A Novel Conducting Charge-transfer Salt: (BEDT-TTF)$_3$Cl$_2$·2H$_2$O

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The bis(ethylenedithio) tetrathiafulvalene salt (BEDT-TTF)$_3$Cl$_2$·2H$_2$O (**1**) has been prepared and characterised by single crystal *X*-ray diffraction, four probe electrical conductivity, and e.s.r. measurements, showing a metallic 2D network of BEDT-TTF molecules, separated by complex anions consisting of units of 4 Cl$^-$ and 4 H$_2$O molecules (σ = 0.6 S cm^{-1} at 300 K) with a metal–insulator transition at 100 K; activated behaviour of the spin susceptibility in the metallic regime is tentatively ascribed to Peierls fluctuations, lowering $N(\varepsilon_F)$ with temperature.

In recent years, molecular solid-state chemistry has experienced rapid growth, through the discovery of molecular crystals that exhibit metallic conductivity and even become superconducting at low temperature.[1,2] Of particular interest are the organic superconductors (BEDT-TTF)$_2$X, where X = ReO$_4$, I$_3$, IBr$_2$, or AuI$_2$, which are salts of the donor molecules, bis(ethylenedithio) tetrathiafulvalene.[3—6] The family of BEDT-TTF salts has been shown to encompass a wide range of cation : anion ratios, and several crystal morphologies and structures, thus resulting in a variety of electrical and magnetic properties. As an extension of our research on conductive molecular crystals based on BEDT-TTF containing inorganic linear anions [*e.g.* AuX$_2$, X = Cl, Br, or I; M(CN)$_2$, M = Ag or Au and CuCl$_2$],[6,7] we have made crystals with organic anions, still retaining a linear geometry, (CF$_3$SO$_3$, MeSO$_3$ or *p*-MeC$_6$H$_4$SO$_3$).[8] In the course of electro-oxidation of BEDT-TTF in CH$_2$Cl$_2$ with dibenzyl dithiocarbamate [(C$_5$H$_5$CH$_2$)$_2$NCS$_2$]$^-$, (BEDT-TTF)$_3$Cl$_2$·2H$_2$O (**1**) was isolated.† Herein, we describe its synthesis, crystal structure, electrical, and magnetic properties. This salt is not only the first BEDT-TTF chloride‡ to be isolated but also the first to contain water.

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† Crystals were prepared by electrochemical oxidation of BEDT-TTF in CH$_2$Cl$_2$ with (C$_4$H$_9$)$_4$N[(C$_5$H$_5$CH$_2$)$_2$NCS$_2$] as electrolyte at a constant voltage of 1.4 V for a period of 10 days. A three compartment cell fitted with platinum electrodes was used. The presence of chlorine was confirmed by energy dispersive *X*-ray fluorescence measurements. Also, the failure to produce crystals in a non-chlorinated solvent, tetrahydrofuran (THF), and subsequent addition of CH$_2$Cl$_2$ to the THF solution to induce crystal growth, indicate that the crystals contain chloride ions.

‡ (BEDT-TTF)$_3$Br$_2$, triclinic, $P\bar{1}$, a = 9.606 (2), b = 16.194 (3), c = 7.743(1) Å, α = 95.00(1), β = 99.05 (2), γ = 84.92 (2)°, U = 1181.5 Å^3, and Z = 1, has been reported.[9a] (BEDT-TTF)$_3$Br$_2$·2H$_2$O has recently been grown, using (Bu$_4$N)Br as electrolyte, and only if the solvent is contaminated with water. It is metallic with a metal–insulator transition at *ca.* 150 K.[9b]

The crystal structure belongs to the triclinic system, with an asymmetric unit (Figure 1a) containing three independent cations, two chlorine atoms, and two water molecules.[§] The BEDT-TTF molecules are arranged in sheets in the *ab* plane separated by anions. The mean-planes of the cations are all parallel and are tilted by an angle of 63° to the *b*-axis and thus direct $S \cdots S$ interactions along the stacking axis *b* [*cf.* β″-(BEDT-TTF)$_2$AuBr$_2$][7a] are weak and are even weaker along axis *a*. The anion is present as a complex, hydrogen bonded unit of four chlorine atoms and four water molecules (increasing the effective anion size[10]), which fits in cavities formed by the ethylenic hydrogen atoms of the cations (Figure 1b).

The structure of (**1**) is different from most of the 3 : 2 salts of BEDT-TTF, except γ-(BEDT-TTF)$_3$(ReO$_4$)$_2$.[9a] The main structural difference is that the chloride salt has three crystallographically independent cations while the per-rhenate has only two. This difference results in a larger number of cation–cation interactions in the present case (Figure 1a). The only short interplanar distance is between molecules I and II (3.59 Å) and the others are greater than 3.67 Å. In general, there is no direct face-to-face overlap between the BEDT-TTF molecules, thus $p\pi$–$p\pi$ $S \cdots S$ interaction is weak. On the other hand, along [320], the BEDT-TTF molecules lie almost in one plane and there are some very short $S \cdots S$ contacts (3.33—3.46 Å) between peripheral sulphur atoms on adjacent BEDT-TTF molecules. Thus, the structure would suggest dominant one-dimensional interactions along this axis in contrast with the 2D nature of the superconducting β-phase (BEDT-TTF)$_2$X, X = I$_3$ or AuI$_2$.[4,7b]

The temperature dependence of the conductivity[||] of (**1**) is shown in Figure 2. The material is metallic ($\sigma = 0.6$ S cm^{-1} at 300 K) with a metal–insulator transition (T_{MI}) at 100 K and an activation energy of 0.04 eV. This behaviour is common in most 3 : 2 salts of BEDT-TTF, for example the T_{MI} is observed at 10 K for γ-ReO$_4$, 50 K for BrO$_4$, and 170 K for ClO$_4$, which has been ascribed to the Peierls instability with a $4k_F$ distortion (for a 2/3 filled band).[11]

X-band e.s.r. was performed on single crystals between 5 and 300 K. The spectra were characterised by a single asymmetric (Dysonian line shape) peak due to the conduction electrons ($g = 2.003$), the asymmetry being much more marked when the oscillating magnetic field is normal to the plane of the crystal (plate) than when parallel, indicative of anisotropic conductivity. By deconvolution of the spectrum at each temperature into its real (χ') and imaginary (χ'') contributions, we have obtained the relative skin depth and thus the microwave conductivity (Figure 2). There is good agreement with the results obtained by the 4-probe technique. The spin susceptibility, derived from the integrated intensity of the imaginary (χ'') part, is weakly temperature dependent, suggestive of Pauli paramagnetism between 200 and 300 K. Below 200 K, the change in χ_{spin} is much more pronounced. However, fitting the data to $\chi_{spin} = (C/T)\exp(-\Delta/2kT)$ for the temperature region 60—300 K, good correlation with a gap $\Delta = 0.03$ eV was obtained. This activated behaviour of the spin susceptibility in the metallic regime is tentatively ascribed to Peierls fluctuations, lowering $N(\varepsilon_F)$ with temperature.

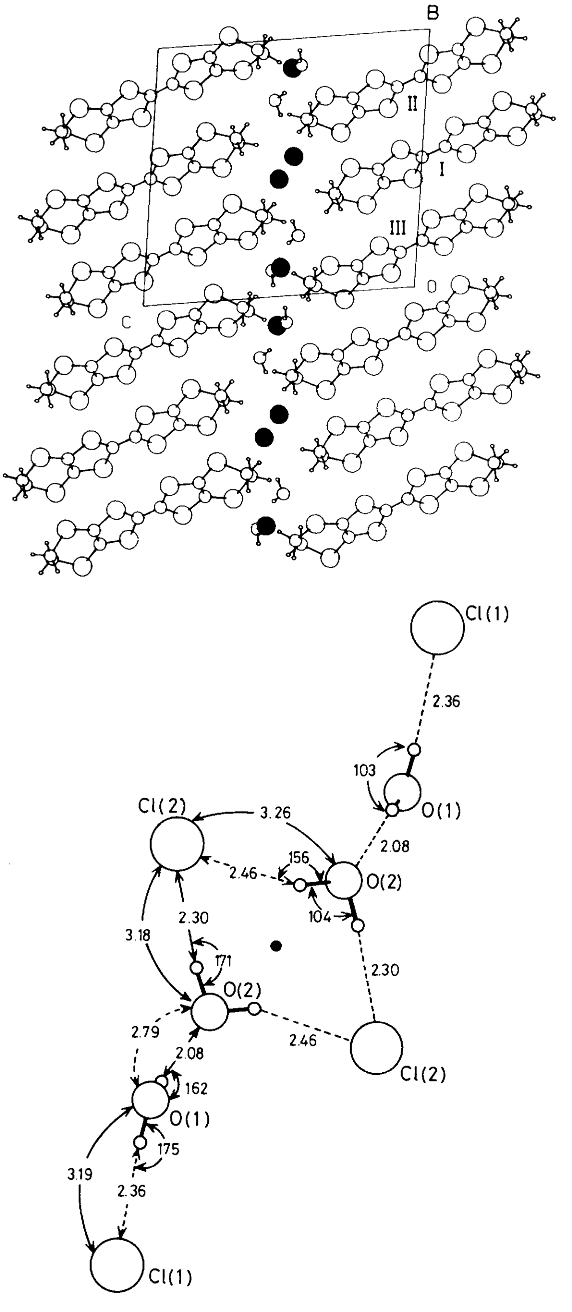

Figure 1. (a) View of the unit cell of (**1**) along the *a*-axis; (b) view of the complex anion in the *ab* plane.

In conclusion, although (**1**) was prepared by a reaction whose mechanism has still not been explained, it is a most unusual compound, both structurally and in its properties. The mode of cation stacking in (**1**) is uncommon for BEDT-TTF salts and the inclusion of H$_2$O in the lattice

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[§] *Crystal data* for (**1**): C$_{30}$H$_{28}$Cl$_2$O$_2$S$_{24}$, $M = 1261$, triclinic, space group $P\bar{1}$, $a = 11.214(2)$, $b = 13.894(2)$, $c = 15.924(2)$ Å, $\alpha = 94.74(1)$, $\beta = 109.27(1)$, $\gamma = 97.03(1)°$, $U = 2304.3$ Å^3, $D_c = 1.817$ gcm^{-3}, $Z = 2$, $F(000) = 1284$, λ(Cu-K_α) = 1.5418 Å, μ(Cu-K_α) = 116.5 cm^{-1}. 12 614 intensities were collected on an Enraf-Nonius CAD-4 diffractomer giving 9467 unique data, 6013 observed [$I > 3\sigma(I)$], which were corrected for Lorentz and polarisation effects and for absorption. Refinement by large block-diagonal matrix least-squares based on F led to $R = 0.045$ ($R_w = 0.06$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[||] Conductivity was measured by a 4-probe method using both A.C.(110 Hz) and D.C. techniques, applying a maximum current of 10 μA. Contacts were made with silver paint on evaporated gold pads (*ca.* 20 Ohms per pair). E.s.r. spectra were measured using a Varian reflection spectrometer and a continuous flow Oxford Instruments cryostat.

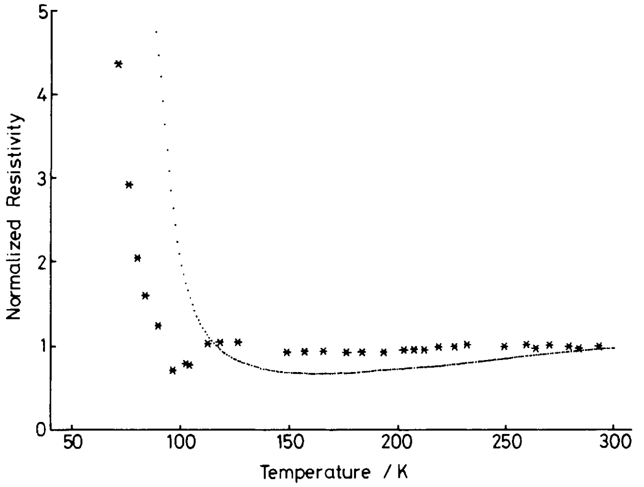

Figure 2. Temperature dependence of the resistivity determined by 4-probe technique (· · · ·) and as deduced from e.s.r. measurements (*****).

(apparently a prerequisite to crystal growth of BEDT-TTF with halides) is observed for the first time. There is close agreement between the conductivity measured by 4-probe technique and microwave (e.s.r.) methods in so far as the metal–insulator transition is observed at 100 K.

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