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

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The complex formation between racemic Co $\mathrm{pn_3}^{3+}$ and $\mathrm{I^-}$ has been studied at 25 °C at the constant ionic strengths ($\mathrm{NaClO_4}$) $I=1$ M and 4 M by potentiometric, spectrophotometric, and solubility methods. The following stability constant values were found (errors within parentheses), $I=1$ M: $\beta_1=1.7(1)\ \mathrm{M^{-1}}$; $I=4$ M: $\beta_1=1.9(1)\ \mathrm{M^{-1}}$, $\beta_3=0.62(15)\ \mathrm{M^{-3}}$. The results are compared with those reported earlier for tris(ethylenediamine)cobalt and hexaamminecobalt halide systems.

This study is part of a series of investigations on outersphere complexes formed by inert complex cations, with the emphasis on high ligand concentrations. Studies on Co $\mathrm{en_3}^{3+}-\mathrm{I^-}$, $\mathrm{Co(NH_3)_6}^{3+}-\mathrm{I^-}$ and $\mathrm{Co(NH_3)_6}^{3+}-\mathrm{Br^-}$ complexes have been reported earlier.[1-3] These systems differ in the respect that Co $\mathrm{en_3}^{3+}$ prefers one or three iodide ions, while $\mathrm{Co(NH_3)_6}^{3+}$ adds ligands more regularly. If this is due to the different symmetries of the cations, Co $\mathrm{pn_3}^{3+}$ is expected to behave like Co $\mathrm{en_3}^{3+}$. No detalied studies on the Co $\mathrm{pn_3}^{3+}-\mathrm{I^-}$ system have appeared in the literature.[4]

In the present investigation, potentiometric and spectrophotometric methods and solubility measurements have been employed, at the constant ionic strengths 1 M and 4 M, $\mathrm{NaClO_4}$ being used as supporting electrolyte. By ionic strength is as before [1-3] meant the sum of perchlorate and ligand concentrations.

EXPERIMENTAL

Chemicals. Analytical grade chemicals were used when available. Racemic Co $\mathrm{pn_3Cl_3}$ was prepared as described in the literature.[5] Co $\mathrm{pn_3I_3}$ was prepared from the chloride by repeated precipitation with NaI. Co $\mathrm{pn_3(ClO_4)_3}$ was obtained from the chloride by repeated precipitation with $\mathrm{HClO_4}$ until the salt was chloride free. It was recrystallized in ca 97 % ethanol. The potential *explosion risk* of Co $\mathrm{pn_3(ClO_4)_3}$ should be noted.[6]

The iodide was analyzed for I as described.[1] Found 57.3 % (calc. 57.50 %). In the visible, solutions of the iodide and perchlorate salts showed identical spectra, well in accord with literature data.[7]

Potentiometric measurements. In principle, the change in iodide concentration upon the addition of Co $\mathrm{pn_3}^{3+}$ was measured using the $\mathrm{I^-,I_3^-/Pt}$ electrode.[8] The element was constituted as follows (the same notation is used as in previous papers [1-3])

$$\mathrm{Ag,AgCl}\left|\begin{array}{l}0.01\ \mathrm{M\ NaCl}\\ \\ I-0.01\ \mathrm{M\ NaClO_4}\end{array}\right|\begin{array}{l}I\ \mathrm{M}\\ \\ \mathrm{NaClO_4}\end{array}$$

$$\left|\begin{array}{l}C_\mathrm{L}\ \mathrm{M\ NaI}\\ C_\mathrm{T}\ \mathrm{M\ NaI_3}\\ C_\mathrm{M}\ \mathrm{M\ Co\ pn_3(ClO_4)_3}\\ (I-C_\mathrm{L}-C_\mathrm{T}-3C_\mathrm{M})\ \mathrm{M\ NaClO_4}\end{array}\right|\mathrm{Pt}$$

$C_\mathrm{T}\approx 1$ mM was obtained by adding a weighed amount of $\mathrm{I_2}$. Bright platinum foils were used as electrodes. C_L and C_M ranged from 0 to 0.1 M. The test solution was oxygen free, and the electrode vessel was kept stoppered to prevent iodine vapour leakage. The whole element was thermostated. The emf was measured by a Radiometer PHM 52 potentiometer.

The $\mathrm{I^-}$, $\mathrm{I_3^-/Pt}$ electrode is known to behave well.[8] The various electrode combinations normally gave identical and stable emfs.

Spectrophotometric measurements. The M-method, described earlier,[1,9] was employed. The solutions contained C_L M NaI, $0\leqslant C_\mathrm{L}\leqslant 0.01$ M, C_M M Co $\mathrm{pn_3(ClO_4)_3}$, $0\leqslant C_\mathrm{M}\leqslant 0.1$ M and $(I-C_\mathrm{L}-3C_\mathrm{M})$ M $\mathrm{NaClO_4}$. The absorbances were measured at the wavelengths 280, 290, 300, and 310 nm. For experimental details, see Ref. 1.

Solubility measurements. Solutions of the composition C_L M NaI, $(I-C_\mathrm{L})$ M $\mathrm{NaClO_4}$,

Table 1. Iodide content w_1 (weight percent; error ± 0.2 %) and mol fraction x_2 of Co $pn_3(ClO_4)_3$ in the salt equilibrated with solutions of various C_L ($I = 4$ M).

C_L M	w_1 %	$x_2 \times 10^3$
Theory	57.50	0
4.0	57.5	0
3.0	57.1	8
2.6	57.0	10
2.2	56.8	14
1.8	56.0	30
1.4	55.6	38
1.0	55.1	47
0.8	53.7	75

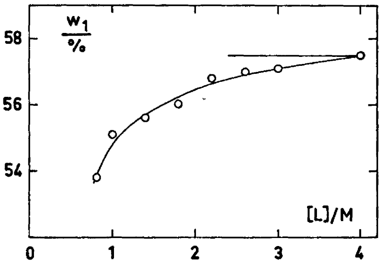

Fig. 1. Solubility measurements at 4 M ionic strength. Iodide content of solid phase *versus* iodide concentration in solution. Points: experimentally observed values. Best curve drawn. Horizontal line: theoretical value for Co pn_3I_3.

$1 \leq C_L \leq 4$ M, ($I = 4$ M only), were equilibrated with Co pn_3I_3(s) in a solubility column, as described earlier.[1,10] Samples of the solid were frequently withdrawn and analyzed for the iodide content. As shown in Table 1 and Fig. 1, Co pn_3I_3(s) is not stable; the iodide content decreases as C_L is decreased. It is natural to assume that some iodide is replaced by perchlorate. To confirm this it was shown (by an ion exchanger) that the solid phase contained the expected number of equivalents. As I^- and ClO_4^- are the only anions present, the missing I^- ions must necessarily have been replaced by ClO_4^-. The same behaviour was observed with Co en_3I_3,[1] but there the change set in at a much lower C_L. As a consequence of the solid solution formation, the equilibria were attained slowly. Care was taken to assure that equilibrium was really reached. Below $C_L = 1$ M, no reproducible solubilities were obtained.

The saturated solutions were analyzed spectrophotometrically at 340 and 470 nm.

RESULTS, CALCULATIONS

Potentiometric measurements

If activity coefficients and liquid junction potentials are constant, the emf E of the described element may be written

$$E = (E' + 0.5k \log [I_3^-]) - 1.5k \log [L] \qquad (1)$$

where E' and $k = RTF^{-1} \ln 10$ are constants. Provided $[I_3^-]$ is constant, the expression within parentheses is a constant. If E is measured for a particular C_L with and without M present in the solution, the difference may be taken

$$E_L = E(C_M > 0) - E(C_M = 0) \qquad (2)$$

According to eqn. (1), then

$$E_L = 1.5k \log C_L/[L] \qquad (3)$$

The triiodide ion is actually dissociated, although very slightly [8,11]

$$I_3^- \rightleftharpoons I_2 + I^-$$

If this dissociation is different for $C_M > 0$ and $C_M = 0$, eqn. (3) is no longer valid. A small correction has to be introduced:

$$E_L = 1.5k \log \delta C_L/[L] \qquad (4)$$

where

$$\delta = \left(\frac{1 - (K_{tri}[L])^{-1}}{1 - (K_{tri}C_L)^{-1}}\right)^{\frac{1}{3}} \qquad (5)$$

The correction may be calculated from known [8,11] values of K_{tri} and preliminary values of [L] obtained by eqn. (3).

Thus, from E_L we may compute [L], as well as the ligand number,

$$\bar{n}/[L] = (C_L/[L] - 1)/C_M \qquad (6)$$

The possible formation of Co $pn_3^{3+} - ClO_4^-$ complexes is neglected (*cf.* Discussion). Since $\bar{n}/[L]$ approaches β_1 for small [L], it follows from eqns. (3) and (6) that

$$E_L \approx 1.5k \log (\beta_1 C_M + 1) \approx \text{const. } C_M$$

Thus, E_L is roughly independent of [L], but roughly proportional to C_M. The precision of β_1 is thus favoured by high C_M, but not by high C_L. It has not been possible to study complexes higher than ML by this method, primarily due to the limited solubility of Co pn_3 salts. From $\bar{n}$, the stability constants can in principle be extracted by standard methods. However, at the low C_L used here, higher

Table 2. Potentiometric measurements, 1 M ionic strength.

$C_L \times 10^3$ M	$C_M \times 10^3$ M	E_L mV	$[L] \times 10^3$ M	δ	$\bar{n}/[L]$ M^{-1}	β_1 M^{-1}
49.0	100.0	5.1	42.9	0.9987	1.430	1.52
49.0	50.0	2.75	45.6	0.9993	1.495	1.60
39.0	100.0	3.8	33.6	0.9981	1.646	1.74
39.0	50.0	2.6	36.5	0.9992	1.413	1.49
29.0	100.0	5.9	24.9	0.9973	1.685	1.76
29.0	50.0	3.0	26.8	0.9987	1.648	1.72
19.0	100.0	5.8	16.2	0.9958	1.673	1.72
19.0	50.0	3.0	17.5	0.9978	1.668	1.72

complexes than ML may certainly be neglected. A value of β_1 may then be readily computed from each value of E_L.

The triiodide ion might also be complexed to Co pn_3^{3+}, and although we have to assume that such complexes are absent, it may be of interest to look at their consequences. If a complex $M(I_3)$ is formed, stability constant β_1', eqn. (4) takes the form

$$E_L = 1.5k \log \frac{\delta C_L/[L]}{(C_T/[I_3^-])^{1/3}} \qquad (7)$$

or, roughly

$$E_L = 1.5k \log \delta \frac{1+\beta_1 C_M}{1+\frac{1}{3}\beta_1' C_M} \qquad (8)$$

Thus, triiodide complexes cannot be revealed by variation of C_L or C_T.

In Table 2, the results of the measurements at $I = 1$ M are reported. Only random variation in β_1 is shown. The average value is 1.66(10) M^{-1}. (Throughout this paper, the errors given refer to the 99 % confidence level.)

At 4 M ionic strength, the E_L values were generally lower, and decreased with increasing C_L (up to $C_L = 0.1$ M) at a rate that could not possibly be due to complex formation only. At low [L] a value $\beta_1 \approx 1$ M^{-1} was approached, but no significance should be attached to this value.

Spectrophotometric measurements

The pertinent equations for the M-method have been derived in an earlier paper.[1] In Tables 3–4 the observed absorbances are given as well as the β_1 values obtained. No significant variation of β_1 with the wavelength or with C_L was observed. The random errors, however, have a minimum at 290–300 nm.

Table 3. Spectrophotometric measurements at 1 M ionic strength. Absorbances (cell length 1.000 cm) for the ligand concentrations $C_L = 0$ (A_0) and 4.95×10^{-3} M (A_5). Each value is the average of at least two measurements. The absorbances are corrected for the slight absorption by I^-. Values of β_1 with errors within parentheses referring to the 99 % confidence level.

$C_M \times 10^3$ M	280 nm A_0	A_5	290 nm A_0	A_5	300 nm A_0	A_5	310 nm A_0	A_5
15.0	0.294	0.415	0.126	0.234	0.204	0.296	0.420	0.492
20.0	0.384	0.548	0.157	0.299	0.262	0.383	0.542	0.636
39.3	0.707	1.031	0.270	0.546	0.483	0.714	1.047	1.227
45.0	0.847	1.200	0.302	0.612	0.540	0.803	1.184	1.388
59.5	1.054	1.515	0.392	0.795	0.711	1.052	1.555	1.822
75.0	1.303	1.853	0.480	0.978	0.880	1.298	1.949	2.272
79.1	1.381	1.979	0.507	1.032	0.936	1.378		
105.0			0.653	1.307				
β_1/M^{-1} ⟶		1.56(40)		1.65(15)		1.54(10)		1.62(30)

Table 4. Spectrophotometric measurements at 4 M ionic strength. Ligand concentrations: 0 (A_0), 5.00×10^{-3} M (A_5) and 10.00×10^{-3} M (A_{10}). *Cf.* Table 3.

$C_M \times 10^3$	290 nm			300 nm			310 nm		
M	A_0	A_5	A_{10}	A_0	A_5	A_{10}	A_0	A_5	A_{10}
20.0	0.164	0.271	0.370	0.261	0.355	0.444	0.538	0.608	0.680
39.9	0.293	0.491	0.688	0.487	0.659	0.834	1.040	1.174	1.314
60.1	0.424	0.718	–	0.718	0.972	–	1.549	1.745	–
61.5	0.441	–	1.027	0.730	–	1.241	1.560	–	1.964
79.9	0.553	0.933	1.324	0.942	1.273	1.619	2.050	2.300	2.588
β_1/M^{-1} $\longrightarrow$		1.89(15)	1.95(15)		1.86(30)	2.01(30)		2.04(20)	1.94(30)

Solubility measurements

As Table 1 shows, the iodide content of the solid decreases as the ratio of ClO_4^- to I^- in the solution increases. Evidently a *solid solution* of Co $pn_3(ClO_4)_3$ (MA_3, mol fraction x_2, Table 1) in Co pn_3I_3 (ML_3, mol fraction x_1) is formed. The complex formation in the aqueous solution can nevertheless be elucidated if the data are treated in the following way (*cf.* Holmberg[12]).

The activities of the components of the solid phase are denoted a_1 and a_2. Then for the equilibria

$ML_3(s, a_1) \rightleftharpoons M + 3L$

and $MA_3(s, a_2) \rightleftharpoons M + 3A$

the equations apply

$$K_{s1} = [M][L]^3/a_1 \tag{9}$$

$$\text{and } K_{s2} = [M][A]^3/a_2 \tag{10}$$

where K_{s1} and K_{s2} are constants. As before it is assumed that activity coefficients are constant *in the aqueous solution.* As expressed by eqn. (9), the product $[M][L]^3$ is now variable, in contrast to the more common situation of pure ML_3, when a_1 is constant (usually taken as unity) and $[M][L]^3$ consequently also constant (= the solubility product).

Since the solubility S is expressed by

$$S = [M]X \tag{11}$$

$$\text{or } S[L]^3/a_1 = K_{s1}X \tag{12}$$

$$\text{where } X = 1 + \beta_1[L] + \cdots \tag{13}$$

the stability constants can be computed once a_1 is known.

The two activities are connected by the Gibbs-Duhem equation

$$x_1 \,\mathrm{d} \ln a_1 + x_2 \,\mathrm{d} \ln a_2 = 0 \tag{14}$$

$$\text{or } -\mathrm{d} \ln a_2 = x_1/x_2 \,\mathrm{d} \ln a_1 \tag{15}$$

Eqns. (9) and (10) yield, upon combination, taking logarithms and differentiating

$$\mathrm{d} \ln a_1 - \mathrm{d} \ln a_2 = 3 \,\mathrm{d} \ln [L]/[A] \tag{16}$$

Eqn. (15) is inserted

$$\mathrm{d} \ln a_1 = 3x_2 \,\mathrm{d} \ln [L]/[A] \tag{17}$$

In integral form

$$\int_1^2 \mathrm{d} \log a_1 = 3 \int_1^2 x_2 \,\mathrm{d} \log [L]/[A] \tag{18}$$

The integration was performed graphically. The fraction x_2 (Table 1) was plotted *vs.* log [L]/[A]. The area under the curve between any two points yields the difference in log a_1 between these points. Since log [L]/[A] grows infinitely as [L] approaches 4.0 M, it was difficult to estimate the "tail" of the integral between [L] = 3.8 M and [L] = 4.0 M. However, when (log a_1 − log a_1 (3.8)) was plotted *vs.* [L], a practically linear curve resulted, which could be easily extrapolated the short path to [L] = 4.0 M, hence giving a reliable value of $a_1(3.8)/a_1(4.0)$. The a_1 values of Table 5 are calculated setting $a_1(4.0) = 1.000$. It may be noted that the values of a_1 are not very sensitive to the random errors in x_2.

[L] and C_L are equal except at the lowest C_L. Strictly, [L] is given by the expression

$$[L] = C_L + (3x_1 - \bar{n})S \tag{19}$$

The perchlorate concentration, [A], is not significantly different from its initial concentration (*cf.*, however, Discussion).

$K_{s1}X$ was computed according to eqn. (12). The function could be fitted using the constants

Table 5. Solubility at 4 M ionic strength. Observed solubilities, S_0, and solubilities calculated from the constants given in the text, S_c. Deviation $=100(S_0-S_c)/S_c$. The activity a_1 was calculated according to eqn. (18) and [L] according to eqn. (19).

C_L M	[L] M	a_1	$S_0\times10^3$ M	$S_c\times10^3$ M	Dev %	$K_{s1}X$ M^4
4.0	$=C_L$	1.000	0.681	0.674	+1.1	43.6
3.8		0.994	0.680	0.683	−0.5	37.5
3.6		0.987	0.695	0.694	+0.1	32.9
3.4		0.980	0.702	0.708	−0.9	28.2
3.0		0.966	0.741	0.747	−0.9	20.7
2.6		0.950	0.815	0.810	+0.6	15.1
2.2		0.932	0.927	0.917	+1.1	10.59
1.8	1.801	0.910	1.112	1.112	±0.0	7.17
1.4	1.402	0.876	1.514	1.513	+0.1	4.76
1.0	1.004	0.822	2.519	2.542	−0.9	3.10

$K_{s1}=0.9(2)\times10^{-3}$ M^4, $K_{s1}\beta_1=1.65(10)\times10^{-3}$ M^3, and $K_{s1}\beta_3=0.56(2)\times10^{-3}$ M. Hence $\beta_1=1.8(4)$ M^{-1} and $\beta_3=0.62(15)$ M^{-3}. (The large errors in β_1 and β_3 are thus due mainly to the uncertainty in K_{s1}.) As shown by Fig. 2, the formation of ML_2 or ML_4 is not needed to explain the data.

For comparison, the calculation of stability constants was also attempted neglecting the solid solution formation, *i.e.* the solid phase was assumed to be $\mathrm{Co\,pn_3I_3(s)}$. Then, $K_{s1}<0.2\times10^{-3}$ and hence $\beta_1\geqslant10$ M^{-1} were obtained. Moreover, the formation of ML_4 had to be assumed in order to fit the data at high [L]. Evidently, when the solid solution formation is taken into consideration, the overall picture of the system is much improved.

At 1 M ionic strength, the solubility was so high already when $C_L=1$ M ($S\approx15\times10^{-3}$ M) that it was judged impracticable to study the system with the solubility method.

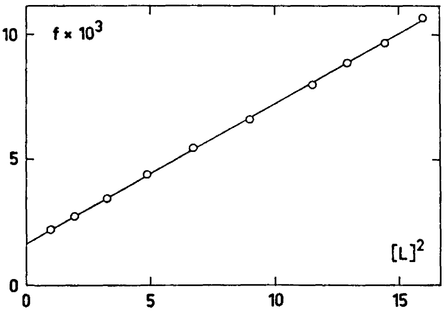

Fig. 2. Solubility measurements at 4 M ionic strength. $f=(K_{s1}X-K_{s1})[L]^{-1}$ *vs.* $[L]^2$

DISCUSSION

The results of the present study are summarized in Table 6. At both ionic strengths, different methods gave β_1 values that agree within the limits of error. These values may thus be regarded with confidence. It seems reasonable to assume that this conclusion is valid also for the higher complexes studied although only the solubility method was applicable in the region of high ligand concentration.

As discussed in previous papers,[1-3,13] ClO_4^- quite probably forms complexes with cobaltammine cations to some degree. If this is the case, methods like the potentiometric and spectrophotometric methods used here would give higher β_1 values than the solubility method.[13] The difference found at 4 M ionic strength is, however, although in the right direction, far from being significant. As moreover the precision of the β_1 value from the solubility method is rather low, no safe conclusion about perchlorate complex may be drawn.

Table 6. Stability constant values of the $\mathrm{Co\,pn_3^{3+}-I^-}$ system obtained in the present study.

I M	Method	β_1 M^{-1}	β_3 M^{-3}
1	Pot.	1.7(1)	
	Spectr.	1.6(1)	
4	Spectr.	1.9(1)	
	Soly.	1.8(4)	0.62(15)

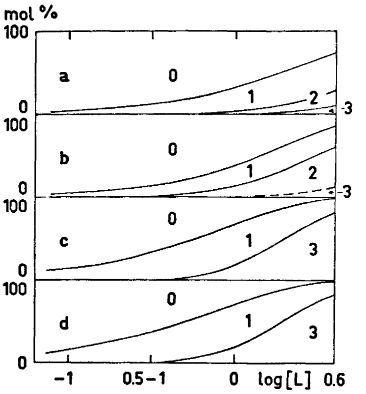

Fig. 3. Distribution of C_M between different species ML_n (n given in the figure). (*a*). Co-$(NH_3)_6^{3+}-Br^-$. (*b*). $Co(NH_3)_6^{3+}-I^-$. Dashed curve: only qualitative evidence of ML_3. (*c*). Co $en_3^{3+}-I^-$. (*d*). Co $pn_3^{3+}-I^-$. Ionic strength: 4 M, temperature: 25 °C.

Anyhow, perchlorate association may affect the value of β_1 slightly; it is not thought to have any influence on the formation of higher complexes.[3]

As discussed in Ref. 2, no serious medium effects should occur when I^- is substituted for ClO_4^-.

The studies on cobaltammine halides may now be summarized. Fig. 3 clearly shows the difference between the hexaamminecobalt systems on the one hand and the trisdiaminecobalt systems on the other. In the first place, the hexaamminecobalt complexes are significantly weaker. Secondly, in the hexaamminecobalt systems, the data are best fitted if it is assumed that halide ions are added successively and regularly. In the trisdiaminecobalt systems, on the other hand, only the first and third complexes are needed to fit the data well. It should perhaps be pointed out that although also this difference is statistically significant, only quite modest systematic errors are required to change the picture appreciably. However, the consistency of the four systems speaks against systematic errors, and the difference between the systems is thought to be real. It is reasonable to ascribe this difference to the difference in shape between the hexaamminecobalt ion and the trisdiaminecobalt ions. This would imply that forces other than electrostatic ionic attraction are involved.

Although it is shown beyond doubt for all systems that complexes higher than the first are formed, the question of the maximum coordination number is not settled. In the hexaamminecobalt systems complex formation is evidently far from completed even at [L] = 4 M. In the trisdiaminecobalt systems, however, ML_3 is formed to about 80 % at 4 M iodide concentration. Nevertheless, in neither system was there any indication of the formation of ML_4. Thus, one tends to conclude that here ML_3 is the final complex, or at least that the complex formation function has a pronounced halt at 3, the negatively charged ML_4 being formed only very reluctantly. This of course indicates that electrostatic forces are important.

All four systems were studied at different ionic strengths. The original intention was to study variations with the ionic strength in some detail. However, the changes in the range studied, 0.5 – 4 M, are not very spectacular. Stability constants of outer-sphere complexes often pass through a shallow minimum [1,14–16] or stay constant within the limits of error;[2] more rapid changes may occur for very low and very high I. Different ionic strengths have therefore primarily been used as a means of providing different series of measurement of essentially the same quantities. Results in accord have increased the confidence in the conclusions drawn.

As far as possible the results have also been tested by using more than one experimental method. The agreement has as a rule been good. In the region of high [L], of particular interest in these studies, unfortunately only the solubility method has been applicable. However, when this method gives results at low [L] in accord with other methods, it is reasonable to assume it to be reliable at high [L] as well.

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