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The New Semiconducting Magnetic Charge Transfer Salt (BEDT-TTF)$_4$ • H_2O • $Fe(C_2O_4)_3$ • $C_6H_5NO_2$: Crystal Structure and Physical Properties

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The New Semiconducting Magnetic Charge Transfer Salt (BEDT-TTF)$_4$ • H_2O • $Fe(C_2O_4)_3$ • $C_6H_5NO_2$: Crystal Structure and Physical Properties

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The structure, resistivity and ESR of a new molecular charge transfer salt β-(salt(BEDT-TTF)$_4$ • H_2O • $Fe(C_2O_4)_3$ • $C_6H_5NO_2$ (BEDT-TTF = bis (ethylenedithio)tetrathiofulvalene) are studied. The structure of the salt consists of successive layers of BEDT-TTF which are packed according to β-type and layers of approximately hexagonal geometry containing alternating H_2O and $Fe(C_2O_4)_3^{3-}$, with $C_6H_5NO_2$ lying within the hexagonal cavity. Its main crystallographic parameters are found to be: M = 1999.6(1), a = 10.31(8), b = 20.14(8), c = 35.34(4) Å, β = 92.21(9)°; V = 7342.0(5) Å^3, space group C_2/c; Z = 4. The conductivity of this salt at room temperature is 10 S cm^{-1} and shows semiconducting behaviour from 20 to 300 K. The ESR line width is found to be 38.1 (300 K), which is substantially wider than a typical line width for BEDT-TTF based radical cation salts of the β-type, indicating a two-dimensional character. The comparison of crystal structure and properties of the title compound with other salts of this family (BEDT-TTF)$_4$ • A • $Fe(C_2O_4)_3$ • $C_6H_5NO_2$, where A = H_2O, K^+ or NH_4^+, is also carried out.

Keywords: BEDT-TTF; organic conductors; charge transfer salt; crystal structure; physical properties

1. INTRODUCTION

Charge transfer salts of organic donor molecule bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF) have been of great interests for the last decades

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because of the wide range of physical properties which they exhibit [1 – 5]. In addition, one aspect of the potential flexibility of the structures in this class of compound that has received much attention recently is the incorporation of anions carrying a magnetic moment, although superconductivity and magnetism have long been considered inimical to one another [6, 7]. In 1992, Day *et al.* [8] reported one example, $[BEDT\text{-}TTF]_3CuCl_4 \bullet H_2O$, which remains metallic down to 400 mK without becoming superconducting. Until recently, Kurmoo *et al.* [9] and Zhu *et al.* [10] showed that β''-$(BEDT\text{-}TTF)_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5CN$ and $(BEDT\text{-}TTF)_2 \bullet K \bullet FeCN_5NO$ phases exhibit a sharp superconducting transition with a T_c of 7.0 K respectively, which is rather high for molecular based system.

It is well known that the incorporation of different shapes of anion and conditions of crystal growth can lead to a change in the packing of the BEDT-TTF molecules, which can result in marked variations in the physical properties. In superconductor β''-$(BEDT\text{-}TTF)_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5CN$, the solvent molecules are incorporated into the crystal. In this paper, we illustrate how small chemical modifications may result in drastic changes in the physical properties of molecular charge transfer salts. The crystal structure and physical properties of the compound β-$(BEDT\text{-}TTF)_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5NO_2$ obtained by substituting $C_6H_5NO_2$ for C_6H_5CN are reported.

2. EXPERIMENTAL

2.1. Preparation

BEDT-TTF was prepared by literature method [11] and recrystallized from C_6H_5Cl. $(NH_4)_3Fe(C_2O_4)_3$ was purchased from Beijing Chemical Agent Company and recrystallized from water. $C_6H_5NO_2$ was dried over CaH_2 and distilled prior to use. 18-crown-6 ether (from Across) was used as received. Electrocrystallization was carried out in a conventional two-compartment H-shaped cell by a porous frit, which minimize the influence of unwanted side reactions of reduced species generated at the cathode. The Pt (ϕ = 1 mm) electrodes were soaked in 1:1 HNO_3, rinsed in deionised water, then acetone, and dried at about at 110°C. The cells were cleaned by the same procedure.

Crystal growth was carried out under galvanostatic conditions in a constant temperature. Each cell contained 15 mg of BEDT-TTF and 120 mg $(NH_4)_3Fe(C_2O_4)_3 \bullet 3H_2O$ together with 200 mg 18-crown-6 ether in 40 ml of $C_6H_5NO_2$. Two weeks later, black needle-like crystals with metallic lustre can be obtained when the current was kept at 1 μA.

2.2. Structure Determination

Crystallographic parameters are: $C_{52}H_{39}FeNO_{15}S_{32}$; $M = 1999.61$; $a = 10.31(8), b = 20.14(8), c = 35.34(4)$ Å, $\beta = 92.21(9)°$; $V = 7342.0(5)$ Å^3, space group C2/c; $Z = 4$. $d_{calc} = 1.81$ g/cm^3; $F(000) = 3665.0$.

The X-ray data were collected on a Mac Science DIP 2000 (Mac Science Co. Ltd.) diffractometer with Mo-Kα radiation (Kα = 0.71073 Å). The size of the crystal used for measurement was $0.7 \times 0.2 \times 0.1$ mm^3. An area detector was applied. A total of 3511 reflections was collected of which 3427 reflections [$I > 2\sigma(I)$] were used for structure determination. The structure was solved by SIR 92 method [12] and refined by the full-matrix least-squares method by using the CrystanG software package. All atoms were refined isotropically. Final R and Rw values and the largest peak and hole in the final difference map were 0.0650, 0.0634 and 0.64, -0.68 e Å^{-3}, respectively. Figure 1 shows the view of molecular structure with number labeling. The final coordinates are tabulated in Table I.

2.3. Electrical Conductivity

Temperature dependent electrical conductivity of single crystals were carried out by using the standard d.c. four probe technich from 20 to 300 K along the long side of the crystals. The gold wires were connected to the crystals by gold paste. The wire diameter was 7 μm. The conductivity of the crystals in the highly conducting ab plane was 10 S cm^{-1} at room temperature. The

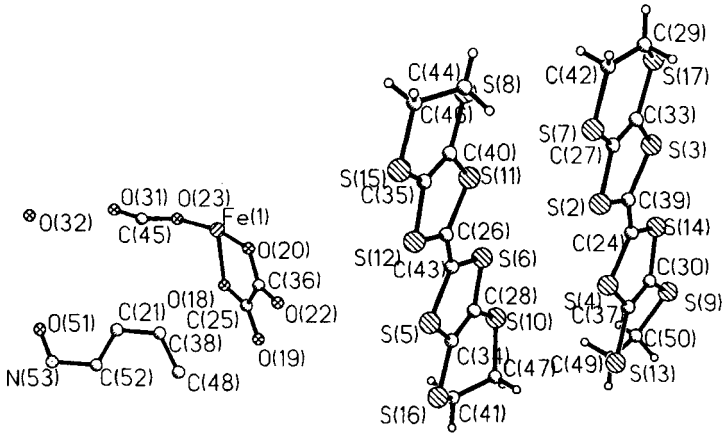

FIGURE 1 Molecular structure together with the labeling scheme.

TABLE 1 Fractional atomic coordinates and isotropic thermal parameters of non-hydrogen atoms for the complex

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*
Fe(1)	0.00000	0.42306(15)	0.25000	0.061
S(2)	0.2547(3)	1.0120(2)	0.5436(1)	0.064
S(3)	0.0246(3)	1.0887(2)	0.5194(1)	0.065
S(4)	0.3843(3)	1.0431(2)	0.4637(1)	0.065
S(5)	0.5778(3)	0.7856(2)	0.4919(1)	0.067
S(6)	0.3375(3)	0.8564(2)	0.4690(1)	0.064
S(7)	0.1657(4)	0.9837(2)	0.6207(1)	0.073
S(8)	0.0863(4)	0.8073(2)	0.6211(1)	0.073
S(9)	0.2526(4)	1.1578(2)	0.3655(1)	0.080
S(10)	0.4180(4)	0.8891(2)	0.3919(1)	0.071
S(11)	0.2184(3)	0.8254(2)	0.5494(1)	0.065
S(12)	0.4556(3)	0.7541(2)	0.5736(1)	0.065
S(13)	0.5267(4)	1.0723(2)	0.3941(1)	0.072
S(14)	0.1522(3)	1.1185(2)	0.4396(1)	0.066
S(15)	0.3753(4)	0.7264(2)	0.6508(1)	0.080
S(16)	0.7074(4)	0.8070(2)	0.4203(1)	0.074
S(17)	0.1113(4)	−1.0720(2)	0.5897(1)	0.087
O(18)	0.1507(9)	0.4401(5)	0.2161(3)	0.067
O(19)	0.3221(10)	0.5071(5)	0.2119(3)	0.086
O(20)	0.1050(9)	0.4848(4)	0.2839(3)	0.063
C(21)	0.3984(18)	0.2814(10)	0.2677(6)	0.096
O(22)	0.2896(10)	0.5426(5)	0.2872(3)	0.077
O(23)	−0.0738(9)	0.3460(5)	0.2192(3)	0.073
C(24)	0.2306(12)	1.0727(7)	0.4754(4)	0.054
C(25)	0.2320(17)	0.4836(9)	0.2287(5)	0.067
C(26)	0.3754(12)	0.7980(7)	0.5380(4)	0.058
C(27)	0.1311(13)	1.0207(7)	0.5761(4)	0.057
C(28)	0.4588(13)	0.8517(7)	0.4359(4)	0.058
C(29)	−0.0634(18)	1.0472(10)	0.6366(5)	0.095
C(30)	0.2837(13)	1.1179(7)	0.4089(4)	0.060
O(31)	−0.0881(11)	0.2358(6)	0.2193(3)	0.091
O(32)	0.0000	0.1030(8)	0.2500	0.099
C(33)	0.0284(13)	1.0549(7)	0.5650(4)	0.057
C(34)	0.5664(14)	0.8201(7)	0.4466(4)	0.063
C(35)	0.3299(13)	0.7606(7)	0.6062(4)	0.058
C(36)	0.2116(16)	0.5065(8)	0.2694(5)	0.069
C(37)	0.3875(14)	1.0835(7)	0.4205(4)	0.064
C(38)	0.3979(17)	0.3522(11)	0.2686(7)	0.091
C(39)	0.1805(12)	1.0598(7)	0.5088(4)	0.057
C(40)	0.2257(13)	0.7932(7)	0.5950(4)	0.055
C(41)	0.6510(14)	0.8314(8)	0.3734(5)	0.072
C(42)	0.0190(19)	0.9973(13)	0.6427(6)	0.105
C(43)	0.4226(13)	0.8106(6)	0.5038(4)	0.057
C(44)	0.1584(16)	0.8036(9)	0.6679(5)	0.089
C(45)	−0.0446(17)	0.2887(10)	0.2329(5)	0.080
C(46)	0.2269(16)	0.7390(10)	0.6764(5)	0.089
C(47)	0.5745(14)	0.8941(8)	0.3715(4)	0.067
C(48)	0.5000	0.3860(15)	0.2500	0.097
C(49)	0.0455(2)	1.075(1)	0.349(1)	0.109
C(50)	0.3616(19)	1.1157(12)	0.3348(6)	0.093
O(51)	0.3934(17)	0.1493(8)	0.2485(5)	0.109
C(52)	0.5000	0.2503(13)	0.2500	0.088
N(53)	0.5000	0.1733(13)	0.2500	0.097

anistropic conductivity was not measured due to the small size of the crystals.

2.4. ESR Measurement

The ESR spectrum was recorded on a Bruker ESP-300 spectrometer at room temperature.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure

Relative bond lengths and angles are shown in Table II. The asymmetric unit consists of two independent BEDT-TTF molecules, and half of $H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5NO_2$. The structure consists of alternating layers containing only BEDT-TTF and only $H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5NO_2$, as is customary in these charge transfer salts [13].

When projected on to the mean plane of the H_2O and Fe, the arrangement of the anion layer is rather similar to that in β''-(BEDT-

TABLE II Selected bond lengths and angles for the complex

Fe(1) —O(18)	2.029(10)	S(5) —C(43)	1.746(14)
S(5) —C(34)	1.746(16)	S(6) —C(43)	1.745(15)
S(6) —C(28)	1.749(15)	S(10) —C(28)	1.766(16)
S(10) —C(47)	1.796(15)	C(21) —C(52)	1.39(3)
S(16) —C(34)	1.775(15)	S(16) —C(41)	1.806(17)
O(18) —C(25)	1.28(2)	O(19) —C(25)	1.22(3)
C(26) —C(43)	1.35(3)	C(21) —C(38)	1.43(3)
C(28) —C(34)	1.32(2)	C(25) —C(36)	1.54(3)
C(41) —C(47)	1.49(3)	C(38) —C(48)	1.43(3)
C(52) —N(53)	1.47(4)	O(51) —N(53)	1.24(3)
O(18) —Fe(1) —O(20)	87.2(4)	C(28) —S(6) —C(43)	95.1(7)
O(20) —Fe(1) —O(23)	88.4(4)	C(28) —S(10) —C(47)	100.9(7)
C(34) —S(5) —C(43)	94.3(7)	C(34) —S(16) —C(41)	101.4(8)
C(38) —C(21) —C(52)	117.6(19)	Fe(1) —O(20) —C(36)	114.6(10)
O(19) —C(25) —C(36)	118.3(15)	Fe(1) —O(18) —C(25)	114.6(10)
S(6) —C(28) —C(34)	116.8(12)	O(18) —C(25) —C(36)	114.9(15)
S(5) —C(34) —C(16)	113.1(8)	S(12) —C(26) —C(43)	125.0(11)
S(16) —C(34) —C(28)	128.3(13)	S(6) —C(28) —S(10)	114.5(8)
O(22) —C(36) —C(25)	122.8(15)	S(10) —C(28) —C(34)	128.7(12)
S(5) —C(34) —C(28)	118.6(12)	O(20) —C(36) —C(25)	114.5(14)
C(21) —C(38) —C(48)	117.5(20)	S(5) —C(43) —C(26)	121.9(11)
S(10) —C(47) —C(41)	114.7(11)	C(21) —C(52) —N(53)	116.8(13)
S(16) —(41) —C(47)	115.0(12)	S(5) —C(43) —S(6)	115.2(9)
S(6) —C(43) —C(26)	122.9(11)	O(51) —N(53) —C(52)	117.2(14)

TTF)$_4$ • A • Fe$(C_2O_4)_3$ • C_6H_5CN, where $A = H_2O$, K^+ or NH_4^+. There is a clear honeycomb arrangement in the anion layer, with alternate H_2O and Fe forming an approximately hexagonal network (Fig. 2). The Fe are octahedrally coordinated by three bidentate oxalate ions, giving rise to a trigonal component of the crystal field. The mean Fe—O bond lengths (2.029 Å) is a bit longer than that found in β''-(BEDT-TTF)$_4$ • A • Fe$(C_2O_4)_3$ • C_6H_5CN [9]. The O atoms of the oxalate which are not coordinated to Fe form cavities occupied by H_2O. The mean plane of the nitrobenzene coincides with the hexagonal shape cavities formed by H_2O and Fe, therefore we can also doubt that it performs an important "templating" role in stabilizing the lattice as found in (BEDT-TTF)$_4$ • K • Fe$(C_2O_4)_3$ • C_6H_5CN [7]. In addition, in the title compound the included nitrobenzene are fully ordered, with the $-NO_2$ groups oriented toward Fe, so the hexagonal network of Fe and H_2O elongated along one axis. The volume is increased from 7157 Å^3 for β''-(BEDT-TTF)$_4$ • H_2O • Fe$(C_2O_4)_3$ • C_6H_5CN to 7342 Å^3 for the title compound due to the substitution of $C_6H_5NO_2$ for C_6H_5CN. It appears that in the

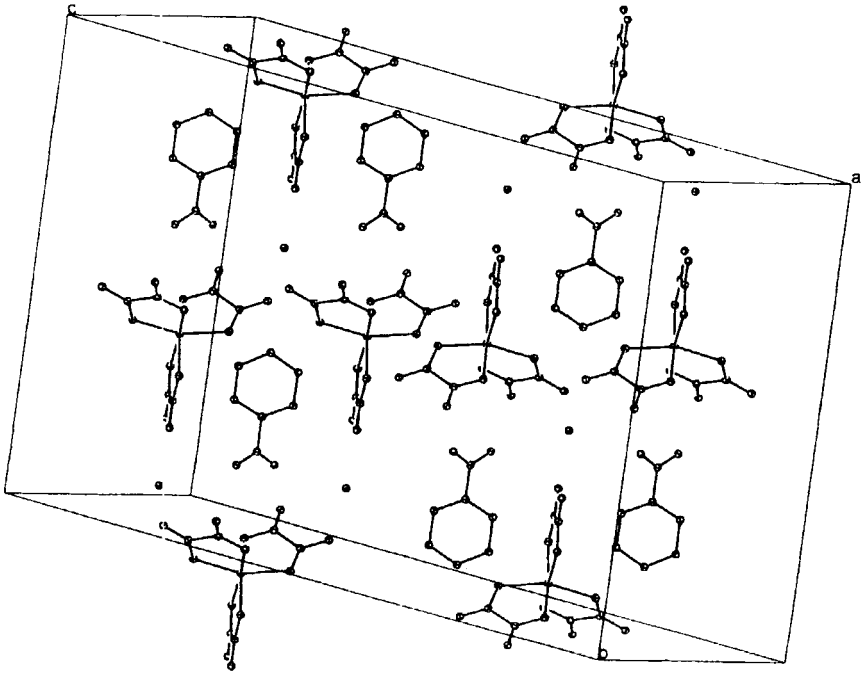

FIGURE 2 The anion and solvent layer in the complex.

$C_6H_5NO_2$ salt the lattice is loosely packed probably as a result of the volume of $C_6H_5NO_2$ is a bit larger than that of C_6H_5CN which results in the enlargement of the hexagonal cavities. The difference of $\sim 185\,Å^3$ is equivalent to an extra 8–9 atoms.

In the BEDT-TTF layer, stacks are formed with S···S contacts shorter than the sum of van der Waals radii (3.70 Å) between them (Fig. 3 and Tab. III). Overall the packing closely resembles that of the β-structure (Fig. 4) found in $(BEDT\text{-}TTF)_2X$ [14]. Finally, the planes of BEDT-TTF molecules in adjacent layers are twisted with respect to one another, an unusual feature in BEDT-TTF salts, the only other two examples known being one phase of

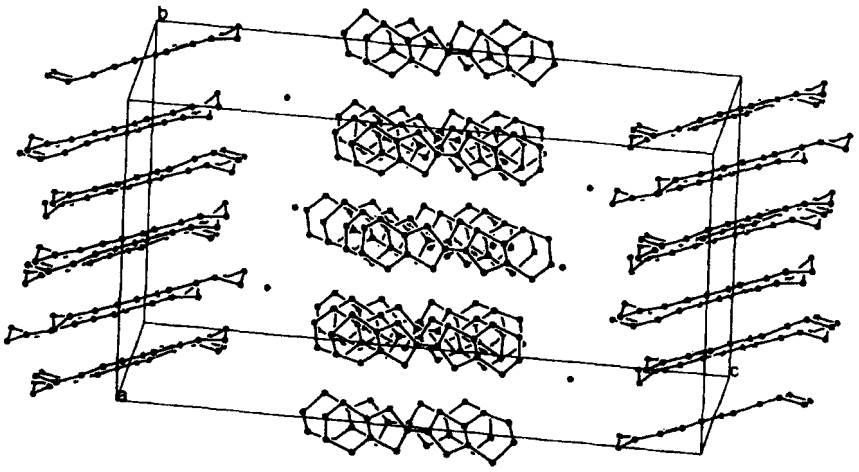

FIGURE 3 The layers of BEDT-TTF in the complex.

TABLE III Intermolecular S···S distances shorter than van der Waals radii

Atom (1)	*Atom* (2)	*dist*	*e.s.d.*	*ns*	*np*	*Ta*	*Tb*	*Tc*	*x*(2)	*y*(2)	*z*(2)
S(2)	–S(13)	3.5258	0.0057	1*	1	1	2	1	0.47334	0.92772	0.60588
S(6)	–S(17)	3.3859	0.0059	1*	1	0	2	1	0.11126	0.92798	0.41029
S(7)	–S(13)	3.4276	0.0054	1*	1	1	2	1	0.47334	0.92772	0.60588
S(8)	–S(9)	3.6154	0.0059	1*	1	0	2	1	–0.25256	0.84218	0.63453
S(8)	–S(14)	3.5338	0.0058	1*	1	0	2	1	–0.15224	0.88154	0.56042
S(9)	–S(16)	3.6160	0.0062	1	2	–1	0	0	0.20741	1.30697	0.42032
S(10)	–S(17)	3.3484	0.0057	1*	1	0	2	1	0.11126	0.92798	0.41029
S(12)	–S(13)	3.6813	0.0056	1*	1	1	2	1	0.47334	0.92772	0.60588
S(12)	–S(16)	3.6873	0.0054	1*	2	1	1	1	0.79259	0.69303	0.57968

ns is the symmetry operator number – (* denotes inversion indicator).
np is the lattice point number.
Ta, Tb & Tc are unit cell translations.

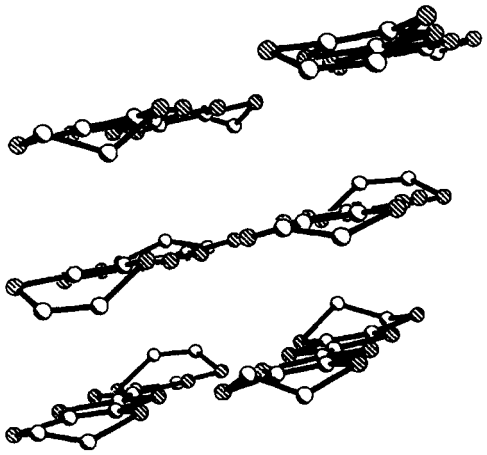

FIGURE 4 Stacking mode of BEDT-TTF molecules (β-type).

$(BEDT\text{-}TTF)_2Ag(CN)_2$ [15] and β''-$(BEDT\text{-}TTF)_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5CN$ [9].

3.2. Conductivity Measurements

At room temperature the conductivity of the title compound is $10\,S\,cm^{-1}$. Figure 5 shows the temperature dependence of the resistance of in the long side of the crystals for a typical sample. One can see that the resistance monotonically increases by a factor of 2.5 from room temperature down to 20 K. Although it shows a semiconducting feature in the whole temperature range measured, the conductivity at low temperature (20 K) is rather high ($4\,S\,cm^{-1}$). This indicates that the interaction between BEDT-TTF molecules in the crystal is rather strong.

3.3. ESR Measurement

Figure 6 shows the ESR spectrum of the salt under study. There is only one broad resonance ($g_0 = 2.005$ and $\Delta H = 38.1$ G), which was assigned to the conduction electrons. The value of the linewidth is quite broad which is not typical for a β-type BEDT-TTF radical cation salts, but two times larger than the expected value. It is known that the broad linewidths are characteristic of two-dimensional organic conductors, such as κ-type BEDT-TTF based cation radical salts [16, 17]. Quite narrow linewidths were obtained for two-dimensional BEDT-TTF salts: β-$(BEDT\text{-}TTF)_2BrICl$; β-

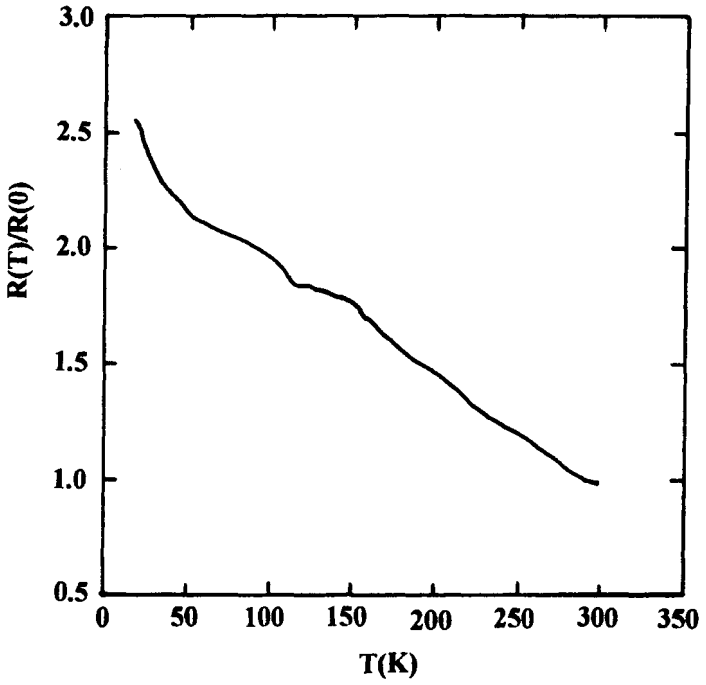

FIGURE 5 Temperature dependence of the resistance along the longest side (*b* axis).

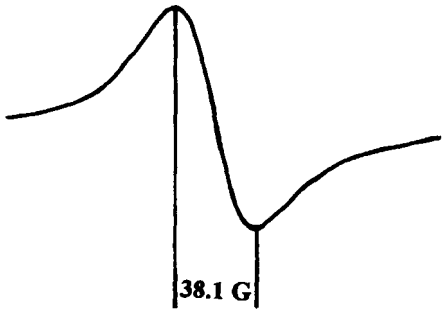

FIGURE 6 ESR spectrum of the complex at room temperature.

BEDT-TTF)$_2$ICl$_2$; β-(BEDT-TTF)$_2$I$_2$Cl [18] and β-(BEDT-TTF)$_2$AuCl$_2$ [19] in which there was a characteristic quasi-one-dimensional type of conducting band according to the tight-binding band-structure calculations.

The broad linewidth of the salt under study can be understood by taking into account the peculiarities of its structure. According to the X-ray analysis, the planes of BEDT-TTF molecules in adjacent layers are twisted

with respect to one another, thus the conducting stacks of the BEDT-TTF molecules are projected in two directions in the crystal and this results in a two-dimensional conducting network in the salt. Finally, the narrow resonance of Fe^{3+} ($g_0 = 2.002$ and $\Delta H = 1.5$ G) observed in β''-(BEDT-TTF)$_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5CN$ was not found in this case.

4. CONCLUSION

Single crystal of β-(BEDT-TTF)$_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5NO_2$ was prepared by substituting $C_6H_5NO_2$ for C_6H_5CN. In the crystal, the lattice is stabilized by $C_5H_5NO_2$ molecules included in the hexagonal cavities. By this method, transition metal ions carrying localized magnetic moments are introduced in to the lattice of a molecular charge transfer salt. The packing of the BEDT-TTF is of β-type. However, the twisting of the adjacent BEDT-TTF molecule layers result in the formation of a fairly broad ESR linewidth, characteristic of two-dimensional salts rather than β-type BEDT-TTF salts. The loosely packed lattice compared with β''-(BEDT-TTF)$_4 \bullet H_2O \bullet Fe(C_2O_4)_3 \bullet C_6H_5CN$ may be resulted from the fact that the size of $C_6H_5NO_2$ molecule is a bit bigger than that of C_6H_5CN.

Acknowledgements

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