

RADICAL CATION SALTS OF AN UNSYMMETRICAL BEDT-TTF DERIVATIVE: DIMET**

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ABSTRACT

Crystal structures, temperature dependent conductivity measurements and thermopower data of several DIMET radical salts are presented and discussed.

INTRODUCTION

A surprising fact in the structures of the organic superconductors $(\text{TMTSF})_2\text{ClO}_4$ and $\beta\text{-(BEDT-TTF)}_2\text{X}$ ($\text{X} = \text{I}_3^-$, IBr_2^- and AuI_2^-) is that there exists a slight dimerisation of the donor molecules within the stacks of these radical cation salts. Therefore, the question arises whether a more pronounced dimerisation in organic radical salts of this type leads to stronger intra- and interstack interactions and to stronger couplings between the unpaired electrons. This might result in an increase of the transition temperature to superconductivity. A step in this direction is the preparation of "unsymmetrical" donors like DIMET, which was synthesized recently [1-4]. This new donor was electrocrystallized by us in different solvents using tetrabutylammonium salts of various anions [1,2] like ClO_4^- , ReO_4^- , NO_3^- , I_3^- , $(\text{AuI}_2)^-$, PF_6^- , AsF_6^- and SbF_6^- as electrolytes. With all these anions radical salts were obtained and in some cases even several crystallographic different phases. Nevertheless, in the electrocrystallization exists the problem that solvent molecules are easily incorporated into the radical salts. Due to this inclusion of the solvent molecules metal-insulator transitions occur often already at relatively high temperatures. In order to prevent

** DIMET = 4,5-Dimethyl-4',5'-ethylenedithiotetrathiafulvalene = $\text{C}_{10}\text{H}_{10}\text{S}_6$.

this incorporation of solvents crystals have to be prepared from solvents where the molecules - due to their size - can not be incorporated. Here we report investigations on some of the above mentioned DIMET radical salts and show an example of a salt without incorporated solvent molecules.

EXPERIMENTAL

The synthesis of the donor DIMET was described recently [1,2]. The donor was electrocrystallized in different solvents using tetrabutylammonium salts at various anions as electrolytes in an arrangement described earlier [5,6]. The electrical conductivity was measured by the standard four probe method (dc and ac at 4-10 Hz) in the temperature range between 4.2K and 300K. Gold leads were attached to the samples with silver or gold paint on previously evaporated gold pads, yielding contact resistencies of a few ohms. Thermopower measurements were performed in the temperature range between 20 - 300K. The X-ray investigations were done with a Syntex R 3 diffractometer with monochromated MoK_α radiation as described earlier [2,7].

RESULTS AND DISCUSSION

The electrocrystallization of DIMET in solvents like THF and CH_2Cl_2 results in an incorporation of solvent molecules into the radical salts. This can be seen for example from the structures of $(\text{DIMET})_2\text{ClO}_4 \cdot x\text{THF}$ (1) (fig. 1) and $\text{DIMET} \cdot \text{ReO}_4 \cdot x0.5\text{CH}_2\text{Cl}_2$ (2) (fig. 2).

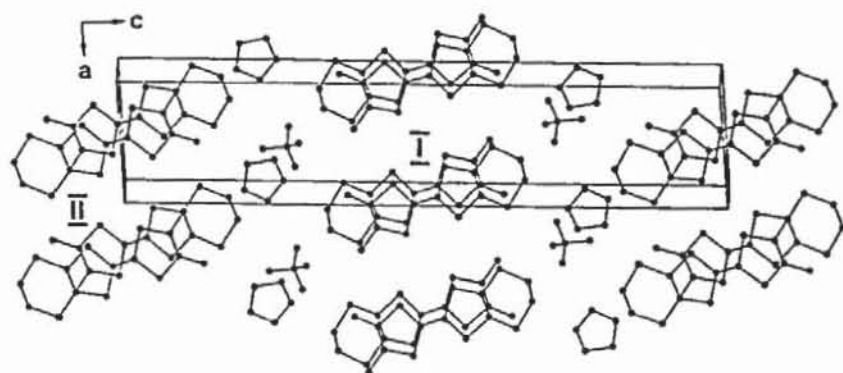


Fig. 1. Parallel projection of the crystal packing of 1 seen from a direction inclined at 10° to the b-axis.

The crystallographic data are: 1 = triclinic $\bar{P}1$, $a = 6.731(5)$, $b = 7.632(3)$, $c = 33.32(3)\text{\AA}$, $\alpha = 96.53(5)$, $\beta = 92.99(6)$, $\gamma = 103.13(5)^\circ$, $V = 1650.7\text{\AA}^3$, $Z = 2$; 2 = monoclinic $P2_1/n$, $a = 8.413(4)$, $b = 22.201(7)$, $c = 9.663(3)$, $\beta = 100.14(3)^\circ$, $V = 1776.6\text{\AA}^3$, $Z = 2$.

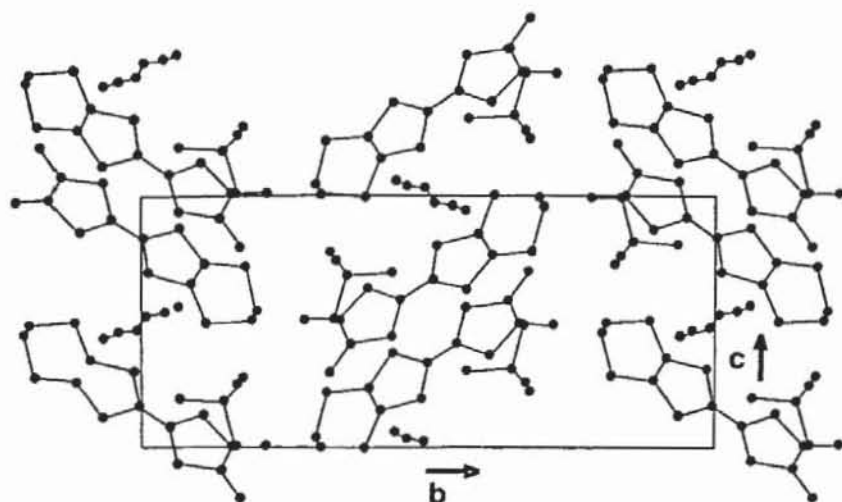


Fig. 2. Perspective projection of the crystal packing of 2 along a.

The typical room temperature conductivity of the needle-shaped crystals of 1 range around $100 (\Omega\text{cm})^{-1}$. By lowering the temperature from room temperature a weak increase (see fig. 3) in conductivity is observed until 220K, indicating a metallic behaviour.

The cube-like crystals of 2 are more or less insulators due to the dimeric arrangement of the DIMET molecules in the unit cell. The DIMET dimers are surrounded by the ReO_4^- anions and CH_2Cl_2 molecules.

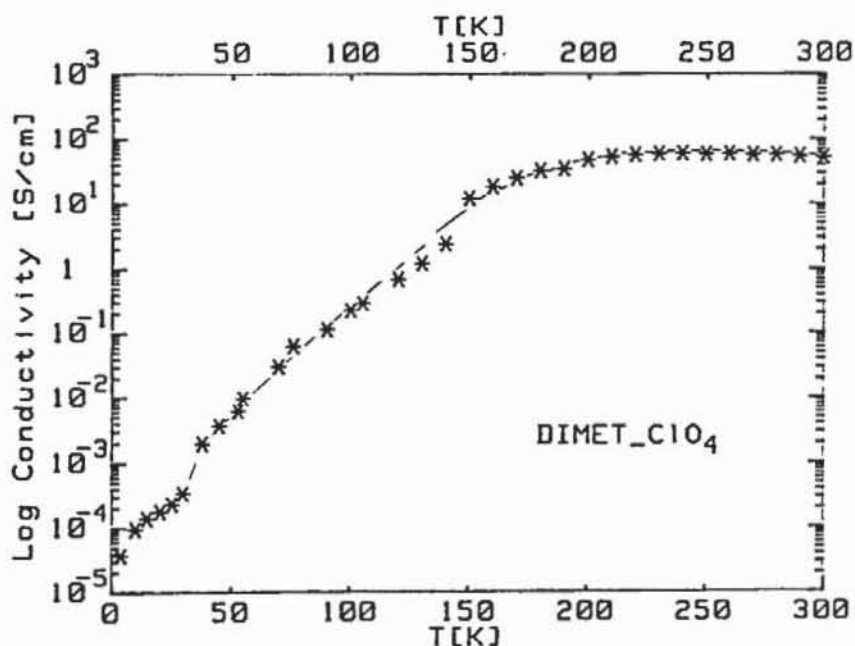


Fig. 3. Temperature dependence of the conductivity of 1 measured along the needle axis.

Nevertheless, from the solvent TMF one obtains another phase $(\text{DIMET})_x(\text{ReO}_4)_y(\text{THF})_z$ (3) which forms needles. These crystals have room temperature conductivities around $50 (\Omega\text{cm})^{-1}$ and show also a weak increase in conductivity by lowering the temperature (see fig. 4). The elucidation of the crystal structure is now under progress.

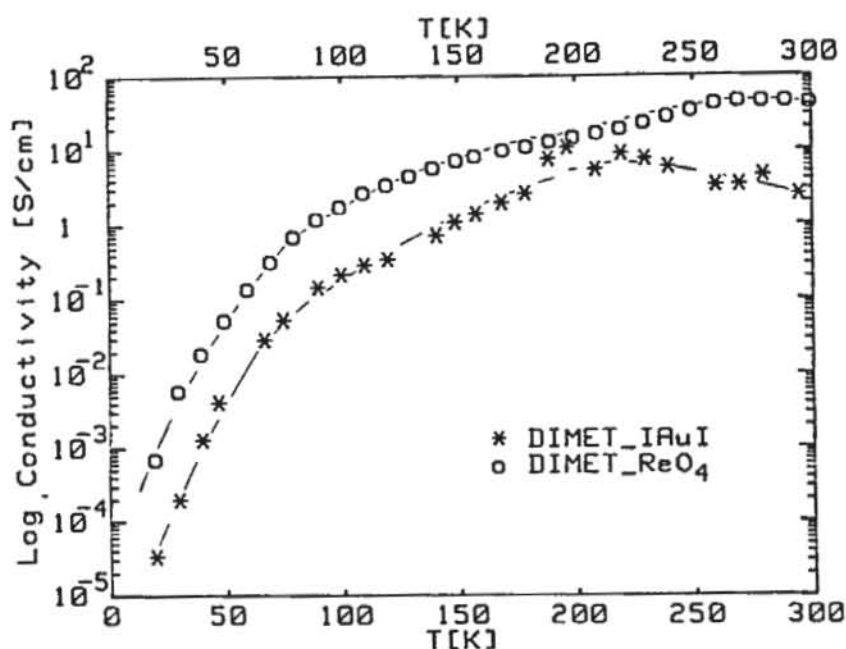


Fig. 4. Temperature dependence of the conductivity of 3 and 4.

A metallic-like conductivity behaviour is also observed in crystals of $(\text{DIMET})_x(\text{IAuI})_y(\text{THF})_z$ (fig. 4) and of $(\text{DIMET})_x(\text{NO}_3)_y \times (\text{THF})_z$ (5). This is confirmed by thermopower data (see fig. 5) which show in this temperature region a weak linear temperature dependence. The thermopower data of crystals of $(\text{DIMET})_x(\text{PF}_6)_y(\text{THF})_z$ (6) which are semiconducting at room temperature are added in fig. 5.

In order to prevent an incorporation of solvent molecules we prepared radical salts from trichlorethane. With ClO_4^- anions we obtained crystals of $(\text{DIMET})_2\text{ClO}_4$ (7) with a new type of structure for organic conductors. The crystals of 7 have the following data: triclinic P1, $a = 7.000(2)$, $b = 7.824(3)$, $c = 27.010(14)\text{\AA}$, $\alpha = 88.10(4)$, $\beta = 89.02(4)$, $\gamma = 74.58(3)^\circ$, $V = 1425\text{\AA}^3$ and $Z = 2$. As a very unusual feature in organic radical salts two donor species are arranged in crystallographically inequivalent stacks running parallel to a and b as can be seen from a projection along a in fig. 6. The stacks are arranged side by side perpendicular to the long molecular axes forming sheet-like arrangements. Due to

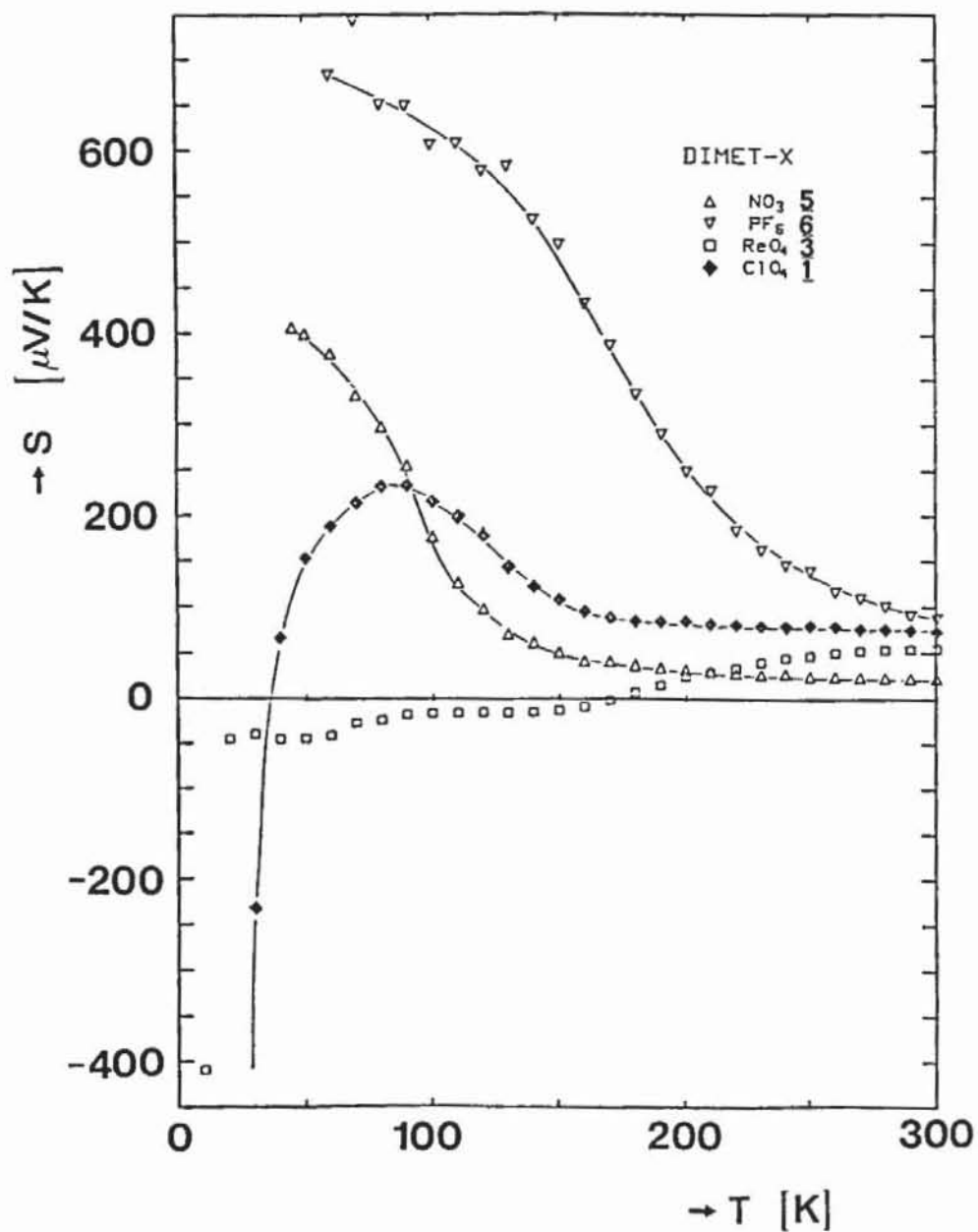


Fig. 5. Temperature dependence of the thermopower of crystals of 1, 3, 5 and 6.

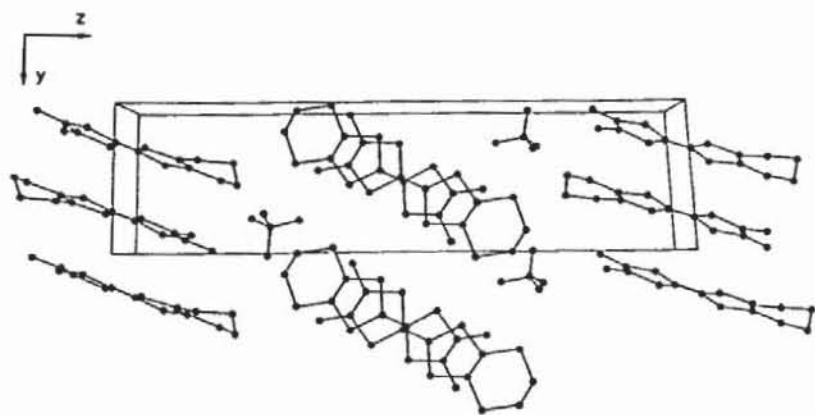


Fig. 6. Projection of the unit cell of $(\text{DIMET})_2\text{ClO}_4$ (7) along a.

the short interstack S...S contacts this leads to a more or less two-dimensional character within each sheet. Due to the nearly perpendicular arrangement of the sheets the crystals show a three-dimensional conducting behaviour. Further crystallographic and physical details [7] will be reported separately.

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