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Crystal Structure and Magnetic Properties of Organic Radical Cation Salt, α-(Benzo[1,2-*d*:4,5-*d*′]bis[1,3,2]dithiazole)$_2$ReBr$_6$

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A new molecule-based magnet, α-(benzo[1,2-*d*:4,5-*d*′]bis-[1,3,2]dithiazole (BBDTA))$_2$ReBr$_6$, comprised a one-dimensional network composed of an alternative alignment of BBDTA$^+$ ($S = 1/2$) and ReBr$_6^{2-}$ ($S = 3/2$) and an $S = 1/2$ regular chain network of the other BBDTA$^+$. This material became a ferromagnet below 12.2 K. The magnetization curve showed complex field dependence, which might be related to the orientation of the one-dimensional alternative network in its crystal.

Cyclic thiazyl radicals exhibit strong intermolecular interactions via the characteristic S···N and/or S···S contacts between molecules and easily form multi-dimensional networks in the solid state. Magnetic ordering,[1] room-temperature magnetic bistability,[2] photoinduced phase transition,[3] metallic conduction,[4] negative resistance,[5] etc. have been reported in materials composed of these radicals, which have resulted in their attracting a great deal of interest as building blocks of functional molecular materials. We systematically investigated the crystal structure and magnetic properties of the monocation salts of a cyclic thiazyl radical, BBDTA (=benzo[1,2-*d*:4,5-*d*′]bis[1,3,2]-dithiazole; Chart 1), with various diamagnetic anions to identify new magnetic materials having higher magnetic transition temperatures.[6] Recently, we reported a ferrimagnet, comprising the monocation, BBDTA$^+$ ($S = 1/2$), and a paramagnetic anion, FeCl$_4^-$ ($S = 5/2$), which had a relatively high transition temperature (T_c) of 44 K,[7] as compared to other molecule-based ferromagnetic materials. Thus, the combination of BBDTA$^+$ and various paramagnetic anions ($S > 1/2$) may yield high-T_c ferrimagnetic materials.

In the present study, we report a novel molecule-based magnet, BBDTA$_2$ReBr$_6$. It has been reported that Re(IV) compounds have a spin quantum number of $S = 3/2$ and exhibit a remarkable spin delocalization from the metal atom to the ligands.[8] Such characteristics may result in strong antiferromagnetic interactions between BBDTA$^+$ ($S = 1/2$) and ReBr$_6^{2-}$ ($S = 3/2$) and in ferrimagnetic spin alignment at higher temperatures. Herein, we describe the crystal structure and magnetic properties of the α phase of this salt.

Figure 1 shows the crystal structure of α-BBDTA$_2$ReBr$_6$ at 180 K.[9] The two BBDTA$^+$ cations and one octahedral ReBr$_6^{2-}$ anion were crystallographically independent.[10] Figure 1a shows the projection drawing of the *ab* plane from the c^* axis direction. The two types of BBDTA$^+$ cations were labeled as cation A, whose molecular plane was inclined to the *ab* plane, and cation B, which was parallel to the *ab* plane. Cation A was regularly aligned along the *c* axis and formed a one-dimensional network via the short intermolecular interatomic contact of S···S (3.535(2) Å), as shown in Figure 1b. We estimated the intermolecular overlap integrals in the nearest neighboring A cations, based on the singly occupied molecular orbital (SOMO) obtained using the extended Hückel method.[11] The value of the intermolecular overlap integral thus obtained was large (1.01×10^{-2}), suggesting a strong antiferromagnetic correlation between the A cations. Cation B aligned alternatively with the anion ReBr$_6^{2-}$ toward the [110] direction, as shown in Figure 1a. This molecular alignment may be governed by the Coulombic interaction between the anion and the cation. In this crystal, the symmetry operation of the *c*-glide plane perpendic-

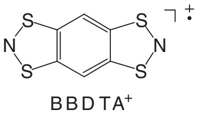

Chart 1.

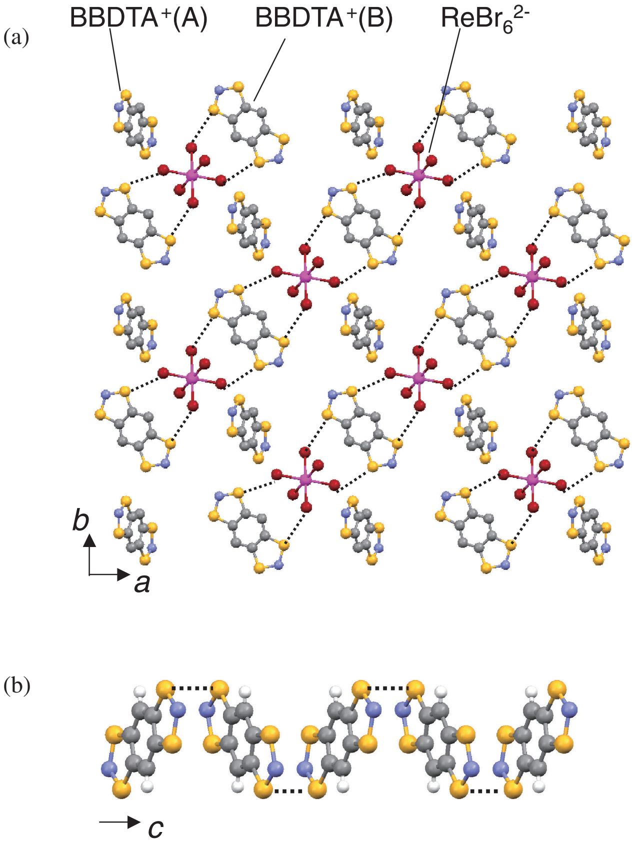

Figure 1. Crystal structure of α-BBDTA$_2$ReBr$_6$ at 180 K. (a) Molecular alignment onto the *ab* plane and (b) molecular alignment of cation A along the *c* axis. Dotted lines indicate short interatomic distances.

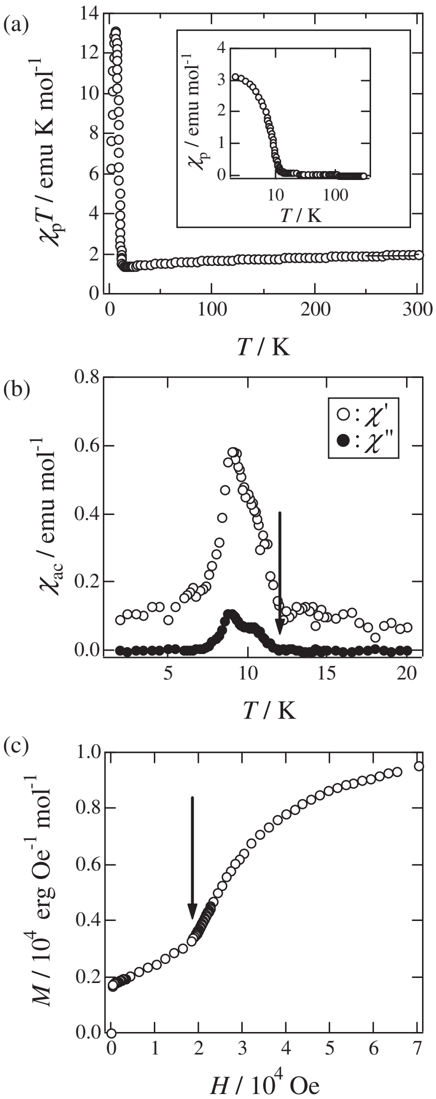

Figure 2. Magnetic properties of α-BBDTA$_2$ReBr$_6$. (a) Temperature dependence of the product of the paramagnetic susceptibilities and temperature, χ_pT. The solid line in the range of 250–300 K shows the theoretical curve of the Curie–Weiss law. (Inset) Temperature dependence of the paramagnetic susceptibility. (b) Temperature dependence of the ac susceptibilities (χ': in-plane, χ'': out-of-plane). (c) A magnetization curve at 2 K.

ular to the *b* axis also resulted in an alternative alignment of the cation B and ReBr$_6{}^{2-}$ toward the $[\bar{1}10]$ direction. Cation B had no short intermolecular contacts with the other BBDTA$^+$ cations; however, there were close interatomic S···Br contacts between cation B and ReBr$_6{}^{2-}$ (3.5169(18) and 3.533(2) Å). These findings suggest that the interatomic contacts produce antiferromagnetic interactions in cation B and ReBr$_6{}^{2-}$, which are favorable for realizing ferrimagnetic properties. The Coulombic interaction works on alternative alignments of magnetic species with different spin multiplicities.

Figure 2 shows the magnetic properties of α-BBDTA$_2$ReBr$_6$.[9] We adopted BBDTA$_2$ReBr$_6$ as the molar unit. Figure 2a shows the χ_pT vs. T plots of this material. The χ_pT value at 300 K was 1.84 emu K mol^{-1}, which is smaller than the theoretical value of 2.35 emu K mol^{-1}.[12] The theoretical value was estimated assuming that no magnetic interaction existed between 2 mol of $S = 1/2$ ($g = 2.00$) spins and 1 mol of $S = 3/2$ ($g = 1.85$ for Re(IV)) spins,[13] which indicates the dominance of intermolecular antiferromagnetic interactions between their magnetic ions. As the temperature decreased from 300 K, χ_pT decreased gradually; the minimum value (1.38 emu K mol^{-1}) was observed at 18 K. Below 18 K, the value of χ_pT increased with decreasing temperature; the maximum value (13.1 emu K mol^{-1}) was observed at 6 K. Data in the range of 250–300 K were fitted according to the Curie–Weiss law,[12] with $C = 2.29$ emu K mol^{-1} and $\theta = -51$ K, where C and θ were the Curie and Weiss constants, respectively. It has been difficult to estimate the magnetic exchange coupling constants of this material because a Re(IV) compound has a large zero-field splitting constant of $|D|/k_B \approx 50$ K[13] and there are weak interchain magnetic interactions between cation A chains and the alternative networks. The inset of Figure 2a shows χ_p vs. T plots. The χ_p value was found to increase rapidly around 10 K. Figure 2b shows the temperature dependence of the ac susceptibilities (χ': in-plane, χ'': out-of-plane) for the same sample at lower temperatures. The plots of χ'' showed an anomaly below 12.2 K; a rapid increase in χ' indicates a ferromagnetic ordering at this temperature. The magnetic transition temperature of this material is relatively low, as compared to that of the several high-T_c molecule-based magnets with organic radicals.[1,14]

This material exhibited complex field dependence of magnetization. Figure 2c depicts the magnetization curve for α-BBDTA$_2$ReBr$_6$ at 2 K. The magnetization value increased abruptly when the magnetic field was considerably weak and then gradually increased; such behavior is typical of ferromagnetic materials. The spontaneous magnetization value was estimated to be 1720 erg Oe^{-1} mol^{-1} at 2 K. Around 2 T, the magnetization abruptly increased again. Common ferromagnetic materials usually do not exhibit the field dependence of magnetization. Furthermore, in the case of this material, when a higher magnetic field was applied, the magnetization value approached 10000 erg Oe^{-1} mol^{-1}. This value is close to the theoretical value of 9908 erg Oe^{-1} mol^{-1} for the ferrimagnetic ordered state of 1 mol of the $S = 3/2$ ($g = 1.85$) spin and 1 mol of the $S = 1/2$ ($g = 2.00$) spin.[12] These findings indicate that the magnetic behaviors are associated with a ferrimagnetic spin alignment in the alternative chain of cation B and ReBr$_6{}^{2-}$ below 12.2 K. It is believed that the contribution of cation A to the magnetization at 2 K is small because of the strong intermolecular antiferromagnetic interactions between A cations.

Magnetic anomalies around 2 T might be associated with the orientation of the one-dimensional alternative network of cation B and ReBr$_6{}^{2-}$. There are the two types of directions in the alternative networks; [110] and $[\bar{1}10]$. The easy axes of magnetization in these two types of the alternative networks may be aligned in different directions. Hence, it is thought that the magnetization vector of the alternative network toward the [110] direction is inclined to that of the alternative network toward the $[\bar{1}10]$ direction. When a critical magnetic field of 2 T was applied, the magnetization vectors of the alternative chains oriented toward the magnetic field. These results suggest that this material is not a genuine ferrimagnet. In order to understand the detailed spin alignment of this material, it is necessary to carry out neutron diffraction studies using large single crystals.

In summary, we identified a novel molecule-based ferromagnet, α-BBDTA$_2$ReBr$_6$, having a magnetic transition temperature of 12.2 K. This material comprised an alternative chain of two magnetic species with different spin quantum numbers, BBDTA$^+$ with $S = 1/2$ and ReBr$_6{}^{2-}$ with $S = 3/2$, as well as a strong antiferromagnetic chain of BBDTA$^+$. The origin of the ferromagnetic properties may be related to the ferrimagnetic spin alignment of the alternative chain. An anomaly in the magnetization curve around 2 T might be related to the orientation of the one-dimensional alternative network in its crystal. Finally, this material provides us with a new approach for the construction of molecule-based ferrimagnetic materials. In an ionic crystal, cations and anions are usually aligned alternatively because of the Coulombic interactions. If the spin multiplicity of the cation differs from that of the anion, a desirable molecular alignment attributable to ferrimagnetism will be easily achieved in ionic radical crystals.

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10 Crystal data at 180(2) K: C$_{12}$H$_4$Br$_6$N$_4$ReS$_8$, $M_r = 1126.33$, monoclinic, space group $C2/c$, $a = 17.959(3)$, $b = 16.0497(17)$, $c = 9.4117(13)$ Å, $\beta = 115.216(5)°$, $V = 2454.3(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 3.048$ g cm^{-3}, 142 parameters were refined using 2441 reflections to give $R = 0.0351$ and $R_w = 0.0745$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-783592. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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