# Kinetics and Mechanism of the Reduction of Thiocyanato-, Azido-, and Isothiocyanato-penta-amminecobalt(III) by Hexa-ammineruthenium(II), Tris(ethylenediamine)ruthenium(II), and Tris(2,2'-bipyridyl)chromium(II) in Aqueous Solutions

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The kinetics of reduction of $[Co(NH_3)_5X]^{2+}$ (X = SCN, $N_3$, or NCS) by $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ (en = ethylenediamine) in aqueous solutions have been investigated. All the reactions follow second-order rate equations, and the kinetic parameters obtained at 25 °C, $I$ = 0.20 mol dm$^{-3}$, and $[H^+]$ = 0.10 mol dm$^{-3}$ are as follows: $[Ru(NH_3)_6]^{2+}$, $k_{SCN} = 379 \pm 7$, $k_{N_3} = 1.82 \pm 0.10$, $k_{NCS} = 0.74 \pm 0.06$ dm$^3$ mol$^{-1}$ s$^{-1}$, $\Delta H_{SCN}^{\ddagger} = 6.4 \pm 0.2$ kcal mol$^{-1}$, $\Delta S_{SCN}^{\ddagger} = -(25.3 \pm 1.0)$ cal K$^{-1}$ mol$^{-1}$, $\Delta H_{N_3}^{\ddagger} = 9.4 \pm 0.8$ kcal mol$^{-1}$, $\Delta S_{N_3}^{\ddagger} = -(25.9 \pm 2.6)$ cal K$^{-1}$ mol$^{-1}$, $\Delta H_{NCS}^{\ddagger} = 14.9 \pm 0.7$ kcal mol$^{-1}$, $\Delta S_{NCS}^{\ddagger} = -(9.5 \pm 1.8)$ cal K$^{-1}$ mol$^{-1}$; $[Ru(en)_3]^{2+}$, $k_{SCN} = 45.3 \pm 4.0$, $k_{N_3} = 0.26 \pm 0.01$, $k_{NCS} = 0.15 \pm 0.02$ dm$^3$ mol$^{-1}$ s$^{-1}$; $[Cr(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl), $k_{SCN} \geqslant 7.0 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$. The small $k_{N_3} : k_{NCS}$ ratios for these reactions confirm that they proceed by the outer-sphere mechanism. The $k_{SCN} : k_{N_3}$ ratio is generally higher for reactions of the outer-sphere mechanism than for reactions of the inner-sphere type in which the bridging ligands are only $[SCN]^-$, $[N_3]^-$, and $[NCS]^-$. This mechanism-dependent reactivity pattern is attributed to the fact that in outer-sphere reactions the sole determinant of the reactivity pattern is $\Delta G^{\ominus}$, while the crucial factor in inner-sphere reactions is the relative stability of the precursor complexes. Additional confirmatory evidence for this conclusion stems from the excellent correlation obtained when Marcus' theory is employed to compare the rates of reduction of some penta-ammineanionocobalt(III) complexes by $[Cr(bipy)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$.

In the kinetic investigations of the reduction of penta-amminecobalt(III) complexes by metal aqua-ions, mechanistic classification into the inner- or outer-sphere type has often been based on the relative rates of reduction of the azido- and the isothiocyanato-complexes.[1,2] Such rate comparisons have been extended[3-6] to the thiocyanato-complex, and the reactivity order for almost all the aqua-ions is $k_{SCN} > k_{N_3} > k_{NCS}$. This reactivity order has been attributed to a combination of three possible factors,[6] *viz.*: (*a*) free-energy changes in the reactions; (*b*) changes in the stability of the precursor complexes as the bridging ligand changes; (*c*) the greater ease of stretching the Co–S compared to the Co–N bond in the precursor complexes. The relative importance of each factor is unknown. Moreover, the much higher reactivity of *S*-bonded cobalt complexes towards such aqua-ions has also been attributed to the special electron-mediating ability of a sulphur bound to a cobalt centre.[5,7]

As a means of assessing, at least qualitatively, the importance of (*b*) in relation to the other factors, the reactivity order for the reduction of such complexes by $[Ru(NH_3)_6]$,$^{2+}$ $[Ru(en)_3]^{2+}$ (en = ethylenediamine), and $[Cr(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl) has now been investigated. These complexes have been shown, through the retention of their co-ordination integrity during the electron-transfer process, and from other evidence, to be good examples of outer-sphere reducing agents.[8,9] Since precursor-complex formation in such reactions does not entail bond formation, it is presumed that the ambiguity of adjacent or remote attack of the ambidentate bridging ligand does not further complicate the interpretation of the results obtained.

## EXPERIMENTAL

*Materials.* $[Co(NH_3)_5(SCN)]Cl_2 \cdot 1.5H_2O$, $[Co(NH_3)_5(N_3)][ClO_4]_2$, 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] Tris(ethylenediamine)-ruthenium(II) was prepared by zinc-amalgam reduction of tris(ethylenediamine)ruthenium(III) tetrachlorozincate(II), a procedure first adopted by Meyer[13] and fully reported by Elsbernd and Beattie.[14] The complex $[Ru(en)_3]^{2+}$ prepared by this method gave identical spectral characteristics with those reported by these workers, *viz.* well defined shoulders at 370 and 304 nm (ε 120 and 1 000 dm$^3$ mol$^{-1}$ cm$^{-1}$) respectively. We also tried the method of Allen and Senoff[15] for the preparation of $[Ru(en)_3]Cl_2$. The products obtained gave low absorption coefficients (45 and 140 dm$^3$ mol$^{-1}$ cm$^{-1}$ respectively) at these wavelengths, and had no reducing properties, at least as shown in the reactions with the penta-ammineaniono-complexes used in this work. A commercial sample of $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey), from which $[Ru(NH_3)_6]^{2+}$ was prepared by zinc-amalgam reduction, was first purified by dissolving it (1 g) in 10$^{-3}$ mol dm$^{-3}$ HCl (40 cm$^3$), filtering off solid impurities, cooling the filtrate to 0 °C, and adding an equal

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volume of chilled concentrated HCl. The resulting precipitate was filtered off and recrystallised at least twice from $10^{-3}$ mol dm$^{-3}$ HCl. The final pure product was dried in air.

The concentrations of the penta-amminecobalt(III) complexes were determined from their measured absorbances and the reported [10-12] absorption co-efficients at the absorbance peaks: $[Co(NH_3)_5(SCN)]^{2+}$, $\lambda_{max.}$ 288, ε 15 600; $[Co(NH_3)_5(N_3)]^{2+}$, $\lambda_{max.}$ 302, ε 7 830; $[Co(NH_3)_5(NCS)]^{2+}$, $\lambda_{max.}$ 306 nm, ε 1 541 dm$^3$ mol$^{-1}$ cm$^{-1}$. The concentrations of the $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ ions were determined by the addition of excess of acidic iron(III) solution, complexing the $Fe^{II}$ formed with 1,10-phenanthroline (phen) solution in potassium hydrogenphthalate [16] and measuring the absorbance of the resulting $[Fe(phen)_3]^{2+}$ at 510 nm where the absorption co-efficient is 11 000 dm$^3$ mol$^{-1}$ cm$^{-1}$.

*Kinetics*.—All the reactions with $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ were followed by conventional techniques using a Unicam SP 500 spectrophotometer. The cell compartments were well thermostatted by circulating water from a water-bath regulated to the desired temperature which was maintained constant to within ±0.1 °C. The rates of the reactions were monitored by following absorbance decreases at selected wavelengths where the cobalt(III) complexes absorb much more intensely than either $Ru^{II}$ or $Ru^{III}$. The wavelengths used were 288, 498, and 516 nm for the thiocyanato-, isothiocyanato-, and azido-complexes respectively. In all the runs, $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ were in such large excesses that pseudo-first-order conditions in the cobalt(III) complexes prevailed throughout the courses of the reactions. Since perchlorate ion is known to easily oxidise $Ru^{II}$ to $Ru^{III}$ $\{k_2$ for $[Ru(NH_3)_6]^{2+} + [ClO_4]^-$ is *ca.* $3.0 \times 10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C and $I = 0.62$ mol dm$^{-3}\}$, HCl–LiCl was used to maintain the ionic strength at 0.20 mol dm$^{-3}$. However, lithium perchlorate was employed in some of the runs with $[Co(NH_3)_5(N_3)]^{2+}$ when the effects of chloride ions were investigated. All the solutions were thoroughly freed from air by passing argon which had been previously scrubbed in chromium(II) towers.

## RESULTS

*Stoicheiometry*.—It was shown from spectrophotometric determinations of the concentrations of the complexes in the visible region that, for the thiocyanato- and isothiocyanato-complexes, 1 mol of the ruthenium(II) complex reacts with 1 mol of the cobalt(III) complex, but 1 mol of the azido-complex reacts with 1.5 mol of $[Ru(NH_3)_6]^{2+}$. The latter result agrees with the earlier stoicheiometric results of Endicott and Taube,[8] and is explained in terms of the subsequent reaction of the liberated $[N_3]^-$ with $[Ru(NH_3)_6]^{2+}$ according to equation (1).

$$2[Ru(NH_3)_6]^{2+} + 4[N_3]^- + 6H^+ \longrightarrow 2[Ru(NH_3)_6]^{3+} + 5N_2 + 2NH_3 \quad (1)$$

*Reactions*.—$[Ru(NH_3)_6]^{2+} + [Co(NH_3)_5X]^{2+}$ (X = SCN, $N_3$, *or* NCS). The rate data obtained were analysed on the assumption that these reactions are first order in $[Ru(NH_3)_6{}^{2+}]$ and first order in the cobalt(III) concentration. This assumption was shown to be valid from the linearity of pseudo-first-order plots to more than 90% completion of reaction [the ruthenium(II) complex was always present in large excess]. The independence of the second-order rate constants of the ruthenium(II) complex concentration confirms that the reaction is also first order in $[Ru(NH_3)_6{}^{2+}]$. Consequently, rate equation (2) was employed to

$$-d[Co(NH_3)_5X^{2+}]/dt = k_X[Ru(NH_3)_6{}^{2+}][Co(NH_3)_5X^{2+}] \quad (2)$$

analyse all the data, and values of $k_X$ under different kinetic conditions are presented in Tables 1—3.

TABLE 1

Rate constants for the $[Ru(NH_3)_6]^{2+} + [Co(NH_3)_5(SCN)]^{2+}$ reaction at $[Co(NH_3)_5(SCN)^{2+}] = 3.0 \times 10^{-6}$—$8.0 \times 10^{-6}$, $I = 0.20$, and $[H^+] = 0.10$ mol dm$^{-3}$

| $\theta_c$/°C | $10^5[Ru(NH_3)_6{}^{2+}]$/mol dm$^{-3}$ | $k_{SCN}$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 25.0 | 2.01 | 381.9 |
| | 2.68 | 365.2 |
| | 4.02 | 385.2 |
| | 5.36 | 375.2 |
| 17.0 | 2.18 | 259.9 |
| | 4.02 | 280.7 |
| | 5.36 | 272.1 |
| | 6.70 | 271.5 |
| 21.5 | 1.88 | 324.6 |
| | 2.50 | 332.3 |
| | 3.75 | 343.7 |
| | 5.00 | 335.1 |
| 29.0 | 3.00 | 437.5 |
| | 4.50 | 429.5 |
| | 9.00 | 433.8 |
| | 12.00 | 438.2 |

TABLE 2

Rate constants for the $[Ru(NH_3)_6]^{2+} + [Co(NH_3)_5(N_3)]^{2+}$ reaction at $I = 0.2$ and $[Co(NH_3)_5(N_3)^{2+}] = 1.5 \times 10^{-4}$—$2.5 \times 10^{-4}$ mol dm$^{-3}$

| $\theta_c$/°C | $10^3[Ru(NH_3)_6{}^{2+}]$/mol dm$^{-3}$ | $[H^+]$/mol dm$^{-3}$ | $k_{N_3}$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 25.0 | 1.6 | 0.10 | 1.86 |
| | 2.4 | 0.10 | 1.69 |
| | 3.2 | 0.10 | 1.88 |
| | 3.92 | 0.10 | 1.76 |
| | 4.80 | 0.10 | 1.86 |
| | 1.60 | 0.02 | 1.63 |
| | 2.67 | 0.04 | 1.61 |
| | 3.20 | 0.15 | 1.61 |
| | 3.20 | 0.20 | 0.75 |
| 12.0 | 4.51 | 0.10 | 0.71 |
| | 3.76 | 0.10 | 0.61 |
| 18.5 | 1.53 | 0.10 | 1.15 |
| | 2.29 | 0.10 | 1.28 |
| | 3.05 | 0.10 | 1.29 |
| | 4.58 | 0.10 | 1.04 |
| 32.0 | 1.02 | 0.10 | 2.56 |
| | 1.55 | 0.10 | 2.25 |
| | 2.04 | 0.10 | 2.31 |
| | 2.16 | 0.10 | 2.47 |
| | 3.06 | 0.10 | 2.46 |
| | 3.16 | 0.10 | 2.21 |
| | | $I$ [a]/mol dm$^{-3}$ | |
| 25.0 | 3.20 | 0.04 | 0.68 |
| | 3.20 | 0.10 | 1.61 |
| | 3.20 | 0.24 | 2.17 |
| | 3.20 | 0.40 | 2.83 |
| | 3.20 | 0.50 | 3.37 |
| | | $[Cl^-]$ [b]/mol dm$^{-3}$ | |
| 25.0 | 2.40 | 0.2 | 3.20 |
| | 2.40 | 0.3 | 3.49 |
| | 2.40 | 0.4 | 3.19 |
| | 2.40 | 0.5 | 3.39 [c] |

[a] Adjusted with LiCl. [b] $I = 0.5$ mol dm$^{-3}$ ($Li[ClO_4]$ + LiCl). [c] Solution contained only HCl and LiCl, no $Li[ClO_4]$.

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TABLE 3

Rate constants for the $[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_5(NCS)]^{2+}$ reaction at $[Co(NH_3)_5(NCS)^{2+}] = 1.8 \times 10^{-4}$—$2.6 \times 10^{-4}$, $[H^+] = 0.10$, and $I = 0.20$ mol dm$^{-3}$

| $\theta_c$ / °C | $10^3[Ru(NH_3)_6{}^{2+}]$ / mol dm$^{-3}$ | $k_{NCS}$ / dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 11.0 | 2.24 | 0.22 |
| | 3.73 | 0.16 |
| | 4.48 | 0.21 |
| 20.5 | 2.26 | 0.38 |
| | 3.01 | 0.40 |
| | 3.76 | 0.39 |
| | 4.51 | 0.44 |
| 25.0 | 1.49 | 0.74 |
| | 1.87 | 0.78 |
| | 2.24 | 0.86 |
| | 2.99 | 0.68 |
| | 3.73 | 0.64 |
| 32.0 | 1.47 | 1.13 |
| | 1.84 | 1.39 |
| | 2.11 | 1.31 |
| | 2.57 | 1.15 |

Although Endicott and Taube showed [8] that the $[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_5X]^{2+}$ reaction is complicated by the subsequent reaction of the free $[N_3]^-$ with $[Ru(NH_3)_6]^{2+}$ to give $N_2$, $NH_3$, and $[Ru(NH_3)_6]^{3+}$, the amount of the hexa-ammine consumed in this side reaction is so insignificant that the pseudo-first-order condition, *viz.* $[Ru(NH_3)_6{}^{2+}]_0 \sim [Ru(NH_3)_6{}^{2+}]_t$, remains valid throughout the course of the reactions. Moreover, our kinetic analysis is unaffected by this side reaction because we monitored the course of the reaction by following the decrease in the absorbance of the cobalt(III) complex as a function of time and the side reaction of free $[N_3]^-$ and $[Ru(NH_3)_6]^{2+}$ is at least 20 times faster than the reduction of $[Co(NH_3)_5(N_3)]^{2+}$ by the $[Ru(NH_3)_6]^{2+}$.

The effect of changes in chloride and hydrogen-ion concentrations and in ionic strength on the reduction of the azido-complex was also investigated. The rate constant $k_{N_3}$ was insensitive to changes in the concentration of these ions in the range investigated, but increased with increasing ionic strength as expected since both reactant ions are positively charged. The effect of ionic strength was not quantitatively analysed because it is not relevant to the theme of our investigation, but was examined in order to allow for a greater variation in the range of chloride concentrations while determining the effect of chloride. Our results give the following values for $k_X$ at 25 °C, $I = 0.2$ mol dm$^{-3}$ (LiCl), and $[H^+] = 0.10$ mol dm$^{-3}$: $k_{SCN} = 379 \pm 7$, $k_{N_3} = 1.82 \pm 0.10$, and $k_{NCS} = 0.74 \pm 0.06$ dm$^3$ mol$^{-1}$ s$^{-1}$.

From plots of log $k_X/T$ against $1/T$, activation parameters were determined as follows: $\Delta H_{SCN}{}^\ddagger = 6.4 \pm 0.2$ kcal mol$^{-1}$, $\Delta S_{SCN}{}^\ddagger = -(25.3 \pm 1.0)$ cal K$^{-1}$ mol$^{-1}$, $\Delta H_{N_3}{}^\ddagger = 9.4 \pm 0.8$ kcal mol$^{-1}$, $\Delta S_{N_3}{}^\ddagger = -(25.9 \pm 2.6)$ cal K$^{-1}$ mol$^{-1}$, $\Delta H_{NCS}{}^\ddagger = 14.9 \pm 0.7$ kcal mol$^{-1}$, and $\Delta S_{NCS}{}^\ddagger = -(9.5 \pm 1.8)$ cal K$^{-1}$ mol$^{-1}$.* Our rate constants for the reduction of $[Co(NH_3)_5(N_3)]^{2+}$ compare reasonably well with the approximate value of 1.2 dm$^3$ mol$^{-1}$ s$^{-1}$ obtained by Endicott and Taube.[8]

$[Co(NH_3)_5X]^{2+}$ + $[Ru(en)_3]^{2+}$. These reactions also followed a second-order rate equation under conditions similar to those of the reactions of $[Ru(NH_3)_6]^{2+}$ and values of the rate constants at $I = 0.2$ mol dm$^{-3}$, 25 °C, and $[H^+] = 0.10$ mol dm$^{-3}$ are as follows: $k_{SCN} = 45.3 \pm 4.0$, $k_{N_3} = 0.26 \pm 0.01$, and $k_{NCS} = 0.15 \pm 0.02$ dm$^3$ mol$^{-1}$ s$^{-1}$. Details of the individual rate constants obtained are in Table 4.

TABLE 4

Rate constants for the reduction of $[Co(NH_3)_5X]^{2+}$ (X = SCN, $N_3$, or NCS) by $[Ru(en)_3]^{2+}$ at $I = 0.20$ and $[H^+] = 0.10$ mol dm$^{-3}$ and 25 °C

| X | $10^4[Ru(en)_3{}^{2+}]$ / mol dm$^{-3}$ | $10^4[Co(NH_3)_5X^{2+}]$ / mol dm$^{-3}$ | $k$ / dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| SCN | 0.5 | 0.05 | 49.9 |
| | 0.7 | 0.05 | 42.6 |
| | 0.9 | 0.05 | 42.6 |
| $N_3$ | 25.0 | 2.7 | 0.28 |
| | 30.0 | 2.7 | 0.25 |
| | 40.0 | 2.16 | 0.26 |
| NCS | 28.0 | 3.0 | 0.12 |
| | 40.0 | 3.0 | 0.17 |
| | 60.0 | 3.0 | 0.16 |

$[Co(NH_3)_5(SCN)]^{2+}$ + $[Cr(bipy)_3]^{2+}$. The rate of this reaction was too fast for the stopped-flow spectrophotometer under pseudo-first-order conditions. At low concentrations (*ca.* $10^{-5}$ mol dm$^{-3}$ of each reactant), after repeated attempts, we estimated the rate constant of the reaction to be $\geqslant 7.0 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C and $I = 0.2$ mol dm$^{-3}$. The traces of the rate curves obtained from the oscilloscopes at such fast scanning speeds were extremely noisy, and also showed that a reasonable proportion of the reaction had occurred during the mixing of the reactant solutions prior to their arrival at the observation chamber of the equipment.

## DISCUSSION

The substitution characteristics [17] of the two ruthenium complexes employed in this work, and the obtained rate data ($k_{redox} \gg k_{sub.}$), lead to the unequivocal conclusion that the reductions of the cobalt(III) complexes by $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ proceed by the outer-sphere mechanism. The low values for the ratio $k_{N_3} : k_{NCS}$ {$[Ru(NH_3)_6]^{2+}$, 2.5; $[Ru(en)_3]^{2+}$, 1.7} provide additional evidence for this conclusion. The above ratios are at least $10^3$ times lower than values obtained for the reduction of these cobalt(III) complexes by aqua-ions, which have been shown to proceed by the inner-sphere mechanism.[6] As in the previously reported reactions of the aqua-ions, the observed reactivity order obtained for these outer-sphere reducing ions is also $k_{SCN} > k_{N_3} > k_{NCS}$. For purposes of comparison, rate ratios for all such related systems are presented in Table 5.

Two prominent qualitative differences are evident in Table 5. (1) The ratio $k_{N_3} : k_{NCS}$ is very large ($>10^3$) for all reactions proceeding by the inner-sphere mechanism, and these are mostly reactions of the aqua-ions. The exceptions to this generalisation are: (*i*) $[CrX]^{2+}$ + $U^{3+}$ reactions where either $[OH]^-$ and/or $X^-$ acts as a bridging ligand; [18] (*ii*) $V^{2+}$ + $[Co(NH_3)_5X]^{2+}$ reactions which, although proceeding by the inner-sphere mechanism, have their rates determined by the rate of formation of the precursor complex [4,19] rather than by the electron transfer within the complex, and therefore the rate is

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* Throughout this paper: 1 cal = 4.184 J.

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TABLE 5

Relative rates of the reactions of thiocyanato-, azido-, and isothiocyanato-complexes with some reducing ions at 25 °C

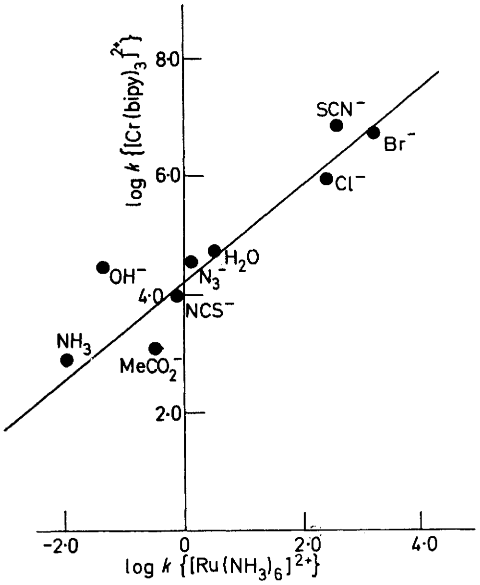
| Reaction[a] | $k_{SCN}$ | : | $k_{N_3}$ | : | $k_{NCS}$ | $k_{SCN}/k_{N_3}$ | Mechanism[b] | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[CrX]^{2+} + Cr^{2+}$ | 280 000 | : | 4 300 | : | 1 | 6.4 | i.s. | 3, 19 |
| $[CrX]^{2+} + V^{2+}$ | 182 000 | | | | 1 | | i.s. | 3, 19 |
| $[CrX]^{2+} + U^{3+}$ | 38 461 | | 188 | | 1[c] | 204 | i.s. | 18 |
| $[Co(NH_3)_5X]^2 + Cr^{2+}$ | 4 200 | | 16 000 | | 1[d] | 0.25 | i.s. | 5, 9 |
| | 10 000 | | 16 000 | | 1[e] | 0.625 | i.s. | 5 |
| $+ Eu^{2+}$ | 62 000 | | 3 860 | | 1 | 16 | i.s. | 6 |
| $+ V^{2+}$ | 100 | | 43 | | 1 | 25 | i.s. | 4, 9 |
| $+ Fe^{2+}$ | 40 000 | | 3 000 | | 1 | 13.3 | i.s. | 4, 2 |
| $+ U^{3+}$ | | | 44 000 | | 1 | | i.s. | *f* |
| $+ Ti^{3+}$ | 2 460 000 | | 390 000 | | 1 | 6.3 | i.s. | *g* |
| $+ [Co(CN)_5]^{3-}$ | $100 < 1\,250$ | | 1.6 | | 1 | $62.5 < 1\,250$ | i.s. | 5, *h* |
| $+ [Cr(bipy)_3]^{2+}$ | 172 | | 4.0 | | 1 | 43 | o.s. | *i*, 9 |
| $+ [Ru(NH_3)_6]^{2+}$ | 512 | | 2.5 | | 1 | 200 | o.s. | *i* |
| $+ [Ru(en)_3]^{2+}$ | 302 | | 1.7 | | 1 | 178 | o.s. | *i* |

[a] X = SCN, $N_3$, or NCS. [b] i.s. = Inner sphere, o.s. = outer sphere. [c] Bridging ligands are either $[OH]^-$ or $[OH]^-$ and $X^-$. [d] The precursor complex is formed by adjacent attack on S in the thiocyanato-complex. [e] The precursor complex is formed by remote attack on N in the thiocyanato-complex. [f] R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, 1971, **93**, 380. [g] A. Adegite and J. F. Ojo, *Inorg. Chem.*, 1977, in the press; J. P. Birk, *ibid.*, 1975, **14**, 1724. [h] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 1963, **85**, 2517. [i] This work.

not very sensitive to the nature of $X^-$; and (*iii*) the $[Co(CN)_5]^{3-} + [Co(NH_3)_5X]^{2+}$ reaction where the stability of the final product has an important influence on the overall rate of the redox reaction. (2) The ratio $k_{SCN} : k_{N_3}$ is much smaller for reactions of the inner-sphere type than for reactions of the outer-sphere mechanism, the only exceptions, and for the same reasons, being (*i*)—(*iii*) noted in (1) above.

The reactivity order observed for the inner-sphere reduction of the thiocyanato-, isothiocyanato-, and azido-cobalt(III) ammine complexes by aqua-ions has been rationalised on the basis of the effect of the relative stability of the precursor complexes on the energetics of the activation processes.[4,6] In addition, the concept of Pearson's hard acids[20] has also been invoked[2,4,6] to explain the preferences of the metal ions for the N or S end of the ambidentate bridging ligands in the formation of these precursor complexes. However, when discussing the behaviour of the outer-sphere reducing ions, solace cannot be found in these explanations because there are no bonds formed in the precursor complexes.

As in many other outer-sphere redox reactions, the dominant factor in the observed reactivity pattern seems to be the free energy, *i.e.* $\Delta G^{\ominus}$, of the reactions.[21,22] The ratio $k_{SCN} : k_{N_3}$ is *ca.* 200 for the reductions of the cobalt(III) complexes by both $[Ru(en)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$. From purely thermodynamic considerations, this implies that the Co–S bond is *ca.* $4 \times 10^4$ times weaker than the Co–N bond in these penta-amminecobalt(III) complexes. The relative bond strengths obtained from our kinetic data are consistent with the factor $5 \times 10^5$ in the $Cr^{III}$–S and $Cr^{III}$–N bond strengths obtained[3,5] from kinetic studies of the isomerisation of $[Cr(SCN)]^{2+}$ to the more stable $[Cr(NCS)]^{2+}$. Additional evidence in support of a free-energy-dependent reactivity pattern is the good correlation obtained when Marcus theory is employed to compare the rates of reduction of some penta-amminecobalt(III) complexes by $[Ru(NH_3)_6]^{2+}$ and $[Cr(bipy)_3]^{2+}$, both these ions being generally accepted as outer-sphere reductants. For this purpose, the modified form of the Marcus[24] equation, (3), is employed. Precedent for this type of comparison is found in the



log–log plot of the specific rates of outer-sphere reduction of some penta-amminecobalt(III) complexes $[Co(NH_3)_5X]$ by $[Ru(NH_3)_6]^{2+}$ and $[Cr(bipy)_3]^{2+}$. Rate constants for the $[Cr(bipy)_3]^{2+}$ reactions are from ref. 9, and for $[Ru(NH_3)_6]^{2+}$ the values are from ref. 8 and this work. The value plotted for the $[Cr(bipy)_3]^{2+} + [Co(NH_3)_5(SCN)]^{2+}$ reaction is the lower limit of the estimated rate constant

$$\log k\{[Cr(bipy)_3]^{2+}\} = a \log k\{Ru(NH_3)_6]^{2+}\} + b \quad (3)$$

studies of Guenther and Linck,[23] Chen and Gould,[24]

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and Hutchital *et al.*,[25] and, more recently, Hand *et al.*[26] applied this semiquantitative approach to the reduction of μ-superoxo-bis[penta-amminecobalt(III)] by some aqua-ions and $[Ru(NH_3)_6]^{2+}$. It is expected that, if a common mechanism exists in the reactions of the two reductants under consideration with the common oxidants, a linear plot, of unit gradient, should be obtained if equation (3) is applied to the rate data.[27] A plot of the data available for the reactions of $[Cr(bipy)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ with some cobalt(III) ammine complexes gave a satisfactory linear correlation [equation (4)] of gradient $0.83 \pm 0.09$ which is quite close to unity. The most significant deviation from the

$$\log k\{[Cr(bipy)_3]^{2+}\} = 0.83 \log k\{[Ru(NH_3)_6]^{2+}\} + 4.19 \quad (4)$$

plot is that of the reduction of the hydroxo-complex, which tends to suggest that this reaction might not be of the same mechanism for both reductants (Figure 1).

This good correlation based on Marcus' correlation of rates, with $\Delta G^{\ominus}$, and the previous deduction of the relative strengths of the Co–S and Co–N bonds from purely thermodynamic considerations, confirm that the observed reactivity patterns in these outer-sphere reactions are a reflection of the thermodynamic properties of the systems, and that the special electron-mediating ability associated[5,7] with the Co–S bond in inner-sphere reactions is unimportant in the present reactions. The activation enthalpies for the $[Ru(NH_3)_6]^{2+}$ reactions follow the observed order of reactivity, $k_{SCN} > k_{N_3} > k_{NCS}$, showing that differences in the rates are manifested in the magnitudes of $\Delta H^{\ddagger}$. There is no apparent reason why $\Delta S_{NCS}^{\ddagger}$ should be more favourable than the activation entropies for the other complexes.

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