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A new stable organic metal in the well known family of radical cation α-salts: α-(BETS)$_2$TlHg(SeCN)$_4$. Synthesis, structure and properties

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The stable organic metal α-(BETS)$_2$TlHg(SeCN)$_4$ has been obtained by means of electrochemical oxidation of bis(ethylenedithio)tetraselenafulvalene (BETS) in 1,1,2-trichloroethane (TCE) with the addition of absolute ethanol in the presence of an electrolyte consisting of 18-crown-6, TlSeCN and Hg(SeCN)$_2$. The salt is isostructural with the ET-based salt with the same anion and ET and BETS salts with KHg(SCN)$_4$ as well. The number of the side-by-side Se···Se, Se···S and S···S contacts in each radical cation layer was twice that in comparison with the corresponding ET salt. Reflectivity spectra and magnetoresistance were studied. The Shubnikov–de Haas effect and angular oscillations of the magnetoresistance were observed. Optical and transport properties of α-(BETS)$_2$TlHg(SeCN)$_4$ were compared with those of the analogous ET salt.

All radical cation salts obtained with the highest superconducting transition temperatures (over 10 K) are based on bis(ethylenedithio)tetrathiafulvalene (ET).[1–5] They have layered structures consisting of alternating conducting radical cation layers of k-type and insulating anion sheets. One of the major directions of molecular design strategy for the preparation of new metallic and superconducting organic compounds is chemical modification of ET. Among the known ET derivatives, only its closest analogue, bis(ethylenedithio)-tetraselenafulvalene (BETS), forms superconductors with relatively high T_c values: (BETS)$_2$GaCl$_4$ ($T_c = 8$ K[6,7]), (BETS)$_2$GaCl$_x$Y$_{4-x}$ (Y = Br, F; $0 < x < 4$), ($T_c = 3.6$–8 K depending on x and Y[8,9]). The BETS superconductors are characterized by the availability of radical cation layers of λ-type. The anion layers consist of GaCl$_4$ or mixed GaCl$_x$Y$_{4-x}$ tetrahedra, respectively. It should be noted that the ET salt with the GaCl$_4$ anion does not possess the same crystal packing as λ-(BETS)$_2$GaCl$_4$ and is a semiconductor.[10] The preparation of new BETS salts, most notably with polymeric complex anions of cupper {Cu[N(CN)$_2$X], X = Cl, Br} and mercury [MHg(XCN)$_4$, M = K, NH$_4$, Tl, Rb; X = S, Se] is of considerable interest. ET salts with cuprate anions have exhibited the highest T_c values (11.5–12.8 K)[2,3] among the low-dimensional molecular metals. ET salts with mercurate anions have provided a series of intriguing physical results (Shubnikov–de Haas effect, gigantic angular dependent magnetoresistance oscillations and magnetic phase transitions[11]). The electronic properties of these isostructural salts essentially depend on M and ligands (SCN or SeCN) in the mercurate anion. Recently, the radical cation BETS-based salts with Cu[N(CN)$_2$Br] and MHg(SCN)$_4$ (M = K, NH$_4$) have been synthesized.[12–15] The salts are isostructural with the corresponding ET salts. This is very important since it allows the study of the effect of replacement of the fulvalene sulfur atoms by selenium on the properties of the electron system of the BETS compounds.

Here, we report the first radical cation BETS salt with the tetrakis(selenocyanato)mercurate anion, α-(BETS)$_2$TlHg(SeCN)$_4$. Its crystal structure, optical and magnetotransport properties were studied and compared with those of the isostructural ET salt.

Experimental

Synthesis

Crystals of the α-(BETS)$_2$TlHg(SeCN)$_4$ salt were obtained by employing a standard electrochemical procedure.[16] A 1,1,2-TCE–ethanol mixture (10% absolute ethanol by volume) was used as solvent for the electrocrystallization of the BETS salt. The electrolyte consisted of 18-crown-6, TlSeCN and Hg(SeCN)$_2$ in a molar ratio of 1 : 2 : 1, respectively. Because of the limited solubility of BETS in TCE (also in most organic solvents) the electrocrystallization (under dry argon) was carried out at 50 °C. A constant current of 0.5–0.7 µA cm^{-2} was applied and thin dark plate-shaped crystals grew on the Pt anode after two months.

X-Ray structure determination

The crystal data of α-(BETS)$_2$TlHg(SeCN)$_4$ were: $a = 10.149(4)$, $b = 21.187(3)$, $c = 10.081(3)$ Å, $a = 103.41(2)$, $\beta = 90.45(2)$, $\gamma = 93.22(2)°$, $V = 2104.8$ Å^3, $Z = 2$, space group $P\bar{1}$, C$_{24}$H$_{16}$N$_4$S$_8$Se$_{12}$TlHg, $F(000) = 1770$, $M = 1969.25$, $D_c = 3.106$ g cm^{-3}, μ(Mo-Kα) = 191.27 cm^{-1}. X-Ray diffraction data for 4071 independent reflections from a $0.40 \times 0.40 \times 0.06$ mm single crystal were collected at room temperature on an Enraf-Nonius CAD 4 diffractometer [Mo-Kα radiation, ω scan technique, up to (sin $\Theta/\lambda)_{\max} = 0.594$]. Starting atomic coordinates were obtained from the analogous α-(ET)$_2$TlHg(SeCN)$_4$ salt.[17,18] The structure was refined by the least-squares method in anisotropic (for all the non-hydrogen atoms) approximation using AREN programs to $R=0.104$ for 3926 reflections with $F_o \geqslant 3\sigma(F_o)$. No absorption corrections were applied.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/79.

Resistance and magnetoresistance

Crystal resistance along the *a*-axis was measured by the standard dc four-probe method from room temperature down to 1.5 K. Magnetoresistance (MR) was studied in magnetic fields up to 14.3 T using an ac four-probe method at 330 Hz. The current was directed perpendicular to the conducting (*ac*) plane for all MR experiments. A measuring unit which allowed crystal rotation around the polar and azimuthal angles was used.

Optical measurements

The reflectivity spectra of the α-$(BETS)_2TlHg(SeCN)_4$ salt were measured at room temperature in the range 450–10 000 cm^{-1} in polarized light using a Perkin-Elmer 1600 Fourier transform spectrometer (450–4400 cm^{-1}) and an SF-8 grating spectrophotometer (4000–10 000 cm^{-1}). One single crystal with typical dimensions of 2 × 2 × 0.3 mm was used for the study. The spectra were taken from the *ac*-plane of conducting BETS layers. The optical conductivity spectra were obtained from the reflectivity spectra by means of Kramers–Kronig analysis. The result of this analysis in the region of 450–5000 cm^{-1} does not qualitatively depend on the kind of extrapolation at low and high frequencies. We have presumed that the reflectivity reaches unity at low frequencies (which is typical for metals) and is constant at high frequencies.

Results and Discussion

Crystal structure

The X-ray analysis has shown that the single crystals obtained for α-$(BETS)_2TlHg(SeCN)_4$ are isostructural with α-$(ET)_2TlHg(SeCN)_4$ [parameters: $a=10.105(1)$, $b=20.793(3)$, $c=10.043(1)$ Å, $\alpha=103.51(1)$, $\beta=90.53(1)$, $\gamma=93.27(1)°$, $V=2047.9$ Å^3, $Z=2$, space group $P\bar{1}$].[17,18] The largest difference is 0.394 Å (*ca.* 2%) for the *b*-axis. A detailed description of the layered crystal structure of α-$(ET)_2TlHg(SeCN)_4$ has been published and the overall features of the present salt are the same. As shown in Fig. 1, the α-$(BETS)_2TlHg(SeCN)_4$ structure includes three BETS radical cations in the asymmetric unit. One of them (I) occupies a general position, whereas two others (II and III) are located at centres of symmetry. Labeling of the atoms for BETS I, II, III is shown in Fig. 2. All the radical cations show the same, eclipsed, conformation of ethylene groups without orientational disorder. The projection of the radical cation layer along the *b*-direction is shown in Fig. 3. It is formed of two non-equivalent stacks parallel to the *c*-axis. One of them consists of parallel I, I_i and I_c radical cations while the other stack contains the non-parallel II, III and III_c radical cations (dihedral angle II–III = 5.6°). There are many short inter-radical cation Se···Se, Se···S, S···S contacts which are listed in Table 1. It should be noted that the number of short contacts in α-$(BETS)_2TlHg(SeCN)_4$ salt is almost twice that found in α-$(ET)_2TlHg(SeCN)_4$.

The structure of the anion layer is shown in Fig. 4. Each SeCN group of this layer forms a bridge between the Tl^+ and Hg^{2+} cations leading to a polymeric network in the *ac*-plane. This network contains Hg^{2+} ions tetrahedrally coordinated to

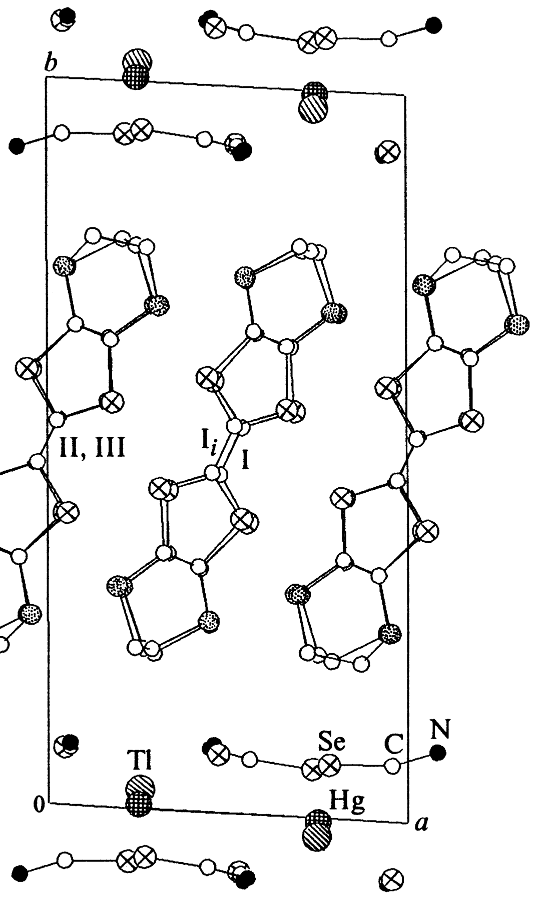

Fig. 1 The structure of α-$(BETS)_2TlHg(SeCN)_4$ projected along the *c*-axis. The symmetry operations for BETS I, II, III (x, y, z) and I_i ($1-x$, $1-y$, $1-z$)

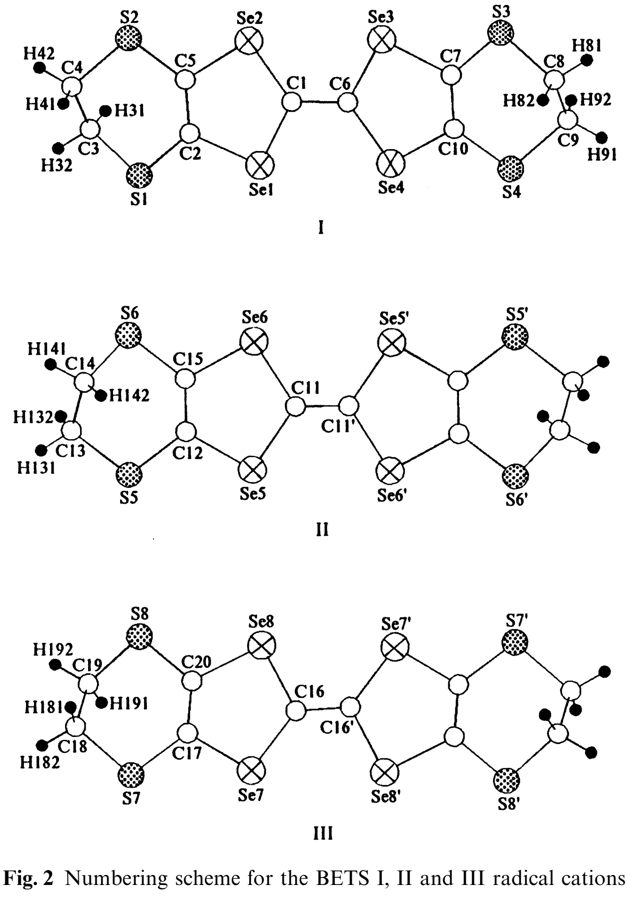

Fig. 2 Numbering scheme for the BETS I, II and III radical cations

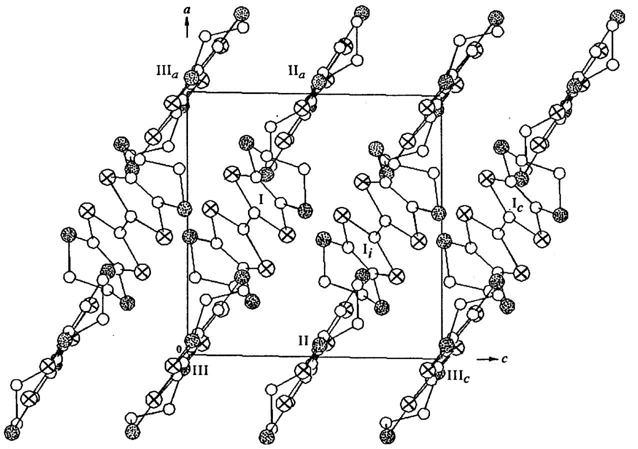

Fig. 3 The projection of the radical cation layer along the *b*-axis. The symmetry operations for BETS are II$_a$, III$_a$ $(1+x, y, z)$; I$_c$, III$_c$ $(x, y, 1+z)$; for other symmetry operations see Fig. 1.

Table 1 Short contacts S···S ($r \leqslant 3.70$ Å), Se···S ($r \leqslant 3.80$ Å) and Se···Se ($r \leqslant 3.90$ Å) between the radical cations in the α-(BETS)$_2$-TlHg(SeCN)$_4$ salt

contact	r/Å	BETS[a]	contact	r/Å	BETS[a]
Se1···Se4	3.869(5)	I–I$_i$	Se4···Se5	3.895(4)	I–II
Se1···Se5	3.821(5)	I–II	Se4···Se6′	3.865(5)	I–II
Se1···Se7	3.817(5)	I–III	Se4···Se7	3.803(6)	I–III
Se1···S5	3.62(1)	I–II	Se4···Se8′	3.798(5)	I–III
Se1···S7	3.52(1)	I–III	S1···S5	3.59(2)	I–II
Se2···Se5′	3.804(6)	I–II$_a$	S1···S7	3.50(1)	I–III
Se2···Se6	3.712(5)	I–II$_a$	S2···Se6	3.66(1)	I–II$_a$
Se2···Se7′	3.806(4)	I–III$_a$	S2···Se8	3.57(1)	I–III$_a$
Se2···Se8	3.791(5)	I–III$_a$	S2···S6	3.66(1)	I–II$_a$
Se3···Se5′	3.850(5)	I–II$_a$	S2···S8	3.55(2)	I–III$_a$
Se3···Se7′	3.741(5)	I–III$_a$	S3···S7′	3.67(2)	I–III$_a$
Se3···S5′	3.62(1)	I–II$_a$	S4···Se6′	3.59(1)	I–II
Se3···S7′	3.64(1)	I–III$_a$	S4···Se8′	3.65(1)	I–III
			S4···S6′	3.66(2)	I–II

[a] For symmetry operations of BETS, see captions to Fig. 1 and 3.

four Se atoms from the SeCN groups. The Hg—Se interatomic distances are in the range 2.636–2.651 Å while the corresponding distances for α-(ET)$_2$TlHg(SeCN)$_4$ are in the range 2.640–2.651 Å.[18,19] The coordination of the Tl$^+$ ion is quite typical: four short bonds on one side of the ion and four longer bonds on the other.[20] The Tl ion is placed at the top of a pyramid and bonded to four N atoms from the SeCN groups. The Tl—N interatomic distances are in the range 2.99–3.06 Å. The corresponding parameters for the ET analogues are in the range 2.935–3.019 Å. Four longer Tl—Se bonds (3.461–3.624 Å) complete the Tl coordination up to eight (a tetragonal antiprism).

Resistance and magnetoresistance

Crystals of α-(BETS)$_2$TlHg(SeCN)$_4$ demonstrate well pronounced metallic properties. The temperature dependence of the resistance is shown in Fig. 5. The resistance decreases with the temperature decreasing down to helium temperature with R^3 *ca.* 200 [$R^3 = R(295\ \mathrm{K})/R(4.2\ \mathrm{K})$] without any peculiarities. The value of R^3 exceeds, by almost one order of magnitude, that in the isostructural compound α-(ET)$_2$TlHg(SeCN)$_4$.[17]

Under a magnetic field $H = 14$ T perpendicular to the conducting plane the resistance grows almost six times without saturation at a temperature $T = 1.45$ K. This growth is considerably more than that in the ET salt.[21] Shubnikov–de Haas (SdH) oscillations have been observed in the α-(BETS)$_2$TlHg(SeCN)$_4$ samples (Fig. 6). These oscillations have only one fundamental frequency, $F_0 = 660$ T, which depends on the angle θ as $F(\theta) = F_0/\cos\theta$, where θ is the angle between the field direction and the direction b^*. Such behavior is characteristic of the cylindrical sheet of the Fermi surface. The analogous oscillations with the same frequency have also been observed earlier in the isostructural ET salt.[21] However, the parameters describing these oscillations differ significantly. The cyclotron mass in the BETS sample, $m^* = 1.1m_c$, is almost half that in the ET salt while the Dingle temperature, T_D *ca.* 4 K, is almost seven times the value in the ET salt.

The latter results indicate the considerably lower quality of the BETS samples. However, in this case it is difficult to explain the large values of R^3 and $R(H)/R(0)$. It should be noted that similar values of the cyclotron mass and Dingle temperature were also found in isostructural salts of α-(BETS)$_2$NH$_4$Hg(SCN)$_4$ and α-(BETS)$_2$KHg(SCN)$_4$.[22] One can suppose that the small cyclotron mass is typical for organic

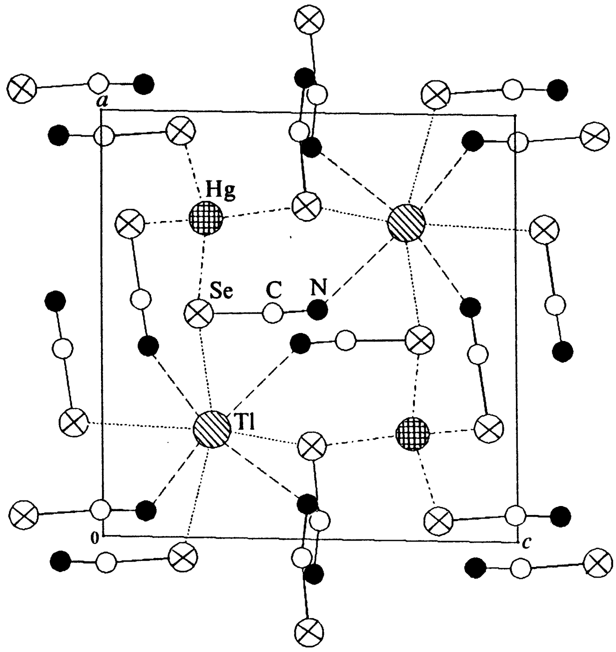

Fig. 4 Projection of the anion layer along the *b*-axis

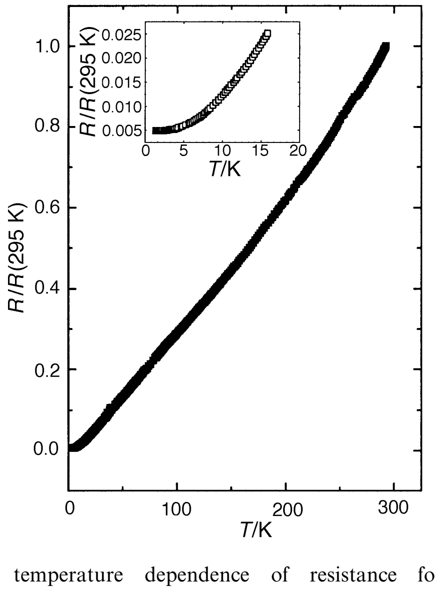

Fig. 5 The temperature dependence of resistance for the α-(BETS)$_2$TlHg(SeCN)$_4$ salt. The inset shows the low-temperature part of the curve.

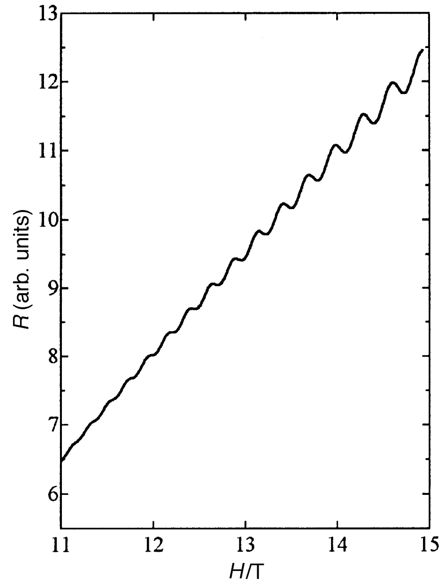

Fig. 6 Shubnikov–de Haas oscillations in the α-$(BETS)_2TlHg(SeCN)_4$ salt. $H \| b^*$, $T = 1.45$ K.

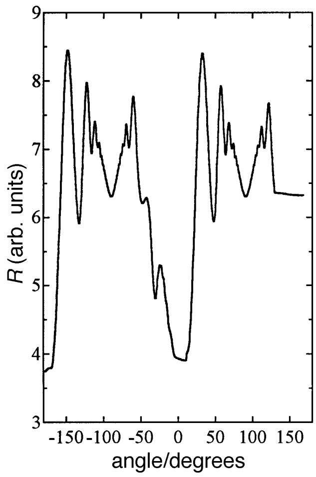

Fig. 7 Angle dependence of the magnetoresistance in the α-$(BETS)_2TlHg(SeCN)_4$ salt. $H = 14.2$ T, $T = 1.45$ K.

metals of this class. Clarifying such behaviour will require further investigations.

The angular oscillations of the magnetoresistance (AMRO) observed in α-$(BETS)_2TlHg(SeCN)_4$ (Fig. 7) are periodical in $\tan\theta$ and close to those in the ET salt.[21] Preliminary studies of the AMRO at different azimuthal angles have shown that they are connected to the cylindrical sheet of the Fermi surface. The size and exact form of this cylinder can be defined only after more detailed investigations which are in progress.

Optical properties

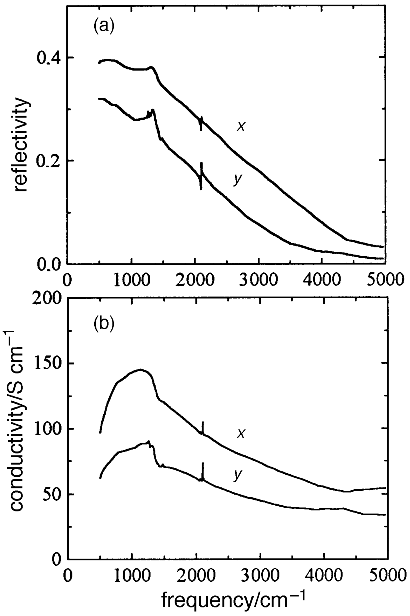

Fig. 8 Reflectivity (a) and optical conductivity (b) spectra of the α-$(BETS)_2TlHg(SeCN)_4$ crystals for two main optical directions x and y

Table 2 Electronic structure parameters of α-$(BETS)_2TlHg(SeCN)_4$ and α-$(ET)_2TlHg(SeCN)_4$ for the two main optical directions

	α-$(BETS)_2TlHg(SeCN)_4$		α-$(ET)_2TlHg(SeCN)_4$	
parameter	x ($E \perp c$)	y ($E \| c$)	x ($E \perp c$)	y ($E \| c$)
ε_∞	2.5	2.0	2.0	2.5
ω_p/cm^{-1}	3850	3100	4200	3500
2Δ/cm^{-1}	1400	1300	0	0
Γ/cm^{-1}	3000	2850	3000	3500
m/m_e	2.4	4.7	2.5	2.9
t/eV	0.09	0.06	0.09	0.08

Fig. 8(a) shows the polarized reflectivity spectra of α-$(BETS)_2TlHg(SeCN)_4$ in the region 450–5500 cm^{-1} for the two main optical directions, x and y, for which the maximal difference in reflectivities is observed. The reflectivity in the region 5500–10 000 cm^{-1} is weak and structureless. Fig. 8(b) shows the optical conductivity spectra for the same main optical directions. The spectra resemble those of the analogous isostructural compound α-$(ET)_2TlHg(SeCN)_4$.[23] By analogy with the ET salt, one may conclude that x and y directions correspond to polarizations with the electric vector perpendicular and parallel to the c crystallographic axis, respectively. This means that the electronic reflectivity is greater for the polarization perpendicular to the BETS stacks owing to a large number of short contacts between S(Se) atoms in the BETS cations of adjacent stacks. Similarly to α-$(ET)_2TlHg(SeCN)_4$, no pronounced plasma edge at *ca.* 4000 cm^{-1} is observed in the spectra of the BETS salt. This also results in the absence of a maximum in conductivity at *ca.* 3000 cm^{-1} which may be evidence of the absence of an energy gap in the spectrum of the electronic states, similarly to α-$(ET)_2TlHg(SeCN)_4$.

The reflectivity spectra of α-$(BETS)_2TlHg(SeCN)_4$ may be described in terms of the Drude–Lorentz model used for α-$(ET)_2I_3$.[24] The obtained parameters of this model (relative permittivities at high frequencies, ε_∞; plasma frequency, ω_p; electron energy gap, 2Δ; electronic damping, Γ) are given in Table 2 for x and y directions. High electron damping may be a reason for the absence of the pronounced plasma edge at *ca.* 4000 cm^{-1}. Carrier effective masses m_x and m_y were obtained from the equation $\omega_p{}^2 = 4\pi ne^2/m$ [e is electron charge and n is concentration of carriers accepted ($n = 1 \times 10^{21}$ cm^{-3} from structural data supposing one electron charge per two BETS molecules)]. Transfer integrals t_x and t_y were calculated from the effective masses by numerical integration by analogy with ref. 25 (intermolecular distances were accepted as half periods along a and c, $a_x = 5$ Å and $a_y = 5$ Å) (Table 2). We have also evaluated the Drude–Lorentz parameters for α-$(ET)_2TlHg(SeCN)_4$. The results are given in Table 2. Effective masses and transfer integrals for ET and BETS salts are almost equal in the x direction (perpendicular to stacks). In y direction the effective mass of the BETS compound is higher and the transfer integral is lower than in the ET salt. Similarly to the α-$(ET)_2TlHg(SeCN)_4$ salt, a doublet electron-vibrational band with a slight reflectivity minimum near 1280 cm^{-1} is observed in the polarization parallel to the BETS stacks (y direction) while the electron reflectivity is more intense in the polarization perpendicular to the stacks (Fig. 8). Maxima of this doublet are shifted to higher frequencies comparing with those of α-$(ET)_2TlHg(SeCN)_4$ (1270 and 1340 cm^{-1} *cf.* 1258 and 1316 cm^{-1} for the ET salt). Narrow bands near 2100 cm^{-1} are due to vibrations of CN fragments in the anionic layers (Fig. 8). Maxima of these bands are slightly shifted to higher frequencies compared with those of α-$(ET)_2TlHg(SeCN)_4$ (2110 and 2105 cm^{-1} for x and y directions *cf.* 2104 and 2102 cm^{-1} for the ET salt).

Summary

The first BETS salt with the tetrakis(selenocyanato)mercurate anion, α-$(BETS)_2TlHg(SeCN)_4$, has been synthesized. Its structure, magnetotransport and optical properties were studied and compared with those of the corresponding ET salt. The comparison of the lattice parameters and the short contacts in the conducting layer of α-$(BETS)_2TlHg(SeCN)_4$ with those of the isostructural ET salt has shown that the BETS compound is 'more of a two-dimensional' molecular metal than α-$(ET)_2TlHg(SeCN)_4$. SdH oscillations observed in α-$(BETS)_2TlHg(SeCN)_4$ salt show only one fundamental frequency, $F = 660$ T, and are similar to those in the ET analogue. However, the parameters which describe the oscillations differ significantly for these compounds. In particular, the cyclotron mass is lower (half) and the Dingle temperature higher (seven times) for the BETS sample. It is probable that the values of these parameters are distinctive features of the α-BETS salts. The reflectivity spectra of the BETS and ET salts are similar. However, their analysis in terms of the Drude–Lorentz model has shown that the effective mass and transfer integral of the BETS compound in the y direction are different from those of the ET salt while they are almost equal in the x direction for both salts. The probable reason for some differences in the magnetotransport and optical properties of the α-ET and α-BETS salts with $TlHg(SeCN)_4$ anion is the larger bandwidth of the BETS compounds as a result of substitution of sulfur atoms for selenium.[7]

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