

# Crystal and electronic structure of a new metallic modification of $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$

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A new room-temperature metallic modification of the well known radical cation salt  $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$  has been prepared by electrochemical oxidation of ET. Its crystal and electronic structure have been examined at 110 K. The salt has a layered structure in which the conducting layers are characterized by the  $\delta$ -type packing.

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## 1. Introduction

Molecular conductors with the general formula  $(\text{ET})_2[\text{MHg}(\text{SCN})_4]$ , where  $M = \text{NH}_4, \text{Li}, \text{K}, \text{Rb}, \text{Cs}$  or  $\text{Tl}$  [ET = bis(ethylenedithio)tetrathiafulvalene] have attracted much attention. These salts are organic conductors with a three-component anionic system which contains two cations of a different nature and charge ( $M^+$  and  $\text{Hg}^{2+}$ ) as well as  $\text{SCN}^-$  anions. These salts exhibit a number of interesting physical properties. For instance,  $\beta$ - $(\text{ET})_3[\text{Li}_{0.5}\text{Hg}(\text{SCN})_4](\text{H}_2\text{O})_2$  and  $\alpha'$ - $(\text{ET})_2[\text{CsHg}(\text{SCN})_4]$  exhibit metal-semiconductor transitions at 170 and 210 K, respectively (Mori *et al.*, 1991), the isostructural salts  $\alpha$ - $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$ ,  $\alpha$ - $(\text{ET})_2[\text{RbHg}(\text{SCN})_4]$  and  $\alpha$ - $(\text{ET})_2[\text{TlHg}(\text{SCN})_4]$  (Mori *et al.*, 1990; Kushch *et al.*, 1992) are metals and exhibit interesting low-temperature resistivity anomalies related to density wave instabilities (Kartsovnik *et al.*, 1993; Sasaki & Toyota, 1994; Caufield *et al.*, 1995), and  $\alpha$ - $(\text{ET})_2[\text{NH}_4\text{Hg}(\text{SCN})_4]$  is isostructural with the previous three salts and indeed does not show such resistivity anomalies and enters into a superconducting state at 0.8 K (Wang *et al.*, 1990). It should be added that the  $\delta$ - $(\text{ET})_2[\text{TlHg}(\text{Se}_{0.875}\text{S}_{0.125}\text{CN})_4]$  salt (Shibaeva *et al.*, 1997), with the same composition as the metallic  $\alpha$ -type salt (Rousseau *et al.*, 1996), proved to be a semiconductor. In the present work we report the crystal and electronic structure of a new polymorphic modification of a salt of such type,  $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$  (1), which behaves as a metal at room temperature.

## 2. Experimental

The X-ray crystal study of the  $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$  (1) radical cation salt prepared by electrochemical oxidation of ET was performed at 110 K on a Bruker AXS SMART 1000 instrument equipped with a CCD detector (Mo  $K\alpha$  line, graphite monochromator,  $\omega$  scanning, scanning pitch 0.3, frame measuring time 30 s). Crystal data for the  $(\text{ET})_2[\text{KHg}(\text{SCN})_4]$

**Table 1**

Experimental details.

Crystal data	
Chemical formula	(C <sub>10</sub> H <sub>10</sub> S <sub>8</sub> ) <sub>2</sub> [KHg(SCN) <sub>4</sub> ]
Chemical formula weight	1245.33
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.648 (1), 14.888 (3), 20.380 (4)
$\alpha$ , $\beta$ , $\gamma$ (°)	86.20 (3), 86.02 (3), 81.00 (3)
<i>V</i> (Å <sup>3</sup> )	1984.3 (6)
<i>Z</i>	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	2.084
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	5.065
Temperature (K)	110 (2)
Crystal form, colour	Rhombic plate, black
Crystal size (mm)	0.58 × 0.25 × 0.12
Data collection	
Diffractionmeter	Bruker AXS SMART 1000
Data collection method	$\omega$ scans
Absorption correction	Semi-empirical
<i>T</i> <sub>min</sub>	0.188
<i>T</i> <sub>max</sub>	0.658
No. of measured, independent and observed parameters	9096, 8123, 5862
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.1139
$\theta$ <sub>max</sub> (°)	30.02
Range of <i>h</i> , <i>k</i> , <i>l</i>	−9 → <i>h</i> → 9 −20 → <i>k</i> → 11 −24 → <i>l</i> → 28
Refinement	
Refinement on	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.0555, 0.1403, 0.804
No. of reflections and parameters used in refinement	8123, 462
H-atom treatment	None
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.003
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	2.748, −2.067

Computer programs used: diffractometer software (Bruker, 1997), *SHELXS97*, *SHELXL97* (Sheldrick, 1997).

salt are given in Table 1.<sup>1</sup> The crystal structure was solved by direct methods and subsequent Fourier synthesis using the *SHELXS97* (Sheldrick, 1997) software package. The structure was refined by full-matrix least-squares procedures using an anisotropic approximation for all non-H atoms with the *SHELXL97* (Sheldrick, 1997) program. The S2 atom of the thiocyanate group was found to be statistically disordered on two positions with populations equal to 0.380 (5) and 0.646 (5). An absorption correction was applied using the *SADABS* (Sheldrick, 1997) program. The bond lengths and angles are reported in Table 2.

### 3. Results and discussion

The low-temperature X-ray study showed that (1) is a new polymorph of the  $\alpha$ -phase first described in 1989 (Oshima *et al.*,

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV0050). Services for accessing these data are described at the back of the journal.

*et al.*, 1989) and the  $\delta$ -phase first described in 1997 (Shibaeva *et al.*, 1997). The crystal structure of the salt (1) contains two crystallographically independent ET radical cations (*A* and *B*) and the [KHg(SCN)<sub>4</sub>]<sup>−</sup> anion in the asymmetric part of the unit cell (Fig. 1). Crystals of (1) have a layered structure in which the conducting layers composed of the ET cations, *A* and *B*, alternate along the *c* axis with the non-conducting anion layers (Fig. 2).

The conducting layer is shown in Fig. 3. The layers are packed as in the  $\delta$ -type packing which was earlier discovered in the  $\delta$ -(ET)<sub>2</sub>AuI<sub>2</sub> compound (Kobayashi *et al.*, 1986). The ET cations *A* and *B* stack in a sequence  $\cdots(A\cdots A\cdots B\cdots B)\cdots$  in such a way that the cation radicals of one type (*A*, *A* or *B*, *B*) are parallel to each other. The dihedral angle between the ET planes of different types (*A* and *B*) is 5.1°, which is close to 5.5° found in  $\delta$ -(ET)<sub>2</sub>[TiHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>], which is isostructural with the  $\delta$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] crystals (Shibaeva *et al.*, 1997). The donor pairs (*A*, *A*) and (*B*, *B*) of the stack are turned with respect to each other with an angle of 25.3°, which is a dihedral angle between the planes drawn through the S6, S8, S10, S12 and S14, S16, S18, S20 atoms. The corresponding angle in the  $\delta$ -(ET)<sub>2</sub>[TiHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>] salt is 32.5°. The interplanar distances between the *A*···*A* and *B*···*B* molecules are 3.63 and 3.50 Å, respectively {in the  $\delta$ -(ET)<sub>2</sub>[TiHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>] salt the distances between the *A*···*A* and *B*···*B* molecules are 3.65 and 3.66 Å, respectively}. The layer contains a great number of short side-by-side intermolecular S···S contacts between the ET cation radicals from the neighbouring stacks of *A*···*A* and *B*···*B* types in the range 3.340 (2)–3.579 (2) Å (Table 3) {in the  $\delta$ -(ET)<sub>2</sub>[TiHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>] salt the S···S contacts are of the *A*···*B* type with the distances 3.426–3.660 Å}. Within the stacks there are S···S contacts shorter than the sum of the van der Waals radii only within the ET pairs of type *A* [the distance S7···S11 is 3.627 (2) Å]. The atoms C5, C6, C13 and C14 are out of the average plane of ET(*A*) by −0.60, 0.26, −0.05 and 0.76 Å, respectively. Three C atoms of the ethylene groups of the cation radicals of type *B* lie on one side of the molecular plane (the displacement of the atoms is C15 0.23, C16 0.66 and C23 0.65 Å) and C24 atom lies on the opposite site with a displacement of 0.17 Å.

The structure of the anion layer is shown in Fig. 4. The Hg atom is coordinated through the S atoms by four SCN groups as a distorted tetrahedron. The Hg–S bond lengths and the S–Hg–S angles range from 2.420 (4) to 2.617 (2) Å and from 102.51 (8) to 125.64 (13)°, respectively. The Hg–S–CN and S–C–N angles lie within the ranges 68.2 (3)–99.2 (2)° and 156.8 (6)–177.6 (9)°, respectively.

The immediate coordination environment of the K<sup>+</sup> cations is shown in Fig. 4 and the main distances are reported in Table 4. Comparing the distances from the K<sup>+</sup> cation to the nearest neighbouring atoms (Table 4) with the sums of van der Waals and ionic radii (2.80 for K<sup>+</sup>···N, 3.21 K<sup>+</sup>···S), it can be concluded that only the contacts K1–N and K1–S might be associated with weak interatomic interactions. The interaction between the K<sup>+</sup> cations and the SCN<sup>−</sup> anions is thus essentially electrostatic.

**Table 2**  
Bond lengths (Å) and angles (°) for (1).

Hg1—S2'	2.420 (4)	S14—C17	1.757 (5)
Hg1—S1	2.504 (2)	S14—C15	1.772 (7)
Hg1—S2	2.601 (3)	S15—C19	1.737 (5)
Hg1—S3	2.602 (2)	S15—C18	1.741 (5)
Hg1—S4	2.617 (2)	S16—C19	1.736 (5)
S1—C1	1.583 (9)	S16—C17	1.744 (5)
S2—S2'	1.110 (6)	S17—C20	1.744 (5)
S2—C2	1.641 (7)	S17—C22	1.756 (5)
S2'—C2	1.876 (8)	S18—C20	1.740 (5)
S3—C3	1.663 (7)	S18—C21	1.747 (5)
S4—C4	1.685 (7)	S19—C22	1.749 (5)
S5—C7	1.749 (5)	S19—C24	1.818 (5)
S5—C5	1.809 (5)	S20—C21	1.739 (5)
S6—C8	1.753 (5)	S20—C23	1.816 (5)
S6—C6	1.826 (5)	N1—C1	1.174 (12)
S7—C9	1.755 (5)	N2—C2	1.136 (9)
S7—C7	1.757 (5)	N3—C3	1.165 (9)
S8—C9	1.746 (5)	N4—C4	1.138 (8)
S8—C8	1.754 (5)	C5—C6	1.526 (7)
S9—C10	1.741 (5)	C7—C8	1.340 (7)
S9—C11	1.745 (5)	C9—C10	1.343 (6)
S10—C10	1.747 (5)	C11—C12	1.353 (7)
S10—C12	1.761 (5)	C13—C14	1.521 (7)
S11—C11	1.749 (5)	C15—C16	1.417 (12)
S11—C13	1.813 (5)	C17—C18	1.343 (7)
S12—C12	1.733 (5)	C19—C20	1.368 (6)
S12—C14	1.814 (5)	C21—C22	1.360 (7)
S13—C18	1.756 (5)	C23—C24	1.532 (7)
S13—C16	1.789 (8)		

S2'—Hg1—S1	103.91 (13)	C8—C7—S5	127.9 (4)
S2'—Hg1—S2	25.22 (13)	C8—C7—S7	116.1 (4)
S1—Hg1—S2	124.61 (8)	S5—C7—S7	116.0 (3)
S2'—Hg1—S3	106.81 (11)	C7—C8—S6	129.2 (4)
S1—Hg1—S3	111.00 (7)	C7—C8—S8	118.1 (4)
S2—Hg1—S3	107.14 (7)	S6—C8—S8	112.7 (3)
S2'—Hg1—S4	125.64 (13)	C10—C9—S8	123.3 (4)
S1—Hg1—S4	105.92 (6)	C10—C9—S7	122.5 (4)
S2—Hg1—S4	102.51 (8)	S8—C9—S7	114.2 (3)
S3—Hg1—S4	103.35 (5)	C9—C10—S9	123.2 (4)
C1—S1—Hg1	96.2 (3)	C9—C10—S10	121.9 (4)
S2'—S2—C2	83.6 (4)	S9—C10—S10	114.8 (3)
S2'—S2—Hg1	68.2 (3)	C12—C11—S9	118.4 (4)
C2—S2—Hg1	96.8 (3)	C12—C11—S11	128.5 (4)
S2—S2'—C2	60.4 (3)	S9—C11—S11	112.8 (3)
S2—S2'—Hg1	86.5 (3)	C11—C12—S12	128.1 (4)
C2—S2'—Hg1	96.9 (3)	C11—C12—S10	115.4 (3)
C3—S3—Hg1	94.5 (2)	S12—C12—S10	116.3 (3)
C4—S4—Hg1	99.2 (2)	C14—C13—S11	112.8 (3)
C7—S5—C5	100.7 (2)	C13—C14—S12	112.8 (4)
C8—S6—C6	102.2 (2)	C16—C15—S14	121.8 (6)
C9—S7—C7	96.1 (2)	C15—C16—S13	119.3 (7)
C9—S8—C8	95.5 (2)	C18—C17—S16	116.7 (4)
C10—S9—C11	95.3 (2)	C18—C17—S14	128.3 (4)
C10—S10—C12	96.0 (2)	S16—C17—S14	115.1 (3)
C11—S11—C13	102.6 (2)	C17—C18—S15	117.9 (4)
C12—S12—C14	100.5 (2)	C17—C18—S13	127.3 (4)
C18—S13—C16	100.1 (3)	S15—C18—S13	114.8 (3)
C17—S14—C15	103.5 (3)	C20—C19—S16	122.0 (4)
C19—S15—C18	94.5 (2)	C20—C19—S15	122.3 (4)
C19—S16—C17	95.1 (2)	S16—C19—S15	115.6 (3)
C20—S17—C22	95.3 (2)	C19—C20—S18	122.1 (4)
C20—S18—C21	95.6 (2)	C19—C20—S17	122.6 (4)
C22—S19—C24	101.5 (2)	S18—C20—S17	115.3 (3)
C21—S20—C23	99.9 (2)	C22—C21—S20	128.7 (4)
N1—C1—S1	177.6 (9)	C22—C21—S18	116.9 (4)
N2—C2—S2	166.3 (7)	S20—C21—S18	114.4 (3)
N2—C2—S2'	156.8 (6)	C21—C22—S19	128.8 (4)
S2—C2—S2'	36.0 (2)	C21—C22—S17	116.9 (3)
N3—C3—S3	177.5 (6)	S19—C22—S17	114.3 (3)
N4—C4—S4	179.4 (5)	C24—C23—S20	112.2 (3)

**Table 2 (continued)**

C6—C5—S5	112.9 (3)	C23—C24—S19	113.9 (4)
C5—C6—S6	113.0 (3)		

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x + 1, -y + 2, -z$ ; (iv)  $-x, -y + 2, -z$ .

**Table 3**  
Short S...S ( $r \leq 3.68$  Å) and N...S ( $r \leq 3.34$  Å) contacts (Zefirov, 1997) in the (ET)<sub>2</sub>[KHg(NCS)<sub>4</sub>] salt.

S1—S1 <sup>i</sup>	3.484 (5)	S13—S14 <sup>ii</sup>	3.435 (2)
S5—S6 <sup>ii</sup>	3.361 (2)	S13—S16 <sup>ii</sup>	3.548 (2)
S6—S7 <sup>iii</sup>	3.579 (2)	S17—S20 <sup>ii</sup>	3.488 (2)
S7—S11 <sup>iv</sup>	3.627 (2)	S19—S20 <sup>ii</sup>	3.462 (2)
S10—S11 <sup>iii</sup>	3.576 (2)	N1—S2 <sup>iii</sup>	3.132 (7)
S11—S12 <sup>ii</sup>	3.340 (2)	N1—S4 <sup>iii</sup>	3.295 (9)

Symmetry codes: (i)  $2 - x, 1 - y, -z$ ; (ii)  $x + 1, y, z$ ; (iii)  $x - 1, y, z$ ; (iv)  $2 - x, -y, 1 - z$ .

**Table 4**  
The immediate coordination environment of the K<sup>+</sup> cation (contact distances in Å).

K1—S3	3.379 (2)	K1—N3 <sup>ii</sup>	2.928 (6)
K1—S4 <sup>i</sup>	3.352 (2)	K1—N4 <sup>ii</sup>	2.979 (6)
K1—N3 <sup>i</sup>	2.891 (7)	K1—N4	2.815 (6)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y + 2, -z$ .

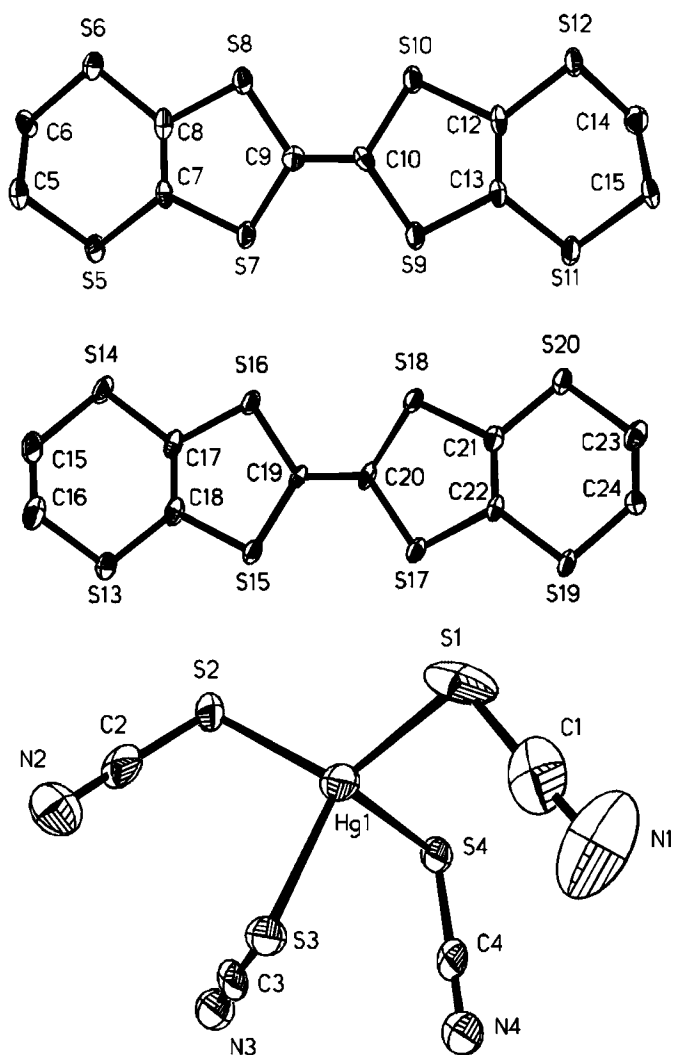
Unlike the anion layer of the  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt (Mori *et al.*, 1990), where the Hg<sup>2+</sup> and K<sup>+</sup> cations are staggered, the anion layer of the new polymorph shows a zigzag sequence of K<sup>+</sup> cations along the *a* axis fenced on both sides by two rows of translationally identical [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions. Whereas in the  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt each K<sup>+</sup> cation is surrounded by four [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions, in the new polymorph every K<sup>+</sup> cation is surrounded by only three [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions with a triangular coordination (the range of Hg—K—Hg angles is 94.4–133.8°). It should also be noted that because of the existence of a short intermolecular S1...S1 contact of 3.484 (5) Å, every [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anion really forms a dimer with its centrosymmetric analogue. These dimers lead to bands along the *a* axis through N1...S2 and N1...S4 short contacts of 3.132 (7) and 3.295 (9) Å, respectively. Thus, the anion layer has a polymeric structure in which the [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions and K<sup>+</sup> cations are held together by van der Waals and electrostatic interactions.

The new polymorph (1) is a room-temperature metal, but around 80 K the conductivity becomes activated. In order to correlate the crystal structure and the transport properties we carried out tight-binding band structure calculations for the donor layers of the present salt. These calculations used an extended Hückel-type Hamiltonian (Whangbo & Hoffmann, 1978) and a modified Wolfsberg–Helmholz formula (Ammeter *et al.*, 1978) to calculate the non-diagonal matrix elements. Double- $\zeta$  Slater-type orbitals were used for C and S and single- $\zeta$  Slater-type orbitals for H. The exponents, contraction coefficients and ionization potentials were taken from the previous work (Pénicaud *et al.*, 1992). The repeat unit of the

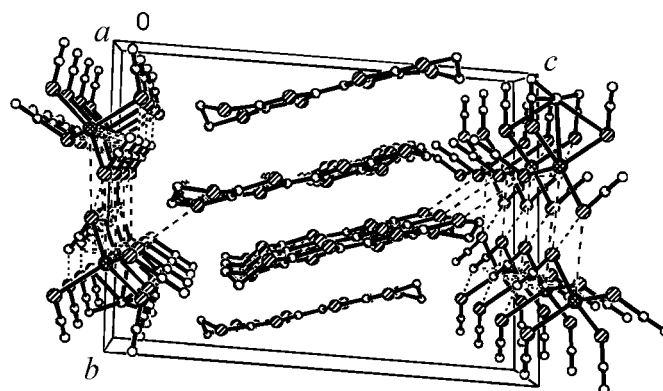
layer contains four ET donors (two of type *A* and two of type *B*) so that the band structure in the vicinity of the Fermi level contains four bands. These bands are mainly built from the HOMO of the ET donors and thus, in the following, they will be referred to as HOMO bands. The calculated band structure for the donor lattice is shown in Fig. 5. Given the stoichiometry and the usual charges of  $K^+$ ,  $Hg^{2+}$  and  $SCN^-$ , there must be two holes in these four HOMO bands. As shown in Fig. 5, the two upper bands are well separated along the directions  $\Gamma$ -Y,  $\Gamma$ -M and  $\Gamma$ -S but they almost touch along the  $\Gamma$ -X direction. The crossing of the two upper bands is not allowed by the low symmetry of the lattice ( $P\bar{1}$ ), but the gap is so small that it may be even difficult to see it in Fig. 5. A careful exploration of the band structure all along the Brillouin zone shows that the band gap is only 2.9 meV. Although the band gap could be somewhat underestimated by the present calculations, it must definitely be very small. Such a small band gap will be ignored by the electrons at room temperature because the thermal energy would exceed it and, consequently, the present  $(ET)_2[KHg(SCN)_4]$  polymorph should exhibit a room-

temperature metallic behaviour in agreement with the conductivity measurements.

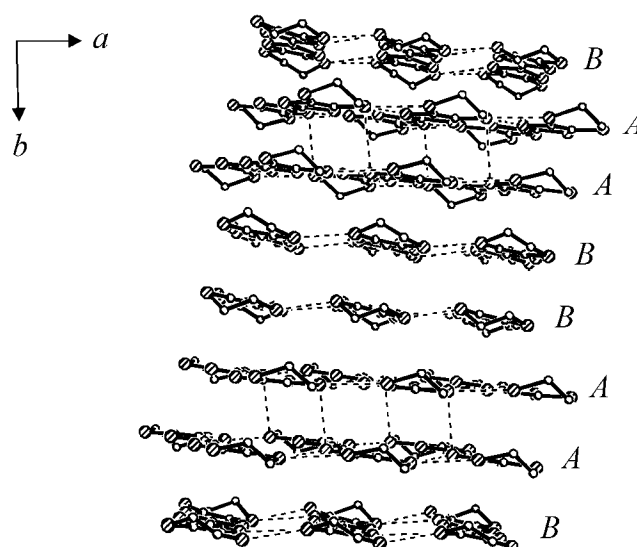
The loss of the metallic behaviour at low temperatures can be attributed to the small energy gap which may become relevant when the thermal energy of the electrons decreases. However, we believe that the conductivity change around the transition temperature is somewhat too abrupt to be just due to this thermal effect. Let us note that of the two bands implicated in this weakly avoided crossing, the upper and flat one is associated with ET donors of type *B* (*i.e.* is due to the strips of dimers of ET donors of type *B*, see Fig. 3), whereas the second and highly dispersive one is associated with ET donors of type *A* (*i.e.* is due to the strips of dimers of ET donors of type *A*, see Fig. 3). Thus, any small structural change increasing the coupling between the HOMOs of the type *A* and type *B* donors will make the crossing more avoided and the band gap larger. We believe that the metal to semiconductor transition is probably due to a small structural



**Figure 1**  
Atomic labelling used for  $(ET)_2[KHg(SCN)_4]$ .

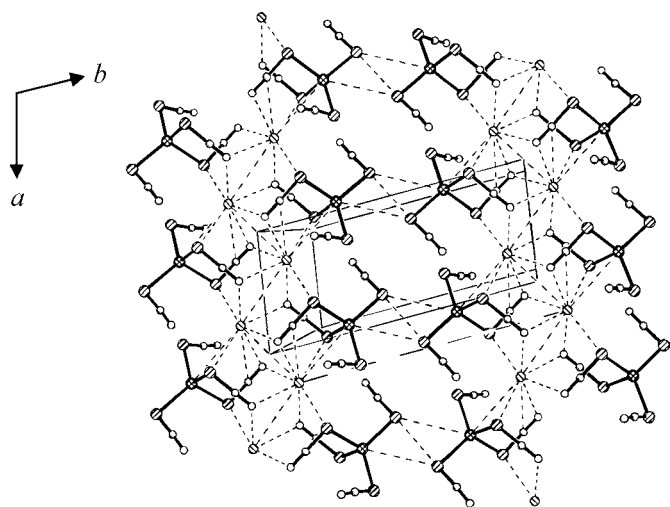


**Figure 2**  
A view of the crystal structure of  $(ET)_2[KHg(SCN)_4]$  showing the alternation of the conducting radical cation layers and the non-conducting anionic layers along the *c* axis. The dashed lines show short intermolecular contacts.

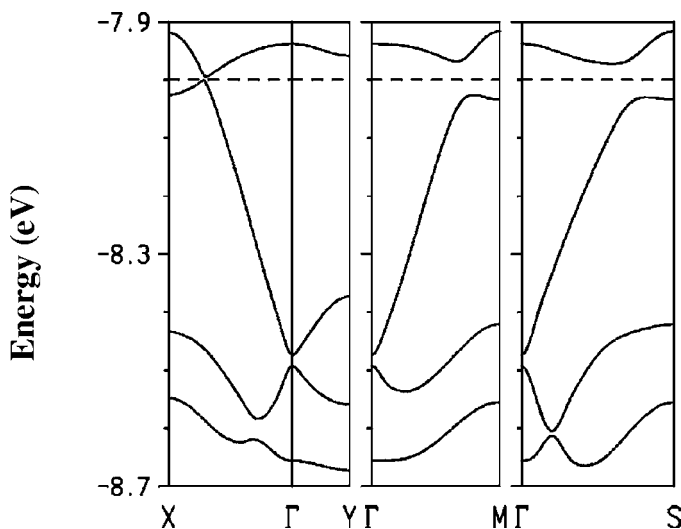


**Figure 3**  
The  $\delta$ -packing of the ET radical cations in the conducting layers of  $(ET)_2[KHg(SCN)_4]$ . The dashed lines show short intermolecular contacts.

change occurring at around 80 K, which leads to a stronger coupling of the strips of ET dimers of type *A* and type *B* and results in a larger band gap. It is interesting to point out that the large dispersion in the band structure is along the direction perpendicular to the stacks. It is because of the very short side-by-side contacts between the type *A* donors that there is the very dispersive band which ultimately leads to the metallic behaviour at room temperature. If the *A*···*B* contacts had been stronger, the very small band gap would have been larger and the salt would have been a room-temperature semiconductor. In fact, this happens in the  $\delta$ -(ET)<sub>2</sub>[TlHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>] and  $\delta$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salts (Shibaeva *et al.*, 1997) where, among other structural differences, the important interstack interactions are of the *A*···*B* type. However, the more important difference between these salts and the present polymorph (1) is that the *A* and *B* donors



**Figure 4**  
A view of the anion layers of (ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>].



**Figure 5**  
Calculated HOMO bands for a donor layer of (ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>]. The dashed line refers to the Fermi level and  $\Gamma = (0, 0)$ ,  $X = (a^*/2, 0)$ ,  $Y = (0, b^*/2)$ ,  $M = (a^*/2, b^*/2)$  and  $S = (-a^*/2, b^*/2)$ .

were shown to exhibit different charges (ET<sup>+</sup> and ET<sup>0</sup>) in  $\delta$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] and  $\delta$ -(ET)<sub>2</sub>[TlHg(Se<sub>0.875</sub>S<sub>0.125</sub>CN)<sub>4</sub>]. This charge localization is the ultimate reason for the room-temperature semiconducting behaviour of the later salts.

#### 4. Conclusion

Three basic structural features distinguish the previously known  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt (Mori *et al.*, 1990) from the new polymorph (1) reported here. First, the radical cation layers of  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] are packed as in the  $\alpha$ -type, whereas in the new modification they are packed as in the  $\delta$ -type. Second, the relative orientation of the thiocyanato groups of the anion layers is different. Third, whereas in  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] (Mori *et al.*, 1990) the Hg<sup>2+</sup> and K<sup>+</sup> cations are staggered, in the new polymorph there is a zigzag sequence of the K<sup>+</sup> cations along the *a* axis fenced on both sides by two rows of translationally identical [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions. Thus, in the case of the  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt every K<sup>+</sup> cation is surrounded by four [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions with a tetrahedral coordination, but in the new polymorph (1) every K<sup>+</sup> cation is surrounded by three [Hg(SCN)<sub>4</sub>]<sup>2-</sup> anions with a triangular coordination. In both salts the anion layers have a polymeric structure: in the  $\alpha$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt it is realised through the thiocyanate group ambidexterity and in the new polymorph (1) through intermolecular S···S and S···N contacts. In contrast with the previous  $\delta$ -(ET)<sub>2</sub>[KHg(SCN)<sub>4</sub>] salt, where the two donors have different charges and the side-by-side contacts are of the *A*···*B* type, the strong side-by-side *A*···*A* contacts and the similarity in the HOMO energies of donors *A* and *B* lead to the metallic room-temperature behaviour of the present polymorph.

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