ACTA CHEMICA SCANDINAVICA 25 (1971) 3752–3762

Outer-sphere Complex Formation Between Tris-(ethylenediamine)cobalt(III) Ion and Iodide Ion in Aqueous Solution

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The complex formation between $Coen_3^{3+}$ and I^- has been studied at 25°C and at constant ionic strengths ($NaClO_4$) ranging from 0.5 to 4 M. Solubility and spectrophotometric methods have been employed. Typically, the following constants were obtained at 1 M ionic strength: $\beta_1 = 1.73 \pm 0.15$ M^{-1} (spectrophotometry), $\beta_1 = 1.42 \pm 0.05$ M^{-1} (solubility), $\beta_3 = 0.51 \pm 0.05$ M^{-3} (solubility).

The results are discussed in terms of the geometry of the $Coen_3^{3+}$ ion.

Some trends found when the ionic strength was varied, as well as the discrepancy in β_1 shown above, can be explained if a slight association $Coen_3^{3+} - ClO_4^-$ is assumed.

Considerable interest has been paid to outer-sphere complex formation between inert complex ions and various ligands, theoretically [1] as well as experimentally.[2] The vast majority of investigations have been concerned only with the 1:1 complex; the ligand concentration has been kept low. For this first complex, different methods of investigation have sometimes given very different results.

The aim of the present paper has been to study outer-sphere complex formation over as broad as possible a range of ligand concentration, taking also the possible formation of higher complexes into consideration. Since the study of weak complex formation is always a difficult task, it has been judged desirable to use more than one method of investigation whenever possible.

The $Coen_3^{3+} - I^-$ system has been chosen for various reasons. The cation is very inert; $Coen_3I_3(s)$ has a solubility of suitable magnitude; $Coen_3(ClO_4)_3(s)$ has a solubility high enough to permit high ionic strengths to be employed. The system has been studied earlier by Evans and Nancollas,[3] who used a spectrophotometric method at 0.3 M ionic strength.

The bulk of the results in the present study were obtained from the solubility of $Coen_3I_3(s)$. Different constant ionic strengths were used, *viz.* 0.5,

1, 2, and 4 M, $NaClO_4$ being the supporting electrolyte. By "ionic strength" is here meant the sum of perchlorate and iodide concentrations. Unless otherwise stated, minor deviations from constancy caused by dissolution and complex formation have been neglected.

Solubility measurements employing $Coen_3I_3(s)$ could be used at 4 M, 2 M, and 1 M but not at 0.5 M ionic strength, since the solubility grew inconveniently high when $[I^-] < 0.5$ M. The high ionic strengths make it possible to use a high ligand concentration and thus better to study higher complexes. At 4 M ionic strength also the solubility of $Coen_3(ClO_4)_3(s)$ could be measured (if $[I^-]$ was kept low).

The lower ionic strengths were necessary since it was judged desirable to support the solubility results by spectrophotometric measurements. However, as is shown in the preceding paper,[4] absorbance measurements at varying ligand concentration (L-method) are very unreliable. The more reliable method of varying the central ion concentration [3,5] (M-method), on the other hand, could only be applied at 0.5 M and 1 M ionic strength, due to the low solubility of $Coen_3(ClO_4)_3(s)$, at higher perchlorate concentrations.

The solubility of $Coen_3I_3(s)$ was also measured in NaI with no $NaClO_4$ added to see if S might have a minimum at high [L].

EQUATIONS

It is assumed that activity factors and absorption coefficients are constant. No polynuclear complexes nor complexes involving the inert salt are assumed to be formed. The notation is the same as in Ref. 4.

Solubility of $Coen_3I_3(s)$

The total concentration of $Coen_3$ at equilibrium, the solubility, is denoted S. Indexed C stand for total initial concentrations. $K_s(I)$ is the solubility product of $Coen_3I_3(s)$. The following equations hold [6] ($\beta_0 = 1$)

$$S = \sum_{n=0}^{N} [ML_n] = \sum_{n=0}^{N} K_s(I)\ \beta_n [L]^{n-3} \tag{1}$$

$$[L] = C_L + (3 - \bar{n})\ S \tag{2}$$

The difference between C_L and [L] was with few exceptions small, so that only rough values of $\bar{n}$ were needed for the calculation of [L] (eqn. (2); *cf.* Ref. 7). Then, $S[L]^3$ was computed (eqn. (1)) and treated graphically according to standard procedures, yielding $K_s(I)$ and the various β_n.

Solubility of $Coen_3(ClO_4)_3(s)$

Here

$$S = \sum_{n=0}^{N} [ML_n] = [ClO_4^-]^{-3} \sum_{n=0}^{N} K_s(ClO_4)\ \beta_n\ [L]^n \tag{3}$$

$K_s(ClO_4)$ being the solubility product of $Coen_3(ClO_4)_3(s)$,

$$[L] = C_L - \bar{n}S \quad (4)$$

and

$$[ClO_4^-] = I - C_L + 3S \quad (5)$$

(I = initial ionic strength).

Using $[L] = C_L$ as a first approximation $S[ClO_4^-]^3$ was treated graphically to yield a preliminary set of $K_s(ClO_4)$, β_n and $\bar{n}$. Hence, better (and final) values of [L] (eqn. (4)) and the constants (eqn. (3)) were obtained.

Spectrophotometric M-method

C_L is kept so low that formation of complexes higher than ML can be neglected. If this neglect is not completely justified, only a minor correction is introduced, quite contrary to the situation on the L-method,[4] where higher complexes may have a much more serious effect. C_M is varied, and the apparent absorption coefficient ε is measured. Then

$$\frac{C_L}{\varepsilon - \varepsilon_0} = \frac{[M]}{\varepsilon_1 - \varepsilon_0} + \frac{1}{(\varepsilon_1 - \varepsilon_0)\beta_1}(1 + \beta_1 C_L) \quad (6)$$

and

$$[M] \approx C_M/(1 + \beta_1 C_L) \quad (7)$$

The left member of eqn. (6) is first plotted *vs.* C_M, and a first value of β_1 is obtained. When necessary the plot is repeated using values of [M] obtained from eqn. (7).

EXPERIMENTAL

Chemicals. All chemicals used were of analytical grade, when available. Sodium perchlorate solutions were prepared as described earlier.[8] Sodium iodide solutions were prepared by weighing the salt (Mallinckrodt), dried at 120°C. Samples gave the calculated amount of I within 0.1 %, when titrated with $AgNO_3$.

Cobalt salts. $Coen_3Cl_3$ was prepared as described in the literature.[9] From a solution of the chloride the corresponding iodide was precipitated by sodium iodide, recrystallized several times, washed and dried at 120°C. A sample was analyzed for C and N (by the Department of Analytical Chemistry, Chemical Center, Lund). Found: 11.6 % C, 13.6 % N. Silver nitrate titrations (see below) of several samples gave an average of 61.2 ± 0.2 % I. Calculated for $Coen_3I_3$: 11.62 % C, 13.56 % N, 61.4 % I.

$Coen_3(ClO_4)_3$ was prepared from the iodide: the salt was slurried in *ca.* 6 M $HClO_4$. A vigorous air stream rapidly oxidized I^- and expelled the formed iodine. The perchlorate was recrystallized several times, washed and dried. Its absorption spectrum was in agreement with those given in the literature.[10] The potential *explosion risk* of $Coen_3(ClO_4)_3$ should be noted.[11]

Solubility measurements. Solutions, composed of C_L M NaI and $I - C_L$ M $NaClO_4$, (or only C_L M NaI) were equilibrated with $Coen_3I_3$(s) or $Coen_3(ClO_4)_3$(s) at 25°C in a solubility column, as described earlier.[6,8] Black tape was wound around the column to protect the solid and the solutions from light. It was checked frequently that equilibrium was really reached. Two samples of each solution were equilibrated, with results normally in agreement within 0.5 %.

The equilibrated solutions were analyzed spectrophotometrically after proper dilution with a solution of the same C_L and I. For calibration purposes, the absorbances of solutions of known C_M and varying C_L were determined. (These measurements are in fact those described as the "L-method" in the preceding paper.[4]) As suitable wavelengths

were chosen 300, 320, and 340 nm when $I = 1$ and 2 M, 340 and 470 nm when $I = 4$ M. There was no difference in the solubilities, as obtained at different wavelengths.

$Coen_3I_3(s)$, treated with various solutions, was analyzed for I in the following way. A sample was washed with 95 % ethanol and ether, dried and weighed. Since additional washing did not change the weight or I content, this procedure was assumed to be sound. The samples were dissolved in water, passed through a cation exchanger in the sodium form, and titrated with silver nitrate, using dichloro fluorescein as indicator. As Table 1 shows, the salt had the calculated iodide content over the entire range of [L] employed, for the ionic strengths 1 and 2 M, while, at 4 M ionic strength, low iodide contents were found when $[L] \leq 1.0$ M. Evidently, small amounts of ClO_4^- enter the solid phase as a result of the high ratio $[ClO_4^-]/[I^-]$ of the solution. Solubilities from this region consequently should not be used.

Table 1. Iodide content in $Coen_3I_3(s)$, equilibrated with solutions of various compositions. Reproducibility ± 0.3 %.

Ionic strength	1 M		2 M		4 M			
C_L, M	1.0	0.3	2.0	0.5	1.5	1.0	0.5	0
% I in solid	61.5	61.3	61.4	61.3	61.3	61.1	59.9	Trace

Spectrophotometric measurements. All absorbance measurements (including those mentioned above) were performed with a Zeiss PMQ II spectrophotometer, using quartz cells of carefully determined lengths. Water blanks were used, the absorbance of I^- being determined separately and introduced as a small correction. The perchlorate medium did not absorb at the wavelengths employed.

Since I_3^- absorbs strongly in the wavelength region studied,[12] the solutions were treated with nitrogen in order to retard the oxidation of I^- by air. Further, small amounts of sodium thiosulfate were added to the solutions prior to measurements. The concentration used, $[S_2O_3^{2-}] \approx 3 \times 10^{-5}$ M, effectively reduced traces of I_3^-, without otherwise affecting the spectra.[13] All solutions were filtered to remove dust particles. The solutions were protected from light as much as possible. The cell compartment was carefully thermostated to 25°C with water, and the spectrophotometer was placed in a room maintained at 25°C. The solutions were allowed to attain this temperature before the cells were filled. The absorbance readings were stable for at least 1 h.

For the measurements with the M-method the wavelengths 280, 290, and 300 nm were chosen. The solutions had the composition C_M M $Coen_3(ClO_4)_3$, C_L M NaI — $C_L \ll C_M$ — and $(I - 3C_M - C_L)$ M $NaClO_4$.

RESULTS

The solubility, S_{obs}, of $Coen_3I_3(s)$ in various media is given in Table 2. [L], $K_s(I)$, and the stability constants were calculated according to eqns. (1) and (2). At all ionic strengths, a good fit was obtained if it was assumed that the complexes ML and ML_3 were formed. This may be judged from Figs. 1a – c, where $(S[L]^3 - K_s(I))\,[L]^{-1}$ is plotted *vs.* $[L]^2$. The plots are linear within the experimental errors. It is thus *not necessary* to include ML_2 and/or ML_n, $n > 3$, to explain the data. On the other hand, since experimental scatter is inevitable, the existence of these complexes in small amounts naturally cannot be excluded.

Table 2. Solubility of $Coen_3I_3(s)$ in various media. S_{obs} is experimentally determined, S_{calc} is calculated from the constants in Table 3.

C_L M	[L] M	$S_{obs} \times 10^3$ M	$S_{calc} \times 10^3$ M	Dev. %	C_L M	[L] M	$S_{obs} \times 10^3$ M	$S_{calc} \times 10^3$ M	Dev. %
$I = 1$ M					$I = 4$ M				
					0.800	0.812	6.01	(6.61)	(−9)
0.400	0.457	22.7	21.9	+3.7	1.200	1.205	2.930	2.942	−0.4
0.500	0.537	14.95	14.64	+2.1	1.600	1.603	1.866	1.845	+1.1
0.600	0.624	10.16	10.19	−0.3	2.000	2.002	1.412	1.392	+1.4
0.700	0.717	7.36	7.37	−0.2	2.400	2.402	1.156	1.165	−0.8
0.800	0.812	5.54	5.59	−0.9	2.800	2.801	1.028	1.036	−0.8
0.900	0.909	4.393	4.386	+0.2	3.20	3.20	0.957	0.956	+0.1
1.000	1.007	3.557	3.556	±0	3.60	3.60	0.903	0.903	±0
					4.00	4.00	0.867	0.866	+0.1
$I = 2$ M					Variable I				
0.500	0.548	20.10	19.99	+0.6	1.5	$\approx C_L$	2.182		
0.600	0.633	14.12	14.20	−0.5	2.0		1.582		
0.700	0.724	10.44	10.42	−0.2	2.5		1.285		
0.800	0.817	7.93	7.95	−0.2	3.0		1.109		
0.900	0.913	6.22	6.25	−0.5	3.5		0.977		
1.000	1.010	5.05	5.07	−0.4	4.0		0.867		
1.200	1.206	3.580	3.576	+0.1	4.5		0.804		
1.400	1.405	2.739	2.719	+0.7	5.0		0.741		
1.600	1.603	2.200	2.187	+0.6	5.5		0.714		
1.800	1.803	1.842	1.835	+0.4	6.0		0.682		
2.000	2.002	1.582	1.593	−0.7					

Table 3 shows the various constants found. The solubilities, S_{calc}, calculated from these constants are also given in Table 2, as well as the percentual deviations $100(S_{obs} - S_{calc})/S_{calc}$. The increased deviation at low [L] when $I = 1$ M can be partly explained as a result of the increase in $I = [ClO_4^-] + [I^-]$ due to the high solubility. It was actually shown that if $[ClO_4^-]$ was decreased to give a more constant I, the percentual deviation was de-

Table 3. Constants obtained from solubility measurements, with estimated errors.

Salt	I M	$K_s \times 10^3$ M^4	$K_s\beta_1 \times 10^3$ M^3	$K_s\beta_3 \times 10^3$ M	β_1 M^{-1}	β_3 M^{-3}
$Coen_3I_3(s)$	1	1.23 ± 0.03	1.75 ± 0.03	0.63 ± 0.05	1.42 ± 0.05	0.51 ± 0.05
	2	1.60 ± 0.05	2.9 ± 0.1	0.67 ± 0.04	1.8 ± 0.1	0.42 ± 0.04
	4	1.65 ± 0.05	1.85 ± 0.15	0.725 ± 0.020	1.12 ± 0.09	0.44 ± 0.03
$Coen_3(ClO_4)_3(s)$	4	1490 ± 10	1640 ± 80	–	1.10 ± 0.05	–

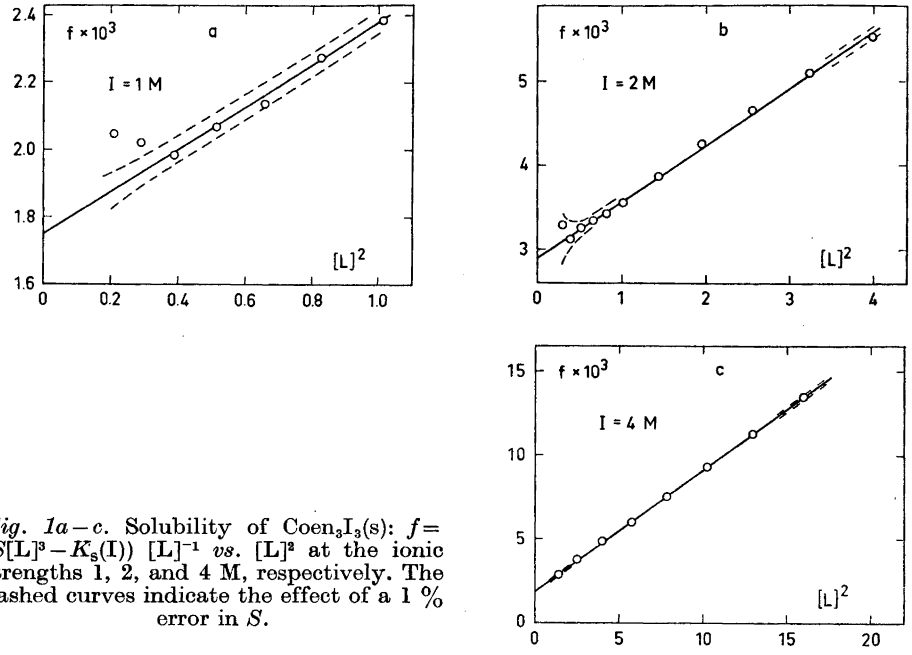

Fig. 1a–c. Solubility of $Coen_3I_3(s)$: $f = (S[L]^3 - K_s(I))\ [L]^{-1}$ *vs.* $[L]^2$ at the ionic strengths 1, 2, and 4 M, respectively. The dashed curves indicate the effect of a 1 % error in S.

creased (but not eliminated). Moreover, the high solubility makes the calculation of [L] uncertain (eqn. (2)), and thus, since ε depends on [L], also S itself grows uncertain.

At 4 M ionic strength, the solubility was lower than calculated, when $[L] \leq 1$ M. This is a result of the instability of the solid phase (see Experimental).

The solubility of $Coen_3I_3(s)$ in sodium iodide shows no tendency to pass through a minimum (Table 2). Since the ionic strength was not kept constant, no calculations based on these data have been attempted.

Table 4 shows the solubility of $Coen_3(ClO_4)_3$ as a function of [L] at 4 M ionic strength. (Actually, $I = [L] + [ClO_4^-] = 4$ M *initially*. Due to the high

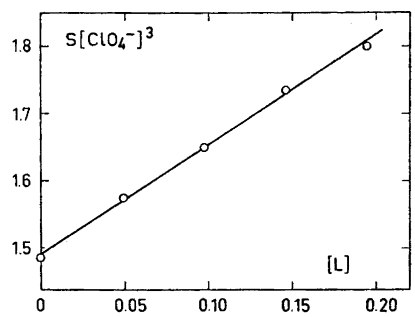

Fig. 2. Solubility of $Coen_3(ClO_4)_3(s)$ at 4 M ionic strength: $S[ClO_4^-]^3$ *vs.* [L].

Table 4. Solubility of $Coen_3(ClO_4)_3(s)$ at 4 M ionic strength. S_{obs} is experimentally determined, S_{calc} is calculated from the constants in Table 3.

C_L M	[L] M	$[ClO_4^-]$ M	$S_{obs} \times 10^3$ M	$S_{calc} \times 10^3$ M	Dev. %
0.000	0.000	4.066	22.08	22.22	−0.3
0.050	0.0488	4.023	24.20	24.12	+0.3
0.100	0.0974	3.979	26.17	26.19	−0.1
0.150	0.1460	3.935	28.48	28.38	+0.3
0.200	0.1945	3.892	30.54	30.69	−0.5

solubility, the ionic strength at equilibrium had increased to 4.08 ± 0.01 M.) As shown in Fig. 2, $S[ClO_4^-]^3$ *vs.* [L] is a straight line within the experimental errors (eqns. (3) and (4)). Assuming the values of β_3 given above (Table 3) to be correct, it can be shown that $[ML_3]$ is completely negligible also at the highest [L] of Table 4. The intercept and slope in Fig. 2 thus give $K_s(ClO_4)$ and $K_s(ClO_4)\ \beta_1$, respectively (eqn. (3)). The two solubility methods employed at $I = 4$ M give β_1 values of excellent agreement (Table 3).

Data from the spectrophotometric measurements are given in Table 5 ($I = 1$ M) and 6 ($I = 0.5$ M). Plots according to eqn. (6) give the values of $\varepsilon_1\beta_1$ and β_1 recorded in Table 7. At $I = 1$ M, the values of $C_L/(\varepsilon - \varepsilon_0)$ for the two values of C_L concurred within the experimental error. Only one β_1 at each wavelength is therefore given. The uncertainties in β_1 given in Table 7 have been estimated from the errors in the absorbances. The better agreement of the β_1 values obtained at different wavelengths is probably accidental.

Table 5. Spectrophotometric measurements. Absorbances (cell length 1.000 cm) at 1 M ionic strength for different ligand concentrations: $C_L = 10.00 \times 10^{-3}$ M (A_{10}), 5.00×10^{-3} M (A_5) and 0 (A_0). The absorbances are corrected for the slight absorption by I^-.

$C_M \times 10^3$	280 nm			290 nm			300 nm		
M	A_{10}	A_5	A_0	A_{10}	A_5	A_0	A_{10}	A_5	A_0
40.0	0.991	0.676	0.359	0.768	0.482	0.199	0.919	0.684	0.450
60.0	1.450	1.000	0.538	1.120	0.710	0.299	1.353	1.014	0.675
80.0	1.906	1.310	0.718	1.463	0.929	0.398	1.778	1.334	0.900
100.0	2.351	1.622	0.902	1.790	1.143	0.498	2.190	1.657	1.125

Measurements were also attempted at 2 M and 4 M ionic strength. Since the limited solubility of $Coen_3(ClO_4)_3(s)$ did not permit high enough C_M to be employed, no reproducible values of β_1 could be obtained. These measurements gave, however, rough estimates of $\varepsilon_1\beta_1$ (Table 7).

Table 6. Spectrophotometric measurements. Absorbances (cell length 1.000 cm) at 0.5 M ionic strength for the ligand concentrations $C_L = 5.00 \times 10^{-3}$ M (A_5) and 0 (A_0). The absorbances are corrected for the slight absorption by I^-.

$C_M \times 10^3$ M	280 nm		290 nm		300 nm	
	A_5	A_0	A_5	A_0	A_5	A_0
40.0	0.651	0.349	0.554	0.198	0.741	0.449
60.0	1.102	0.521	0.812	0.297	1.094	0.673
80.0	1.442	0.696	1.057	0.396	1.439	0.897
100.0	1.777	0.870	1.293	0.496	1.776	1.122

Table 7. Constants obtained from spectrophotometric measurements.

Medium	0.5 M			1 M			2 M	4 M
Wavelength, nm	280	290	300	280	290	300	300	300
$\varepsilon_1\beta_1$	2220	1950	1620	1730	1550	1280	≈1040	≈1000
β_1 M^{-1}	2.11	2.16	2.11	1.73	1.71	1.74	–	–
β_1 (average)	2.13 ± 0.10			1.73 ± 0.15			–	–
ε_1	1040	910	760	1000	900	740	570[a]	900[a]

[a] Obtained using β_1 from solubility measurements (Table 3).

DISCUSSION

The β_1 values shown in Tables 3 and 7 can be summarized as follows. At 4 M ionic strength, two solubility methods have been employed giving β_1 values of excellent agreement. At 1 M ionic strength, β_1 has been obtained from solubility and spectrophotometric measurements. The agreement is acceptable. At 2 M and 0.5 M, only one method of investigation has been employed.

Table 8. Values of ε_0, the absorption coefficient of $Coen_3^{3+}$, at different wavelengths and perchlorate ion concentrations.

Medium	280 nm	300 nm	340 nm
0.5 M	8.7	11.22	–
1 M	9.0	11.25	76.7
2 M	9.0	11.4	78.5
4 M	11.1	11.7	79

As mentioned, the product $\varepsilon_1\beta_1$ could be determined at all ionic strengths (Table 7). When ε_1 is computed, using these $\varepsilon_1\beta_1$ values and the various β_1 values, it appears that, at 0.5 and 1 M ionic strengths, where spectrophotometric β_1 can be used, essentially the same values of ε_1 are obtained, while, at 2 M and 4 M, where β_1 from solubility had to be used, the ε_1 values were different from those at 0.5 and 1 M (Table 7).

It was also found that ε_0, the absorption coefficient of $Coen_3^{3+}$, showed a slight increase with increasing $[ClO_4^-]$, more pronounced at lower wavelengths (Table 8). This quite clearly indicates some interaction between $Coen_3^{3+}$ and ClO_4^-. It is therefore natural to see what effect such an interaction might have on the $Coen_3^{3+} - I^-$ complex formation.

Assume $Coen_3^{3+}$ and ClO_4^- form a complex $MClO_4$, stability constant γ_1. (Higher complexes are not likely to be formed. The neglect of mixed complexes is perhaps more dubious.) The solubility of $Coen_3I_3$(s) or $Coen_3(ClO_4)_3$(s) will then be (*cf.* eqns. (1) and (3))

$$S = [M] + [MClO_4] + [ML] + \ldots$$

Since $[ClO_4^-] = I - [L]$ (provided $S \ll I$):

$$S = [M](1 + \gamma_1 I + (\beta_1 - \gamma_1)[L] + \ldots) \qquad (8)$$

Depending on the salt used, $[M] = K_s(I)[L]^{-3}$ or $[M] = K_s(ClO_4)[ClO_4^-]^{-3}$. The observed constant, β_1(obs), believed to be the stability constant of ML, would then in reality be, according to eqn. (8)

$$\beta_1(\text{obs}) = \frac{\beta_1 - \gamma_1}{1 + \gamma_1 I} \quad \text{(solubility)}$$

where β_1 in the right member is the "true" β_1.

The corresponding adjustment of the spectrophotometric equations is more lengthy, so only the results are given:

$$\varepsilon_1(\text{obs}) = \varepsilon_1 \qquad \text{(M-method)}$$

$$\beta_1(\text{obs}) = \frac{\beta_1}{1 + \gamma_1 I} \quad \text{(M-method)}$$

Solubility and spectrophotometry would thus give different values of β_1(obs). That so was actually found at $I = 1$ M is in accord with this hypothesis. It can be readily shown that $\beta_1 = 2.5$ and $\gamma_1 = 0.45$ fit the data at $I = 1$ M. The concurrent values of β_1(obs) obtained by the two solubility methods at $I = 4$ M are also in accord with the hypothesis. Moreover, if we assume ε_1 to be independent of I (as indicated at $I = 0.5$ M and 1 M), we can estimate what β_1(obs) the M-method would have given at $I = 4$ M:

$$\frac{\varepsilon_1\beta_1(\text{obs})}{\varepsilon_1(\text{obs})} = \beta_1(\text{obs}) \approx \frac{1000}{750}$$

Thus

$$\frac{\beta_1}{1 + \gamma_1 I} = 1.3 \qquad \text{(M-method)}$$

Since

$$\beta_1(\text{obs}) = \frac{\beta_1 - \gamma_1}{1 + \gamma_1 I} = 1.11 \qquad \text{(solubility)}$$

the data at 4 M also agree with the hypothesis of a $Coen_3^{3+} - ClO_4^-$ complex. It is more difficult, however, to fit the constant at 2 M ionic strength ($\beta_1(\text{obs}) = 1.8$) into the scheme. The estimated result of the M-method at $I = 2$ M is $\beta_1(\text{obs}) \approx 1.4$. Before more conclusive evidence is obtained the question whether perchlorate complexes are formed or not has to be left unanswered. However, taking the above estimations for what they might be worth, the following "true" β_1 values are obtained: 2.6, 2.5, 2.6, and 3.7 at 0.5, 1, 2, and 4 M ionic strength, respectively. The trend is in accord with what other authors have found on various systems.[14-16]

Evans and Nancollas[3] obtained, using the M-method, $\beta_1 = 8.5$ M^{-1} at the ionic strength 0.3 M, which is in reasonable agreement with the results of the present study.

It can be shown that a slight complex formation between $Coen_3^{3+}$ and ClO_4^- would in no way alter the conclusions in the preceding paper[4] about the unreliability of the L-method.

An interesting feature of the above results is the occurrence of a complex ML_3, while the second complex is apparently absent. It is unfortunate that the region of high [L] could by studied only by the solubility method. However, as shown in the preceding paper,[4] the fact that the L-method gives completely wrong β_1-values, is *clear evidence* that higher complexes are involved. Moreover, several facts indicate that the solubility results are reliable. The most important indication is the fact that the same picture of the complex formation is obtained at the three different ionic strengths (Figs. 1 a–c). Further, if we look at the constant $K_s(I) \times \beta_3$, we find a value that is essentially independent of the ionic strength. This is what should be expected, since $K_s(I) \times \beta_3$ refers to the equilibrium

$$ML_3(s) \rightleftharpoons ML_3(aq)$$

where no ions are involved. Thirdly, the check of the composition of the solid phase (p. 3755) eliminates one possible source of error. The risk of changes in the solid phase would, though, be small at the high [L] where ML_3 is studied.

The shape of the $Coen_3^{3+}$ ion might give some indication as to why $Coen_3I_3$ is preferred to $Coen_3I_2^+$: the ion looks like a "propeller", the chelate ligands acting as three "blades". It does not seem unreasonable that a configuration with three iodides between the ligands would be more stable than one with one iodide at each end of the complex. Some interesting features of the crystal structure[17] of $Coen_3Cl_3$ (no description of the iodide has been found in the literature) may be noted in this connexion. The three chloride ions are indeed placed between the chelate ligands. The smallest N–Cl distance is 3.1 Å, which is quite close, bearing in mind that the crystallographic radius of Cl^- is 1.8 Å and that one of the hydrogen ions of the NH_2 group is directed approximately towards the Cl^- ion. Hydrogen bond formation is suggested.[17] However, halide ions are reported[18] to have little effect on the PMR spectrum of $Coen_3^{3+}$.

To shed more light on the problem, an investigation of the hexammine-cobalt–iodide system is planned. A more regular trend in the strengths of the complexes would be expected. It would also be interesting to study the other halide systems of $Coen_3^{3+}$, or, perhaps better, as I^- is rather different to Br^- and Cl^- in size and polarizability, the iodide systems of ions similar to $Coen_3^{3+}$.

This work was supported by a grant from the *Swedish Natural Science Research Council*. The skilful technical assistance of Miss Irene Gustavsson and Mr. Bengt Falk is gratefully acknowledged.

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Received February 24, 1971.