Kinetics and Mechanism of the Reduction of Thiocyanato- and Isothiocyanato-penta-amminecobalt(III) Ions by Europium(II)

By **A. Adegite** * and **T. A. Kuku**, Chemistry Department, University of Ife, Nigeria

The kinetics of reduction of $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ by Eu^{2+} have been investigated in acid solution. For both complexes the reactions are first order in concentrations of the cobalt complex and Eu^{2+}. At 25 °C, $[H^+] = 0.1$M, and $I = 1.0$M ($Li[ClO_4]$), $k = (3.1 \pm 0.1) \times 10^3$ and $(4.95 \pm 0.13) \times 10^{-2}$ l mol^{-1} s^{-1} for $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ respectively. The corresponding activation parameters are $\Delta H^‡ = 2.7 \pm 0.2$ kcal mol^{-1} and $\Delta S^‡ = -33.4 \pm 5.6$ cal K^{-1} mol^{-1}, and $\Delta H^‡ = 7.5 \pm 0.7$ kcal mol^{-1} and $\Delta S^‡ = -39.7 \pm 2.7$ cal K^{-1} mol^{-1}. The reactivity order $[Co(NH_3)_5(SCN)]^{2+} > [Co(NH_3)_5(N_3)]^{2+} > [Co(NH_3)_5(NCS)]^{2+}$ ($k_{SCN} : k_{N_3} : k_{NCS} = 6.5 \times 10^4 : 3.9 \times 10^3 : 1$) is discussed in terms of an inner-sphere mechanism in which Eu^{2+} attacks the ambidentate bridging ligand at the end remote from the cobalt centre. Differences in activation enthalpy for the reduction of the complexes are attributed to differences in (*a*) the enthalpy of formation of the precursor complex and (*b*) the ease of stretching the Co–S or Co–N bond in the precursor complex.

FOR redox reactions of the type (1) (X = anion), mechanistic classification as inner or outer sphere has been most

$$Co(NH_3)_5X]^{2+} + M^{2+} + 5H^+ \longrightarrow Co^{2+} + 5[NH_4]^+ + M^{3+} + X^- \quad (1)$$

readily demonstrated where M^{3+} is sufficiently inert and $[MX]^{2+}$ could be identified as the final or immediate product of the reaction. The reaction in which M = Cr and Fe are typical.[1,2] In many others, where the above criterion cannot be applied because of the lability of

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[1] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

[2] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1966, **88**, 5343.

M^{3+}, indirect criteria such as the relative rates of reduction of $[Co(NH_3)_5(NCS)]^{2+}$ and $[Co(NH_3)_5(N_3)]^{2+}$ have been employed.[3,4] Soon after Buckingham *et al.*[5] prepared $[Co(NH_3)_5(SCN)]^{2+}$, and Haim and Sutin[6] prepared $[Cr(SCN)]^{2+}$, this criterion was extended to include these *S*-bonded isomers. The kinetics of the reaction of $[CrX]^{2+}$ (X = SCN, N, or NCS) with Cr^{2+} and V^{2+} have been reported[3,7–9] and also the reduction of the complexes $[Co(NH_3)_5X]^{2+}$ by Fe^{2+}, Cr^{2+}, and $[Co(CN)_5]^{2-}$ have been investigated.[10–15] In almost all these cases the reactivity order follows the sequence $[M(SCN)]^{2+} > [M(N_3)]^{2+} > [M(NCS)]^{2+}$ [M = Cr or $Co(NH_3)_5$]. We have extended these investigations to Eu^{2+}, and in an effort to elucidate the possible causes of the observed reactivity order we have determined the activation parameters for the $[Co(NH_3)_5(SCN)]^{2+} + Eu^{2+}$ and the previously, but briefly, investigated $[Co(NH_3)_5(NCS)]^{2+} + Eu^{2+}$ reactions.

EXPERIMENTAL

The salts $[Co(NH_3)_5(SCN)]Cl_2\cdot 1.5H_2O$ and $[Co(NH_3)_5(NCS)][ClO_4]_2$ were prepared by previously reported methods.[5,16] In order to ascertain the purity of the complexes their spectra were run on a Cary 16 spectrophotometer and the results [$\lambda_{max.} = 288$ (ε 1.56×10^4) and 512 nm (ε 74 l mol^{-1} cm^{-1}) and $\lambda_{max.} = 306$ (ε 1 488) and 498 nm (ε 179 l mol^{-1} cm^{-1}) respectively] agree with values reported in the literature. Concentrations of solutions of these complexes were determined spectrophotometrically using the above absorption coefficients. The complex $[Co(NH_3)_5(SCN)]^{2+}$ is reported[5] to undergo isomerization very slowly and its crystals were therefore kept in a deep freeze before use. Europium(II) perchlorate solutions were prepared by zinc-amalgam reduction of $Eu[ClO_4]_3$ which was made by dissolution of Eu_2O_3 in $HClO_4$. The reduction was carried out in capped serum bottles, and with continuous flushing with argon to maintain an inert atmosphere over the Eu^{2+} solutions. Concentrations of Eu^{2+} solutions were determined by direct or indirect iodometry. In the former, a known volume of Eu^{2+} solution was introduced into properly deaerated $[I_3]^-$ solutions and excess of $[I_3]^-$ was determined by titration against $Na_2[S_2O_3]$. In the latter method, a known volume of Eu^{2+} was introduced into properly deaerated Ce^{IV} solution and the excess of Ce^{IV} was determined by iodometry.

The kinetics of reaction of $[Co(NH_3)_5(SCN)]^{2+}$ were followed by monitoring absorbance changes at 300 nm, where, for the concentration range employed, the complex is the dominant absorbing species. Since the kinetics were investigated under pseudo-first-order conditions with the Eu^{2+} concentration at least 10-fold larger than that of $[Co(NH_3)_5(SCN)]^{2+}$, and hence approximately constant throughout the course of reaction, the small absorbance due to Eu^{2+} had no effect on the rate constants obtained for the reaction. Teflon needles and plastic syringes were employed in the transfer of solutions.

The $[Co(NH_3)_5(NCS)]^{2+} + Eu^{2+}$ reaction is sufficiently slow to be followed by conventional techniques on a Unicam SP 500 spectrophotometer fitted with a thermostatted cell compartment. The rate of this reaction was monitored by measuring absorbance changes at 498 nm, an absorption peak for $[Co(NH_3)_5(NCS)]^{2+}$. In order to facilitate early measurements of the absorbance after initiation of reaction, the reactants were mixed directly in a 40 mm cell in which calculated amounts of $HClO_4$ and the complex had been placed and required amounts of Eu^{2+} were added to the properly deaerated contents of the cell to initiate the reaction. Constant ionic strengths were maintained with $Li[ClO_4]$, after due consideration for the concentrations of the other ions in solution.

RESULTS

The $[Co(NH_3)_5(SCN)]^{2+} + Eu^{2+}$ *Reaction.*—Rate curves depicted on the oscilloscope were smooth and exponential, and their subsequent analysis with a pseudo-first-order rate equation gave linear plots to more than 90% completion of reaction. From the resulting pseudo-first-order rate constants, second-order rate constants at different initial concentrations of reactants, acid, and temperature were obtained (Table 1). Activation parameters for this reaction were calculated from a plot of log (k/T) against $(1/T)$ as $\Delta H^\ddagger = 2.7 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -33.4 \pm 5.6$ cal K^{-1} mol^{-1}.*

TABLE 1

Rate constants for the reduction of $[Co(NH_3)_5(SCN)]^{2+}$ by Eu^{2+} at $I = 1.0$M ($Li[ClO_4]$)

$\frac{\theta_c}{°C}$	$\frac{[H^+]}{M}$	$\frac{[Co(NH_3)_5(SCN)^{2+}]}{M}$	$\frac{10^4[Eu^{2+}]}{M}$	$\frac{10^{-3}k}{l\ mol^{-1}\ s^{-1}}$
13	0.10	2.7	4.7	1.9
	0.10	2.7	9.4	1.8
	0.10	2.7	14.1	2.0
25	0.1	1.5	7.2	2.9
	0.1	1.5	14.6	3.0
	0.1	2.7	4.8	3.0
	0.1	2.7	9.7	3.2
	0.1	3.0	2.4	3.0
	0.1	3.0	4.8	3.1
	0.1	3.0	9.7	3.2
	0.1	4.6	14.6	3.1
	0.1	6.1	14.6	3.5
	0.15	3.0	4.8	3.2
	0.20	3.0	4.8	3.0
	0.25	3.0	4.8	3.3
	0.30	3.0	4.8	3.0
37	0.10	2.7	4.8	4.0
	0.10	2.7	9.6	4.0
	0.10	2.7	14.4	4.1
45	0.10	2.7	6.6	4.5
	0.10	2.7	9.5	4.7

The $[Co(NH_3)_5(NCS)]^{2+} + Eu^{2+}$ *Reaction.*—An approximate value for the rate constant for this reaction was

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* 1 cal = 4.184 J, 1M = 1 mol dm^{-3}.

[3] D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, 1958, **80**, 1091; R. Snellgrove and E. L. King, *Inorg. Chem.*, 1963, **3**, 288.

[4] J. H. Espenson, *Inorg. Chem.*, 1965, **4**, 121.

[5] D. A. Buckingham, I. I. Creases, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 655.

[6] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1965, **87**, 4210.

[7] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1966, **88**, 434.

[8] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, 1967, **89**, 722.

[9] M. Orhanovic, N. Po, and N. Sutin, *J. Amer. Chem. Soc.*, 1968, **70**, 7224.

[10] D. P. Fay and N. Sutin, *Inorg. Chem.*, 1970, **9**, 1291.

[11] A. Haim, *J. Amer. Chem. Soc.*, 1963, **85**, 1016.

[12] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 3055.

[13] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.

[14] C. Shea and A. Haim, *Inorg. Chem.*, 1973, **12**, 3013.

[15] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 1963, **85**, 2517.

[16] R. L. Carlin and J. O. Edwards, *J. Inorg. Nuclear Chem.*, 1958, **6**, 217.

reported by Candlin *et al.*[13] as 0.7 l mol^{-1} s^{-1} at 25 °C and at an ionic strength of presumably 1.0M. Our results (Table 2), also at an ionic strength of 1.0M, differ considerably from this approximate value. In order to ascertain that impurities were not responsible for the difference in these results, we measured the rate constant for the V^{2+} reduction of $[Co(NH_3)_5(NCS)]^{2+}$. Our results, which agree with the earlier work,[13] gave 0.30 l mol^{-1} s^{-1}. For reasons discussed later, the approximate value of 0.7 l mol^{-1} s^{-1} is considered too high for the rate of the present reaction. The low solubility of $[Co(NH_3)_5(NCS)][ClO_4]_2$ might have been responsible for this high value. Activation parameters obtained from log (k/T) against $(1/T)$ plots were $\Delta H^{\ddagger} = 7.5 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -39.7 \pm 2.7$ cal K^{-1} mol^{-1}.

TABLE 2

Rate constants for the reduction of $[Co(NH_3)_5(NCS)]^{2+}$ by Eu^{2+} at $[Co(NH_3)_5(NCS)^{2+}] = 2.0 \times 10^{-4} - 2.5 \times 10^{-4}$M, $[H^+] = 0.1$M, and $I = 1.0$M $(Li[ClO_4])$

θ_c / °C	$10^2[Eu^{2+}]$ / M	10^2k / l mol^{-1} s^{-1}
18	8.46	2.42
	6.77	2.51
	5.07	2.57
25	4.93	4.79
	3.94	4.87
	3.96	5.07
	2.50	4.98
	2.00	5.06
36	3.35	7.32
	2.51	7.16
45	4.19	8.66
	3.35	8.59
	1.68	8.75

DISCUSSION

The rates of reaction of $[Co(NH_3)_5X]^{2+}$ ($X = SCN^-$, N_3^-, or NCS^-) with the reducing ions so far investigated (Table 3) generally follow the reactivity pattern $[M(SCN)]^{2+} > [M(N_3)]^{2+} > [M(NCS)]^{2+}$ $[M = Co(NH_3)_5]$. The only exception is the path of remote attack in which the azido-complex is reduced faster than the thiocyanato-complex by Cr^{2+}. The ratio $k_{SCN} : k_{N_3} : k_{NCS}$ is generally high for a given reductant, apart from the V^{2+} reactions in which replacement of a co-ordinated water molecule on the vanadium(II) ion is rate limiting.[10]

TABLE 3

Comparison of the rate constants for the reduction of thiocyanato-, isothiocyanato-, and azido-penta-ammine-cobalt(III) complexes by some metal ions

Reductant	$k_{SCN} : k_{N_3} : k_{NCS}$	Ref.
Cr^{2+}	4 200 : 16 000 : 1 [a]	13
Cr^{2+}	10 000 : 16 000 : 1 [b, c]	13
Fe^{2+}	40 000 : 3 000 : 1	4, 6, 11
$[Co(CN)_5]^{3-}$	2 000 : 1.6 : 1	14, 15
V^{2+}	100 : 4.3 : 1	6, 13
Eu^{2+}	62 000 : 3 860 : 1	This work, 13

[a] Adjacent attack. [b] Remote attack. [c] It was assumed that $[Co(NH_3)_5(N_3)]^{2+}$ reacts mainly by remote attack.

High values for $k_{N_3} : k_{NCS}$ have been invoked[4] as evidence for the inner sphere mechanism in the reduction reactions of $[Co(NH_3)_5(N_3)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ by Fe^{2+}. The validity of this conclusion was subsequently confirmed by the more definitive product criterion in the reduction of Co^{III} complexes by Fe^{2+}. However, an effort to extend this criterion to characterize the type of mechanism obtaining in the reactions of Eu^{2+} with Co^{III} complexes was inconclusive because of the low magnitude (300 : 1) of this ratio compared to the values of 3×10^3 and $1.6 \times 10^4 : 1$ found for Fe^{2+} and Cr^{2+} respectively. The rationale for the higher rate of reaction of the azido-complex is the preference of a hard acid (reducing metal ion) for co-ordination to a nitrogen rather than a sulphur atom in the formation of the precursor complex. Considering the criteria[17,18] that distinguish a hard from a soft acid, Eu^{2+} should be at least as hard as Fe^{2+} or Cr^{2+}. This relative hardness is expected to be reflected in the stabilities of the *S*- or *N*-bonded complexes. Consequently, the ratio $k_{N_3} : k_{NCS}$ should not differ very widely for these aqua-ions if the reactions proceed by formation of binuclear intermediates in which $[N_3]^-$ and $[NCS]^-$ are the bridging ligands. Therefore, the previously reported[13] value of 300 : 1 for this ratio is considered too low for Eu^{2+}. Our present result, $k_{N_3} : k_{NCS} = 3.9 \times 10^3 : 1$, supports this conclusion, and resolves the doubt on the basis of this criterion as to whether Eu^{2+} reduction of these penta-amminecobalt(III) complexes proceeds by the inner-sphere mechanism.

The activation parameters obtained (Table 4) for the reduction of $[Co(NH_3)_5(NCS)]^{2+}$ and $[Co(NH_3)_5(SCN)]^{2+}$ by Eu^{2+}, and those previously obtained by other workers for $[Co(NH_3)_5(N_3)]^{2+}$, show that differences in the magnitudes of the activation enthalpy are responsible for the reactivity order $k_{SCN} > k_{N_3} > k_{NCS}$. Explanation of these ligand-dependent values of $\Delta H^{\ddagger}$ entails detailed consideration of the elementary paths that make up the reaction mechanism, assuming that the three complexes react by the inner-sphere mechanism. Therefore, following Sutin,[7,10,19,20] the important stages in the reaction mechanism are formation of the precursor

TABLE 4

Activation parameters for the reduction of some cobalt(III) complexes by Eu^{2+}

Oxidant	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}	Ref.
$[Co(NH_3)_5Cl]^{2+}$	5.0	−30	14
$[Co(NH_3)_5Br]^{2+}$	4.7	−32	14
$[Co(NH_3)_5(N_3)]^{2+}$	5.5	−30	14
$[Co(NH_3)_5(SCN)]^{2+}$	2.7	−33	This work
$[Co(NH_3)_5(NCS)]^{2+}$	7.5	−39	This work

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[17] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *Science*, 1965, **151**, 172.

[18] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' John Wiley, London, 1968.

[19] N. Sutin, *Electrochim. Acta*, 1968, **13**, 1175.

[20] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

complex [equation (2)], reorganisation of the inner and

$$\mathrm{Eu^{2+} + [Co(NH_3)_5X]^{2+} \rightleftharpoons [Eu^{II}\cdots X\cdots Co^{III}(NH_3)_5]^{4+}} \qquad (2)$$

outer co-ordination shells of the precursor complex [equation (3)], electron transfer within the precursor

$$\mathrm{[Eu^{III}\cdots X\cdots Co^{III}(NH_3)_5]^{4+} \rightleftharpoons [Eu^{II}\cdots X\cdots Co(NH_3)_5]^{4+\ddagger}} \qquad (3)$$

complex [equation (4)], and reorganisation within and

$$\mathrm{[Eu^{II}\ldots X\cdots Co(NH_3)_5]^{4+\ddagger} \rightleftharpoons [Eu^{III}\cdots X\cdots Co^{II}(NH_3)_5]^{4+\ddagger}} \qquad (4)$$

outside the co-ordination shell of the successor complex and its dissociation to the products [equation (5)].

$$\mathrm{[Eu^{III}\cdots X\cdots Co^{II}(NH_3)_5]^{4+\ddagger} \rightleftharpoons Eu^{3+} + Co^{2+} + 5[NH_4]^+ + X^-} \qquad (5)$$

The ions $\mathrm{Eu^{2+}}$, $\mathrm{Eu^{3+}}$, and $\mathrm{Co^{2+}}$ are labile and consequently steps (2) and (5) are much faster than the redox steps. Although step (2) is a fast equilibrium, Fay and Sutin,[10] and also Haim,[21] have pointed out that the stability of the precursor complex considerably influences the overall rate of the reaction. The energetics of this process must, therefore, have an effect on the enthalpy of activation of the overall reaction. From the properties of the donor atom in the bridging ligand, the expected order of exothermicity for the formation of the precursor complex should be $\Delta H_{\mathrm{N_3}^{\ominus}} > \Delta H_{\mathrm{SCN}^{\ominus}} > \Delta H_{\mathrm{NCS}^{\ominus}}$. This order does not explain the higher activation enthalpy of the azido- as compared to the thiocyanato-complex. Consequently, the contributions to $\Delta H^{\ddagger}$ from paths (3) and (4) must be important. Based on the electronic structures of the bridging ligands, the nature of the orbitals on the cobalt centre into which the transferred electron enters, and the role of the bridging ligands [22] in electron transfer within such binuclear intermediates, the contribution from path (4) (the electron-transfer step) to $\Delta H^{\ddagger}$ should not differ significantly between the azido- and thiocyanato-complexes. It is, therefore, suggested that the ease of stretching the Co–N or Co–S bond is the crucial factor in rationalizing the observed differences in $\Delta H^{\ddagger}$. The work of Taube and his co-workers [23,24] has shown that extensive stretching of the cobalt–ligand bond occurs in precursor complexes formed in redox reactions that proceed by the inner-sphere mechanism. The aquation rates of the complexes $\mathrm{[Co(NH_3)_5(NCS)]^{2+}}$ (5.0×10^{-10}),[25] $\mathrm{[Co(NH_3)_5(N_3)]^{2+}}$ (2.1×10^{-9}),[26] and $\mathrm{[Co(NH_3)_5(SCN)]^{2+}}$ $(8 \times 10^{-7}\ \mathrm{s^{-1}})$ [5] could be used as a rough estimate of the ease of stretching the Co–N or Co–S bond in these complexes, and the order is in accord with the observed order of activation enthalpies for the redox reactions. The higher reactivity of $\mathrm{[Co(en)_2(SCH_2O_2)]^+}$ ($k = 10^6$ l mol^{-1} s^{-1}) compared to $\mathrm{[Co(en)_2(OCH_2O_2)]^+}$ ($k = 10^3$ l mol^{-1} s^{-1}) in their reduction by $\mathrm{Cr^{2+}}$ has also been partly attributed to the ease of stretching the metal–ligand bond in the precursor complex.[27]

The activation entropies (Table 4) of the complexes are almost the same within experimental error as those reported for the penta-amminehalogeno-complexes. This suggests that in these reactions the probability of electron transfer and the steric factors in the binuclear intermediate are quite similar. In the reactions where ambidentate ligands are bridging the binuclear intermediate could be formed by adjacent and/or remote attack on the bridging ligand. These possibilities have been demonstrated by Shea and Haim [12,14] in the $\mathrm{Cr^{2+}}$ and $\mathrm{[Co(CN)_5]^{3-}}$ reductions of $\mathrm{[Co(NH_3)_5(SCN)]^{2+}}$, and also in the $\mathrm{Cr^{2+} + [Fe(NCS)]^{2+}}$ reactions reported by Haim and Sutin.[28] Although activation parameters for the two possibilities have not been reported, it is considered likely on purely steric grounds that remote attack should lead to a more favourable entropy of activation than adjacent attack. The similarities in the activation entropies for the three complexes and of the reactions of penta-amminehalogenocobalt(III) complexes seem to suggest that the $\mathrm{Eu^{2+}}$ reduction of the thiocyanato-, isothiocyanato-, and azido-cobalt(III) complexes proceeds by remote attack on the bridging ligand.

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[21] A. Haim, *Inorg. Chem.*, 1968, **7**, 1475.

[22] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, 1960, **29**, 32.

[23] M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, 1965, **4**, 1184; H. Diebler, P. H. Dodel, and H. Taube, *ibid.*, 1966, **5**, 1688.

[24] R. K. Murmann, H. Taube, and F. A. Posey, *J. Amer. Chem. Soc.*, 1957, **79**, 262.

[25] D. L. Gay and G. C. Lalor, *J. Chem. Soc.* (*A*), 1966, 1179.

[26] G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1963, 1560.

[27] R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 1970, **92**, 1089.

[28] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1965, **87**, 4210.