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 $\beta_4$ for the chloro-
cobalt(II) complexes in 10 M H(ClO$_4$) aqueous solutions are calculated from spectrophotometric measurements to have the values $10^{1.34}$ l/mol and $10^{5.57}$ 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 concentra-
tion has been the subject of numerous studies, and it is now generally recognized that the colour
change is caused by the reaction:

$$\text{Co(H}_2\text{O)}^2^+ + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{2-} + 6\text{H}_2\text{O}$$

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 hydro-
chloric acid, and in a recent paper 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 it was shown that a common set of activity con-
stants is valid for the complex equilibria in solutions of cobalt(II) in lithium chloride, calcium chloride and hydrochloric acid at high chloride ion concen-
trations ($\text{Cl}^- \approx 5$ 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 accom-
panying change in configuration of the complexes in cobalt(II) chloride solutions are strongly pro-
duced by lowering the water activity. In order to
clarify this influence on the chloro complex forma-
tion and to prove the general validity of the effective
stepwise formation constants, the stability constants
in 10 M H(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.

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 com-
plexometric and alkalimetric titrations, respectively.
Perchloric acid and hydrochloric acid were of
Fig. 1. Absorption spectra of $\sim 10^{-3} \text{ M Co(II)}$ 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$_3$CoCl$_4$ crystal (in arbitrary absorbance units). The ○ 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 $\approx 13 \text{ M lithium chloride}$. 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$_3$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 $\sim 5 \text{ nm}$ towards longer wavelengths. It can thus be concluded that formation of the tetrachlorocobaltate(II) ion in 10.0 M H(ClClO$_4$) 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(ClClO$_4$) 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 ($\varepsilon_\lambda$) 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).

$$K_n = \frac{[\text{CoCl}_n^{2- \cdot n}]}{[\text{CoCl}_2^{2- \cdot 2}][\text{Cl}^-]^n}$$ \hspace{1cm} (1)

The following relationships are valid for each solution:

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

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

$$\alpha_n = \frac{[\text{CoCl}_n^{2- \cdot n}]}{C_{\text{Co(ClO}_4)_2}} = \beta_n[\text{Cl}^-]^n / \sum_{n=0}^{4} \beta_n[\text{Cl}^-]^n$$ \hspace{1cm} (4)

$$\varepsilon_\lambda = \sum_{n=0}^{4} \alpha_n \varepsilon_{\lambda,n}$$ \hspace{1cm} (5)

The experiments determine $\varepsilon_\lambda$ as a function of the total concentrations $C_{\text{HCl}}$ and $C_{\text{Co(ClO}_4)_2}$. For a given set of stability constants, $[\text{Cl}^-]$ and $[\text{Co}^{2+}]$ were calculated from $C_{\text{HCl}}$ 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:

$$\sum_{i} \sum_{j} \left[ \varepsilon_{ij}(\text{calc}) - \varepsilon_{ij}(\text{obs}) \right]^2 / \sigma_{ij}^2$$

where the index $i$ refers to solution-numbers. The uncertainties $\sigma_i$ were assumed to be proportional to the observed $\varepsilon_i$ 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. 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: 
\[ \varepsilon_i = \varepsilon_i^{(0)} \cdot \varepsilon_i \cdot \beta_i \] 

The spectrum of Co(II) in 0.1146 M HCl, 9.88 M HClO₄ (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 CoCl₂ and CoCl₃⁺ have a negligibly small range of existence. This seems to be even more pronounced in 10.0 M H(Cl,ClO₄) than in lithium chloride solutions. 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: 
\[ \log K_1 = 1.34 \pm 0.11 \] 
\[ \log K_2 = 2.57 \pm 0.09 \] 

The molar absorptivity of the tetrachloro complex ($\varepsilon_4$) 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 Co²⁺ 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>
<thead>
<tr>
<th>$C_{CoClO_4}^2$</th>
<th>$C_{HCl}$</th>
<th>$[Cl^-]$</th>
<th>$\varepsilon_{641}$</th>
<th>calc.</th>
<th>$\varepsilon_{662}$</th>
<th>calc.</th>
<th>$\varepsilon_{690}$</th>
<th>calc.</th>
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<td>261</td>
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<td>0.598</td>
<td>0.594</td>
<td>281</td>
<td>280</td>
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<td>0.643</td>
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<td>424</td>
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<td>0.693</td>
<td>299</td>
<td>307</td>
<td>437</td>
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<td>0.001239</td>
<td>0.796</td>
<td>0.791</td>
<td>317</td>
<td>325</td>
<td>463</td>
<td>471</td>
<td>491</td>
<td>485</td>
</tr>
<tr>
<td>0.001526</td>
<td>0.893</td>
<td>0.887</td>
<td>333</td>
<td>337</td>
<td>490</td>
<td>487</td>
<td>514</td>
<td>502</td>
</tr>
</tbody>
</table>

*($\varepsilon$(obs.) are apparent molar absorptivities based on the total Co(II) concentrations. ($\varepsilon$(calc.) are calculated from the estimated stability constants and molar absorptivities for the complex ions; see text.*

10.0 M H(Cl,CIO₄) alters the molar absorptivities of CoCl₂⁻ by less than 3%.

The molar absorptivities of CoCl₂⁻ calculated by regression analysis are as much as 6% smaller than those measured directly in 10.0 M H(Cl,CIO₄). This is only an apparent difference. It reflects accumulated errors from the rather lengthy extrapolation with x₄ ≈ 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 ε₄ 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 ε₉₉₀/ε₆₂₅ ≈ 1.55 is constant in 7.0 M Na(Cl,CIO₄) 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,CIO₄) reported by Belousov et al.³

Chloride ion activity. The overall effective formation constant determined previously¹ is assumed to approximate to the true activity constant:

\[ \beta_4^* \approx \frac{[\text{CoCl}_4^{2-}]}{[\text{Co}^{2+}] \cdot a_{\text{Cl}^-}^2} \]

By combining \( \beta_4^* \left( = 10^{-6.62} \right) \) with the concentration constant \( \beta_4 \left( = 10^{-2.57} \right) \) valid in 10.0 M H(Cl,CIO₄) it is possible to estimate the effective activity coefficient based on molar concentrations for the chloride ion in this actual medium:

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

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 \( \log \gamma_\text{Cl}^- \) and molality of an electrolyte in binary electrolyte mixtures at constant total molality is known as Harne's rule.⁹ For \( \gamma_\text{Cl}^- \) (the mean activity coefficient based on molar concentrations) in an H(Cl,CIO₄) medium this rule can be formulated as eqn. (6).

\[ \log \gamma_\text{Cl}^- = \log \gamma_{\text{Cl}^-}^\text{m} - x_{\text{Cl}^-} m_{\text{ClO}_4^-} \]  

(6)

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

<table>
<thead>
<tr>
<th>Medium</th>
<th>log ( K_1 )</th>
<th>log ( K_2 )</th>
<th>log ( K_3 )</th>
<th>log ( K_4 )</th>
<th>log ( \beta_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0 M H(Cl,CIO₄) ⁴</td>
<td>1.34 ± 0.11</td>
<td>0.44</td>
<td>0.35</td>
<td>-0.17</td>
<td>2.57 ± 0.09</td>
</tr>
<tr>
<td>10.0 M H(Cl,CIO₄) ⁴</td>
<td>0.82 ± 0.09</td>
<td>-2.69 ± 0.90</td>
<td>-1.54 ± 0.89</td>
<td>-1.34 ± 0.13</td>
<td>1.43 ± 0.22</td>
</tr>
<tr>
<td>LiCl - H₂O ⁵</td>
<td>-1.05 ± 0.38</td>
<td>-2.69 ± 0.90</td>
<td>-1.54 ± 0.89</td>
<td>-1.34 ± 0.13</td>
<td>-6.62 ± 0.24</td>
</tr>
</tbody>
</table>

⁴ This paper. Constants based on concentrations. ⁵ Belousov et al.⁴ Constants based on concentrations. ⁶ Bjerrum et al.¹ Constants are effective constants, denoted in the text by an asterisk.

**Table 3.** Molar absorptivities of CoCl₂⁻ in cm⁻¹ M⁻¹ at 25 °C.

<table>
<thead>
<tr>
<th>Medium</th>
<th>( \varepsilon ) ₆₁₀</th>
<th>( \varepsilon ) ₆₂₄</th>
<th>( \varepsilon ) ₆₄₁</th>
<th>( \varepsilon ) ₆₆₂</th>
<th>( \varepsilon ) ₆₉₀</th>
<th>( \varepsilon ) ₆₉₀/( \varepsilon ) ₆₂₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl - H₂O ⁴</td>
<td>279</td>
<td>380</td>
<td>372</td>
<td>550</td>
<td>600</td>
<td>1.58</td>
</tr>
<tr>
<td>HCl - H₂O ⁴</td>
<td>279</td>
<td>380</td>
<td>380</td>
<td>560</td>
<td>610</td>
<td>1.61</td>
</tr>
<tr>
<td>1.59 M HCl</td>
<td>277</td>
<td>370</td>
<td>378</td>
<td>557</td>
<td>597</td>
<td>1.61</td>
</tr>
<tr>
<td>8.40 M HClO₄ ⁴</td>
<td>277</td>
<td>370</td>
<td>378</td>
<td>557</td>
<td>597</td>
<td>1.61</td>
</tr>
<tr>
<td>10.0 M H(Cl,CIO₄) ⁴</td>
<td>258 ± 5</td>
<td>356 ± 5</td>
<td>362 ± 4</td>
<td>532 ± 5</td>
<td>564 ± 6</td>
<td>1.58</td>
</tr>
<tr>
<td>7.0 M Na(Cl,CIO₄) ⁴</td>
<td>258 ± 5</td>
<td>356 ± 5</td>
<td>362 ± 4</td>
<td>532 ± 5</td>
<td>564 ± 6</td>
<td>1.55</td>
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<tr>
<td>9.0 M H(Cl,CIO₄) ⁴</td>
<td>180d</td>
<td>615</td>
<td>3.42d</td>
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⁴ Extrapolated from data for solutions saturated with LiCl and HCl, respectively; see Ref. 1. ⁵ Calculated by nonlinear regression; see text. ⁶ From Ref. 8, ratio \( \varepsilon_{\text{690}}/\varepsilon_{\text{625}} \). ⁷ From Ref. 3, ratio \( \varepsilon_{\text{690}}/\varepsilon_{\text{625}} \).

where $\gamma_{HCl}^a$ is the activity coefficient for HCl in pure hydrochloric acid at the molality in question. $\kappa_{HCl}$ 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 $\gamma_{Cl^-} \approx 200$ (corresponding to $\gamma_{HCl}^a \approx 200/1.75 = 114$) seems to be a reasonable assumption. From data in the literature$^{10}$ it can be estimated that $\gamma_{HCl}^m \approx 60$ in 17.5 m HCl. When these values for $\gamma_{HCl}^a$ and $\gamma_{HCl}^m$ together with $m_{HClO_4} = 17.5$ are inserted in (6), $\kappa_{HCl}$ 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$_2$ClO$_4$)$_4$, where $\kappa_{HCl} \approx -0.020^{11}$.

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 

![Diagram](image)

**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 $a_{Cl^-} = [Cl^-] \times 10^{[Cl^-]^{-0.5}}$, with $B=0.170$ and $B=0.185$ in the case of LiCl and HCl, respectively. The measurement in 10.0 M H(Cl$_2$ClO$_4$)$_4$ is from the present investigation, and the chloride activity is calculated to be $a_{Cl^-} = 200[Cl^-]$.}


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**REFERENCES**


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