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Outer-Sphere Complexes of the $\mathrm{Ru(NH_3)_6}^{3+}$ Ion: Stability Measurement using Charge-Transfer Spectra

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When colourless solutions containing $\mathrm{Ru(NH_3)_6}^{3+}$ and $\mathrm{I^-}$ are mixed, a colour appears due to formation of ion-pairs with strong anion–metal charge-transfer [1]. When certain other anions such as $\mathrm{SO_4}^{2-}$ are added, the colour is discharged owing to competing ion-pair formation [2]. This effect provides a method of comparing ion-pair formation constants in media of high ionic strength.

We assume the equilibria

$$\mathrm{Ru(NH_3)_6}^{3+} + \mathrm{A^{a-}} \overset{K_A}{\rightleftharpoons} \mathrm{Ru(NH_3)_6}^{3+}\cdot\mathrm{A^{a-}} \qquad (1)$$

$$\mathrm{Ru(NH_3)_6}^{3+} + \mathrm{B^{b-}} \overset{K_B}{\rightleftharpoons} \mathrm{Ru(NH_3)_6}^{3+}\cdot\mathrm{B^{b-}} \qquad (2)$$

where $\mathrm{A^{a-}}$ denotes an anion with a high charge-transfer tendency (*e.g.* $\mathrm{I^-}$, $\mathrm{N_3}^-$, $\mathrm{S_2O_3}^{2-}$) and $\mathrm{B^{b-}}$ denotes a competing anion of low charge-transfer tendency. The absorbance A is thus given by

$$\frac{A}{[\mathrm{Ru}]_T l} = \frac{\epsilon_0 + \epsilon_A K_A[\mathrm{A^{a-}}] + \epsilon_B K_B[\mathrm{B^{b-}}]}{1 + K_A[\mathrm{A^{a}}-] + K_B[\mathrm{B^{b-}}]} \qquad (3)$$

where $[\mathrm{Ru}]_T$ is the total ruthenium concentration, l is the path length and ϵ_0, ϵ_A, ϵ_B, are the extinction coefficients of $\mathrm{Ru(NH_3)_6}^{3+}$ and of the two ion pairs. Absorption by the free anions is neglected.

In our experiments, two sodium salts $\mathrm{Na_aA}$ and $\mathrm{Na_bB}$ were used, and in each set of measurements the total sodium ion concentration was held constant. Thus, in cases where the ion charges a and b were equal, the ionic strength was constant. In other cases the ionic strength varied as shown below. Writing the total sodium ion concentration as c we have

$$a[\mathrm{A^{a-}}] + b[\mathrm{B^{b-}}] = c \qquad (4)$$

hence the anion concentrations in a set of experiments are $[\mathrm{B^{b-}}] = x/b$, $[\mathrm{A^{a-}}] = (c - x)/a$, where x varies from 0 to c, and equation 3 becomes

$$\frac{A}{[\mathrm{Ru}]_T l} = \frac{\epsilon_0 + \epsilon_a(K_A/a)(c - x) + \epsilon_B(K_B/b)x}{1 + (K_A/a)(c - x) + (K_B/b)x} \qquad (5)$$

The absorbances when x = 0 and x = c are given by $A(0) = (\epsilon_0 + \epsilon_A c K_A/a)(1 + cK_A/a)^{-1}\,[\mathrm{Ru}]_T l$ and $A(c) = (\epsilon_0 + \epsilon_B c K_B/b)(1 + cK_B/b)^{-1}[\mathrm{Ru}]_T l$, hence equation (5) leads to

$$R = \frac{(A - A(0))(c - x)}{(A(c) - A)x} = \frac{1 + cK_B/b}{1 + cK_A/a} \qquad (6)$$

For each set of experiments, values of R were calculated, as shown in Table I. For a given anion $\mathrm{A^{a-}}$, values of R are expected to increase as K_B increases. The two series of data, with $\mathrm{A^{a-}} = \mathrm{S_2O_3}^{2-}$ and $\mathrm{N^{3-}}$, are seen to be satisfactorily consistent, with K_B increasing in the order $\mathrm{Cl^-} < \mathrm{NO_3}^- \sim \mathrm{ClO_3}^- < \mathrm{SO_4}^{2-}$. This agrees with the order of stabilities of the corre-

TABLE I. Ion-Pair Formation Constants K_B[a] from Spectrophotometric Measurements[b].

Anion $\mathrm{B^{b-}}$	Anion $\mathrm{A^{a-}}$ $\mathrm{Na^+}$/M	$\mathrm{S_2O_3}^{2-}$[d] 1.0		$\mathrm{N_3}^-$[e] 0.5		log K $\mathrm{Co(NH_3)_6}^{3+} + \mathrm{B^{b-}}$
		R[c]	log K_B	R[c]	log K_B	
$\mathrm{SO_4}^{2-}$		0.95 ± 0.06	1.12[f,k]	1.52 ± 0.23	1.19[f,m]	1.97[h]
$\mathrm{S_2O_6}^{2-}$				1.43 ± 0.10	1.09[f,m]	
$\mathrm{IO_3}^-$				1.18 ± 0.04	0.75[f,n]	
$\mathrm{ClO_3}^-$		0.69 ± 0.05	0.65[f,l]	1.16 ± 0.10	0.73[f,n]	
$\mathrm{NO_3}^-$		0.62 ± 0.04	0.60[f,l]	1.23 ± 0.08	0.77[f,n]	0.94[i]
$\mathrm{Cl^-}$		0.48 ± 0.02	0.45[g,l]	0.96 ± 0.10	0.62[g,n]	−0.31[j]
$\mathrm{BrO_3}^-$				0.78 ± 0.05	0.48[f,n]	
$\mathrm{CH_3COO^-}$				0.58 ± 0.06	0.24[f,n]	

[a] See text, equation 2. [b] Data were recorded with a Cary 14 spectrophotometer, at the wavelengths noted below. T = 25.0 ± 0.2 °C, pH = 7.0, $[\mathrm{Ru}]_T = 2.0 \times 10^{-3}$ M, chloride ion present, 6.0×10^{-3} M, in addition to the ions listed. A nitrogen atmosphere was maintained in all experiments to avoid side-reactions (cf. [3]). [c] See text, equation 8. Values listed are mean and standard error, from 7–10 readings evenly spaced over the range x = 0 to c. [d] $\lambda = 403$ nm. [e] $\lambda = 375$ nm. [f] Calculated from the values of R and K_{Cl} listed in the same column. [g] Calculated from data of [1], Table I. [h] I = 1.0 *M*, [4]. [i] Calculated from values at I = 0.05 *M* [5], assuming the same ionic strength dependence as for $\mathrm{Ru(NH_3)_6}^{3+}\cdot\mathrm{Cl^-}$ [1]. [j] I = 1.0 M, [6]. [k] I = 1.5 *M*. [l] I = 1.0–1.5 *M*. [m] I = 0.5–0.75 *M*. [n] I = 0.5 *M*.

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sponding complexes of $Co(NH_3)_6^{3+}$, at high ionic strengths, as shown in the Table. Absolute values of K_B can be calculated if one value is already known. We have taken K_B for the Cl^- ion pair from the data of Waysbort *et al.* [1] and thence calculated the other values of K_B, at the two sodium ion concentrations used, as shown in Table I.

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