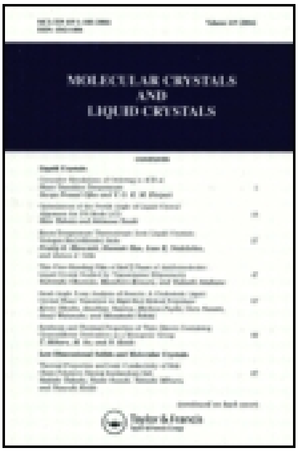

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Crystal Structure and Magnestism of [Ni(dmit) 2] - Salts With Supramolecular Cations of M + (15-Crown-5)

Tomoyuki Akutagawa [a b c], Nobuhiro Takamatsu [c], Tatsuo Hasegawa [a c], Takayoshi Nakamura [a c] & Tamotsu Inabe [d]

[a] Research Institute for Electronics Science, Hokkaido University, Sapporo, 060-0812, Japan

[b] PRESTO, Japan Science and Technology Corporation (JST), Japan

[c] Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan

[d] Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

Version of record first published: 18 Oct 2010

To cite this article: Tomoyuki Akutagawa, Nobuhiro Takamatsu, Tatsuo Hasegawa, Takayoshi Nakamura & Tamotsu Inabe (2002): Crystal Structure and Magnestism of [Ni(dmit) 2] - Salts With Supramolecular Cations of M + (15-Crown-5), Molecular Crystals and Liquid Crystals, 376:1, 39-46

To link to this article: http://dx.doi.org/10.1080/10587250210736

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 39-46
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1058-725X/02 \$12.00 + .00

Crystal Structure and Magnestism of $[Ni(dmit)_2]^-$ Salts With Supramolecular Cations of M^+ (15-Crown-5)

TOMOYUKI AKUTAGAWA[a,b,c*],
NOBUHIRO TAKAMATSU[c], TATSUO HASEGAWA[a,c],
TAKAYOSHI NAKAMURA[a,c,*] and TAMOTSU INABE[d]

[a]*Research Institute for Electronic Science, Hokkaido University, Sapporo 060-0812, Japan,*
[b]*PRESTO, Japan Science and Technology Corporation (JST), Japan,*
[c]*Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan and*
[d]*Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

The crystals of M^+(15-crown-5)$_2$[Ni(dmit)$_2$] ($M^+ = K^+$ (**1**), Rb^+ (**2**) and NH_4^+ (**3**)) were prepared. In the crystal, M^+ and 15-crown-5 formed a barrel-shape supramolecular cation structure, which filled the space between the $[Ni(dmit)_2]^-$ layers. The $[Ni(dmit)_2]^-$ formed the π - π dimers which were connected through the side-by-side S ~ S contacts. The interactions between $[Ni(dmit)_2]^-$ within the dimer were not strong enough and the crystals showed Curie-Weiss magnetic susceptibility with the Weiss temperature θ of -3.8, -2.8 and –3.2 K for the salts **1**, **2** and **3**, respectively.

Keywords [Ni(dmit)$_2$], crown ether, supramolecular cation, magnetism, crystal structure

INTRODUCTION

[Ni(dmit)$_2$] (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) is a good building block for constructing molecular conductors and magnets in the partially charged and monovalent state, respectively [1]. In both cases, the interaction (or overlap of molecular orbitals) between [Ni(dmit)$_2$] molecules is essential to assert bulk electric and magnetic properties. We are interested in regulating the assembly structure of [Ni(dmit)$_2$] in the crystal by introducing crown-ether based supramolecular cation (SC$^+$) structures [2]. We can change the shape and valence of the SC$^+$ by appropriate design, through which we can control the intermolecular interactions between [Ni(dmit)$_2$].

We have already reported that the ion-channel structure composed of 15-crown-5 and Li$^+$ can coexist with highly conducting [Ni(dmit)$_2$] one-dimensional column in the crystal [3]. The K$^+$(4,13-diaza-18-crown-6) formed a typical disc-shape SC$^+$ structure which regulates the [Ni(dmit)$_2$]$^-$ to a one-dimensional antiferromangetic chain [4]. In this paper, we report the assembly structure of [Ni(dmit)$_2$]$^-$ induced by the barrel-type SC$^+$ structure composed of M$^+$ (M$^+$ = K$^+$, Rb$^+$ and NH$_4^+$) and 15-crown-5. Preliminary results for the NH$_4^+$ salt have been appeared in ref. 5

EXPERIMENTAL

Monovalent (*n*-Bu$_4$N)[Ni(dmit)$_2$] was prepared according to the literature [6]. Single crystals were prepared by slow diffusion in CH$_3$CN. Inorganic salt, KClO$_4$, RbClO$_4$ or NH$_4$BF$_4$, and 15-crown-5 were placed one of the leg of diffusion cell, and (*n*-Bu$_4$N)[Ni(dmit)$_2$] was placed in the other side.

Crystal data were collected on a Rigaku AFC-7R or a Rigaku Raxis-Rapid diffractometers with Mo-Kα (λ = 0.71073 Å) radiation using a graphite monochromator. The structures were solved and refined using the teXsan program [7]. The structure refinements were performed by the full matrix least-squares method. Table 1 summarizes the crystal data of salts **1**, **2** and **3**. Parameters were refined using the anisotropic temperature factors in all crystals, and the hydrogen atoms were removed from the refinements.

TABLE 1 Crystal data of the salts **1** ~ **3**.

	1	**2**	**3**[a)]
Chemical formula	$C_{26}H_{40}O_{10}S_{10}$ NiK	$C_{26}H_{40}O_{10}S_{10}$ NiRb	$C_{26}H_{44}O_{10}NS_{10}$ Ni
Formula weight	930.99	977.36	909.93
Space group	*C*2/c (#15)	*C*2/c (#15)	*C*2/c (#15)
a, Å	33.394(2)	33.660(2)	33.611(8)
b, Å	12.539(1)	12.5654(7)	12.502(8)
c, Å	19.193(2)	19.283(1)	19.196(1)
β, deg	91.405(2)	91.263(2)	91.34(2)
V, Å^3	8034(1)	8153.9(6)	8063(5)
Z	10	10	10
D_{calc}, gcm^{-1}	1.924	1.990	1.874
T	297	297	297
μ, cm^{-1}	14.42	27.73	13.09
R[b]	0.092	0.083	0.079
R_w[b]	0.105	0.088	0.069

a) From ref. 5.

b) $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

The temperature dependent magnetic susceptibility was measured by a SQUID magnetometer (Quantum Design Model MPMS-5) for polycrystalline samples. The magnetic field applied was 1 T for all measurements. The transfer integrals (t) were calculated within the tight-binding approximation using the extended Hückel molecular orbital calculation. The LUMO of the [Ni(dmit)$_2$] molecule was used as the basis function [8]. The semiempirical parameters for Slater-type atomic orbitals were taken from ref. 8. The t value between each pair of molecules is assumed to be proportional to the overlap integral (S), $t = -10S$ eV.

RESULTS AND DISCUSSION

Crystal Structure

The salts **1**, **2** and **3** were isostructural ($C2/c$) each other with the crystal stoichiometry of $M^+(15\text{-crown-}5)_2[Ni(dmit)_2]$ ($M^+ = K^+$ (**1**), Rb^+ (**2**) and NH_4^+ (**3**)). Figures 1a and 1b show the unit cell of salt **1** viewed along the b- and a-axis, respectively. The salts have a sandwich-type $M^+(15\text{-crown-}5)_2$ SC^+ structure (Figure 1c), which filled the space between $[Ni(dmit)_2]^-$ dimer chains within the same ac-plane. The larger ion radii of K^+ (1.34 Å), Rb^+ (1.52 Å) and NH_4^+ (1.48 Å) than the cavity radius of 15-crown-5 resulted in the outer-coordination of M^+ ions to the 15-crown-5 cavity. The observed average $K^+ \sim O$ (2.91 Å), $Rb^+ \sim O$ (3.01 Å) and $NH_4^+ \sim O$ (3.02 Å) distances were almost the same as the sum of ion radii and van der Waals contacts ($K^+ \sim O$ (2.85), $Rb^+ \sim O$ (3.04) and $NH_4^+ \sim O$ (3.02 Å)) [9]. The $M^+(15\text{-crown-}5)_2$ units were further dimerized forming a barrel-type $[M^+(15\text{-crown-}5)_2]_2$ structure, in which two M^+ ions were appart far enough to reduce the Coulomb repulsive energy ($K^+ \sim K^+$ (8.8), $Rb^+ - Rb^+$ (8.9) and $NH_4^+ - NH_4^+$ (9.0 Å).

The $[Ni(dmit)_2]^-$ formed the $\pi - \pi$ dimer in the ab-plane, and each dimer was connected along the c-axis through the side-by-side S ~ S contacts. The magnitude of intermolecular interactions was evaluated by the transfer integrals ($t \times 10^{-2}$ eV). Since the magnetic exchange energy (J) is proportional to t^2, the magnetic behavior can be dictated by t. The intradimer π-π interaction ($t_1 = 4.90$) in the salt **1** was about five times larger than the interdimer S-S interaction ($t_2 = 0.85$). Similar magnitude of intermolecular interactions were observed in the salts **2** (t_1 = 5.10 and t_2 = 0.47) and **3** (t_1 = 5.82 and t_2 = 1.01). Although the ion radii of K^+, Rb^+ and NH_4^+ are different in the order of $Rb^+ > NH_4^+ > K^+$, the same size of SC^+ structure is maintained through the inclusion of the cations in the structurally flexible 15-crown-5 molecules.

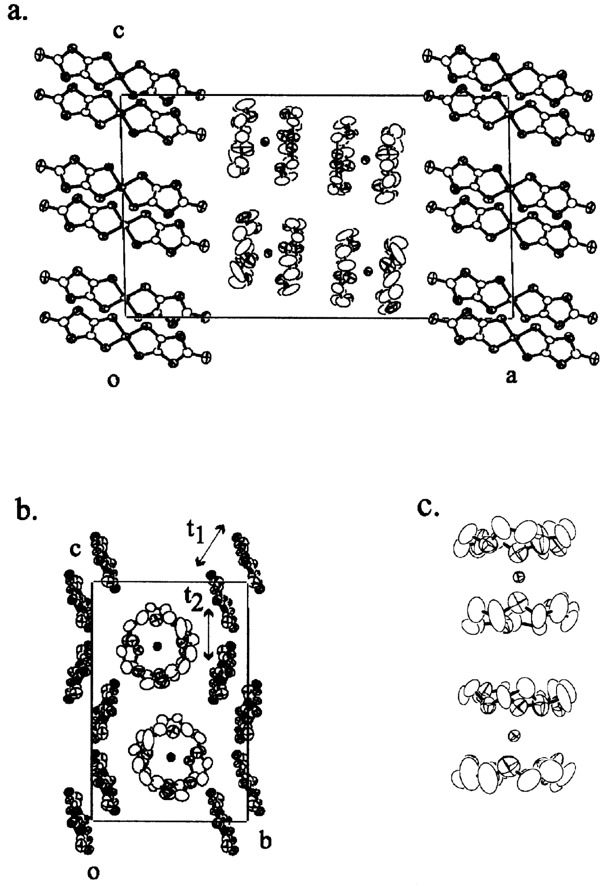

FIGURE 1 Crystal structure of K^+(15-crown-5)$_2$[Ni(dmit)$_2$] (**1**) viewed along the a) b-axis and b) along the a-axis. The transfer integrals t_1 and t_2 correspond to the intradimer and interdimer interactions, respectively. c) Structure of the supramolecular cation.

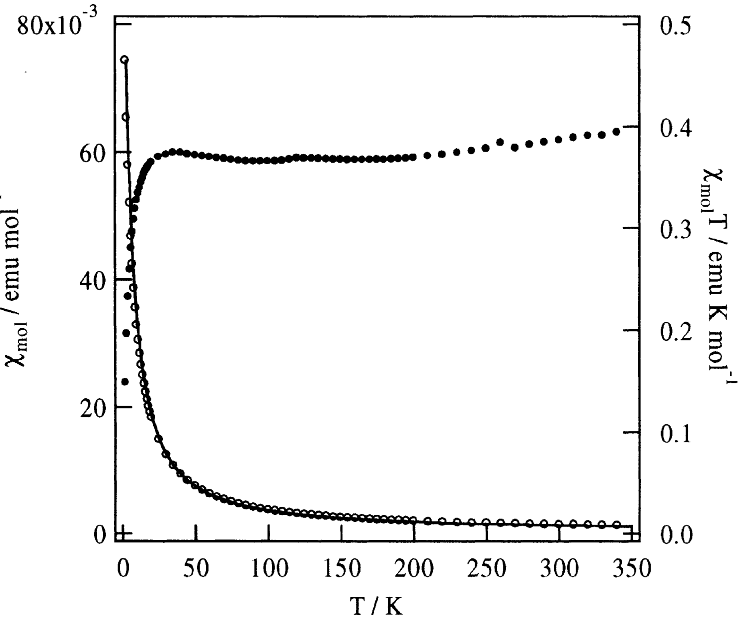

FIGURE 2 Temperature dependent magnetic susceptibility of salt **1**.

Magnetic Properties

The temperature dependent χ_m value in the salt **1** obeyed the Curie-Weiss behavior (Figure 2). The $\chi_m T$ value was constant above 20 K (0.37 emu K mol^{-1}), and a weak antiferromagnetic interaction (θ = –3.8 K) was observed below 20 K. The spin on each [Ni(dmit)$_2$]$^-$ behaved as a free spin at higher temperatures without the singlet pair formation despite relatively large intermolecular interaction within the dimer. The salts **2** and **3** also showed a similar magnetic behavior with the $\chi_m T$ values of 0.34 and 0.31 emu K mol^{-1}, respectively, and the Weiss temperature θ= -2.8 and -3.2 K.

In the case of K$^+$(4,13-diaza-18-crown-6)[Ni(dmit)$_2$], π-π dimer formation in the crystal was prevented by disc-shape K$^+$(4,13-diaza-18-crown-6) cation through the alternate stack of the K$^+$(4,13-diaza-

18-crown-6) and [Ni(dmit)$_2$]$^-$. The intermolecular interaction at the terminal sulfur atom (thione moiety) was small (t = 1.03) and the regular chain of [Ni(dmit)$_2$]$^-$ showed one-dimensional aniferromagnetic behavior with the exchange energy of $|J/K_B|$ = 24.7 K [4]. Although the face-to-face π-π interaction was possible in the present salts, the magnitude of the exchange interactions were not strong engough and the Curie-type magnetic behavior was predominant.

CONCLUSION

We have demonstrated that M$^+$/15-crown-5 forms a barrel-shape SC$^+$ structure, which induces the dimer chain of [Ni(dmit)$_2$]$^-$ in the crystal. The [Ni(dmit)$_2$]$^-$ spin arrangement strongly depends on the shape and valence state of SC$^+$ structures. Further design to obtain desired magnetic properties of [Ni(dmit)$_2$]-based magnetic system will be necessary from the supramolecular-cation approach. The SC$^+$ of trivalent cations should be a next target for bring about the diversity of [Ni(dmit)$_2$] assemblies.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science, Sports, and Culture of Japan and by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) in Japan. The authors thank Dr. M. Wakeshima and Prof. Y. Hinatsu for the use of SQUID magnetometer.

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