

Preparation and Thermal Square Planar-Octahedral Transformation of Nickel(II) Complexes Containing 1,2-Butanediamine or 3,3-Dimethyl-1,2-butanediamine in Solid Phase

Yoshinori IHARA,* Akiko WADA, Yutaka FUKUDA,[†] and KOZO SONE[†]
Laboratory of Chemistry, Faculty of Education, Kanazawa University,
Marunouchi, Kanazawa 920

[†]Department of Chemistry, Faculty of Science, Ochanomizu University,
Otsuka, Bunkyo-ku, Tokyo 112
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Nickel(II) complexes of 1,2-butanediamine(1,2-bn) and 3,3-dimethyl-1,2-butanediamine(dmbn), were prepared, and their thermal behavior was investigated in solid phase. The original complexes were all violet, octahedral diaquabis(diamine) complexes $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn/dmbn})_2]\text{X}_2$; X=Cl, Br, NO_3 , or ClO_4 . The 1,2-bn complexes with Cl^- or Br^- and the dmbn complex with NO_3^- showed a two-step thermochromism, violet→yellow→violet blue, upon heating. These steps correspond to structural changes to a square planar anhydride, and then to an octahedral dianiono complex. The complexes of both ligands with ClO_4^- underwent only thermal deaquation, changing into orange square planar anhydride. Other salts, the 1,2-bn complex with NO_3^- and the dmbn complexes with Cl^- or Br^- , were converted into octahedral dianiono complexes by thermal deaquation-anation which occurs in one step. The differences among the thermal reactivities of the complexes with different diamines can be understood on the basis of steric hindrance caused by the substituent groups on the diamine.

It has been well-known that the bis(*N*- or *C*-substituted ethylenediamine) complexes of Ni(II) have either an octahedral structure, $[\text{Ni}(\text{A})_2(\text{diamine})_2]\text{X}_2$ or $[\text{NiX}_2(\text{diamine})_2]$ (A: neutral unidentate ligand, X: univalent anion), or a square planar one, $[\text{Ni}(\text{diamine})_2]\text{X}_2$, depending upon the structure of the diamines and the nature of X^- ions. Among the alkyl-substituted ethylenediamine complexes, in particular, two effects due to the substituent groups on the diamines seem to influence the coordination structure of the complexes. One is their inductive effect, and another is their steric hindrance. The former tends to raise the ligand field strength(l.f.s.) in the octahedral complex,¹⁾ whereas the latter disturbs the coordination of A and X^- and thus favors the formation of square planar structure.

Both of these effects are reflected in the modes of the thermal reactions of these complexes in solid phase.^{2–4)} Such reactions are, in general, accompanied by distinct color changes, and can be classified into the following four types.

- a) $[\text{Ni}(\text{H}_2\text{O})_2(\text{diamine})_2]\text{X}_2 (\text{Oh}) \xrightarrow[\Delta]{-2\text{H}_2\text{O}} [\text{NiX}_2(\text{diamine})_2] (\text{Oh}')$
- b) $[\text{Ni}(\text{H}_2\text{O})_2(\text{diamine})_2]\text{X}_2 (\text{Oh}) \xrightarrow[\Delta]{-2\text{H}_2\text{O}} [\text{Ni}(\text{diamine})_2]\text{X}_2 (\text{Sp})$
- c) $[\text{Ni}(\text{H}_2\text{O})_2(\text{diamine})_2]\text{X}_2 (\text{Oh}) \xrightarrow[\Delta]{-2\text{H}_2\text{O}} [\text{Ni}(\text{diamine})_2]\text{X}_2 (\text{Sp}) \xrightarrow{\Delta} [\text{NiX}_2(\text{diamine})_2] (\text{Oh}')$
- d) $[\text{Ni}(\text{diamine})_2]\text{X}_2 (\text{Sp}) \xrightarrow{\Delta} [\text{NiX}_2(\text{diamine})_2] (\text{Oh}')$

Here, Oh(or Oh') and Sp represent an octahedral diaqua(or dianiono) species and a square planar one,

respectively.

In the case of the *N*-substituted ethylenediamine complexes, only reactions of the type (a) or (b) are observed on heating; in certain instances, no diaqua complex can be prepared at room temperature, and the square planar complex obtained scarcely show any structural change until it decomposes on strong heating. Thus it is comparatively easy to see which kind of structure(Oh, Oh', or Sp) is favored by a particular ligand. This situation is probably due to the fact that, in these complexes, the substituent groups are bound directly to the donor N atom(s) of diamines, so that they can exert highly selective influence on the stabilities of the complexes.

On the other hand, in the case of the *C*-substituted ethylenediamine complexes, thermal reactions of the type (c) or (d) often take place,⁵⁾ which include the transformation of a square planar species into an octahedral ones on heating, in addition to those of the pattern (a) or (b), so that the correlation between structure and reactivity becomes much more complicated.^{7–9)} In these complexes, the substituent groups are bound somewhat apart from the donor N atoms, often forming specific conformations; the mode of the thermal reaction thus seems to depend on more delicate structural factors than in the case of the *N*-substituted diamine complexes.

In continuation of these studies, thermal reactions of the nickel(II) complexes with 1,2-butanediamine or 3,3-dimethyl-1,2-butanediamine in solid phase were investigated. The obtained results will be reported in this paper.

Experimental

Materials. 1,2-Butanediamine(1,2-bn)¹⁰⁾ was prepared

by the reaction of 2-ethylaziridine¹¹⁾ with liquid ammonia. 3,3-Dimethyl-1,2-butanediamine(dmbn)¹²⁾ was obtained by reducing 3,3-dimethyl-1,2-butanedione dioxime¹³⁾ with Raney nickel.

The complexes with these ligands were prepared by the following method. To an ethanolic solution of a nickel(II) salt, $\text{NiX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_3$, or ClO_4), an ethanolic solution of 1,2-bn or dmbn was added in the molar ratio of 1:2.¹⁴⁾ The solutions were allowed to stand for several days to precipitate the desired bis-type complexes. The violet crystals obtained were collected by filtration and washed with ethanol and/or diethyl ether.

The products of the thermal reactions of these complexes were obtained by isothermal heating at the temperatures of the respective DTA peaks, using an electric furnace in static air. They were studied directly after preparation, or in carefully dried atmosphere, to avoid the occurrence of backward reactions towards the original complexes(see later).

Visual Observations of Thermochromic Changes. The mode of thermochromic color change of each complex, which usually occurs within a temperature range of several degrees, was observed by putting a small amount of finely powdered sample on the bulb of a spiral-formed thermometer, and heating it on a hot plate with a rate of ca. 5°C min^{-1} .

Measurements. Simultaneous TG-DTA or TG-DSC measurements were carried out with a Sinku Riko TGD-3000M or a Rigaku Denki standard TG-DSC apparatus. The conditions of the runs are given in the captions of Figs. 3 and 4.

The electronic spectra in solid phase were measured by the diffuse reflectance method with a Hitachi 340 spectrophotometer equipped by reflection attachments for the visible(850—300 nm) and near IR(1400—850 nm) parts of the spectrum. The spectra at elevated temperatures were obtained by using a powder cell attached to a heating block.¹⁵⁾ The IR spectra were measured with a JASCO IR-A3 spectrophotometer in Nujol mulls.

Magnetic susceptibility measurements were performed with a Shimadzu Torsion Magnetometer MB-100 at room temperature.

Results and Discussion

Structure of the Original Complexes. The analyt-

ical data and magnetic moments in Table 1 show that all the complexes prepared are of the composition, $\text{NiX}_2 \cdot 2(\text{diamine}) \cdot n\text{H}_2\text{O}$ (n is 2.5 for perchlorate with 1,2-bn or 2 for others), and are high spin. The spectrum of one of them, the 1,2-bn complex with Br^- , is shown in Fig. 1 (together with those of its thermal reaction products; see later). The number of observed bands and their modes of splitting clearly indicate that the original complex has a *trans*-octahedral structure.^{16,17)} The spectra of the other 1,2-bn complexes and all the dmbn complexes are all similar, leading to the formulas of these complexes given in Table 1.

Thermochromism of the Complexes. Figure 2 shows the results of visual observations on the solid phase thermochromism of the complexes. All the complexes except for *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2](\text{NO}_3)_2$ change their color from violet to yellow, orange, or violet blue at a relatively low temperature (ca. 100°C or lower). Among them, the changes observed in the 1,2-bn complexes with Cl^- and Br^- and in the dmbn complex with NO_3^- are especially remarkable, since they show a second color change from yellow to violet blue upon continued heating, leading to a two-step thermochromism(violet→yellow→violet blue).

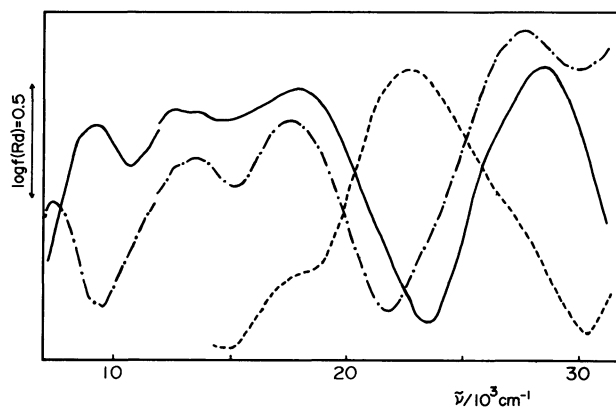


Fig. 1. Electronic spectra of *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2]\text{Br}_2$ at room temperature(—), at 100°C (---), and at 160°C (-·-·-).

Table 1. Data on the Elemental Analyses, Electronic Spectra, and Magnetic Moments of the Original Complexes

Complexes	Analytical data ^{a)}			Absorption maxima					μ_{eff} B. M.
	H (%)	C (%)	N (%)	$\bar{\nu}/10^3 \text{ cm}^{-1}$					
<i>trans</i> -[Ni(H ₂ O) ₂ (1,2-bn) ₂]Cl ₂	8.43 (8.25)	27.65 (28.10)	16.12 (16.38)	9.3	12.5	13.5	17.4	28.1	3.12
<i>trans</i> -[Ni(H ₂ O) ₂ (1,2-bn) ₂]Br ₂	6.68 (6.55)	21.97 (22.30)	12.58 (13.00)	9.3	12.5	13.5	17.9	28.4	3.13
<i>trans</i> -[Ni(H ₂ O) ₂ (1,2-bn) ₂](NO ₃) ₂	7.37 (7.16)	24.33 (24.32)	21.70 (21.27)	8.8	12.8	13.5	18.2	28.4	3.17
<i>trans</i> -[Ni(H ₂ O) ₂ (1,2-bn) ₂](ClO ₄) ₂ ·0.5H ₂ O	5.98 (6.11)	19.65 (20.01)	11.08 (11.70)	8.8	12.8	13.5	18.2	28.4	3.27
<i>trans</i> -[Ni(H ₂ O) ₂ (dmbn) ₂]Cl ₂	8.98 (9.12)	35.92 (36.21)	14.16 (14.08)	8.8	12.8	13.5	18.5	28.4	3.29
<i>trans</i> -[Ni(H ₂ O) ₂ (dmbn) ₂]Br ₂	7.34 (7.45)	29.16 (29.60)	11.42 (11.51)	9.3	12.8	13.5	18.5	29.1	3.18
<i>trans</i> -[Ni(H ₂ O) ₂ (dmbn) ₂](NO ₃) ₂	7.87 (8.04)	31.98 (31.95)	18.64 (18.63)	9.3	12.8	13.5	18.2	28.4	3.22
<i>trans</i> -[Ni(H ₂ O) ₂ (dmbn) ₂](ClO ₄) ₂	6.42 (6.90)	27.25 (27.40)	10.66 (11.43)	8.5	12.8	13.8	18.2	28.7	3.15

a) Calculated values are in parentheses.

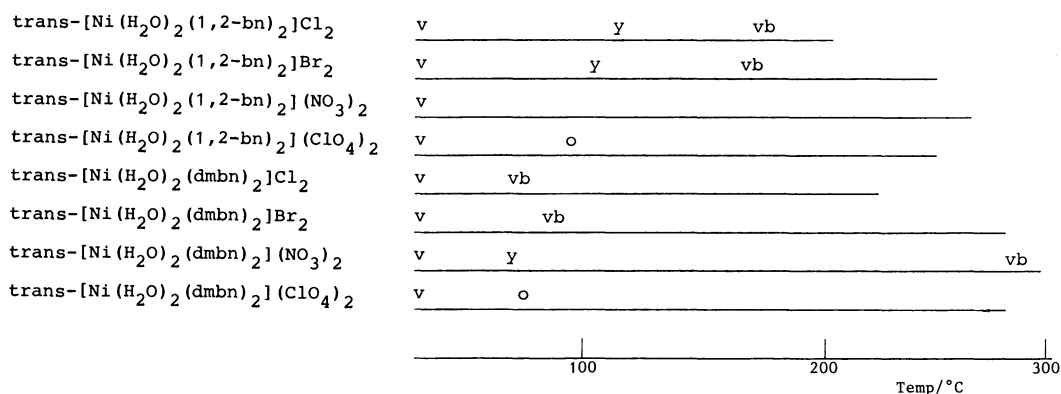


Fig. 2. Results of visual observations on the thermochromic changes of the complexes. v: violet, vb: violet blue, y: yellow, o: orange. The high-temperature colors are shown at the spots on the temperature scale(horizontal lines) where they begin to appear; the right-hand ends of the lines correspond to the decomposition points.

These color changes are reversible; in particular, the violet blue product of the dmbn complex with NO_3^- returns to yellow immediately on cooling. Also in the case of the 1,2-bn complexes with Cl^- and Br^- , reverse changes from violet blue or yellow to an original violet are observed on cooling for a few minutes. The violet blue product of the former complex and the yellow and violet blue products of the latter ones are thus stable only at the correspondingly elevated temperatures. The yellow product of the dmbn complex with NO_3^- could be cooled to room temperature and identified; however, it also returned to the original violet complex on standing for some days in open air. The violet blue products of the dmbn complexes with Cl^- and Br^- , and the violet one of the 1,2-bn complex with NO_3^- (anhydrous salt; see later) also revert to the original diaqua species more or less gradually.

Thermal Analyses. The results of simultaneous TG-DTA analyses for the 1,2-bn complexes with Cl^- and Br^- are shown in Fig. 3. The abrupt weight losses observed in both TG curves before 100°C , and the corresponding endothermic DTA peaks, are due to the liberation of two moles of coordinated water, which is responsible for the color change from violet to yellow. The endothermic peaks near $160^\circ\text{C}(\text{Cl}^-)$ and $150^\circ\text{C}(\text{Br}^-)$, on the other hand, apparently correspond to the second color changes from yellow to violet blue, in which the TG curves remain flat.

Figure 4 depicts the results of TG-DTA analysis of $\text{trans-[Ni(H}_2\text{O)}_2(\text{dmbn})_2](\text{NO}_3)_2$, as another example of the complexes showing the two-step thermochromism. The DTA curve at the heating rate of 2°C min^{-1} gives no peak for the second color change (yellow $\rightarrow$ violet blue), until the complex decomposes exothermically near 260°C . When the heating rate is increased to 8°C min^{-1} , however, the endothermic peak begins to appear, and becomes very apparent at $10^\circ\text{C min}^{-1}$, as can be seen in the same Figure. It is considered that this endothermic peak corresponds

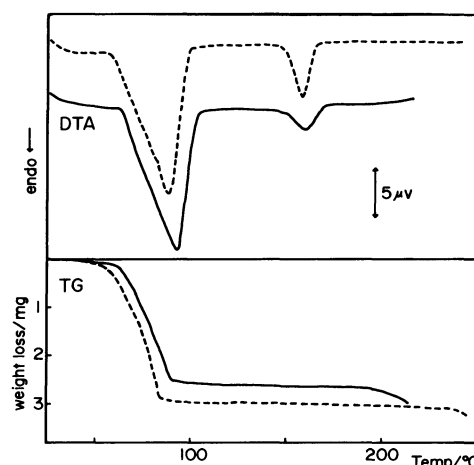


Fig. 3. TG-DTA patterns of $\text{trans-[Ni(H}_2\text{O)}_2(1,2\text{-bn)}_2]\text{Cl}_2$ (—) and $\text{trans-[Ni(H}_2\text{O)}_2(1,2\text{-bn)}_2]\text{Br}_2$ (----). Heating rate: 2°C min^{-1} ; DTA sensitivity: $\pm 25 \mu\text{V}$ with Pt-Rh thermocouple; gas flow: N_2 at 20 ml min^{-1} ; amounts of samples: 24.8 mg for chloride and 34.8 mg for bromide.

to the color change (yellow $\rightarrow$ violet blue).

The features of TG-DTA curves of the remaining five complexes are quite similar to those of the complexes in Figs. 3 and 4, except for that the second endothermic peak does not appear. The results obtained by TG-DTA analyses of all the complexes studied are summarized in Table 2. The enthalpy changes for the reactions of the type (yellow $\rightarrow$ violet blue), also shown in Table 2, were estimated from the DSC measurements carried out separately.

Spectral Changes of the Complexes on Heating.

The spectra of the 1,2-bn complexes with NO_3^- and ClO_4^- after dehydration are shown in Fig. 5. In the former case, the spectral pattern remains nearly unchanged after dehydration, showing that the *trans*-octahedral configuration is retained. In the latter case, however, there is a drastic spectral change, and a broad band characteristic to the spectrum of a square

planar Ni(II) complex appears. It is thus clear that the reactions of types (a) and (b) take place in these two cases, respectively; the reason why a distinct change in color does not occur in the former case can also be understood, since the ligands exchanged (H_2O and NO_3^-) are both O-ligands with nearly the same ligand field strength.

Figure 1 gives a comparison of the spectra of the yellow and violet blue species of the 1,2-bn complex with Br^- with that of the original violet one. The spectra of both products were measured at the elevated temperatures where the respective species form, because they change rapidly into the original complex on cooling (see above). As shown in the Figure, it is clear that the yellow product formed by dehydration has a square planar structure and the violet blue product has a *trans*-octahedral one, which is similar to that of the original violet specimen. The

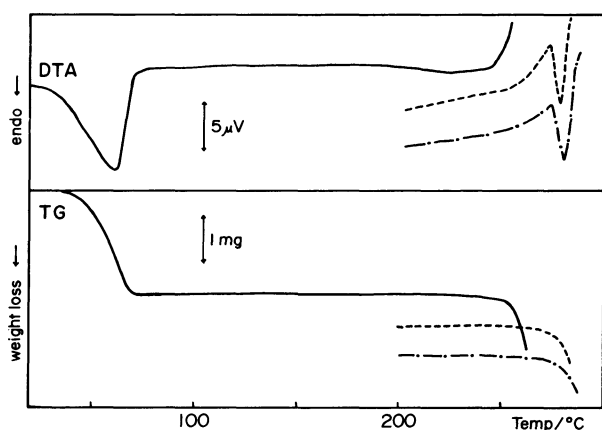


Fig. 4. TG-DTA patterns of *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(\text{dmbn})_2](\text{NO}_3)_2$. Heating rate: 2°C min^{-1} (run 1, —), 8°C min^{-1} (run 2, ---), and $10^\circ\text{C min}^{-1}$ (run 3, -·-·-). DTA sensitivity: $\pm 25 \mu\text{V}$ with Pt-Rh thermocouple; gas flow: N_2 at 20 ml min^{-1} ; amounts of samples: 26.5 mg for run 1, 25.8 mg for 2, and 26.3 mg for 3, respectively. The first (dehydration) step observed in run 2 and run 3 is essentially the same as that in run 1, except for a gradual shift to higher temperature like that observed with the second step.

spectral data on the same color change, violet $\rightarrow$ yellow $\rightarrow$ violet blue, of the 1,2-bn complex with Cl^- , which are not shown, are quite similar to those in Fig. 1. In these cases, the reactions which take place are clearly of type (c).

Confirmation of the Structures of the Thermal Reaction Products. It was also tried to isolate the products of the thermal reactions and to confirm their structures separately. Although they readily revert to the original diaqua species on cooling, such reverse changes are sometimes slow enough to allow rapid measurements. In addition, they (except those of the $\text{Oh}' \rightarrow \text{Sp}$ type) can be stopped by operating in extremely dry air to avoid the reaquation of the dehydrated species. The data in Table 3 were obtained by making use of these facts; some of the spectra were obtained at high temperatures. It can be seen that all these data, and the structures deduced from them are compatible with the modes of the formation of these complexes proposed above.

The mode of coordination in the nitrato complex (Oh') with 1,2-bn was also studied by means of its IR spectrum. In general, NO_3^- ion in a metallic complex gives rise to a weak combination band in the range of $1700\text{--}1800 \text{ cm}^{-1}$. When it is coordinat-

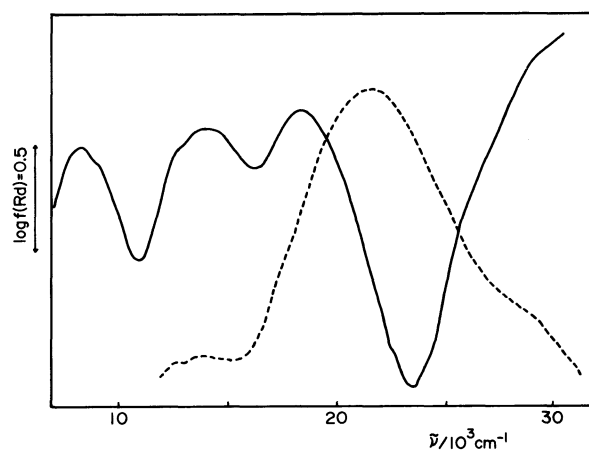


Fig. 5. Electronic spectra of *trans*- $[\text{Ni}(\text{NO}_3)_2(1,2\text{-bn})_2]$ (—) and $[\text{Ni}(1,2\text{-bn})_2](\text{ClO}_4)_2$ (---).

Table 2. The Results of Thermal Analyses

Complexes	Dehydration		Sp $\rightarrow$ Oh' Transformation	
	Temp/ $^\circ\text{C}$	Weight loss/% ^{a)}	Temp/ $^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2]\text{Cl}_2$	65—95	11.0 (10.5)	148—170	21.3
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2]\text{Br}_2$	50—85	8.6 (8.4)	140—160	8.02
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2](\text{NO}_3)_2$	60—90	9.2 (9.1)		
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bn})_2](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$	35—75	8.7 (9.4)		
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(\text{dmbn})_2]\text{Cl}_2$	RT—53	9.0 (9.1)		
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(\text{dmbn})_2]\text{Br}_2$	RT—70	7.4 (7.4)		
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(\text{dmbn})_2](\text{NO}_3)_2$	RT—48	7.6 (8.0)	280—290	—
<i>trans</i> - $[\text{Ni}(\text{H}_2\text{O})_2(\text{dmbn})_2](\text{ClO}_4)_2$	RT—62	6.5 (6.8)		

a) Calculated values are in parentheses.

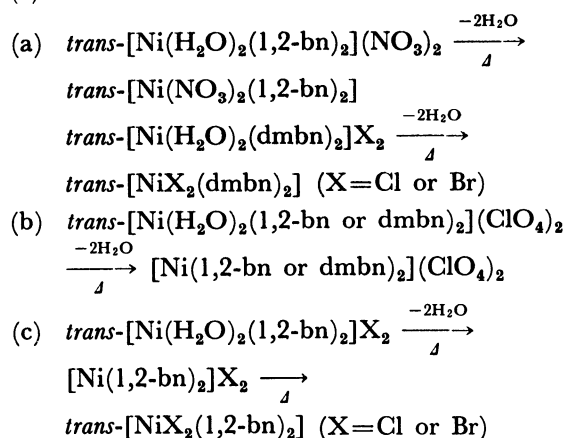
Table 3. Data on the Elemental Analyses, Electronic Spectra, and Magnetic Moments of the Complexes Obtained by Heating the Complexes in Table 1

Complexes	Color	Analytical data ^{a)}			Absorption maxima ^{b)} $\bar{\nu}/10^3 \text{ cm}^{-1}$					μ_{eff} B. M.
		H (%)	C (%)	N (%)						
[Ni(1,2-bn) ₂]Cl ₂	Yellow						22.8			Diamag.
<i>trans</i> -[NiCl ₂ (1,2-bn) ₂]	Violet blue	7.65 (7.92)	30.86 (31.40)	17.84 (18.32)	8.3*	12.5 sh*	13.9*	17.2*	27.5*	3.15
[Ni(1,2-bn) ₂]Br ₂	Yellow						22.6			Diamag.
<i>trans</i> -[NiBr ₂ (1,2-bn) ₂]	Violet blue	6.29 (6.14)	24.39 (24.33)	13.88 (14.19)	7.3*	12.0 sh*	13.5*	17.5*	27.5*	3.15
<i>trans</i> -[Ni(NO ₃) ₂ (1,2-bn) ₂]	Violet	6.67 (6.75)	26.70 (26.76)	23.26 (23.41)	8.3	12.8 sh	13.9	18.5	28.5 sh	3.18
[Ni(1,2-bn) ₂](ClO ₄) ₂	Orange	5.40 (5.59)	21.43 (22.14)	12.53 (12.91)			21.6			Diamag.
<i>trans</i> -[NiCl ₂ (dmbn) ₂]	Violet blue	9.29 (8.91)	39.33 (39.81)	15.26 (15.48)	8.4	13.2 sh	13.9	18.2	27.8	3.21
<i>trans</i> -[NiBr ₂ (dmbn) ₂]	Violet blue	7.42 (7.15)	31.57 (31.96)	12.49 (12.43)	7.5	12.8 sh	13.9	18.2	27.8	3.17
[Ni(dmbn) ₂](NO ₃) ₂	Yellow	7.35 (7.77)	34.61 (34.72)	20.14 (20.24)			22.5			Diamag.
[Ni(dmbn) ₂](ClO ₄) ₂	Orange	6.56 (6.58)	29.41 (29.41)	11.52 (11.43)			21.8			Diamag.

a) Calculated values are in parentheses. b) The data obtained at high temperatures are marked with.*

ed as a monodentate ion, a small splitting into two components (less than 25 cm⁻¹) takes place. When it acts as a bidentate ligand, the splitting becomes much larger (20–50 cm⁻¹).^{18,19} The band at 1768 cm⁻¹ in the original complex is found to split into two bands at 1752 cm⁻¹ and 1773 cm⁻¹ with a separation of 21 cm⁻¹ after heating. This is compatible with the view that the two NO₃⁻ ions are coordinated at the axial positions as unidentate ligands to form the *trans*-octahedral complex.

The thermochemical changes of all the complexes observed can thus be represented by the following equations, and classified into the types (a), (b), and (c) mentioned above:



The data for the violet blue product of the dmbn complex with NO₃⁻ are lacking in Table 3, because it reverts so easily to the yellow species on cooling, at a temperature which is quite close to the decomposition point (see above and Figs. 2 and 4). The first step, violet→yellow, of its formation is, however,

clearly a structural change to a square planar anhydrous complex (Table 3), and the general features of the second steps, yellow→violet blue, indicates that a type (c) reaction also takes place here.

Effects of Structures of Diamines upon Thermal Reactions. Table 4 summarizes the results on the thermal reactions of 1,2-bn and dmbn complexes, and those of 1-phenyl-1,2-ethanediamine(phenen) complexes already studied.⁹ When heated, they change in one of the three ways, Oh→Oh'(type (a)), Oh→Sp(type (b)), and Oh→Sp→Oh'(type (c)). On the other hand, when the original species are square planar, they remain unchanged upon heating until decomposition; only one such example is shown in the Table, i. e., [Ni(phenen)₂](ClO₄)₂.

It can be seen that both 1,2-bn and dmbn complexes easily undergo deaquation-anation either in one step or in two, producing aniono complexes, retaining their octahedral configuration. Perchlorates are exceptions, undergoing deaquation to Sp only, because of the poor coordination ability of ClO₄⁻ ions.

The tendency of favoring an octahedral configuration observed in C-monosubstituted ethylenediamine complexes, such as those in Table 4, is more remarkable than that in 1,1-di- or 1,2-disubstituted ethylenediamine complexes.^{3,7,20} The main reason for such a differences can be found in the magnitudes of steric hindrance caused by the substituent groups on the diamines. From NMR studies on Co(III),²¹ Pt(II),^{22,23} and Ni(II)^{24,25} complexes with several C-substituted ethylenediamines, it is known that, when there is only one substituent group on the diamine, it almost always occupies the equatorial position on

Table 4. Classification of Thermal Reactions of Nickel(II) Complexes Containing C-Mono Substituted Ethylenediamines

	Cl	Br	NO ₃	ClO ₄
1,2-bn	Oh→Sp→Oh'	Oh→Sp→Oh'	Oh→Oh'	Oh→Sp
dmbn	Oh→Oh'	Oh→Oh'	Oh→Sp→Oh'	Oh→Sp
phenen ⁹⁾	Oh→Oh'	Oh→Oh'	Oh→Sp→Oh'	Sp

the plane containing two diamines at room temperature. It is clear that, in such a case, there is enough space above and below to permit the approach of the additional ligands such as water molecules and counter anions. On the other hand, in the complexes with 1,1-di- or *meso*-1,2-disubstituted ethylenediamines, at least one of the substituents in each diamine ligand is forced to occupy the axial positions.^{26,27)} Such a configuration generates a larger steric hindrance, preventing the approach of other ligands from the axial direction and stabilizing the square planar structure.

For the square planar species to occur in the C-monosubstituted ethylenediamine complexes, therefore, it is tempting to suppose that the substituent group in the diamine protruding on the equatorial plane should be so bulky that they can influence the axial coordination to some extent. In fact, except for the case of perchlorates, such a species is formed in the 1,2-bn complexes with Cl⁻ and Br⁻, and in the dmbn complex with NO₃⁻. However, since the substituent group in dmbn (i.e., (CH₃)₃C-) is much larger than that in 1,2-bn (C₂H₅-), the tendency observed in the complex halides is rather unexpected.

A possible explanation for this apparent anomaly is as follows. At high temperature, the conformation of the diamine chelate ring will not be rigid, and a conformational equilibrium will finally be brought about by thermal agitation, in which the equatorial group(R) on the ligand temporarily "stands up" as the axial one.^{28,29)} Such a "stand up" motion will occur more easily when R is small, hindering the coordination of X⁻ at trans positions of Ni(II), but when R is as large as (CH₃)₃C-, it will be hard to move in crystals, so that dianion complexes can be formed more easily.³⁰⁾ It seems probable that the occurrence of such thermal deformation of the ligands is complicating the observed situations also in the case of related complexes.

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- 1) If the l.f.s. is raised strongly, it is also conceivable that a crossover into the square planar (i.e., low spin) structure is brought about by this effect. In the present case, however, it seems that the steric effect is more important when the square planar structure is favored.
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- 5) Such kind of thermal transformation was first observed by Tsuchiya et al.⁶⁾ with tetrakis(benzimidazole)-nickel(II) nitrate, but our studies on the complexes of C-substituted ethylenediamines added a number of new examples.⁷⁻⁹⁾
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- 30) T. W. Hambley, C. J. Hawkins, J. Martin, J. A. Palmer, and M. R. Snow, *Aust. J. Chem.*, **34**, 2505 (1981); according to these authors, the energies needed for such a "stand up" motion in $[\text{Co}(\text{NH}_3)_4(\text{pn})]^{3+}$ and $[\text{Co}(\text{NH}_3)_4(\text{dmbn})]^{3+}$ are 4.64 kJ mol⁻¹ and 18.25 kJ mol⁻¹, respectively. They show that dmbn favors the equatorial conformation much more strongly than pn.
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