rapid mixing device this interval can be shortened by at least 10^3, putting it in the range of many group ionizations.

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Registry No. Triose phosphate isomerase, 9023-78-3; D_2O, 7789-20-0.

Crystal Structure of a New Type of Two-Dimensional Organic Metal, $(C_{10}H_8S_8)_2ClO_4(C_2H_3Cl_3)_{0.5}$

Hayao Kobayashi*

Department of Chemistry, Faculty of Science
Toho University, Funabashi, Chiba 274, Japan

Akiko Kobayashi and Yukiyoshi Sasaki

Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Tokyo 113, Japan

Gunzi Saito, Toshiaki Enoki, and Hiroo Inokuchi

Institute for Molecular Science, Okazaki 444, Japan

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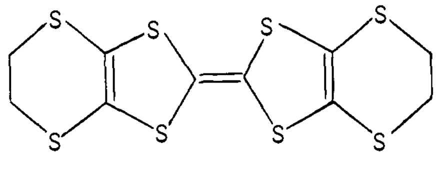
All organic metals known to date are composed of planar donor and/or acceptor molecules with π-conjugated systems. Most of them are regarded as quasi-one-dimensional compounds. The molecules are stacked face to face to form segregated columns. The one-dimensional properties are considered to arise from the intermolecular π–π interaction along the columns.[1-3] Since the CDW and SDW instabilities inherent in one-dimensional metals tend to break the metallic state,[4] interchain interactions must be introduced in order to stabilize this state. However, if the interchain interaction is sufficiently strong, the column structure will be unfavorable and the conduction pathway will become more complicated.

In this paper, we report on the structure of a new type of organic metal where the planar molecules are not stacked face to face but are arranged side by side to form a two-dimensional system. The two-dimensionality of the structure originates from short intermolecular contacts between the sulfur atoms of the donor molecules.



BEDT–TTF

Saito et al. have grown the crystals of the perchlorate salt of bis(ethylenedithiolo)tetrathiafulvalene (abbreviated as BEDT-TTF)[5,6] by the electrochemical oxidation method. The single-crystal resistivity along the elongated direction ($\rho_\parallel$), which is close to the *a* axis in the (010) plane, decreases monotonically from the room-temperature value (3.8×10^{-2} Ω cm) to the minimum at 16 K ($T_{\min}$, 1.0×10^{-3} Ω cm). Metallic conduction is retained even at the lowest measured temperature (1.4 K, 1.5×10^{-3} Ω cm). The anisotropy of the resistivity is very small in the *a*–*c* plane ($\rho_\parallel/\rho_\perp = 0.4$–$0.9$), but the room-temperature resistivity parallel to the b^* direction is 10^2–10^3 times bigger. The stoichiometry of BEDT-TTF to ClO_4 is 2:1, and the crystals contain solvent molecules (1,1,2-trichloroethane). The formal charge on the BEDT-TTF molecule is $^1/_2$. The crystal structure is shown in Figure 1.[7] The unit cell contains four BEDT-TTF, two ClO_4, and $C_2H_3Cl_3$. The two crystallographically independent BEDT-

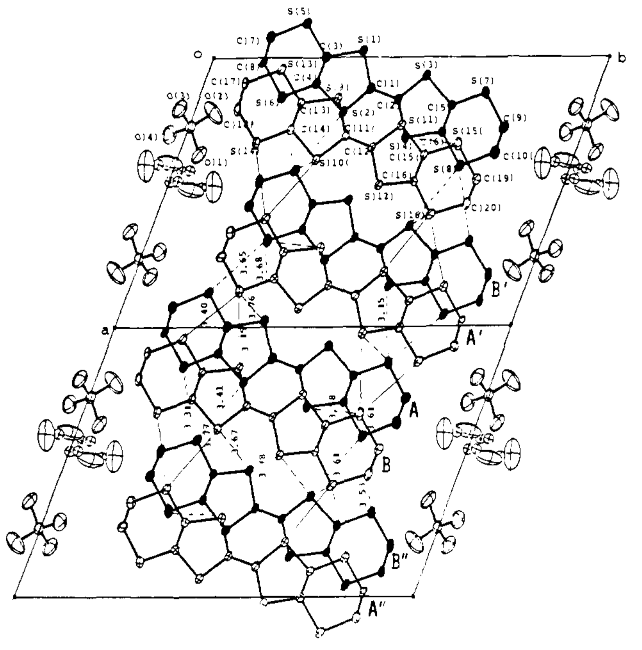


Figure 1. Crystal structure viewed along the c^* axis. Molecules A and B indicate two crystallographically independent BEDT-TTF molecules. The coordinates of the center of molecule A are (0.10, 0.48, -0.26) and those of molecule B are (0.34, 0.43, 0.21). Molecules A′ and A″ (B′ and B″) are the molecules related to A (B) by symmetry operations. The symmetry operations are A(x, y, z), B(x, y, z), A′($-x$, $1-y$, $-z$), B′($-x$, $1-y$, $-z$), A″($1-x$, $1-y$, $-z$), and B″($1-x$, $1-y$, $-z$). Molecules A, B′, and B″ are approximately on the same plane at $z = 0.25$, and molecules B, A′ and A″ are approximately on the plane at $z = 0.25$.

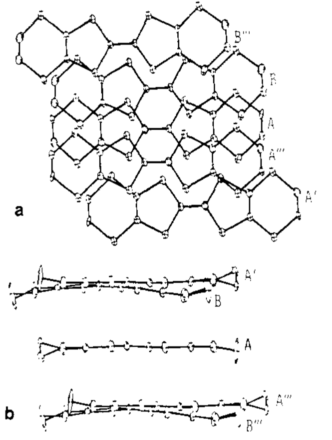


Figure 2. Arrangement of the neighboring BEDT-TTF molecules. The symmetry operations are A(x, y, z), A′($-x$, $1-y$, $-z$), A‴($-x$, $1-y$, $-1-z$), B(x, y, z), and B‴($x, y, -1+z$) (see also Figure 1): (a) mode of the intermolecular overlapping; (b) side view of the moelcular planes.

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(6) The formal name of BEDT-TTF is 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin.

(7) The crystal data (room temperature) are as follows: $(C_{10}H_8S_8)_2ClO_4(C_2H_3Cl_3)_{0.5}$, triclinic; space group $P\bar{1}$; $a = 12.966$ (7), $b = 18.620$ (13), $c = 7.740$ (5) Å; $\alpha = 79.32$ (6), $\beta = 104.80$ (5), $\gamma = 110.85$ (5)°; $V = 1684$ (2) Å^3; $Z = 2$. A total of 8112 reflections were measured (Rigaku automated diffractometer) for $2\theta \leq 60°$ with Mo Kα radiation, of which 3797 reflections were considered to be observed ($|F_o| \geq 3\sigma|F_o|$). Block-diagonal least-squares refinement produced a final agreement factor $R = 0.087$. Fourier syntheses gave fairly large peaks corresponding to the position of chlorine atoms of the trichloroethane molecules, but they are highly disordered and could not be located definitely.

TTF molecules are named hereafter as molecules A and B (see Figure 1). The atomic parameters of one of the two ethylene groups of molecule A and both ethylene groups of molecule B indicate their positional disorder. The perchlorate anion also has large thermal parameters, suggesting molecular rotation as frequently observed in such similar cation radical salts as $(TMTTF)_2ClO_4$[8] and $(TMTSF)_2ClO_4$[9] (TMTTF, tetramethyltetrathiafulvalene; TMSTF, tetramethyltetraselenafulvalene). X-ray diffuse spots indicating the doubling of the lattice constant *c* below ca. 100 K suggest the ordering of the molecular orientation of ClO_4^- at low temperature. The molecular plane of molecule A is almost parallel to that of molecule B. The dihedral angle of the two least-squares planes is 2.9°. The mode of intermolecular overlapping is shown in Figure 2a. Figure 2b shows the molecular arrangement viewed along the direction parallel to the molecular plane.

Unlike the other organic metals with column structures, $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ exhibits only a slight intermolecular overlapping (see Figure 2). As shown in Figures 1 and 2b, the molecules B′, A, and B″ are approximately on the same plane at $z = -1.4$. Similarly the molecules A′, B, and A″ are approximately on the plane $z = {}^1/_4$. Thus the molecules related to A by symmetry operations and those related to B are alternately arranged side by side to form a strip along the *a* axis. This arrangement is in contrast with the face to face stacking typically observed in organic metal systems. The intermolecular S–S contacts in the strip are short compared with the van der Waals distance (3.70 Å). They are given in Figure 1. The shortest distance is 3.34 Å, which is reduced to 3.317 Å at 153 K. Similar side by side arrangement and intermolecular short S–S contacts are found in $(BEDT\text{-}TTF)_2PF_6$.[10] There are also some short S–S contacts between the molecules arranged along the $[10\bar{2}]$ direction. Thus the crystal has a two-dimensional nature, which is consistent with the anisotropy of the conductivities.

Recently we have made the band-structure calculation in order to obtain a better understanding of the two-dimensional conducting properties. The 2s and 2p atomic orbitals of C and the 3s and 3p atomic orbitals of S were used. The intermolecular overlap integral of HOMO is largest along $[10\bar{2}]$ and smallest along [102]. As shown in Figure 2, there is no face to face overlapping along $[10\bar{2}]$ (B‴, A, A′, ...). In spite of the shortest S···S distance, the overlap integrals along [100] are in the middle of the others. This is due to the $p\pi$ character of the HOMO. In an organic metal with face to face stacking, the Fermi surface is expected to be a plane. In fact, the band calculation in TTF-TCNQ gave one-dimensional plane Fermi surface.[11] Similar one-dimensional band structure has been obtained even in the organic superconductor $(TMTSF)_2X$ (X: ClO_4, PF_6, BF_4, ...).[12] However, owing to the two-dimensional molecular arrangement, the band-structure calculation of $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ leads to a very different band structure, indicating that this compound is a two-dimensional organic semimetal or a narrow-gap semiconductor.[13]

The importance of the intermolecular contacts between chalcogen atoms has been already revealed in some low-dimensional conductors. Underhill and Ahmad have found a new type of highly conducting planar platinum complex, $Li_{0.75}[Pt(C_4N_2S_2)_2]\cdot 2H_2O$, where the conduction pathway is considered to be formed by intermolecular contacts of the sulfur atoms of the ligands.[14,15] The crystals of the organic superconductors $(TMTSF)_2X$ suggest the importance of the formation of the two-dimensional Se–Se "sheet-network".[16] The crystal structure of $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ suggests a way to introduce a two-dimensional interaction in the organic conductors, which will be effective in the design new organic metal systems.

Registry No. $(BEDT\text{-}TTF)_2ClO_4\cdot(C_2H_3Cl_3)_{0.5}$, 83314-73-2.

Supplementary Material Available: Table of atomic coordinates (2 pages). Ordering information is given on any current masthead page.

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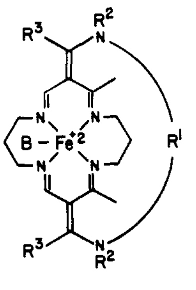
A Totally Synthetic (Nonporphyrin) Iron(II) Dioxygen Carrier That Is Fully Functional under Ambient Conditions

Norman Herron, James H. Cameron, Gary L. Neer, and Daryle H. Busch*

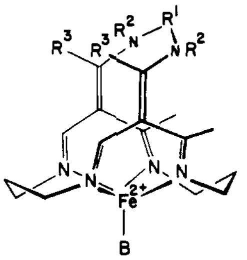
The Chemistry Department, The Ohio State University
Columbus, Ohio 43210

Received November 22, 1982

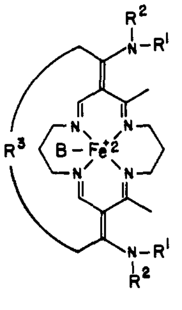
The iron–oxygen chemistry that is well-known among heme proteins has long remained without parallel among the usual coordination compounds of that metal. Even the history of nonporphyrin iron(II)–dioxygen carriers is fraught with misinterpretation and uncertainty.[1] Only relatively recently have unchallenged examples of such iron–dioxygen carriers been reported. Baldwin and Huff[2] synthesized an iron(II) complex with a hindered 14-membered macrocycle that showed reversible O_2 binding in anhydrous solvents at −85 °C but lost all trace of reversible binding by −50 °C. The only other example was our lacunar iron(II) complex[3] of structure I (R^1 = *m*-xylylene; $R^2 = R^3 = CH_3$). The O_2 adduct of this complex shows complete reversibility up to temperatures of about −35 °C, and the O_2 adduct is still detectable at temperatures above 0 °C. We now report iron-based O_2 carriers that are fully functional under ambient conditions.



Ia



Ib



II

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