

Kinetics and Mechanism of the Reductions of Azido- and Isothiocyanatopentacyanocobaltate(III) by Ruthenium(II) Ammine Species in Aqueous Solution

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Abstract

The reductions of azido- and isothiocyanatopentacyanocobaltate(III) by hexaammine- and aquapentammineruthenium(II) have been investigated in aqueous solution at $I = 0.20 \text{ mol dm}^{-3}$ (LiCl) and the values at 25 °C of the rate constants ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) are $k_{\text{N}_3} = 1.71$ and $k_{\text{NCS}} = 0.81$ for the $\text{Ru}(\text{NH}_3)_6^{2+}$ reactions and $k_{\text{N}_3} = 2.06$ and $k_{\text{NCS}} = 0.99$ for the $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ reactions.

The reductions are acid-independent in the acid concentration range $[\text{H}^+] = (0.01\text{--}0.10) \text{ mol dm}^{-3}$ (HCl), but they are dependent on ionic strength. The low $k_{\text{N}_3}/k_{\text{NCS}}$ ratios obtained and conformity with the modified Marcus equation (based on linear free-energy) of the data suggest an outer-sphere mechanism for the reductions.

Activation parameters obtained for the reductions by hexaammine-ruthenium(II) are

$$\Delta H^\ddagger_{\text{N}_3} (\text{kJ mol}^{-1}) = (83.1 \pm 5.7),$$

$$\Delta S^\ddagger_{\text{N}_3} (\text{J mol}^{-1} \text{ K}^{-1}) = (38.6 \pm 1.9)$$

$$\Delta H^\ddagger_{\text{NCS}} (\text{kJ mol}^{-1}) = (84.0 \pm 2.2),$$

$$\Delta S^\ddagger_{\text{NCS}} (\text{J mol}^{-1} \text{ K}^{-1}) = (35.9 \pm 7.9)$$

Introduction

Previously, investigations [1, 2] of the reductions of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{N}_3^-, \text{NCS}^-, \text{SCN}^-$) by ruthenium(II) species in aqueous solution have been reported. The reductions of these pentaammine-cobalt(III) complexes by ruthenium(II) complexes were classified as outer-sphere using the relative rates $k_{\text{N}_3}/k_{\text{NCS}}$ and log-log plots based on a linear free-energy correlation and Marcus equation. In the reductions of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{NCS}^-, \text{SCN}^-$) by $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$, observation of absorbance increase [2] leading to the initial formation of $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$ only after the electron-transfer process further provides direct evidence for an outer-sphere mechanism.

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We report here the reductions of the pentacyano analogues $\text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X} = \text{N}_3^-, \text{NCS}^-$) of these cobalt(III) complexes by ruthenium(II) species in aqueous solution. The replacement of the five σ -coordinated NH_3 ligands by five π -bonded CN^- ligands might have a remarkable difference on the relative reactivities of these cobalt(III) complexes. Moreover, the charge differences between $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}(\text{CN})_5\text{X}^{3-}$ might manifest coulombic interactions between the ruthenium(II) species and the cobalt(III) complexes through their relative rates. The redox chemistry of $\text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X} = \text{N}_3^-, \text{NCS}^-$) is much less exhaustively [3a, b] documented in the literature than those of the corresponding pentaammine-cobalt(III) complexes.

In view of the anticipated mechanistic differences outlined above, there is therefore the need to investigate more redox reactions involving $\text{Co}(\text{CN})_5\text{X}^{3-}$.

Experimental

Materials

A commercial sample of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Johnson Matthey Co. Ltd.) from which $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared, was purified as described previously [1]. The complex $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared from purified $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ by the usual literature method [4] and its absorption peak and absorption coefficient agree with literature data [5]. Aquapentammine-ruthenium(II) and hexaammine-ruthenium(II) were generated respectively by zinc amalgam reduction [6] of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ [2] in an inert argon atmosphere. The complexes $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ and $\text{K}_3[\text{Co}(\text{CN})_5\text{NCS}]$ were prepared, purified and characterized by means of their IR and UV-Vis spectra as reported in the literature [7–11]. Their analytical concentrations agreed well with those calculated from their absorbances and the reported absorption coefficients [7a] at the absorption peaks. All the kinetic runs were performed in an inert gas (argon) medium. HCl and twice recrystallised LiCl were the usual ionic strength reagents. The ionic strength used in the runs was maintained at 0.20 mol dm^{-3} (except where effect of the ionic strength

TABLE I. Average Second-order Rate Constants (k_{obs})^a Obtained for $\text{Ru}(\text{NH}_3)_6^{2+} + \text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X} = \text{N}_3^-, \text{NCS}^-$) Reactions

T (°C)	$10^3 \times [\text{Ru}(\text{NH}_3)_6^{2+}]$ (mol dm ⁻³)	$10^4 \times [\text{Co}(\text{CN})_5\text{X}^{3-}]$ (mol dm ⁻³)	$[\text{H}^+]$ (mol dm ⁻³)	I (LiCl) ^b (mol dm ⁻³)	k_{obs} (dm ³ mol ⁻¹ s ⁻¹)	
X = N₃⁻						
25.0	1.29	1.29	0.10		1.72	
	1.92	1.29	0.07		1.62	
	1.92	1.29	0.05		1.64	
	1.92	1.29	0.10		1.66	
	2.56	1.29	0.10		1.78	
	5.12	1.29	0.10		1.76	
					mean = (1.71 ± 0.07)	
30.0	1.29	1.29	0.10		2.74	
	1.92	1.29	0.10		2.78	
35.0	1.29	1.29	0.10		4.90	
	1.92	1.29	0.10		4.86	
40.0	1.29	1.29	0.10		9.80	
	1.92	1.29	0.10		10.40	
X = NCS⁻						
20.5	0.16	21.8	0.10		0.55	
	0.16	32.6	0.10		0.52	
25.0	0.16	21.8	0.01		0.82	
	0.16	21.8	0.02		0.82	
	0.16	21.8	0.05		0.78	
	0.16	32.6	0.10		0.85	
	0.16	43.5	0.10		0.82	
	0.16	65.2	0.10		0.83	
						mean = (0.81 ± 0.05)
		0.16	21.8	0.10	0.11	1.60
	0.16	21.8	0.10	0.15	1.16	
	0.16	21.8	0.10	0.20	0.76	
	0.16	21.8	0.10	0.30	0.62	

^a k_{obs} listed in Tables I and II is the average of at least 3 runs at each of the reactant concentrations in excess. ^b $I = 0.20$ mol dm⁻³ (LiCl) except where indicated otherwise.

on the rate constant was investigated). The required aqueous aliquots of the oxidants (Co(III)) were removed from the daily freshly prepared thermostatted stock aqueous Co(III) solution and added last to the reaction mixture to minimise acid hydrolysis [7a, 9]. (The aqueous solutions of the Co(III) complexes used in this study have aquation rates of $\sim 10^{-7}$ s⁻¹ at 40 °C and unit ionic strength [7a].)

Kinetics

All the reactions were followed by conventional techniques using a Pye-Unicam Sp 500 Series 2 UV-Vis Spectrophotometer. Absorbance changes were monitored at $\lambda = 380$ nm, the absorption peak [7a] for $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ ($\epsilon = 666$ dm³ mol⁻¹ cm⁻¹) under pseudo first-order conditions, with the concentration

of the two ruthenium(II) ammine complexes in at least ten fold excess over that of the Co(III) complex. For the $\text{Co}(\text{CN})_5\text{NCS}^{3-}$, absorbance changes were followed at $\lambda = 350$ nm (following rate of disappearance of the two Ru(II) ammine complexes) under pseudo first-order conditions with the concentration of the Co(III) complex in at least ten fold excess over those of the two Ru(II) ammine complexes. The cell compartment was well-thermostatted to the desired temperature to within ± 0.1 °C. All ruthenium(II) solutions were freshly prepared and thoroughly deaerated with pure argon prior to kinetic runs and during the kinetic runs an argon gas blanket was maintained over the solution mixture in the serum-capped 2 cm or 4 cm spectrophotometric cell. Nitrogen was not used because it is known to complex [12] with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$.

TABLE II. Average Second-order Rate Constants (k_{obs}) Obtained for $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} + \text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X} = \text{N}_3^-$, NCS^-) Reactions at $I = 0.20 \text{ mol dm}^{-3}$ (LiCl), $T = 25^\circ\text{C}$

$10^4 \times [\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}]$ (mol dm^{-3})	$10^4 \times [\text{Co}(\text{CN})_5\text{X}^{3-}]$ (mol dm^{-3})	$[\text{H}^+]$ (mol dm^{-3})	k_{obs} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
X = N_3^-			
12.9	1.29	0.10	2.11
19.4	1.29	0.02	1.90
19.4	1.29	0.05	2.10
19.4	1.29	0.10	2.00
22.5	1.29	0.10	1.97
22.5	1.29	0.05	2.26
25.8	1.29	0.02	1.90
51.6	1.29	0.02	1.96
			mean = (2.06 ± 0.15)
X = NCS^-			
0.56	6.4	0.10	0.98
0.56	11.1	0.10	0.90
0.56	13.9	0.10	1.03
0.56	16.7	0.10	0.96
			mean = (0.99 ± 0.03)

Results

The observed absorbance changes indicate that the stoichiometry of all the reactions is 1 mol of Ru(II) consumed by 1 mol of Co(III) thereby giving 1 mol each of Ru(III) and Co(II). Pseudo first-order rate plots were linear to at least four half-lives in all cases. The second-order rate constants obtained from these were independent of the concentration of the reactant in excess at constant temperature. The observed second-order rate constants k_{obs} fit the rate law:

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

and are independent of the acid concentration in the range $[\text{H}^+] = (0.01-0.10) \text{ mol dm}^{-3}$ (see Tables I and II). At 25°C , and $I = 0.20 \text{ mol dm}^{-3}$ (LiCl), the observed average second-order rate constants ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the reductions by $\text{Ru}(\text{NH}_3)_6^{2+}$ are $k_{\text{N}_3} = 1.71$, $k_{\text{NCS}} = 0.81$ and by $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ are $k_{\text{N}_3} = 2.06$ and $k_{\text{NCS}} = 0.99$. From the temperature dependence of the second-order rate constants in Table 1, the activation parameters obtained using least-squares analysis are for the $\text{Ru}(\text{NH}_3)_6^{2+}$ reaction

$$\Delta H^\ddagger_{\text{N}_3} = (83.1 \pm 5.7) \text{ kJ mol}^{-1};$$

$$\Delta S^\ddagger_{\text{N}_3} = (38.6 \pm 1.9) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H^\ddagger_{\text{NCS}} = (84.0 \pm 2.2) \text{ kJ mol}^{-1};$$

$$\Delta S^\ddagger_{\text{NCS}} = (35.9 \pm 7.9) \text{ J mol}^{-1} \text{ K}^{-1}$$

It was found that in the reaction of $\text{Co}(\text{CN})_5\text{NCS}^{3-}$ with $\text{Ru}(\text{NH}_3)_6^{2+}$ (Table I), the observed

second-order rate constant varies with the ionic strength used. As the ionic strength is increased, the second-order rate constant decreases – a result which agrees qualitatively with the Bronsted theoretical prediction of the dependence of the rate constant on the product of the ionic charges for this pair of oppositely charged reactants.

It was also found that the slow decomposition/hydrolysis of $[\text{Co}(\text{CN})_5\text{N}_3]^{3-}$ in acidic solution [9] did not affect our results under the experimental conditions used as judged from the values of the rate constants obtained (Tables I and II). Moreover, since the cobalt azido complex was not the species in excess, its absolute concentrations are not crucial in determining the rate constants under pseudo first-order conditions.

Discussion

We have previously [13] measured the second-order rate constant for the substitution of free SCN^- ion into the coordination sphere of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and its value at 25°C and $I = 0.20 \text{ mol dm}^{-3}$ (LiCl) is $0.21 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate constant for the substitution of the coordinated thiocyanate in $\text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X} = \text{SCN}^-$, NCS^-) should be much smaller than the value $0.21 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is less than the measured redox rate constant obtained in this study ($k_{\text{NCS}} \sim 1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $I = 0.20$ and $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$) for the reduction of $\text{Co}(\text{CN})_5\text{NCS}^{3-}$ by $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$. The redox reaction between $\text{Co}(\text{CN})_5\text{NCS}^{3-}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ is therefore suggested to occur by an outer-sphere mechanism.

TABLE III. Relative Rates for the Various Oxidants ($X = \text{NCS}^-$, N_3^-) with the Reductants at 25 °C

Reductant	Oxidant	$k_{\text{N}_3}/k_{\text{NCS}}$	Mechanism	Reference
(1) Cr^{2+}	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	2×10^4	inner-sphere	3b
(2) Fe^{2+}	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	3×10^3	inner-sphere	3b
(3) Cr^{2+}	CrX^{2+}	4×10^4	inner-sphere	3b
(4) Fe^{2+}	FeX^{2+}	10^2	inner-sphere	3b
(5) $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{3-a}$	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	1.6	inner-sphere	3b ^a
(6) $\text{Cr}^{2+ a}$	FeX^{2+}	1	inner-sphere	3b ^a
(7) $\text{Cr}(\text{bpy})_3^{2+}$	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	4	outer-sphere	3b
(8) V^{2+}	FeX^{2+}	~ 1	outer-sphere	3b
(9) $\text{Ru}(\text{NH}_3)_6^{2+}$	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	1.5	outer-sphere	2
(10) $\text{Ru}(\text{en})_3^{2+}$	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	1.7	outer-sphere	2
(11) $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$	$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	2.2	outer-sphere	2
(12) $\text{Ru}(\text{NH}_3)_6^{2+}$	$\text{Co}(\text{CN})_5\text{X}^{3-}$	2.1	outer-sphere	this work
(13) $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$	$\text{Co}(\text{CN})_5\text{X}^{3-}$	2.1	outer-sphere	this work

^aThese are the exceptions mentioned in the text.

TABLE IV. Second-order Rate Constants for the Reduction of some Cobalt(III) Complexes by $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ at $I = 0.20 \text{ mol dm}^{-3}$ and $T = 25 \text{ }^\circ\text{C}$

Oxidant	k_a ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	k_b ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	Reference ^a	Reference ^b
(1) $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$	6.7×10^3	2.5×10^3	18	19
(2) $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	1.6×10^3	1.6×10^2	18	19
(3) $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	2.6×10^2	1.8×10^2	18	19
(4) $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$	3.79×10^2	1.67×10^2	20	2
(5) $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$	118.1	7.18	21	21
(6) $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	80	3.3×10^{-2}	19	19
(7) $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$	7.8	3.7	21	21
(8) $\text{Co}(\text{CN})_5\text{N}_3^{3-}$	1.71	2.06	this work	this work
(9) $\text{Co}(\text{CN})_5\text{NCS}^{3-}$	0.81	0.99	this work	this work
(10) $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$	1.82	0.61	20	2
(11) $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	0.74	0.28	20	2
(12) $\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4^{2+}$	0.50	0.10	21	21

^aSource of k_a for $\text{Ru}(\text{NH}_3)_6^{2+}$ reactions. ^bSource of k_b for $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ reactions.

It has been pointed out [3b, 14–16] that the difference in rates observed with symmetrical and unsymmetrical bridging groups could form the basis for determining whether a particular reaction proceeds by an inner-sphere or outer-sphere mechanism. In particular, the value of the relative rates of the reduction of azido and isothiocyanato complexes, $k_{\text{N}_3}/k_{\text{NCS}}$ have normally been used. As can be seen from Table III, large values of $k_{\text{N}_3}/k_{\text{NCS}}$ of $\geq 10^2$ have usually been associated with inner-sphere redox reactions while low values of ≤ 10 have indicated an outer-sphere mechanism since bond formations are not required in outer-sphere redox reactions. Exceptions to this fairly general rule could be seen in reactions (5) and (6) in Table III and the probable reasons for these were cited [3b] but these do not apply to $\text{Ru}(\text{II})$ used as reductant in this

study. The very slow acid hydrolysis of hexaammine–ruthenium(II) [12] does not interfere with the redox reactions herein reported. $\text{Ru}(\text{NH}_3)_6^{2+}$ does not have active substitution sites and therefore will react with $\text{Co}(\text{CN})_5\text{X}^{3-}$ ($X = \text{N}_3^-$, NCS^-) by an outer-sphere mechanism. The value of $k_{\text{N}_3}/k_{\text{NCS}} = 2.1$ is in full agreement with the assignment of an outer-sphere mechanism for the reactions of $\text{Ru}(\text{NH}_3)_6^{2+}$ (Table III) with both $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ and $\text{Co}(\text{CN})_5\text{NCS}^{3-}$. Similarly, the low value of $k_{\text{N}_3}/k_{\text{NCS}} = 2.1$ for the $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ reduction of these two $\text{Co}(\text{III})$ complexes would suggest an outer-sphere mechanism for these reactions.

Modified Marcus equation plots [2, 17] (based on linear free-energy relationship) for the reduction of various $\text{Co}(\text{III})$ complexes by $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ obtained from the data in Table IV,

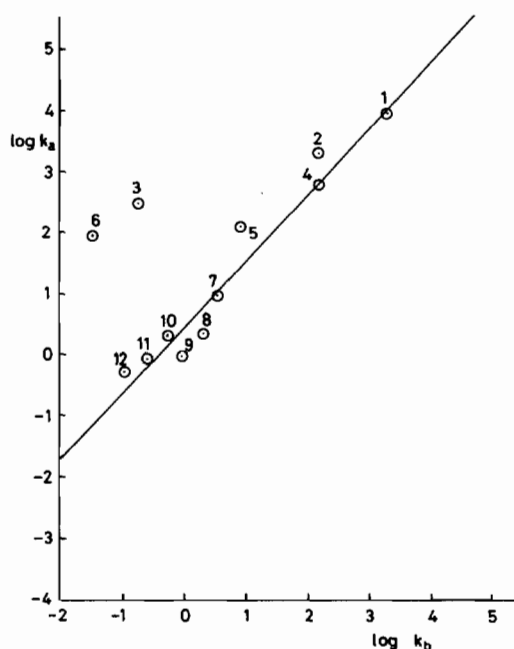


Fig. 1. Log-log plots for the reduction of some cobalt(III) complexes by $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$. Numbering is as in Table IV.

are presented in Fig. 1. Reactions involving $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{F}^-$, Cl^-) with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ have been previously shown [21] to proceed through an inner-sphere mechanism and these two points fall off the line defined by eqn. (2)

$$\log k_a = (1.05 \pm 0.08) \log k_b + 0.44 \quad (2)$$

(where k_a represents the rate constants for reactions involving $\text{Ru}(\text{NH}_3)_6^{2+}$ and k_b those involving $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$) which has a correlation factor of 0.97. All the other Co(III) reactions except those involving pentacyanocobaltate(III) ions have been shown to go by an outer-sphere mechanism. Since the points for the azido- and isothiocyanatopentacyanocobaltate(III) ions clearly fall close to the line defined by eqn. (2), their reactions with the reductants $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ could be said to proceed through an outer-sphere mechanism too.

Based solely on their redox potentials [12] $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ should be less reactive than $\text{Ru}(\text{NH}_3)_6^{2+}$ for any given oxidant. However, the reverse is obtained in this study. The reason for this anomaly is not immediately apparent but it may be due to the favourable coulombic interaction between the positively charged Ru(II) species and the negatively

charged cobalt(III) complexes ($\text{Co}(\text{CN})_5\text{X}^{3-}$). This favourable coulombic interaction could enhance the rate constant through a larger outer-sphere formation constant in the reactions of the two pentacyanocobaltate(III) ions with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ (when compared with $\text{Ru}(\text{NH}_3)_6^{2+}$) because of the greater lability of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ relative to $\text{Ru}(\text{NH}_3)_6^{2+}$. Previously, those outer-sphere reactions, in which $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ proceeds at slower rates than $\text{Ru}(\text{NH}_3)_6^{2+}$, involve cationic oxidants [2, 21].

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