COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Formation of a molecular spin ladder induced by a supramolecular cation structure

Sadafumi Nishihara,[a] Tomoyuki Akutagawa,[abc] Tatsuo Hasegawa[ab] and Takayoshi Nakamura*[ab]
[a] *Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[b] *Research Institute for Electronic Science, Hokkaido University, Sapporo 060-0812, Japan. E-mail: tnaka@imd.es.hokudai.ac.jp*
[c] *PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Japan*

Received (in Cambridge, UK) 13th November 2001, Accepted 23rd January 2002
First published as an Advance Article on the web 11 February 2002

A novel molecular spin ladder structure of a nickel dithiolate complex has been constructed using a supramolecular cation composed of anilinium and 18-crown-6.

Even-leg ladders of $S = 1/2$ Heisenberg antiferromagnetic spins are in a resonating valence bond state[1] at low-temperature and have a finite spin-gap.[2] Recently, open-shell organic molecules have been utilized for constructing two-leg spin ladders, and the crystals with a relatively high spin-gap temperature (Δ) have been reported.[3] Herein, we present a supramolecular approach to construct molecular spin ladders. The $[Ni(dmit)_2]^-$ (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) having an $S = 1/2$ spin is an excellent building block for molecular magnetic materials. Since the interacting spins are located in singly occupied molecular orbitals, magnetic properties can be modified by regulating intermolecular interactions in the crystals.[4] We have been studying the control of $[Ni(dmit)_2]^-$ arrangements by supramolecular cations composed of inorganic ions and crown ethers.[5] In the present study, we have constructed dimer chains of $[Ni(dmit)_2]^-$ by using newly designed supramolecular cations composed of arylammonium and 18-crown-6 aimed at forming spin ladders. Ammonium or amine moieties are known to be included into the 18-crown-6 cavity through N–H···O hydrogen bonding.[6] We have utilized this strong interaction for constructing spool-shaped supramolecular cations of $\{[Ph(NH_3)](18\text{-crown-}6)\}_n$ and $[p\text{-}Ph(NH_3)_2](18\text{-crown-}6)_2$. A pair of $[Ni(dmit)_2]^-$ molecules formed a dimer embedded between two adjacent 18-crown-6 moieties of a spool, and the one-dimensional array of the $\{[Ni(dmit)_2]^-\}_2$ gave dimer chain structures, one of which exhibited the magnetic behavior of a spin ladder.

Single crystals of $[Ph(NH_3)](18\text{-crown-}6)[Ni(dmit)_2]$ (**1**) and $[p\text{-}Ph(NH_3)_2](18\text{-crown-}6)_2[Ni(dmit)_2]_2(CH_3CN)_2$ (**2**) were prepared from $(n\text{-}Bu_4N)[Ni(dmit)_2]$, 18-crown-6 and the corresponding arylammonium–(BF_4) in acetonitrile by a diffusion method. The crystal structures of the salts **1** and **2** are shown in Fig. 1. The $[Ni(dmit)_2]^-$ assemblies in crystals **1** and **2** are similar to each other.†

The NH_3^+ part of $[Ph(NH_3)]^+$ cation was included in 18-crown-6, which stacked regularly along the *c*-axis forming an ionic channel-like, one-dimensional spool array in the salt **1**. The $[Ph(NH_3)]^+$ cations were oriented in the same direction within a column and were opposite to those in the neighboring columns. The NH_3^+ group is located at the center of a 18-crown-6 cavity, 0.91 Å above the 18-crown-6 molecular plane, forming $NH^+\cdots O$ hydrogen bonds with oxygen atoms. The average hydrogen-bond length is 2.92 Å, which is slightly longer than the standard $NH^+\cdots O$ distance (2.87 Å).[7]

Each pair of $[Ni(dmit)_2]^-$ molecules forms a dimer through face-to-face interaction, embedded between the adjacent 18-crown-6 molecules. The dimer is located on a pair of spools in neighboring columns, and is aligned along the (011) direction guided by the ditch of the supramolecular cations giving a dimer chain structure.

The $[p\text{-}Ph(NH_3)_2]^{2+}$ part in salt **2** is sandwiched by 18-crown-6 molecules forming a spool-shape supramolecular cation. The NH_3^+ groups are located 0.91and 0.97 Å above the center of the 18-crown-6 with average hydrogen-bond lengths of 2.92 and 2.94 Å. The supramolecular cations are further stacked alternately with CH_3CN molecules forming a one-dimensional spool array along the *b*-axis. Pairs of $[Ni(dmit)_2]^-$ molecules are embedded between the 18-crown-6 molecules, not only on $[p\text{-}Ph(NH_3)_2]^{2+}$ but also on CH_3CN, and are stacked along the *c*-axis forming a one-dimensional array as in the case of salt **1**.

We evaluated the transfer integrals between $[Ni(dmit)_2]^-$ using extended Hückel molecular orbital calculations to estimate the magnetic exchange interactions in the crystals.[8] The transfer integral within the dimer of salt **1**, which corresponds to the ladder rung direction (A–A′), is $t' = 45.3$ meV, and that in the ladder leg direction (A–A and A′–A′) is $t = 15.9$ meV. Since the magnetic exchange interaction is proportional to the square of the transfer integral, the ratio of exchange interaction between the ladder rung (J') and ladder leg (J) directions (J'/J) of salt **1** was estimated to be 8.1. On the other hand, there are two kinds of dimer pairs in salt **2**, although they are almost in the same $[Ni(dmit)_2]^-$ arrangement. The interactions within the dimer (A–A′ and B–B′) are $t' = 74.2$ and 76.0 meV, respectively, whereas those in the ladder leg direction (t) were 11.5 meV in both cases (A–A, A′–A′, B–B and B′–B′). The ratio of J'/J was estimated to be 43.

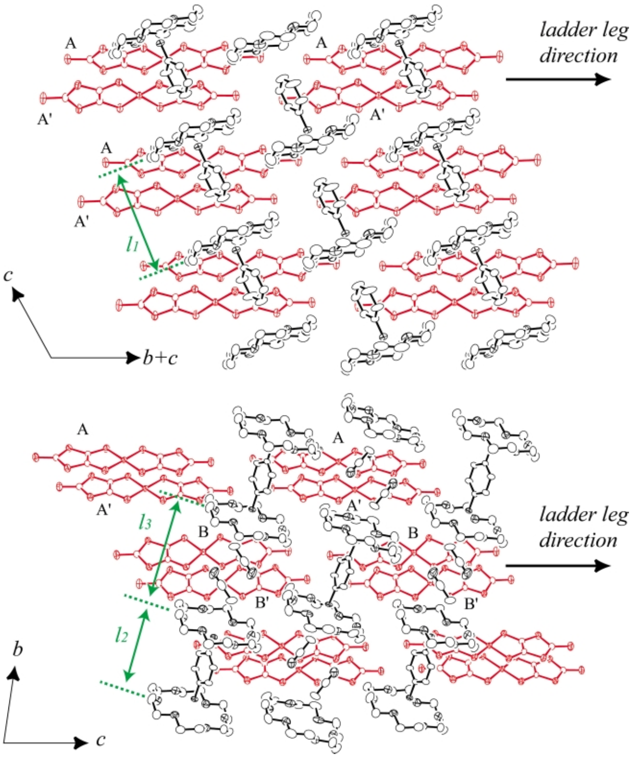

Fig. 1 Crystal structure of the salts **1** (above) and **2** (below). The molecular arrangement of $[Ni(dmit)_2]^-$ forming dimer chain structures (red) is overlaid with spool arrays (black).

DOI: 10.1039/b110368g

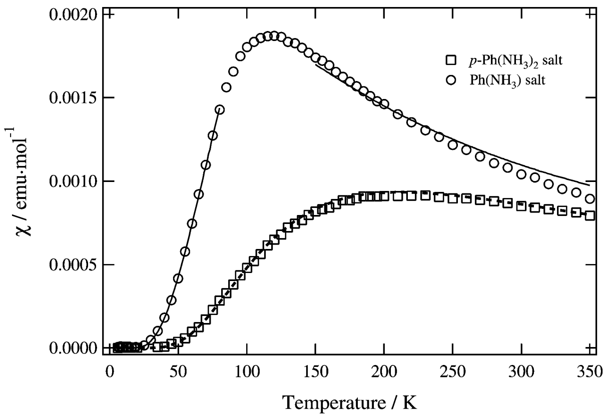

Fig. 2 Temperature dependence of the magnetic susceptibility of salts **1** (○) and **2** (□). The solid lines are fitted curves of eqn. (1) (< 80 K) and eqn. (3) (> 150 K) (see text), and the dashed line is a fit by eqn. (4).

Fig. 2 shows the temperature dependence of the magnetic susceptibility (χ) of the salts **1** and **2** after subtracting the Curie component, $C = 0.0060$ and 0.0063 emu K mol^{-1}, for salts **1** and **2**, respectively. The magnetic susceptibility was measured on a Quantum Design MPMS-XL SQUID susceptometer in a field of 1 T. The susceptibility of salt **1** had a maximum at 120 K, and reached 0 emu mol^{-1} around 15 K. The low-temperature-limit equation of a two-leg spin ladder,[9]

$$\chi_{\rm Low} = \alpha T^{-1/2}\exp(-\Delta/T) \qquad (1)$$

reproduced the observed susceptibility below 80 K with the spin gap $\Delta = 190$ K. Since the gap is related to J and J' as,

$$\Delta \approx J' - J + \frac{1}{2}J^2 / J' \qquad (2)$$

we can estimate the magnetic exchange energies $J = 20$ K and $J' = 200$ K by assuming $J'/J = 10$. The magnetic susceptibility at higher temperatures (> 150 K) is well reproduced by the high-temperature equation,[9]

$$\chi_{\rm High} = C\left[T^{-1} - \frac{1}{2}\left(J + \frac{1}{2}J'\right)T^{-2} + \frac{3}{16}JJ'T^{-3}\right] \qquad (3)$$

using these parameters and $C = 0.394$ emu K mol^{-1} determined from EPR.

In the case of salt **2**, χ increased with the decrease in temperature down to 210 K, and decreased exponentially at lower temperatures. A fitting by the singlet–triplet thermal excitation model,

$$\chi_{\rm Singlet-Triplet} = \frac{C}{T}\frac{4\exp(-2J/T)}{1 + 3\exp(-2J/T)} \qquad (4)$$

using $C = 0.394$ emu K mol^{-1} gave a good result, and the magnetic exchange interaction $2J$ was around 340 K. The ratio of $J'/J = 43$ may be too large to realize the spin-ladder state in salt **2**. It should be noted that eqn. (4) does not give a good fit in the case of salt **1**.

The stronger face-to-face π–π interaction within the [Ni(dmit)$_2$]$^-$ dimer reflects the larger value of J'/J in salt **2**. The interaction depends on the distance between the [Ni(dmit)$_2$]$^-$ units forming the dimer, which should be related to the distance between crown ethers. The distances between the 18-crown-6 molecular planes sandwiching the [p-Ph(NH$_3$)$_2$]$^{2+}$ and CH$_3$CN are $l_2 = 7.49$ and $l_3 = 8.80$ Å (Fig 1). Since each dimer is on both of [p-Ph(NH$_3$)$_2$]$^{2+}$ and CH$_3$CN, the interaction should be determined by the shorter l_2. The distance between the adjacent crown ethers in the salt **1** is $l_1 = 8.13$ Å, which is quite a bit longer than l_2.

In conclusion, we have constructed a novel molecular spin ladder using a spool-type supramolecular cation. According to theory,[10] hole doping to two-leg spin ladders will lead to superconductivity due to that effective attraction between extra holes may arise from the magnetic interactions. In fact, superconducting transitions have been reported in hole-doped spin ladders of calcium cuprates.[11] In the case of salt **1**, the hole doping will be accomplished without significant lattice distortion by replacing a fraction of the ammonium cations with the corresponding amines. Studies on this are in progress.

The authors thank Dr K. Ichimura and Professor K. Nomura for the use of the SQUID magnetometer. This work was partly supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

† *Crystal data*: for **1**: $C_{24}H_{32}NO_6S_{10}Ni$, $M = 809.82$, $T = 296$ K, triclinic, space group $P\bar{1}$, $a = 14.217(1)$, $b = 16.666(2)$, $c = 8.1271(6)$ Å, $\alpha = 97.120(2)$, $\beta = 92.599(3)$, $\gamma = 112.846(2)°$, $V = 1751.6(3)$ Å^3, $D_c = 1.535$ g cm^{-3}, $Z = 2$, $F(000) = 838$, μ(Mo-Kα) = 11.87 cm^{-1}, final R, $R_w = 0.051$, 0.118. $I_o = 5677$ 'observed' [$I > 3.0\sigma(I)$] reflections out of $N = 7594$ unique. GOF = 1.69.

For **2**: $C_{46}H_{64}O_{12}N_4S_{20}Ni_2$, $M = 1623.63$, $T = 296$ K, triclinic, space group $P\bar{1}$, $a = 13.1321(4)$, $b = 16.3032(5)$, $c = 17.6903(5)$ Å, $\alpha = 73.5786(9)$, $\beta = 76.2712(8)$, $\gamma = 82.426(1)°$, $V = 3520.6(2)$ Å^3, $D_c = 1.531$ g cm^{-3}, $Z = 2$, $F(000) = 1680$, μ(Mo-Kα) = 11.82 cm^{-1}, final R, $R_w = 0.055$, 0.094. $I_o = 8095$ 'observed' [$I > 3.0\sigma(I)$] reflections out of $N = 16043$ unique. GOF = 1.11. Crystallographic data collected on a Rigaku RAXIS-RAPID Imaging Plate. All H atoms placed in calculated positions.

CCDC reference numbers 176980 and 176981. See http://www.rsc.org/suppdata/cc/b1/b110368g/ for crystallographic data in CIF or other electronic format.

1 P. W. Anderson, *Science*, 1987, **235**, 1196.

2 E. Dagotto and T. M. Rice, *Science*, 1996, **271**, 618; D. J. Scalapino, *Nature*, 1995, **377**, 12; Z. Hiroi and M. Takano, *Nature*, 1995, **337**, 41.

3 C. Rovira, J. Veciana, E. Ribera, J. Tarrés, E. Candell, R. Rousseau, M. Mas, E. Molins, M. Almeida, R. T. Henriques, J. Morgado, J. P. Schoeffel and J. P. Pouget, *Angew. Chem., Int. Ed. Engl.*, 1997, **109**, 2418; H. Imai, T. Inabe, T. Otsuka, T. Okuno and K. Awaga, *Phys. Rev. B*, 1996, **54**, R6338; T. Komatsu, N. Kojima and G. Saito, *Solid State Commun.*, 1997, **103**, 519; M. Fourmigué, B. Domerq, I. V. Jourdain, P. Molinié, F. Guyon and J. Amaudrut, *Chem. Eur. J.*, 1988, **4**, 1714.

4 C. Rovira, *Chem. Eur. J.*, 2000, **6**, 1723.

5 N. Takamatsu, T. Akutagawa, T. Hasegawa, T. Nakamura, T. Inabe, W. Fujita and K. Awaga, *Inorg. Chem.*, 2000, **39**, 870; T. Akutagawa, S. Nishihara, N. Takamatsu, T. Hasegawa, T. Nakamura and T. Inabe, *J. Phys. Chem. B*, 2000, **104**, 5871.

6 E. Weber, L. J. Toner, I. Goldberg, F. Vögtle, A. D. Laidler, F. J. Stoddart, A. R. Bartsch and L. C. Liotta, *Crown Ethers and Analogs*, S. Patai and Z. Rappoport, ed., John Wiley & Sons, New York, 1989.

7 G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*,Freemann, San Francisco, 1960.

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

9 M. Troyer, H. Tsunetsugu and D. Würtz, *Phys. Rev. B*, 1994, **50**, 13 515.

10 T. M. Rice, S. Gopalan and M. Sigrist, *Europhys. Lett.*, 1993, **23**, 445.

11 M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori and K. Kinoshita, *J. Phys. Soc. Jpn.*, 1996, **65**, 2764; J. H. Schön, M. Dorget, F. C. Beuran, X. Z. Xu, E. Arushanov, M. Lagues and C. Deville Cavellin, *Science*, 2001, **293**, 2430.