (2)
S15	−0.2266 (6)	0.9258 (6)	0.7757 (7)	0.047 (2)
S16	−0.0977 (6)	1.1383 (6)	0.7007 (7)	0.048 (2)
C1	0.1996 (14)	0.7607 (13)	0.4295 (15)	0.039 (2)
C2	0.3061 (14)	0.5805 (13)	0.4886 (15)	0.041 (2)
C3	−0.0158 (14)	0.8710 (13)	0.3393 (15)	0.044 (2)
C4	0.0482 (14)	0.9515 (13)	0.3128 (15)	0.041 (2)
C5	0.4707 (14)	0.4920 (13)	0.6081 (15)	0.042 (2)
C6	0.5263 (14)	0.5746 (14)	0.5809 (15)	0.045 (2)
C7	−0.2038 (12)	0.7765 (12)	0.3638 (14)	0.029 (2)
C8	0.0775 (15)	1.1686 (14)	0.2397 (16)	0.051 (2)
C9	0.5756 (14)	0.2326 (14)	0.5415 (16)	0.053 (2)
C10	0.8134 (15)	0.4382 (14)	0.4634 (16)	0.056 (2)
C11	0.2432 (14)	0.7284 (14)	0.9724 (15)	0.045 (2)
C12	0.1416 (14)	0.8086 (13)	0.9065 (15)	0.042 (2)
C13	0.4149 (14)	0.5353 (13)	1.0779 (15)	0.043 (2)
C14	0.4715 (14)	0.6157 (13)	1.0541 (15)	0.045 (2)
C15	−0.0762 (14)	0.9128 (13)	0.8093 (15)	0.045 (2)
C16	−0.0225 (14)	0.9963 (13)	0.7876 (15)	0.045 (2)
C17	0.3482 (15)	0.3402 (14)	1.1664 (16)	0.049 (2)
C18	0.6203 (15)	0.5778 (15)	1.3118 (16)	0.073 (2)
C19	−0.3564 (14)	1.0464 (14)	0.9395 (16)	0.054 (2)
C20	−0.1389 (14)	1.2527 (14)	0.8659 (16)	0.056 (2)
CU1	0.0960 (6)	0.3903 (5)	0.7903 (7)	0.040 (1)
CU2	0.3556 (6)	0.0983 (5)	0.5996 (7)	0.040 (1)
CL1	0.2558 (9)	0.2046 (8)	0.8553 (10)	0.053 (2)
CL2	0.1772 (9)	0.2685 (8)	0.5466 (10)	0.055 (2)
CL3	0.0089 (9)	0.4711 (9)	1.0516 (11)	0.049 (2)
CL4	−0.0368 (9)	0.5579 (9)	0.6898 (11)	0.053 (2)
CL5	0.4938 (9)	−0.0696 (9)	0.6930 (10)	0.059 (2)
CL6	0.4520 (9)	0.0178 (9)	0.3434 (11)	0.062 (2)

SUMMARY

In summary, we have prepared four new CT salts with Cu-containing binuclear polyhalide complex anions and studied their electrical properties, determined the crystal structures of two of them. At the same time, we have also discussed the structure-property relationship and the degree of charge transfer between the donor

TABLE IV

Selected bond lengths (Å) and angles (°) in $(TTM\text{-}TTF)_2Cu_2Cl_6$ with e.s.d.'s in parentheses

Bond lengths			
S1—Cl	1.674 (22)	S10—C11	1.796 (22)
S1—C3	1.699 (16)	S10—C14	1.737 (16)
S2—C1	1.763 (18)	S11—C12	1.688 (21)
S2—C4	1.674 (18)	S11—C15	1.743 (16)
S3—C2	1.722 (17)	S12—C12	1.767 (17)
S3—C5	1.729 (17)	S12—C16	1.738 (17)
S4—C2	1.734 (22)	S13—C13	1.722 (15)
S4—C6	1.739 (16)	S13—C17	1.879 (21)
S5—C3	1.745 (18)	S14—C14	1.722 (18)
S5—C7	1.816 (17)	S14—C18	1.864 (16)
S6—C4	1.741 (15)	S15—C15	1.739 (19)
S6—C8	1.736 (22)	S15—C19	1.788 (13)
S7—C5	1.728 (15)	S16—C16	1.757 (15)
S7—C9	1.796 (17)	S16—C20	1.810 (17)
S8—C6	1.786 (19)	C1—C2	1.372 (19)
S8—C10	1.815 (13)	C3—C4	1.413 (26)
S9—C11	1.670 (19)	C5—C6	1.364 (26)
S9—C13	1.765 (19)	C11—C12	1.371 (19)
C13—C14	1.348 (26)	CU2—CL1	2.292 (10)
C15—C16	1.358 (26)	CU2—CL2	2.264 (10)
CU1—CL1	2.306 (9)	CU2—CL5	2.198 (10)
CU1—CL2	2.298 (10)	CU2—CL6	2.202 (10)
CU1—CL3	2.242 (10)	CU1—CL4	2.204 (11)
Bond angles			
C3—S1—C1	96.5 (10)	C15—S11—C12	97.0 (9)
C4—S2—C1	94.4 (9)	C16—S12—C12	94.4 (8)
C5—S3—C2	97.2 (9)	C17—S13—C13	99.9 (8)
C6—S4—C2	95.4 (9)	C18—S14—C14	115.7 (7)
C18—S4—C2	105.2 (8)	C19—S15—C15	101.4 (8)
C18—S4—C6	70.1 (6)	C20—S16—C16	100.1 (7)
C7—S5—C3	102.1 (7)	S2—C1—S1	116.0 (9)
C8—S6—C4	105.4 (9)	C2—C1—S1	124.8 (14)
C9—S7—C5	103.4 (8)	C2—C1—S2	119.1 (14)
C10—S8—C6	101.5 (8)	S4—C2—S3	114.3 (8)
C13—S9—C11	97.4 (10)	C1—C2—S3	122.8 (15)
C14—S10—C11	94.7 (9)	C1—C2—S4	122.8 (14)
S5—C3—S1	122.3 (12)	S13—C13—S9	120.5 (11)
C4—C3—S1	115.2 (12)	C14—C13—S9	115.7 (11)
C4—C3—S5	122.5 (10)	C14—C13—S13	123.8 (12)
S6—C4—S2	121.2 (12)	S14—C14—S10	120.6 (11)
C3—C4—S2	117.7 (11)	C13—C14—S10	117.6 (12)
C3—C4—S6	121.1 (12)	C13—C14—S14	121.8 (11)
S7—C5—S3	118.5 (11)	S15—C15—S11	114.9 (11)
C6—C5—S3	115.6 (11)	C16—C15—C11	115.4 (12)
C—C5—S7	125.9 (13)	C16—C15—S15	129.7 (11)
S8—C6—S4	116.0 (11)	S16—C16—S12	120.3 (11)
C5—C6—S4	117.3 (13)	C15—C16—S12	117.7 (10)
C5—C6—S8	126.7 (11)	C15—C16—S16	121.6 (12)
S10—C11—S9	114.6 (9)	S14—C18—S4	121.1 (8)
C12—C11—S9	123.2 (15)	CL2—CU1—CL1	81.1 (3)
C12—C11—S10	121.8 (14)	CL3—CU1—CL1	90.8 (4)
S12—C12—S11	115.0 (8)	CL3—CU1—CL2	166.6 (5)
C11—C12—S11	121.2 (14)	CL4—CU1—Cl1	171.3 (4)
C11—C12—S12	123.7 (15)	CL4—CU1—CL2	91.1 (4)
CL4—CU1—CL3	97.6 (4)	CL2—CU2—CL1	82.1 (3)
CL6—CU2—CL2	93.7 (4)	CL5—CU2—CL1	90.4 (4)
CL6—CU2—CL5	94.6 (4)	CL5—CU2—CL2	167.7 (5)
CU2—CL1—CU1	97.3 (4)	CL6—CU2—CL1	173.0 (5)
CU2—CL2—CU1	98.3 (4)		

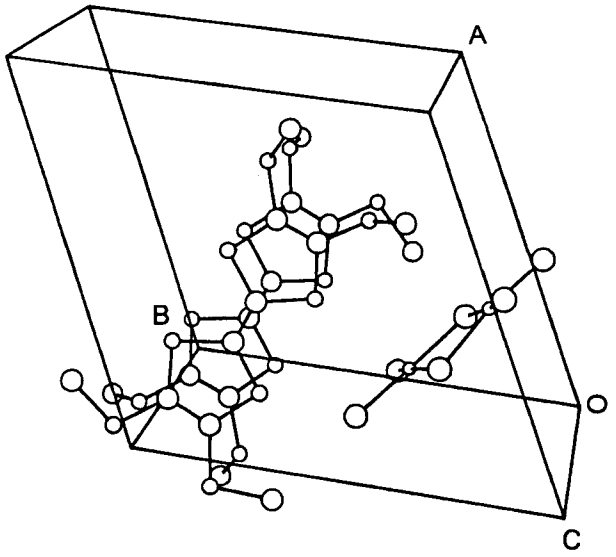


FIGURE 8 Dimeric structure of TTM-TTF moities in $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D).

molecules ET or TTM-TTF and the binuclear polyhalide metal complex anions by means of electrical conductivity and XPS spectra measurements as well as crystal structure determination. The rather high conductivity of $(TTM\text{-}TTF)Cu_2Br_{4.72}$ (C) might be considered due to the 2-dimensional interactions in the cation columns and the very low conductivity of $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D) is considered due to full charge transfer resulted in $TTM\text{-}TTF^{+1}$ and $(Cu_2Cl_6)^{2-}$ dianion. The existence of Cu(II) in compounds $ET_3Cu_2Br_x(x \sim 5)$ (A) and $(TTM\text{-}TTF)_2Cu_2Cl_6$ (D) may indicate the possible existence of localized spins in the anion layers.

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