

Preparation of Nickel(II) Complexes with 2,3-Butanediamines and Their Thermal Octahedral-Square Planar Transformation

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The following nickel(II) complexes with *meso*- or *dl*-2,3-butanediamine (abbreviated to *meso*-bn and *dl*-bn, respectively) were prepared: $[\text{Ni}(\text{meso-bn})_3]\text{X}_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{meso-bn})_2]\text{X}_2$ and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$). It was found from the changes in the absorption spectra and magnetic susceptibilities that $[\text{Ni}(\text{meso-bn})_3]\text{X}_2 \cdot 2\text{H}_2\text{O}$ complexes, when heated to 188 ($\text{X} = \text{Cl}$) and to 233 °C ($\text{X} = \text{Br}$), respectively, undergo transformations from octahedral to square planar structures with the loss of two moles of lattice water and one mole of coordinated *meso*-bn. $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{X}_2$ complexes were similarly found to transform from octahedral to square planar structures at 120 ($\text{X} = \text{Cl}$) and at 110 °C ($\text{X} = \text{Br}$), respectively with the evolution of two moles of coordinated water. After this transformation, the resulting complexes underwent the inverse transformation from square planar to octahedral structure at 170 °C, without any weight change. The effect of the configurational difference between *meso*- and *dl*-bn on the formation of tris and bis(2,3-butanediamine) complexes is also discussed.

Nickel(II) ions form complexes of various structures, *e.g.*, octahedral, tetrahedral and square planar structures, depending upon the ligands, with mutual transformations often occurring among them.¹⁾ Tsuchiya *et al.* have reported structural transformations of $[\text{Ni}(\text{H}_2\text{O})_2(\text{NN-deen})_2]\text{X}_2$, where *NN-deen* is *N,N*-diethylethylenediamine and *X* is a halide ion;²⁾ the chloride, upon heating, evolved two moles of coordinated water accompanied by the anation of chloride ions with the retention of the original octahedral structure, whereas the bromide transformed from an octahedral to a square planar structure without anation of bromide ions after the liberation of water molecules.

The structural transformation of nickel(II) complexes upon heating in solid phase is characterized by a change in the coordination number from six to four, as is seen for the above bromide. On the other hand, an interesting thermal equilibrium has been reported on the basis of spectral measurements that the structure of bis(*N,N*-diethylethylenediamine)copper(II) tetrafluoroborate, perchlorate and nitrate changes to square planar as the temperature is lowered, but to octahedral as the temperature is raised.³⁾ Tsuchiya *et al.* also recently found a novel example of a transformation from square planar to octahedral structure in the benzimidazole complex, $[\text{Ni}(\text{bimd})_4](\text{NO}_3)_2 \cdot 2.5\text{C}_2\text{H}_5\text{OH}$, in the solid phase.⁴⁾

In addition to nickel(II) complexes containing *N*-substituted diamine, the thermal behavior of complexes with the *C*-substituted diamines, 2-methyl-1,2-propanediamine and 1,2-diphenylethylenediamine, have been studied in the solid phase by Farago *et al.*⁵⁾ and by Lifschitz *et al.*,⁶⁾ respectively. Transformations from octahedral to square planar structure are observed in these examples.

The present study was undertaken to prepare various types of the nickel(II) complexes containing *meso*- and *dl*-2,3-butanediamines, as *C*-substituted ethylenediamines, and to investigate thermal transformations in the solid phase and steric effects due to alkyl substitution.

Experimental

Preparation and Identification of 2,3-Butanediamines. A solution containing a mixture of *meso*- and *dl*-2,3-butanediamines (*meso*-bn and *dl*-bn, respectively) was obtained by the method described in Ref. 7. From the solution, *meso*-bn and *dl*-bn were separated as dihydrochlorides by the addition of hydrochloric acid, and were identified from IR and NMR spectra.⁸⁾

The yields were about 20% for *meso*-bn and 9% for *dl*-bn.

Preparation of the Complexes. Tris(*meso*-2,3-butanediamine)-nickel(II) Halide Dihydrates, $[\text{Ni}(\text{meso-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (I) and $[\text{Ni}(\text{meso-bn})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (II). A methanolic solution of nickel chloride or bromide was added to a solution of excess amounts of the free *meso*-diamine obtained by adding KOH to the diamine dihydrochloride. The resulting solution was allowed to stand for about three days in a refrigerator, with a bluish-violet *meso*-bn complex obtained. Recrystallization was carried out from ethanol.

Bis(*meso*-2,3-butanediamine)nickel(II) Halides, $[\text{Ni}(\text{meso-bn})_2]\text{Cl}_2$ (III) and $[\text{Ni}(\text{meso-bn})_2]\text{Br}_2$ (IV). These complexes were prepared in a manner similar to that used for complexes I and II, except for ligand molar ratios of 2:1. A mixture of methanol and water (1:1) was used as a solvent, and yellow plates were obtained.

Diabiquis(*dl*-2,3-butanediamine)nickel(II) Halides, $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Cl}_2$ (V) and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Br}_2$ (VI). By a method similar to that used for complexes III and IV, blue crystals were obtained by recrystallization from water.

Analytical data for all the complexes obtained are summarized in Table 1.

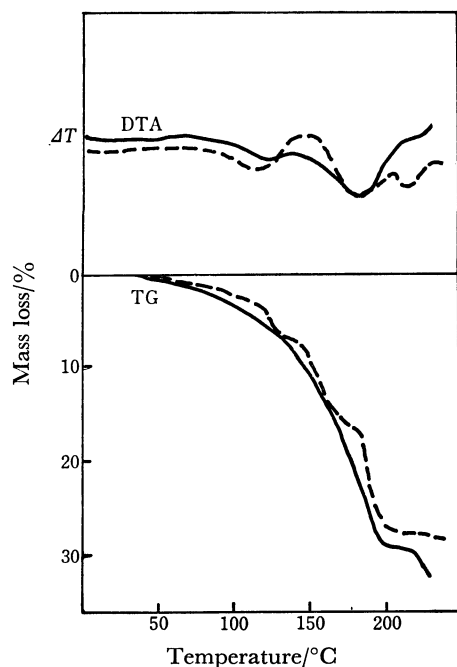
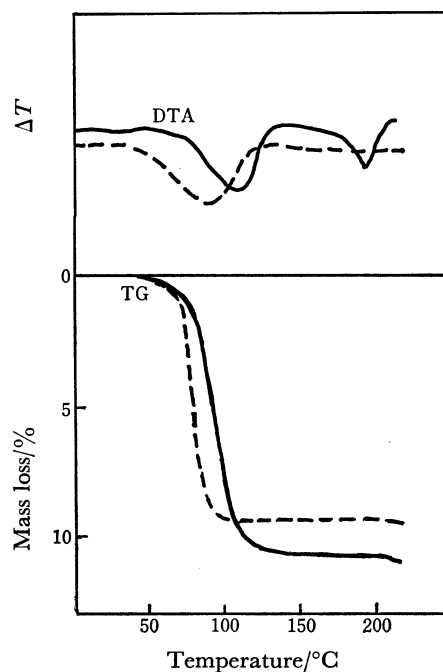
Measurements. Derivatograms for thermal reactions of the complexes, electronic spectra and magnetic susceptibilities were measured in the manner previously reported.^{2,4)}

Results and Discussion

Derivatography. The derivatograms for complexes I and II are shown in Fig. 1. The former chloride shows a 28.6% mass loss in the TG curve in the temperature range from 50 to 188 °C, which just corresponds to the total liberation of two moles of lattice water and one mole of *meso*-bn. On the other hand, in the latter

TABLE 1. ANALYTICAL DATA FOR NICKEL(II) COMPLEXES WITH *meso*- AND *dl*-2,3-BUTANEDIAMINES

Complex	C %		H %		N %	
	Found	Obsd	Found	Obsd	Found	Obsd
(I) $[\text{Ni}(\text{meso-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	33.65	33.51	9.71	9.37	18.84	19.54
(II) $[\text{Ni}(\text{meso-bn})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$	27.70	27.77	8.16	7.77	16.22	16.19
(III) $[\text{Ni}(\text{meso-bn})_2]\text{Cl}_2$	31.49	31.41	8.16	7.91	17.85	18.31
(IV) $[\text{Ni}(\text{meso-bn})_2]\text{Br}_2$	24.20	24.34	6.16	6.13	14.15	14.19
(V) $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Cl}_2$	27.31	28.10	8.34	8.25	16.21	16.39
(VI) $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Br}_2$	22.30	22.29	6.55	6.56	13.00	12.41

Fig. 1. Derivatograms of $[\text{Ni}(\text{meso-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (—) and $[\text{Ni}(\text{meso-bn})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (---).Fig. 2. Derivatograms of $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Cl}_2$ (—) and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Br}_2$ (---).

bromide, three steps due to mass losses corresponding to the successive liberation of two moles of lattice water, that of a half mole of *meso*-bn and that of another half mole were found at 122, 192, and 233 °C, respectively.

The derivatograms for complexes V and VI are shown in Fig. 2. The former chloride shows a 10.4% mass loss in the TG curve between 70 and 120 °C. This mass loss matches the liberation of two moles of coordinated water. It is worth noting that an endothermic peak appears at 170 °C without any change in the TG and DTG curves, which is the basis of new information described in a later section.

For complex VI, a 8.4% mass loss was found in the range from 35 to 100 °C. This corresponds to the liberation of two moles of coordinated water. The endothermic peak was, however, not as distinctly observed as for complex V.

Electronic Spectra. Color changes of the complexes in each heating step are summarized in Table 2. This table also includes the magnetic moments which will be discussed in a later section.

The electronic spectral changes corresponding to these color changes were measured in the solid state. The diffuse reflection spectra of complex I, the sample

TABLE 2. COLOR AND MAGNETIC MOMENT OF THE COMPLEXES IN EACH HEATING STEP

Complex	Color	Magnetic moments (μ_{eff} B.M.)		Color	Magnetic moments (μ_{eff} B.M.)	Color	Magnetic moments (μ_{eff} B.M.)
(I) $[\text{Ni}(\text{meso-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	bluish violet	3.33	50—188 °C	yellow	diamag.		
(II) $[\text{Ni}(\text{meso-bn})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$	bluish violet	3.24	122—223 °C	yellow	diamag.		
(V) $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Cl}_2$	blue	3.39	70—120 °C	yellow	diamag.	180 °C → green	3.11
(VI) $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Br}_2$	blue	3.28	35—110 °C	yellow	diamag.	170 °C → gray	3.44

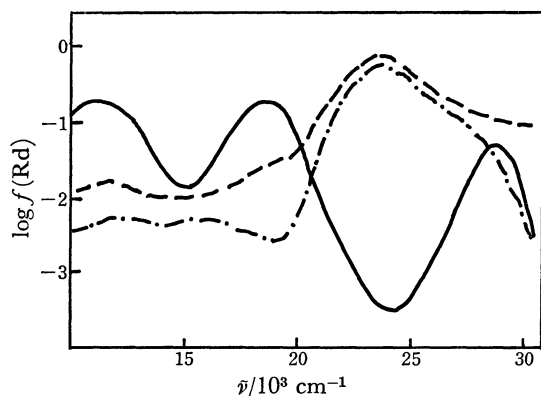


Fig. 3. Electronic spectra of $[\text{Ni}(\text{meso-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (—), the sample obtained by heating it at 180°C (---) and of $[\text{Ni}(\text{meso-bn})_2]\text{Cl}_2$ prepared in aqueous solution.

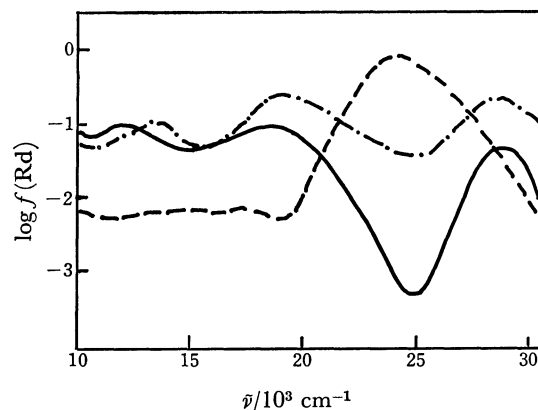


Fig. 5. Electronic spectra of $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Cl}_2$ (—), the samples obtained by heating it at 120°C (---) and at 180°C (-·-·-).

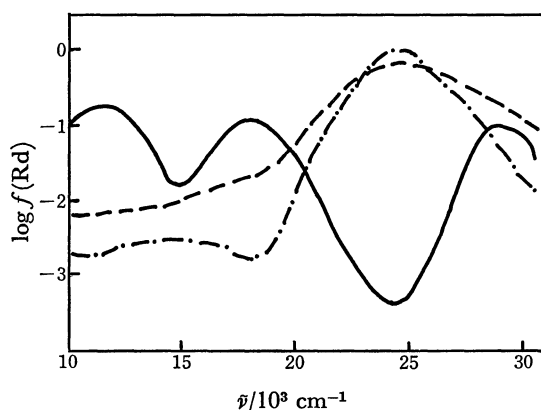


Fig. 4. Electronic spectra of $[\text{Ni}(\text{meso-bn})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (—), the sample obtained by heating it at 220°C (---) and of $[\text{Ni}(\text{meso-bn})_2]\text{Br}_2$ prepared in aqueous solution.

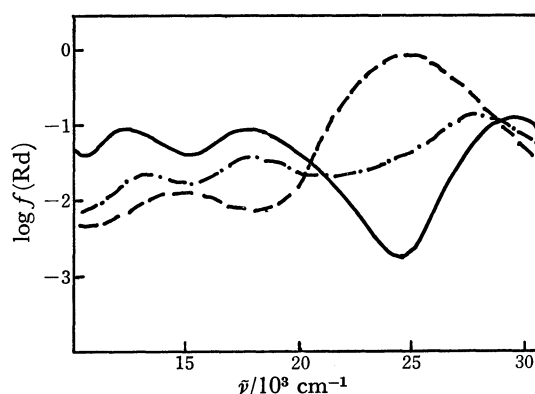


Fig. 6. Electronic spectra of $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-bn})_2]\text{Br}_2$ (—), the samples obtained by heating it at 110°C (---) and at 170°C (-·-·-).

obtained by heating complex I to 180°C , and of complex III are compared in Fig. 3, and the corresponding spectra of complex II, the sample obtained by heating complex II to 220°C , and of complex IV in Fig. 4. Complexes I and II gave three characteristic maxima at 11 , 18 , and $28 \times 10^3 \text{ cm}^{-1}$, which are assignable to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions in the octahedral nickel(II) complex at room temperature. After heating, these absorption bands were almost quenched and one strong band appeared at $24 \times 10^3 \text{ cm}^{-1}$, which was assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ transition in the square planar nickel(II) complex.⁹⁾

The spectra of complex V and the samples obtained by heating this complex to 120 and 180°C are shown in Fig. 5. At 120°C , a new strong absorption band due to the formation of the square planar structure appears after the disappearance of the three absorption bands attributed to the octahedral structure, as was observed for complexes I and II. It is notable, however, that when heated to 180°C , the three original absorption bands reappear after the disappearance of the strong band observed at 120°C . This suggests the occurrence of a second thermal transformation from square planar to octahedral structure, an exceptional change for

nickel(II) complexes.

The spectra of complex VI and the samples obtained by heating it to 110 and 170°C are shown in Fig. 6. In a manner similar to that for complex V, the three original absorption bands disappear and one strong band appears upon heating at 110°C , showing that the transformation from octahedral to square planar structure occurs. On the other hand, above 170°C , the three absorption bands weakly reappear. Partial transformation from square planar to octahedral structure appears to occur.

Magnetic Moments. The magnetic moments at room temperature for complexes I, II, V, and VI and the samples obtained by heating them to each temperature at which a transformation occurs are listed in Table 2. For complexes I and II, the paramagnetic species change to diamagnetic species. By combining these results with the spectral changes due to heating, it is concluded that the change in the structure from octahedral to square planar occurs during the thermal reaction.

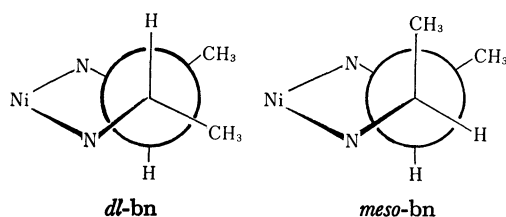
On the other hand, for complexes V and VI, the paramagnetic species change to diamagnetic species with the first heating step in a manner similar to that for complexes I and II. In the second heating step, however, the paramagnetism is recovered. Although the

tetrahedral nickel(II) complex is paramagnetic, it is known that its magnetic moment (3.7 B.M.) is significantly larger than that for the octahedral complex (3.3 B.M.).¹⁰ A stepwise structural transformation, octahedral→square planar→octahedral, is concluded to occur in complex V.

On the other hand, in complex VI having a magnetic moment of 3.44 B. M. and the three weak absorption bands when heated above 170 °C, the partial transformation from square planar to either octahedral or tetrahedral structure is presumed to take place in a second heating step. It is to be noted that such a novel transformation including the subsequent inverse change from square planar to octahedral structure was found.

Relationship between the Conformation of 2,3-bn Coordinated and Ease of Complex Formation. In the present study, diaquabis(*dl*-bn)nickel(II) complexes were prepared, but the corresponding *meso*-bn complexes could not be prepared. This difference is probably due to the difference in the conformational structures of the coordinated 2,3-bn.

The conformations of *dl*-bn and *meso*-bn coordinated to the nickel ion are depicted below.



In complexes containing two moles of *dl*-bn in a

square planar structure, the four methyl groups are all equatorial and the apical positions will admit the coordination of water molecules easily forming diaquabis(*dl*-bn)nickel(II) complexes easily.

For complexes containing two *meso*-bn, on the other hand, two of the four methyl groups are axial and, therefore, the water molecules are not easily coordinated in the apical positions. This may be the principal reason why diaquabis(*meso*-bn)nickel(II) complexes could not be prepared.

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