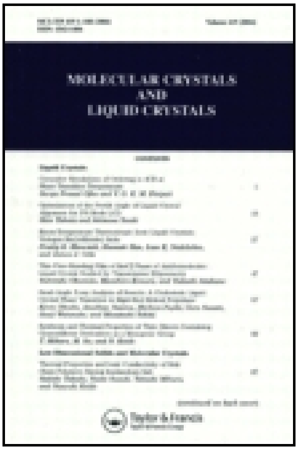

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Structure, magnetic and electronic properties of charge transfer complex containing hexacyanoferrate chain and bedt-ttf column

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STRUCTURE, MAGNETIC AND ELECTRONIC PROPERTIES OF CHARGE TRANSFER COMPLEX CONTAINING HEXACYANOFERRATE CHAIN AND BEDT-TTF COLUMN

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A novel charge transfer complex containing of hexacyanoferrate ($Fe(CN)_6$) unit, which has been exhibited variety of magnetic topics in prussian blue systems, was synthesized. X-ray analysis of the single crystal obtained by electrolysis of BEDT-TTF (ET) and hexacyanoferrate suggests that this complex contains 1D magnetic hexacyanoferrate chain perpendicular to the conducting ET column. This significant structure implies that significant properties can be expected caused by the interaction between the spin momentum on d-electrons and a conducting π-electrons influenced vertically by the applied magnetic field. From the result of the electrical conducting measurement, it is suggested that is a semiconductor, with the activation energy and the conductivity at room temperature to be 0.113 eV and 0.46 S/cm, respectivity. Detailed X-ray analysis suggests that the occupancies of Fe and C elements in the 1D hexacyanoferrate chain are 0.5, that of N element is 1.0.

Keywords: BEDT-TTF; hexacyanoferrate; charge transfer complex; crystal structure; magnetic properties

INTRODUCTION

One of the current trends in molecular magnetic materials is dealing with the design and the study of materials with multiple physical properties such as conductivity [1,2,3,4,5,6] or superconductivity [7,8,9] and magnetism [10]. For example, the aim of the synergy between electrical conductivity and

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magnetism is to obtain a long range ferromagnetic coupling of localized magnetic moments of the d-transition metals supported by the delocalized π-electrons of conducting organic molecular networks. Recently it was reported that there is a possibility of new magnetic superconducting of complexes containing of nitroprusside ($M(NO)_5$) unit and ET. In this study, a new type of charge transfer complex containing hexacyanoferrate and ET[11] is obtained from electrochemical synthesis, and characterized its electronic and magnetic properties.

EXPERIMENTAL

The single crystal of the compound was synthesized by the electrochemical oxidation of BEDT-TTF in a H-shaped cell with Pt electrodes separated by a sintered-glass filter of CH_2Cl_2 in the presence of the potassium hexacyanoiron, MeOH and 18-crown-6-ether. After three weeks, the single crystals of $ET_3[Fe(CN)_6]\cdot 4H_2O$ (**1**) which is suitable for X-ray structural analysis were collected and the measurements of magnetic and electronic properties were characterized.

RESULTS AND DISCUSSIONS

The crystal structure of the compound exhibits the layer structure of cation and the organic ET molecules are stacked direct to the c-axis (Figure 1).

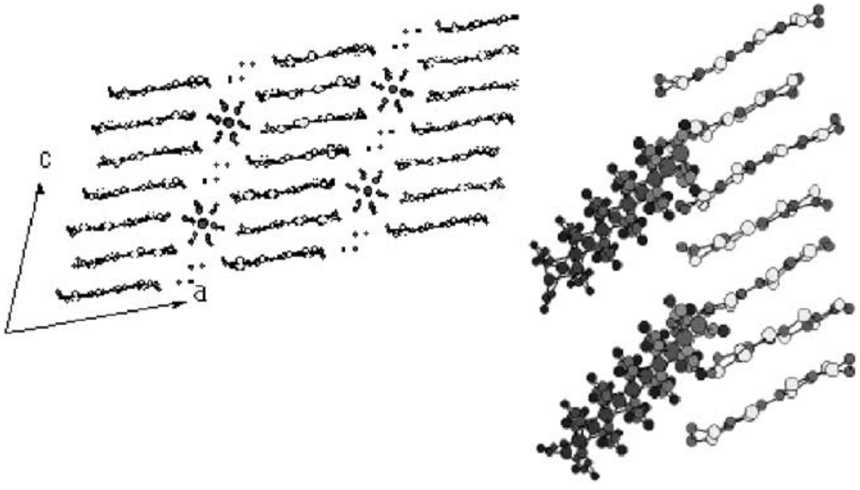
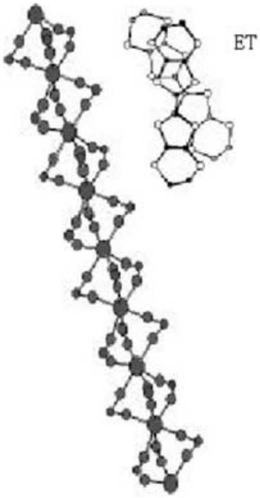


FIGURE 1 Molecular packing in **1**.



Structural data of $FeC_{36}N_6S_{24}O_4H_{24}$ (**1**)
a = 38.642(2)Å
b = 6.6330(3)Å β = 115.372(2)•
c = 23.199(1) Å
V = 5372.7(5) $Å^3$
Z = 4
F.W. = 1429.91
D_{cal} = 1.77 g/cm^3
Space group C2/c (#15)

FIGURE 2 Structure of 1-D chain of $Fe(CN)_6$ and stacked ET molecules in **1**.

The first example that involves a trianion of $[Fe(CN)_6]^{3-}$ in two isostructural α-phase can be obtained. The $[Fe(CN)_6]^{3-}$ anion is located on the inversion center and is formed a 1D chain structure bridged by the terminal N atom. Each anion is connected to the neighbors by two terminal nitrogen atoms, resulting to the 1D chains along to the b-axis.

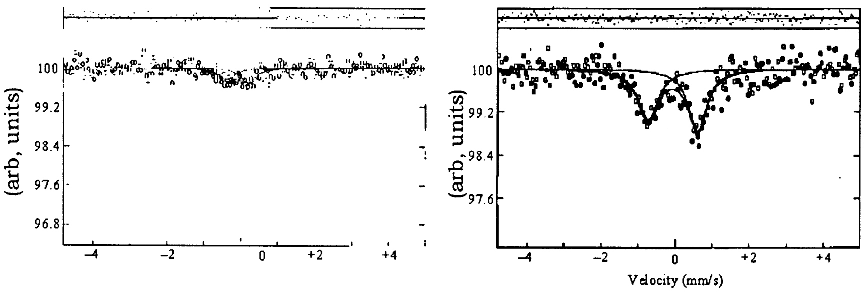


FIGURE 3 Mössbauer spectra of **1** at room temperature (left) and 77 K (right). Open circles and solid lines denote the observed and fitted data, respectively.

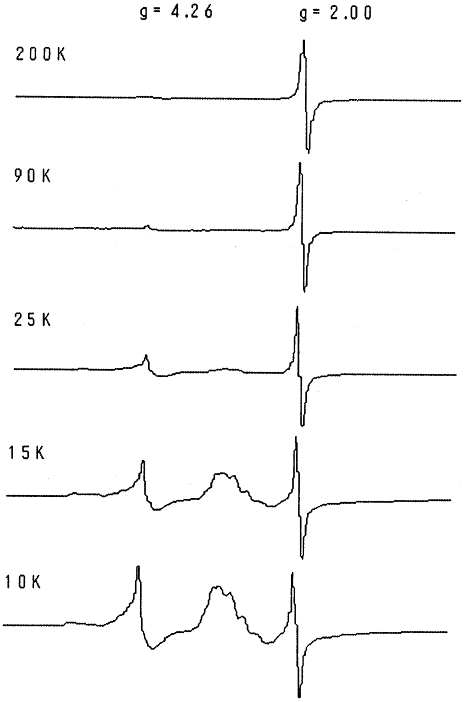


FIGURE 4 ESR spectra of $ET_3[Fe(CN)_6]·4H_2O$.

The Mössbauer spectra observed at room temperature and 77 K are given in Figure 3. These results suggested that the low-spin state of Fe(III) ions can be existed in the compound. An asymmetrical doublet peaks are observed at low temperature, suggesting that there is a possibility of two kinds of ferric Fe(III) species coexistence in the unit cell.

Temperature dependence of the ESR spectrum was measured, as shown in Figure 4. Signals originated by Fe^{III} ions are observed at around $g = 2$. An additional signal at around $g = 4$, which is originated by the interaction between two Fe^{III} ions, becomes larger as the temperature is lowered. This result implies that there is the antiferromagnetic interaction between the low-spin Fe^{III}– Fe^{III} spins, as described later.

The magnetic susceptibility was measured by means of Quantum Design MPMS SQUID, as shown in Figure 5. Weak antiferromagnetic interaction is observed at low temperatures, caused by the presence of a antiferromagnetic exchange interaction between the low-spin Fe^{III}–Fe^{III} ions through the cyanide bridge. This result corresponds to the decreasing of the ESR signals around $g = 4$.

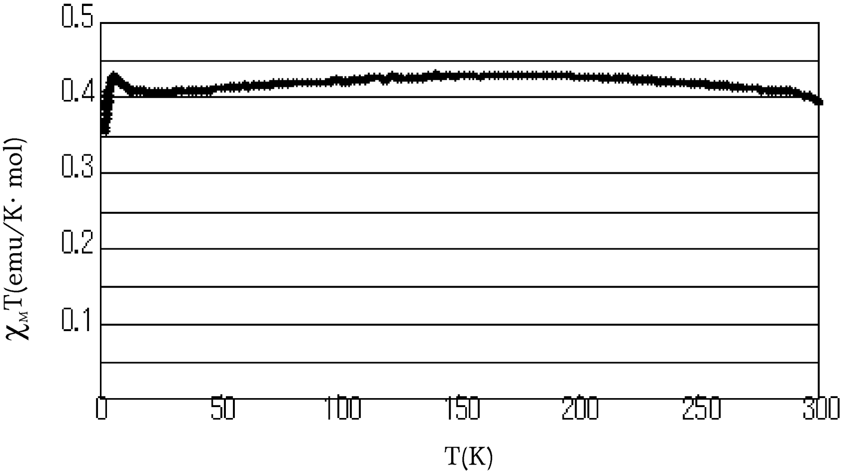


FIGURE 5 Temperature dependence of $\chi_M T$ for $ET_3[Fe(CN)_6]{\cdot}4H_2O$.

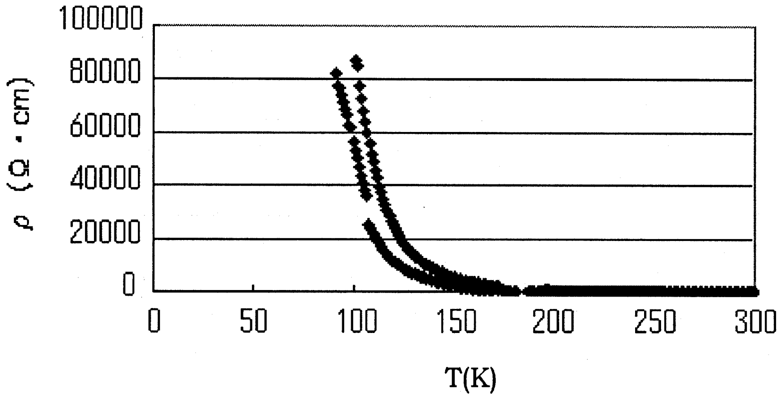


FIGURE 6 Temperature dependence of resistivity for $ET_3[Fe(CN)_6]{\cdot}4H_2O$.

The electrical conductivity was measured with the four contacts method in the single crystal of this salt. This is a semiconductor with conductivity of 0.457 S/cm at room temperature and an activation energy of 0.133 eV (see Figure 6).

REFERENCES

[1] Coronado, E. *et. al.* (1997). ***Adv. Mater.***, ***9***, 984–987.

[2] Ouahab, L., Golhen, S., LeHoerff, T., Gnilievic, J., Tual, L., Helou, N., Amiell, J., Delhaes, P., Binet, L., & Fabre, J. M. (1999). ***Synthetic Metals***, ***102***, 1642–1645.

[3] Kushch, L., Buravov, L., Tkacheva, V., Yagubskii, E., Zorina, L., Khasanov, S., Shibaeva, R. (1999). ***Synthetic Metals***, ***102***, 1646–1649.

[4] Le Magueres, P., Ouahab, L., Briard, P., Even, J., Bertault, M., Toupet, L., Ramos, J., Gomez-Garcia, C. J., & Delhaes, P. (1997). ***Mol. Cryst. Liq. Cryst.***, ***305***, 479–489.

[5] Pierre Le Magueres, Lahcene Ouahab, Nathalie Conan. (1996). ***Solid State Commun.***, ***97***, 27–32.

[6] Mallah, T., Hollis, C., Bott, S., Kurmoo, M., and Day, P. (1990). ***J. Chem. Soc., Dalton Trans.***, *859*.

[7] Williams, J. M. *et al.* (1991). ***Science***, ***252***, 1501–1508.

[8] Day, P. *et al.* (1992). ***J. Am. Chem. Soc.***, ***114***, 10722–10729.

[9] Kurmoo, M. *et. al.* (1995). ***J. Am. Chem. Soc.***, ***117***, 12209–12217.

[10] Miller, J. S., & Epstein, A. J. (1994). ***Angew. Chem. Int. Ed. Engl.***, ***33***, 385–415.

[11] Hngbin Yu and Daoben Zhu. (1997). ***Physica C***, 282–287, 1893–1894.