Orbitally similar situations occur in a number of other binuclear complexes (e.g., edged-sharing or confacial bioctahedral complexes,[2e,3b,16,20] dibridged trivalent titanocene complexes[3d]) where relatively large exchange interactions have been attributed to direct exchange between ions separated by ~3 Å or less. Since internuclear M–M separations in **3a–e** vary from 2.90 to 3.04 Å, strong direct exchange interactions seem highly probable.

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**Supplementary Material Available:** Magnetic data for **3b** and the Ti/V and V/Cr mixed-metal dimers, including temperature-dependent magnetizations, bucket correction terms (BC), sample magnetizations, and experimental and calculated molar and inverse-molar susceptibilities ($\chi_M$ and $1/\chi_M$) (Tables S1–S5), and X-ray crystal data for **3b** and **3e**, including textual summaries of experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (Tables S6–S17) (29 pages); listings of calculated and observed structure factors for **3b** and **3e** (40 pages). Ordering information is given on any current masthead page.

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# Polymeric Anions Leading to Novel Packing Motifs in Donor-Radical Salts: Synthesis and Crystal and Band Electronic Structure of (BEDT-TTF)BiI$_4$

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In an attempt to synthesize a 2:1 salt of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET, $C_{10}H_8S_8$) with soft C—H···anion contacts, which promote an increase in the superconducting transition temperature, $T_c$, in $\beta$-(ET)$_2$X salts, we carried out slow electrocrystallization of ET with BiI$_3$ and $[(n\text{-}C_4H_9)_4N]I$ in 1,1,2-trichloroethane. This led to an unexpected 1:1 salt, (ET)BiI$_4$, which was characterized by X-ray single-crystal diffraction. The polymeric anion, a $[\mathrm{BiI_4^-}]_\infty$ chain, contains [BiI$_6$] octahedra sharing edges, such that the two terminal iodide ligands are in a cis configuration. ET$^+$ cations form a network of (ET$^+$)$_2$ dimers, connected by S···S contacts shorter than the sum of the van der Waals radii (3.6 Å). The spin susceptibility as a function of temperature, derived from ESR measurements, follows Curie's law down to 20 K, but a spin count indicates that the ESR signal is due to an impurity (less than 1%). Band electronic structure calculations on the (ET$^+$)$_2$ layer predict (ET)BiI$_4$ to be a semiconductor with a band gap of order 0.4 eV. Crystal data: triclinic, space group P$\bar{1}$, lattice constants $a$ = 8.265 (3) Å, $b$ = 11.118 (3) Å, $c$ = 14.424 (4) Å, $\alpha$ = 110.76 (2)°, $\beta$ = 96.41 (2)°, $\gamma$ = 103.57 (2)°, $V$ = 1176.8 (7) Å$^3$, and $Z$ = 2.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) is the most extensively used electron-donor molecule in the search for new organic superconductors.[1] At least ten ET-based ambient-pressure superconductors have been found to date, including that with the highest superconducting transition temperature, $T_c$, of any organic material, i.e., $\kappa$-(ET)$_2$Cu(SCN)$_2$, with $T_c$ = 10 K.[2] Several structural families of superconducting ET salts exist, of which the best known is the $\beta$-(ET)$_2$X group, where X can be a number of linear trihalide or dihalometalate anions, e.g., X$^-$ = IBr$_2^-$ ($T_c$ = 2.8 K),[3] AuI$_2^-$ ($T_c$ = 4.9 K),[4] and I$_3^-$ ($T_c$ = 1.5,[5] 8 K).[6] The ET molecular packing arrangements, and hence the electrical properties, are largely determined by the size, shape, and charge distribution of the anions.

Structure–property correlations developed for the $\beta$-(ET)$_2$X family of organic superconductors[1,7] indicated that large anions with polarizable end groups in general show more promise for the discovery of new superconductors. The late-period terminal halide ligands found in the large anions lead to soft C—H···X contacts, which correlate with $T_c$ enhancement.[7] The iodine atom is the largest and most polarizable halogen atom, and its bonds with late-period main-group metals are among the longest covalent bonds known. In an attempt to synthesize a 2:1 salt of ET with soft C—H···I contacts, we carried out electrocrystallization of ET with bismuth iodide complex anions. This attempt led to an unexpected 1:1 salt, (ET)BiI$_4$, in which the counteranion exists as a $[\mathrm{BiI_4^-}]_\infty$ chain. In the following we describe the synthesis,

**Table I.** Crystal and Refinement Parameters for (ET)BiI$_4$

| | |
|---|---|
| $C_{10}H_8S_8BiI_4$ | fw = 1101.25 |
| $a$ = 8.265 (3) Å | triclinic, space group $P\bar{1}$ (No. 2) |
| $b$ = 11.118 (3) Å | $T$ = 295 K |
| $c$ = 14.424 (4) Å | $\lambda$ = 0.71073 Å |
| $\alpha$ = 110.76 (2)° | $\rho_{calcd}$ = 3.108 g cm$^{-3}$ |
| $\beta$ = 96.41 (2)° | $\mu$ = 133.5 cm$^{-1}$ |
| $\gamma$ = 103.57 (2)° | transm coeff = 0.246–0.646 |
| $V$ = 1176.8 (7) Å$^3$ | $R(F_o)^a$ = 0.035 |
| $Z$ = 2 | $R_w(F_o)^b$ = 0.032 |

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

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**Table II.** Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] in (ET)BiI$_4$

| atom | $x$ | $y$ | $z$ | $10^4U_{eq}$ |
|---|---|---|---|---|
| Bi | 0.24602 (5) | −0.04685 (4) | 0.06849 (3) | 335 (1) |
| I1 | −0.00287 (10) | 0.12758 (7) | 0.14800 (5) | 541 (3) |
| I2 | 0.50625 (10) | 0.19607 (7) | 0.02016 (6) | 625 (3) |
| I3 | 0.44207 (10) | 0.05587 (8) | 0.27982 (5) | 571 (3) |
| I4 | 0.03711 (9) | −0.28751 (7) | 0.08091 (6) | 576 (3) |
| S1 | 0.3845 (3) | 0.1246 (2) | 0.5621 (2) | 366 (9) |
| S2 | 0.1879 (3) | 0.1410 (2) | 0.7195 (2) | 416 (10) |
| S3 | 0.1357 (3) | −0.1826 (2) | 0.4292 (2) | 410 (10) |
| S4 | −0.0542 (3) | −0.1510 (3) | 0.5908 (2) | 455 (10) |
| S5 | 0.6261 (4) | 0.3950 (3) | 0.6709 (2) | 521 (11) |
| S6 | 0.3930 (4) | 0.4216 (3) | 0.8549 (2) | 469 (10) |
| S7 | −0.0541 (4) | −0.4690 (3) | 0.3092 (2) | 636 (13) |
| S8 | −0.2776 (4) | −0.4256 (3) | 0.5082 (2) | 696 (14) |
| C1 | 0.2134 (11) | 0.0479 (9) | 0.6014 (6) | 320 (35) |
| C2 | 0.1084 (11) | −0.0799 (9) | 0.5440 (6) | 345 (36) |
| C3 | 0.4484 (12) | 0.2748 (9) | 0.6698 (6) | 351 (36) |
| C4 | 0.3541 (12) | 0.2828 (9) | 0.7422 (6) | 347 (36) |
| C5 | −0.0237 (11) | −0.3251 (9) | 0.4170 (7) | 371 (38) |
| C6 | −0.1121 (13) | −0.3104 (10) | 0.4919 (7) | 459 (42) |
| C7 | 0.690 (2) | 0.5194 (12) | 0.8015 (9) | 662 (54) |
| C8 | 0.6218 (12) | 0.4720 (11) | 0.8789 (7) | 497 (45) |
| C9 | −0.238 (2) | −0.5813 (13) | 0.3197 (10) | 919 (70) |
| C10 | −0.277 (2) | −0.5784 (14) | 0.4118 (14) | 1252 (95) |

[a] The equivalent isotropic temperature factor expression is $\exp(-8\pi^2U_{eq}(\sin^2\theta)/\lambda^2)$, where $U_{eq} = {}^1/_3\sum_{ij}U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$ in units of Å$^2$.

crystal structure, ESR properties as a function of temperature, and band electronic structure of (ET)BiI$_4$.

## Experimental Section

The title compound was synthesized by electrocrystallization from a solution of 1.74 mM ET (Strem Chemical Co., Inc.), 0.020 M BiI$_3$, and 0.027 M [($n$-C$_4$H$_9$)$_4$N]I in 1,1,2-trichloroethane on a Pt electrode and with a current density of 3 μA cm$^{-2}$. The crystals were harvested after 2 weeks of growth on the anode. They formed as heavily intergrown aggregates of black, slanted plate-shaped individual crystallites of typically less than 0.3-mm size. A single crystal was carved out of such an aggregate for the structure determination.

The crystal structure of (ET)BiI$_4$ was determined at room temperature on a Nicolet P3/F four-circle diffractometer. The data were corrected for Lorentz, polarization, and absorption (Gaussian integration method), but not for extinction, effects. The structure was partially solved by direct methods and completed in subsequent cycles of full-matrix least-squares refinement and Fourier techniques. No hydrogen atoms were located. The most important crystal and refinement parameters are summarized in Table I, final atomic coordinates are given in Table II, and further details have been deposited as supplementary material.[8] The atomic labeling is indicated in Figure 1, and bond lengths and angles are given in Table III.

The magnetic properties of (ET)BiI$_4$ were measured on an X-band ESR spectrometer (IBM ER-200 with a TE$_{102}$ rectangular cavity) in the temperature range 4.2–300 K. Cryogenic temperatures were achieved in an Oxford Instruments EPR-900 gas (nitrogen or helium, depending on the temperature range) flow cryostat regulated by an ITC4 temperature controller. A cluster sample containing about 10 crystallites in approximately the same orientation was aligned with the *ab* plane roughly parallel to the microwave electric field vector. The absolute integrated intensity of the ESR signal was estimated from a comparison with 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH, 98%, Aldrich Chemical Co.) whose molar susceptibility (proportional to the integrated ESR intensity) was assumed to correspond to the theoretical value, 1.25 × 10$^{-3}$ cgsu.[9] Spin susceptibilities obtained by this method are estimated to be

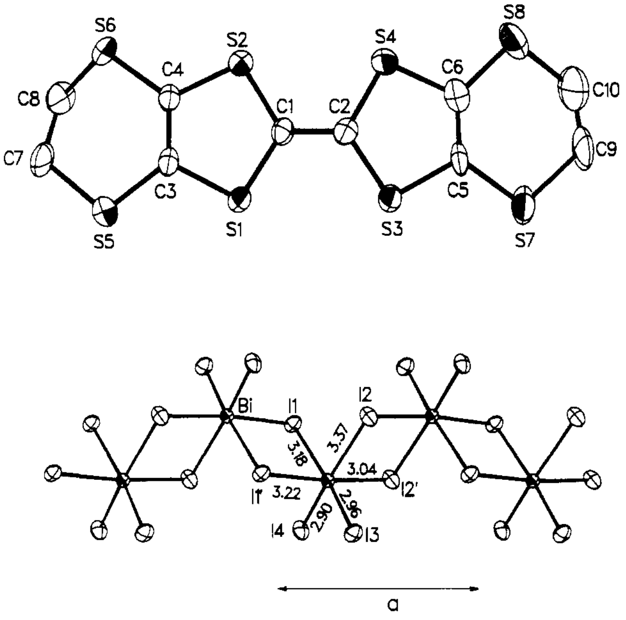

**Figure 1.** The ET$^+$ cation (not shown are hydrogen atoms attached to ethylene groups C7–C8 and C9–C10) and the polymeric [BiI$_4^-$]$_\infty$ anion in (ET)BiI$_4$. The atomic labeling is indicated, and thermal ellipsoids are drawn at the 50% probability level. The cation and the anion fragments are drawn on different scales.

**Table III.** Bond Lengths and Angles in (ET)BiI$_4$[a]

| | | | |
|---|---|---|---|
| Interatomic Distances (Å) | | | |
| Bi–I4 | 2.9005 (11) | S6–C4 | 1.732 (9) |
| Bi–I3 | 2.9634 (13) | S6–C8 | 1.797 (10) |
| Bi–I2$^{i}$ | 3.0421 (12) | S7–C5 | 1.733 (9) |
| Bi–I1 | 3.1828 (12) | S7–C9 | 1.786 (13) |
| Bi–I1$^{ii}$ | 3.2188 (13) | S8–C6 | 1.741 (10) |
| Bi–I2 | 3.3689 (12) | S8–C10 | 1.78 (2) |
| S1–C1 | 1.732 (9) | C1–C2 | 1.373 (12) |
| S1–C3 | 1.745 (9) | C3–C4 | 1.362 (12) |
| S2–C1 | 1.717 (8) | C5–C6 | 1.354 (13) |
| S2–C4 | 1.731 (9) | C7–C8 | 1.50 (2) |
| S3–C2 | 1.720 (9) | C9–C10 | 1.39 (2) |
| S3–C5 | 1.746 (9) | S1–S4$^{iii}$ | 3.449 (4) |
| S4–C2 | 1.724 (9) | S2–S3$^{iii}$ | 3.460 (4) |
| S4–C6 | 1.750 (10) | S3–S5$^{iv}$ | 3.455 (4) |
| S5–C3 | 1.733 (9) | S5–S7$^{iv}$ | 3.393 (4) |
| S5–C7 | 1.825 (11) | | |
| Bond Angles (deg) | | | |
| I4–Bi–I3 | 93.03 (4) | C6–S8–C10 | 101.1 (6) |
| I4–Bi–I2$^{i}$ | 90.69 (3) | C2–C1–S2 | 122.0 (7) |
| I4–Bi–I1 | 94.42 (3) | C2–C1–S1 | 122.6 (7) |
| I4–Bi–I1$^{ii}$ | 88.64 (4) | S2–C1–S1 | 115.3 (5) |
| I4–Bi–I2 | 170.24 (2) | C1–C2–S3 | 124.3 (7) |
| I3–Bi–I2$^{i}$ | 93.49 (3) | C1–C2–S4 | 119.6 (7) |
| I3–Bi–I1 | 89.25 (3) | S3–C2–S4 | 115.9 (5) |
| I3–Bi–I1$^{ii}$ | 171.64 (2) | C4–C3–S5 | 128.3 (7) |
| I3–Bi–I2 | 92.30 (4) | C4–C3–S1 | 116.5 (7) |
| I2$^{i}$–Bi–I1 | 174.07 (2) | S5–C3–S1 | 115.3 (5) |
| I2$^{i}$–Bi–I1$^{ii}$ | 94.68 (3) | C3–C4–S2 | 116.5 (7) |
| I2$^{i}$–Bi–I2 | 80.82 (3) | C3–C4–S6 | 124.7 (7) |
| I1–Bi–I1$^{ii}$ | 82.46 (3) | S2–C4–S6 | 118.8 (5) |
| I1–Bi–I2 | 93.82 (3) | C6–C5–S7 | 127.1 (7) |
| I1$^{ii}$–Bi–I2 | 87.26 (3) | C6–C5–S3 | 116.5 (7) |
| Bi–I1–Bi$^{ii}$ | 97.54 (3) | S7–C5–S3 | 116.4 (6) |
| Bi$^{i}$–I2–Bi | 99.18 (3) | C5–C6–S8 | 130.7 (8) |
| C1–S1–C3 | 95.4 (4) | C5–C6–S4 | 116.7 (7) |
| C1–S2–C4 | 96.2 (4) | S8–C6–S4 | 112.6 (6) |
| C2–S3–C5 | 95.6 (5) | C8–C7–S5 | 115.6 (8) |
| C2–S4–C6 | 95.3 (4) | C7–C8–S6 | 112.6 (7) |
| C3–S5–C7 | 104.6 (5) | C10–C9–S7 | 123.8 (11) |
| C4–S6–C8 | 98.1 (5) | C9–C10–S8 | 120.8 (12) |
| C5–S7–C9 | 101.9 (6) | | |

[a] Symmetry transformations: (i) $1-x, -y, -z$; (ii) $-x, -y, -z$; (iii) $-x, -y, 1-z$; (iv) $1-x, -y, 1-z$.

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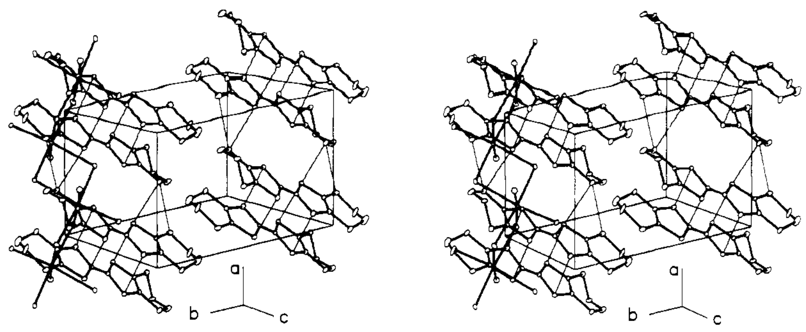

**Figure 2.** Stereoview of a unit cell of (ET)BiI$_4$. Intermolecular S···S contacts shorter than 3.60 Å are drawn as thin lines. Only one anion chain is drawn and the ellipsoids are arbitrarily small for clarity.

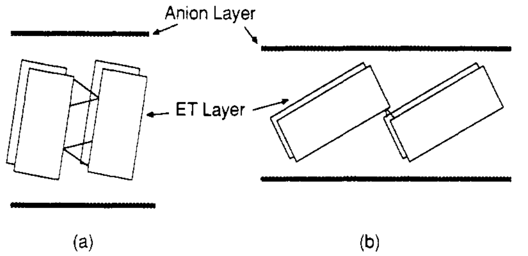

**Figure 3.** Schematic representations of ET molecular *inter*stack packing arrangements: (a) typical ET salt, e.g., superconducting $\beta$-(ET)$_2$I$_3$; (b) (ET)BiI$_4$. The rectangles represent individual ET molecules, and the thin lines connecting them indicate typical S···S contact directions. The details of the *intra*stack packing are not shown in these schematic drawings.

accurate within approximately 20%. The method was further tested with a related compound, $\beta''$-(BEDT-TTF)$_2$ICl$_2$,[10] where we obtained results which were in agreement with static susceptibility measurements.[11]

## Results

The crystal structure of (ET)BiI$_4$ contains stacks of ET donor-radical cations (+1 charge per molecule) and infinite chains of BiI$_4^-$ anions, both running along the *a* axis. A stereoview of the unit cell is shown in Figure 2. Within each donor molecule stack, the ET molecules form face-to-face dimers, with short intermolecular contacts of 3.45–3.46 Å between inner sulfur atoms, which are shorter than the sum of the van der Waals radii, 3.60 Å.[12] The ET molecules are slightly bent away from the center of the dimer, such that the contacts between outer sulfur atoms are ca. 0.3 Å longer than 3.60 Å. Short S···S contacts also exist between dimers, but they involve the outer sulfur atoms of the ET molecules, and they are in a much more side-by-side fashion than within the dimers (see Figure 2).

The principal novelty of this structure lies in the orientation of the donor stack within the unit cell. Adjacent stacks are arranged into layers parallel to the *ab* plane, but unlike that of any other known ET salt, the long axis of the donor molecules is more *in the plane* rather than approximately perpendicular to it[1] (see Figure 3). This leads to intermolecular S···S contacts between stacks involving only outer sulfur atoms (S5–S8). In addition, these contacts are between atoms located on opposite (with respect to the long molecular axis) ends of the molecule in (ET)BiI$_4$ (i.e., corner-to-corner contacts) as compared to those in a conventional ET salt (Figure 3a), where the contacts connect the same ends (side-by-side contacts). The bond distances within the ET molecule are consistent with a +1 charge, but the standard deviations are too large to warrant further discussion.

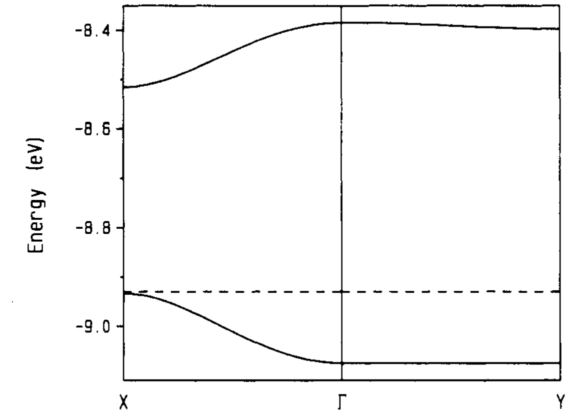

**Figure 4.** Dispersion relations of the valence and conduction bands in (ET)BiI$_4$ calculated for a layer of (ET$^+$)$_2$ dimers, where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, and $Y = (0, b^*/2)$. The dashed line refers to the highest occupied level for low-spin band filling at $T = 0$ K.

The anion chain consists of [BiI$_6$] octahedra. Two of the iodine atoms are terminally bound, whereas pairs of the other iodine atoms form bridges to two neighboring bismuth atoms along the chain. Due to the cis configuration of the terminal ligands, there is an approximately 90° angle between adjacent Bi–Bi vectors, resulting in a zigzag chain. Only (2-picolinium)BiI$_4$[13] exhibits this type of chain among the reported ternary bismuth iodide compounds, but it is quite common in antimony salts.[14] The bond lengths within the anion are very similar to those in (2-picolinium)BiI$_4$.[13] The terminal Bi–I bonds are shortest (2.90 and 2.96 Å), and among the bridging Bi–I bonds (3.04–3.37 Å), those trans to the terminal iodine atoms are the longest. In the present structure, neighboring bismuth atoms are approximately 0.1 Å further apart (4.82 and 4.89 Å), resulting in slightly larger Bi–I–Bi bridging angles (98–99°, rather than 92–95° in the picolinium salt).

The ESR spectra consisted of a weak single transition of Lorentzian shape at all temperatures, with a peak-to-peak line width of 36 G at 300 K. Upon lowering the temperature, the line width increased slightly to 44 G at 4.2 K. The temperature dependence of the spin susceptibility (proportional to the integrated transition intensity) was essentially that of a paramagnet and followed a Curie law ($\chi^{-1} \propto T$) above ca. 20 K, below which the susceptibility values were slightly reduced. The ESR peaks were slightly asymmetric at room temperature, as is often seen in electrically conducting samples, but the asymmetry disappeared at lower temperatures. The room-temperature susceptibility was estimated to be $7 \times 10^{-6}$, i.e., only 0.5% of the calculated value of an $S = {}^1/_2$ paramagnet with $g \approx 2$. We therefore conclude that the ESR signal is due to an impurity (either chemical or stacking fault) and that (BEDT-TTF)BiI$_4$ is diamagnetic. Unfortunately, no crystals large enough for four-probe electrical

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conductivity measurements could be grown.

The band electronic structure[15] calculated for a layer of $(ET^+)_2$ dimers is shown in Figure 4. In each $(ET^+)_2$ dimer, the HOMO's of the $ET^+$ cations interact to give the bonding and antibonding levels $\psi_+$ and $\psi_-$, respectively. The lower and upper bands are largely described by the bonding and antibonding combinations of the HOMO's in each $(ET^+)_2$ dimer, respectively. These two bands are slightly dispersive along the *a* direction but almost dispersionless along the *b* direction. This reflects the fact that short interdimer S···S contacts of less than 3.60 Å occur only along the *a* direction. With the formal oxidation state of $ET^+$, only the lower band is filled if a low-spin band filling is adopted, as indicated by the diamagnetic properties (vide supra). This leads to a band gap of 0.42 eV, and $(ET)BiI_4$ is expected to be a semiconductor with high activation energy.

## Discussion

The original intent of our work was to obtain a 2:1 salt of ET with a very large polarizable, "tetrahedral" anion $BiI_4^-$, and hence with soft C—H···I contacts between the donor molecules and the anions. This attempt led to an unexpected 1:1 salt $(ET)BiI_4$ that contains polymeric anions, i.e., $[BiI_4^-]_\infty$ chains. As is often the case, this result may reflect the fact that the $[BiI_4^-]_\infty$ anions are too large to allow formation of a 2:1 salt with ET. Soft C—H···anion contacts are expected from a large, polarizable anion, but such an anion may prevent the formation of a 2:1 salt. Thus, a balance of polarizability and size appears to be crucial in obtaining a 2:1 salt with soft C—H···anion contacts.

The packing motif for the ET donor molecule network in $(ET)BiI_4$ is novel and does not resemble that of any other ET salt. Due to the unavailability of sufficiently large crystals, the electrical conductivity of $(ET)BiI_4$ has not yet been measured directly, but the ESR measurements (i.e., lack of an *intrinsic* signal) and band electronic structure calculations indicate that the compound is a semiconductor or insulator. When the electronic structure of an $(ET^+)_2$ dimer is described by the configuration $(\psi_+)^2$ (ignoring the weaker *inter*dimer interactions), $(ET)BiI_4$ would be diamagnetic in the absence of impurities. If the electronic structure of $(ET^+)_2$ were described by the configuration $(\psi_+)(\psi_-)$, as appropriate when the intermolecular interaction in each $(ET^+)_2$ dimer is weak, the singlet and triplet states of each dimer would have a small energy difference, thereby giving rise to an ESR signal from the thermally populated triplet state. However, the observed ESR signal is so weak as to rule out that possibility, and the electronic structure of (BEDT-TTF)$BiI_4$ is best described as composed of strongly antiferromagnetically coupled dimers.

$(ET)BiI_4$ is an example of an ET salt with polymeric counteranions. The latter include not only the superconductors $\kappa$-$(ET)_2Cu(SCN)_2$[16] and $(ET)_4Hg_{3-x}X_8$ (X = Cl, Br)[17,18] but also the nonsuperconducting salts $(ET)Ag_4(CN)_5$,[19] $(ET)_3Ag_{6.4}I_8$,[20] $\kappa$-$(ET)_2Ag(CN)_2(H_2O)$,[21] $(ET)Ag_{1.6}(SCN)_2$,[22] $(ET)Ag_{2.4}Br_3$,[23] $(ET)Cu_2(NCS)_3$,[22] $(ET)_2Cu_5I_6$,[24] and $(ET)_2HgBr_3(TCE)$.[25]

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**Supplementary Material Available:** Tables of details of X-ray diffraction data collection and anisotropic thermal parameters (2 pages); a listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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# Optical Spectrum of $K_2CuF_4$

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The absorption, magnetic circular dichroism (MCD), and Zeeman spectra of $K_2CuF_4$ single crystals were measured below 5 K. An unambiguous assignment of the d–d transitions can be made from the experimental spectra. Two zero-phonon magnetic dipole origins were observed, and their energies, intensities, polarization properties, and MCD parameters agree with those given by a ligand field model for a tetragonally elongated complex. The extensive vibrational fine structure on one of the transitions has been partially analyzed. An electric dipole vibronic origin must be interpreted on the basis of a $D_{4h}$ factor group rather than the $D_{2h}$ site symmetry of the $CuF_6^{4-}$ chromophore.

## Introduction

Although copper(II) complexes display a wide variety of coordinations and geometries, there are to date only a few known examples of a pure copper(II) compound with a compressed octahedral geometry.[1] Until recently, $K_2CuF_4$ was also often cited as having a compressed geometry.[2] This prompted magnetic[3]

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