

## Acid Dissociation of Aquaamminerhodium(III) Complexes in Aqueous Solution

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The acid dissociation constants for several aquaamminerhodium(III) complexes have been determined from potentiometric titrations. The  $pK_a$  values measured in 1.0 M  $\text{NaClO}_4$  solution at 25.0 °C are as follows:  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ,  $pK_a = 6.93$ ; *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ,  $pK_{a1} = 6.40$ ,  $pK_{a2} = 8.32$ ; *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ,  $pK_{a1} = 4.92$ ,  $pK_{a2} = 8.26$ ; *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ ,  $pK_a = 7.84$ ; *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ ,  $pK_a = 6.75$ ; *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$ ,  $pK_a = 7.89$ ; *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$ ,  $pK_a = 6.87$ . The syntheses of the previously unknown *trans*- and *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$  salts were accomplished using the hydrido complex  $[\text{Rh}(\text{NH}_3)_5\text{H}]\text{SO}_4$  and the hydroxo aqua complex *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$  as the respective precursors. The various acidities of coordinated  $\text{H}_2\text{O}$  as a function of the remaining ligand field are rationalized in terms of combined  $\pi$ - and  $\sigma$ -bonding and electrostatic effects.

Dichloro- and dibromo-tetraamminerhodium(III) salts of both the *trans*- and the *cis*-series are well characterized compounds, and high yield syntheses are known.<sup>1,2</sup> These dihalo complexes have recently been used as precursors for the aquahalo-tetraamminerhodium(III) analogues<sup>3</sup> and also for *cis*-diaquatetraamminerhodium(III).<sup>4</sup> In each case, the aqua complexes are synthesized by thermal aquation of one or both of the coordinated halides. Attempts to prepare the *trans*-diaqua ion, *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  by analogous thermal aquation or by base hydrolysis were unsuccessful, but a procedure (reported here) utilizing the hydrido complex  $[\text{Rh}(\text{NH}_3)_5\text{H}]^{2+}$  as a precursor proved successful. These aqua ions and the hydroxo ana-

logues are quite active photochemically, undergoing both ligand substitution and stereoisomerization processes<sup>3,5</sup> but are thermally robust. The latter property allows the measurement of the acid dissociation constants for these ions by simple titrations in aqueous solution. The current series of complex ions provides an interesting opportunity to evaluate how the acidity of coordinated  $\text{H}_2\text{O}$  is a function of the composition and stereochemistry of the balance of the ligand field. Furthermore, these constants are of interest in characterizing fully the photochemical reaction patterns of various aquaammine- and hydroxoamminerhodium(III) complexes.<sup>3,5</sup>

### EXPERIMENTAL

**Materials.** Pentaamminehydridorhodium(III) sulfate,<sup>6</sup> pentaammineaquarhodium(III) perchlorate,<sup>7</sup> *cis*- and *trans*-tetraammineaquachlororhodium(III) dithionate,<sup>3</sup> *cis*- and *trans*-tetraammineaquabromorhodium(III) dithionate,<sup>3</sup> and *cis*-tetraammineaquahydroxorhodium(III) dithionate 0.2 hydrate<sup>4</sup> were all synthesized and purified by published methods. Other chemicals were of analytical or reagent grade. Doubly distilled water was used throughout. Analyses were made by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

**Instruments.** Electronic absorption spectra were recorded on a Cary Model 118C spectrophotometer. pH-Measurements were performed with a Sargent-Welch pH-meter model NX with a combination glass electrode modified to contain 1.0 M NaCl in the reference part.

*pH-Measurements.* The equilibrium studies reported were all done in a 1.0 M perchlorate medium. The definition  $\text{pH} = -\log[\text{H}^+]$  was employed throughout, using solutions of standardized perchloric acid in 1.0 M  $\text{NaClO}_4$  as pH-standards.

*Determination of  $pK_a$  values.* A weighed amount of complex (between 0.04 and 0.08 mmol) were dissolved in 10 ml of 1.0 M  $\text{NaClO}_4$  in a thermostatted beaker at 25.0 °C and titrated with  $\sim 0.04$  M NaOH in 0.96 M  $\text{NaClO}_4$  to  $\text{pH} \sim 10.5$  and then immediately backtitrated with  $\sim 0.05$  M  $\text{HClO}_4$  in 0.95 M  $\text{NaClO}_4$ . Due to slow dissolution of pentaammineaquarhodium(III) perchlorate in the actual medium, the concentration of this complex was evaluated from the titration curve. At each titration point, the function  $\bar{n}(\text{pH})$  was evaluated

$$\bar{n} = N + \frac{C_{\text{HClO}_4} - C_{\text{NaOH}} + [\text{OH}^-] - [\text{H}^+]}{C_{\text{complex}}}$$

where  $C_x$  denotes the concentrations of added perchloric acid, sodium hydroxide and complex ion, respectively, and  $N = 1$  for the monobasic,  $N = 2$  for the dibasic complex ions.  $[\text{OH}^-]$ , the concentration of hydroxide ion, was calculated using the value  $10^{-13.95} \text{ mol}^2/\text{l}^2$  for the ionic product of water in 1.0 M  $\text{NaClO}_4$ .<sup>8</sup> Calculations of  $pK_a$  values were done from the formula  $pK_a = \text{pH} + \log[\bar{n}/(1-\bar{n})]$  for the monobasic acids, and from:

$$pK_{a,1} = \text{pH} + \log \frac{\bar{n}-1}{2-\bar{n}} + \log \left( 1 + \frac{\bar{n}K_{a,2}}{(\bar{n}-1)[\text{H}^+]} \right)$$

$$2 < \bar{n} < 1$$

$$pK_{a,2} = \text{pH} + \log \frac{\bar{n}}{1-\bar{n}} - \log \left( 1 + \frac{(2-\bar{n})[\text{H}^+]}{(1-\bar{n})K_{a,1}} \right)$$

$$1 < \bar{n} < 0$$

for the dibasic acids.<sup>9</sup>

*Syntheses. cis-Tetraamminediaquarhodium(III) perchlorate, cis-[Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.* A 0.18 g portion of *cis*-tetraammineaquahydroxorhodium(III) dithionate 0.2 hydrate (0.50 mmol) was dissolved in 2 ml of 0.5 M  $\text{HClO}_4$ . The addition of 2 ml of 70 %  $\text{HClO}_4$  acid gave an almost white precipitate, which after cooling in ice was filtered off, washed with 5 drops of ice cold 2 M  $\text{HClO}_4$  and then with 0.5 ml of absolute ethanol. The product was dissolved in 2 ml of water and reprecipitated, then washed as before and air dried. Yield: 0.20 g (80 %). Anal. H, N, Cl.

*Crude trans-tetraammineaquahydroxorhodium(III) dithionate, trans-[Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(OH)]S<sub>2</sub>O<sub>6</sub>.* 1.00 g of pentaamminehydridorhodium(III) sulfate (3.7 mmol) was dissolved in 25 ml of 0.5 M  $\text{HClO}_4$  and heated to 50 °C for 5 min. The warm solution

was filtered and 1.5 ml of 30 %  $\text{H}_2\text{O}_2$  was added dropwise. The resulting yellow solution was heated to 90 °C for 1 h, protected against light, then 1.5 g of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  was dissolved in the warm solution. After cooling to room temperature the solution was filtered and pH adjusted to 7 by dropwise addition of 2 M NaOH. A cream colored product formed rapidly, and after cooling the mixture in ice for 2 h, this was filtered off, washed with 2 ml of ice water, twice with 3 ml of 95 % ethanol and finally with ether. Yield: 0.90 g (66 %). This product was purified as the *trans*-tetraamminediaquarhodium(III) perchlorate.

*trans-Tetraamminediaquarhodium(III) perchlorate, trans-[Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.* 0.90 g of crude *trans*-tetraammineaquahydroxorhodium(III) dithionate (2.5 mmol) was converted into the diaqua product by the procedure used for the *cis*-isomer (adjusting all volumes relatively). The reprecipitation was, however, performed once more for the *trans*-isomer. Yield 0.52 g (41 %). Anal.: H, N, Cl.

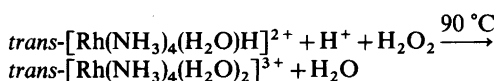
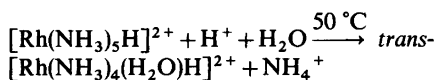
*trans-Tetraammineaquahydroxorhodium(III) dithionate, trans-[Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(OH)]S<sub>2</sub>O<sub>6</sub>.* 0.20 g of *trans*-tetraamminediaquarhodium(III) perchlorate (0.40 mmol) and 0.20 g of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  was dissolved in 2 ml of water. The solution was filtered and pH adjusted to 7 by addition of 2 M NaOH. The formed precipitate was filtered off after cooling in ice for 2 h, washed with 5 drops of icewater, than with 0.5 ml of 95 % ethanol. The product was recrystallized from the minimum volume of 90 °C warm water. Pale yellow crystals were slowly formed. After isolation and washing as before the yield was 0.12 g (82 %). Anal. H, N, S.

*Anation of the trans-tetraamminediaquarhodium(III) ion.* 14 mg of *trans*-[Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> was dissolved in 4 ml of 4 M HBr and boiled gently for 1 h. After cooling to room temperature and dilution to 10 ml the absorption spectrum ( $\lambda_{\text{max}}$ ,  $\epsilon$ ; 437 nm,  $142 \text{ mol}^{-1} \text{ l cm}^{-1}$ ) matched that of *trans*-tetraamminedibromorhodium(III) bromide<sup>1</sup> heated in HBr by the same procedure ( $\lambda_{\text{max}}$ ,  $\epsilon$ ; 437, 141).

*Base hydrolysis.* The extent of base hydrolysis of the complex ions was estimated by the following experiments. Spectral changes of solutions of the complex ions in 0.040 M NaOH and 0.96 M  $\text{NaClO}_4$  were monitored for 90 min at 25 °C. Such hydrolysis for rhodium(III) complexes are stereoretentive,<sup>10</sup> and from the spectral changes the following degrees of hydrolysis were calculated: *cis*-[Rh(NH<sub>3</sub>)<sub>4</sub>(OH)Cl]<sup>+</sup> 8 %; *cis*-[Rh(NH<sub>3</sub>)<sub>4</sub>(OH)Br]<sup>+</sup> 6 %; *trans*-[Rh(NH<sub>3</sub>)<sub>4</sub>(OH)Cl]<sup>+</sup> <0.7 %; *trans*-[Rh(NH<sub>3</sub>)<sub>4</sub>(OH)Br]<sup>+</sup> 1.5 %. For *trans*- and *cis*-[Rh(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>]<sup>+</sup> no hydrolysis was detectable under the experimental conditions used.

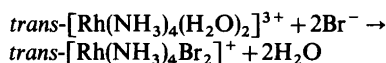
## RESULTS

*cis*-Tetraamminediaquarhodium(III) perchlorate has been synthesized by a simple conversion of the *cis*-tetraammineaquahydroxorhodium(III) dithionate. The synthesis of the latter by acid hydrolysis of the *cis*-tetraamminedichlororhodium(III) ion has recently been reported by Hancock.<sup>4</sup> Attempts to use the same method to prepare the *trans*-isomer were unsuccessful. No experimental conditions were found for the *trans*-tetraamminedichlororhodium(III) ion where both of the coordinated chlorides could be hydrolyzed without extensive hydrolysis of the coordinated ammonias. The *trans*-tetraamminediaquarhodium(III) ion was instead achieved according to the following reaction scheme:



The product was first isolated as the *trans*-tetraammineaquahydroxorhodium(III) dithionate. This salt, however, proved to be difficult to purify as such. A conversion to the *trans*-tetraamminediaquarhodium(III) perchlorate greatly aided the

purification process. The constant absorption spectrum obtained on repeated recrystallization displayed an absorption minimum sensitive to impurities ( $\lambda_{\text{min}}$ ,  $\epsilon$ ; 227 nm, 13 l mol<sup>-1</sup> cm<sup>-1</sup>; in 1.0 M HClO<sub>4</sub>). This spectral characteristic can be used as a criterion for purity. The assignment of this product to the *trans*-series was done on the basis of the well-documented<sup>1,6</sup> *trans*-labilizing effect of coordinated hydride in rhodium(III) ammine complexes and of the quantitative conversion of the complex ion into the *trans*-tetraamminedibromorhodium(III) ion by the stereoretentive anation with Br<sup>-</sup> (see Experimental):



The ligand field spectra of the aqua- and hydroxo complexes in aqueous 1.0 M perchlorate solution are tabulated in Table 1.

The estimated concentration acid dissociation constants, determined from at least two full titration curves for each complex, are given as pK<sub>a</sub> values in Table 2. No systematic deviations between the titrations with NaOH and the backtitrations with HClO<sub>4</sub> were observed. This observation indicates that neither hydrolysis nor polymerization reactions were important during the titration experiments, a conclusion confirmed by the spectrophotometric

Table 1. Ligand field spectra in 1.0 M aqueous perchlorate solution.

Complex Ion	Medium	$\lambda_{\text{max}}$ in nm ( $\epsilon$ in l mol <sup>-1</sup> cm <sup>-1</sup> )	
$[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$	0.10 M HClO <sub>4</sub> , 0.90 M NaClO <sub>4</sub>	315 (106),	263 (95)
$[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	319 (130),	277 (119)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	1.0 M HClO <sub>4</sub>	326 (107),	268 (89)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]^{2+}$ <sup>a</sup>	1.0 M NaClO <sub>4</sub> , pH = 7.35	329 (122),	279 (104)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})_2]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	335 (125),	283 (120)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	1.0 M HClO <sub>4</sub>	353 (52),	273 (94)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]^{2+}$ <sup>a</sup>	1.0 M NaClO <sub>4</sub> , pH = 6.59	347 (83),	291 (124)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})_2]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	347 (96),	303 (120)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$	0.10 M HClO <sub>4</sub> , 0.90 M NaClO <sub>4</sub>	348 (111),	283 (94)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Cl}]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	350 (121),	287 (98)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$	0.10 M HClO <sub>4</sub> , 0.90 M NaClO <sub>4</sub>	389 (55),	284 (117)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Cl}]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	372 (102),	289 (110)
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$	0.10 M HClO <sub>4</sub> , 0.90 M NaClO <sub>4</sub>	363 (126),	
<i>cis</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Br}]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	364 (131)	
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$	0.10 M HClO <sub>4</sub> , 0.90 M NaClO <sub>4</sub>	466 (39), <sup>b</sup>	406 (61)
<i>trans</i> - $[\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Br}]^+$	0.040 M NaOH, 0.96 M NaClO <sub>4</sub>	382 (119),	288 (115) <sup>b</sup>

<sup>a</sup> The spectrum reported is that of the mixture at pH =  $\frac{1}{2}(\text{p}K_{a,1} + \text{p}K_{a,2})$ . For the *cis*-complex the distribution at pH = 7.35 is  $\alpha_{(\text{H}_2\text{O})_2} = 0.09$ ,  $\alpha_{(\text{OH})(\text{H}_2\text{O})} = 0.82$ ,  $\alpha_{(\text{OH})_2} = 0.09$ . For the *trans*-complex at pH = 6.59:  $\alpha_{(\text{H}_2\text{O})_2} = 0.02$ ,  $\alpha_{(\text{OH})(\text{H}_2\text{O})} = 0.96$ ,  $\alpha_{(\text{OH})_2} = 0.02$ . <sup>b</sup> Shoulders.

Table 2.  $pK_a$  values for some aquaamminerhodium(III) complexes in 1.0 M sodium perchlorate at 25.0 °C.<sup>a</sup>

Complex	$pK_a$	$\delta^b$
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	6.93	
$\text{cis-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	6.40	-0.53
$\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	4.92	-2.01
$\text{cis-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$	7.84	+0.91
$\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$	6.75	-0.18
$\text{cis-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$	7.89	+0.96
$\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$	6.87	-0.06
$\text{cis-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]^{2+}$	8.32 <sup>c</sup>	+1.39
$\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]^{2+}$	8.26 <sup>c</sup>	+1.33

<sup>a</sup>  $pK_a = -\log K_a$ . The  $K_a$ 's are measured in mol/l. <sup>b</sup>  $\delta = pK_a(\text{complex}) - pK_a(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+})$ . <sup>c</sup>  $pK_{a,2}$  of the analogous diaqua complex.

monitored hydrolysis experiments (see Experimental).

The final calculations of the  $pK_a$  values were done from at least the part of the titrations curves corresponding to between 15 and 85 % neutralization, and good agreement between model and experiment were found. The standard deviation on the mean values of the reported  $pK_a$  values were calculated to be 0.01–0.02.

A spectrophotometric determination of  $pK_a$  for the *trans*-tetraammineaquachlororhodium(III) ion and for the *trans*-tetraammineaquabromorhodium(III) ion confirmed the potentiometric determined values. At room temperature in 1.0 M  $\text{NaClO}_4$  the spectrophotometric determined values were 6.67 and 6.84, respectively. For the corresponding *cis*-complexes, the spectral differences between the hydroxo- and the aqua complexes are only minor (Table 1) and no spectrophotometric  $pK_a$  determination was attempted.

## DISCUSSION

The  $pK_a$  of pentaammineaquarhodium(III) has previously been determined, but under different conditions. Thus, in 0.5 M  $\text{NaClO}_4$  at 25.0 °C the value 6.78 was found,<sup>13</sup> in reasonable agreement with the value reported here, taking the different ionic strengths into account.

The pattern shown by the  $pK_a$  values reported here for various aquaamminerhodium(III) complexes follows qualitatively trends noted for some other hexacoordinate complexes. For example, the *trans* diaqua ion  $\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  is more acidic than the *cis*-analogue which has a  $pK_{a,1}$  value near that of the pentaammine complex  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  (Table 2). In addition, the presence of hydroxide in the coordination sphere of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]^{2+}$  decreases the acidity of the remaining  $\text{H}_2\text{O}$  (i.e.,  $pK_{a,2} \gg pK_{a,1}$ ) as would be expected from electrostatic considerations. Notably electrostatic factors alone are not sufficient to make  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  a stronger acid than  $\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ .

When one considers the effect of a ligand X in the coordination sphere of  $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}]^{n+}$ , the acidity order is different for *trans*-X ( $pK_a$  as a function of X follows:  $\text{H}_2\text{O} \ll \text{Cl}^- < \text{Br}^- \sim \text{NH}_3 \ll \text{OH}^-$ ) than for *cis*-X ( $pK_a$ 's:  $\text{H}_2\text{O} < \text{NH}_3 < \text{Cl}^- \sim \text{Br}^- < \text{OH}^-$ ). In both series the diaqua and the aqua-hydroxo complexes are the most and least acidic members of the series, respectively, but the range is much narrower for the *cis* stereochemistry (1.92  $pK_a$  units) than for the *trans* stereochemistry (3.34  $pK_a$  units). Notably the narrower *cis* range parallels closely the behavior seen for Co(III) and Cr(III) tetraammine complexes (Table 3) as does the observation that the *trans* diaqua complex is consistently more acidic than the *cis* analogue.

These trends can be rationalized partially by the

Table 3.  $pK_a$  values for some *cis*- and *trans*-tetraamminediaqua complexes.<sup>a</sup>

	<i>cis</i>			<i>trans</i>			Medium	$t/^\circ\text{C}$	Ref.
	$pK_{a,1}$	$pK_{a,2}$	$\Delta_{cis}$	$pK_{a,1}$	$pK_{a,2}$	$\Delta_{trans}$			
$[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	4.96	7.53	2.57	4.38	7.78	3.40	1.0 M $\text{NaClO}_4$	25.0	11
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	5.69	7.99	2.30				0.1 M $\text{NaClO}_4$	20.0	12
$[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	6.40	8.32	1.92	4.92	8.26	3.34	1.0 M $\text{NaClO}_4$	25.0	This work
$[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$	4.75	7.35	2.60	4.11	7.71	3.60	1.0 M $\text{NaClO}_4$	25.0	11
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$	6.06	8.19	2.13	4.45	7.94	3.49	1.0 M $\text{NaNO}_3$	25.0	9

<sup>a</sup>  $\Delta = pK_{a,2} - pK_{a,1}$ . en = 1,2-ethanediamine.

two dimensional bonding properties of these ligands, *i.e.*, the ligand  $\sigma$ - and  $\pi$ -donor properties in the equilibrium



Hydroxide is both a stronger  $\sigma$ -donor and a stronger  $\pi$ -donor than  $\text{H}_2\text{O}$ . Thus variations of X which disfavor either of the bonding contributions between M and  $\text{OH}^-$  will decrease the acidity of the coordinated  $\text{H}_2\text{O}$ . The proposed order for  $\sigma$ -donor strengths in hexacoordinate first row transition metal complexes is  $\text{OH}^- > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^- > \text{Br}^-$ , while that for  $\pi$  donor strengths is  $\text{OH}^- > \text{Cl}^- \sim \text{Br}^- > \text{H}_2\text{O} > \text{NH}_3$ .<sup>14</sup> Relative to the reference complex  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  with  $\text{X} = \text{NH}_3$ , the  $\pi$ -bonding contributions for  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$  should all increase the  $\text{pK}_a$ , while the  $\sigma$ -bonding contribution should increase  $\text{pK}_a$  for  $\text{X} = \text{OH}^-$  but decrease it for  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$ . Generally it is found that electronic effects (especially  $\sigma$ -bonding effects) are more sharply defined in the *trans* position owing to the direct overlap of the *trans* ligand orbitals with the same metal orbitals, hence the greater sensitivity of  $\text{pK}_a$  to X in the *trans* series. Thus, when  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  and  $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  are compared, both of the diaqua ions are more acidic ( $\delta$  is negative, Table 2) than the pentaammine complex despite the weak  $\pi$ -donor ability of  $\text{H}_2\text{O}$ . However, given the statistical factor of two (0.3  $\text{pK}_a$  units) favouring ionization of the diaqua complexes, the *cis* complex is but marginally more acidic than the pentaammine. In contrast, the *trans* ion is considerably more acidic than the *cis* or the pentaammine, suggesting the dominance of the  $\sigma$ -donor effects in this case.

Each of the other X's are anionic, a feature complicating comparisons to the  $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  reference, since in these cases electrostatic considerations alone should increase the  $\text{pK}_a$ 's. For the *cis* series, this factor alone appears to be dominant,  $\delta$  is positive in each case. The somewhat larger value of  $\delta$  for  $\text{X} = \text{OH}^-$  can easily be attributed to its stronger  $\sigma$  and  $\pi$ -donor strengths relative to either  $\text{Cl}^-$  or  $\text{Br}^-$ . In the *trans* series, however, the electrostatic effect is no longer dominating and small but negative  $\delta$ 's are noted when  $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ . This apparently can be rationalized by the approximate balancing of electrostatic and  $\pi$ -donor effects by the  $\sigma$ -donor effects in the *trans* site, the halides being much weaker  $\sigma$ -donors than  $\text{NH}_3$ .

In contrast,  $\text{OH}^-$  is a stronger  $\pi$ - and  $\sigma$ -donor than  $\text{NH}_3$ , thus  $\delta$  is understandably positive when  $\text{X} = \text{trans} - \text{OH}^-$ .

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## REFERENCES

- Poë, A. J. and Twigg, M. V. *Can. J. Chem.* 50 (1972) 1089.
- Hancock, M. P. *Acta Chem. Scand. A* 29 (1975) 468.
- Skibsted, L. H., Strauss, D. and Ford, P. C. *Inorg. Chem.* 18 (1979) 3171.
- Hancock, M. P. *Acta Chem. Scand. A* 33 (1979) 499.
- Skibsted, L. H. and Ford, P. C. *J. Chem. Soc. Chem. Commun.* (1979) 853.
- Osborn, J. A., Thomas, K. and Wilkinson, G. *Inorg. Synth.* 13 (1972) 213.
- Bushnell, G. U., Lalor, G. L. and Moelewyn-Hughes, E. A. *J. Chem. Soc. A* (1966) 719.
- Anderegg, G. *Helv. Chim. Acta* 50 (1967) 2333.
- Bjerrum, J. and Rasmussen, S. E. *Acta Chem. Scand.* 6 (1952) 1265.
- Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd Ed., Wiley, New York 1967, p. 273.
- Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 30 (1976) 202.
- Schwarzenbach, G., Boesch, J. and Egli, H. *J. Inorg. Nucl. Chem.* 33 (1971) 2141.
- Palmer, D. A. and Harris, G. M. *Inorg. Chem.* 13 (1974) 965.
- Glerup, J., Mønsted, O. and Schäffer, C. E. *Inorg. Chem.* 15 (1976) 1399 and references therein.

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