Thermal Reactions of the Nickel(II) Complexes Containing 1-Phenyl-1,2-ethanediamine in the Solid Phase

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Nickel(II) complexes [Ni(phenen)$_2$](ClO$_4$)$_2$ and [Ni(H$_2$O)$_2$(phenen)$_2$]X$_2$ (phenen=1-phenyl-1,2-ethanediamine, X=Cl, Br, or NO$_3$) were prepared, and their thermal behavior was investigated in the solid phase. The nitrate showed a thermochromism consisting of two steps, violet→yellow→violet, which corresponds to a structural change from an octahedral diaqua complex to a square planar anhydride, and then to the octahedral dinitrato complex, respectively. Both the chloride and bromide were converted into the octahedral dianiono complexes by thermal deaquation-anation, retaining their octahedral configuration. However, no change was observed in the perchlorate, which is invariably square planar.

When two molecules of a *N*- and/or *C*-substituted ethylenediamine are coordinated to a nickel(II) ion, the resulting bis(diamine) complex is generally either square planar ([Ni(diamine)$_2$]X$_2$) or octahedral ([NiX$_2$(diamine)$_2$] or [NiA$_2$(diamine)$_2$]X$_2$: X=a univalent anion, A=a solvent molecule). Two main factors for deciding whether X or A are coordinated or not can be distinguished: (i) the coordinating ability of these ligands, and (ii) the steric hindrance resulting from *N*- or *C*-substituents of the diamine.

Tsuchiya et al. have studied the relative stabilities of these two structures, and the ease of their interconversions, using many complexes containing different types of diamines, on the basis of their thermal reactions in the solid phase.[1-3] Recently, the author found more interesting examples of such a thermal transformation, including some octahedral→ square planar→octahedral changes which are peculiarly thermochromic (violet→yellow→violet or blue), in the nickel(II) complexes with butanediamines[4] or 1,2-diphenyl-1,2-ethanediamines[5] in the solid phase. Such transformations were found to occur most easily in the case of the complex chloride or nitrate of *dl*-form diamines.

In a continuation of these studies, thermal reactions of the nickel(II) complexes of 1-phenyl-1,2-ethanediamine (phenen) were studied. The obtained results are reported in this paper. It is interesting to note that it was just these complexes, and those of 1,2-diphenyl-1,2-ethanediamines, that Lifschitz et al. studied and discussed in their historical paper on the structure of the nickel(II) complexes.[6]

Experimental

Preparation.   Methyl 2-amino-2-phenylacetate[7] was converted into 2-amino-2-phenylacetamide by the method of Arpesella.[8] 1-Phenyl-1,2-ethanediamine was obtained by reducing the amide with LiAlH$_4$ according to the procedure described by Yano et al.[9]

The complexes were prepared following the method of Lifschitz et al.[6] with slight modifications.

(i) Complex chloride, nitrate, and perchlorate: To an aqueous solution of nickel(II) chloride or nitrate, an ethanolic solution of phenen was added in the molar ratio of 1:2. The violet crystals which separate out on standing were recrystallized from boiling water. The same procedure with nickel(II) perchlorate gave orange crystals of the complex perchlorate.

(ii) Complex bromide: When nickel(II) bromide was used in the method (i), a mixture of violet blue and violet crystals was almost always obtained irrespective of the organic solvent used (methanol or ethanol) and its concentration. The mixture was dissolved in boiling water, and the resulting solution was cooled rapidly on ice to yield pure violet crystals.

Measurements.   Simultaneous TG and DSC measurements were carried out with a Rigaku Denki standard TG-DSC apparatus under a constant flow of nitrogen (20 ml/min). The heating rates and amounts of samples used are given in the figures.

The electronic spectra in the solid phase were measured by the diffuse reflectance method on a JASCO UVIDEC-410 spectrophotometer. The effective magnetic moments were evaluated from the susceptibilities measured by Gouy's method at room temperature.

Results and Discussion

Structures of the Original Complexes.   The reflectance spectra of the chloride and perchlorate are shown in Fig. 1. The bromide and nitrate revealed
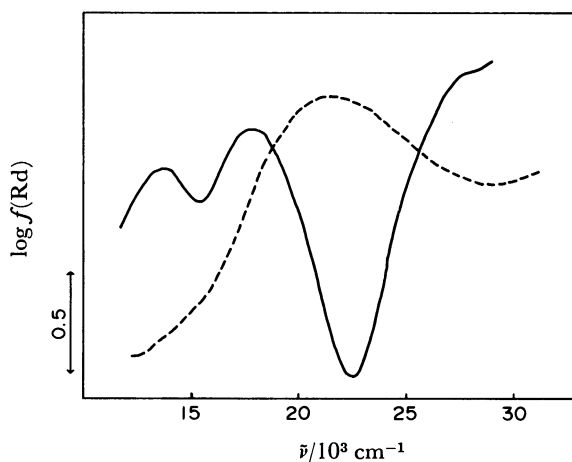

Fig. 1.   Electronic spectra of [Ni(H$_2$O)$_2$(phenen)$_2$]Cl$_2$ (——) and [Ni(phenen)$_2$](ClO$_4$)$_2$ (----).

TABLE 1.   DATA ON THE ELEMENTAL ANALYSES, ELECTRONIC SPECTRA AND MAGNETIC MOMENTS
OF THE ORIGINAL COMPLEXES

| Complexes | Color | Analytical data[a] | | | Absorption maxima | μ_{eff} |
		H (%)	C (%)	N (%)	$\bar{\nu}/10^3$ cm^{-1}	B.M.
[Ni(H$_2$O)$_2$(phenen)$_2$]Cl$_2$	Violet	6.24(6.44)	43.52(43.87)	12.72(12.79)	13.5 17.9 28.1 sh	3.26
[Ni(H$_2$O)$_2$(phenen)$_2$]Br$_2$	Violet	5.40(5.36)	36.44(36.47)	10.57(10.63)	13.5 18.2 29.4	3.17
[Ni(H$_2$O)$_2$(phenen)$_2$](NO$_3$)$_2$	Violet	5.75(5.66)	39.13(39.46)	17.11(17.35)	13.5 17.9 27.5 sh	3.28
[Ni(phenen)$_2$](ClO$_4$)$_2$	Orange	4.56(4.53)	36.26(36.69)	10.57(10.24)	22.3	Diamag.

a) Calculated values are in parentheses.

similar spectral patterns to that of the chloride. The spectral data of all the complexes are summarized in Table 1, together with their magnetic moments and analytical data. It is well understood from Fig. 1 and Table 1 that the violet complexes have an octahedral geometry and the orange perchlorate has a square planar one, leading to the formulas of the complexes

Fig. 2.   TG–DSC patterns of [Ni(H$_2$O)$_2$(phenen)$_2$]X$_2$, where X=Cl (——), Br (----), and NO$_3$ (—·—). Heating rate: 1.25 °C min^{-1} for all complexes. Amount of sample used: 28.5 mg (chloride), 25.5 mg (bromide), and 20.1 mg (nitrate).

given in Table 1.

Thermal Analyses.   The results of simultaneous TG–DSC measurements of the complexes are shown in Fig. 2. The results of the perchlorate are not shown, because it did scarcely show any change on TG and DSC curves before its decomposition. The weight losses observed below 100 °C correspond to the liberation of two moles of the coordinated water in the respective complexes (obsd. 8.07%, calcd. 8.23% for chloride; 6.86%, 6.84% for bromide; 7.46%, 7.34% for nitrate, respectively). The colors of the chloride and bromide were changed to violet blue and that of nitrate to yellow, after the dehydration.

On the DSC curves, a small exothermic peak is observed at 175 °C in the case of the chloride and an endothermic one at 215 °C in the case of the nitrate, after the peak caused by the dehydration. It is likely that these changes are not so drastic to bring about a distinct structural transformation, because no appreciable change was observed in the reflectance spectra of the complexes before and after the peak temperature.

On the other hand, the nitrate is strongly thermochromic, changing from yellow to violet at about 130 °C, after the color change by dehydration (violet→yellow) is over. This change indicates that, upon heating the yellow anhydrous complex a square planar-octahedral transformation takes place. But, the DSC curve remains nearly linear in this range irrespective of the obvious color change. Thus,
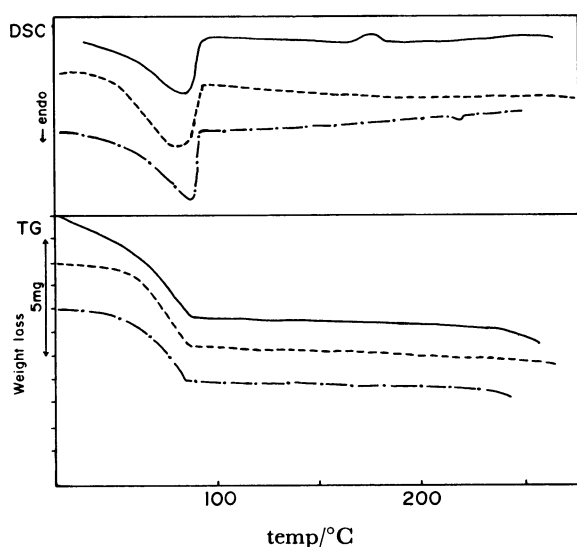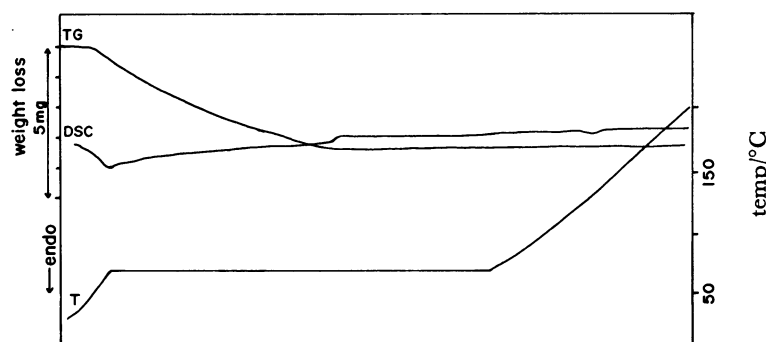

Fig. 3.   TG–DSC pattern of [Ni(H$_2$O)$_2$(phenen)$_2$](NO$_3$)$_2$.   Heating rate: 2.5 °C min^{-1} until 70 °C. After the dehydration was completed at 70 °C, heating was continued at the same rate. The sensitibity of DSC was the same as that of Fig. 2.

a more detailed measurement regarding this thermal reaction was tried, with the result is shown in Fig. 3. Avoiding an overlap with the dehydration peak, a measurement was performed by using an isothermal technique at 70 °C, under the conditions given in the caption of the figure.

The new small peak observed at about 130 °C revealed the existence of an endothermic reaction, which seems to correspond to the color change
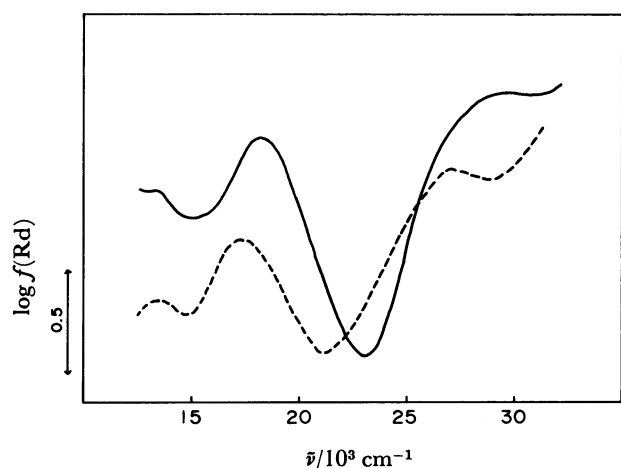

Fig. 4. Electronic spectra of [Ni(H$_2$O)$_2$(phenen)$_2$]Br$_2$ before heating (——) and after heating (- - - -).
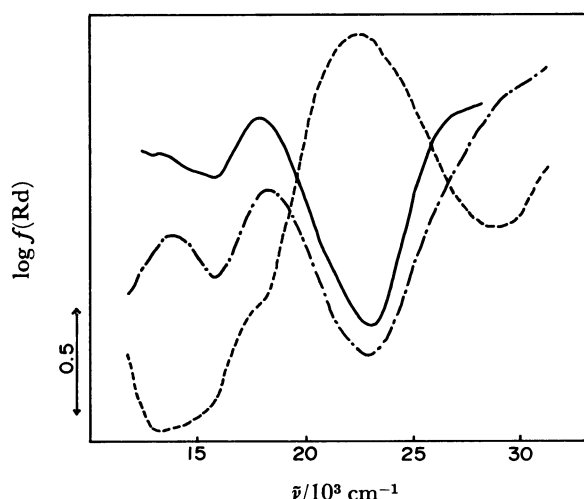
Fig. 5. Electronic spectra of [Ni(H$_2$O)$_2$(phenen)$_2$]-(NO$_3$)$_2$ before heating (——) and after heating at 70 °C (- - - -) and at 150 °C (—·—).

(yellow→violet). The peak is, however, too weak for estimating the amount of heat absorbed in the reaction.

Structures of the Complexes Obtained by Heating.
The products of the thermal reactions were obtained by isothermal heating at the temperatures of the respective DSC peaks using an electric furnace in static air.

The reflectance spectra of the complex bromide and nitrate before and after heating are compared in Figs. 4 and 5, respectively. As shown in Fig. 4, the spectrum of the anhydrous complex bromide obtained upon heating is almost identical with that of the mother complex, except for a slight shift of the maximum peaks to longer wavelengths. The shifts can be attributed to an exchange of the coordinated species, i.e., that of water molecules by bromide ions. A similar spectral change is also observed in the case of the chloride (Table 2). Consequently, both the chloride and bromide are found to undergo thermal deaquation-anation (Eq. 1; see below).

On the other hand, the spectrum of the yellow product of the nitrate is very similar to that of the complex perchlorate, but is completely different from those of the two violet species (Fig. 5). The violet product obtained by heating at 150 °C shows a spectral pattern nearly identical with that of the original octahedral dihydrate, while the pattern of the yellow product is that of a square planar nickel(II) complex, which have a broad and strong absorption band in the blue part of the spectrum. The data of the magnetic moments in Table 2 support these discussions.

The thermochemical changes observed can thus be represented by the following equations (as to the notations Oh, Oh′, and Sp, see below):

$$[\mathrm{Ni(H_2O)_2(phenen)_2]X_2} \xrightarrow[\Delta]{-2\mathrm{H_2O}} [\mathrm{NiX_2(phenen)_2}]$$

$$\mathrm{Oh} \qquad\qquad\qquad\qquad\qquad \mathrm{Oh'}$$

$$(\mathrm{X = Cl \ or \ Br}), \qquad (1)$$

$$[\mathrm{Ni(H_2O)_2(phenen)_2](NO_3)_2} \xrightarrow[\Delta]{-2\mathrm{H_2O}}$$

$$\mathrm{Oh}$$

$$[\mathrm{Ni(phenen)_2](NO_3)_2} \xrightarrow{\Delta} [\mathrm{Ni(NO_3)_2(phenen)_2]}. \qquad (2)$$

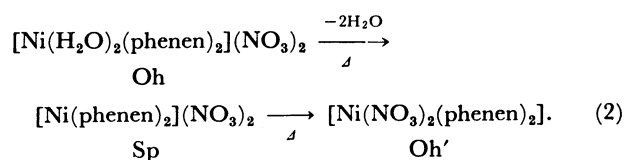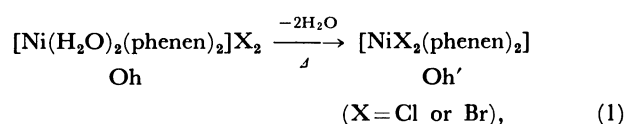$$\mathrm{Sp} \qquad\qquad\qquad\qquad \mathrm{Oh'}$$

TABLE 2. DATA ON THE ELEMENTAL ANALYSES, ELECTRONIC SPECTRA AND MAGNETIC MOMENTS
OF THE COMPLEXES OBTAINED BY HEATING

Complexes	Color	Analytical data[a]			Absorption maxima			μ_{eff}
		H (%)	C (%)	N (%)	$\bar{\nu}/10^3 \mathrm{cm^{-1}}$			B.M.
[NiCl$_2$(phenen)$_2$]0.75H$_2$O[b]	Bluish violet	5.99 (6.19)	46.11 (46.25)	13.41 (13.48)	13.5	17.6	27.8 sh	3.23
[NiBr$_2$(phenen)$_2$]	Violet blue	4.82 (4.93)	39.67 (39.15)	11.50 (11.41)	13.5	17.4	27.2	3.13
[Ni(phenen)$_2$](NO$_3$)$_2$	Yellow					21.7		Diamag.
[Ni(NO$_3$)$_2$(phenen)$_2$]0.75H$_2$O[b]	Violet	5.16 (5.48)	41.28 (41.01)	17.53 (17.93)	13.7	18.3	27.0<	3.27

a) Calculated values are in parentheses.   b) Very hygroscopic.

TABLE 3. CLASSIFICATION OF THERMAL REACTIONS OF NICKEL(II) COMPLEXES
CONTAINING C-SUBSTITUTED ETHYLENEDIAMINES

	Cl	Br	I	NO₃	ClO₄
pn[10]	Oh→Oh'	Oh→Oh'		Oh→Oh'	Oh→Sp
phenen	Oh→Oh'	Oh→Oh'		Oh→Sp→Oh'	Sp
i-bn[4]	Sp→Oh'	Sp	Sp	Sp	Sp
m-bn[4]	Sp	Sp	Sp	Sp→Oh'	Sp
dl-bn[4]	Oh→Sp→Oh'	Oh→Sp→Oh'		Oh→Sp	Oh→Sp
m-stien[5]	Sp	Sp	Sp	Sp	Sp
dl-stien[5]	Oh→Sp→Oh'	Oh→Sp→Oh'	Sp	Oh→Sp→Oh'	Sp

Abbreviations pn, phenen, i-bn, m-bn, dl-bn, m-stien, and dl-stien are 1,2-propanediamine, 1-phenyl-1,2-ethane-diamine, 2-methyl-1,2-propanediamine, *meso-* and dl-2,3-butanediamine, and *meso-* and dl-1,2-diphenyl-1,2-ethane-diamine, respectively. Oh and Sp denote an octahedral and a square planar structure. As to Oh→Oh', Oh→Sp, Oh→Sp→Oh', and Sp→Oh', see text.

Only in the case of the nitrate, a square planar structure is observed as a stable product of the thermal reaction. The reason for the peculiarity of the nitrate showing such a transformation had been discussed in the preceding paper.[4,5]

Effects of Structures of Diamines upon Thermal Reactions. Table 3 summarizes the results of the thermal reactions of phenen complexes and those of the nickel(II) complexes with other C-substituted ethylenediamines already studied.

When the original species are octahedral, *i.e.* the diaqua bis(diamine)nickel(II) complexes, they are denoted by Oh in this Table. They contain monosubstituted, or *m-* or dl-disubstituted ethylene-diamines, as shown below the table. When heated, they change in one of the three ways, *i.e.*: (i) simple deaquation leading to a square planar (Sp) species: Oh→Sp; (ii) single-step deaquation-anation leading to an octahedral dianiono species (Oh'): Oh→Oh' (*cf.* Eq. 1); and (iii) two-step deaquation-anation: Oh→ Sp→Oh' (*cf.* Eq. 2). On the other hand, when the original species are square planar, they may remain unchanged upon heating, or may be converted into the octahedral dianiono species (simple anation, Sp→Oh').

It can be seen that the phenen complexes easily undergo deaquation-anation either in one step or in two, producing dianiono complexes, retaining (or restoring) their octahedral configuration. An important reason for this easy anation can be found in the structure of the planar complex, [Ni(phenen)₂]²⁺. It is clear that there is enough space above and below it to permit the anation of counter ions since the bulky phenyl groups can occupy the equatorial positions on the plane containing two diamines. On the other hand, in the complexes with i-bn, m-bn, or m-stien, at least two of their substituents are forced to occupy the axial positions. Such a conformation generates a

large steric hindrance, preventing the approach of the other ligands and stabilizing the Sp structure.

The data in Table 3 (especially the comparison of phenen with bn and stien) lead, finally, to an impression that, for the square planar-to-octahedral transformation to occur, the steric hindrance of the ligands should be intermediate; it can be neither too large, nor too small. Diamines satisfying the following two conditions seemingly favor the trans-formation: (i) The substituent groups in the diamine protruding on the equatorial plane should be so bulky that they can influence the strength of axial coordination to some extent. (ii) The substituent groups protruding toward the axial directions are unnecessary for the reaction; if they exist, they should be as small as possible (*e.g.* methyl).

References

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

2) H. Nishimoto, T. Yoshikuni, A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **51**, 1068 (1978).

3) Y. Ihara, E. Izumi, A. Uehara, R. Tsuchiya, S. Nakagawa, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, **55**, 1028 (1982).

4) Y. Ihara, T. Kamishima, and R. Tsuchiya, *Thermochim. Acta*, **67**, 23 (1983).

5) Y. Ihara and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **57**, 2829 (1984).

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

7) E. L. Smith, D. H. Speckman, and J. Polglase, *J. Biol. Chem.*, **199**, 801 (1952).

8) L. Arpesella, A. La Manna, and M. Grassi, *Gazz. Chim. Ital.*, **85**, 1354 (1955).

9) S. Yano, M. Saburi, S. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **49**, 101 (1976).

10) Y. Ihara and N. Nakamura, unpublished results.