

NEW RADICAL SALTS OF BEDO-TTF: STRUCTURES AND ELECTRONIC PROPERTIES OF ORGANIC METALS AND SUPERCONDUCTORS

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ABSTRACT

Structural data as well as some measurements on the electronic properties of a few organic metals of the donor BEDO-TTF are reported.

INTRODUCTION

Since the highest values for the superconducting transition temperature T_c in organic superconductors are observed in radical salts of the donor BEDT-TTF (bisethylenedithiotetrathiafulvalene), it was expected after the synthesis of the new donor BEDO-TTF [1] (bisethylenedioxytetrathiafulvalene) – which is structurally strongly related to BEDT-TTF – that similar radical salts with superconducting properties can be obtained from this donor by electrochemical preparations. In fact, up to now a large number of organic metals was prepared with the donor BEDO-TTF, but only in two radical salts superconductivity was observed. RF-penetration depth measurements on crystals of $(\text{BEDO-TTF})_3 \cdot \text{Cu}_2(\text{NCS})_3$ [2] show the occurrence of superconductivity below 1K but resistivity measurements were not reported up to now. In $(\text{BEDO-TTF})_2\text{ReO}_4(\text{H}_2\text{O})$ the onset for superconductivity in resistivity was found at 2.5 K while the onset in the rf-penetration depth measurement was found only at 0.9K [3,4]. It was concluded that the broad superconducting transition in the second type of crystals might be due to structural disorder.

Usually the crystal quality of the BEDO-TTF salts is rather poor and in fact up to now only a few have been characterized structurally [2,5,6]. Even in the few cases in which the structures were solved, relative large R-values are given in the structural data, indicating disorder and bad crystal quality, in contrast to radical salts of the donor BEDT-TTF, which show normally a quite good crystal quality.

The electrocrystallisation of radical salts of the donor BEDO-TTF results – similar as in the case of BEDT-TTF – often in several structural different phases, depending on the conditions of the electrocrystallisation. In order to optimize the crystal quality we varied those conditions and obtained a number of known as well as a few new organic metals. Here we report structural data as well as electronic properties of a few BEDO-TTF radical salts.

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EXPERIMENTAL

BEDO-TTF was synthesised as described by Suzuki et al [1]. Single crystals of (BEDO-TTF)₂ Cu₂(NCS)₃ (**1**), (BEDO-TTF)₂ReO₄·(H₂O) (**2**) and a BEDO-TTF-chloride phase (**3**) were prepared using the crown ether route in the electrochemical preparation [7]. The crystal preparation was similar as described earlier for (BEDT-TTF)₂ Cu(NCS)₂ [8].

For the crystal structure determination black plate-like crystals (0.05 × 0.25 × 0.65 mm³ for **2** and 0.06 × 0.57 × 0.57 mm³ for **3**) were used. Lattice parameters were obtained from setting angles of 15 reflections ($4 < 2\theta < 21^\circ$) for **2** and 10 reflections ($9 < 2\theta < 21^\circ$) for **3** centered on a diffractometer (Syntex R3, Mo K α radiation). Data collection at room temperature by Ω scan ($3 < 2\theta < 58^\circ$) yielded 3112 observed independent reflections for **2** and 1533 observed independent reflections for **3** with $I > 2\sigma(I)$. The structures were solved by direct methods and Fourier synthesis. Calculations were performed with the SHELXTL program package [9].

The resistivity measurements were carried out by the usual four point method. On all measured crystals four gold contacts were deposited by evaporation techniques and gold wires with gold paint connected to these contacts.

The real part of the complex susceptibility was measured by using a standard low frequency (117 Hz) mutual inductance technique. The ac- magnetic field was about $5 \cdot 10^{-5}$ Tesla. The measurements were performed in an adiabatic demagnetization cryostat down to 30 mK.

RESULTS

Superconductivity in **1** was observed by rf-penetration depth measurements [2]. We have reproduced this result on crystals of **1**. Figure 1 shows the normalized susceptibility signal as a function of temperature. Due to the very small mass of the samples, the absolute value of χ is not exactly known. The half value of the transition is obtained at $T = 0.6$ K while the onset temperature is observed at 1.1 K (same as in ref. 2). Usually an onset in change in ac-susceptibility in organic superconductors is observed at about the temperature where zero resistivity is found. Therefore we have measured in addition the temperature dependence of the resistivity (fig. 2) down to 1.5 K but did not find an onset for superconductivity (see insert in fig. 1) at this temperature. Figure 3 shows the temperature dependence of the thermopower of crystals of **1**. The crystals of **1** were characterized by x-ray methods as well as by the ESR linewidth of the conduction electrons.

The crystal structure determination of (BEDO-TTF)₂ ReO₄(H₂O) (**2**) at room temperature gives a monoclinic cell P2 1/a, with $a = 12.16$ (1) Å, $b = 34.05$ (3) Å, $c = 8.091$ (4) Å, $\beta = 123.44$ (4)°, $V = 2795.5$ Å³, $d_c = 2.16$ g/cm³, $Z = 4$. Refinement of 280 variables converged with $R_w = 0.069$. Atomic coordinates are listed in table 1. Figure 4 shows a projection of the unit cell of crystals of **2**. Strong S-S and S-O contacts between the molecules are shown as well, indicating the typical two dimensional electronic character of the material. Hydrogen atoms are not drawn in the figure but the hydrogen bonds between the water molecules and the oxygens of the ReO₄⁻ anions are indicated. Since often for a fast characterisation of crystals of organic metals the ESR- linewidth is used, we have measured the angle dependence of the ESR- linewidth (see fig. 5) at room temperature. Superconductivity in crystals of **2** was reported recently [3,4].

For the x-ray investigation we selected plate-like crystals of the obtained BEDO-TTF-chloride phases (**3**). These have the following cell dimensions: Monoclinic cell P2 1/a, with $a = 8.593$ (6) Å, $b = 5.108$ (7) Å, $c = 16.27$ (1) Å, $\beta = 98.05$ (6)°, $V = 707.1$ Å³, $d_c = 1.75$ g/cm³, $Z = 2$. Refinement of 105 variables converged with $R_w = 0.043$. Atomic coordinates are listed in table 2. Beside the atomic positions for each BEDO-TTF molecule there are two additional crystallographic sites in the lattice. These are statistically occupied either by Cl⁻ anions solely (occupation factor 0.667) or by Cl⁻ anions and H₂O molecules (occupation factor 0.5 each).

Since the IR-spectrum indicates H_2O in the crystal system we conclude that the latter model is more appropriate. This would lead to a composition of $(BEDO-TTF)Cl(H_2O)$ (**3**) for this plate-like phase. Because of the statistic occupation of the two mentioned sites it cannot be distinguished between the positions of Cl^- and O (in H_2O) which are marked with $Cl1(a.....j)$ in fig. 6. Figure 6 shows as well the arrangement of the donor molecules in the unit cell of crystals of **3**. In fig. 7 the temperature dependence of the resistivity of crystals of **3** is presented.

TABLE 1

Atomic coordinates ($\times 10^4$) of crystals of $(BEDO-TTF)_2ReO_4(H_2O)$ (**2**).

Atom	x	y	z	Atom	x	y	z
S (1)	-640 (6)	-2745 (2)	230 (11)	S (8)	-552 (6)	-1796 (2)	5274 (11)
S (2)	1913 (6)	-2723 (2)	529 (11)	O (5)	1786 (15)	-3546 (4)	5433 (29)
S (3)	-712 (6)	-1812 (2)	262 (11)	O (6)	-689 (16)	-3523 (5)	5218 (28)
S (4)	1827 (6)	-1774 (2)	492 (11)	O (7)	2058 (15)	-1049 (5)	5532 (27)
O (1)	-526 (15)	-3527 (4)	297 (27)	O (8)	-369 (15)	-1016 (5)	5460 (30)
O (2)	1923 (16)	-3509 (4)	521 (31)	C (11)	1223 (25)	-3894 (7)	5823 (43)
O (3)	-798 (16)	-1031 (4)	235 (27)	C (12)	-294 (23)	-3876 (7)	4628 (43)
O (4)	1657 (16)	-995 (5)	378 (31)	C (13)	1137 (24)	-3206 (7)	5364 (40)
C (1)	-38 (28)	-3860 (6)	-195 (46)	C (14)	29 (26)	-3206 (6)	5378 (39)
C (2)	1508 (26)	-3854 (7)	1135 (42)	C (15)	628 (22)	-2477 (7)	5400 (35)
C (3)	87 (28)	-3187 (6)	369 (40)	C (16)	654 (24)	-2096 (7)	5368 (41)
C (4)	1247 (22)	-3179 (6)	456 (37)	C (17)	1336 (23)	-1370 (6)	5420 (38)
C (5)	630 (22)	-2456 (7)	398 (36)	C (18)	224 (28)	-1350 (7)	5453 (44)
C (6)	578 (22)	-2078 (6)	352 (37)	C (19)	1709 (25)	-717 (7)	6300 (43)
C (7)	-92 (24)	-1345 (6)	315 (39)	C (20)	214 (29)	-679 (7)	5080 (53)
C (8)	1046 (24)	-1334 (7)	351 (39)	O (10)	2192 (21)	238 (6)	5152 (38)
C (9)	-385 (24)	-690 (8)	-465 (45)	Re (1)	6007 (1)	-54 (1)	8333 (2)
C (10)	1079 (26)	-660 (8)	660 (45)	O (11)	6507 (24)	-141 (9)	6870 (38)
S (5)	1876 (6)	-2764 (2)	5476 (11)	O (12)	7151 (36)	-143 (12)	10681 (61)
S (6)	-647 (6)	-2743 (2)	5253 (11)	O (13)	5347 (28)	407 (7)	7795 (50)
S (7)	1964 (6)	-1832 (2)	5497 (11)	O (14)	4825 (23)	405 (5)	7522 (36)

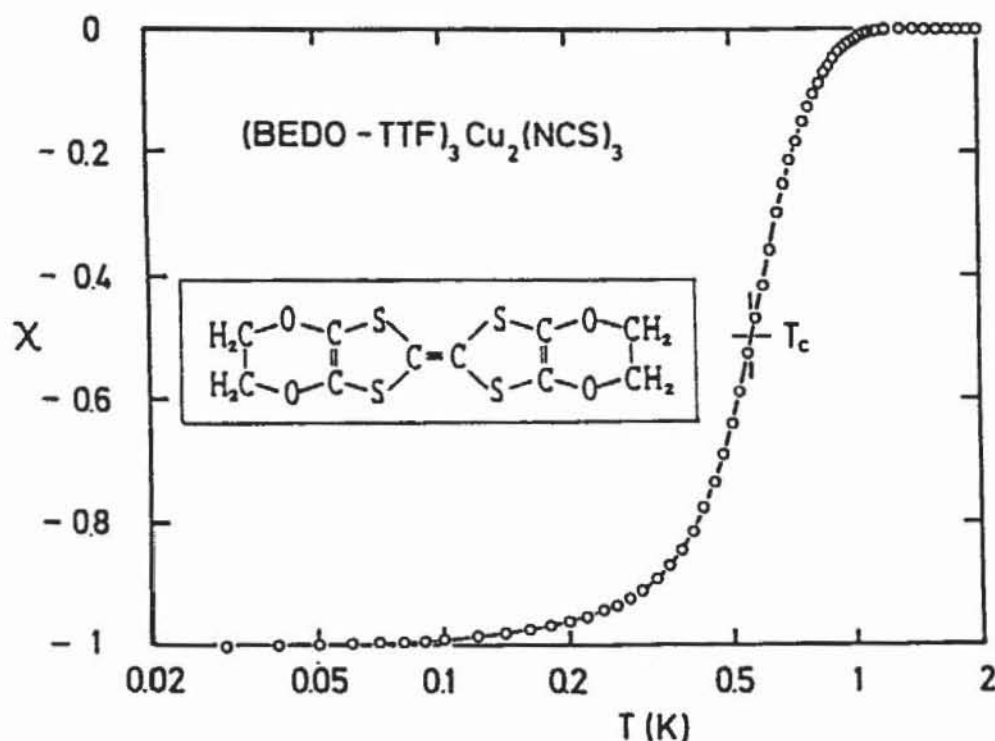
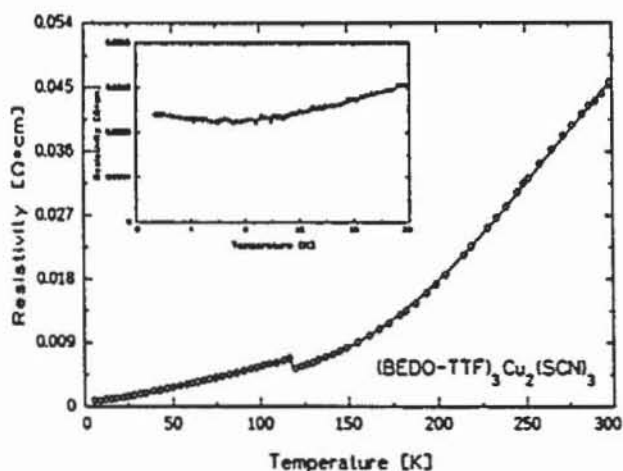
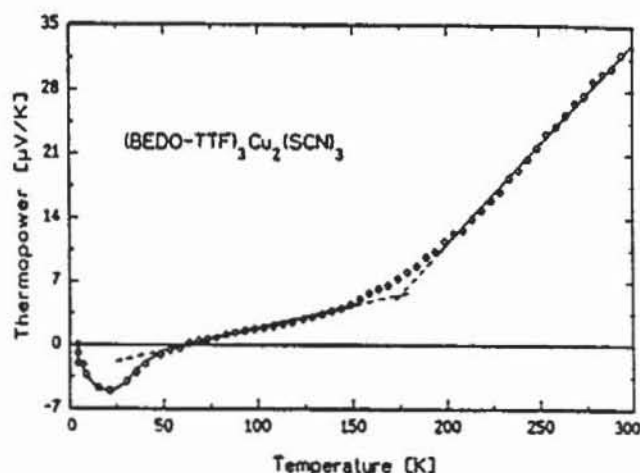


Fig. 1. Normalized susceptibility signal as a function of the temperature for crystals of $(BEDO-TTF)_3Cu_2(NCS)_3$ (**1**). The insert shows the molecule BEDO-TTF.

TABLE 2

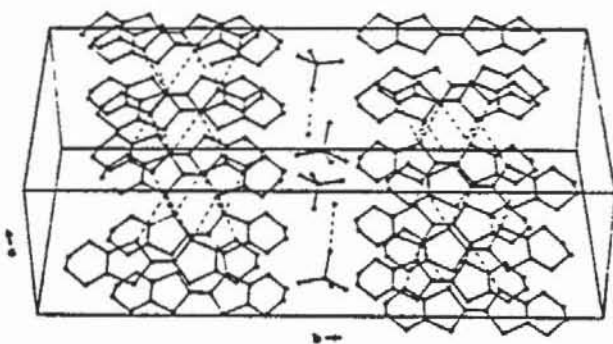
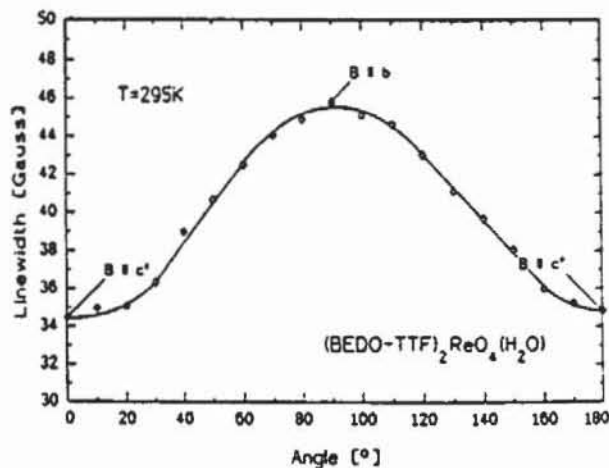
Atomic coordinates ($\times 10^4$) of crystals of (BEDO-TTF)Cl(H₂O) (3).

Atoms	x	y	z	Atom	x	y	z
S(1)	-1474 (1)	-2215 (2)	5740 (1)	C(2)	-1038 (4)	-1255 (7)	6780 (2)
S(2)	922 (1)	1945 (2)	6164 (1)	C(3)	27 (4)	614 (7)	6968 (2)
O(1)	-1816 (3)	-2528 (5)	7338 (1)	C(4)	-1006 (6)	-2081 (11)	8172 (2)
O(2)	-492 (3)	1579 (5)	7742 (1)	C(5)	-553 (6)	661 (10)	8311 (2)
C(1)	-120 (3)	-63 (6)	5403 (2)	Cl(1) [O(3)]	6683 (3)	-265 (5)	9863 (1)

Fig. 2. Temperature dependence of the resistivity of crystals of (BEDO-TTF)₃Cu₂(NCS)₃ (1)Fig. 3. Temperature dependence of the thermopower of crystals of 1.

DISCUSSION

In ref. 3 a broad superconducting transition in the crystals of (BEDO-TTF)₂ReO₄(H₂O) (2) was found with an onset for superconductivity at 2.5 K in resistivity and 0.9 K in the ac-susceptibility. Since the origin of this broad transition is still not totally clarified (under relative low pressure the transition sharpens drastically [4]) it was interesting to investigate the electronic

Fig. 4. Projection of the unit cell of crystals of (BEDO-TTF)₂ReO₄(H₂O) (2).Fig. 5. Angle dependence of the ESR-line-width in the bc*-plane for crystals of 2.

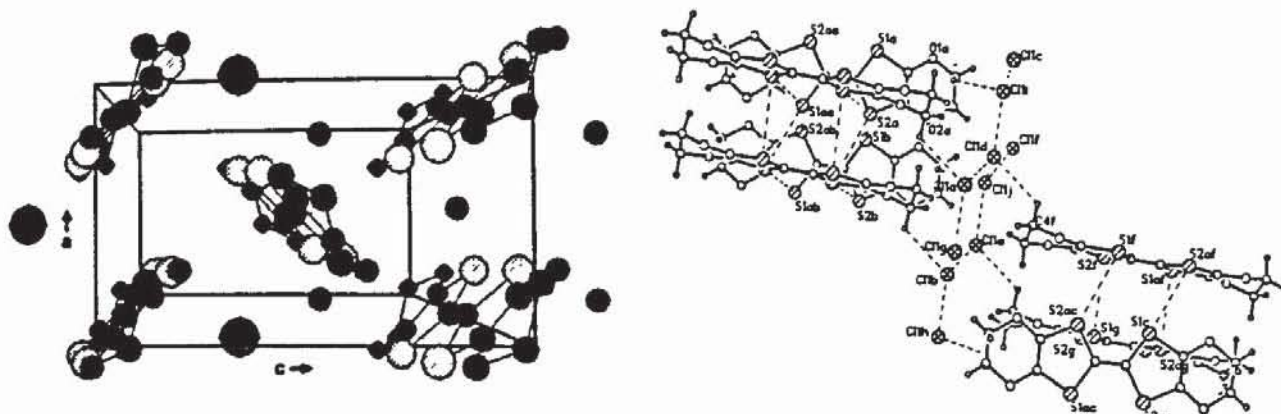


Fig. 6. Projection of the unit cell of single crystals of (BEDO-TTF)Cl(H₂O) (**3**) (see text).

properties of the other superconductor in the BEDO-TTF family, (BEDO-TTF)₃Cu₂(NCS)₃ (**1**), in more detail. From fig. 1 it can be seen that the superconducting transition observed in the rf-penetration depth signal is again rather broad. While the onset for superconductivity lies at around 1.1 K in the ac-susceptibility (fig. 1) the signal starts to saturate only at about 0.3 K. Usually in crystals of organic superconductors of the BEDT-TTF family the onset for superconductivity in the ac-susceptibility is observed at a temperature where the resistivity is already zero within the experimental facilities. Therefore it is surprising that in the temperature dependence of the resistivity down to 1.5 K no onset in superconductivity can be observed as can be seen from the insert in fig. 2. This indicates again that the superconducting transition is rather broad and that probably the resistivity is not zero at the temperature where the onset in the ac-susceptibility is observed. Such a behaviour was found as well in the crystals of **2** [3]. On the other hand the resistivity characteristic (fig. 2) demonstrates a clear metallic behaviour of the crystals of **1** and does not show an increase in resistivity in any temperature range as e.g. the crystals of **2** [3,4] but as well the crystals of (BEDT-TTF)₂Cu(NCS)₂. The jump in resistivity at around 120 K (fig. 2) is probably due to a crack in the crystal and not due to a phase transition. A broad phase transition seems to exist at around 180 K as can be seen from the change in the slope of the thermopower in fig. 3, while the nonlinear signal in the thermopower below 60 K might be due to a phase transition as well, or due to a phonon drag.

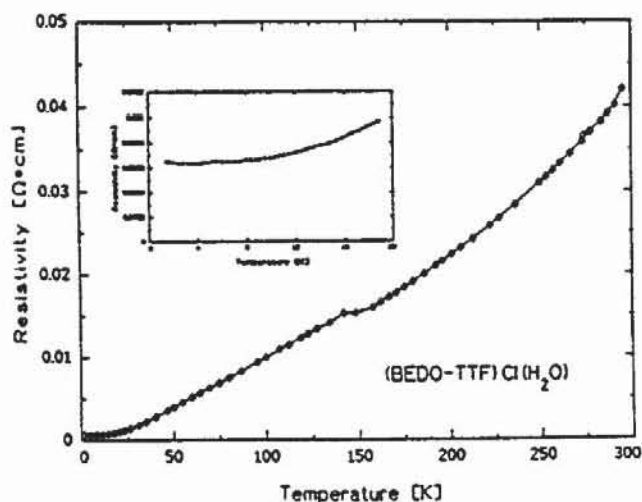


Fig. 7. Temperature dependence of the resistivity of crystals of **3**.

In ref. 3 only the unit cell parameter of the crystals of (BEDO-TTF)₂ReO₄(H₂O) (**2**) were presented. Therefore in table 1 the atomic coordinates of **2** are given and in fig. 4 a somewhat different view of the unit cell with respect to the one in ref. 3 is shown. In this view here the diversity of the two dimensional contacts can nicely be seen. The ESR - linewidth of the crystals of **2** is typically of the order of 40 Gauss and varies between 34 Gauss when the magnetic field is arranged parallel to the crystal needle axis (parallel c*), that means into the direction of the highest conductivity, and 46 Gauss when the magnetic field is parallel to the b-axis, the direction of the lowest conductivity. Further electronic properties under pressure as well as measurements of the magnetoresistance of crystals of **2** and IR- investigations are presented in references 10 and 11.

Crystals of **3** are organic metals down to low temperature as can be seen from the resistivity characteristic in fig. 7. In the low temperature resistivity data down to 1.5K (see insert) no onset to superconductivity is seen. Therefore a measurement of the temperature dependence of the ac- susceptibility down to 30mK was performed but did not show any sign of superconductivity as well. This might be due to the fact that the positions of the Cl⁻ - anions and the H₂O molecules are statistically occupied.

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