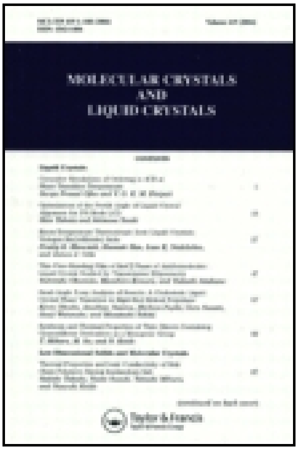

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M^+ (Crown Ether) Supramolecular Cations ($M^+ = K^+, Rb^+, NH_4{}^+$) for Controlling Magnetic Properties of Monovalent $[Ni(dmit)_2]^-$ Salts

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M^+(Crown Ether) Supramolecular Cations ($M^+= K^+, Rb^+, NH_4^+$) for Controlling Magnetic Properties of Monovalent $[Ni(dmit)_2]^-$ Salts

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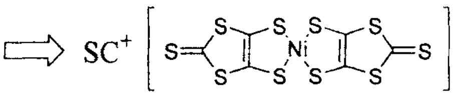
Supramolecular cations (SC^+) of K^+, Rb^+, or NH_4^+(crown ether) were incorporated into the monovalent $[Ni(dmit)_2]^-$ salts. The K^+ and Rb^+(DA18-crown-6) units had a planar disk-shaped SC^+ structure, while the $[NH_4^+(15\text{-crown-}5)_2]_2$ was the barrel type SC^+ structure. The $[Ni(dmit)_2]^-$ arrangement and magnetic properties of these salts depended on the coordination properties in the cation structures.

INTRODUCTION

Anion radical salts of $Ni(dmit)_2$ (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) have been extensively studied from the viewpoint of molecular superconductors and metals.[1] Highly electrically conducting $Ni(dmit)_2$ salts are composed of the partially oxidized $[Ni(dmit)_2]^{-\delta}$ anion ($\delta < 1$) and closed-shell counter cation.[1] On the other hand, the crystal structures of monovalent $[Ni(dmit)_2]^{-\delta}$ ($\delta = 1$) salts have not been examined extensively due to the insulating electrical behavior. The monovalent [Ni(dmit)$_2$]$^-$ has a S = 1/2 spin, which has a potential for constructing molecular magnets. Through the crystal engineering of monovalent [Ni(dmit)$_2$]$^-$ salts to regulate the π–π stacking arrangements in addition to the side by side intermolecular sulfur – sulfur contacts within the crystal, the ferromagnetic interaction and spin-ladder system have been already reported for the [Ni(dmit)$_2$]$^-$ anion system.[2-3]

The supramolecular cation (SC$^+$) structures have a structural diversity according to the size and shape of host and guest species.[4] For example, crown ethers can include a variety of cation within the cavity. According to the size of cavity and cation, a large number of SC$^+$ structures such as planar disk shaped M$^+$(crown ether), sandwiched M$^+$(crown ether)$_2$, and pyramidal M$^+$(crown ether) etc have been reported.[4] These SC$^+$ structures can also incorporated into the electrically conducting [Ni(dmit)$_2$]$^{-\delta}$ salts as a counter cation.[5-9] Among them, a regular array of Li$^+_{0.6}$(15-crown-5) structure of an ion-conducting channel coexisting with highly electrical conducting Ni(dmit)$_2$ column recently reported.[10]

1: K$^+$(DA18-crown-6)
2: Rb$^+$(DA18-crown-6)
3: NH$_4^+$(15-crown-5)$_2$



The SC$^+$ structures can utilize for the counter cation in the monovalent [Ni(dmit)$_2$]$^-$ salts, which expand a variation of the S = 1/2 spin arrangement within the crystal. Here we report the crystal structures and magnetic properties of K$^+$(DA18-crown-6)[Ni(dmit)$_2$]$^-$ **1**, Rb$^+$(DA18-crown-6)[Ni(dmit)$_2$]$^-$ **2** (DA18-crown-6 is 4,13-diaza-18-crown-6), and NH$_4^+$(15-crown-5)$_2$[Ni(dmit)$_2$]$^-$ **3** together with those of (tetrabutyl ammonium (TBA))[Ni(dmit)$_2$]$^-$ **4**.

EXPERIMENTAL

The salts **1** and **2** were prepared by the electrocrystallization of (TBA)[Ni(dmit)$_2$] in presence of K$^+$ or Rb$^+$ ions with DA18-crown-6,[11] while the salt **3** was prepared by the diffusion method between (TBA)[Ni(dmit)$_2$] and NH$_4^+$ with 15-crown-5 molecule.[7] The stoichiometries of salts **1**, **2**, and **3** were determined by the elemental and X-ray structural analyses.[7, 11] Static magnetic susceptibilities were measured by a SQUID magnetometer (Quantum Design MPMS-5) in a field of 1.0 T.

RESULTS AND DISCUSSION

CRYSTAL STRUCTURES

Salts **1** and **2** are an isostructural to each other. Figs. 1a and 1b show the SC^+ structures of K^+(DA18-crown-6) and $[NH_4^+(15\text{-crown-}5)_2]_2$, respectively. The SC^+ structure M^+(DA18- crown-6) in salts **1** and **2** has a planar-disk shape. Figs. 2a and 2b show the $[Ni(dmit)_2]^-$ anion arrangements in the salts **1** and **3**, respectively. The SC^+ units are schematically illustrated by closed circles. The alternate stack of $[Ni(dmit)_2]^-$ anion and M^+(DA18-crown- 6) was observed along the a-axis in salts **1** and **2** (Fig. 2a), which prevents the effective intermolecular π–π interaction between $[Ni(dmit)_2]^-$. The $[Ni(dmit)_2]^-$ anions arranged along the b-axis through the side by side sulfur - sulfur intermolecular contacts, which forms the one-dimensional regular S =

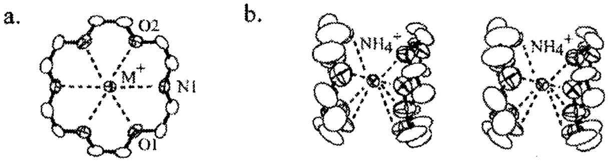


Figure 1. Supramolecular cation structures of a) K^+(DA18-crown-6) and b) $[NH_4^+(15\text{-crown-}5)_2]_2$ in the salts **1**, and **3** respectively.

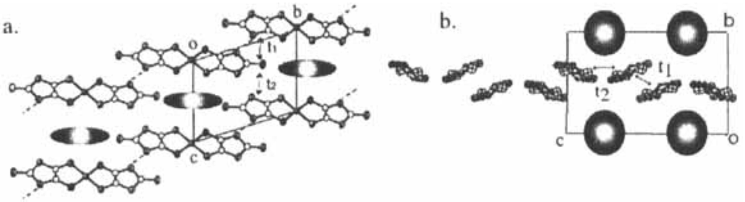


Figure 2. $[Ni(dmit)_2]^-$ anion arrangements of salts **1** and **3**. a) One-dimensional regular chain of $[Ni(dmit)_2]^-$ in the salt **1**. b) One-dimensional zig-zag chain of the $[Ni(dmit)_2]^-$ through S ~ S contacts in the salt **3**

1/2 chain. Each chain is further interacted through side by side fashion along the c-axis resulting in the two -dimensional sheet structure. However, the intermolecular interactions are highly one-dimensional character because of larger transfer integral of t_1 (1.03 and 2.77 x 10^{-2} eV for **1** and **2**, respectively) along the b-axis than that of t_2 (-0.15 and –0.62 x 10^{-2} eV for **1** and **2**, respectively) along the c-axis.[12].

A fundamental SC^+ unit in the salt **3** is the sandwiched NH_4^+(15-crown-5)$_2$ structure, which is further dimerized to the barrel type [NH_4^+(15-crown-5)$_2$]$_2$ structure (Fig. 1b). Since the size of the barrel structure is quite significantly larger than that of disk shaped M^+(DA18-crown-6), the [Ni(dmit)$_2$]$^-$ anion arrangement in the salt **3** is quite different to that in the salt **1** or **2**. The [Ni(dmit)$_2$]$^-$ anions in the salt **3** form a face to face π–π dimer structure, which is further connected by side by side S ~ S contacts along the c-axis. The transfer integral within the dimer (t_1 = 5.82 x 10^{-2} eV) is ca. six times larger than that of the side by side S ~ S interaction (t_2 = 1.01 x 10^{-2} eV).

The crystal structure of (TBA)[Ni(dmit)$_2$] has been reported,[13] in which the [Ni(dmit)$_2$]$^-$ anions were isolated to each other.[13] According to the structure of the SC^+ structures, the [Ni(dmit)$_2$]$^-$ arrangements within the crystal is tuned drastically.

MAGNETIC PROPERTIES

The magnetic properties of salts **1** ~ **4** depend on the [Ni(dmit)$_2$]$^-$ arrangements within the crystal. We measured the magnetic susceptibilities of three types of [Ni(dmit)$_2$]$^-$ arrangements, i) one-dimensional regular chain in the salts **1** and **2**, ii) zig-zag chain of dimerized [Ni(dmit)$_2$]$^-$ in the salt **3**, and iii) isolated [Ni(dmit)$_2$]$^-$ in the salt **4**. Fig. 3 shows the temperature dependence of the molar magnetic susceptibilities (χ_m) of the salts **1**, **2**, **3**, and **4**.

The temperature dependence of the χ_m of the salts **1** and **2** showed the same behavior due to the same [Ni(dmit)$_2$]$^-$ arrangements within the crystal. The χ_m value increases by lowering the temperature from 350 to 30 K, then a broad maxima is appeared at around 30 K. The temperature dependence is fitted well by using one-dimensional Heisenberg antiferromagnetic chain model (solid lines in Fig. 3a).[14] The magnitude of magnetic interaction within the chain ($|J/k_B|$) in the salts **1** and **2** are 24.7 and 22.7 K, respectively. The magnetic behaviors of these salts are consistent with the one-dimensional regular chain of [Ni(dmit)$_2$]$^-$ anions along the b-axis.

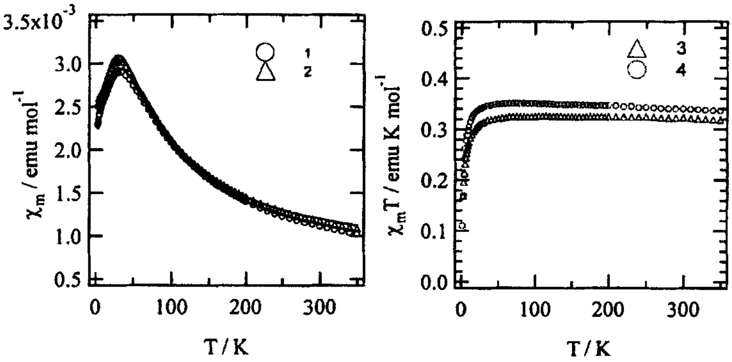


Figure 3. Temperature dependence of magnetic susceptibilities. a) χ_m vs. T plots of salt **1** and **2**. b) $\chi_m T$ vs. T plots of salts **3** and **4**.

The temperature dependence of χ_m in the salts **3** and **4** showed Curie like behavior. In the case of salt **3**, the constant $\chi_m T$ value (C = 0.35 emu K mol^{-1}) was observed in the temperature range from 20 to 350 K.The [Ni(dmit)$_2$]$^-$ overlap within the dimer was the ring over bond type, which is not effective to increase the transfer integral within the dimer. As a result, two S = 1/2 spins on the [Ni(dmit)$_2$]$^-$ dimer behave as free spin without antiferromagnetic coupling. Since the [Ni(dmit)$_2$]$^-$ anions in the salt **4** are completely isolated to each other, the Curie-type magnetic behavior is consistent with the constant $\chi_m T$ value (C = 0.33 emu K mol^{-1}) in the temperature range from 20 to 350 K.

SUMMARY

The supramolecular cation (SC$^+$) structures were incorporated into the monovalent [Ni(dmit)$_2$]$^-$ salts. The K$^+$ or Rb$^+$(DA18-crown-6) unit and [Ni(dmit)$_2$]$^-$ anion formed a mixed-stack structure, which regulated the [Ni(dmit)$_2$]$^-$ anions to the one-dimensional Heisenberg antiferromagnetic chain. The barrel type [NH$_4^+$(15-crown-5)$_2$]$_2$ units coexisted with the one-dimensional zig-zag chain of dimerized [Ni(dmit)$_2$]$^-$ anions. Within the dimer, two S = 1/2 spins behave as free spin without antiferromagnetic coupling, which resulted in the Curie-type magnetic behavior. The design of SC$^+$ structures is important for controlling the magnetic properties of S = 1/2 spins on the [Ni(dmit)$_2$]$^-$ anions.

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References

[1] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, *Coord. Chem. Rev.*, **110,** 115 (1991).

[2] W. E. Broderick, J. A. Thompson, M. R. Godfrey, M. Sabat, B. M. Hoffman, *J. Am. Chem. Soc.*, **111**, 7653 (1989).

[3] H. Imai, T. Inabe, T. Otsuka, T. Okuno, K. Awaga, *Phys. Rev. B.* **54,** 6838 (1994).

[4] G. Gokel, *"Crown Ethers & Cryptands"*, edited by J. F. Stoddart, The Royal Society of Chemistry (1994).

[5] T. Akutagawa, T. Nakamura, T. Inabe and A. E. Underhill, *J. Mater. Chem.*, **7**, 183 (1997).

[6] T. Akutagawa, T. Nakamura, T. Inabe and A. E. Underhill, *Synthetic Metals,* **86,** 1861 (1997).

[7] T. Akutagawa, T. Nakamura, T. Inabe and A. E. Underhill, *Thin Solid Films,* **331**, 264 (1998).

[8] T. Akutagawa, T. Nakamura, T. Inabe and A. E. Underhill, *Chemm. Commun.,* 2599 (1998).

[9] T. Akutagawa, T. Hasegawa, T. Nakamura, T. Inabe, K. Sugiura, Y. Sakata, A. E. Underhill, *Synthetic Metals,* **102,** 1747 (1999).

[10] T. Nakamura, T. Akutagawa, K. Honda, A. E. Underhill, A. T. Coomber and R.H. Friend, *Nature,* **394,** 159 (1998).

[11] N. Takamatsu, T. Akutagawa, T. Hasegawa, T. Nakamura, T. Inabe, W. Fujita, K. Awaga, submitted.

[12] T. Mori, A. Kobayashi, Y. Sasaki. H. Kobayashi, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.,* **57,** 627 (1984).

[13] O. Lindqvist, L. Andersen, J. Sieler, G. Steinmecke, E. Hoyer, *Acta Chem. Scand. A* **36,** 855 (1982).

[14] J. C. Bonner, M. E. Fisher, *Phys. Rev., A.* **3,** 640 (1964).