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## Synthesis of Pentaammine(phosphato)rhodium(III) and Kinetics of Formation of Its Diprotonated Form

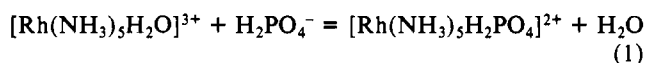
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The compound  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]\cdot 3\text{H}_2\text{O}$  has been prepared in pure form and characterized. The kinetics of formation of its diprotonated form,  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}$  from  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  and  $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ , has been studied in aqueous solution at 80, 90, and 97 °C ( $[\text{H}^+] = 0.8 \times 10^{-3}$ – $1.3 \times 10^{-1}$ );  $I = 1.0$  ( $\text{LiClO}_4$ ). Both  $\text{H}_3\text{PO}_4$  ( $k_1$  path) and  $\text{H}_2\text{PO}_4^-$  ( $k_2$  path) are reactive, but no evidence for outer-sphere association has been found. Values of the rate constants at 80, 90, and 97 °C are as follows:  $10^4 k_1$  ( $\text{M}^{-1} \text{s}^{-1}$ ) = 2.1, 5.4, 14;  $10^3 k_2$  ( $\text{M}^{-1} \text{s}^{-1}$ ) = 1.7, 5.5, 10. The results are interpreted in terms of a mechanism with associative activation. A comparison with existing data for anation of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  is made.

### Introduction

Whereas anation reactions of pentaammineaquocobalt(III) and pentaammineaquochromium(III) have been well studied,<sup>1-6</sup> the corresponding reactions of pentaammineaquorhodium(III) are not so well-known.<sup>7</sup> Following our interest in complexes containing phosphorus oxoanions,<sup>8,9</sup> we report in this paper the synthesis of pure  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]\cdot 3\text{H}_2\text{O}$  (hereafter referred to as the phosphato complex) and its characterization and a study of the kinetics of formation of its diprotonated form from the corresponding aquo complex (eq 1) in order to provide more data on the reactivity and substitution mechanisms of pentaammine complexes of Rh(III).



### Experimental Section

**Materials.** Stock solutions of phosphoric acid, lithium dihydrogen phosphate, and lithium perchlorate were prepared as previously described.<sup>3</sup>  $\text{RhCl}_3(\text{aq})$  (Johnson Matthey Chemicals) was used as a source of rhodium.  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  was prepared<sup>10</sup> from  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .<sup>11</sup> The spectrum of the aquo complex, maxima at 315 nm ( $\epsilon = 111 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 263 nm ( $\epsilon = 98 \text{ M}^{-1} \text{ cm}^{-1}$ ), was in good agreement with literature values.<sup>12</sup>  $[\text{Rh}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$  was prepared by the method of Palmer et al.<sup>13</sup> and characterized spectrophotometrically.

**Preparation of  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]\cdot 3\text{H}_2\text{O}$ .**  $[\text{Rh}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$  (0.4 g) and 85% phosphoric acid (40 mL) were heated at 80–85 °C on a water bath for 7 h. The resulting syrup was allowed to cool to room temperature and treated with distilled methanol (ca. 350 mL) under constant stirring until a precipitate started to form. The suspension was left in the refrigerator overnight and then centrifuged. The solid, which easily becomes an oil, was dissolved in the minimum amount of water and poured onto a 150 × 15 mm column of Lewatit MP 64 weakly basic anion-exchange resin (OH<sup>-</sup> form) and the effluent collected. The column was washed with water until the washings gave no basic reaction. The combined effluent and washings were treated with a 1/10 volume of concentrated ammonia and then with an excess of distilled ethanol that had been previously treated with activated charcoal (the ethanol used should be very pure, otherwise the UV bands of the impurities mask the bands of the phosphato complex). The yellow-white solid that precipitated

was filtered and washed with ethanol and air-dried. Anal. Calcd for  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]\cdot 3\text{H}_2\text{O}$ : PO<sub>4</sub>, 28.19; NH<sub>3</sub>, 25.22. Found: PO<sub>4</sub>, 28.1; NH<sub>3</sub>, 25.1. A solution of the diprotonated phosphato complex was obtained by dissolving the neutral species in 0.1 M HClO<sub>4</sub>.

**Analyses.** Phosphates were determined gravimetrically as quinolinium phosphomolybdate.<sup>14</sup> Ammonia was determined by distillation in the presence of Devarda alloy.

**Kinetic Runs.** The reaction was followed in situ at 340 nm in the cell compartment of a Beckman UV 5230 spectrophotometer that was thermostated by circulating water (80, 90 ± 0.1 °C) or ethylene glycol (97 ± 0.1 °C) from a Hetto 05 ultrathermostat. The temperature control was achieved with a copper–constantan thermocouple directly connected to the cell. Absorbance values were read from the recording chart. In the acidity range used ( $[\text{H}^+] = 0.8 \times 10^{-3}$ – $1.3 \times 10^{-1}$ ) the only relevant species derived from phosphoric acid are  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$ ; furthermore, given the low acidity constant of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ,  $\text{p}K_a = 6.9$  at 25 °C, the contribution of  $[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$  can be neglected since even at the lowest acidity the concentration ratio of  $[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$  to  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  is ca.  $2 \times 10^{-4}$ . The reaction was carried out with a great excess of total phosphate concentration,  $[\text{PO}_4]_{\text{T}} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-]$ , over that of aquo complex,  $7.00 \times 10^{-3} \text{ M}$  in all runs, thus ensuring pseudo-first-order conditions. Values of  $[\text{H}^+]$ ,  $[\text{H}_3\text{PO}_4]$ , and  $[\text{H}_2\text{PO}_4^-]$  were calculated from added HClO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and LiH<sub>2</sub>PO<sub>4</sub>. The ionic strength was adjusted to 1.0 with LiClO<sub>4</sub> in all runs. The runs carried out at low  $[\text{PO}_4]_{\text{T}}$  and/or low temperature (i.e., most at 80 °C, about half at 90 °C, and a few at 97 °C) do not reach 100% completion as can be shown by comparing experimental and calculated  $A_{\infty}$  values. To eliminate the contribution of the back-reaction (the aquation reaction) (see below), only the values of absorbance/time corresponding to the first approximately 20% of the reaction were used in computing first-order rate constants ( $k_{\text{obsd}}$ ).<sup>2</sup> These were obtained from the slopes of the plots of  $-\ln(A_{\infty} - A)$  vs. time, which were linear, thereby

$$-d[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}]/dt = k_{\text{obsd}}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] \quad (2)$$

The  $A_{\infty}$  values used in this formula correspond to those calculated on the assumption of 100% conversion. Errors quoted are standard deviations.

### Results and Discussion

**Characterization of the Phosphato Complex.** Seel and Bohnstedt<sup>15</sup> prepared the neutral phosphato complex, heavily contaminated by ammonium carbonate, and did not report spectra. We have been able to prepare it in a pure form, using a different procedure.  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]\cdot 3\text{H}_2\text{O}$  is a yellow-white stable solid, easily soluble in water. The IR spectrum (Figure 1) clearly shows the presence of monodentate phosphate group ( $C_{3v}$  symmetry) and is very similar to that of the cobalt<sup>16</sup> and chromium<sup>8</sup> analogues. Conductivity measurements ( $10^{-3} \text{ M}$ , 25 °C) give  $\Lambda = 23 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , a value somewhat high due to partial protonation of the neutral species but consistent with its formulation as a nonelectrolyte. The compound does not give an immediate precipitate

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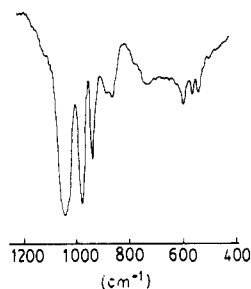


Figure 1. Infrared spectrum (KBr disk) of  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4] \cdot 3\text{H}_2\text{O}$ .

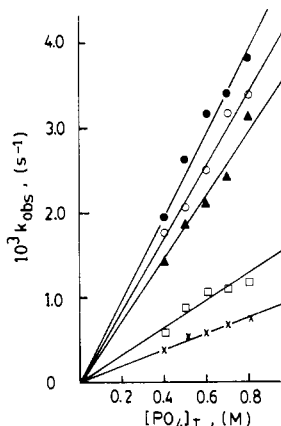
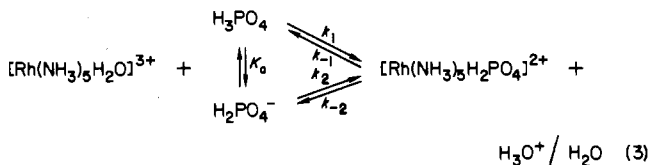


Figure 2. Variation of  $k_{\text{obs}}$  with  $[\text{PO}_4]_{\text{T}}$  for the reaction of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  and  $\text{H}_3\text{PO}_4$  at  $90^\circ\text{C}$ ,  $I = 1.0$  ( $\text{LiClO}_4$ ).  $[\text{H}^+]$  (M): 0.121 (x); 0.033 (□); 0.008 (▲); 0.0034 (○); 0.0008 (●).

with barium chloride in ammonia. The spectrum of the phosphato complex in aqueous solution changes with the pH, as with the Co and Cr analogues.<sup>8,17</sup> Seel and Bohnstedt<sup>15</sup> estimated by  $^{31}\text{P}$  NMR  $pK$  values for the different stages of protonation of the phosphato complex. According to their data, the species present in 0.01 M NaOH is the neutral complex,  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]$ :  $\lambda_{\text{max}}$  332 nm ( $\epsilon$  164  $\text{M}^{-1} \text{cm}^{-1}$ ), 272 (148). In the acidity range used in the kinetics study (e.g.,  $\text{HClO}_4$  (0.1 M)), the only spectrophotometrically significant species is the diprotonated complex,  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}$ :  $\lambda_{\text{max}}$  327 nm ( $\epsilon$  124  $\text{cm}^{-1} \text{M}^{-1}$ ), 267 (109).

**Kinetic Study.** A good retention of isosbestic points was obtained on running successive spectra of pentaammineaquo-rhodium(III) perchlorate with  $[\text{PO}_4]_{\text{T}} = 0.8 \text{ M}$  and  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$  at  $90^\circ\text{C}$ , indicating that the only significant reaction is (1). Table I gives  $k_{\text{obs}}$  as a function of total phosphate,  $[\text{PO}_4]_{\text{T}}$ , at different acidities and at each temperature. The plots of  $k_{\text{obs}}$  against  $[\text{H}_2\text{PO}_4^-]$  do not show any clear trend, which suggests that  $\text{H}_3\text{PO}_4$  is also a reacting species. The plots of  $k_{\text{obs}}$  against  $[\text{PO}_4]_{\text{T}}$  (Figure 2) are linear, indicating that the outer-sphere complexation of the aquo complex with phosphate species is not important. The reaction scheme (3) involving both  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  as reacting



species is proposed. The rate law corresponding to this scheme is (4), which can be rearranged to (5) by using the usual ex-

$$\begin{aligned}
 \text{rate} = -d[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} / dt = & \\
 & k_1[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}[\text{H}_3\text{PO}_4] + \\
 & k_2[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}[\text{H}_2\text{PO}_4^-] - \\
 & k_{-1}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}[\text{H}^+] - k_{-2}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}
 \end{aligned}
 \quad (4)$$

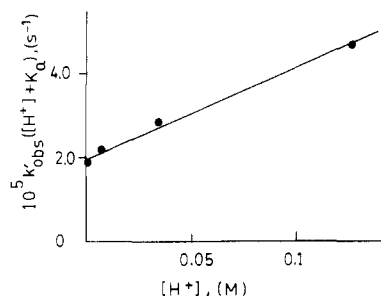
Table I. First-Order Rate Constants,  $k_{\text{obs}}$ , for the Anation of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  ( $7.00 \times 10^{-3} \text{ M}$ ) by Phosphate,  $I = 1.0$  ( $\text{LiClO}_4$ )

temp, °C	$10^2[\text{H}^+], \text{M}$	$[\text{PO}_4]_{\text{T}}, \text{M}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$		
80.0	0.08	0.8	1.16		
		0.7	1.10		
		0.6	0.98		
		0.5	0.80		
		0.8	0.89		
		0.7	0.78		
	0.8	0.6	0.77		
		0.5	0.59		
		0.4	0.52		
		3.5	0.8	0.50	
		0.7	0.42		
		0.5	0.34		
	90.0	0.08	12.7	0.8	0.295
			0.7	0.202	
			0.5	0.180	
			0.4	0.137	
0.8			3.8		
0.7			3.4		
0.34		0.6	3.3		
		0.5	2.66		
		0.4	1.95		
		0.8	3.4		
97.0	0.07	0.7	3.3		
		0.6	2.50		
		0.5	2.20		
		0.4	1.77		
		0.8	3.1		
		0.7	2.41		
	0.7	0.6	2.11		
		0.5	1.89		
		0.4	1.43		
		3.3	0.8	1.18	
		0.7	1.10		
		0.6	1.08		
		0.5	0.88		
		0.4	0.58		
11.9	12.1	0.8	0.75		
		0.7	0.68		
		0.6	0.58		
		0.5	0.53		
		0.4	0.36		
		0.8	6.8		
	3.1	0.7	6.2		
		0.6	5.0		
		0.5	4.9		
		0.7	5.0		
0.7	0.6	4.7			
	0.5	4.3			
	0.4	3.3			
	0.8	3.0			
11.9	0.7	2.62			
	0.5	2.28			
	0.4	1.98			
	0.8	1.68			
	0.7	1.44			
	0.5	1.42			
0.4	0.89				

$$\text{rate} = \frac{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}[\text{PO}_4]_{\text{T}}}{[\text{H}^+] + K_a} \frac{k_1[\text{H}^+] + k_2 K_a}{[k_1[\text{H}^+] + k_2]} \quad (5)$$

$$\begin{aligned}
 \text{expressions of } K_a \text{ as a function of } [\text{PO}_4]_{\text{T}} \text{ and } [\text{H}^+] \text{ or to (6) with} \\
 \text{rate} = a[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - b[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+} \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 a = \frac{[\text{PO}_4]_{\text{T}}(k_1[\text{H}^+] + k_2 K_a)}{([\text{H}^+] + K_a)} \text{ and } b = \frac{k_{-1}[\text{H}^+] + k_{-2}}{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}} \\
 \ln \frac{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}}{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}_0 - [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{PO}_4]^{2+}_0} = -(a + b)t \quad (7)
 \end{aligned}$$



**Figure 3.** Variation of  $k_{\text{obs}}' / ([\text{H}^+] + K_a)$  with  $[\text{H}^+]$  for the reaction of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  with  $\text{H}_3\text{PO}_4$  at 80 °C,  $I = 1.0$  ( $\text{LiClO}_4$ ).

absorbance (8) is obtained where (9) holds true.

$$-\ln [(A_{\text{eq}} - A) / (A_{\text{eq}} - A_0)] = k_{\text{app}} t \quad (8)$$

$$k_{\text{app}} = [\text{PO}_4]_{\text{T}} \frac{k_1[\text{H}^+] + k_2 K_a}{[\text{H}^+] + K_a} + k_{-1}[\text{H}^+] + k_{-2} \quad (9)$$

In about half of the runs, only the forward reaction is significant (see above) due to the combined effect of the increase of the equilibrium constant with the temperature and the shift of the equilibrium with the concentration of phosphate. Therefore, we have considered only the forward pathways for which their contributions in the value of  $k_{\text{app}}$  are always present. Then

$$k_{\text{obsd}} = [\text{PO}_4]_{\text{T}} (k_1[\text{H}^+] + k_2 K_a) / ([\text{H}^+] + K_a) \quad (10)$$

This expression will always hold in the first stages of the reaction, a region where the value of  $A_{\text{eq}}$  can be replaced by  $A_{\infty}$  (calculated on the assumption of 100% completion). Thus, (8) becomes

$$-\ln [(A_{\infty} - A) / (A_{\infty} - A_0)] = k_{\text{obsd}} t$$

(10) can be rearranged to

$$k_{\text{obsd}} = k_{\text{obsd}}' [\text{PO}_4]_{\text{T}} \quad (11)$$

with

$$k_{\text{obsd}}' = (k_1[\text{H}^+] + k_2 K_a) / ([\text{H}^+] + K_a) \quad (12)$$

The values of  $k_{\text{obsd}}'$  at each acidity are obtained from the plots of  $k_{\text{obsd}}$  against  $[\text{PO}_4]_{\text{T}}$ , which are linear (Figure 2). With knowledge of  $k_{\text{obsd}}'$  and  $K_a$  (obtained at the relevant temperatures by extrapolation of data at 25, 40, and 50 °C at  $I = 1.0$  ( $\text{LiClO}_4$ )),  $k_1$  and  $k_2$  can be obtained by plotting  $k_{\text{obsd}}' / ([\text{H}^+] + K_a)$  against  $[\text{H}^+]$  (Figure 3). The values of  $k_1$  and  $k_2$  at the three temperatures together with the activation parameters obtained from the usual Eyring plots are given in Table II. By using experimental values of  $A_{\infty}$  (i.e.,  $A_{\text{eq}}$ ) for some of the runs at 80 and 90 °C that do not reach completion, and doing additional equilibrium experiments at 70 °C, values of the equilibrium constant for reaction 1 can be determined spectrophotometrically. The values obtained are  $3.6 \pm 1.7$ ,  $8.2 \pm 2.5$ , and  $11.3 \pm 1.2$  M at 70, 80, and 90 °C, respectively.

The plots of  $k_{\text{obsd}}$  against  $[\text{PO}_4]_{\text{T}}$  are linear (Figure 2), indicating that the equilibrium constant for outer-sphere association of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  with  $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{PO}_4^-$  ( $K_{\text{OS}(1)}$  and  $K_{\text{OS}(2)}$ , respectively) are less than ca.  $0.2 \text{ M}^{-2}$ . The system  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{H}_2\text{PO}_4^-$  has been found to behave similarly.<sup>3</sup> Contrary to this, the same plots for the system  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$  show marked curvature,<sup>4</sup> allowing the determination of  $K_{\text{OS}}$ . These observations may be explained by outer-sphere association being less favorable on increasing the  $t_{2g}$  level population ( $\text{Cr}^{3+} t_{2g}^3$ ;  $\text{Co}^{3+}$ ,  $\text{Rh}^{3+} t_{2g}^6$ ).

The question as to whether anation reactions of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  proceed through an  $I_a$  or  $I_d$  mechanism is unsettled.<sup>2,7</sup> The volume of activation for the water-exchange process of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  is clearly negative ( $\Delta V^\ddagger = -4.1 \text{ cm}^3 \text{ mol}^{-1}$ ),<sup>18</sup> suggesting an associative mechanism. It is accepted<sup>6,19</sup> that a method to distinguish between an associatively activated mechanism, a, from a dissociatively activated mechanism, d, for the

**Table II.** Summary of Kinetic Data for the Anation of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  by  $\text{H}_3\text{PO}_4$  ( $k_1$ ) and  $\text{H}_2\text{PO}_4^-$  ( $k_2$ ),  $I = 1.0$  ( $\text{LiClO}_4$ )

temp, °C	$10^5 k_1, \text{M}^{-1} \text{s}^{-1}$	$10^5 k_2, \text{M}^{-1} \text{s}^{-1}$
80.0	$21.4 \pm 11.1$	$169 \pm 6$
90.0	$54.0 \pm 4.8$	$552 \pm 25$
97.0	$139 \pm 13.2$	$1030 \pm 79$
$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$26.5 \pm 3.2$	$27.1 \pm 1.0$
$\Delta S^\ddagger$ , cal K <sup>-1</sup> mol <sup>-1</sup>	$-0.91 \pm 8.8$	$5.0 \pm 2.7$

**Table III.** Summary of Rate Constants for Anation of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  by Different Entering Ligands, at 65 °C

entering ligand	$10^4 k_i, \text{s}^{-1}$	$10^4 k, \text{M}^{-1} \text{s}^{-1}$	ref
$\text{N}_3^-$	50	10.0	a
$\text{SO}_4^{2-}$	17	12.1	b
$\text{AcO}^-$	15	5.24	a
HGly		3.72	c
HProp		2.70	d
Prop <sup>-</sup>	6.13	9.56	d
$\text{Ox}^{2-}$	1.74	12.4	7
$\text{HOx}^-$	1.77	4.20	7
$\text{H}_2\text{Ox}$		1.79	7
$\text{Cl}^-$	39.7	7.15	e, b
$\text{Br}^-$	79	6.32	b
$\text{H}_2\text{PO}_4^-$		2.87	this work
$\text{H}_3\text{PO}_4$		0.35	this work
$\text{H}_2\text{O}$	14.9		7 <sup>f</sup>

<sup>a</sup> Chatterjee, C.; Chandhuri, P. *Indian J. Chem.* 1973, 11, 777.

<sup>b</sup> Monacelli, F. *Inorg. Chim. Acta* 1968, 2, 263. <sup>c</sup> Chatterjee, C.; Basak, A. K. *Bull. Chem. Soc. Jpn.* 1979, 52, 2710. <sup>d</sup> Chatterjee, C.; Bali, A. S. *J. Coord. Chem.* 1981, 11, 179. <sup>e</sup> Bott, H. L.; Poë, A. J.; Shaw, K. *J. Chem. Soc. A* 1970, 1745. <sup>f</sup> Monacelli, F.; Viel, E. *Inorg. Chim. Acta* 1967, 1, 467.

anation reaction (13) is the examination of the span of values of  $\text{ML}_5\text{S} + \text{X} \rightarrow \text{ML}_5\text{X} + \text{S}$  S = solvent (13)

rate constants for a wide series of different entering ligands, X. Although second-order rate constants ( $k = k_i K_{\text{OS}}$ ) are often used for such a purpose (with ligands of the same charge), it is more reliable that comparisons be made among first-order constants, since in this way differences in  $K_{\text{OS}}$  arising from both charge and nature of the entering ligand can be obviated. Thus, if the span of  $k_i$  values is small, the mechanism is d, and if it is sufficiently large, then the mechanism is a. Table III gives first- and second-order rate constants for the anation reaction of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  by a series of ligands at 65 °C and  $I = 1.0$ . The span of second-order rate constants for uninegative anions has been expanded a little by the  $\text{H}_2\text{PO}_4^-$  value and is  $(2.87-9.95) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . The small span for the Rh system does not seem to indicate a mechanism, but as we have indicated, the comparison should preferably be made among first-order rate constants. (Since we have not found any curvature in the plots of  $k_{\text{obsd}}$  vs. ligand concentration, which means that approximately  $K_{\text{OS}} < 0.1 \text{ M}^{-1,2}$  we have been unable to determine  $K_{\text{OS}}$  or  $k_i$ , but an estimated value of  $k_{i(2)}$  should be at least  $2.9 \times 10^{-4}/0.1$  or  $29 \times 10^{-4} \text{ s}^{-1}$ .) The span of first-order rate constants,  $k_i (=k/K_{\text{OS}})$ , is much larger,  $(1.79-79) \times 10^{-4} \text{ s}^{-1}$ . (Apparently  $K_{\text{OS}}$  values depend not only on the charge of the ligand but also on its nature.) The corresponding spans of  $k_i$  for the analogous Co(III) and Cr(III) systems are  $(1.6-7.4) \times 10^{-4}$  (70 °C)<sup>3</sup> and  $(1.45-14.2) \times 10^{-4}$  (50 °C).<sup>5</sup> According to this, the associative character of the anation reaction of  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  is greater than in  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ , which in turn is greater than in  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ . This trend can be associated<sup>19</sup> with the increasing size of the central metals ( $\text{Co} < \text{Cr} < \text{Rh}$ ). The value of the rate constant for the water exchange is smaller than some  $k_i$  values, a fact that again points to an a mechanism.<sup>6</sup>

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**Registry No.**  $[\text{Rh}(\text{NH}_3)_5\text{PO}_4]$ , 65584-33-0;  $[\text{Rh}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$ , 50600-90-3;  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ , 15337-79-8.

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