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Mohamedally Kurmoo [a b c], Hiroshi Kitagawa [a], Tadaoki Mitami [a], Katsuyuki Morii [a] & Peter Day [c]

[a] Japan Institute of Science and Technology, 15 Asahidai, Tatsunokuchi, Ishikawa, 923-12, Japan

[b] Institut de Physique et Chimie des Matériaux de Strasbourg, Groupes des Matériaux Inorganiques, 23 rue du Loess, F-67037, Strasbourg Cedex, France

[c] The Royal Institution of Great Britain, 21 Albemarle Street, London, W1X4BS, UK

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# A MOLECULAR CHARGE TRANSFER SALT OF BEDT-TTF WITH $[Cr(C_2O_4)_3]^{3-}$ : SYNTHESIS AND PHYSICAL PROPERTIES

MOHAMEDALLY KURMOO,[a,b,c] * HIROSHI KITAGAWA,[a] TADAOKI MITANI,[a] KATSUYUKI MORII[a] AND PETER DAY[c]

[a]Japan Institute of Science and Technology, 15 Asahidai, Tatsunokuchi, Ishikawa 923-12, Japan; [b]Institut de Physique et Chimie des Matériaux de Strasbourg, Groupes des Matériaux Inorganiques, 23 rue du Loess, F-67037 Strasbourg Cedex, France; [c]The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

Abstract The synthesis of BEDT-TTF, bis(ethylenedithio)-tetrathiafulvalene, charge transfer salts with isostructural magnetic and non-magnetic anions $M(C_2O_4)_3^{3-}$, where $M^{III}$ is Cr, Co or Al is reported. $(BEDT\text{-}TTF)_4[Cr(C_2O_4)_3]\cdot C_6H_5CN$ is a semiconductor ($\sigma_{RT}$= 1-10 $Scm^{-1}$, $E_A$= 0.09 eV). The EPR spectrum is characterised by one single resonance with a g-value average between those of BEDT-TTF radical and $Cr^{3+}$. The linewidth is exchange narrowed. The temperature dependence of the susceptibility indicates antiferromagnetic interactions. Infrared data give an optical gap (~0.2eV) which is consistent with that obtained by the electrical measurement.

## INTRODUCTION

Materials with new properties or new combinations of properties are attracting much attention because of their potential importance for technological applications. Electro-luminescent materials in screen displays and high density storage system employing magneto-optical Kerr effects are two examples.[1,2] Materials used in electronic equipment are polymers, metallic thin films, and semiconductor multilayers. Accordingly, there is a major effort to develop crystalline organic-inorganic hybrids with desirable and tuneable properties. The early research in this field was based on the chemistry of intercalation.[3] More recently, the research trend is to start with building blocks that favour the required structures and properties. For example, Clément[4] has recently synthesised a ferromagnetically ordered layered compound with an organic molecule that has non linear optical properties inserted between the layers. Our own efforts to make organic conductors with inorganic magnetic spacers have resulted,[5-7] at

the beginning of this year, in the synthesis of the first layered organic superconductor interleaved with an inorganic sheet of paramagnetic ion. We made use of the paramagnetic anion, $Fe(C_2O_4)_3^{3-}$ (S=5/2), which favours a layered hexagonal lattice due to its secondary binding ability of the oxalate ligand. Two different crystal phases were identified and characterised; one is a semiconductor and the other is a metal with a superconducting transition at $T_c$~8K.[7] The study of their electrical, magnetic and optical properties indicates no interaction between the conduction electrons and the localised moments on the anion.

We are currently exploring this field by replacing the metal centre by chromium (S=3/2), cobalt and aluminium (S=0), as well as replacing the oxalate by thio-oxalates. We believe extension of the π-orbital radius on going from oxygen to sulphur may promote larger effects through π(inorganic)-π(organic) interaction. Here we report the synthesis of charge transfer salts with different central metals and the characterisation of one salt, $(BEDT\text{-}TTF)_4[Cr(C_2O_4)_3]\cdot C_6H_5CN$ by electrical conductivity, EPR, magnetic susceptibility and infrared reflectivity.

We present evidence that this compound contains layers of BEDT-TTF probably with a regular linear chain of $Cr(C_2O_4)_3^{3-}$ channelled between them. It is a semiconductor and the single crystal EPR spectra and magnetic susceptibility indicate the existence of interaction between the two spin systems.

## EXPERIMENTAL

### Synthesis

BEDT-TTF (Tokyo Kasei) was used as received. Benzonitrile, dried over $CaH_2$ overnight, and absolute ethanol were distilled just before use. Oxalic acid was recrystallised from water. The anions $K_3M(C_2O_4)_3\cdot 3H_2O$, M=Cr, Co or Al, were prepared and recrystallised as described by Bailar and Jones.[8]

Electrocrystallisation of the charge transfer salts was performed in two compartment cells (35ml) with platinum wire electrodes at constant current of 1μA for 12 days. Each cell contained 20mg of BEDT-TTF, 200mg of the appropriate anion and 300mg of 18Crown6. Three different methods were employed. For the first, only the anion and the crown ether were partially dissolved in neat benzonitrile and BEDT-TTF was placed in one arm of the cell. For the second, 200mg of oxalic acid was also added For the third, we dissolved the anion and the crown ether in 2ml of water before adding a saturated solution of BEDT-TTF in benzonitrile. To mix the less miscible solvents (water and benzonitrile) and to partially dissolve the anion, all the cells were sonicated for approximately 5 minutes and allowed to settle for a few hours.

Crystals of differing quality and quantity were obtained in every case, except for Co in water. The crystals were diamond shaped, either as large thin transparent plates or small thick opaque needles or plates. For M=Fe or Cr in the water cells some crystals were as large as 5 x 3 x 0.02mm$^3$. These crystals were "fish" shape, possibly as a result of the solubility of the charge transfer salts in the aqueous media. For M=Co, the crystals were very small. We also note that in this case the anion has decomposed to pink Co(II) oxalate during the electrocrystallisation.

X-Ray Diffraction

Two crystals (0.3x0.1x0.1 and 0.15x0.08x0.05 mm$^3$) of the Cr salt were selected and mounted on glass fibres . Their lattice parameters were determined from the angles of 30 reflections using a Rigaku diffractometer (graphite monochromatized Cu K$\alpha$ 1.540598Å). Both crystals belong to the monoclinic system and have the same lattice parameters, a =11.106(2), b=4.229(1), c = 37.69(1)Å, $\beta$ = 95.71(2)°, V = 1761.3(5)Å$^3$. A full set of data was collected on the large crystal because the other had very weak reflections at high angles. Intensities of 3217 reflections were obtained with 1481 having $I \geq 3\sigma(I)$.

Electrical Transport

Four probe DC resistivity measurements were made along the long axis of the crystal (also the b-crystallographic axis) with applied current of 1$\mu$A. The contacts were made with 25$\mu$ gold wire and gold paste. The temperature was measured by a calibrated Pt-Co resistor; the sample and the sensor were thermally anchored to a copper block surrounded by helium exchange gas.

Electron Spin Resonance

Spectra were recorded on single crystals by use of a JEOL-RE3X spectrometer operating in a $TE_{011}$ mode at 9GHz and 100KHz field modulation. Frequency was measured by an Advantest R5372 counter. Temperature of the sample was measured by a Au-Fe(0.07%) / Chromel thermocouple by use of a APD cryogenics continuous flow cryostat and a Lakeshore 330 controller. Crystals were mounted on a cut flat face of 3mm diameter Teflon rods using a smear of silicone grease, which was then placed in a quartz tube containing helium exchange gas. The alignment was such that the applied field is in the bc plane. A manganese marker and a TEMPOL sample were used to calibrate the magnetic field and g-values.

Static Magnetic Susceptibility

The susceptibility was measured on a Métronique SQUID magnetometer in an applied field of 5000G. The sample (0.69±0.05 mg) was wrapped in cling film and held on a

cotton string. The data were corrected for the sample holder and the diamagnetic contribution estimated using Pascal constants.

Optical Reflectivity

Mid-infrared reflectivity data of single crystals were recorded at room temperature by use of a Perkin-Elmer 1710 FT-spectrometer in conjunction with an IR-PLAN microscope and a KRS5 polariser.



## RESULTS AND DISCUSSIONS

### X-ray Structure

Numerous attempts at solving the crystal structure failed because the Bragg reflections were double peak and secondly, the number of observables is too small compared to the number of parameters. However, we can infer from the lattice parameters and speculate on the phase it may have.

First, we compare this present compound to the other fully characterised tris-oxalatometallate salts of BEDT-TTF, $(BEDT\text{-}TTF)_4[AFe(C_2O_4)_3]\cdot C_6H_5CN$, where $A=K^+$, $NH_4^+$ or $H_2O$. The volume of the cell is smaller than the Fe salts, suggesting there is no potassium ion in the lattice which was confirmed by microanalysis using X-ray fluorescence. There is only one common lattice parameter (c-axis ~35Å), which corresponds to two BEDT-TTF layers per cell. The c-axis is longer than the Fe analogues meaning either the docking of the BEDT-TTF on the anion layer, if Cr adopts the same layered structure as Fe, is more perpendicular in the Cr salt than in the Fe compounds or that the anion is a monomer and sits in cavities created by the ethylene groups. The lattice parameters b=4.229Å implies that the layers are one molecule thick along the stacking axis and a=11.106Å is for two molecules with short interconnecting side-by side S···S distances. The a and b dimensions are close to those found for the many known α and θ phases,[9-17] especially those with a 4-5Å lattice parameter. We have recently established a correlation between the dihedral angles between the BEDT-TTF molecules in adjacent stacks and the electrical conductivity.[9] If we apply a similar correlation using, this time, the ratio of the crystallographic axes defining the conducting plane divided by the number of molecules in that direction for the α, θ or η-phase, we arrive at a dihedral angle of ~45° and thus a semiconductor for the present compound.

The anion $M(C_2O_4)_3$ has the shape of a disk of diameter 7.6Å (10.2Å including the van der Waals radii of the peripheral atoms) and a thickness 2.8Å (5.4Å).[7] For the two known salts of Fe the lattice parameters within the BEDT-TTF layer is ~10x20Å, thus it can accommodate the anions parallel to the BEDT-TTF layer; resulting in alternate organic conducting and polymeric inorganic magnetic layers. In the present

case the unit cell dimensions are only 4x11Å, we can accommodate the anion only if it is perpendicular to the BEDT-TTF layer. As a result the structure will be made up of layers of the conducting organic molecules and regular chains of the anions perpendicular to these layers. If this is the case, it will be an example of a regular magnetic (S=3/2) linear chain.



Electrical Conductivity

The temperature dependence of the resistivity of a crystal is shown in Figure 1. The room temperature conductivity for several crystals ranges from 1 to $10Scm^{-1}$, which lies between that of $(BEDT\text{-}TTF)_4[KFe(C_2O_4)_3]\cdot C_6H_5CN$ ($10^{-4}Scm^{-1}$) and $(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3]\cdot C_6H_5CN$ ($10^{2}Scm^{-1}$).[7] The activation energy (0.09eV) is also smaller than for $(BEDT\text{-}TTF)_4[KFe(C_2O_4)_3]\cdot C_6H_5CN$. The room temperature conductivity and the activation energy are similar to those found for the α-phase compounds with magnetic anions, $(BEDT\text{-}TTF)_3CuBr_4$ and $(BEDT\text{-}TTF)_8PMo_{12}O_{40}\cdot(CH_3CN\cdot H_2O)_2$.[6,11]

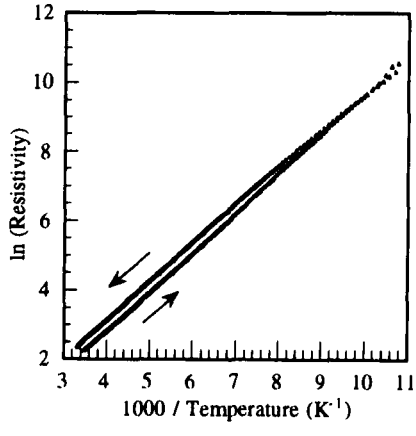


FIGURE 1 Temperature dependence of the resistivity of a single crystal along the b-axis. Arrows indicate the cooling and warming cycle.

Electron Spin Resonance

The spectrum at each temperature and orientation studied is characterised by a single Lorentzian line centred near g=2. The g-values, peak-to-peak linewidth and intensity of the resonance as a function of temperature are shown in Figures 2-4 for the applied field either parallel or perpendicular to the conducting plane (bc-plane).

The observed g-values are lower than those for BEDT-TTF radical salts[18,19] containing non-magnetic anions (2.003-2.011), depending on the direction of the applied

field with respect to the BEDT-TTF molecule. The g-value for chromium is 1.98 when in a cubic and 1.984 in trigonal symmetry and very little anisotropy.[20] For a system which satisfies the condition for "Bottleneck",[21,22] that is close proximity of the g-values of the two spin systems and similar relaxation (linewidth), the observed g-value is intermediate between those of the two individual spins and is given by

$$g_{obs} = \frac{g_{org}\ \chi_{org} + g_{Cr}\ \chi_{Cr}}{\chi_{org} + \chi_{Cr}} \quad (1)$$

If we take the maximum and minimum values expected for the BEDT-TTF molecule and g=1.98 for the chromium atom as well as assuming the susceptibility at room temperature does not deviate from that expected for one S=1/2 localised spins (*vide supra)* for the organic moiety per formula unit and for Cr ($d^3$, S=3/2) we get, using equation (1), maximum and minimum g-values of 1.985 and 1.984 respectively. These values are 1.9919 and 1.9888 if there are three S=1/2 for the BEDT-TTF moiety. These calculated absolute values are still lower than those observed.

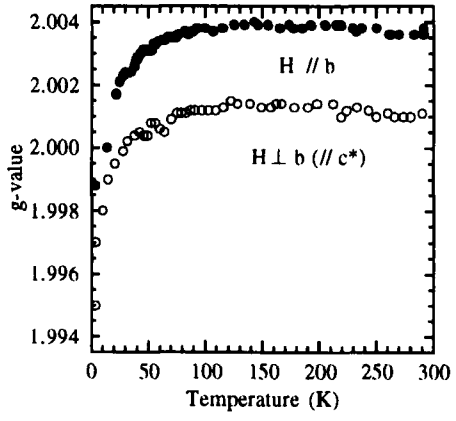


FIGURE 2 Temperature dependence of the g-value of the resonance for the applied field parallel (filled circles) and perpendicular (open circles) to the crystal plate (bc-plane).

The linewidth of the resonance is almost isotropic in the bc-plane. It decreases gradually to a minimum at ~75K before diverging rapidly at low temperature to 5 times that at 300K. The lineshape analysis of the resonance is Lorentzian and there is no evidence for a second resonance within its envelope. If there were two resonances at the expected g-values for the individual spins, we would observe a non-Lorentzian line

shape. The value of 4.5mT at room temperature is comparable to many BEDT-TTF salts. However, it is narrower than those expected for chromium oxalate complexes, which has very wide line (>100mT) at room temperature. The narrow linewidth reinforces the point that due to exchange between the two spin systems the resonance is exchange narrowed. Furthermore, the lack of fine structure for $^{53}Cr$ (9.55%) may also be due to exchange between the moment on the organic molecules and that on the metal. We also note that the linewidth and g-values start to diverge at the same temperature.

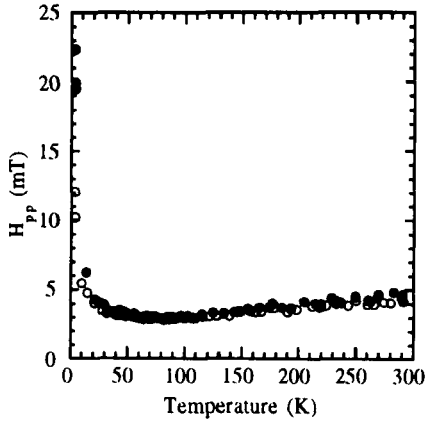


FIGURE 3 Temperature dependence of the peak-to-peak linewidth of the resonance for the applied field parallel (filled circles) and perpendicular (open circles) to the crystal plate (bc-plane).

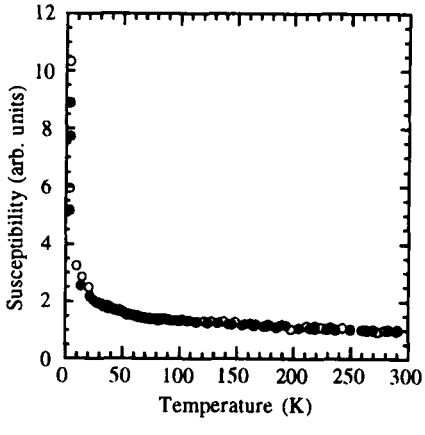


FIGURE 4 Temperature dependence of the spin susceptibility for the applied field parallel (filled circles) and perpendicular (open circles) to the crystal plate.

The spin susceptibility derived from the intensity of the resonance is shown in Figure 4. The temperature dependence of the susceptibility, the g-values and linewidths is very smooth suggesting there is no structural, electronic or magnetic transition. The intensity increases as the temperature of the sample is lowered, but not according to a Curie-Weiss law. The observed ratio $\chi(4K)/\chi(300K)$ ~10 being smaller than that expected (75), if we assume the exchange between all type of spins is absent, suggests considerable interaction between the moments.

Bulk Magnetic Susceptibility

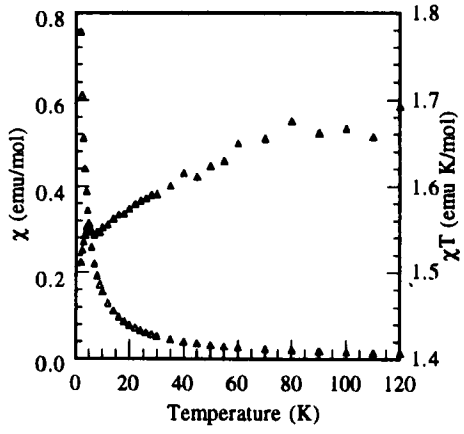


FIGURE 5 Temperature dependence of the bulk magnetic susceptibility (open triangles) and of the $\chi T$ product (filled triangles).

Isothermal magnetisation at 4.5K up to 5000G is linear. The measurement is only good for the temperature range 2-120K; above 120K the signal too small. The susceptibility (Figure 5) was obtained by analysis of each SQUID response. The value of the susceptibility at 120K is that expected for one S=3/2 magnetic ion. The increase to low temperature is approximately that expected for a Curie-Weiss law with $\theta$= -2±0.2K and C=1.70 emuK/mol. The latter is close to the value (1.84 emu K/mol for g=1.98) expected for Cr ($d^3$, S=3/2). The contribution from the BEDT-TTF is therefore nil. The reason for which is not clear. We expected three holes for the formulation and if there is dimerisation of the BEDT-TTF molecules the resultant number of spins will be one. Thus the minimum value for the Curie constant should be 2.2 emu K/mol. There is sign of short range antiferromagnetic interaction, but the magnitude of which is not so large that the Curie constant is only 75% of the theoretical. In addition, there is indication of

3D-magnetic order at 6±1K. The lack of a maximum in the susceptibility curve makes it difficult to estimate the exchange interactions or to assign a model to the behaviour.[6,11]

IR Reflectivity

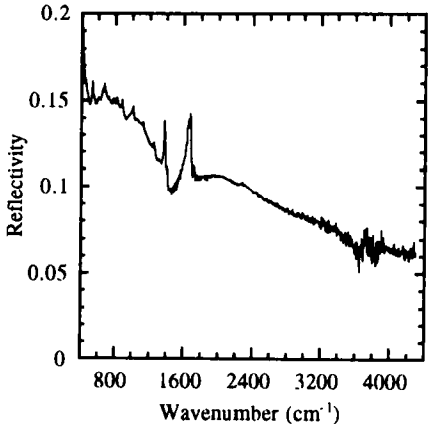


FIGURE 6 Mid-infrared reflectivity of a single crystal at room temperature.

The mid infrared reflectivity spectrum is shown in Figure 6. The first observation is that the absolute reflectivity is low compared to metallic BEDT-TTF salts. The spectra with the plane of polarisation within the crystal plate (ab-plane) are quite isotropic and are characterised by a broad electronic background superposed by several vibrational bands. There are two possible interpretations of the electronic contribution. Firstly, there are two bands centred at ~1200 and ~2000$cm^{-1}$, the first can be assigned to the band gap which is expected at ~1400$cm^{-1}$ from the conductivity measurement and the second is another intraband transition. Secondly, there is only one very broad electronic band corresponding to the expected band gap and the dip at ~1400$cm^{-1}$ is due to a Fano structure[23] (strong *e-mv* coupling) via the interaction of the electronic dipole moment to the vibrational C=C modes of the BEDT-TTF molecules. The latter is more plausible. The spectrum is similar to those observed for $(BEDT\text{-}TTF)_3CuBr_4$ and $(BEDT\text{-}TTF)_8PMo_{12}O_{40}\cdot(CH_3CN\cdot H_2O)_2$; both of which are small band gap semiconductors. Two sharp vibrational modes of the $Cr(C_2O_4)_3$ anion are observed in the range of frequency measured, $C{=}O_{ter}$ 1660$cm^{-1}$ and $C\text{-}O_{br}$ 1350$cm^{-1}$, similar to those in $Fe(C_2O_4)_3^{3-}$. The other weak vibrational structures are those of BEDT-TTF and benzonitrile. Assignment of the vibrational structure of the BEDT-TTF molecule can be seen in the literature.[24]

SUMMARY

Several new charge transfer salts of BEDT-TTF have been prepared containing the anion $M(C_2O_4)_3^{3-}$ where the metal is paramagnetic $Cr^{III}$ or diamagnetic $Co^{III}$ and $Al^{III}$. The structure of one of the Cr-salts is proposed to be of α-phase consisting of layers of BEDT-TTF separated by regular chains of stacked disks of $Cr(C_2O_4)_3^{3-}$. It is small gap semiconductor. The temperature dependence of the EPR g-values, linewidths and intensities suggest considerable interaction between the spin sublattices. The electrical, magnetic and optical properties of this salt are very similar to those of the two α-phase compounds, $(BEDT\text{-}TTF)_3CuBr_4$ and $(BEDT\text{-}TTF)_8PMo_{12}O_{40}\cdot(CH_3CN\cdot H_2O)_2$, which show magnetic exchange interaction between the conduction electrons and the localised moments on the magnetic anions. On the other hand, β"-phase[24] compounds, $(BEDT\text{-}TTF)_3CuCl_4\cdot H_2O$ and $(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3]\cdot C_6H_5CN$,[5,7] show two resonances in their EPR spectra implying no interaction. The structures and properties of the compounds with cobalt and aluminium are in currently being studied.

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