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A Calorimetric Study on the Relative Thermal Stability in Some Nickel(II) Complexes Containing *N*,*N*′- or *N*,*N*-Diethylethylenediamine

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(Received November 24, 1981)

The enthalpy changes (ΔH) in the reaction of $Ni(AA)_2X_2 \cdot nH_2O$ type complexes with aqueous potassium cyanide were calorimetrically measured at 25 °C, where AA is *N*,*N*′-diethylethylenediamine (*NN*′-deen) or *N*,*N*-diethylethylenediamine (*NN*-deen); X is Cl^-, Br^-, I^-, or NO_3^- ion; and *n* is 0 or 2. On the basis of the enthalpy data measured, the thermal stability was compared among chloride, bromide, iodide, and nitrate in the following each group of compounds: Ni(*NN*′-deen)$_2$X$_2$·2H$_2$O, Ni(*NN*′-deen)$_2$X$_2$, Ni(*NN*-deen)$_2$X$_2$·2H$_2$O, and Ni(*NN*-deen)$_2$X$_2$. The thermal stability was found to decrease in the order, chloride>bromide>nitrate>iodide in each group. Comparison of the enthalpy data between the chlorides of the *NN*′-deen and *NN*-deen complexes revealed the difficulty of anation in the latter rather than in the former. [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Br$_2$ was, when heated, converted into [Ni(*NN*-deen)$_2$]Br$_2$ without anation differing from the chloride. The difference was also discussed on the basis of the enthalpy data.

Nickel(II) complexes are fascinating compounds from the viewpoint that they have a possibility to take various coordination structures easily capable of transforming to each other in the solution and in the solid phase.[1] The equilibria and mutual conversions are most familiarly investigated among their tetrahedral, square planar, and octahedral configurations.[2]

We have already reported that the compounds [Ni(*NN*′-deen)$_2$(H$_2$O)$_2$]X$_2$ (*NN*′-deen: *N*,*N*′-diethylethylenediamine; X: Cl^-, Br^-, I^-, or NO_3^- ion) undergo anation to form [NiX$_2$(*NN*′-deen)$_2$] upon heating in the solid phase still keeping the octahedral environment.[3] On the other hand, the complexes [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]X$_2$ (*NN*-deen: *N*,*N*-diethylethylenediamine; X: Cl^- or Br^-) display some different thermal reactions from the *NN*′-deen complexes: *i.e.*, the chloride undergoes anation in a manner similar to the corresponding *NN*′-deen compounds, but the bromide deaquates to form square planar complexes. In addition, in the case of the iodide and nitrate, we always failed in attempting to prepare the octahedral diaqua complexes like the chloride or bromide, but exclusively obtained the square planar [Ni(*NN*-deen)$_2$]X$_2$.[4]

It is therefore worthwhile to know why such differences take place in the thermal reaction. The present study was undertaken (1) to measure calorimetrically the enthalpy changes (ΔH) in the reaction of $Ni(AA)_2X_2 \cdot nH_2O$ (AA: *NN*′- or *NN*-deen; X: Cl^-, Br^-, I^-, or NO_3^- ion; *n*: 0 or 2) with aqueous potassium cyanide, (2) to compare the thermal stability of these complexes on the basis of the enthalpy changes obtained, and (3) to try to interprete the difference of the features appearing in the thermal reactions in the solid phase.

Experimental

Preparation of Complexes. Ni(*NN*′-deen)$_2$X$_2$·*n*H$_2$O,[5] and Ni(*NN*-deen)$_2$X$_2$·*n*H$_2$O[6] (X=Cl^-, Br^-, I^-, and NO_3^-; $n=0$ and 2) were prepared by the known method and identified by the chemical analysis and the electronic spectra.

Calorimetric Measurements. In order to discuss the thermal stability of these complexes, the enthalpy changes in the reaction of them in the powder state with potassium cyanide solution were measured with Tokyo-Riko twin isoperibol calorimeter TIC-2S at 25 °C. In each run, the diamine complexes employed were accurately weighed in the range of order of 1×10^{-4} mol and the aqueous potassium cyanide employed was 100 cm^3 of 6×10^{-2} mol dm^{-3} solution. The reactions proceeded quantitatively, for example, according to the Eqs. 1 and 2, and the enthalpy changes (ΔH) for each reaction were estimated as mentioned in the later section.

Results and Discussion

Thermal Stability in the NN′-*deen Complexes.* The enthalpy changes for the *NN*′-deen and *NN*-deen complexes measured are summarized in Table 1. The enthalpy changes for the reaction of diaquabis(*NN*′-deen)chromium(III) chloride and bromide with potassium cyanide solution are given as below,

$$\begin{aligned}&[Ni(NN'\text{-deen})_2(H_2O)_2]Cl_2(s) + 4CN^-(aq)\\ &\quad = Ni(CN)_4{}^{2-}(aq) + 2NN'\text{-deen}(aq) + 2Cl^-(aq)\\ &\quad + 2H_2O(l) \qquad \Delta H = -128\ 8\ \text{kJ mol}^{-1} \qquad (1)\end{aligned}$$

$$\begin{aligned}&[Ni(NN'\text{-deen})_2(H_2O)_2]Br_2(s) + 4CN^-(aq) =\\ &\quad Ni(CN)_4{}^{2-}(aq) + 2NN'\text{-deen}(aq) + 2Br^-(aq)\\ &\quad + 2H_2O(l) \qquad \Delta H = -103.3\ \text{kJ mol}^{-1}. \qquad (2)\end{aligned}$$

Table 1. Enthalpy changes for the reaction of nickel(II)–bis(diamine) complexes with CN^- (kJ mol^{-1})[a)]

X^-	AA=*NN*′-deen		*NN*-deen	
Cl^-	Oh −128.8	Oh′ −143.5	Oh −121.4	Oh′ −155.6
Br^-	Oh −103.3	Oh′ −128.3	Oh −96.2	Sq −102.0
I^-	Oh −81.6	Oh′ −177.8	Sq −111.6	
NO_3^-	Oh −91.3	Oh′ −124.3	Sq −113.6	

a) Oh designates the octahedral diaquabis(diamine) complexes [Ni(AA)$_2$(H$_2$O)$_2$]X$_2$, Oh′, the octahedral diacidobis(diamine) complexes [NiX$_2$(AA)$_2$]produced by the anation of the former, and Sq means the square-planar bis(diamine) complexes [Ni(AA)$_2$]X$_2$.

By combining these two enthalpy changes with the following values,

$Cl^-(aq) = Cl^-(g)$ $\Delta H = -76.5$ kJ mol^{-1} 7)

$Br^-(aq) = Br^-(g)$ $\Delta H = -110.5$ kJ mol^{-1}, 8)

the enthalpy change for the reaction,

$[Ni(NN'\text{-deen})_2(H_2O)_2]Cl_2(s) + 2Br^-(g)$

$= [Ni(NN'\text{-deen})_2(H_2O)_2]Br_2(s) + 2Cl^-(g)$,

was calculated as $\Delta H = 42.5$ kJ mol^{-1}. This value corresponds to the difference of lattice energy between the chloride and bromide: this result reflects that the bromide is thermally more unstable by this value than the chloride.

In the same way, by using the enthalpy data measured for the iodide ($\Delta H = -81.6$ kJ mol^{-1}) and nitrate ($\Delta H = -91.3$ kJ mol^{-1}) and those for the following changes,

$I^-(aq) = I^-(g)$ $\Delta H = -154\ 0$ kJ mol^{-1} 9)

$NO_3^-(aq) = NO_3^-(g)$ $\Delta H = -128.9$ kJ mol^{-1}, 10)

the enthalpy changes for the substitution reaction of the chloride by iodide or nitrate ion were obtained as follows:

$[Ni(NN'\text{-deen})_2(H_2O)_2]Cl_2(s) + 2X^-(g)$

$= [Ni(NN'\text{-deen})_2(H_2O)_2]X_2(s) + 2Cl^-(g)$

$\Delta H = 107.9$ kJ mol^{-1} for $X = I^-$

$\Delta H = 67.4$ kJ mol^{-1} for $X = NO_3^-$

These values are the difference of the lattice energies between the iodide or nitrate and the chloride.

As seen from Table 1, the enthalpy changes for the octahedral diacido complexes $[NiX_2(NN'\text{-deen})_2]$ formed by the anation of the octahedral diaqua complexes $[Ni(NN'\text{-deen})_2(H_2O)_2]X_2$ were measured as −143.5, −128.3, −117.8, and −124.3 kJ mol^{-1} for the chloride, bromide, iodide, and nitrate, respectively. By analogous calculations to the diaqua complexes, the enthalpy changes for the following substitution reactions were estimated. These values correspond to the

$[NiCl_2(NN'\text{-deen})_2](s) + 2X^-(g)$

$= [NiX_2(NN'\text{-deen})_2](s) + 2Cl^-(g)$

$\Delta H = 52.8$ kJ mol^{-1} for $X = Br^-$

$\Delta H = 129.4$ kJ mol^{-1} for $X = I^-$

$\Delta H = 85.7$ kJ mol^{-1} for $X = NO_3^-$

decrements of lattice energy of the bromide, iodide, and nitrate from that of the chloride. As expected from the equation of lattice energy by Kapustinskii,11) the lattice energy decreases as the radius of anion increases if the cation is the same. The radius of Cl^-, Br^-, I^-, and NO_3^- are 1.18,12) 1.96,12) 2.16,13) and 1.89 Å,14) respectively. The order of decrement of lattice energy observed in the diaqua and diacido complexes is, therefore, parallel to the increasing order of the radius except for the case of the nitrate.

The enthalpy level diagram for the NN'-deen complexes by using the enthalpy data obtained above is illustrated in Fig. 1. It is obvious from the figure that the thermal stability decreases in the order, chloride> bromide>nitrate>iodide, both in the diaqua and diacido series. The enthalpy changes in the dehydration followed by the anation were obtained by combining the heat of vaporization of water with the enthalpy changes measured for the reaction of $[Ni(NN'\text{-deen})_2(H_2O)_2]X_2$ or $[NiX_2(NN'\text{-deen})_2]$ type complexes with potassium cyanide solution. The value found in the dehydration of the chloride is 102.8 kJ mol^{-1} (Fig. 1).

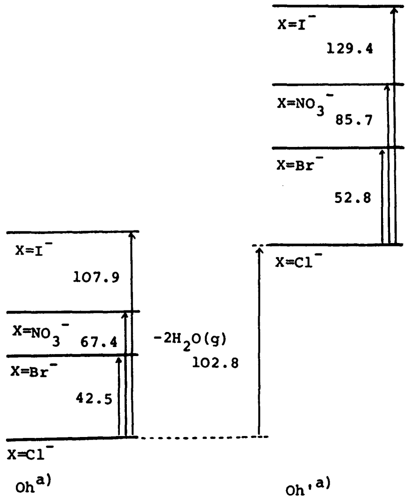

Fig. 1. Enthalpy level diagram for the NN'-deen complexes. The numerals are expressed by the unit of kJ mol^{-1}.

a) These designations are the same as those employed in Table 1.

Thermal Stability in the NN-*deen Complexes.* The enthalpy changes for the reaction of $[Ni(NN\text{-deen})_2(H_2O)_2]Cl_2$ and $[Ni(NN\text{-deen})_2(H_2O)_2]Br_2$ with aqueous potassium cyanide corresponding to Eqs. 1 and 2 were measured as $\Delta H = -121.4$ kJ mol^{-1} and $\Delta H = -96.2$ kJ mol^{-1}, respectively, in a manner similar to those for the NN'-deen complexes (Table 1). The difference of the lattice energy between the chloride

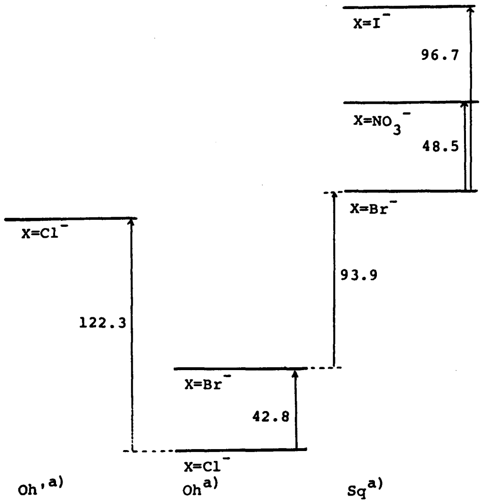

Fig. 2. Enthalpy level diagram for the NN-deen complexes. The numerals are expressed by the unit of kJ mol^{-1}.

a) These designations are the same as those employed in Table 1.

and bromide was estimated as $\Delta H=42.8$ kJ mol^{-1}. The enthalpy level diagram for the *NN*-deen complexes, including the latter value, is presented in Fig. 2.

In the thermal reaction of the *NN'*-deen complexes in the solid phase, the anation was generally found, but only a slight difference was shown in ease of anation depending upon the kind of anations. It is probably due to the lesser steric effect of two equatorial ethyl groups in *NN'*-deen upon anation relative to *NN*-deen. On the contrary, the *NN*-deen complexes have at least one axial ethyl group in each *NN*-deen chelate ring, and hence notable steric effect may be expected. For example, as stated in the introduction, the chloride of the *NN*-deen complex undergoes anation, whereas the corresponding bromide is converted into square planar complex after losing the coordinated water.

The enthalpy change in the dehydration accompanied by the anation, from [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Cl$_2$ to [NiCl$_2$(*NN*-deen)$_2$], was obtained as $\Delta H=122.3$ kJ mol^{-1} in the same way as that for the corresponding *NN'*-deen complex. In [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Br$_2$, on the other hand, the enthalpy change in the dehydration followed by the formation of square planar complex without anation was obtained as $\Delta H=93.9$ kJ mol^{-1} by employing the measured value for [Ni(*NN*-deen)$_2$]Br$_2$, $\Delta H=-102.0$ kJ mol^{-1} (Table 1, Fig. 2). In the iodide and nitrate, the diaqua complexes were not obtained, but prepared only in anhydrous square planar configuration as mentioned in the introduction. For these square planar complexes, the differences of lattice energies of the iodide and the nitrate from the bromide were calculated as $\Delta H=96.7$ and 48.5 kJ mol^{-1}, respectively. From Fig. 2, the thermal stability for the square planar complexes decreases in the order, bromide>nitrate>iodide.

Difference in Thermal Stability between the NN'*-deen and* NN*-deen Complexes.* The enthalpy change for the reaction of [Ni(NN'-deen)$_2$(H$_2$O)$_2$]Cl$_2$ with aqueous potassium cyanide expressed by Eq. 1, $\Delta H=-128.8$ kJ mol^{-1}, and that for the reaction of the corresponding *NN*-deen complex, $\Delta H=-121.4$ kJ mol^{-1} (Table 1), were combined with the following values:

NN'-deen(l) = *NN'*-deen(aq) $\Delta H=-48.5$ kJ mol^{-1}

NN'-deen(l) = *NN'*-deen(g) $\Delta H=37.6$ kJ mol^{-1}

NN-deen(l) = *NN*-deen(aq) $\Delta H=-44.0$ kJ mol^{-1}

NN-deen(l) = *NN*-deen(g) $\Delta H=37.0$ kJ mol^{-1}.

Here, the heats of dissolution of *NN'*-deen ($\Delta H=-48.5$ kJ mol^{-1}) and *NN*-deen ($\Delta H=-44.0$ kJ mol^{-1}) were measured with the calorimeter, and the heats of vaporization of *NN'*-deen ($\Delta H=37.6$ kJ mol^{-1}) and *NN*-deen ($\Delta H=37.0$ kJ mol^{-1}) were calculated from their boiling points and Trouton's constant. The enthalpy change in the reaction,

$$[\mathrm{Ni}(NN'\text{-deen})_2(\mathrm{H_2O})_2]\mathrm{Cl_2(s)} + 2NN\text{-deen(g)}$$
$$= [\mathrm{Ni}(NN\text{-deen})_2(\mathrm{H_2O})_2]\mathrm{Cl_2(s)} + 2NN'\text{-deen(g)},$$

was thus calculated as $\Delta H=2.8$ kJ mol^{-1}. The enthalpy change for substituting *NN'*-deen by *NN*-deen in the bromide was obtained as $\Delta H=3.1$ kJ mol^{-1} in the same way as that employed in the chloride.

Figure 3 illustrates the enthalpy level diagram for the chlorides and bromides of the *NN'*-deen and *NN*-deen complexes. It is found from the figure that the enthalpy ($\Delta H=122.3$ kJ mol^{-1}) required for [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Cl$_2$ to form [NiCl$_2$(*NN*-deen)$_2$] is greater than that ($\Delta H=102.8$ kJ mol^{-1}) for [Ni(*NN'*-deen)$_2$(H$_2$O)$_2$]Cl$_2$ to form [NiCl$_2$(*NN'*-deen)$_2$]. This suggests that the former undergoes anation with more difficulty than the latter. It is probably due to the presence of an exial ethyl group in the *NN*-deen complex and its absence in the *NN'*-deen complex. Such a difference between *NN*-deen and *NN'*-deen complexes is also expected in the bromide, but we were unable to estimate the difference because [NiBr$_2$(*NN*-deen)$_2$] was not prepared. It is, however, assumed that the anation of [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Br$_2$ is not so easy as that of the corresponding chloride because bromide ion has larger radius than chloride ion. Therefore, the enthalpy level for the imaginary [NiBr$_2$(*NN*-deen)$_2$] may be expected to be higher by >24 kJ mol^{-1} than that of the corresponding *NN'*-deen complex as shown by a broken line (Fig. 3). In addition, as seen obviously in the diagram, the enthalpy level for the imaginary [NiBr$_2$(*NN*-deen)$_2$] is much higher (>40 kJ mol^{-1}) than that for [Ni(*NN*-deen)$_2$]Br$_2$. This might be the reason why [Ni(*NN*-deen)$_2$(H$_2$O)$_2$]Br$_2$ is, when heated in the solid phase, converted into the square planar complex without anation.

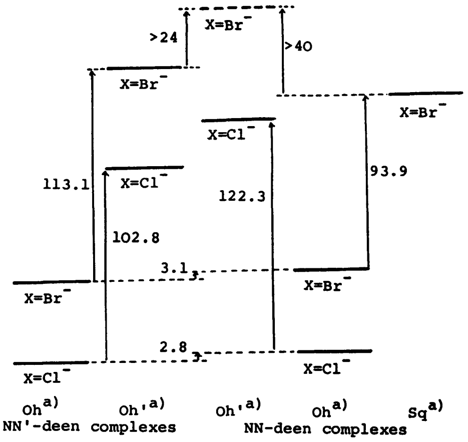

Fig. 3. Enthalpy level diagram for the chlorides and bromides of the *NN'*-deen and *NN*-deen complexes. The numerals are expressed by the unit of kJ mol^{-1}. a) These designations are the same as those employed in Table 1.

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