A BEDT-TTF Complex Including a Magnetic Anion, $(BEDT\text{-}TTF)_3(MnCl_4)_2$

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(Received July 30, 1987)

Synopsis. The title charge-transfer complex is prepared and its crystal structure is determined (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene). One third of the BEDT-TTF molecules is incorporated in the anion sheet, and holds about 2+ charge. The remaining donors form a conducting sheet with a similar arrangement to β'-$(BEDT\text{-}TTF)_2ICl_2$.

In the past few years, a considerable number of BEDT-TTF complexes have been prepared and their structural and physical properties have been investigated. It has been observed that some of these BEDT-TTF complexes exhibit superconductivity; actually these BEDT-TTF superconductors form a most important family of organic superconductors. On the other hand, though magnetic impurity had been believed to be very harmful to superconductivity, the discoveries of the ternary rhodium borides and the Chevrel series compounds including lanthanoids demonstrated the coexistence of superconductivity and long-range magnetic order.[1] The recent investigations of the high-temperature oxide superconductors show that the substitution of magnetic lanthanides is no more harmful to the Y-Ba-Cu-O series of superconductors.[2] Very little investigation has been, however, done concerning the interrelation of localized spins and conduction electrons in organic systems. Thus it is interesting to explore the BEDT-TTF complexes including magnetic anions. In the present paper, we report the preparation and the crystal structure of $(BEDT\text{-}TTF)_3(MnCl_4)_2$, where the anion has a localized spin on Mn^{2+}.

Experimental

Crystals were obtained by electrochemical crystallization of BEDT-TTF in benzonitrile. The electrolyte $(Me_4N)MnCl_3$ (TMMC), which is well-known as a linear-chain antiferromagnet,[3] was prepared by the reaction of $(Me_4N)Cl$ and $MnCl_4 \cdot 4H_2O$ in hot ethanol, and pale pink crystals were recrystallized from ethanol.

Crystal data: $C_{30}H_{24}S_{24}Mn_2Cl_8$, F.W. 1547.46, triclinic, space group $P1$, a=9.714(1), b=20.595(2), c=6.802(1) Å, α=89.70(1), β=101.66(1), γ=93.75(1)°, V=1329.8(3) Å^3, Z=1, and D_x=1.932 g cm^{-1}. Intensity data were measured by the θ-2θ scan technique on a Rigaku automated four-circle diffractometer with monochromatized Mo $K\alpha$ radiation. The structure was solved by the Patterson method and the succeeding Fourier syntheses and refined by the block-diagonal least-squares procedure to an R value of 0.033 by using 3479 independent reflections ($|F_o| > 3\sigma(|F_o|)$). Anisotropic thermal parameters were adopted for all non-hydrogen atoms, and the hydrogen atoms were refined isotropically.

Results and Discussion

For the electrolyte of electrochemical crystal growth of organic conductors, tetrabutylammonium salts are usually used because of their high solubilities in organic solvents. However, many tetrabutylammo-

Table 1. Atomic Parameters ($\times 10^4$) of $(BEDT\text{-}TTF)_3(MnCl_4)_2$

Atom	x	y	z	B_{eq}
Mn	6256(1)	3278(1)	−181(1)	2.9
Cl(1)	4077(1)	3071(1)	−2416(2)	3.9
Cl(2)	7970(1)	2488(1)	−51(2)	3.6
Cl(3)	5721(2)	3322(1)	3040(2)	4.3
Cl(4)	7383(1)	4274(1)	−849(2)	4.4
S(1)	219(1)	−911(1)	2180(2)	2.6
S(2)	2613(1)	194(1)	4083(2)	2.7
S(3)	999(1)	−747(1)	−1713(2)	2.7
S(4)	3410(1)	358(1)	197(2)	2.5
S(5)	−1929(1)	−1976(2)	946(2)	2.9
S(6)	4755(1)	1143(1)	6247(2)	3.7
S(7)	−958(1)	−1775(1)	−3767(2)	3.5
S(8)	5616(1)	1403(1)	1488(2)	3.1
SS(1)	13274(1)	4392(1)	3351(2)	3.5
SS(2)	13747(1)	4934(1)	7288(2)	3.9
SS(3)	10390(2)	3878(1)	3201(2)	5.3
SS(4)	10970(2)	4408(1)	8103(2)	4.7
C(1)	1277(4)	−497(2)	753(6)	2.5
C(2)	2310(4)	−31(2)	1598(6)	2.3
C(3)	−678(4)	−1432(2)	272(6)	2.3
C(4)	4011(4)	758(2)	3968(6)	2.4
C(5)	−305(4)	−1348(2)	−1548(6)	2.3
C(6)	4362(4)	847(2)	2151(6)	2.4
C(7)	−2073(7)	−2560(3)	−1058(8)	4.8
C(8)	5868(5)	1799(3)	5501(7)	3.3
C(9)	−2332(7)	−2300(3)	−3054(9)	5.1
C(10)	6674(5)	1607(2)	3942(7)	3.1
CC(1)	14350(5)	4842(2)	5146(7)	2.9
CC(2)	11900(5)	4276(2)	4580(7)	3.1
CC(3)	12146(5)	4519(2)	6485(7)	3.1
CC(4)	9400(7)	3640(4)	5090(11)	6.8
CC(5)	10191(6)	3626(3)	7146(10)	4.9

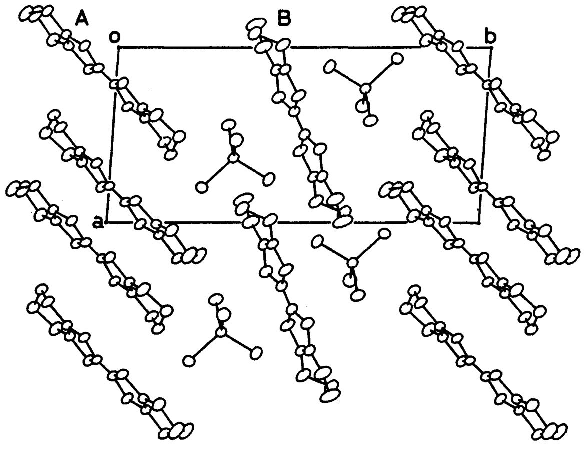

Fig. 1. Crystal structure of $(BEDT\text{-}TTF)_3(MnCl_4)_2$.

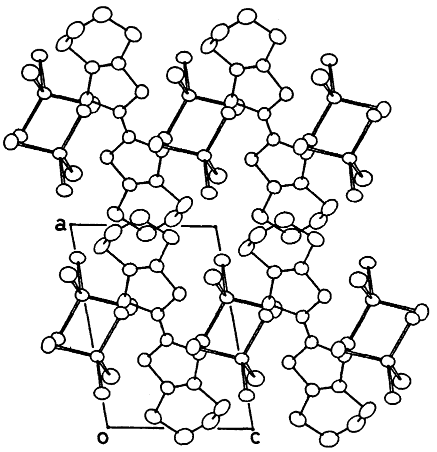

Fig. 2. Structure of the anion and the donors B sheet.

Table 2. Bond Lengths (Å) of the TTF Skeleton of BEDT-TTF, and the Average with the mmm Symmetry

	A	B	D$^+$
C(1)-C(2)	1.381(6)	1.431(7)	1.38(3)
C(1)-S(1)	1.733(5)	1.677(5)	
C(1)-S(3)	1.720(4)	1.693(5)	
C(2)-S(2)	1.717(4)		
C(2)-S(4)	1.728(5)		
Average	1.725	1.685	1.72(1)
S(1)-C(3)	1.741(4)	1.716(6)	
S(3)-C(5)	1.741(4)	1.713(5)	
S(2)-C(4)	1.743(4)		
S(4)-C(6)	1.741(4)		
Average	1.739	1.715	1.73(1)
C(3)-C(5)	1.365(6)	1.361(7)	
C(4)-C(6)	1.356(6)		
Average	1.361		1.37(2)

D$^+$: (BEDT-TTF)ReO$_4$(THF)$_{0.5}$.[6]

nium salts of halogeno transition metals tend to become oily liquid. Tetraethyl- and tetramethylammonium salts are prepared as solids and can be recrystallized easily,[3] while the solubilities of these salts in organic solvents are generally low. Benzonitrile, which shows moderately high polarizability, can fairly dissolve both BEDT-TTF and these ammonium salts. Then we used the combination of the tetramethylammonium salt and benzonitrile. Nitrobenzene is sometimes applicable for the same purpose.

The atomic coordinates are listed in Table 1.[5] The crystal structure is shown in Fig. 1. The anion consists of discrete tetrahedron, MnCl$_4^{2-}$. In a unit cell, 1.5 donor molecules are crystallographically independent. The donors A present on general positions form an ordinary conducting sheet parallel to the (010) plane. On the other hand, the molecules B on inversion centers are incorporated in the anion sheet. Figure 2 shows the structure of the anion and the donors B sheet.

In order to estimate the positive charge present on the donors, the bond lengths of the TTF skeleton are listed in Table 2. In comparison with the reported data,[6] the charge on the molecule A is estimated to be about 1+. Therefore, from the neutrality of the crystal, the molecule B must hold 2+ charge. This agrees with the change of the bond lengths; in the B molecule, the central C=C distance is anomalously long, and the C-S distances are very short. This systematic change originates in the symmetry of the highest occupied molecular orbital (HOMO), which has nodes on each C-S bond, and bonding nature concerning to every C=C bond. Because even in the 2+ molecule all bond distances change systematically so as to keep the mmm symmetry of the molecule, it can be concluded that in the energy band there is no overlap between the highest occupied band and the next highest band. This observation justifies the energy band calculation which is done by using the HOMO only.[7] The molecule like B, which holds 2+ charge and incorporated in the anion sheet, has also found in (BEDT-TTF)$_5$Hg$_3$Br$_{11}$.[8]

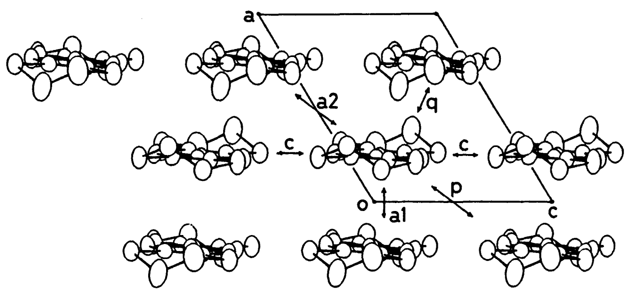

Fig. 3. Arrangement of the donors A in the conducting sheet.

Table 3. Overlap Integrals of the HOMO, the Parameter ϕ: the Angle between the Molecular Plane and the Interaction Direction, and D: the Slip Distance along the Molecular Long Axis[7]

Direction	Overlap/ ×10^{-3}	D/Å	ϕ/°
A a1	27.1	1.8	87
a2	14.0	4.0	36
c	6.1	1.8	5
p	4.9	0.0	24
q	−4.3	5.8	60
B a	−5.7	8.8	85
c	−1.0	2.0	15
a—c	−0.2	10.8	20

The arrangement of the donors A in the conducting sheet is depicted in Fig. 3. The modes of the intermolecular interactions are analyzed according to the method in Ref. 7 (Table 2). Though there are some overlap between the donors B, these molecules contribute very little to the electron transport, because there is no (or little) conduction electrons. The arrangement of the donors A has close resemblance to that of β'-(BEDT-TTF)$_2$ICl$_2$.[9,10] Along the a axis the 90° interaction (a1) and the 30° interaction (a2) are repeated alternatingly to form a one-dimensional conducting path where the intermolecular overlap integrals are considerably larger than the other interactions. Thus the resulting energy band structure is essentially the same as that of the β'-salt. A very important difference is the band occupancy: 3/4-filled for the β'-salt and 1/2-filled for the present salt. It is interesting that donor sheets with different electron filling exhibit the same structure.

The electrical resistivity is 0.04 Ωcm at room temperature and activated with an activation energy, 0.04 eV in the temperature range between room temperature and (at least down to) 60 K. Though the temperature dependence is semiconducting, it is surprising that the resistivity is lower than that of the β'-salts (>10 Ωcm), because the simple one-electron band model affords a metallic energy band for the β'-salts, and a semiconducting band for the present complex. The semiconducting resistivities of the β'-salts have been attributed to the electron correlation.^{9–11)} On the other hand, the comparatively low resistivity and the small activation energy of the present salts suggest that the semiconducting transport is not due to the intrinsic one-electron gap in the energy band but due to the electron correlation, where the charge distribution may be a little deviated from $A_2^+B^{2+}$ to result in a metallic one-electron energy band. Since the conduction mechanism of these salts seems to be dominated by the electron correlation, the simple one-electron picture is not helpful to estimate the magnitude of conductivity.

In a preliminary ESR work, there has been observed a rather wide signal whose peak-to-peak linewidth is as large as 360 G at room temperature.

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