

Magnetism of Metallic Molecular Crystals with Rare-Earth Complex Anions

Takeo Otsuka,* HengBo Cui,* Akiko Kobayashi*,¹ Yohji Misaki,† and Hayao Kobayashi‡

*Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan;

†Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-8501, Japan;

and ‡Institute for Molecular Science, Okazaki 444-8585, Japan

Received December 17, 2001; in revised form March 28, 2002; accepted April 2, 2002

Novel molecular metal salts comprising an organic donor 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and lanthanide nitrate complex anions $[M(\text{NO}_3)_y]^{-(y-3)}$ were synthesized as the composition $(\text{BDT-TTP})_x[M(\text{NO}_3)_y]$. Attempts on X-ray crystal structure analyses gave rise to a detection of two polymorphs. One of the polymorph, which had a composition of $(\text{BDT-TTP})_5[M(\text{NO}_3)_5]$ for $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd , was analyzed in detail. Five crystallographically independent BDT-TTP molecules were stacked face-to-face to form a pentad, which was jointed one after another by crystallographic inversion centers into a one-dimensional column. The calculated overlap integrals of the highest occupied molecular orbitals revealed that not only intracolumnar orbital overlaps but also transverse intermolecular interactions were important in the electronic band formation. Consequently, the system has two-dimensional Fermi surfaces that explain the stable metallic states. Magnetic measurements on the four salts, with $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd , showed Curie paramagnetic moments on rare-earth ions which were superimposed on the Pauli paramagnetism of metallic π electrons. Especially, the magnetic susceptibility of the isolated Eu^{3+} ion was written using Curie term and extremely large Van Vleck term. © 2002

Elsevier Science (USA)

INTRODUCTION

Lately, the interdisciplinary studies on conductivity and magnetism of the molecular crystals have attracted much interest (1–3). Most of the conductive molecular crystals are substantially the salts of a donor or an acceptor, and salts of organic electronic donor/acceptor with magnetic counter ion have been examined recently. Accordingly, many molecular compounds that consist of organic donors and paramagnetic anions are studied (4), some of which

show both paramagnetism and high conductivity, or metallic behavior, or even superconductivity, simultaneously (1). In some complexes, moreover, the conducting electrons were found to be coupled with the localized unpaired electrons, resulting in a wide variety of cooperative phenomena (5–7). These materials are called ‘ π - d systems’ as they are consisted of delocalized π and localized d electron systems, where novel transport phenomena such as a superconductor-to-insulator transition, a successive transitions from paramagnetic metal to antiferromagnetic metal to antiferromagnetic superconductor, and a magnetic-field-induced superconducting transition have been recently discovered (8, 9). Compared with the d block elements, the f block elements, namely lanthanide, will show still more unique electronic properties because of their peculiar magnetic properties of its f orbital spins, and large magnetic moments. Since the f electrons are well shielded by outer closed-shell electrons, the spin-orbit coupling is considered to play essential role in their magnetic properties. Hence, their total magnetic moments, J , are expressed as $J = L + S$, where L denotes an angular moment and S a spin moment. The ground states of these ions are $J = L \pm S$, where the sign depends on the number of f electrons ($J = L - S$ for lighter than Gd , $J = L + S$ for heavier than Gd). Though the molecular metals incorporating localized f electrons are still very limited (10), the study of the ‘ π - f system’ will undoubtedly expand the range of functional molecular materials. One of the reasons why these materials are still rare is in the fact that the lanthanides tend to form complex anions which are much larger in size and charge compared with the d block ions so that the systems with good crystallinity is very rare. Here we focus on the lanthanide nitrate complex anions, $[M(\text{NO}_3)_y]$ ($y = 5$ or 6), which have relatively smaller volume in anionic lanthanide complexes and show favorable crystallinity with a number of organic cations (11). In the course of our pursuance of complex salts of organic

¹To whom correspondence should be addressed. Fax: +81-3-5841-4417. E-mail: akiko@chem.s.u-tokyo.ac.jp.

donors and lanthanide-centered anions, an organic donor with a highly extended π orbital, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, abbreviated as BDT-TTP (Fig. 1), was found to give fairly fine crystalline salts with lanthanide nitrato complexes. In this paper, the crystal structures, electronic conductivity and magnetic properties of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ ($M = (\text{La}), (\text{Ce}), (\text{Pr}), (\text{Sm}), (\text{Eu}), (\text{Nd}), (\text{Gd})$), are reported.

EXPERIMENTAL

Synthesis and X-Ray Crystal Structure Analysis

BDT-TTP were prepared according to the literature method (12). The crystals of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ were prepared electrochemically applying the constant current of $0.1 \mu\text{A}$ for 1 or 2 weeks (electrodes: ϕ 1 mm platinum wires, supporting electrolytes: $(n\text{-Bu}_4\text{N})_{y-3}[\text{M}(\text{NO}_3)_y]$ ($y = 5$ or 6)).

The X-ray reflection data of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ were collected on a RIGAKU MERCURY CCD auto-crystal structure analysis system. The composition of the crystals of $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd were determined as $x = y = 5$, and they were isomorphous to each other. Only unit-cell parameters refinement was performed for $M = \text{Ce}$ crystals, which was found to be anisomorphous to the former systems. Both systems have triclinic unit cells. The

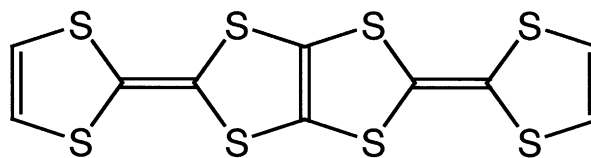


FIG. 1. A schematic diagram of a BDT-TTP molecule.

harvested crystals of $M = \text{Pr}$ were found to be a mixture of these two polymorphic systems. Crystal data and experimental conditions are listed in Table 1.

Physical Properties

The four-probe resistivity measurements of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ were performed along the long axis of the rectangular platelet samples applying *ac* technique from room temperature down to 4.2 K.

The isotropic dc magnetic susceptibilities were measured using polycrystalline samples in the temperature range of 2–300 K on a SQUID magnetometer MPMS7XL (Quantum Design). The typical mass of the samples was approx. 6 mg. The paramagnetic susceptibilities, χ_p , were calculated by subtracting the diamagnetic susceptibilities, which were obtained assuming Pascal's law in whole temperature range.

TABLE 1
Crystal Data and Experimental Conditions for $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ Salts

	$M = \text{Ce}$	$M = \text{Nd}$	$M = \text{Sm}$	$M = \text{Eu}$	$M = \text{Gd}$
Chemical formula	$x \approx 7, y \approx 6$	$x = y = 5$	$x = y = 5$	$x = y = 5$	$x = y = 5$
Temperature (K)	298	298	298	298	298
Formula weight	1671.29	2357.61	2363.73	2365.34	2370.62
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.18	11.56	11.56	11.56	11.60
b (Å)	13.61	19.53	19.55	19.54	19.63
c (Å)	20.77	21.95	21.96	21.94	22.06
α (deg)	75.35	68.96	68.86	68.86	68.83
β (deg)	88.73	76.57	76.66	76.70	76.70
γ (deg)	67.08	78.85	78.75	78.77	79.097
V (Å ³)	2971	4464	4469	4462	4528
Z	2	2	2	2	2
d (g cm ⁻³)	1.786	1.754	1.756	1.760	1.738
Sample dimensions (mm)	$0.2 \times 0.2 \times 0.03$	$0.3 \times 0.2 \times 0.03$	$0.3 \times 0.2 \times 0.03$	$0.5 \times 0.2 \times 0.03$	$0.3 \times 0.2 \times 0.03$
Radiation			MoK α		
Data collection			A CCD detector (RIGAKU MERCURY)		
μ (cm ⁻¹)	14.35	15.74	16.50	16.95	17.13
$2\theta_{\text{max}}$ (deg)	55.0	47.6	47.6	55.0	47.6
Reflcn. collected	21883	25410	26325	37457	26468
Reflcn. unique	13852	13482	13532	19947	13573
R	0.128	0.088	0.085	0.089	0.077
R_w	0.180	0.110	0.114	0.108	0.101
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$

RESULTS AND DISCUSSION

Crystal Structures of $(BDT-TTP)_x[M(NO_3)_y]$ and Band Structures

The analyses of the crystal structures of the $(BDT-TTP)_x[M(NO_3)_y]$ salts were attempted on all samples, and two compositions of polymorph were identified: $(BDT-TTP)_x[M(NO_3)_6]$, $x \approx 7$ for $M = Ce$ and Pr and $(BDT-TTP)_5[M(NO_3)_5]$ for $M = Pr, Nd, Sm, Eu$ and Gd . The samples of former polymorph were relatively inferior in quality to the ones of latter, so the crystal structure analysis was not made satisfactorily. The samples of latter polymorph showed good quality, except the salt of $M = Pr$ which was grown as a mixture with the former polymorph. Then, we concentrate our structural discussion below on the latter polymorph with $M = Nd, Sm, Eu$ and Gd .

The X-ray crystal structure analyses of all crystals of $M = Nd, Sm, Eu$ and Gd were performed and these crystals were found to be isomorphous. Figure 2a shows the unit cell of $(BDT-TTP)_5[M(NO_3)_5]$ ($M = Eu$ is chosen as an arbitrary example). One $[M(NO_3)_5]^{2-}$ anion and five BDT-TTP donor molecules are crystallographically independent in the lattice.

The lanthanide ions (M^{3+}) are surrounded approximately in trigonal bipyramidal manner by NO_3^- ions and consequently deca-*O*-coordinated by five bidentated NO_3^- ligands: $M-O$ distances = 2.46–2.54 Å (Eu) and $\angle OMO = 49.7$ – 52.5° (Eu). This is the first example of deca-*O*-coordinated trigonal bipyramidal penta-nitrato lanthanide complex materials because all penta-nitrato lanthanide complexes ever reported have square-pyramidal coordination geometry (11). Owing to the 5:1 stoichiometry of donors and anions, the highest occupied molecular orbital (HOMO) of BDT-TTP forms a 4/5-filled band.

The five BDT-TTP molecules, as indexed A–E in Fig. 2b, are stacked face-to-face right above to form a columnar pentad as shown in Fig. 2a. Two pentads are joined with each other by a crystallographic inversion center as shown in Fig. 2b. A periodic unit comprises these stacking 10 BDT-TTP molecules, and causes an infinite one-dimensional columnar structure of BDT-TTP. The stackings of two BDT-TTPs across inversion centers (namely E–E' and A–A') have slips (≈ 0.8 Å) along the molecular long axis. Overlap integral calculation on the basis of extended Hückel *MO* indicates that these slips have little influence on the magnitude of overlap integrals. It should be also pointed out that the transverse intermolecular overlaps of orbitals are comparable to the intracolumnar ones (see Fig. 2c). The 10 energy dispersion curves obtained by tight-binding band calculation are shown in Fig. 3a, which gave intricate two-dimensional Fermi surfaces, as depicted in Fig. 3b.

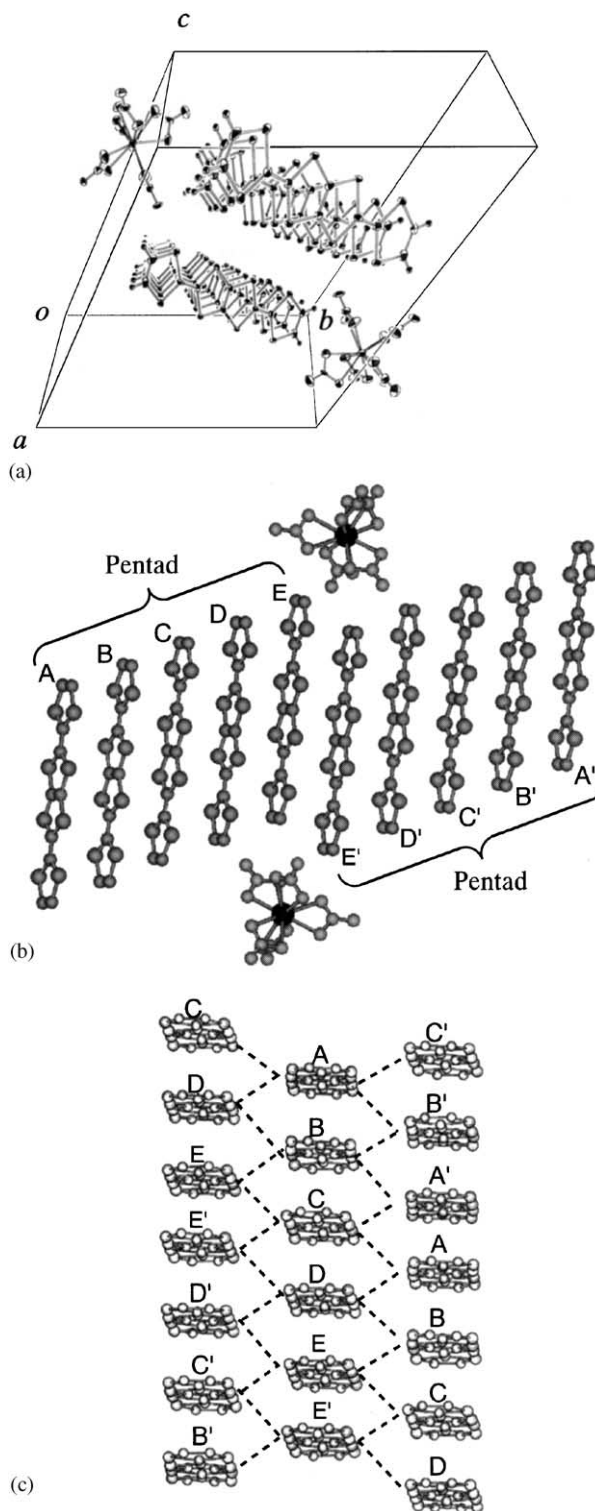


FIG. 2. Crystal structure of $(BDT-TTP)_5[M(NO_3)_5]$. (a) A view of a unit cell. (b) A side view of a repeat unit of a donor column. (c) A projection perpendicular to the conduction plane. Broken lines represent the transverse intermolecular S...S contacts which are shorter than the sum of van der Waals radii.

Electrical Conductivity

The room-temperature conductivities were 1×10^2 ($M = \text{Ce}$), 3×10^2 ($M = \text{Pr}$), 1×10^2 ($M = \text{Nd}$), 5×10^1 ($M = \text{Sm}$), 7×10^1 ($M = \text{Eu}$) and, $4 \times 10^1 \text{ S cm}^{-1}$ ($M = \text{Gd}$). The sample of $M = \text{Pr}$ belongs to a polymorph of the $M = \text{Nd}$ – Gd group.

Figure 4 shows the temperature dependencies of the resistivity of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ salts. Stable metallic behaviors are consistent with two-dimensional electronic band structures (see Fig. 3).

Magnetic Behavior of $(\text{BDT-TTP})_5[\text{M}(\text{NO}_3)_5]$ Salts ($M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd)

Due to its uncertain composition of $M = \text{Ce}$ salt, our magnetic measurements are restricted to $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd salts. The open circles in Fig. 5a show the

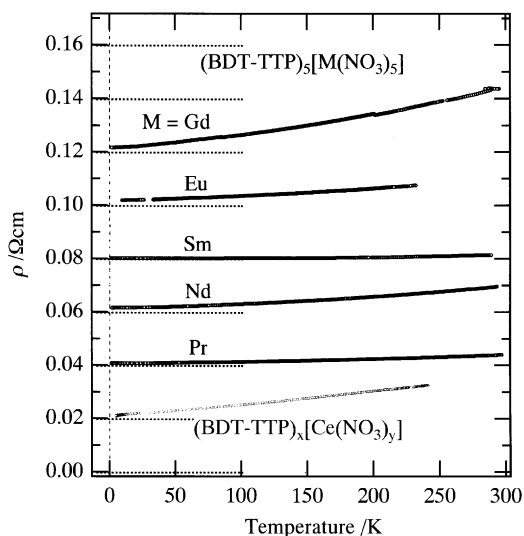


FIG. 4. The temperature dependences of the resistivities of $(\text{BDT-TTP})_x[\text{M}(\text{NO}_3)_y]$ along the directions parallel (ρ_{\parallel}) to the ab plane.

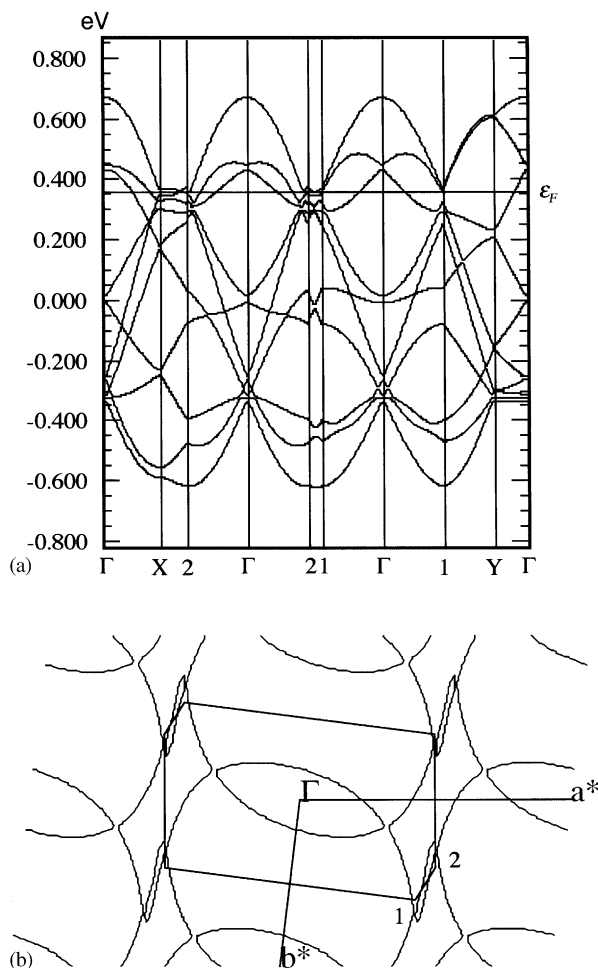


FIG. 3. The calculated band structure and Fermi surface of $(\text{BDT-TTP})_5[\text{Eu}(\text{NO}_3)_5]$. (a) Energy dispersion curves. (b) First Brillouin zone and Fermi surfaces.

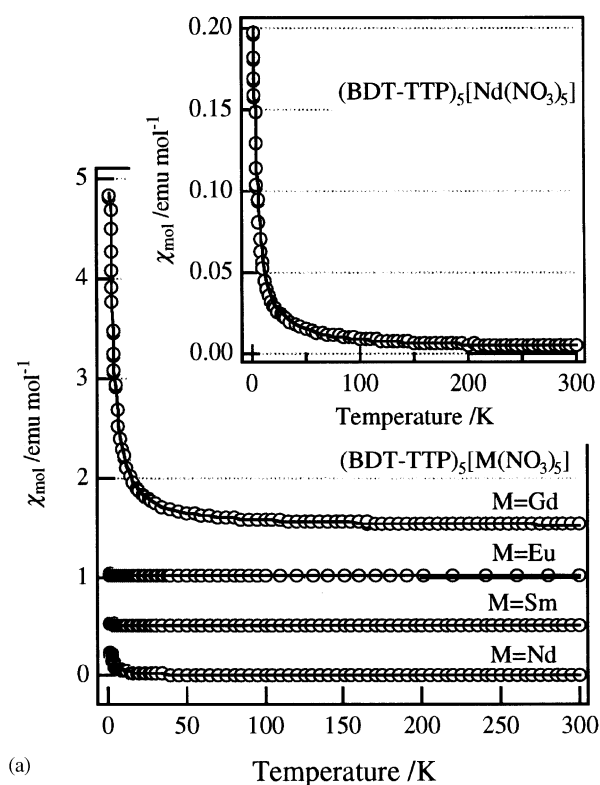
temperature dependence of the paramagnetic susceptibilities χ_p of $(\text{BDT-TTP})_5[\text{M}(\text{NO}_3)_5]$ salts with $M = \text{Nd}(4f^4)$, $\text{Sm}(4f^5)$, $\text{Eu}(4f^6)$ and $\text{Gd}(4f^7)$.

$M = \text{Nd}$: The total magnetic moment J of Nd^{3+} ion is $\frac{9}{2}$ ($S = \frac{3}{2}$ and $L = 6$). The magnetic behavior of this salt (Fig. 5a) shows a sharp increase in the low-temperature region. This behavior of the χ_p value seems to follow Curie–Weiss law in whole temperature range.

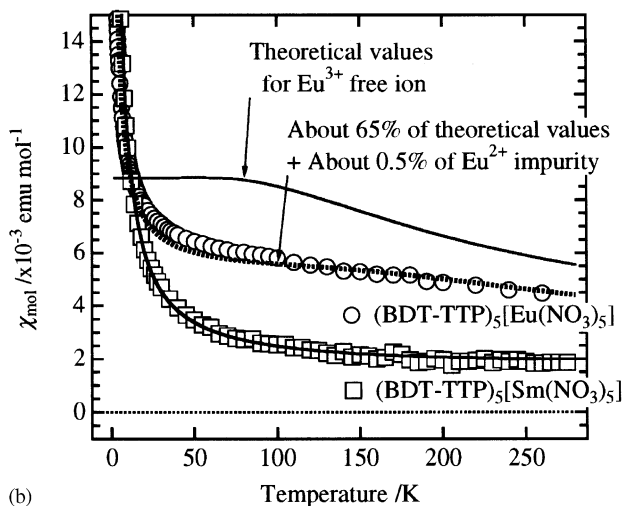
The solid line in Fig. 5a denotes the best-fit curve to Curie–Weiss law, with following parameters: Curie constant $C = 0.63 \text{ emu K mol}^{-1}$ and Weiss constant $\theta = -1.28 \text{ K}$. The obtained value $C = 0.63$ coincides approximately to the value calculated using $J = \frac{9}{2}$, $S = \frac{3}{2}$ and $L = 6$ (13).

$M = \text{Gd}$: This salt has the largest magnetic moment, originated from Gd^{3+} ion. Its magnetic behavior, however, is rather straightforward because the Gd^{3+} ion has no orbital angular momentum ($L = 0$). Then, total magnetic moment $J = S = \frac{7}{2}$ on Gd^{3+} ion shows a Curie-like temperature dependence. The experimental data were fitted to the Curie–Weiss law, and the results were plotted in Fig. 5(a) as a solid line with the parameters $C = 7.607 \text{ emu K mol}^{-1}$ and $\theta = -0.37 \text{ K}$. The fitted value of Curie constant is also consistent with the quantum moments of $J = S = \frac{7}{2}$. In spite of the large moment of Gd^{3+} ion, however, the quite small value of θ means that there is no evidence of any interaction between the local magnetic moment of f electrons and the conducting π electrons.

$M = \text{Eu}$ and Sm : Magnetic susceptibilities of these two salts were quite small compared with the Nd or Gd salts, so the experimental data of these two salts were enlarged in Fig. 5b. The value of χ_p increases slightly and continuously



(a)



(b)

FIG. 5. The magnetic susceptibilities of $(\text{BDT-TTP})_5[\text{M}(\text{NO}_3)_5]$. (a) Plots for $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd . Zero levels of the plots are shifted (denoted as thick solid lines) for clarity. The expanded plot for $M = \text{Nd}$ is insetted. (b) Expanded plots for $M = \text{Sm}$ and Eu .

with decreasing temperature down to 50 K. After passing a faint plateau, it turns to increase again that seems inversely proportional to the temperature.

Eu^{3+} ion possesses six unpaired electrons (spin and orbital moments $S=3$ and $L=3$) and the total magnetic

moment $J = L - S = 0$. The slight change of the χ_p value in the high-temperature range is thought to be due to the Pauli paramagnetism of metallic π electrons at first sight. The susceptibility value, however, exceeds $1 \times 10^{-3} \text{ emu mol}^{-1}$, which is too large for the Pauli paramagnetism of the ordinal organic conductor. A contribution from Eu^{3+} ion should be taken into account. The energy levels of the lowest $J = 0$ state and the excited $J = 1$ state are very close to each other for Eu^{3+} ion, thereby the excited state can be easily accessed by an external magnetic field. In this case, a second-order mixture between the ground state and the excited states, namely the Van Vleck paramagnetic compensation term, becomes important. In addition, a thermal excitation effect is not negligible particularly for Eu^{3+} ion. Consequently, the magnetic susceptibility of the isolated Eu^{3+} ion is written using Curie term and Van Vleck term as follows (14):

$$\chi_{\text{Eu}} = \frac{\sum_J (2J + 1) \exp(-E_J/k_B T) [\chi_{\text{Curie}} + \chi_{\text{vanVleck}}]}{\sum_J (2J + 1) \exp(-E_J/k_B T)},$$

where

$$\chi_{\text{Curie}} = \frac{N_A g^2 \mu_B^2 J(J + 1)}{3k_B T},$$

$$\chi_{\text{Van Vleck}} = \frac{N_A \mu_B^2}{6(2J + 1)} \left[\frac{F(J + 1)}{E_{J+1} - E_J} - \frac{F(J)}{E_J - E_{J-1}} \right],$$

$$\left(F(J) = \frac{[(S + L + 1)^2 - J^2][J^2 - (S - L)^2]}{J} \right),$$

with N_A being the Avogadro number, k_B the Boltzmann constant, μ_B a Bohr magneton, g an effective g -factor. If the ion is well isolated so that the Landé interval rule is satisfied, the difference of the energy $E_J - E_{J-1}$ is presented as $E_J - E_{J-1} = \lambda J$, where the symbol λ is a spin-orbit coupling constant and given as $\lambda/k_B = 337 \text{ K}$ for an isolated Eu^{3+} ion. The calculated χ_{Eu} (dotted line in Fig. 5b reproduces the tendency of the experimental data, but only qualitatively. The experimental value is approximately 65% of the calculated value. The cause of this considerable difference cannot be explicitly reasoned now, but it may be explained as the effect of crystal field. In most of the lanthanide complexes, the interaction between $4f$ electrons and the crystal field is very small, so the crystal field hardly affects the paramagnetic susceptibility of the $4f$ electrons. In the case of $M = \text{Eu}^{3+}$ salt, however, the effect of the crystal field, namely Stark effect, is no longer negligible because (1) the Eu^{3+} ion in the $(\text{BDT-TTP})_5[\text{Eu}(\text{NO}_3)_5]$ salt is deca- O -coordinated, which causes a crystal field which is not negligible, (2) the difference between the ground state and the first excited state of the

Russel–Saunders levels E_J is extremely small ($E_1 - E_0 = \lambda/k_B = 337\text{ K}$) and (3) the Curie contribution of the ground state ($J = 0$) is explicitly zero. The sharp increase of the χ_p value in the low-temperature range ($T < 50\text{ K}$) is fitted to the Curie rule. Since Eu^{3+} ion has a tendency being reduced to Eu^{2+} , it may be possible that impurity Eu^{2+} is included in the lattice. The 0.5% contamination of Eu^{2+} ($S = \frac{7}{2}, L = 0$) ion in place of Eu^{3+} ion explains the Curie tail of the magnetic susceptibility satisfactorily. Thus, $(\text{BDT-TTP})_5[\text{Eu}(\text{NO}_3)_5]$ is revealed to be a very rare organic metal exhibiting huge Van Vleck paramagnetism, which is never expected in π - d conducting systems (15).

$(\text{BDT-TTP})_5[\text{Sm}(\text{NO}_3)_5]$ showed almost temperature-independent paramagnetism ($\approx 1.8 \times 10^{-3} \text{ emu mol}^{-1}$) at high-temperature region. Since the temperature-independent paramagnetic susceptibility of π metal electrons is about $5 \times 10^{-4} \text{ emu mol}^{-1}$ in usual organic conductors, the main part of the paramagnetic susceptibility of about $1.3 \times 10^{-3} \text{ emu mol}$ will be ascribed to $[\text{Sm}(\text{NO}_3)_5]^{2-}$ ions. Similar to Eu^{3+} , the Van Vleck paramagnetism is expected also in Sm^{3+} , though it is not so large: the calculated Van Vleck paramagnetic susceptibility was $1.3 \times 10^{-3} \text{ emu mol}^{-1}$ at room temperature ($\lambda/k_B = 348\text{ K}$), which agrees well with the expected value. At first sight, very weak Curie behavior is peculiar because Sm^{3+} free ion ($4f^5$) is expected to be paramagnetic ($S = \frac{5}{2}, L = 5, J = L - S = \frac{5}{2}$). However, this is reasonable because g -factor of Sm^{3+} is very small ($g = \frac{3}{2} + [S(S+1) - L(L+1)]/2J(J+1) = 0.286$). By subtracting the contributions from Van Vleck paramagnetism and Curie term, the paramagnetic susceptibility of π metal electrons is estimated to be $5.0 \times 10^{-4} \text{ emu mol}^{-1}$.

CONCLUSION

We succeeded in the development of a new series of metallic molecular crystals, $(\text{BDT-TTP})_x[M(\text{NO}_3)_y]$ salts, and crystal structure analyses were successfully made for the lanthanoids of $J = L - S$ group, i.e., $M = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd . To our knowledge, these are the first example of complete structure analysis on the metallic molecular materials coexistent with a magnetic rare-earth complex anions. These four salts were determined to be isomorphous. Electric and magnetic measurements clarify the crystal structures and electrical and magnetic behaviors of π - f conducting systems, $(\text{BDT-TTP})_5[M(\text{NO}_3)_5]$ ($x = y = 5$). In the case of $M = \text{Eu}$ and Sm , the weakly temperature-dependent large paramagnetic susceptibilities and stable metallic state of $(\text{BDT-TTP})_5[M(\text{NO}_3)_5]$ suggest these systems to be π metal systems exhibiting unique Van Vleck paramagnetism. Contrary to the widely accepted image of shielded f orbitals, the susceptibility of $(\text{BDT-}$

$\text{TTP})_5[\text{Eu}(\text{NO}_3)_5]$ suggests the importance of the crystal field effect on the magnetism of the complexes.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

1. M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. M. Caufield, J. Singleton, L. Ducasse, and P. Guionneau, *J. Am. Chem. Soc.* **117**, 12,209 (1995).
2. H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe, and P. Cassoux, *J. Am. Chem. Soc.* **118**, 368 (1996).
3. E. Coronado, J. R. Galán-Mascars, C. J. Gomes-Garcia, V. Laukhin, *Nature* **408**, 447 (2000).
4. H. Kobayashi, A. Kobayashi, and P. Cassoux, *Chem. Soc. Rev.* **29**, 325 (2000).
5. E. Ojima, H. Fujiwara, K. Kato, H. Kobayashi, H. Tanaka, A. Kobayashi, M. Tokumoto, and P. Cassoux, *J. Am. Chem. Soc.* **121**, 5581 (1999); H. Fujiwara, E. Ojima, Y. Nakazawa, B. Zh. Narymbetov, K. Kato, H. Kobayashi, A. Kobayashi, M. Tokumoto, and P. Cassoux, *J. Am. Chem. Soc.* **123**, 306 (2001).
6. T. Otsuka, A. Kobayashi, Y. Miyamoto, J. Kiuchi, N. Wada, E. Ojima, F. Fujiwara, and H. Kobayashi, *Chem. Lett.* 732–733 (2000); T. Otsuka, A. Kobayashi, and Y. Miyamoto, J. Kiuchi, S. Nakamura, N. Wada, E. Fujiwara, H. Fujiwara, and H. Kobayashi, *J. Solid State Chem.* **159**, 407 (2001).
7. H. Kobayashi, A. Sato, E. Arai, H. Akutsu, A. Kobayashi, and P. Cassoux, *J. Am. Chem. Soc.* **119**, 12392 (1997); A. Sato, E. Ojima, H. Akutsu, Y. Nakazawa, H. Kobayashi, H. Tanaka, A. Kobayashi, and P. Cassoux, *Chem. Lett.* 673 (1998).
8. H. Tanaka, H. Kobayashi, A. Kobayashi, and P. Cassoux, *Adv. Mater.* **12**, 1685 (2000).
9. S. Uji, H. Shinagawa, T. Terashima, C. Terakura, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, *Nature* **410**, 908 (2001).
10. T. Imakubo, H. Sawa, H. Tajima, and R. Kato, *Synth. Met.* **86**, 2047 (1997); M. Tamura, F. Matsuzaki, Y. Nishio, K. Kajita, T. Kitazawa, H. Mori, and S. Tanaka, *Synth. Met.* **102**, 1716 (1999); O. A. Dyachenko, O. N. Kazheva, V. V. Gritsenko, N. D. Kushch, *Synth. Met.* **120**, 1017 (2001).
11. H. Jing, X. Wang, Z. Hou, S. Chen, and D. Li, *Polyhedron* **13**, 1035 (1994); I. M. Walker, and D. H. Weeden, *Inorg. Chem.* **12**, 772 (1973).
12. Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe, and M. Shiro, *Chem. Lett.* 1337 (1993).
13. L. Carlin, "Magnetochemistry." Springer-Verlag, Berlin Heidelberg, 1986.
14. J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities." Oxford University Press, Oxford, 1931.
15. To our best knowledge, $(\text{BDT-TTP})_5[\text{Eu}(\text{NO}_3)_5]$ is the first example of organic metal in which Van Vleck paramagnetism was clearly observed.