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# Supramolecular Rotor: Adamantylammonium([18]crown-6) in $[Ni(dmit)_2]^-$ Salt

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Adamantylammonium ($ADNH_3^+$) was complexed with [18]crown-6, forming a supramolecular cation of ($ADNH_3^+$)([18]crown6), which was introduced into a $[Ni(dmit)_2]^-$ salt as a supramolecular rotor. The cation layers were alternately arranged with $[Ni(dmit)_2]^-$ layers in the crystal, in which the molecular rotation of ($ADNH_3^+$)([18]-crown-6) was confirmed from the temperature-dependent solid-state $^1$H NMR.

The molecular motor should be one of the most important prototypes of nanoscale mechanical systems because they can convert various kinds of energies into kinetic energy with high conversion efficiency.[1−3] Although complex molecules such as triptycenes, catenanes, and rotaxanes have been employed as model compounds to develop such molecular systems,[2] real artificial molecular rotors comparable to those in the living system have not been developed yet. While molecular motors on substrate surfaces and in polymer matrixes may be suggested,[4] those in crystalline solids have been limited in molecular structure to molecular gyroscopes and turnstiles, for example.[5] The molecules in a crystal tend to form a closely packed structure, which allows little space for molecular rotation.

Molecular rotations have been typically observed in plastic and liquid crystals, where rotation occurred around the high-symmetry axes of the molecules. High-symmetry molecules such as $CCl_4$, cyclohexane, $C_{60}$, and adamantane can form plastic crystals.[6] As a result, high-symmetry molecules have the potential to form molecular rotors in crystals. Thus, we designed a solid-state molecular rotator using the adamantyl group.

We have previously introduced supramolecular cations of ammonium−crown ether molecular assemblies in electrically conducting and magnetically active $[Ni(dmit)_2]$ salts (dmit$^{2-}$ = 2-thione-1,3-dithiole-4,5-dithiolate).[7,8] This approach allows us to design structurally diverse cations in the $[Ni(dmit)_2]$ crystals. For example, the simple combination of alkali-metal ions ($M^+$) and crown ethers yielded a molecular rotator of $(Cs^+)_2$([18]crown-6)$_3$ in $[Ni(dmit)_2]$ salts.[7,8] Quaternary ammoniums ($R-NH_3^+$) are capable of forming molecular assemblies of ($R-NH_3^+$)([18]crown-6) in solids, where the size of the $-NH_3^+$ moiety fits the cavity of [18]-crown-6.[9] On the basis of these designing strategies, we have already reported the supramolecular cations of ($R-NH_3^+$)-([18]crown-6) in the $[Ni(dmit)_2]^-$ salts.[10] Although the random rotation of [18]crown-6 has already been established in a $(Cs^+)_2$([18]crown-6)$_3[Ni(dmit)_2]^-_2$ salt, the designs of

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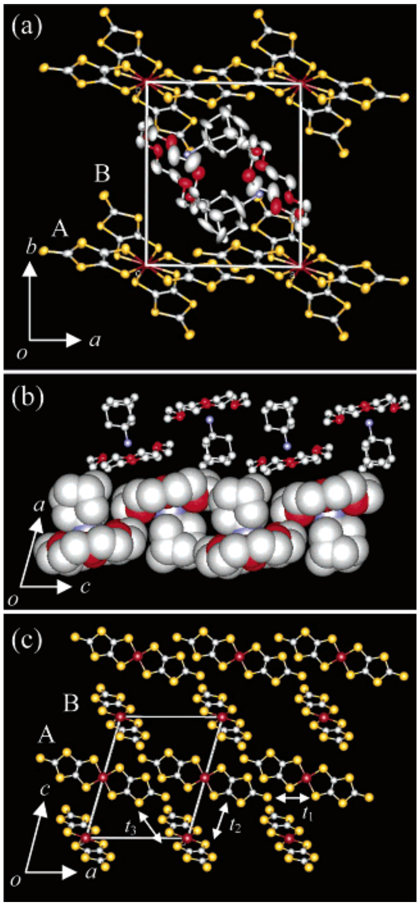

**Figure 1.** Crystal structure of salt **1**. (a) Unit cell viewed along the *c* axis. (b) $(ADNH_3^+)$([18]crown-6) cation layer viewed along the *b* axis. A half-unit was depicted by a Corey−Pauling−Koltun representation. (c) $[Ni(dmit)_2]^-$ anion layer viewed along the *b* axis. H atoms were omitted in these figures.

rotary modes, i.e., rotation symmetry, rotation speed, etc., are difficult. All organic $(R{-}NH_3^+)$([18]crown-6) structures have the potential to realize diverse design of molecular rotors in a crystalline solid. It is expected that a highly symmetric three-dimensional molecule will lead to molecular motion in a solid.[11] Thus, we used the high-symmetry adamantylammonium $(ADNH_3^+)$ as a molecular assembly unit complexed with [18]crown-6, which was introduced into the $[Ni(dmit)_2]^-$ salt as a countercation. Dual rotations of [18]crown-6 and $R{-}NH_3^+$ units were realized in the solid.

Single crystals of $(ADNH_3^+)$([18]crown-6)$[Ni(dmit)_2]^-$ (**1**) were grown by the standard diffusion of $(ADNH_3^+)(BF_4^-)$, [18]crown-6, and $(n\text{-}Bu_4N^+)[Ni(dmit)_2]^-$ in $CH_3CN$.[12] The magnetic properties of the salt were evaluated by a SQUID magnetometer (Quantum Design model MPMS-XL) at a magnetic field of 1 T.

Figure 1a shows the unit cell of salt **1** ($T = 160$ K).[13] One $ADNH_3^+$, one [18]crown-6, and two half-units of $[Ni(dmit)_2]^-$ molecules (**A** and **B**) were the crystallographically asymmetric units. The $ADNH_3^+$ cation sits on the cavity of [18]crown-6, forming a $(ADNH_3^+)$([18]crown-6) supramolecular cation structure. Six $N{-}H^+{\sim}O$ hydrogen bonds with an average N−O distance of 2.98 Å were observed within the range of the standard hydrogen-bond distance.[14] Although the average thermal parameter of $ADNH_3^+$ at 160 K ($B_{eq} = 7.8$) was close to that at 300 K ($B_{eq} = 9.45$), the average thermal parameter of [18]crown-6 at 160 K ($B_{eq} = 6.85$) was quite smaller than that at 300 K ($B_{eq} = 12.87$). Thermal motion in the adamantyl group in the cation structure occurred even at 160 K, while that in the [18]crown-6 was suppressed by a decrease of the temperature down to 160 K (see Tables S3 and S4 in the Supporting Information).

Two kinds of $[Ni(dmit)_2]^-$ units **A** and **B** were arranged within the *ac* plane, while the cations of $(ADNH_3^+)$([18]crown-6) were also arranged within the *ac* plane. An alternate layer structure of cations and anions was observed along the *b* axis. There were effectively no interatomic contacts between the cation and anion layers stronger than a van der Waals interaction. Thus, the cation and anion layers were independent of each other.

In the cation layer, the nearest-neighboring $(ADNH_3^+)$([18]crown-6) units were related by an inversion symmetry along the *c* axis (Figure 1b). Although the adamantyl group was sandwiched by two nearest-neighboring [18]crown-6 molecules along the *c* axis, there was enough space for the molecular rotation of the adamantyl group in the crystal owing to the high-symmetry molecular structure of adamantane.

Figure 1c shows the $[Ni(dmit)_2]^-$ arrangement in the *ac* plane. The magnitude of intermolecular interactions was estimated from the transfer integral ($t$) of the lowest unoccupied molecular orbital of $[Ni(dmit)_2]^-$ by the extended Hückel molecular orbital calculation, and the magnetic exchange energy ($J$) was deduced from the $t$ value via $J \sim 4t^2/U_{eff}$, where $U_{eff}$ is the effective on-site Coulomb repulsive energy in the solid.[15] A regular array of $[Ni(dmit)_2]^-$ **A** was observed along the *a* axis with $t_1 = 38.4$ meV. No effective intermolecular interaction between the **B** molecules was detected within the *ac* plane, while interactions between the **A** and **B** molecules were observed along the *c* and $-(a + c)$ axes. The magnitudes of the interactions of $t_2 = 18.0$ along the *c* axis and of $t_3 = 12.8$ meV along the $-(a + c)$ axis were smaller than that of the $t_1$ interaction.

Figure 2 shows the temperature dependence of the magnetic susceptibility of salt **1** ($\chi_{mol}$ vs $T$). $\chi_{mol}$ increased monotonically with decreasing temperature. From the $\chi_{mol}T$ vs $T$ plots (right scale in Figure 2), the antiferromagnetic

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(12) Synthesis of $[Ni(dmit)_2]$ salt: A solution of $(n\text{-}Bu_4N)[Ni(dmit)_2]$ (40 mg), $(ADNH_3^+)(BF_4^-)$ (80 mg), and [18]crown-6 (400 mg) in $CH_3CN$ was slowly diffused in an H-shaped cell (50 mL). The solution was allowed stand for about 1 week at room temperature.

(13) Crystal data: salt **1**, 160 K, triclinic, $P\bar{1}$, $a = 10.958(5)$ Å, $b = 13.411(5)$ Å, $c = 14.512(7)$ Å, $\alpha = 68.578(14)°$, $\beta = 73.430(16)°$, $\gamma = 84.413(14)°$, $V = 1902.8(14)$ Å$^3$, $Z = 2$, $D_c = 1.515$ g cm$^{-3}$, $2\theta_{max} = 55°$, $\mu$(Mo K$\alpha$) = 10.99 cm$^{-1}$. A total of 18 748 collected reflections and 5783 reflections of $I > 1\sigma(I)$ were used for refinement based on $F^2$. The final $R$ values were R1 = 0.066, wR2 = 0.134, and GOF = 0.919.

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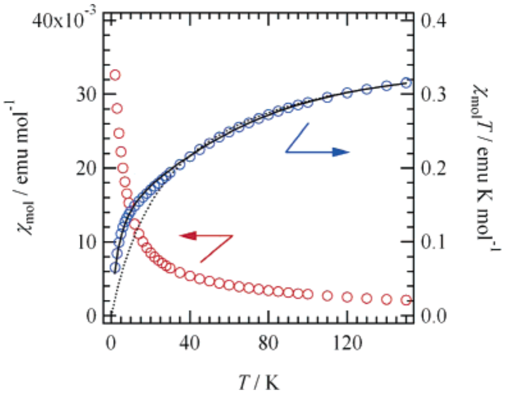

**Figure 2.** Temperature dependence of molar magnetic susceptibility ($\chi_{mol}$) of salt **1** per $[Ni(dmit)_2]^-$. $\chi_{mol}$ vs $T$ (red) and $\chi_{mol}T$ vs $T$ (blue) were plotted using the left and right scales, respectively. Dashed and solid lines were the fitting results (see text).

interaction between the $[Ni(dmit)_2]^-$ anions was identified. The Curie−Weiss (CW) equation with a fixed Curie constant ($C$) of 0.376 emu K mol$^{-1}$ almost exactly reproduced the temperature-dependent behavior with a Weiss temperature ($\theta$) of −29.6 K. However, a deviation from the theoretical curve (dashed line in Figure 2) was observed in the temperature range below 40 K. Because three kinds of intermolecular interactions were observed between $[Ni(dmit)_2]^-$ anions in the *ac* plane, it was expected that the magnetic susceptibility of salt **1** would be characterized by three magnetic exchange energies, namely, $J_1$, $J_2$, and $J_3$. The ratio of these $J$ values, as calculated from $t_1$, $t_2$, and $t_3$, was $J_1$:$J_2$:$J_3$ = 1:0.2:0.1. Thus, the $J_1$ interaction will presumably be dominant in the $\chi_{mol}$ vs $T$ behavior.

The magnitudes of the $J_2$ and $J_3$ interactions between $[Ni(dmit)_2]^-$ **A** and **B** were smaller than that of the one-dimensional (1D) linear interaction of $J_1$ between the **A** molecules along the *a* axis. Thus, we employed a linear combination of the equation of the 1D Heisenberg antiferromagnetic chain model for **A** and the CW model for **B**.[16] The $\chi_{mol}$ vs $T$ behavior between 4 and 300 K was reproduced by this equation almost exactly with a $J_1$ of −46 K for the 1D Heisenberg antiferromagnetic chain and a $\theta$ of −4 K (solid line in Figure 2).

To examine the molecular motion of supramolecular cations in salt **1**, temperature-dependent solid-state $^1$H NMR measurements were carried out (Figure 3). While we would have expected the protons of the adamantyl group (15H), the amino group (3H), and [18]crown-6 (24H) of salt **1** to all be detected in the NMR spectra (see Figure S5 in the Supporting Information), the spectrum was largely dominated by the two components, adamantyl (15H) and [18]crown-6 (24H), because amino protons (3H) were present in a relatively small amount. The full width at half-maximum ($\Delta H_A$) and peak-to-peak line width ($\Delta H_B$) of the differential spectra, which corresponded to molecular motions of [18]-crown-6 and $ADNH_3^+$, respectively, were plotted against the temperature. The $\Delta H_B$ value at low temperature corresponds to the line width of the sharp signal (motional $ADNH_3^+$ unit).

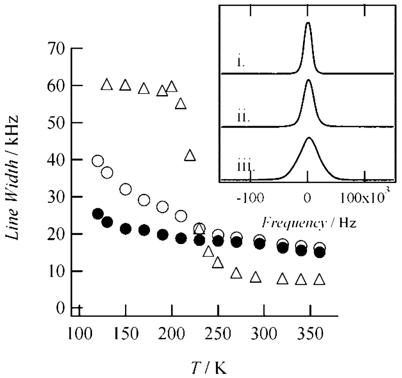

**Figure 3.** Temperature dependence of the full width at half-maximum ($\Delta H_A$: open circles) and the peak-to-peak line width of the differential spectrum ($\Delta H_B$: filled circles) of $^1$H NMR for salt **1** together with $\Delta H_A$ of salt **2** (triangles).[8a] The inset shows the temperature variation of $^1$H NMR spectra at (i) 360 K, (ii) 230 K, and (iii) 120 K.

The $\Delta H_A$ value in the temperature range above 250 K was ∼20 kHz, while that at 120 K ($\Delta H_A$ = 40 kHz) was twice that at room temperature. Lowering of the temperature was observed to lead to broadening of the $\Delta H_A$ value in the temperature range from 360 to 120 K. The molecular rotation of [18]crown-6 in $(Cs^+)_2([18]crown\text{-}6)_3[Ni(dmit)_2]^-{}_2$ (**2**) has been identified as a thermally activated motion in the temperature range above 220 K, resulting in a rapid decrease in $\Delta H_A$ from 60 kHz ($T$ < 220 K) to ∼8 kHz ($T$ > 220 K) as shown in Figure 3 (triangles).[8a] The $\Delta H_A$ value of thermally frozen [18]crown-6 has been estimated as ∼60 kHz in salt **2**,[8a] suggesting that the maximum rotation frequency of [18]crown-6 at 220 K was about 60 kHz. Because the $\Delta H_A$ (∼40 kHz) value of salt **1** at 120 K was lower than 60 kHz, molecular rotation of [18]crown-6 occurred even at 120 K. Thus, the potential barrier to molecular rotation was lower in salt **1** than in salt **2**. The rotation frequency of the adamantyl group is presumably much faster that that of [18]-crown-6. The $\Delta H_B$ value corresponds to the rotation of the adamantyl group in the low-temperature region, which showed a weaker temperature dependence than $\Delta H_A$. Thus, the rotation frequency of the adamantyl group was much higher than that of [18]crown-6 at 120 K. The ammonium group $ADNH_3^+$ is also a rotation unit, whose frequency is presumably much higher than that of the adamantyl group. Three kinds of rotation units should be considered in the supramolecular rotor $(ADNH_3^+)$([18]crown-6).

In conclusion, the supramolecular cation $[ADNH_3^+]$([18]-crown-6) was introduced into a $[Ni(dmit)_2]^-$ salt as the countercation. Both $ADNH_3^+$ and [18]crown-6 molecules formed a molecular rotator with different rotation frequencies. The high-symmetry molecular structure of the adamantyl group was effective in constructing the rotation space in the solid state.

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**Supporting Information Available:** Crystal data (in PDF and CIF formats) of salt **1**, intermolecular interaction modes of $[Ni(dmit)_2]^-$ anions, and $^1$H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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