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Low temperature crystal and electronic band structure of the $(BEDO\text{–}TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ stable organic metal

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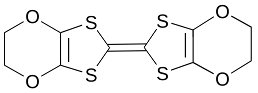
A bis(ethylenedioxy)tetrathiafulvalene (BEDO–TTF) chloride was synthesized by a combined diffusion-electrocrystallization method using the $[(C_2H_5)_4N]_2CuCl_4$ salt as supporting electrolyte. An X-ray analysis has been carried out at both room and low (160 K) temperatures: $a = 5.097(1)$, $b = 8.592(2)$, $c = 16.236(2)$ Å, $\alpha = 98.13(1)°$, $V = 703.8$ Å^3 (293 K) and $a = 5.069(2)$, $b = 8.435(6)$, $c = 16.137(4)$ Å, $\alpha = 97.82(4)°$, $V = 683.6$ Å^3 (160 K); space group $P2_1/b$. This salt seems to be the same BEDO–TTF chloride previously reported by several groups although its composition was never firmly established. The crystal structure is characterized by the presence of Θ-type radical cation layers alternating along the *c*-direction with honeycomb-like polymeric networks including Cl^- anions, H_2O molecules and H_3O^+, hydroxonium ions. The band structure and Fermi surface for different electron transfers at both 160 and 293 K have been calculated. The combination of these results with IR spectral data and analysis of the physical properties led to the conclusion that the real composition of this salt is $(BEDO\text{–}TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$.

Using a crown ether route Schweitzer *et al.*[1] prepared for the first time a (BEDO–TTF) chloride which is a stable organic metal. On the basis of X-ray and IR studies they proposed the composition $(BEDO\text{–}TTF)Cl\cdot H_2O$ for this salt. This was a surprising result because it was the first stable metallic radical cation salt with a half-filled band. Later, the formation of the same (BEDO–TTF) chloride with Bu_4NCl as a supporting electrolyte was described by Mori *et al.*[2] However, they proposed the composition $(BEDO\text{–}TTF)_2Cl\cdot 3H_2O$. Very recently, we tried to synthesize a radical cation salt of BEDO–TTF with the magnetic anion $CuCl_4^{2-}$. Salts of the bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) donor and its selenium analog—bis(ethylenedithio)tetraselenafulvalene (BETS)—with this anion have already been reported.[4–8] However, an X-ray study of the single crystals obtained showed that no Cu atoms were present and that the radical cation salt prepared was really a BEDO–TTF chloride with unit cell parameters very close to those reported by Schweitzer *et al.*[1] Almost simultaneously, the same BEDO–TTF chloride was accidentally prepared by another group,[9] while trying to synthesize BEDO–TTF salts with HgX_4^{2-} anions in the presence of supporting electrolytes with the composition $Bu_4NHgX_3 + Bu_4NX$ (X = I, Br, Cl).



BEDO-TTF

The exact composition of this BEDO–TTF chloride has not yet been firmly established, *i.e.* the exact content of H_2O molecules and Cl^- anions is still not clear. The problem lies in the statistical occupation of four symmetrically equivalent crystallographic positions in the unit cell by the Cl^- anions and H_2O molecules. However, determination of the real composition of this salt is an essential step in understanding its physical properties. As shown below, neither the $(BEDO\text{–}TTF)Cl\cdot H_2O$ nor the $(BEDO\text{–}TTF)_2Cl\cdot 3H_2O$ formulae seem to be entirely appropriate for this molecular metal. This is why we considered it worth restudying this salt in order to elucidate its true composition.

Here, we report our work concerning the synthesis as well as the room and low temperature (160 K) crystal structures of this BEDO–TTF chloride. We assumed that when lowering the temperature the thermal motion of the atoms will become slower and thus, the refinement of the occupation factors for the Cl and O atoms would be more precise. We also report IR spectral measurements as well as local X-ray microprobe analysis (LRMA) in order to check the chlorine content. Finally, we also analyze the band structure and Fermi surface at both room temperature and 160 K in an attempt to correlate the results of these studies with magnetoresistance measurements. As a result of this combined effort we believe that the true composition of this BEDO–TTF chloride can now be given as $(BEDO\text{–}TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$.

Experimental

Synthesis

Crystals of the BEDO–TTF chloride were obtained by a combined diffusion–electrocrystallization method from a BEDO–TTF solution in benzonitrile with addition of ethanol (10% vol) at 20 °C. A constant current of 0.2 μA was applied. The $[(C_2H_5)_4N]_2CuCl_4$ salt was used as supporting electrolyte.

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Addition of BEDO–TTF to the electrolyte solution led to the almost instantaneons precipitation of the products of the chemical oxidation of the donor by the Cu^{2+} ions. In order to avoid this, BEDO–TTF (1.5×10^{-3} mol l^{-1}) and the electrolyte (5×10^{-3} mol l^{-1}) were placed in different compartments of an H-like electrochemical cell. After approximately 30 min the cell was connected to the current source.

The use of this method leads to the oxidation of BEDO–TTF both electrochemically and chemically (because of the diffusion of $CuCl_4{}^{2-}$ or $CuCl_3{}^{-}$ anions through the glass frit separating the cell compartments). The appearance of the Cl^- anions in the solution was probably caused by the dissociation of the electrolyte ($CuCl_4{}^{2-} \rightleftharpoons CuCl_{3-} + Cl^-$) and/or BEDO–TTF oxidation by Cu^{2+} ions. Note that BEDO–TTF is a stronger reducing agent than BEDT–TTF and BETS donors. Within 18–20 days BEDO–TTF chloride crystals grow on the anode as rhombic- or hexagonal-like plates.

X-Ray structure determination

X-Ray experimental data were collected at room temperature and at 160 K on an Enraf-Nonius CAD-4F diffractometer [λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scan]. At room temperature the intensities of 956 non-zero reflections were measured up to $(\sin\theta/\lambda)_{max} = 0.549$; 572 were unique ($R_{int} = 0.029$) with $I \geqslant 2\sigma(I)$. The structure was solved by direct methods and refined by a least-squares technique in the full-matrix anisotropic approximation to $R = 0.044$ using the AREN programs.[10] The unit cell parameters ($T = 293$ K) are as follows: $a = 5.097(1)$, $b = 8.592(2)$, $c = 16.236(2)$ Å, $\alpha = 98.13(1)°$, $V = 703.8$ Å^3, space group $P2_1/b$. Crystal data and experimental details of the BEDO–TTF chloride single crystals at $T = 160$ K are listed in Table 1. The atomic coordinates and the room temperature crystal structure were used as a starting point and the low temperature structure was refined by a full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms by using the SHELXL-93 package of programs.[11] The hydrogen atoms were located from a difference synthesis and only their position parameters were refined. Their thermal parameters were kept equal to those of the atoms to which they are bonded. The final coordinates of the atoms and their thermal parameters are listed in Table 2. The bond distances and angles of the BEDO–TTF radical cation are given in Table 3. 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 1145/86.

Table 1 Crystal and experimental data

formula	$C_{20}H_{21.72}S_8O_{10.72}Cl_{1.28}$
M	735.47
T/K	160
crystal system	monoclinic
space group	$P2_1/b$
a/Å	5.069(2)
b/Å	8.435(6)
c/Å	16.137(4)
α/°	97.82(4)
V/Å^3	683.55
Z	1
F(000)	378.5
D_c/g cm^{-3}	1.787
μ(Mo-Kα)/cm^{-1}	7.1
$2\Theta_{max}$ (°)	50
h, k, l limits	$\pm h$, $-k$, $\pm l$
	5, 10, 19
data collected	2028
independent data	1026
$R_{int}(F^2)$	0.031
observed data, $F > 4\sigma(F)$	1023
parameters refined	116
R^a	0.026
goodness of fit	0.656
$\Delta\rho_{max}$/e Å^{-3}	0.37
$\Delta\rho_{min}$/e Å^{-3}	−0.24

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Table 2 Atomic coordinates and equivalent isotropic parameters for $(BEDO\text{–}TTF)_2Cl_{1.28}(H_3O)_{0.28} \cdot 2.44H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x/a	y/b	z/c	U_{eq}
S(1)	0.2250(1)	0.8499(1)	0.0741(0)	0.0137(2)
S(2)	−0.1965(1)	1.0923(1)	0.1172(0)	0.0142(2)
O(1)	0.2623(3)	0.8162(2)	0.2350(1)	0.0192(4)
O(2)	−0.1566(3)	1.0476(2)	0.2759(1)	0.0180(4)
C(1)	0.0054(4)	0.9876(3)	0.0408(1)	0.0124(5)
C(2)	0.1312(5)	0.8928(3)	0.1789(1)	0.0149(5)
C(3)	−0.0606(5)	1.0015(3)	0.1982(1)	0.0144(5)
C(4)	−0.0663(5)	0.9394(3)	0.3331(1)	0.0215(5)
C(5)	0.2223(5)	0.9007(3)	0.3188(1)	0.0212(5)
Cl[a]	0.9722(3)	0.3295(2)	0.5171(1)	0.031(1)
O_w[a]	0.9722(3)	0.3295(2)	0.5171(1)	0.081(3)
H(41)	−0.168(6)	0.845(3)	0.324(2)	0.0215(5)
H(42)	−0.095(6)	0.992(3)	0.387(2)	0.0215(5)
H(51)	0.330(6)	0.998(3)	0.323(2)	0.0212(5)
H(52)	0.283(6)	0.833(3)	0.357(2)	0.0212(5)
$H_w(1)$[a]	0.96(1)	0.442(3)	0.510(5)	0.081(3)
$H_w(2)$[a]	1.07(1)	0.337(8)	0.569(2)	0.081(3)

[a] Occupancy factors are 0.32 for Cl and 0.68 for O_w, $H_w(1)$ and $H_w(2)$.

IR spectra

The smallest single crystals under investigation had dimensions of 1 × 0.5 × 0.06 mm. As a result, the measurements of the infrared transmittance and reflectance spectra were carried out using the IR microscope of a Fourier-transform spectrometer. Spectra were measured at 300 K in the spectral range 600–6000 cm^{-1}. The electrical vector of the light beam was parallel to the highly conductive *ab*-plane of the BEDO–TTF chloride single crystals. The absorption spectra were calculated from the transmittance ones.

Electrical resistivity measurements

Resistivity was measured by the standard four-probe dc technique (in the *ab* plane). Contacts to the crystals were glued with a graphite paste using 10–30 μm diameter platinum wires. The room temperature conductivity was found to be about 60 ohm^{-1} cm^{-1}.

Table 3 Bond lengths and angles for BEDO–TTF in $(BEDO\text{–}TTF)_2Cl_{1.28}(H_3O)_{0.28} \cdot 2.44H_2O$

bond distances/Å		bond angles (°)	
S(1)—C(1)	1.746(2)	C(1)—S(1)—C(2)	93.8(1)
S(1)—C(2)	1.745(2)	C(1)—S(2)—C(3)	93.8(1)
S(2)—C(1)	1.746(2)	C(2)—O(1)—C(5)	109.6(2)
S(2)—C(3)	1.744(2)	C(3)—O(2)—C(4)	110.4(2)
O(1)—C(2)	1.355(3)	S(1)—C(1)—S(2)	116.8(1)
O(1)—C(5)	1.455(3)	S(1)—C(1)—C(1)′	121.3(2)
O(2)—C(3)	1.352(3)	S(2)—C(1)—C(1)′	122.0(2)
O(2)—C(4)	1.458(3)	S(1)—C(2)—O(1)	117.3(2)
C(1)—C(1)′	1.362(4)	S(1)—C(2)—C(3)	117.8(2)
C(2)—C(3)	1.344(3)	O(1)—C(2)—C(3)	124.9(2)
C(4)—C(5)	1.510(4)	S(2)—C(3)—O(2)	116.9(2)
		S(2)—C(3)—C(2)	117.8(2)
		O(2)—C(3)—C(2)	125.2(2)
		O(2)—C(4)—C(5)	110.4(2)
		O(1)—C(5)—C(4)	110.2(2)

Band structure calculations

The tight-binding band structure calculations are based upon the effective one-electron Hamiltonian of the extended Hückel method.[12] The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg–Helmholz formula.[13] All valence electrons were explicitly taken into account in the calculations and the basis set consisted of double-ζ Slater-type orbitals for C, S and O and single-ζ Slater type orbitals for H. The exponents, contraction coefficients and atomic parameters were taken from previous work.[14]

Results and Discussion

The temperature dependence of the resistivity of our crystals is analogous to that of the BEDO–TTF chloride crystals previously prepared by electrochemical oxidation of BEDO–TTF using the crown ether route.[1] The crystals exhibit a metallic behavior down to 1.3 K (Fig. 1) and the ratio $R_{1.3\ \mathrm{K}}/R_{293\ \mathrm{K}}$ is 7×10^{-3}.

Fig. 2 shows a projection of the 160 K BEDO–TTF chloride structure along the *a*-direction. The structure is characterized by layers of the BEDO–TTF radical cation alternating along the *c*-direction with honeycomb-like polymeric anion networks. The BEDO–TTF radical cations (see Fig. 3 for atom labelling) are located on an inversion center and have an eclipsed conformation of the terminal ethylene groups: the C(4) and C(5) atoms deviate from the average plane of the molecule by +0.27 and −0.49 Å, respectively. The ethylene groups are ordered. The nature of the bond lengths and angle distribution (Table 3) probably corresponds to (BEDO–TTF)$^{0.5+}$. It is noteworthy that the C=C double bonds C(1)=C(1′) [1.362(4) Å] and C(2)=C(3) [1.344(3) Å] are longer than the corresponding bonds in the neutral (BEDO–TTF)^{0} molecule. Their values are close to those found in the 2:1 salts $(\mathrm{BEDO{-}TTF})_2\mathrm{AuBr}_2$,[15] $(\mathrm{BEDO{-}TTF})_2\mathrm{ReO}_4\cdot\mathrm{H_2O}$[16] and $(\mathrm{BEDO{-}TTF})_2\mathrm{CF_3SO_3}$.[17]

The projection of the radical cation layer along the *c*-direction is shown in Fig. 4(*a*). It is a layer of the Θ-type first discovered in the organic superconductor Θ-$(\mathrm{BEDT{-}TTF})_2\mathrm{I}_3$[18] and later in a number of organic metals. This type of conducting layer is built from regular BEDO–TTF stacks parallel to the short *a*-axis. The overlap mode of adjacent radical cations in the stack is shown in Fig. 4(*b*) and it is the same at room and low temperatures. The mean BEDO–TTF interplanar distances in the stack are 3.532 (293 K) and 3.475 Å (160 K). The planes of the radical cations from neighboring stacks are approximately perpendicular to each other. There are several short S···S and S···O intermolecular contacts (see Table 4) which allow the electron delocalization within the slabs.

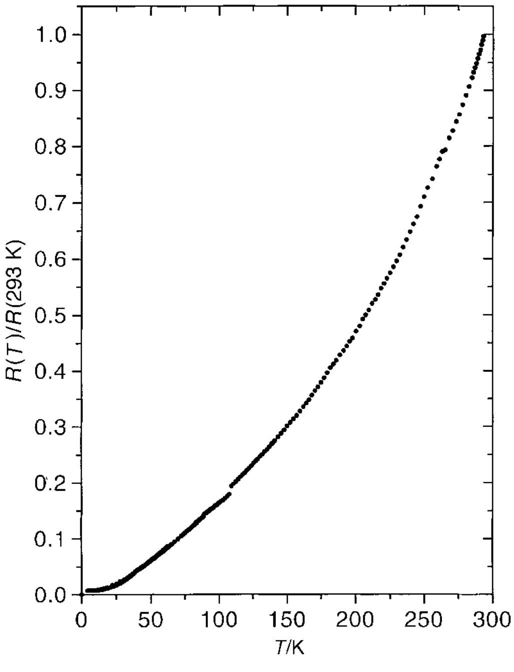

Fig. 1 Temperature dependence of the relative resistivity of $(\mathrm{BEDO{-}TTF})_2\mathrm{Cl}_{1.28}(\mathrm{H_3O})_{0.28}\cdot2.44\mathrm{H_2O}$

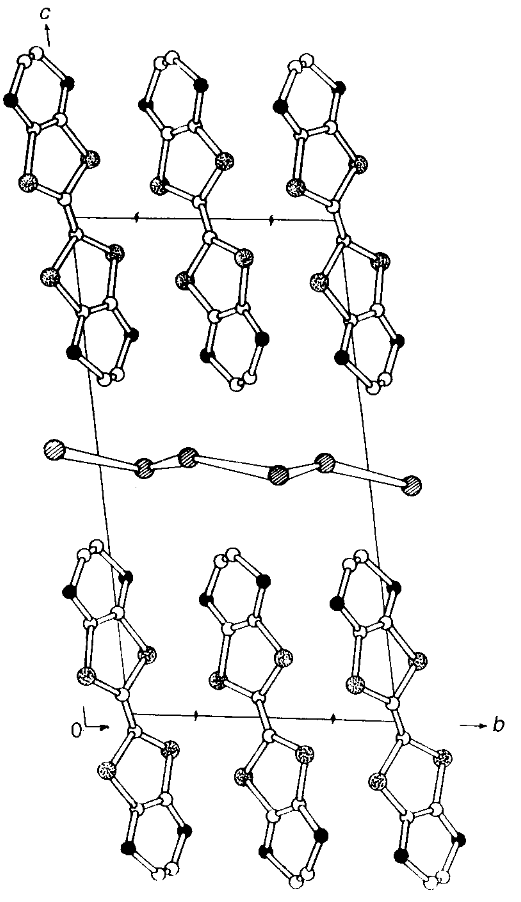

Fig. 2 $(\mathrm{BEDO{-}TTF})_2\mathrm{Cl}_{1.28}(\mathrm{H_3O})_{0.28}\cdot2.44\mathrm{H_2O}$ viewed along the *a*-axis

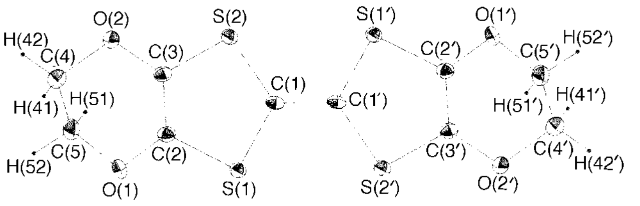

Fig. 3 Atomic labelling for the BEDO–TTF radical cation

As mentioned above, the main goal of our study is the establishment of the true composition of this ubiquitous BEDO–TTF chloride. A projection of the arrangement of the anion layer is shown in Fig. 5. By analogy with the works of Schweitzer *et al.*[1] and Mori *et al.*[2] we have assumed that the BEDO–TTF chloride single crystals contain water molecules.

Table 4 Short S···S ($r<4.0$ Å) and S···O ($r<3.5$ Å) distances and absolute values of the $\beta_{\mathrm{HOMO{-}HOMO}}$ interaction energies (eV) for the two different donor···donor interactions in the 160 and 293 K crystal structures of $(\mathrm{BEDO{-}TTF})_2\mathrm{Cl}_{1.28}(\mathrm{H_3O})_{0.28}\cdot2.44\mathrm{H_2O}$

interaction	S···S/Å	S···O/Å	$\beta_{\mathrm{HOMO{-}HOMO}}$
interstacks (160 K)	3.365, 3.576, 3.726	3.324	0.2975
(293 K)	3.428, 3.621, 3.767	3.375	0.2747
intrastack (160 K)	3.588 (×2)		0.2238
(293 K)	3.630 (×2)		0.2173

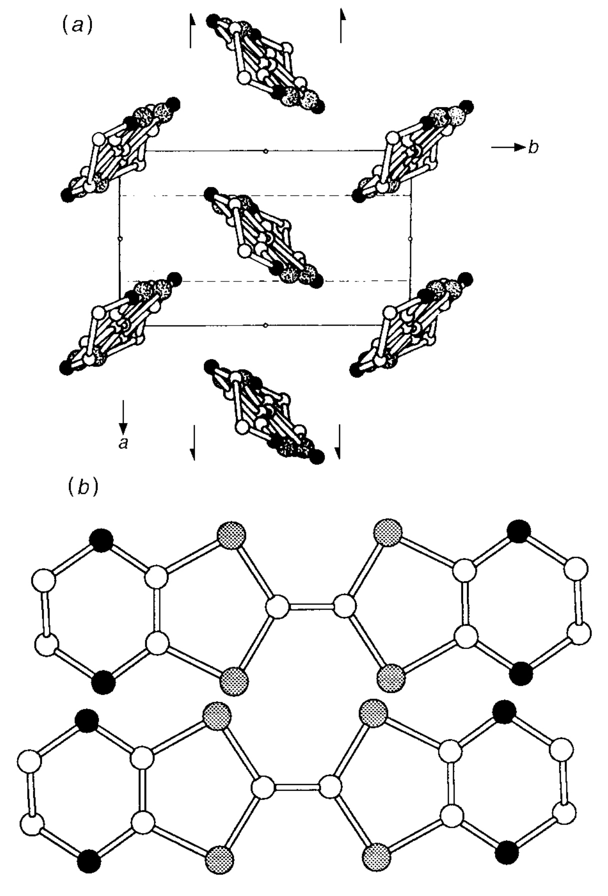

Fig. 4 (*a*) Projection of the radical cation layer along the *c*-axis; (*b*) overlap mode of the BEDO–TTF radical cations along the stack

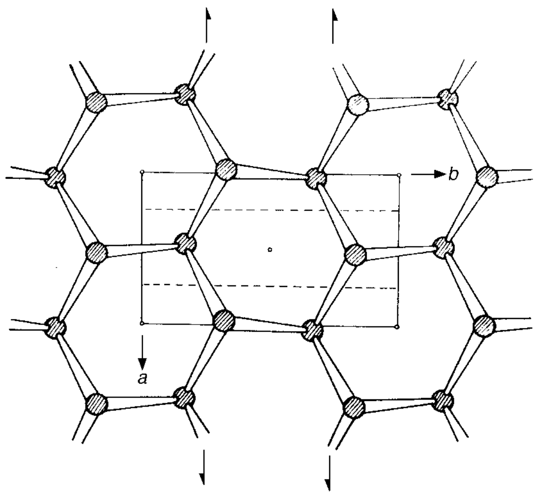

Fig. 5 The polymeric $[Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O]^-$ anion layer viewed down the *c*-axis

The unit cell of the crystal has four symmetrically equivalent positions for the (Cl, O) atoms. Consequently, we can represent its composition as $(BEDO\text{–}TTF)_2Cl_x\cdot(4-x)H_2O$. The refinement of the occupancy factors for the Cl and O atoms as well as their corresponding positions gave the same value for x at both temperatures ($x=1.28$). This value is close to that found by LRMA ($x=1.25$). Note that the hydrogen atoms of the water molecules have been unambiguously localized in difference Fourier maps. Thus, for the time being we can conclude that the composition of the BEDO–TTF chloride can be written as $(BEDO\text{–}TTF)_2Cl_{1.28}\cdot 2.72H_2O$.

At this point we must examine the electronic structure of the BEDO–TTF chloride. The calculated low temperature band structure near the Fermi level is shown in Fig. 6(*a*) (the band structure and Fermi surfaces for the room temperature structure are almost identical—except for a slightly smaller band dispersion—and are not reported here). Since there are two donor molecules per unit cell there are two HOMO bands (*i.e.* two bands mainly built from the highest occupied molecular orbital of the BEDO–TTF donor). The sticking together of the two bands is due to the non-symmorphic symmetry elements along the *a*- and *b*-directions. There are only two different types of BEDO–TTF···BEDO–TTF intermolecular interactions in the slab: those along the stacks and those between stacks. The absolute values of the $\beta_{\text{HOMO–HOMO}}$ interaction energies[19] for these intermolecular interactions as well as the associated short S···S and S···O distances are reported in Table 4. The interaction energies are a measure of the strength of the interaction between a pair of donor HOMOs in adjacent sites of the crystal and give important insight concerning the correlation between the crystal and electronic structures of molecular solids.[19]

As shown in Fig. 4(*b*) the intrastack donor···donor interaction is such that the p orbitals of the S atoms in the HOMOs are engaged in a very favorable σ-type overlap. On the basis of this and the fact that there are two relatively short S···S contacts, it is easy to understand the quite high value of the corresponding $\beta_{\text{HOMO–HOMO}}$ interaction energy. In contrast, because of the almost orthogonal arrangement of the two donors in the interstack interaction, the overlap between the S p orbitals in the HOMOs is much less favorable. A considerably smaller $\beta_{\text{HOMO–HOMO}}$ could be expected. However there is a very short S···S contact (3.365 Å at 160 K) associated with the interstack interaction. This very short contact overrides the effect of the less favorable geometric arrangement and leads, in fact, to a slightly larger interaction energy (at this point it should be noted that the relatively short S···O contact has only a minor contribution to the $\beta_{\text{HOMO–HOMO}}$ because the HOMO of BEDO–TTF has a very small contribution from the O p orbitals). Thus, the interaction between a BEDO–TTF and the six nearest neighbors in the slab is expected to be very isotropic at both room temperature and 160 K. Consequently, for any reasonable filling of the HOMO bands the Fermi surface should have an almost circular shape.

We have carried out a complete study of the Fermi surface of these slabs as a function of the electrons transferred per BEDO–TTF donor (ρ). As shown in Fig. 6(*b*)–(*d*) for $\rho=0.25$, 0.50 and 0.75, respectively, the Fermi surface is just a circle of increasing area, as expected. (Note: because of the degeneracy of the HOMO bands along the Brillouin zone boundary it is more convenient to represent the Fermi surface in an extended zone scheme.) With such a simple Fermi surface, the Shubnikov–de Haas frequency observed in the magnetoresistance measurements gives directly the number of holes in the HOMO bands and consequently, the average charge of the BEDO–TTF radical cations.

The Shubnikov–de Haas oscillations observed for our single crystals (data by S. I. Pesotski and R. B. Lyubovsky, practically identical to those reported by the same authors for single crystals prepared by a different method[9]) consist of a single fundamental frequency corresponding to a closed orbit associated with an area of 51% of the first Brillouin zone. Thus, within the limits of experimental accuracy, the upper HOMO band should be half-empty (or equivalently, the whole HOMO band should be a quarter-empty). Consequently, this result strongly suggests that the BEDO–TTF chloride should be a 2:1 radical cation salt as first suggested by Mori *et al.*[2] It is thus quite puzzling that our X-ray study seems to provide evidence against such a conclusion (*i.e.* according to the $(BEDO\text{–}TTF)_2Cl_{1.28}\cdot 2.72H_2O$ formula there should be a 64% empty upper HOMO band). However, the magnetoresistance and X-ray results can be easily reconciled if it is assumed that the extra negative charge (0.28) is compensated by the presence

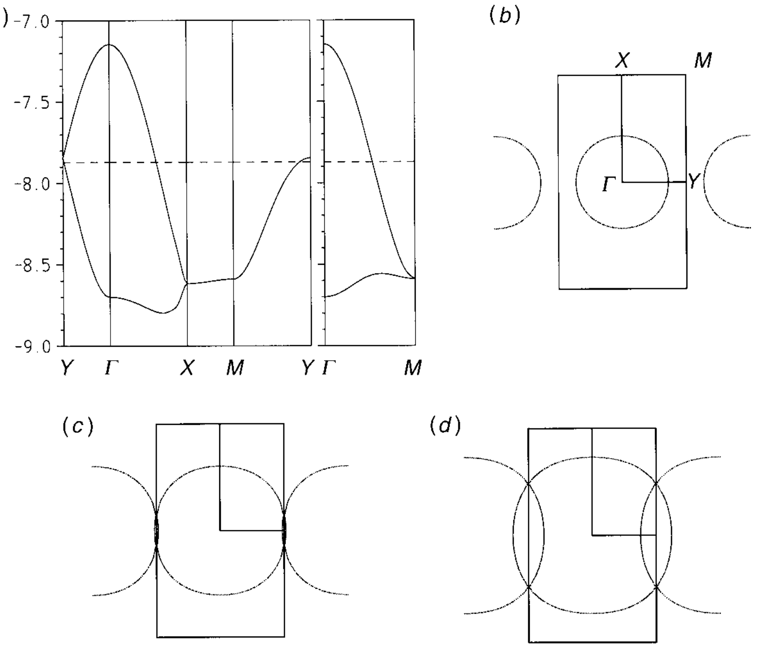

Fig. 6 Electronic structure of $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ calculated on the basis of its low temperature crystal structure. Dispersion relations (*a*) and Fermi surface for different values of the charge per BEDO–TTF donor (ρ): (*b*) +0.25, (*c*) +0.50 and (*d*) +0.75. The dashed line in (*a*) indicates the Fermi level for $\rho = 0.5$. Γ, *X*, *Y* and *M* are refer to the (0, 0), ($a^*/2$, 0), (0, $b^*/2$) and ($a^*/2$, $b^*/2$) wave vectors, respectively.

of H_3O^+ hydroxonium ions in the lattice. Such hydroxonium cations have been previously found in other radical cation salts like $(BT)_2Cl_2(H_5O_2)$ [BT = bis(butylenedithio)tetrathiafulvalene][20] and $(BEDT–TTF)_3Cl_{2.5}(H_5O_2)$.[21] The BEDO–TTF chloride would then have the composition $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$.

In order to test our suggestion we studied the IR spectra of the BEDO–TTF chloride single crystals and compared the results with those for the organic metal $(BEDO–TTF)_2ReO_4\cdot H_2O$ and BEDO–TTF itself. Fine structure of the IR spectra is observed in both absorption and reflection although it is more clearly seen in the absorption spectra (Fig. 7). The insert in Fig. 7 shows that the spectra of the $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ and $(BEDO–TTF)_2ReO_4\cdot H_2O$ salts differ from that of the BEDO–TTF single crystal in that they exhibit broad backgrounds. Intraband transitions of free carriers and, maybe, interband transitions, contribute to these backgrounds. Vibrational features are superimposed upon the electronic backgrounds. Some of them are modified molecular vibrations of the BEDO–TTF single crystal. Strong vibrational features around 3500 cm^{-1} are observed in the spectra of $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ and $(BEDO–TTF)_2ReO_4\cdot H_2O$ single crystals. We have subtracted the electronic backgrounds and presented these features in Fig. 7 for the spectral range 3000–4000 cm^{-1}.

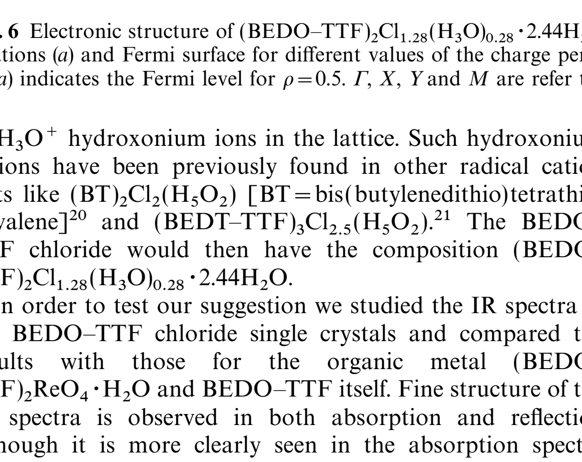

Fig. 7 Vibrational features of the O—H bonds in the absorption spectra of (*a*) $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ and (*b*) $(BEDO–TTF)_2ReO_4\cdot H_2O$ single crystals in the spectral range of the O—H vibrations. The insert shows the full spectra of the same crystals as well as of (*c*) BEDO–TTF single crystals in a wider spectral range ($T = 300$ K).

The features around 3500 cm^{-1} in the spectra of $(BEDO–TTF)_2ReO_4\cdot H_2O$ and $(BEDO–TTF)_2Cl_{1.28}\cdot(H_3O)_{0.28}\cdot 2.44H_2O$ correspond to the stretching vibrations of the OH groups in the H_2O molecules. The ratio of integrals in these spectra is approximately 3, which is in fair agreement with the H_2O content found in the X-ray structural determinations. The narrow lines at 3570 and 3690 cm^{-1} in the spectrum of $(BEDO–TTF)_2ReO_4.H_2O$ are due to the vibrations of the two nonequivalent OH groups of the water molecules in the room temperature crystal structure of this salt.[16] The strong and broad line in the spectral range 3320–3900 cm^{-1}—with a maximum at 3380 cm^{-1}—in the spectrum of $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ can also be ascribed to the stretching vibration of the H_2O molecules. It is important to point out the remarkable difference between the shape of this line and those observed in ordinary water and ice. The sharp low energy side of the line in the spectrum of $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ is indicative of the strong interaction of the H_2O molecules with the neighboring atoms in the crystal.

In the context of the present work, the more important feature of the IR spectra of $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ is the line at 3250 cm^{-1} which should be ascribed to the hydroxonium ion H_3O^+.[22] This result reconciles the magnetoresistance and X-ray studies and suggests that the $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ composition is a reasonable one. The very good coincidence in the transport properties of our single crystals with those of the different BEDO–TTF chlorides reported by Schweitzer *et al.*,[1] Mori *et al.*[2] and Lyubovskaya *et al.*,[9] suggests that despite the different synthetic routes all of the BEDO–TTF chlorides are the same $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28}\cdot 2.44H_2O$ salt.

Thus, the anionic part of the BEDO–TTF chloride (see Fig. 5) is a complex anion including the Cl^- anions, H_2O water molecules and the H_3O^+ cations. It is a polymeric corrugated network in which all positions are statistically occupied either by Cl or O atoms, Each position in this network is surrounded by three neighbors in a pyramidal arrangement with bond angles 108.2, 118.5 and 122.9° at 160 K and 111.2, 121.2 and 121.5° at room temperature. The height of the pyramid is 0.547 at 160 K and 0.421 Å at room temperature. The distances between two successive positions of this network along the zig-zag chains parallel to the *a*-axis (see Fig. 5) are 2.886(2) (160 K) and 2.920(7) Å (293 K) whereas those between zig-zag chains are 3.015(2) (160 K) and 2.976(7) Å (293 K). Such a corrugated hexagonal network seems to be quite able to accommodate H_3O^+ hydroxonium ions. The tendency of water molecules towards formation of polymeric networks in the solid state probably plays a major role in leading to the structure of this anionic network.[23] It is worth pointing out that polymeric networks containing infinite chains of Cl^- ions and H_2O molecules (or hydroxonium ions) have also been found in the crystal structure of the radical cation salts $(BEDT–TTF)_4Cl_2 \cdot 4H_2O$,[24,25] $(BEDT–TTF)_4Cl_2 \cdot 6H_2O$[26–28] and $(BEDT–TTF)_3Cl_{2.5}(H_5O_2)$.[21] In the well known organic metal $(BEDT–TTF)_3Cl_2 \cdot 2H_2O$[24,29,30] the Cl^- ions and H_2O molecules lead to a discrete complex anion. No structurally characterized BEDT–TTF or BEDO–TTF salts containing chloride ions alone are known.

Conclusion

A hydrated BEDO–TTF chloride was previously reported by several groups although the composition was never firmly established. The same BEDO–TTF chloride has been obtained through an alternative (unexpected) route. As a result of a combined study of the IR spectra, magnetoresistance and low temperature (160 K) crystal and electronic structures, we conclude that this salt can be adequately described as $(BEDO–TTF)_2Cl_{1.28}(H_3O)_{0.28} \cdot 2.44H_2O$. This salt is a two-dimensional organic metal stable down to 1.3 K, containing radical cation layers of the so-called Θ-type and a corrugated hexagonal network of Cl^- anions, water molecules and H_3O^+ hydroxonium cations. It is the second radical cation salt of BEDO–TTF with halogen ions, the first one, $(BEDO–TTF)_2(I_3)_{0.83}$,[31,32] exhibiting a radically different crystal structure. It is also worth noting that after completion of this work we have obtained BEDO–TTF chloride single crystals as long thin plates, with unit cell parameters $a=4.015(2)$, $b=5.344(1)$, $c=33.245(8)$ Å, $\gamma=98.38(1)°$, $V=705.7(5)$ Å^3 (space group $P2_1/b$). The structural study of this phase will be carried out as soon as appropriate single crystals can be found.

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