

A New Nickel Coordination Polymer with Dynamic Channels that Mechanically Capture and Release Including Guest Molecules Responding to a Temperature Variation

Mitsuru Kondo,* Yusuke Shimizu, Makoto Miyazawa, Yasuhiko Irie, Akira Nakamura,[†] Tetsuyoshi Naito,^{††} Kenji Maeda,^{††} Fumio Uchida,^{††} Tadahiro Nakamoto,^{#†††} and Akira Inaba^{†††}

Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422-8529

[†]OM Research, 7-2-1308 Ohgimachi, Kita-ku, Osaka 530-0052

^{††}Hautform Division, Fuji Chemical Co. Ltd., 1683-1880, Nakagaito, Nasubigawa, Nakatsugawa, Gifu 509-9132

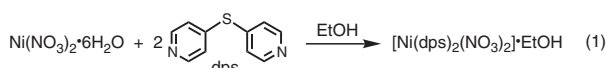
^{†††}Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received January 9, 2004; CL-040042)

A new 1-D nickel(II) coordination polymer with dynamic channels was prepared and characterized. This compound has two structural phases that are switched by a temperature variation. The closed channel created at the low temperature mechanically captures the including guests in the channels.

Coordination channel frameworks that change their structures in response to the physical stimuli have received intense attention because of their new functions such as molecular storage.¹ Nevertheless, such dynamic coordination frameworks have not yet been well developed. We have studied coordination polymers with sulfide in organic backbone,² and we have recently succeeded in synthesis of a new coordination polymer with such dynamic channels, in which the channel structures open and close above and below a critical temperature.

The new porous coordination polymer [Ni(dps)₂(NO₃)₂]₂·EtOH (dps = 4,4'-dipyridylsulfide) (**1**) was conveniently obtained as light-blue crystals by diffusion of dps into the Ni(NO₃)₂·6H₂O in an ethanol solution (Eq 1). As mentioned below, **1** has two structural phases that reversibly transform, depending on the temperature. The critical temperature is in the range of -18 to 2 °C, which is easily attainable. The two structural phases observed above and below the critical temperature are designated by **1** α and **1** β , respectively.



Figures 1 and 2 compare the arrangements of the 1-D chains and channel structures of **1** α and **1** β .³ **1** α , prepared at room temperature, crystallizes in *Ccc2*. The structural determination shown in Figure 1 (left) was carried out at 23 °C. The nickel cen-

ter is based on a distorted octahedron with four pyridine nitrogen donors and two oxygen donors from nitrate anions. Each nickel center is bridged by two dps ligands to yield 1-D chains along the *c* axis. Of the four 1-D chains, 1-D channels with a compressed octahedral shape (ca. 5 × 5 Å) are created (Figure 2). Although elemental and structural analyses at lower temperatures show that **1** α contains one ethanol molecule per nickel atom, the expected electron densities were not observed in the channels (Elemental analysis (%) Calcd for C₂₂H₂₂N₆NiO₇S₂: C, 43.66; H, 3.66; N, 13.88; Found: C, 43.39; H, 3.49; N, 14.11%). This is likely due to the remarkable disorders at this temperature. As a result, no atoms could be located in the channels for the X-ray refinement models.

The formation of the second structural phase was confirmed by differential scanning calorimetry (DSC) measurement and X-ray single crystal analysis. When the bulk sample of **1** α was cooled, followed by heating, exo- and endothermic peaks were observed between -6 and -32 °C and between -19 and 2 °C, respectively. The crystal structure of the second phase, **1** β , which forms below the critical temperature, was determined by X-ray analysis at -40 °C by using the single crystal (**1** α) that was prepared at room temperature. The space group *Ccc2* for **1** α is changed to *Pnc2* for **1** β . In contrast to **1** α , **1** β contains two crystallographically independent nickel centers, which yield two types of 1-D chains that are made of equivalent nickel centers. The two chains are designated chain-A and chain-B as illustrated in Figure 1. The phase transformation accompanies a slide of the chain-B of about 1 Å along the *c* axis. The guest ethanol molecules, which are not structurally defined in **1** α , are clearly observed in the channel-like cavities of **1** β . The oxygen atom of the ethanol forms a weak hydrogen bond with an oxygen atom of a coordinating nitrate anion (O–O = 3.065(2) Å).

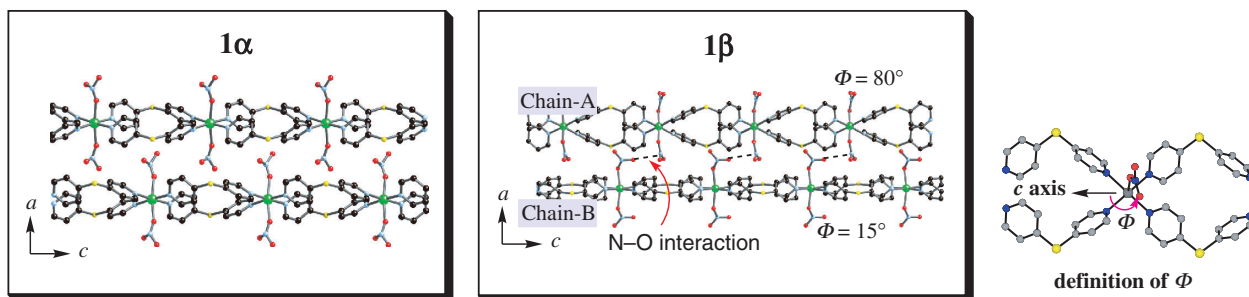


Figure 1. 1-D chains of **1** α (left) and **1** β (middle) are illustrated for comparison. The ethanol molecules in the channels of **1** β and hydrogen atoms of both compounds are omitted for clarity. The channel structures are controlled by the rotation of NO₃ anions, in which the rotation angles Φ is illustrated (right).

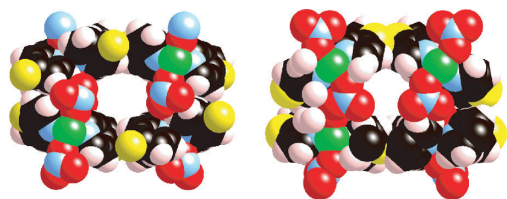


Figure 2. Channel structures with van der Waals radii of 1α (left) and 1β (right).

The slide of the chains is linked to the rotations of the nitrate anions to form electrostatic interactions⁴ between nitrogen and oxygen atoms ($N-O = 2.989(2) \text{ \AA}$) in the chain-A and B. The rotation of the coordinating nitrate anions establishes the most significant effects of this transformation on the channel structures. When the angle of the NO_3 plane of the coordinating anion to the channel direction, i.e. the c axis, is defined as Φ , (Figure 1) the angles of nitrate anions in 1α are about 45° (and -45°). However, the Φ of nitrate anions in 1β are about 80° (and -80°) and 15° (and -15°) for chain-A and chain-B, respectively. That is, the planes of the nitrate anions of chain-A are adjusted to nearly perpendicular to the channel direction. The rotations divide channel-like cavities to each cavity, in which the shape of the channel windows is changed from the “compressed hexagon” of 1α to the “T-shape” ($5 \times 2 + 2 \times 3 \text{ \AA}$) by the jutting of the nitrate anions of chain-A into the channels. The structural transformation narrows the channel width from about 5 to 2 \AA for the lower half of the channel window. This diminishment is sufficient to significantly change the guest capturing properties. This second phase with diminished channels is regarded as the *closed* channel phase induced by the temperature switch.

The finding of the dynamic channel framework prompted us to study the amount of ethanol molecules released from the *open* and *closed* channels. We preliminarily monitored the guest ethanol molecules released from the bulk crystalline samples of **1** as the temperature changed from -50 to 30°C (Figure 3). When the crystalline sample was heated from -50 to 30°C in *m*-xylene media only small concentrations of ethanol were observed, indicating that ethanol molecules are essentially not released from the cavities below -18°C . The release of ethanol molecules was suddenly observed at -18°C with an apparent discontinuity. Above this temperature the concentration increases with the increase in temperature, which is a typical property of physical adsorption for open channels.

A sample cooled to -40°C , followed by heating to room temperature, displayed similar X-ray powder diffraction (XRPD) pattern to 1α , and retained capturing properties for the capture and release experiment. These results demonstrate that the *closing* and *opening* mechanism of the channels of **1** proceeds reversibly.

This dynamic porous mechanism is unprecedented and is attractive for achieving new functionality. Further studies of the dynamic channel framework of **1** to understand the effects of the including guests on the phase transition temperature and the capturing functions against various guest molecules in gas- and liquid states are currently undergone.

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 15036227, “Reaction control of dynamic complexes”) from the Ministry of Education, Culture,

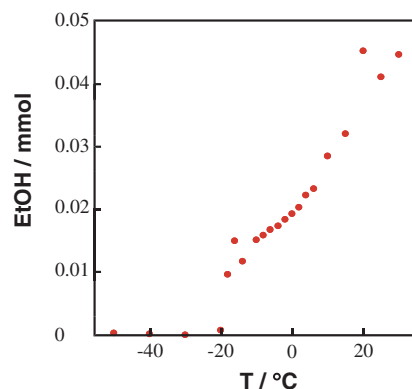


Figure 3. Plot of the amount of ethanol released from the channels of $[\text{Ni}(\text{dps})_2(\text{NO}_3)_2] \cdot \text{EtOH}$ against temperature. The crystalline sample (100 mg, 1.7×10^{-4} mol) was cooled to -50°C , then immersed in *m*-xylene (3 mL) containing a small amount of methanol ($5.89 \mu\text{L}$, 1.7×10^{-4} mol) at -50°C . The methanol molecules in *m*-xylene were added to promote the release of ethanol molecules from the channels by replacement with methanol. The amount of ethanol molecules released in the *m*-xylene media was monitored by gas chromatography as the temperature was increased to 30°C .

Sports, Science, and Technology, Japan. The authors greatly thank to Prof. K. Kaneko of Chiba University and Prof. G. R. Desiraju of University of Hyderabad for their helpful discussion.

References and Notes

- # Present address: Toray Research Center, Inc., 3-3-7 Sonoyama, Otsu, Shiga 520-8567
- a) J. L. Atwood, L. J. Barbour, and A. Jerga, *Science*, **296**, 2367 (2002). b) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, **71**, 1739 (1998). c) P. J. Hagrman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed.*, **38**, 2638 (1999). d) O. M. Yaghi, H. Li, C. Davis, D. Richardson, and T. L. Groy, *Acc. Chem. Res.*, **474**, 31 (1998). e) C. Janiak, *J. Chem. Soc., Dalton Trans.*, **2003**, 2781. f) S. Takamizawa, E.-I. Nakata, H. Yokoyama, K. Mochizuki, and W. Mori, *Angew. Chem., Int. Ed.*, **42**, 4331 (2003). g) K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.-C. Chang, and T. Mizutani, *Chem.—Eur. J.*, **8**, 3587 (2002). h) M. Albrecht, M. Lutz, A. L. Spek, and G. van Koten, *Nature*, **406**, 970 (2000).
- M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, and F. Uchida, *Chem. Commun.*, **2002**, 2156.
- Crystal data for 1α : fw = 605.27, orthorhombic, space group *Ccc2* (no. 37), $a = 13.27(1)$, $b = 19.88(2)$, $c = 10.100(9) \text{ \AA}$, $V = 2665(3) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.508 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.937 \text{ mm}^{-1}$, $T = 296 \text{ K}$, $\lambda = 0.07107 \text{ \AA}$, ω scans, $R = 0.076$, $wR = 0.099$ for 1641 unique reflections ($R_{\text{int}} = 0.040$) with $I > 2\sigma(I)$ and 158 parameters, CCDC 225114. Crystal data for 1β : fw = 605.27, triclinic, space group *Pnc2* (no. 30), $a = 13.1233(8)$, $b = 19.468(1)$, $c = 10.1241(5) \text{ \AA}$, $V = 2586.6(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.554 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.966 \text{ mm}^{-1}$, $T = 233 \text{ K}$, $\lambda = 0.07107 \text{ \AA}$, ω scans, $R = 0.038$, $wR = 0.052$ for 5334 unique reflections ($R_{\text{int}} = 0.027$) with $I > 2\sigma(I)$ and 344 parameters, CCDC 225115. The data collection was performed on a Rigaku-CCD Mercury system. The structures were solved by direct methods using SIR-92.⁵ All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were included but not refined.
- R. K. R. Jetti, P. K. Thallapally, A. Nangia, C.-K. Lam, and T. C. W. Mak, *Chem. Commun.*, **2002**, 952.
- A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.*, **26**, 343 (1993).