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The Reductions of Hydroxo- and Aquapentaammine-cobalt(III); and of Hydroxo- and Aquapentacyano-cobaltate(III) by Aquapentaammine-ruthenium(II) in Aqueous Solution

J. FOLORUNSO OJO, OLUSEGUN OLUBUYIDE* and OLAYINKA OYETUNJI

Department of Chemistry, University of Ife, Ile-Ife, Nigeria

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The hydroxo ligand (OH) has been shown to be a more effective bridging ligand than the aqua ligand (H_2O), to the extent that the rate ratios $k_{OH}:k_{H_2O}$ have been used [1–4] to diagnose the mechanisms of some electron-transfer reactions. When substitution-labile reductants such as U^{3+}, Cr^{3+}, Eu^{2+}, Cu^+, V^{2+} [1–4] reduce hydroxo and aqua complexes, very high rate ratios $k_{OH}:k_{H_2O}$ are obtained and inner-sphere mechanism is proposed; but when substitution-inert reductants such as $Ru(NH_3)_6{}^{2+}$ [5] and $Cr(bipy)_3{}^{2+}$ [2] are employed, low rate ratios are obtained and outer-sphere mechanism is proposed.

Here we report the reductions of $Co(NH_3)_5X^{n+}$ ($X = H_2O$, OH, $n = 2$ or 3) and the pentacyano-analogues $Co(CN)_5X^{n-}$ by the mild and moderately substitution-labile reductant $Ru(NH_3)_5H_2O^{2+}$. This reductant is much less substitution-labile than U^{3+}, Cr^{2+}, Eu^{2+} etc., but more substitution-labile than $Ru(NH_3)_6{}^{2+}$ [6]. The inclusion of the pentacyano analogues of the oxidants ($Co(CN)_5X^{n-}$) is aimed at investigating the effect which the replacement of the five σ-bonded ammonia ligands in $Co(NH_3)_5X^{n+}$ by five π-bonded cyano ligands ($Co(CN)_5X^{n-}$) could have on the redox reactivity of cobalt(III) ion centre. Moreover, these two types of cobalt(III) complexes are oppositely charged and their interactions with $Ru(NH_3)_5H_2O^{2+}$ could lead to different redox behaviours.

Experimental

Materials

$Co(NH_3)_5H_2O^{3+}$ was synthesised and characterised as described in literature [7]. $Co(CN)_5H_2O^{2-}$ was prepared *in situ* from $Co(CN)_5N_3{}^{3-}$ [8, 9] as described in literature and it was kept in vessels wrapped with aluminium foil because of its light-sensitivity [9]. It was certified pure by its IR and UV–Vis absorption spectra [10]. $Co(NH_3)_5OH^{2+}$ and $Co(CN)_5OH^{3-}$ were generated *in situ* from the aqua analogues at alkaline pH using NH_3/NH_4Cl buffer [5].

$Ru(NH_3)_5H_2O^{2+}$ was generated by the zinc amalgam reduction of purified $[Ru(NH_3)_5Cl]Cl_2$ in an argon atmosphere [6]. HCl used was Analar grade, and the ionic strength reagent LiCl (Hopkins and Williams reagent grade) was twice recrystallised.

Kinetics

All the reactions were monitored on a Pye Unicam UV–Vis SP500 spectrophotometer equipped with a direct read-out absorbance recorder, and in an argon gas atmosphere as a result of the oxygen-sensitivity of $Ru(NH_3)_5H_2O^{2+}$. The ionic strength was maintained at 0.20 mol dm^{-3} with LiCl as a result of the limited solubility of Ru(II) [11]. Absorbance changes were monitored at the UV absorption peak [12] of $Ru(NH_3)_5H_2O^{2+}$ (λ_{max} = 300 nm, $\epsilon = 1.18 \times 10^3$ dm^3 mol^{-1} cm^{-1}) with the concentrations of the Co(III) complexes in excess ($\geqslant$10 fold) over those of the Ru(II) reductant. The reaction temperature was maintained at 25.0 ± 0.1 °C by circulating water from a regulated water-bath around the cell compartment. Pseudo first-order rate plots were linear to at least four half-lives in all cases.

Results

The stoichiometry of each reaction was checked as usual [12] and confirmed to be 1 mol of Co(III) consumed by 1 mol of Ru(II).

All the kinetic data fit the second-order rate law:

$$\frac{-d[\mathrm{Ru(II)}]}{dt} = k_{obs}[\mathrm{Ru(II)}][\mathrm{Co(III)}] \qquad (1)$$

The observed second-order rate constants k_{obs} are independent of acid concentration in the range $[H^+] = 0.02$–0.10 mol dm^{-3}, and of pH in the range pH = 8–10 (Table I).

Discussion

All the second-order rate constants obtained in this study, are higher than the characteristic substitution rate constants [12, 13] for $Ru(NH_3)_5H_2O^{2+}$ and therefore we suggest that the redox reactions occur by outer-sphere mechanism.

The rate ratios $k_{OH}:k_{H_2O}$ for the hydroxo/aqua pairs $Co(NH_3)_5OH^{2+}/Co(NH_3)_5H_2O^{3+}$ and $Co(CN)_5OH^{3-}/Co(CN)_5H_2O^{2-}$ as obtained from Table I are 2.0 and 0.6, respectively. These, when compared with others (Table II) suggest that the reductions of

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*Author to whom correspondence should be addressed.

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TABLE I. Observed Second-order Rate Constants (k_{obs}) for the Reductions of $Co(NH_3)_5X^{n+}$ and $Co(CN)_5X^{n-}$ (n = 2 or 3, X = OH, H_2O) by $Ru(NH_3)_5H_2O^{2+}$ at 25 °C, I = 0.20 mol dm^{-3} (LiCl)

Reaction	10^4 [Co(III)]$_0$ (mol dm^{-3})	10^5 [Ru(II)]$_0$ (mol dm^{-3})	[H$^+$] (mol dm^{-3})	k_{obs} (dm^3 mol^{-1} s^{-1})
$Ru(NH_3)_5H_2O^{2+} + Co(NH_3)_5H_2O^{3+}$	8.0	6.0	0.02	0.42
	16.0	10.0	0.02	0.45
	32.0	20.0	0.02	0.41
	32.0	20.0	0.05	0.43
	16.0	10.0	0.10	0.46
	20.0	10.0	0.10	0.44
	32.0	20.0	0.10	0.41
	35.0	25.0	0.10	0.39
				Average k_{obs} = 0.43 ± 0.02
$Ru(NH_3)_5H_2O^{2+} + Co(CN)_5H_2O^{2-}$	8.1	6.0	0.02	0.91
	9.1	6.0	0.02	0.96
	15.2	10.0	0.02	0.95
	22.3	10.0	0.05	1.08
	25.0	10.0	0.05	1.02
	8.1	6.0	0.10	0.94
	15.0	10.0	0.10	0.91
	25.0	15.0	0.10	0.93
				Average k_{obs} = 0.96 ± 0.06
			pH	
$Ru(NH_3)_5H_2O^{2+} + Co(NH_3)_5OH^{2+}$	8.0	6.0	8.0	0.84
	10.0	10.0	8.0	0.90
	15.0	8.0	9.0	0.86
	20.0	10.0	9.0	0.94
	25.0	15.0	9.0	0.90
	10.0	10.0	10.0	0.80
	20.0	10.0	10.0	0.85
				Average k_{obs} = 0.87 ± 0.06
$Ru(NH_3)_5H_2O^{2+} + Co(CN)_5OH^{3-}$	8.1	6.0	8.0	0.58
	9.1	6.0	8.0	0.56
	15.0	8.0	9.0	0.65
	20.0	10.0	9.0	0.59
	15.0	8.0	10.0	0.58
	24.2	20.0	10.0	0.63
				Average k_{obs} = 0.60 ± 0.02

TABLE II. k_{OH}:k_{H_2O} Ratios for the Reductions of some $Co(NH_3)_5X^{n+}$, $Co(CN)_5X^{n-}$ $Ru(NH_3)_5X^{n+}$ and $Fe(H_2O)_5X^{n+}$ (n = 2 or 3, X = OH, H_2O) Complexes by some Reductants

Reaction	k_{OH}:k_{H_2O}	Mechanism[a]	Reference
$U^{3+} + Co(NH_3)_5X^{n+}$	very large	I.S.	1
$Cu^{2+} + Co(NH_3)_5X^{n+}$	3.8×10^5	I.S.	3
$Cr^{2+} + Co(NH_3)_5X^{n+}$	3.0×10^5	I.S.	2
$V^{2+} + Co(NH_3)_5X^{n+}$	$<1 \times 10^5$	I.S.	2
$Cr^{2+} + Fe(H_2O)_5X^{n+}$	1.4×10^3	I.S.	4
$Eu^{2+} + Fe(H_2O)_5X^{n+}$	1.35×10^3	I.S.	4
$V^{2+} + Fe(H_2O)_5X^{n+}$	<20	O.S.	2
$Ru(NH_3)_5H_2O^{2+} + Co(NH_3)_5X^{n+}$	2.0	O.S.	this work
$Ru(NH_3)_5H_2O^{2+} + Co(CN)_5X^{n-}$	0.6	O.S.	this work
$U^{3+} + Ru(NH_3)_5X^{n+}$	0.5	O.S.	17
$Ru(NH_3)_6^{2+} + Co(NH_3)_5X^{n+}$	1.3×10^{-2}	O.S.	5
$Cr(bipy)_3^{2+} + Co(NH_3)_5X^{n+}$	1.0×10^{-2}	O.S.	2

[a] I.S., inner sphere; O.S., outer sphere.

$Co(NH_3)_5X^{n+}$ and $Co(CN)_5X^{n-}$ by $Ru(NH_3)_5H_2O^{2+}$ occur by outer-sphere mechanism. K_a for $Co(NH_3)_5$-H_2O^{3+} as represented by the equilibrium:

$$Co(NH_3)_5H_2O^{3+} \overset{K_a}{\rightleftharpoons} Co(NH_3)_5OH^{2+} + H^+ \qquad (2)$$

is 6.1×10^{-7} mol dm^{-3} [14] at 25 °C and $I = 0.30$ mol dm^{-3} ($LiClO_4$). In acid medium, such as the one used in this study ($[H^+] = 0.02–0.10$ mol dm^{-3}), only a very small amount of the hydroxo species is present in equilibrium with the aqua species. Since the $k_{OH}:k_{H_2O}$ ratio is small, no detectable acid-dependence of k_{obs} was observed (Table I). In other previous systems involving labile reductants [1–4], for which inner-sphere mechanism has been proposed, the rate ratios $k_{OH}:k_{H_2O}$ are very large and the small amounts of the hydroxo species present in equilibrium with the aqua species are sufficient to make acid-dependence detectable.

The ammonia ligands in $Co(NH_3)_5X^{n+}$ are more weakly bound to cobalt than the cyano ligands in $Co(CN)_5X^{n-}$ [15, 16] and therefore greater reactivity is expected from $Co(NH_3)_5X^{n+}$. While the ratio $k_{NH_3}:k_{CN}$ for the hydroxo species is 1.5, it is 0.5 for the aqua species (Table I). There is therefore not much reactivity difference between the pentaammine- and the pentacyano- species. However, the expected reactivity difference in terms of non-bridging ligand effects [3, 15, 16], might have possibly been cancelled by the more favourable coulumbic interactions between the negatively charged pentacyano- complexes $Co(CN)_5X^{n-}$ and $Ru(NH_3)_5H_2O^{2+}$ than between $Co(NH_3)_5X^{n+}$ and $Ru(NH_3)_5H_2O^{2+}$.

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