Co²⁺(15-crown-5) Magnetic Supramolecular Cation in [Ni(dmit)₂]⁻ π-Spin System

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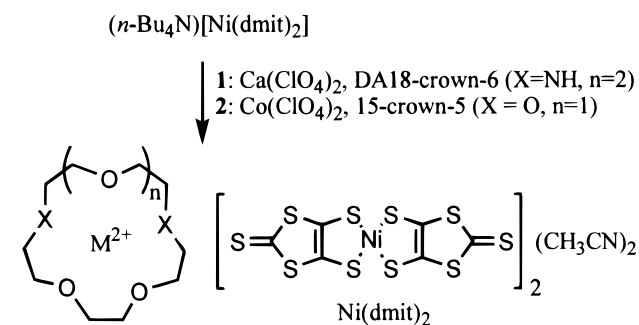
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Magnetic cation of Co²⁺ was incorporated in a monovalent [Ni(dmit)₂]⁻ (2-thioxo-1,3-dithiole-4,5-dithiolate) salt by using the supramolecular framework of 15-crown-5. The π-spins of [Ni(dmit)₂]⁻ formed a one-dimensional Heisenberg antiferromagnetic linear chain, while the d-spin of Co²⁺ behaved as a free S = 3/2 spin within the crystal.

The partially oxidized [metal(dithiolate)₂]$^{-\delta}$ ($\delta < 1$) salts show high electrical conductivity and have been widely examined.[1] Although the monovalent [metal(dithiolate)₂]⁻ anions such as [Ni(mnt)₂]⁻ and [Ni(dmit)₂]⁻ (mnt and dmit are maleonitriledithiolate and 2-thioxo-1,3-dithiole-4,5-dithiolate, respectively) form insulating salts, each anion bears S = 1/2 spin and a potential to form molecular magnets through inter-molecular interactions in the crystal.[2] The ferromagnetic order of the spins has been observed in the NH₄⁺[Ni(mnt)₂]⁻(H₂O),[3] and the spin-ladder chains have been constructed in [Ni(mnt)₂]⁻ or [Ni(dmit)₂]⁻ salts.[4] For the long range magnetic ordering, appropriate molecular arrangements in the crystals are indispensable. We have reported that the supramolecular cations (SC) such as M⁺(crown ether) can control the molecular arrangements of [Ni(dmit)₂]⁻ within the crystal.[5] For example, one-dimensional antiferromagnetic [Ni(dmit)₂]⁻ chain has been obtained in the M⁺(crown ethers)[Ni(dmit)₂]⁻ (M⁺ = K⁺ and Rb⁺) salts.[6] To decrease the Coulombic repulsive energy, the planar M⁺(crown ether) and [Ni(dmit)₂]⁻ anion stack alternately in the crystal. The M⁺(crown ether) prevents the face-to-face π−π overlap of the [Ni(dmit)₂] anions that form one-dimensional chain through side-by-side sulfur−sulfur contacts.

The crystal structure should be largely modified by replacing the monovalent M⁺ to divalent M²⁺ within the SC unit due to the change in Madelung energy.[7] In addition, the magnetic ions can be introduced into the crystal utilizing the SC structure through the design of coordination environment. We show here an unusual arrangement of [Ni(dmit)₂]⁻ anions in the divalent SC²⁺ salts and the incorporation of d-spin species into the SC structure.

The cation exchange of (*n*-Bu₄N)[Ni(dmit)₂]⁻ with Ca²⁺/DA18-crown-6 and Co²⁺/15-crown-5 gave the SC salts of the Ca²⁺(DA18-crown-6)[Ni(dmit)₂]₂(CH₃CN)₂ (**1**) and Co²⁺(15-crown-5)[Ni(dmit)₂]₂(CH₃CN)₂ (**2**), respectively (Scheme 1).

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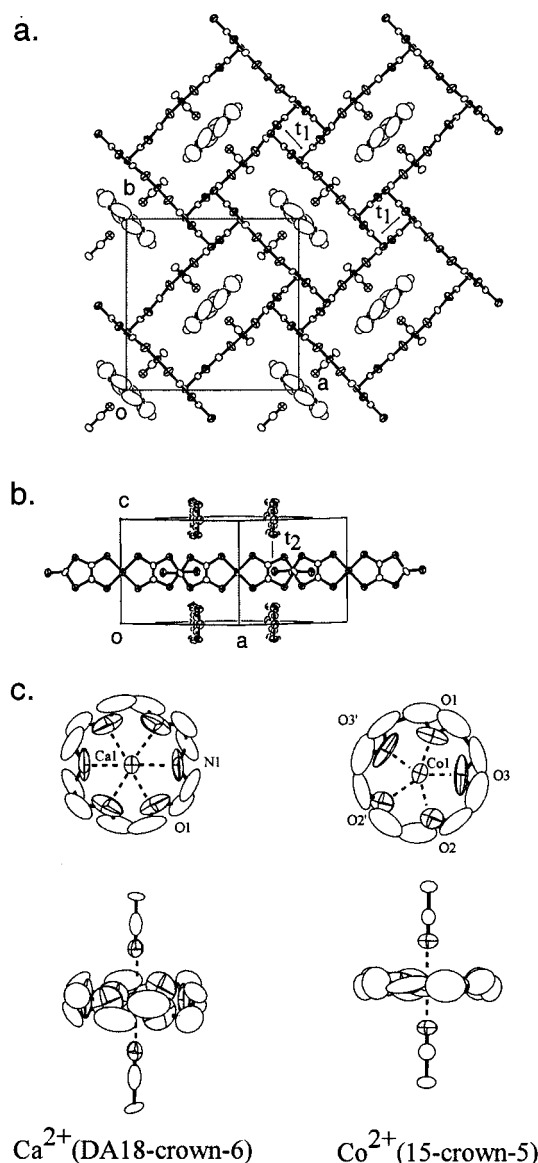§ PRESTO, JST.
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SCHEME 1

(*n*-Bu₄N)[Ni(dmit)₂]

1: Ca(ClO₄)₂, DA18-crown-6 (X=NH, n=2)
2: Co(ClO₄)₂, 15-crown-5 (X = O, n=1)

Ni(dmit)₂

The M²⁺(crown ether) and [Ni(dmit)₂]⁻ self-assembled to the isostructural crystals (tetragonal *P*4₂/*mnm*) as expected,[8] al-though the SC unit of Co²⁺(15-corwn-5) has a magnetic spin of S = 3/2.

Since the divalent Co²⁺ and Ca²⁺ ions are stoichiometrically incorporated into the crystals, the [Ni(dmit)₂]⁻ is in a completely ionized electronic state with S = 1/2 spin. Figure 1a shows the unit cell of the salt **1** viewed along the *c*-axis. The molecular plane of [Ni(dmit)₂]⁻ anions is orthogonal to the *ab*-plane, and the [Ni(dmit)₂]⁻ anions form a parallel cross lattice. The long axes of [Ni(dmit)₂]⁻ anions within the same plane is parallel to each other and are orthogonal to that of the next layer. Figure 1b shows the π−π overlap mode of the [Ni(dmit)₂]⁻ anions viewed along the $a - b$ axis. The π−π overlap ($t_1 = 3.71$ and 4.03×10^{-2} eV for salts **1** and **2**, respectively[9]) was found between the [Ni(dmit)₂]⁻ anions around the terminal sulfur atoms forming a uniform zigzag chain along the $a + b$ and $a - b$ axes. No interchain contacts were observed within the *ab*-plane. However, these chains were further connected through the weak side-by-side interactions ($t_2 = 0.79$ and 0.83×10^{-2} eV for salt **1** and **2**, respectively) along the *c*-axis. From the magnitude of t_1 and t_2, the intermolecular interaction is dominant in the one-dimensional zigzag chain of [Ni(dmit)₂]⁻ anions.

Figure 1c shows the SC structures of Ca²⁺(DA18-crown-6)(CH₃CN)₂ and Co²⁺(15-crown-5)(CH₃CN)₂ viewed along the normal and parallel to the crown ether plane. Since the ion radius of Co²⁺ (0.72 Å) and Ca²⁺ (0.99 Å) fits well to the cavity radius of 15-crown-5 (0.85−1.1 Å) and DA18-crown-6 (1.3−1.6 Å),

Figure 1. Crystal structure of salt **1**. (a) Unit cell viewed along the *c*-axis. (b) $\pi-\pi$ Overlap mode and the zigzag chain of $[\mathrm{Ni(dmit)_2}]^-$ anions viewed along the $a-b$ axis. (c) $\mathrm{Ca^{2+}}$(DA18-crown-6)(CH$_3$CN)$_2$ and $\mathrm{Co^{2+}}$(15-crown-5)(CH$_3$CN)$_2$ structures viewed normal (upper figures) and parallel (lower figures) to the crown ether plane, respectively. The 15-crown-5 molecule has an orientational disorder. One of the orientations is indicated in the figure.

respectively, the divalent ions are tightly included into the crown ether cavities. The average $\mathrm{M^{2+}-O}$ (or N) distances are 0.15 Å shorter than the corresponding van der Waals contacts.[10] The disk-shaped $\mathrm{M^{2+}}$(crown ether) units are further coordinated axially by the nitrogen atoms of two CH$_3$CN molecules. The $\mathrm{M^{2+}}$(crown ethers)(CH$_3$CN)$_2$ SC units are located at the residual space of the parallel cross lattice of $[\mathrm{Ni(dmit)_2}]^-$.

Figure 2 shows the temperature dependence of magnetic susceptibility of salts **1** and **2**. Salt **1** has a broad χ_m maximum at around 20 K. The temperature dependence of χ_m is fitted well by the one-dimensional Heisenberg antiferromagnetic linear chain model,[11] which is consistent with the arrangement of the $[\mathrm{Ni(dmit)_2}]^-$ anions in the crystal. The intrachain exchange energy ($|J/k_B| \sim 12.2$ K) on the $[\mathrm{Ni(dmit)_2}]^-$ chain of salt **1** is small due to the weak $\pi-\pi$ overlap of $[\mathrm{Ni(dmit)_2}]^-$ anions. The $\chi_m T$ vs T plot of salt **1** (Figure 2b) is constant above 40 K ($C = 0.76$ emu K mol^{-1}) and the magnetic moment corresponds to S = 1/2 spin on every $[\mathrm{Ni(dmit)_2}]^-$ anion. On the other hand,
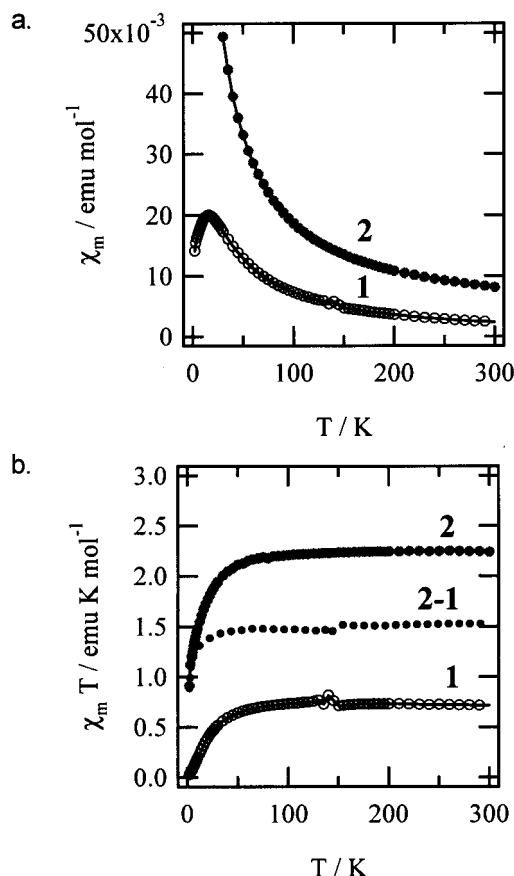

Figure 2. Magnetic properties of salts **1** and **2**. (a) Temperature (T/K) dependence of molar magnetic susceptibilities (χ_m/emu mol^{-1}). (b) $\chi_m T$ vs T plots of salts **1** and **2**. Line **2−1** is obtained by subtracting $\chi_m T$ values of salt **1** from that of salt **2** ($\chi_m T$ (**2**) $- \chi_m T$ (**1**)).

the absolute χ_m value of the **2** is much larger than that of salt **1** due to the contribution from the Co^{2+} spin (S = 3/2). Since the $\chi_m T$ vs T plot of the **2** shows a constant ($C = 2.20$ emu K mol^{-1}) above 40 K, the magnetic susceptibility is explained by the sum of two S = 1/2 spins of $[\mathrm{Ni(dmit)_2}]^-$ anions and one S = 3/2 spin of Co^{2+} ion. By assuming that the $[\mathrm{Ni(dmit)_2}]^-$ lattice shows the same magnetic behavior in salts **1** and **2**, we can estimate the magnetic behavior of Co^{2+} in salt **2** by subtracting $\chi_m T$ value of salt **1** from that of salt **2**. The residual magnetic moment is almost constant ($C = 1.47$ emu K mol^{-1}) in the measuring temperature range (**2−1** in Figure 2b), showing that the d-spin of Co^{2+} behaves as a free S = 3/2 spin within the crystal.

We have shown the incorporation of magnetic d-spin into divalent $\mathrm{M^{2+}}$(crown ether) supramolecular cation structure, which coexisted with the $[\mathrm{Ni(dmit)_2}]^-$ π-spin. The $\mathrm{M^{2+}}$(crown ether)(CH$_3$CN)$_2$ cation ($\mathrm{M^{2+}} = \mathrm{Ca^{2+}}$ or Co^{2+}) afforded the isostructural crystals in which $[\mathrm{Ni(dmit)_2}]^-$ formed a parallel cross lattice and the supramolecular cations were located at the residual space. By introducing the d- and π-spins within the crystal simultaneously, it should be possible to construct d$-\pi$ molecular magnets whose magnetic structures are dominated by the supramolecular cation structures.

References and Notes

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(8) Crystal data for salt **1**: $C_{22}H_{32}O_4N_4S_{20}Ni_2Ca$, $M = 1215.2$, crystal dimensions $0.80 \times 0.20 \times 0.20$ mm^3, Rigaku-AFC7R diffractometer, Mo$-$Kα radiation ($\lambda = 0.71069$ Å), tetragonal, space group $P4_2/mnm$ (no. 136), $a = 15.562(1)$, $c = 10.218(2)$ Å, $U = 2474.8(5)$ Å^3, $T = 298$ K, $Z = 2$, $D_c = 1.631$ gcm^{-3}, $F(000) = 1240.0$, μ(Mo$-$Kα) 17.41 cm^{-1}, Lorentz polarization and absorption corrections applied, 1581 reflections measured, 1581 independent reflections, 1046 reflections with $I > 3.00\sigma(I)$. $(\Delta\rho)_{max} = 0.88$e Å^{-3}, $(\Delta\rho)_{min} = -1.32$e Å^{-3}, $R = 0.046$, $R' = 0.038$. For salt **2**: $C_{36}H_{26}O_5N_2S_{20}CoNi_2$, $M = 1384.2$, crystal dimensions $0.30 \times 0.30 \times 0.02$ mm^3, Rigaku RAXIS$-$RAPID diffractometer, Mo$-$Kα radiation ($\lambda = 0.71069$ Å), tetragonal, space group $P4_2/mnm$ (no. 136), $a = 15.3048(4)$, $c = 10.0251(3)$ Å, $U = 2348.2(1)$ Å^3, $T = 298$ K, $Z = 2$, $D_c = 1.957$ g cm^{-3}, $F(000) = 1398.0$, μ(Mo$-$Kα) 20.80 cm^{-1}, Lorentz polarization and absorption corrections applied, 21443 reflections measured, 1495 independent reflections, 906 reflections with $I > 3.00\sigma(I)$. $(\Delta\rho)_{max} = 0.41$e Å^{-3}, $(\Delta\rho)_{min} = -0.34$e Å^{-3}, $R = 0.030$, $R' = 0.042$. Calculations were performed using teXsan crystallographic software packages with refinements based F. Solution by direct method: non-hydrogen atoms refined anisotropically and no refinement of hydrogen atoms.

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