The Dissociative Interchange Substitution of the Pentacyanocobaltate(III) Series of Complexes, $[Co(CN)_5X]^{n-}$, $n = 2$ or 3

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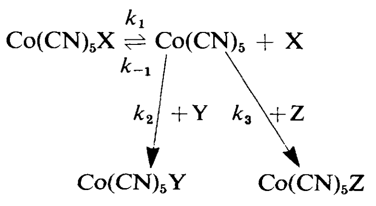
The efficiency of nucleophiles, (N_3^-, NCS^- and Me_2SO) in combining with the intermediate $[Co(CN)_5]^{2-}$ depends on the ion from which the intermediate is formed, $[Co(CN)_5(OH_2)]^{2-}$, $[Co(CN)_5Cl]^{3-}$, or $[Co(CN)_5(N_3H)]^{2-}$, thereby suggesting that the substitution of these ions takes place by dissociative interchange, I_d.

One of the most convincing demonstrations of a *D*-type mechanism involves the measurement of nucleophile competition during substitution proceeding at the limiting dissociative rate.[1] The pentacyanocobaltate(III) family of complexes has been supposed[2] to form an ideal group for the demonstration of this class of substitution. Recently,[3] however, some of the data in the case of N_3^-–$[Co(CN)_5(OH_2)]^{2-}$ have been corrected and it is no longer considered to be a case of limiting *D*-type mechanism. On the other hand, part of the experimental evidence in favour of such a reaction in the NCS^-–$[Co(CN)_5(OH_2)]^{2-}$ system has been confirmed.[4] The remaining kinetic evidence also concerns the NCS^- nucleophile and, in view of its apparently unique character, we have repeated and extended the original competition studies.[5]

The original experiments involved the acid catalysed hydrolysis of $[Co(CN)_5N_3]^{3-}$ *via* $[Co(CN)_5(N_3H)]^{2-}$ in the presence of added thiocyanate ion. We have repeated the experiments using an improved monitoring system and computer modelling to fit the constants k_1, and k_1k_2/k_3 to the experimental absorbance–time curves. The computer model was based on the simple dissociative Scheme 1.† In the particular case of $X = N_3H$, the rate of the back reaction reforming $[Co(CN)_5(N_3H)]^{2-}$ may be neglected.



Scheme 1

Further experiments have also been performed using $[Co(CN)_5Cl]^{3-}$ and the nucleophiles thiocyanate, azide, and dimethyl sulphoxide. The results of the corresponding anation reaction of $[Co(CN)_5(OH_2)]^{2-}$ are also given in Table 1.

None of the anation studies reported here or elsewhere,[6] except the thiocyanate case, show any evidence of the high nucleophile concentration fall-off in rate constant, k_{obs}, required by Scheme 1, ([Z] = 0 and X = OH_2), and predicted by the rate equation (1). The maximum or minimum limiting values possible but still consistent with the experiments are quoted in Table 1 together with values of k_1k_2/k_{-1} calculated from k_{obs} using the rate equation,

$$\frac{d[Co(CN)_5(OH_2)]}{dt} = \frac{k_1k_2[Co(CN)_5(OH_2)][Y]}{k_2[Y] + k_{-1}[H_2O]} = k_{obs}[Co(CN)_5(OH_2)] \quad (1)$$

Table 1. Relative nucleophile efficiencies in $[Co(CN)_5X]^{n-}$ substitution, $n = 2$ or 3.[a]

Nucleophile[b] Y	Leaving group	$10^5k_1/s^{-1}$	$10^2(k_1k_2/k_{-1})/s^{-1}$	k_2/k_3[b]
NCS^-	OH_2[d]	233	3.5	15
NCS^-	N_3H	330[c]	—	13[c]
NCS^-	Cl^-	45	—	0
N_3^-	OH_2[d]	(>700)	3.7	(<5)
N_3^-	Cl^-	45	—	*ca.* 5
Me_2SO	OH_2	(>400)	2.2	(<5)
Me_2SO	Cl^-	45	—	13

[a] At 40 °C and unit ionic strength maintained by $Na[ClO_4]$; u.v. measurement of concentration. [b] Z = H_2O in all cases. [c] Calculated using $pK([Co(CN)_5(N_3H)]^{2-}) = 0.67$ taken from ref. 5 in which $k_2/k_3 = 19$, $k_1 = 3.2 \times 10^{-3}\ s^{-1}$. [d] Ref. 4.

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† The ion charges have been omitted for clarity but $Co(CN)_5X$, $Co(CN)_5Y$, and $Co(CN)_5Z$ are all (3−) ions when X, Y, or Z = Cl^-, NCS^-, or N_3^- but are (2−) ions when X, Y, or Z = OH_2, N_3H, or Me_2SO. The intermediate, $Co(CN)_5$, is a (2−) ion.

Table 2. Relative nucleophile efficiency in $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5Cl]^{3-}$ substitutions.[a]

	k_2/k_3	
Y[b]	$[Co(CN)_5Cl]^{3-}$ [c]	$[Co(CN)_5(OH_2)]^{2-}$ [d]
N_3^-	*ca.* 0.4	1.7
NCS^-	0	1.6

[a] At 40 °C and unit ionic strength maintained by $Na[ClO_4]$. [b] Z = Me_2SO in all cases. [c] Calculated from k_2/k_3 values in Table 1. [d] Calculated from k_1k_2/k_{-1} values in Table 1.

assuming that $k_2[Y]$ may be neglected. The relative nucleophile efficiencies for Me_2SO, N_3^-, and NCS^- may be estimated from these data for Y = N_3^- or NCS^- and Z = Me_2SO.

Values of k_2/k_3 for $[Co(CN)_5OH_2]^{2-}$ found in this way are compared in Table 2 with corresponding values calculated for $[Co(CN)_5Cl]^{3-}$ from data in Table 1. There is clear evidence that the origin of the hypothetical intermediate $[Co(CN)_5]^{2-}$ markedly changes the observed relative nucleophile efficiencies. This confirms the conclusion from the direct competition measurements in Table 1. Although these latter data are consistent with the requirements of a limiting dissociative mechanism in that the hydrolysis rate constants for $[Co(CN)_5Cl]^{3-}$ and $[Co(CN)_5(N_3H)]^{2-}$ were both unaffected by the added nucleophile, the nucleophile efficiency ratios k_2/k_3 varied with the leaving group X. This behaviour is typical of a dissociative interchange reaction (I_d) rather than a true dissociative reaction (*D*).

Other evidence from solvent effects[7] and activation volumes[8] correctly suggested a dissociative path but the fact they were also supposed to indicate a *D*-type mechanism must cast doubt on their value as probes of detailed mechanism.

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