Outer-sphere Complex Formation between the Hexaamminecobalt(III) Ion and Bromide Ion in Aqueous Solution

LARS JOHANSSON

Division of Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The complex formation between Co(NH₃)₆³⁺ and Br⁻ has been studied at 25°C, at the constant ionic strengths (NaClO₄) I = 1 M and 4 M, and in NaBr of varying ionic strength. The solubility measurement data give evidence for the formation of outer-sphere complexes with one, two, and three bromide ions. At the constant ionic strengths, the following constants fit the data (errors within parentheses): I = 1 M: β₁ = 0.40(2) M⁻¹, β₂ = 0.04(2) M⁻², I = 4 M: β₁ = 0.43(5) M⁻¹, β₂ = 0.045(10) M⁻², β₃ = 0.006(4) M⁻³. Possible systematic errors are discussed. The results are compared with earlier studies on the same and similar systems.

This study is part of a series of investigations on outer-sphere complexes formed by inert complex cations. Previously, iodide complexes of Coen₃³⁺ and Co(NH₃)₆³⁺ have been studied.¹,² These systems differ in the respect that Coen₃³⁺ prefers one or three iodide ions while Co(NH₃)₆³⁺ forms iodide complexes in a more regular manner. The differences are thought to be due to the different shapes of the inert cations. If this is true, the hexaamminecobalt bromide system should be similar to the hexaamminecobalt iodide system.

The present system has been subject to several earlier studies.²⁻¹¹ The majority of these have dealt with the formation of the first complex only. However, Larsson ⁹ challenged the commonly adopted view that predominantly electrostatic forces are responsible for outer-sphere complex formation. For Co(NH₃)₆³⁺ and a number of ligands, including Br⁻, he attempted to show that a series of consecutive complexes is formed, and not only those explicable by electrostatic attraction. Thus, for Br⁻ it was inferred from anion exchange measurements that the complexes ML²⁺, ML₄⁺, ML₉ and ML₁₄⁻ were formed. Since the ionic strength could not be kept constant, no evaluation of stability constants was attempted.⁹

In the present investigation, the hexaamminecobalt bromide system has been studied by solubility measurements in mixtures of NaBr and NaClO₄ of constant ionic strengths (1 M and 4 M). A quantitative interpretation should

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then be possible. On the other hand, ClO₄⁻ probably forms, as discussed below, complexes with Co(NH₃)₆³⁺, a fact which affects the results of the measurements. To see if the picture is substantially different when ClO₄⁻ is omitted, at the cost of the constant ionic strength, the solubility has also been measured in pure NaBr. A closer comparison with Larsson's results⁹ is then also possible.

It would have been desirable to study this weak complex formation with different methods, but no suitable complement to the solubility measurements has been found. Spectrophotometric¹,¹² measurements, for instance, are rendered impracticable by the low solubility of Co(NH₃)₆(ClO₄)₃.

EXPERIMENTAL

**Chemicals.** Analytical grade chemicals were used when available. Co(NH₃)₆Cl₂ and Co(NH₃)₆(ClO₄)₂ were prepared and analyzed as described earlier.² Co(NH₃)₆Br₃ was precipitated from the chloride by HBr and recrystallized several times. Its bromide content was found to be 59.6(3) % (calculated 59.80 %).

**Solubility measurements.** Solutions were equilibrated in a saturator and analyzed spectrophotometrically as described earlier.² The same precautions as before were taken to assure good reproducibility. The wavelengths 470 and 340 nm were chosen when I=1 M, and 270 nm in the remainder of the measurements. The solubilities were reproducible within 1 % when I=1 M otherwise within 1−2 %. Below Cₗ=1.0 M (I=4 M) no reproducible solubilities could be obtained.

Samples of the solid phase were frequently withdrawn and analyzed for bromide in the same manner as described for iodide¹ (Table 1).

**Table 1.** Bromide content in the solid phase equilibrated with solutions of various compositions.

<table>
<thead>
<tr>
<th>Phase</th>
<th>I M</th>
<th>Cₗ M</th>
<th>% Br</th>
</tr>
</thead>
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<tr>
<td>ML₂</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>4</td>
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<td>59.3</td>
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<tr>
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<tr>
<td>MA₂</td>
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<tr>
<td>1</td>
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<td>0</td>
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</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>0</td>
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</tr>
</tbody>
</table>

**RESULTS, CALCULATIONS**

The same notation is used as in Refs. 1 and 2. For the two constant ionic strengths 1 M and 4 M, the observed solubilities are given in Tables 2 and 3, respectively. A striking difference between the present system and the iodide system² is the appearance of a well-defined intermediate phase, MB₃(CIO₄)(s), between MB₃(s) at high [Br⁻] and M(CIO₄)₃(s) at low [Br⁻]. As is obvious from Table 1, no solid solution formation¹ was observed. All three phases had,
Table 2. $I=1$ M. Solubilities: experimentally observed ($S_o$) and calculated from the constants of Table 4 ($S_o$ vs. bromide ([L]) and perchlorate ([A]) concentration. Deviation $= 100(S_o - S_c)/S_c$. Ligand number: by eqn. (4) or eqn. (5) ($\tilde{n}_o$) and calculated from the constants ($\tilde{n}_c$). Metastable points are marked (*).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_L$ M</th>
<th>$[L]$ M</th>
<th>$[A]$ M</th>
<th>$S_o \times 10^4$ M</th>
<th>$S_c \times 10^4$ M</th>
<th>Dev. %</th>
<th>$\tilde{n}_o$</th>
<th>$\tilde{n}_c$</th>
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<td>0.000</td>
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<td>0.965</td>
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<td>0.802</td>
<td>0.2014</td>
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<td>1.385</td>
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<td>0.700</td>
<td>0.702</td>
<td>0.3012</td>
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<td>0.702</td>
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<td>0.1922</td>
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Table 3. $I=4$ M. Cf. Table 2. Here, $[L] = C_L$ and $[A] = 4.000 - C_L$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_L$ M</th>
<th>$S_o \times 10^4$ M</th>
<th>$S_c \times 10^4$ M</th>
<th>Dev. %</th>
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<td>0.725</td>
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however, a tendency to be metastable just outside their stability ranges. Once a transition had started, though, it proceeded rapidly and completely, in the saturator. The phase transition points generally were approached both from

*Acta Chem. Scand. 27 (1973) No. 7*
high and from low \([\text{Br}^-]\). It was always possible to return over a phase transition point and, once the earlier phase was reestablished, obtain the same solubilities as before.

When \(I = 1\) M, some indications of the formation of the phase \(\text{MBr(ClO}_4\text{)}_2(s)\) around \(C_L = 0.45\) M were observed. Later attempts to confirm these findings failed, however. This could possibly be due to a persistent metastability of the adjacent phases, and we shall not exclude the possibility that \(\text{MBr(ClO}_4\text{)}_2(s)\) has a narrow range of existence between \(\text{MBr}_3\text{(ClO}_4\text{)}_2(s)\) and \(\text{M(ClO}_4\text{)}_3(s)\).

If \(\text{Br}^-\) is denoted by \(L\) and \(\text{ClO}_4^-\) by \(A\), the solubility of the solid phase \(\text{ML}_{j}\text{A}^{3-j}\) \((0 \leq j \leq 3)\) is given by

\[
S = K_s(j) \cdot X[L]^{-j} [A]^{i-3}
\]

(1)

where \(X = \sum_{n=0}^{N} \beta_n[L]^n\)

represents the complex formation in the solution, and \(K_s(j)\) is the solubility product. Complexes involving \(\text{ClO}_4^-\) are assumed to be absent.

At equilibrium, \([L]\) and \([A]\) may differ slightly from the initial values, \(C_L\) and \(I-C_L\):

\[
[L] = C_L + (j - \bar{n})S
\]

(2)

\[
[A] = I - C_L + (3 - j)S
\]

(3)

(See Tables 2 and 3.)

The minor changes in ionic strength have been neglected.

---

**Fig. 1.** 1 M ionic strength: \(\log S\) vs. \(\log [L]\). The points are the observed values; the curves are calculated from the constants given in Table 4. The left part is raised and conforms to the inner ordinate scale. Metastability is indicated by dashed curve and filled symbols.

**Fig. 2.** 4 M ionic strength: \(\log S\) vs. \(\log [L]\). See Fig. 1.

The slope of a plot of \(\log S\) vs. \(\log [L]\) (Figs. 1 and 2) yields important information \(^{13}\) on the complex formation as well as on changes in the solid phase. The following derivative is obtained from eqn. (1) (provided \(I = [L] + [A]\))

Thus, as soon as the composition (i.e. $j$) of the solid phase is known, $\bar{n}$ can be estimated from the slope of the solubility curve. A few $\bar{n}$ values estimated in this way are given in Tables 2 and 3.

For $\text{MA}_3$(s) it may be an advantage to plot $\log S$ vs. $\log [A]$. From eqn. (1) ($j = 0$) then

\[
\frac{d \log S}{d \log [A]} = -\left(\frac{\bar{n}}{[L]} + 3\right)
\]  

(5)

The limiting value of this derivative as $[L]$ approaches zero is $-(\beta_1 I + 3)$. When $I = 1$ M, the $\bar{n}$ values for $\text{MA}_3$(s) given in Table 2 were obtained from a plot of $\log S$ vs. $\log [A]$. The limiting value of the slope was $-3.4$, indicating a value of $\beta_1 \approx 0.4$.

As eqn. (4) shows, an intermediate phase like $\text{ML}_2\text{A}(s)$ may exhibit a minimum solubility, even if no complex formation takes place ($\bar{n} = 0$) or, as in the present case, $\bar{n}$ is small and varies only slightly. If no complexes were formed, the minimum would occur at $[L] = \frac{2}{3} I$; it is found here at somewhat lower values, $[L] \approx 0.65$ M and $[L] \approx 2.26$ M, when $I = 1$ and 4 M, the displacements being caused by the complex formation.

Close to a phase transition point, the slopes for both phases (characterized by $j_1$ and $j_2$, respectively) can be estimated at the same $[L]$. Eqn. (4) then gives

\[
D_1 - D_2 = (j_2 - j_1) \frac{I}{(I - [L])}
\]  

(6)

Thus, when $I = 1$ M, we find at $[L] = 0.89$ M $D_1 = 6.2(3)$ and $D_2 = -2.7(1)$ (estimated errors in the last digit given within parentheses). Hence, $j_2 - j_1 = 0.98(4)$. For $[L] = 0.45$ the slopes are $2.7(1)$ and $-0.92(3)$, respectively, giving a change in $j$ of $1.99(6)$. The corresponding changes in $j$ when $I = 4$ M are $0.96(4)$ and $2.0(2)$, respectively. The changes found by analysis of the solid phase (Table 1) are thus amply confirmed by the solubility data.

The stability constants were computed in the following way. According to eqn. (1)

\[
S[L][A]^{3-j} = K_s(j)X
\]  

(7)

$S$, $[L]$, and $[A]$ being known, $K_s(j)X$ can thus always be computed. When $I = 1$ M, $K_s(j)X$ was plotted vs. $[L]$ separately for the phases $\text{MA}_3$(s) and $\text{ML}_2\text{A}(s)$. Good straight lines resulted, thus implying that only the first complex, $\text{ML}$, is formed. However, the values of $\beta_1$ obtained were slightly different: 0.42(1) and 0.48(2). This fact, in conjunction with the findings when $I = 4$ M (below), leads one to conclude that also $\text{ML}_2$ is formed to a slight degree. It was found that an assumed value of $\beta_2 = 0.10 \beta_1$ (cf. 4 M ionic strength, Table 4) gave the same value of $\beta_1 = 0.40(2)$ for both phases, $\text{MA}_3$(s) and $\text{ML}_2\text{A}(s)$. The phase $\text{ML}_2$(s) has too narrow a range of existence to allow an independent evaluation of $\beta_1$ (and $\beta_2$). However, the $K_{s}(3)X$ values for this phase were divided by $X$, as calculated from the $\beta_1$ and $\beta_2$ values just obtained. The re-

resulting $K_s(3)$ showed no systematic variation. Thus, the ML$_3$(s) data also fit
to these stability constant values (Table 2).

When $I = 4$ M, only ML$_2$A(s) could be studied in a broad range of [L] (Fig. 2). For this phase, $K_s(2)X$ was plotted vs. [L]. Then, $K_s(j)X$ for MA$_3$(s) and ML$_2$A(s) were multiplied by suitable factors, $a$ and $b$ respectively, so that they fell on the same curve as $K_s(2)X$. From the resulting data set the constants $K_s(2)$, $\beta_1$, $\beta_2$, and $\beta_3$ were extracted (graphically). The other solubility products were obtained as

$$K_s(0) = K_s(2)/a \text{ and } K_s(3) = K_s(2)/b$$

As is obvious from Table 3, the data for all three phases fit to the common set of stability constants.

**Table 4.** Solubility products of Co(NH$_3$_5)Br$_2$(s), Co(NH$_3$_6)Br$_2$(ClO$_4$)(s), and Co(NH$_3$_6)Br$_2$(ClO$_4$)$_2$(s). Stability constants of the Co(NH$_3$_6)$^{3+}$$-$$Br^-$$ system. The estimated error of
the last digit is given within parentheses.

<table>
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<tr>
<th>$I$ M</th>
<th>$K_s(3) \times 10^a$ M</th>
<th>$K_s(2) \times 10^a$ M</th>
<th>$K_s(0) \times 10^a$ M</th>
<th>$\beta_1$ M$^{-1}$</th>
<th>$\beta_2$ M$^{-2}$</th>
<th>$\beta_3$ M$^{-3}$</th>
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<tbody>
<tr>
<td>1</td>
<td>1.34(2)</td>
<td>0.133(2)</td>
<td>0.193(1)</td>
<td>0.40(2)</td>
<td>0.04(2)</td>
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</tr>
<tr>
<td>4</td>
<td>3.3(2)</td>
<td>0.44(3)</td>
<td>1.32(10)</td>
<td>0.43(5)</td>
<td>0.045(10)</td>
<td>0.006(4)</td>
</tr>
</tbody>
</table>

From the solubility products now being known, [L] of the phase transition points can be determined. In a transition point, eqn. (1) is valid for both phases, with $S$, [A], and [L] and hence also $X$ equal. This gives the following expression

$$K_s(j_1)/K_s(j_2) = ([L]/[A])^{i_i}$$

By eqn. (8) it was found that MA$_3$(s) changes to ML$_2$A(s) for [L] = 0.455 M and ML$_2$A(s) changes to ML$_3$(s) for [L] = 0.915 M, when $I = 1$ M. The corresponding points at 4 M ionic strength are 1.46 M and 3.53 M.

**Table 4** summarizes the various constants obtained.

**Table 5.** Floating ionic strength. Solubility of Co(NH$_3$_6)Br$_2$(s) vs. bromide concentration:

\[ C_L \times 10^4; 4.0, 1.96; 3.5, 2.54; 3.0, 3.45; 2.5, 4.50; 2.0, 6.39; 1.5, 10.47; 1.0, 19.18. \]

The solubility of ML$_3$(s) in NaBr (floating ionic strength) is given in Table 5. In the plot of log $S$ vs. log [L] (Fig. 3), the slope tends to decrease with increasing [L]. This unexpected behaviour can be explained only by medium effects. Probably, it mainly reflects a maximum in the solubility product of ML$_3$(s) caused by the minimum in activity factors usually encountered around $I = 2$ M.\textsuperscript{16} It may be noted that the same trend was found in the Co(NH$_3$_6)$^{3+}$$ - $$[\Gamma^-]$$ system (Table 2 of Ref. 2: $[\Gamma^-] = 1$, 2, and 4 M).

Fig. 3. Floating ionic strength: log S vs. log [L]. Best curve drawn.

DISCUSSION

Table 6 shows the result of earlier determinations of $\beta_1$ in the hexaamminem-
cobalt bromide system. In addition, some more qualitative studies have been
reported.\textsuperscript{9–11}

Table 6. Earlier studies on the Co(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} – Br\textsuperscript{−} system at 25°C.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>$I$ M</th>
<th>$\beta_1$ M\textsuperscript{−1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bjerrum\textsuperscript{14,15}</td>
<td>Theory</td>
<td>0</td>
<td>66</td>
</tr>
<tr>
<td>Nancollas \textit{et al.}\textsuperscript{3,15}</td>
<td>Spectr.</td>
<td>0.054</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rightarrow$ 0</td>
<td>240</td>
</tr>
<tr>
<td>King \textit{et al.} (35°C) \textsuperscript{4}</td>
<td></td>
<td>0.9</td>
<td>$&lt; 0.2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rightarrow$ 0</td>
<td>$&lt; 5$</td>
</tr>
<tr>
<td>Tanaka \textit{et al.}\textsuperscript{5}</td>
<td></td>
<td>0.07</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rightarrow$ 0</td>
<td>9</td>
</tr>
<tr>
<td>Katayama \textit{et al.}\textsuperscript{4}</td>
<td>Cond.</td>
<td>0.3</td>
<td>45</td>
</tr>
<tr>
<td>Miranov \textit{et al.}\textsuperscript{7}</td>
<td>Soly.</td>
<td>$\sim$ 0.2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rightarrow$ 0</td>
<td>95</td>
</tr>
<tr>
<td>Heck\textsuperscript{8}</td>
<td>Spectr.</td>
<td>0.0120</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0048</td>
<td>37.7</td>
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<tr>
<td></td>
<td></td>
<td>0.0024</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rightarrow$ 0</td>
<td>60</td>
</tr>
</tbody>
</table>

In all studies summarized in Table 6, attempts have been made to assign
a value to $\beta_1$ at zero ionic strength. When these values are compared, it is
obvious that the spectrophotometric L-method gives, as explained earlier,\textsuperscript{12}
completely irrelevant values of $\beta_1$. Disregarding these values,\textsuperscript{4,5,8} the remainder
fall in the range 45 to 240 M\textsuperscript{−1}. Bearing in mind that none of the latter studies
are completely unambiguous, and that the extrapolations to zero ionic strength
are always more or less uncertain, the agreement is satisfactory. There is little
doubt that the correct value is positioned somewhere within this range.

\textit{Acta Chem. Scand.} 27 (1973) No. 7
With reference also to the present work, the spectacular decrease of $\beta_1$, when the ionic strength is increased from zero to $\approx 1$ M, is noted. At least three factors can be mentioned as possible causes of this decrease: the decrease of activity factors with increasing ionic strength, medium effects at constant ionic strength, and perchlorate association. The first is the most significant factor and is the one that should be eliminated on extrapolation to zero ionic strength. The other two may be termed systematic errors and have been discussed in detail earlier. In the present study, activity factors may change, at constant ionic strength, due to the exchange of NaClO$_4$ for NaBr. The effect is probably not negligible, as it was in the iodide case, but the crude estimates outlined indicate it to be of a modest magnitude ($\approx 10\%$ in $\beta_1$). Moreover, the medium effects in this case tend to increase the stability constants, the observed values being higher than the "true" ones.

Perchlorate association, on the other hand, necessarily decreases the observed stability constants. The effect is believed to be of some significance as far as $\beta_1$ is concerned. From a comparison with the measurements in perchlorate-free solutions (Table 5), no safe conclusions can be drawn about the perchlorate effect, as strong medium effects are evidently on hand here.

Regarding the higher complexes, ML$_2$ and, especially, ML$_3$, the effects of medium changes as well as of perchlorate association should reasonably be smaller. Therefore, there cannot be any doubt about the existence of these species. On the other hand, there is no indication of the formation of ML$_4$, either at constant (Fig. 2) or floating (Fig. 3) ionic strength. Actually, the curves are far from any minimum ($n = 3$) in both cases. It might be argued that the appearance of ML$_4$ is masked by perchlorate association and medium changes. However, it is difficult to imagine these effects to be of the required magnitude. It seems safe to conclude that ML$_4$ is formed only in negligible amounts for $[L] \leq 4$ M. This naturally does not mean to say that ML$_4$ cannot be formed. That question has to be left unanswered by the present measurements. The views held by Larsson are thus partially confirmed: species higher than ML do exist. It is probable, however, that the degree of complex formation at high ligand concentration, as inferred from the anion exchange measurements, is strongly overestimated.

The smooth decrease of $\beta_n$ as $n$ increases confirms the earlier findings that Co(NH$_3$)$_6^{3+}$ forms halide complexes in a more regular way than does Coen$_3^{2+}$.

In conclusion, the present study gives reliable evidence for the existence of ML$_2$ and ML$_3$. Together with a suitably weighted average value of $\beta_1$ at zero ionic strength (Table 6), this is believed to give a fairly true description of the hexaamminecobalt bromide system. From various lines of evidence it is inferred that ClO$_4^-$ associates to Co(NH$_3$)$_6^{3+}$ (and similar ions). A more quantitative knowledge of the degree of this association at different ionic strengths is lacking but would be very valuable.

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