The Relative Nucleophilic Efficiency of Water and the Azide and Thiocyanate Ions in the Aqueous Substitution of Chloropentacyanocobaltate(III)

Moustafa H. M. Abou-El-Wafa
Department of Chemistry, University of Assiut, Qena, Egypt
Michael G. Burnett* and John F. McCullagh
Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG

The kinetics of the substitution of Cl^- in $[Co(CN)_5Cl]^{3-}$ by solvent H_2O and by $X^- = NCS^-$ or N_3^- may be quantitatively interpreted by a stepwise mechanism, equations (i) and (ii). High-performance liquid chromatographic analysis confirms the absence of direct chloride substitution by reaction (iii). These results support the view that the substitution occurs by an I_d interchange mechanism.

$$[Co(CN)_5Cl]^{3-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} + Cl^- \qquad (i)$$

$$[Co(CN)_5(OH_2)]^{2-} + X^- \longrightarrow [Co(CN)_5X]^{3-} + H_2O \qquad (ii)$$

$$[Co(CN)_5Cl]^{3-} + X^- \longrightarrow [Co(CN)_5X]^{3-} + Cl^- \qquad (iii)$$

The substitution of the pentacyanocobaltate(III) family of complex ions is widely used in accounts of the substitution chemistry of six-co-ordinate complex ions as an ideal example of a purely dissociative system.[1] The original investigation[2] concentrated on the substitution of $[Co(CN)_5(OH_2)]^{2-}$ by azide and thiocyanate ions.

The theoretical basis for the kinetic test for the thiocyanate ion depended on the mechanism shown by equations (1)—(4).

$$[Co(CN)_5(OH_2)]^{2-} \longrightarrow [Co(CN)_5]^{2-} + H_2O \qquad (1)$$

$$[Co(CN)_5]^{2-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} \qquad (2)$$

$$[Co(CN)_5]^{2-} + NCS^- \longrightarrow [Co(CN)_5(SCN)]^{3-} \qquad (3)$$

$$[Co(CN)_5]^{2-} + NCS^- \longrightarrow [Co(CN)_5(NCS)]^{3-} \qquad (4)$$

An expression for the second-order substitution rate constant, k_{NCS}, was derived [equation (5)] assuming that the intermediate

$$k_{NCS} = \frac{k_1(k_3 + k_4)}{k_2[H_2O] + (k_3 + k_4)[NCS^-]} \qquad (5)$$

$[Co(CN)_5]^{2-}$ was in the steady-state concentration, and since the absorption coefficients of the products were derived from measurements on the fully reacted solution it was thought unnecessary to identify the thiocyanate isomer formed in the reaction. It has been already shown[3] that the relative amounts of the linkage isomers formed in the anation reaction are constant throughout an experiment so that this procedure is fully justified. We have independently confirmed the predicted deviation from first-order kinetics for the thiocyanate ion reported previously[2] but despite the fact that the rates of aqua substitution[2,4] by pyridine, N_3^-, and NCS^- are comparable, no similar effects for pyridine and N_3^- have been established. The original report[2] that it had been detected in the case of N_3^- was subsequently disproved.[5,6] The second-order rate constant for each of these nucleophiles has the same form as equation (5) and the difficulty lies in detecting the term equivalent to $(k_3 + k_4)[NCS^-]$. This term always, it seems, makes a relatively small contribution to the denominator and the variation in the rate constant is hard to detect. In the case of NCS^- the observed rate constant only changed by 30% over the available concentration range and this is comparable to the sort of effect which could be expected for the failure of the constant ionic strength principle at unit ionic strength.[5]

Although evidence from the anation reactions of $[Co(CN)_5(OH_2)]^{2-}$ is ambiguous, a study[7] of the acid-catalysed substitution of $[Co(CN)_5(N_3)]^{3-}$ independently showed that $(k_3 + k_4)/k_2$ agreed with the value calculated from the anation study.[2] Unfortunately although we have been able to confirm this work in broad outline[3] we were forced to conclude that the method was not sufficiently sensitive to show conclusively that the ratio $(k_3 + k_4)/k_2$ derived from the substitution was the same as that found from the study of anation. In the present work we have studied the competition of water with both N_3^- and NCS^- in the thermal substitution of $[Co(CN)_5Cl]^{3-}$. The results have been interpreted using the full dissociative mechanism which includes reactions (1)—(4) and (6) for NCS^- and reactions (1), (2), (6), and (7) for N_3^-.

$$[Co(CN)_5Cl]^{3-} \longrightarrow [Co(CN)_5]^{2-} + Cl^- \qquad (6)$$

$$[Co(CN)_5]^{2-} + N_3^- \longrightarrow [Co(CN)_5(N_3)]^{3-} \qquad (7)$$

The results of the kinetic analysis show that the ratios for both the NCS^- competition, $(k_3 + k_4)/k_2$, and for the N_3^- competition, k_7/k_2, are close to zero. This ratio should be compared in the case of NCS^- with that of 15 from the anation of $[Co(CN)_5(OH_2)]^{2-}$ and 8 from competition reactions with $[Co(CN)_5(N_3H)]^{2-}$. The corresponding ratio for the N_3^- competition is consistent with the value of zero found in the anation reaction.[5,6] These results suggest that although the mechanism is a dissociative process, it has some interchange characteristics since the relative reaction rate of the intermediate depends on the ion from which it is formed.

Experimental

Reagents.—G.P. sodium azide, thiocyanate, perchlorate, and tetraethylammonium chloride were used as received. Perchloric acid solutions were prepared from a 60% AnalaR supply and standardised by titration. The complex $K_3[Co(CN)_5Cl]$ was prepared[8] from $[Co(NH_3)_5Cl]Cl_2$. Methods used to prepare

Table 1. Mean absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) from kinetic spectroscopic data for $[Co(CN)_5X]^{n-}$ (n = 2 or 3)

X	ε_{278}	ε_{280}	ε_{380}
OH_2	144	137 (100[a])	278 (301[a])
OH^-		238 (250[a])	226 (250[a])
Cl^-	459	430 (410[b])	195 (204[c])
NCS^-[d]	9 540 (10 000[a])		251 (246[a])
N_3^-		8 790 (8 800[a])	748 (737[a])

[a] From ref. 3. [b] From ref. 8. [c] J. Fujita and Y. Shimura, *Bull. Chem Soc. Jpn.*, 1963, **36**, 1281. [d] A 1:4 mixture of $[Co(CN)_5(NCS)]^{3-}$ and $[Co(CN)_5(SCN)]^{3-}$.

$K_3[Co(CN)_5(NCS)]$, $K_3[Co(CN)_5(SCN)]$, $K_3[Co(CN)_5(N_3)]$, and $K_2[Co(CN)_5(OH_2)]$ have been described previously.[3] The high-pressure liquid chromatography (h.p.l.c.), spectral, and microchemical analyses of the complexes were satisfactory.

Apparatus.—The apparatus used for h.p.l.c. analyses of the reactants and products has already been described.[3,9] Absorbance measurements were made using a Unicam SP6-800 spectrometer.

Kinetic measurements were made on suitably diluted samples taken from a reaction mixture held in a 100-cm^3 stoppered conical flask thermostatted at 40.0 ± 0.02 °C. The samples, cooled to *ca.* −10 °C in an ice–salt mixture, did not vary in absorbance in the time required to make all the necessary spectral measurements, *ca.* 2 h.

Results

H.P.L.C. and Spectroscopic Analyses.—The methods of h.p.l.c. analysis and calibration have been reported previously.[3] A detailed h.p.l.c. investigation of this and allied systems is at present being carried out but it has already been established that the substitution reactions of $[Co(CN)_5Cl]^{3-}$ are clean and that the concentration ratio of the linkage isomers $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ in 0.1 mol dm^{-3} perchloric acid is *ca.* 4:1 for $[Co(CN)_5Cl]^{3-}$, $[Co(CN)_5(N_3H)]^{2-}$, and $[Co(CN)_5(OH_2)]^{2-}$. This explains the fact that the measured absorption coefficients shown in Table 1 for the thiocyanate products in the present work are very similar to those reported previously[3,5] from studies of the reactions of $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(N_3H)]^{2-}$. The absorption coefficients for $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(OH)]^{3-}$ are from completely hydrolysed solutions of $[Co(CN)_5Cl]^{3-}$ and show some discrepancies from standard values used previously,[5] particularly at 280 nm. Since the absorption contribution by $[Co(CN)_5(OH_2)]^{2-}$ is very small in comparison with the other complexes present, any error in this value is unlikely to have a serious effect. The h.p.l.c. results obtained for the N_3^-– and NCS^-–$[Co(CN)_5Cl]^{3-}$ systems generally agree with the analytical results using spectroscopy except for the case of NCS^- substitutions in a phosphate buffered medium. In the latter case the spectroscopic results suggest that the ratio k_7/k_2 is *ca.* 5 but the result is at the limit of detection for the method.

Numerical Methods.—Since h.p.l.c. shows that the concentration ratio of the linkage isomers is constant, it is possible to treat the thiocyanate products as a single species. The kinetic data are analysed by two methods.

Method 1. The concentrations of $[Co(CN)_5Cl]^{3-}$, $[Co(CN)_5(OH_2)]^{2-}$, and either the sum of the concentrations of $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ or the concentration of $[Co(CN)_5(N_3)]^{3-}$ are represented by a, b, and c respectively. The values of a, b, and c can be calculated by solving equations (8)—(10). Equations (8) and (9) are based on absorbance measurements at two different wavelengths, A_1 and A_2, and expressed in terms of the concentrations of the reactants and products, a, b, and c, combined with the corresponding absorption coefficients ε_{1a}, ε_{1b}, and ε_{1c} at wavelength 1 and ε_{2a}, ε_{2b}, and ε_{2c} at wavelength 2.

Equation (10) uses the fact that the initial concentration of the reactant, c_0, is always equal to the sum of the concentrations of the complexes present.

$$a\varepsilon_{1a} + b\varepsilon_{1b} + c\varepsilon_{1c} = A_1 \qquad (8)$$

$$a\varepsilon_{2a} + b\varepsilon_{2b} + c\varepsilon_{2c} = A_2 \qquad (9)$$

$$a + b + c = c_0 \qquad (10)$$

The method of analysis is very convenient for calculating the overall rate constant [equation (11)] for the removal of the

$$k_{obs.} = (1/a)\mathrm{d}a/\mathrm{d}t \qquad (11)$$

reactant $[Co(CN)_5Cl]^{3-}$, using the conventional plot of ln a *versus* time.

The absorption coefficients required for each experiment were derived from the initial absorbance readings extrapolated to zero time and the readings after complete reaction. The values for $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(OH)]^{3-}$ were taken from blank experiments on the decomposition of $[Co(CN)_5Cl]^{3-}$ in the absence of added nucleophile.

Method 2. Although method 1 is convenient it is not the most reliable method for measuring the competition ratio of either NCS^- or N_3^- and H_2O for the reaction intermediate $[Co(CN)_5]^{2-}$. The ratio c/b rises in the course of the reaction, due to anation of $[Co(CN)_5(OH_2)]^{2-}$. The most direct method for determining the competition ratios is through the direct fitting of the observed absorbance–time curves using integrated rate equations in which only the rate constants k_{12}, k_{13}, and k_{14} are allowed to vary. The model system used to fit the experiments is reduced to three pseudo-unimolecular reactions, equations (12)—(14) (X = NCS^- or N_3^-). The values of $k_{12} + k_{13}$ and k_{13}/k_{12} are fitted and k_{14} taken from previous experimental work.[7]

$$[Co(CN)_5Cl]^{3-} \longrightarrow [Co(CN)_5(OH_2)]^{2-} \qquad (12)$$

$$[Co(CN)_5Cl]^{3-} \longrightarrow [Co(CN)_5X]^{3-} \qquad (13)$$

$$[Co(CN)_5(OH_2)]^{2-} \longrightarrow [Co(CN)_5X]^{3-} \qquad (14)$$

The rate constants of the simplified scheme are directly related to those corresponding to the full mechanism given above, by equation (15) and by equations (16) (X = N_3^-) and (17) (X = NCS^-).

$$k_{12} + k_{13} = k_6 \qquad (15)$$

$$k_{13}/k_{12} = k_7[N_3^-]/k_2[H_2O] \qquad (16)$$

$$k_{13}/k_{12} = (k_3 + k_4)[NCS^-]/k_2[H_2O] \qquad (17)$$

The differential equations used and their solutions are identical in algebraic form to those described earlier.[3]

Kinetic Measurements.—Rate constants derived by methods 1 and 2 described above are shown in Tables 2 and 3. The absorbance–time curves were in each case fitted over two half-lives and the divergence between experimental and calculated results was usually comparable to the experimental error in the

Table 2. Rate constants[a] used in fitting the absorption–time results for the reaction of $[Co(CN)_5Cl]^{3-}$ with NCS^-

$[NCS^-]$/ mol dm^{-3}	$10^4(k_{12} + k_{13})/s^{-1}$ *b*	*c*	$10^4k_{14}/s^{-1}$ [d]	k_{13}/k_{12} [c]	$\frac{(k_3 + k_4)}{k_2}$
0	4.37	4.6			
0.1	4.30	3.3	0.62	<0.01	<5
0.2	4.27	4.0	1.20	<0.04	<11
0.5	4.27	3.7	2.79	<0.02	<3
0.7	4.62	4.6	3.72	<0.02	<1
0.956	5.16	4.4	4.80	<0.02	<1

[a] At 40 °C; unit ionic strength maintained by $NaClO_4$ in 0.01 mol dm^{-3} phosphate buffer, pH 6.4; initial complex concentration 4×10^{-3} mol dm^{-3}. [b] Calculated using method 1. [c] Calculated using method 2. [d] Calculated from equation (4) of ref. 5, X = NCS^-.

Table 3. Rate constants[a] used in fitting the absorption–time results for the reaction of $[Co(CN)_5Cl]^{3-}$ with N_3^-

$[N_3^-]$/mol dm^{-3}	$10^4(k_{12} + k_{13})/s^{-1}$ *b*	*c*	$10^4k_{14}/s^{-1}$ [d]	k_{13}/k_{12} [c]	k_7/k_2
0[e]	4.48	4.4			
0[f]	5.27	4.0			
0.1[e]	4.40	3.7	0.66	0.01	6
0.2[e]	4.64	4.8	1.32	0.03	8
0.5[e]	4.60	4.0	3.31	0.06	7
0.7[e]	4.57	4.1	4.63	0.02	2
0.956[e]	5.60	4.0	6.33	0.06	3
0.876[f]		4.0	0.03	<0.01	<1
0.876[g]		3.3	0.24	<0.01	<1
0.876[h]		4.0	0.53	<0.05	<3
0.876[i]		3.5	5.80	0.11	7

[a] At 40 °C; unit ionic strength maintained by $NaClO_4$; initial complex concentration 4×10^{-3} mol dm^{-3}. [b] Calculated using method 1. [c] Calculated using method 2. [d] From Ref. 5, $k_{14} = 6.62 \times 10^{-4}[N_3^-]$ s^{-1} for pH 6.4; corrected by equation (3) of ref. 5 for the effect of increasing pH. [e] In 0.01 mol dm^{-3} phosphate buffer, $Na[H_2PO_4]$–$Na_2[HPO_4]$; pH 6.4. [f] In 0.1 mol dm^{-3} NaOH. [g] In 0.01 mol dm^{-3} NaOH. [h] In 0.01 mol dm^{-3} $Na[H_2PO_4]$–$Na_3[PO_4]$, pH 10.8. [i] In 0.01 mol dm^{-3} $Na[HCO_3]$–Na_2CO_3, pH 9.6.

Table 4. Average values for the rate constant k_6 (= $k_{12} + k_{13}$) at 40 °C and unit ionic strength ($NaClO_4$)

	$10^4k_6/s^{-1}$ Average value	Standard deviation	No. of observations
Table 2: method 1	4.79	0.45	6
method 2	4.0	0.40	11
Table 3: method 1	4.50	0.35	6
method 2	4.1	0.53	6

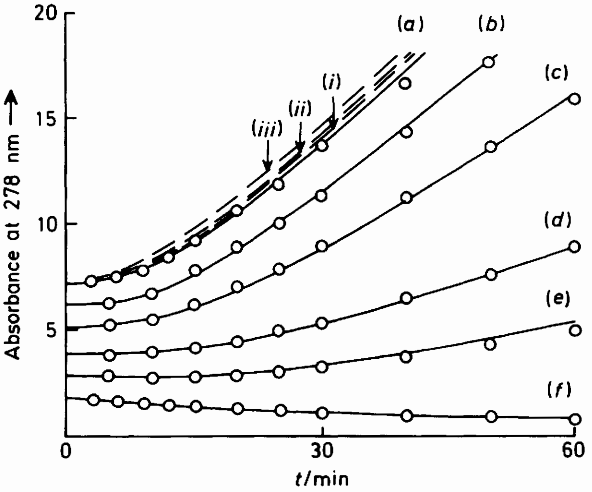

Figure. Absorbance–time curves for the reaction of $[Co(CN)_5Cl]^{3-}$ (4×10^{-3} mol dm^{-3}) with NCS^- [(*a*) 0.956, (*b*) 0.7, (*c*) 0.5, (*d*) 0.2, (*e*) 0.1, and (*f*) 0 mol dm^{-3}] at 40 °C, unit ionic strength ($NaClO_4$), and pH 6.4: (○) experimental observations; (——) calculated for k_{13}/k_{12} = 0; (– – – –) calculated for k_{13}/k_{12} = 0.02 (*i*), 0.04 (*ii*), and 0.08 (*iii*). The *y*-axis zero has been displaced by unit absorbance for each successive experiment

absorption measurements, *ca.* 2%. The results show that data treatment can produce apparently dramatic alterations in the rate constants. However there are no significant differences between the mean results, Table 4, and the differences in individual cases probably represent systematic errors normally concealed by the conventional analysis of method 1. Disagreement between methods 1 and 2 originates in the different weight attributed to observations at later times. The conventional method 1 tends to ignore the later observations since the concentration of the reactant has by then fallen to such a low value that it can only be measured inaccurately. However, method 2 requires an adequate fit for all wavelengths over the whole reaction profile.

Thiocyanate Substitution.—The spectroscopic and h.p.l.c. analyses agree that there is no detectable competition between the nucleophiles NCS^- and H_2O at zero time. The preliminary h.p.l.c. result suggests that $(k_3 + k_4)/k_2$ is less than 0.6. The ratio of S- to N-bonded isomer found later in the reaction, *ca.* 4:1, is identical to that measured during the anation of $[Co(CN)_5(OH_2)]^{2-}$. This validates the method of spectroscopic analysis and also supports the hypothesis that the greater part of the thiocyanate product is formed *via* $[Co(CN)_5(OH_2)]^{2-}$. The effect of reactions (3) and (4) should be observed at 278 nm since this wavelength is dominated by the effect of the absorption due to thiocyanate products. The results obtained during the runs summarised in Table 2 are shown for 278 nm in the Figure. The observations generally fit the zero competition prediction and such discrepancies as exist show less thiocyanate products to be formed than are calculated. The upper limits to $(k_3 + k_4)/k_2$ were found by assessing the greatest value which still gave a reasonable fit to the experimental absorbance–time plot. Examples are shown for 0.956 mol dm^{-3} NCS^- for various values of the ratio.

Azide Substitution.—The results shown in Table 3 for a phosphate buffered reaction mixture suggested that there was a small but detectable direct nucleophilic attack by N_3^- on $[Co(CN)_5Cl]^{3-}$. However the h.p.l.c. results limited the ratio k_7/k_2 to less than 0.4. Additional experiments were performed under alkaline conditions where the competing effect of anation would be greatly reduced.[5] When the product is present mainly as $[Co(CN)_5(OH)]^{3-}$, method 1 becomes inaccurate due to the similar absorption coefficients of $[Co(CN)_5Cl]^{3-}$ and $[Co(CN)_5(OH)]^{3-}$ at 380 nm. Method 2, on the other hand, remains effective since it uses the complete observational set and is particularly sensitive to the early appearance of $[Co(CN)_5(N_3)]^{3-}$. The value found for k_7/k_2 fell below the limit of detection at 1 and was confirmed by h.p.l.c. measurements which suggested a value of *ca.* 0.2.

Discussion

The results obtained in this study confirm the general theoretical scheme which has been developed in previous papers.[3,5,10]

The original supposition[2] that the negative charge of the $[Co(CN)_5]^{2-}$ intermediate combined with the electron-donor character of the cyano-ligands should favour an S_N1 or D type path is still plausible but the experimental facts suggest that the mechanism is generally within the I_d classification. The original concept of Langford and Gray[11] pictured substitution mechanisms in terms of a spectrum of behaviour in which individual cases lay between the purely interchange and the extreme cases of the purely associative, A, and dissociative, D. The evidence for the pentacyanocobaltate(III) family suggests beyond reasonable doubt that the mechanism is I_d and that in individual cases the $[Co(CN)_5]^{2-}$ intermediate may be sufficiently long lived for the mechanism to be classed as D type. Unfortunately in all the cases so far investigated the reactivity of the intermediate for water is too high for a successful kinetic demonstration such as that originally attempted for the N_3^- and NCS^- substitution of $[Co(CN)_5(OH_2)]^{2-}$. It seems likely that minor failures in the ionic strength principle[5] are distorting the effects of the kinetics of the reactions. These effects however should be much less important in competition studies. The activity of singly-charged nucleophiles in an unchanging primary solvation sphere of water and sodium cations should be free of variation. Consequently we have been attempting a systematic investigation of competition experiments of the type described earlier.[3,7] It is ironic that the pentacyanocobaltate(III) family of complexes seems generally to substitute *via* the aqua intermediate although historically supposed to be D type, whereas the evidence for the classic case[12] of an aqua-intermediate, the NCS^- substitution of $[Co(NH_3)_5(NO_3)]^{2+}$, has recently[13] been shown to be in error.

In a preliminary account of some of this work[10] a value for k_7/k_2, of *ca.* 5, was given which we now consider to be a serious overestimate. The added technique of h.p.l.c. has now shown the value to be less than 0.4, although the spectroscopic experiments under neutral conditions continue to support a value of *ca.* 5. At present we have no proven explanation for the systematic tendency of the spectroscopic experiments to exaggerate the competition ratio. The fact that the additional experiments performed under alkaline conditions provide an upper limit of 0.5 and that the apparently erroneous value reappears at the lowest alkaline pH, 9.6, seems to imply that the measured values of the constant k_{14} taken from previous work[5] must be low. The value of this constant under alkaline conditions is so small that it has little effect on the fitted ratio, k_7/k_2. However it is still a matter of opinion as to whether the low anation rate at high pH is due to the effects of OH^- competition[2] or the slow substitution[7] of $[Co(CN)_5(OH)]^{3-}$, but it is clearly possible to explain the low competition ratio at high pH by the former theory, *i.e.* by hydroxide ion competition. It was precisely these difficulties of interpretation which first led us to attempt the measurement of the competition ratios under neutral conditions. The spectroscopic result only seemed reliable because of its repeatability since in any individual experiment the fitted ratio was close to the limit of detection for the method. It should always be borne in mind in assessing the results of such experiments that the final competition ratio is systematically dependent on the values of the anation constant, k_{14}, and the absorption coefficient for $[Co(CN)_5(N_3)]^{3-}$ at 280 nm. An unrecognised source of error in either of these constants of *ca.* 20% would reduce k_7/k_2 to zero. The h.p.l.c. data on the other hand are fortunately unambiguous.

The theoretical conclusion from this study is quite unaffected by the precise upper limit which is set to the competition ratios for NCS^- or N_3^-. The upper limit of the ratio $(k_3 + k_4)/k_2$, 0.6, is far smaller than the values estimated from the study[5] of $[Co(CN)_5(OH_2)]^{2-}$, 15, or that[3] of $[Co(CN)_5(N_3H)]^{2-}$, 8. Although it is possible to argue that the latter two values are as close as might be expected in view of possible medium effects, the order of magnitude difference between them and the first value must point to a mechanistic effect. The most obvious difference between the systems is that in the latter cases the leaving group is neutral but that in the former is negatively charged. Provided the transition state for the substitution reaction still includes a partial bond to the leaving chloride anion, the dramatic decrease in the competition ratio may be understood on electrostatic grounds alone. The low upper limit for the competition ratio of the azide ion is explicable on the same basis. It must therefore be concluded that the substitution of $[Co(CN)_5Cl]^{3-}$ is by dissociative interchange, I_d, although the anation of $[Co(CN)_5(OH_2)]^{2-}$ could represent a closer approximation to the purely dissociative D type model.

References

1 K. F. Purcell and J. C. Kotz, in 'Inorganic Chemistry,' W. B. Saunders Co., Philadelphia, 1972, p. 715.
2 A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573.
3 M. H. M. Abou-El-Wafa, M. G. Burnett, and J. F. McCullagh, *J. Chem. Soc., Dalton Trans.*, 1986, 2083.
4 R. Barca, J. Ellis, M-S. Tsao, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 243.
5 M. G. Burnett and W. M. Gilfillan, *J. Chem. Soc., Dalton Trans.*, 1981, 1578.
6 A. Haim, *Inorg. Chem.*, 1982, **21**, 2887.
7 A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 583.
8 R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 237.
9 M. G. Burnett and M. H. M. Abou-El-Wafa, *J. Chem. Soc., Dalton Trans.*, 1984, 2341.
10 M. H. M. Abou-El-Wafa and M. G. Burnett, *J. Chem. Soc., Chem. Commun.*, 1983, 833.
11 C. H. Langford and H. B. Gray, 'Ligand Substitution Mechanism,' Benjamin, New York, 1965.
12 R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1964, **3**, 1334.
13 W. G. Jackson, S. S. Jurisson, and B. C. McGregor, *Inorg. Chem.*, 1985, **24**, 1788.

Received 15*th April* 1986; *Paper* 6/732