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Thermal Reactions of Octahedral Nickel(II) Complexes Containing *N,N*- and *N,N′*-Dialkylethylenediamines in a Solid Phase

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Thermal reactions of the $[Ni(H_2O)_2(AA)_2]X_2 \cdot nH_2O$ complexes in a solid phase were investigated, where AA is *N,N′*-diethylethylenediamine (*NN′*-deen), *N,N*-dimethylethylenediamine (*NN*-dmen), or *N,N*-′dimethylethylenediamine (*NN′*-dmen), and where X^- is Cl^-, Br^-, I^-, NO_3^- or ClO_4^-. By means of thermal analyses and spectral and magnetic measurements in a series of these complexes before and after heating, the following results were obtained. In the case of the *NN′*-deen complexes, only the perchlorate deaquates to change from octahedral to square-planar, but the other salts, such as the chloride, bromide, iodide, and nitrate, undergo deaquation-anation keeping their octahedral configuration. The deaquation-anation was also observed in the chloride, bromide, and nitrate of the *NN*-dmen complexes, but the iodide deaquated, and so was transformed from octahedral to square-planar. In the *NN′*-dmen complexes, only deaquation-anation was detected, irrespective of the anions (Cl^-, Br^-, I^-, and NO_3^-). The effects of *N*-substituents in the diamines and the anions on the above transformation were discussed.

There are three main types of nickel(II) complexes: the first group consists of blue or green, paramagnetic complexes with an octahedral configuration; the second consists of analogously paramagnetic complexes, but with a tetrahedral configuration, and the third consists of red, orange or yellow, diamagnetic complexes with a square-planar configuration.[1)] In 1939, Lifschitz *et al.*[2)] pointed out that the $[Ni(\text{stien or phenen})_2]X_2 \cdot nH_2O$ complexes (stien: 1,2-diphenyl-1,2-ethanediamine; phenen: 1-phenyl-1,2-ethanediamine; X: Cl^-, $ClCH_2COO^-$, $HCOO^-$, and $1/2SO_4^{2-}$; *n*: 0 to 4) easily undergo mutual transformation (yellow diamagnetic ↔blue paramagnetic species), with a slight variation depending upon the kind of X and the hydration states. Since then, such mutual configurational change or equilibration between any two of the three types has often been found in aqueous and some organic solvents.[3,4)] Such changes have also been observed in a solid phase in some limited cases. An example of the change from a square-planar to a tetrahedral configuration was reported in nickel(II) complexes with *N*-methylsalicylideneamine and its derivatives in a solid phase.[5,6)] One of the examples of the octahedral-to-square-planar change is seen in $[Ni(H_2O)_2(NN\text{-deen})_2]Br_2 \cdot H_2O$, where *NN*-deen is *N,N*-diethylethylenediamine,[7)] while the reverse change, square-planar-to-octahedral, is found in the nickel(II) complex with 2-aminobenzimidazole.[8)]

In a series of $[Ni(H_2O)_2(NN\text{-deen})_2]X_2 \cdot nH_2O$-type complexes,[7)] the chloride undergoes anation by the counter-chloride ion after the liberation of coordinated water, keeping the octahedral configuration, whereas the bromide loses the coordinated water to form a square-planar structure without anation upon heating in a solid phase, as has been described above. For the iodide and perchlorate, the octahedral complexes were not obtained with two coordinated water molecules; only anhydrous square-planar complexes were formed. In addition to the kind of counter ion, the structure of *N*-alkylethylenediamines is expected to affect the feature of the configurational change of nickel(II) complexes.

The present study aimed to investigate what different changes appear when $Ni(AA)_2X_2 \cdot nH_2O$ are heated. As the diamines, AA, *N,N′*-diethylethylenediamine (*NN′*-deen), *N,N*-dimethylethylenediamine (*NN*-dmen), and *N,N′*-dimethylethylenediamine (*NN′*-dmen) were selected; X^- was Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-.

Experimental

Preparation of Complexes. The *NN′*-deen, *NN*-dmen, and *NN′*-dmen were of a commercial-reagent grade and were used without further purification. The $[Ni(H_2O)_2(NN'\text{-deen})_2]X_2$ (X^-=Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-),[9)] $[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$,[10)] $[Ni(H_2O)_2(NN\text{-dmen})_2]X_2$($X^-$=$Br^-$, I^-, and NO_3^-),[10)] and $[Ni(H_2O)_2(NN'\text{-dmen})_2]X_2 \cdot 2H_2O$ (X^-= Cl^-, Br^-, I^-, and NO_3^-)[10)] complexes were prepared by a method similar to that of the literature, their chemical formulas being identified by means of elemental analyses and spectral measurements. The perchlorates containing *NN*-dmen and *NN′*-dmen were not obtained in a pure form.

Thermal Analyses. The TG, DTA, and DSC measurements were made with a MOM Derivatograph, Typ-OD-102, and a Rigaku Denki Standard TG-DSC apparatus.

Spectral Measurements. The visible and ultraviolet spectra in a solid state were measured by the diffuse reflectance method with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment. The IR spectra were obtained with JASCO-IR-E and -IR-F infrared spectrophotometers.

Magnetic Measurements. The effective magnetic moments were evaluated from the magnetic susceptibilities, as measured by the Gouy method at room temperature.

Results and Discussion

$[Ni(H_2O)_2$(NN′-$deen)_2]X_2$. *DSC Measurements*: The TG and DSC curves of $[Ni(H_2O)_2(NN'\text{-deen})_2]X_2$ (X^-=Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-) are given in Fig. 1. From the DSC peak temperatures in Fig. 1, the coordinated water molecules are found to be easily evolved in this order: perchlorate (103 °C)<bromide (96 °C) <iodide (93 °C)<nitrate (74 °C)<chloride (66 °C).

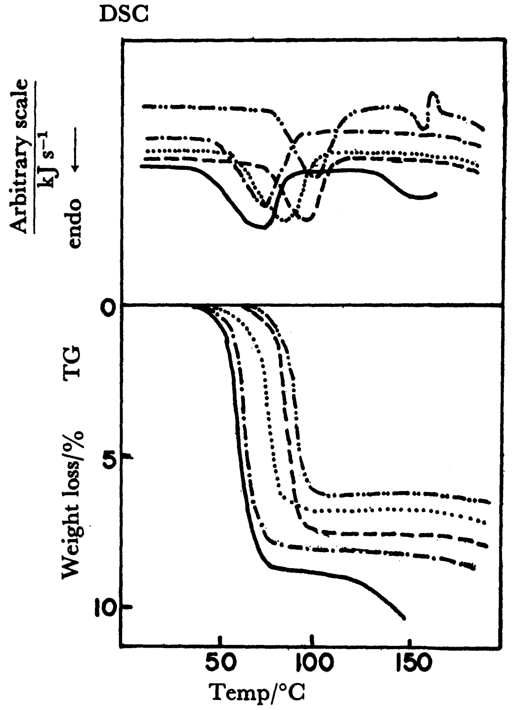

Fig. 1. DSC curves for $[Ni(H_2O)_2(NN'\text{-deen})_2]X_2$, where $X^- = Cl^-$ (——), Br^- (----), I^- (......), NO_3^- (-·-·-), and ClO_4^- (-··-··-).

A striking difference is, however, seen in the DSC curve for $[Ni(H_2O)_2(NN'\text{-deen})_2](ClO_4)_2$; the successive endo- and exothermic peaks appear at about 160 °C, where no change is observed in the TG curve, which retains a plateau.

Absorption Spectra: The absorption spectra measured by the diffuse-reflectance method for $[Ni(H_2O)_2(NN'\text{-deen})_2]Cl_2$ and $[Ni(H_2O)_2(NN'\text{-deen})_2]Br_2$ before and after heating at 130 °C are shown in Fig. 2.

It can be seen from this figure that both of the aqua complexes give three absorption bands, at 12.5, 17.6, and 27.8×10^3 cm^{-1} at room temperature; these bands can be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) electron transitions respectively, irrespective of the kind of counter ion, Cl^- or Br^-. The spectra of the anhydrous salts obtained upon heating are almost identical with those of the mother complexes, except for a slight shift of the maximum peaks to the longer-wavelength region (*e.g.*, the third absorption peaks in the chloride and bromide shift to 26.7×10^3 cm^{-1}).

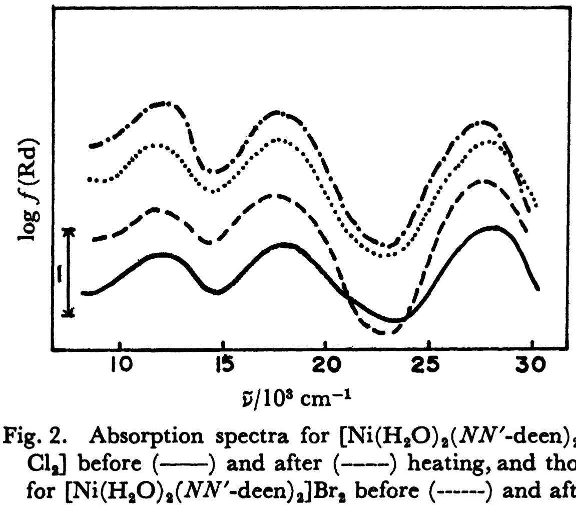

Fig. 2. Absorption spectra for $[Ni(H_2O)_2(NN'\text{-deen})_2]Cl_2$ before (——) and after (----) heating, and those for $[Ni(H_2O)_2(NN'\text{-deen})_2]Br_2$ before (......) and after (-·-·-) heating.

Similar patterns were observed in the spectra of the iodide and nitrate (not shown): the third absorption peaks in the iodide and nitrate shift from 28.1 to 26.9×10^3 cm^{-1} and from 28.1 to 27.5×10^3 cm^{-1} respectively. In all these complexes, a color change from violet to blue was observed upon heating, except that the iodide gives a color change from violet to green.

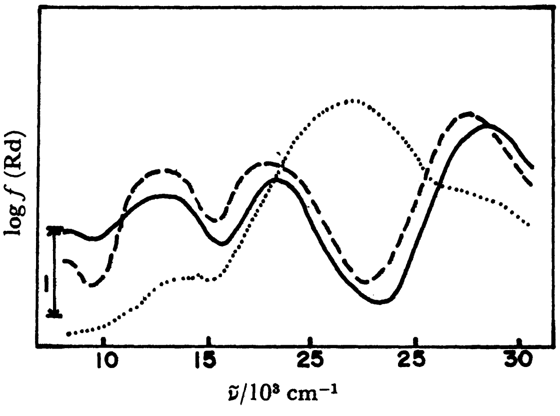

Fig. 3. Absorption spectra for $[Ni(H_2O)_2(NN'\text{-deen})_2](ClO_4)_2$ before (——) and after heating at 130 °C (----) and at 160 °C (......).

On the other hand, a color change from violet to orange through gray was observed in the $[Ni(H_2O)_2(NN'\text{-deen})_2](ClO_4)_2$ complex at 160 °C, where a complicated DSC peak appears. The absorption spectra measured at room temperature and those measured at 130 ° and at 165 °C areshown in Fig. 3. As may be seen in the figure, the former two spectra are very similar to each other, indicating three absorption bands characteristic of six-coordinated nickel(II) complexes, although slight shifts are observable in each absorption peak at 130 °C. At 165 °C, however, these three absorption bands disappear, and a strong band at 21.5×10^3 cm^{-1}, characteristic of the square-planar structure and probably assignable to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, appears instead.

IR Spectra. The representative infrared absorption spectra before and after heating are given in Fig. 4 for $[Ni(H_2O)_2(NN'\text{-deen})_2](ClO_4)_2$. The figure shows that the considerably weak absorption peak at *ca.* 930 cm^{-1} assignable to the Cl–O stretching vibration grows upon heating at 130 °C as a result of the coordination of ClO_4^- to the metal and is then weakened at 165 °C. This rise and fall of the absorption peak corresponds to the color change of the complex: violet→gray→orange. This suggests that the complex loses the coordinated water to undergo the anation of ClO_4^- at 130 °C, and that ClO_4^- is then liberated from the coordination sphere upon further heating.[11]

Magnetic Susceptibilities. The values of the effec-

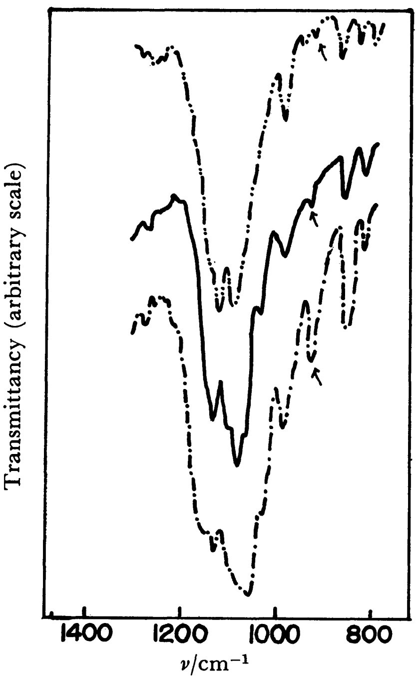

Fig. 4. IR spectra for [Ni(H$_2$O)$_2$(*NN'*-deen)$_2$](ClO$_4$)$_2$ at room temperature (——), upon heating at 130 °C (–•–•–) and at 165 °C (–••–••–).

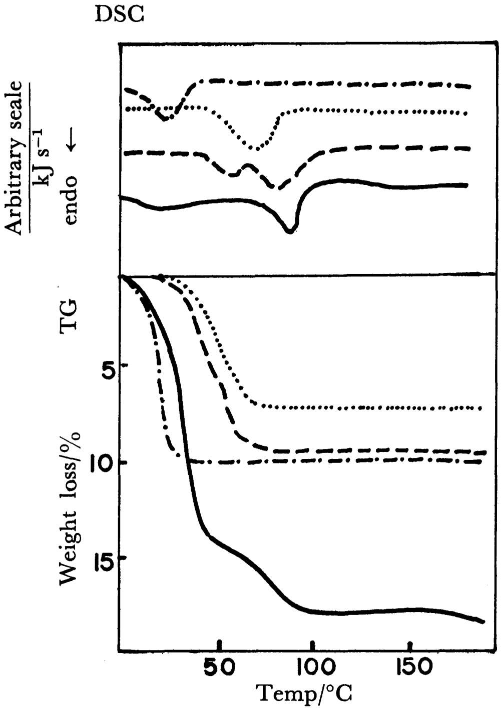

Fig. 5. DSC curves for [Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Cl$_2$·2H$_2$O (——), [Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]X$_2$, where X= Br$^-$ (– – – –), I$^-$ (······), and NO$_3$$^-$ (–•–•–).

tive magnetic moments of the complexes before and after heating are summarized in Table 1. All the [Ni(H$_2$O)$_2$(*NN'*-deen)$_2$]X$_2$ complexes have paramagnetism corresponding to the two unpaired electrons in octahedral nickel(II) complexes. Upon heating, all except for the perchlorate keep the original paramagnetism. This suggests that the octahedral configuration is still kept as a result of the anation of counter ions in the chloride, bromide, iodide, and nitrate. Only the perchlorate, however, gives a change in the magnetic behavior, paramagnetism→diamagnetism, corresponding to the gray→orange color change. This suggests that ClO$_4$$^-$ once coordinates to the nickel ion, yielding a six-coordinated complex, and then gets free from the coordination sphere to form a square-planar complex.

[Ni(H$_2$O)$_2$(NN-dmen)$_2$]X$_2$·nH$_2$O. *DSC Measurements*: The TG and DSC curves for [Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Cl$_2$·2H$_2$O and [Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]X$_2$ (X$^-$= Br$^-$, I$^-$, and NO$_3$$^-$) are shown in Fig. 5. The temperature giving DSC peaks becomes lower in this order: chloride (88 °C) > bromide (83 °C) > iodide (70 °C) > nitrate (30 °C).

Absorption Spectra: The absorption spectra of [Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]X$_2$·*n*H$_2$O (X$^-$=Cl$^-$, Br$^-$, I$^-$, and NO$_3$$^-$) before and after heating are given in Fig. 6. In the chloride, bromide, and nitrate, the three absorption bands characteristic of the six-coordinated nickel(II) complexes are not quenched, but show a shift to a somewhat longer wavelength region upon heating, the

Table 1. Effective magentic moments of the complexes before and after heating

Complex	Magnetic moments μ_{eff}/BM	
	Before heating	After heating
[Ni(H$_2$O)$_2$(*NN'*-deen)$_2$]Cl$_2$	2.96	2.90
[Ni(H$_2$O)$_2$(*NN'*-deen)$_2$]Br$_2$	3.03	2.95
[Ni(H$_2$O)$_2$(*NN'*-deen)$_2$]I$_2$	2.96	2.92
[Ni(H$_2$O)$_2$(*NN'*-deen)$_2$](NO$_3$)$_2$	2.94	2.94
[Ni(H$_2$O)$_2$(*NN'*-deen)$_2$](ClO$_4$)$_2$	2.91	2.94,$^{a)}$ diamag$^{b)}$
[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Cl$_2$·2H$_2$O	3.13	2.90
[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Br$_2$	3.02	2.91
[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]I$_2$	3.26	diamag
[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$](NO$_3$)$_2$	2.96	3.17
[Ni(H$_2$O)$_2$(*NN'*-dmen)$_2$]Cl$_2$·2H$_2$O	3.18	3.00
[Ni(H$_2$O)$_2$(*NN'*-dmen)$_2$]Br$_2$·2H$_2$O	3.08	2.95
[Ni(H$_2$O)$_2$(*NN'*-dmen)$_2$]I$_2$·2H$_2$O	3.18	2.93
[Ni(H$_2$O)$_2$(*NN'*-dmen)$_2$](NO$_3$)$_2$·2H$_2$O	3.16	3.17

a) Upon heating at 130 °C. b) Upon heating at 165 °C.

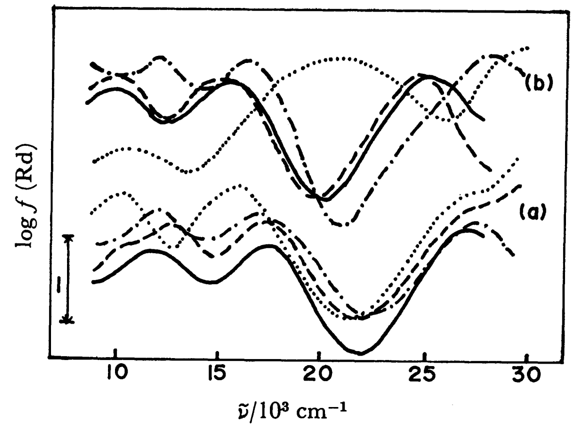

Fig. 6. Absorption spectra for $[Ni(H_2O)_2(NN\text{-dmen})_2]X_2$ before (a) and after (b) heating, where $X^- = Cl^-$ (——), Br^- (– – –), I^- (······) and NO_3^- (–·–·–).

color changing from pale blue to greenish blue, to green, and to blue respectively. Only in the iodide does the color change from the original pale blue to orange, and a new strong band due to the formation of a square-planar complex appears after the liberation of the coordinated water.

Magnetic Susceptibilities: As is shown in Table 1, the effective magnetic moments of $[Ni(H_2O)_2(NN\text{-dmen})_2]X_2 \cdot nH_2O$ are all paramagnetic. After heating, the paramagnetism is not lost in the chloride, bromide, and nitrate, indicating that the octahedral configuration is still maintained as a result of the anation of counter ions, whereas only the iodide gives diamagnetism upon heating, suggesting that it undergoes the configurational change to square-planar from octahedral.

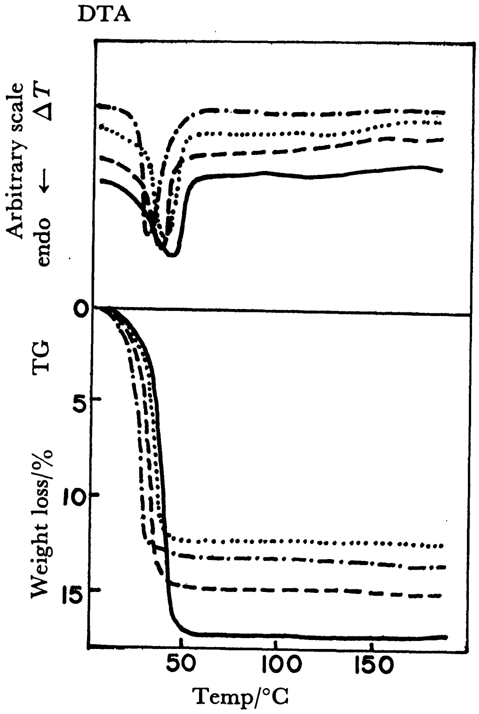

Fig. 7. TG and DTA curves for $[Ni(H_2O)_2(NN'\text{-dmen})_2]X_2 \cdot 2H_2O$, where $X^- = Cl^-$ (——), Br^- (– – –), I^- (······), and NO_3^- (–·–·–).

$[Ni(H_2O)_2($NN'-dmen$)_2]X_2 \cdot nH_2O$. DTA Measurements: The DTA measurements were carried out in this series of compounds because these compounds deaquated even below 50 °C and because our DSC apparatus could not be employed below that temperature. The TG and DTA curves for these compounds are shown in Fig. 7. The temperature giving DTA peaks becomes lower in this order: chloride (52 °C)>iodide (38 °C)>bromide (34 °C)>nitrate (32 °C).

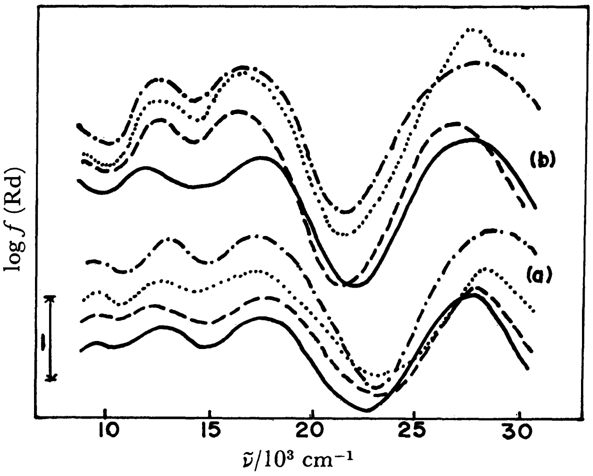

Fig. 8. Absorption spectra for $[Ni(H_2O)_2(NN'\text{-dmen})_2]X_2 \cdot 2H_2O$ before (a) and after (b) heating, where $X^- = Cl^-$ (——), Br^- (– – –), I^- (······), and NO_3^- (–·–·–).

Absorption Spectra: The absorption spectra of $[Ni(H_2O)_2(NN'\text{-dmen})_2]X_2 \cdot 2H_2O$ ($X = Cl^-$, Br^-, I^-, and NO_3^-) before and after heating are given in Fig. 8. In this case, all the complexes are pale blue and give the three absorption bands. After heating, they are still blue, and these absorption bands remain, except for a slight shift to the longer-wavelength region.

Magnetic Susceptibilities: The data in Table 1 show that all the complexes containing *NN'*-dmen, both before and after heating, give paramagnetism, indicating that these complexes undergo the anation of counter ions while keeping their six-coordinated, octahedral configuration.

Effect of N-*Substituents in Ethylenediamine upon Configurational Change*: Table 2 summarizes the configurational changes in $[Ni(H_2O)_2(AA)_2]X_2 \cdot nH_2O$-type complexes.

TABLE 2. CONFIGURATIONAL CHANGES IN $[Ni(H_2O)_2(AA)_2]X_2 \cdot nH_2O$-TYPE COMPLEXES

AA	X^-				
	Cl^-	Br^-	I^-	NO_3^-	ClO_4^-
NN'-dmen	A[a]	A	A	A	—
NN'-deen	A	A	A	A	A[b], B[c]
NN-dmen	A	A	B	A	—
NN-deen[d]	A	B[a]	C[a]	C	C

a) A denotes that the complexes undergo deaquation-anation, keeping an octahedral configuration; B, that the complexes deaquate to form square-planar complexes, and C, that square-planar complexes are exclusively obtained. b) At 130 °C. c) At 165 °C. d) Ref. 7.

It shows that the feature of the configurational change is dependent upon the position to which the substituents are attached and upon the kind of substituent, methyl or ethyl. First, in the complexes containing *NN'*-dmen or *NN'*-deen, where two methyl or ethyl groups are combined with different nitrogen atoms, all the complexes undergo anation after liberating coordinated water except for the perchlorate containing *NN'*-deen. On the other hand, in the complexes having *NN*-dmen, where two substituents are combined in the same nitrogen atom, the iodide undergoes the configurational change from octahedral to square-planar after dehydration. In *NN*-deen complexes, on the other hand, the bromide undergoes a similar change to the iodide of the *NN*-dmen complex, while the iodide and perchlorate only give the anhydrous square-planar structure, without any anation. Such differences between the complexes containing *N,N'*- and *N,N*-disubstituted diamines are probably due to the larger steric hindrance of the *N,N*-disubstituent against the anation than that of the *N,N'*-disubstituent. This was because, in the stable form of the *NN'*-dmen and *NN'*-deen complexes, the substituents can all be equatorial, whereas in the *NN*-dmen and *NN*-deen complexes, at least one of the substituents in these diamines is forced to take the axial position.

By inspecting the different behavior in configurational change observed upon heating between octahedral *NN*-dmen and *NN*-deen complexes, the latter has been found more easily to turn or take a square-planar configuration than the former. That is, in the bromide, the *NN*-dmen complex only undergoes anation, while the *NN*-deen complex does not undergo anation, but gives a square-planar configuration, upon heating. In the iodide, where the iodide ion has a larger radius than the bromide ion, the *NN*-dmen complex gives a square-planar configuration after liberating the coordinated water upon heating, but the *NN*-deen complex does not form an octahedral complex with coordinated water, but forms only a square-planar complex. The perchlorate containing *NN*-deen also shows the same behavior as the corresponding iodide. Such differences between *NN*-dmen and *NN*-deen complexes are possibly attributable to the bulkiness of the ethyl group relative to the methyl group. Moreover, the easier formation of square-planar complexes in the iodide than in the bromide is probably also attributable to the larger size of an iodide ion.

References

1) R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

2) I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allg. Chem.*, **242**, 97 (1939).

3) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

4) D. R. Eaton, W. D. Philips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

5) L. Sacconi, P. Paoletti, and R. Cini, *J. Am. Chem. Soc.*, **80**, 3583 (1958).

6) H. C. Clark and R. J. O'Brien, *Can. J. Chem.*, **39**, 1030 (1961).

7) R. Tsuchiya, S. Joba, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, **46**, 1454 (1973).

8) Y. Ihara and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **53**, 1614 (1980).

9) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, **1963**, 616.

10) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, **1963**, 5909.

11) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, **1961**, 3091.