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Dehydration Associated with High-spin to Low-spin Conversion of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Halide Dihydrate

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(Received July 3, 1980)

Synopsis. The title compounds, orange, diamagnetic four-coordinate complexes, $[NiL]X_2 \cdot 2H_2O$ (X=Cl, Br, I for *meso*-L and X=Cl, Br for *rac*-L) were converted, upon dehydration by heating in the solid state, to violet, paramagnetic six-coordinate complexes, $[NiX_2L]$. The enthalpies of the dehydration reactions were close to those for many simple inorganic hydrates and that for the ice-water vapor equilibrium in spite of the presence of the large organic ligand.

Nickel(II) halides (Cl, Br, and I) and the *meso*-form of the title macrocyclic ligand ((7*RS*,14*SR*)-form) form orange low-spin complexes, $[Ni(meso\text{-}L)]X_2 \cdot 2H_2O$, and violet high-spin complexes, $[NiX_2(meso\text{-}L)]$.[1)] The macrocyclic ligand is constrained by the steric requirements to coordinate in a single plane. From their electronic spectra and magnetic properties,[1)] and the X-ray analyses of $[Ni(meso\text{-}L)]Cl_2 \cdot 2H_2O$,[2)] $[NiCl_2(meso\text{-}L)]$,[2)] and $[Ni(meso\text{-}L)]Br_2 \cdot 2H_2O$,[3)] it has been shown that the orange dihydrate is a square-planar four-coordinate complex having a singlet ground state, whereas the violet paramagnetic anhydride is a *trans*-dihalogeno six-coordinate complex having a triplet ground state. The solid, violet, paramagnetic anhydrous complex readily reverts to $[Ni(meso\text{-}L)]X_2 \cdot 2H_2O$ when moisture is available.[1)]

In the present study, the orange four-coordinate dihydrate was found to be converted to $[NiX_2(meso\text{-}L)]$ upon dehydration by heating in the solid state. The isomeric complex containing the racemic ligand ((7*RS*,14*RS*)-form),[4)] $[Ni(rac\text{-}L)]X_2 \cdot 2H_2O$ (X=Cl and Br)[5)] underwent exactly the same reaction, yielding the anhydrous six-coordinate complex, *trans*-$[NiX_2(rac\text{-}L)]$. In the present note, the enthalpies of the dehydration reactions are reported.

Figure 1 shows a typical example of the thermogravimetry (TG) and the differential scanning calorimetry (DSC). When $[Ni(meso\text{-}L)]Cl_2 \cdot 2H_2O$ was heated at a heating rate of 3 °C min^{-1}, the weight loss due to the dehydration began at 58 °C and constant weight attained at 110 °C. The weight loss of $8.2 \pm 0.2\%$ was in accord with the calculated value for the loss of two mols of water (8.00%). Corresponding to the weight loss, an endothermic peak appeared on a DSC curve. The heat of dehydration was estimated to be 100 ± 1 kJ mol^{-1} by comparing the peak area with that for melting of naphthalene crystals ($\Delta H = 18.98$ kJ mol^{-1}).[6)] Experiments for other systems were carried out similarly. The results are summarized in Table 1. Values given in Table 1 are mean values for at least four experimental runs. The product was identified by elemental analysis, electronic spectrum,[1,7,8)] and infrared spectrum.[8)] All the results indicated that the reaction proceeds as follows:

$$[NiL]X_2 \cdot 2H_2O \xrightarrow{\Delta} [NiX_2L] + 2H_2O.$$

This is the reverse reaction reported by Busch[1)] and involves the change in the coordination number from four to six, *viz.*, the singlet to triplet spin-state change.

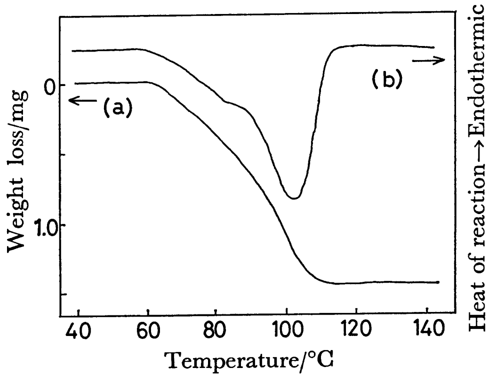

Fig. 1. TG (a) and DSC (b) curve for the thermal dehydration of $[Ni(meso\text{-}L)]Cl_2 \cdot 2H_2O$.
Heating rate: 3 °C min^{-1}. Sample: 18.52 mg.

As shown in Table 1, the ΔH values are not largely different from each other except for the iodide system of $[Ni(meso\text{-}L)]$, though the difference in ΔH caused by the kind of halide ion and the ligand may be significant. It is worth while to mention that the enthalpies found in the present study can be compared to the calculated enthalpy value for sublimation of ice, where ΔH(sublimation)$=51.9$ kJ mol^{-1} at 25 °C.[9)] (Note that the ΔH values given in Table 1 correspond to the loss of two mols of water.) Except for the iodide system, the enthalpy values found in the present study are significantly larger than those usually found for dehydration reactions of coordination compounds. For example, ΔH for dehydration of $[Ni(abi)_4]X_2 \cdot nH_2O$ (abi=2-aminobenzimidazole) has been reported to be 8.8 (X=Cl, n=3), 8.8 (X=Br, n=3), and 7.1

Table 1. Enthalpy of the thermal dehydration reaction of $[NiL]X_2 \cdot 2H_2O$

L	X	$\Delta H(-2H_2O)$ / kJ mol^{-1}	Temperature of incipient reaction/°C[a)]
meso-L	Cl	100 ± 1	58
	Br	104 ± 3	75
	I	78 ± 2	58
rac-L	Cl	99 ± 4	76
	Br	96 ± 4	65

a) Heating rate: 3 °C min^{-1}.

kJ mol^{-1} (X=NO$_3$, n=1).$^{10)}$ Fogel *et al.* studied dehydration reactions of many simple inorganic hydrates$^{9,11,12)}$ and reported that, for many reactions, ΔH=55.2x kJ mol^{-1} (x designates mol number of lost water), which is close to what is observed for the ice system.$^{12)}$ They concluded on this basis that, when only small structural changes occur during dehydration reactions, the thermodynamic value is close to that for the vaporization of ice.$^{9)}$

It is striking that the ΔH values given in Table 1 are close to those reported by Fogel and that for the sublimation of ice, even though the present complexes bear the large organic ligand. This indicates that the water molecules in the dihydrates of the present complexes are involved in the strong hydrogen-bonds such as those in ice and many simple inorganic hydrates. It has been shown that, in the crystals of [Ni(*meso*-L)]Cl$_2$·2H$_2$O$^{2)}$ and [Ni(*meso*-L)]Br$_2$·2H$_2$O,$^{3)}$ all the water molecules are disposed above the hydrogen atoms of N–H groups and are involved in the strong hydrogen-bonds, N–H···OH$_2$ and OH$_2$···X, forming hydrogen-bonded chelate rings of the type Ni–N–H···$\underset{\text{H}}{\text{O}}$–H···X···H–N. The magnitude of ΔH seems to reflect at least qualitatively the strength of the hydrogen-bonds in the hydrate, although many other factors affect the magnitude of ΔH. The small ΔH value for the iodide system probably indicates the weaker hydrogen-bond in the crystal as expected. Busch pointed out the importance of the role played by water in the spin-state conversions such as the anhydrous spin-free–hydrate spin-paired type.$^{13)}$ When the anhydrous [NiX$_2$L] takes up the two water molecules from the atmospheric moisture to produce [NiL]X$_2$·2H$_2$O, the incorporated water molecules displace the halogen ions from the coordination sites but are not involved in the coordination in the product. This is unexpected in the light of the fact that water has much higher coordinating ability as compared with the halide ion. In view of the crystal structures of [Ni(*meso*-L)]Cl$_2$·2H$_2$O$^{2)}$ and [Ni(*meso*-L)]Br$_2$·2H$_2$O,$^{3)}$ the dispositions of the water molecules above the N–H bonds would be much more favorable over the hypothetical occupation by the water molecules at the axial coordination sites. This situation could be explained by the larger ΔH values observed in the present study. The N–H···OH$_2$ and OH$_2$···X hydrogen-bond networks operating in the vicinity of the nickel(II) ion are strong enough to prevent the coordination of water.

Experimental

Materials. Orange dihydrates, [Ni(*meso*-L)]X$_2$·2H$_2$O (X=Cl, Br, and I) and [Ni(*rac*-L)]X$_2$·2H$_2$O (X=Cl and Br), were prepared from the corresponding perchlorates$^{4)}$ by ion exchange (Dowex 1-X8). Elemental analyses gave satisfactory results.

Measurements. Thermal analyses were carried out on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C.

Elemental Analyses of the Reaction Products. (a) [NiX$_2$(*meso*-L)]=NiC$_{16}$H$_{36}$N$_4$X$_2$. Found: C, 46.35; H, 8.89; N, 13.44; Cl, 17.16%. Calcd for X=Cl: C, 46.41; H, 8.76; N, 13.53; Cl, 17.12%. Found: C, 38.08; H, 7.30; N, 11.30; Br, 31.96%. Calcd for X=Br: C, 38.20; H, 7.21; N, 11.14; Br, 31.77%. Found: C, 31.96; H, 6.16; N, 9.42; I, 42.69%. Calcd for X=I: C, 32.19; H, 6.08; N, 9.39; I, 42.51%. (b) [NiX$_2$(*rac*-L)]=NiC$_{16}$H$_{36}$N$_4$X$_2$. Found: C, 45.53; H, 8.81; N, 12.89; Cl, 16.83%. Calcd for X=Cl: C, 46.41; H, 8.76; N, 13.53; Cl, 17.12%. [NiBr$_2$(*rac*-L)] is very sensitive to moisture. Accurate data for the anhydrous complex could not be obtained because of rapid absorption of water vapor during weighing the sample.

The authors wish to thank Professor Yoshio Matsunage for the kindness in the DSC measurements.

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