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Charge-Transfer Salts Derived from the New Electron-Donor Molecule BEDO-TTF: ESR, Superconductivity and Electrical Properties, and Crystal and Band Electronic Structure

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CHARGE-TRANSFER SALTS DERIVED FROM THE NEW ELECTRON-DONOR MOLECULE BEDO-TTF: ESR, SUPERCONDUCTIVITY AND ELECTRICAL PROPERTIES, AND CRYSTAL AND BAND ELECTRONIC STRUCTURE

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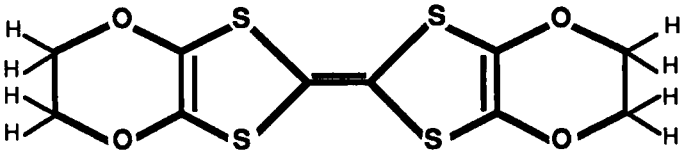
ABSTRACT. Charge transfer salts of bis(ethylenedioxy)tetrathiafulvalene, BEDO-TTF, namely $(BEDO\text{-}TTF)_2AuBr_2$, and charge transfer salts $(BEDO\text{-}TTF)_mX_n$ where X^- is I_3^-, AuI_2^-, $Au(CN)_2^-$, ClO_4^-, BrO_4^-, BF_4^-, PF_6^-, AsF_6^-, NO_3^-, $C(CN)_3^-$, and $HgBr_3^-$ have been synthesized. The $AuBr_2^-$ salt is the first BEDO-TTF salt to be structurally characterized. Crystallographic investigations of several of the other $(BEDO\text{-}TTF)_mX_n$ salts have shown that (with the exception of the I_3^- salt) these new synmetals are structurally very similar to $(BEDO\text{-}TTF)_2AuBr_2$. Therefore, a 2:1 stoichometry is expected for BEDO-TTF salts. The observation of similar ESR linewidths for all the BEDO-TTF salts reinforces this conclusion. While $(BEDO\text{-}TTF)_2PF_6$ is semiconducting and the $AuBr_2^-$, $Au(CN)_2^-$, and ClO_4^- salts are metallic only near room temperature and semiconducting at low temperatures, $(BEDO\text{-}TTF)_2AuI_2$ shows metallic conductivity to low temperatures. RF penetration depth measurements on crystals derived from BEDO-TTF/KSCN/CuSCN show the occurence of superconductivity near 1 K. Band electronic structure calculations on $(BEDO\text{-}TTF)_2AuBr_2$ and $(BEDO\text{-}TTF)_2ClO_4$ indicate that they are one-dimensional metals.

INTRODUCTION

Research on organic metals has produced a steady increase in the ambient pressure superconducting transition temperatures (T_c) from T_c = 1.2 K for $(TMTSF)_2ClO_4$, to T_c = 1.5, 2.8, 5.0 K for the β-$(BEDT\text{-}TTF)_2X$ salts where X^- = I_3^-, IBr_2^-, and AuI_2^- [1] respectively, and to T_c = 10.4 K in κ-$(BEDT\text{-}TTF)_2Cu(SCN)_2$ [2]. In the isostructural β-phase $(BEDT\text{-}TTF)_2X$ salts, we have shown that the anion size[3] and anion–CH_2 hydrogen interactions[4,5] are critical factors that control the packing of the BEDT-TTF donor molecule and thus determine the transport properties of the resulting charge-transfer salts. Changes in the donor-to-anion "hydrogen bonding" interactions that accompany variations in anion size have been correlated to the lattice softness and phonon frequencies and, therefore, to the superconducting T_c values.[5] Rather than systematic variations in the anions, an

alternative approach that may be used to tailor the electrical properties of synmetals is the replacement of the BEDT-TTF donor with similar organic molecules. Examples of this strategy are the variation of the end groups of the BEDT-TTF molecule from ethylene to propylene (PT), or methylene (MT), and the mixed end group asymmetric molecules MET, MPT and EPT[6,7]. Another approach to modification of the donor molecule is substitution for the chalcogen atoms. Examples of this approach are the substitution of Se or O



1.

atoms for the outer S atoms in BEDT-TTF to synthesize the BEDSe-TTF (BEST)[8] and BEDO-TTF (**1**)[9] donor molecules, respectively. We have previously reported on charge-transfer salts derived from BEST[10]. In this paper, we elucidate the structures, physical properties and band electronic structures of charge transfer salts derived from the organic donor molecule BEDO-TTF. We also report the first indications of superconductivity in a BEDO-TTF salt (vide infra).

Table I Interatomic Distances and Angles in Neutral BEDO-TTF at 125 K.

Atoms	Dist. (Å)	Atoms	Dist. (Å)	Atoms	Dist. (Å)
S1-C1	1.766(7)	S1-C3	1.771(7)	S2-C1	1.753(7)
S2-C4	1.757(7)	S3-C2	1.761(7)	S3-C5	1.771(7)
S4-C2	1.755(7)	S4-C6	1.761(7)	O1-C3	1.361(8)
O1-C7	1.439(8)	O2-C4	1.363(8)	O2-C8	1.454(8)
O3-C5	1.369(8)	O3-C9	1.445(9)	O4-C6	1.382(9)
O4-C10	1.446(8)	C1-C2	1.342(9)	C3-C4	1.317(9)
C5-C6	1.289(10)	C7-C8	1.508(10)	C9-C10	1.530(11)

Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
C1-S1-C3	91.9(3)	C1-S2-C4	92.6(3)	C2-S3-C5	92.1(3)
C2-S4-C6	92.9(4)	C3-O1-C7	109.1(5)	C4-O2-C8	108.5(5)
C5-O3-C9	109.2(5)	C6-O4-C10	108.2(5)	C2-C1-S2	121.7(5)
C2-C1-S1	123.0(5)	S2-C1-S1	115.3(4)	C1-C2-S4	122.8(5)
C1-C2-S3	121.3(5)	S4-C2-S3	115.8(4)	C4-C3-O1	125.9(6)
C4-C3-S1	117.8(5)	O1-C3-S1	116.2(4)	C3-C4-O2	125.4(6)
C3-C4-S2	118.1(5)	O2-C4-S2	116.3(5)	C6-C5-O3	125.9(7)
C6-C5-S3	118.7(5)	O3-C5-S3	114.9(5)	C5-C6-O4	126.0(7)
C5-C6-S4	118.4(6)	O4-C6-S4	115.6(5)	O1-C7-C8	110.8(6)
O2-C8-C7	110.1(6)	O3-C9-C10	108.5(6)	O4-C10-C9	110.9(6)

NEUTRAL BEDO-TTF

To verify the unusual acentric structure of the BEDO-TTF donor molecule, as well as to provide accurate positional parameters for molecular orbital calculations and intermolecular C-H···X (X = O or S) interactions[11], we determined the structure of neutral BEDO-TTF at 125 K by use of single crystal x-ray diffraction methods. BEDO-TTF synthesized by the method reported by Suzuki, et. al.[9], crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters (125 K) a = 7.409(2)Å, b = 7.455(2) Å, c = 21.678(7) Å, and V_c = 1197.5(6) Å^3 with Z=4. Interatomic distances and angles for BEDO-TTF at 125 K appear in Table I and the positional parameters are given in Table II.

Table II Positional and Equivalent Isotropic Thermal Parameters for BEDO-TTF at 125 K.

Atom	x	y	z	U_{eq}*10^4 [a]
S1	0.4824(2)	0.3910(3)	0.98284(8)	162(6)
S2	0.1710(2)	0.4691(3)	0.90062(8)	173(5)
S3	0.7374(3)	0.3473(3)	0.86352(8)	183(5)
S4	0.4276(2)	0.4371(3)	0.78152(9)	188(6)
O1	0.3084(6)	0.5543(7)	1.0748(2)	155(15)
O2	-0.0014(7)	0.6170(7)	0.9954(2)	165(15)
O3	0.9591(6)	0.4035(8)	0.7692(2)	202(16)
O4	0.6573(7)	0.4820(8)	0.6881(2)	196(17)
C1	0.4018(9)	0.4203(10)	0.9069(3)	169(16)[b]
C2	0.5070(10)	0.4025(10)	0.8568(3)	170(15)[b]
C3	0.2959(8)	0.5083(9)	1.0142(3)	118(15)[b]
C4	0.1575(9)	0.5405(10)	0.9777(3)	144(14)[b]
C5	0.7816(9)	0.4131(10)	0.7865(3)	159(15)[b]
C6	0.6471(9)	0.4457(10)	0.7505(4)	179(15)[b]
C7	0.1646(11)	0.6763(11)	1.0898(3)	212(22)
C8	-0.0114(10)	0.6135(11)	1.0624(3)	183(22)
C9	0.9696(10)	0.3825(12)	0.7031(3)	228(26)
C10	0.8436(10)	0.5196(12)	0.6730(3)	211(24)

[a] The complete temperature factor is $\exp(-8\pi^2 U_{eq} \sin^2\theta/\lambda^2)$, where $U_{eq} = 1/3\ \Sigma_{ij}\ U_{ij}\ a^*_i a^*_j\ a_i\ a_j$ in units of Å^2.

[b] Isotropic thermal parameters.

CHARGE TRANSFER SALTS DERIVED FROM BEDO-TTF

Bis(ethylenedioxy)tetrathiafulvalene, or simply BEDO-TTF, has yielded several conducting charge-transfer salts.[9] The first of these to be structurally characterized was $(BEDO\text{-}TTF)_2AuBr_2$[12]. With the exception of the I_3^- salt which is reported elsewhere[13], crystals of charge-transfer salts derived by electrocrystallization of BEDO-TTF in TCE (1,1,2-trichloroethane) or THF (tetrahydrofuran) are very small and in many cases form as

intergrown thin plates. The small size, poor crystal habit and the chronic occurrence of twinning makes crystallographic studies on salts of this donor especially challenging.

Crystals of (BEDO-TTF)$_2$AuBr$_2$ are thin plates twinned along the (0 1 0) faces. An extremely small single crystal (0.1 x 0.2 x ~0.01 mm) of (BEDO-TTF)$_2$AuBr$_2$ obtained from the tip of an intergrown crystal was used for a single x-ray structure determination.

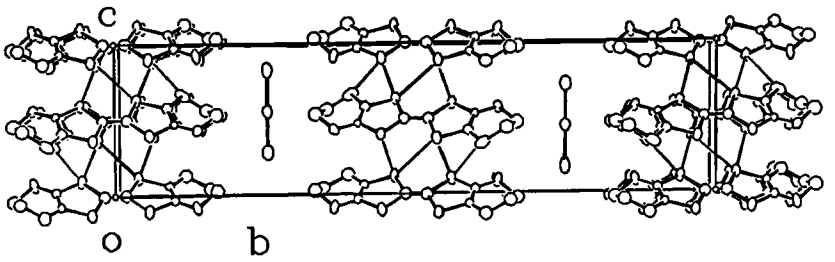


FIGURE 1. The BEDO-TTF donor molecules in (BEDO-TTF)$_2$AuBr$_2$ stack along the *a*-axis and are connected by short (less than the van der Waals radius sum) intermolecular S···S (3.8 Å) and S···O (3.3 Å) contacts.

Table III Crystallographic data for (BEDO-TTF)$_2$X salts.

Anion	$AuBr_2^-$	ClO_4^-	PF_6^-	KSCN/CUSCN
Space Group	$P2_1/m$	$P2_1/m$	$P\bar{1}$	$P2_1/m$
a (Å)	5.308(2)	5.340(1)	5.358(5)	4.240(3)
b (Å)	32.47(1)	33.43(1)	17.04(2)	33.47(2)
c (Å)	8.165(6)	8.069(2)[a]	8.080(9)	5.25(1)[a]
α			92.68(10)	
β	98.47(5)°	98.25(2)	97.91(8)	97.83(5)
γ			94.76(9)	
V_c (Å^3)	1392.(1)	1425.8(7)	726.7(14)	739(2)
Z	2	2	1	1
2θ range	4° – 45°	4° – 50°		
total refl.	3276	3837		
independent refl.	1874	2561 subcell (1283)		
refl. > 3σ	1049	1701 1140(subcell)		
parameters refined	111	103 (subcell)		
$R(F_o)$	0.15	0.066		
refl. > 3σ	0.11	0.060		
$wR(F_o^2)$	0.10	0.089		
refl. > 3σ	0.09	0.081		
"goodness of fit"	1.29	2.36		

[a]Crystals may have a (*a*, *b*, 3*c*) super cell.

Crystallographic data for $(BEDO\text{-}TTF)_2AuBr_2$ along with that for other BEDO-TTF salts appears in Table III. The unit cell contains two $AuBr_2^-$ anions, located at crystallographic mirror planes (y = 1/4 and 3/4), and four BEDO-TTF molecules.

The two independent BEDO-TTF molecules in each donor layer are located with the central carbon-carbon double bond on an inversion center so that the stacks of donor molecules are equally spaced along the crystallographic *a*-axis (see Fig. 1). A non-crystallographic translational symmetry operation (x,y,z+1/2) relates the two half BEDO-TTF molecules so that reflections (hkl) where l is odd are weak, i.e., a (*a,b,c*/2) subcell is observed for the donor molecules. The translational pseudo-symmetry of the donor layers is not found in the anion layers however. Positional parameters for $(BEDO\text{-}TTF)_2AuBr_2$ are given in Table IV, while intramolecular distances and angles appear in Table V. The poor quality and small size of crystals of BEDO-TTF charge transfer salts is reflected in the agreement factors given in Table III and the high standard deviations of the derived structural parameters. There is, however, no doubt about the basic crystal and molecular structure derived herein.

Table IV Positional and Equivalent Isotropic Thermal Parameters for $(BEDO\text{-}TTF)_2AuBr_2$.

Atom	x	y	z	$U_{eq}*10^4$ [a]
Au1	0.6943(4)	0.2500	0.5563(2)	447(7)
Br1	0.7878(12)	0.2500	0.2812(6)	798(25)
Br2	0.5944(14)	0.2500	0.8298(7)	968(29)
S1	0.3218(11)	0.0340(2)	0.6309(9)	311(23)
S2	-0.1349(11)	0.0594(2)	0.3992(8)	288(22)
S11	0.3204(12)	0.0368(2)	0.1208(9)	338(23)
S12	-0.1524(12)	0.0583(2)	-0.1015(9)	394(25)
O1	0.474(3)	0.1098(5)	0.665(2)	441(48)[b]
O2	0.036(3)	0.1367(5)	0.428(2)	295(41)[b]
O11	0.452(3)	0.1147(5)	0.133(2)	448(49)[b]
O12	-0.016(3)	0.1360(5)	-0.079(2)	453(48)[b]
C1	0.038(5)	0.0209(7)	0.502(3)	352(67)[b]
C2	0.274(4)	0.0854(7)	0.581(3)	265(57)[b]
C3	0.074(4)	0.0978(7)	0.470(3)	191(53)[b]
C4	0.481(5)	0.1494(8)	0.566(3)	450(75)[b]
C5	0.192(6)	0.1679(8)	0.531(4)	519(77)[b]
C11	0.035(5)	0.0185(7)	0.002(3)	330(67)[b]
C12	0.266(4)	0.0884(6)	0.065(3)	208(53)[b]
C13	0.051(4)	0.0981(7)	-0.028(3)	252(59)[b]
C14	0.424(5)	0.1549(9)	0.043(3)	459(75)[b]
C15	0.121(5)	0.1690(9)	0.030(4)	506(80)[b]

[a] The complete temperature factor is $\exp(-8\pi^2 U_{eq} \sin^2\theta/\lambda^2)$, where $U_{eq} = 1/3\ \Sigma_{ij}\ U_{ij}\ a^*_i a^*_j\ a_i\ a_j$ in units of $Å^2$.

[b] Isotropic atoms.

The structure of $(BEDO\text{-}TTF)_2ClO_4$ is similar to that of the $AuBr_2^-$ salt. Layers of BEDO-TTF donor molecules in the *ac* plane located at y = 0 and y = 1/2 are separated by

anion layers on the mirror planes at y = 1/4 and 3/4. The subcell, (*a,b,c*/2), reflections in this case are much stronger , with the average intensity of the odd *l* reflections only 2.6% of that for the even *l* data. The positional and thermal parameters derived for the (*a,b,c*/2) subcell are given in TableVI. At present, a definitive structure for the anion layers has not been determined. The ClO_4^- anions appear to be disordered on the mirror plane and also appear to possess non-crystallographic symmetry, (x,y,z+1/2). This structure may be an example of a commensurate columar stack structure[14] in which the unit cell for the donor layers is half the size of that for the ClO_4^- anions. It may be possible to derive a better model for the anion layers with diffraction data collected at reduced temperatures. Distances and angles calculated for the BEDO-TTF donor molecules are given in Table VII.

Table V Interatomic Distances and Angles in $(BEDO\text{-}TTF)_2AuBr_2$.

Atoms	Dist. (Å)	Atoms	Dist. (Å)	Atoms	Dist. (Å)
S1-C2	1.73(2)	S1-C1	1.76(2)	S2-C1	1.69(2)
S2-C3	1.71(2)	O1-C2	1.42(3)	O1-C4	1.52(3)
O2-C3	1.32(2)	O2-C5	1.49(3)	C1-C1	1.42(5)
C2-C3	1.35(3)	C4-C5	1.63(4)		
S11-C12	1.75(2)	S11-C11	1.78(2)	S12-C11	1.77(2)
S12-C13	1.73(2)	O11-C12	1.36(3)	O11-C14	1.50(3)
O12-C13	1.33(3)	O12-C15	1.51(3)	C11-C11	1.26(5)
C12-C13	1.31(3)	C14-C15	1.66(4)		
Au1-Br1	2.370(7)	Au1-Br2	2.370(7)		

Atoms	Angle (°)	Atoms	Angle (°)
C2-S1-C1	90.5(11)	C12-S11-C11	94.7(10)
C1-S2-C3	95.3(11)	C13-S12-C11	95.8(11)
C2-O1-C4	106.8(18)	C12-O11-C14	109.1(18)
C3-O2-C5	117.1(17)	C13-O12-C15	113.0(19)
C1-C1-S2	124.6(24)	C11-C11-S12	123.0(26)
C1-C1-S1	117.1(24)	C11-C11-S11	123.8(27)
S2-C1-S1	118.1(14)	S12-C11-S11	113.1(12)
C3-C2-O1	128.0(21)	C13-C12-O11	127.2(21)
C3-C2-S1	121.3(17)	C13-C12-S11	118.4(17)
O1-C2-S1	110.7(15)	O11-C12-S11	114.3(15)
O2-C3-C2	122.4(20)	C12-C13-O12	124.8(22)
O2-C3-S2	122.8(16)	O12-C13-S12	117.3(16)
C2-C3-S2	114.6(17)	C12-C13-S12	117.8(18)
O1-C4-C5	107.9(21)	O11-C14-C15	107.4(22)
O2-C5-C4	106.2(20)	O12-C15-C14	102.6(21)
Br1-Au1-Br2	179.2(3)		

Crystals grown by electrocrystallization of BEDO-TTF in TCE or THF solvent in the presence of $(n\text{-}Bu_4N)AuI_2$ are poorly formed thin plates bunched in branching, tree-like clusters. Single crystal x-ray diffraction studies on thin plates cut from these clusters indicate that $(BEDO\text{-}TTF)_2AuI_2$ may be isostructural to the $AuBr_2^-$ salt.

Octhedral anions such as AsF_6^- or PF_6^- have not as yet produced single crystals suitable for full structural studies. The unit cell constants for a sample of

$(BEDO\text{-}TTF)_2PF_6$ are given in Table III. The unit cell, while triclinic, is very similar to those observed for $(BEDO\text{-}TTF)_2ClO_4$ and $(BEDO\text{-}TTF)_2AuBr_2$. Therefore a 2:1 stoichometry is assumed for this salt.

Electrocrystallization of the polymeric anion $Cu(NCS)_2^-$ (KSCN/CuSCN, crown ether) with the BEDO-TTF donor produces small crystals with morphologies of needles and blocks. The monoclinic unit cell for one of the needles-like crystals is given in Table III. The BEDO-TTF layers in this structure appear to be very similar to those shown in Figure1. The structure of the anion layers has not yet been determined.

Table VI Positional and Equivalent Isotropic Thermal Parameters for $(BEDO\text{-}TTF)_2ClO_4$.

Atom	x	y	z	$U_{eq}*10^4$ [a]
S1	0.3194(2)	0.03447(4)	1.2460(3)	333(4)
S2	-0.1466(2)	0.05718(4)	0.7956(3)	339(4)
O1	0.4552(7)	0.11058(10)	1.2871(10)	451(12)
O2	0.0003(7)	0.13306(10)	0.8435(10)	465(12)
C1	0.0359(8)	0.01968(13)	1.0084(11)	282(12)
C2	0.2742(8)	0.08493(14)	1.1505(12)	347(14)
C3	0.0634(9)	0.09465(14)	0.9427(12)	359(14)
C4	0.4294(11)	0.1487(2)	1.113(2)	531(19)
C5	0.1539(11)	0.1619(2)	1.054(2)	535(19)
Cl1	0.617(2)	0.2500	0.638(3)	1153(36)
O3	0.694(4)	0.2192(6)	0.691(6)	1728(97)
O4	0.402(5)	0.2500	0.513(11)	202(20)[b]

[a] The complete temperature factor is $\exp(-8\pi^2 U_{eq} \sin^2\theta/\lambda^2)$, where $U_{eq} = 1/3\ \Sigma_{ij}\ U_{ij}\ a^*_i a^*_j\ a_i\ a_j$ in units of $Å^2$.
[b] $U_{eq}*10^3$

Table VII. Interatomic Distances and Angles in $(BEDO\text{-}TTF)_2ClO_4$.

Atoms	Dist. (Å)	Atoms	Dist. (Å)	Atoms	Dist. (Å)
S1-C1	1.740(4)	S1-C2	1.742(5)	S2-C3	1.728(5)
S2-C1	1.737(4)	O1-C2	1.349(6)	O1-C4	1.454(7)
O2-C3	1.375(6)	O2-C5	1.456(7)	C1-C1	1.371(9)
C2-C3	1.341(7)	C4-C5	1.518(8)		

Atoms	Angle (°)	Atoms	Angle (°)
C1-S1-C2	94.2(2)	C3-S2-C1	93.8(2)
C2-O1-C4	110.5(4)	C3-O2-C5	110.9(4)
C1-C1-S2	122.6(4)	C1-C1-S1	121.0(4)
S2-C1-S1	116.5(3)	C3-C2-O1	125.9(4)
C3-C2-S1	116.8(4)	O1-C2-S1	117.4(3)
C2-C3-O2	123.9(4)	C2-C3-S2	118.7(4)
O2-C3-S2	117.4(4)	O1-C4-C5	110.6(4)
O2-C5-C4	110.4(4)		

Although results for some salts are preliminary, thus far crystallographic studies on BEDO-TTF salts have shown remarkable consistency in the molecular packing of the donor molecules. This suggests that, similar to the case for TMTSF salts where one primary donor packing was observed, the donor packing observed in $(BEDO\text{-}TTF)_2ClO_4$ and $(BEDO\text{-}TTF)_2AuBr_2$ may persist in all 2:1 BEDO-TTF charge transfer salts.

As noted earlier,[11] the donor-molecule layers of $(BEDO\text{-}TTF)_2AuBr_2$ and $(BEDO\text{-}TTF)_2ClO_4$ have a packing pattern in which adjacent donor molecules make short C-H···O contacts not only within each donor stack (see Figures 2b and 2c) but also between adjacent donor stacks (see Figure 2c). The most likely reason for this observation is that the stabilization energy associated with a C-H···donor contact of the type C-H···O is much greater than that associated C-H···donor contacts of the type C-H···S or C-H···$C(sp^2)$,[11] and is also comparable in magnitude to the stabilization energy resulting from a C-H···anion contact.[11]

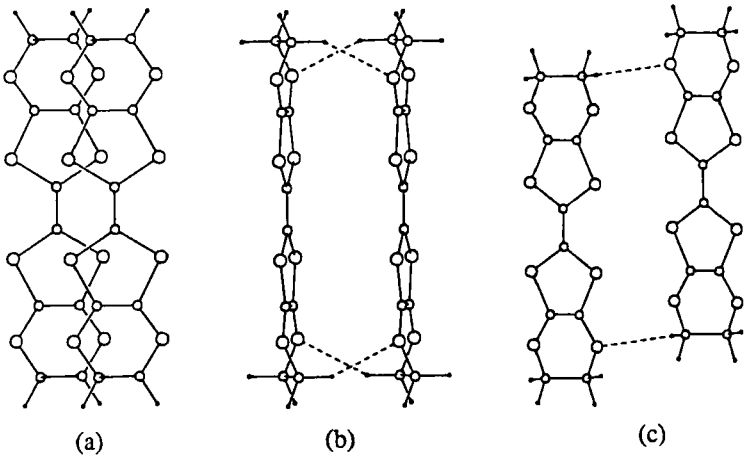


FIGURE 2. Arrangements of adjacent donor molecules in the donor layers of $(BEDO\text{-}TTF)_2AuBr_2$ and $(BEDO\text{-}TTF)_2ClO_4$: (a) Projection view of two adjacent donor molecules within a donor stack. (b) Short C-H···O contacts (dashed lines) within a donor stack. (c) Short C-H···O contacts (dashed lines) between donor stacks.

CONDUCTIVITY MEASUREMENTS

Conductivities of five BEDO-TTF salts which had crystals of reasonable quality and sufficiently large size were determined from 300 K to 15 K with the use of a standard 4-probe resistance-measuring technique. The conductivities at room temperature (300 K) and other conductive parameters are summarized in Table VIII. Crystals of $(BEDO\text{-}TTF)_2X$ with the linear anions $X^- = AuBr_2^-$ and $Au(CN)_2^-$ exhibited weak metallic conductivity near room temperature and metal-to-insulator (MI) transitions at 260 K and ~190 K, respectively. The change in conductivity between 300 K and the onset of the MI transition amounted to only ~10%. The resistance (conductance) curves for $(BEDO\text{-}TTF)_2Au(CN)_2$ showed strong hysteretic differences between the cooling and warming cycles, so that it is difficult to define a MI transition temperature precisely. The conductivity curves for this salt showed T (MI) ≅ 170 K on cooling and T (MI) ≅ 210 K on warming with some resistive jumps indicative of problems with contact resistances or the development of microcracks. The third salt with a linear anion, $(BEDO\text{-}TTF)_2AuI_2$, exhibited metallic conductivity throughout the temperature range and gave a conductivity ratio σ (15 K) / σ (300 K) ≅ 100.

Table VIII Conductivity data for BEDO-TTF salts.

Salt	σ (300 K) $(\Omega\ cm)^{-1}$	T (MI) (K)	E_a (eV)
$(BEDO\text{-}TTF)_2AuBr_2$	68	260	0.07 (220–80 K)
$(BEDO\text{-}TTF)_2AuI_2$	10	Metallic to 15 K	
$(BEDO\text{-}TTF)_2Au(CN)_2$	2	~190[a]	
$(BEDO\text{-}TTF)_2ClO_4$	100	~200[a]	
$(BEDO\text{-}TTF)_2PF_6$	20	semiconducting to 15 K[b]	0.03

[a]Hysteretic effects in the resistance occurred with cooling and warming cycles (see text). A metal to metal transition occurs for a ClO_4^- as reported in ref. 9(b).
[b]Possible semiconductor-semiconductor transition near 160 K. A PF_6^- salt in ref. 9(b) shows metallic behavior, these samples may be structurally distinct.

Crystals of the $(BEDO\text{-}TTF)_2ClO_4$ salt exhibited similar strong hysteretic effects in the conductivity curves. On cooling, this salt was very weakly metallic to 200 K and weakly semiconductive to lower temperatures. On warming, the low-temperature semiconductive behavior persisted to about 260 K. Crystals of $(BEDO\text{-}TTF)_2PF_6$ exhibited weak semiconductive behavior at all temperatures and examination of plots of $\ln(\sigma)$ vs 1/T indicated a possible semiconductor-semiconductor transition occurring near 160 K. RF penetration depth measurements for metallic $(BEDO\text{-}TTF)_2AuI_2$ at 0.6 K gave no indication of superconductivity in this salt, while measurements of crystals derived form electrocrystallization of BEDO-TTF/KSCN/CuSCN showed evidence of superconductivity near 1 K. Further details on this salt will be reported elsewhere.

ESR MEASUREMENTS

ESR measurements were carried out by use of an IBM ER-200 X-band spectrometer equipped with a VT-4111 temperature controller (300 to 100 K). The spin susceptibility of each salt was calibrated a against DPPH standard (Aldrich) at 300 K. The results are summarized in Table IX. The room temperature ESR peak-to-peak linewidths of $(BEDO\text{-}TTF)_2X$ ($X^- = AuI_2^-$, $AuBr_2^-$, $Au(CN)_2^-$, ClO_4^-, BrO_4^- and BF_4^-) salts are almost

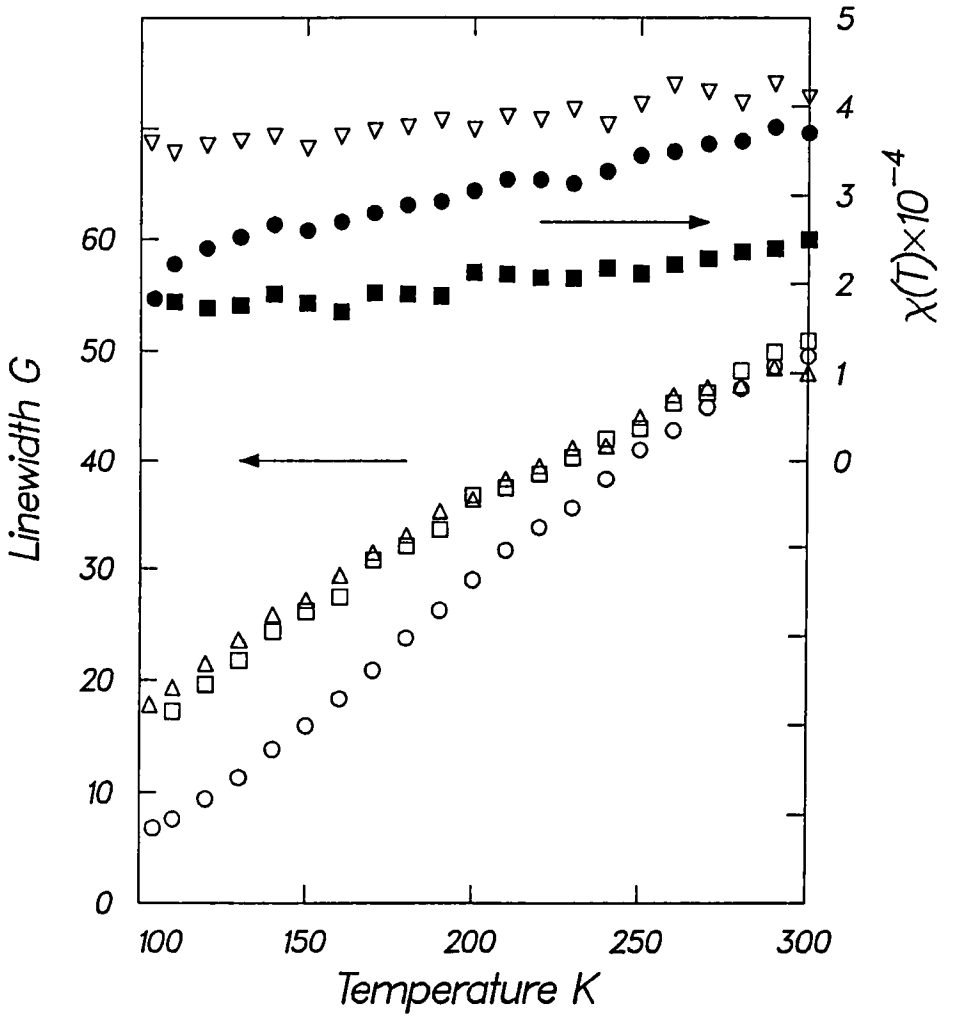


FIGURE 3. The temperature dependent linewidths and spin susceptibilities for $(BEDO\text{-}TTF)_2X$ salts, $X^- = AuI_2^-$ (up triangle and down triangle), $AuBr_2^-$ (hollow circle and filled circle), and ClO_4^- (hollow square and filled square), respectively.

identical, indicating that these salts are likely to be isostructural. The linewidths for the PF_6^- and AsF_6^- salts are slightly narrower which is consistent with the slightly different unit cell parameters (see Table III) observed for the PF_6^- salt.

Variable temperature measurements were done with several needle crystals of the $AuBr_2^-$ and AuI_2^- salts, and a distorted hexagon, plate-like crystal of the ClO_4^- salt. Crystals were oriented vertically in the ESR cavity with the static magnetic field normal to the crystal plane. The temperature dependent linewidths and spin susceptibilities are shown in Figure 3. The spin susceptibility of $(BEDO\text{-}TTF)_2AuI_2$ is almost constant between 100 and 300 K, which is consistent with its observed metallic conductivity. In contrast to the four probe resistivity measurements, no abrupt changes were observed in the spin susceptibilities or linewidths of $(BEDO\text{-}TTF)_2AuBr_2$ and $(BEDO\text{-}TTF)_2ClO_4$. However, the spin susceptibilities drop gradually by 50% for the $AuBr_2^-$ salt, and 30% for the ClO_4^- salt between 100 and 300 K. The decrease in the spin susceptibilities suggests spin pairing occurs at low temperature for these two salts.

Table IX ESR data for BEDO-TTF salts.

	300 K		100 K	
Anion	ΔH(G)	χ (emu / mole)	ΔH(G)	χ (emu / mole)
AuI_2^-	48	4.1×10^{-4}	18	3.6×10^{-4}
$AuBr_2^-$	50	3.7×10^{-4}	6.8	1.8×10^{-4}
$Au(CN)_2^-$	47			
ClO_4^-	50	2.5×10^{-4}	17	1.8×10^{-4}
BrO_4^-	45	3.3×10^{-4}		
BF_4^-	43			
PF_6^-	37			
AsF_6^-	36			

Band Electronic Structure

Figure 4a shows the dispersion relations of the two highest occupied bands calculated[15] for a donor-molecule layer of $(BEDO\text{-}TTF)_2AuBr_2$, which has two nonequivalent donor molecules per unit cell. These two bands are mainly represented by the HOMO of each donor molecule, and are more dispersive along the $\Gamma \rightarrow X$ (i.e., stacking) direction. With the formal oxidation state $(BEDO\text{-}TTF)_2^+$, the upper band is half-filled and therefore has the Fermi surface shown in Figure 4b. This Fermi surface is open along the $\Gamma \rightarrow Z$ (i.e., interstack) direction, so that $(BEDO\text{-}TTF)_2AuBr_2$ is calculated to be a one-dimensional (1D) metal with good electrical conductivity along the $\Gamma \rightarrow X$ direction. The MI transition of $(BEDO\text{-}TTF)_2AuBr_2$ is likely to be associated with the 1D nature of its Fermi surface.

Figure 5a shows the dispersion relations of the two highest occupied bands calculated

for a donor-molecule layer of $(BEDO\text{-}TTF)_2ClO_4$ taken from its subcell crystal structure. This latter donor layer has one unique donor molecule per unit cell, but our calculations employed a double unit cell size (and hence two equivalent donor molecules per unit cell per layer as was the case in $(BEDO\text{-}TTF)_2AuBr_2$) for ease of comparison with Figure 4a. The Fermi surface associated with the bands of Figure 5a is shown in Figure 5b. This Fermi surface is essentially derived from slightly overlapping ellipses when the overlapping lines at crossing points are made noncrossing. Hence, the Fermi surface consists of wave-like 1D lines and small 2D pockets.

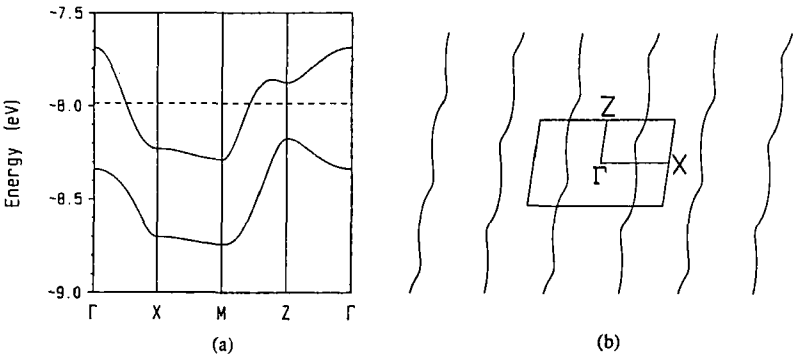


FIGURE 4 (a) Dispersion relations of the two highest occupied bands calculated for a donor-molecule layer of $(BEDO\text{-}TTF)_2AuBr_2$. The dashed line refers to the Fermi level, $\Gamma = (0,0)$, $X = (a^*/2,0)$, $Z = (0,b^*/2$, and $M = (a^*/2, b^*/2)$. (b) Fermi surface associated with the half-filled band of Figure 4a in an extended zone scheme. The parallelogram represents a primitive unit cell in reciprocal space.

The donor layer of $(BEDO\text{-}TTF)_2AuBr_2$ taken from the crystal structure determined for its subcell is quite similar in structure to the corresponding layer of $(BEDO\text{-}TTF)_2ClO_4$, and consequently has band dispersions, and a Fermi surface, almost identical with those shown in Figures 5a and 5b, respectively. Thus, it is clear from Figures 4a and 5a that the lower symmetry of the donor layer in $(BEDO\text{-}TTF)_2AuBr_2$ is responsible for the noncrossing of its two highest occupied bands. The 1D Fermi surface of Figure 4b is derived from the wave-like 1D lines of Figure 5b by flattening them. By analogy, the 'supercell' (i.e., real) structure of $(BEDO\text{-}TTF)_2ClO_4$ which has yet to be determined, should possess band dispersions and a Fermi surface similar to those in Figures 4a and 4b, respectively. Then the occurrence of an MI transition in $(BEDO\text{-}TTF)_2ClO_4$ can be explained in terms of the 1D nature of its Fermi surface, as in the case of $(BEDO\text{-}TTF)_2AuBr_2$.

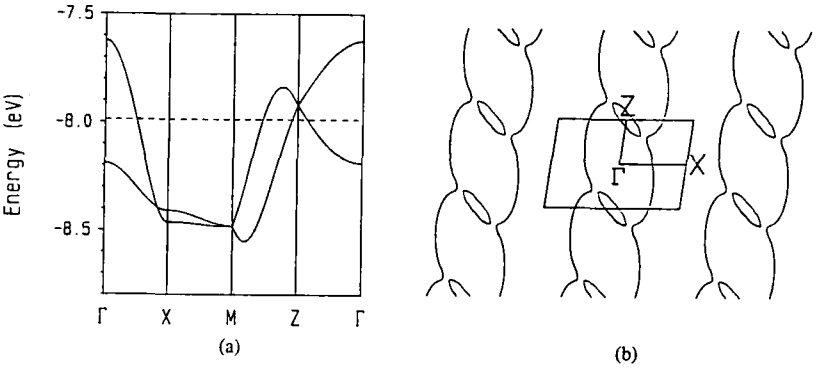


FIGURE 5 (a) Dispersion relations of the two highest occupied bands calculated for a donor-molecule layer of (BEDO-TTF)$_2$ClO$_4$. The dashed line refers to the Fermi level approximated for the oxidation state (BEDO-TTF)$_2^+$. (b) Fermi surfaces associated with the partially filled bands of Figure 5a in an extended zone scheme.

Micro-reflectance measurements were made at room temperature on the (BEDO-TTF)$_2$X salts, where X = ClO_4^-, AuI_2^- and $(I_3^-)_{1.25}$. A Digilab FTS-40 interferometer interfaced with a UMA300A microscope and a Cadmium-Mercury-Telluride detector was used. Measurements were made at 4 cm^{-1} resolution and 256 scans were taken. The reflectance spectra of (BEDO-TTF)$_2$ClO$_4$ resembled that of a 1D metal, e.g. α-(BEDT-TTF)$_2$I$_3$, with perchlorate vibrations observed at 1100 cm^{-1}. No splitting occurred in the vibronic region (1200-1400 cm^{-1}) for the salts.[19,20]

CONCLUDING REMARKS

Our crystal structure studies show that the donor molecule layers of (BEDO-TTF)$_2$AuBr$_2$ and (BEDO-TTF)$_2$ClO$_4$ have a very similar packing pattern, in which adjacent donor molecules both within a donor stack and between donor stacks have short C-H···O contacts. This similarity, which occurs despite the large differences in the anion shapes, implies that the C-H···O interactions are strong and hence are a primary governing factor in determining the donor-packing pattern. Thus, we believe that this stacking pattern is likely to be found in most BEDO-TTF/anion salts. Our band electronic structure study reveals that both (BEDO-TTF)$_2$AuBr$_2$ and (BEDO-TTF)$_2$ClO$_4$ are 1D metals, and that the observed MI transitions in these materials are associated with the 1D nature of the Fermi surfaces. Finally, our discovery of superconductivity in the BEDO-TTF/KSCN/CuSCN system strongly suggests that this donor molecule has great future promise.

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