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The Stability of Metal Halide Complexes in Aqueous Solution

V. The Chloride and Bromide Complexes of Thallium(III)

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The complex formation of Tl^{3+} with Cl^- and Br^- has been investigated by measuring the variation of the Tl(III)/Tl(I) redox potential when adding the respective ligand. The measurements have been performed at 20°C in an approximately constant medium of the ionic strength 4 M, the acidity of which has been kept 3 M in order to suppress the hydrolysis of Tl^{3+} to a negligible value. The first four mononuclear complexes are formed with both ligands, while other complexes cannot be proved within the range of concentrations studied. The determined constants are in Tables 7 and 8, together with the data available from previous investigations. The relative stabilities of the complexes formed, Table 9 and Fig. 6, follows a distinct pattern which is intermediate between that found for Hg^{2+} (or Ag^+) and that found for Cd^{2+}.

The characteristic properties of class (*b*) acceptors seem to depend on the availability of electrons from the lower *d*-orbitals of the metal for dative π-bonding to ligands, able to participate in the formation of bonds of a partially multiple character. For ligands coordinating through the heavier atoms of groups 5a, 6a, and 7a (from the 3rd period on), the extra electrons involved as the bond order exceeds one, may be accomodated in the otherwise vacant outer *d*-shell present in these atoms. For the light ligand atoms B, C, N, O, and F on the other hand, this possibility does not exist. In these cases a dative π-bond can only be formed if the ligand already contains a multiple bond, whose bond order may be decreased so as to provide an orbital for the extra bond to the metal [1,2].

If the easy availability of *d*-electrons within the outer shell of the acceptor atom is really the main point, then elements situated in that part of the triangular class (*b*) area, which is to the right of the central copper group, should display a stronger class (*b*) character the higher the redox state, as an oxidation will remove the outermost *s*-electrons, thus making the *d*-electrons more available for bonding. On the other hand elements within the left part of the class (*b*) triangle should be more pronounced (*b*) acceptors the lower the redox state, as an oxidation in these cases will remove *d*-electrons, and furthermore those possessing energies especially favourable for bond formation [1]. These consequences of the theory advocating dative π-bonding to account for the complex formation of class (*b*) acceptors are open to experimental verification.

There is much experimental evidence in support of the latter part of the deduction above. Thus copper(I), nickel(0), cobalt(0) and iron(0) are all very typical class (*b*) acceptors, while copper(II), nickel(II) and cobalt(II) are on the border, having a weak class (*b*) character towards ligand atoms of the oxygen group, but a weak class (*a*) character towards halide ions, and iron(III) is clearly a typical class (*a*) acceptor. On the other hand, the evidence pertaining to elements to the right of the copper group is fairly scanty. The only data available for a quantitative comparison are those referring to halide complexes of mono- and trivalent thallium. As to thallium(I), its weak class (*b*) character has been fully established by the thorough investigation of Nilsson [3]. For thallium(III) on the other hand, the information is still incomplete and in part even contradictory, *e.g.* as to the number of complexes really formed within the halide systems [4–7, 7a]. Though the available data certainly bear out the stronger class (*b*) character of the trivalent state, nevertheless it therefore seems worthwhile to check the results so far reported by an independent method of measurement and also to extend the investigations to further ligands.

This paper presents a study of the chloride and bromide complexes of thallium(III), performed by measurements of the variation of the Tl(III)/Tl(I) redox potential when ligand is added to the solutions. In order to determine the equilibria pertaining to one of the redox states present it is, however, necessary to know the complex formation of the other state in the actual medium. Moreover, this complex formation should preferably be much weaker than that of the state under investigation, as the accuracy of the determined constants otherwise will be seriously impaired. In the present case, the data already available certainly show that the complex formation of Tl(I) will only show up as a small correction in the measurements. This correction can be found with quite adequate accuracy from Nilsson's measurements. These relate to a medium of the same ionic strength as the one used here, *i.e.* 4 M, though it is qualitatively different, sodium perchlorate being the only supplementary electrolyte. With Tl(III) present, however, the acidity of the solutions must be kept high in order to suppress the hydrolysis to a negligible value. In the present measurements, the acidity has been chosen = 3.00 M, and the sodium ion concentration is thus only about 1 M. However, as the corrections due to the complexes of Tl(I) are so small, the difference of medium is certainly of no consequence.

At an acidity h = 3 M, the degree of hydrolysis is only about 3 % even in the pure perchlorate solution,[8] and it certainly decreases further as the complex formation proceeds.

The measurements have been performed at 20°C.

CALCULATION OF THE STABILITY CONSTANTS FROM THE MEASURED POTENTIALS

The emf E of cells of the following type has been measured:

$-$Au	3 M $HClO_4$ 1 M $NaClO_4$ quinhydrone (s).	3 M $HClO_4$ 1 M $NaClO_4$	C_M mM Tl(III) C_P mM Tl(I) C_A mM ligand $h = 3$ M $I = 4$ M	Pt +

This emf is constituted as follows:

$$E = e^0 + \frac{RT}{2F} \ln \frac{[M] \cdot f_M}{[P] \cdot f_P} - E_{RE} - E_d \tag{1}$$

where M and P denote Tl^{3+} and Tl^+, respectively. Here the standard potential e^0 of the Tl(III)/Tl(I) couple and the potential of the quinhydrone reference electrode, E_{RE}, are constants. In the approximately constant medium used, the same may be considered as true for the activity factors f_M and f_P and for the liquid junction potential E_d too. Hence

$$E = E^0 + \frac{RT}{2F} \ln \frac{[M]}{[P]} \tag{2}$$

where E^0 is a constant. In the special case when no ligand has been added, $C_A = 0$:

$$E' = E^0 + \frac{RT}{2F} \ln \frac{C_M}{C_P} \tag{3}$$

Hence

$$E' - E = E_{MP} = \frac{RT}{2F} \ln \frac{C_M}{[M]} \cdot \frac{[P]}{C_P} \tag{4}$$

The thallium(I) systems contain only mononuclear complexes and the quantity $C_p/[P]$ can therefore be expressed as:

$$C_P/[P] = 1 + \sum_{q=1}^{Q} \beta_q' [A]^q = X_P \tag{5}$$

For any value of the free ligand concentration $[A]$,$C_P/[P]$ can be calculated from the known values [3] of the constants β_q'. Thus $C_M/[M]$ can be found, and from this function the stability constants β_n of the thallium(III) system can be computed according to the methods given by Leden and Fronaeus (described in Ref.[9]). The main problem in this connexion is to find the value of [A], corresponding to a certain value of $C_M/[M]$ measured. Depending upon whether [A] is of the same order of magnitude as C_A or very much smaller, it has to be determined in two essentially different ways.

If it is preliminarily assumed that also the thallium(III) complexes are solely mononuclear, then

$$C_M/[M] = 1 + \sum_{n=1}^{N} \beta_n [A]^n = X_M \tag{6}$$

and $$E_{MP} = \frac{RT}{2F} \ln \frac{X_M}{X_P} \quad (7)$$

i.e. $C_M/[M]$ and, consequently, E_{MP} are functions of [A] only. The same will also apply to the ligand numbers $\bar{n}_M$ and $\bar{n}_P$ of thallium(III) and thallium(I), respectively [9]. Thus if E_{MP} is measured as a function of C_A for a set of values of C_M while C_P is kept constant, and the resulting family of curves cut at constant values of E_{MP}, then [A], $\bar{n}_M$ and $\bar{n}_P$ will all be constant along these lines of intersection. These quantities are, however, connected according to

$$C_A - [A] = \bar{n}_M . C_M + \bar{n}_P . C_P \quad (8)$$

Thus at constant E_{MP}, C_A is a linear function of C_M with the slope $= \bar{n}_M$ and an intercept on the C_A-axis $= [A] + \bar{n}_P \cdot C_P$. As the thallium(I) complexes are quite weak, $\bar{n}_P$ is, however, small within the range of [A] investigated. Moreover C_P has been chosen as low as is compatible with a satisfactory adjustment of the redox potential, in order to avoid a precipitation of slightly soluble thallium(I) halides, which would highly complicate the measurements. The result is that $\bar{n}_P \cdot C_P$ is quite negligible relative to [A] in the whole range of concentration covered, and thus the intercept will in fact be [A].

For very strong complexes like those formed in the thallium(III) systems under investigation, the complex formation, however, starts already at values of [A], which are several powers of ten lower than the corresponding values of C_A. In such cases all the C_A, C_M-lines will in the beginning pass through the origin within the limits of experimental accuracy, and the intercept will not yield a useful value of [A]. On the other hand, the slope will be well defined and thus give a quite reliable value of $\bar{n}_M$. As C_A increases however, the part consumed by complex formation becomes relatively smaller and [A] will grow to a size comparable with C_A. The intercepts of the C_A, C_M-lines will then start to yield useful values of [A], while the slopes still give the corresponding values of $\bar{n}_M$ with fair accuracy. At a further increase of C_A to large excess over C_M, the part bound in complexes will finally be insignificant, *i.e.* $[A] \rightarrow C_A$. The value of [A] determined by the small extrapolation needed under such circumstances will be very reliable, but the slopes of the C_A, C_M-lines will on the other hand be very uncertain and the values of $\bar{n}_M$ hence determined subjected to large errors.

The value of [A], corresponding to a certain value of $C_M/[M]$ can thus be found by extrapolation only in the later stages of the complex formation. The low values of [A] in the beginning are instead evaluated by means of the integrated Bodländer equation [9]

$$\log \frac{[A]_0}{[A]} = \int_{X_M([A])}^{X_M([A]_0)} \frac{1}{\bar{n}_M} \, d \log X_M \quad (9)$$

The integration is performed graphically. The upper limit of integration $X_M([A]_0)$ is chosen so that the corresponding value of $[A] = [A]_0$ can be reliably determined by extrapolation of (8), while the slope still gives a good values of $\bar{n}_M$.

From corresponding values of X_M and [A], the constants β_n are calculated in the usual way,[9] and hence the complex formation function $\bar{n}_M = f([A])$. Within that region of [A] where the C_A, C_M-lines give measurable intercepts on the C_A-axis, this function can be compared with the values of $\bar{n}_M$ found from the slopes of the lines. If these are lower than the values calculated from the stability constants, then the existence of polynuclear complexes is indicated [10]. In such a case, the intercepts for $C_M = 0$ will still give [A], and corresponding values of X_M will be found from eqn. (7), but eqn. (9) will no longer be valid and the determination of the lower part of the complex formation curve, where [A] cannot be found from the intercepts, will thus be rendered impossible.

EXPERIMENTAL

Chemicals. All chemicals used were of analytical grade and used without further purification. Thallium(I) perchlorate was prepared by dissolving the carbonate in an excess of warm, concentrated perchloric acid. The salt was recrystallized three times from water. A 0.2 M stock solution was prepared and analysed by titration with iodate [11]. A solution of thallium(III) perchlorate was prepared by anodic oxidation of 0.2 M thallium(I) perchlorate in 2 M perchloric acid [12,8]. In the resulting solution, the residual concentration of Tl(I) was determined by direct iodate titration. The concentration of Tl(III) was found by titrating the solution after complete reduction by means of SO_2 and then subtracting the known concentration of Tl(I) from the total. The acidity was determined after reduction of the easily hydrolysed Tl(III) by hydrogen peroxide, according to the reaction $Tl^{3+} + H_2O_2 \rightarrow Tl^+ + 2H^+ + O_2$. The acidity wanted is thus found by subtracting twice the original concentration of Tl(III) from the acidity of the reduced solution. Sodium perchlorate was prepared by almost neutralizing perchloric acid with sodium carbonate, boiling off CO_2, and finally completing the neutralization by carbonate free sodium hydroxide solution. The solution was analysed by running a sample through a cation exchange column saturated with H^+ and then titrating it alkalimetrically. The stock solutions of perchloric, hydrochloric and hydrobromic acid, and of sodium chloride were also analysed alkalimetrically, the last-mentioned after cation exchange treatment.

Procedure. The thallium half-cell initially contained a known volume of a ligand-free solution S of the composition C_M mM thallium(III) perchlorate, C_P mM thallium(I) perchlorate, 3 M perchloric acid, and sodium perchlorate so as to make $I = 4$ M. Two platinized Pt-foils were used as electrodes. The halfcell was connected with a quinhydrone reference electrode, and the emf E' measured. The equilibrium potential was reached most rapidly with platinized electrodes, but even then the adjustment took about half an hour. Bright gold or platinum electrodes were considerably more sluggish. After E' had been measured, portions of a solution T containing ligand, but otherwise of the same composition as S, were added from a burette. At the lowest ligand concentrations, the potential adjustment was still slow, but with growing C_A it soon became more and more rapid so that at last equilibrium was reached immediately upon mixing (which was rapidly brought about by a stream of pure nitrogen, passing through the solution during the whole measurement). This is in accordance with the fact that the Tl(III)/Tl(I) electron exchange proceeds much faster at high concentrations of chloride or bromide than if these are present only in low concentrations or not at all [7,13-15]. Once reached, the emfs measured were quite stable and the two foils as a rule gave the same value within 0.1 mV. On repetition of a series, however, the initial emf E' was sometimes found to deviate as much as 2 mV from the value measured previously, and for the lowest halide concentrations even larger deviations were occasionally found, evidently due to the slow electrode kinetics in these media. To minimize the errors caused by this inaccuracy, mean values of E' have been used for the calculation of E_{MP}. In this way considerably more concordant values of E_{MP} were found when a titration was repeated than if the accidental value of E' read for each titration was used when forming the difference E_{MP}.

The mean values were determined by special series of measurements, also arranged in order to check that the Tl(III)/Tl(I) electrode obeys the law of Nernst. If so, E^0 of eqn.

Table 1. The validity of Nernst's law for the Tl^{3+}/Tl^{+}-couple.

$C_P \times 10^3$ M	2.5		1.0		0.25	
$C_M \times 10^3$ M	E' mV	E^0 mV	E' mV	E^0 mV	E' mV	E^0 mV
1.43	—	—	—	—	617.8	595.8
2.27	—	—	609.4	596.5	626.1	595.7
4.17	606.8	599.9	—	—	—	—
5.00	608.1	599.3	617.3	597.0	633.9	596.1
6.00	—	—	619.8	597.1	636.5	596.2
8.33	615.2	599.9	—	—	—	—
10.00	—	—	626.4	597.3	642.3	595.8
10.73	618.3	599.9	—	—	—	—
12.87	—	—	629.7	597.5	—	—
15.00	622.4	599.8	631.6	597.4	647.4	595.7
18.00	—	—	634.0	597.5	—	—
20.00	—	—	—	—	652.2	596.9
21.45	—	—	636.7	598.0	—	—
22.50	—	—	—	—	653.5	596.7

(2) and (3) should be a constant, provided that the use of an approximately constant medium really keeps f_M, f_P and E_d constant, as it is postulated. In eqn. (3), valid for ligand free solutions, all quantities except E^0 can be easily found, and the check has therefore been performed as follows. A thallium(I) solution, S′, in a perchlorate medium of the same acidity and ionic strength as in the ligand titrations was titrated with a solution, T′, containing thallium(III) but otherwise of the same composition as S′. Series were performed with three different values of the thallium(I) concentration, C_P, Table 1. The value of E^0 shows a slight but significant increase with C_P. On the other hand E^0 seems to be independent of C_M up to $C_M \approx 20$ mM. Provided C_P is kept constant, the electrode thus shows the theoretical behaviour within a rather wide range of C_M.

In the ligand titrations, C_M has been kept ≤ 10 mM. As to C_P, the values 2, 1, and 0.25 mM have been used in the chloride measurements. From Table 1 it is deducted that these correspond to $E^0 = 599.8$, 597.3, and 595.9, respectively, and hence the value of E' wanted for a certain series is easily calculated from eqn. (3). In the bromide measurements, values of C_P higher than 0.25 mM cannot be used if an early precipitation is to be avoided. Even at $C_P = 0.25$, precipitation occurs when [A] reaches about 30 mM. For the extension of the measurements to higher values of [A], C_P was chosen as low as 0.02 mM. Such a value of C_P, however, will give reliable potentials only if a fairly high concentration of bromide is present, and it is thus impossible to determine E' (or E^0) by direct measurement. The difference E_{MP} is instead found as follows. With $C_P = 0.02$ mM, E is determined not only for values of C_A so high that they cannot be covered, if higher values of C_P are used, but also in as wide a range of C_A as possible which has already been measured with $C_P = 0.25$ mM. From the constant difference between the two series within the region of overlapping, E' for the series with $C_P = 0.02$ can be calculated and hence E_{MP} for that upper region of C_A where measurements can be performed only with $C_P = 0.02$ mM.

In the strongly acid solution of the reference half-cell the quinhydrone electrode showed a drift in the first few hours amounting to about 0.1 mV/h, which later became more and more rapid. The values of E have been corrected for this drift. As the electrode was freshly prepared each day, the correction never exceeded 1 mV.

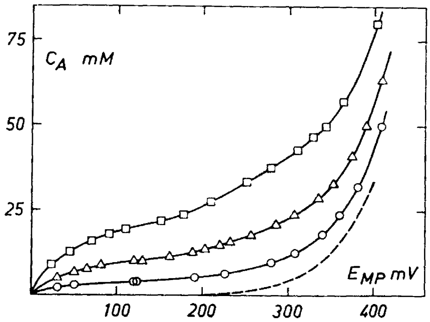

Fig. 1. The chloride system: The connexion between E_{MP} and C_A for $C_M = 10$ (□), 5 (△) and 2 mM (○), up to $E_{MP} \approx 410$ mV. Dashed curve denotes the extrapolated function for $C_M = 0$. For the sake of clarity, the experimental points below $E_M = 20$ mV are not given in the figure.

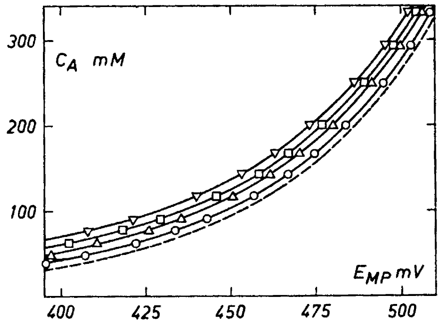

Fig. 2. The chloride system: The connexion between E_{MP} and C_A for $C_M = 8$ (▽), 6(□), 4 (△) and 2 mM (○) in the intermediate range of E_{MP}. Dashed curve denotes the extrapolated function for $C_M = 0$.

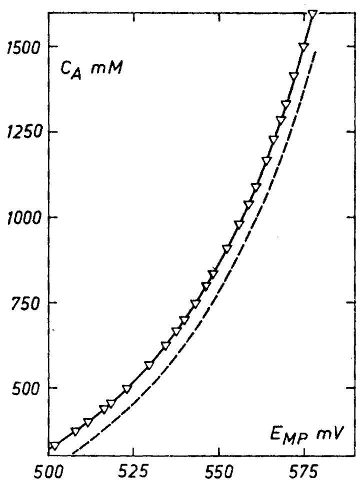

Fig. 3. The chloride system: The connexion between E_{MP} and C_A for $C_M = 8$ mM (▽) and the extrapolated curve for $C_M = 0$ (dashed) when $E_{MP} > 500$ mV. For the sake of clarity, the intermediate curves of $C_M = 6$, 4 and 2 mM have been omitted.

RESULTS

Chloride system. Figs. 1, 2, and 3 contain E_{MP} as a function of C_A for the different values of C_M chosen. These curves have been cut at a number of values of E_{MP}, and corresponding values of C_M and C_A determined, Tables 2 and 4. The connexion between C_A and C_M turned out to be linear, as expected for a mononuclear complex formation (*cf.* p. 1570). The slopes $\bar{n}_{obs}$ of these lines have been read up to and including the line of $E_{MP} = 440$ mV, corresponding to an intercept [A] = 76.5 mM. For higher values of E_{MP}, the slopes become more and more ill-defined. Furthermore they tend to improbably high values ($\approx$ 15 at the highest values of E_{MP} reached) which are believed to

Table 2. The chloride system: Determination of corresponding values of [A], n and X_M for $E_{MP} \leq 390$ mV.

$C_M \times 10^3$ M	10	5	2	0				
E_{MP} mV	$C_A \times 10^3$ M			$C_A = [A]$	$[A]_{int}$ M	$\bar{n}_{obs}$	X_P	X_M
10	5.4	2.6	1.0		3.18×10^{-8}	0.530		2.21
20	8.2	4.0	1.6		1.04×10^{-7}	0.807		4.87
40	11.9	5.9	2.4		4.94×10^{-7}	1.19		23.7
60	14.8	7.5	3.0		1.61×10^{-6}	1.50		1.16×10^{2}
80	17.3	8.8	3.5		4.24×10^{-6}	1.75		5.63×10^{2}
100	18.9	9.6	3.7		1.00×10^{-5}	1.91		2.74×10^{3}
120	20.1	10.0	3.9		2.24×10^{-5}	2.01		1.34×10^{4}
140	21.1	10.5	4.2		4.85×10^{-5}	2.10		6.51×10^{4}
160	22.3	11.2	4.5	0.1	0.10×10^{-3}	2.22		3.17×10^{5}
180	24.1	12.1	4.9	0.1	0.20×10^{-3}	2.39		1.55×10^{6}
200	26.4	13.4	5.4	0.2	0.38×10^{-3}	2.63		7.52×10^{6}
220	29.0	14.9	6.2	0.4	0.67×10^{-3}	2.88		3.66×10^{7}
240	31.7	16.4	7.0	0.8	1.13×10^{-3}	3.11	1.001	1.79×10^{8}
260	34.6	18.2	8.2	1.6	1.84×10^{-3}	3.32	1.001	8.70×10^{8}
280	37.5	20.3	9.7	2.8	2.91×10^{-3}	3.49	1.003	4.25×10^{9}
300	40.8	22.7	11.5	4.2	4.51×10^{-3}	3.67	1.004	2.07×10^{10}
320	44.5	25.8	14.2	6.6	6.90×10^{-3}	3.83	1.006	1.01×10^{11}
340	49.1	29.9	17.9	10.2	10.5×10^{-3}	3.92	1.009	4.94×10^{11}
370	59.4	39.2	27.3	19.3		4.00	1.017	5.35×10^{12}
390	70.2	49.5	36.9	28.5		4.20	1.026	2.63×10^{13}

Table 3. The chloride system: Derivation of the stability constants by extrapolation of the corresponding X-functions.

E_{MP} mV	X_1 M^{-1}	$X_2 \times 10^{-13}$ M^{-2}	$X_3 \times 10^{-16}$ M^{-3}	$X_4 \times 10^{-19}$ M^{-4}
0	*3.5×10^{7}*	*2.4*	*6.2*	*3.8*
10	3.8×10^{7}			
20	3.7×10^{7}			
40	4.6×10^{7}			
60	7.1×10^{7}			
80	13.3×10^{7}			
100	27.4×10^{7}	2.4		
120	59.6×10^{7}	2.5		
140	1.34×10^{9}	2.7		
160	3.14×10^{9}	3.1		
180	7.7×10^{9}	3.8	7.0	4.0
200	19.9×10^{9}	5.3	7.7	4.0
220	54.5×10^{9}	8.1	8.5	3.4
240	1.58×10^{11}	13.9	10.2	3.5
260	4.73×10^{11}	25.7	12.7	3.5
280	14.6×10^{11}	50.1	16.4	3.5
300	45.9×10^{11}	102	22.2	3.5
320	1.46×10^{13}	212	30.4	3.5
340	4.72×10^{13}	451	43.0	3.4
370	27.7×10^{13}	1440	74.5	3.5
390	92.3×10^{13}	3240	119	3.9

Table 4. The chloride system: Determination of corresponding values of [A], X_M, X_3 and X_4 for $E_{MP} \geqq 400$ mV.

$C_M \times 10^3$ M	8	6	4	2	0					
E_{MP} mV	$C_A \times 10^3$ M				$C_A = [A]$	$\bar{n}_{obs}$	X_P	X_M	$X_3 \times 10^{-18}$ M^{-3}	$X_4 \times 10^{-19}$ M^{-4}
400	70.3	60.5	51.0	42.0	33.5	4.5	1.03	5.83×10^{13}	1.55	4.4
410	79.0	68.5	60.0	50.3	41.5	4.7	1.04	1.30×10^{14}	1.81	4.2
420	89.0	79.0	70.5	60.0	51.0	4.8	1.05	2.88×10^{14}	2.17	4.1
430	102	91.5	83.0	72.0	63.0	4.9	1.06	6.43×10^{14}	2.57	4.0
440	118	107	98.0	86.0	76.5	5.2	1.07	1.44×10^{15}	3.21	4.1
450	136	126	117	103	93		1.09	3.22×10^{15}	4.00	4.2
460	160	147	140	125	115		1.11	7.23×10^{15}	4.75	4.1
470	189	176	167	152	141		1.13	1.63×10^{16}	5.82	4.1
480	224	211	200	185	173		1.16	3.70×10^{16}	7.14	4.1
490	266	253	243	226	215		1.20	8.44×10^{16}	8.50	3.9
500	319	305	295	275	264		1.25	1.94×10^{17}	10.5	4.0
504	346	330	321	300	290		1.27	2.71×10^{17}	11.1	3.8
508	373	356	346	326	314		1.30	3.80×10^{17}	12.3	3.9
514	419	400	390	368	357		1.34	6.31×10^{17}	13.9	3.9
520	469	452	441	417	407		1.39	1.05×10^{18}	15.6	3.8
524	508	489	477	457	443		1.43	1.48×10^{18}	17.1	3.8
528	550	531	518	498	485		1.47	2.09×10^{18}	18.4	3.8
532	596	577	563	542	527		1.52	2.96×10^{18}	20.3	3.8
536	645	626	611	590	574		1.57	4.21×10^{18}	22.3	3.9
540	699	679	665	643	627		1.63	6.00×10^{18}	24.4	3.9
542	729	709	694	673	655		1.66	7.16×10^{18}	25.5	3.9
544	759	740	724	703	683		1.69	8.54×10^{18}	26.8	3.9
546	793	772	755	735	715		1.72	1.02×10^{19}	27.9	3.9
548	828	806	789	770	750		1.76	1.22×10^{19}	28.9	3.8
550	864	842	824		783		1.80	1.46×10^{19}	30.5	3.9
552	903	879	860		818		1.84	1.75×10^{19}	32.0	3.9
554	942	918	899		856		1.89	2.11×10^{19}	33.6	3.9
556	980	956	936		892		1.93	2.51×10^{19}	35.6	4.0
558	1023	999	979		934		1.98	3.03×10^{19}	37.2	4.0
560	1069	1045	1024		978		2.03	3.64×10^{19}	39.0	4.0
562	1118	1093	1070		1021		2.08	4.37×10^{19}	41.1	4.0
564	1170	1144	1121		1073		2.15	5.29×10^{19}	42.9	4.0
566	1226	1198	1174		1121		2.21	6.38×10^{19}	45.3	4.0
568	1283	1254	1227		1171		2.27	7.67×10^{19}	47.8	4.1
570	1341	1312	1284		1227		2.34	9.27×10^{19}	50.2	4.1
572	1403	1374	1344		1285		2.42	1.12×10^{20}	53.0	4.1
574	1470	1440	1408		1346		2.50	1.36×10^{20}	55.7	4.1
576	1542	1510	1476		1410		2.58	1.64×10^{20}	58.6	4.2
578	1615	1583	1549		1483		2.69	2.01×10^{20}	61.5	4.2

have no physical meaning, for the following reason. In the range in question, the C_A, E_{MP}-curves are so close together and rise so steeply (*cf.* Fig. 2 and 3) that even a very modest error in the determination of E_{MP} will have disastrous consequences for the determination of $\bar{n}$ from the slopes. Thus at the highest C_A measured, as small a displacement as between 1 and 2 mV of the curves of $C_M = 4$ and 8 mM relative to each other will be sufficient to cause the ano-

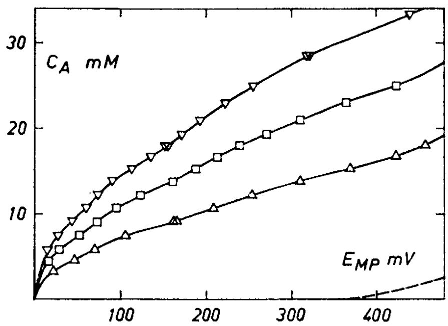

Fig. 4. The bromide system: The connexion between E_{MP} and C_A for $C_M = 8$ (▽), 6 (□) and 4 mM (△) up to $E_{MP} = 480$ mV. Extrapolated curve for $E_M = 0$ coincides with the E_{MP}-axis except at the extreme right.

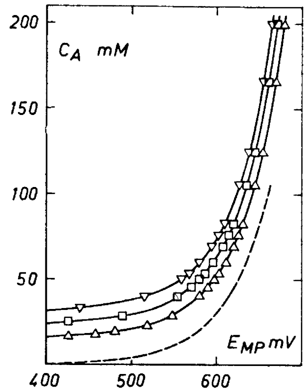

Fig. 5. The bromide system: The connexion between E_{MP} and C_A for $E_{MP} > 400$ mV. The symbols mean the same as in Fig. 4.

malous slopes observed. The extrapolated values of [A] should, on the other hand, be fairly reliable in this region, as [A] is not very different from C_A. This is also confirmed by the following computation of the stability constants. The values of [A] used for this calculation have been found by extrapolation when $E_{MP} \geqq 370$ mV, *i.e.* all values of [A] $\geqq$ 19.3 mM have been found in this way. For values of [A] $<$ 19.3 mM, the determination by means of eqn. (9) is to be preferred, and as [A] decreases, this method will rather soon be the only one practicable. Values found by eqn. (9) are marked $[A]_{int}$ in Table 2. In a transitional range, [A] can however be determined according to both methods. The results agree quite well, which evidently is a good criterion of the validity of eqn. (9) in the present case. The functions X_1, X_2, and X_3 (Tables 3 and 4) give by extrapolation to [A] = 0 the constants β_1, β_2 and β_3. The function X_4 is a constant = β_4 from the lowest value of [A] where it can still be computed, *viz.* 0.20 mM, up to the highest value of [A] reached, 1483 mM. Consequently, higher complexes than the fourth one do certainly not exist within the range of [A] investigated here. The ligand number evidently approaches $\bar{n} = N = 4$, and the inference is thus confirmed that the high values of the slopes of the C_A, C_M-lines observed for high values of [A] have no physical meaning. From the constants β_n thus determined, $\bar{n}$ can be calculated as a function of [A] and compared with the values found from the slopes,[9,10] Fig. 6 a. For values of [A] determined by means of eqn. (9) (= $[A]_{int}$) the method of evaluation of β_n certainly ensures that a good overall fit is obtained, but nevertheless significant deviations are found for the very highest values within this range, where the slopes yield higher values of $\bar{n}$ than those which are calculated from the constants. Thus at the upper limit $[A]_0$ = 19.3 mM, $\bar{n}$ = 4.00 is found from the slope as compared with 3.91 from the constants. As it has been stated above, this deviation is most probably due to a systematic error and has therefore been corrected for by the following process of reiteration. The values of $\bar{n}$ found from the first set of constants calculated as described above are introduced into eqn. (9) and slightly modified values of [A] hence obtained. These are used to calculate better values of β_n and so on. In practice, the second set of constants will be the definitive one, which is recorded in Table 7.

Bromide system: In Figs. 4 and 5, the C_A, E_{MP}-curves of different C_M have been plotted. The corresponding values of C_A and C_M for a number of suitably chosen E_{MP} are found in Tables 5 and 6. As was the case for chloride, C_A is a linear function of C_M at constant E_{MP}. These lines still pass through the origin at values of E_{MP} where the chloride lines yield an easily measurable intercept, thus demonstrating the stronger complex formation in the bromide system. For very high values of E_{MP}, the slopes give improbably high values of $\bar{n}_{obs}$, Table 6, though the anomaly for a certain value of E_{MP} is considerably smaller than in case of chloride. In the main this certainly depends upon the better

Table 5. The bromide system: Determination of corresponding values of [A], $\bar{n}$ and X_M for $E_{MP} \leqq 340$ mV. Derivation of the stability constants by extrapolation of the X-functions.

[$\times 10^3$ M	8	6	4							
[P mV	$C_A \times 10^3$ M			[A]int M	$\bar{n}_{obs}$	X_M	X_1 M^{-1}	$X_2 \times 10^{-17}$ M^{-2}	$X_3 \times 10^{-22}$ M^{-3}	$X_4 \times 10^{-26}$ M^{-4}
0							*4.2 × 10⁹*	*1.16*	*3.9*	*5.4*
1	0.62	0.55	0.31	1.96×10^{-11}	0.08	1.08	4.17×10^{9}			
2	1.18	0.88	0.59	4.10×10^{-11}	0.15	1.17	4.18×10^{9}			
3	1.70	1.28	0.84	6.39×10^{-11}	0.21	1.27	4.19×10^{9}			
4	2.22	1.64	1.05	8.84×10^{-11}	0.28	1.37	4.21×10^{9}			
5	2.67	1.98	1.26	1.15×10^{-10}	0.33	1.49	4.22×10^{9}			
6	3.10	2.27	1.45	1.44×10^{-10}	0.38	1.61	4.23×10^{9}			
7	3.48	2.55	1.64	1.75×10^{-10}	0.43	1.74	4.23×10^{9}			
10	4.55	3·30	2.18	2.85×10^{-10}	0.55	2.21	$4{\cdot}23 \times 10^{9}$			
20	6.57	4.97	3.15	8.99×10^{-10}	0.82	4.87	4.30×10^{9}	1.12		
30	7.80	5.90	3.75	2.19×10^{-9}	0.97	10.75	4.45×10^{9}	1.15		
40	8.70	6.60	4.23	4.76×10^{-9}	1.08	23.7	4.78×10^{9}	1.20		
50	9.45	7.27	4.70	9.59×10^{-9}	1.18	52.4	5.36×10^{9}	1.20		
60	10.6	8.07	5.23	1.81×10^{-8}	1.32	1.16×10^{2}	6.33×10^{9}	1.17		
80	12.9	9.70	6.40	5.31×10^{-8}	1.61	5.63×10^{2}	1.06×10^{10}	1.20		
00	14.5	11.0	7.3	1.33×10^{-7}	1.82	2.74×10^{3}	2.06×10^{10}	1.23		
20	15.8	12.0	7.9	3.07×10^{-7}	1.99	1.34×10^{4}	4.36×10^{10}	1.28		
40	16.9	12.9	8.4	6.63×10^{-7}	2.12	6.51×10^{4}	9.81×10^{10}	1.42	3.9	
60	18.3	13.8	9.0	1.36×10^{-6}	2.29	3.17×10^{5}	2.33×10^{11}	1.68	3.8	
80	19.9	14.9	9.7	2.64×10^{-6}	2.49	1.54×10^{6}	5.85×10^{11}	2.20	3.96	
00	21.4	16.0	10.4	4.88×10^{-6}	2.66	7.52×10^{6}	1.54×10^{12}	3.16	4.11	
20	22.8	17.1	11.1	8.66×10^{-6}	2.85	3.66×10^{7}	4.33×10^{12}	4.88	4.25	
40	24.1	18.0	11.8	1.49×10^{-5}	3.01	1.79×10^{8}		8.09	4.63	5.4
60	25.2	18.9	12.4	2.49×10^{-5}	3.16	8.70×10^{8}		14.1	5.16	5.2
80	26.4	19.7	13.0	4.07×10^{-5}	3.28	4.24×10^{9}		25.6	5.99	5.3
00	27.5	20.6	13.6	6.53×10^{-5}	3.42	2.06×10^{10}		48.4	7.23	5.2
20	28.6	21.4	14.1	1.03×10^{-4}	3.56	1.01×10^{11}		95.2	9.17	5.2
40	29.4	22.2	14.5	1.59×10^{-4}	3.68	4.90×10^{11}		193	12.1	5.2

Table 6 The bromide system: Determination of [A], X_M, X_3 and X_4 for $E_{MP} \geq 360$ mV.

$C_M \times 10^3$ M	8	6	4	0						
E_{MP} mV	$C_A \times 10^3$ M			$C_A =$ [A]	$[A]_{int}$ M	$\bar{n}_{obs}$	X_P	X_M	X_3 M^{-3}	$X_4 \times 10^{-26}$ M^{-4}
360	30.2	22.9	15.0	0.0	2.43×10^{-4}	3.79	1.000	2.39×10^{12}	1.66×10^{23}	5.2
400	31.7	24.2	16.1	0.5	5.53×10^{-4}	3.92	1.001	5.67×10^{13}	3.35×10^{23}	5.3
440	33.3	25.6	17.3	1.5	1.24×10^{-3}	3.98	1.003	1.35×10^{15}	7.06×10^{23}	5.4
480	35.8	27.7	19.3	2.6	2.76×10^{-3}	4.16	1.005	3.20×10^{16}	1.53×10^{24}	5.4
520	40.6	32.0	23.4	6.1		4.32	1.013	7.66×10^{17}	3.38×10^{24}	5.5
540	44.4	36.0	26.8	9.1		4.44	1.02	3.75×10^{18}	4.98×10^{24}	5.4
560	50.1	41.7	32.3	13.5		4.64	1.03	1.85×10^{19}	7.53×10^{24}	5.5
580	59.8	50.0	40.0	20.1		5.0	1.04	9.11×10^{19}	1.12×10^{25}	5.5
600	73.5	62.8	52.0	30.3		5.4	1.07	4.54×10^{20}	1.63×10^{25}	5.4
620	95.0	82.5	69.5	44.8		6.3	1.10	2.27×10^{21}	2.53×10^{25}	5.6
640	128	114	97	67.5		7.6	1.15	1.16×10^{22}	3.78×10^{25}	5.5
650	152	136	116	82.5		8.8	1.18	2.62×10^{22}	4.67×10^{25}	5.6

spacing of the bromide C_A, E_{MP}-curves which is a consequence of the stronger complex formation. On the other hand, a reliable value of the intercept that can be used as the upper limit of integration $[A]_0$ in eqn. (9) is reached only at such a high value of E_{MP}, that nevertheless the slope may be somewhat erratic. In practice, $E_{MP} = 520$ mV has been selected, corresponding to an intercept $[A]_0 = 6.1$ mM and a slope $\bar{n}_{obs} = 4.32$. The values of [A] found from the intercepts and by eqn. (9) ($= [A]_{int}$) are all given in Tables 5 and 6. The functions X_1 to X_4 are then calculated and hence the constants β_1 to β_4. Also for the bromide system, the function X_4 is a constant within very wide limits of [A], *viz.* from 0.015 to 82.5 mM, and no complexes beyond the fourth one can thus be proved within this system either. The ligand numbers used in eqn. (9) are thus rather much too high as [A] approaches $[A]_0$. For $[A]_0$ the constants β_n yield in fact $\bar{n} = 3.99$, as against 4.32 from the slope. The reiteration procedure therefore results in larger adjustments of the preliminary constants than what was found for the chloride system. Nevertheless the second set of constants will be the definitive one which is given in Table 7.

Table 7. The stability constants of the thallium(III) chloride and bromide complexes, with maximum random errors.

	Cl^-	Br^-
β_1 M^{-1}	$(3.5 \pm 0.3) \times 10^7$	$(4.2 \pm 0.1) \times 10^9$
β_2 M^{-2}	$(2.4 \pm 0.2) \times 10^{13}$	$(1.16 \pm 0.05) \times 10^{17}$
β_3 M^{-3}	$(6.2 \pm 0.5) \times 10^{16}$	$(3.9 \pm 0.3) \times 10^{22}$
β_4 M^{-4}	$(3.8 \pm 0.4) \times 10^{19}$	$(5.4 \pm 0.2) \times 10^{26}$
β_5 M^{-5}	$< 2.5 \times 10^{18}$	$< 2 \times 10^{26}$

CONCLUSIONS, COMPARISON WITH PREVIOUS WORK

The very strong affinity to chloride and bromide ions, increasing quite considerably in the mentioned order, characterizes Tl^{3+} as a much more typical class (*b*) acceptor than Tl^{+}. On this point the experimental evidence thus strongly favours the notion, consequential of the theory of dative π-bonding, that the more accessible the *d*-electrons, the more pronounced the class (*b*) character of the acceptor.

Within the range of concentration investigated for each ligand, four mononuclear complexes are formed in both systems. If a fifth complex is formed at even higher ligand concentrations, it must at any rate be much weaker than the preceding ones, Table 8. Most of the complexes have rather wide ranges of existence, Fig. 6 b, c, which is also apparent from the wawy appearance of the complex formation curves, Fig. 6 a. Quantitatively this is demonstrated by the very high values found for most of the ratios K_n/K_{n+1} between the consecutive stability constants, defined [9] according to $K_n = \beta_n/\beta_{n-1}$; $K_1 = \beta_1$ (Tables 8 and 9). Within the chloride system, the second complex has a wider range of existence than its neighbours. As one passes on to the bromide system, however, the second complex becomes relatively less important, while the first and third complex both become relatively more important, Fig. 6 b, c and Table 9. In fact the range of the first complex grows larger than that of the second one.

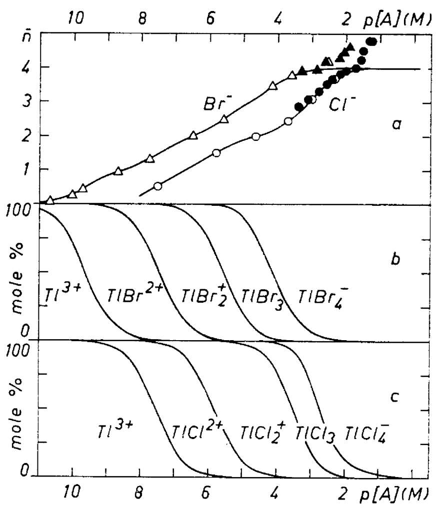

Fig. 6a. The complex formation functions of the systems investigated. Fulldrawn curves calculated with the constants of Table 7. Circles and triangles denote $\bar{n}_{obs}$ of Tables 2 and 4; 5 and 6, respectively. Open signs refer to $[A]_{int}$, obtained by eqn. (9), filled signs to [A] determined as intercepts, eqn. (8). The points above $\bar{n} = 4$ are presumably erratic (*cf.* p. 1573). Of $[A]_{int}$, only every third value is given in the figure. — *Fig. 6 b and c.* The distribution of thallium(III) between different complexes in the bromide and chloride systems.

Table 8. Comparison of the values of log K_n found by different investigators under the conditions stated.

Ref.	Method	I M	t°C	log K_n					
n →				1	2	3	4	5	6
Chloride									
This work	Tl^{3+}/Tl^{+}	4.0	20	7.54 ± 0.04	5.84 ± 0.08	3.41 ± 0.08	2.79 ± 0.08	< −1.2	—
4	Ag/AgCl	0.0	18	8.1	5.5	2.2	2.2	—	—
5	Ag/AgCl	1.2	21	6.25	5.15	3.10	2.5	2.15	1.80
6	Tl^{3+}/Tl^{+}*	0.5	25 *	7.05	4.97	2.41	1.89	—	—
6	Tl^{3+}/Tl^{+}*	3.0	25 *	7.78	5.09	3.29	2.16	—	—
7	Ag/AgCl	3.0	30	7.30	5.18	3.08	2.36	—	—
7a	Ag/AgCl	0.4	20	7.50	4.50	2.75	2.25	1.95	1.75
Bromide									
This work	Tl^{3+}/Tl^{+}	4.0	20	9.62 ± 0.01	7.44 ± 0.03	5.53 ± 0.06	4.14 ± 0.05	< −0.4	—
4	Ag/AgBr	0.0	18	9.7	6.9	4.6	2.7	—	—
5	Ag/AgBr	1.2	25	8.9	7.5	5.7	4	3.1	2.4
7a	Ag/AgBr	0.4	20	8.3	6.3	4.6	3.1	2.5	1.7

* Private communication from Dr. E. L. King through Dr. D. Dyrssen.

Table 9. Comparison of the ratios K_n/K_{n+1} found by different investigators.

Ref.	I M	K_1/K_2	K_2/K_3	K_3/K_4	K_4/K_5
Chloride					
This work	4.0	51	230	4.3	> 9 000
4	0.0	400	2000	1	—
5	1.2	13	110	4	2
6	0.5	120	380	3.3	—
6	3.0	490	61	14	—
7	3.0	130	120	5	—
7a	0.4	1000	60	3	2
Bromide					
This work	4.0	150	82	24	> 38 000
4	0.0	600	200	80	—
5	1.2	25	60	50	8
7a	0.4	100	50	30	4

A comparison of this work with previous investigations [4-7,7a] of the thallium(III) chloride and bromide systems is also contained in Tables 8 and 9. In view of the differences in method of measurement, medium and temperature, the results may be considered as giving a fairly coherent general picture, except for the coordination of six ligands in solution, as claimed by Peschanski and Valladas-Dubois[5] and also by Busev, Tiptsova and Sokolova [7a]. Like several other investigators,[4,6,7] however, we have not been able to find any complexes beyond the fourth one, though our measurements have been arranged in such a way that those higher complexes would certainly have shown up, if they had existed. As to the finer points, it is generally agreed that the second complex is more prominent in the chloride than in the bromide system, while the opposite is true of the first and, especially, the third complex. Remarkable deviations from this pattern are reported, however, by Busev *et al.*[7a] and also by Hugus [6] who has evaluated data provided by E. L. King. For the series of $I = 3.0$ M, he finds an exceptionally wide range of existence for the first chloride complex, as compared with the second one. The same conclusion is drawn by Busev *et al.* from their data at $I = 0.4$ M, Table 9. A later reappraisal of King's data has however resulted in essentially altered values of the constants K_n (according to a private communication from Dr. King through Dr. D. Dyrssen). These new values indicate the first complex to have a much narrower range of existence than the second one, in accordance with the view of most investigators.

In fact it is rather surprising that the silver halide electrodes, which have been used by most investigators [4,5,7,7a], really yield any reasonable results at all. From the known values of the standard potentials and stability constants involved, it is quite plain that these electrodes should be oxidized by thallium (III) in all solutions investigated. As the electrodes nevertheless seem to work at least tolerably well, this redox reaction must evidently be strongly inhibited. It is possible, however, that the effect ascribed to formation of complexes beyond the fourth one [5,7a] is in reality due to an oxidation of the electrodes.

The property of Tl^{3+} of coordinating in solution four halide ions at the most is shared [16] by the isoelectronic Hg^{2+}, and also [17,18] by Cd^{2+} and Ag^{+} which are mutually isoelectronic and have an electron configuration analogous to that of Tl^{3+} and Hg^{2+}. On the other hand Bi^{3+}, with the same charge as Tl^{3+}, and in the same period, but possessing two more electrons, is able to coordinate six halide ions [19] (*cf.* also Ref.[20]).

The relative stabilities of the consecutive complexes are however very different among the four-coordinating ions mentioned, the extremes being represented by Hg^{2+} and Cd^{2+}. For Hg^{2+}, the second complex has an extremely wide range of existence, both in terms of the range of [A] where it is dominating, and relative to its neighbours, and this becomes more and more pronounced in the sequence [16] Cl^-, Br^-, I^-. The same pattern, though not so strongly marked, is presented by Ag^+ (see Appendix, p. 1582, for further discussion). For Cd^{2+}, on the contrary, the second complex has an unusually narrow range of existence, which moreover gets narrower in the sequence Cl^-, Br^-, I^-. The state of Tl^{3+} is obviously intermediate. The broad range of the second chloride complex is a feature in common with Hg^{2+} and Ag^+, but the narrower range of the corresponding bromide complex resembles the behaviour of Cd^{2+}.

Both effects are however less pronounced than for the typical cases of Hg^{2+} (or Ag^{+}) and Cd^{2+}, respectively.

The coordination number $N = 4$ found in solution may look somewhat strange in view of the existence of solid salts of the types [21] $M_3(I)[TlCl_6]$ and $M_3(I)[TlCl_5.H_2O]$. Moreover an octahedral arrangement of six halide ions around Tl^{3+} has been inferred [22] from X-ray examinations for $K_3[TlCl_6].2\ H_2O$, and also for $Rb_3[TlBr_6].8/7\ H_2O$. However, great care should always be exercised when drawing conclusions about the conditions in solution from structures found for solid phases. It may also be significant that, as the strength of the complex formation grows in the sequence $Cl^- < Br^- < I^-$, the maximum number of halide ions coordinated tends to four even in the solid state [21]. Thus most bromo thallates, and all iodo thallates known so far, are of the type $M(I)[TlX_4]$.

In this connexion it should be noted (*cf.* Refs.[16,23]) that in the solid compound NH_4HgCl_3 each Hg^{2+} is surrounded octahedrally by six Cl^-. The octahedron is distorted in so far that two Cl^- are especially close to the central ion, which reflects the high stability of the second complex, but the remaining four Cl^- are all equidistant, in spite of the established fact that the maximum coordination number in solution is four. Also in solid K_2HgCl_4, a similar octahedral arrangement has been found, though in this case not only the first two ligands are preferred but also, to some extent, the two next ones. In the case of I^- on the other hand, a tetrahedral configuration around Hg^{2+} is found not only for Ag_2HgI_4 and Cu_2HgI_4, but also, more surprisingly, for the red modification of HgI_2. From the conditions ruling in solution, a linear twocoordinated group would rather be expected to exist in this compound, as it in fact does in the yellow mofidication of HgI_2, stable above 127°C, as well as in $HgBr_2$ and $HgCl_2$. A trend common to Hg^{2+} and Tl^{3+} in solid compounds thus seems to be that a maximum coordination number of six is favoured in case of Cl^-, as against four in the case of I^-.

APPENDIX

Note on the complex formation of the silver halides. Dr Leden has told us that he does not regard his value of the constant β_1 for the silver iodide system [24,25] as very reliable, because he did not have at the time the adequate means for a good determination of those extremely low solubilities where AgI is a main component of the system. The highest activity of ^{110m}Ag obtainable did not give a sufficient number of counts with the experimental setup at his disposal. Instead ^{131}I had to be used as a tracer which permitted a higher activity in the original solutions. In the fairly intense field of radiation however, an oxidation of the iodide to free iodine was very likely to occur to some extent, which would result in too high a figure for the solubility. In fact the solubility curve found from the ^{110m}Ag-series did point to a lower value of the minimum solubility than that which was actually found from the ^{131}I-series. The stability of the first complex might thus have been considerably overestimated, and consequently, that of the second complex underestimated. It seems in fact most likely that the complex formation curve of the silver iodide system has a main stop at $\bar{n} = 2$ and a less marked one at $\bar{n} = 1$. This conclusion is much strengthened by the results of Lieser [26] who has also measured the solubility of the silver halides by tracer methods. For the iodide system, the lowest solubilities were determined by means of ^{111}Ag which permits the use of a sufficiently high activity. A very wide range of existence was found for the second complex, $K_2/K_3 = 1700$ at $I = 0$ and 18°C. Though this value may be somewhat too high in view of the fact that, contrary to expectation, the ratio $K_1/K_2 = 26$ comes out lower than the corresponding ratio for the bromide system, $K_1/K_2 = 51$, it leaves no doubt about the high stability of the second complex relative to its neighbours. The complex formation of the silver halides thus comforms to that of the mercury(II) halides,[16] though the characteristic features are considerably less marked.

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