Studies on Cobalt(II) Halide Complex Formation. II.

Cobalt(II) Chloride Complexes in 10 M Perchloric Acid Solution

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The stability constants K_1 and β_4 for the chlorocobalt(II) complexes in 10 M $H(Cl,ClO_4)$ aqueous solutions are calculated from spectrophotometric measurements to have the values $10^{1.34}$ l/mol and $10^{2.57}$ l^4/mol^4, respectively. The dichloro and trichloro complexes are shown to have a negligibly small range of existence. The greatly increased stability of the tetrachlorocobaltate(II) ion relative to that in dilute aqueous solutions can be accounted for entirely by the change in the chloride ion activity coefficient, and the general validity of so-called "effective formation constants" is discussed.

The change in colour of cobalt(II) chloride solutions from red to blue with increasing chloride concentration has been the subject of numerous studies, and it is now generally recognized that the colour change is caused by the reaction:

$$Co(H_2O)_6^{2+} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 6H_2O$$
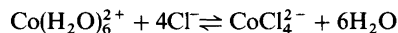
Chloride ion activities sufficiently large for almost complete conversion of the hexaaqua ion into the tetrachlorocobaltate(II) ion are reached in saturated aqueous solutions of lithium chloride and hydrochloric acid, and in a recent paper[1] the present authors have estimated values of the stepwise formation constants for the tetrachloro complex from spectrophotometric measurements. The latter study utilized the fact that the tetrachloro ion is the only complex absorbing in the wavelength range 610–690 nm for chloride concentrations higher than 5 M. Activity corrections were included semiquantitatively by means of a one-parameter function for the chloride ion activity, and using the

concept of effective stepwise formation constants[2] it was shown that a common set of activity constants is valid for the complex equilibria in solutions of cobalt(II) in lithium chloride, calcium chloride and hydrochloric acid at high chloride ion concentrations ($C_{Cl^-} \gtrsim 5$ M).

Since the so-called effective stepwise formation constants are approximately equal to the true activity formation constants, they ought to be valid for any aqueous solution when combined with the appropriate activity function.

The chloro complex formation and the accompanying change in configuration of the complexes in cobalt(II) chloride solutions are strongly promoted by lowering the water activity.[2,3] In order to clarify this influence on the chloro complex formation and to prove the general validity of the effective stepwise formation constants, the stability constants in 10 M $H(Cl,ClO_4)$ medium were determined, in concentration terms, spectrophotometrically. In 10 M $HClO_4$ the water activity is less than 4 % of that in pure water.[4]

EXPERIMENTAL

Cobalt(II) hydroxide-carbonate from MERCK was dissolved in perchloric acid and cobalt(II) perchlorate was precipitated by addition of 70 % perchloric acid. The cobalt(II) perchlorate was dissolved in sufficient water and 70 % perchloric acid to give a perchloric acid concentration of 10.0 M. Cobalt(II)- and acid concentrations in the stock solutions were determined by standard complexometric and alkalimetric titrations, respectively. Perchloric acid and hydrochloric acid were of
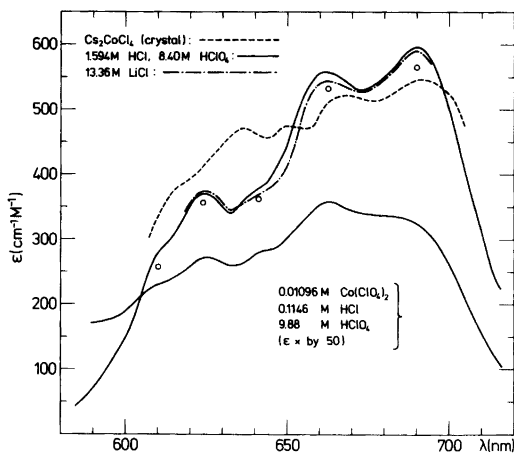
Fig. 1. Absorption spectra of $\sim 10^{-3}$ M Co(II) in 13.36 M LiCl[1] and in 1.594 M HCl plus 8.40 M HClO$_4$ compared with the solid state spectrum[5,6] of Cs$_2$CoCl$_4$ crystal (in arbitrary absorbance units). The O points indicate the molar absorptivities of the tetrachlorocobaltate(II) ion obtained from regression analysis at selected wavelengths; see text. The spectrum of 0.01096 M Co(ClO$_4$)$_2$ in 0.1146 M HCl + 9.88 M HClO$_4$ with the molar absorptivities multiplied by 50 is also shown.

analytical grade. The water used was doubly-distilled.

Densities were determined by weighing known volumes at 25 °C.

Spectrophotometric measurements were made on a Zeiss DMR 21 recording spectrophotometer using 1 and 5 cm cells thermostatted at 25.0 °C. Since the hydrogen-chloride vapour pressure over a 10.0 M acid solution is considerable, spectra were recorded immediately after mixing the solutions.

DETERMINATION OF STABILITY CONSTANTS

Formation of the tetrachlorocobaltate(II) ion is nearly complete in ≈ 13 M lithium chloride. As shown in Fig. 1, almost the same absorption spectrum is observed for a solution with hydrochloric and perchloric acid concentrations of 1.6 and 8.4 M, respectively. Fig. 1 also outlines the solid-state spectrum of Cs$_2$CoCl$_4$ which is known to contain tetrahedral tetrachlorocobaltate(II) ions. This spectrum (in arbitrary absorbance units[5,6]) displays the same characteristic absorption bands between 600 and 700 nm, although they are shifted

~ 5 nm towards longer wavelengths. It can thus be concluded that formation of the tetrachloro-cobaltate(II) ion in 10.0 M H(Cl,ClO$_4$) solutions is nearly complete at hydrochloric acid concentrations of around 1.6 M.

In order to determine the concentration stability constants in this medium, absorption spectra of a series of solutions of Co(ClO$_4$)$_2$ in 10.0 M H(Cl,ClO$_4$) were recorded. One such spectrum is shown in Fig. 1. The hydrochloric acid concentration ranged from *ca.* 0.07 to *ca.* 0.9 M. To ensure a fair constancy of the ionic medium, higher concentrations were not included in the series. After correction for the absorption of the medium, the apparent molar absorptivities (ε_λ) at the wavelengths $\lambda = 610, 624, 641, 662,$ and 690 nm were calculated for each solution.

The concentration stability constants in a constant salt medium are defined according to eqn. (1).

$$K_n = \frac{[\text{CoCl}_n^{2-n}]}{[\text{CoCl}_{n-1}^{3-n}][\text{Cl}^-]}, \text{ where } \beta_n = K_1 K_2 ... K_n \quad (1)$$

The following relationships are valid for each solution:

$$[\text{Cl}^-] = C_{\text{HCl}} - \sum_{n=1}^{4} n\beta_n [\text{Co}^{2+}][\text{Cl}^-]^n \quad (2)$$

$$[\text{Co}^{2+}] = C_{\text{Co(ClO}_4)_2} - \sum_{n=1}^{4} \beta_n [\text{Co}^{2+}][\text{Cl}^-]^n \quad (3)$$

$$\alpha_n = \frac{[\text{CoCl}_n^{2-n}]}{C_{\text{Co(ClO}_4)_2}} = \beta_n [\text{Cl}^-]^n \bigg/ \sum_{n=0}^{4} \beta_n [\text{Cl}^-]^n \quad (4)$$

$$\varepsilon_\lambda = \sum_{n=0}^{4} \alpha_n \varepsilon_{\lambda,n} \quad (5)$$

The experiments determine ε_λ as a function of the total concentrations C_{HCl} and $C_{\text{Co(ClO}_4)_2}$. For a given set of stability constants, $[\text{Cl}^-]$ and $[\text{Co}^{2+}]$ were calculated from C_{HCl} and $C_{\text{Co(ClO}_4)_2}$ [eqns. (2) and (3)] by Newton-Raphson iteration. Within the framework of non-linear regression analysis, the following expression was minimized as a function of the stability constants and the molar absorptivities for the complexes:

$$\sum_\lambda \sum_i \frac{[\varepsilon_{\lambda,i}(\text{calc}) - \varepsilon_{\lambda,i}(\text{obs})]^2}{\sigma_{\lambda,i}^2}$$

where the index *i* refers to solution-numbers. The uncertainties σ_λ were assumed to be proportional to the observed $\varepsilon_{\lambda,i}$ values.

Attempts to calculate the four stability constants and the molar absorptivities for the five species present showed that further information or certain assumptions had to be introduced. The ambiguities which arise in such simultaneous calculation of absorptivities and stability constants have recently been discussed by the present authors.[7] A preliminary calculation was therefore made based on the assumption that only the tetrachlorocobaltate(II) ion absorbs in the wavelength range of interest, justifying the use of the simple relationship: $\alpha_4 = \varepsilon_\lambda/\varepsilon_{\lambda,4}$. The spectrum of Co(II) in 0.1146 M HCl, 9.88 M HClO$_4$ (multiplied by 50; see Fig. 1) shows that this assumption is not of general validity under the present conditions. Not only the intensity but also the shape (especially the ratio $\varepsilon_{690}/\varepsilon_{662}$) of the absorption band changes with increasing chloride ion concentration. However, these preliminary calculations showed clearly that the species CoCl$_2$ and CoCl$_3^-$ have a negligibly small range of existence. This seems to be even more pronounced

in 10.0 M H(Cl,ClO$_4$) than in lithium chloride solutions.[1] Calculations based on eqns. (1)–(5) confirmed the validity of this assumption, and in the final calculations the dichloro and trichloro complexes were not taken into account. Table 1 gives the observed absorptivities together with the values calculated from the final numerical treatment at the three wavelengths 641, 662 and 690 nm. The resulting estimates of the stability constants are: log $K_1 = 1.34 \pm 0.11$ and log $\beta_4 = 2.57 \pm 0.09$. The molar absorptivity of the tetrachloro complex (ε_4) for the 5 wavelengths (given in Fig. 1 and Table 3) was obtained by regression analysis of the data for each wavelength. The molar absorptivities of Co^{2+} and CoCl$^+$ appear, within the estimated uncertainties, to be equal to zero at these wavelengths.

DISCUSSION

Spectra of chlorocobalt(II) complexes. These near-infrared ligand field spectra are not significantly influenced by the medium. For example, it can be seen from Table 3 and Fig. 1 that changing the salt medium from 13.4 M LiCl to 1.6 M HCl in

Table 1. Observed and calculated molar absorptivities (in cm^{-1} M^{-1}) of Co(II) in 10.0 M H(Cl,ClO$_4$) at 641, 662, and 690 nm.[a]

$C_{Co(ClO_4)_2}$	C_{HCl}	[Cl$^-$]	ε_{641} obs.	calc.	ε_{662} obs.	calc.	ε_{690} obs.	calc.
0.01147	0.0738	0.0669	1.52	1.50	1.78	1.77	1.45	1.46
0.01126	0.0905	0.0830	2.61	2.69	3.13	3.20	2.74	2.70
0.01096	0.1146	0.1064	5.57	5.56	7.14	7.04	6.48	6.39
0.01068	0.1374	0.1286	9.87	9.81	13.01	12.99	12.27	12.34
0.01059	0.1447	0.1357	11.56	11.53	15.51	15.43	14.64	14.81
0.01041	0.1590	0.1497	15.56	15.45	21.1	21.0	20.4	20.5
0.01016	0.1796	0.1697	23.1	22.4	31.6	31.0	30.8	30.7
0.00999	0.1928	0.1825	28.1	27.7	38.7	38.6	37.6	38.5
0.00968	0.218	0.207	40.1	39.6	55.7	55.8	54.9	56.2
0.00911	0.264	0.251	66.3	66.7	94.1	95.1	94.0	96.7
0.001526	0.361	0.358	144.0	147.3	208	212	210	217
0.001239	0.379	0.376	164.6	161.3	237	232	243	238
0.001526	0.397	0.393	176.0	173.9	250	251	254	257
0.001239	0.498	0.494	243	237	350	343	363	352
0.001239	0.548	0.544	261	261	376	377	394	388
0.001239	0.598	0.594	281	280	406	405	425	417
0.001239	0.647	0.643	291	295	424	427	444	439
0.001239	0.697	0.693	299	307	437	445	458	458
0.001239	0.796	0.791	317	325	463	471	491	485
0.001526	0.893	0.887	333	337	490	487	514	502

[a] ε(obs.) are apparent molar absorptivities based on the total Co(II) concentrations. ε(calc.) are calculated from the estimated stability constants and molar absorptivities for the complex ions; see text.

10.0 M $H(Cl,ClO_4)$ alters the molar absorptivities of $CoCl_4^{2-}$ by less than 3 %.

The molar absorptivities of $CoCl_4^{2-}$ calculated by regression analysis are as much as 6 % smaller than those measured directly in 10.0 M $H(Cl,ClO_4)$. This is only an apparent difference. It reflects accumulated errors from the rather lengthy extrapolation with $\alpha_4 \approx 0.90$ at the highest chloride ion concentration included in the final numerical treatment. A series of measurements on solutions with chloride ion concentrations varying up to 1.6 M was tentatively incorporated in the calculations. This treatment gave values for ε_λ which were a few percent higher but it was clear that the ionic medium had been changed too much to justify the use of the concentration constants defined according to eqn. (1).

The ratio $\varepsilon_{690}/\varepsilon_{625} \approx 1.55$ is constant in 7.0 M $Na(Cl,ClO_4)$ over a 1000-fold change in absorption, indicating that one species, the tetrachloro complex, is mainly responsible for the absorption in this wavelength range.[8] Almost the same value for this ratio is calculated from the limiting spectra measured with the other salt media quoted in Table 3, except for the spectrum in 9.0 M $H(Cl,ClO_4)$ reported by Belousov et al.[3]

Chloride ion activity. The overall effective formation constant determined previously[1] is assumed to approximate to the true activity constant:

$$\beta_4^* = \frac{[CoCl_4^{2-}]}{[Co^{2+}] a_{Cl^-}^4} \approx \frac{a_{CoCl4^{2-}}}{a_{Co^{2+}} + a_{Cl^-}^4}$$

By combining β_4^* ($= 10^{-6.62}$) with the concentration constant β_4 ($= 10^{2.57}$) valid in 10.0 M $H(Cl,ClO_4)$ it is possible to estimate the effective activity coefficient based on molar concentrations for the chloride ion in this actual medium:

$$\gamma_{Cl^-}^C = \sqrt[4]{\beta_4/\beta_4^*} \approx 200,$$

and it is satisfying that a similar estimate using the values for K_1 and K_1^* (see Table 2) leads to a value of the same order of magnitude.

A linear relationship between $\log \gamma_\pm^m$ and molality of an electrolyte in binary electrolyte mixtures at constant total molality is known as Harned's rule.[9] For γ_{HCl}^m (the mean activity coefficient based on molal concentrations) in an $H(Cl,ClO_4)$ medium this rule can be formulated as eqn. (6).

$$\log \gamma_{HCl}^m = \log \gamma_{HCl}^{m,o} - \varkappa_{HCl} m_{HClO_4} \tag{6}$$

Table 2. Comparison of stability constants for the cobalt(II) chloride system.

Medium	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log \beta_4$
10.0 M $H(Cl,ClO_4)^a$	1.34 ± 0.11				2.57 ± 0.09
10.0 M $H(Cl,ClO_4)^b$	0.82 ± 0.09	0.44	0.35	-0.17	1.43 ± 0.22
$LiCl - H_2O^c$	-1.05 ± 0.38	-2.69 ± 0.90	-1.54 ± 0.89	-1.34 ± 0.13	-6.62 ± 0.24

[a] This paper. Constants based on concentrations. [b] Belousov et al.[3] Constants based on concentrations. [c] Bjerrum et al.[1] Constants are effective constants, denoted in the text by an asterisk.

Table 3. Molar absorptivities of $CoCl_4^{2-}$ in $cm^{-1} M^{-1}$ at 25 °C.

Medium	ε_{610}	ε_{624}	ε_{641}	ε_{662}	ε_{690}	$\varepsilon_{690}/\varepsilon_{624}$
$LiCl - H_2O^a$	279	380	372	550	600	1.58
$HCl - H_2O^a$	279	380	380	560	610	1.61
1.59 M HCl 8.40 M $HClO_4$	277	370	378	557	597	1.61
10.0 M $H(Cl,ClO_4)^b$	258 ± 5	356 ± 5	362 ± 4	532 ± 5	564 ± 6	1.58
7.0 M $Na(Cl,ClO_4)^c$						1.55^c
9.0 M $H(Cl,ClO_4)^d$		180^d			615	3.42^d

[a] Extrapolated from data for solutions saturated with LiCl and HCl, respectively; see Ref. 1. [b] Calculated by nonlinear regression; see text. [c] From Ref. 8, ratio $\varepsilon_{690}/\varepsilon_{625}$. [d] From Ref. 3, ratio $\varepsilon_{690}/\varepsilon_{623}$.

where $\gamma_{HCl}^{m,o}$ is the activity coefficient for HCl in pure hydrochloric acid at the molality in question. $\varkappa_{HCl}$ denotes the Harned coefficient. 10.0 M HClO$_4$ has a density of 1.575 and a molality m of 17.5. The activity coefficient of HCl in 17.5 m HClO$_4$ is not known, but $\gamma_{Cl^-}^C \approx 200$ (corresponding to $\gamma_{HCl}^m \approx 200/1.75 = 114$) seems to be a reasonable assumption. From data in the literature[10] it can be estimated that $\gamma_{HCl}^{m,o} \approx 60$ in 17.5 m HCl. When these values for γ_{HCl}^m and $\gamma_{HCl}^{m,o}$ together with $m_{HClO_4} = 17.5$ are inserted in (6), $\varkappa_{HCl}$ is calculated to be -0.016. For comparison it can be mentioned that Harned's rule is known to be approximately valid in 1.0 m H(Cl,ClO$_4$), where $\varkappa_{HCl} \approx -0.020$.[11]

The remarkable increase in the stability of the tetrachlorocobaltate(II) ion which is observed can therefore be accounted for entirely by the dramatic change in the activity of the chloride ion. Fig. 2 shows the molar absorptivity of Co(II) at 624 nm as a function of increasing chloride ion activity. The curve is calculated from the effective constants and the molar absorptivity of the tetrachlorocobaltate-(II) ion. The measurements in lithium chloride and
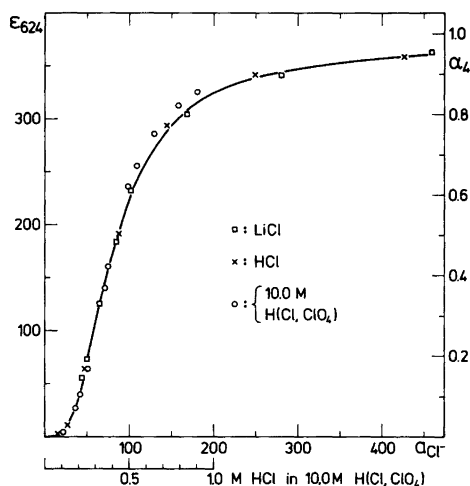

Fig. 2. The molar absorptivity of Co(II) at 624 nm as a function of chloride ion activity. The curve is calculated from the effective formation constants (see Table 2) and the molar absorptivity of CoCl$_4^{2-}$. The values for LiCl and HCl are from Ref. 1 and the chloride ion activity is calculated to be $a_{Cl^-} = [Cl^-] \times 10^{B[Cl^-]-0.5}$, with $B = 0.170$ and $B = 0.185$ in the case of LiCl and HCl, respectively. The measurement in 10.0 M H(Cl,ClO$_4$) is from the present investigation, and the chloride activity is calculated to be $a_{Cl^-} = 200[Cl^-]$.

in hydrochloric acid solutions are seen to follow this curve. With the estimated value of $\gamma_{Cl^-}^C \approx 200$ in 10.0 M H(Cl,ClO$_4$), the experimental absorptivities in this medium lie close to this same curve. This indicates the general validity of the effective formation constants.

Intermediate complexes. Smithson and Williams[8] showed the existence of CoCl$^+$ and CoCl$_4^{2-}$ species in 7.0 M Na(Cl,ClO$_4$) spectrophotometrically but found no intermediate complexes. The same conclusion can be drawn from the present calculations based on the measurement of the absorbance of Co(II) in 10.0 M H(Cl,ClO$_4$). In the previous investigation[1] of chlorocobalt(II) complex formation in lithium chloride solutions it was shown that the dichloro and trichloro complexes have a very small range of existence, and the calculated values for K_2^* and K_3^* were only crude estimates. The principal conclusion to be drawn concerning these two species, however, is that they can normally be neglected in calculations relating to aqueous solutions.

The above results contrast with the rather large range of existence for the dichloro and trichloro complexes which is predicted by the constants determined by Belousov et al.[3] in 10.0 M H(Cl,ClO$_4$) and the latter values are undoubtedly incorrect for aqueous solutions. However, a complex distribution of the type predicted by Belousov et al.[3] is observed in non-aqueous solvents such as acetic acid.[12] In acetone[13] and dimethyl sulfoxide[14] the dominant species have been shown to be CoCl$_3^-$ and CoCl$_4^{2-}$. These solvents have lower solvating power toward Co(II), and in addition to the different complex distribution a much stronger complex formation is found. In aqueous solution the entirely different distribution, with CoCl$^+$ and CoCl$_4^{2-}$ as the dominant complexes, does not seem to be significantly influenced by the bulk of electrolyte present.

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