

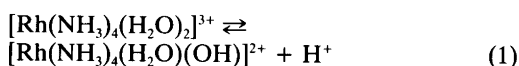
Temperature Dependence of the Acid Dissociation of *cis*- and *trans*-Tetraamminediaquarhodium(III)

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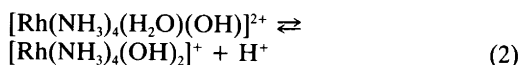
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For octahedral tetraamminediaqua cobalt(III),¹ rhodium(III),²⁻⁴ and iridium(III)⁵ complexes, significantly higher aqueous solution acidities for the *trans* than for the *cis* isomers have been noted. In the case of tetraamminediaquarhodium(III),² the acidity of the coordinated water corresponding to the equilibrium



has been rationalized on the basis of the donor properties of the ligand which is involved in σ orbital overlap with the same metal orbital as the water ligand, i.e., the *trans* ligand. Since hydroxide is a stronger σ donor than water,⁶ a weak σ donor present in the *trans* position would favour bonding of hydroxide relative to water, thus increasing the acidity of the coordinated water. The higher acidity of *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ than of *cis*-[Rh(NH₃)₄(H₂O)₂]³⁺ is, on the basis of these arguments, fully consistent with the stronger σ donor properties of ammonia than those of water. Similarly, the higher acidity of *trans*- than of *cis*-[Rh(NH₃)₄(H₂O)X]²⁺ (X = Cl, Br) is consistent with the stronger σ donor properties of ammonia than of halide.² However, the acidity of the second water ligands in the two isomeric tetraamminediaquarhodium(III) complexes described by the equilibrium



is surprisingly independent of the stereochemistry, in spite of the difference in donor properties of the *trans* ligands (ammonia for the *cis* isomer and hydroxide for the *trans* isomer, respectively).² The differences in donor properties between related ligands such as ammonia, water, and hydroxide are expected to be derived from differences in the reaction enthalpies, whereas differences in specific solvation influence primarily the reaction entropies. To acquire a better understanding of the factors controlling the aqueous solution acidities of d⁶-metal ion complexes such as *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺, a determination of ΔH° and ΔS° for the reactions of eq. (1) and (2) in 1.0 M NaClO₄ was undertaken.

Both *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ were titrated at a number of temperatures between 0 and 35°C (each titration in duplicate). From the full titration curves, pK_{a,1} and pK_{a,2} were calculated by nonlinear regression analysis.⁷ Figure 1 shows the experimental data, together with the regression curves computed from pK_{a,n} = ($\Delta H_n^\circ / T - \Delta S_n^\circ$)/2.303R which yield the values for the parameters ΔH_n° and ΔS_n° , which are given in Table 1 together with pK_{a,n} at 25.0°C.

For *cis*-[Rh(NH₃)₄(H₂O)₂]³⁺, in which both aqua ligands are *trans* to an ammine ligand, the reaction enthalpies for the two dissociation steps are almost equal ($\Delta H_2^\circ - \Delta H_1^\circ = -2.3 \pm 1.9$ kJ mol⁻¹), in agreement with the arguments presented above. The difference between pK_{a,2} and pK_{a,1} is largely determined by statistical factors and specific solvation effects ($T(\Delta S_2^\circ - \Delta S_1^\circ) =$

Table 1. Thermodynamic parameters for the acid dissociation of the isomeric tetraamminediaquarhodium(III) complexes in aqueous 1.0 M sodium perchlorate.^a

	$\text{pK}_{a,1}^b$ (25 °C)	ΔH_1° (kJ mol ⁻¹)	ΔS_1° (J mol ⁻¹ K ⁻¹)	$\text{pK}_{a,2}^b$ (25 °C)	ΔH_2° (kJ mol ⁻¹)	ΔS_2° (J mol ⁻¹ K ⁻¹)
<i>cis</i> -[Rh(NH ₃) ₄ (H ₂ O) ₂] ³⁺	6.391(9)	44.9(1.6)	28(5)	8.356(7)	42.6(1.1)	-17(4)
<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O) ₂] ³⁺	4.860(11)	34.0(1.1)	21(4)	8.294(11)	36.7(1.0)	-36(4)

^aOne standard deviation is given in parenthesis.

^b $\text{pK}_a = -\log K_a$. The K_a 's are measured in mol/l.

-13.4 ± 1.9 kJ mol⁻¹ at 25 °C), and is consequently almost temperature-independent. *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ is, with respect to dissociation of the first proton, a stronger acid than its *cis* counterpart, which is clearly a result of a smaller ΔH_1° and is in agreement with the weaker σ donor properties noted for the *trans* aqua ligand compared to ammonia.⁶ The difference between $\text{pK}_{a,1}$ for the *cis* and *trans* isomers thus depends on the temperature, and for $\text{pK}_{a,2}$ a similar temperature dependence of the *cis/trans* differences was also found. The equality of the second dissociation

constants for *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ near room temperature is thus coincidental (in 1.0 M NaClO₄, $\text{pK}_{a,2}(\textit{cis}) = \text{pK}_{a,2}(\textit{trans})$ at 37 °C), and the difference in bonding properties between the *trans* ligands in the two isomers is manifested in the difference in ΔH_2° . Hydroxide is a stronger σ donor than ammonia, and, in keeping with the arguments presented for ΔH_1° , ΔH_2° is expected to be larger for the *trans* than for the *cis* isomer. However, the opposite was found, implying that π bonding effects are important. The proposed order for σ donor strength is OH⁻ > NH₃ > H₂O, whereas that for π donor strength is OH⁻ > H₂O > NH₃.⁶ Hydroxide as a ligand increases the electron density in the t_{2g} -(d_{xy} , d_{yz} , d_{zx}) and in the t_{1u} (p) metal orbitals relative to water and, more significantly, relative to ammonia. The metal p orbitals are also involved in σ bonding, and a strong π donor will increase the energy of the p orbitals involved in σ bonding with the *cis* ligands. As a consequence, the bonding of a hydroxide instead of water *cis* to a hydroxide is disfavoured. Evidently, this *cis* effect is important since $\Delta H_2^\circ(\textit{cis}) > \Delta H_2^\circ(\textit{trans})$. In contrast, a π acceptor such as cyanide *cis* to water has the opposite effect, rendering *cis*- a stronger acid than *trans*-[Rh(NH₃)₄(H₂O)(CN)]²⁺.¹¹

ΔS_1° is independent of stereochemistry for [Rh(NH₃)₄(H₂O)₂]³⁺; the positive sign is in keeping with the decrease in solvation taking place upon proton dissociation and the reduction in the charge on the cationic complex. In contrast, ΔS_2° is negative and dependent on stereochemistry. The values $\Delta S_2^\circ(\textit{trans}) = -36$ and $\Delta S_2^\circ(\textit{cis}) = -17$ J mol⁻¹ K⁻¹ indicate strong solvation of the tetraamminedi-hydroxide rhodium ions, although more pronounced for the D_{4h} than for the C_{2v} symmetry. The partial molar volume for anionotetraammineaquarhodium(III) ions has been found to be independent of stereochemistry (*i.e.*

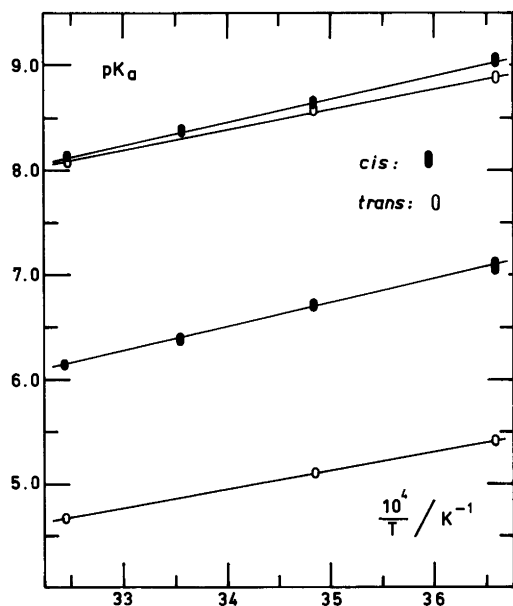


Fig. 1. Temperature dependence of $\text{pK}_{a,1}$ and $\text{pK}_{a,2}$ for *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ in 1.0 M NaClO₄. Experimental data are given with a range corresponding to ± the estimated uncertainties.

$[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$; *cis*: 83.0; *trans*: 85.5 $\text{ml} \cdot \text{mol}^{-1}$), whereas *cis*-tetraamminedianionorhodium(III) ions are significantly smaller than their *trans* counterparts (*i.e.* $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$; *cis*: 87.1; *trans*: 107.6 $\text{ml} \cdot \text{mol}^{-1}$).¹² The dissociation of a proton from $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]^{2+}$ is thus expected to be accompanied by a large expansion for the *trans* but not for the *cis* isomer, again indicating differences in the solvation of the two isomeric tetraammineaquahydroxorhodium(III) ions.

Experimental. *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{S}_2\text{O}_6$ and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ were prepared and purified according to published procedures.^{8,9} The titrations were performed as previously described² and the pH was standardized relative to perchloric acid in 1.0 M NaClO_4 using the definition $\text{pH} = -\log[\text{H}^+]$.

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