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Effect of Methyl Substitution in 1,2-Ethanediaminenickel(II) Complexes upon Their Thermal Stabilities

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The enthalpy changes (Δ*H*) in the reaction of three types of the nickel(II) complexes, $[Ni(AA)_2(H_2O)_2]X_2 \cdot nH_2O$, $[NiX_2(AA)_2]$, and $[Ni(AA)_2]X_2$, with aqueous potassium cyanide solution were calorimetrically measured at 25 °C, where AA denotes a diamine selected from 1,2-ethanediamine (en), *N*-methyl-1,2-ethanediamine (*N*-men), *N*,*N*-dimethyl-1,2-ethanediamine (*NN*-dmen), *N*,*N'*-dimethyl-1,2-ethanediamine (*NN'*-dmen), and *N*,*N*,*N'*-trimethyl-1,2-ethanediamine (*NNN'*-tmen); X is Cl, Br, I, NO_3, or ClO_4; $n=0$, 2, or 3. The thermal stabilities of the complexes in the solid state defined by the enthalpy changes (not by the free energy changes) were compared with one another, so that the thermal stabilities of the complexes are highly dependent on numbers and/or positions of *N*-methyl groups on diamines. In the series of $[NiX_2(AA)_2]$ and $[Ni(AA)_2]X_2$ type complexes, the *NN'*-dmen complexes are the most stable. Except for the *NN'*-dmen complexes, as the numbers of *N*-methyl group(s) contained in the diamines increase, the complexes have the tendency to become less stable. The relative thermal stabilities of the present complexes were discussed in terms of the basicities of diamines and steric effect of *N*-methyl groups.

We have systematically studied the structural and thermochemical changes in the course of the solid phase thermal reactions of the nickel(II) complexes containing a variety of diamines.[1)] In the preceding paper, the relative thermal stabilites of the octahedral and square planar nickel(II) complexes containing *N*,*N*- and *N*,*N'*-diethyl-1,2-ethanediamines were discussed on the basis of their calorimetric data.[2)]

In the present study, our interest is focused on the information on the relative thermal stabilities of the nickel(II) complexes containing *N*-methyl, *N*,*N*(or *N*,*N'*)-dimethyl, and *N*,*N*,*N'*-trimethyl substituted diamines. The diamines selected are 1,2-ethanediamine (en), *N*-methyl-1,2-ethanediamine (*N*-men), *N*,*N*-dimethyl-1,2-ethanediamine (*NN*-dmen), *N*,*N'*-dimethyl-1,2-ethanediamine (*NN'*-dmen), and *N*,*N*,*N'*-trimethyl-1,2-ethanediamine (*NNN'*-tmen). The enthalpy changes for the following reactions were also estimated; the dehydration ($[Ni(AA)_2(H_2O)_2]X_2 \cdot nH_2O \rightarrow [Ni(AA)_2(H_2O)_2]X_2 + nH_2O$), the dissociation ($[Ni(AA)_2(H_2O)_2]X_2 \rightarrow [Ni(AA)_2]X_2 + 2H_2O$), and the deaquation anation ($[Ni(AA)_2(H_2O)_2]X_2 \rightarrow [NiX_2(AA)_2] + 2H_2O$).

Experimental

Preparation of Complexes. The en,[3)] *N*-men, *NN*-dmen, *NN'*-dmen and *NNN'*-tmen[4)] complexes were prepared by the known methods or a slight modification thereof, if necessary.

Calorimetric Measurements. In order to discuss the difference in the thermal stabilities of these complexes, the enthalpy changes (Δ*H*) for the reactions of the accurately weighed complexes in the range of order of 1×10^{-4} mol in the powder state with 100 dm^{-3} of aqueous potassium cyanide solution of 6×10^{-2} mol dm^{-3} were measured with Tokyo Riko TIC-2S isoperibol calorimeter at 25 °C. Three or more measurements were carried out every one sample, and three values within ±0.5 kJ mol^{-1} were averaged. In these reactions, $[Ni(CN)_4]^{2-}$ is formed. The formation constant of $[Ni(CN)_4]^{2-}(aq)$ is 31.3 (25 °C)[5)], the concentration of $Ni^{2+}(aq)$ remained being calculated to be in the order of 10^{-27} mol dm^{-3}, so that the reactions were concluded to take place completely.

Results and Discussion

Thermal Stability in the en Complexes. Table 1 summarizes the enthalpy changes for the bis(en), bis(*N*-men), bis(*NN*-dmen), bis(*NN'*-dmen) and bis(*NNN'*-tmen) nickel(II) complexes measured. The enthalpy changes for the reaction of $[Ni(en)_2(H_2O)_2]X_2$ ($X=NO_3$, I, and ClO_4) with aqueous potassium cyanide solution are given as below,

$$[Ni(en)_2(H_2O)_2]X_2(s) + 4CN^-(aq) \\ = Ni(CN)_4{}^{2-}(aq) + 2en(aq) + 2X^-(aq) + 2H_2O(l),$$

where $\Delta H = -58.6$ kJ mol^{-1} for $X=NO_3$, $\Delta H = -60.8$ kJ mol^{-1} for X=I and $\Delta H = -63.4$ kJ mol^{-1} for $X=ClO_4$. By combining the above values with the hydration enthalpies of the respective anions, ΔH_x for the reactions of $X^-(g) = X^-(aq)$ (Table 2),[6)] the enthalpy changes for the exchange reaction of anions,

$$[Ni(en)_2(H_2O)_2](NO_3)_2(s) + 2X^-(g) \\ = [Ni(en)_2(H_2O)_2]X_2(s) + 2NO_3{}^-(g),$$

are calculated. The values thus obtained are 61 kJ mol^{-1} for $X^- = I^-$ and 172 kJ mol^{-1} for $X^- = ClO_4^-$. As was mentioned before, the above enthalpy changes correspond to the difference in the lattice energy between the nitrate and iodide, and between the nitrate and perchlorate, respectively. These results reflect that the iodide and perchlorate are thermally less stable than the nitrate.

The enthalpy changes for the substitution reaction

TABLE 1. ENTHALPY CHANGES FOR THE REACTION OF NICKEL(II)-BIS(DIAMINE) COMPLEXES WITH CN^- ION (ΔH/kJ mol^{-1})[a)]

X \ AA	en	*N*-men	*NN′*-dmen	*NN*-dmen	*NNN′*-tmen
Cl	$\mathrm{Oh'}$ −105.6	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −76.6 −95.5 −114.1	$\mathrm{Oh(3)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −88.8 −124.1	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh(*)}^{b)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −98.1 −126.5 −153.5	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −128.4 −171.2
Br	$\mathrm{Oh'}$ −97.0	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −65.3 −71.5 −96.5	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −87.3 −106.9	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −89.4 −101.4 −141.1	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −120.7 −155.6
NO_3	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −58.6 −82.0	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −63.1 −87.2	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −72.7 −105.6	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −87.0 −102.6	$\mathrm{Oh'}$ −143.8
I	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −60.8 −73.4	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −69.9 −85.3	$\mathrm{Oh(2)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −67.7 −97.7	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq}$ −87.8 −117.3	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −115.8 −166.8
ClO_4	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq}$ −63.4 −76.0	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq}$ −67.5 −84.6	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq}$ −86.6 −105.3	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq}$ −99.1 −105.0	$\mathrm{Oh(0)} \xrightarrow[\Delta]{} \mathrm{Sq} \xrightarrow[\Delta]{} \mathrm{Oh'}$ −113.9 −148.0 −151.9

a) Oh(n) designates the octahedral diaquabis(diamine) complex hydrates $[Ni(AA)_2(H_2O)_2]X_2 \cdot nH_2O$, Oh′ the octahedral dianiono-bis(diamine) complexes $[NiX_2(AA)_2]$ produced by the anation of the formers, and Sq means the square-planar bis(diamine) complexes $[Ni(AA)_2]X_2$. b) Oh(*): $[NiCl(NN\text{-dmen})_2(H_2O)]Cl$.

TABLE 2. THE HYDRATION ENTHALPIES, ΔH_x, FOR THE REACTIONS, $X^-(g) = X^-(aq)$ AND ΔH_{AA} FOR $AA(g) = AA(aq)$

ΔH_x/kJ mol^{-1}					ΔH_{AA}/kJ mol^{-1}				
Cl^-	Br^-	NO_3^-	I^-	ClO_4^-	en	*N*-men	*NN′*-dmen	*NN*-dmen	*NNN′*-tmen
−351.5	−318.0	−309.6	−280.3	−225.9	−64.7	−67.1	−79.6	−74.1	−78.2

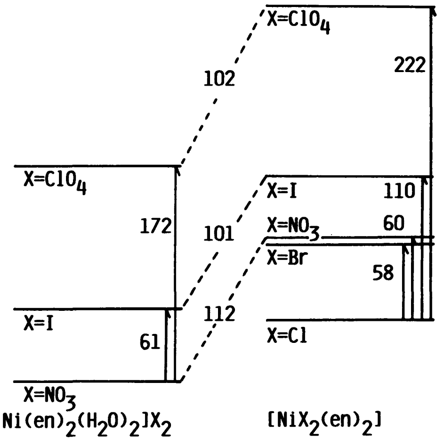

Fig. 1. Enthalpy level diagram for Ni(II)–en complexes (kJ mol^{-1}).

of the dianiono complexes,

$$[Ni(en)_2Cl_2](s) + 2X^-(g) = [NiX_2(en)_2](s) + 2Cl^-(g),$$

were obtained as ΔH=58 kJ mol^{-1} for X^-=Br^-, ΔH=60 kJ mol^{-1} for X^-=NO_3^-, and ΔH=110 kJ mol^{-1} for X^-=I^-, by using the enthalpy data measured (Table 1) for the octahedral dianiono complexes, $[NiX_2(en)_2]$, where X^- is Cl^-, Br^-, NO_3^-, or I^-, and the ΔH_x values listed in Table 2. These values correspond to the decrements in lattice energies of the dibromo, dinitrato, and diiodo complexes as compared with that of dichloro complex.

From the above enthalpy data, the diagram of enthalpy level for the en complexes can be illustrated as seen in Fig. 1. It is obvious from the figure that the thermal stability decreases in the order, nitrate> iodide>perchlorate in the diaqua series, and dichloro> dibromo>dinitrato>diiodo in the aniono series.

The enthalpy changes for the deaquation-anation,

$$[Ni(en)_2(H_2O)_2]X_2(s) = [NiX_2(en)_2](s) + 2H_2O(g),$$

are also given in Fig. 1. The values were estimated to be ΔH=112 kJ mol^{-1} for X=NO_3 and ΔH=101 kJ mol^{-1} for X=I by combining the heat of vaporization of water, ΔH=44.2 kJ mol^{-1}[7)] with the enthalpy data concerned (Table 1). The dissociation enthalpy for the reaction,

$$[Ni(en)_2(H_2O)_2](ClO_4)_2(s)$$
$$= [Ni(en)_2](ClO_4)_2(s) + 2H_2O(g),$$
$$\Delta H = 102 \text{ kJ mol}^{-1}$$

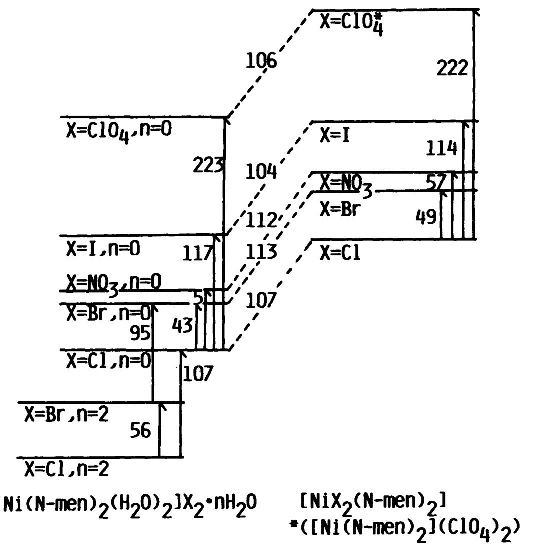

Fig. 2. Enthalpy level diagram for Ni(II)–N-men complexes (kJ mol^{-1}).

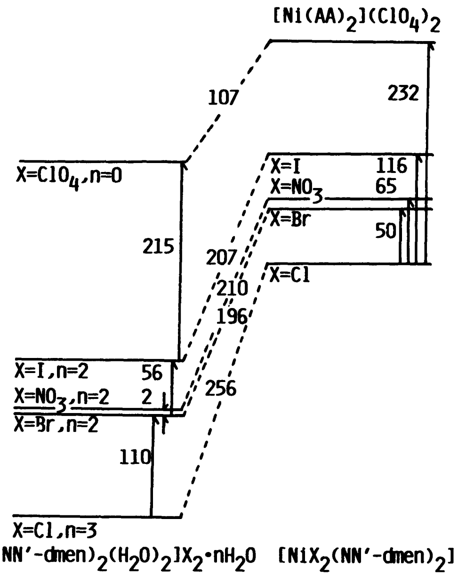

Fig. 4. Enthalpy level diagram for Ni(II)–NN'-dmen complexes (kJ mol^{-1}).

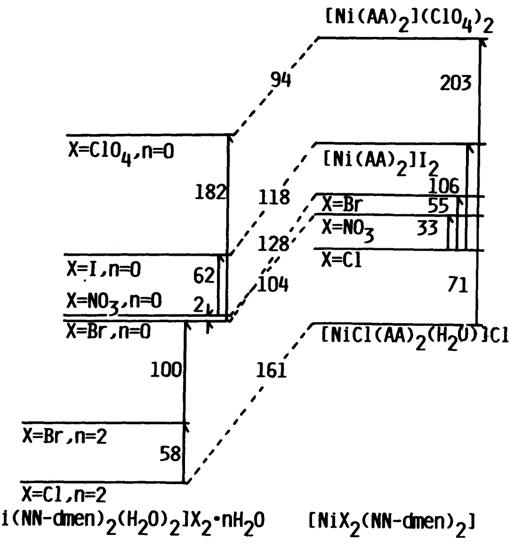

Fig. 3. Enthalpy level diagram for Ni(II)–NN-dmen complexes (kJ mol^{-1}).

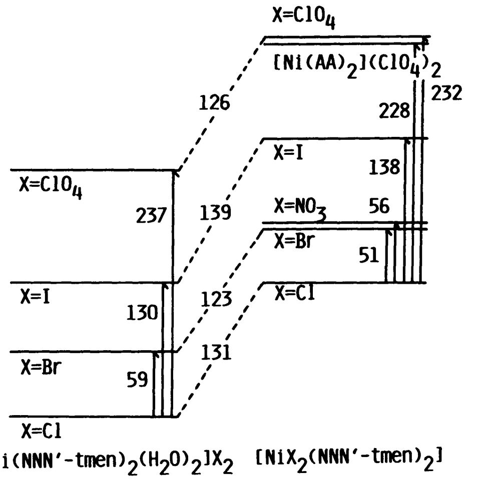

Fig. 5. Enthalpy level diagram for Ni(II)–NNN'-tmen complexes (kJ mol^{-1}).

is also shown in Fig. 1.

Thermal Stability in the N-*men Complexes.* The enthalpy changes for the substitutions of counter anion and of aniono ligand, the dehydration, the deaquation-anation, and the dissociation of the N-men complexes were calculated in a manner similar to that carried out for the en complexes. The enthalpy level diagram thus obtained is represented in Fig. 2. The figure exhibits that [Ni(N-men)$_2$(H$_2$O)$_2$]X$_2$·nH$_2$O become thermally less stable in the order, chloride dihydrate>bromide dihydrate (n=2), and chloride>bromide>nitrate>iodide> perchlorate (n=0); the thermal stabilities of [Ni(N-men)$_2$X$_2$] decrease in the order, dichloro>dibromo >dinitrato>diiodo complexes.

Thermal Stability in the NN-*dmen,* NN'-*dmen, and* NNN'-*tmen Complexes.* In the same way as that shown in the N-men complexes, the enthalpy level diagrams of the NN- and NN'-dmen, and NNN'-tmen complexes are obtained, which are represented in Figs. 3, 4, and 5, respectively. These figures indicate that the thermal stabilities decrease in the order, chloride>bromide>nitrate>iodide in the di-aqua series, and dichloro>dibromo>dinitrato>diiodo in the aniono series except for NN-dmen complexes, which are consistent with the orders of the stability appearing in the *N*-men complexes. The orders of decrement in lattice energy observed in the diaqua and dianiono complexes are parallel to the increasing order of the anionic radii.[8]

Influence of Numbers of N-*Methyl Groups upon Thermal Stability.* The relative thermal stabilities of a series of $[Ni(AA)_2(H_2O)_2]X_2$ can be estimated by comparing the enthalpy changes for the following substitution reaction of diamines:

$$[Ni(AA)_2(H_2O)_2]X_2(s) + 2AA'(g) \\ = [Ni(AA')_2(H_2O)_2]X_2(s) + 2AA(g)$$

For example, the enthalpy change (ΔH) for the reaction,

$$[Ni(en)_2(H_2O)_2](NO_3)_2(s) + 2N\text{-men}(g) \\ = [Ni(N\text{-men})_2(H_2O)_2](NO_3)_2(s) + 2en(g)$$

was calculated as $-0.3\,kJ\,mol^{-1}$ by using the following equation,

$$\Delta H = \Delta H_1 - \Delta H_2 - \Delta H_{en} + \Delta H_{N\text{-men}},$$

where ΔH_1 and ΔH_2 are the enthalpy changes for the following reactions, respectively (Table 1):

$$[Ni(en)_2(H_2O)_2](NO_3)_2(s) + 4CN^-(aq) \\ = Ni(CN)_4{}^{2-}(aq) + 2en(aq) + 2NO_3{}^-(aq) \\ + 2H_2O(l) \cdots \Delta H_1$$

$$[Ni(N\text{-men})_2(H_2O)_2](NO_3)_2(s) + 4CN^-(aq) \\ = Ni(CN)_4{}^{2-}(aq) + 2N\text{-men}(aq) + 2NO_3{}^-(aq) \\ + 2H_2O(l) \cdots \Delta H_2,$$

and ΔH_{en} and $\Delta H_{N\text{-men}}$ are the heats for the reactions of en(g)=en(aq) and *N*-men(g)=*N*-men(aq), respectively (Table 2). The same procedures as those described above were employed for the calculation of the corresponding enthalpy changes for the reactions of the *NN*-dmen, *NN'*-dmen and *NNN'*-tmen complexes. In these calculations, the enthalpy changes for the reaction of AA(g)=AA(aq) in the various diamine systems should be referred. These values were calculated from the heats of vaporization and the heats of solution. The former heats were estimated from the Trouton's constant and the

Table 3. The heats of dissolution of the diamines in aqueous potassium cyanide solution (/kJ mol^{-1})

en	*N*-men	*NN'*-dmen	*NN*-dmen	*NNN'*-tmen
−30.4	−32.9	−45.0	−40.6	−43.8

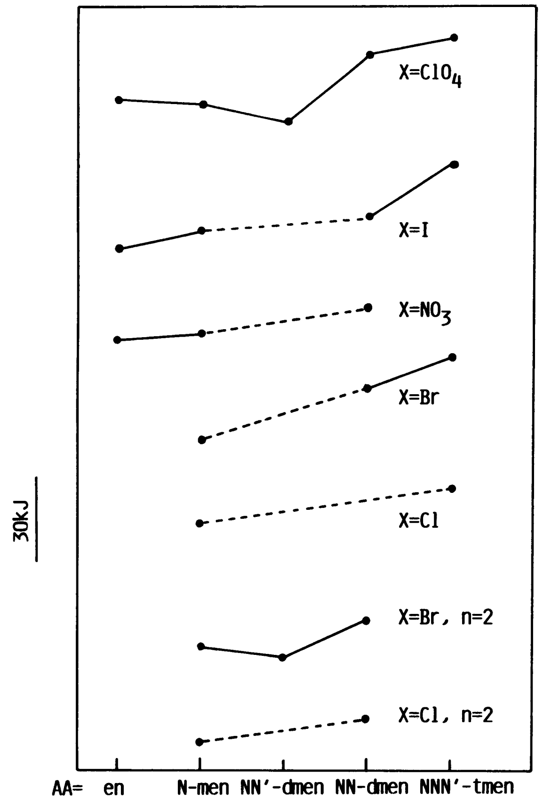

Fig. 6. Enthalpy change diagrams depending upon the displacement of diamines for $[Ni(AA)_2(H_2O)_2]X_2 \cdot nH_2O$ type complexes. The lines to which *n* values are not given are referred to the anhydrates.

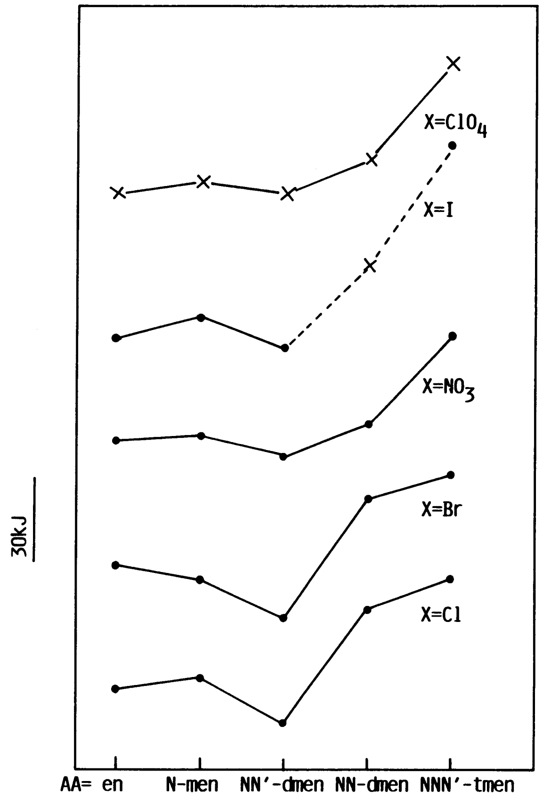

Fig. 7. Enthalpy change diagrams depending upon the displacement of diamines for $[NiX_2(AA)_2]$ (--●--) and $[Ni(AA)_2]X_2$ (--×--) type complexes.

boiling points of diamines within about 5% errors. The latter heats were measured in the concentration of diamine similar to that liberated by the reaction of complexes with CN^- solution. These data measured are listed in Table 3.

Additionally, the enthalpy changes for the substitution reactions of diamines in $[NiX_2(AA)_2]$ and $[Ni(AA)_2]X_2$ were estimated from the data obtained above. The enthalpy change diagrams for $[Ni(AA)_2(H_2O)_2]X_2 \cdot nH_2O$ are depicted in Fig. 6, and those for $[NiX_2(AA)_2]$ and $[Ni(AA)_2]X_2$, in Fig. 7.

The most striking feature is that, in the series of $[NiX_2(AA)_2]$ and $[Ni(AA)_2]X_2$ type complexes, the *NN′*-dmen complexes are the most stable as can be seen in Fig. 7. Except for the *NN′*-dmen complexes, as the number of *N*-methyl groups on diamines increases, the relative thermal stabilities of the complexes generally decrease: namely the complexes become unstable in the order of the en, *N*-men, *NN*-dmen, *NNN′*-tmen complexes (Figs. 6 and 7). This may be partly attributable to an increase of steric repulsion between *N*-methyl groups and the ligands in the apical positions. In the *N*-methyl substituted en complexes, the orientation of methyl group(s) is expected to have an significant influence on the thermal stability of the complexes. In the *NN′*-dmen complexes, two methyl groups are equatorial with respect to the N_4 plane. On the other hand, the *NN*-dmen and *NNN′*-tmen complexes have at least one axial methyl group, which causes a stronger steric repulsion with the ligands in the apical positions than equatorial methyl group and makes the complexes less stable.

The stability of the complexes in the solid state would be mainly dependent not only on the steric interaction but also on the size and shape of the complex cation and the basicity of diamines. In fact, as the numbers of *N*-methyl groups increase, the size of complex cations becomes larger, leading the complexes less stable in the order, en>*N*-men *NN*-dmen>*NNN′*-tmen complexes. This is in line with the results observed in the effect arising from variation of anion size.

So far as the order of the thermal stability between *N*-men and *NN′*-dmen complexes is concerned, however, the interpretation is not so clear only from the steric factor. It has been shown that the formation constant of nickel(II)-*N*-men complex in aqueous solution is larger than that of nickel(II)-*NN′*-dmen complex.[9] In general, the stronger the basicity of the ligand is, the more stable the complex becomes, if no steric hindrance is present within the complex, and the basicity of *N*-men is known to be larger than that of *NN′*-dmen.[10] The observed order of the stabilities between *N*-men and *NN′*-dmen complexes, therefore, is not in harmony with that expected from the formation constant and basicity arguments. In spite of the above discussions, the interpretation on the difference of the thermal stabilities between *N*-men and *NN′*-dmen complexes is not so clear.

References

1) R. Tsuchiya, S. Joba, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, **46**, 1454 (1973); R. Tsuchiya, E. Kyuno, A. Uehara, S. Joba, and S. Ohba, *Chem. Lett.*, **1976**, 911; H. Nishimoto, T. Yoshikuni, A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **51**, 1068 (1978); Y. Ihara and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **53**, 1614 (1980).

2) R. Tsuchiya, A. Uehara, and Y. Ohtsuka, *Bull. Chem. Soc. Jpn.*, **55**, 1858 (1982).

3) M. E. Farago, L. M. James, and V. C. G. Trew, *J. Chem. Soc.*, **A1967**, 820.

4) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, **1963**, 616, 5909; S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

5) L. G. Sillén and A. E. Martell, Ed., "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

6) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963); V. P. Vasil'ev, E. K. Zolobarev, A. F. Kapustinskii, K. P. Mischenko, E. A. Podgornaya, and K. B. Yatsimirskii, *Russ. J. Phys. Chem.*, **34**, 840 (1960); M. F. C. Ladd and W. H. Lee, *Prog. Solid St. Chem.*, **2**, 378 (1965).

7) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Thermodynamic Properties," U. S. Governm. Printing Office, Washington, D. C. (1962), p. 31.

8) V. M. Goldschmidt, *Ber.*, **60**, 1263 (1927); L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927); K. B. Yatsimirskii, Izv. *Akad. Nauk SSSR, Otdel, Khim. Nauk*, **1943**, 398.

9) F. Basolo and R. K. Murman, *J. Am. Chem. Soc.*, **74**, 5243 (1952); **76**, 211 (1954).

10) F. Basolo, R. K. Murman, and Y. T. Chen, *J. Am. Chem. Soc.*, **75**, 1478 (1953); F. Basolo and R. K. Murman, *J. Am. Chem. Soc.*, **74**, 2373 (1952).