Kinetics and Mechanism of the Reduction of Thiocyanato-, Isothiocyanato-, and Azido-penta-amminecobalt(III) by Penta-ammineaquaruthenium(II) in Aqueous Solutions

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Kinetic measurements have been made on the reactions of $[Ru(NH_3)_5(OH_2)]^{2+}$ with $[Co(NH_3)_5X]^{2+}$ (X = SCN, NCS, or N_3) in aqueous solution. The reactions obey second-order rate laws with the following kinetic parameters at 25 °C, $I = 0.20$ mol dm^{-3} (LiCl), and $[H^+] = 0.10$ mol dm^{-3} (HCl): $k_{SCN} = (1.7 \pm 0.10) \times 10^2$, $k_{N_3} = 0.61 \pm 0.02$, and $k_{NCS} = 0.28 \pm 0.01$ dm^3 mol^{-1} s^{-1}; $\Delta H^‡_{SCN} = 35.1 \pm 2.9$ kJ mol^{-1}, $\Delta S^‡_{SCN} = -84.5 \pm 7.5$ J K^{-1} mol^{-1}, $\Delta H^‡_{N_3} = 55.2 \pm 1.7$ kJ mol^{-1}, $\Delta S^‡_{N_3} = -(63.2 \pm 8.4)$ J K^{-1} mol^{-1}, $\Delta H^‡_{NCS} = 61.9 \pm 3.3$ kJ mol^{-1}, $\Delta S^‡_{NCS} = -47.3 \pm 5.9$ J K^{-1} mol^{-1}. The reactions are not affected by added acid or chloride ion. The small ratio $k_{N_3} : k_{NCS}$ obtained for these reactions confirms that they occur by an outer-sphere mechanism. In agreement with other outer sphere reactions previously reported, the ratio $k_{SCN} : k_{N_3}$ for these reactions is larger than that in inner-sphere redox reactions and an excellent linear free-energy correlation is obtained when the modified form of the Marcus equation is used to compare the rates of the reduction of the cobalt(III) complexes by $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[Ru(NH_3)_6]^{2+}$.

THE cations $[Ru(NH_3)_6]^{2+}$, $[Ru(en)_3]^{2+}$, and $[Cr(bipy)_3]^{2+}$ are now confidently classified as typical outer-sphere reductants [1-5] as a result of their substitution inertness and redox properties (en = ethylenediamine, bipy = 2,2′-bipyridine). Unlike $[Ru(NH_3)_6]^{2+}$, a normal co-ordination position is available in $[Ru(NH_3)_5(OH_2)]^{2+}$ for possible occupation, during a redox reaction, by a good bridging ligand X from an oxidant $[RX]^{2+}$ [R = $Co(NH_3)_5$, $Ru(NH_3)_5$, *etc.*]. Although some reports have been made [3,6,7] of the co-ordination of penta-ammineaquaruthenium(II) with nitrogen and nitrogen-containing ligands, little is known of its redox properties. In fact, only indirect estimates [8,9] have been made of the rate constants of the outer-sphere reactions of $[Ru(NH_3)_5(OH_2)]^{2+}$ with penta-amminehalogenoruthenium(III) ions. The reactions of $[Ru(NH_3)_6]^{2+}$ with $[Co(NH_3)_5X]^{2+}$ (X = SCN, N_3, NCS, Cl, Br, or I) occur by an outer-sphere mechanism as evidenced [1] by the substitution inertness of $[Ru(NH_3)_6]^{2+}$ and the low ratio of $k_{N_3} : k_{NCS}$. In view of the considerably greater substitution lability of $[Ru(NH_3)_5(OH_2)]^{2+}$ compared with $[Ru(NH_3)_6]^{2+}$, the mechanism of the redox reactions between $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[Co(NH_3)_5X]^{2+}$ (X = SCN, N_3, or NCS) should be of considerable interest. We have therefore made direct measurements of the rate parameters for these reactions in aqueous solution and compared them with the reactions of the less labile $[Ru(NH_3)_6]^{2+}$.

EXPERIMENTAL

Materials.—The complexes $[Co(NH_3)_5(SCN)]Cl_2 \cdot 1.5H_2O$, $[Co(NH_3)_5(N_3)][ClO_4]_2$, and $[Co(NH_3)_5(NCS)]Cl_2$ were prepared, purified, and characterised by means of their u.v.–visible spectra as reported in the literature.[10-12] Their concentrations were determined from their measured absorbances and the reported absorption co-efficients [10-12] at the absorption peaks: $[Co(NH_3)_5(SCN)]^{2+}$, 288 nm, 15 600; $[Co(NH_3)_5(N_3)]^{2+}$, 302 nm, 7 830; and $[Co(NH_3)_5(NCS)]^{2+}$, $\lambda_{max.}$ 306 nm, ε 1 541 dm^3 mol^{-1} cm^{-1}. A commercial sample of $[Ru(NH_3)_6]Cl_3$ (Johnson, Matthey Co. Ltd.), from which $[Ru(NH_3)_5Cl]Cl_2$ was prepared, was purified as described previously.[5] The complex $[Ru(NH_3)_5Cl]Cl_2$ was prepared from purified $[Ru(NH_3)_6]Cl_3$ by the usual literature method [13] and its absorption peak and absorption coefficient agree with literature data.[8] Penta-ammineaquaruthenium(II) was generated by the zinc-amalgam reduction [6] of $[Ru(NH_3)_5Cl]Cl_2$ in an argon atmosphere. The concentration of $[Ru(NH_3)_5(OH_2)]^{2+}$ was determined [14] by adding excess of an acidic solution of Fe^{III}, complexing the Fe^{II} so formed with 1,10-phenanthroline solution in potassium hydrogenphthalate, and measuring the absorbance of the resulting $[Fe(phen)_3]^{2+}$ at 510 nm ($\varepsilon_{max.}$ 11 000 dm^3 mol^{-1} cm^{-1}).

Kinetics.—The reactions between $[Co(NH_3)_5(SCN)]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$ were monitored by following the decrease in absorbance of $[Co(NH_3)_5(SCN)]^{2+}$ at 512 nm (ε 74 dm^3 mol^{-1} cm^{-1}) on a Durrum–Gibson stopped-flow spectrophotometer. The slower reactions of $[Ru(NH_3)_5(OH_2)]^{2+}$ with $[Co(NH_3)_5(N_3)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ were followed [11] at 516 (ε 275) and 498 nm (ε 179 dm^3 mol^{-1} cm^{-1}) respectively on a Unicam SP 500 spectrophotometer. At these wavelengths $[Ru(NH_3)_5(OH_2)]^{2+}$ has negligible absorption. The cell compartments were well thermostatted (to ±0.1 °C) by circulating water from a water-bath regulated to the desired temperature. All the solutions were thoroughly deoxygenated with pure argon before the kinetic runs. Nitrogen was not used because

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it is known to be able to complex [3] with $[Ru(NH_3)_5(OH_2)]^{2+}$. Perchlorate ion readily oxidises [3] Ru^{II} to Ru^{III} {for $[Ru(NH_3)_5(OH_2)]^{2+} + [ClO_4]^-$ at 25 °C, $k_2 = 2.6 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}} so a HCl–LiCl mixture was used to maintain the ionic strength at 0.20 mol dm^{-3}. However, in runs where the effects of chloride ions were investigated for the reactions between $[Co(NH_3)_5(N_3)]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$, $Li[ClO_4]$ was used to maintain the ionic strength at 0.20 mol dm^{-3}. The reactions were studied under pseudo-first-order conditions with $[Ru(NH_3)_5(OH_2)]^{2+}$ in large excess.

RESULTS

Stoicheiometry.—From spectrophotometric determinations of the concentrations of the cobalt(III) complexes at the appropriate regions of the visible [11] spectrum it was found that 1 mol of the cobalt(III) complex reacts with 1 mol of the ruthenium(II) complex for the thiocyanato- and isothiocyanato-complexes, while for the azido-complex 1 mol of Co^{III} reacts with 1.5 mol of Ru^{II}. These results agree with the earlier stoicheiometric results of Endicott and Taube,[1] and of Adegite *et al.*[5] using $[Ru(NH_3)_6]^{2+}$ as the reductant.

Reactions of $[Ru(NH_3)_5(OH_2)]^{2+}$ *and* $[Co(NH_3)_5X]^{2+}$ (X = SCN *or* NCS).—Pseudo-first-order plots for these reactions were linear to >95% completion of reaction. The second-order rate constants obtained from these were independent of the ruthenium(II) concentrations. The results at different temperatures are shown in Tables 1 and 2. These confirm that the reactions are first order in both $[Ru^{II}]$ and $[Co^{III}]$, giving the overall rate equation (1).

$$-d[Co(NH_3)_5X^{2+}]/dt = k[Ru(NH_3)_5(OH_2)^{2+}][Co(NH_3)_5X^{2+}] \quad (1)$$

From the temperature dependence of the second-order rate constants the activation parameters obtained were $\Delta H^‡_{SNC} = 35.1 \pm 2.3$ kJ mol^{-1}, $\Delta S^‡_{SCN} = -84.5 \pm 7.5$ J K^{-1} mol^{-1}, $\Delta H^‡_{NCS} = 61.9 \pm 3.3$ kJ mol^{-1}, and $\Delta S^‡_{NCS} = 47.3 \pm 5.9$ J K^{-1} mol^{-1}.

TABLE 1

Rate constants for the $[Ru(NH_3)_5(OH_2)]^{2+} + [Co(NH_3)_5(SCN)]^{2+}$ reaction at $[Co(NH_3)_5(SCN)^{2+}] = 8.0 \times 10^{-4}$, $I = 0.20$ (LiCl), and $[H^+] = 0.10$ mol dm^{-3}

θ_c / °C	$10^2[Ru(NH_3)_5(OH_2)^{2+}]$ / mol dm^{-3}	$10^{-2}k_{SCN}$ / dm^3 mol^{-1} s^{-1}
18.5	0.75	1.2
	1.13	1.1
	1.35	1.2
25.0	0.75	1.8
	0.83	1.6
	0.90	1.5
	1.13	2.0
	1.35	1.7
	2.00	1.4
29.0	0.75	2.2
	1.13	2.1
	1.35	2.1
36.0	0.75	3.0
	1.13	2.9
	1.35	2.7

TABLE 2

Rate constants for the $[Ru(NH_3)_5(OH_2)]^{2+} + [Co(NH_3)_5(NCS)]^{2+}$ reaction at $[Co(NH_3)_5(NCS)^{2+}] = 2.4 \times 10^{-4}$—$6.0 \times 10^{-4}$, $I = 0.20$ (LiCl), and $[H^+] = 0.10$ mol dm^{-3}

θ_c / °C	$10^2[Ru(NH_3)_5(OH_2)^{2+}]$ / mol dm^{-3}	k_{NCS} / dm^3 mol^{-1} s^{-1}
10.0	0.90	0.071
	1.20	0.062
	2.00	0.081
15.0	0.60	0.13
	0.90	0.093
	1.20	0.11
17.5	0.60	0.15
	0.90	0.14
	1.20	0.17
23.0	0.30	0.21
	0.45	0.20
	0.60	0.27
	0.75	0.24
	0.90	0.23
	0.90	0.25
25.0	0.30	0.30
	0.60	0.26
	0.90	0.27
	1.20	0.28

TABLE 3

Rate constants for the $[Ru(NH_3)_5(OH_2)]^{2+} + [Co(NH_3)_5(N_3)]^{2+}$ reaction at $[Co(NH_3)_5(N_3)^{2+}] = 2.08 \times 10^{-4}$—$4.16 \times 10^{-4}$ and $I = 0.20$ mol dm^{-3}

θ_c / °C	$10^2[Ru(NH_3)_5(OH_2)^{2+}]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[Cl^-]$ / mol dm^{-3}	k_{N_3} / dm^3 mol^{-1} s^{-1}
8.0	0.90	0.10	0.20	0.16
	1.20	0.10	0.20	0.18
	2.40	0.10	0.20	0.12
	2.80	0.10	0.20	0.14
15.5	0.90	0.10	0.20	0.30
	1.20	0.10	0.20	0.31
	1.80	0.10	0.20	0.27
	2.40	0.10	0.20	0.29
22.5	0.40	0.10	0.20	0.49
	0.48	0.10	0.20	0.53
	0.60	0.10	0.20	0.55
	1.20	0.10	0.20	0.45
	1.80	0.10	0.20	0.46
	1.20	0.05	0.20	0.52
	1.20	0.15	0.20	0.53
	1.20	0.20	0.20	0.50
	0.60	0.10	0.05	0.55
	0.60	0.10	0.10	0.51
	0.60	0.10	0.15	0.54
	0.60	0.10	0.20	0.50
25.0	0.24	0.10	0.20	0.56
	0.36	0.10	0.20	0.66
	0.48	0.10	0.20	0.61
	0.72	0.10	0.20	0.59
	0.96	0.10	0.20	0.64
30.0	0.24	0.10	0.20	0.85
	0.36	0.10	0.20	0.95
	0.48	0.10	0.20	0.91
	0.72	0.10	0.20	0.92

After the redox reactions between $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[Co(NH_3)_5X]^{2+}$ (X = SCN or NCS) there was a gradual increase in absorbance. The colour of the primary reaction mixture changed slowly from yellowish green {colour of excess of $[Ru(NH_3)_5(OH_2)]^{2+}$} to orange-red. This was found to be due to the formation of a complex between excess of $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[NCS]^-$ released from reacted $[Co(NH_3)_5X]^{2+}$ according to equations (2) and (3). The new complex has an absorption peak at

$$[Ru(NH_3)_5(OH_2)]^{2+} + [Co(NH_3)_5X]^{2+} \longrightarrow [Ru(NH_3)_5(OH_2)]^{3+} + Co^{2+} + X^- + 5NH_3 \quad (2)$$

$$[Ru(NH_3)_5(OH_2)]^{2+} + X^- \longrightarrow [Ru(NH_3)_5X]^+ \quad (3)$$

490 nm. Infrared spectra of the isolated product {which must have been converted into $[Ru(NH_3)_5X]^{2+}$ in the air} showed absorption ν_1 at 2 070 cm^{-1} only, indicating[15] that the thiocyanate is bonded to Ru^{II} *via* the nitrogen atom after the primary redox reaction. This subsequent complex formation between excess of $[Ru(NH_3)_5(OH_2)]^{2+}$ and released $[NCS]^-$ did not interfere with the primary redox reaction because pseudo-first-order rate plots for these reactions were linear to >95% completion of reaction. A separate experiment using $[Ru(NH_3)_5(OH_2)]^{2+}$ and free $[NCS]^-$ (from ammonium thiocyanate solution) mixed in a well deoxygenated spectrophotometric cell gave the same complex, identified as above.

Reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ *and* $[Co(NH_3)_5(N_3)]^{2+}$.—Pseudo-first-order plots for this reaction were linear to >95% completion of reaction. The second-order rate constants obtained were independent of [Ru^{II}], [H$^+$], and [Cl$^-$]. The results are shown in Table 3. From the temperature dependence of the second-order rate constants, the activation parameters obtained were $\Delta H^\ddagger_{N_3} = 55.2 \pm 1.7$ kJ mol^{-1} and $\Delta S^\ddagger_{N_3} = -63.2 \pm 8.4$ J K^{-1} mol^{-1}. There was no complex formation between excess of $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[N_3]^-$ after the redox reaction.

DISCUSSION

The rate constant for the substitution of free thiocyanate ion into the co-ordination sphere of $[Ru(NH_3)_5(OH_2)]^{2+}$ in the presence of pyrazine was estimated roughly by Shepherd and Taube[6] as 4 dm^3 mol^{-1} s^{-1} at 25 °C. The rate constant for substitution of thiocyanate of $[Co(NH_3)_5X]^{2+}$ (X = SCN or NCS) into the co-ordination sphere of $[Ru(NH_3)_5(OH_2)]^{2+}$ is likely to be much less than 4 dm^3 mol^{-1} s^{-1} at 25 °C, which is very much less than the measured rate constant $\{k_{SCN} = (1.7 \pm 0.10) \times 10^2$ dm^3 mol^{-1} s^{-1} at $I = 0.20$ and $[H^+] = 0.10$ mol dm$^{-3}\}$ for the reduction of $[Co(NH_3)_5(SCN)]^{2+}$ by $[Ru(NH_3)_5(OH_2)]^{2+}$ at 25 °C in the present study. This is supported by our observation that complex formation between $[NCS]^-$ {from consumed $[Co(NH_3)_5X]^{2+}$} and $[Ru(NH_3)_5(OH_2)]^{2+}$ occurred after the primary redox reactions. The redox reaction between $[Co(NH_3)_5(SCN)]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$ is therefore suggested to occur by an outer-sphere mechanism.

The reactivity order for the three cobalt(III) complexes, $k_{SCN} > k_{N_3} > k_{NCS}$, is the usual order obtained for redox systems involving these three complexes.[5] Table 4 shows the relative rates of the reactions of $[Co(NH_3)_5X]^{2+}$ (X = SCN, N$_3$, or NCS) with some reductants. This lends support for the assignment of an outer-sphere mechanism to the reactions with $[Ru(NH_3)_5(OH_2)]^{2+}$ in two ways.

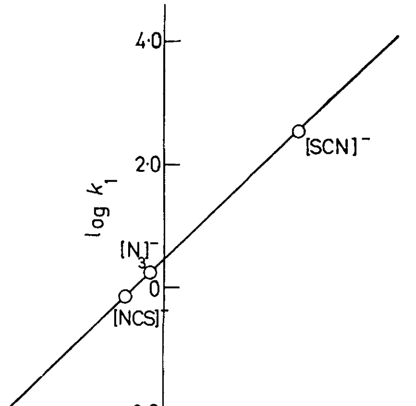
(*i*) $(k_{N_3} : k_{NCS})_{o.s.} \ll (k_{N_3} : k_{NCS})_{i.s.}$. The effect of the stability of the precursor complexes on the energetics of the activation processes, in which 'hard' acids prefer[5] to form *N*- rather than *S*-bonded complexes, is responsible for the large $k_{N_3} : k_{NCS}$ ratios in inner-sphere redox reactions. Such bond formations are not required in outer-sphere redox reactions and hence the

TABLE 4

Relative rates of the reactions of $[Co(NH_3)_5X]^{2+}$ (X = SCN, N$_3$, or NCS) with some reductants

Reductant	$k_{N_3} : k_{NCS}$	$k_{SCN} : k_{N_3}$	Mechanism[a]	Ref.
Cr^{2+}	1.6×10^4	0.63	i.s.	*b*
Eu^{2+}	3.9×10^3	16.0	i.s.	*c*
Fe^{2+}	3.0×10^3	13.3	i.s.	*d*
U^{3+}	4.4×10^4		i.s.	*e*
Ti^{3+}	3.9×10^5	10.5	i.s.	*f*
Cu^+	10^3		i.s.	*g*
$[Ru(NH_3)_6]^{2+}$	1.5	200	o.s.	5
$[Ru(en)_3]^{2+}$	1.7	178	o.s.	5
$[Cr(bipy)_3]^{2+}$	4.0	43	o.s.	5, *h*
$[Ru(NH_3)_5(OH_2)]^{2+}$	2.2	278	o.s.	This work

[a] i.s. = Inner sphere, o.s. = outer sphere. [b] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 3055; *Inorg. Chem.*, 1973, **12**, 3013. [c] A. Adegite and T. Kuku, *J.C.S. Dalton*, 1976, 158. [d] D. P. Fay and N. Sutin, *Inorg. Chem.*, 1970, **9**, 1291; J. H. Espenson, *ibid.*, 1965, **4**, 121. [e] R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, 1971, **93**, 380. [f] A. Adegite and J. F. Ojo, *Inorg. Chem.*, 1977, **16**, 477; J. P. Birk, *ibid.*, 1975, **14**, 1724. [g] O. J. Parker and J. S. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1968. [h] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.



Log–log plot comparing the rates of outer-sphere reduction of some $[Co(NH_3)_5X]^{2+}$ complexes and $[ClO_4]^-$ by $[Ru(NH_3)_6]^{2+}$ (k_1) and $[Ru(NH_3)_5(OH_2)]^{2+}$ (k_2). Rate constants for $[Ru(NH_3)_6]^{2+}$ are from ref. 5; for the reduction of $[ClO_4]^-$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$, values are from ref. 2

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rate constants are less sensitive to the nature of the ligands.

(*ii*) $(k_{\mathrm{SCN}} : k_{\mathrm{N_3}})_{\mathrm{o.s}} > (k_{\mathrm{SCN}} : k_{\mathrm{N_3}})_{\mathrm{i.s.}}$. The extra stability acquired by the precursor complex for the azido- relative to the thiocyanato-complex is probably responsible for reducing the reactivity gap[5] between $[\mathrm{Co(NH_3)_5(SCN)}]^{2+}$ and $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ for inner-sphere redox reactions. The extra stability is acquired by the precursor azido-complex through the greater exothermicity (by resonance) accompanying its formation.

Application of the modified form of the Marcus equation[4,5] to the reactions of these penta-amminecobalt(III) complexes and $[\mathrm{ClO_4}]^-$ with $[\mathrm{Ru(NH_3)_6}]^{2+}$ and $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ (Figure) indicates that free-energy changes constitute the dominant factor controlling the reactivity pattern in these outer-sphere redox reactions. An excellent linear correlation was obtained of the form (4) where k_1 is the rate constant for $[\mathrm{Ru(NH_3)_6}]^{2+}$ and k_2 that for $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$. Perchlorate ion clearly does not fall on this linear plot.

$$\log k_1 = (1.00 \pm 0.04) \log k_2 + 0.45 \qquad (4)$$

The cation $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ was found[2,3,15] to be more reactive towards $[\mathrm{ClO_4}]^-$ than $[\mathrm{Ru(NH_3)_6}]^{2+}$, opposite to what is found for their reactions with $[\mathrm{Co(NH_3)_5X}]^{2+}$ (X = SCN, $\mathrm{N_3}$, or NCS) in the present study and with $\mathrm{Fe^{3+}}$.[17] The greater lability[3] of $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ compared with $[\mathrm{Ru(NH_3)_6}]^{2+}$ is said to be responsible for its higher reactivity. The redox potentials[3] for the couples (5) and (6) suggest that

$$[\mathrm{Ru(NH_3)_6}]^{2+} - e^- \longrightarrow [\mathrm{Ru(NH_3)_6}]^{3+} \quad E^\ominus = -0.10\ \mathrm{V} \qquad (5)$$

$$[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+} - e^- \longrightarrow [\mathrm{Ru(NH_3)_5(OH_2)}]^{3+} \quad E^\ominus = -0.16\ \mathrm{V} \qquad (6)$$

$[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ should be a poorer outer-sphere reducing agent than $[\mathrm{Ru(NH_3)_6}]^{2+}$. Table 5 and the Figure suggest that this is so for $[\mathrm{Co(NH_3)_5X}]^{2+}$ (X = SCN, $\mathrm{N_3}$, or NCS) and $\mathrm{Fe^{3+}}$ but not so for $[\mathrm{ClO_4}]^-$ and $[\mathrm{Fe(OH)}]^{2+}$,[3,17] supporting the idea that the reactions of $[\mathrm{Co(NH_3)_5X}]^{2+}$ (X = SCN, $\mathrm{N_3}$, or NCS) and $\mathrm{Fe^{3+}}$ with $[\mathrm{Ru(NH_3)_6}]^{2+}$ and $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ occur by an outer-sphere mechanism while the reactions of these reductants with $[\mathrm{ClO_4}]^-$ and $[\mathrm{Fe(OH)}]^{2+}$ occur by a different mechanism.

The activation enthalpies of these reactions are in agreement with the order of reactivity, $k_{\mathrm{SCN}} > k_{\mathrm{N_3}} > k_{\mathrm{NCS}}$, and this more than compensates for the apparently more favourable entropies of activation for the less reactive penta-amminecobalt(III) complexes.

TABLE 5

Rate constants for the reactions of $[\mathrm{Ru(NH_3)_6}]^{2+}$ and $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$ with $[\mathrm{Co(NH_3)_5X}]^{2+}$ (X = SCN, $\mathrm{N_3}$, or NCS) and some oxidants

	k/dm^3 mol^{-1} s^{-1}		Ref.	
Oxidant	$[\mathrm{Ru(NH_3)_6}]^{2+}$	$[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$	*b*	*c*
$[\mathrm{Co(NH_3)_5(SCN)}]^{2+}$	379 [a]	167 [a]	5	This work
$[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$	1.82 [a]	0.61 [a]	5	This work
$[\mathrm{Co(NH_3)_5(NCS)}]^{2+}$	0.74 [a]	0.28 [a]	5	This work
$\mathrm{Fe^{3+}}$	31×10^4 [d]	8×10^4 [d]	17	17
$[\mathrm{Fe(OH)}]^{2+}$	5×10^4 [d]	4.8×10^5 [d]	17	17
$[\mathrm{ClO_4}]^-$	3×10^{-4} [a]	2.6×10^{-2} [a]	2	2

Rate constants for $\mathrm{Fe^{3+}}$ and $[\mathrm{Fe(OH)}]^{2+}$ were not plotted in the Figure since these values were supplied at 10 °C and $I = 0.10$ mol dm^{-3}.

[a] 25 °C, $I = 0.20$ mol dm^{-3}. [b] For $[\mathrm{Ru(NH_3)_6}]^{2+}$. [c] For $[\mathrm{Ru(NH_3)_5(OH_2)}]^{2+}$. [d] 10 °C, $I = 0.10$ mol dm^{-3}.

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