Derivatographic Studies on Transition Metal Complexes. XIII.[1) Thermal Decomposition of $[Ni(N_2H_4)_6]X_2$ Complexes[2)

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The thermal decomposition of $[Ni(N_2H_4)_6]X_2$ (X=Cl, Br, I) in solid phase was investigated by means of derivatography and IR spectral measurement. It was found from the derivatography that the decomposition of the chloride and bromide proceeded *via* tris-, bis-, and mono-hydrazine complexes as metastable reaction intermediates, while tetra-hydrazine complex was produced in the decomposition of the iodide instead of the tris-one which appeared in the chloride and bromide. IR spectra showed that, although the hexa-hydrazine complex as a starting material contains only unidentate hydrazine coordinated by either one of terminal nitrogen atoms, all the reaction intermediates have bidentate one bridging between two nickel ions. In particular, it was of much interest that the decomposition of these hydrazine complexes was remarkably exothermic, a part of the reasons being discussed.

Systematic studies on thermal decomposition in solid phase for $[Ni(II)N_6]$-type complexes seem to be still rare except for $[Ni(NH_3)_6]X_2$.[3) Tanaka *et al.*[4) proposed from the thermogravimetry for hexaamminenickel(II) complexes that it decomposed in two or three steps through lower ammine intermediates $NiX_2 \cdot nNH_3$: n=2, 1 for X=Cl; n=2 for X=Br, I and n=4 for X=NO_3.

Because of d^8 electronic configuration in nickel(II) ion, the tendency of the complex formation of either octahedral (O_h symmetry) six-coordinated, square planar (D_{4h}) or tetrahedral (T_d) four-coordinated structure apparently could exist depending upon the changes in trivial steric hindrance or the nature of surroundings for the central metal ion.[5,6) In the thermal decomposition of hexaamminenickel(II) complexes described above, however, the latter two forms, square planar and tetrahedral, could not be found, but the intermediates were presumed to be polymers from the diffuse reflectance spectral measurement in which nickel ions were octahedrally coordinated with ammonia molecules and bridging halogen atoms.

Hydrazine (NH_2NH_2), in general, behaves either as unidentate ligand coordinated by either one of terminal nitrogen atoms or as bidentate one bridging between two metals[7–9) because of the difficulty of the formation of bidentate coordination with a same metal ion owing to its short N–N distance despite of keeping two nitrogen atoms capable of coordinating to metal in one hydrazine molecule itself.

From these standpoints, hydrazine may be expected to form the complex like $[NiN_6]$-type. On the other hand, the thermal decomposition of the complexes of nickel(II),[10) iron(II),[11) and cobalt(II)[12) oxalates with hydrazine had been investigated.

Thus, as the object of the present work, it was undertaken to find whether or not the nickel(II) complexes with hydrazine undergo the analogous structural transformation to that of hexaamminenickel(II) complexes in the course of thermal decomposition, and whether or not any unique changes can be found in terms of the peculiar behavior of hydrazine to coordination form as described above.

Experimental

Preparation of Complexes. Complexes $Ni(N_2H_4)_6X_2$ (X=Cl, Br, I) were prepared in the similar manner to that described in the literature.[13) Compounds of $Ni(N_2H_4)_3X_2$ type as well as $Ni(N_2H_4)_2X_2$ type were also obtained by the known method[8) to identify the corresponding intermediates in the thermal reaction of hexehydrazinenickel(II) complexes. Their chemical formulae were determined by elemental analysis and spectral measurement.

Derivatographic Measurements. The derivatograms were obtained with a MOM Derivatograph Typ-OD-102. All the measurements were carried out in a constant flow of nitrogen stream under the heating rate of 1 °C/min. In each run 0.4 or 0.5 g sample was used. The thermal functions, activation energies (E_a) and enthalpy changes (ΔH), were calculated in each step of thermal reaction by analyzing the DTA curves in the derivatograms obtained.[14)

Spectral Measurements. In order to examine the structural change or bonding feature of the reaction intermediates during the course of the thermal decomposition, the reaction intermediates were taken out of a furnace at various desired temperatures during the continuous heating by a Shimadzu TM-1A thermobalance and their electronic and infrared absorption spectra were measured with a Hitachi EPS and EPU-2A spectrophotometers in both solution and powder state and with a JASCO Model IR-E spectrophotometer in mull state, respectively.

Magnetic Measurements. The effective magnetic moments of the samples as well as the reaction intermediates were evaluated from the magnetic susceptibilities of the sample corrected by applying the Pascal's constant of the elements involved.

X-Ray Powder Diffraction. X-ray powder diffraction patterns of the sample and its thermal reaction intermediates were obtained with a Rigaku-denki Geiger-flex X-ray Analyzer.

Results and Discussion

Derivatography. When $Ni(N_2H_4)_6X_2$ (X=Cl, Br) was heated in solid phase, the decomposition accompanying the liberation of hydrazine took place stepwise with some color changes. Figure 1 shows the derivatograms for the chloride and bromide.

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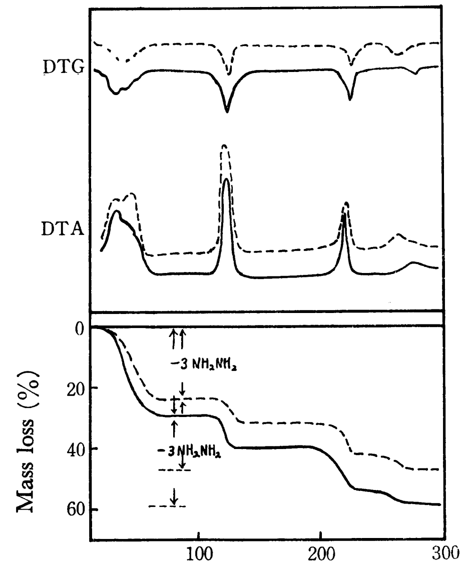


Fig. 1. Derivatograms for $Ni(N_2H_4)_6Cl_2$ (——) and $Ni(N_2H_4)_6Br_2$ (------).

As seen in this figure, two reaction intermediates formed as the result of the evolution of three and four moles of hydrazine are obviously detected successively in the TG curves up to 60 °C and in the temperature range of 100—140 °C, respectively, being confirmed to have the compositions, $Ni(N_2H_4)_3X_2$ (X=Cl, Br) and $Ni(N_2H_4)_2X_2$, by the electronic and IR spectra which will be described in the later sections. The further heating of these compounds leads to the decomposition to nickel(II) halides as the final products at 240—320 °C *via*, as a whole, the formation of monohydrazine complexes, $Ni(N_2H_4)X_2$ (Cl, Br), at 190—230 °C as the third reaction intermediates.

The DTA curves show one broad and two sharply exothermic peaks in the three decomposition steps, $Ni(N_2H_4)_6X_2$ to $Ni(N_2H_4)_3X_2$, $Ni(N_2H_4)_3X_2$ to $Ni(N_2H_4)_2X_2$ and $Ni(N_2H_4)_2X_2$ to $Ni(N_2H_4)X_2$, and a small exothermic peak in the last step of the decomposition to nickel(II) halides.

Although the evolution of ammonia or water molecules in the thermal decomposition of aquo or ammine cobalt(III) or chromium(III) complexes gives, in general, endothermic peak,[14,15] an appearance of exothermic peaks as mentioned above is of much interest. Such a phenomenon will be attributed to the characteristic properties of hydrazine, and the discussion concerned will be briefly made in the later section.

In the case of the iodide, on the other hand, the tetrahydrazine complex was found in place of tris(hydrazine) complex in the case of chloride and bromide, and bis(hydrazine) complex undersent the complete decomposition without the formation of monohydrazine complex as shown in Fig. 2: the two decomposition steps, hexa-to-tetra and tetra-to-bis complex, appear at about 30—85 °C and at 100—135 °C, respectively, and the final decomposition occurs at 240—290 °C. The most striking difference between the chloride, bromide and iodide is that, in the former two, the final decomposition product is nickel(II) halides, whereas the iodide finally decomposes without the formation of nickel(II) iodide. It may be in part due to the essential decomposition with iodine liberation.

Magnetic Susceptibilities. The effective magnetic moments evaluated from the magnetic susceptibilities of the hexahydrazine complexes and their thermal reaction intermediates are listed in Table 1 together with their colors.

The complexes $Ni(N_2H_4)_6X_2$ (Cl, Br) did not give a constant value on account of the sensitivity of the composition in air exposure, and hence are expressed as paramagnetic. That the complexes, $Ni(N_2H_4)_3X_2$ and $Ni(N_2H_4)_2X_2$, give the magnetic moments corresponding to the electronic structure with two free spins suggests that their structures are not, at least, the square planar. The values for the iodide could not be obtained because of the comparative instability against the chloride and bromide.

Electronic Spectra. In order to clarify the coordination structures of the hexahydrazinenickel(II) complexes, $Ni(N_2H_4)_6X_2$, and their thermal reaction intermediates, their electronic spectra were measured in the powdered state by the diffuse reflectance method, which are shown in Fig. 2 for the chloride, in Fig. 3 for the bromide and in Fig. 4 for the iodides.

As seen in these figures and in Table 1, tris(hydrazine)nickel(II) chloride, $Ni(N_2H_4)_3Cl_2$, and the bromide, $Ni(N_2H_4)_3Br_2$, and tetra-hydrazine iodide, $Ni(N_2H_4)_4I_2$, as well as the hexahydrazinenickel(II)

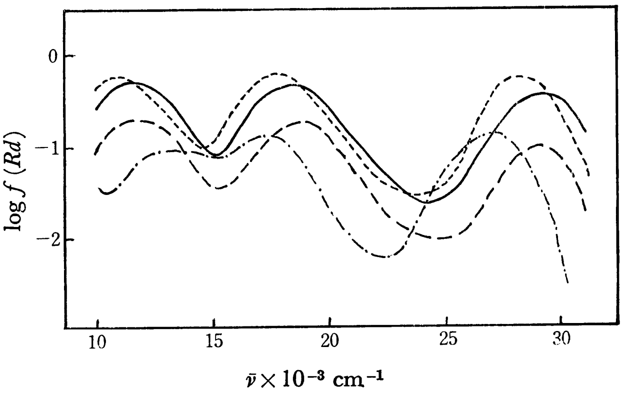


Fig. 2. Electronic spectra of $[Ni(N_2H_4)_6]Cl_2$ (——), $Ni(N_2H_4)_3Cl_2$ (-----), $Ni(N_2H_4)_2Cl_2$ (— — —), and $[Ni(NH_3)_6]Cl_2$ (-------).

TABLE 1. MAGNETIC MOMENTS (25 °C) AND COLORS OF $[Ni(N_2H_4)_n]X_2$

n	X	μ_{eff}(B.M.)	Color	n	X	μ_{eff}(B.M.)	Color	n	X	Color
6	Cl	paramag.	pale violet	6	Br	paramag.	pale violet	6	I	pale violet
3	Cl	2.96	pale violet	3	Br	3.43	pale violet	4	I	pale violet
2	Cl	3.17	pale blue	2	Br	3.20	grayish blue	2	I	yellowish green
1	Cl		yellow	1	Br		yellowish brown			

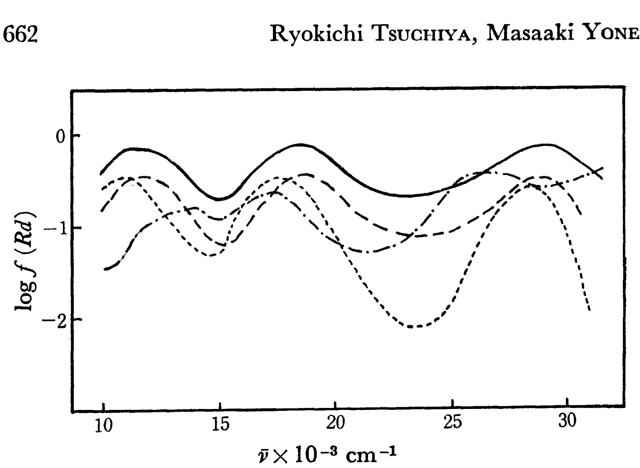


Fig. 3. Electronic spectra of $[Ni(N_2H_4)_6]Br_2$ (——), $Ni(N_2H_4)_3Br_2$ (----), $Ni(N_2H_4)_2Br_2$ (– – –) and $[Ni(NH_3)_6]Br_2$ (-------).

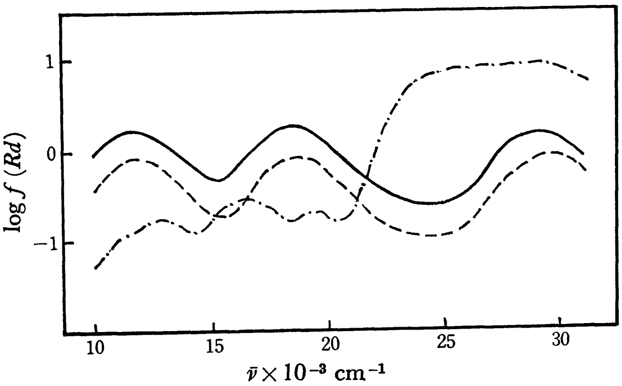


Fig. 4. Electronic spectra of $[Ni(N_2H_4)_6]I_2$ (——), $Ni(N_2H_4)_4I_2$ (----) and $Ni(N_2H_4)_2I_2$ (– – –).

complexes as the starting materials are all pale violet in color, and their spectra are in approximate agreement with each other in the chlorides, bromides and iodides, respectively. These facts exhibit that these complexes have commonly the same $[NiN_6]$-type coordination structure.

In the bis-type complexes, $Ni(N_2H_4)_2X_2$, on the other hand, the spectra assigned to $^3T_{2g}\leftarrow{}^3A_{2g}$, $^3T_{1g}\leftarrow{}^3A_{2g}$, and $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ are found to slightly shift to the longer wavelength region than that of hexahydrazine complexes without the remarkable change of the spectral form. These shifts are understood to be attributed to the substitution of the ligand hydrazine by halide ions in the lower position of the spectrochemical series, and they support the color change to pale blue for the chloride, grayish blue for the bromide and yellowish green for the iodide from yellow in the starting complexes upon heating, in a similar manner in the case of heating $Ni(NN\text{-}deen)_2Cl_2 \cdot 2H_2O$(NN-deen=*N*,*N*-diethylethylenediamine), where two chloride ions existing as a counter ion anate by entering the coordination sphere after the liberation of water.[5]

IR Spectra. Closely related to the structural determination from electronic spectra, it may be very important to know whether the hydrazine coordinates as unidentate or as bidentate ligand bridging between two nickel ions from IR spectral measurement in the course of thermal reaction. Above all, the strikingly decisive factor for the above informations is the N–N stretching vibration, ν_{N-N}.

It is well known that the vibration ν_{N-N} in the hydrazine coordinated as unidentate ligand by either one of terminal nitrogen atoms appears in the 920—940 cm^{-1} region with considerably high intensity, whereas in the hydrazine coordinated as bidentate ligand bridging between two metal ions, the ν_{N-N} frequency is expected to shift to higher wave number side, lying in the 960—985 cm^{-1} region.[8,9] Therefore, the ν_{N-N} frequency mentioned above is thought to be the most immediately useful identification method which type of coordinated hydrazine are contained in the complexes.

The IR spectra of the hexahydrazinenickel(II) complexes and their thermal reaction intermediates were given in Fig. 5.

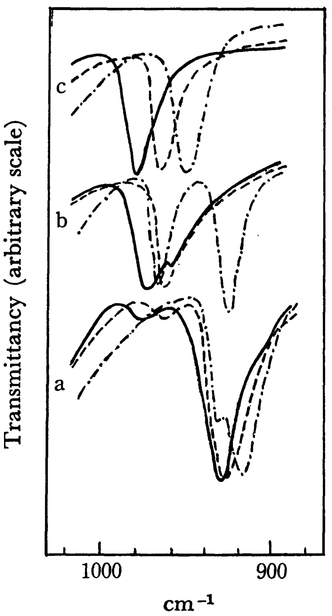


Fig. 5. IR spectra of (a) $[Ni(N_2H_4)_6]X_2$, (b) $Ni(N_2H_4)_4X_2$ (X=I) and $Ni(N_2H_4)_3X_2$ (X=Cl, Br) and (c) $Ni(N_2H_4)_2X_2$.
—— chloride, ---- bromide, – – – iodide

As seen in this figure, the N–N stretching vibration are found at around 932, 928, and 936(sh)—915 cm^{-1} for the chloride, bromide and iodide of $[Ni(N_2H_4)_6]X_2$ complexes as starting materials, respectively. These facts indicate that all the hydrazine molecules coordinate to central nickel(II) ion as unidentate ligand with either one of terminal nitrogen atoms in these type complexes. In $Ni(N_2H_4)_3X_2$ type complexes of the first reaction intermediates, on the other hand, the ν_{N-N} band is shifted to 968 cm^{-1} for the chloride and 966 cm^{-1} for the bromide, respectively.

Upon heating $[Ni(N_2H_4)_6]I_2$, the original peak, 936—915 cm^{-1}, is diminished gradually and a new peak at 966 cm^{-1} grows strong until $Ni(N_2H_4)_4I_2$ is formed, with the liberation of two moles of hydrazine. These facts suggest that tris(hydrazine)nickel(II) chloride and bromide contain bidentate bridging hydrazine alone, while the tetrahydrazinenickel(II) iodide does both unidentate terminal and bidentate bridging hydrazine as ligands.

In the bis(hydrazine)nickel(II) chloride and bromide as the second reaction intermediates, the ν_{N-N} band is observed at around 980 and 966 cm^{-1}, respectively, as the same as the corresponding tris complexes, and in the bis(hydrazine)nickel(II) iodide, only the band at 966 cm^{-1} remains, the band at a around 930 cm^{-1} being quenched. These results indicate that all the hydrazines are the bidentate bridging ligand.

It was concluded, therefore, from the information shown by IR spectra as above along with no color change in the first reaction step for $[Ni(N_2H_4)_6]X_2$ to tris(hydrazine)nickel(II) chloride and bromide or to tetrahydrazinenickel(II) iodide that these processes are "Dehydrazination-Bridging" reaction, and from the electronic spectra that the second step reactions are "Dehydrazination-Anation."

X-Ray Powder Diffraction Pattern. The structural determination of $[Zn(N_2H_4)_2]Cl_2$ has been done by X-ray diffraction method.[16] The powder patterns of $Ni(N_2H_4)_2Cl_2$ and $Ni(N_2H_4)_2Br_2$ obtained in the present work were similar to that of the corresponding Zn(II) complex, as shown in Fig. 6. Therefore, they seem to have isostructure, which is also supported by the spectral measurements.

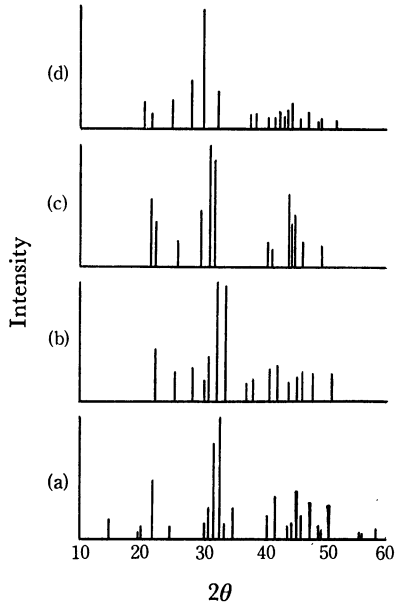
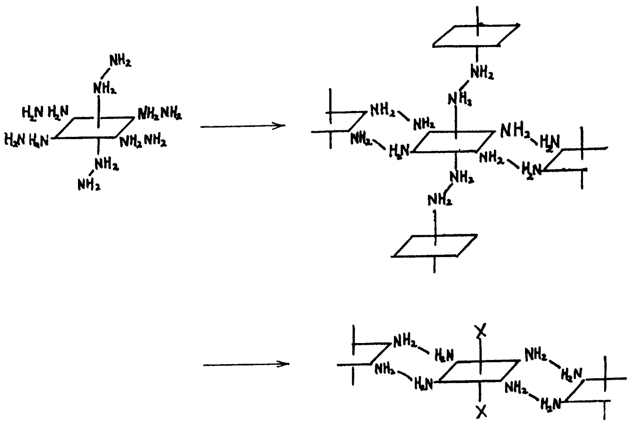


Fig. 6. X-ray diffraction patterns of (a) $ZnCl_2(NH_2NH_2)_2$, (b) $NiCl_2(NH_2NH_2)_2$, (c) $NiBr_2(NH_2NH_2)_2$ and (d) $NiI_2(NH_2NH_2)_2$.

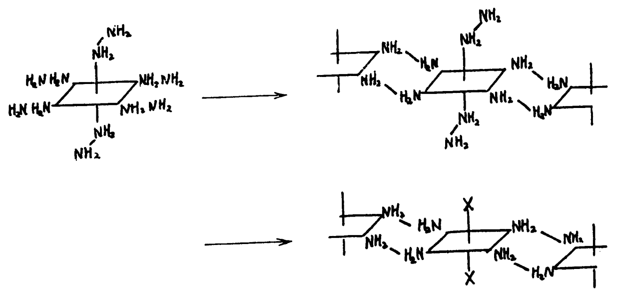
In the case of $Ni(N_2H_4)_2I_2$, however, the powder pattern may be somewhat different from those of the chloride and bromide. Although details on the structure except by the informations in the electronic and IR spectra are still unknown the tetra-, tris-, and bis-(hydrazine) type complexes probably have polymer structures.

Summarily, on the basis of the experimental results obtained above, the thermal reactions of hydrazine complexes are presumed to be portrayed by the following schemes:

for chloride and bromide:



for iodide:



Thermochemical Functions. The values of the enthalpy changes (ΔH) and the activation energies (E_a) were calculated from the derivatograms, which are summarized in Table 2, along with the temperatures of each decomposition step.

As shown in derivatograms and in Table 2, the striking feature appearing in the hydrazine complexes treated in the present work is great exothermicity in the dehydrazination in contrast to the endothermicity in the general dehydration. This abnormal character may be considered to be in part attributed to the following reaction predicted to occur in the dehydrazination process.

TABLE 2. THERMOCHEMICAL FUNCTIONS FOR DECOMPOSITION OF $[Ni(N_2H_4)_6]X_2$ (X=Cl, Br)

Decomposition step		Complex	
		$[Ni(N_2H_4)_6]Cl_2$	$[Ni(N_2H_4)_6]Br_2$
$Ni(N_2H_4)_6X_2$ to $Ni(N_2H_4)_3X_2$	T(°C)[a]	−60	−50
	ΔH[b]	−20.5	−18.6
	E_a[c]	—	—
$Ni(N_2H_4)_3X_2$ to $Ni(N_2H_4)_2X_2$	T(°C)	100—140	110—140
	ΔH	−19.6	−13.7
	E_a	46.5	43.8
$Ni(N_2H_4)_2X_2$ to $Ni(N_2H_4)X$	T(°C)	190—230	190—230
	ΔH	−16.8	−8.5
	E_a	26.3	33.7
$Ni(N_2H_4)X_2$ to NiX_2	T(°C)	240—320	250—310
	ΔH	−16.7	−8.6
	E_a	—	—

a) Decomposition temperature. b) kcal per one mole of hydrazine liberated. c) kcal per one mole of complexes.

If hydrazine is decomposed by the following mode,

$$NH_2NH_2\ (g) = 4/3NH_3\ (g) + 1/3N_2\ (g),$$

the enthalpy change is expected as $\Delta H_1 = -36.77$ kcal/mol.[17] On the other hand, the enthalpy change of deammonation in the reaction,

$$Ni(NH_3)_6Br_2\ (s) = Ni(NH_3)_2Br_2\ (s) + 4NH_3\ (g),$$

is known as $\Delta H_2 = 15.79$ kcal/mol,[18] which is assumed to be equal to the energy required to break the bond between nickel(II) ion and four nitrogen atoms.

$$Ni(NH_2NH_2)_3Br_2\ (s) = Ni(NH_2NH_2)_2Br_2\ (s) + 4/3NH_3\ (g) + 1/3N_2\ (g),$$

Therefore, for example, the enthalpy change of the thermal decomposition of tris(hydrazine)nickel(II) bromide is calculated as $\Delta H = \Delta H_1 + 2\Delta H_2 = -5.19$ kcal/mol. Although this value is relatively lower than the observed value, $\Delta H = -13.7$ kcal/mol in Table 2, the exothermicity can be, to some extent, explained by the results calculated as above.

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