The Relative Nucleophilic Efficiency of Water and the Thiocyanate Ion in the Acid-catalysed Substitution of Azidopentacyanocobaltate(III)

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The acid-catalysed substitution of $[Co(CN)_5(N_3)]^{3-}$ by NCS^- in water yields $[Co(CN)_5(OH_2)]^{2-}$, $[Co(CN)_5(SCN)]^{3-}$, and $[Co(CN)_5(NCS)]^{3-}$. Spectroscopic and high-performance liquid chromatographic analytical data are quantitatively consistent with an acid-catalysed dissociative mechanism [equations (1)—(5)], in which $K_1 = 4.47 \pm 0.22$ dm^3 mol^{-1}, $k_2 = (3.46 \pm 0.17) \times 10^{-3}$ s^{-1},

$$[Co(CN)_5(N_3)]^{3-} + H_3O^+ \overset{K_1}{\rightleftharpoons} [Co(CN)_5(N_3H)]^{2-} + H_2O \quad (1)$$

$$[Co(CN)_5(N_3H)]^{2-} \xrightarrow{k_2} [Co(CN)_5]^{2-} + HN_3 \quad (2)$$

$$[Co(CN)_5(OH_2)]^{2-} \xrightarrow{k_3} [Co(CN)_5]^{2-} + H_2O \quad (3)$$

$$[Co(CN)_5]^{2-} + H_2O \xrightarrow{k_4} [Co(CN)_5(OH_2)]^{2-} \quad (4)$$

$$[Co(CN)_5]^{2-} + NCS \xrightarrow{k_{5a}} [Co(CN)_5(SCN)]^{3-} \quad (5a)$$

$$[Co(CN)_5]^{2-} + NCS \xrightarrow{k_{5b}} [Co(CN)_5(NCS)]^{3-} \quad (5b)$$

$k_3 = 6.07 \times 10^{-4}$ s^{-1}, $(k_{5a} + k_{5b})/k_4[H_2O] = 0.14 \pm 0.02$ dm^3 mol^{-1}, and $k_5/k_{5b} \approx 4$ at 40 °C and unit ionic strength. Equilibrium spectroscopic measurements of K_1 (4.67 ± 0.09 dm^3 mol^{-1}) agree with the fitted kinetic result.

The substitution of the pentacyanocobaltate(III) family of complex ions has recently been the subject of reinvestigation[1,2] and the kinetic evidence in favour of a simple *D*-type substitution of the azide ion in $[Co(CN)_5(OH_2)]^{2-}$ has been found to be incorrect.[2] However, the analogous evidence for substitution by the thiocyanate ion has been confirmed[1] although the size of the effect is sufficiently small to raise the possibility that it could be due to the failure of the constant ionic strength principle.[1]

One of the remaining powerful kinetic arguments for the validity of the mechanism depends on a classic series of competition experiments.[3] In view of the crucial importance of this study we have attempted to repeat some of the original work as a preliminary to additional similar competition studies on the same family of complexes.[4] The reaction was less clean than was anticipated partly due to the formation of trace amounts of polynuclear complex anions and partly due to side-reactions of the thiocyanate ion in acid solution giving coloured products.[5] In addition it was found that the rate of the thiocyanate reaction was inhibited by a high surface-to-volume ratio. These effects were shown not to be responsible for the results of the competition experiments by means of a final test performed in a large-volume stirred reactor. The spectroscopic data have been analysed using integrated rate equations based on the steps (1)—(5). The products of reactions (5a) and (5b) are not distinguished by the spectroscopic measurements and they may be treated in the calculations as a single species formed with a rate constant k_5 since the ratio of their concentrations does not change during a run ($k_5 = k_{5a} + k_{5b}$).

$$[Co(CN)_5(N_3)]^{3-} + H_3O^+ \overset{K_1}{\rightleftharpoons} [Co(CN)_5(N_3H)]^{2-} + H_2O \quad (1)$$

$$[Co(CN)_5(N_3H)]^{2-} \xrightarrow{k_2} [Co(CN)_5]^{2-} + HN_3 \quad (2)$$

$$[Co(CN)_5(OH_2)]^{2-} \xrightarrow{k_3} [Co(CN)_5]^{2-} + H_2O \quad (3)$$

$$[Co(CN)_5]^{2-} + H_2O \xrightarrow{k_4} [Co(CN)_5(OH_2)]^{2-} \quad (4)$$

$$[Co(CN)_5]^{2-} + NCS^- \begin{cases} \xrightarrow{k_{5a}} [Co(CN)_5(SCN)]^{3-} & (5a) \\ \xrightarrow{k_{5b}} [Co(CN)_5(NCS)]^{3-} & (5b) \end{cases}$$

The results confirm that direct competition occurs between water and the thiocyanate ion in the primary substitution process. Preliminary high-performance liquid chromatography (h.p.l.c.) results show that *ca.* 20% of the thiocyanate complex product is in the form of the nitrogen-bound linkage isomer.

Experimental

Reagents.—G.P. sodium azide, thiocyanate, and hydroxide, potassium hexacyanocobaltate(III), tributylmethylammonium bromide, and tetraethylammonium chloride were used as received. Perchloric acid (60% w/w) was AnalaR grade. The salt $K_3[Co(CN)_5(N_3)]$ was prepared[6] *via*[7] $[Co(NH_3)_5(N_3)]Cl_2$. Solutions of $K_2[Co(CN)_5(OH_2)]$ were prepared by photolysis[1] of $K_3[Co(CN)_6]$. The salt $K_3[Co(CN)_5(SCN)]$ was prepared[8] from $[Co(NH_3)_5(SCN)]SO_4$ and also by isolation of the product of reaction of $K_2[Co(CN)_5(OH_2)]$ with potassium thiocyanate. The salt $[NBu^n{}_4]_3[Co(CN)_5(NCS)]$ was prepared from $K_3[Co(CN)_5(SCN)]$.[8] The h.p.l.c., spectral, and microchemical analyses of these complexes were satisfactory.

Apparatus.—The reactants and products were analysed by h.p.l.c. using apparatus which has been described previously.[9] The speed of analysis was found to be improved in the later experiments by using an eluant consisting of 10% (v/v) methanol–water containing 0.1 mol dm^{-3} tetraethylammonium chloride with a 5-μm ODS Partisil column.

The greater part of the kinetic and equilibrium data was obtained spectroscopically using a thermostatted reaction cell in a Unicam SP6-800 spectrometer monitoring at either 278 or 280, and 380 nm. Some kinetic runs were performed by taking 1-cm^3 samples from a thermostatted conical flask (100 cm^3) and quenching them in 0.5 cm^3 of 1 mol dm^{-3} sodium hydroxide at room temperature. In one set of experiments the absorbance was subsequently measured using the digital absorbance readings of suitably diluted samples at 278 or 280, and 380 nm, while in another the analysis was performed by h.p.l.c. A further group of experiments using reactant concentrations between 10^{-3} and 10^{-4} mol dm^{-3} were monitored directly in a thermostatted 10-mm quartz cell. The cell path was reduced to 0.18 mm using a quartz block for a group of experiments with 0.014 mol dm^{-3} of reactant.

The final kinetic run was performed in a jacketted stirred reaction vessel (250 cm^3) containing 125 cm^3 of reactant from which 0.85 cm^3 min^{-1} were pumped and mixed continuously with 14.3 cm^3 min^{-1} of 1 mol dm^{-3} sodium hydroxide. The absorbance at 278 nm was recorded continuously using a 10-mm flow cell and the quenched solution was collected in 5-cm^3 samples whose absorbance was later measured at 380 nm using a 40-mm cell.

Results

Reactant and Product Analyses.—The absorption coefficients used in this work are given in Table 1 together with data transcribed from the literature.[8] The h.p.l.c. data were calculated from either peak heights or peak areas using sensitivity factors obtained by direct calibration using solutions of known composition. The column's stability was poor over periods of 100 h. The plate number and both the absolute and the relative retention volumes varied so that calibration with synthetic mixtures during each experiment was essential in order to be sure of the relative sensitivities of the detector to each ion, and of the elution pattern. A typical chromatogram recorded during experiments on the acid-catalysed thiocyanate substitution is shown in Figure 1.

$[Co(CN)_5(OH_2)]^{2-}$. This complex is formed in solution during the photolysis of acidified $[Co(CN)_6]^{3-}$ in stoicheiometric yield, although continued photolysis[10] eventually produces *trans*-$[Co(CN)_4(OH_2)_2]^-$. Fortunately, any traces of the latter product rapidly revert to $[Co(CN)_5(OH_2)]^{2-}$ and the sole impurity is $[Co(CN)_6]^{3-}$ (1—5%). The h.p.l.c. analysis shows a single sharp peak and although cyanide-bridged polymer has been shown[11] to form slowly in solution the process does not occur sufficiently rapidly to be detected during anation experiments at 40 °C. However $[Co(CN)_5(OH_2)]^{2-}$ formed by slight hydrolysis during the storage of 10^{-3} mol dm^{-3} $[Co(CN)_5X]^{3-}$, X = Cl^- or N_3^-, does show a characteristic peak distortion[9] attributable to polymer formation.

$[Co(CN)_5(N_3)]^{3-}$. This complex is readily synthesised but it is frequently isolated contaminated with 10—30% by weight of potassium chloride. The sample used for the original competition study seems to have been contaminated in this way since both the bands at 278 and 380 nm are less intense than they should be although they still preserve almost the correct intensity ratio (Table 2). The absorption coefficients quoted here and by authors who have attempted a thorough recrystallisation[8,12] are in good agreement (Table 2), and the h.p.l.c. analysis shows a single sharp peak.

$[Co(CN)_5(SCN)]^{3-}$. The spectroscopic and h.p.l.c. results confirm that the sulphur-bonded isomer is the major product in both of the synthetic routes used. The absorption coefficients calculated for the final product of the acid-catalysed reaction of $[Co(CN)_5(N_3)]^{3-}$ and NCS^- only change slowly after 4—5 h and it is those values which are reported in Table 1. The absorption coefficient at 380 nm is reproducible but the values at 278 and 280 nm are never really constant. Despite the

Table 1. Absorption coefficients[a] for reactants and products

	ε_{278}	ε_{280}	ε_{380}
$[Co(CN)_5(OH_2)]^{2-}$ [b]	100	100	301
$[Co(CN)_5(OH)]^{3-}$ [b]	300	250	250
$[Co(CN)_5(N_3)]^{3-}$ [c]	8 700	8 800	737
$[Co(CN)_5(N_3H)]^{2-}$ [d]	*ca.* 140	—	260
NCS^-–$[Co(CN)_5(N_3)]^{3-}$ obs.[d]	10 000	8 700	246
calc.[e]	8 630	7 560	231
$[Co(CN)_5(SCN)]^{3-}$ [f]	10 300	9 000	190
$[Co(CN)_5(NCS)]^{3-}$ [f]	1 960	1 820	397

[a] In units of dm^3 mol^{-1} cm^{-1}. [b] W. M. Gilfillan, Ph.D. Thesis, University of Belfast, 1973. [c] Purified reactant in aqueous solution. [d] The mixture of linkage isomers produced by the reaction of $[Co(CN)_5(N_3)]^{3-}$ in 0.1 mol dm^{-3} $HClO_4$ with 0.9 mol dm^{-3} NaNCS in water at 40 °C. [e] From h.p.l.c. analysis and absorption coefficients for the thiocyanate and isothiocyanate complexes in this table. [f] From Figures 5 and 6 of ref. 8.

Table 2. Absorption coefficients[a] of $[Co(CN)_5(N_3)]^{3-}$

Ref.	*b*	*c*	*d*	*e*
380 nm	737	666	743	724
278 nm	8 700	7 300	8 580	—
$\varepsilon_{278}/\varepsilon_{380}$	11.8	11.0	11.6	—

[a] In units of dm^3 mol^{-1} cm^{-1}. [b] This work. [c] Ref. 3. [d] Ref. 8, the values were quoted for maxima at 383 and 281 nm for $[NBu^n{}_4]_3[Co(CN)_5(N_3)]$ in water. [c] Ref. 11.

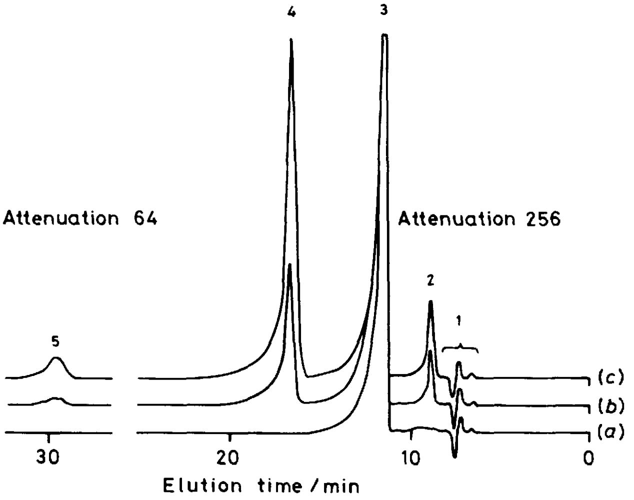

Figure 1. Chromotogram at 265 nm of the acid-catalysed decomposition of $[Co(CN)_5(N_3)]^{3-}$ (0.04 mol dm^{-3}) in 0.091 mol dm^{-3} $HClO_4$ and 0.67 mol dm^{-3} NaNCS at 40 °C and unit ionic strength: (*a*) zero time, (*b*) after 10 min, and (*c*) after 20 min. Peaks: (1) injection and background peaks, (2) $[Co(CN)_5(OH_2)]^{2-}$, (3) $[Co(CN)_5(N_3)]^{3-}$, (4) $[Co(CN)_5(SCN)]^{3-}$, and (5) $[Co(CN)_5(NCS)]^{3-}$. Eluant: 10% methanol–water + 0.1 mol dm^{-3} $[NEt_4]Cl$ at 1 cm^3 min^{-1}. Sample volume: 20 μl

product's evident lack of long-term stability at 40 °C, the spectral results fully support its assignment as being predominantly in the sulphur-bound form.

Heating aqueous or methylene chloride solutions of $[Co(CN)_5(SCN)]^{3-}$, as well as storing $[NBu^n_4]_3[Co(CN)_5(SCN)]$ for periods of several days, produces ultra-violet spectral changes indicating the formation of the nitrogen-bound isomer and this is accompanied by the development of the appropriate h.p.l.c. peak (Figure 1). These reactions do not produce single products since smaller late-running peaks also appear as well as that attributed to $[Co(CN)_5(NCS)]^{3-}$. It is probably these other products which make the determination of the final absorption coefficients of the thiocyanate substitution uncertain in the kinetic spectroscopic experiments.

$[Co(CN)_5(NCS)]^{3-}$. Although we were unable to obtain $[Co(CN)_5(NCS)]^{3-}$ entirely free from $[Co(CN)_5(SCN)]^{3-}$, the sample could be used to calibrate the h.p.l.c. system. The spectroscopic results, after allowing for $[Co(CN)_5(SCN)]^{3-}$ present, approximately agreed with the literature values[8] and the latter, being more accurate, have been adopted for reference purposes (Table 1). The h.p.l.c. analysis of the reaction of $[Co(CN)_5(OH_2)]^{2-}$ or $[Co(CN)_5(N_3H)]^{2-}$ with aqueous thiocyanate shows that about 20% of the thiocyanate complex product is in the nitrogen-bound form (Figure 1). Peak 3 in Figure 1 contains a small contribution due to the free thiocyanate anion but this is removed in quantitative analyses by a background blank chromatogram recorded separately.

The Acid-catalysed Hydrolysis of $[Co(CN)_5(N_3)]^{3-}$.—The h.p.l.c. analysis of the acid-catalysed hydrolysis shows that $[Co(CN)_5(N_3)]^{3-}$ is stoicheiometrically converted into $[Co(CN)_5(OH_2)]^{2-}$ [equations (1) and (6)]. Although at this stage the

$$[Co(CN)_5(N_3)]^{3-} + H_3O^+ \rightleftharpoons [Co(CN)_5(N_3H)]^{2-} + H_2O \quad (1)$$

$$[Co(CN)_5(N_3H)]^{2-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} + HN_3 \quad (6)$$

results need not be interpreted in terms of the dissociative mechanism *via* steps (2) and (4) given previously, the evidence given below on the acid-catalysed thiocyanate substitution supports this mechanism and the rate constant for (6) can

$$[Co(CN)_5(N_3H)]^{2-} \longrightarrow [Co(CN)_5]^{2-} + HN_3 \quad (2)$$

therefore be identified with that for reaction (2). The constants K_1 and k_2 were then evaluated from kinetic and equilibrium measurements.

Equilibrium Measurements.—Volumes of 2—10 µl of *ca.* 0.5 mol dm^{-3} $[Co(CN)_5(N_3)]^{3-}$ were injected into the appropriate background electrolyte at 40 °C. The cell was shaken while still in the thermostatted holder and the absorbance at 278 nm was recorded for sufficient length of time to allow an accurate extrapolation back to the time of mixing. The experiments were performed in groups, each covering a range of hydrogen-ion concentrations between zero and 1 mol dm^{-3}. The values of the absorption coefficient of $[Co(CN)_5(N_3)]^{3-}$ in neutral solution (ε_0) showed considerable variations in some cases due to the contamination of some of the samples of $[Co(CN)_5(N_3)]^{3-}$ with potassium chloride (groups 1, 3, 8, and 9). The observed absorption coefficients in each group (ε) were therefore expressed as ratios of ε_0. The results expressed in this way were mutually consistent and showed no dependence on the sample of $[Co(CN)_5(N_3)]^{3-}$ used.

The data were fitted by use of equation (7), which may be

$$K_1 = (1 - \varepsilon/\varepsilon_0)/(\varepsilon/\varepsilon_0 - \varepsilon_\infty/\varepsilon_0)[H_3O^+] \quad (7)$$

derived from the equilibrium constant K_1, expressed in concentrations, by the customary substitution of the absorption coefficients ε, ε_0, and ε_∞. The absorption coefficient for the fully protonated complex, found in the form $\varepsilon_\infty/\varepsilon_0$, was obtained by extrapolation of the linear plot $\{\varepsilon/\varepsilon_0$ *vs.* $(1 - \varepsilon/\varepsilon_0)/[H_3O^+]\}$ of

$$\varepsilon/\varepsilon_0 = (1 - \varepsilon/\varepsilon_0)/K_1[H_3O^+] + \varepsilon_\infty/\varepsilon_0 \quad (8)$$

equation (8). The absorption coefficient of $[Co(CN)_5(N_3H)]^{2-}$ is so very much less than that of $[Co(CN)_5(N_3)]^{3-}$ at 278 nm that the extrapolated value is only accurate to ± 20%. However, the resulting systematic error is always negligible compared to the random error even at 1 mol dm^{-3} perchloric acid.

The results shown in Table 3 are poor in quality until the absorbance change on adding acid is more than 20%, but they improve from 0.087 to 1 mol dm^{-3} perchloric acid, $K_1 = 4.67 \pm 0.09$ dm^3 mol^{-1}. The values are unaffected by complex concentration and by replacing the perchlorate by the thiocyanate anion. There is also no evidence for any failure of equation (8) down to 0.01 mol dm^{-3} perchloric acid.

Kinetic Measurements.—The experiments in Table 3 also provided values of the hydrolysis rate constant k_2 from the high sensitivity measurements (0.2 absorbance units full-scale deflection) of the early changes in the absorbance A at 278 nm. The constants were calculated from equation (9), in which A is the

$$k_{obs.} = [1/(A - A_\infty)]dA/dt \quad (9)$$

absorbance equivalent to the stoicheiometric conversion of $[Co(CN)_5(N_3)]^{3-}$ into $[Co(CN)_5(OH_2)]^{2-}$. In the case of experiments with a perchloric acid concentration greater than 0.65 mol dm^{-3} A_∞ was observed directly, but for reactions at lower acid concentrations the values were calculated. Since in the latter cases $A/A_\infty > 20$, the possible systematic error introduced by this procedure is negligible. The results, shown in Table 3, were fitted to equation (10), in which $k_2 = (3.46 \pm 0.17) \times 10^{-3}$ s^{-1} and $K_1 = 4.47 \pm 0.22$ dm^3 mol^{-1}.

$$k_{obs.} = k_2K_1[H_3O^+]/(1 + K_1[H_3O^+]) \quad (10)$$

The Acid-catalysed Substitution of $[Co(CN)_5(N_3)]^{3-}$.—The preliminary h.p.l.c. analyses for this reaction confirm that $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ are formed approximately in the ratio of 4:1 for up to 5 half-lives of the reaction. During that period the proportion of $[Co(CN)_5(SCN)]^{3-}$ to $[Co(CN)_5(OH_2)]^{2-}$ increases 20-fold. There is no evidence of isomerisation between the linkage isomers. Thus, although the thiocyanate product is present as two isomers, they behave spectroscopically as a single species.

Numerical Methods.—The rate of removal of $[Co(CN)_5(N_3)]^{3-}$ is unaffected by the presence of the thiocyanate ion and may be expressed in all that follows by equation (11), where a

$$-da/dt = k_2'a \quad (11)$$

$$k_2' = k_2K_1/(1 + K_1[H_3O^+]) \quad (12)$$

represents the sum of the concentrations of $[Co(CN)_5(N_3)]^{3-}$ and $[Co(CN)_5(N_3H)]^{2-}$.

Assuming $[Co(CN)_5]^{2-}$ is in the steady state, the total rate of formation of $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ in the presence of added thiocyanate is given by equation (13)

$$db/dt = k_a a - k_b b \quad (13)$$

Table 3. The equilibrium constant[a] K_1 and rate constant[a] k_1

	$[H_3O^+]$	$10^4[\text{Complex}]_0$[c]			k_1/s^{1}	
Group[b]	mol dm^{-3}		$\varepsilon/\varepsilon_0$[d]	K_1[e]/ dm^3 mol^{-1}	obs.	calc.[f]
1	0.0100	1.23	0.895	11.9	0.148	0.150
1	0.0200	1.54	0.902	5.5	0.280	0.284
2	0.0200	2.05	0.896	5.9	0.291	0.284
1	0.0300	1.56	0.847	6.2	0.418	0.409
1	0.0400	1.23	0.818	5.7	0.540	0.525
2	0.0400	2.05	0.845	4.7	0.468	0.525
3	0.0503	2.17	0.878	2.8	0.637	0.636
1	0.0503	1.53	0.790	5.4	0.639	0.636
3	0.0737	1.56	0.775	7.3	0.874	0.858
4	0.0869	117	0.754	3.8	—	—
5	0.0869	140	0.772	3.48	—	—
5	0.0869	141	0.696	5.15	—	—
5	0.0869	140	0.704	4.96	—	—
5	0.0869	137	0.710	4.82	—	—
5	0.0869	1.47	0.674	5.45	—	—
6	0.0911	1.32	0.707	4.67	—	—
7	0.0911	1.27	0.725	4.27	1.04	1.00
6	0.0911	1.30	0.686	5.16	—	—
3	0.0997	2.88	0.712	4.16	1.09	1.07
3	0.154	3.60	0.608	4.31	1.42	1.41
8	0.203	3.59	0.530	4.52	1.66	1.65
2	0.203	2.07	0.539	4.35	1.70	1.65
8	0.252	4.32	0.460	4.84	1.83	1.83
8	0.303	5.05	0.400	5.17	2.01	1.99
2	0.303	2.05	0.401	5.15	2.06	1.99
8	0.452	5.76	0.322	4.92	2.36	2.32
9	0.651	9.25	0.253	4.86	2.52	2.58
8	0.651	7.19	0.256	4.78	2.61	2.58
2	0.651	2.05	0.254	4.83	2.67	2.58
7	0.980	1.28	0.191	4.74	—	—
9	1.00	9.25	0.191	4.65	2.78	2.83
8	1.00	8.38	0.199	4.40	2.78	2.83
8	1.00	7.19	0.200	4.37	2.84	2.83
2	1.00	2.04	0.184	4.89	2.99	2.83

[a] Temperature 40 °C, unit ionic strength. [b] Groups 1—3 and 7—9 contain $NaClO_4$ as the background electrolyte, groups 4—6 contain NaNCS. [c] Calculated from the standard dilution experiment, which contained no added acid, using the absorption coefficient quoted in Table 1 (8 800 dm^3 mol^{-1} cm^{-1}). [d] ε_0 values at 278 nm; 5 680 (1), 6 980 (2), 7 370 (4), 8 880 (5), 7 690 (6), 7 690 (7), 5 620 (8), and 5 200 dm^3 mol^{-1} cm^{-1} (9). The first number is the standard absorption coefficient in neutral solution for the group shown in parentheses. [e] The extrapolated value of $\varepsilon_\infty/\varepsilon_0$, 0.016 ± 0.003, is based on the observations for $[H_3O^+] > 0.6$ mol dm^{-3} combined with the best-fit slope. [f] Calculated from equation (6).

where the concentration of $[Co(CN)_5(OH_2)]^{2-}$ is b and k_a and k_b are defined by equations (14) and (15). The integrated forms

$$k_a = k_2'k_4[H_2O]/(k_4[H_2O] + k_5[NCS^-]) \quad (14)$$

$$k_b = k_3k_5[NCS^-]/(k_4[H_2O] + k_5[NCS^-]) \quad (15)$$

of these equations used in the thiocyanate-substitution studies are given in equations (16)—(18) in which a_0 is the initial

$$a = a_0 \exp(-k_2't) \quad (16)$$

$$b = k_a a_0[\exp(-k_b t) - \exp(-k_2't)]/(k_2' - k_b) \quad (17)$$

$$c = a_0 - (a + b) \quad (18)$$

concentration of $[Co(CN)_5(N_3)]^{3-}$ and c is the sum of the concentrations of the thiocyanate complexes formed.

The rate constant k_a is found by directly fitting the results of the integrated equations to the absorbance curves. The observed initial and final absorbance values are used to find the absorption coefficients for the reactants and products, except for the complexes $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(OH)]^{3-}$ whose values are taken from previous work[1] (Table 1). The rate constant k_2' is taken from measurements in the absence of thiocyanate ion for those experiments in which the absorbance is monitored at a single wavelength and k_b is taken from earlier work.[1]

The analysis used in the original study depended on the assumption that there was one isosbestic point at 380 nm for the thiocyanate products with $[Co(CN)_5(OH)]^{3-}$ and a second isosbestic point with $[Co(CN)_5(N_3)]^{3-}$ at 278 nm. A plot of $\ln(A - A_\infty)$ against time yields the rate constants k_{380} and k_{278}. The value of A_∞ at 380 nm could be measured directly but at 278 nm the conversion of the initially formed $[Co(CN)_5(OH_2)]^{2-}$ into $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ later in the reaction makes it necessary to calculate A_∞' for the hypothetical reaction to $[Co(CN)_5(OH_2)]^{2-}$. Thus k_{278} must be measured as a tangent at zero time to a curved plot of $\ln(A - A_\infty')$ against time. The ratio k_{380}/k_{278} may be shown to be $(k_4[H_2O] + k_5[NCS^-])/k_4[H_2O]$, using the mechanism given previously, so that the competition ratio $k_5/k_4[H_2O]$ may be found directly. We have used this method only in order to compare our results with the original data.[3]

Kinetic Measurements.— (*a*) *Aliquot analysis.* The original method[3] was repeated using the conditions specified for Figure

Table 4. Thiocyanate and water competition measurements at 40 °C at unit ionic strength

Run[a]	$10^4\,a$	$[NCS]^-$	$[H_3O^+]$	$10^4\,k_2'/s^{-1}$		$k_5/k_4[H_2O]$
		mol dm^{-3}		obs.	calc.[b]	dm^3 mol^{-1}
1	10.5	0.90	0.091	9.0	10.0	0.06
2	10.2	0.90	0.091	9.5	10.0	0.06
3	9.5	0.90	0.091	10.1	10.0	0.31
4	11.2	—	0.091	9.4	10.0	—
5	153	0.82	0.087	10.0	9.7	0.12
6	138	0.82	0.087	9.5	9.7	0.06
7[c]	1.43	0.83	0.092	—	10.1	0.12
8[c]	1.34	0.83	0.092	—	10.1	0.11
9[c]	1.33	—	0.092	10.4	10.1	—
10	1.28	0.91	0.091	—	10.0	0.11
11	1.29	0.91	0.091		10.0	0.14
12	139	0.82	0.087	—	9.7	0.14
13	137	0.82	0.087	—	9.7	0.18
14	124	0.82	0.087	—	9.7	0.23
15	139	0.82	0.087	9.8	9.7	—
16	10.1	0.91	0.092	10.1	10.1	0.24

[a] Runs 1—6 were performed in a 100-cm^3 conical flask (aliquot samples), 7—11 in a 10-mm optical cell, 12—15 in a 0.18-mm optical cell, and 16 in a stirred 250-cm^3 cylindrical reactor, continuously sampled *via* a 10-mm flow cell. [b] Calculated values from equation (10). [c] Ionic strength 0.92 mol dm^{-3}.

1 of that reference. Although the complex concentration was not given, unit ionic strength is only possible for the perchloric acid and sodium thiocyanate concentrations given (0.091 and 0.90 mol dm^{-3} respectively) if the reactant concentration is *ca.* 10^{-3} mol dm^{-3}. We repeated this experiment three times taking observations every minute but the increased number of points merely revealed a serious scatter of ±5% in our measurements at 278 nm occurring at the start of the reaction. When a blank experiment was performed in the absence of complex, the absorbance at 278 nm initially rose by 0.1 absorbance unit per hour. Although the absorbance at 380 nm also increased, the rate was only 0.0024 absorbance unit per hour. Furthermore, the values of the absorbance at 278 nm varied irregularly by *ca.* 0.02 absorbance unit about the overall trend. When the kinetic results were corrected for the drift in background absorbance from the blank experiment, the three sets of results (Table 4) varied from one extreme where they reproduced the original data[3] to the other where they were in complete disagreement. That is, the ratio of the rate constants k_{380}/k_{278} ranged from 1.06 to 1.31, compared to the original result of 1.31. Any attempt to improve the reproducibility by using the integrated equations throughout a run rather than by taking initial tangents to the rate plots was unsuccessful. The fitting of the integrated equations was extremely sensitive to the exact initial value of the absorbance at 278 nm and also to the precise rate of absorbance change in the first 20 min of reaction. We repeated the experiment twice more using *ca.* 0.015 mol dm^{-3} $[Co(CN)_5(N_3)]^{3-}$ in order to reduce the effect of the irregular changes in background absorbance. In this case the general reproducibility was excellent and the results closely resembled those for the original experiment. Despite this improvement, the accuracy of the data was still inadequate because of the sensitivity of the fitting procedure to the initial absorbance and its rate of change in the first 10 min (Table 4).

(*b*) *Continuous monitoring.* The experiments were repeated using spectroscopic cells of pathlength 10 and 0.18 mm as reaction vessels. The concentration of $[Co(CN)_5(N_3)]^{3-}$ was 1.4×10^{-4} and 0.014 mol dm^{-3} respectively. The continuous record was made at 278 nm only since the reproducibility at 380 nm was excellent and showed no significant difference between experiments with and without added thiocyanate (Table 4). Unfortunately, although the fit of the integrated equations and the observed results at 278 nm was excellent, the results still showed considerable variability between runs (Table 4).

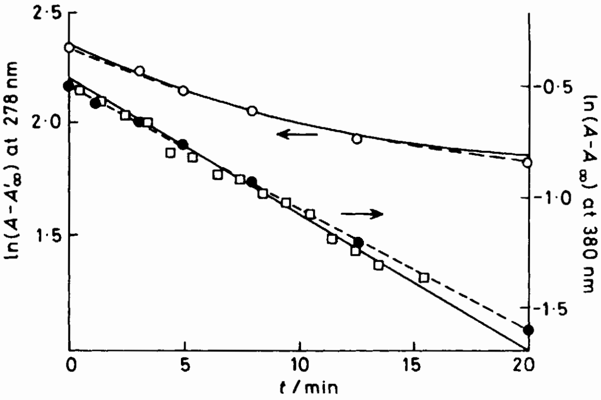

Figure 2. Comparison of spectroscopic results. The fitted lines for this work (solid) and for ref. 3 (broken) have been drawn using the constants in Table 5. At 380 nm: (□) this work, (●) ref. 3. At 278 nm: the theoretical line and recorder trace coincide, (○) ref. 3

The difficulty at low concentrations of reactant may be due to drifts in the background absorbance caused by acidified sodium thiocyanate. Initially the absorbance of the background electrolyte increased after heating to 40 °C and although these changes had always ceased before the complex was added, the disturbance needed to mix the reactants might produce a further background drift. The fitted constant k_a at 278 nm could apparently be measured with sufficient accuracy but the value found was only 10% less than the value measured in the absence of thiocyanate.

The problem of the background absorbance changes was eliminated by using a complex concentration of 0.014 mol dm^{-3}. The rate constant k_a in the presence of 0.82 mol dm^{-3} thiocyanate ion was up to 23% less than the corresponding value in the absence of thiocyanate. Unfortunately the surface-to-volume ratio in the short path cell was 110 cm^{-1} and a test experiment using the previous 'aliquot' method showed that both k_{278} and k_{380} could be surface inhibited. Both rate constants decreased by 25% when the surface-to-volume ratio was raised to 30 cm^{-1} by filling the reaction volume with 3-mm soda-glass beads {0.091 mol dm^{-3} $HClO_4$, 0.92 mol dm^{-3} NaNCS, and 0.015 mol dm^{-3} $[Co(CN)_5(N_3)]^{3-}$}. However, the integrated equations no longer fitted the absorbance–time plots and since the high-concentration results in the 0.18-mm cell are fitted very well by the equations it seems probable that heterogeneous inhibition is not important.

The continuously sampled stirred glass reactor was finally constructed so as to avoid the difficulties of all the previous methods. The record at 278 nm was uninterrupted from time zero and one absorbance measurement per minute was available at 380 nm. The crucial observations occur in the first 10 min (Figure 2). There is excellent broad agreement with the original data which have been superimposed for comparison by an arbitrary shift on the *y* axis.

Discussion

The mechanism of the acid-catalysed hydrolysis of $[Co(CN)_5(N_3)]^{3-}$ is fully confirmed by the present work although special precautions are needed to obtain adequate experimental data. The original measurements have been reproduced and the quality of the data improved. The equilibrium estimate of K_1 = 4.67 dm^3 mol^{-1} closely agrees with the present kinetic value, 4.47 dm^3 mol^{-1}, and the previously published[3] value of 4.5. The rate constant for reaction (2), 3.46×10^{-3} s^{-1}, also agrees with the previous determination, 3.2×10^{-3} s^{-1}.

The product of the thiocyanate acid-catalysed substitution of $[Co(CN)_5(N_3)]^{3-}$ and the thiocyanate anation of $[Co(CN)_5(OH_2)]^{2-}$ is mainly the sulphur-bonded isomer and the ratio of the isomers, *ca.* 4S- : 1N-bonded, does not appear to vary during the reactions. Thus, provided the absorption coefficients for the thiocyanate complex used to analyse the spectroscopic results are based on values drawn from each individual run, the total thiocyanate complex concentration can be calculated. The agreement of the observed and calculated coefficients shown in Table 1 for the mixed thiocyanate product is well within the uncertainties of the coefficients and isomer ratio which have been used in the calculation. The value at 380 nm is the most reliable absorption coefficient and it definitely suggests the presence of the more strongly absorbing nitrogen linkage isomer.

The spectroscopic evidence which has been interpreted as showing the initial formation of a nitrogen-bonded isomer during the anation of $[Co(CN)_5(OH_2)]^{2-}$ followed by a slow isomerisation to the sulphur-bonded form[13] is inconsistent with the h.p.l.c. and preparative results. However, slow spectroscopic changes do take place which seem to be associated with cyanide bridge formation.[10,14] The preliminary h.p.l.c. studies have so far revealed that the main product of $[Co(CN)_5(OH_2)]^{2-}$ anation is $[Co(CN)_5(SCN)]^{3-}$.

Table 5. Concentrations, rate constants, and absorption coefficients used in Figure 2

Complex	ε_{278}	ε_{380}	Source
$[Co(CN)_5(N_3)]^{3-}$	8 288 (7 300)[a]	716 (666)[a]	This expt.
$[Co(CN)_5(OH)]^{3-}$	250 (219)[a]	250 (226)[a]	*b*
$[Co(CN)_5(NCS)]^{3-}$[c]	9 316 (7 300)[a]	260 (226)[a]	This expt.

$k_a = 4.60 \times 10^{-4}$ s^{-1} (ref. 1) (3.74×10^{-4})[a]
$k_2' = 1.012 \times 10^{-3}$ s^{-1} (fitted)[d] (0.91×10^{-3})[a]
$k_5/k_4[H_2O] = 0.24$ dm^3 mol^{-1} (fitted) (0.34)[a]

$a_0 = 1.32 \times 10^{-3}$ mol dm^{-3}

[NaNCS] = 0.906 mol dm^{-3} (0.9)[a]
$[HClO_4]$ = 0.0916 mol dm^{-3} (0.91)[a]

[a] Data from ref. 3 used to calculate broken lines in Figure 2. [b] W. M. Gilfillan, Ph.D. Thesis, University of Belfast, 1973. [c] NCS/SCN isomer mixture. [d] The complete set used for fitting extends to 40 min.

In the light of these results the spectroscopic data for the acid-catalysed substitution can be analysed by the integrated equations (16)—(18). The immediate conclusion from the success of this treatment is that the dissociative step (2) is rate controlling and that the mechanism possesses at least one of the characteristics of a *D*-type substitution.[15]

The values of $k_5/k_4[H_2O]$ recorded in Table 4 vary from run to run more than would be expected judging by the sensitivity of the fitting procedure. However, these variations may be reasonable in view of the systematic errors to which the experiments are liable. The effects of background absorbance changes or heterogeneous inhibition tend to increase the ratio, while errors in the selection of absorption coefficients and also in the initial time and absorbance readings can either consistently increase or decrease the final result.

The original method of determining $k_5/k_4[H_2O]$ can produce a systematic bias. The difficulty can be seen from Figure 2 when it is remembered that the rate constant for the thiocyanate-ion substitution is proportional to the difference in slope of the 380-nm plot and the tangent to the origin of the 278-nm plot. The original measurements, replotted in Figure 2, were analysed assuming that over the first 5—6 min the 278-nm plot was linear so that k_{278} was systematically reduced. The apparent linearity seems to originate in a slight scatter in the early observations and this may reflect the same difficulties which we have experienced in obtaining reproducible early observations. This relatively trivial discrepancy is largely responsible for changing $k_5/k_4[H_2O]$ from 0.24 to 0.34 dm^3 mol^{-1} (Figure 2).

A further systematic bias may be introduced by using a standard set of absorption coefficients or, as in this case, by assuming certain wavelengths to be isosbestic. The latter assumption at 380 nm seems quite reliable since none of the absorbing species has markedly changing absorption coefficients at that wavelength but the same is not true at 278 nm. The full expression for the thiocyanate-substitution rate constant can be given exactly in terms of $(k_{380} - k_{278})$ and the absorption coefficients ε, ε_b, and ε_c for $[Co(CN)_5(N_3)]^{3-}$, $[Co(CN)_5(OH)]^{3-}$, and the mixed product, $[Co(CN)_5(SCN)]^{3-}$ and $[Co(CN)_5(NCS)]^{3-}$ [equation (19)]. Our measurements from

$$k_2'k_5[NCS^-]/(k_4[H_2O] + k_5[NCS^-]) = (k_{380} - k_{278})(\varepsilon - \varepsilon_b)/(\varepsilon_c - \varepsilon_b) \quad (19)$$

Table 1 suggest that assuming ε and ε_c to be equal overestimates $k_5/k_4[H_2O]$ by 15% but, since the value of ε_c is measured on the edge of an absorption band rapidly rising towards the ultraviolet, the possibility of error is very high. In any case, although the complexes of the $[Co(CN)_5X]^{3-}$ family are easy to prepare, it is difficult to obtain reproducible absorption coefficients (Table 2), even where isomer mixtures are not present.

Experiment (16) was designed to avoid all the identified sources of positive systematic bias but despite this the result fell at the upper limit defined by the other data in Table 4. We conclude that the method is too sensitive to minor disturbances of the absorbance–time readings at 278 nm and that the best estimate of $k_5/k_4[H_2O]$ available is the mean 0.14 ± 0.02 dm^3 mol^{-1}. The statistical error of the mean is based on the standard deviation of 0.08 for 13 independent observations. The apparently dramatic contrast between the present and previous work[3] is a consequence of relatively minor differences in experimental results and data treatment.

The difficulties of the spectroscopic method are such that we are at present extending the h.p.l.c. results since these alone seem to offer sufficient analytical accuracy for the determination of $k_5/k_4[H_2O]$. The present work, however, qualitatively supports the original investigation and permits some comparison with other systems. It is noteworthy that the mean, 0.14 $dm^3\ mol^{-1}$, is comparable with estimates derived from two previous examinations of the thiocyanate anation of $[Co(CN)_5(OH_2)]^{2-}$, 0.34[16] and 0.27.[1] In view of the discrepancy between the two latter values and the difficulties of ion-activity variation at constant ionic strength,[17] the competition results for $[Co(CN)_5]^{2-}$ derived from both $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(N_3H)]^{2-}$ cannot be said to be inconsistent. Other work[4] using $[Co(CN)_5Cl]^{3-}$ indicates, in contrast, that when the departing ligand is anionic the ratio is much smaller. The ratio of the nitrogen- to sulphur-bonded linkage isomers has not yet been determined by h.p.l.c. in this case but the spectroscopic data suggest that the major substitution product is again $[Co(CN)_5(SCN)]^{3-}$.

In short, though the evidence is not extensive,[4] it seems that in the substitutions of $[Co(CN)_5X]^{n-}$ (n = 2 or 3) the influence of the departing and entering ligands is sufficiently strong to imply that the substitutions have some interchange character.[15] The fact that the ratio of sulphur- to nitrogen-bonded thiocyanate can now be measured in these systems makes it possible that the nature of the intermediate may be detected by the method[18] successfully used in the substitution of $[Co(NH_3)_5X]^{2+}$.

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