## Cold Crystallization in Bis[1-(3-methylphenyl)iminomethylnaphthalen-2-olato]nickel(II) Studied by Thermal Analysis and X-ray Diffraction

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Bis[1-(3-methylphenyl)iminomethylnaphthalen-2-olato]nickel(II) was synthesized to see a potential use of this type of compounds as heat-storage materials utilizing cold crystallization. Its thermal, structural, and energetic properties were investigated by thermal analysis, X-ray diffraction, and DFT calculation. Some principles in designing complexes for this purpose are deduced.

Global ecology demands highly fuel-efficient vehicles such as hybrid vehicles (HV). Although the transportation is certainly of the primary importance for any vehicles, the comfort is also crucial for the modern life. The improved fuel efficiency generally accompanies the lowered temperature of exhaust heat (200–300 °C), which is to be utilized for the improved *net* efficiency of vehicles. In this respect, the development of heatstorage materials that are workable reliably and safely in this temperature range is strongly desired. Principal demands for heat-storage materials are the controllability of storage and release and the heat capacity.

Thermal storage materials can be grouped into two: thermophysical<sup>1,2</sup> and thermochemical materials.<sup>3,4</sup> Thermophysical ones utilize sensible and latent heats and usually need thermal insulation to prevent the heat losses to the environment, except for those utilizing supercooling and cold crystallization.<sup>5</sup> On the other hand, in thermochemical materials, chemical reactions (breakage and formation of covalent bonds) are utilized to reversibly store and withdraw energy without the need for thermal insulation. Despite the high energy density and insulation-free long-term storage, however, thermochemical technologies have not been used in automobiles because of needs for high temperatures (over 300 °C), which is closely related to a large energy of a covalent bond.

The use of the change in coordination bonds, energy of which lies in between van der Waals interaction used in a thermophysical system and covalent bond in the thermochemical one, would lower the working temperature while maintaining relatively high energy density. Thermal properties and the cold crystallization with the change in the coordination mode was reported for a Schiff-base metal complex, bis[*N*-isopropyl-5,6-benzosalicylideneaminato]nickel(II), by Wang et al.<sup>6</sup> The aim of this letter is to report the synthesis of a complex exhibiting cold crystallization as the first attempt at developing heat-storage materials of coordination complexes. The mechanism of cold crystallization is discussed on the basis of results of thermal analysis, X-ray diffraction, and quantum chemical calculation.

For a possible application in HVs, a high-melting point complex with a substituted phenyl group as an N-substituent, bis[1-(3-methylphenyl)iminomethylnaphthalen-2-olato]nickel(II)



Figure 1. Atomic numbering and ORTEP drawing of the molecular structure in Form 1 crystal. Hydrogen atoms are omitted for clarity.

(Figure 1), was synthesized<sup>7</sup> and characterized by X-ray crystallography on a single crystal.<sup>8</sup> This as-synthesized crystal is designated as Form 1 hereafter.

The phase-transition behavior of the complex was investigated utilizing a commercial differential scanning calorimeter (DSC) (Mettler Toledo, DSC-1). Open pans of aluminum were used under a nitrogen gas (50 mL min<sup>-1</sup>). The scanning rate was  $\pm 15.0$  °C min<sup>-1</sup>. Transition temperatures were determined as onset temperatures.

Figure 2 shows DSC curves with marked A-F peaks. Run 1 is the first heating process of Form 1. Form 1 melts at 241.5 °C (A) with the enthalpy of fusion of  $104 \text{ kJ mol}^{-1}$ . On cooling the liquid (run 2), it shows supercooling and finally undergoes a glass transition (B) around 90 °C without any anomalies suggesting crystallization. On heating (run 3), this glass exhibits two stepped anomalies at 97.2 (C) and 149.7 °C (D). The two anomalies are tentatively assigned to two-step softening (glass transitions), suggesting that a softening process of translational degrees of freedom of molecules is not closely coupled with that of orientations. Above the second softening, the sample is in the supercooled liquid, which relaxes to a crystalline form (the socalled cold crystallization) at 191.4 °C (E) on further heating. The enthalpy involved in the cold crystallization is estimated as  $60 \text{ kJ mol}^{-1}$ . The resultant crystal melts at 243.7 °C (F) with the enthalpy of fusion of 79 kJ mol<sup>-1</sup>. Since the temperature and enthalpy of fusion are different from Form 1, the crystal obtained after the cold crystallization (E) is referred to as Form 2. After the second cooling (run 4), essentially the same behavior as runs 2 and 3 was observed. The detailed thermodynamics quantities are given in Table S1.12 Since the melting



**Figure 2.** DSC traces of the complex measured under nitrogen with a scanning rate of  $15.0 \,^{\circ}\text{C}\,\text{min}^{-1}$ . A, F, melting; B, C, D, glass transition; E, cold crystallization.

temperature of Form 2 (observed at F) is slightly higher by ca. 2 °C than that of Form 1 (A), Form 2 is more stable thermodynamically than Form 1 is in this temperature region. The enthalpies involved in F in run 3, 5, and 7 were approximately the same, implying the similar extent of cold crystallization. If the extent was full, thermodynamic stabilities of Forms 1 and 2 will be interchanged at a low temperature. The interchange temperature (the expected temperature of the phase transition) was calculated as ca. 233 °C. On the one hand, the temperature of the cold crystallization (E) is 192 °C. Form 2 is metastable at that temperature, accordingly. Hence, the behavior of the cold crystallization is in accordance with Ostwald's step rule, which says the solid first formed from the melt is the least-stable polymorph with the highest Gibbs energy.

As explained above, bis[1-(3-methylphenyl)iminomethylnaphthalen-2-olato]nickel(II) exhibits an exothermic process upon the cold crystallization; this can be regarded as heat storage in the first heating process and heat release in the second or later heating process at an arbitrary moment by a thermal stimulus. Note that the state storing heat is practically stable below  $T_g \approx 90$  °C. The changes in the enthalpy of melting and cold crystallization, corresponding to the heat storage capacity of Form 2, are 79–84 and 60–62 kJ mol<sup>-1</sup>, respectively. Since the change in coordination bonds is not involved in this process as described later, the latent heat utilized here relies on van der Waals interaction.

To see structural changes associated with thermal anomalies observed by DSC, simultaneous powder X-ray diffraction and DSC (XRD–DSC) analysis was employed. Despite slightly different sample environments, thermal behavior observed in DSC (Figure 2) was essentially reproduced. The result of XRD– DSC is presented in Figure S1 in Supporting Information.<sup>12</sup>



**Figure 3.** Experimental powder diffraction patterns of Form 1 (blue line), Form 2 (red line), and glass (black line) compared with simulated pattern based on crystal structures determined independently.

Amorphous nature of the glass (after B in Figure 2) was confirmed as shown in Figure 3. Form 1 (as-synthesized crystal before A) and Form 2 (obtained through cold crystallization E) gave completely different diffraction patterns.

Single-crystal pieces were picked up from the sample after cooling the cold-crystallized sample to room temperature. After some trials, the crystal structure of Form 2 was successfully solved at room temperature.<sup>8</sup> Resultant crystallographic data reasonably explain the powder X-ray diffraction patterns for both Forms 1 and 2, as shown in Figure 3. Therefore, we confirm that both forms are the predominant crystals in the bulk composition.

The peaks of the lowest angles in Forms 1 and 2 are indexed as  $(10\overline{1})$  and (100), respectively. If the setting of the space group of Form 1 ( $P2_1/n$ ) is changed to  $P2_1/c$ , the structural similarity between the corresponding planes becomes clear (Figure S2).<sup>12</sup> This suggests superior structural stability of molecular packing within these planes. In other words, Forms 1 and 2 structurally differ in stacking of these planes. On the other hand, the powder X-ray pattern of the glass shows two broad peaks. The first broad peak has the peak centered around  $8.05^\circ$ , which is roughly equal to the lowest angle of Form 1 ( $8.05^\circ$ ). In contrast, the second peak is very broad ( $16.0-27.0^\circ$ ).

For the comparison of molecular structures in Forms 1 and 2, three planes are defined: Plane P1, which serves as the reference in the followings, is defined as that on which the five central atoms sit. Plane P2 is the plane of the ligand except a substituent on N1 atom. P2 is, in practice, determined as the "best plane," from which the sum of squares of distances of C9–C18 atoms is the minimum. Although P2 of Form 2 (2-P2) is almost flat (as indicated by  $\pm 0.01$  Å) in terms of the distance of atoms, the planarity of 1-P2 is worse ( $\pm 0.03$  Å). Plane P3 is the best plane of the benzene ring consisting of C1–C6 atoms. P3 is practically flat in both Forms 1 and 2.

Now, the molecular structures can be compared. The bending angle between 1-P1 and 1-P2 was  $18.1^{\circ}$ . 1-P3 is



**Figure 4.** Molecular energy starting from the structures in Forms 1 and 2 as a function of the twist angle of the phenyl moiety in the molecule in  $15^{\circ}$  steps from 40 to  $100^{\circ}$ . Crosses indicate the angles corresponding to the structures in crystals. Diamond corresponds to the fully optimized structure.

twisted from 1-P1 by 71.2°. The corresponding angles in Form 2 are 14.7 and 81.5°, respectively. If the step distance is defined as the vertical distance between P2 and P2', those of Forms 1 and 2 are 0.00 and 0.62 Å, respectively. It is reported<sup>13</sup> that complexes with bulkier side groups as substituents on N1 atom exhibit larger step distances. Hence, the substituent (3-methylphenyl group) on the N atom turned to an effectively bulkier structure by twisting.

The energy profiles of isolated molecules were calculated by varying the twist angle  $\phi$  of the phenyl moiety (expressed by the dihedral angle of C8–N1–C1–C2 in the molecule) at every 15° from 40 to 100°, while fixing structures of other parts at those observed crystallographically. DFT calculation was performed utilizing the Gaussian03 package at level of B3LYP/ 6-311G<sup>\*\*</sup>.<sup>14</sup>

Results of the calculation, i.e., the intramolecular stability, are shown in Figure 4. Although the molecular energy in Form 1 is calculated to be slightly lower than that of Form 2 by ca.  $5 \text{ kJ mol}^{-1}$ , this magnitude is too small to deduce a definite conclusion concerning the relative stability of molecules in Forms 1 and 2. Considering thermal energy at temperatures of present interest [ $R \times (500 \text{ K}) \approx 4 \text{ kJ mol}^{-1}$ ], on the other hand, the minima of the energy curves obtained for both Forms are very shallow. This implies that molecules in melt have a wide range of the twist angle, resulting in the ease of supercooling, i.e., the difficulty in crystallization on cooling. In this respect, a flexible molecular structure is preferred in designing molecules exhibiting cold crystallization.

In conclusion, we considered the possibility of utilizing organic metal complexes as heat-storage materials, and we prepared bis[1-(3-methylphenyl)iminomethylnaphthalen-2olato]nickel(II) as a trial material. Thermal, crystallographic, and computational analyses revealed the cold crystallization behavior of the compound. Molecular flexibility enhances the ease of supercooling, possibly leading to the occurrence of the desired cold crystallization. Since Ostwald's step rule practically applies, avoiding metastable polymorphs is preferable to achieve a large storage capacity. Considering the potential advantages, the flexibility in coordination geometry should be pursued in future.

## **References and Notes**

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- 7 Nickel(II) acetate hydrate (4.24 g, 16.0 mmol) in THF (20 mL) and ethanol (30 mL) was mixed with *N*-(*m*-tolyl)-2-hydroxy-1-naphthaldimine (2.00 g, 8.0 mmol) in ethanol (50 mL). The liquid solution was heated at 70 °C. After 1 h, a platelet-shaped crystals started appearing. We confirmed the purity of complex which is high enough to pass <sup>1</sup>H NMR, Karl-Fisher (water content ca. 270 ppm).
- 8 X-ray measurements of single crystals of Form 1 and Form 2 were carried out using a R-AXIS RAPID imaging plate diffractometer with Mo K $\alpha$  radiation (0.71075 Å) and a Rigaku Saturn724 diffractometer using multilayer mirror monochromated MoK $\alpha$  radiation at 20 ± 1 °C, respectively. The structures were solved by the direct method (SIR20089) and refined by the full-matrix least-squares method on |F|.<sup>2</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Absorption correction was applied using an empirical procedure. All calculations were performed using the CrystalStructure<sup>10</sup> crystallographic software package except for refinement, which was performed using SHELXL-97.1 Crystal Data for Form 1:  $C_{36}H_{28}N_2NiO_2$ , M = 579.33, green platelet, crystal dimensions  $0.200 \times 0.090 \times 0.030 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ , a = 12.076(1) Å, b = 2.8739(5) Å, c =19.484(2) Å,  $\beta = 99.593(7)^{\circ}$ , V = 1362.8(2) Å<sup>3</sup>, Z = 2,  $D_{calcd} = 1.412 \text{ g cm}^{-3}$ , 9040 reflections collected. 3080 independent , 9040 reflections collected, 3080 independent  $(R_{\text{int}} = 0.0515), \text{ GOF} = 1.006, R_1 = 0.0511$   $(I > 2.00\sigma(I)),$  $wR_2 = 0.1368$  for all reflections. Crystal Data for Form 2:  $C_{36}H_{28}N_2NiO_2$ , M = 579.33, brown block, crystal dimensions  $0.080 \times 0.077 \times 0.020 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ , a = 9.318(4) Å, b = 11.799(5) Å, c = 13.690(6) Å,  $\beta =$  $108.253(5)^{\circ}$ ,  $V = 1429.4(11) \text{ Å}^3$ , Z = 2,  $D_{\text{calcd}} = 1.346 \text{ g cm}^{-3}$ , 11239 reflections collected, 3272 independent ( $R_{int} = 0.0378$ ), GOF = 0.916,  $R_1 = 0.0401$  ( $I > 2.00\sigma(I)$ ),  $wR_2 = 0.1054$  for all reflections.
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