Studies on Cobaltammines

VI. A Polarimetric Investigation of Some Outer-sphere Complexes of the *d*-Trisethylenediaminecobalt(III) Ion

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The optical rotation of the d-[Coen$_3$]$^{3+}$ ion has been measured in aqueous solutions of increasing concentrations of sulphate, thiosulphate, fluoride, chloride and perchlorate ions. In the first two cases a minimum of the rotatory power was obtained. This result indicates the existence of the first two outer-sphere complexes in these systems. For the thiosulphate system there are also some indications of the third outer-sphere complex as well as of a slight tendency to the formation of polynuclear complexes.

The other three systems showed a monotonous change of the rotatory power, the chloride system towards greater values, the fluoride and the perchlorate systems towards smaller values than that of the free d-[Coen$_3$]$^{3+}$ ion.

The relation between the changes observed and the polarizabilities of the ions is discussed.

It is a well known fact [1,2] that changes in the composition of the second coordination sphere of transition metal complexes do not cause great changes in the visible spectrum of the complex. However, it was demonstrated already by Werner [3] that the optical rotation of a complex ion in solution is strongly dependent upon the nature of the counter-ion. Following the work of Werner, Jaeger [4] measured the rotation dispersion of a series of complexes and found considerable differences for different counter-ions. To the best of the author's knowledge, it was not until the repetition and extension of these investigations by Kirschner and coworkers [5], that this effect was used for the investigation of outer-sphere complexity.

However, the above-mentioned authors [5] seem to have been measuring the optical rotation at only one concentration of the counter-ions, *viz.* that determined by the concentration of the complex ion and the stoechiometry of the salt in question. The rotations obtained by this method must depend on the degree of the outer-sphere affinity of the different counter-ions and on the molar rotations of the outer-sphere complexes. Thus they cannot be used directly as a measure of the complexity.

A better approach would be to measure the optical rotation of the complex central ion, as the concentration of the ligand is gradually changed. Then one may obtain evidence of a consecutive outer-sphere complex formation. The situation must be especially favorable, if the molar rotations of the consecutive complexes differ very much.

Such measurements have been performed in this paper. The rotatory power of the d-[Coen$_3$]$^{3+}$ ion has been determined for solutions holding varying amounts of sulphate, thiosulphate, fluoride, chloride and perchlorate ions, respectively.

METHOD AND FORMULAE

During the measurements no attempt was made to maintain a constant ionic strength. Thus the stability constants β_n used below are not to be regarded as true constants. Nevertheless, valuable information may be obtained from a quantitative formulation of the dependence of the rotatory power on the ligand concentration.

Let ϑ be the observed rotation, when the cobalt complex concentration is $C_{\mathrm{Men_3}}$, when the total ligand concentration is C_{B} and the cell length is d dm. Then we define

$$\psi = \frac{\vartheta - \vartheta_0}{d \cdot C_{\mathrm{Men_3}}} \tag{1}$$

where ϑ_0 is ϑ for $C_{\mathrm{B}} = 0$.

If we assume that only mononuclear complexes exist, it is easily deduced that

$$\psi = \frac{\sum\limits_{n=0}^{N} \delta_n \beta_n [\mathrm{B}]^n}{\sum\limits_{n=0}^{N} \beta_n [\mathrm{B}]^n} - \delta_0 \tag{2}$$

and

$$\frac{\mathrm{d}\psi}{\mathrm{d}\ln[\mathrm{B}]} = \sum\limits_{n=0}^{N} (n - \bar{n})(\delta_n - \delta_n)\alpha_n \tag{3}$$

Here δ_n denotes the molar rotation of the complex [(Coen$_3$)B$_n$] and β_n is the stability constant of that complex. $\bar{n}$ is the mean ligand number and α_n is the fraction of the cobalt existing as the n:th outer-sphere complex at the concentration [B] of free ligand.

Eqn. (3) is derived under the assumption of constant β_n and is thus valid only within a limited concentration range. It is obvious that if $\delta_1 < \delta_0$ and $\delta_2 > \delta_0$, γ will exhibit a minimum value. The position of this minimum can be estimated from eqn. (3). If only the first two terms in the right member of this equation are taken into account, we get:

$$\frac{\mathrm{d}\psi}{\mathrm{d}\ln[\mathrm{B}]} = (1 - \bar{n})(\delta_1 - \delta_0)\alpha_1 + (2 - \bar{n})(\delta_2 - \delta_0)\alpha_2 \tag{4}$$

The first term of the right side changes sign, when $\bar{n} = 1$. The second term is positive, when $\bar{n} < 2$, but as α_2 is rather small when $\bar{n} \approx 1$, this term does

contribute only little to the value of $d\psi/d \ln[B]$. We may then conclude that, when $\bar{n}$ is only slightly less than one, $d\psi/d \ln[B]$ changes sign. This relation will be exemplified below.

EXPERIMENTAL

Chemicals used. d-[Coen$_3$]Cl d-tartrate was prepared as described by Werner [1]. This salt was dissolved and the perchlorate was precipitated with concentrated perchloric acid, washed with alcohol and ether and air-dried. Other chemicals were of *pro analysi* quality.

The polarimeter was a Hilger M 323, three-field Lippich-type for visual observation. The light source was a conventional sodium lamp and the instrument was equipped with a bichromate filter. The readings could be reproduced within 0.01°. Every reading was repeated 3—4 times to minimize random errors. The polarimeter tubes were kept at a constant temperature (20°C) by passing thermostated water through jackets on the tubes. The length of the tube was 4 dm in all cases but for the measurements at $C_M = 32$ mM, when a 2 dm tube was used.

RESULTS

The measurements of the sulphate and thiosulphate systems are reported in Tables 1 and 2. A graphical comparison between the two systems is given in Fig. 1. It can immediately be seen that whereas the minimum values are of the same order of magnitude, the subsequent increase of ψ is much more pronounced in the thiosulphate system. The minimum occurs at a lower value of C_B for the thiosulphate system than for the sulphate one. As the measurements reported in Fig. 1 were made at the same C_{Men_3} and as the minima are expected to occur at approximately the same value of $\bar{n}$, this means that the minimum also occurs at a smaller value of [B] for the thiosulphate system. This result indicates that the complexity is stronger in the system first men-

Table 1. Determination of ψ for the sulphate and thiosulphate systems. $C_{Men_3} = 16.00$ mM. $d = 4$ dm. $\delta_0 = 52.7$ degr. dm^{-1} M^{-1}.

The sulphate system			The thiosulphate system		
C_B mM	ϑ degr.	ψ degr.dm^{-1} M^{-1}	C_B mM	ϑ degr.	ψ degr.dm^{-1} M^{-1}
0	3.37$_4$	0	0	3.37$_4$	0
15.7	3.22$_5$	-2.3_3	14.0	3.25$_0$	-1.9_4
31.4	3.16$_0$	-3.3_4	31.4	3.17$_5$	-3.1_1
59	3.09$_6$	-4.3_4	58	3.12$_0$	-3.9_7
87	3.08$_6$	-4.5_0	87	3.15$_9$	-3.3_6
126	3.09$_1$	-4.4_2	157	3.31$_1$	-0.9_8
157	3.10$_2$	-4.2_5	330	3.65$_1$	$+4.3_3$
222	3.13$_6$	-3.7_2	595	4.11$_8$	$+11.6$
331	3.19$_3$	-2.8_3	900	4.59$_8$	$+19.1$
440	3.24$_3$	-2.0_5	1440	5.23$_5$	$+29.1$
595	3.33$_0$	-0.6_9	1800	5.57$_8$	$+34.4$
790	3.40$_6$	$+0.5_0$	2400	6.10$_0$	$+42.6$
990	3.47$_8$	$+1.6_3$	3000	6.42$_8$	$+47.7$

Table 2. Determination of ψ for the thiosulphate system. (Continued)

C_{Men_3} = 8.00 mM d = 4 dm			C_{Men_3} = 32.0 mM d = 2 dm		
C_B mM	ϑ degr.	ψ degr.dm^{-1} M^{-1}	C_B mM	ϑ degr.	ψ degr.dm^{-1} M^{-1}
15.7	1.58_3	$- 3.2_5$	47.7	3.21_4	$- 2.5_0$
47.2	1.52_6	$- 5.0_3$	72	3.19_2	$- 2.8_4$
79	1.56_3	$- 3.8_8$	358	3.69_7	$+ 5.0_5$
450	1.95_2	$+ 8.2_8$	596	4.10_5	$+ 11.4$
900	2.28_5	$+ 18.7$	1125	4.85_3	$+ 23.1$
1200	2.45_5	$+ 24.0$	1800	5.54_9	$+ 34.0$

tioned. This is in agreement with the results of ion-exchange measurements of the analogous $Co(NH_3)_6^{3+}$ systems [6].

In Fig. 2 the results for different C_{Men_3} in the thiosulphate case are given. It can be seen that the minimum of ψ is not independent of C_{Men_3}. This means that the assumptions made at the deduction of eqn. (2) are not fulfilled. The
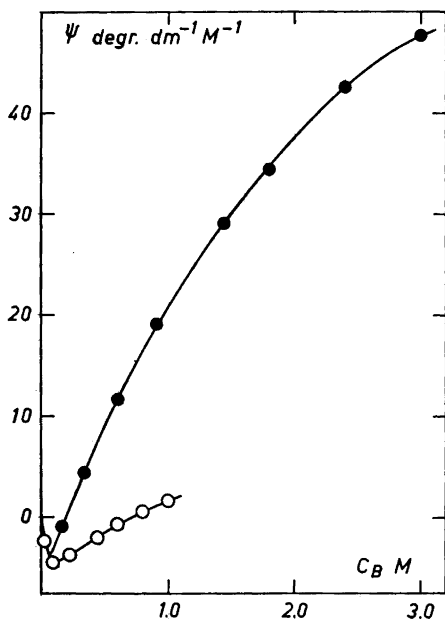

Fig. 1. ψ for the sulphate (O) and the thiosulphate (●) systems. C_{Men_3} = 16.00 mM.

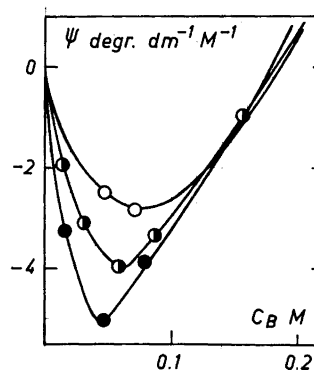*Fig. 2.* The thiosulphate system. C_{Men_3} = 32.0 mM (O); C_{Men_3} = 16.00 mM (◑) and C_{Men_3} = 8.00 mM (●).
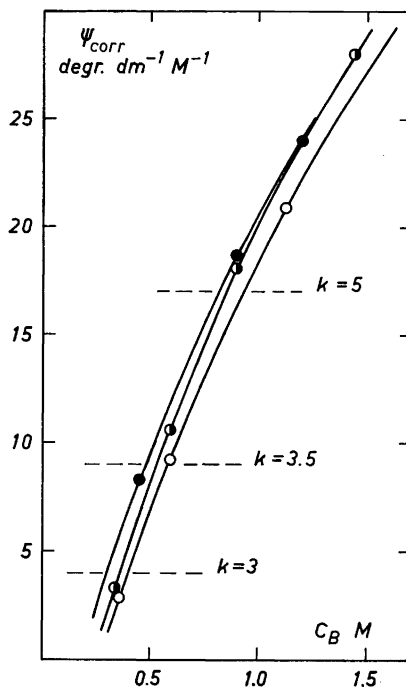
Fig. 3. The thiosulphate system. The ψ-curves after the correction mentioned in the text. The k-values are the means of the readings for ($C''_{\mathrm{Men_3}}$ = 32 mM, $C'_{\mathrm{Men_3}}$ = 8 mM) and ($C''_{\mathrm{Men_3}}$ = 32 mM, C'_{M} = 16 mM). $C_{\mathrm{Men_3}}$ = 32 mM (O); $C_{\mathrm{Men_3}}$ = 16 mM (◑); $C_{\mathrm{Men_3}}$ = 8 mM (●).

author therefore proposes that there is some tendency towards formations of polynuclear complexes within the studied system. This proposal is supported by the observation that the ψ values at high C_{B} and $C_{\mathrm{Men_3}}$ = 8 and 32 mM (Table 2) do not lie in a proper position in relation to the line drawn in Fig. 1. In a situation similar to this one, Fronæus (Ref.[7], p. 129) has used an approximative correction, implying the adjustment of the ψ values with a certain constant value, so that the extreme values of the curves coincide. The present author is well aware of the arbitrariness of this correction if the difference between the minimum values is not very small, and especially at ψ values far from the extreme point. Nevertheless, such a correction has been attempted, by reducing the ψ values for $C_{\mathrm{Men_3}}$ = 16 mM and $C_{\mathrm{Men_3}}$ = 32 mM with 1.05 and 2.20 degrees dm^{-1} M^{-1}, respectively. This operation makes the minima of the three curves (Fig. 2) to coincide. The resulting ψ values are given in Fig. 3. The sequence of the curves is now the one expected if no polynuclear complexes are formed. Then for a constant value of ψ, corresponding to a constant value of [B], we form the quotient $k = (C''_{\mathrm{B}} - C'_{\mathrm{B}})/(C''_{\mathrm{Men_3}} - C'_{\mathrm{Men_3}})$ for two points ($C'_{\mathrm{Men_3}}$, C'_{B}) and ($C''_{\mathrm{Men_3}}$, C''_{B}) of the selected ψ. Some k-values
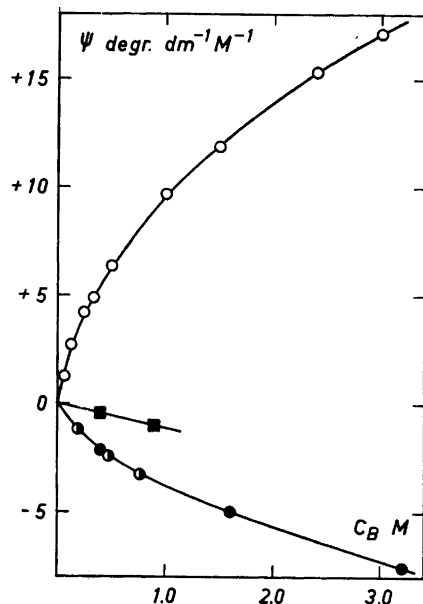
Fig. 4. ψ for the chloride (O) fluoride (◑: NaF; ●:KF) systems, $C_{\text{Men}_3} = 16.00$ mM, $d = 4$ dm; and for the perchlorate system (■), $C_{\text{Men}_3} = 8.00$ mM, $d = 4$ dm.

obtained in this way are indicated in Fig. 3. In the ideal case k should be equal to $\bar{n}$. The results are certainly too high. This is obviously due to an overcorrection and the correct $\bar{n}$ should be somewhat lower, as the degree of formation of polynuclear complexes is probably lower at these high values of C_B, compared to what was the case in the vicinity of the minimum.

The most important point of the argumentation is that the result of the correction makes it probable that the difference in magnitude of the minima for different C_{Men_3} (Fig. 2) is due to the existence of polynuclear complexes. An equally likely explanation is, however, that the difference in ionic strength in the three cases, which is noticeable in the low C_B-range, may have caused the difference in the magnitude of the minimum. It is improbable, however, that such an effect should persist up to the high C_B-range, where the *relative* difference in ionic strengths is small, and thus the result of the correction would be the same.

In the series of measurements with $C_{\text{Men}_3} = 32$ mM, precipitation occurred for $C_B = 100$ mM. Analysis of the precipitate showed that its composition was $[\text{Coen}_3]_2$ $(S_2O_3)_3$. No precipitation was encountered for the other C_B-values. This obviously means that there is a minimum of solubility somewhere in the range 70 mM $< C_B <$ 350 mM. This fact, implies that $\bar{n} = 1.5$ somewhere in this concentration range.

The results of the measurements of the fluoride, chloride and perchlorate systems are reported graphically in Fig. 4. For these systems ψ varies monoto-

nously with ligand concentration. In order to reach high fluoride concentrations, potassium fluoride was used. It can be seen from Fig. 4 that ψ is apparently not influenced by a change from a sodium salt medium to a potassium one.

It is a matter of choice if the slight decrease of ψ found in the measurements of the perchlorate solutions should be ascribed to complex formation or to the variation of δ_0 with the ionic strength.

DISCUSSION

From the submitted results it follows that the existence of at least the first two sulphato- and thiosulphato complexes has been proved. The very steep rise of ψ for the thiosulphato system makes it probable that also a third complex exists. Indeed, even at as high a ligand concentration as 3 M the curve is still rising, indicating the fact that the complex formation has not yet come to a stop. It is difficult to see how this continued rise can be compatible with values of $\bar{n} = 1$ at so small a ligand concentration as [B] $\approx$ 0.05 M and $n = 1.5$ at [B] $\approx$ 0.2 M, without assuming the existence of a third complex. In connection with this it should be observed that anion-exchange measurements [6] of the similar system $Co(NH_3)_6^{3+}-S_2O_3^{2-}$ gave positive evidence of the existence of a third complex.

In an effort to obtain a more definite indication of the third complex the following approximate calculations were performed: From the values ($\bar{n} = 1$; [B] $= 0.05$ M) and ($\bar{n} = 1.5$; [B] $= 0.2$ M) the stability constants were obtained; $\beta_1 = 65$ M^{-1}, $\beta_2 = 400$ M^{-2}. Furthermore d ψ/d ln [B] was estimated from Figs. 2 and 1 at [B] $\approx$ 0.01 M and 0.2 M, respectively. Using the values of β_1 and β_2 given above, α_1, α_2 and $\bar{n}$ were calculated at the [B] values given. (Table 3.) Hence, $\delta_1 - \delta_0$ and $\delta_2 - \delta_0$ could be obtained from eqn. (4). Then d ψ/d ln [B] was calculated at [B] $= 2.8$ M, assuming that eqn. (4) is still valid, $i.e.$ that only the first two complexes exist at this concentration. One then obtained d ψ/d ln [B] $= 1.1$ degr. dm^{-1} M^{-1} (Table 3). An estimation from Fig. 1 gave d ψ/d ln [B] $= 24$ degr. dm^{-1} M^{-1} at this value of [B].

The discrepancy is of such a magnitude that we must conclude that the assumptions made are not correct, $i.e.$, more than two complexes must exist at large ligand concentrations.

The most striking result of the present investigation is the large effect of the outer-sphere ligands on the rotatory power of the complex. $E.g.$, at the

Table 3. Calculation of d ψ/d ln [B] at [B] $= 2.8$ M from $\beta_1 = 65$ M^{-1} and $\beta_2 = 400$ M^{-2} (cf. the text).

[B] M	α_1	α_2	$\bar{n}$	d ψ/d ln [B] degr. dm^{-1} M^{-1}	
0.01	0.39	0.02	0.43	-1.3 (obs.)	$\delta_1 - \delta_0 = -5.8$
0.2	0.43	0.53	1.5	5.9 (obs.)	$\delta_2 - \delta_0 = 17.3$
2.8	0.05	0.95	1.95	1.1 (calc.)	

largest thiosulphate concentrations the rotatory power of the present species is almost twice that of the free d-[Coen$_3$]$^{3+}$ ion.

As it has not been possible to resolve the data into stability constants (β_n) and molar rotation coefficients (δ_n) we cannot make any quantitative comparisons between the different systems.

There is one puzzling problem, however, which presents itself readily. For the sulphate and thiosulphate systems $\delta_1 < \delta_0$ and $\delta_2 > \delta_0$, and for the fluoride system all δ_n (if there is more than one complex) are less than δ_0. On the other hand $\delta_n > \delta_0$ in the chloride system for all complexes that may exist.

It may be reasonable that the change of the rotatory power of the d-[Coen$_3$]$^{3+}$ ion is dependent on the position of the ligand in relation to the reference frame of the inner-sphere ligand. Especially the variation of the directions of greatest and smallest polarization in relation to this reference frame seems to be important [8]. It is thus possible to understand that $S_2O_3^{2-}$ exerts a greater effect than SO_4^{2-} does, as SO_4^{2-} has a lower polarizability. It also seems plausible that the highly polarizable chloride ion changes the rotation towards higher values, whereas the less polarizable fluoride ion changes it towards lower values in comparison with the free [Coen$_3$]$^{3+}$ ion.

But it is strange that the first thiosulphate complex has $\delta_1 > \delta_0$, $i.e.$ follows the same trend as the first fluoride complex with its much less polarizable ligand. Perhaps at least two important factors must be considered: the charge of the ligand and its polarizability. These two factors seem to exert opposite effects resulting in the above-mentioned observations. Another factor of importance may be any kind of specific preference of the various ligands for different coordination sites, $e.g.$ caused by different affinity towards hydrogen bond formation.

Although the interpretation given above is very vague, it seems to the present author, that, if a complete theory of the phenomenon of optical rotation of transition metal complexes were at hand (there have been interesting discussions recently [8,9]), it should be possible to make assignments of the coordination sites, occupied by the ligands in association complexes such as those investigated here. Then the concept of the second coordination sphere can be promoted from the twilight of a disputed possibility into the daylight of established reality.

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