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Magnetism of [Ni(dmit)$_2$] Salts with [*Meso*- and (1*S*, 2*S*)-Diphenyl-1,2-Ethanediammonium]([18]crown-6)$_2$ Supramolecular Cations

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Meso- and (1*S*, 2*S*)-diphenyl-1,2-ethanediammonium (DPEDA^{2+}) complexed with [18]crown-6 were introduced into [Ni(dmit)$_2$]-based magnetic salts as countercations. The configurational difference of DPEDA^{2+} modulated the crystal structure and magnetic behavior of the salts. A two-dimensional (2D) Heisenberg antiferromagnetic square lattice was observed in (*meso*-diphenyl-1,2-ethane diammonium^{2+})([18]crown-6)$_2$[Ni(dmit)$_2$]$^-{}_2$, which was the first example of a 2D magnetic lattice in [Ni(dmit)$_2$]$^-$ salts.

Sulfur-rich planar π-conjugated molecules such as tetrathiafulvalene and metal(ditholate)$_2$ are useful building blocks for molecular magnets owing to their open-shell electronic structure and strong intermolecular interactions through S−S contacts.[1] The anion radical of [Ni(dmit)$_2$]$^-$ (dmit^{2-} = 2-thione-1,3-dithiole-4,5-dithiolate), possessing one $S = {}^1/_2$, is a typical example. By controlling the packing arrangement of such magnetic molecules in the crystal, we are able to obtain a diversity of magnetic properties. We have discussed the use of supramolecular cation structures as countercations to [Ni(dmit)$_2$]$^-$ salts,[2,3] and obtained various types of [Ni(dmit)$_2$]$^-$ arrangements that exhibit magnetism of one-dimensional (1D) Heisenberg chain, spin-ladder, or ferromagnetic interaction.[2,3] In these [Ni(dmit)$_2$]$^-$ salts, the shapes and sizes of the cations are adjustable by complexation with crown ethers, which yields novel [Ni(dmit)$_2$]$^-$ arrangements in the crystals. The introduction of crown ethers also promotes the production of high-quality single crystals, an added advantage over using simple-cation [Ni(dmit)$_2$]$^-$ salts. Among the cation−crown ether−[Ni(dmit)$_2$]$^-$ salts, organic ammonium exhibits a variety of different sizes, valences, and chiralities, and thus has the potential to form novel [Ni(dmit)$_2$]$^-$ arrangements in the crystals.[4] Here we report new supramolecular structures between *meso*- or (1*S*, 2*S*)-diphenyl-1,2-ethanediammonium (DPEDA^{2+}) and [18]crown-6, which were introduced into [Ni(dmit)$_2$]$^-$ -based magnetic salts (Scheme 1).

Single crystals of (*meso*-DPEDA^{2+})([18]crown-6)$_2$-[Ni(dmit)$_2$]$^-{}_2$ (**I**) and [(1*S*, 2*S*)-DPEDA^{2+}]$_2$([18]crown-6)$_4$-[Ni(dmit)$_2$]$^{-0.8}{}_5$ (**II**) were grown by standard mixing of (DPEDA^{2+})(BF$_4{}^-$)$_2$, [18]crown-6, and (n-Bu$_4$N$^+$)[Ni(dmit)$_2$]$^-$ in CH$_3$CN.[4] Since the organic ammonium cations in salts **I**

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(1) (a) Kurmoo, M.; Graham, A. M.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. M.; Singleton, J.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209. (b) Kobayashi, H.; Sato, A.; Arai, E.; Akutsu, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1997**, *119*, 12392. (c) Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garća, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (d) Broderick, W. E.; Thompson, J. A.; Godfrey, M. R.; Sabat, M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 7657. (e) Coomber, A. T.; Beljonne, D.; Friend, R. H.; Brédas, J. J.; Charlton, A.; Robertson, N.; Underhill, A. E.; Kurmoo, M.; Day, P. *Nature* **1996**, *380*, 144. (f) Kato, R. *Chem. Rev.* **2004**, 104, 5319. (g) Smucker, B. W.; Hudson, J. M.; Omary, M. A.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 4714. (g) Roger, M.; Arliguie, T.; Thuery, P.; Fourmigue, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 584.

(2) (a) Takamatsu, N.; Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Fujita, W.; Awaga, K. *Inorg. Chem.* **2000**, *39*, 870. (b) Akutagawa, T.; Nishihara, S.; Takamatsu, N.; Hasegawa, T.; Nakamura, T.; Inabe, T. *J. Phys. Chem. B* **2000**, *104*, 5871. (c) Akutagawa, T.; Takamatsu, N.; Shitagami, K.; Hasegawa, T.; Nakamura, T.; Inabe, T. *J. Mater. Chem.* **2001**, *11*, 2118. (d) Nishihara, S.; Akutagawa, T.; Hasegawa, T.; Nakamura, T. *Inorg. Chem.* **2003**, *42*, 2480. (e) Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T. *J. Am. Chem. Soc.* **2002**, *124*, 8903. (f) Akutagawa, T.; Shitagami, K.; Nishihara, S.; Takeda, S.; Hasegawa, T.; Nakamura, T.; Hosokoshi, Y.; Inoue, K.; Ikeuchi, S.; Miyazaki, Y.; Saito, K. *J. Am. Chem. Soc.* **2005**, *127*, 4397.

(3) (a) Nishihara, S.; Akutagawa, T.; Hasegawa, T.; Nakamura, T. *Chem. Commun.* **2002**, 408. (b) Akutagawa, T.; Hashimoto, A.; Nishihara, S.; Hasegawa, T.; Nakamura, T. *J. Supramol. Chem.* **2002**, *2*, 175. (c) Akutagawa, T.; Hashimoto, A.; Nishihara, S.; Hasegawa, T.; Nakamura, T. *J. Phys. Chem. B* **2003**, *107*, 66.

(4) Synthesis of [Ni(dmit)$_2$] salts. A solution of (n-Bu$_4$N)[Ni(dmit)$_2$] (19.8 μmol), (*meso*-DPEDA^{2+})(BF$_4{}^-$)$_2$ (100 μmol), and [18]crown-6 (1 mmol) in CH$_3$CN (20 mL) was gently heated until (n-Bu$_4$N)[Ni(dmit)$_2$] was completely dissolved. The solution was slowly cooled to room temperature. [Ni(dmit)$_2$] salts precipitated in the form of black plates (0.2 × 0.1 × 0.1 mm^3), which were washed with CH$_3$CN and C$_2$H$_5$OH and dried. Salt **II** was prepared by the same procedure using chiral cations of (1*S*, 2*S*)-DPEDA^{2+}. Elemental analysis calcd. (%) for salt **I**, C$_{25}$H$_{33}$O$_6$S$_{10}$NNi: C 42.21, H 2.74, N 17.90. Found: C 42.03, H 2.67, N 17.79. Salt **II**, C$_{106}$H$_{132}$O$_{24}$S$_{50}$N$_4$Ni$_5$, C 42.21, H 2.74, N 17.90. Found: C 41.45, H 2.53, N 17.64.

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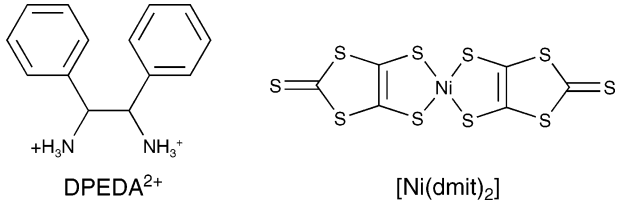
Scheme 1. Chemical Structures of $DPEDA^{2+}$ and $[Ni(dmit)_2]$



and **II** were achiral and chiral, the space groups of salts **I** and **II** were $P\bar{1}$ and $P1$, respectively.[5] The magnetic properties of these two salts were evaluated by a SQUID magnetometer at a magnetic field of 1 T.

Figure 1a and b show the cation structures of (*meso*-$DPEDA^{2+}$)([18]crown-6)$_2$ and [(1*S*, 2*S*)-$DPEDA^{2+}$] ([18]-crown-6)$_2$ in salts **I** and **II**, respectively ($T = 100$ K).[6] The cation was assembled by the sandwich-type coordination of two $-NH_3^+$ groups of $DPEDA^{2+}$ from two upper and lower [18]crown-6 molecules. Two phenyl rings of *meso*-$DPEDA^{2+}$ were symmetrically projected due to the *S*- and *R*-configurations of two chiral carbons, while those of (1*S*, 2*S*)-$DPEDA^{2+}$ were extended in the same direction forming a 90-degree angle. Although the [18]crown-6 molecules in salt **II** exhibited a planar conformation, those in salt **I** were largely warped into a *V*-shaped conformation in order to reduce steric repulsion from two phenyl rings. The difference of chirality of two carbon atoms changed the cation structure of ($DPEDA^{2+}$)([18]crown-6)$_2$, which also modified the $[Ni(dmit)_2]^-$ arrangement and magnetic properties of the crystals.

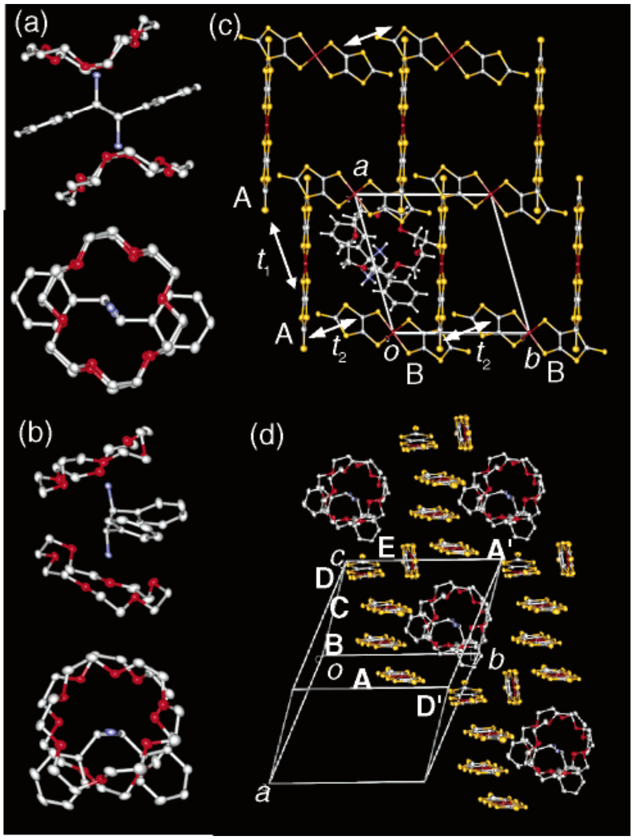


Figure 1. Crystal structures of salts **I** and **II**. Cation structures of (a) (*meso*-$DPDEA^{2+}$)([18]crown-6)$_2$ and (b) [(1*S*, 2*S*)-$DPDEA^{2+}$]([18]crown-6)$_2$. $[Ni(dmit)_2]^-$ arrangements (c) in salt **I** viewed along the *c*-axis and (d) in salt **II**.

Figure 1c and d show the $[Ni(dmit)_2]^-$ arrangements and cation packing in salts **I** and **II**, respectively. In salt **I**, two crystallographically independent $[Ni(dmit)_2]^-$ anions (**A** and **B**) occurred on the inversion centers. The π-overlap at the terminal five-membered rings of $[Ni(dmit)_2]^-$ anion **A** formed linear 1D chains along the *a*-axis, while weak lateral S∼S interactions between the **B** anions yielded 1D linear chains along the *b*-axis. Transfer integrals (*t*) based on the extended Hückel molecular orbital calculations were used to evaluate the magnitude of the intermolecular interaction between $[Ni(dmit)_2]^-$ anions.[7] The magnetic exchange energy (*J*) is proportional to the square of the transfer integral, $J \sim 4t^2/U_{eff}$, where U_{eff} is the on-site Coulomb repulsive energy.[7] The magnitude of transfer integrals within the $[\mathbf{A}^- - \mathbf{A}^-]_\infty$ chain ($t_1 = 22.9$ meV) was much larger than that in the $[\mathbf{B}^- - \mathbf{B}^-]_\infty$ chain ($t_3 = 0.75$ meV).[8] Effective intermolecular interaction ($t_2 = 12.4$ meV) was observed between the $[\mathbf{A}^- - \mathbf{A}^-]_\infty$ chains and $[Ni(dmit)_2]^-$ anion **B** along the *b*-axis, which resulted in a two-dimensional (2D) square lattice of $[Ni(dmit)_2]^-$ anions within the *ab*-plane. From the relationship between *J* and *t*, magnetic anisotropy of $J_1/J_2/J_3$ was estimated to be 3:1:0.001, suggesting that J_1 and J_2 interactions in the 2D square lattice were dominant in the crystal.

There were four crystallographically independent $[Ni(dmit)_2]^-$ and one $[Ni(dmit)_2]$ molecules (**A**, **B**, **C**, **D**, and **E**) in salt **II**. The crystal stoichiometry of [(1*S*, 2*S*)-$DPEDA^{2+}]_2$([18]crown-6)$_4[Ni(dmit)_2]^{-0.8}{}_5$ suggested that one of these five was a formally neutral $[Ni(dmit)_2]$ molecule without a $S = {}^1/_2$ spin. The π-stacks of $[Ni(dmit)_2]^-$ yielded π-tetramer with an [**A**−**B**−**C**−**D**] arrangement along the $a + b$ axis. The transfer integrals within the tetramer ($t_{C-D} = 117$, $t_{C-B} = 126$, and $t_{A-B} = 101$ meV) evidenced strong π-interactions between the $[Ni(dmit)_2]^-$. On the other hand, the π-plane of $[Ni(dmit)_2]$ **E** was normal to those of the tetramer, which connected the [**A**−**B**−**C**−**D**] tetramers via intermolecular π−*S* interactions with $t_{D-E} = 25.5$ and $t_{E-A} = 17.3$ meV.

Figure 2 shows temperature-dependence of molar magnetic susceptibilities (χ_{mol} vs *T*) per $[Ni(dmit)_2]^-$ for salts **I** and

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(5) Crystal data. Salt **I**, 100 K, triclinic, $P\bar{1}$, $a = 12.058(2)$ Å, $b = 12.234(2)$ Å, $c = 13.187(2)$ Å, $\alpha = 111.542(3)°$, $\beta = 94.241(5)°$, $\gamma = 103.080(4)°$, $V = 1735.8(4)$ Å^3, $Z = 2$, $D_c = 1.574$ gcm^3, 2θmax = 55°, μ(Mo Kα) = 12.00 cm^{-1}. 7527 collected reflections, 5962 reflections of $I > 3\sigma(I)$] were used for refinement based on F^2. The final *R* values were $R = 0.050$, $wR2 = 0.067$, GOF = 1.180. Salt **II**, 100 K, triclinic, $P1$, $a = 15.729(3)$ Å, $b = 16.030(3)$ Å, $c = 17.204(5)$ Å, $\alpha = 96.66(1)°$, $\beta = 93.658(1)°$, $\gamma = 118.535(8)°$, $V = 3749(1)$ Å^3, $Z = 2$, $D_c = 1.657$ gcm^3, 2θmax = 55°, μ(Mo Kα) = 13.76 cm^{-1}. 98770 collected reflections, 23812 reflection of $I > 2\sigma(I)$] were used for refinement based on F^2. The final *R* values were $R = 0.053$, $wR2 = 0.097$, GOF = 0.912.

(6) (a) Larsen, A. O.; White, P. S.; Gagné, M. R. *Inorg. Chem.* **1999**, *38*, 4824. (b) Garcia-Granda, S.; Diaz, M. R.; Barrio, C.; Gómetz-Beltrá. *Acta Crystallogr. Sect C* **1990**, *46*, 377. (c) Ghizdavu, L.; von Zelewsky, A.; Stoeckli-Evans, H. *Eur. J. Inorg. Chem.* **2001**, 993.

(7) Scott, J. C. *Highly Conducting Quasi-One-Dimensional Organic Crystals*; Semiconductors and Semimetals Series Vol. 27; Conwell, E., Ed.; Academic Press: New York, 1988, 385. (b) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(8) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627.

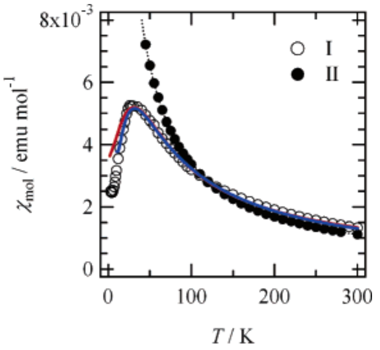

Figure 2. Temperature-dependence of molar magnetic susceptibility (χ_{mol}) of salts **I** (○) and **II** (●) per $[Ni(dmit)_2]^-$. Solid lines are fits of χ_{mol} vs T plots (see text).

II. Salt **II** showed the Curie−Weiss behavior with $C = 0.31$ emu K mol^{-1} (solid circles), which almost corresponds to 0.8 spins per $[(1S,\ 2S)\text{-DPEDA}^{2+}]_{0.4}([18]\text{crown-6})_{0.8}[Ni(dmit)_2]^{-0.8}$ ($C = 0.30$ emu K mol^{-1}). A weak antiferromagnetic interaction was observed between $[Ni(dmit)_2]^-$ anions in salt **II** ($\theta = -4.5$ K). On the other hand, the χ_{mol} vs T plot for salt **I** showed a broad maximum at around 30 K, which is typical for 1D linear Heisenberg antiferromagnetic chains.[9] However, this model failed to reproduce low-temperature behavior (red line in Figure 2) well. Since a 2D square arrangement of $[Ni(dmit)_2]^-$ anions was observed in the X-ray crystal structural analysis, we applied a 2D Heisenberg antiferromagnetic square lattice model to fit the χ_{mol} vs T behavior of salt **I** (blue line in Figure 2).[10] This model reproduced the low-temperature χ_{mol} vs T behavior with a J of -32.3 K and a fixed C of 0.376 emu K mol^{-1} for one $S = {}^1/_2$ spin ($g = 2.0$). To the best of our knowledge, salt **I** represents the first example of a $[Ni(dmit)_2]^-$ salt having magnetic interactions of 2D Heisenberg antiferromagnetic square lattice.

In conclusion, [*meso*- and (1*S*, 2*S*)-diphenyl-1,2-ethanediammonium]([18]crown-6)$_2$ were introduced into magnetic $[Ni(dmit)_2]^-$ salts as countercations. The cation conformations differed from each other, depending on the configuration of two carbon atoms, which also changed the $[Ni(dmit)_2]^-$ arrangements and magnetic properties of the crystals. A two-dimensional Heisenberg antiferromagnetic square lattice was observed in (*meso*-diphenyl-1,2-ethanediammonium^{2+})([18]-crown-6)$_2[Ni(dmit)_2]^-{}_2$, the first example of a 2D magnetic lattice in $[Ni(dmit)_2]^-$ salts. The supramolecular cation approach was found to be effective in generating a variety of $[Ni(dmit)_2]^-$ arrangements in the crystal.

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Supporting Information Available: Crystal data (CIF) of salts **I** and **II**, and overlap modes of $[Ni(dmit)_2]^-$ anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *135*, A640.
(10) Lines, M. E. *J. Phys. Chem. Solids* **1970**, *31*, 101.