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THERMAL SQUARE PLANAR-TO-OCTAHEDRAL TRANSFORMATION OF $[Ni(bimd)_4](NO_3)_2 \cdot 2.5C_2H_5OH$ IN SOLID PHASE

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The reaction involving the increase of the coordination number from four to six, viz, the transformation from square planar to octahedral was found in the benzimidazole complex, $[Ni(bimd)_4](NO_3)_2 \cdot 2.5C_2H_5OH$ upon heating. The transformation was considered to be due to the approach of the nitrate ions toward the central ion along the vertical axis.

It is known that the nickel (II) ion forms the complexes which have various coordination structures, e.g, octahedral, tetrahedral and square planar etc, depending upon the kind of ligands owing to the d^8-electronic configuration of the central ion. Although it is also well-known that the mutual transformations among the above coordination structures occur and there are equilibria in various solvents,$^{1)}$ no papers on such studies in solid phase have been found, except for the studies on the N,N-diethylethylenediaminecopper(II) tetrafluoroborate, perchlorate and nitrate on the basis of the spectral measurements, in which the coordination structure moves on toward the square planar as the temperature is lowered, but to the octahedral as the temperature is raised.$^{2)}$

In the previous paper, the configurational transformation of $[Ni(H_2O)_2(NN\text{-}deen)_2]X_2$, where NN-deen is N,N-diethylethylenediamine and X is halide ions, had been reported;$^{3)}$ it liberates two coordinated water molecules upon heating and the counter ion coordinates instead to keep the original octahedral configuration in the case of the chloride, whereas, in the corresponding bromide, the complex undergoes the transformation from paramagnetic, octahedral to diamagnetic, square planar without the coordination of counter ions after the liberation of water molecule coordinated.

The transformation described above exclusively belongs to the change of the coordination number from six to four when the complexes are heated in the solid phase, and such tendencies are normally expected to appear upon heating the nickel(II) complexes.

On the other hand, when the nickel(II) complexes contain the unidentate ligand which has a fair bulkiness and gives somewhat strong ligand field, it might be predicted that the square planar complexes are prepared even at room temperature without the additional coordination of another ligands toward tha vertical sites over and below the square plane. Moreover, since the heating of the complexes gives rise to some increases of metal-ligand bond distance, the steric requirement as discribed above will be partially relaxed to change the square planar complexes to the octahedral owing to the approach of the counter ions toward nickel(II) atom along the vertical axis.

In the present work, benzimidazole was employed as one of the typical ligands capable of forming square planar nickel(II) complexes which undergo the above peculiar thermal behaviors. It has already been reported, however, that the nickel(II) complexes with benzimedazole undergo the transformation from paramagnetic to diamagnetic species only in the acetone adduct of the bromide upon heating at 140°, as usually seen, while the paramagnetism is kept in the corresponing chloride.4) It was also known that the corresponding iodide and perchlorate were obtained in the orange, diamagnetic state at the beginning.4)

The present paper was, therefore, undertaken to examine whether or not such diamagnetic complexes are prepared in addition to the iodide and perchlorate and whether or not the thermal behavior such as square planar-to-octahedral transformation appears when the counter ion is varied.

Experimental

Preparation of Complexes. Tetrakisbenzimidazolenickel(II) Nitrate Di- and Hemi-Alcoholate, $[Ni(bimd)_4](NO_3)_2\cdot 2.5C_2H_5OH$ (bimd=benzimidazole). Nickel (II) nitrate hexahydrate and benzimidazole were separately dissolved in ethanol as much as possible. The two solutions were mixed so as to give the specified molar ratio of their solutes 1:4. The resulting bluish green solution was evaporated on standing at room temperature to obtain yellow crystals. Recrystallization was carried out from ethanol. Anal. found: Ni, 7.41; C, 49.65; N, 18.23; H, 4.91%. Calcd for $[Ni(C_7N_2H_6)_4](NO_3)_2\cdot 2.5C_2H_5OH$: Ni, 7.35; C, 51.44; N, 18.18; H, 4.92%.

Tetrakisbenzimidazolenickel(II) Iodide and Perchlorate, $[Ni(bimd)_4]X_2$(X=I, ClO_4). These complexes were prepared by the method according to the literature.4) Found: C, 42.68; N, 14.11; H, 3.09% for the iodide. Calcd for $[Ni(C_7N_2H_6)_4]I_2$: C, 42.83; N, 14.28; H, 3.08%. Found: C, 46.26; N, 15.23; H, 3.35% for the perchlorate. Calcd for $[Ni(C_7N_2H_6)_4](ClO_4)_2$: C, 46.06; N, 15.34; H, 3.31%.

Measurements. The thermal reactions of the complexes were traced with a MOM Derivatograph Typ-OD-102 under the nitrogen stream at the heating rate of 1°C min^{-1}. The electronic and IR absorption spectra of the complexes before and after heating were measured with Hitachi EPS spectrophotometer in a solid state and with JASCO model IR-E spectrophotometer in Nujol mull state, respectively. The magnetic moments were evaluated from the magnetic susceptibility measured by Gouy method.

Results and Discussion

Derivatography. The derivatogram of the ntirate is shown in Fig. 1. The weight loss observed in the TG curve at 130° amounts to 14.8%, which is close to the calculated value of 14.42% corresponding to the liberation of 2.5 mole of alcohol. On the other hand, no weight losses were found both in the TG curves of the iodide and perchlorate until their decomposition begins.

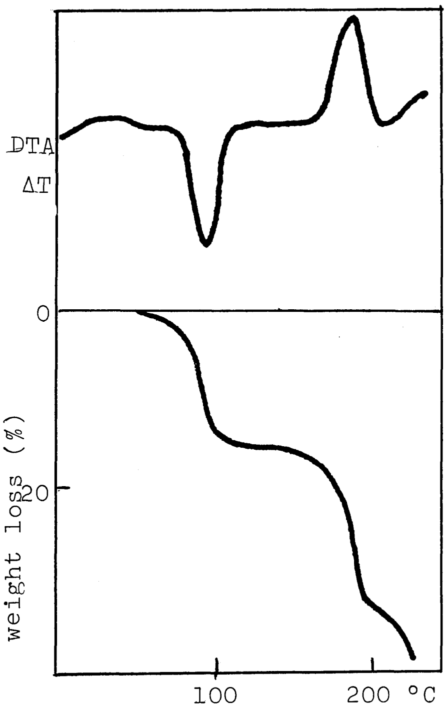

Fig. 1. Derivatogram of $[Ni(bimd)_4](NO_3)_2 \cdot 2.5C_2H_5OH$.

Electronic and IR Spectra. It was observed in the course of the derivatography that the tetrakisbenzimidazolenickel(II) nitrate di and hemi-alcoholate gave changes in color from yellow to blue at 130° as the ethanol is evolved, while the corresponding iodide exhibited the color change from yellow to green at 190° without any weight losses.

The electronic absorption spectra of the above nitrate at room temperature and of that obtained by heating it at 130° are shown in Fig.2. 2. It is found from this figure that the yellow, starting complex gives a strong absorption band at ca. 25×10^3 cm^{-1} probably assigned to the transition, $^1A_{1g} \longrightarrow {}^1A_{2g}$, which is characteristic to square planar configuration in nickl(II) complexes. On the other hand, in the blue complex obtained by heating the former planar complex at 130°C, the three bands appear at ca. 8×10^3, 17×10^3 and $26\times10^3 cm^{-1}$ assigned to the transitions, $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, respectively.

Ferraro and Walker5) pointed out that anhydrous metal nitrates, $Cu(NO_3)_2$and $Co(NO_3)_2$, exhibit the peak in the range 350 ~ 250 cm^{-1} assigned to the metal-oxygen vibration owing to the coordination of nitrate ion to central metal. In the IR spectra of the nitrate of the benzimidazole complexes, the peak assigned to ν_{OH} of ethanol disappeared upon heating it at 130° and a peak appeared instead at ca. 300 cm^{-1} assigned to the $Ni-O(NO_3)$ vibration, as shown in Fig. 3. It means that, after the evolution of ethanol, nitrate ions approach to the vertical sites over and below the square plane to form octahedral configuration.

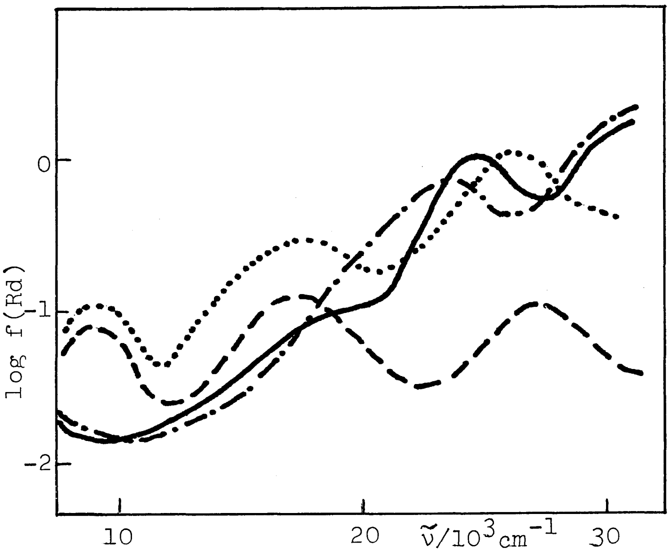

Fig. 2. Electronic absorption spectra of $[Ni(bimd)_4](NO_3)_2 \cdot 2.5C_2H_5OH$ in solid state before(———) and after heating at 130°(----), and those of $[Ni(bimd)_4]I_2$ before (-·-·-) and after heating at 190° (····).

The corresponding electronic absorption spectra of the tetrakisbenzimidazolenickel(II) iodide are also shown in Fig.2. It is also found in the iodide that one strong band disappears and new three bands are produced upon heating it at 190° as similarly seen in the nitrate except for the results that no weight losses are observed. The information will be given from this change of the spectra that the square planar complex partially turns the octahedral one.

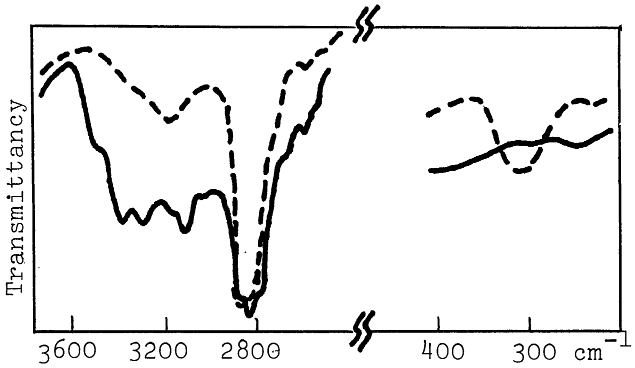

Fig. 3. IR spectra of $[Ni(bimd)_4](NO_3)_2\cdot 2.5C_2H_5OH$ before (——) and after heating at 130° (----).

Magnetic Moments. The magnetic moments of the complexes and those obtained by heating the nitrate at 130° and the iodide at 190° are listed in Table 1. It is found in this table that the nitrate and iodide of tetrakisbenzimidazolenickel(II) complexes which have diamagnetic configuration both undergo the transformation to paramagnetic complexes.

As far as the tetrakisbenzimidazolenickel(II) complexes reported by Goodgame et al.[4] are concerned, the coordination structure is kept in the orginal form or, even if changed, decreases, for example, six to four upon heating.

Nevertheless, in the present study, the reverse transformations from diamagnetic square-planar to paramagnetic octahedral were found in the corresponding nitrate and iodide as predicted in the introduction of this paper, which is considered to be one of unique reactions in a solid phase.

Table 1. Magnetic moments of the complexes before and after heating

Complexes	before heating μ_{eff} (B.M.)	after heating μ_{eff} (B.M.)
$[Ni(bimd)_4](NO_3)_2\cdot 2.5C_2H_5OH$	diamag.	3.11
$[Ni(bimd)_4]I_2$	diamag.	3.19

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