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Derivatographic Studies on Transition Metal Complexes. X.[1] Thermal Octahedral-to-Square Planar Transformation of Ni(*NN*-deen)$_2$X$_2$·*n*H$_2$O in Solid Phase[2]

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Thermal reactions of the complexes $[Ni(H_2O)_2(NN\text{-deen})_2]X_2 \cdot nH_2O$ (*NN*-deen is *N*,*N*-diethylethylenediamine and X is Cl or Br) were investigated. It was found by derivatography and spectral and magnetic measurements that the bromide undergoes transformation from octahedral to square planar structure by "deaquation" upon heating, whereas the chloride turned to the dichloro complex by thermal "deaquation-anation" losing the coordinated water and drawing chloride ion into the coordination sphere with retention of octahedral structure around the central metal. No such transformation could be found in the corresponding iodide and nitrate, since only diamagnetic complexes, $[Ni(NN\text{-deen})_2]X_2$ (X is I or NO_3), and no paramagentic complexes were obtained.

When a nickel(II) atom is surrounded by the same six ligands forming a regular octahedral configuration, it forms a blue type complex with magnetic moment 3.1—3.2 B.M. due to two unpaired electrons in 3d orbital with a small orbital contribution.[3] The red, brown and yellow nickel(II) complexes show a diamagnetic behavior due to the lower energy of the triplet ground state relative to the singlet state,[4,5] taking a planar structure in a strong field with coordination number 4. Some green and blue nickel(II) complexes are known,[3] which take a tetrahedral structure with coordination number 4 having two unpaired 3d electrons.

Since the three types of nickel(II) complexes give characteristic electronic spectra as regards symmetry,[6,7] the structure of the complexes and their thermal reaction products can be assigned by observing the spectra and other physical properties.

It is of interest to investigate the structural transformation of nickel(II) complexes upon heating. Structural transformations after complete dehydration of nickel(II) complexes containing *C*,*C*′-substituted ethylenediamine are known.[8,9] Nickel(II) complexes containing ethylenediamine itself[3] or its *N*-alkyl-substituted products[6] as diamine such as Ni(diamine)$_2$X$_2$·*n*H$_2$O or Ni(diamine)$_2$X$_2$, are known. However, no detailed studies on the structural change upon heating have been made.

Studies on the thermal structural transformation of some metal complexes have been carried out recently by means of derivatography.[1,10–12] The present work was undertaken to find whether or not the nickel(II) complexes with *N*,*N*-diethylethylenediamine undergo structural transformation from octahedral to square planar in the solid phase depending upon the kind of counter anions.

Experimental

Preparation of Complexes. *N*,*N*-Diethylethylenediamine was of commercial reagent grade and used without purification. Complexes Ni(*NN*-deen)$_2$Cl$_2$·2H$_2$O, Ni(*NN*-deen)$_2$Br$_2$·3H$_2$O, Ni(*NN*-deen)$_2$I$_2$ and Ni(*NN*-deen)$_2$(NO$_3$)$_2$ were prepared by the known method,[6] their chemical formulas being identified by elemental analysis and spectral measurement.

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[1] Part IX in this series; See R. Tsuchiya, S. Nakagawa, A. Uehara, and E. Kyuno, This Bulletin, **46**, 169 (1973).

[2] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[3] R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

[4] G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162, 1129 (1958).

[5] C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, **81**, 538 (1959).

[6] D.M.L. Goodgame and L.M. Venanzi, *J. Chem. Soc.*, **1963**, 616, 5909.

[7] C. Furlani and G. Sartori, *J. Inorg. Nucl. Chem.*, **8**, 126 (1958).

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

[9] I. Lifschitz and J. G. Bos, *Rec. Trav. Chim.*, **59**, 407 (1940).

[10] R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, This Bulletin, **43**, 1383 (1970).

[11] R. Tsuchiya, Y. Nakata, and E. Kyuno, *ibid.*, **44**, 705 (1971).

[12] R. Tsuchiya, M. Suzuki, and E. Kyuno, *ibid.*, **44**, 709 (1971).

Derivatographic Measurements. The derivatograms were obtained with a MOM Derivatograph Typ-OD-102.[13] 0.5 g of finely powdered sample (100—200 mesh inch^{-1}) was used in each run. Measurements were carried out under a constant flow of nitrogen stream with a heating rate of 1 °C min^{-1} unless otherwise stated.

Spectral Measurements. Visible and UV spectra in the solid state were measured by the diffuse reflectance method with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment. 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 measured by the Gouy method at room temperature. Hg[Co(NCS)$_4$] was used as reference material. Susceptibilities of the complexes were corrected by applying Pascal's constants of the elements involved.

Results and Discussion

Derivatography. The derivatograms of Ni(*NN*-deen)$_2$Cl$_2$·2H$_2$O and Ni(*NN*-deen)$_2$Br$_2$·3H$_2$O are shown in Fig. 1. The former shows a loss of two moles of water upon heating at 80—110 °C in the TG curve, an endothermic peak appearing in the DTA curve. It seems that the anhydrous complex Ni(*NN*-deen)$_2$Cl$_2$ is produced.

The bromide complex loses one mole of water at 30—65 °C and two moles at 70—110 °C, giving two endothermic peaks in the corresponding dehydration temperature ranges in the DTA. The anhydrous complex Ni(*NN*-deen)$_2$Br$_2$ seems to be formed.

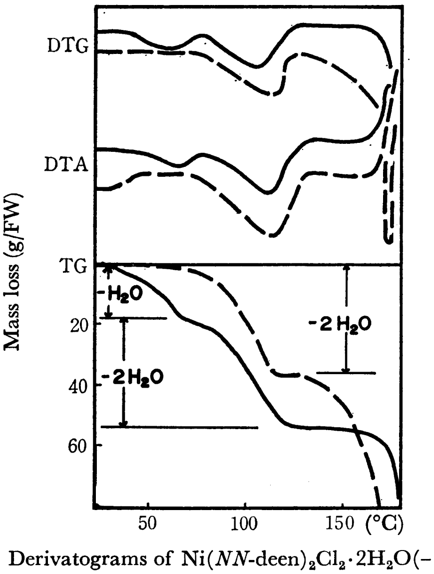

Fig. 1. Derivatograms of Ni(*NN*-deen)$_2$Cl$_2$·2H$_2$O(----) and Ni(*NN*-deen)$_2$Br$_2$·3H$_2$O (——).

Absorption Spectra. The visible absorption spectra of the complexes Ni(*NN*-deen)$_2$X$_2$·nH$_2$O measured in solid state by the diffuse reflectance method are shown in Fig. 2, together with those of the anhydrous complexes Ni(*NN*-deen)$_2$X$_2$ (X is Cl or Br), obtained by heating the corresponding hydrated complexes at 110 °C.

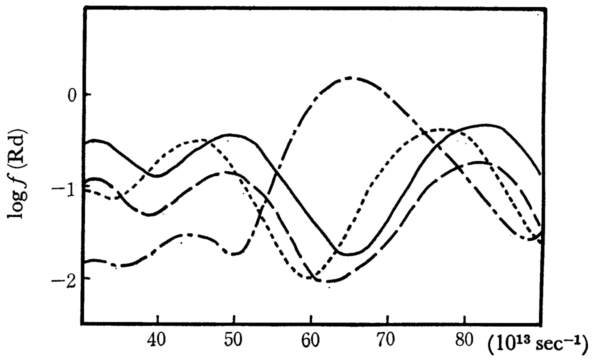

Fig. 2. Electronic spectra of Ni(*NN*-deen)$_2$Cl$_2$·2H$_2$O (——), Ni(*NN*-deen)$_2$Br$_2$·3H$_2$O (———) and those after heating them at 110 °C (----) and at 110 °C (———).

We see from Fig. 2 that the hydrated complexes Ni(*NN*-deen)$_2$X$_2$·nH$_2$O both give three absorption bands at 30, 49, and 80×10^{13} sec^{-1}, which can be assigned to the electron transitions taking place in the Oh symmetry complexes of d^8 metal,[6,7] $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P), respectively, irrespective of the kind of counter ions such as Cl$^-$ or Br$^-$.

The absorption spectra of the anhydrous complexes Ni(*NN*-deen)$_2$X$_2$, where X is I or NO$_3$, are given in Fig. 3. They show that the anhydrous complexes Ni(*NN*-deen)$_2$X$_2$ both give a relatively strong absorption band at 64—65×10^{13} sec^{-1}, characteristic of the square planar structure in nickel(II) complexes and probably assignable to the transition $^1A_{1g}\rightarrow{}^1A_{2g}$.

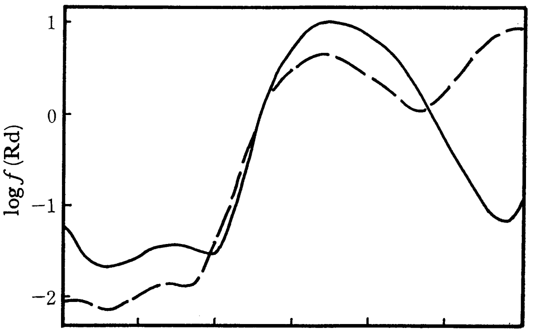

Fig. 3. Electronic spectra of Ni(*NN*-deen)$_2$I$_2$ (———) and Ni(*NN*-deen)$_2$(NO$_3$)$_2$ (——).

We see that the spectrum of the anhydrous chloride obtained upon heating is analogous to that of the mother hydrated chloride except for a slight shift of maximum peak to the longer wavelength region (Fig. 2), whereas the spectrum of the anhydrous bromide is analogous to that of the anhydrous iodide and nitrate (Fig. 3). The results suggest that the hydrated chloride turns to the dichloro complex through deaquation-anation upon heating with retention of the octahedral coordination, while the bromide is converted into the square planar coordination as the result of dehydration alone. Thus, the hydrated chloride and bromide are both diaquo octahedral complexes and their thermal reactions can be assumed to proceed as follows.

$$[\mathrm{Ni(H_2O)_2}(NN\text{-deen})_2]\mathrm{Cl_2} \longrightarrow [\mathrm{NiCl_2}(NN\text{-deen})_2] + 2\mathrm{H_2O}$$

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[13] F. Paulik, J. Paulik, and L. Erdey, *Talanta*, **13**, 1405 (1966).

$$[Ni(H_2O)_2(NN\text{-deen})_2]Br_2 \cdot H_2O \longrightarrow [Ni(NN\text{-deen})_2]Br_2 + 3H_2O$$

From the similarity of spectra of the anhydrous complex bromide (Fig. 2) and of the iodide and nitrate (Fig. 3), the complex iodide and nitrate can be represented by $[Ni(NN\text{-deen})_2]I_2$ and $[Ni(NN\text{-deen})_2](NO_3)_2$, respectively.

IR Spectra. Infrared and far-infrared absorption spectra were measured in order to see whether the anions in the complexes are coordinated and to obtain configurational information. The IR spectra of the diaquo complexes exhibit an absorption peak assigned to the stretching vibration, ν_{OH}, at *ca.* 3200 cm^{-1} and that for the bending vibration, δ_{OH}, at *ca.* 1600 cm^{-1}, the patterns of the chloride and bromide being the same. This supports the results given by electronic absorption measurement and derivatography where the diaquo complex chloride and bromide are represented by $[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$ and $[Ni(H_2O)_2(NN\text{-deen})_2]Br_2 \cdot H_2O$ respectively.

The IR spectra of the anhydrous complex chloride and bromide obtained by heating the corresponding diaquo complexes are shown in Fig. 4, together with those of the iodide and nitrate. The absorption peaks of the OH group in the former two complexes are quenched as a result of dehydration, and the patterns of the bromide, iodide, and nitrate are approximately analogous to each other but differ from that of the chloride. These results confirm the chemical formulas $[Ni(NN\text{-deen})_2]Br_2$, $[Ni(NN\text{-deen})_2]I_2$, $[Ni(NN\text{-deen})_2](NO_3)_2$, and $[NiCl_2(NN\text{-deen})_2]$ for the bromide, iodide, nitrate, and chloride, respectively, in which the former three have a square planar structure and the last one has an octahedral structure with chloride ions in coordination.

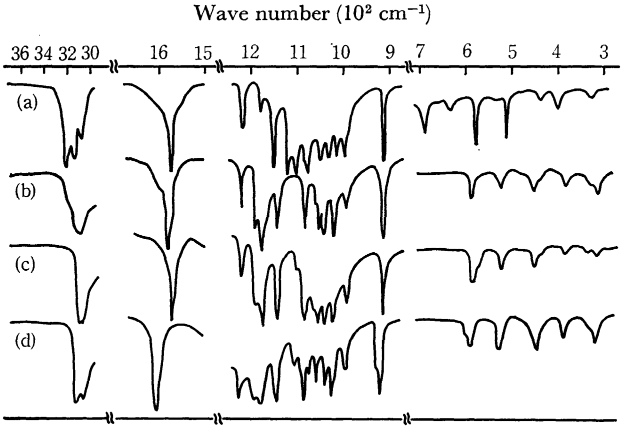

Fig. 4. IR and Far-IR spectra of (a) $Ni(NN\text{-deen})_2Cl_2$, (b) $Ni(NN\text{-deen})_2Br_2$, (c) $Ni(NN\text{-deen})_2I_2$, and (d) $Ni(NN\text{-deen})_2(NO_3)_2$.

Magnetic Susceptibility Measurement. The values of the effective magnetic moments of the complexes are summarized in Table 1 together with their colors. The fact that the diaquobis(diamine) complex chloride and bromide, including the dichloro complex formed by heating the former, show paramagnetism and the anhydrous iodide and nitrate diamagnetism confirms the respective structures predicted by spectral measurements. It was found that the hydrated diaquo complex bromide lost paramagnetism remarkably upon heating (Table 1).

Table 1. Magnetic moments and colors of the complexes

Complex	Color	Magnetic moment μ_{eff} (B.M.)
$[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$	blue	3.21 (28 °C)
$[Ni(H_2O)_2(NN\text{-deen})_2]Br_2 \cdot H_2O$	blue	3.30 (20 °C)
$[Ni(NN\text{-deen})_2]I_2$	orange	diamag.
$[Ni(NN\text{-deen})_2](NO_3)_2$	orange	diamag.
$[NiCl_2(NN\text{-deen})_2]$	green	3.19 (20 °C)
$[Ni(NN\text{-deen})_2]Br_2$	orange yellow	0.9 (20 °C)

It is concluded that the diaquo complex bromide undergoes structural transformation from octahedral to square planar configuration by way of thermal deaquation in a solid phase, whereas the diaquo complex chloride undergoes no structural transformation but a thermal deaquation-anation reaction, forming the dichloro complex simultaneously (Fig. 5).

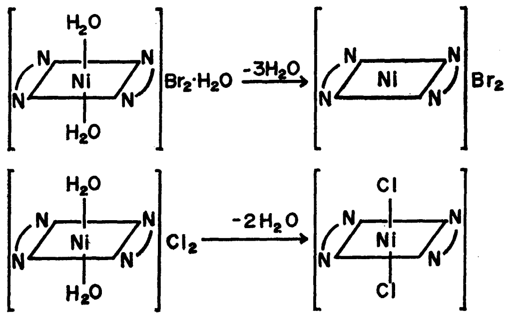

Fig. 5. Thermal reaction schemes of $[Ni(H_2O)_2(NN\text{-deen})_2]Br_2 \cdot H_2O$ and $[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$.