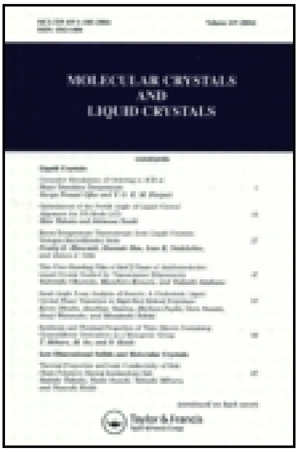

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Preparation, Structure and Electronic Properties of some Organic Donor Salts of Rare-earth Complex Anions: Novel 4 f -π Composite Conductors

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Preparation, Structure and Electronic Properties of some Organic Donor Salts of Rare-earth Complex Anions: Novel 4*f*-π Composite Conductors

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We have obtained a new molecular metal containing a rare-earth complex anion, β″-$(BO)_2[YbCl_4(H_2O)_2]$. This salt retains metallic conductivity down to 4 K. This crystal is metastable at room tmperature; it gradually tranforms into another phase, α-$(BO)_2[YbCl_4(H_2O)_x]$, which becomes insulating below 210 K. The β″-phase crystal have a chain structure of the anions, formed by OH···Cl hydrogen bonding. This is the first example of a π molecular conductor based on an assembled rare-earth complex. Preparation, structure and resistivity of $(BO)_2[YbCl_4(H_2O)_x]$ system is reported.

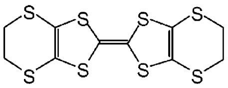
Keywords: Rare-earth; molecular conductors; structure; *f*-electrons

INTRODUCTION

From both chemical and physical points of view, the 4*f* electrons of the rare earth (lanthanides; abbreviated as Ln) ions make a unique category among localized electron systems. The 4*f* electrons exhibit large and structure-sensitive magnetic moments as a result of spin-orbital coupling and the Hund coupling. The interactions between the 4*f* and πelectrons, if sufficiently large, are expected to afford peculiar physical properties. Although the Ln^{3+} ions are not redox active in most cases, the relatively large charge and size provide peculiar coordination structures with variety of coordination numbers. These physical and chemical features are expected to afford a novel effect on the properties of the π conduction electrons. Only a few examples of rare-earth containing π donor conductors have been known[1-4].

TABLE 1 π-*f* Composite conductors obtained in the present study.

Compounds	Properties
$(ET)_4[Ln(NCS)_6]\cdot CH_2Cl_2$	Insulator, AF order below 4 K
β''-$(BO)_x[Ln(NCS)_6]$ ($x \sim 8$)	Metallic
$(TTP)_x[Ln(NCS)_6]$ ($x \sim 8$)	Metallic
$(DIEDO)_6[Ln(NCS)_6]$	M-I around 70 K
β''-$(BO)_2[YbCl_4(H_20)_2]$	Metallic
α-$(BO)_2[YbCl_4(H_20)_x]$	M-I at 210 K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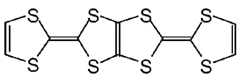
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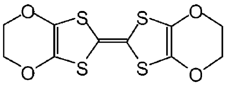
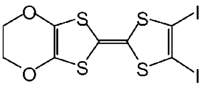

BO


DIEDO

In the search for a 4*f*-πhybrid system, we prepared several salts of π donors and stable complex anions, $[Ln(NCS)_6]^{3-}$ [2,3]. Some of them retain metallic conductivity at low temperatures for the first time as a 4*f*-π donor compound, while others are insulating or exhibit increasing resistivity at low temperature. (Table 1) The metallic behavior is observed for the salts of self-assembling donors, BO, TTP and DIEDO. In these cases, however, the anions are disordered. The large charge of the anions, referring to the repulsion between the anions, may prevent them from a well-organized structure.

In order to avoid such a situation, we are examining the conditions for the crystal growth. Simple ligands with bridging ability has been applied for this purpose. Reduction of the charge of the anions is also taken into account. In this way, we have obtained a new molecular metal, β''-$(BO)_2[YbCl_4(H_2O)_2]$, in which the Yb complex anion forms a supramolecular chain structure. The preparation and crystal structure of this salt is presented, together with those of the related material α-$(BO)_2[YbCl_4(H_2O)_x]$.

PREPARATION OF SAMPLES

All the crystals were grown by electrochemical oxidation of the donors in CH_2Cl_2 solutions. For the $[Ln(NCS)_6]$ salts, $[(n\text{-}C_4H_9)_4N]_3[Ln(NCS)_6]$ (Ln = Ho, Er, Yb, Y), prepared from $LnCl_3{\cdot}6H_2O$ and $[(n\text{-}C_4H_9)_4N]SCN$ in MeOH, was used. $YbCl_4^-$ anion was generated in a solution from $YbCl_3{\cdot}6H_2O$, by adding $[(n\text{-}C_4H_9)_4N]Cl$ or benzoic acid. The addition of $[(n\text{-}C_4H_9)_4N]Cl$ gave only the α-phase; β''-$(BO)_2[YbCl_4(H_2O)_2]$ crystals were obtained by use of benzoic acid. For the BO salts, the temperature was kept below 10 K during the crystal growth over a few days.

CRYSTAL STRUCTURE OF β''-$(BO)_2[YbCl_4(H_2O)_2]$

Figure 1 shows the crystal structure of β''-$(BO)_2[YbCl_4(H_2O)_2]$. Crystal data are, triclinic, space group $P\bar{1}$, $a = 7.161(2)$ Å, $b = 19.298(4)$ Å, $c = 6.167(1)$ Å, $\alpha = 97.69(1)$ °, $\beta = 102.71(1)$ °, $\gamma = 90.02(2)$ °, $V = 823.5(3)$ Å^3, $Z = 1$. The final R value of 0.089 was obtained for 4787 unique diffractions. The molecular packing in the conduction layers are the so-called β″-type, as is often found in BO compounds. The complex anions $[\mathrm{YbCl_4(H_2O)_2}]^-$ form a chain structure running along the *c*-direction. In the chain, the anions are linked to each other by double bridging, ···HO-Yb-Cl···HO-Yb-Cl···. The intermolecular Cl···O distance is 3.15 Å. This is the first example of an assembled rare-earth complex found in a molecular conductor, with a "polymeric" or "supramolecular" architecture. Unlike the $[\mathrm{Ln(NCS)_6}]^{3-}$ salts, the lower charge of the anion is considered to favor the anion-anion linkage.

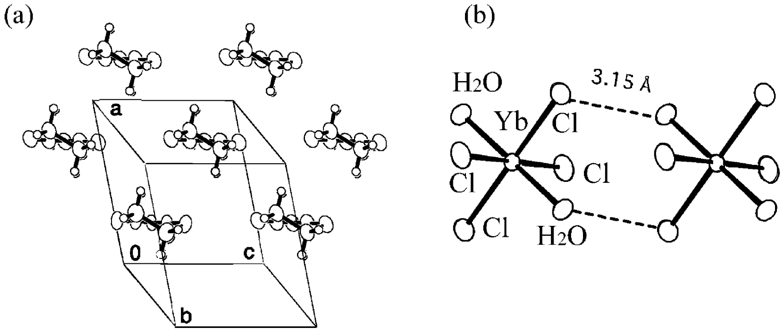


FIGURE 1 Crystal structure β″-$\mathrm{(BO)_2[YbCl_4(H_2O)_2]}$. (a) Donor Layer and (b) Anion-anion linkage

BEHAVIOR OF β″-$\mathrm{(BO)_2[YbCl_4(H_2O)_2]}$ CRYSTAL

Figure 2 (a) shows the temperature dependence of electric resistivity measured for crystals of β″-$\mathrm{(BO)_2[YbCl_4(H_2O)_2]}$ picked up from the same batch. One of the sample exhibited metallic conductivity over the

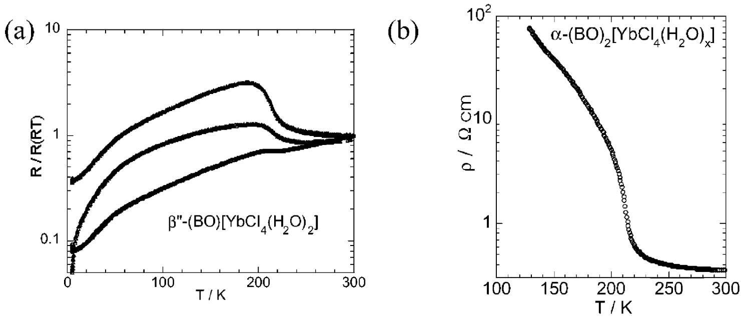


FIGURE 2 Resistivity of (a) β''- $(BO)_2[YbCl_4(H_2O)_2]$ samples, and (b) α- $(BO)_2[YbCl_4(H_2O)_x]$, plotted against temperature.

temperature range 4-300 K, except a small anomaly at 210 K. The anomaly appeared more obviously for the other samples. X-ray photographs of the samples with an appreciable anomaly shows that the crystals contain another polycrystalline material. It is also observed that a β''-$(BO)_2[YbCl_4(H_2O)_2]$ sample looses metallic behavior after keeping over one month, accompanied by a change in X-ray diffraction pattern.

From these observations, it is concluded that the β''-crystals gradually transforms into another phase, α-phase, when kept at room temperature. The β''-phase itself is metallic down to 4 K, whereas the α-phase undergoes a transition to insulator at 210 K.

The α-phase crystals can be directly obtained as mentioned above. Figure 2 (b) shows the temperature dependence of resistivity of an α-phase crystal. X-ray structure analysis shows that the α-phase, α-$(BO)_2[YbCl_4(H_2O)_x]$, has a herring-bone type donor packing (α-structure, Figure 3) and the anions are disordered. (The crystal data for the α-phase are, triclinic, space group $P\,\bar{1}$, $a = 8.392$ Å, $b = 10.162$ Å, $c = 20.165$ Å, $\alpha = 95.30°$, $\beta = 96.10°$, $\gamma = 89.80°$, $V = 1702.6$ Å^3, $Z = 2$.) It is known that this donor packing often exhibits a charge ordering transition[5], whereas the β''-packing stabilizes metallic state. This accounts for the present results.

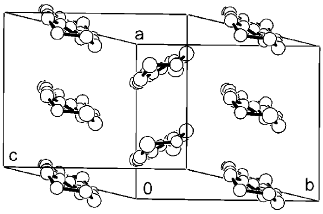


FIGURE 3 Donor packing in α-$(BO)_2[YbCl_4(H_2O)_x]$

The existence of the anion-anion linkage comes up to our expectation for the intermolecular couplings related to the 4*f* electrons. However, we have not yet obtained an indication such as magnetic ordering or field effect on the conductivity.

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