\( \pi-f \) Composite metals

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Abstract

Using the heavy rare-earth complex anions, \([\text{Ln(NCS)}_6]^{2-}\) (Ln = Ho, Er, Yb and Y), we have synthesized three series of metallic compounds, \((\text{BO})_x[\text{Ln(NCS)}_6]\), \((\text{TTP})_x[\text{Ln(NCS)}_6]\) (\(x = 8\)) and \((\text{DIEDO})_x[\text{Ln(NCS)}_6]\). The BO and TTP salts are metallic down to very low temperature, while the resistivity of the DIEDO salts increases below about 40 K. These are the first examples of stable metals based on organic \(\pi\)-donors and rare-earth 4f/ions.

Keywords: (Organic conductors based on radical cation salts, Transport measurements, conductivity, X-ray diffraction, Magnetic measurements)

1. Introduction

\(4f\) electrons of rare-earth ions have unique characters, such as very large anisotropic magnetic moments, as a result of the strong spin-orbit coupling and the high degeneracy due to strong correlation in a well-localized \(4f\) orbital. This feature is never found in 3d ions, organic \(\pi\) molecules nor the other systems. Thus, it is interesting to see what will occur when \(4f\) electrons are incorporated into a conduction \(\pi\) electron system. Imakubo et al. synthesized the first metallic examples using rare-earth chloride complexes [1]. Unfortunately, these compounds are not stable in air. On the other hand, stable heavy rare-earth complex anions, \([\text{Ln(NCS)}_6]^{2-}\) (Ln = Ho, Er, Yb or Y), were found to afford stable ET salts, \((\text{ET})_x[\text{Ln(NCS)}_6]\), \(\text{CH}_2\text{Cl}_2\) [2], by means of electrocrystallization in \(\text{CH}_2\text{Cl}_2\) solutions. These salts are insulators as a result of intradimer Coulomb repulsion and charge separation [2].

We have found that other \(\pi\)-donors, BO, TTP and DIEDO, form stable metallic salts with \([\text{Ln(NCS)}_6]^{2-}\), by a similar method. We report here the structures and physical properties of these novel \(f-\pi\) metals.

2. \((\text{BO})_x[\text{Ln(NCS)}_6] \) (\(x = 8\))

The donor BO provides many metallic compounds [3]. The BO salts of \([\text{Ln(NCS)}_6]^{2-}\) crystallize in a monoclinic form, with a strong disorder in the anion layers. Only the structure refinement of the BO layers was possible [4]. The BO molecules form a so-called \(\beta\)-structure (Fig. 1), like other conductive BO salts [3]. The salts retain metallic conductivity down to 1 K (Fig. 1), which is almost

![Fig. 1. Left: Packing of BO molecules viewed along the molecular long axis. Right: Resistivity of the Yb compound plotted against T.](image-url)
independent of rare-earth ion. No magnetic field effect on conductivity was found. As exemplified in Fig. 2, the \( f \) electrons exhibit magnetic susceptibility (\( \chi \)) of Curie-like behavior at high temperatures (> 100 K). The \( Y (f^{0}) \) compound shows Pauli-like behavior of \( \chi \) of \( \pi \) electrons. From the Curie constant of the Ho compound (\( f^{10}, J = 8, g = 5/4 \)), the composition was estimated as \( x = 8 \). The magnetic moment of the Ho ions shrinks at low temperatures. As pointed out in the case of the ET salts [2], it is most likely to attribute this to the crystal field effect.

![Fig. 2. \( \chi T \) of the Ho compound as a function of \( T \).](image)

3. (TTP)\(_{2}\)[Ln(NCS)\(_{3}\)] (\( x = 8 \))

TTP is also known to give metallic salts with various anions [5]. The TTP salts of [Ln(NCS)\(_{3}\)]\(^{3-}\) contain disorder in the anion layers, similarly to the BO case. The TTP molecules are alternatingly stacked along the \( a \) direction (Fig. 3) [6], like other TTP salts [5]. Though considerably affected by cracking, metallic conductivity was observed down to 1.7 K (Fig. 3). The magnetic properties are similar to those of the BO salts. The \( x \) value, ca. 8, was estimated from the high temperature Curie constant of \( 4f \) electrons.

![Fig. 3. Left: Packing of TTP molecules viewed along the molecular long axis. Right: Resistivity of the TTP salt plotted against \( T \).](image)

4. (DIEDO)\(_{2}\)[Ln(NCS)\(_{3}\)]

The most outstanding character of DIEDO [7] is the coordination ability of the iodine atoms to electro-negative atoms. In fact, short I–S contacts are formed between the donor and ligand, as shown in Fig. 4 [8]. The resistivity of the DIEDO salts gradually decreases with lowering temperature, forming broad minimum around 50-80 K, followed by steep increase below ca. 40 K (Fig. 5). This behavior in independent of the rare-earth ion, suggesting negligible \( \pi-f \) interactions inspite of the I–S contacts. The insulating behavior at low temperature is accompanied by no magnetic anomaly, indicating that this is neither a density wave nor a Mott transition, but a disorder effect.

![Fig. 4. Crystal structure of the DIEDO salt projected along the \( a \)-axis. The short I–S contacts are indicated by broken lines.](image)

![Fig. 5. Temperature dependence of resistivity of the DIEDO salt.](image)

In summary, the use of the self-assembling donors and [Ln(NCS)\(_{3}\)]\(^{3-}\) have afforded the first examples of stable \( \pi-f \) composite metals, though disorder is introduced in the [Ln(NCS)\(_{3}\)]\(^{3-}\) layers. To realize a \( \pi-f \) interplay, a more efficient medium for \( \pi-f \) interactions is desired.

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References

[4] The crystal data for the BO lattice of the Er compound are, space group \( Pm \), \( Z = 2 \) (for BO), \( a = 5.340(1), b = 32.758(7), c = 4.0439(7) \, \text{\AA}, \beta = 98.81(1)^\circ, V = 699.0(2) \, \text{\AA}^3 \). The final \( R \) values, \( R = 0.118; 0.155 \) were obtained for 2100 unique diffractions.
[6] The crystal data for the TTP lattice of the Y compound are, triclinic, space group \( P T \), \( Z = 2 \) (for TTP), \( a = 6.937(8), b = 16.92 (1), c = 6.390(3) \, \text{\AA}, \alpha = 100.35(5)^\circ, \beta = 100.40(6)^\circ, \gamma = 85.56(8)^\circ, V = 724(1) \, \text{\AA}^3 \). The final \( R \) values, \( R = 0.077; 0.085 \) were obtained for 3320 unique diffractions in the refinement of the TTP structure.
[8] The crystal data of (DIEDO)\(_{2}\)[Ho(NCS)\(_{3}\)]\(_{2}\) are, orthorhombic, space group \( Cmca \), \( Z = 4, a = 7.21(4), b = 13.295(8), c = 34.85(3) \, \text{\AA}, V = 3339(7) \, \text{\AA}^3 \). The \( R \) values, \( R = 0.133; 0.168 \) were obtained for 2025 unique diffractions, with 1/3 occupancy of the anion site.