One-Dimensional Antiferromagnetic Chain in [Ni(dmit)$_2$]$^-$ Salts of [K$^+$ or Rb$^+$(4,13-diaza-18-crown-6)] Supramolecular Cation

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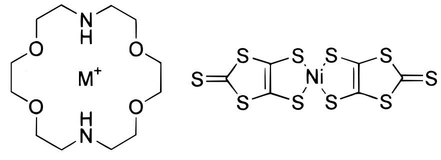
Crown ether macrocycles can include cations into their cavity to form supramolecular cation (SC$^+$) structures of various size, shape, and coordination environments.[1] We introduced the SC$^+$ structures into highly conducting Ni(dmit)$_2$ (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) salts as a countercation.[2] It was possible to exercise control the structure of SC$^+$, the valence state, and the stacking mode of the Ni(dmit)$_2$, as well as the electrical conducting properties of the resultant salts.[2] For example, an ion-channel Li$^+_{0.6}$(15-crown-5) structure was introduced into the crystal which has partially oxidized uniform Ni(dmit)$_2$ stacks of metallic character.[3]

The monovalent [Ni(dmit)$_2$]$^-$ with spin ($S = {}^1/_2$) on each molecule may show a long-range magnetic order, provided an appropriate packing arrangement of [Ni(dmit)$_2$]$^-$ anions within the crystal. For example, a spin-ladder type magnetic chain has been reported in a [Ni(dmit)$_2$]$^-$ salt of pyridinium cation in which the large cation regulated the arrangement of [Ni(dmit)$_2$]$^-$ anions.[4] Control over the packing arrangements of [Ni(dmit)$_2$]$^-$ anions within the crystal should also be possible by utilizing a large structural diversity of SC$^+$ units. In this paper, we describe the K$^+$(DA18-crown-6)[Ni(dmit)$_2$] (**1**) and Rb$^+$(DA18-crown-6)[Ni(dmit)$_2$] (**2**) salts (DA18-crown-6 is 4,13-diaza-18-crown-6) in which the arrangement of [Ni(dmit)$_2$]$^-$ anions is regulated by the planar large SC$^+$ unit to form a one-dimensional Heisenberg antiferromagnetic linear chain.



M$^+$(DA18-crown-6)[Ni(dmit)$_2$], M$^+$ = K$^+$ and Rb$^+$

From the stoichiometry and X-ray crystal structural analysis of the salts **1** and **2**, the completely ionized state of [Ni(dmit)$_2$]$^-$ was confirmed.[5] The UV−vis−NIR spectra of the salts **1** and **2** in KBr pellets exhibited the charge-transfer transition of monovalent [Ni(dmit)$_2$]$^-$ at 1240 nm, which was consistent with that of monovalent (n-Bu$_4$N$^+$)[Ni(dmit)$_2$]$^-$ (1190 nm).

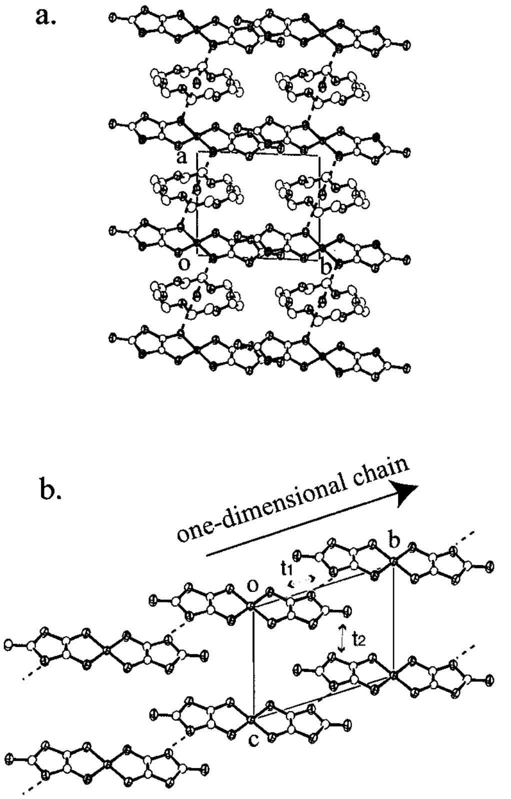


Figure 1. Crystal structure of K$^+$(DA18-crown-6)[Ni(dmit)$_2$]: (a) unit cell viewed along the c-axis; (b) one-dimensional [Ni(dmit)$_2$]$^-$ linear chain viewed along the a-axis.

The salts **1** and **2** were isostructural. Figure 1a shows the unit cell of salt **1** viewed along the c-axis. The half units of [Ni(dmit)$_2$]$^-$ and K$^+$(DA18-crown-6) are the crystallographically

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(5) Rigaku AFC-7R diffractometer using a graphite monochromator, Mo Kα radiation (λ = 0.710 69 Å). For salt **1**: black needle, $1.0 \times 0.\underline{1} \times 0.1$ mm^3, C$_{18}$H$_{26}$O$_4$N$_2$ S$_{10}$KNi, M = 752.81, triclinic, space group $P\bar{1}$, a = 8.920(3) Å, b = 10.911(2) Å, c = 8.373(1) Å, α = 106.86(1)°, β = 97.37(2)°, γ = 92.28(2)°, V = 770.8(3) Å^3, T = 298 K, Z = 1, $2\theta_{max}$ =55.0°, 3765 reflections measured, 3538 independent reflections, 2425 reflections with $I > 3\sigma(I)$, $(\Delta\rho)_{max}$ = 0.55 eÅ^{-3}, $(\Delta\rho)_{min}$ = −0.29 e Å^{-3}, R = 0.042, R' = 0.046, refinement on F^2. For salt **2**: black plate, $0.8 \times 0.\underline{4} \times 0.3$ mm^3, C$_{18}$H$_{26}$N$_2$O$_4$S$_{10}$RbNi, M = 799.18, triclinic, space group $P\bar{1}$, a = 8.815(5) Å, b = 11.04(2) Å, c = 8.51(1) Å, α = 107.8-(1)°, β = 97.53(9)°, γ = 91.5(1)°, V = 779(2) Å^3, T = 298 K, Z = 1, $2\theta_{max}$ = 55.0°, 3809 reflections measured, 3577 independent reflections, 2768 reflections with $I > 3\sigma(I)$, $(\Delta\rho)_{max}$ = 0.86 e Å^{-3}, $(\Delta\rho)_{min}$ = −0.48 e Å^{-3}, R = 0.058, R' = 0.069, refinement on F^2.

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asymmetric units. The alternate stack of $[Ni(dmit)_2]^-$ and K^+-(DA18-crown-6) units is elongated along the *a*-axis. Since the ion radii of K^+ (1.33 Å) and Rb^+ (1.48 Å) fit well to the cavity radius of DA18-crown-6 molecule (1.3−1.6 Å), the K^+ and Rb^+ ions are completely included into the DA18-crown-6 cavity through the coordination of four oxygen and two nitrogen atoms. The average K^+-O (2.84 Å) and Rb^+-O (2.89 Å) distances are similar to those of van der Waals contact ($K^+-O = 2.85$ Å and $Rb^+-O = 3.00$ Å), respectively.[6] The cations were further interacted axially by the sulfur atom of $[Ni(dmit)_2]^-$ through the weak interatomic contacts ($K^+-S = 3.60$ Å and $Rb^+-S = 3.71$ Å).

Figure 1b shows the $[Ni(dmit)_2]^-$ arrangement in the salt **1** viewed along the *a*-axis. The transfer integrals (t_1 and $t_2 \times 10^{-2}$ eV) were obtained from the extended Hückel molecular orbital calculations.[7] The face to face $\pi-\pi$ interaction of $[Ni(dmit)_2]^-$ molecules along the *a*-axis was completely prevented by the M^+-(DA18-crown-6) due to the mixed-stack structure, while the side-by-side t_1 interactions (1.03 for salt **1**, S2−S2 = 3.762(2) Å, S1−S3 = 3.777(3) Å, and S2−S3 = 3.782(2) Å, 2.77 for salt **2**, S4−S4 = 3.660(4) Å, S3−S4 = 3.740(3) Å, and S3−S5 = 3.786(3) Å) connect the $[Ni(dmit)_2]^-$ anions along the *b*-axis. Since the t_2 interactions (−0.15 for salt **1**, S4−S4 = 3.464(3) Å, and S3−S4 = 3.622(2) Å; −0.62 for salt **2**, S2−S2 = 3.395(4) Å and S2−S3 = 3.579(3) Å) along the *c*-axis are small, the $[Ni(dmit)_2]^-$ in the salts **1** and **2** are arranged quasi one-dimensionally along the *b*-axis from the electronic point of view. The electrical conductivity at room temperature along the *b*- and *c*-axes of salt **1** was 1.2×10^{-6} and 3×10^{-7} S cm^{-1} (two-probe method), while that of salt **2** was 3.1×10^{-7} and 1.2×10^{-7} S cm^{-1}, respectively. The planar SC^+ unit for the 1:1 salts has a tendency to form a mixed-stack structure in order to reduce the Coulomb repulsion, which results in a quasi one-dimensional chain of $[Ni(dmit)_2]^-$ anions through the side-by-side S−S interaction.

Figure 2 shows the temperature dependence of molar magnetic susceptibility (χ_m) of the salt **1**. The salt **2** showed a similar behavior. The χ_m increased by lowering the temperature from 350 to 50 K; then a broad maximum was observed at around 30 K. The temperature dependent χ_m was fitted well by using the one-dimensional Heisenberg antiferromagnetic linear chain model.[8] The intrachain magnetic exchange energy $|J/k_B|$ of salts **1** and **2** is 24.7 and 22.7 K, respectively. The magnetic behavior of the one-dimensional Heisenberg antiferromagnetic linear chain is in good agreement with the one-dimensional interaction between $[Ni(dmit)_2]^-$ estimated by the transfer integral calculations.

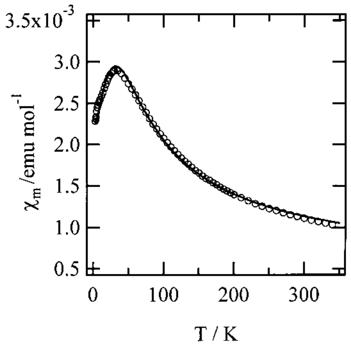

Figure 2. Temperature (*T*/K) dependent molar magnetic susceptibility (χ_m) of the salt **1**. The solid curve is a fit of the one-dimensional Heisenberg antiferromagnetic linear chain model with $S = ^1/_2$. The data was measured by a SQUID magnetometer at a magnetic field of 1 T.

In conclusion, the mixed-stack structure of $[Ni(dmit)_2]^-$ and M^+(DA18-crown-6) supramolecular cation ($M^+ = K^+$ and Rb^+) decreases the effective $\pi-\pi$ of $[Ni(dmit)_2]^-$ molecules, which results in the one-dimensional Heisenberg antiferromagnetic linear chain of $S = ^1/_2$ spins within the crystal. Further control over the magnetic properties of the $[Ni(dmit)_2]^-$ salt will be possible through the design of supramolecular cation structures.

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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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