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Outer-sphere Complex Formation between the Hexaammine-cobalt(III) Ion and Iodide Ion in Aqueous Solution

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The complex formation between $Co(NH_3)_6{}^{3+}$ and I^- has been studied at 25°C and at the constant ionic strengths ($NaClO_4$) $I=1$ M, 2 M, and 4 M, by solubility measurements. The 1:1 complex is formed at all ionic strengths. At 2 M and 4 M ionic strength, the formation of the 1:2 complex has been clearly demonstrated. This complex is probably of some importance also when $I=1$ M. The formation of even higher complexes, at high iodide concentration, is indicated.

Possible medium effects and perchlorate association have been discussed. While activity coefficient changes probably are of minor importance, perchlorate association probably occurs to some degree. The qualitative interpretation of the data is not changed by this possibility.

The data are consistent with the following constants (errors within parentheses):

$I=1$ M: $\beta_1=0.4(1)$ M^{-1}, $\beta_2=0.04(4)$ M^{-2}
$I=2$ M: $\beta_1=0.5(1)$ M^{-1}, $\beta_2=0.15(5)$ M^{-2}
$I=4$ M: $\beta_1=0.4(2)$ M^{-1}, $\beta_2=0.2(1)$ M^{-2}

In an earlier paper,[1] the results from a study of $Coen_3{}^{3+}-I^-$ outer-sphere complexes were reported. It was found that besides the 1:1 complex the 1:3 complex was formed as well at high iodide concentration. The 1:2 complex could not be detected.

The aim of the present study has been to study the system $Co(NH_3)_6{}^{3+}-I^-$, especially at high ligand concentration, to show whether or not higher complexes than the well-established 1:1 complex are formed also in this system. In view of the results on the ethylenediamine system just mentioned, particular attention has been paid to the relative strengths of the complexes formed. The hexaamminecobalt iodide system has been studied earlier by several authors.[3–11] Their interest has invariably been focussed on the 1:1 complex. A discussion of the results is given on p. 1643.

Compared to $Coen_3{}^{3+}-I^-$, the hexaamminecobalt iodide system is less suited for experimental study. The solubilities of $Co(NH_3)_6I_3$(s) and $Co(NH_3)_6(ClO_4)_3$(s) are low, making spectrophotometric measurements [1,2] impracticable and solubility measurements difficult, especially at high ionic strengths. The hexaamminecobalt ion is also less stable kinetically than the ethylenediaminecobalt ion (see Experimental).

The solubility of $Co(NH_3)_6I_3(s)$ has been studied at the ionic strengths 1, 2, and 4 M, $NaClO_4$ being used as supporting electrolyte. Attempts to study the solubility of $Co(NH_3)_6(ClO_4)_3(s)$ were not successful (see Experimental).

EXPERIMENTAL

Chemicals. Analytical grade chemicals were used, when available.

Cobalt salts. $Co(NH_3)_6Cl_3$ was prepared according to Bjerrum's [12] method. Samples of the salt were analyzed for Co spectrophotometrically, using the thiocyanate method, after boiling with NaOH and subsequent acidifying with HCl. Found 21.90 % Co, calculated for $Co(NH_3)_6Cl_3$ 22.05 % Cl. From the chloride, $Co(NH_3)_6(ClO_4)_3$ and $Co(NH_3)_6I_3$ were precipitated by $HClO_4$ and NaI, respectively, and recrystallized several times. A spectrum of the perchlorate dissolved in water was recorded. The following peak values were obtained: 56.6 M^{-1} cm^{-1} (475 nm) and 45.4 M^{-1} cm^{-1} (340 nm). Heck[13] reported 56.4 and 45.5 M^{-1} cm^{-1}, respectively. The iodide content of the hexaamminecobalt iodide was found to be 70.2 % (calculated 70.26 %).

Solubility measurements. (Notation, see Refs. 1 and 2.) Solutions, composed of C_L M NaI and $(I-C_L)$ M $NaClO_4$ ($I=1$, 2, or 4 M) were equilibrated with $Co(NH_3)_6I_3(s)$ at 25°C in a solubility column, as described earlier.[14,15] Black tape wound around the column protected the solid and the solutions from light. It was checked frequently that equilibrium was really reached. At least two samples of each solution were equilibrated, with results normally in agreement within 1 %($I=1$ M) or 2 % (2 M and 4 M). At the highest [L], when $I=4$ M, the reproducibility was poorer. On the other hand, several samples were equilibrated here, in order to improve the precision of the averages.

The equilibrated solutions were analyzed spectrophotometrically on a Zeiss PMQ II spectrophotometer. 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. For calibration purposes, the absorbances of solutions of known C_M and varying C_L were determined. As the solubilities were low, long cells (4 cm) had to be used, and special care had to be taken in order to assure reproducible results. Thus, to avoid the oxidation of I^- to I_3^-, all solutions were treated with nitrogen. Minute amounts of sodium thiosulfate were added to the solutions before measurement.[1] At first, high and not very reproducible absorbances were obtained for $NaClO_4-NaI$ mixtures, and consequently also for the calibration solutions. This was probably due, at least in part, to iodide complexes of metals present in the solutions as trace impurities, originating from the stock chemicals, and/or from dust particles. Satisfactory results were obtained when the following measures were taken. Stock solutions were prepared avoiding dust as much as possible. The sodium perchlorate solutions, prepared as described earlier,[15] were percolated through a cation exchanger, in the sodium form. A different brand of NaI (Merck *p.a.* or Suprapur) was used. At short wavelengths, large spreads were nevertheless obtained when $I=2$ or 4 M. As the cobalt absorption increased with decreasing wavelength, a compromise had to be reached. As an optimal wavelength, 320 nm was chosen when $I=2$ and 4 M. When $I=1$ M, 320 and 300 nm gave consistent solubilities.

The hexaamminecobalt ion is rather sensitive to light. It was found that in a solution with $C_M=0.2\times10^{-3}$ M, $C_L=1$ M, when exposed to daylight for a few hours, most of the cobalt had precipitated as hydroxide. On the other hand, if the same solution was completely protected from light, the absorbance changed less than 1 % in 4 h. The solutions were consequently always handled so as to minimize their exposure to light.

Samples of $Co(NH_3)_6I_3(s)$, treated with various solutions, were analyzed for I as described earlier [1] (Table 1). The time of contact between the solid and the solution was about equal to or somewhat longer than the normal contact time in the saturator. When $I=4$ M, the salt was apparently stable down to $C_L=1.0$ M, which seemed to be relatively low, compared to the corresponding values when $I=1$ M and 2 M. It was also found

Table 1. Iodide content in $Co(NH_3)_6I_3(s)$ treated with solutions of various compositions (calculated value 70.26 %).

C_L M	% I	C_L M	% I
$I = 1$ M		$I = 4$ M	
0.48	70.2	1.4	70.2
0.42	Trace	1.3	70.3
$I = 2$ M		1.2	70.4
		1.1	69.9
1.0	70.3	1.1[a]	55
0.9	70.0	1.0	70.3
0.8	70.0	0.9	Trace
0.7	Trace		

[a] Extended contact time; see text.

with one of the solutions ($I = 4$ M, $C_L = 1.1$ M) that a considerably longer contact time resulted in a lower I content in the solid (Table 1). Since the solid did not change during the normal contact time and the solubility in this range does not behave abnormally (Table 2), it may be concluded that $Co(NH_3)_6I_3(s)$ is metastable, probably in the range $1.0 \lesssim C_L \lesssim 1.3$ M, when $I = 4$ M.

At low iodide concentrations, $Co(NH_3)_6(ClO_4)_3(s)$ is the stable salt. Its low solubility, in conjunction with the low absorption coefficients at these low iodide concentrations, made it impossible to obtain reproducible solubilities of the perchlorate with the present technique. Moreover, the values obtained, however uncertain, were such that they could not be easily interpreted in terms of complex formation. The composition of the solid phase was constant. In view of their low precision, these measurements have been disregarded.

RESULTS, CALCULATIONS

The same notation is used as in Refs. 1 and 2. Table 2 shows the observed solubility, S_0, as a function of the solution composition. Stability constants have been calculated from these solubilities. Assuming activity factors to be constant and polynuclear complexes or complexes involving the inert salt to be absent (*cf.* Discussion on p. 1642), the following equation is valid:

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

When [L], the free ligand concentration in the saturated solutions, differs appreciably from the initial ligand concentration, C_L, it can be calculated by the equation

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

Since S is always much smaller than C_L, only rough estimates of the ligand number $\bar{n}$ are needed. S and [L] being known, $S[L]^3$ was computed (eqn. (1)) and treated graphically according to standard procedures, to yield K_s and the various β_n.

Table 2. Solubility of $Co(NH_3)_6I_3(s)$. S_0 is experimentally determined, S_c is calculated from the constants given in the text.

C_L M	[L] M	$S_0 \times 10^4$ M	$S_c \times 10^4$ M	Dev. %
		$I = 1$ M		
0.484	0.486	8.07	8.09	−0.3
0.520	0.5215	6.70	6.64	+0.9
0.544	0.545	5.81	5.87	−1.0
0.605	0.606	4.37	4.366	+0.1
0.665	0.666	3.36	3.364	−0.1
0.720	0.721	2.708	2.707	0.0
0.800	0.8005	2.047	2.037	+0.5
0.880	0.880	1.577	1.579	−0.2
1.000	1.000	1.125	1.125	0.0
		$I = 2$ M		
0.800	0.801	2.969	2.968	0.0
0.900	0.901	2.194	2.194	0.0
1.000	1.000	1.677	1.684	−0.4
1.100	1.100	1.347	1.329	+1.4
1.200	1.200	1.069	1.075	−0.5
1.300	1.300	0.893	0.887	+0.7

$C_L = [L]$ M	$S_0 \times 10^4$ M	$S_c \times 10^4$ M	Dev. %
	$I = 2$ M, ctd.		
1.400	0.738	0.744	−0.8
1.500	0.632	0.634	−0.3
1.600	0.552	0.546	+1.0
1.700	0.475	0.476	−0.3
1.800	0.433	(0.419)	
1.900	0.384	(0.373)	
2.000	0.351	(0.334)	
	$I = 4$ M		
1.100	0.835	0.842	−0.9
1.400	0.474	0.470	+0.8
1.700	0.309	0.302	+2.3
2.000	0.208	0.2125	−2.0
2.500	0.135	0.1352	−0.3
3.000	0.097	0.096	+1
3.500	0.083	(0.073)	
4.000	0.073	(0.058)	

For $I = 1$ M, the function $S[L]^3$ *vs.* [L] is shown in Fig. 1. The values follow closely a linear relationship, and it may be concluded that the free central ion and the first complex ML suffice to explain the data, *i.e.* $S[L]^3 = K_s + K_s\beta_1[L]$; $K_s = 7.41 \times 10^{-5}$ M^4 and $K_s\beta_1 = 3.82 \times 10^{-5}$ M^3 fit the line.

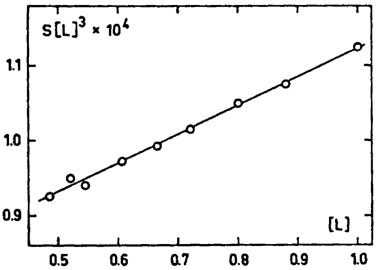

Fig. 1. 1 M ionic strength: $S[L]^3$ *vs.* [L] Straight line of best fit drawn (see text).

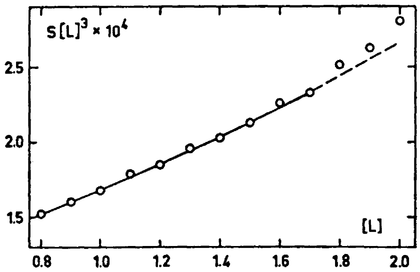

Fig. 2. 2 M ionic strength: $S[L]^3$ *vs.* [L]. The function is curved. The curve drawn is calculated from the constants given in the text.

However, the data at $I = 2$ and 4 M (below) show that also the second complex ML_2 is formed, at higher [L]. It is then natural to check whether the formation of ML_2 is consistent with the data at $I = 1$ as well. It was indeed found that an increase of the ratio β_2/β_1 from 0 to ≈ 0.25 did not affect the fit (error square sum assuming constant relative errors) significantly. The ratio $\beta_2/\beta_1 = 0.3$ (*cf.* values at $I = 2$ M) gave a slightly poorer fit. The values S_c in Table 2 are calculated assuming the constants to be $K_s = 7.72 \times 10^{-5}$, $K_s\beta_1 = 2.94 \times 10^{-5}$, and $K_s\beta_2 = 0.59 \times 10^{-5}$, *i.e.*, $\beta_2/\beta_1 = 0.2$. It is obvious, however, that the data at $I = 1$ M alone do not permit us to conclude whether only ML or both ML and some higher complex(es) are formed. This, of course, is due to the fact that $[ML_2]$ amounts to at most about 5 % of the total concentration of M. The important fact to notice, is, however, that β_1 is altered quite significantly, from 0.52 to 0.38, when β_2 is changed from its minimum to its maximum permissible value.

When $I = 2$ (Fig. 2) and 4 M, the function $S[L]^3$ *vs.* [L] is curved, and it may safely be concluded that complexes higher than the first are formed. In both cases a good fit is obtained except at the highest [L], when it is assumed that ML and ML_2 are formed. At the highest [L], the solubilities tend to higher values, thus indicating the formation of one or more complexes beyond ML_2. Since the data at high [L] (= low solubilities) are not very reliable, no attempts have been made to estimate the compositions or stabilities of these complexes. S_c of Table 2 are calculated assuming

$$K_s = 10 \times 10^{-5}\ M^4,\ K_s\beta_1 = 5.3 \times 10^{-5} M^3,\ K_s\beta_2 = 1.5 \times 10^{-5} M^2\ (I = 2\ M),\ \text{and}$$
$$K_s = 7.0 \times 10^{-5} M^4,\ K_s\beta_1 = 2.4 \times 10^{-5} M^3,\ K_s\beta_2 = 1.3 \times 10^{-5} M^2\ \ (I = 4\ M).$$

It should be noted, though, that since ML_3, *etc.*, have been neglected in the calculations at $I = 2$ and 4 M, in an analogous manner as ML_2 was neglected at $I = 1$ M (above), the β_2 values probably come out somewhat high.

That complexes higher than the first are formed can be inferred also from the spectrophotometric calibration data (not given). When such data are plotted according to eqn. (3) of Ref. 2, straight lines with slope $-\beta_1$ should result if no higher complexes are formed. In the present case, the slopes were very small, positive or negative, and varied erratically with the wavelength. As is elucidated in Ref. 2, this is a strong indication of the formation of complexes higher than ML.

An attempt to exclude ML_2, *i.e.* to fit the data ($I = 2$ M) with M, ML, and ML_3 only (and possibly higher complexes; *cf.* the $Coen_3^{3+} - I^-$ system [1]), did not give an acceptable fit.

Table 3. Constants obtained from the solubility data. The estimated error in the last digit is given within parentheses.

I M	$K_s \times 10^5$ M^4	β_1 M^{-1}	β_2 M^{-2}	Higher complexes
1	7.6(3)	0.4(1)	0.04(4)	
2	10(1)	0.5(1)	0.15(5)	Evidence
4	7(1)	0.4(2)	0.2(1)	Evidence

DISCUSSION

The study of such weak complexes as are encountered here is subject to several limitations. In the first place, in order to get any complex formation, it is necessary to change the medium, in this case from I M $NaClO_4$ to I M NaI. It is well known [16-18] that activity coefficients may then change despite the constant ionic strength.

In the present system, it may thus, perhaps, be asked if such medium effects alone are responsible for the solubility changes, or, as a milder alternative, if only the first complex is formed, the higher ones being artefacts due to the medium effects. It can be checked, firstly, if the experimental data are at all compatible with these hypotheses, secondly, if the required medium effects are of a reasonable magnitude.

When an electrolyte, ML, is substituted for another at constant ionic strength, activity coefficients usually follow [16] the (empirical) equation

$$\log y_{\pm} = \log y_{\pm}^0 + \alpha[\mathrm{L}] \tag{3}$$

where $y_{\pm}$ and $y_{\pm}^0$ are the mean activity coefficients at the given [L], and at $[\mathrm{L}]=0$, respectively, and α is a constant. Assuming (a) no complexes are formed and (b) only the first complex is formed, in the $Co(NH_3)_6^{3+} - I^-$ system, we find:

1. The data of Table 2 are at least roughly compatible with both hypotheses.

2. The following approximate α values for the variation in the mean activity coefficient of $Co(NH_3)_6I_3$ are required: (a) -0.045 ($I=1$ M), -0.05 ($I=4$ M); (b) -0.03 ($I=4$ M). Making the somewhat bold assumption that mean activity coefficients for different electrolytes vary approximately in the same way, we compare the given values with literature values.

Ginstrup [17] studied how $y_{\pm}$ for HCl varied when the composition of the background electrolyte was changed. *E.g.*, when $NaClO_4$ was exchanged for NaCl, $\alpha = -0.022$ was found. The α values are largely independent of the ionic strength. On the other hand, they are highly dependent on the nature of the exchanging electrolytes. For various halides, this is perhaps best illustrated by the data of Nilsson.[19] From the variation in solubility product of the thallium(I) halides, the following α values for $y_{\pm}$(TlL) may be computed: -0.018 ($NaClO_4$ − NaCl), -0.008 ($NaClO_4$ − NaBr) and $|\alpha| < 0.002$ ($NaClO_4$ − − NaI; the solubility product of TlI(s) did not change significantly between 4 M $NaClO_4$ and 4 M NaI). The chloride value [19] (for TlCl) is in good agreement with Ginstrup's [17] value (for HCl). The trend towards decreasing medium effect in the halide series is found also in other studies.[17,20-23] Therefore it seems safe to conclude that in the present study, medium effects, if present at all, are much smaller than those required by the above hypotheses.

Secondly, the study of weak complexes may be affected by *perchlorate ion association.* As has been briefly outlined earlier,[1] the basic equation (eqn. (1), p. 1639) is then still valid, but instead of the "true" constants β_n, composite constants are obtained. If only one perchlorate complex $MClO_4^{2+}$ is formed, its stability constant being γ_1, the composite constants $(\beta_1 - \gamma_1)/(1+\gamma_1 I)$, $\beta_2/(1+\gamma_1 I)$, *etc.* result. When, as in the present case, positive constants are obtained, it can be immediately concluded that even if $\gamma_1 > 0$, the corresponding β_n must also be > 0. In other words, the qualitative interpretation of the M − L system is still correct. It is also clear that it cannot be judged from the present data whether perchlorate complexes are formed or not. However, in the ethylenediaminecobalt iodide system,[1] data indicated a perchlorate association with $\gamma_1/\beta_1 \approx 0.2$. Heck[10,11,13] has studied various hexaamminecobalt systems spectrophotometrically; from his data at low ionic strengths a ratio γ_1/β_1 in the range 0.3 to 1.0 can be estimated. The higher limit is of course inconsistent with the data in the present investigation. However, it is most likely that $Co(NH_3)_6^{3+}$ and ClO_4^- do form associates to a significant degree. The "true" β_n are somewhat higher than those given in Table 3.

The perchlorate association is a medium effect, although of a different kind than the activity coefficient variation discussed above. As it is necessary sometimes to employ high ionic strengths, such medium effects are unavoidable. At first sight it may seem to be merely a matter of taste whether the apparent constants in the specific medium are reported or if "true" constants are sought. However, when only weak complexes are involved, different methods of study do not necessarily give the same composite constants.[1] This, on the one hand, provides a means of evaluating γ_1 and β_n independently. On the other hand, it makes it obvious that a constant cannot be reported as *the* constant, in the medium used; at least the method should also be specified.

Table 4. Earlier studies on the $Co(NH_3)_6^{3+} - I^-$ system at 25°C.

Reference	Method	I M	β_1 M^{-1}
Bjerrum[24,7]	Theory	0	66
Linhard[3]	Spectr.	Var.; ≤ 0.06	38[a]
Nancollas *et al.*[4,25]	»	0.054	17
»	»	$\rightarrow 0$	90
Kubota[5]	»	Var.; ≤ 0.1	16
Tanaka *et al.*[6]	»	0.07	0.7
»	»	$\rightarrow 0$	3
Katayama *et al.*[7]	Cond.	0	24
Mironov *et al.*[8]	Soly.	~ 0.2	0.5
»	»	$\rightarrow 0$	60
Yokoyama *et al.*[9]	Spectr.	0.06	9
Heck[11]	»	0.012	32
»	»	$\rightarrow 0$	60

[a] 17–22°C

Several authors have studied the hexaamminecobalt iodide system (Table 4). The ionic strength has been kept low in all studies. Consequently, only the first complex has been subject to study. Disregarding the results[6] obtained by the unreliable L-method,[2] the β_1 values are in fair, though not good, agreement. The strong decrease of β_1 with increasing ionic strength is noticeable.

In the present investigation attention has primarily been paid to the higher complexes. Therefore, high ionic strengths have been employed, and a closer comparison with the earlier studies is not possible. However, the present results, in conjunction with the earlier ones, give a fairly complete picture of the system.

To sum up, the present investigation adds the new information that, in the $Co(NH_3)_6^{3+} - I^-$ system, besides ML, also ML_2 and very probably some higher complex(es) are formed. The order of complex strength is more regular than in the $Coen_3^{3+} - I^-$ system.[1] Possible medium effects, probably of minor importance, or perchlorate association, probably more prominent, cannot invalidate these qualitative conclusions.

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