New BETS Salt with Iodomercurate Anion: $(BETS)_4Hg_3I_8$

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Two phases of new BETS salt of $(BETS)_4Hg_3I_8$ are synthesized. X-ray analysis of θ-phase revealed a strong interstack interaction in organic layers and the occurrence of infinite chains of iodomercurate anions.

It is well known that the most of radical cation salts on the base of bis(ethylenedithio)tetraselenafulvalene (BETS) behave as metals down to low temperatures.[1-3]

The synthesis of the first BETS based superconductor λ-$(BETS)_2GaCl_4$[4] gave rise to the intense investigations of BETS salts with tetrahedral anions. Some more new superconductors isostructural to λ-$(BETS)_2GaCl_4$, were synthesized by a partial substitution of Cl for Br and F.[5-7]

It is known that bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) bromomercurate (BEDT-TTF is a sulfur containing analog of BETS) is an organic superconductor.[8] The conductivity measurements of BETS bromomercurates also showed the fall of the resistance at 5 K for one sample.[3] Therefore we studied the preparation of BETS halomercurates of different compositions.

We present here the synthesis of a new BETS salt with iodomercurate anion $(BETS)_4Hg_3I_8$ together with the results of X-ray analysis and resistivity measurements.

BETS was prepared according to the novel method developed by Kato et al[1]. $(BETS)_4Hg_3I_8$ single crystals were prepared at least as a two-phase mixture by a galvanostatic (i=1 μA/cm^2) oxidation of BETS in the presence of $(n\text{-}Bu_4)NHgI_3/HgI_2$ as a supporting electrolyte at 48 °C. Both phases are black thin plates. Electron probe microanalysis of the crystals obtained from different experiments, showed the crystals of both phases to have the same composition, namely, $(BETS)_4Hg_3I_8$. However conductivity measurements showed a different behavior of the crystals of these phases. Temperature dependent resistivity of both salts is shown in Figure 1. The phase 1 is metallic down to 4.6 K (σ_{RT} = 200 Ω^{-1}cm^{-1}). The resistivity of phase 2 attains its minimum at 95 K and then rises (σ_{RT} = 100 Ω^{-1}cm^{-1}). Recently Montgomery et al[9] have reported the preparation of $(BETS)_4Hg_3I_8$ which belongs to a triclinic system and has the temperature of metal-insulator transition equal to 200 K. This is probably one more phase of the same composition.

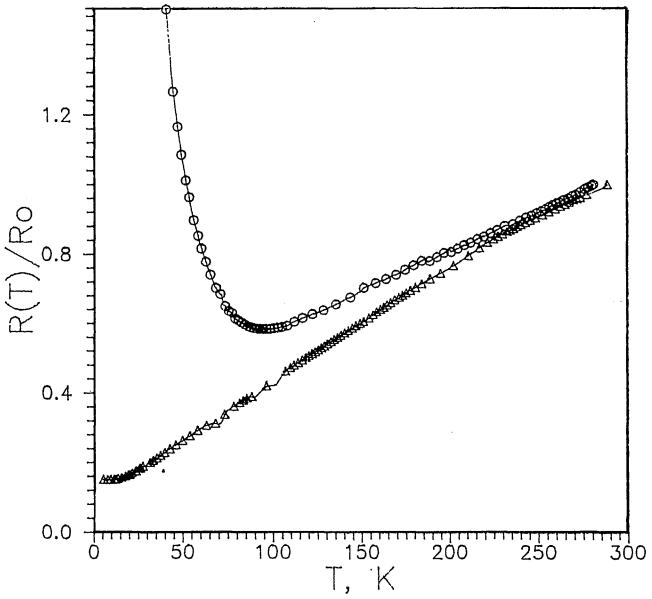

Figure 1. Temperature dependency of resistivity for $(BETS)_4Hg_3I_8$: o - θ-phase , Δ - phase 1.

The X-ray studies of the phase 2 showed it to have the following crystal parameters: space group $C2$, a = 11.971(5), b = 41.45(1), c = 8.462(2) Å, β = 110.49(4)°, V = 3933(10) Å^3, Z = 2, d_{calc} = 3.29 g/cm^3, F(000) = 3440. The independent reflections were collected by a KM-4 four-circle automatic diffractometer with a monochromated Cu-Kα radiation. The structure was solved by a direct method and refined by using full-matrix least-squares procedure in an anisotropic approximation to R = 0.086.

The crystal structure of the salt 2 (Figure 2) appears as an alternation of organic and inorganic layers along the b axis of the crystal. An organic layer is formed by the packing of four crystallographically independent BETS radical cations denoted as A, B, C, and D. There are two types of stacks: the AB stack composed of A and B cations and the CD one composed of C and D cations. The AB and CD stacks differ from each other by the manner of overlapping: the overlapping of the CD cations is characterized by the shift along the short molecular axis, and that of the AB stack is characterized by the shift similar to that along the short axis together with the shift along the long molecular axis. The interplanar distances in the AB and CD stacks are equal to 3.99 and 3.95 Å, respectively. The dihedral angles between the molecules are 41.2°, 44.9°, 46.9° and 50.6° for A-C, A-D, B-C and B-D pairs, respectively. The molecular arrangement is θ-

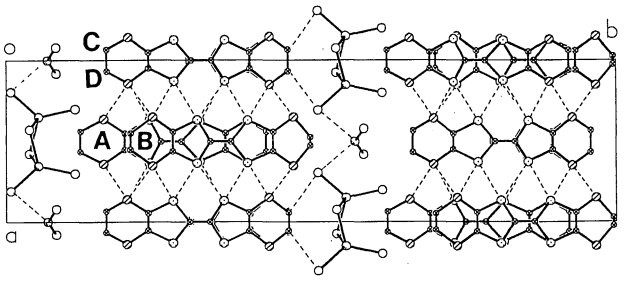

Figure 2. Projection of the crystal structure of θ-$(BETS)_4Hg_3I_8$ on the *ab* plane. Dashed lines correspond to shortened contacts.

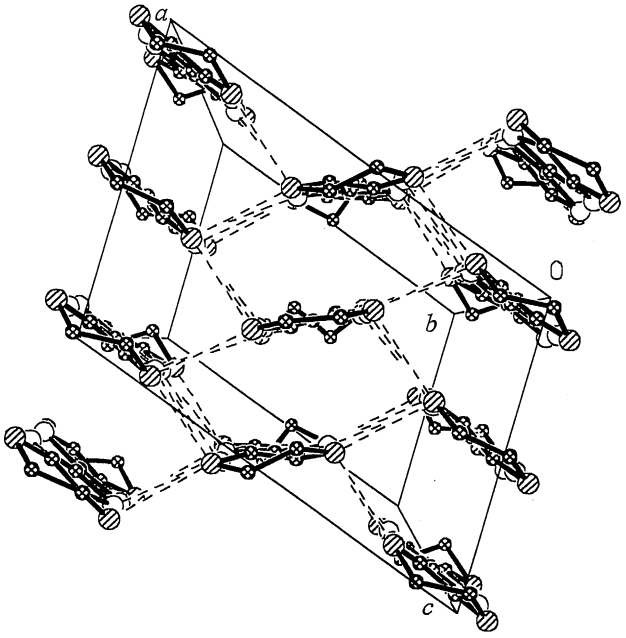

Figure 3. The arrangement of BETS radical cations in the conducting layer of θ-$(BETS)_4Hg_3I_8$. Dashed lines correspond to shortened contacts.

type. The shortened intrastack chalcogen...chalcogen distances are not found (Figure 3). On the other hand many shortened chalcogen...chalcogen contacts are found between the molecules of the neighboring stacks. The shortened Se...Se contacts are within 3.68-3.93 Å, Se...S ones are within 3.49-3.63 Å, and S...S ones are within 3.60-3.64 Å.

The inorganic layer is formed by dimeric $[Hg_2I_6]^{2-}$ anions and HgI_2 molecules. $[Hg_2I_6]^{2-}$ anions are linked with HgI_2 molecules by strongly shortened intermolecular Hg(1)...I(2) contacts of 3.365 Å in infinite chains along the *a* axis. The I(2) atoms are also involved in shortened contacts with C atoms of BETS radical cations in the conducting layer.

θ-$(BETS)_4Hg_3I_8$ is isomorphic to θ-$(BEDT\text{-}TTF)_4Hg_3I_8$ synthesized by us earlier.[10] The structure of anion sheets completely coincides in both compounds. The shortened intrastack S...S contacts are absent in the BEDT-TTF salt similarly to the BETS one, every BEDT-TTF radical cation forming six shortened S...S contacts which lie within 3.48-3.60 Å, with radical cations from the neighboring stacks. One observes more similar side-by-side contacts in the BETS salt. Therefore one could suggest stronger interstack interactions in the BETS salt as compared with the BEDT-TTF one. Such interactions seem to affect the conductivity of the salts: θ-$(BEDT\text{-}TTF)_4Hg_3I_8$ is a semiconductor at room temperature with the first order phase transition at 265K[10] whereas θ-$(BETS)_4Hg_3I_8$ behaves as a metal down to 95 K.

We have performed X-ray analysis for the crystal which behaves as metal (phase 1). Unfortunately, the lattice parameters are very close to those found for the phase 2 with metal-insulator transition. The difference is only in that Hg atoms in the phase 1 are somewhat disordered as compared with those in the phase 2. Probably slight changes in the crystal structure can result in such changes in conductivity. We would like to define this unambiguously. Now X-ray studies of the crystals of the phase 1 are carried out.

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