Structure and Optical Spectrum of $(TMTTF)_2IO_4$. The Role of Coulomb Interaction

Kyuya Yakushi,* Sukekazu Aratani, Koichi Kikuchi, Hiroyuki Tajima, and Haruo Kuroda
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received September 4, 1985)

The semiconductive $(TMTTF)_2IO_4$ salt was prepared by using the electrochemical method. The crystal structure was determined to be isomorphous to the metallic $(TMTTF)_2X$ salts. The polarized infrared reflectance spectra of $(TMTTF)_2IO_4$ and $(TMTTF)_2BF_4$ were measured and were interpreted on the basis of the extended Hubbard model.

Over the past few years, the bis(tetramethyltetrathiafulvalenium) salts $[(TMTTF)_2X]$ have been widely studied.[1] All of these salts exhibit a metallic character as regards the temperature dependence of electrical resistivity near room temperature.[2] On the other hand, the optical spectra of $(TMTTF)_2PF_6$ and $(TMTTF)_2Br$ do not show a Drude-like spectral shape, but show a shape which suggests the localization of charges due to the Coulomb interaction.[3] We found a new semiconductive TMTTF salt, $(TMTTF)_2IO_4$, which has an isomorphous structure to other $(TMTTF)_2X$ salts. Although this salt is a semiconductor, its optical spectrum was found to be very similar to that of the metallic $(TMTTF)_2PF_6$, showing a non Drude-like spectral shape. These facts suggest that the Coulomb interaction cannot be neglected also in the metallic $(TMTTF)_2PF_6$, and if this is the case, the transfer integrals, which were given for $(TMTTF)_2PF_6$ from the analysis of its reflectance data by use of the Drude model, should be reexamined by taking account of the Coulomb interaction. In this paper we describe the characteristic structure of the TMTTF column of $(TMTTF)_2IO_4$, and estimate the band parameters of the extended Hubbard model through the analysis of the reflectance spectrum. The reflectance spectrum of the metallic $(TMTTF)_2BF_4$ was also measured for the purpose of comparison.

Experimental

The single crystals of $(TMTTF)_2IO_4$ and $(TMTTF)_2BF_4$ were obtained in the tetrahydrofuran solutions of $(n\text{-}Bu_4N)BF_4$ and $(n\text{-}Bu_4N)IO_4$ by using the electrochemical method. The temperature of the electrochemical cell was controlled to be 0 °C and the constant current, 5 μA, was applied for 2 d. The largest crystal thus obtained was of the dimension of $5\times1\times0.2\,\mathrm{mm}^3$ for $(TMTTF)_2BF_4$ and $20\times2.5\times0.5\,\mathrm{mm}^3$ for $(TMTTF)_2IO_4$. The low frequency electrical resistivity was measured along the a-axis by using a standard four-probe method. The electrical contacts were made by 20 μm gold wires with carbon paint onto the (001) crystal face. The reflectance measurement on the (001) crystal faces was conducted over the spectral range from $720\,\mathrm{cm}^{-1}$ to $25000\,\mathrm{cm}^{-1}$ by using the microspectrophotometric technique. The intensities of X-ray diffraction were collected with Rigaku automated diffractometer using Mo *Kα* radiation in the range of 2θ from 2° to 60°. The 1107 independent diffractions which are larger than three times of the standard deviations were used for the analysis. The full-matrix-least-squares refinement reduced the R-value to 0.079.

Results and Discussion

The temperature dependence of the electrical conductivity of $(TMTTF)_2IO_4$ is shown in Fig. 1. The electrical behavior is semiconductive throughout the observed temperature region below 300 K. The room-temperature dc conductivity along the a-axis was $\approx10\,\Omega^{-1}\mathrm{cm}^{-1}$. The activation energy around 150 K was obtained to be 0.09 eV, which is about twice the values of other $(TMTTF)_2X$ salts. Among the $(TMTTF)_2X$ salts, $(TMTTF)_2IO_4$ is the first example which exhibits the semiconductive behavior at room temperature.

The crystal of $(TMTTF)_2IO_4$ belongs to the triclinic system, the space group $P\bar{1}$, the lattice constants being $a=7.226(6)$ Å, $b=7.664(3)$ Å, $c=13.226(4)$ Å, $\alpha=81.99(3)°$, $\beta=96.54(4)°$, $\gamma=106.68(5)°$, $Z=1$. The final values of the fractional coordinates were listed in Table 1. The crystal structure is isomorphous to other $(TMTTF)_2X$ salts as shown in Fig. 2, in which the two orientations, of IO_4 occupying the center of symmetry are drawn separately although those two orientations are randomly distributed. The intrastack S–S distances are significantly shorter than the interstack S–S distances.

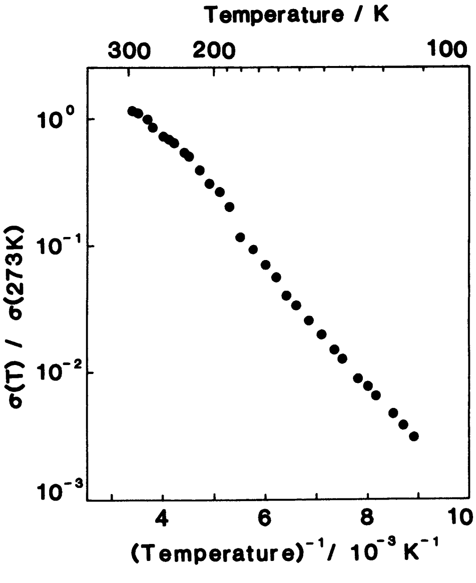

Fig. 1. Temperature dependence of the electrical conductivity.

Table 1. Fractional Atomic Coordinates ($\times 10^4$) of $(TMTTF)_2IO_4$. The e.s.d.'s are Given in Parentheses

Atom	x	y	z	$B_{eq}(A^2)$[a]
I	0000(0)	5000(0)	5000(0)	6.3
S1	3435(7)	3140(6)	1017(4)	4.1
S2	2514(8)	−545(6)	2115(4)	4.1
S3	2720(8)	1424(6)	−1135(4)	4.2
S4	1853(7)	−2261(6)	−55(4)	3.9
C1	2817(25)	825(22)	924(13)	3.3
C2	2483(28)	62(21)	33(15)	4.0
C3	3600(27)	2971(27)	2370(15)	4.4
C4	3128(28)	1265(23)	2863(14)	4.2
C5	2169(24)	−406(23)	−1885(13)	3.4
C6	1738(27)	−2078(24)	−1392(12)	3.6
C7	4176(31)	4751(25)	2828(14)	5.1
C8	3157(35)	803(27)	4026(13)	5.9
C9	2241(32)	177(25)	−3039(13)	4.8
C10	1226(30)	−3894(24)	−1852(14)	4.8
O1	260(108)	3184(55)	4484(39)	15.3
O2	1661(137)	6110(77)	5441(44)	18.0
O3	−1977(83)	5051(91)	4986(53)	15.3
O4	−320(113)	3630(56)	6228(32)	18.3

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i a_j)$.

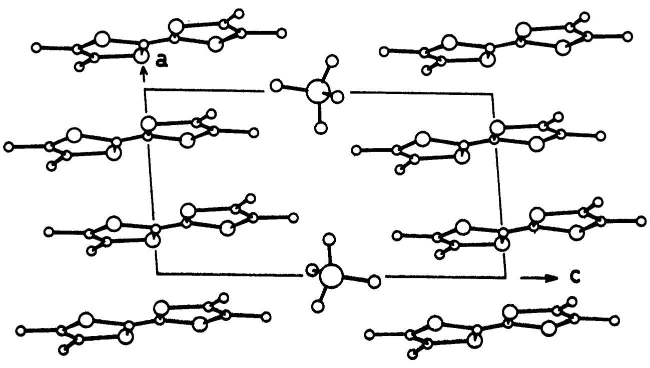

Fig. 2. Crystal structure of $(TMTTF)_2IO_4$ projected along the b-axis.

Table 2. Inter-Planar Spacings in the TMTTF Stack[a]

Anion	d1	d2	d2−d1	(d1+d2)/2
Br	3.50	3.53	0.03	3.52
I	3.50	3.54	0.04	3.52
SCN	3.49	3.56	0.07	3.53
NO_3	3.50	3.57	0.07	3.54
BF_4	3.54	3.56	0.02	3.55
ClO_4	3.52	3.59	0.07	3.56
PF_6	3.52	3.62	0.10	3.57
ReO_4	3.57	3.59	0.02	3.58[b]
AsF_6	3.54	3.64	0.10	3.59
IO_4	3.58	3.63	0.05	3.61[c]

a) The values of d1 and d2 except for IO_4 and BF_4 salts are given in Ref. 4. b) Ref. 12. c) This work.

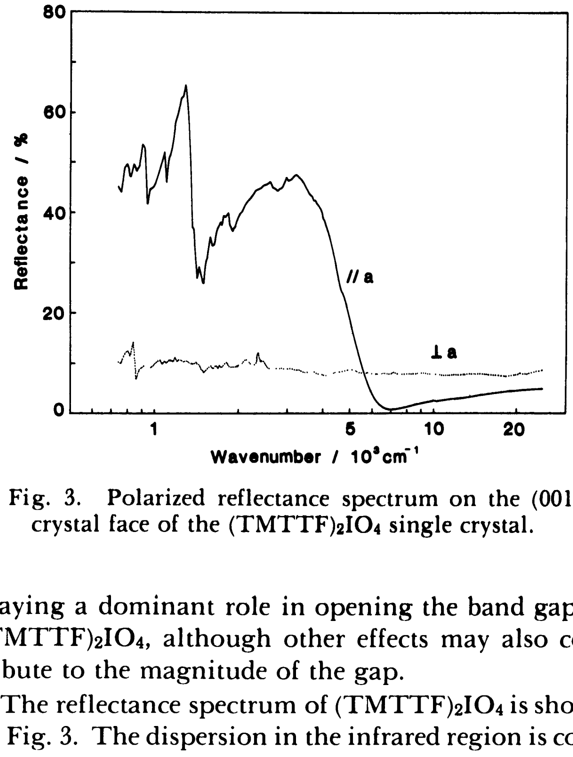

Fig. 3. Polarized reflectance spectrum on the (001) crystal face of the $(TMTTF)_2IO_4$ single crystal.

This result indicates that this salt possesses a strong one-dimensional nature like other $(TMTTF)_2X$ salts. The TMTTF molecules are stacking diadically along the a-axis. The interplanar spacings between the TMTTF molecules are listed in Table 2 together with the corresponding values of other $(TMTTF)_2X$ salts. In a $(TMTTF)_2X$ crystal, the semiconductive gap is introduced by the periodic potentials,[5] the difference of the transfer integrals,[5] and the nearest-neighbor Coulomb interaction, V,[6] if the on-site Coulomb repulsion, U, is very large as compared with the average transfer integral, t. The difference of the transfer integrals increases with the increase of the value of the difference between the interplanar spacings, (d2−d1), found in a TMTTF stack, while the normalized Coulomb interaction, V/t, increases with the increase of the average spacing. The most characteristic feature of the semiconductive $(TMTTF)_2IO_4$ is that it shows the largest average spacing among the $(TMTTF)_2X$ salts hitherto investigated. This fact suggests that the Coulomb interaction, V, is playing a dominant role in opening the band gap in $(TMTTF)_2IO_4$, although other effects may also contribute to the magnitude of the gap.

The reflectance spectrum of $(TMTTF)_2IO_4$ is shown in Fig. 3. The dispersion in the infrared region is completely polarized along the stacking axis. The spectrum is very similar to that of $(TMTTF)_2PF_6$, which was reported by Jacobsen et al.[3] We calculated the optical conductivity spectrum through the Kramers-Kronig transformation of the reflectance data. The spectrum thus obtained is shown in Fig. 4 together with the spectrum of $(TMTTF)_2BF_4$, which is known to be metallic. Four prominent peaks, A, B, C, and D were observed in the infrared region. The maximum position of the peak A is 2300 cm^{-1} for $(TMTTF)_2IO_4$ and 2100 cm^{-1} for $(TMTTF)_2BF_4$. This broad band is assignable to the charge-transfer transition from $TMTTF^0$ to $TMTTF^+$ or interband transition between the subbands separated mainly by Coulomb energy, V. The positions of peaks, B, C, and D are 1180 cm^{-1}, 1080 cm^{-1}, and 900 cm^{-1} both for $(TMTTF)_2IO_4$ and $(TMTTF)_2BF_4$. These peaks correspond to the a_{1g} vibrational transitions of TMTTF mixed with the charge-transfer excitation.[7] The total oscillator strength, which can be the measure of the

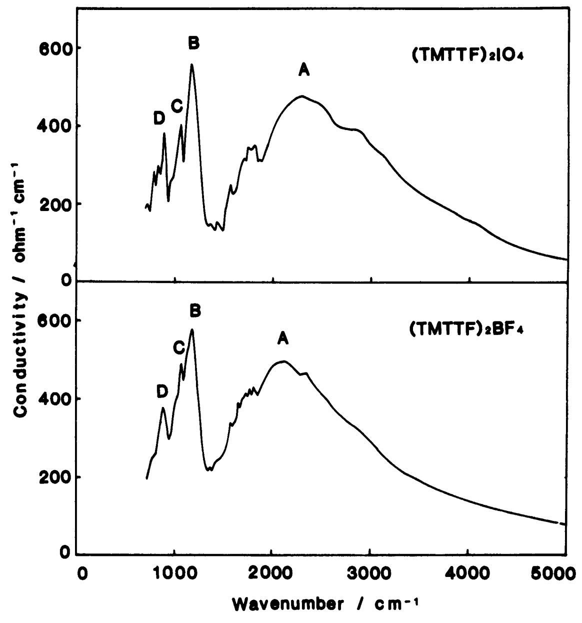

Fig. 4. Conductivity spectra in the infrared region.

magnitude of transfer integral, was obtained by the numerical integration of the conductivity curve from 0 to 10000 cm^{-1}, where the conductivity curve in the region from 720 cm^{-1} to 0 cm^{-1} was drawn by a smooth extrapolation to the dc conductivity at zero frequency. The oscillator strengths thus obtained were about 0.4 both for $(TMTTF)_2IO_4$ and $(TMTTF)_2BF_4$. This value is slightly smaller in comparison with alkali-metal–TCNQ salt, which gave the oscillator strength value of about 0.5.[8,9]

We should consider that the band-gap in $(TMTTF)_2IO_4$ arises from the electron–electron Coulomb interactions, since the one-electron theory predicts a metallic state without a gap for a diadically stacked TMTTF column. If the on-site Coulomb repulsion, U, is much larger than the average transfer integrals, t, the band-gap is introduced by the periodic potentials due to anions, by the nonequivalent transfer integrals in the diadically stacked column, and/or by the nearest-neighbor Coulomb repulsion, V. As we have already mentioned, the crystal structure of $(TMTTF)_2IO_4$ suggests the importance of V for opening a semiconductive gap. The difference of the two kinds of transfer integrals is rather small and is not likely to be the main factor. Thus, let us make a rough estimation of the band parameters, U, V, and t within the framework of the extended Hubbard model. In the case $U \gg t$, the exact solution of the 3/4-filled extended Hubbard chain predicts that $V/2t=1$ is the boundary between a metal and a semiconductor.[6] Thus, we can consider that $V>2t$ in $(TMTTF)_2IO_4$, because it is semiconductive at room temperature. No theory is known to predict the excitation energy and the oscillator strength of the optical transition in such a case. However, we could estimate the parameters in the following way. Mazumdar and Soos calculated the band structure of a one-dimensional chain in the limit of $V \gg 2t$, and concluded the optical gap to be $V+2t^2/V$.[6] Since the electronic transition (peak A) appears at about 0.3 eV, we should consider that $2t<V<0.3$ eV. From the magnetic susceptibility study, Delhaes et al.[10] proposed that $(U-V)/4t \simeq 2$ for the $(TMTTF)_2X$ salts. If we assume this relation for $(TMTTF)_2IO_4$, we obtain the following relations: $U<1.5$ eV and $2t<V<0.3$ eV. Thus the parameters in $(TMTTF)_2IO_4$ are likely to be comparable with those of K·TCNQ[8] and Rb·TCNQ[9], and consistent also with the powder optical spectrum of TMTTF–Br.[11] As shown in Fig. 4, the optical conductivity spectrum of the semiconductive $(TMTTF)_2IO_4$ is quite similar to that of the metallic $(TMTTF)_2BF_4$. This fact indicates that the band structures of these two salts are similar to each other. Mortensen et al. proposed from their thermopower studies that the apparent metallic behavior observed for several $(TMTTF)_2X$ salt comes not from the absence of a band gap but from the narrowness of their semiconductive gap.[12] According to their model, we can consider that the difference between the semiconductive $(TMTTF)_2IO_4$ and other metallic $(TMTTF)_2X$ salts exists only in the magnitude of the band gap. The similarity of the reflectance spectrum between $(TMTTF)_2BF_4$ and $(TMTTF)_2IO_4$, shown in the present study, indeed supports their model.

We thank Dr. A. Kobayashi and Dr. K. Ichida for their kind assistance to the crystal structure analysis. This work was supported by the Grant-in-Aid for the Special Project Research on "The Properties of Molecular Assemblies"(No.59112002) from the Ministry of Education, Science and Culture.

References

1) See "Proceedings of the International Conferences on the Physics and Chemistry of Organic Metals" [*J. Phys. (Paris) Colloq.* **44**, C3 (1983)].

2) P. Delhaes, C. Coulon, J. Amiell, S. Flandrois, E. Toreilles, J. M. Fabre, and L. Giral, *Mol. Cryst. Liq. Cryst.*, **50**, 43 (1979).

3) C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, *Phys. Rev.* **B28**, 7019 (1983).

4) B. Liautard, S. Peytavin, G. Brun, and M. Maurin, *J. Phys. (Paris) Colloq.* **44**, C3-951 (1983).

5) R. Bosio, M. Meneghetti, and C. Pecile, *J. Chem. Phys.*, **76**, 5782 (1982).

6) S. Mazumdar and Z. G. Soos, *Phys. Rev.*, **B23**, 2810 (1981).

7) M. J. Rice, V. M. Yartsev, and C. S. Jacobsen, *Phys. Rev.*, **B21**, 3437 (1980).

8) K. Yakushi, T. Kusaka, H. Kuroda, *Chem. Phys. Lett.*, **68**, 139 (1979).

9) K. Yakushi, S. Miyajima, T. Kusaka, H. Kuroda, *Chem. Phys. Lett.*, **114**, 68 (1985).

10) P. Delhaes, C. Coulon, J. Amiell, S. Flandrois, E. Toreilles, J. M. Fabre and L. Giral, *Mol. Cryst. Liq. Cryst.*, **50**,

43 (1972).

11) J. B. Torranace, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev.*, **B19**, 730 (1979).

12) K. Mortensen, E. M. Conwell, and J. M. Fabre, *Phys. Rev.*, **B28**, 5856 (1983).