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Crystal Structure and Reflectance Spectrum of β''-$(BEDT\text{-}TTF)_2IAuBr$

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$(BEDT\text{-}TTF)_2IAuBr$ was synthesized and the crystal structure of this material was determined to be of the β''- type, being isomorphous to β''-$(BEDT\text{-}TTF)_2AuBr_2$. The polarized reflectance spectrum indicates that the electronic structure of this salt is of considerable two-dimensional character.

Discovery of the superconductivity in β-$(BEDT\text{-}TTF)_2AuI_2$[1] has raised a strong interest in the series of $(BEDT\text{-}TTF)_2X$, where X is a linear metal-halide anion. Depending on the anion, the arrangement of BEDT-TTF molecules was found to be a little different from that of β-$(BEDT\text{-}TTF)_2AuI_2$, and this type of structure was called β'-type.[2,3] Recently, another new type was found by Mori et al. on $(BEDT\text{-}TTF)_2AuBr_2$ and named β''-type.[4] We prepared $(BEDT\text{-}TTF)_2X$ salt with a new metal-halide anion $IAuBr^-$, and found it to be of the β''-type. In this letter, we present the crystal structure and reflectance spectrum of β''-$(BEDT\text{-}TTF)_2IAuBr$.

Single crystals of β''-$(BEDT\text{-}TTF)_2IAuBr$ were obtained by the electrochemical oxidation of BEDT-TTF in THF, by using tetra-n-butylammonium bromoiodoaurate(I)[5] as the supporting electrolyte. Reflection data were collected by the ω-2θ scan technique with a Rigaku automated four-circle diffractometer. The used X-ray was CuK_α radiation monochromatized with graphite. The shape of the sample crystal was a distorted hexagon of the dimension , 0.50 x 0.30 x 0.10 mm^3. The crystal belongs to the triclinic system with the space group $P\bar{1}$, the lattice parameters being a = 9.071(1), b = 16.406(2), c = 5.770(2) Å, α = 97.61(2), β = 103.43(2), γ = 91.70(1)°, V = 826.3(3) $Å^3$, and Z = 1. We obtained 2643 independent reflections ($|F_o| > \sigma(F)$) and solved the structure by the direct method combined with the Monte-Carlo method[6] for the selection of initial phases. The refinement was carried out by the full-matrix least-squares method after applying the absorption corrections. The final values of R and R_w were 0.053 and 0.061, respectively. The atomic coordinates are given in Table 1. The anisotropic thermal parameters and the list of the structure factors are available upon request.

Figure 1 shows the crystal structure of β''-$(BEDT\text{-}TTF)_2IAuBr$, which is isostructural to β''-$(BEDT\text{-}TTF)_2AuBr_2$. Since under the assumption of the $P\bar{1}$ space group, asymmetric $IAuBr^-$ anion lies on an inversion center, Br and I atoms cannot

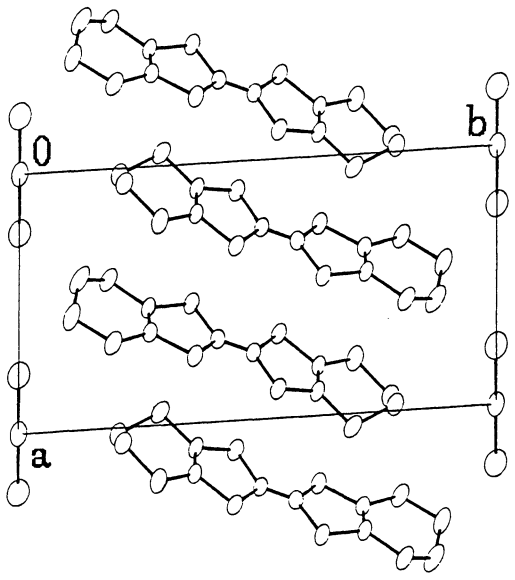

Fig. 1. Crystal structure of β''-(BEDT-TTF)$_2$IAuBr, projected along the c axis.

Table 1. Atomic parameters (x10^4) and equivalent thermal factors $B_{eq}=(4/3)\sum\sum_{ij}\beta_{ij}\cdot a_i a_j$(Å^2)

Atom	X	Y	Z	B_{eq}
Au	0	0	0	4.5
IBr	2269(1)	3(1)	-1583(2)	6.4
S(1)	7394(2)	3699(1)	7712(3)	3.3
S(2)	8866(2)	5443(1)	7236(3)	3.4
S(3)	5376(2)	3616(1)	2898(3)	3.4
S(4)	6744(2)	5448(1)	2542(3)	3.3
S(5)	6716(2)	1989(1)	8340(4)	4.1
S(6)	10505(2)	7018(1)	7189(4)	3.9
S(7)	4279(2)	1880(1)	2564(4)	4.0
S(8)	7867(3)	7046(1)	1691(4)	4.1
C(1)	6802(7)	4172(4)	5146(12)	2.8
C(2)	7399(7)	4916(4)	4980(12)	2.7
C(3)	6394(8)	2762(4)	6474(13)	3.0
C(4)	9054(8)	6276(4)	5702(13)	3.0
C(5)	5443(8)	2723(4)	4278(13)	3.1
C(6)	8061(8)	6288(4)	3580(12)	2.8
C(7)	5612(12)	1112(5)	6485(20)	5.6
C(8)	9756(10)	7900(5)	5906(17)	4.4
C(9)	4201(12)	1273(6)	4881(19)	5.9
C(10)	9407(9)	7792(5)	3182(16)	4.3

be distinguished from one another. Attempts to refine the data assuming the noncentrosymmetric space group, P1, led to the result that I-Au and Au-Br distances were equal to each other. Therefore, we adopted the space group, $P\bar{1}$, and concluded that $IAuBr^-$ anions are completely in an orientationally disordered state. The intramolecular bond lengths and bond angles of BEDT-TTF are shown in Fig. 2, which is the typical geometry of $BEDT\text{-}TTF^{1/2+}$.[8]

The BEDT-TTF molecules and $IAuBr^-$ anions are on separate sheets parallel to the (010) plane, and these molecular sheets are alternately stacked along the b-axis. The molecular arrangement in the BEDT-TTF sheet is illustrated in Fig. 3.

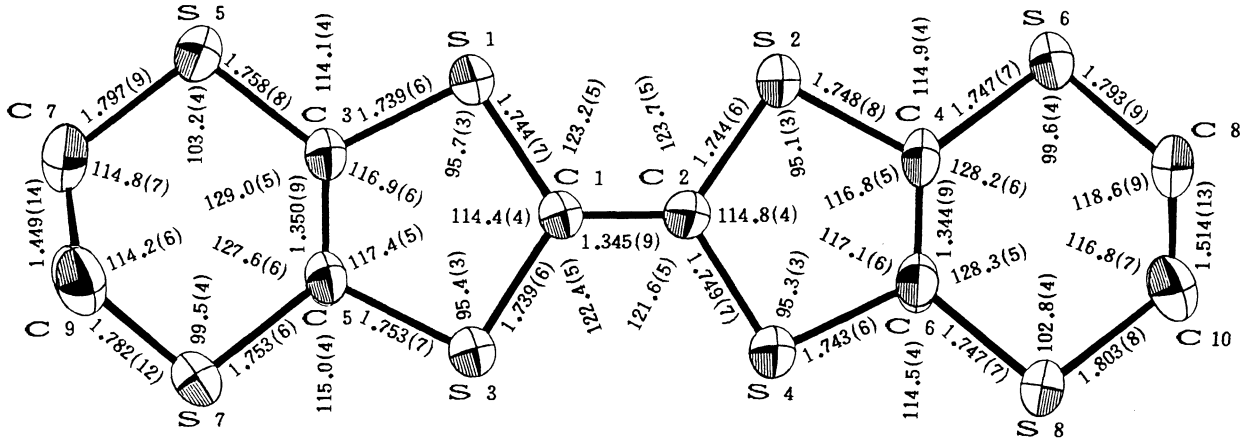

Fig. 2. Bond lengths and bond angles of BEDT-TTF in β''-(BEDT-TTF)$_2$IAuBr.

Table 2. Intermolecular S···S contacts shorter than 4 Å. The symbols of the interactions a1, a2, etc. are shown in Fig. 3

a1	S(3)-S(4)	3.800(3)	c	S(5)-S(7)	3.668(3)	p	S(7)-S(8)	3.471(3)
				S(5)-S(3)	3.916(3)		S(3)-S(8)	3.504(3)
a2	S(1)-S(6)	3.843(3)		S(1)-S(3)	3.868(2)		S(3)-S(4)	3.816(3)
	S(2)-S(2)	3.828(3)		S(1)-S(4)	3.884(2)		S(4)-S(4)	3.878(3)
	S(6)-S(3)	3.918(3)		S(2)-S(4)	3.977(3)			
				S(2)-S(8)	3.712(3)	q	S(5)-S(6)	3.360(3)
				S(6)-S(8)	3.917(3)		S(1)-S(6)	3.481(3)
							S(2)-S(2)	3.857(3)

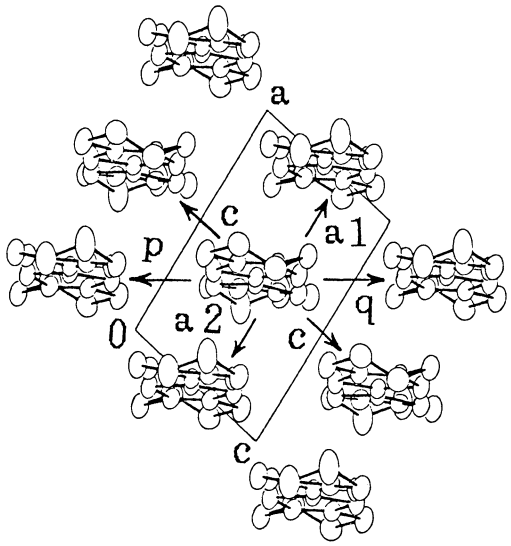

Fig. 3. The arrangement of the donor molecules in β''-(BEDT-TTF)$_2$IAuBr, viewed along the molecular long axis.

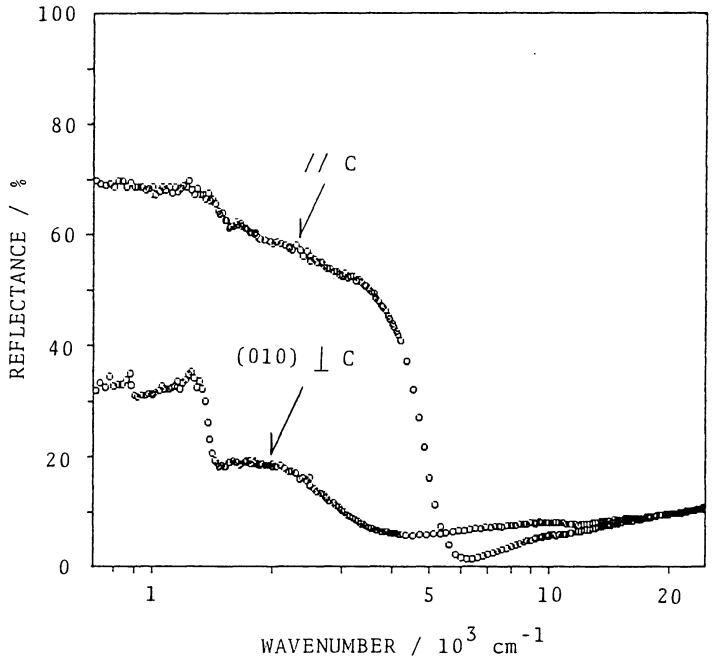

Fig. 4. Polarized reflectance spectrum of β''-(BEDT-TTF)$_2$IAuBr on the (010) crystal face.

Leung et al. and Mori et al. proposed an empirical relation between the packing mode of BEDT-TTF and the anion size.[2,4] According to this relation, the structure of (BEDT-TTF)$_2$IAuBr is expected to be of the β'-type. However, this material takes β''-type lattice, despite that the anion length of $IAuBr^-$(8.98Å) is almost the same as that of $BrICl^-$ (9.0Å) which forms the salt of β'-type. The intermolecular S···S contacts are summarized in Table 2. All of these are very similar to the corresponding distances in β''-(BEDT-TTF)$_2$AuBr$_2$. Therefore, the band structure is essentially the same as that of β''-(BEDT-TTF)$_2$AuBr$_2$, the electronic structure of which was predicted to be one-dimensional along the c direction.[4]

Figure 4 shows the reflectance spectra measured on the (010) crystal face at 293 K, over the spectral range from 720 cm^{-1} to 25,000 cm^{-1}, for the two light polarizations parallel and perpendicular to the c-axis. The infrared reflectivity was found to be maximum when the polarization direction is parallel to the c-axis, which is the direction of the maximum intermolecular orbital overlap according to Mori et al.[4] Although the anisotropy is fairly large, the infrared dispersion is clearly observed also in the $\perp$ c spectrum, indicating a considerable two-dimensional character of the electronic structure of this salt. The reflectance spectrum of β''-(BEDT-TTF)$_2$IAuBr is similar to that of (BEDT-TTF)$_3$(ClO_4)$_2$,[9] which has the arrangement of BEDT-TTF very similar to β''-(BEDT-TTF)$_2$IAuBr. Details of the interpretation of the reflectance data will be described elsewhere.

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