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# THERMAL REACTION OF FIVE-COORDINATED NICKEL(II) COMPLEXES CONTAINING *N,N*-BIS[2-(DIMETHYLAMINO)ETHYL]METHYLAMINE IN THE SOLID STATE

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## ABSTRACT

The following two types of 5-coordinated nickel(II) complexes of *N,N*-bis[2-dimethylamino)ethyl]methylamine (PMDN) were prepared; $[NiX(NH_3)pmdn]X \cdot nH_2O$ where X: Cl, Br or I; $n$: 0 or 1, and $[Ni(A)_2pmdn]X_2$ where A: $NH_3$ or $CH_3CN$; X: $ClO_4$ or $BF_4$. In the solid-phase thermal reaction of $[NiX(NH_3)pmdn]X$, the complexes evolved 1 mol of ammonia to undergo anation. On the other hand, the compounds $[Ni(A)_2pmdn]X_2$ were found to evolve 1 mol of A to convert into square planar complexes.

## INTRODUCTION

Among the first divalent transition metal ions, the nickel(II) ion, having a $d^8$ electronic configuration, is peculiar in that the field strength and the steric requirement of coordinated ligands dictate whether the ion forms paramagnetic octahedral, paramagnetic tetrahedral or diamagnetic square-planar complex [1,2a]. We have systematically studied the structural and thermochemical changes during the solid state thermal reactions of octahedral, tetrahedral and square-planar bis(diamine)nickel(II) complexes containing a variety of diamines [2]. We have also reported the relative thermal stabilities of the octahedral and square-planar nickel(II) complexes containing *N,N*- and *N,N'*-diethyl (or dimethyl)-1,2-ethanediamines as indicated by calorimetric studies [3].

Additionally, Ni(II) ion is characteristic in that it easily forms 5-coordinated complexes as well as 4- and 6-coordinated complexes [4]. The

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structural conversion of the 5-coordinated complexes in solution has been examined extensively, but little is known of the conversion in the solid state.

Therefore a series of 5-coordinated nickel(II) complexes containing *N,N*-bis[2-(dimethylamino)ethyl]methylamine (PMDN) was prepared and their thermal behavior in the solid state was investigated. It is well known that PMDN forms 5-coordinated bivalent metal complexes in addition to 4- and 6-coordinated species [5].

## EXPERIMENTAL

### *Preparation of* N,N*-bis[2-(dimethylamino)ethyl]methylamine*

The amine was prepared according to a modification of the known method [6]: a solution of *N,N*-bis(2-aminoethyl)amine (51.5 g, 0.5 mol) in water (50 ml) was added to a mixture of formaline (300 ml) and 85% formic acid (420 ml). The mixture was refluxed on an oil-bath for about 10 h, and allowed to cool at ambient temperature, when 6 M hydrochloric acid was added in sufficient quantity to produce the amine trichloride which was collected by filtration. Sufficient saturated sodium hydroxide solution was then added to neutralize the trichloride. Two layers appeared: the upper layer contained the desired amine. This was extracted from the upper layer with ether. To the ethereal solution was added potassium hydroxide to remove residual water. The ether was removed by distillation and the amine was distilled at 97.9–98.1°C (25 mmHg). Yield 50 g for the trichloride: found: C, 38.28; H, 9.53; N, 14.53%; calcd. for $C_9H_{23}N_3 \cdot 3HCl$: C, 38.24; H, 9.29; N, 14.86%.

### *Preparation of complexes*

$[NiCl(NH_3)pmdn]Cl \cdot H_2O$. To a solution of $NiCl_2 \cdot 6H_2O$ (5 mmol) in ethanol, $[Ni(NH_3)_6]Cl_2$ (5 mmol) and PMDN (6.6 mmol) were added. The solution turned dark green. The mixture was stirred for about 20 h, and was then allowed to stand in a refrigerator. The green product thus obtained was collected by filtration and washed three times with ethanol. Yield 0.5 g; found: C, 32.23; H, 8.31; N, 16.77%; calcd. for $[NiCl(NH_3)(C_9H_{23}N_3)]Cl \cdot H_2O$: C, 31.99; H, 8.35; N, 16.58%.

$[NiBr(NH_3)pmdn]Br$ and $[NiI(NH_3)pmdn]I$. These were prepared in a manner similar to that used for the chloride above except that $NiBr_2 \cdot 6H_2O$ and $NiI_2 \cdot 6H_2O$ were used in place of $NiCl_2 \cdot 6H_2O$. Yield 0.9 g for the bromide and 1.7 g for the iodide; found: C, 26.17; H, 6.35; N, 13.53%; calcd. for $[NiBr(NH_3)(C_9H_{23}N_3)]Br$: C, 26.44; H, 6.41; N, 13.70%; found: C, 21.43; H, 5.01; N, 11.22%; calcd. for $[NiI(NH_3)(C_9H_{23}N_3)]I$; C, 21.50: H, 5.21; N, 11.14%.

$[Ni(NH_3)_2pmdn]X_2$ ($X = ClO_4$, $BF_4$). Hexaamminenickel(II) perchlorate (2 mmol) and nickel(II) perchlorate (4 mmol) were dissolved in ethanol and PMDN (6.6 mmol) was added. After the solution was stirred overnight, the desired products were obtained. These were dissolved in a small amount of DMSO, and hot ethanol was added when a green precipitate was obtained. This was dried overnight in a desiccator. Yield 1.4 g; found: C, 23.74; H, 6.36; N, 13.98%; calcd. for $[Ni(NH_3)_2(C_9H_{23}N_3)](ClO_4)_2$: C, 23.25; H, 6.29; N, 15.06%.

The corresponding tetrafluoroborate was obtained by a procedure similar to that for the perchlorate.

$[Ni(CH_3CN)_2pmdn]X_2$ (X: $ClO_4$, $BF_4$). Nickel(II) perchlorate (4 mmol) was dissolved in ethanol, and acetonitrile (12 mmol) was added. When PMDN (4.4 mmol) was added to the mixture, a greenish-blue precipitate was formed, which was collected by filtration and dried overnight in a desiccator.

The complex (1.6 g) thus obtained was dissolved in hot acetonitrile (10 ml) and the solution was filtered while hot. Hot ethanol (40 ml) was added to the solution. The resulting solution was permitted to stand overnight in a refrigerator. The product thus obtained was collected by filtration and dried overnight in a desiccator. Yield 0.8 g; found: C, 29.30; H, 5.73; N, 12.88%; calcd. for $[Ni(CN_3CN)_2(C_9H_{23}N_3)](ClO_4)_2$: C, 30.44; H, 5.70; N, 13.65%.

The tetrafluoroborate was obtained by a procedure similar to that for the perchlorate.

### *Derivatographic measurements*

The derivatograms of the complexes were obtained with a MOM Derivatograph Typ-OD-102. Measurements were carried out in a nitrogen atmosphere at a heating rate of 1.2°C $min^{-1}$. Finely powdered samples (0.4–0.5 g, 100–200 mesh) were used in each run.

### *Spectral measurements*

Visible and near IR spectra of the starting materials and the products obtained during heating were measured by the diffuse reflectance method with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment, Type R-3. IR spectra of the samples were measured by the KBr method with a JASCO-A-3 infrared spectrophotometer.

### *Magnetic measurement*

Effective magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method at room temperature. $Hg[Co(NCS)_4]$ was used as the standard material. The susceptibilities of the complexes were corrected by Pascal's constants for each element or atomic group contained.

## RESULTS AND DISCUSSION

### *Derivatographies*

Figure 1 shows the derivatograms of the ammine-halogeno complexes. The mass losses in the TG curves are expressed in terms of g per formula weight (g/FW). As seen from the TG curve of the chloride, the complex evolves 1 mol of lattice water and 1 mol of ammonia at 30–140°C, with a plateau being obtained. On the other hand, the bromide and iodide lose 1 mol of ammonia up to 200°C.

Figure 2 depicts the derivatograms of the diamine and the bis(acetonitrile) complexes. The diammine complex loses 1 mol of ammonia at 60–130°C, a plateau being obtained. On the other hand, the bis(acetonitrile) complex lose 1 mol of acetonitrile at 30–115°C, a plateau being obtained.

### *Colors and magnetic moments*

Table 1 shows the colors and magnetic moments of the starting complexes and the reaction products. In the ammine-halogeno complexes, the original green was changed into brown after the deammonation. However, significant changes in magnetic moments were not detected: the changes were only from about 3.1–3.2 to about 3.3–3.5. The results suggest that the ammine-halogeno complexes undergo deammonation–anation during derivatogra-

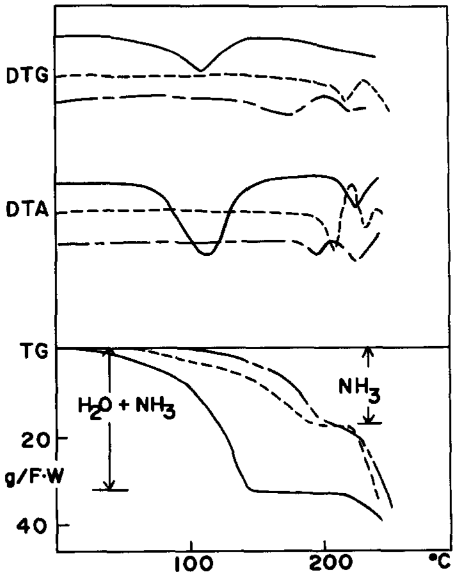

Fig. 1. Derivatograms of $[NiCl(NH_3)pmdn]Cl \cdot H_2O$ (———), $[NiBr(NH_3)pmdn]Br$ (– – –) and $[NiI(NH_3)pmdn]I$ (— - —). g/F·W stands for grams per formula weight.

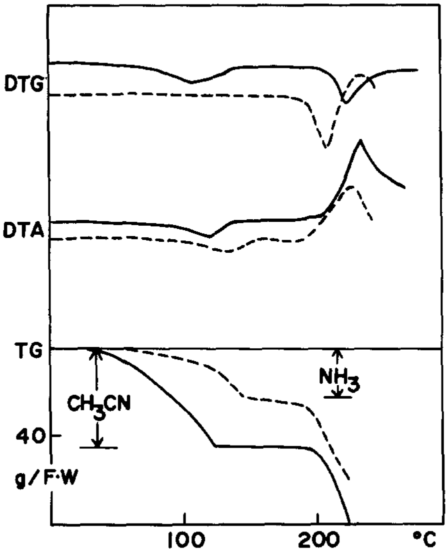

Fig. 2. Derivatograms of $[Ni(NH_3)_2pmdn](BF_4)_2$(- - -) and $[Ni(CH_3CN)_2pmdn](BF_4)_2$ (———).

phies. On the other hand, both the amine and bis(acetonitrile) complexes changed in color from original green or blue to orange and they changed from paramagnetic (about 3.2 B.M.) to diamagnetic, indicating the formation of 4-coordinated square-planar complexes.

## *Electronic spectra*

Figure 3 shows the electronic spectra of $[NiCl(NH_3)pmdn]Cl \cdot H_2O$ before and after heating. As seen from the Figure, the bands found in the

TABLE 1

Colors and magnetic moments ($\mu_{eff}$) of the starting complexes and reaction products

| Complexes | Colors | | $\mu_{eff}$ | |
|---|---|---|---|---|
| | Starting complexes | Reaction products [a] | Starting complexes | Reaction products [a] |
| $[NiCl(NH_3)pmdn]Cl \cdot H_2O$ | green | yellowish brown | 3.18 | 3.34 |
| $[NiBr(NH_3)pmdn]Br$ | green | brown | 3.27 | 3.37 |
| $[NiI(NH_3)pmdn]I$ | yellowish green | brown | 3.25 | 3.51 |
| $[Ni(NH_3)_2pmdn](ClO_4)_2$ | green | reddish orange | 3.29 | diamagnetic |
| $[Ni(NH_3)_2pmdn](BF_4)_2$ | green | reddish orange | 3.33 | diamagnetic |
| $[Ni(CH_3CN)_2pmdn](ClO_4)_2$ | blue | orange | 3.21 | diamagnetic |
| $[Ni(CH_3CN)_2pmdn](BF_4)_2$ | blue | orange | 3.15 | diamagnetic |

[a] Reaction products = products obtained at the plateaus in the TG curves.

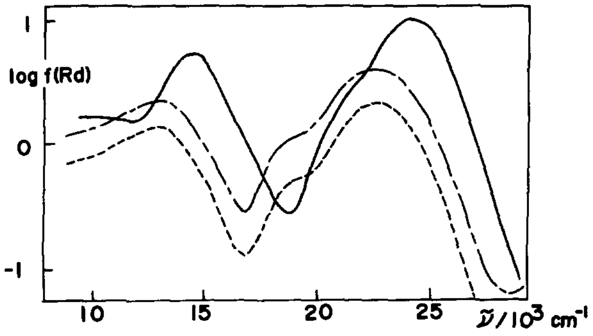

Fig. 3. Electronic spectra of [NiCl($NH_3$)pmdn]Cl·$H_2O$ before (———) and after heating (— - —), and the reference complex [$NiCl_2$pmdn] (- - -).

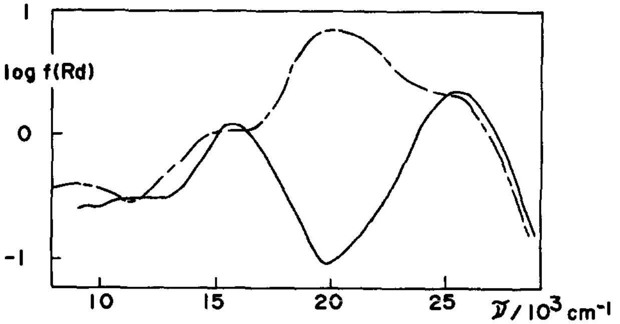

Fig. 4. Electronic spectra of [Ni($NH_3$)$_2$pmdn]($BF_4$)$_2$ before (———) and after heating (— - —).

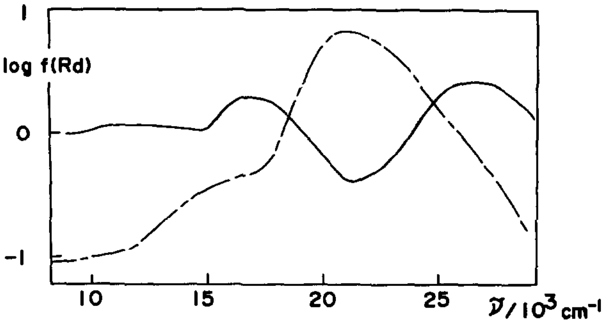

Fig. 5. Electronic spectra of [Ni($CH_3CN$)$_2$pmdn]($BF_4$)$_2$ before (———) and after heating (— - —).

spectrum of the product obtained by heating shift by 2000 $cm^{-1}$ to a lower wave-number region than those of the complex before heating. In addition, the spectrum of the product is almost the same as that of the reference material $[NiCl_2pmdn]$ [7]. This, when considered with the results of magnetic moment measurement suggests that the complex undergoes anation during heating. This is also true for the bromide and the iodide.

Figures 4 and 5 show the spectra of the diammine $[Ni(NH_3)_2pmdn](BF_4)_2$ and the bis(acetonitrile)complex $[Ni(CH_3CN)_2pmdn](BF_4)_2$ before and after heating. As may be seen, the spectra of both the complexes after heating show strong bands at about 21,000 $cm^{-1}$ characteristic of 4-coordinated square-planar complexes.

## SUMMARY

On the basis of the above results, the thermal reactions of the complexes in the present study can be divided into two classes. In the ammine-halogeno series, the complexes evolve 1 mol of ammonia to undergo anation to produce the dihalogeno complexes (deammonation-anation). On the other hand, as for the diammine and the bis(acetonitrile) complexes, they lose one mole of ammonia or acetonitrile to convert into 4-coordinated square-planar complexes (structural conversion).

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