

Derivatographic Studies on Transition Metal Complexes. XX.¹⁾ Thermal Electron Transfer Reactions of Cobalt(III) Complexes Containing Phenylbiguanide in the Solid Phase²⁾

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The following six cobalt(III) complexes containing phenylbiguanide were prepared and the thermal reactions were followed both isothermally and non-isothermally (derivatographically) in the solid phase: *trans*-[Co(A)₂(phbgH)₂]X₃·*n*H₂O, where A denotes volatile ligands such as NH₃, CH₃NH₂ or C₅H₅N; phbgH denotes 1-phenylbiguanide, X chloride or bromide ion; and *n* is 2 or 3. From the electronic, IR and far-IR spectra and magnetic susceptibilities of these complexes before and after heating, the products obtained by evolving volatile ligands were found to be uniform bivalent cobalt complexes without rupture of the bonds of phbgH to cobalt in spite of the reduction of central cobalt(III) ion, except for the complexes containing ammonia. The reaction seems to be caused by the electron transfer from the coordinated phbgH to cobalt, not from the outer-sphere anions.

Werner found that the hydroxo-aqua-cobalt(III) complexes *cis*-[Co(OH)(NH₃)₄(H₂O)]X₂ (X=Cl or Br) evolve water at *ca.* 100 °C to form the corresponding diol complexes in the solid phase.³⁾ Since then, thermal reactions of several cobalt(III) complexes have occasionally been investigated in the solid phase; *e.g.*, anation of [Co(H₂O)(NH₃)₅]X₃ (X=NO₃,^{4a)} Br,^{4b)} or ReO₄,^{4c)}, *cis*↔*trans* isomerization of [CoCl₂(NH₃)₄]-IO₃,⁵⁾ [CoCl₂pn₂](H₅O₂)Cl₂,⁶⁾ and [CoCl₂(NH₃)₂en]-SCN,⁷⁾ and kinetics of the thermal decomposition of [Co(NH₃)₆]X₃ (X=Cl, Br, or I).⁸⁾

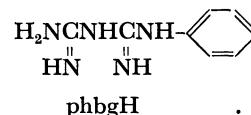
Few systematic investigations have been carried out for cobalt(III) complexes to clarify their reactions in the solid phase. This is mainly due to the instability of cobalt(III) complexes upon heating. Most cobalt(III) complexes are apt to undergo a reduction of Co(III) to Co(II) ions followed by rapid and complicated decomposition. In fact, Tanaka and Nagase pointed out that the decomposition of the ammine complexes is initiated by the electron transfer from outer-sphere anions to central Co(III) ions.⁸⁾

It was found that *trans*-[Co(CH₃NH₂ or C₅H₅N)₂(bgH)₂]X₃ (bgH=biguanide and X=Cl or Br) lose two moles of methylamine or pyridine to yield uniform bivalent cobalt(II) complexes without destruction of the bond of the bgH with cobalt ion upon heating.⁹⁾ The stiffness of the complexes was thought to be due to the inherent characteristics of biguanide; namely biguanide can form extremely stable planar complexes¹⁰⁾ containing pseudoaromaticity.¹¹⁾

The present study was undertaken (1) to prepare such instructive model complexes in which the skeletons are indestructible even at the end of the reduction of Co(III) to Co(II) ions, (2) to investigate isothermally and non-isothermally overall reaction processes of the complexes obtained, and (3) to confirm the origin of the electron transfer; *i.e.*, whether it is promoted from counter anion or ligand to Co(III) ion.

As compounds suitable for our purposes, *trans*-[Co(A)₂(phbgH)₂]X₃·*n*H₂O were selected. PhbgH has the following characteristics: two molecules of each bidentate ligand can occupy the opposite four coordination sites of octahedral cobalt(III) ion with

planar geometry; pseudoaromaticity can be induced by coordination to Co(III) ion. PhbgH has the following constitutional formula:



It is π -electron-rich as compared with bgH by virtue of the electron-donating effect of an introduced -C₆H₅ group.

Experimental

Preparation of Ligand. 1-Phenylbiguanide (C₆H₅NHC(=NH)NHC(=NH)NH₂·HCl) was prepared by the method reported.¹²⁾

Preparation of Complexes. *trans*-[Co(A)₂(phbgH)₂]X₃·*n*H₂O (A=NH₃, CH₃NH₂ or C₅H₅N; X=Cl or Br). These complexes were prepared by the method of Rây¹³⁾ modified as follows: 6.5 g of phbgH·HCl was dissolved in 150 ml of 10% sodium hydroxide solution. To this was added drop by drop with stirring a solution of CoCl₂·6H₂O (3.5 g) in 10 ml of water. When the solution turned yellow from brown, yellow precipitates (probably [Co(phbg)₂]) were obtained. After filtration, the precipitates were suspended in appropriate bases and oxidized by addition of a few drops of 35% hydrogen peroxide solution. As the bases, 120 ml of 28% aqueous ammonia, 120 ml of 40% methylamine solution and 120 ml of 60% pyridine solution were used to prepare *trans*-diammine, *trans*-bis(methylamine) and *trans*-bis(pyridine) complexes, respectively. After a small portion of cobalt(II) hydroxide deposited had been filtered off, the filtrate was neutralized by using concentrated hydrochloric acid. The use of concentrated hydrobromic acid instead of concd HCl gave the corresponding bromide complexes. As soon as neutralization was complete, pink crystals were obtained. They were recrystallized from water, and then washed with cold ethanol and ether. Yield about 2 g for each complex.

The analytical data of the six complexes are summarized in Table 1, together with deamination temperatures and isothermal conditions which were determined from the respective derivatograms (Figs. 1 to 3).

Derivatographic Measurements. The derivatograms for the above complexes were recorded with a MOM Derivatograph Typ-OD-102. All the measurements were carried out

TABLE 1. ANALYTICAL DATA, DEAMINATION TEMPERATURES, AND ISOTHERMAL CONDITIONS OF THE STARTING COMPLEXES

Complex	Analytical data						Deamina- tion Temp (°C)	Isothermal conditions	
	C %		H %		N %			Temp (°C)	Time (h)
	Found	Calcd	Found	Calcd	Found	Calcd			
<i>trans</i> -[Co(NH ₃) ₂ (phbgH) ₂]Cl ₃ ·2H ₂ O (I)	32.62	32.58	5.40	5.47	28.53	28.50	—	—	—
<i>trans</i> -[Co(NH ₃) ₂ (phbgH) ₂]Br ₃ ·3H ₂ O (II)	25.77	25.93	4.40	4.35	22.76	22.68	—	—	—
<i>trans</i> -[Co(CH ₃ NH ₂) ₂ (phbgH) ₂]Cl ₃ ·2H ₂ O (III)	34.89	34.99	5.75	5.87	26.88	27.20	148	160	13
<i>trans</i> -[Co(CH ₃ NH ₂) ₂ (phbgH) ₂]Br ₃ ·2H ₂ O (IV)	28.72	28.78	4.63	4.83	22.42	22.37	172	175	7
<i>trans</i> -[Co(py) ₂ (phbgH) ₂]Cl ₃ ·2H ₂ O (V)	43.34	43.74	4.74	5.08	23.29	23.54	86	160	10
<i>trans</i> -[Co(py) ₂ (phbgH) ₂]Br ₃ ·2H ₂ O (VI)	36.86	36.86	4.62	4.28	19.32	19.84	106	165	7

under a constant flow of nitrogen at a heating rate 1.0–1.5 °C min.⁻¹.

Isothermal Measurements. The products from which methylamine or pyridine was eliminated were obtained by an isothermal method using Cho 100-L thermobalance in static air. The isothermal conditions for obtaining uniform

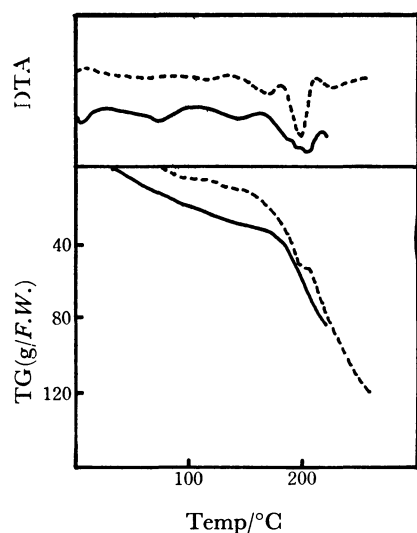


Fig. 1. Derivatograms of complexes I (—) and II (---).

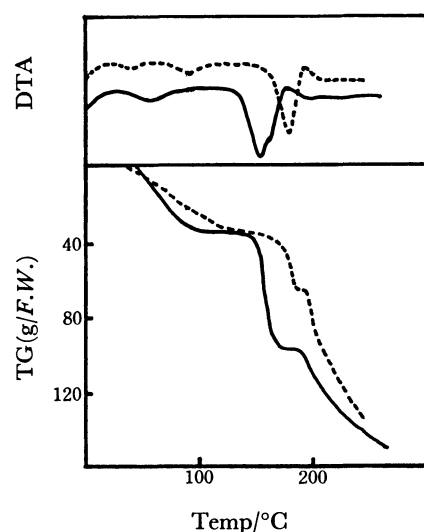


Fig. 2. Derivatograms of complexes III (—) and IV (---).

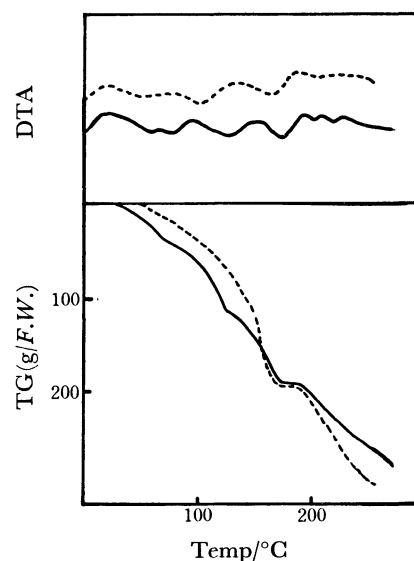


Fig. 3. Derivatograms of complexes V (—) and VI (---).

products are given in Table 1.

Spectral Measurements. The electronic spectra in the solid state were measured by a diffuse reflectance method with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment (Type R-3). The IR and far-IR spectra were measured by the KBr disk method with a JASCO-A-3 infrared spectrophotometer and by the Nujol method with a JASCO IR-F far-infrared spectrophotometer.

Measurements of Magnetic Susceptibilities. The effective magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method at room temperature. Hg[Co(NCS)₄] was employed as a reference material. The susceptibilities of the complexes were corrected by using Pascal's constants for each element or atomic group contained.

Results and Discussion

Derivatography. The derivatograms of a series of *trans*-[Co(A)₂(phbgH)₂]X₃·*n*H₂O are shown in Figs. 1–3, the complexes being numbered according to Table 1. The TG and DTA curves in complex IV exhibit two distinct thermal steps, the first corresponding to the evolution of water and the second to the liberation of one mole of methylamine coordinated. Two thermal steps are also observed in complexes III, V, and VI, the second step corresponding to the liberation of

two moles of amines. On the other hand, no such distinct steps accompanied by the liberation of ammonia could be observed in complexes I and II owing to rapid decomposition. The liberation of amines in each complex was confirmed.

Thermal Two-mol-deamination Reaction ($[\text{Co}(A)_2(\text{phbgH})_2]X_3 \cdot n\text{H}_2\text{O} \rightarrow \text{Co(II)-product} + 2A + n\text{H}_2\text{O}$). Complexes III, V, and VI fall in this category; complex III is discussed in detail. The gas evolved from complex III by isothermal heating at 160 °C in a silicon bath was dissolved in water. The resulting solution turned violet by addition of an ethanol containing chloranil ($\text{C}_6\text{Cl}_4\text{O}_2$). The solution was neutralized with dilute hydrochloric acid and concentrated to obtain white precipitates. The IR spectrum of the precipitates resembles that of methylamine hydrochloride prepared as a reference material. The results support the view that the evolved gas is not ammonia formed by the decomposition of phbgH , but methylamine itself.

Figure 4 shows the IR spectra of complex III before and after heating together with the spectrum of complex IV. By comparing their IR spectra with that of methylamine hydrochloride, the peaks at 1419, 1293, and 817 cm^{-1} before heating are considered to be characteristic bands with respect to methylamine. They disappeared completely after heating. Thus, the liberated molecule was found to be two moles of the coordinated methylamine in *trans* position.

Figure 5 shows the far-IR spectra of complex III before and after heating. The peak at 498 cm^{-1} , which is due to the $\text{Co-N}(\text{CH}_3\text{NH}_2)$ stretching vibration, disappears upon heating. On the other hand, the

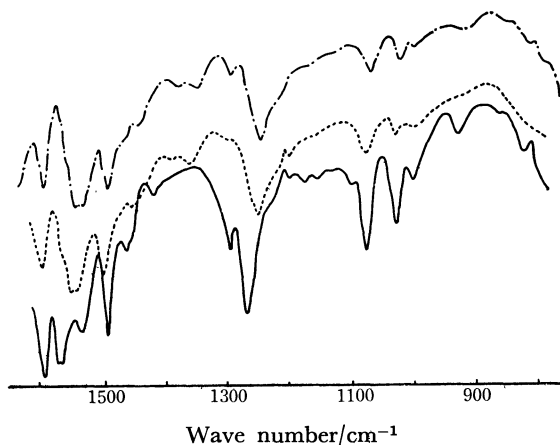


Fig. 4. IR spectra of complex III before heating (—) and after heating (----), and complex IV after heating (—·—).

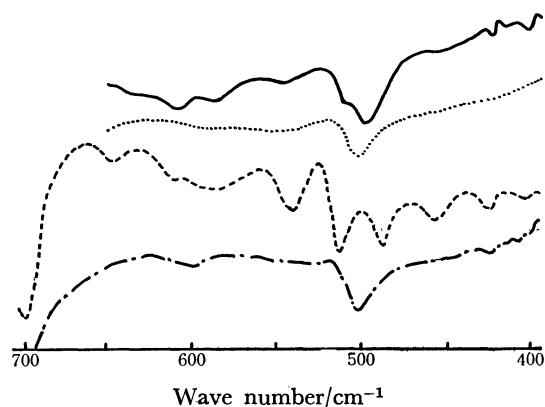


Fig. 5. Far-IR spectra of complex III before heating (—) and after heating (.....), and complex VI before heating (----) and after heating (—·—).

peak at 510 cm^{-1} assignable to the $\text{Co-N}(\text{phbgH})$ stretching vibration remains even after heating. The assignments of these peaks were made by a comparison of the two peaks appearing in the other *trans*-diamine-bis(phbgH) complexes.

The analytical data, absorption maxima and magnetic moments for all the complexes obtained upon heating are summarized in Table 2. The electronic spectrum of complex III in the solid state changes remarkably upon heating (Fig. 6). The distinct feature of the spectra commonly found in these complexes before heating lies in the strong charge transfer band, which covers the second absorption band, suggesting the presence of the strong π -bond character

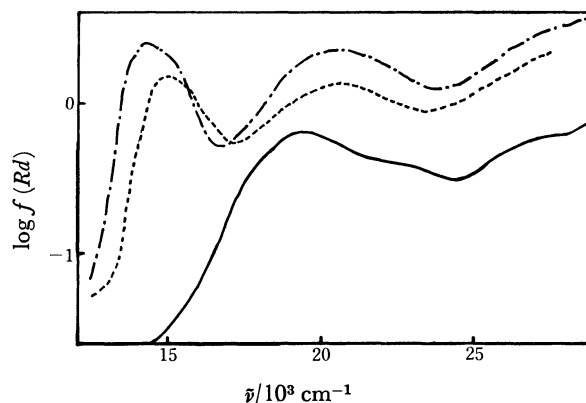


Fig. 6. Electronic spectra of complex III before heating (—) and after heating (----), and complex IV after heating (—·—).

TABLE 2. ANALYTICAL DATA, ABSORPTION MAXIMA, AND MAGNETIC MOMENTS OF THE PRODUCTS OBTAINED

Starting complex	Product	Analytical data						Absorption maxima ($\bar{\nu}/10^3 \text{ cm}^{-1}$)		μ_{eff} (B.M.)
		C %		H %		N %				
		Found	Calcd	Found	Calcd	Found	Calcd			
III	[CoCl(phbgHCl) ₂]	36.57	36.98	4.40	4.27	26.85	26.95	14.8	20.7	2.40
IV	[Co(CH ₃ NH ₂)(phbgHBr) ₂]Br	30.08	29.85	3.98	3.98	22.18	22.52	14.3	20.7	2.57
V	[CoCl(phbgHCl) ₂]	37.19	36.98	4.35	4.27	25.23	26.95	14.9	20.7	2.74
VI	[CoBr(phbgHBr) ₂]·2H ₂ O	29.25	29.42	3.95	3.40	21.09	21.45	14.7	20.5	2.96

of the phbgH to the metal. On the other hand, three bands including charge transfer band are observed after heating at 160 °C. The obvious difference in the spectra before and after heating is the appearance of the peak at $14.8 \times 10^3 \text{ cm}^{-1}$ after heating. The peak has a narrow half-width characteristic of bivalent cobalt complexes.¹⁴⁾ In studies on the low spin five-coordinated cobalt(II) complexes, three peaks are often detected at 6—9, 14—17, and 19—25 $\times 10^3 \text{ cm}^{-1}$.¹⁵⁾ The spectral pattern of the product resembles them, especially those of the five-coordinated complexes, $[\text{CoCl}(\text{dpe})_2]\text{ClO}_4$ ^{15d)} and $\beta\text{-Co}(\text{paphy})\text{Cl}_2$,^{15e)} where dpe and paphy are 1,2-bis-(diphenylphosphino)ethane and 1,3-bis-(2'-pyridyl)-2,3-diaza-1-propene, respectively.

The value of 2.4 B. M. for the heated product of complex III suggests it to be the low spin cobalt(II) complexes.¹⁶⁾ Since the coordination structure of the C_{4v} symmetry mode is considered to require low spin state from the ligand field splitting pattern¹⁷⁾ and two molecules of biguanides coordinated have a tendency to occupy the plane containing a metal ion in the bis-type complexes,^{10,11)} the product is presumed to be the low spin, square pyramidal five-coordinated cobalt(II) complex.

The evolved gas analyses for chlorine were carried out to confirm whether or not the reduction by halide ions takes place. However, neither the color reaction by *o*-tolidine (3,3'-dimethylbenzidine) nor KI-starch method denied the evolution of gaseous chlorine. In order to detect chlorine, the solution containing the evolved gas was acidified with sodium hydrogensulfite which can convert chlorine into chloride ion. However, addition of silver nitrate to the solution produced no precipitates of silver chloride. Furthermore, no mass losses corresponding to the evolution of gaseous chlorine were observed in the TG curve. Thus, it is conceivable that the reduction is not due to the chloride ions in outer-sphere. The coordinated methylamines are also not responsible for the reaction since they were liberated without any change in structure.

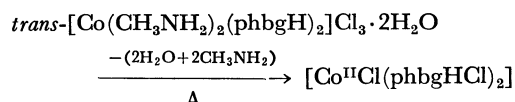
The cause might be attributed to the ligand (phbgH), which forms a six-membered chelate ring with π -electron delocalization with a metal ion. The reduction of Co(III) to Co(II) ion can be understood to be due to the electron transfer from the two π -electron-rich phbgH's to the central cobalt ion. This is supported by the IR and far-IR data. As is shown in Fig. 4, both bands at 1572 and 1267 cm^{-1} in complex III which are assigned to the stretching vibrations of C=N and C-N bonds, respectively, shift to lower wavenumber regions by about 20 cm^{-1} . The shifts may arise from the decrease of π -electron delocalization in the phbgH due to the electron transfer from the phbgH to the cobalt(III) ion.

The decrease in the stretching vibration of Co-N (phbgH) is also observed in far-IR region upon heating (510 sh \rightarrow 502 cm^{-1} , Fig. 5). The decrease may result from the difference in the force constants of Co(III)-N and Co(II)-N bonds. Actually, the values of the force constants in the hexaammine complexes are reported to be 1.05 and 0.33 mdyn/\AA(UBF) for Co(III)-N and

Co(II)-N, respectively,¹⁸⁾ the energy difference in the stretching vibrations being beyond 100 cm^{-1} . Taking the above value into account, the energy difference observed in the stretching vibrations of Co(III)-N (phbgH) and Co(II)-N(phbgH) is considerably smaller. Such difference between the known and the observed values may be ascribed to the increasing character of the covalent bond between cobalt and phbgH in the bivalent cobalt complex, which supports the occurrence of the inner-sphere electron transfer reaction.

The final problem is to determine the outcome of the chloride ions upon heating, which are generally known to enter into the coordination sphere through anation. A key to this lies in the appearance of a peak at 1355 cm^{-1} in the IR region which is newly observed after heating (Fig. 4). PhbgH is thought to have the coordination mode with a positive charge at N(4) site due to the six membered ring aromaticity.¹¹⁾ The positive charge will increase owing to the electron transfer. It is reasonable to consider that the band is attributable to the vibration of the $\text{NH}^+\text{-Cl}^-$ which seems to be formed after heating. Thus, of the three chloride ions, two are added to the phbgH, and the remaining one enters into the coordination sphere.

The following reaction scheme can be represented for the thermal electron transfer reaction of complex III.



The product is stable in the solid state, but unstable in various solvents; it decomposes even by the addition of ethanol separating white crystals. The IR spectrum of the crystals shows the structure of the phbgH to remain even after the electron transfer reaction.

The patterns of the thermal reactions of complexes V and VI can be understood in a similar way. As an example, the far-IR spectra of complex VI are shown in Fig. 5. The three peaks at 645, 487, and 455 cm^{-1} which are specified to be in-plane ring deformation of pyridine molecule, Co-N(py) stretching vibration and out of plane ring deformation of pyridine molecule, respectively, are entirely quenched by the thermal treatment. This indicates the liberation of two moles of the coordinated pyridine.

The band shifts and the appearance of the peak near 1350 cm^{-1} upon heating of complexes V and VI are summarized in Table 3. The bands of the Co-N (phbgH) stretching vibration are also shifted to lower

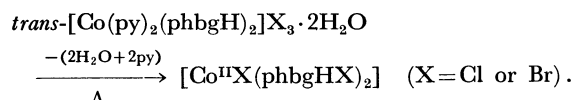
TABLE 3. IR DATA OF COMPLEXES V AND VI BEFORE AND AFTER HEATING

	Complex V		Complex VI	
	Before heating (cm^{-1})	After heating (cm^{-1})	Before heating (cm^{-1})	After heating (cm^{-1})
$\nu_{\text{C}=\text{N}}$	1550	1540	1550	1538
$\nu_{\text{C}-\text{N}}$	1270	1247	1273	1248
δ_{NH_2}	1674	1685	1668	1679
$\delta_{\text{NH}^+-\text{X}^-}$	—	1354	—	1356

wavenumber regions in the far-IR spectra ($510 \rightarrow 504 \text{ cm}^{-1}$, and $513 \rightarrow 502 \text{ cm}^{-1}$ for complexes V and VI, respectively).

The electronic spectral pattern of both products obtained upon heating are identical with the pattern of complex III. The absorption maxima and the values of magnetic moments are given in Table 2 for the products of complexes V and VI.

The following thermal electron transfer reactions are considered to proceed during the course of thermal treatment in complexes V and VI:

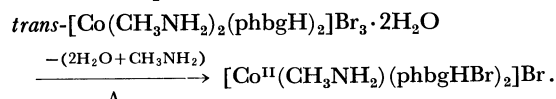


Thermal One-mol-deamination Reaction ($[\text{Co}(\text{A})_2(\text{phbgH})_2]\text{X}_3 \cdot n\text{H}_2\text{O} \rightarrow \text{Co}(\text{II})\text{-product} + \text{A} + n\text{H}_2\text{O}$).

The IR spectrum of complex IV after heating is shown in Fig. 4. The peaks at 1292 , 1000 , and 820 cm^{-1} , characteristic of methylamine, remain even in the heated product. Shifts similar to those of complexes III, V, and VI are observed in the IR region upon heating ($\nu_{\text{C}=\text{N}}$, $1561 \rightarrow 1545 \text{ cm}^{-1}$; $\nu_{\text{C}-\text{N}}$, $1258 \rightarrow 1243 \text{ cm}^{-1}$), suggesting the occurrence of electron transfer from the phbgH to the cobalt(III) ion. A new peak assignable to the vibration of the NH^+-Br^- bond appears at 1350 cm^{-1} .

The electronic spectral pattern of the product was analogous to those of complexes III, V, and VI. However, the absorption maximum of the product from complex IV ($14.3 \times 10^3 \text{ cm}^{-1}$) appears in a lower wavenumber region to some extent as compared with those ($14.7\text{--}14.9 \times 10^3 \text{ cm}^{-1}$) of complexes III, V, and VI (Table 2). The shift is attributable to the coordination of the remaining one mole of methylamine.

The following equation might hold for the thermal reaction of complex IV:



Difference in the Ease of Electron Transfer. A comparison of the liberation temperatures of amines is suitable for estimating the reactivity in the thermal reaction. The temperatures observed in the derivatograms are summarized as deamination temperatures in Table 1. We see the following order of reactivity depending upon the kind of the coordinated amine and counter ion.

- i) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{py}$
- ii) $\text{Br}^- < \text{Cl}^-$

Order i), the reverse of that in the strength of the ligand field, is the order of the ease of the liberation of the coordinated amine. This is understandable if the liberation of the coordinated amines is considered to

be a trigger of the reactions. The fact that ammine complexes I and II decomposed without a distinct liberation step of ammonia upon heating can be explained by the fact that the temperatures of complexes I and II reached the decomposition points prior to the liberation of the coordinated ammonia. The liberation temperatures of ammonia in these complexes might be higher than those of the methylamine or pyridine complexes.

Order ii) is related to the order of the ease of anation and addition of the halide ions to phbgH.

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