

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF  
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## Synthesis and Isomerization of Nitritopentammine Complexes of Rhodium(III), Iridium(III), and Platinum(IV)

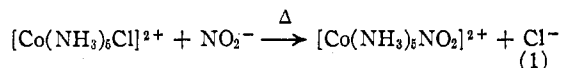
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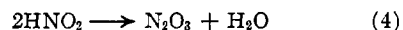
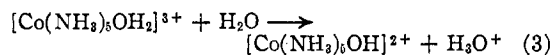
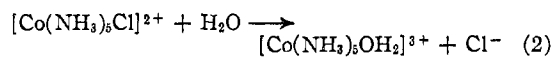
The syntheses and properties of the new nitritopentammine complexes,  $[(\text{NH}_3)_5\text{M-ONO}]^{n+}$  where  $\text{M} = \text{Rh(III)}$ ,  $\text{Ir(III)}$ , and  $\text{Pt(IV)}$ , are reported. The method of preparation of these complexes was based on the mechanism proposed earlier for the formation of the known  $\text{Co(III)}$  compounds. The rates of formation of these nitrito complexes and of their rearrangement to the nitro isomers,  $[(\text{NH}_3)_5\text{M-NO}_2]^{n+}$ , were determined.

Mechanisms of reactions of metal complexes have been studied in some detail and progress has been made toward a better understanding of these reaction processes. It is hoped that such knowledge will lead to the synthesis of new compounds and to new methods for the preparation of known compounds.<sup>2</sup> Recently the compounds  $[(\text{NH}_3)_5\text{Co-O}(\text{C}=\text{O})\text{C}_6\text{H}_5\text{COOH}](\text{ClO}_4)_2$ <sup>3</sup> and  $\text{K}_6[(\text{NC})_5\text{Fe}(\text{CNC})\text{Co}(\text{CN})_5]^{4-}$  were prepared by making use of information on the mechanism of oxidation-reduction reactions in these systems.

A few years ago the apparently simple reaction



was studied<sup>5</sup> and found to be complex. The following five steps appear to be involved



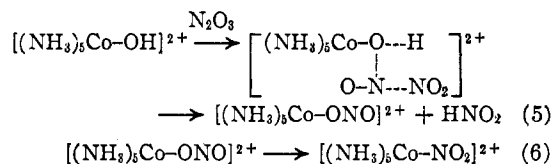
(1) Taken in part from the Ph.D. Thesis of G.S.H., Northwestern University, 1961.

(2) F. Basolo, *Chem. and Eng. News*, **39**, 86 (1961).

(3) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **82**, 4152 (1960).

(4) A. Haim and W. K. Wilmarth, *ibid.*, **83**, 509 (1961).

(5) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *ibid.*, **76**, 5920 (1954).



Of particular significance in this reaction scheme is the O-nitrosation step (5), which suggests that the Co-O bond is not cleaved and that the kinetic product is therefore the unstable nitrito (Co-ONO) isomer. This then rearranges to the stable nitro (Co-NO<sub>2</sub>) linkage isomer. Oxygen-18 experiments<sup>6</sup> subsequently have confirmed the fact that there is no rupture of the Co-O bond during this process.

This mechanistic concept for the formation of nitrito complexes of cobalt(III) suggests that other analogous metal systems should yield similar materials. However, no other example of linkage isomerism for metal complexes had been reported. One reason that previous investigators had not been successful is that the platinum group metal complexes are usually very slow to react and rather drastic reaction conditions had been used. As a result the stable nitro product rather than the kinetic nitrito product had been isolated. Since the formation

(6) R. K. Murmann and H. Taube, *ibid.*, **78**, 4896 (1956).

of M-ONO does not involve M-O bond cleavage, the reaction as shown in equation 5 is expected to occur even at rather mild experimental conditions. This was found to be the case and salts of the new complexes  $[(\text{NH}_3)_5\text{M-ONO}]^{n+}$ , where  $\text{M} = \text{Rh(III)}, \text{Ir(III)}, \text{and Pt(IV)}$ , have been prepared.<sup>7</sup> The syntheses and the kinetics of formation and isomerization of these complexes are described here.

### Experimental

**Preparation of Compounds.**—The desired nitropentamine complexes of Rh(III), Ir(III), and Pt(IV) were prepared and isolated by almost the same procedure in each case. Metal powders obtained from Baker and Co. were used as the starting materials. The metals were converted by standard methods into  $\text{K}_3\text{RhCl}_6$ ,  $\text{Na}_3\text{IrCl}_6$ , and  $(\text{NH}_4)_2\text{PtCl}_6$ , respectively. For rhodium and iridium this involved passing  $\text{Cl}_2$  over a mixture of the metal plus alkali metal halide at a temperature of approximately  $580^\circ$ . The aqueous filtrate, after removal of unreacted metal by filtration, was used directly to prepare the pentamine complexes. For platinum the procedure was to dissolve the metal in aqua regia and then add  $\text{NH}_4\text{Cl}$  to precipitate  $(\text{NH}_4)_2\text{PtCl}_6$ .

Except for the preparation of  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , all of the known compounds were prepared by methods described previously. Thus the reaction of the above mentioned aqueous filtrate containing Rh(III) with  $\text{NH}_4\text{Cl}$  plus  $(\text{NH}_4)_2\text{CO}_3$  yielded  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .<sup>8</sup> This then was allowed to react with  $\text{KOH}$  and the reaction mixture finally acidified to give  $[\text{Rh}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_3$ .<sup>9</sup>

The methods reported for the synthesis of  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  are somewhat troublesome and give rather low yields. It was found that the method used for rhodium can be applied to iridium. This procedure is much easier and gives better yields than the methods reported previously. A reaction mixture of 2.5 g. of Ir and 5.0 g. of  $\text{NaCl}$  was chlorinated at  $580^\circ$  for 40 min. and the resulting solid was extracted with acetone to remove  $\text{Na}_2\text{IrCl}_6$ . The remaining solid then was extracted with 75 cc. of water and the unreacted Ir was removed by filtration. To this filtrate was added 15 g. of  $\text{NH}_4\text{Cl}$  and 25 g. of  $(\text{NH}_4)_2\text{CO}_3$ . The reaction mixture was heated on a steam-bath. During the first hour the solution changed in color from greenish-black to yellow. Upon continued heating for a period of approximately 6 hr. a yellow precipitate slowly formed. This yellow precipitate was collected and extracted with 100 cc. of 3 *M*  $\text{HCl}$  to remove most of the  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . The insoluble material was largely  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and this was purified as described previously.<sup>10</sup> A yield of 1.3 g. of  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was obtained. This was converted into  $[\text{Ir}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_3$  by refluxing in aqueous  $\text{KOH}$  for 8 hr. and then acidifying with excess 12 *M*  $\text{HCl}$  in the cold.<sup>11</sup>

(7) F. Basolo and G. S. Hamaker, *J. Am. Chem. Soc.*, **82**, 1001 (1960).

(8) Gmelin, "Handbuch der anorganischen Chemie," **64**, 134 (1938).

(9) Reference 8, p. 109.

(10) Gmelin, "Handbuch der anorganischen Chemie," **67**, 157 (1939).

(11) Reference 10, p. 144.

The reaction of  $(\text{NH}_4)_2\text{PtCl}_6$  with liquid  $\text{NH}_3$  at room temperature was used to prepare  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ .<sup>12</sup> Again, refluxing an aqueous solution of this complex with caustic and acidification yielded  $[\text{Pt}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_4$ .<sup>12</sup>

The compounds  $[\text{M}(\text{NH}_3)_5\text{ONO}]\text{Cl}_n$  were prepared by the reaction between  $[\text{M}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_n$  and  $\text{NaNO}_2\text{-HCl}$  at  $0^\circ$ . The method of synthesis can be illustrated by that used for  $[\text{Rh}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ . An aqueous solution containing 0.5 g. of  $[\text{Rh}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_3$  in 15 cc. of water was cooled in an ice-bath. To this was added 0.8 g. of solid  $\text{NaNO}_2$ . As soon as it dissolved, 1 cc. of cold 12 *M*  $\text{HCl}$  was added with stirring. A white crystalline precipitate started to separate almost immediately. After about 30 min. the solid product was collected on a filter, washed with ethanol and acetone, and air-dried at room temperature; yield, 0.37 g. (76% of theory).

*Anal.* Calcd. for  $[\text{Rh}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ : Rh, 33.8; N, 27.5; Cl, 23.3; H, 4.92. Found: Rh, 33.9; N, 28.0; Cl, 23.3; H, 4.69.

Exactly the same procedure was used to prepare  $[\text{Ir}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ . A reaction mixture containing 0.7 g. of  $[\text{Ir}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_3$  in 20 cc. of water to which was added 1.0 g. of  $\text{NaNO}_2$  and 1 cc. of 6 *M*  $\text{HCl}$  yielded 0.54 g. (83% of theory) of product.

*Anal.* Calcd. for  $[\text{Ir}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ : N, 21.3; Cl, 18.0; H, 3.80. Found: N, 21.2; Cl, 17.6; H, 3.7.

The isolation of  $[\text{Pt}(\text{NH}_3)_5\text{ONO}]\text{Cl}_3$  was plagued with difficulties, but finally a usable method was found and the compound was obtained in suitable yield. A reaction mixture of 1.0 g. of  $[\text{Pt}(\text{NH}_3)_5\text{OH}_2]\text{Cl}_4$ , 25 cc. of water, 1.4 g. of  $\text{NaNO}_2$ , and 1 cc. of 6 *M*  $\text{HCl}$  was allowed to stand for 2 hr. at  $0^\circ$ . Air was bubbled through the solution for 15 min. and then an equal volume of cold 12 *M*  $\text{HCl}$  was added. The crystalline precipitate formed was washed with cold water followed by acetone, and the dried product weighed 0.55 g. (57% of theory).

*Anal.* Calcd. for  $[\text{Pt}(\text{NH}_3)_5\text{ONO}]\text{Cl}_3$ : Pt, 45.2; N, 19.3; H, 3.48. Found: Pt, 45.6; N, 18.0; H, 3.74.

The procedure used for Rh(III) and Ir(III) also gave in good yield  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ . Similar attempts to prepare *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{ONO})_2]$  starting with *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$  yielded only the nitro isomer, *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ .

**Absorption Spectra of Compounds.**—The nitropentamines of Rh(III), Ir(III), and Pt(IV) are colorless to pale yellow and show almost no absorption in the visible region of the spectrum. The ultraviolet absorption spectra of these complexes and also of the analogous nitro- and aquopentamines were determined with a Beckman DK-2 recording spectrophotometer using 1-cm. quartz cells. The infrared spectra of the solids were determined with a Baird AB-2 recording infrared spectrometer. Both the KBr disk and Nujol mull techniques were used.

**Rates of Formation.**—The method used to follow the reaction between  $[\text{M}(\text{NH}_3)_5\text{OH}_2]^{n+}$  and  $\text{HNO}_2\text{-NO}_2^-$  buffer was similar to that described earlier.<sup>5</sup> This was done spectrophotometrically by observing the change in optical density of a reaction mixture at a predetermined wave length where the optical densities of the nitrito and nitro complexes are the same, or almost the same, and both are appreciably different from that of the aquo complex.

(12) Gmelin, "Handbuch der anorganischen Chemie," **68D**, 478 (1953).

For the Co(III) and Cr(III) systems which absorb in the visible region, the presence of  $\text{HNO}_2\text{-NO}_2^-$  does not interfere. However, the absorption of  $\text{HNO}_2\text{-NO}_2^-$  in the ultraviolet region, where the platinum metal systems must be studied, clearly causes trouble. One method that was tried and found to be unsatisfactory was the removal of aliquots from the reaction mixture and addition of these to an excess of sulfamic acid. This procedure removed the  $\text{HNO}_2\text{-NO}_2^-$  but introduced other complications so that the data were badly scattered and reproducible results could not be obtained.

The method finally used was to make measurements in the wave length region 270–320  $\text{m}\mu$  where the  $\text{HNO}_2\text{-NO}_2^-$  buffers have a broad absorption minimum. At buffer concentrations up to 0.1  $M$  there was fortunately still enough light transmitted to permit meaningful measurements. Thus by using the buffer as a blank, the changes in optical density observed gave rate constants which were reproducible with a precision of 5%. Measurements were made using 1-cm. quartz cells with a Beckman DU spectrophotometer equipped with thermo-spacers through which was circulated water from a constant temperature bath to maintain a cell compartment temperature of  $25 \pm 0.1^\circ$ . The complex concentration was approximately  $10^{-3} M$  and the  $\text{HNO}_2\text{-NO}_2^-$  was 0.05  $M$  or greater. Thus the kinetic data were plotted as pseudo-first order reactions and good straight line plots of  $\log(D_\infty - D_t)$  vs.  $t$  were obtained. The experimental values of  $D_\infty$ , optical density at infinite time, were used and these were in good agreement with the calculated values. First order rate constants were obtained from the slopes of these lines.

**Rates of Isomerization.**—The rates of isomerization of nitrito ( $\text{M-ONO}$ ) into nitro ( $\text{M-NO}_2$ ) complexes were studied both in the solid state and in solution. Rearrangement in the solid state was followed by observing the disappearance of the nitrito band at approximately 1060  $\text{cm}^{-1}$ . Most of the runs were made in KBr disks but a few of these were checked using Nujol mulls. Except for the relatively short period of time required for spectral measurements, the disk was kept at constant temperature  $\pm 0.5^\circ$  by placing it in a metal container suspended in a constant temperature bath. The concentration of the complex is proportional to  $\log T_0/T$ , since the cell length remains constant throughout a kinetic run. Zero percent transmittance was determined by placing a glass plate in the light path, since glass is opaque in this spectral region. Estimates of  $T_0$  were made by drawing a line connecting the base line immediately before and immediately after the nitrito band. Straight lines were obtained from plots of  $\log(\log T_0/T)$  vs.  $t$  with slopes equal to  $-k/2.303$ . The rate constants obtained were reproducible to within 5%.

Isomerizations in aqueous solution were followed by observing changes in optical density with a Beckman DU spectrophotometer. Measurements were made at wave lengths of maximum difference in optical density between the nitrito and nitro isomers. Again good first order rate plots were obtained which permitted estimates of the rate constants at various temperatures. In all cases the absorption spectra of the final solutions were in good agreement with the known spectra of the nitropentamine complexes.

## Results

The infrared spectra of the nitropentamine complexes of Rh(III), Ir(III), Pt(IV), and Cr(III) are shown in Fig. 1. Also shown are the

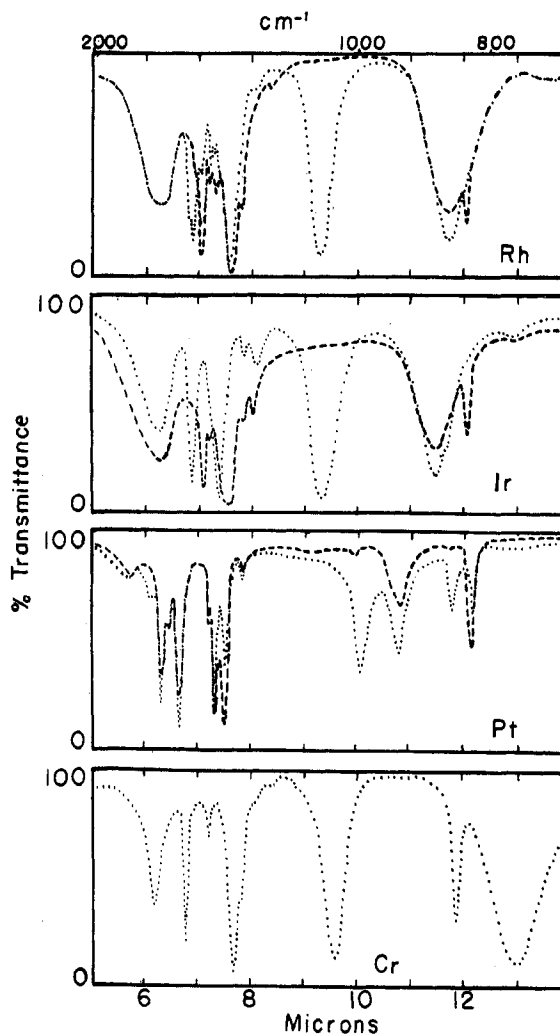


Fig. 1.—Infrared spectra of nitrito- and nitropentamine complexes: .....  $[(\text{NH}_3)_5\text{M-ONO}]^{n+}$ , ----  $[(\text{NH}_3)_5\text{M-NO}_2]^{n+}$ .

spectra of the nitro isomers which form on aging.

The rates of formation of  $[\text{M}(\text{NH}_3)_5\text{ONO}]^{n+}$  at an ionic strength of 1.125 and a temperature of  $25^\circ$  are summarized in Table I. Data for Co(III), reported previously,<sup>5</sup> are included for comparison.

The rates of isomerization  $[(\text{NH}_3)_5\text{M-ONO}]^{n+} \rightarrow [(\text{NH}_3)_5\text{M-NO}_2]^{n+}$  in the solid state are given in Table II and in aqueous solution in Table III. Data for Co(III) also are given for comparison.

## Discussion

The most significant contribution to report here is that it was possible to prepare the new com-

TABLE I  
 RATES OF FORMATION OF NITRITOPENTAMMINE COMPLEXES AT  $\mu = 1.125[\text{NaClO}_4]$  AND  $25^\circ$ 

$$[\text{M}(\text{NH}_3)_5\text{OH}_2]^{n+} \xrightarrow[k]{} [\text{M}(\text{NH}_3)_5\text{ONO}]^{n-1+}$$

[NO <sub>2</sub> <sup>-</sup> ], M	[HClO <sub>4</sub> ], M	$k \times 10^4, \text{sec.}^{-1}$				
		Rh(III) <sup>a</sup>	Ir(III) <sup>b</sup>	Pt(IV) <sup>c</sup>	Cr(III) <sup>d</sup>	Co(III) <sup>e</sup>
0.1	0.0125	6.0	19.	...	25.	10.
.1	.0063	3.2	10.	...	...	5.3
.05	.0063	1.5	4.4	...	6.8	2.7
.05	.0125	2.6	7.7	4.0	9.6	4.0
.05	.00125	0.31	0.90	...	...	...
.20	.0250	...	...	...	100.	42.
.20	.0125	...	...	...	51.	23.
.20	.0063	...	...	...	26.	10.

<sup>a</sup> [Rh(III)] =  $2.0 \times 10^{-3} M$ , measured at 297 m $\mu$ . <sup>b</sup> [Ir(III)] =  $7.5 \times 10^{-4} M$ , measured at 275 m $\mu$ . <sup>c</sup> [Pt(IV)] =  $2.0 \times 10^{-4} M$ , measured at 295 m $\mu$ . <sup>d</sup> [Cr(III)] = 0.02 M, measured at 480 m $\mu$ . <sup>e</sup> From reference 5.

 TABLE II  
 RATES OF ISOMERIZATION OF NITRITOPENTAMMINE  
 COMPLEXES IN THE SOLID STATE<sup>c</sup>

$$[(\text{NH}_3)_5\text{M-ONO}]^{n+} \longrightarrow [(\text{NH}_3)_5\text{M-NO}_2]^{n+}$$

Rhodium(III)		Iridium(III)	
Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>	Temp., °C.	$k \times 10^6$ , sec. <sup>-1</sup>
22	0.55	32	0.42 <sup>b</sup>
32	1.6 <sup>b</sup>	35	0.68
35	1.7	57	6.6
51	5.5	65	16.
$\Delta H^* = 18 \text{ kcal.};$		$\Delta H^* = 22 \text{ kcal.};$	
$\Delta S^* = -16 \text{ e.u.}$		$\Delta S^* = -10 \text{ e.u.}$	
Platinum(IV)		Cobalt(III) <sup>c</sup>	
Temp., °C.	$k \times 10^6$ , sec. <sup>-1</sup>	Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>
51	0.87	58	1.0
95	5.9	75	8.0
		$\Delta H^* = 26 \text{ kcal.};$	
		$\Delta S^* = 3 \text{ e.u.}$	

<sup>a</sup> Except where indicated the reactions took place in KBr disks. Measurements were made at the following cm.<sup>-1</sup>: Rh, 1060; Ir, 1056; Pt, 995. <sup>b</sup> Nujol mull. <sup>c</sup> Taken from reference 15. Measurements were made at 1065 cm.<sup>-1</sup> using KCl disks.

 TABLE III  
 RATES OF ISOMERIZATION OF NITRITOPENTAMMINE  
 COMPLEXES IN AQUEOUS SOLUTION<sup>a</sup>

$$[(\text{NH}_3)_5\text{M-ONO}]^{n+} \longrightarrow [(\text{NH}_3)_5\text{M-NO}_2]^{n+}$$

Rhodium(III)		Iridium(III)	
Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>	Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>
9.9	2.4	25.	0.44
25.	9.6	49.8	6.7
37.2	45.	73.5	46.
$\Delta H^* = 18 \text{ kcal.};$		$\Delta H^* = 19 \text{ kcal.};$	
$\Delta S^* = -12 \text{ e.u.}$		$\Delta S^* = -14 \text{ e.u.}$	
Platinum(IV)		Cobalt(III) <sup>b</sup>	
Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>	Temp., °C.	$k \times 10^4$ , sec. <sup>-1</sup>
25	0.56	20	0.17
		30	0.63
		$\Delta H^* = 22 \text{ kcal.};$	
		$\Delta S^* = -5 \text{ e.u.}$	

<sup>a</sup> Measurements were made at the following  $\mu$ : Rh, 250; Ir, 275; Pt, 300. <sup>b</sup> Taken from reference 16.

plexes  $[(\text{NH}_3)_5\text{M-ONO}]^{n+}$ , where M = Rh(III), Ir(III), and Pt(IV), by a method of synthesis implicit in the mechanism proposed<sup>5</sup> for the formation of  $[(\text{NH}_3)_5\text{Co-ONO}]^{2+}$ . Thus under the conditions of these experiments the low energy reaction path shown by equation 5 first yields the nitrito product because this does not require M-O bond cleavage. Since the rearrangement of this kinetic product to its stable nitro linkage isomer is slow, it is possible to isolate and characterize the nitrito form prior to its isomerization.

An attempt was made to prepare a nitrito complex of Pt(II) but this was not successful. Specifically, the reaction of *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> with HNO<sub>2</sub>-NO<sub>2</sub><sup>-</sup> gave an immediate crystalline precipitate of the nitro complex *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]. Further studies should be made on these systems. However, it may be that nitrite ion, known to be a good nucleophile toward platinum (II) complexes,<sup>13</sup> replaces the coordinated water by a direct attack on platinum(II). Otherwise, if O-nitrosation does occur and the nitrito complex is produced then it must rearrange rapidly into the stable nitro form. It is not difficult to see that such an intramolecular rearrangement may take place much more readily in a square complex than it does in an octahedral one.

The infrared spectra of these nitritopentamine complexes (Fig. 1) are in good agreement with the reported<sup>14</sup> spectrum of  $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ . Thus the bands assigned to Co-ONO stretching vibrations at 1460 and 1065 cm.<sup>-1</sup> are found to appear at approximately these frequencies for the analogous Rh(III) and Ir(III) complexes. For Pt(IV) these are shifted to 1505 and 995 cm.<sup>-1</sup>,

(13) D. Banerjee, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957).

(14) R. B. Penland, T. J. Lane, and J. V. Quagliano, *ibid.*, **78** 887 (1956).

respectively, and a new band appears at 850  $\text{cm}^{-1}$ . This particular M-ONO band is not observed for Co(III), Rh(III), and Ir(III) complexes because it is masked by the ammine rocking band which for these systems occurs in this region. The band however is visible for Cr-ONO (Fig. 1). It also is apparent that the nitrito complex of Pt(IV) contained some of the nitro isomer.

In all cases except Cr(III), the infrared spectra of the nitritopentammine complexes changed on aging to give the spectra expected for the M-NO<sub>2</sub> isomers (Fig. 1). For Rh(III) the bands that appeared on aging were at 1420 and 830  $\text{cm}^{-1}$ ; for Ir(III) at 1410 and 830  $\text{cm}^{-1}$ ; for Pt(IV) at 1330 and 825  $\text{cm}^{-1}$ . In all cases the M-ONO bands disappeared completely indicating that conversion into the stable M-NO<sub>2</sub> is complete within the experimental error of this method. For Co(III) the solid contains some Co-ONO at equilibrium.<sup>16</sup> The Cr(III) nitrito complex shows no sign of rearranging to the nitro form.

The data in Table I show that the rate law for the formation of the nitritopentammine complexes of Rh(III), Ir(III), and Cr(III), like that for Co(III) reported earlier,<sup>5</sup> conforms to the expression

$$\text{Rate} = k[\text{aquo complex}][\text{NO}_2^-][\text{HNO}_2]$$

or to its kinetic equivalent

$$\text{Rate} = k[\text{hydroxo complex}][\text{HNO}_2]^2$$

It therefore would seem that these reactions are all of the same type, involving O-nitrosation as shown in equation 5. In accord with this is the observation that at the same experimental conditions, the rates for all of these systems are of the same order of magnitude. This would not be expected were it necessary to break the M-O bond. Clearly, direct proof regarding M-O bond cleavage requires oxygen-18 experiments of the type used to demonstrate there is no Co-O bond rupture during the formation of Co-ONO.<sup>6</sup>

The rates of isomerization of the nitrito complexes to the nitro isomers are reported both for the solid state (Table II) and for aqueous solution (Table III). The rates of rearrangement in the solid are slower than in solution, as also was

observed for the Co(III) systems.<sup>16</sup> The rates of rearrangement are very similar for Co(III), Ir(III), and Pt(IV), but the rate for Rh(III) is an order of magnitude larger. This seemingly anomalous behavior of Rh(III) is not understood. In contrast to these systems the nitrito complex of Cr(III) appears to be the stable form as it does not isomerize in either the solid state or in solution. This is believed to result from the large affinity of Cr(III) for oxygen.

The results obtained for the rates of isomerization suggest that for these systems, as with Co(III),<sup>5,6</sup> the rearrangement involves an intramolecular process. First, the rates of rearrangement of the nitrito complexes in solutions containing no excess nitrite ion are too great to be compatible with a dissociation-recombination mechanism. Second, the entropies of activation for isomerization are negative suggesting a decrease in degrees of freedom in going from the ground to the transition states. Such would be the case if the activated complex did contain a nitro group at a mid-point in intramolecular rearrangement, where it is bound to the metal through both oxygen and nitrogen.<sup>6</sup>

An attempt was made to prepare nitropentamminechromium(III) by the reaction of  $[\text{Cr}(\text{NH}_3)_5\text{I}]_2$  with  $\text{AgNO}_2$  in N,N-dimethylformamide. This appeared to give only the nitrito isomer. Solid  $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  was irradiated with ultraviolet light for four days, but there was no evidence of isomerization into the nitro form. Similar treatment of the analogous nitro complexes of Rh(III), Ir(III), and Pt(III) showed some nitrito formation only with Ir(III). Adell<sup>17</sup> was able to irradiate  $[\text{Co}(\text{NO}_3)_5\text{NO}_2]\text{Cl}_2$  with sunlight and obtain  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ .

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(15) I. R. Beattie and D. P. N. Satchell, *Trans. Faraday Soc.*, **52**, 1590 (1956).

(16) B. Adell, *Svensk. Kem. Tidskr.*, **56**, 318 (1944).

(17) B. Adell, *Z. anorg. u. allgem. Chem.*, **279**, 219 (1955).