

Studies on Cobaltamines

X. Some Reactions of the (+)-Trisethylenediaminecobalt(III) Ion with the Hexacyanoferrate(II) Ion

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From polarimetric measurements of the association between the (+)-Coen₃³⁺ and the Fe(CN)₆⁴⁻ ions in solutions of a total concentration of sodium ions = 2 M, stability constants for the two first "outer-sphere" complexes have been determined: $\beta_1 = 2.5 \pm 0.5 \text{ M}^{-1}$ and $\beta_2 = 42 \pm 10 \text{ M}^{-2}$.

The light absorption spectra and the circular dichroism spectra have consequently been determined for the species [(+)-Coen₃(Fe(CN)₆)_n]^{[3-4n]+} for $n = 0, 1, \text{ and } 2$ (Figs. 5 and 6).

An attempt has also been made to determine the stability constants at a low, but constant ionic strength ($I = 0.2 \text{ M}$). The results obtained are compared with those for solutions of $C_{\text{Na}^+} = 2 \text{ M}$.

It has been found that the system is considerably sensitive to light. The reaction product has not been isolated, but it is suggested that it contains Co(III)NCFe(II) bonds. Also, in complete darkness a similar substitution reaction takes place. The kinetics of the dark-reaction seems to indicate that the rate-determining step involves a reaction of the first outer-sphere complex.

From previous studies on the bonding of ligands in the outer coordination sphere of such ions as Co(NH₃)₆³⁺ and Coen₃³⁺ the tentative rule has been suggested¹ that these central groups behave as weak b-acceptors in the sense of Ahrlund and Chatt.² *E.g.*, the stabilities of anionic complexes increase¹ in the order $\text{Cl}^- < \text{Br}^-$ and $\text{SO}_4^{2-} < \text{S}_2\text{O}_3^{2-}$.^{1,3} For the "soft"⁴ anion $\text{S}_2\text{O}_3^{2-}$ some evidence⁵ points to a possible coordination of four ligands around the central group Coen₃³⁺.

As this arrangement should result in a formal charge of -5 of the outer-sphere complex, it was considered important to investigate the complexity of the system Coen₃³⁺-Fe(CN)₆⁴⁻. The first outer-sphere complex would in this case have a formal charge of -1, and the second outer-sphere complex would have the charge -5. That the first complex must exist is obvious from Bjerrum's theory of ion-pairs,⁶ but it is not equally certain that a second outer-sphere complex, an iontriplet, should exist in aqueous solution.

THE POLARIMETRIC INVESTIGATION

As previous investigations ^{3,5} have shown that outer-sphere coordination markedly affects the molar rotation of dissymmetric cobaltammines, a polarimetric technique has been used also in this work.

General formulae

The symbols used in the calculations are given below.

C_M , [M] = total, resp. free, concentration of (+)-Coen₃³⁺.

C_L , [L] = total, resp. free, concentration of Fe(CN)₆⁴⁻.

d = length of polarimeter tube.

θ = observed rotation of the plane of polarisation for a solution (C_M , C_L) and cell thickness d .

δ_n = molar rotation of the complex ML_{*n*} (degr. M⁻¹dm⁻¹)

$$D_n = \delta_n - \delta_0 \quad (1)$$

β_n , X , α_n and \bar{n} have their conventional meanings.⁷

We then define the quantity ψ ,

$$\psi = (\theta - \theta_0)/C_M d \quad (2)$$

where θ_0 is the rotation when $C_L = 0$.

Hence

$$\psi = \left(\sum_{n=1}^N D_n \beta_n [L] \right) X^{-1} \quad (3)$$

Experimental details

ψ was measured at a series of C_L , both with and without a supporting electrolyte. In the former case it was not practically possible to maintain a constant ionic strength. Therefore sodium perchlorate was added to such an extent that the sodium ion concentration of all solutions was constant ($C_{Na^+} = 2$ M).

The measurements without supporting electrolyte were undertaken to give qualitative information on the system, while those with supporting electrolyte were used for a calculation of the stability constants.

The polarimeter was a Perkin Elmer 141, photoelectrically recording one. Measurements were made at 589, 578, and 546 nm; 1 dm cells, thermostated at 20.0°C were used in all measurements.

Because of the high light sensitivity of the system, the mixing of the solutions was made in a room with very sparse illumination. The solutions were kept in dark glass bottles which were stored in covered metal cylinders. Thus, protected from light, the solutions were allowed to attain temperature equilibrium. The transfer to the polarimeter tubes was also undertaken with as little illumination as possible.

The chemicals were prepared as before,³ or they were of analytical grade.

Results

In Fig. 1 the values of the function ψ are plotted against C_L in the case when no supporting salt was used. Because of precipitation it was not possible to measure at small values of C_L . However, as $\psi = 0$ for $C_L = 0$ from definition, eqn. (2), one can infer that if such measurements had been possible,

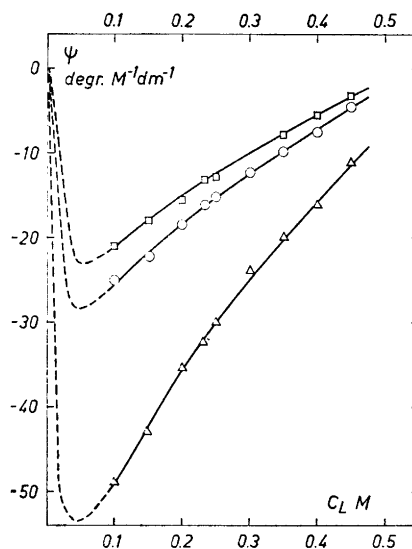


Fig. 1. The function ψ (eqn. (2)) for solutions with no supporting electrolyte, $C_M = 4$ mM. \square , \circ , and \triangle denote $\lambda = 589$, 578, and 546 nm, respectively.

the function ψ would have shown a minimum at $0.01 \text{ M} < C_L < 0.05 \text{ M}$. By arguments analogous to those of the previous investigations,³ one can then conclude that at least two complexes are formed, one with $\delta_1 < \delta_0$, the other one with $\delta_2 > \delta_1$.

Table 1. Experimental values of the function φ . Constant salt normality = 2 M.

C_L M	$-\varphi$ degr. $M^{-1} \text{ dm}^{-1}$			C_M mM
	4.00	6.00	8.00	
0.015	1.9	—	—	$\lambda = 578 \text{ nm}$
0.025	—	3.2	3.3	
0.050	4.9	5.5	5.3	
0.100	6.8	7.0	6.9	
0.125	6.8	—	—	
0.150	6.9	7.2	7.1	
0.200	6.7	7.0	6.9	
0.300	5.3	5.6	5.6	
0.350	4.5	5.0	—	
0.400	3.4	—	—	
0.015	3.2	—	—	$\lambda = 546 \text{ nm}$
0.025	—	6.5	6.0	
0.050	10.0	10.5	9.8	
0.100	13.5	13.3	13.3	
0.125	13.7	—	—	
0.150	14.3	14.3	14.0	
0.200	13.9	14.2	13.8	
0.300	11.5	11.9	11.9	
0.350	9.5	10.2	—	
0.400	8.4	—	—	

Another way to explain the minimum could be the assumption that only one complex exists (still with $\delta_1 < \delta_0$) and that the formation constant of this complex is so drastically decreased by the high ionic strength at large C_L that almost no association could be at hand even at these high C_L . However, it seems highly unlikely that such conditions could be real.

In the series of measurements with a constant salt concentration it was possible to avoid precipitation for all values of C_L when $C_M \leq 8$ mM. The results of these measurements are given in Table 1. As the total metal concentration was rather low and the accuracy of the recorded ψ -values was only about 2–3 % a complete analysis *via* a determination of the mean ligand number ⁷ was not possible. Therefore, a method of successive approximation has been adopted. The assumption was made that not more than two complexes exist. The charges of the reacting species make it impossible that anything else should be the case.

At first only the set of data for $C_M = 4$ mM was considered. Furthermore, $[L]$ was taken to be equal to C_L . Hence eqn. (3) can be written

$$\psi = \frac{D_1\beta_1[L] + D_2\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2} \quad (4)$$

From eqn. (4) it follows that

$$\lim_{[L] \rightarrow 0} \psi/[L] = D_1\beta_1 \quad (5)$$

Table 2. The consecutive steps of approximate results in the estimation of β_1 and β_2 . The units (M^{-1} , etc.) of the calculated quantities are omitted.

		$\lambda = 578 \text{ nm}$	$\lambda = 546 \text{ nm}$
First step, based on (ψ) $C_M=4$ mM	$D_1\beta_1$	–127	–235
	$D_2\beta_2 - D_1\beta_1^2$	550	1000
	Estimated D_1 (from Fig. 1)	–35	–65
	$D_2\beta_2$	105	200
	X (eqn. (7)):		
	β_1 β_2	3 42	3 31
Second step, based on ψ_{mean}	$\psi X/[L]$ (from $\beta_1 = 3$ $\beta_2 = 36$):		
	$D_1\beta_1$ $D_2\beta_2$	–127 117	–239 137
Third step	X (eqn. (7)):		
	β_1 β_2		2.5 ± 0.5 42 ± 10
	ψ/α_1 versus $[L]$ gives:		
	D_1 D_2	–55 3.5	–98 3.5

and

$$\lim_{[L] \rightarrow 0} \frac{d(\psi/[L])}{d[L]} = D_2\beta_2 - D_1\beta_1^2 \quad (6)$$

Hence by plotting $\psi/[L]$ against $[L]$ the intercept gave an approximate value of $D_1\beta_1$ (cf. Table 2).

From the limiting slope one could obtain an approximate value of $D_2\beta_2 - D_1\beta_1^2$.

If now β_1 or D_1 had been known one could have obtained an approximate value of $D_2\beta_2$. For this purpose the results obtained with no supporting electrolyte were used as in this case the formation of the first complex must be almost complete for the ligand concentration where ψ has a minimum value. From the depths of the minima of ψ , one obtains a least value for the absolute magnitude of D_1 . The value actually used was increased a little to partially compensate for the — unknown — deviation of α_1 from unity.

Then, knowing approximative values of $D_1\beta_1$ and $D_2\beta_2$ we can apply eqn. (4) in the form

$$X = (D_1\beta_1[L] + D_2\beta_2[L]^2)\psi^{-1} \quad (7)$$

The values of β_1 and β_2 obtained in this way are included in Table 2.

Now, in order to utilize all the experimental data, the mean of ψ was calculated from the three sets of C_M (Table 3). As before $C_L \approx [L]$.

Table 3. Some of the calculated data used in the estimation of β_1 and β_2 .

[L] M	$-\psi_{\text{mean}} \text{ degr. M}^{-1}\text{dm}^{-1}$		$-\psi X [L]^{-1}$		X (eqn.(7))		$\frac{X_{\text{mean}} - 1}{[L]}$
	578	546	578	546	578	546	
0.015	1.9	3.2	133	224	—	—	
0.025	3.2 ₆	6.2 ₅	140	275			
0.050	5.2 ₃	10.1 ₀	130	250	1.16	1.15	3.1
0.100	6.9 ₀	13.3 ₇	115	222	1.68	1.69	6.8 ₅
0.125	6.8	13.7	106	213	2.07	2.02	8.3 ₅
0.150	7.1 ₀	14.2 ₀	107	214	2.31	2.31	8.7
0.200	6.8 ₆	13.9 ₇	104	212	3.02	3.03	10.1
0.300	5.5	11.7 ₇	94	201	5.01	5.04	13.5
0.350	4.7 ₅	9.8 ₅	88	181	6.34	6.79	15.9
0.400	3.4	8.4	68	167	9.44	8.77	20.3

Then eqn. (4) was transformed into

$$\psi X [L]^{-1} = D_1\beta_1 + D_2\beta_2 [L] \quad (8)$$

Using the mean of the stability constants obtained in the first step the function $\psi X [L]^{-1}$ was calculated for each $[L]$ and plotted against $[L]$. This gave new values of $D_1\beta_1$ and $D_2\beta_2$ (Table 2).

Then, for a check of the stability constants, eqn. (7) was used anew and the function X was obtained as recorded in Table 3.

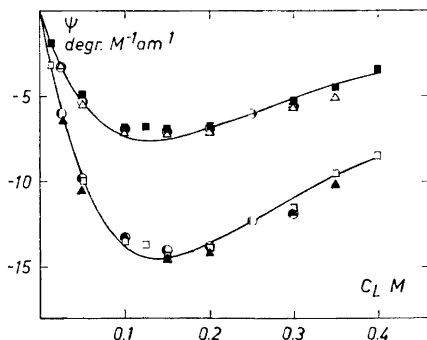


Fig. 2. The function ψ (eqn. (2)) for solutions with a total sodium ion concentration, $C_{\text{Na}^+} = 2$ M. Experimental points: $\lambda = 578$ nm, $C_{\text{M}} = 4, 6,$ and 8 mM: \blacksquare , \blacktriangle , and \bullet . $\lambda = 546$ nm, $C_{\text{M}} = 4, 6,$ and 8 mM: \square , \triangle , and \circ . The full-drawn curves are calculated from the final parameters given in Table 2.

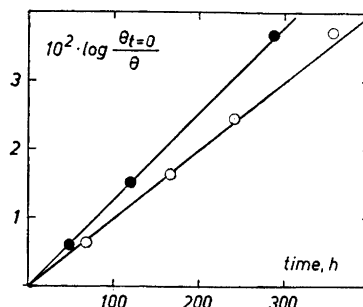


Fig. 3. Some of the kinetic measurements. $C_{\text{M}} = 4$ mM, $C_{\text{L}} = 0.10$ M (\bullet); $C_{\text{M}} = 6$ mM, $C_{\text{L}} = 0.20$ M (\circ). The mean values of the results for the two wavelengths are recorded.

From the mean of $[X-1][L]^{-1}$ for the two wavelengths the final values of the stability constants were calculated (Table 2).

A final calculation of $D_1\beta_1$ and $D_2\beta_2$ from eqn. (8) as above gave the values of D_1 and D_2 recorded in Table 2. It was not considered meaningful to pursue the calculations in further steps. The final values of β_1 , β_2 , D_1 , and D_2 were used for a calculation of ψ . The results together with the experimental points are given in Fig. 2. It can be seen that the calculated curve represents the experimental points rather well.

The kinetic effect

It has been mentioned above that the system $\text{Coen}_3^{3+} - \text{Fe}(\text{CN})_6^{4-}$ is a remarkably light-sensitive one. When the solutions were illuminated, a cherry-red colour developed. However, even when the solutions were carefully protected from light, the optical activity of the solutions decreased slowly and the light absorption was increased. This increase was so pronounced that it proved difficult to follow the reaction polarimetrically to more than about one fifth of a half-life. After that, no good readings could be obtained with the polarimeter. The reaction was followed also spectrophotometrically for a longer period of time, but it proved impossible to use the data for a calculation of the rate constant as the optical density at infinite time was not easy to determine. Although a red colour developed when totally light-protected solutions were heated on the steam bath, the optical densities obtained were never reproducible and it could not be ascertained that the final product at 20°C was the same as at the elevated temperature. It must be said in this connection that all available evidence [absence of analytical reaction for $\text{Co}(\text{II})$; dissimilarity in colour of the reaction product and a mixture of $\text{Co}(\text{II})$ -

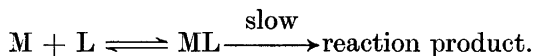
salts, ethylenediamine, and $\text{Na}_4\text{Fe}(\text{CN})_6$] indicates that the product is still one containing Co(III). However, when the circular dichroism of the resultant solutions was measured with a Roussel-Jouan Dichrograph (see below), no deflection was obtained. It was then concluded that the optical activity of the system was lost during the dark reaction. Hence it was possible to use the polarimeter readings to determine the rate constant of the reaction.

The decrease of the optical activity was found to follow a first order rate law (Fig. 3). Thus, $2.303 \log (\theta_{t=0}/\theta) = kt$. In Table 4 the constants k are collected for three values of C_M together with the mean of these values.

Table 4. The first order rate constant k for various values of C_L together with α_1 and k/α_1 .

C_L M	$k \times 10^4$ (h ⁻¹)				α_1	$k\alpha_1^{-1} \times 10^3$
	$C_M = 4$ mM	$C_M = 6$ mM	$C_M = 8$ mM	Mean		
0.015	1.84			1.8 ₄	0.036	5.1
0.025		2.42	2.5	2.4 ₆	0.058	4.2
0.050	2.85	2.83		2.8 ₄	0.102	2.8
0.100	2.91	2.92	2.94	2.9 ₂	0.150	1.9
0.150	2.5	3.21	2.99	2.9	0.162	1.8
0.200	2.71	2.27	2.77	2.6	0.157	1.7
0.300	1.98	2.09	2.93	2.3	0.136	1.7
0.350		1.69		1.7	0.125	1.4
0.400	1.58			1.6	0.115	1.4

The not unexpected result now appears that the first-order rate constant is dependent upon C_L . However, it is not directly proportional to C_L so the reaction cannot be a bimolecular one, the large excess of C_L over C_M making it a pseudo mono-molecular reaction. The close similarity between the variation of k with C_L ($\approx [L]$) and that of the function α_1 , *i.e.* $[\text{ML}]/C_M$, rather suggests that the rate determining step is one involving the first outer sphere complex, ML.



However, if the ratio K/α_1 is calculated, one observes (Table 4) a decrease with C_L . It is difficult but to hint at an explanation of this effect. It may be that even if it has been possible to represent the polarimetric results by two stability "constants" one can not certainly say that these constants are really constant for the whole range of $\text{ClO}_4^- - \text{Fe}(\text{CN})_6^{4-}$ mixtures. Rather the opposite is probable and then α_1 would be slightly in error. However, disregarding the quantitative aspect, the kinetic results seem to confirm the existence of outer-sphere complexes.

ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF THE COMPLEXES

When now the stability constants for the complexes ML and ML_2 have been determined it is possible to determine various molecular parameters. In this case the absorption and the circular dichroism coefficients are of

interest when we try to understand the mechanism of bonding in outer-sphere complexes.

Notations and formulae

Besides the already presented notations we will use the following ones.

A = observed optical density

d = cell thickness

ε_0 = extinction coefficient of M

ε_1 = » » » ML

ε_2 = » » » ML₂

$$\varepsilon = A d^{-1} C_M^{-1} \quad (10)$$

CD = observed circular dichroism

$\Delta_0 = (\varepsilon_1 - \varepsilon_r)_0$ = circular dichroism coefficient of M

$\Delta_1 = (\varepsilon_1 - \varepsilon_r)_1$ = » » » ML

$\Delta_2 = (\varepsilon_1 - \varepsilon_r)_2$ = » » » ML₂

$$\Delta = CD d^{-1} C_M^{-1} \quad (11)$$

Then the following relations are immediately obtained

$$\varepsilon = \sum_{n=0}^2 \alpha_n \varepsilon_n \quad (12)$$

$$\Delta = \sum_{n=0}^2 \alpha_n \Delta_n \quad (13)$$

Eqns. (12) and (13) can be rewritten in the form

$$\frac{\varepsilon - \varepsilon_0 \alpha_0}{\alpha_1} = \varepsilon_1 + \frac{\beta_2}{\beta_1} \varepsilon_2 [L] \quad (14)$$

and

$$\frac{\Delta - \Delta_0 \alpha_0}{\alpha_1} = \Delta_1 + \frac{\beta_2}{\beta_1} \Delta_2 [L] \quad (15)$$

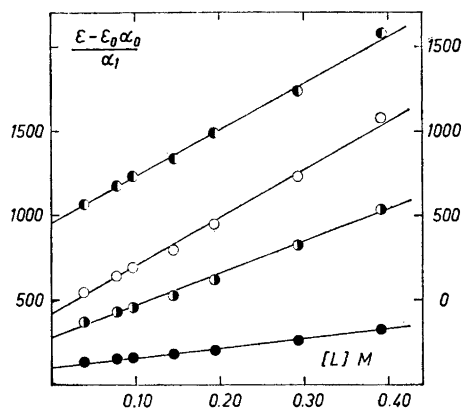
Hence by plotting the quantities on the left side of these equations against [L] the parameters ε_1 , ε_2 , Δ_1 , and Δ_2 can be obtained.

Experimental details

The solutions were made up as in the polarimetric measurements. The absorption spectra for a series of solutions were recorded with a Perkin Elmer Uvicord Spectrophotometer. The solutions were mixed in a dark room and completely protected from light during the time (half an hour) allowed to attain temperature equilibrium. The solutions used for the measurements of CD were prepared in the same way and the spectra were recorded with a Roussel-Jouan Dichrograph. The cell compartment was thermostated to 20.0°C. A deflection on the scale of the instrument of 1 mm was supposed to correspond to 1.5×10^{-4} in observed circular dichroism.

Fig. 4. The determination of ϵ_1 and ϵ_2 . $(\epsilon - \epsilon_0\alpha_0)/\alpha_1$ plotted against $[L]$. Experimental points:

- , $\lambda = 530$ nm; ○, $\lambda = 490$ nm;
- , $\lambda = 460$ nm; all left scale.
- ⊙, $\lambda = 430$ nm; right scale.



Results

The results of the absorption measurements are given in Table 5 and those of the dichroism measurements in Table 6. In both instances the concentration of $(+)\text{Coen}_3(\text{ClO}_4)_3$ was 5.00 mM and the free ligand concentration was calculated from the known stability constants.

In Fig. 4 some of the above-mentioned plots are represented. It can be seen that a fairly good linearity is obtained showing that not more than two complexes exist. The linearity, however, cannot be taken as a criterion that the stability constants are correct, as other values of β_1 and β_2 within reasonable limits also will give linear plots resulting in different values of the spectroscopic parameters.

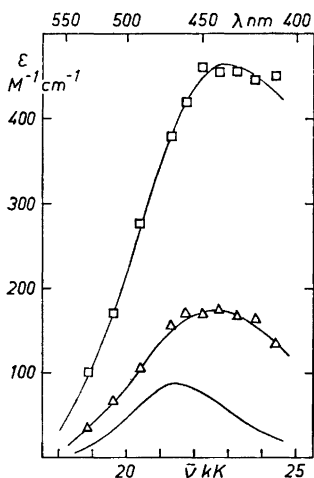


Fig. 5. Absorption spectra of the complexes ML_n . □, $n = 1$; △, $n = 2$. The lower curve corresponds to $n = 0$.

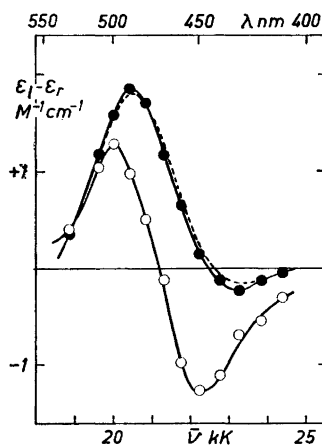


Fig. 6. Circular dichroism spectra of the complexes ML_n . ○, $n = 1$; ●, $n = 2$. The dotted curve corresponds to $n = 0$.

Table 5. The spectrophotometric results. $C_M = 5.00$ mM, $d = 1$ cm, $C_{Na^+} = 2$ M.

C_L M	$[L]$ M	α_0	α_1	ϵ M ⁻¹ cm ⁻¹										
				530 nm	510	490	470	460	450	440	430	420	410	
0				12	33	64	86	86	86	77	63	48	34	23
0.040	0.039	0.84	0.084	20	43	80	113	118	118	115	107	93	80	69
0.080	0.078	0.66	0.132	29	57	98	134	140	140	138	131	120	110	99
0.100	0.097	0.58	0.145	30	60	102	141	149	149	149	144	134	123	112
0.150	0.145	0.42	0.157	33	63	109	151	160	160	161	157	150	141	131
0.200	0.194	0.30	0.152	34	67	114	157	170	170	173	170	165	156	144
0.300	0.293	0.18	0.133	37	71	121	166	179	179	182	180	173	164	149
0.400	0.392	0.11	0.113	38	72	124	173	188	188	195	194	183	164	149

Table 6. The circular dichroism results. $C_M = 5$ mM, $d = 2$ cm, $C_{Na^+} = 2$ M.

C_L mM	$[L]$ mM	α_0	α_1	$\Delta \times 10^{-2}$ (deflection) (mm) cm ⁻¹ M ⁻¹														
				530 nm	510	500	490	480	470	460	450	440	430	420	410			
0	0	1	0	22	72	100	117	111	82	47	15	-4	-11	8	5			
37.5	34	0.85	0.080	23	71	97	111	102	73	37	6	-10	-14	-10	-5			
75	72	0.68	0.127	21	70	95	107	97	66	30	1	-14	-16	-12	-7			
125	121	0.49	0.154	22	70	96	107	96	65	27	-1	-16	-17	-12	-7			
187.5	182	0.33	0.154	23	73	97	107	95	62	25	-4	-17	-17	-12	-6			
250	243	0.23	0.142	22	71	96	107	96	64	27	-3	-17	-18	-12	-6			
375	367	0.13	0.122	23	73	98	109	97	63	26	-3	-17	-18	-12	-6			

The absorption spectra obtained in this way for the spectral range where the ligand did not absorb are given in Fig. 5 and the circular dichroism curves in Fig. 6. It can be seen that the most pronounced change occurs for the first complex in both cases.

THE EFFECT OF THE SUPPORTING ELECTROLYTE

The sequence of the stability constants obtained from the polarimetric measurements is quite unusual. $K_1 = 2.5 \text{ M}^{-1}$ and $K_2 = 17 \text{ M}^{-1}$ yield the very small value of $K_1/K_2 = 0.15$. However, in a system such as this, with highly charged reacting species, deviations from the normal should be expected.

For one thing, association will certainly occur between Na^+ and $\text{Fe}(\text{CN})_6^{4-}$. The effect of this has been minimized by keeping C_{Na^+} constant.

Here another factor will be emphasized. Although we cannot tell for certain that the activity coefficients of the species in solution are "constant" when it is the ionic strength or the normality of the solution that is kept constant at the very high ionic strength used in this work ($I = 2 \rightarrow 5 \text{ M}$), let us suppose that the latter alternative is true.

Furthermore, if K_1° and K_2° are the true thermodynamic formation constants, we have the relations

$$K_1^\circ = K_1 \cdot \frac{f_{\text{ML}^-}}{f_{\text{M}^{3+}} f_{\text{L}^{4-}}} \quad (16)$$

$$K_2^\circ = K_2 \cdot \frac{f_{\text{ML}_2^{2-}}}{f_{\text{ML}^-} f_{\text{L}^{4-}}} \quad (17)$$

Irrespective of the exact formulation of the activity coefficients change with the concentration of supporting electrolyte, the quotient $f_{\text{ML}_2^{2-}}/f_{\text{ML}^-} f_{\text{L}^{4-}}$ must probably be much more insensitive to a change in the normality of the solution than the quotient $f_{\text{ML}^-}/f_{\text{M}^{3+}} f_{\text{L}^{4-}}$ is.

Furthermore, if we make the reasonable assumption that when the solution is as concentrated as in the present experiments, the product of activity coefficients of three- and four-valent ions is much less than the activity coefficient of a univalent ion, it holds that $K_1 \ll K_1^\circ$.

As $K_1 = K_1^\circ$ in the limiting ideal case of a very dilute solution, we can then say that for a solution with less concentrated supporting electrolyte K_1 should be greater than the value observed here but that K_2 should change much less. Because of eqns. (16) and (17) and similar relations, comparisons between sequences of consecutive stability constants should really be made from — the unaccessible — thermodynamic constants.

Measurements at $I = 0.21 \text{ M}$

In order to test these arguments a separate investigation was performed at a formal ionic strength $I = 0.21 \text{ M}$. C_{L^-} was varied between 0 and 20 mM, C_{M} was 2 mM.

The association was observed by measuring the circular dichroism as described above. Readings were made from the recorded spectra at 490, 460, and 430 nm. The results are given in Table 7.

Calculation of the stability constant β_1

Rewriting eqn. (13) to conform with eqn. (4) we obtain

$$\Delta = (\Delta_0 + \Delta_1\beta_1[L] + \Delta_2\beta_2[L]^2)X^{-1} \quad (18)$$

or

$$\frac{\Delta - \Delta_0}{[L]} = [(\Delta_1 - \Delta_0)\beta_1 + (\Delta_2 - \Delta_0)\beta_2[L]]X^{-1} \quad (19)$$

Hence

$$\lim_{[L] \rightarrow 0} \frac{\Delta - \Delta_0}{[L]} = (\Delta_1 - \Delta_0)\beta_1 \quad (20)$$

As $\Delta_1 - \Delta_0$ is known from the earlier measurements one can obtain β_1 .

From a rough estimate using the approximation $C_L = [L]$, an approximate value of $\beta_1 = 100 \text{ M}^{-1}$ was obtained. Using this value and neglecting the second complex, $[L]$ was estimated and $(\Delta - \Delta_0)/[L]$ was calculated. In order to facilitate the extrapolation $(\Delta - \Delta_0)/[L]$ was multiplied with $1 + 100 [L]$. The results of the calculations are included in Table 7. Furthermore, an attempt was made to estimate β_2 from the relation (21), obtained from eqn. (18).

$$\Delta - \Delta_0 = \beta_1(\Delta_1 - \Delta)[L] + \beta_2(\Delta_2 - \Delta)[L]^2 \quad (21)$$

The results obtained showed a very great scattering and also the values for the different wave lengths varied appreciably

$$\beta_2 = (1 \pm 0.5) \times 10^3 \text{ M}^{-2} (\lambda = 490 \text{ nm}), \beta_2 = (8 \pm 3) \times 10^3 \text{ M}^{-2} (\lambda = 460 \text{ nm})$$

and

$$\beta_2 = (12 \pm 4) \times 10^3 \text{ M}^{-2} (\lambda = 430 \text{ nm}).$$

This was to be expected as the second complex does not exist in any greater quantity in the solutions investigated. The approximate determination of $[L]$ also influences the inaccuracy of β_2 . However, the stability constants $\beta_1 = 95 \pm 20 \text{ M}^{-1}$ and $\beta_2 = (7 \pm 5) \times 10^3 \text{ M}^{-2}$ are in accordance with the expectations that K_1 should increase considerably and that K_2 should show only a small change when the concentration of the supporting electrolyte is diminished.

DISCUSSION

As has been pointed out above, the molar circular dichroism coefficients determined at salt concentration = 2 M can be used for a — let be approximate — calculation of stability constants at a much lower ionic strength. These constants conform to a sequence pattern that can be expected from the general behaviour of activity coefficients of ions in electrolyte solutions. This circumstance, so it seems to the present author, gives weight to the

Table 7. The circular dichroism measurements at $I = 0.21$ M and calculation of β_1 . $C_M = 2$ mM, $d = 4$ cm.

C_L mM	[L] mM	Deflection (mm)			$-(\Delta - \Delta_0)$ ($M^{-1}cm^{-1}$)			$-(\Delta - \Delta_0)[L]^{-1}(1 + 100[L])$			
		490	460	430	490	460	430	490	460	430 nm	
0	0	98	42	- 8				81 ± 3	125 ± 10	55 ± 7	
5.00	4.33	85	24	- 16	0.24	0.35	0.15	80	116	50	
6.67	5.87	83	21	- 17	0.28	0.40	0.16	74	107	44	
8.00	7.11	82	20	- 17	0.31	0.43	0.17	75	103	41	
10.00	9.00	80	17	- 18	0.35	0.47	0.19	73	99	40	
13.33	12.19	77	14	- 19	0.40	0.54	0.21	73	98	38	
16.00	13.80	75	12	- 19	0.43	0.57	0.21	74	99	36	
20.00	14.77	74	10	- 21	0.45	0.60	0.23	76	101	39	
	18.67	73	8	- 21	0.47	0.65	0.25	72	100	38	
				$\Delta_1 - \Delta_0$ (Fig. 6)			-0.77			-1.68	-0.53
				β_1 M^{-1}			106			75	104
				β_1 (Mean) M^{-1}						95 ± 20	

interpretation of the polarimetric measurements, *i.e.* that two outer-sphere complexes exist in the investigated system.

The existence of the two $\text{Fe}(\text{CN})_6^{4-}$ outer-sphere complexes then gives added support to the proposal^{5,8} that outer-sphere complexes of the type Coen_3L_n exist, where $\text{L} = \text{S}_2\text{O}_3^{2-}$ or SeO_3^{2-} and $n = 3$ and 4. Also in these cases the unexpectedly high stability constants must to some extent depend upon the high ionic strength of the solutions where these species exist. However, as has been pointed out elsewhere,⁹ the existence of such complexes must depend upon other factors than mere electrostatic forces, probably a charge transfer mechanism. An interpretation of the CD spectra has been given elsewhere,⁸ where one is using the mixing of the $d-d$ transition of the central group with the charge transfer transition between outer sphere ligand and the central group. It seems reasonable that the pronounced increase of the absorption intensity of the $d-d$ transition can also originate from a borrowing of electric dipole intensity from the charge transfer transition.

As there must then also be a significant charge transfer in the ground state it is not surprising that the inert character of the central group is diminished to such an extent that racemization can occur. Although the nature of the reaction product is not yet known, it seems probable that it is a substituted $\text{Co}(\text{III})\text{en}$ complex, possibly containing a $\text{Co}(\text{III})\text{-NC-Fe}(\text{II})(\text{CN})_5$ bridge as found by Adamson¹⁰ and Haim¹¹ in similar cases. The relevant point here is that one must not necessarily assume the formation of $\text{Co}(\text{II})$ species as intermediates, but that the donation of electrons to the antibonding e_g^* orbitals of the central group would tend to loosen the Co-N bonds to such a degree that racemization could occur during the substitution process. Work will be continued to elucidate the interesting relation between outer-sphere coordination and the reactivity of the central group.

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