The Application of High Performance Liquid Chromatography to Analytical Problems in the Synthesis, Substitution and Linkage Isomerism of Cyanocobaltate(III) Complexes

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Abstract

Ion pair reversed phase chromatography has been applied to the analysis of mixtures of $[Co(CN)_5(X)]^{n-}$, $n = 2$, 3 or 4, at ionic strengths from zero to unity using sodium sulphate or perchlorate as background electrolytes. The general principles for optimising these separations using a tertiary ammonium ion-pairing agent have been established and the limitations of the method have been identified. Anomalous competition results in experiments with $[Co(CN)_5Cl]^{3-}$ have been explained by the presence of traces of $[Co(CN)_5(OH_2)]^{2-}$ formed in this and related cyanocomplexes during conventional synthesis. The nucleophile efficiency of the hydroxide ion has been shown to be no greater than is normal for a univalent anion in $[Co(CN)_5X]^{3-}$ substitutions. Trace ion analysis has been used to measure the formation constants for $[Co(CN)_5(S(O)(CH_3)_2]^{2-}$ with dimethyl sulphoxide concentrations from 0.1–6.0 mol dm^{-3}. Separation of the linkage isomers of SCN^- and $S_2O_3{}^{2-}$ has been used as an indication of mechanism.

Introduction

The analysis of charged metal complexes by ion pair high performance chromatography (IPHPLC) was first demonstrated [1] and applied [2] ten years ago by Valenty. Subsequently Buckingham [3] developed the analysis of cationic cobalt(III) nitrogen ligand complexes and in the same paper described successful mechanistic studies using the method. We have presented a series of studies [4–6] of the thermal substitution of $[Co(CN)_5(X)]^{n-}$, $n = 2$ and 3 in which IPHPLC was used to check spectroscopic analyses. In that and subsequent work [7] we have found that many of the anomalies presented by the conventional spectroscopic analysis of the reaction mixtures could be answered by IPHPLC analyses. We also used IPHPLC [8] exclusively in a kinetic study [9] of the substitution of $[Co(ethylenediamine)_2(S_2O_3)(OH_2)]^+$. Despite this success and although analytical methods for specific cases still occasionally appear, actual applications to real synthetic or mechanistic studies are rare. A recent account [10] of analytical separations of the $[Co(CN)_5X]^{n-}$ family has highlighted the improvements possible in the technique although it did not describe a general approach to maximising the speed and resolution of an analysis. The reason for the apparent neglect of IPHPLC seems to be that although the method is effective and simple, its application to routine analysis under real laboratory conditions is not straightforward.

In this paper we describe a general approach to charged complex IPHPLC analysis and present solutions to the common difficulties encountered in practice. The greatest of these lies in the need to analyse accurately small traces of the products in the presence of an excess of unconsumed reactants and also in the presence of an often very large excess of other inert background electrolytes.

Experimental

The complexes $K_3[Co(CN)_5N_3]$ [11], $K_2[Co(CN)_5(H_2O)]$ [12], $K_3[Co(CN)_5Cl]$ [13, 14], $K_4[Co(CN)_5(SO_3)]$ [15], $K_4[Co(CN)_5(S_2O_3)]$ [16], $K_2[Co(CN)_5((CH_3)_2SO)]$ [6], $K_3[Co(CN)_5(SCN)]$ [17], $(N(C_4H_9)_4)[Co(CN)_5(NCS)]$ [17] and *cis*-$Na_4[Co(CN)_4(SO_3)_2)]$ [18] were prepared by the reported methods. The remaining compounds were GP grade reactants and were used as received.

IPHPLC analyses were performed with a Pye Unicam LC3 chromatograph combined with either a Hewlett-Packard 3380 or a Pye-Unicam CDP1 integrator using 5% ODS 5 micron Partisil in either 11 cm Whatman cartridge columns or in 25 cm home-made packed columns. The ion-pairing reagents were all tertiary ammonium halide salts in solutions

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adjusted to pH 6 and filtered by 1.2 micron Millipore filters. Samples of 20 μl were injected by Rheodyne valve.

The substitution experiments were performed in a stirred thermostatted reaction vessel at 40 °C ($[Co(CN)_5X]^{2- \text{ or } 3-}$) or 25 °C ($[Co(CN)_4(SO_3)(OH_2)]^{3-}$). The photolytic experiments were conducted at *c.* 20 °C using a pyrex filtered 125 W Philips mercury lamp.

Results and Discussion

The Optimisation of IPHPLC Analyses

The limited application of IPHPLC may in part be due to a number of minor but not inconsiderable disadvantages. The column lifetime is limited and variable. Although it rarely falls below 100 analyses each of about 10 min duration, it never seems to exceed 500–1000. The greatest lifetime is attained when the same column is used continuously for one type of analysis but the inevitable loss of packing by dissolution in the eluent eventually destroys the column.

The problem of peak splitting reported previously for both cation [3] and anion [10] analyses cannot be completely removed so that any additional peak appearing in a chromatogram should always be initially regarded as an artefact. The splitting of peaks is always linked to the presence of a large sample size, i.e. *c.* 20 μmol, of at least one electrolyte in the sample. In terms of the commonly used standard sample volume of 20 μl, this restricts concentrations to below 1 M. In practice we avoid concentrations above 0.1 M or samples containing more than 2 μmol of any component. Sometimes the concentration of the complex ion giving the peak is itself too large but an inert background electrolyte will also produce exactly the same effect, Fig. 1. The problem may be eliminated by appropriate dilution or by the use of a smaller sample volume but these precautions also reduce the available sensitivity. A considerable improvement is possible by raising the concentration of the ion-pairing agent. The usual concentration is between 1 and 10 mM but we have used concentrations of 100 mM without any undesirable side effects. In fact, the capacity ratio, k', and the relative capacity ratio, α, for adjacent compounds A and B (defined below) both often increase.

$$k' = (V_r - V_m)/V_m \qquad (1)$$

where V_r is the retention volume of any compound, $V_m = V_r$ when the compound is unretained and

$$\alpha = k'_A/k'_B \qquad (2)$$

The larger concentrations are in any case often necessary when added electrolytes are used to create well-distributed chromatograms as described later. A Radial-Pak column (Waters Assoc.) has also been shown [3] to increase the acceptable sample size approximately ten-fold.

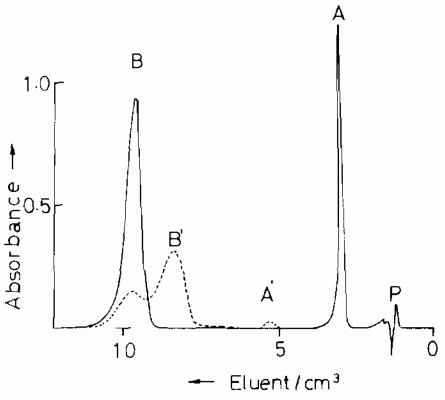

Fig. 1. Chromatogram of a mixture of $[Co(CN)_5(OH_2)]^{2-}$, peak A, and $[Co(CN)_5(dmso)^{2-}$, peak B, containing (——) 0.05 mol dm^3 or (- - - -) 0.1 mol dm^{-3} $NaClO_4$. 11 cm × 0.46 cm 5 μm C18 ODS column, 181 mM $[N(C_2H_5)_4]Cl$ in 100% H_2O, flow rate 1 cm^3 s^{-1}. Peaks A' and B' are artefacts.

We have found that the best separations attainable by IPHPLC are produced by the balancing of the often competing effects of the concentrations of added electrolyte and of methanol in the methanol–water eluent and the size of the substituent R in the ion-pairing agent $[NR_4]^+$. Increase of column temperature shortens the elution time and changes α but we have not examined this method of optimisation since the effect of temperature in HPLC strongly resembles the effects produced by changing the polarity of the eluent [19].

The model described by Knox [20] supplies the best guide to optimising complex ion separations. The complex ion bound to the ion-pairing agent becomes sufficiently hydrocarbon soluble to be retained for the minimum time required to separate it from other species in the sample. The hydrophobic chemically bound C18 chains are interpenetrated [21] by the hydrocarbon chains attached to the tertiary ammonium centre. Peak asymmetry, produced by residual silanol ion exchange sites [22], is removed either by saturation with the ion-pairing agent or by an additional electrolyte included in the eluent [10].

Excellent independent evidence now exists [23] that the counter-ion concentrations commonly used in IPHPLC will produce neutral ion clusters even in the case of highly charged complexes such as $[Co(CN)_6]^{3-}$. Also it has long been recognised [24] that the ion-pairing agent forms a surface film on the hydrocarbon layer of the column packing. Recently [22] experimental evidence has appeared showing that the unreacted silanols of the silica support are responsible for a larger proportion of the retention as the retained species become more polar. Peaks due to ion clusters are therefore uniquely vulnerable to this form of broadening.

The application of the model to the separation of $[Co(CN)_5X]^{n-}$ is exemplified by the analysis of samples from an experiment at unit ionic strength ($NaClO_4$) on the hydrolysis of $[Co(CN)_5Cl]^{3-}$ in the presence of N_3^-. In this case ten-fold sample dilution is sufficient to remove peak splitting by the background electrolyte. The reactant concentration is at least 25 mM to ensure accuracy in product measurement.

The selection of a suitable ion-pairing agent is determined by the need to minimise analysis time and maximise peak resolution. The plate height in HPLC for the flow rates used here varies only slightly in direct proportion to the flow rate [20]. Under these conditions it has been shown [25] that the fastest analysis occurs when the capacity ratio k' is 2, i.e. when the retention volume is three times the dead space volume. A survey of the capacity factors for the longest retained complex, $[Co(CN)_5N_3]^{3-}$ and the relative capacity factors α, (k'_{N3}/k'_{Cl}) for a range of ion-pairing agents, Table 1, shows that although k'_{N3} approaches the ideal value for $R_4 = (C_3H_7)_4$ and $(CH_3)(n\text{-}C_4H_9)_3$, the number of theoretical plates N_{req} required for the separation [25]

$$N_{req} = 36(\alpha(1 + k'_{N3})/k'_{N3}(\alpha - 1))^2$$

is unattainable. The data in Table 1 have been obtained for a minimum ion pair concentration yielding optimum resolution and plate number for the column. In individual applications a survey of both factors might be useful for typical ion-pairing agents. It is well known [26] that individual capacity factors rise to a limit at about 10–20 mM ion pair concentration but it is also true that relative capacity factors and plate numbers increase in the same way. In addition although an increase in the non-aqueous solvent component increases retention, plate number and relative capacity factors both fall, sometimes quite sharply, Table 2. In view of this, it is always worth examining some of the less retained ion-pairing systems when the original survey is made in a methanol-rich eluent. In the present case, Table 3, for $R = C_2H_5$, the separation dramatically improves as the water content of the eluent increases. However although an almost ideal chromatogram can be obtained between 12 and 18% $MeOH/H_2O$, inspection of Table 3 shows that a faster analysis is quite possible using a shorter column and taking advantage of the larger α values for short chain ion-pairing agents in water-rich eluents. This subject has been previously investigated [26] in the context of singly charged organic ions but the range of chain length was insufficient to detect the great variations in α which are possible for short chain lengths in water-rich eluents. We simultaneously improved performance by using the bromide counter ion rather than the chloride. Although the selectivity α deteriorates, it is now so large that this may be sacrificed for the improved analysis time, Table 4. The final tailoring of the analysis to maximise selectivity α and reduce analysis time can be achieved by the use of added inert electrolytes. The effects of added inert, i.e. non-lipophilic, electrolyte have been used to improve column efficiency [10] by reducing peak broadening but their great utility in tailoring the separation has

TABLE 1. The variation[a] of k', α and N_{req} with the chain length of the ion-pairing agent $[NR_4]^+X^-$

R_4 [b]	X^-	k'_{N3}	α	N_{req}
$(CH_3)_4$	Br^-	0.96	1	∞
$H(C_2H_5)_3$	Cl^-	1.00	1	∞
$(C_2H_5)_4$	Cl^-	1.07	1	∞
$(C_3H_7)_4$	Br^-	3.28	1.08	10300
$(C_2H_5)_3(CH_2C_6H_5)$	Cl^-	2.67	1.05	27200
$(CH_3)(n\text{-}C_4H_9)_3$	Br^-	9.78	1.16	2310
$(n\text{-}C_4H_9)_4$	Cl^-	20.87	1.23	1150
$(n\text{-}C_6H_{13})_4$	Cl^-	>66		

[a] 25 cm × 0.46 cm 5 μm C18 ODS column yielding 2000–3000 plates, $V_m = 1.5$ cm^3. [b] 15 mM $[NR_4]^+X^-$ in 45% methanol–water solvent, flow rate 1.00 cm^3 s^{-1}.

TABLE 2. The variation[a] of k', α, N_{req} and N_{obs} with the methanol content of the eluent[b]

Methanol (%)	k'_{N3}	α	N_{req}	N_{obs}
50	5.81	1.11	5040	2700
45	9.78	1.16	2310	2450
40	16.8	1.16	2310	2220

[a] 25 cm × 0.46 cm 5 μm C18 ODS column, $V_m = 1.5$ cm^3.
[b] 11 mM $[N(C_4H_9)_3(CH_3)]^+Br^-$, flow rate 1.00 cm^3 s^{-1}.

TABLE 3. The variation[a] of k', α and N_{req} with the methanol content of the eluent[b]

Methanol (%)	k'_{N3}	α	N_{req}
0	38	1.48	360
4	12	1.27	930
6	8.4	1.24	1200
12	3.8	1.15	3400
18	2.3	1.09	11000
30	1.5	c. 1.2	c. 4000
45	1.07	1.0	∞

[a] 25 cm × 0.46 cm 5 μm C18 ODS column yielding 2000–3000 plates, $V_m = 1.5$ cm^3. [b] 15 mM $[N(C_2H_5)_4]^+Cl^-$, flow rate 1.00 cm^3 s^{-1}.

TABLE 4. The variation[a] of k' and α with the counter ion[b] Y^- of the ion-pairing agent $[NR_4]^+Y^-$

Analyte complex X	Counter ions Y^-					
	F^-		Cl^-		Br^-	
	k'_X	α	k'_X	α	k'_X	α
$[Co(CN)_5(OH_2)]^{2-}$	4.21	0.34	3.71	0.46	3.07	0.41
$[Co(CN)_5Cl]^{3-}$	12.4	1.00	8.14	1.00	7.43	1.00
$[Co(CN)_5(SO_3)]^{4-}$	17.7	1.43	9.43	1.16	8.14	1.10
$[Co(CN)_5N_3]^{3-}$	20.0	1.61	15.9	1.95	11.9	1.60
$[Co(CN)_5((CH_3)_2SO)]^{2-}$	15.0	1.21	14.4	1.77	11.9	1.60
cis-$[Co(CN)_4(SO_3)_2]^{5-}$	15.8	1.27	–	–	7.50	1.01

[a] 11 cm × 0.46 cm 5 μm C18 ODS column yielding 3000–4000 plates, $V_m = 0.7$ cm³. [b] 109 mM $[N(C_2H_5)_4]^+Y^-$ in 100% water eluent, flow rate 1.00 cm³ s⁻¹.

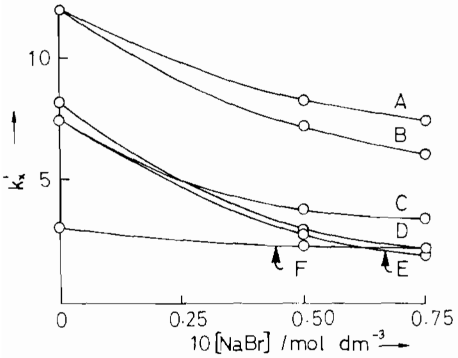

Fig. 2. Variation of capacity factor k' with added NaBr using 100% water containing 100 mM $[N(C_2H_5)_4]Br$ as eluent. Complexes: A, $[Co(CN)_5(dmso)]^{2-}$; B, $[Co(CN)_5N_3]^{3-}$; C, $[Co(CN)_5Cl]^{3-}$; D, $[Co(CN)_5(SO_3)]^{4-}$; E, *cis*-$[Co(CN)_4(SO_3)_2]^{5-}$; F, $[Co(CN)_5(OH_2)]^{2-}$.

not been sufficiently emphasised. Broadly speaking the greater the formal charge on the complex the more the retention is reduced by added inert electrolyte, Fig. 2. This means that retention of $[Co(CN)_5N_3]^{3-}$ may be reduced by a factor of two while preserving the selectivity α.

The conclusion drawn from this survey of the means of optimising HPLC analysis is that the smallest useable group R should be employed preferably in a pure water solvent. The separation should be adjusted using an inert electrolyte and peak splitting should be reduced by increasing the concentration of the ion-pairing agent and finally avoided by sufficient sample dilution. The analysis of mixtures of complex ions now becomes not only possible but relatively fast. The analysis shown in Fig. 3 is only possible because of the fine tuning of the peak positions with added sodium bromide.

HPLC Applications

Synthesis control

The standard synthetic methods for $[Co(CN)_5X]^{3-}$ were re-examined using IPHPLC in view of our failure to detect impurities in $[Co(CN)_5Cl]^{3-}$ by conventional analysis. The standard preparation [13] by the $[Co(CN)_5]^{2-}$ catalysed CN^- substitution of the pentammine $[Co(NH_3)_5X]^{2+}$ is supposed [27] to depend on the speed of reaction (3)

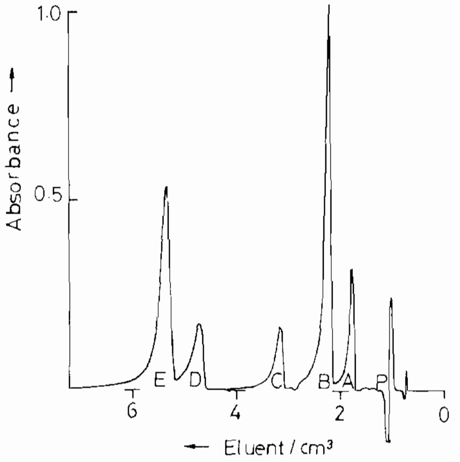

Fig. 3. Analysis of a multicomponent mixture, using 11 cm × 0.46 cm 5 μm C18 ODS column with an eluent of 95 mM $[N(C_2H_5)_4]Br$ containing 50 mM NaBr in 100% water, flow rate 1 cm³ s⁻¹. Peaks: A, $[Co(CN)_5(OH_2)]$; B, $[Co(CN)_5(SO_3)]^{4-}$; C, $[Co(CN)_5Cl]^{3-}$; D, $[Co(CN)_5N_3]^{3-}$; E, $[Co(CN)_5(dmso)]^{2-}$; P, injection pulse.

$$[Co(CN)_5]^{3-} + [Co(NH_3)_5X]^{2+} \longrightarrow [Co(CN)_5X]^{3-} + Co^{2+} + 5NH_3 \qquad (3)$$

in comparison with reactions (4) and (5)

$$[Co(CN)_5]^{3-} + CN^- \rightleftharpoons [Co(CN)_6]^{3-} \qquad (4)$$

$$[Co(CN)_6]^{3-} + [Co(NH_3)_5X]^{2+} \longrightarrow [Co(CN)_6]^{3-} + Co^{2+} + 5NH_3 + X^- \qquad (5)$$

However under preparative conditions the high cyanide concentration so increases the solution pH that the base catalysed hydrolysis of $[Co(NH_3)_5X]^{2+}$ [28] can also compete with reaction (3) for the more labile ligands X. Thus we are unable to detect $[Co(CN)_5(OH_2)]^{2-}$ (i.e. less than 0.1%) in $[Co(CN)_5(N_3)]^{3-}$, $[Co(CN)_5(NCS)]^{3-}$, $[Co(CN)_5(S_2O_3)]^{3-}$ or $[Co(CN)_5(SO_3)]^{3-}$ but find between 5 and 10% in $[Co(CN)_5Cl]^{3-}$ and $[Co(CN)_5Br]^{3-}$. The base catalysed substitution of $X = Cl^-$, Br^- in $[Co(NH_3)_5X]^{2+}$ is approximately a thousand times faster than the substitution of $X = N_3$, NCS^-, $S_2O_3^{2-}$ and SO_3^{2-} [28]. The synthetic procedure proposed by Palmans and D'Olieslager [14] uses a very low cyanide concentration and minimises contamination both by $[Co(CN)_6]^{3-}$ and by $[Co(CN)_5(OH_2)]^{2-}$ but at the cost of reduced product yields and contamination by $[Co(NH_3)_5X]^{2+}$.

It seems that the synthesis of $[Co(CN)_5(OH_2)]^{2-}$ followed by substitution of the aqua-ligand would be the simplest procedure, but in practice the separation of the product from traces of $[Co(CN)_5(OH_2)]^{2-}$ makes achieving the necessary purity very difficult. This may be connected with the fact that $[Co(CN)_5(OH_2)]^{2-}$ solutions at high concentrations are known to contain polymeric complexes [29] which in fact can also be detected by IHPLC at the concentrations used in the synthesis. The separation of these larger and less soluble by-products from $[Co(CN)_5X]^{3-}$ contributes to the problems found in purification.

The detection of reaction intermediates by product analysis

The identification of intermediates in complex substitution has always been difficult. One apparently satisfactory method depends on measuring the ratio of the concentrations of products formed by the competition of two or more nucleophiles for the same intermediate generated using different leaving groups [4–6]. Unfortunately spectroscopic measurements using Cl^- as the leaving group showed that N_3^- was anomalously efficient in scavenging the hypothetical intermediate $[Co(CN)_5]^{2-}$ via reaction (8), where $X = N_3$.

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

$$[Co(CN)_5]^{2-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} \qquad (7)$$

$$[Co(CN)_5]^{2-} + X^- \longrightarrow [Co(CN)_5X]^{3-} \qquad (8)$$

However, a re-analysis of samples of $[Co(CN)_5Cl]^{3-}$ prepared by the standard literature method [13] by IPHPLC shows that up to 10% $[Co(CN)_5(OH_2)]^{2-}$ can be present. The impurity is not detected by microchemical analysis apparently because of the presence of an approximately molar equivalent of KCl. Direct substitution of $[Co(CN)_5(OH_2)]^{2-}$ by N_3^- is known to take place [12] sufficiently rapidly via reaction (9) to allow $[Co(CN)_5N_3]^{3-}$ to form at the start of the reaction.

$$[Co(CN)_5(OH_2)]^{2-} + X^- \longrightarrow [Co(CN)_5X]^{3-} \qquad (9)$$

In this way the initial competition ratio can become anomalously large. The fact that the ratio was overestimated was suspected earlier [5] for $X = N_3$ because it decreased at high pH when the unreactive $[Co(CN)_5(OH)]^{3-}$ replaces the reactive $[Co(CN)_5(OH_2)]^{2-}$. Further experiments using IPHPLC have now confirmed that at 40 °C there is no evidence for direct attack via reaction (8) for either NCS^- or N_3^-. Due to the high concentration of solvent water in these experiments the upper limit of k_8/k_7 could still be unity but experiments performed in 0.1 M hydroxide suggest that the ratio is probably of the order of 0.1.

Unfortunately there is an alternative explanation for the effect of OH^- based on an earlier suggestion [30] that OH^- is 1.7×10^5 more efficient than water in capturing the intermediate. The decrease in competition ratio may therefore be attributed to competition between reaction (8) and reaction (10)

$$[Co(CN)_5]^{2-} + OH^- \longrightarrow [Co(CN)_5(OH^-)]^{3-} \qquad (10)$$

Although this cannot be conclusively dismissed by conventional kinetics [12], it can be tested using IPHPLC. Uncharged reactants are best used for these experiments since the observed competition ratios are larger and easier to measure. The original experiments [6] for dimethyl sulphoxide, dmso, have now been supplemented for this purpose by an IPHPLC study. The results shown in Table 5 have revealed that here too the original data were systematically biased towards a high competition value. The results are shown in Table 5 in which the $[Co(CN)_5Cl]^{3-}$

TABLE 5. The observed competition ratios[a] for $[Co(CN)_5]^{2-}$ calculated from reaction product analyses

$[OH^-]$ (mol dm^{-3})	$10^4 \times k_6$ (s^{-1})	Product[b] ratio	k_8/k_7
c. 0[c]	4.8	0.18	3.8
3.2×10^{-5} [d]	4.8	0.22	4.7
3.2×10^{-3} [e]	5.1	0.12	2.6
c. 0[c]	5.1	0.040	0.86
0.035	4.6	0.042	0.90
0.10	4.7	0.039	0.83
0.88	5.4	0.044	0.94

[a] At 40 °C and unit ionic strength, $(NaClO_4)$, [dmso] = 2.2 mol dm^{-3}, $[H_2O]$ = 47 mol dm^{-3}, *c.* 6% $[Co(CN)_5(OH_2)]^{2-}$ present initially in reactant. [b] Extrapolated initial concentration ratio of $[Co(CN)_5(dmso)]^{2-}$ to $[Co(CN)_5(OH_2)]^{2-}$ corrected for the concentration of $[Co(CN)_5(OH_2)]^{2-}$ observed prior to reaction. [c] Unbuffered solutions, pH *c.* 6. [d] 0.01 mol dm^{-3} borax buffer, pH = 8.85. [e] 0.01 mol dm^{-3} hydrogen phosphate–phosphate buffer, pH = 10.85.

reactant was found to be contaminated by 6.5% $[Co(CN)_5(OH_2)]^{2-}$. The initial competition ratio falls to a limit which is subsequently unaffected by a hundred-fold increase in OH^- concentration. The test unambiguously shows that hydroxide is not a hyper-effective nucleophile and that the anomalous efficiency of N_3^- reported earlier was due to aqua-ion contamination of the reactant.

Trace analysis in equilibrium measurements

In the course of mechanistic work [6] aimed at detecting the competition of water and dmso in the substitution of $[Co(CN)_5(OH_2)]^{2-}$, the rate constant for reaction (11)

$$[Co(CN)_5]^{2-} + \text{dmso} \longrightarrow [Co(CN)_5(\text{dmso})]^{2-} \qquad (11)$$

had to be corrected for the activity variation of dmso at high concentrations. The accuracy of the corrections can in principle be confirmed by the changes in the equilibrium constant for reaction (12)

$$[Co(CN)_5(OH_2)]^{2-} + \text{dmso} \rightleftharpoons [Co(CN)_5(\text{dmso})]^{2-} + H_2O \qquad (12)$$

as the concentration of dmso is increased. Although the trace amounts of $[Co(CN)_5(OH_2)]^{2-}$ remaining in an excess of dmso were too small to be measured spectroscopically., analysis by IPHPLC was possible even in the presence of more than a hundred-fold excess of $[Co(CN)_5(\text{dmso})]^{2-}$. The experimental results shown in Table 6, column 4, are corrected in column 5 for activity variations caused by dimethyl sulphoxide. Although the correction is only approximate, the values are now internally consistent and their mean, 405 ± 13, is not significantly different from the independent spectroscopic value 481 ± 23. The agreement supports the theoretical treatment and emphasises the value of IPHPLC for quantitative trace analysis.

TABLE 6. Values of K_{12} at 40 °C measured by IPHPLC[a] and their correction for reactant non-ideality

[dmso] (mol dm^{-3})	$[H_2O]$ [b] (mol dm^{-3})	$[Co(CN)_5(OH_2)]^{2-}$ [c] (as % total complex)	K_{12}	K_{12} [d]
0.1	54.6	58.5	387	382
0.2	54.1	37.7	447	434
0.5	52.8	18.4	468	434
0.8	51.6	11.9	478	423
1.0	50.8	8.76	529	454
1.5	48.7	5.40	569	450
2.0	46.6	3.98	562	408
3.0	42.7	2.49	558	336
4.0	39.1	1.38	701	347
6.0	31.6	0.426	1232	386

[a] Samples diluted by ×1/20 and analysed on 5 μm C18 ODS column monitored at 250 nm. Eluted by 121 mM $[N(C_2H_5)_4]^+Cl^-$ in 0.05 mol dm^{-3} NaCl in 100% water, flow rate 1.00 cm^3 s^{-1}. [b] Calculated from density measurements. [c] After 15 h equilibration at 40 °C using 0.01 mol dm^{-3} $[Co(CN)_5(OH_2)]^{2-}$ in unit ionic strength maintained by $NaClO_4$. [d] Corrected for water and dmso deviations from ideality [6].

Linkage isomerism

The use of linkage isomerism as a probe for mechanism has already been described [4, 5] for the thiocyanate ion in the substitutions of $[Co(CN)_5(OH_2)]^{2-}$, $[Co(CN)_5(N_3H)]^{3-}$ and $[Co(CN)_5Cl]^{3-}$. In these experiments the ratio of the S- to N-linkage isomers depended on the charge of the leaving group giving rise to the hypothetical intermediate $[Co(CN)_5]^{2-}$. When the leaving group was uncharged, i.e. OH_2 or N_3H, the ratio was 4. In the case of the chloride ion, the only reaction product which could be detected originated from the secondary reaction of $[Co(CN)_5(OH_2)]^{2-}$ formed initially by water. This may explain why the linkage isomer ratio measured for $[Co(CN)_5Cl]^{3-}$ was the same as that for aqua ion substitution although there is now evidence suggesting that the competition ratio is independent of leaving group charge [31]. A parallel investigation of the products of the synthesis of $[Co(CN)_5(SCN)]^{3-}$ using the electron transfer reactions of $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ with $[Co(CN)_5]^{2-}$ showed that no $[Co(CN)_5(NCS)]^{3-}$ could be detected, i.e. less than *c.* 1%. In view of the slow rate of adjacent relative to remote attack already established [32] for electron transfer via the SCN bridge, it is remarkable that $[Co(NH_3)_5(SCN)]^{2+}$ formed no detectable amounts of the nitrogen-bonded isomer.

Sulphur oxygen linkage isomerism has only been detected for $S_2O_3^{2-}$. Dmso and SO_3^{2-} both apparently form the sulphur isomer exclusively [6, 7]. In the case of $S_2O_3^-$, a mixture of isomers is formed both from $[Co(NH_3)_5(S_2O_3)]^+$ by $[Co(CN)_5]^{2-}$ electron transfer and also by $S_2O_3^-$ substitution of $[Co(CN)_5(OH_2)]^{2-}$. The concentration ratio of the isomers is constant during the latter reaction so that their presence would not be detected by spectroscopic analysis. This parallels the failure to detect the N-bonded isomer $[Co(CN)_5(NCS)]^{3-}$ in the corresponding NCS^- anation [4]. The rate of photolytic linkage isomerisation is competitive with photohydrolysis for $[Co(CN)_5(S_2O_3)]^{4-}$ but not for $[Co(CN)_5(SO_3)]^{4-}$. The latter photohydrolyses much more rapidly without forming the O-bonded isomer. Thus one isomer, presumably the O-bonded form, initially increases during the photolysis of $[Co(CN)_5(S_2O_3)]^{4-}$ although during the photolysis of $[Co(CN)_5(SO_3)]^{4-}$ only $[Co(CN)_5(OH_2)]^{2-}$ is formed in stoichiometric amounts.

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