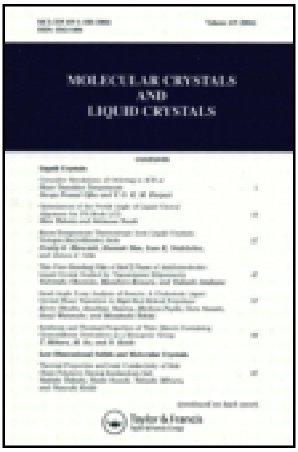

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For both of the single crystals of $(BEDO\text{-}TTF)_9(NiBr_4)_2(CH_2Cl\text{-}CH_2Cl)_5$ and the powder sample of $(BEDO\text{-}TTF)_3[FeCr(ox)_3](H_2O)_{3.5}$ in which the counter ions posses paramagnetic and ferromagnetic localized spins, respectively, the metallic behavior of the electrical conductivity was observed down to low temperatures. The former complex showed the isostructural crystal packing and exhibited the similar properties to those of $(BEDO\text{-}TTF)_9(HgBr_4)_2(CH_2Cl\text{-}CH_2Cl)_5$ in the conducting behavior and spontaneous loss of the solvent of crystallization. The $FeCr(ox)_3$ complex is a metallic molecular ferromagnet below ca. 11 K. The ESR spectra showed the anomalous behavior below around the Curie temperature, though no effects of the magnetically ordered localized spins on the conducting property were detected.

Keywords BEDO-TTF; Metallic Molecular Ferromagnet; Bimetal Oxalate; Organic Metal; Molecular Ferromagnet

INTRODUCTION

The multi-functional molecular crystals are of interest in the lights both of the application and basic science. Recently, intensive works have been carried out to provide the organic metals which show also the magnetic properties. As a promising method, the combination of the conducting organic molecule and magnetic inorganic compound has been examined.[1] Among the conducting component molecules, bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF, BO) shows the peculiarity to produce metallic charge-transfer (CT) complexes regardless the size, shape, and formal charge of the counter components and also ignoring the sample morphology of single crystals, powders, and thin films due to the self-assembling nature.[2] However, the magnetic effects of the counter component have been rarely examined in BO based metallic complexes.[3] This paper describes the complexes with the paramagnetic and ferromagnetic counter ions of $(NiBr_4)^{2-}$ and $[FeCr(ox)_3]^-$, respectively, where ox represents oxalate dianion.

RESULTS AND DISCUSSION

$(BO)_9(NiBr_4)_2(CH_2Cl\text{-}CH_2Cl)_n$ (n = 4 - 5)

The black hexagonal plates of the $NiBr_4$ complex were prepared by the constant current electrocrystallization (1 μA) of BO in the presence of $(Et_4N)_2NiBr_4$ from the 2:1 mixture of 1,2-dichloroethane (DCE) and ethanol. The crystal structure analysis based on the diffraction data taken at 120 K for the fresh sample gave the composition of $(BO)_9\,(NiBr_4)_2(DCE)_n$, where n = 5. However, the data collected 2 - 3 days after the sample preparation at room temperature (RT) resulted in the stoichiometry of $n \approx 4$ indicating the spontaneous loss of the solvent of crystallization.[4] In both cases, the crystal structure consists of the alternating donor and counter component layers along the c-axis, in the former of which BO forms the typical packing pattern for this donor molecule (Fig. 1a). Comparing the donor layer structures between the cases of n = 5 and 4, no significant differences are detected. The calculated band structure[5] shows the complicated Fermi surfaces which can be understood as a folded pattern of an ellipsoid (Fig. 1b). For the counter component layer, the sites, from which the solvent molecules are lost preferentially, are determined to be D and E in Fig. 1c. The crystal structure is isostructural to that of $(BO)_9(HgBr_4)_2(DCE)_5$ reported by Zhilyaeva et al., for which also the spontaneous loss of DCE was reported without specifying the preferential sites.[6]

The ESR spectra showed only one conduction electron resonance (CER) as a slightly distorted Lorentzian signal even at RT.[7] The asymmetry became distinct below 80 K to give a Dysonian line. Along

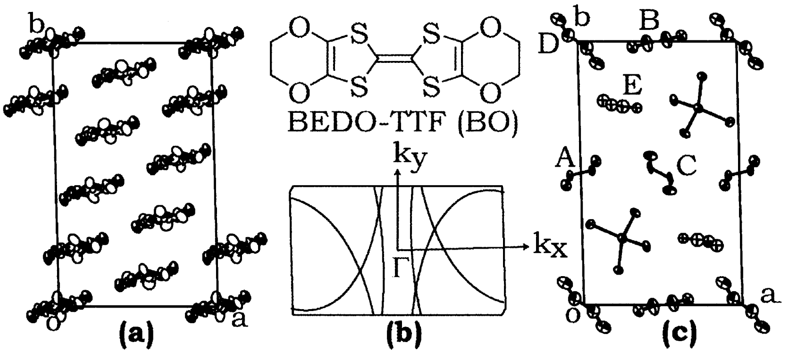

FIGURE 1 Donor (a) and counter component (c) layers in $(BO)_9(NiBr_4)_2(DCE)_5$ projected along the c-axis. At the E site in the latter, only the positions of chlorine atoms were determined with the site occupancy factor of 0.5 at four positions. (b) shows the molecular structure of BO (top) and the calculated Fermi surfaces for this complex.

with the monotonous decrease of ΔHpp, this behavior is consistent with the metallic conductivity described below.

The conductivity (σ) of the fresh crystal was measured by the conventional four-probe method (σ_{RT} = 10 Scm^{-1}). On cooling, the temperature dependence showed the metallic behavior down to ca. 20 K and then slight decrement originated from the disorder and/or microcracks in the crystal. This behavior is the same as that observed for $HgBr_4$ complex which includes only non magnetic counter components.[6] Hence, the effects of the paramagnetic counter anion on the itinerant electrons are concluded to be negligible in the $NiBr_4$ complex.

$(BO)_3[FeCr(ox)_3](H_2O)_{3.5}$

The metathesis between $(BO)_2(BF_4)(H_2O)_x$ ($x \approx 2$) and $K_3Cr(ox)_3(H_2O)_3$ in the presence of $FeSO_4 \cdot 7H_2O$ afforded the bimetallic oxalate complex of BO. The composition of the complex was estimated to be $(BO)_3\,[FeCr(ox)_3](H_2O)_{3.5}$ from the elemental analysis (C, H, N) and the energy dispersion X-ray analysis (Fe, Cr). The composition was supported by the Raman spectra, from which the degree of CT on BO was estimated as 0.4 ± 0.1 by the procedure described in our previous paper.[2b] Also, the IR spectra showed the existence of $BO^{+\cdot}$ and ox^{2-} and the absence of BF_4^-, SO_4^{2-} in the powder sample. The composition is close to that of the recently reported metallic organic ferromagnet of $(ET)_3[MnCr(ox)_3]$, in which ET, the all sulfur analog of BO, plays the role of conducting component.[1c] Concerning the slightly smaller molecular size of BO than that of ET and the fact that the BO complex contains water, it is probable that our BO complex has the similar crystal structure to that of the ET complex.

Fig. 2a shows the plot of μ_{eff} (= $(8\chi T)^{1/2}$) vs. T, which shows the abrupt increase at around 30 K indicating the occurrence of a magnetic transition in the complex. The value of μ_{eff} = 4.82 μ_B at 300 K after subtracting the contribution from the conduction electron based on the ESR spectra is considerably small comparing to that estimated from the spin-only value of 6.24 μ_B for magnetically diluted Fe^{2+} (S = 2) - Cr^{3+} (S = 3/2). Also, the appearance of the round minimum around 40 K suggests the ferrimagnetic ground state of this complex.[8] To clarify the nature of the ordering, so called magnetization curve was measured at

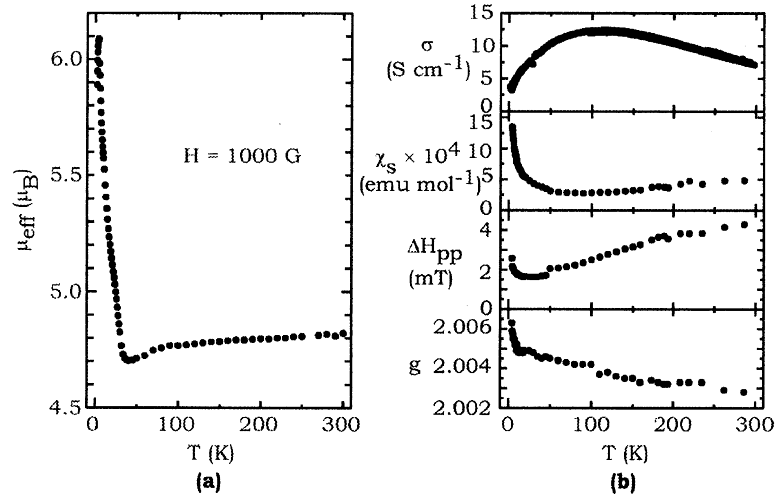

FIGURE 2 The temperature dependences of the magnetic and transport properties of $(BO)_3[FeCr(ox)_3](H_2O)_{3.5}$. In the plot of μ_{eff} vs. T (a), the contribution from the Pascal diamagnetism of the core of all components and the paramagnetism of the conduction electron are subtracted from the observed magnetic susceptibility. In (b), the temperature dependences of the conductivity (σ) and ESR parameters of the conduction electron are compared (from top to bottom, σ, spin susceptibility (χ_s), line width (ΔH_{pp}), and g-value).

1.9 K. Although the maximum filed available was not enough to give the saturation magnetization (M_s), the magnetization at 50 kG of 2.71 μ_B is regarded as the lowest limit of M_s for this complex, which exceeds the M_s for the ferrimagnetically ordered Fe^{2+}-Cr^{3+} network ($M_s = 1\ \mu_B$). Defined as the temperature which gives the maximum zero-field-cooled magnetization, the Curie temperature was determined as T_c = 10.7 K for $(BO)_3[FeCr(ox)_3](H_2O)_{3.5}$ which is about twice that of $(ET)_3[MnCr(ox)_3]$.[1c] The coercieve field of the BO complex (ca. 50 G at 5 K) is also bigger than that of the ET complex (5 - 10 G at 2 K).

The temperature dependence of the conductivity was measured on the compressed pellet by the conventional four-probe method (Fig. 2b, top). Although the maximum is observed at around 120 K and the σ decreases below this temperature, the energy gap (E_g) obtained from the Arrhenius plot is unrealistically small and it decreases in low temperature regime (E_g = 38.5 K in the temperature range of 35 - 70 K, see also below). Hence, the interparticle contacts in the powder sample is regarded to be the origin of the semiconductive behavior below 120 K. The occurrence of a metal-insulator transition is ruled out also by the ESR spectra described below. It should be emphasized that the plot of σ vs. T shows no anomaly around T_c and the small E_g further decreases continuously on cooling indicating that the metallic state persists also below T_c (E_g = 5.70, 3.37, and 1.16 K for the temperature ranges of 20 - 12, 12 - 8, and 8 - 4 K, respectively).

The ESR spectra showed only one Lorentzian signal as the significant one between 286 to 4 K. The g-value, ΔH_{pp}, and the spin susceptibility (χ_s) at 286 K were 2.0028, 42.8 G, and 4.80×10^{-4} emu mol^{-1}, respectively, and the signal is assigned to the CER originated from $BO^{+\cdot}$.

The signal originated from $[FeCr(ox)_3]^-$ could not be detected similar to the case of (decamethylferrocene) $[FeCr(ox)_3]$.[9] There observed no anomaly at around 120 K, while abnormal behavior was observed in the lower temperature region. Although further studies are needed to understand the anomaly, the abrupt increment of g-value below T_c is interpreted as the result of the paramagnetic shielding of the conduction electron by the ferromagnetically ordered localized spins in the bimetallic oxalate.

CONCLUSION

The BO complexes with the magnetic counter anions proved that both of the paramagnetic and ferromagnetic environments provide no affects on the metallic conductivity of the donor layer, however, the conduction electron feels the local magnetic field generated by the ferromagnet in the latter case.

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References

[1] (a) H. Kobayashi, A. Kobayashi, P. Cassoux, Chem. Soc. Rev., **29**,

325(2000). (b) E. Coronado, M. Clemente-León, J. R. Galán-Mascarós C. Giménez-Saiz, C. J. Gómez-García, E. Martínez-Ferrero, J. Chem. Soc., Dalton Trans., 3955(2000). (c) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, V. Laukhin, Nature, **408**, 447(2000).

[2] (a) S. Horiuchi, H. Yamochi, G. Saito, K. Sakaguchi, and M. Kusunoki, J. Am. Chem. Soc., **118**, 8604(1996). (b) O. Drozdova, H. Yamochi, K. Yakushi, M. Uruichi, S. Horiuchi, G. Saito, ibid, **122**, 4436(2000).

[3] The reported BO complexes with the counter anions having the localized magnetic moment; L. V. Zorina, S. S. Khasanov, R. P. Shibaeva, M. Gener, R. Rousseau, E. Canadell, L. A. Kushch, E. B. Yagubskii, O. O. Drozdova, K. Yakushi, J. Mater. Chem., **10**, 2017(2000). M. Tamura, K. Yamanaka, Y. Mori, Y. Nishino, K. Kajita H. Mori, S. Tanaka, J. -I. Yamaura, T. Imakubo, R. Kato, Y. Misaki, K Tanaka, Synth. Met., in press.

[4] Crystal data for $(BO)_9(NiBr_4)_2(DCE)_n$: Triclinic, $P\bar{1}$, black plates at 120 K (n = 5) / room temperature (n = 4), a = 10.781(3) / 10.842(2) Å, b = 17.533(2) / 17.823(3) Å, c = 19.008(3) / 19.141(4) Å, α = 96.335(8) / 96.468(9)°, β = 79.642(7) / 79.85(1)°, γ = 92.66(1) / 92.72(1)°, V = 3512(1) / 3616(1) Å^3, Z = 1, R = 0.0844 / 0.1048 for 7460 / 5311 reflections of $Fo \geq 4\sigma(Fo)$ and 863 / 853 parameters.

[5] T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, Bull. Chem. Soc. Jpn., **37**, 627(1984).

[6] E. I. Zhilyaeva, R. N. Ryubovskaya, S. V. Konovalikhin, O. D. Dyachenko, R. B. Ryubovskii, Synth. Met., **94**, 35(1998).

[7] Although the exact susceptibility (χ) could not be determined by a SQUID magnetometer due to the rapid saturation of the magnetization by the field, the temperature dependency of χ measured at 100 G showed the Curie type behavior and the apparent spin concentration was more than 100 %. This means that the localized spin on Ni^{2+} shows the paramagnetism. Also, it should be mentioned that, since the line width (ΔH_{pp}) of Ni^+ is very large ($\approx$ 450 G for $(Et_4N)_2NiBr_4$ at RT) comparing to the CER (ΔH_{pp} = 51.5 G), the signal could not be detected in the ESR measurement on the single crystal of the complex.

[8] O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, J. Sletten, J. Am. Chem. Soc., **110**, 782(1988).

[9] E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, J. Ensling, P. Gütlich, Chem. Eur. J., **6**, 552(2000).