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Crystal Structure and Magnetic Properties of $Gd_2([18]crown\text{-}6)_2(OH)_2(CH_3CN)_2[Ni(dmit)_2]_4$ Complex Having f- and π-Spins

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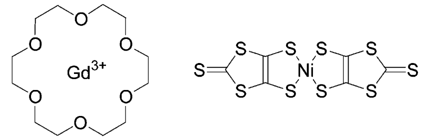
Crystal structure and magnetic properties of $Gd_2([18]crown\text{-}6)_2(OH)_2(CH_3CN)_2[Ni(dmit)_2]_2$ ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate) are reported. Gd^{3+} ions ($S = {}^7/_2$) were introduced into the π-spin network of $[Ni(dmit)_2]^-$ ($S = {}^1/_2$) complex as a binuclear supramolecular cation, $Gd_2([18]crown\text{-}6)_2(OH)_2(CH_3CN)_2$, in which two Gd([18]crown-6) units are bridged with two hydroxide ions. The weak antiferromagnetic interactions between Gd···Gd through hydroxide ions were observed, and $[Ni(dmit)_2]^-$ formed isolated monomers and dimers in the crystal.



Recently, crystals composed of magnetic metal ions and open-shell organic molecules, which often possess interesting magnetic and conductive behaviors under magnetic fields, have attracted much attention. One such example is λ-$(BETS)_2FeCl_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene) complex, which exhibited superconducting transition at $T_c = 0.1$ K when a magnetic field was applied parallel to the conduction layers of the crystal.[1] Within the crystal, the BETS and the $FeCl_4$ layers stack alternately, and in the absence of a magnetic field, interactions between the π-electrons of the BETS molecules and the d-spins of $FeCl_4$ interrupt the superconductivity transition. Other examples include $[\{CuL\}_2Gd(TCNQ)_2]\cdot TCNQ\cdot CH_3OH\cdot 2CH_3CN$ (L^{2-} = *N,N′*-propylenebis(3-methoxysalicylideneiminato); TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane), in which ferromagnetically interacting f-spins of Gd^{3+} and d-spins of Cu^{2+} are incorporated into π-spins of $TCNQ^-$.[2]

Our studies have focused on the manipulation of $[Ni(dmit)_2]^-$ configurations within a crystal by utilizing supramolecular cations, which are composed of metal or organic cations and crown ethers.[3−5] Monovalent species of $[Ni(dmit)_2]^-$ anions, which have $S = {}^1/_2$ spin, have been proven as useful building blocks of molecular magnetic materials. A $[Ni(dmit)_2]^-$ molecule interacts with neighboring molecules through $\pi-\pi$ overlap and sulfur−sulfur atomic contacts and exhibits a variety of magnetism according to the network structure of $[Ni(dmit)_2]^-$ in the crystal. Previously, we have reported a spin ladder structure of $[Ni(dmit)_2]^-$ that was induced by (anilinium)([18]crown-6) supramolecular cation.[4] Subsequently, by using the supramolecular cations approach, we have incorporated magnetic metals into the $[Ni(dmit)_2]^-$-based complexes to afford a variety of d−π-spin systems. Supramolecular cations are favorable in the construction of novel d−π-spin systems because of their ability to regulate $[Ni(dmit)_2]^-$ configurations within a crystal suitable for exhibiting magnetic functions. We have reported on $Co([15]crown\text{-}5)(CH_3CN)[Ni(dmit)_2]_2$, in which the d-spins of Co^{2+} and the π-spins of $[Ni(dmit)_2]^-$ coexist within the crystals and are arranged in a one-dimensional *zigzag* chain. Temperature dependence of χT has suggested that the d-spins of Co^{2+} and the π-spins of $[Ni(dmit)_2]^-$ are isolated from each other in the crystal. Consequently, we have directed our studies toward the synthesis of $[Ni(dmit)_2]^-$ salts that incorporate f-spin. Novel molecular magnetic materials can be expected by the introduction of f-spin using a lanthanide ion, which has a large magnetic moment and a relatively small ionic radius, which allows the ion to be

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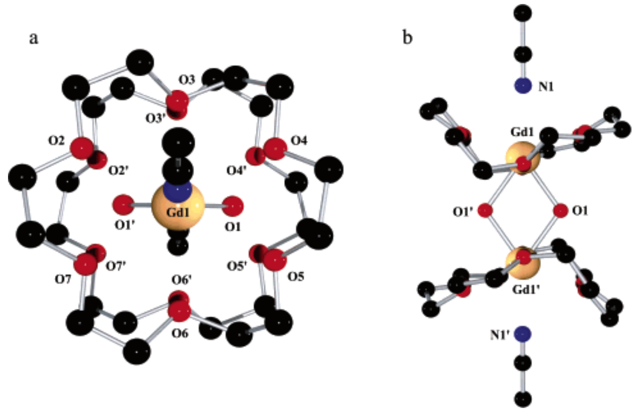

Figure 1. Supramolecular cation structure of Gd^{3+} complex viewed from the top (a) and side (b) of the [18]crown-6 plane.

included within the crown ether cavities. On the basis of the reported ferromagnetic interactions between Gd^{3+} and nitronyl nitroxide,[6] we have selected Gd^{3+} to be incorporated within the [Ni(dmit)$_2$]$^-$ crystals. In this paper, we report the crystal structure and the magnetic properties of the novel Gd$_2$([18]crown-6)$_2$(OH)$_2$(CH$_3$CN)[Ni(dmit)$_2$]$_2$[7], in which the binuclear complex of Gd^{3+} and [18]crown-6 coexists with [Ni(dmit)$_2$]$^-$.

Single crystals of Gd$_2$([18]crown-6)$_2$(OH)$_2$(CH$_3$CN)$_2$[Ni(dmit)$_2$]$_4$ were prepared by combining (n-Bu$_4$N)[Ni(dmit)$_2$], [18]crown-6, 15% aqueous solution of [(CH$_3$)$_4$N]OH, and Gd^{3+}(trifluoromethanesulfonate)$_3$ in acetonitrile.

The supramolecular cation structure of the resulting Gd^{3+} complex is shown in Figure 1. Since the diameter of a Gd^{3+} ion (1.88 Å) is smaller than the cavity of [18]crown-6 (2.6−3.2 Å), a Gd^{3+} ion can be completely included within [18]-crown-6. The supramolecular cation, Gd$_2$([18]crown-6)$_2$(OH)$_2$(CH$_3$CN)$_2$, has an inversion center, and therefore, Gd([18]crown-6) groups exist as binuclear complexes. X-ray crystal structure analysis has shown that two Gd([18]crown-6) units are arranged with two bridge atoms, which were assigned as OH$^-$, to fulfill elemental analysis and the electrically neutral condition of the crystal. The presence of the hydrogen atom of OH$^-$ in the crystal was found by the differntial Fourier method in X-ray analysis. The bond lengths between Gd^{3+} and OH$^-$ [2.282(3) and 2.289(3) Å] and the bond angle defined by O1···Gd1···O1′ [68.0(1)°] were observed, which were comparable to those for [GdCl(OH$_2$)$_2$([18]crown-6)]Cl$_2$·2H$_2$O, in which the bond length between Gd^{3+} and OH$_2$ and the bond angle defined by O···Gd···O were 2.41 Å and 70.2°, respectively.[8] The distance between the nitrogen atom (N1) of acetonitrile and the coordinated Gd1 (Gd1···N1) was 2.589(4) Å. The shortest and average lengths between the oxygen atoms of [18]crown-6 and Gd^{3+} were 2.490(3) and 2.54(1) Å, respectively, and are comparable to those reported previously (the shortest and average lengths between Gd···O were 2.47 and 2.53 Å, respectively).[8] Although the [18]crown-6 molecule generally exists in a flat conformation with a D_{3d} symmetry in the crystal, the [18]crown-6 in the present salt exists in a V-shaped conformation, as shown in Figure 1b. One possible explanation is the steric hindrance between the oxygen atom bridging Gd^{3+} and that of [18]crown-6.

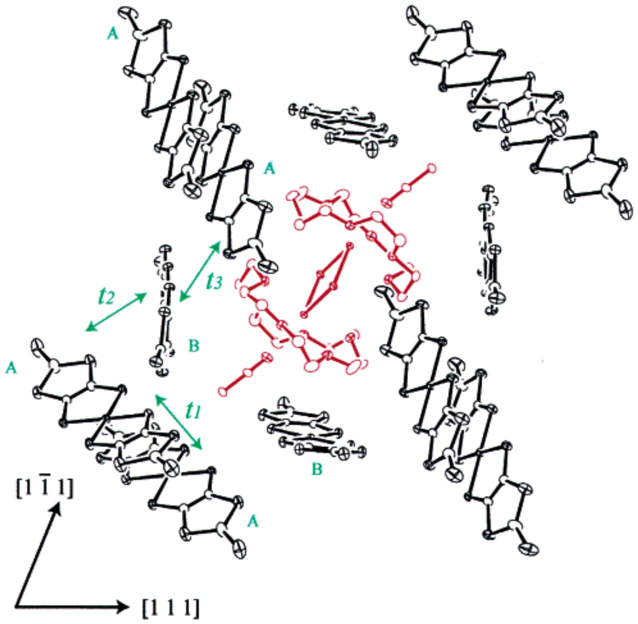

Figure 2. Crystal structure of the Gd^{3+} complex viewed along the [10$\bar{1}$] direction.

Figure 2 shows the crystal structure viewed along the [10$\bar{1}$] direction. Two crystallographically asymmetrical units of [Ni(dmit)$_2$]$^-$ anions (**A** and **B**) were observed; the $\pi-\pi$ dimers of [Ni(dmit)$_2$]$^-$ **A**−**A** and monomers of **B** are arranged alternately along the [111] and [1$\bar{1}$1] directions through side-by-side S···S contacts (**B**···**A**−**A**···**B**). The shortest contact distance for the S···S interaction between neighboring molecules (**A**···**B**) is 3.583 Å, which is shorter than the sum of the van der Waals radius of two S atoms (3.60 Å). The [Ni(dmit)$_2$]$^-$ chains intersect at the dimer sites, thus forming a [Ni(dmit)$_2$]$^-$ net structure, in which the supramolecular cations occupy the holes of the [Ni(dmit)$_2$]$^-$ net.

Using the extended Hückel molecular orbital calculations,[9] transfer integrals between the [Ni(dmit)$_2$]$^-$ molecules of dimer **A**−**A** was determined as $t_1 = 88.4$ meV, and those between the dimer and monomer (**A**-**B**) were calculated as $t_2 = 35.4$ meV and $t_3 = 9.0$ meV (see Figure 2). These values suggest that intradimer interactions should dominate intermolecular interactions within the crystal, and that the dimers are connected through weak dimer−monomer interactions within the two-dimensional network of [Ni(dmit)$_2$]$^-$.

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(7) Rigaku RAXIS-RAPID imaging plate diffractometer using a graphite monochromator Mo Kα radiation ($\lambda = 0.71069$ Å). Crystal data: GdO$_7$C$_{26}$H$_{28}$NNi$_2$S$_{20}$, $M = 1382.36$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.2443(5)$ Å, $b = 23.3557(9)$ Å, $c = 17.1535(6)$ Å, $\beta = 105.628(1)°$, $V = 4724.1(3)$ Å^3, $T = 296$ K, $Z = 4$, $D_{\mathrm{calcd}} = 1.943$ g/cm^3, μ(Mo Kα) = 31.04 cm^{-1}, final R, R_w = 0.040, 0.077. I_o = 8092 “observed” [$I > 3.0\sigma(I)$] reflections out of $N = 10793$ unique ($R_{\mathrm{int}} = 0.039$), and GOF = 1.07. One hydrogen atom of OH$^-$ group was found by differential Fourier search; the other hydrogen atoms were placed in the calculated positions.

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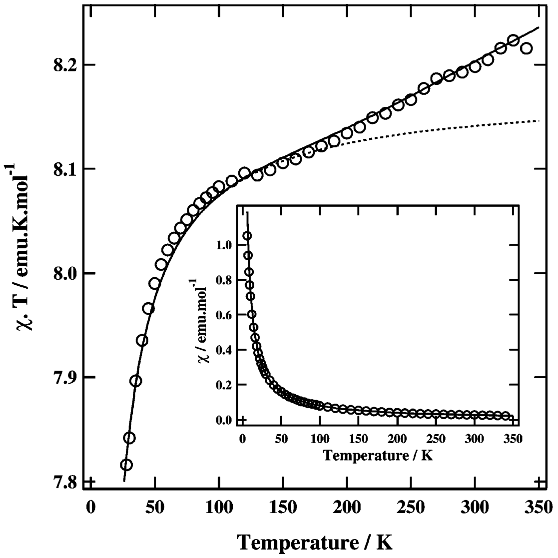

Figure 3. Temperature dependence of χT and the magnetic susceptibility (χ) (inset) of the Gd^{3+} complex. Best fit curves are represented by the solid and dotted lines (see text).

Figure 3 shows the plot of χT as a function of T for Gd([18]crown-6)(OH)(CH_3CN)[Ni(dmit)$_2$]$_2$; the measurements were carried out using a polycrystalline sample in a field of 1 T on a Quantum Design MPMS-XL SQUID susceptometer. The temperature dependence of magnetic susceptibility (χ) is shown in the inset of Figure 3. The relatively large values for χT can be attributed as mainly originating from the moments of Gd^{3+} ($S = {}^7/_2$). Below 120 K, the rapid decrease of χT with the decrease in temperature is attributable to the weak antiferromagnetic interactions between Gd···Gd through superexchange interactions. The $[Ni(dmit)_2]^-$ dimer **A** and monomer **B** ($S = {}^1/_2$) also contributes to the χT. Above 150 K, the χT curve slowly increases with the increase in temperature, which may be attributed to the antiferromagnetic intradimer interactions of the $[Ni(dmit)_2]^-$ dimer. From the transfer integral calculations, relatively strong intradimer interactions can be expected, which are responsible for antiferromagnetic exchange interactions between two $[Ni(dmit)_2]^-$ molecules (**A**). The $[Ni(dmit)_2]^-$ monomer **B** should exhibit Curie−Weiss-type behavior, which may be shadowed by the large magnetic mormant of Gd^{3+}. The temperature-dependent magnetic behavior can be expressed as the sum of Curie−Weiss magnetism of Gd^{3+} and $[Ni(dmit)_2]^-$ monomer, and that of the thermal excitation model of the $[Ni(dmit)_2]^-$ dimer as

$$\chi = \frac{C_{\mathrm{Gd+[Ni(dmit)_2]}}}{T-\theta} + \frac{C_{\mathrm{[Ni(dmit)_2]}}}{T}\,\frac{4\exp(-2J/k_{\mathrm{B}})}{1+3\exp(-2J/k_{\mathrm{B}})}$$

The experimentally derived[4] Curie constant of $[Ni(dmit)_2]^-$, $C_{\mathrm{[Ni(dmit)_2]}} = 0.394$ emu·K·mol^{-1} ($g = 2.050$), was used. The best fit curve was calculated with Curie constant $C_{\mathrm{Gd+[Ni(dmit)_2]}} = 8.175$ emu·K·mol^{-1}, Weiss temperature $\theta = -1.25$ K, and magnetic exchange interaction $2J/k_{\mathrm{B}} = 930$ K. Total χ and the Curie−Weiss component are represented as the solid and dotted lines in Figure 2, respectively. The $C_{\mathrm{Gd+[Ni(dmit)_2]}}$ value should include both the f-spin of Gd^{3+} ($S = {}^7/_2$) and the π-spin of $[Ni(dmit)_2]^-$ monomer **B** ($S = {}^1/_2$). The Curie constant of Gd^{3+} is, therefore, estimated by subtracting $C_{\mathrm{[Ni(dmit)2]}}$ to give $C_{\mathrm{Gd}} = 7.8$ emu·K·mol^{-1}, which is in accord with $S = {}^7/_2$.

The χT value of the Gd^{3+} complex decreased with the decrease in temperature in two steps. The first step is due to the antiferromagnetic interactions between $[Ni(dmit)_2]^-$ π-spins within a dimer, and the second step is due to the weak antiferromagnetic interactions between Gd···Gd through superexchange interactions. A similar two-step decrease in χT was reported for a Gd^{3+} complex, [Gd(Hbpz$_3$)$_2$(dtbsq)]·2CHCl$_3$ (Hbqz$_3$ = hydrotris(pyrazolyl)borate, dtbsq = 3,5-di-*tert*-butylsemiquinonato)[10]. However, the observed magnetic behavior was assigned to the strong coupling between Gd^{3+} and radical ligands directly coordinated to Gd^{3+}, and to the weak antiferromagnetic interaction between neighboring molecules. In the present complex, the f- and π-spins coexist as three spin systems: $[Ni(dmit)_2]^-$ monomer and dimer, as well as a binuclear Gd^{3+} complex with weak antiferromagnetic interactions. Attempts to connect the f- and π-spins to develop new multidimensional magnets are currently in progress.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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