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Novel organic metal of α-$(BETS)_2Cu_5I_6$ with a two-dimensional polymeric anion network; synthesis, structure and properties

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The α-$(BETS)_2Cu_5I_6$ radical cation salt was obtained by electrocrystallization and its crystal structure has been determined by single crystal X-ray diffraction. The salt has a layered crystal structure and shows an unusual two dimensional polymeric anionic network. Crystal resistance and optical properties were studied. At ambient pressure the electrical conductivity of this salt shows metallic behaviour down to 25–30 K and then an M–I transition takes place. It was found this transition was completely suppressed at pressures above *ca.* 10 kbar. After release of pressure the salt shows metallic behaviour down to 1.3 K.

Recently radical cation BETS salts, [BETS = bis(ethylenedithio)tetraselenafulvalene] have attracted special interest due to the unique properties of some of them.[1–9] For instance, the λ-$(BETS)_2FeCl_4$ salt is characterised by coupled metal–insulator and antiferromagnetic transitions owing to the interaction between the conducting π-electrons of BETS radical cations and d-electrons of high occupation molecular orbitals of Fe^{3+} in the anion sheets.[1,2] It was also observed that λ-$(BETS)_2GaCl_4$ and λ-$(BETS)_2GaBr_xCl_{4-x}$ salts are superconductors with $T_c < 10$ K and are isostructural to λ-$(BETS)_2FeCl_4$.[3–7] Superconducting transitions have also been found in the λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.43$, 0.55).[8] In addition to superconducting transitions, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ salts also demonstrate unique superconductor–insulator transitions which are very sensitive to the concentration of magnetic Fe^{3+} ions.[8] Recently, unusual galvanomagnetic properties have been observed in κ-$(BETS)_2C(CN)_3$.[9] BETS is the closest analogue of bis(ethylenedithio)tetrathiafulvalene (ET) and may be considered as being derived from it by substitution of four sulfur atoms by selenium in the central TTF fragment. Obviously, new properties and/or new structures of BETS-based salts in comparison with corresponding ET salts are a result of the substitution of the heteroatoms. In order to understand better the correlations between the structures, properties and compositions of ET and BETS salts it is necessary to prepare corresponding series of the salts. More than a decade ago, we obtained the first organic metal with a two dimensional polymeric anion network, $(ET)_2Cu_5I_6$.[10] The salt was prepared by electrocrystallization of ET in the presence of Bu_4NCuI_2 as electrolyte. One can see that the anion of the radical cation ET salt differs from that in the initial electrolyte.

In this work we report a novel radical cation BETS salt with a two-dimensional polymeric anion network, consisting of $[Cu_5I_6]^-{}_n$ units, its crystal structure and physical properties which are compared with the structure and transport properties of the corresponding ET salt.

Experimental

Synthesis

Crystals of α-$(BETS)_2Cu_5I_6$ were obtained by the electrochemical oxidation of BETS in 1,1,2-trichloroethane at 50 °C in the galvanostatic regime with application of a constant current of 0.2 μA and Bu_4NCuI_2 as the supporting electrolyte. BETS (1.5×10^{-3} mol l^{-1}) was loaded into the anodic chamber of an H-shape electrochemical cell and the electrolyte (2.5×10^{-3} mol l^{-1}) was divided between the two cell chambers. Needle-like crystals grew both on the Pt-anode and in the anodic compartment over a period of 1–1.5 month.

X-Ray structure determination

Analysis of the crystal structure of α-$(BETS)_2Cu_5I_6$ was carried out on a crystal of dimensions $0.34 \times 0.21 \times 0.02$ mm at room temperature. Crystal data $a = 11.629(3)$, $b = 4.246(2)$, $c = 21.853(8)$ Å, $\beta = 100.09(3)^\circ$, $V = 1062.4(6)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $10 < 2\theta < 30^\circ$, $\lambda = 0.71073$ Å), space group $P2_1$, $Z = 1$, $C_{20}H_{16}Cu_5I_6S_8Se_8$, $M = 2223.59$, $D_c = 3.465$ g cm^{-3}, $F(000) = 999$. 2183 independent reflections, 1348 of which with $I > 2\sigma(I)$, were collected on a four-circle automated diffractometer KM-4 (KUMA DIFFRACTION, ω–2θ scan technique, up to $2\theta_{max} = 55.96^\circ$, Mo-Kα radiation with graphite monochromator). Numerical absorption correction [μ(Mo-Kα) = 14.037 mm^{-1}, $T_{max} = 0.76$, $T_{min} = 0.08$) was applied using SHELX-76 according to the crystal shape.[11] The structure was solved by direct methods using SHELX-86[12] and refined by least-squares method using SHELXL-93[13] with anisotropic parameters for Cu(1), I, Se, S atoms and isotropic parameters for C, Cu(2), Cu(3), Cu(4) and Cu(5) to $R = 0.075$ (on |F| for the observed data), $wR = 0.178$ (on F for all data). CCDC reference number 1145/132.

Resistance

Crystal resistance in the conducting *ab*-plane was measured along the *b* axis by the standard dc-four-probe method and also by the contactless method at a frequency of 10^{10} Hz[14] from room temperature down to 1.5 K. Conductivity in the direction perpendicular to the conducting layers was studied as described in ref. 15 and 16. Resistance under pressure was measured by the standard four-probe ac technique at a frequency of 320 Hz down to 1.3 K with the current applied to the single crystal perpendicular to the conducting *ab*-plane. A BeCu clamp cell was used to generate quasihydrostatic pressure up to 14 kbar at room temperature.

Optical properties

Polarised reflectivity spectra were measured at room temperature in the range 450–10000 cm^{-1} by means of Perkin-Elmer 1600 Fourier transform spectrometer (450–4400 cm^{-1}) and SF-8 grating spectrophotometer (4000–10000 cm^{-1}). The sample was made of several single crystals (of typical dimensions 0.25 × 1.5 × 1.5 mm) oriented parallel to each other. Spectra were taken from the *ab*-plane.

Results and discussion

Crystal structure

The radical cation salt α-$(BETS)_2Cu_5I_6$ has a layered crystal structure. The conducting radical cation layers alternate with the inorganic layers along the *c* direction (Fig. 1). The anion sheets consist of $[Cu_5I_6]^-$ anions packed in a two-dimensional polymeric network . The radical cation layers of α-type are constructed of regular $BETS^{+1/2}$ stacks running along the *b* crystal axis (Fig. 2). The BETS radical cations in the stacks are parallel and equidistant (3.87 Å) and overlap with a transverse shift equal to 1/2 of the BETS molecule width. The radical cations have an eclipsed conformation for the ethylene groups without orientation disorder. The dihedral angle between the radical cation planes of neighbouring stacks is 47.1° and there are many short interstack Se···Se, Se···S and S···S contacts. The unusual structure of the anionic polymeric network is of interest. The anion polymeric network consists of a combination of different types of tetrahedral CuI_4 and triangular CuI_3 moieties (Fig. 3). Atoms Cu(1), Cu(2) and Cu(4) have a tetrahedral environment of I atoms with Cu–I interatomic distances in the range 2.60–2.72 Å. Atoms Cu(3) and Cu(5) are bonded to iodine atoms in a triangular configuration with Cu–I interatomic distances in the range 2.41–2.62 Å. The occupancy of the Cu(1) atom position is equal to unity while the total occupation of the four other Cu atom positions sums to 1.5 (Cu(2) = 0.74, Cu(3) = 0.37, Cu(4) = 0.32, Cu(5) = 0.07).

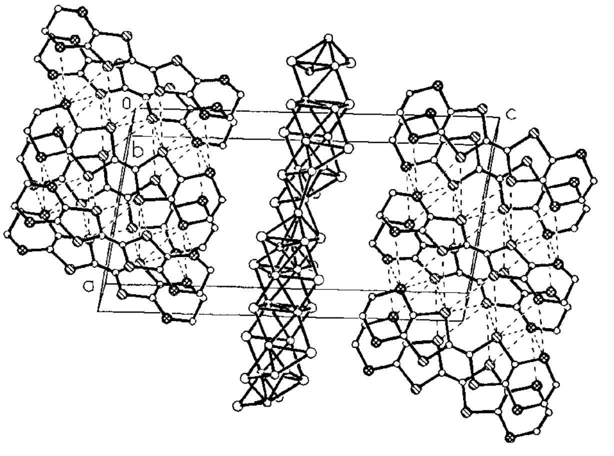

Fig. 1 The structure of the α-$(BETS)_2Cu_5I_6$ salt viewed along the *b* direction.

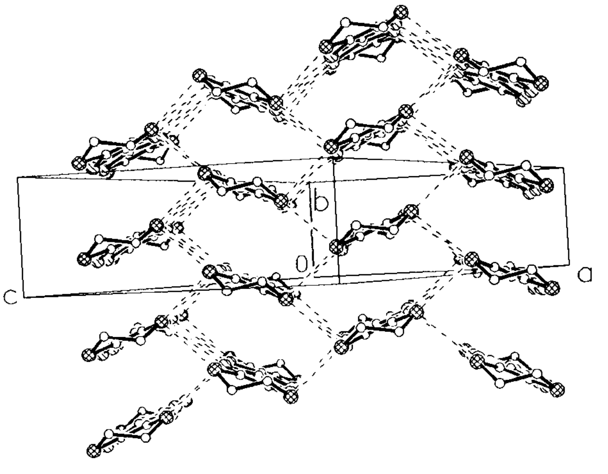

Fig. 2 View of the packing of the BETS radical cations in the α-$(BETS)_2Cu_5I_6$ salt.

Thus, there is some statistical disorder of Cu atoms. It should be noted that the corresponding ET salt, $(ET)_2Cu_5I_6$, is not isostructural to α-$(BETS)_2Cu_5I_6$.[10,17] The ET salt has a different arrangement of the radical cation layers with some positional disorder of the ethylene groups. The disorder associated with partial occupation of Cu atom positions is also present in the anionic layers of the $(ET)_2Cu_5I_6$ crystals. The layers in the latter structure consist of only one type of CuI_4 tetrahedron and display a polymeric honeycomb-like network. All the occupancies of Cu atom positions in $(ET)_2Cu_5I_6$ are equal to 5/6, while each Cu atom position has a different occupancy in α-$(BETS)_2Cu_5I_6$.

Resistance

The temperature dependences of the resistivity along the *b* crystal axis of the sample at ambient pressure for several single α-$(BETS)_2Cu_5I_6$ crystals are shown in Fig. 4. Resistance for all samples decreases by a factor of *ca.* 10–15 with a temperature decrease of 25–30 K and eventually a M–I transition takes place. The resistivity changes are practically the same for all crystals in the temperature range from 295 K to the temperature of the minimum resistivity. After the M–I transition the behaviour of the resistivity differs for each crystal studied as shown in Fig. 4. Note, that the resistance drop observed for several samples at 10 K [Fig. 4(*d*)] does not correspond to a superconducting transition as the resistance behaviour of these crystals do not change in a magnetic field (10 T). However, the nature of the resistivity drop is not clear. A further investigation of this effect is necessary. The distinctions in the resistivity behaviour at low temperature, probably, are caused by different degrees of disorder in the anionic layers of the α-$(BETS)_2Cu_5I_6$ crystals. The corresponding ET salt, $(ET)_2Cu_5I_6$, is a metal down to 2–15 K depending on the crystal quality. At lower temperature there is a weak resistance increase owing to the disorder in the anionic part of the $(ET)_2Cu_5I_6$ crystals.[10,17]

The value of room temperature conductivity along the *b* axis in the plane of BETS layers and perpendicular to this plane for α-$(BETS)_2Cu_5I_6$ crystals are *ca.* 30 and 3×10^{-3} Ω^{-1} cm^{-1}, respectively. The anisotropy of the resistivity ($\rho_{\parallel}/\rho_{\perp}$) is *ca.* 10^4 at room temperature and increases to 60–70% upon lowering the temperature down to 100 K. Both dependences, $\rho_{\parallel}(T)$ and $\rho_{\perp}(T)$ have a minimum at the same temperature (27 K) with dielectrization at lower temperature. A similar value of the anisotropy was found for the corresponding ET salt.[10]

Temperature dependences of dc and microwave resistivity for the same single crystal of α-$(BETS)_2Cu_5I_6$ are given in Fig. 5. These dependences have similar metallic character in the temperature range 295–27 K. By contrast to the dc resistivity, the microwave resistivity only slightly increases on

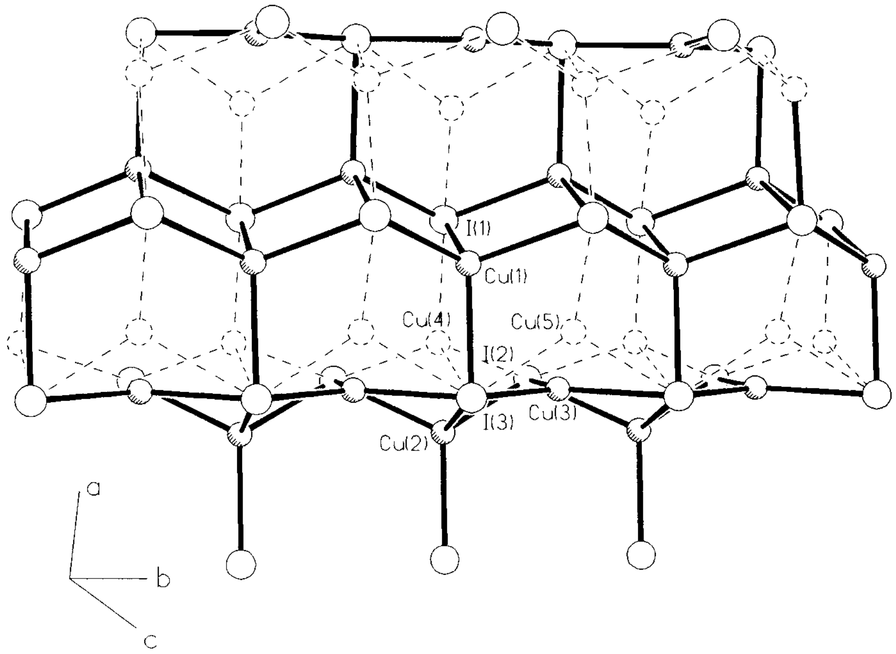

Fig. 3 View of two-dimensional polymeric anion network in the α-$(BETS)_2Cu_5I_6$ salt.

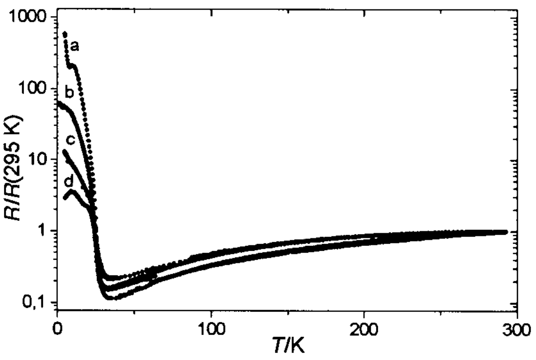

Fig. 4 The temperature dependences of dc-resistance along the *b* direction for four single crystals of α-$(BETS)_2Cu_5I_6$ at ambient pressure.

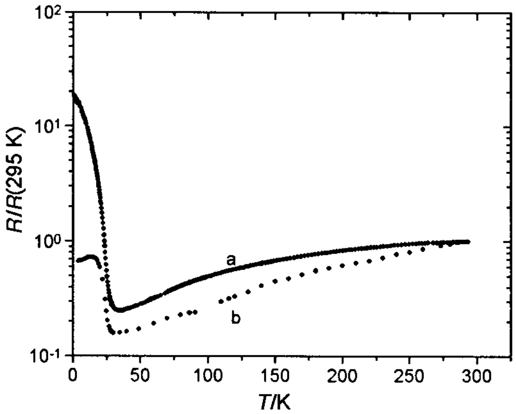

Fig. 5 The temperature dependences of dc- and microwave (10^{10} Hz) resistance along the *b* direction for a single crystal of α-$(BETS)_2Cu_5I_6$; (a) dc, (b) 10^{10} Hz.

cooling from 27 to 20 K and remains almost constant over the temperature range 20–4.2 K. Its value is considerably smaller than the dc resistivity which increases from 27 K down to 4.2 K without any saturation. It should be noted that the microwave resistivity does not change when the microwave power is reduced by a factor of 16. One can suppose that the difference in the behaviour of the dc and microwave conductivities is associated with the formation of a spin density wave at $T < 20$ K in α-$(BETS)_2Cu_5I_6$ crystals. A similar effect was observed previously for $(TMTSeF)_2PF_6$.[18–21]

The temperature dependences of resistance for the same single crystal of α-$(BETS)_2Cu_5I_6$ at ambient and high pressure are shown in Fig. 6. The metal–insulator transition observed in the crystal at 27 K becomes broader and shifts to lower temperature (*ca.* 20 K) with an increase of pressure to 4 kbar. Further increase of pressure to *ca.* 10 kbar completely suppresses this transition. It should be particularly noted that the metallic state created under pressure (14 kbar) is stable and is retained after release of this pressure, (Fig. 7). Probably, high pressure causes some irreversible changes in the structure of the salt stabilising a metallic state. The study of this new metallic phase structure at ambient pressure is in progress.

Optical properties

Fig. 8(a) shows the polarised reflectivity spectra of α-$(BETS)_2Cu_5I_6$ in the region 450–10 000 cm^{-1} for polarisation parallel and perpendicular to the *b* crystal axis. Fig. 8(b) shows the spectra of optical conductivity for the same two polarisations obtained from the reflectivity spectra by means of Kramers–Kronig analysis with usual extrapolations to low and high frequencies.[22–24] It is of interest to compare optical

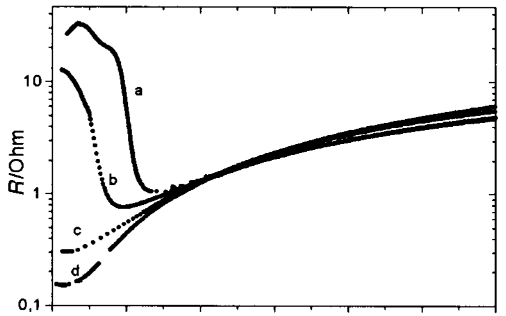

Fig. 6 The temperature dependences of resistance for a single crystal of α-$(BETS)_2Cu_5I_6$ under different pressures; (a) 1 bar, (b) 4 kbar, (c) 9.54 kbar, (d) 14 kbar.

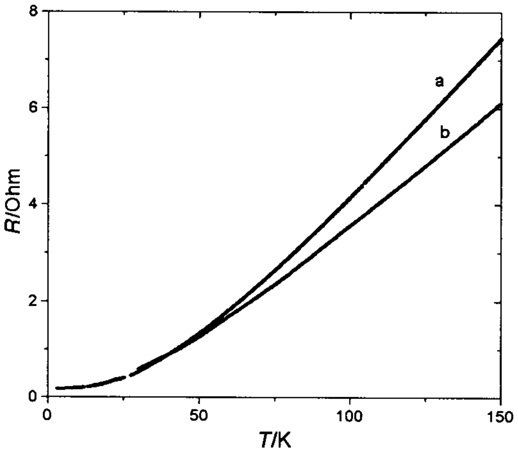

Fig. 7 The temperature dependences of resistance for the α-$(BETS)_2Cu_5I_6$ salt under 14 kbar pressure (b) and after release of pressure (a).

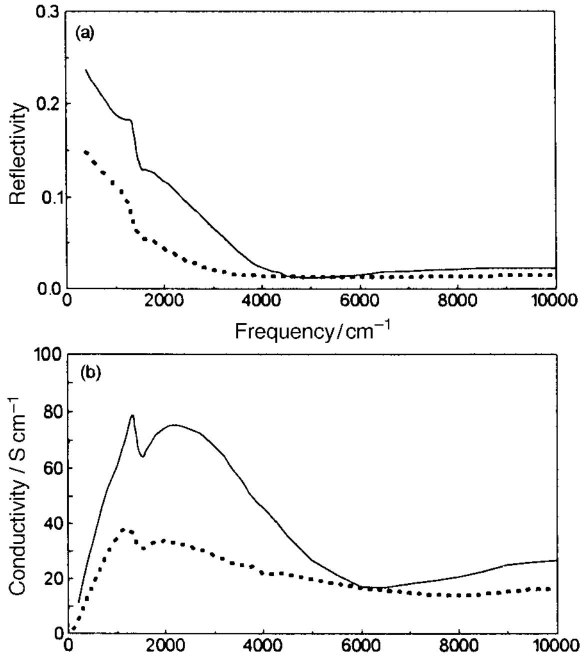

Fig. 8 (a) Polarised reflectivity spectra of α-$(BETS)_2Cu_5I_6$ crystals for the polarisations perpendicular (—) and parallel (- - -) to the *b* crystal axis; (b) spectra of the optical conductivity of α-$(BETS)_2Cu_5I_6$ crystals for the polarisations perpendicular (—) and parallel (- - -) to the *b* crystal axis.

properties of α-$(BETS)_2Cu_5I_6$ with that of previously studied α-type salts, α-$(BETS)_2TlHg(SeCN)_4$,[22] its isostructural ET analogue[23] and also of some other α-type ET salts.[23,24] In the reflectivity spectra of α-$(BETS)_2Cu_5I_6$, the electronic metallic-type reflection with a plasma edge below 4000 cm^{-1} and reflectivity rising to low frequencies are observed which is due to excitation of conducting electrons. Of the two polarisations, the greater electronic reflectivity is observed for the direction perpendicular to BETS stacks. This is consistent with the spectra of previously studied α-type salts and is due to a large amount of short S(Se)···S(Se) contacts between adjacent stacks.[22–24] The important feature of α-$(BETS)_2Cu_5I_6$ is the presence of a maximum in optical conductivity at *ca.* 2300 cm^{-1}. Such a maximum is absent in the optical conductivity spectra of α-$(BETS)_2TlHg(SeCN)_4$[22] and α-$(ET)_2TlHg(SeCN)_4$[22,23] but it is present in the spectrum of α-$(ET)_2I_3$.[23,24] A maximum in the conductivity may provide evidence of an energy gap (or pseudo-gap) in the spectra of electronic states. This possibly correlates with the fact that both α-$(ET)_2I_3$ and α-$(BETS)_2Cu_5I_6$ undergo metal–insulator transitions at low temperatures (*ca.* 137[25] and 27 K respectively) whereas α-$(ET)_2TlHg(SeCN)_4$ and α-$(BETS)_2TlHg(SeCN)_4$ are metals down to 1.3 K.[16,22]

Peculiarities of reflectivity in the region 1100–1300 cm^{-1} are due to electron–vibrational interaction of BETS intramolecular vibrations and conduction electrons.[22–24] The vibrational modes participating in this interaction are mainly connected with C=C stretching vibrations, and therefore the spectral region of electron–vibrational bands do not differ much between BETS and ET salts. For α-$(BETS)_2Cu_5I_6$, an intense electron–vibrational band is observed in the polarisation perpendicular to BETS stacks. For the polarisation parallel to stacks, only a weak broad maximum is observed in the region 1000–1300 cm^{-1}. A similar appearance of electron–vibrational bands is observed for α-$(ET)_2I_3$.[24,23] For α-$(BETS)_2TlHg(SeCN)_4$ and α-$(ET)_2TlHg(SeCN)_4$, by contrast, more intense electron–vibrational bands are observed for the polarisation parallel to stacks.[22,23] The reason for this behaviour is, as yet, not clear. An interesting peculiarity of α-$(BETS)_2Cu_5I_6$ is the absence of a minimum of reflectivity at *ca.* 1290 cm^{-1} for the more intense electron–vibrational band. Such a minimum has been observed for previously studied α-type salts[22–24] and was argued to be due to the presence of centrosymmetric ET or BETS molecules in their crystal structures.[23] In the crystal structure of α-$(BETS)_2Cu_5I_6$ centrosymmetric BETS molecules are absent which correlates with the electron–vibrational spectrum.

Conclusion

A new radical cation salt, α-$(BETS)_2Cu_5I_6$, has been prepared. Its structure, optical properties (at ambient pressure) and conducting properties under different pressures have been studied. The salt has a layered crystal structure with radical cation layers of α-type alternating with anionic layer. The latter is a two-dimensional polymeric network consisting of a combination of a variety of CuI_4 tetrahedra and triangular CuI_3 anions. At ambient pressure the α-$(BETS)_2Cu_5I_6$ salt is a metal to about 27 K at which an M–I transition takes place. This transition was suppressed at a pressure of *ca.* 10 kbar. After release of pressure the α-$(BETS)_2Cu_5I_6$ crystals reveal metallic behaviour down to 1.3 K thus retaining their new state.

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