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Structure of 3,4;3′,4′-Bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene–Dichlorocuprate (BEDT-TTF)$CuCl_2$

By Atsushi Kawamoto and Jiro Tanaka

Department of Chemistry, Faculty of Science, Nagoya Univesity, Nagoya 464, *Japan*

and Masashi Tanaka[*]

Department of Chemistry, College of General Education, Nagoya University, Nagoya 464, *Japan*

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Abstract. $C_{10}H_8S_8.CuCl_2$, $M_r = 519\cdot105$, triclinic, $P\bar{1}$, $a = 6\cdot577\,(2)$, $b = 12\cdot154\,(2)$, $c = 5\cdot781\,(1)$ Å, $\alpha = 100\cdot87\,(1)°$, $\beta = 94\cdot74\,(1)°$, $\gamma = 108\cdot58\,(1)°$, $V = 424\cdot4\,(1)$ Å^3, $Z = 1$, $D_x = 2\cdot031$, $D_m = 2\cdot029$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu = 140\cdot45$ cm^{-1}, $F(000) = 259$, $T = 293$ K, $R = 0\cdot036$ for 1586 observed reflections. BEDT-TTF molecules are stacked to form columns along **c** [interplanar distance 3·39 (3) Å]. Shortest contacts between adjacent BEDT-TTF molecules in a column are S···S 3·712 (1) Å. The central C=C bond in BEDT-TTF is 1·382 (6) Å.

Introduction. A new family of organic conductors has recently been synthesized, namely, the charge-transfer salts of 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF): *e.g.* (BEDT-TTF)$_2ClO_4(C_2H_3Cl_3)_{0.5}$ (Saito, Enoki, Toriumi & Inokuchi, 1982). These include the first sulfur-based organic superconductors, (BEDT-TTF)$_2ReO_4$ ($T_c = 2$ K) at 0·4 GPa pressure (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983) and (BEDT-TTF)I_3 ($T_c = 1\cdot5$ K) at ambient pressure (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984). After these, many BEDT-TTF salts have been synthesized in an attempt to obtain an organic superconductor with high critical temperature. Many known BEDT-TTF salts have a composition (BEDT-TTF)$_2X$ or (BEDT-TTF)$_3X_2$, where X is a univalent anion such as PF_6^- (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1983), AsF_6^- (Leung, Beno, Blackman, Coughlin, Miderski, Joss, Crabtree & Williams, 1984), $InBr_4^-$ (Beno, Cox, Williams & Kwak, 1984), ClO_4^- (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1984), I_3^- (Leung, Emge, Beno, Wang & Williams, 1984; Bender, Hennig, Schweitzer, Dietz, Endres & Keller, 1984; Shibaeva, Kaminskii & Yagubskii, 1985) or other polyhalide series. (BEDT-TTF)X(THF)$_{0.5}$ ($X = ReO_4^-$ and IO_4^-; THF = tetrahydrofuran) salts (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1984) form 4:4 salts which consist of four independent complexes in the unit cell.

In the present paper, we report the crystal structure of the 1:1 salt (BEDT-TTF)$CuCl_2$.

Experimental. Crystal prepared by diffusion of BEDT-TTF and $CuCl_2.2H_2O$ in 1,1,2-trichloroethane; black prism $0\cdot50 \times 0\cdot30 \times 0\cdot30$ mm; D_m by flotation; Rigaku automated four-circle diffractometer AFC-5R; cell dimensions from 20 selected reflections with $25 \le \theta \le 31°$; 1585 measured reflections, $2\theta_{max} = 126\cdot0°$, $-8 \le h \le 8$, $-14 \le k \le 14$, $0 \le l \le 7$, R_{int}

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[*] To whom correspondence should be addressed.

= 0·020; three standard reflections after every 100 reflections (decay less than 1%). Structure solved by the Monte Carlo direct method (Furusaki, 1979) with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 1356 non-zero unique reflections, refined on F^2 by full-matrix least-squares program with absorption correction by analytical method (Katayama, Sakabe & Sakabe, 1972); transmission factors 0·0014 to 0·019. Non-H atoms given anisotropic temperature factors. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to that for bonded C atom. $R = 0.036$, $S = 1.88$, $w = 1/\sigma^2(F)^2$, $(\Delta/\sigma)_{\max} = 0.096$ for x of H(7*B*), $\Delta\rho_{\max} = 1.0\ \text{e Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) employed for drawing molecular structure and crystal structure projection. All calculations made on a FACOM M-382 computer at the Computer Center of Nagoya University.

Discussion. The atomic parameters are given in Table 1.[*] The projection of the structure along the *c* axis is shown in Fig. 1. BEDT-TTF molecules and $CuCl_2$ molecules are on the center of inversion. The BEDT-TTF radicals are stacked to form columns along the *c* axis with an interplanar distance of 3·39 (3) Å. The shortest contacts between the adjacent cations in a column are found between S(5) and S(9) with a distance of 3·712 (1) Å and the shortest intercolumn contacts are found between S(6) and S(9) with a distance of 3·443 (1) Å (see Table 2). These results suggest two-dimensional interaction of BEDT-TTF molecules. Fig. 2 shows the bond lengths and bond angles of the BEDT-TTF molecules. The length of the central C=C bond in BEDT-TTF is comparable with that of the BEDT-TTF cation in the (BEDT-TTF)$ReO_4(THF)_{0.5}$ crystal [R = 1·375 (28) Å] (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1984). However, the *c*-axis polarized reflection spectrum of the crystal shows the metallic reflection in the lower energy region in addition to the CT_1 or *LE* band in the near IR region (~11 000 cm^{-1}) (Tanaka, Kawamoto & Tanaka, 1986). These facts mean that the BEDT-TTF molecules have fractional charge and the dichlorocuprate molecules are a mixture of $Cu^{I}Cl_2^-$ and $Cu^{II}Cl_2$. That is, the Cu atoms in $CuCl_2$ are in a mixed-valence state consisting of mono- and divalent cations. This can be supported by the fact that the Cu—Cl bond length [R = 2·108 (1) Å] is shorter than that of $Cu^{II}Cl_2.2H_2O$ [R = 2·290 (4) Å] (Engberg, 1970).

Table 1. *Positional parameters* (×10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2 × 10^2)
C(1)	−5025 (4)	4636 (2)	−6083 (5)	238 (07)
S(2)	−2714 (1)	4517 (1)	−7148 (1)	279 (02)
C(3)	−4045 (4)	3568 (3)	−9865 (5)	239 (07)
C(4)	−6255 (4)	3180 (2)	−10207 (5)	231 (07)
S(5)	−7452 (1)	3714 (1)	−7854 (1)	257 (02)
S(6)	−24475 (1)	3158 (1)	−11873 (1)	306 (03)
C(7)	−4255 (5)	1634 (3)	−13053 (6)	313 (08)
C(8)	−6365 (5)	1567 (3)	−14426 (6)	310 (08)
S(9)	−8041 (1)	2260 (1)	−12728 (1)	296 (02)
Cu(11)	0	0	0	445 (03)
Cl(12)	1574 (2)	−1028 (1)	−2003 (2)	432 (03)

Table 2. *Selected intermolecular distances* (Å)

S(2)—S(6^{i})	3·758 (1)	Cu(11)—S(9^{iv})	3·377 (1)
S(5)—S(6^{ii})	3·654 (1)	Cl(12)—S(9^{iv})	3·435 (1)
S(5)—S(9^{i})	3·712 (1)	Cl(12)—S(5^{iv})	3·496 (1)
S(6)—S(9^{iii})	3·443 (1)		

Symmetry code: (i) $x, y, 1+z$; (ii) $-1+x, y, z$; (iii) $1+x, y, z$; (iv) $-1-x, -y, -1-z$.

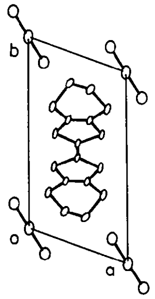

Fig. 1. Projection of the structure along the *c* axis.

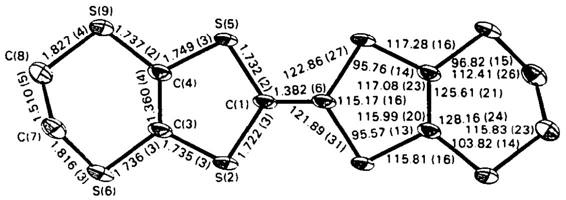

Fig. 2. Molecular dimensions for BEDT-TTF in the (BEDT-TTF)$CuCl_2$ complex.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43339 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of μ-Perchlorato-bis[*N*,*N*′-bis(β-carbamoylethyl)-*N*,*N*′-dimethylethylenediaminecopper(II)] Perchlorate*

BY TIAN-HUEY LU, HSI-CHI SHAN, MIN-SHIUN CHAO AND CHUNG-SUN CHUNG

National Tsing Hua University, Hsinchu, Taiwan 30043

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Abstract. $[\{Cu(C_{10}H_{22}N_4O_2)\}_2(ClO_4)](ClO_4)_3$, $M_r = 985{\cdot}5$, orthorhombic, $Pnma$, $a = 10{\cdot}367\,(1)$, $b = 27{\cdot}545\,(5)$, $c = 12{\cdot}876\,(2)$ Å, $U = 3676{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}75$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7093$ Å, $\mu = 1{\cdot}54$ mm^{-1}, $F(000) = 2024$, 298 (5) K, final $R = 0{\cdot}060$, $wR = 0{\cdot}049$ for 2353 observed reflections. The two copper(II)-diiminodiamide moieties of the binuclear complex are related to each other by a mirror plane containing a Cl and two O atoms of the perchlorate bridge. The Cu of each of these moieties is five-coordinate in a slightly distorted square-pyramidal geometry, and is displaced from the best plane of the two imino nitrogens and the two amide oxygens towards the apex of the pyramid, which is formed by a perchlorate O atom with the Cu—O distance 2·476 Å. The complex has the *RR* or *SS* configuration for the two chiral amine N centers, and the five-membered chelate ring adopts a stable *gauche* conformation. The two six-membered rings are in chair forms.

Introduction. In a previous paper we have reported the crystal structure of copper(II) with $H_2NOC(CH_2)_2NH(CH_2)_2NH(CH_2)_2CONH_2$ (bcen) (Lee, Lu, Liu, Chung & Lee, 1984). As an extension, the crystal structure of the title compound is described here. Detailed structures of these two compounds are compared.

Experimental. The ligand *N*,*N*′-bis(β-carbamoylethyl)-*N*,*N*′-dimethylethylenediamine, *N*-Me$_2$bcen, was prepared by using the following procedure: 13·2 ml (0·2 mol) of *N*,*N*′-dimethylethylenediamine and 28·4 g (0·4 mol) of acrylamide in 50 ml acetonitrile were refluxed for 2 h. The solution was cooled and the product filtered off, washed with chloroform, recrystallized from chloroform, and dried in air; *N*-Me$_2$bcen was reacted with $Cu(ClO_4)_2.6H_2O$ in water. The title compound was crystallized from 9:1 ethanol–water solution (Chao & Chung, 1981; Wei, Chao & Chung, 1979).

CAD-4 diffractometer, graphite monochromator, blue rhombohedral crystal 0·2 × 0·3 × 0·5 mm used for data collection, unit-cell parameters from 25 reflections with $21 \le 2\theta \le 28°$, data collected by ω–2θ scans with scan parameters $2(0{\cdot}7 + 0{\cdot}35\tan\theta)°$ and with scan speed $20/10 \sim 20/3°$ min^{-1}, standard reflections $2,13,\bar{3}$, $6\bar{3}0$, $\bar{5}41$ checked every 2 h varied

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* μ-Perchlorato-bis[3,3′-(*N*,*N*′-dimethylethylenediimino)dipropionamide]copper(II) perchlorate.

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