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Thermal Properties of Solid Bis(2,3-alkanedione dioximato)nickel(II). Crystal Structure Transformation

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The thermal behavior in the solid state of the title complexes was investigated. Here 2,3-alkanedione dioximato is CH_3–C(=NOH)–C(=NO)–R; R includes C_2H_5 (**1**), *n*-C_3H_7 (**2**), *n*-C_4H_9 (**3**), *n*-C_5H_{11} (**4**), *n*-C_6H_{13} (**5**), and *n*-C_8H_{17} (**6**) groups. The complexes, **1**, **2**, **5**, and **6**, underwent thermal crystal structure transformation; the transformation was irreversible for **1** and **5**, and reversible for **2** and **6**. The ΔH_t values, heats of transformation, were found to fall in the 5.3—32.6 kJ mol^{-1} range. The ΔH_m values, heats of melting, were determined for the complexes, **2**—**6**. On the basis of these data, the thermal characteristics for these complex crystals are discussed in relation to the nature of the R groups.

The nickel(II) complexes of 2,3-alkanedione dioximes have been extensively studied in the fields of analytical and coordination chemistries.[1] The current interest has been concentrated rather on the interpretation of the properties and structures in the solid state of the complexes connected with their solubilities: these solubilities closely relate to the function of these dioximes as a specific precipitant for Ni^{2+} and Pd^{2+} ions and also to the proposed presence of a novel, intermetallic interaction[2] in the crystals of these metal-dioximato complexes.

In the crystal of bis(dimethylglyoximato)nickel(II), $Ni(dmgH)_2$,[3] planar complex molecules are stacked face to face along the c_o axis and are rotated alternately by 90° around the c_o axis;[4] this is referred to as the cross-form. The Ni atoms array along the c_o axis apart by 3.5 Å, posing as if there is an intermetallic Ni–Ni interaction.[2] For the $Ni(emgH)_2$ complex, two different forms of crystal are known. In one form, planar complex molecules array like the slats of a venetian blind inclined with an angle of 44°, when the cord of the blind is likened to the a_o axis of the crystal;[5] this is referred to here as the blind-form. In the other form, molecular packing is considered to be like the above mentioned cross-form of $Ni(dmgH)_2$ according to the analysis of the X-ray powder diffractions.[6] Anex and Krist have reported that the slow evaporation of the complex solution gives rise to the precipitation of the blind-form, whereas the hasty evaporation yields the cross-form.[7]

These facts are thought to imply that a crystal structure transformation occurred in the solid of these complexes. However, there has so far been no report which proved the existence of such a thermal crystal structure transformation.[8] In the present paper, the thermal properties of a series of the bis(2,3-alkanedione dioximato)[3] complexes have been investigated by thermal and X-ray powder diffraction analyses. The crystal structure transformation has been found to occur for the complexes whose dioximato ligand is emgH, prmgH, hxmgH, or omgH,[3] and the thermodynamic data have been determined.

Experimental

Preparation of Ligands. Following the general procedure given in the literature,[9] 2,3-alkanedione dioximes were prepared by the condensation reaction of 3-hydroxyimino-2-alkanone and hydroxylamine; the hydroxyimino derivatives were prepared by the isonitrosation of the corresponding 2-alkanones with ethyl nitrite. The dioximes thus obtained were purified by recrystaliization from methanol–chloroform (3 : 7), and were identified by elemental analysis, melting point, and ^{13}C-NMR spectrum.

Preparation of Complexes. The precipitates of the complexes were obtained in the following general manner: an aqueous solution saturated with nickel acetate was added to a hot methanol solution of the dioximes, and then the precipitate produced was collected on a filter. The recrystallization of the complexes was carried out as follows: the complex was added into the boiling solvent indicated in Table 1 for each complex, and then the saturated solution was filtered while it was hot. If the crystals were separated during the filtration, the crystals were dissolved again by heating the filtrate. Then the filtrate was cooled by allowing it to stand at room temperature. The crystals were separated by filtration, and then dried *in vacuo*.

The X-ray diffractions of crystalline $Ni(emgH)_2$ obtained in the above manner indicated it to be the blind-form.[5] The cross-form of $Ni(emgH)_2$ was prepared by the literature method.[6b]

Measurements. The differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were carried out by use of a Rigaku Denki thermal analyzer, Model 8002; the particle size of samples was under 200 mesh. Heats of transformation and of melting were measured by DTA method for $Ni(prmgH)_2$, and by the DSC method for the other complexes; potassium nitrate (transformation temperature, 127.9 °C; heat of transformation, ΔH_t, 5.4 kJ mol^{-1})[10] was employed as the standard compound.

The X-ray powder diffractograms were recorded on a Rigaku Denki Geigerflex diffractometer using Co *Ka* radiation. The sample was heated in a furnace constructed in our laboratory: a sample placed in a holder equipped with a thermocouple was heated in a porcelain, cylindrical skeleton wrapped with a nichrome wire; the temperature was controlled by a PID action thermal controller constructed in our laboratory.

The reflectance spectra were recorded on a Shimadzu UV-300 spectrophotometer, by means of an opal glass method.[11]

Results

The complexes subjected to the investigation are listed in Table 1 along with their thermal character. The ^{13}C-NMR measurements suggested the trans-coordination of the two 2,3-alkanedione dioximato ligands in these complexes, like that in the $Ni(emgH)_2$ complex.[5] The complexes remained diamagnetic on raising temperature until their decomposition initiated.

Table 1. Thermal character of Ni(2,3-alkanedione dioximato)$_2$

Dioximato ligand	Solvent[a)]	Heat of transformation ΔH_t/kJ mol^{-1}	Heat of melting ΔH_m/kJ mol^{-1}	$\Delta H_t + \Delta H_m$	Decomposition t/°C[c)]	Reflectance spectrum peak maximum/nm
emgH	$C_6H_5NO_2$	9.1 (213)[b)]	——	——	251	490 (cross-form)
prmgH	$(CH_3)_2CO$	5.3 (38)	23.4 (156)[b)]	28.7	210	513 (form-I) 518 (form-II)
bmgH	MeOH	——	16.3 (142)	16.3	190	459
pnmgH	MeOH	——	25.2 (145)	25.2	212	463
hxmgH	MeOH	24.4 (80)	21.9 (148)	46.3	174	472 (form-I) 471 (form-II)
omgH	MeOH	32.6 (78)	14.6 (119)	47.2	219	485 (form-I) 466 (form-II)

a) Solvent used for the recrystallization of each complex. b) DTA-peak maximum temperature/°C. c) Initial temperature/°C of decomposition on DTA curve.

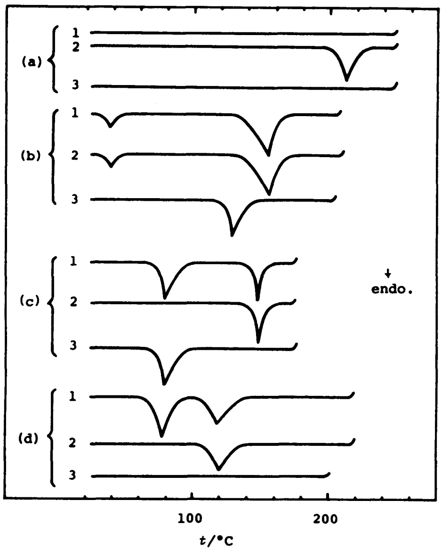

Fig. 1. DTA curves of Ni(2,3-alkanedione dioximato)$_2$. (a) Ni(emgH)$_2$: 1, cross-form; 2, blind-form; 3, cross-form obtained by heating blind-form at *ca.* 200 °C. (b) Ni(prmgH)$_2$: 1, form-II; 2, crystal obtained by heating original form-II at 50—100 °C; 3, sample obtained by heating form-II until melting. (c) Ni(hxmgH)$_2$: 1, form-II; 2, form-I obtained by heating form-II at *ca.* 100 °C; 3, sample obtained by heating form-II until melting. (d) Ni(omgH)$_2$: 1, form-II; 2, form-I obtained by heating form-II at *ca.* 100 °C; 3, sample obtained by heating form-II until melting.

Ni(emgH)$_2$. The DTA curve shown in Fig. 1 indicates that the cross-form crystal of Ni(emgH)$_2$ decomposes exothermally at an initial temperature of 251 °C. The blind-form crystal shows an endothermic DTA peak with a maximum at 213 °C, accompanied by no weight-loss, and then it begins to decompose at 250 °C. The crystal obtained after having heated the blind-form crystal at *ca.* 200 °C no longer shows any DTA peak around 213 °C, and it only shows decomposition initiated at 251 °C, like the authentic cross-form. Moreover, its powder X-ray diffractogram closely corresponded to that of the cross-form.[6b)] These facts indicate that the blind-form is irreversibly transformed into the cross-form in the solid state at *ca.* 200 °C, and the DTA peak at 213 °C is due to this transformation. The thermal analysis showed that the cross-form thus obtained through the transformation could be reformed as the blind-form by the recrystallization from nitrobenzene solution.

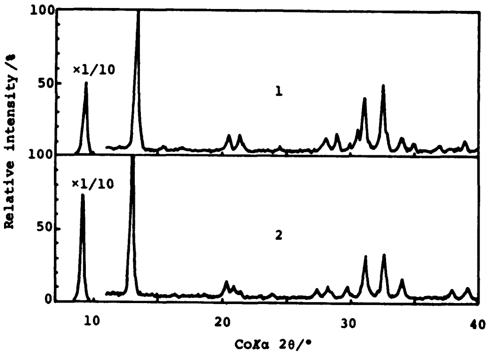

Fig. 2. X-Ray powder diffractograms of Ni(prmgH)$_2$. 1, Form-II; 2, form-I, recorded for form-II at 40 °C.

Ni(prmgH)$_2$. As seen in Fig. 1, the crystal of the complex isolated from acetone solution, noted here as form-II, undergoes two endothermic changes, showing DTA peaks with the maxima at 38 and 156 °C; these changes are accompanied by no weight-loss. The peak at 156 °C is due to melting. The crystal initiate decomposition at 210 °C. The crystal obtainable after keeping the form-II crystal at 50—100 °C, still reproduces a DTA curve which corresponds closely to that shown by the original form-II; this is observed to occur repeatedly. Thus, the form-II obviously undergoes reversible transformation to the form-I at 38 °C. As Fig. 2 shows, there is only a little difference in the X-ray diffractograms between form-II and form-I. However, the sample obtained by heating the form-I to melting shows no DTA peak at 38 °C and only shows one due to the melting at 129 °C, lower than that of the original form-I at 156 °C. And its X-ray diffractogram is quite different from those of the form-II and/or -I; this is in line with the above results obtained by DTA.

Ni(hxmgH)$_2$. The DTA curve given in Fig. 1 shows that the crystal obtained from methanol solution, noted as form-II, undergoes two endothermic changes, showing DTA peaks with the maxima at 80 and 148 °C; both changes cause no weight-loss. The peak at 148 °C is due to melting. Its decomposition initiates at 174 °C. The crystal obtained by heating the form-II at 100 °C, denoted as form-I, does not show any DTA

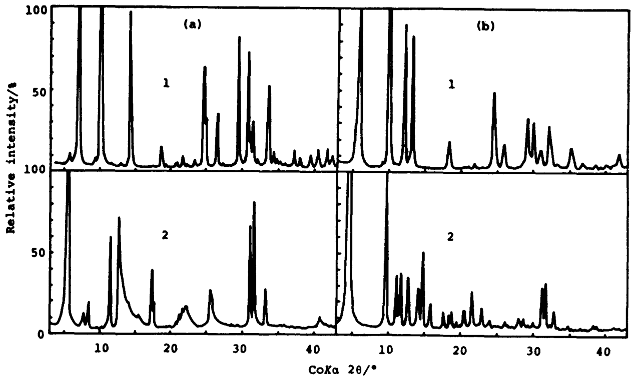

Fig. 3. X-ray powder diffractograms of Ni(hxmgH)$_2$ (a), and Ni(omgH)$_2$ (b).
1, Form-II and 2, form-I.

peak around 80 °C but shows one at 148 °C. Thus, the transformation from form-II to form-I occurs irreversibly at 80 °C. The comparison of the X-ray diffractograms shown in Fig. 3 implies that the above transformation brought about a marked change in the crystal structure. The sample obtained by heating the form-I to melting at 148 °C undergoes melting at 80 °C, lower than the melting point of the form-I at 148 °C.

Ni(omgH)$_2$. As seen in Fig. 1, the thermal character of the crystal obtained from methanol solution, denoted as form-II, resembles those of the form-II crystals of Ni(prmgH)$_2$ and Ni(hxmgH)$_2$; it transforms into its form-I at 78 °C and then melts at 119 °C. For the crystal obtained after having kept the form-II at 100 °C, the DTA peak due to the transformation is not observed at 78 °C. And for the crystal obtained after having heated the form-II until the melting occurred, no DTA peak due either to transformation or to melting is observed. The change in the X-ray diffractogram caused by the transformation at 78 °C is shown in Fig. 3. It is noticed in this case that, on keeping the form-I crystal at room temperature for two or three days, it comes to show the color and X-ray diffractogram characteristic of the form-II, indicating that the transformation of form-I to form-II takes place slowly.

The form-I crystals of Ni(hxmgH)$_2$ and of Ni(omgH)$_2$ yielded by the transformation are rather poorly shaped crystal, as compared with the form-I crystal of Ni(prmgH)$_2$ or with the cross-form crystal of Ni(emgH)$_2$, yielded by the similar transformation. The transformation in the former two cases tends to be accompanied by the formation of an amorphous complex under the conditions employed. The ΔH_t values, heats of transformation, given in Table 1 for the former two cases may partly include the heat needed for a partial crystal-to-amorphous change.

The crystals of Ni(bmgH)$_2$ and Ni(pnmgH)$_2$ were only observed to melt and then to decompose.

The thermal properties for the complexes which undergo the crystal structure transformation are illustrated in Fig. 4.

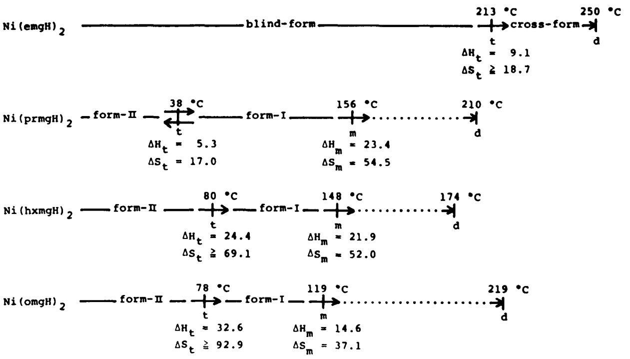

Fig. 4. Illustration for thermal remarks.
t, Transformation; m, melting; d, decomposition. →, Irreversible; and ⇄, reversible changes. ——, Solid; ⋯⋯, liquid states. Temperature/°C indicates DTA peak maximum temperature for transformation and melting, and initial temperature for decomposition. ΔH values are given in kJ mol^{-1}; and ΔS, in J K^{-1} mol^{-1}.

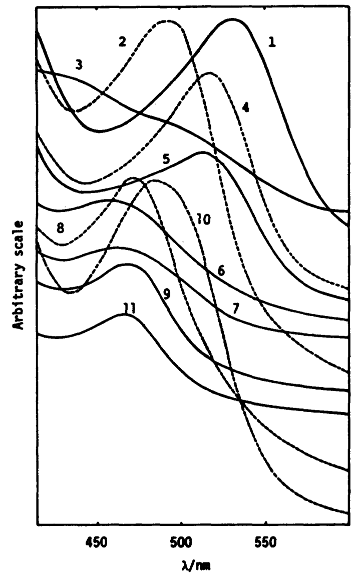

Fig. 5. Reflectance spectra.
1, Ni(dmgH)$_2$; 2, cross-form Ni(emgH)$_2$; 3, blind-form Ni(emgH)$_2$; 4, form-I Ni(prmgH)$_2$; 5, form-II Ni(prmgH)$_2$; 6, Ni(bmgH)$_2$; 7, Ni(pnmgH$_2$); 8, form-I Ni(hxmgH)$_2$; 9, form-II Ni(hxmgH)$_2$; 10, form-I Ni(omgH)$_2$; 11, form-II Ni(omgH)$_2$.

Discussion

Crystal Structure Transformation. The structure of the cross-form crystal of Ni(emgH)$_2$ is similar to that of the cross-form crystal of Ni(dmgH)$_2$; the neighboring Ni atoms in the crystals are 3.44 Å apart for the former and 3.23 Å for the latter.[6b)] As seen in Fig. 5, the cross-form Ni(emgH)$_2$ shows the reflectance spectrum with a distinct peak-maximum at 490 nm that may arise from the same origin as the peak at 530 nm observed for Ni(dmgH)$_2$.[12)] In the blind-form of Ni(emgH)$_2$, the neighboring Ni atoms in the crystal are separated by a distance of 4.74 Å.[5)] This longer Ni–Ni distance, along with the molecular packing in the crystal can hardly indicate the presence of intermetallic Ni–Ni interaction in the blind-form crystal. As Fig. 5 shows, its spectrum has no clear peak in the visible region.[6b]

It is important that the blind- to cross-form transformation is endothermic with a change of enthalpy $\Delta H_\mathrm{t}=9.1$ kJ mol^{-1}, indicating that thermally the cross-form crystals are less stable than the blind-form crystals. The ΔH_t value is considered to be a measure for the difference in the lattice energy between these two forms; it is found to fall, in fact, in the hydrogen-bond energy range, 4—33 kJ mol^{-1}. Assuming the change in free energy of the transformation to be $\Delta G_\mathrm{t}\leqq 0$, change in entropy is calculated to be $\Delta S_\mathrm{t}=S_\mathrm{cross}-S_\mathrm{blind}\geqq 18.7$ J K^{-1} mol^{-1}. Judging from only the symmetry of the crystal system, the orthorhombic cross-form seems to have less entropy than the monoclinic blind-form. The observed increment in the entropy value caused by the blind- to cross-form transformation could be explained in terms of the change in the density of the crystal, that is, as the transformation progresses, the density 1.58 g cm^{-3} of the blind-form[5] decreases to 1.46 g cm^{-3} of the cross-form crystals.[6]

While the crystal structure of Ni(prmgH)$_2$ has so far not been elucidated,[15] the reflectance spectra of both its form-II and form-I crystals show a peak whose position is close to that of Ni(dmgH)$_2$, as seen in Fig. 5. By comparison of the X-ray data for Ni(prmgH)$_2$ with the ones reported for Ni(dmgH)$_2$,[4] the X-ray diffractions with strong intensity of these form-II and -I crystals could be indexed as those of the orthorhombic system. These suggest that the crystal structure of both forms is similar to that of the cross-form Ni(dmgH)$_2$. This is not inconsistent with the fact that the transformation between the form-II and form-I of Ni(prmgH)$_2$ reversibly took place at the low temperature of 38 °C, with a ΔH_t value as small as 5.3 kJ mol^{-1}. The transformation may include a change not like a molecular displacement but like a small conformational displacement of the propyl groups. Since $\Delta G_\mathrm{t}=0$ in this transformation, the ΔS_t value is calculated to be 17.0 J K^{-1} mol^{-1}, which is smaller than that for Ni(emgH)$_2$.

For Ni(hxmgH)$_2$ and Ni(omgH)$_2$, the ΔH_t values of the form-II to -I transformation are, respectively, 24.4 and 32.6 kJ mol^{-1}, as shown in Table 1 and Fig. 4; these are larger than those for the transformations of Ni(emgH)$_2$ and Ni(prmgH)$_2$. And the ΔH_t value for Ni(hxmgH)$_2$ is as large as its ΔH_m value (heat of melting) and that for Ni(omgH)$_2$ is larger than its ΔH_m value. These ΔH_t values may partly include the heat of the crystal-to-amorphous change. As Fig. 5 shows, the above transformation caused no remarkable change in the position of the visible absorption peaks.

Heat of Fusion. Few investigations have dealt with the characterization of the transition metal complexes by such a value as heat of fusion. The stability of the crystal lattice is considered to be reflected on the heat of fusion, which may be represented by the ΔH_m values obtained here.[14] In the cases of the crystals of Ni(hxmgH)$_2$ and Ni(omgH)$_2$ the form-II to -I transformation occurred with the concomitant crystal-to-amorphous change, which brought about inaccuracy in the ΔH_m values measured with their form-II crystals. In addition, the form-II type crystals in the present series of the complexes were obtainable under the conventional preparative conditions. Therefore, the $\Delta H_\mathrm{t}+\Delta H_\mathrm{m}$ values of the form-II type crystals will be considered here. As seen in Table 1, the $\Delta H_\mathrm{t}+\Delta H_\mathrm{m}$ value is the smallest for Ni(bmgH)$_2$. For the complexes with alkyl chains shorter than that of Ni(bmgH)$_2$, the $\Delta H_\mathrm{t}+\Delta H_\mathrm{m}$ values tend to increase. For Ni(prmgH)$_2$ which has an alkyl chain shorter than that of Ni(bmgH)$_2$, the $\Delta H_\mathrm{t}+\Delta H_\mathrm{m}$ value is observed to increase again.

Table 1 shows that the crystal having the larger $\Delta H_\mathrm{t}+\Delta H_\mathrm{m}$ value shows a peak maximum at a higher energy site. From the preliminary result of the X-ray crystallographic investigation on the Ni(prmgH)$_2$ (form-II crystal),[15] the crystal structure may be expected to be similar to that of Ni(dmgH)$_2$ (cross-form),[4] wherein the complex molecules are stacked face to face. This similarity in the molecular array of the crystal is thought to be reflected in the appearance of the peak in the visible reflectance spectrum, as shown in Fig. 2 and Table 1. In fact, the blind-form crystal of Ni(emgH)$_2$ shows no peak.

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3) The following abbreviations are used to denote 2,3-alkanedione dioximato, CH$_3$–C(=NOH)–C(=NO)–R, where R is CH$_3$ (dmgH), C$_2$H$_5$ (emgH), C$_3$H$_7$ (prmgH), C$_4$H$_9$ (bmgH), C$_5$H$_{11}$ (pnmgH), C$_6$H$_{13}$ (hxmgH), and C$_8$H$_{17}$ (omgH).

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12) Ref. 6b); many reports have appeared which deal with the absorption spectra of the analogous dioximato complexes in suspension. The visible absorption peak is known to occur only in the solid complexes; this has so far been discussed in terms of either a proposed Ni–Ni interaction in the crystals[2] or of the intramolecular nature (3d$_{z^2}$→4p$_z$ transition) of the complexes.[13] It might be true that this is a characteristic feature of the molecular packing in the crystal.

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14) Among the analogous complexes, Ni(glyoximato)$_2$, Ni(methylglyoximato)$_2$, and Ni(dmgH)$_2$ showed similarly to Ni(emgH)$_2$ only decomposition without melting on heating.

15) The crystal structure is under investigation by X-ray diffraction analysis.