18-electron intermediates (e.g., $HRh(P{\sim}P)(P{\sim}P)^m$(olefin) or $HRh(P{\sim}P)(PR_3)$(olefin)) that have three phosphine ligands coordinated to Rh at the step in the mechanism where Rh–H addition to coordinated olefin occurs (i.e., the selectivity determining step).

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Thallium-205 Nuclear Magnetic Resonance Study of Thallium(III) Halide Complexes in Aqueous Solutions

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Abstract: A combination of solution and solid-state ^{205}Tl NMR experiments is used to study the formation and geometry of TlX_n^{3-n} complexes (X = Cl, Br). The chemical shifts for the individual species and their stability constants are determined for dilute (0.05 M) and concentrated (1.0 and 2.6 M) aqueous Tl(III) solutions. The existence of $TlCl_5^{2-}$ and $TlCl_6^{3-}$ as well as at least one species higher than $TlBr_4^-$ in solution is shown. The species $TlCl_3$ is 300–400 ppm less shielded in aqueous solutions than in solid phase, indicating a structural difference. The chemical shifts obtained for the individual TlX_n^{3-n} complexes are compared with corresponding shifts for zinc(II) and cadmium(II) halide complexes.

The complexes formed in the thallium(III) halide system are among the strongest metal ion halide complexes known. Several investigations were made on this system,[2-20] and some interesting structural properties can be discerned. Thus, for example, there are indications[15,20] that in aqueous solutions of $Tl(ClO_4)_3$ only two water molecules are strongly bound to Tl^{3+} and that these are replaced by chloride when $TlCl(H_2O)_5^{2+}$ and $TlCl_2(H_2O)_4^+$ are formed. The stability constants and the enthalpy values[10-13,16,20] indicate some structural change between the second and third complex.

The existence of higher complexes $TlCl_n^{3-n}$ ($n > 4$) was for a long time a matter of controversy. In dilute solutions, where all of the emf, solubility, and calorimetric measurements were performed, the formation of higher complexes is generally claimed to be negligible: $K_5 = [TlX_5^{2-}]/([TlX_4^-][X^-]) < 0.07\ M^{-1}$ for X = Cl and $K_5 < 0.37\ M^{-1}$ for X = Br, at 25 °C.[10,11] (The exceptions are some emf works, where silver halide electrodes have been used.[3,4,8,9] These results are probably erroneous because of the oxidation of the electrodes by Tl(III), as was pointed out by some investigators.[10]) However, UV spectra of dilute Tl(III) solutions at very high chloride concentrations[19] indicate the formation of one higher species, $TlCl_5^{2-}$, with the stability constant $K_5 = 0.8\ (2)\ M^{-1}$.

Extraction data for dilute solutions are also interpreted in terms of weak bonding of the fifth chloride ligand ($K_5 = 0.3\ M^{-1}$),[5] although other workers using the same method found no evidence for complexes higher than $TlCl_4^-$ (at least not more than 3% of the total thallium concentration).[14]

In concentrated solutions, Raman spectra clearly show that, in the chloride system, at least one higher complex exists, probably $TlCl_6^{3-}$ ($K_{4,6} = [TlCl_6^{3-}]/([TlCl_4^-][Cl^-]^2) = 0.2\ M^{-2}$).[15,18] NMR data also indicate the formation of complexes with more than four chlorides per Tl(III).[6,7] Figgis[6] postulated that the most stable species at higher halide concentrations is $Tl_2X_9^{3-}$ (X = Cl, Br).

For determination of the compositions and structures of the complexes formed in aqueous solutions containing Tl(III) and one of the halides (Cl, Br), an X-ray diffraction study[21] was undertaken. For the interpretation of the diffraction data the distribution of Tl(III) among the different species has to be known for the concentrated solutions ($[Tl]_{tot} \geq 1$ M). However, all the available stability constants are determined for rather dilute solutions ($[Tl]_{tot} \leq 50$ mM). The aim of the present work is to estimate this distribution. In addition, the ^{205}Tl chemical shifts for the individual TlX_n^{3-n} complexes are obtained, and they may provide some structural information when compared with the chemical shifts for the corresponding solid-state coordination compounds with known structures. The shifts can also be compared with those determined for the halide complexes of the d^{10} ions Zn^{2+} and Cd^{2+}.

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Table I. ^{205}Tl Chemical Shifts (δ) and Line Widths at Half-Height ($\Delta\nu_{1/2}$) for Various Solid Tl(III) Salts[a]

compound	δ	$\Delta\nu_{1/2}$, kHz	configuration around Tl(III)
$Tl(ClO_4)_3 \cdot 6H_2O$	2175	6.8	$Tl(H_2O)_6^{3+}$ regular octahedron[32]
$TlCl_3 \cdot 4H_2O$	2051	8.0	$TlCl_3(H_2O)_2$ trigonal bipyramide[44,45]
$KTlCl_4$	2716	6.0	$TlCl_4^-$ tetrahedron[47,48]
$Cs_2TlCl_5 \cdot H_2O$	2022	5.1	$TlCl_5(H_2O)^{2-}$ octahedron[64,65]
$Na_3TlCl_6 \cdot 12H_2O$	1972	5.0	$TlCl_6^{3-}$ octahedron[66]
$K_3TlCl_6 \cdot (13/7)H_2O$	2007	6.0	$TlCl_6^{3-}$ octahedron and $TlCl_5(H_2O)^{2-}$ octahedron[28,31,38]
$[Co(NH_3)_6]TlCl_6$	2019	3.3	$TlCl_6^{3-}$ octahedron[29,67]
$Cs_3Tl_2Cl_9$	1926	9.0	$TlCl_9^{3-}$ unit (two $TlCl_6^{3-}$ octahedra with one common face)[51,68]
$TlBr_3 \cdot 4H_2O$	1098	14.0	$TlBr_3(H_2O)_2$ trigonal bipyramide[44,45]
$KTlBr_4 \cdot 2H_2O$	1262	15.5	$TlBr_4^-$ tetrahedron[49]
$[Co(NH_3)_6]TlBr_6$	−1271	19.0	$TlBr_6^{3-}$ octahedron[29]
$Cs_3Tl_2Br_9$	−1194	12.0	unknown
$[NBu_4]TlI_4$	−1560	20	slightly distorted TlI_4^- tetrahedron[53]

[a] The shifts are given in ppm toward higher frequency with respect to Tl^+(aq) at infinite dilution.

The following measurements were performed. The ^{205}Tl chemical shifts δ_i^{obsd} for 50 mM, 1.0 M, and 2.6 M aqueous solutions of Tl(III) and varying concentrations of the halide were measured. In the 50 mM solutions, separate signals were obtained for the lower complexes ($n = 0, 1$ for Cl; $n = 0, 1, 2$ for Br), due to slow exchange. In all the other solutions only one average signal was observed due to rapid exchange. The position of this signal is given by

$$\delta_i^{obsd} = \sum_n p_n^i \delta_n \qquad (1)$$

where $p_n^i = [TlX_n^{3-n}]/[Tl]_{tot}$ and δ_n is the chemical shift of TlX_n^{3-n}.

Table II. ^{205}Tl Chemical Shifts (δ) and Line Widths at Half-Height ($\Delta\nu_{1/2}$) for Various Solutions[a]

solution	solvent	δ	$\Delta\nu_{1/2}$, kHz
0.05 M Tl^{3+} in conct HCl	H_2O	2096	0.03
0.05 M Tl^{3+} in conct HBr	H_2O	1169	0.01
0.05 M Tl^{3+} in conct $HClO_4$	H_2O	2056	0.03
0.5 M $[N(C_4H_9)_4]TlI_4$	CH_2Cl_2	−1732	0.2
mother liquor from	H_2O	1944 (90%)	0.6
$Tl(ClO_4)_3 \cdot 6H_2O(s)$		1965 (10%)	0.2

[a] The shifts are given in ppm toward higher frequency with respect to Tl^+(aq) at infinite dilution.

Experimental Section

Materials. Natural abundance Tl chemicals were used throughout. The preparation of the solid phases was described elsewhere.[26-32] The investigated solutions were prepared from stock solutions: 2.1 M $Tl(ClO_4)_3$ in 2.65 M $HClO_4$,[31,33] 2.6 M $TlX_n(ClO_4)_{3-n}$,[31] concentrated $HClO_4$ (p.a., free from halide), 8.4 M $NaClO_4$,[33] and varying amounts of solid LiX (p.a.). They were analyzed for Tl (bromatometric titration[34a] with potentiometric end point), halide (Volhard titration[34b]), and $[H^+]$ (titration with NaOH after reduction of Tl^{3+} to Tl^+ by H_2O_2[33]).

All bromide solutions with $R_{Br} = [Br^-]_{tot}/[Tl]_{tot} \leq 2$ were saturated with Br_2 in order to prevent the reduction of Tl(III) to Tl(I).

The concentration of Tl(I) was lower than 1% of the total thallium in all the solutions investigated.

Measurements. The 51.9 MHz ^{205}Tl spectra were recorded at the ambient probe temperature of 27.2 °C by using a Bruker CXP-100 spectrometer. The field was stabilized with an external field lock. The samples were contained in 10-mm nonspinning sample tubes. The contribution to the line width from field inhomogeneities was 18 Hz.

All ^{205}Tl chemical shifts were reported in parts per million toward higher frequency with respect to an aqueous solution of $TlClO_4$ at infinite dilution. Since the chemical shifts for aqueous solutions of different Tl(I) salts extrapolated to the same value at infinite dilution,[35] this value corresponded to the chemical shift of the free hydrated Tl^+ ion.

The accuracy of the chemical shifts determined depended strongly on the width of the observed peaks. For narrow lines it was better than 0.2 ppm. For the broadest lines the errors were considerably greater. No corrections were made for differences in bulk susceptibilities (they are probably less than ±0.5 ppm[22] and their influence on the results can therefore be neglected).

Results

Solids. The ^{205}Tl chemical shifts and line widths for the salts investigated are given in Table I. As can be seen, the lines are very broad, especially for the bromides. Hence, the accuracy in the determined shifts is rather low (~±25 ppm for the chlorides and ~±50 ppm for the bromides). It was not possible to obtain any information about the individual shielding tensor elements from the solid-state spectra.

In some cases our results differ significantly from earlier reported shifts.[7,36] One possible reason for this difference is that it is often difficult to prepare solid samples that are completely free from mother liquor, and the narrow signal from the mother liquor is relatively easy to observe (see, e.g., Figure 2). For most of the solid samples we have recorded the signal both from the salt and from the mother liquor to assure that no erroneous assignments are made.

Unfortunately, there is no literature data available on any salt containing the fifth bromide complex $TlBr_5(H_2O)^{2-}$ alone. The salt (*N*,*N'*-dimethyltriethylenediammonium)pentabromothallate, (DMTEA)$TlBr_5$, contains highly asymmetric $TlBr_5^{2-}$ units probably because of the packing in the crystal,[37] and this kind of complex is not expected to occur in aqueous solution. The only solid, in which the hydrated complex $TlBr_5(H_2O)^{2-}$ has been found, is $Rb_3TlBr_6 \cdot (^{13}/_7)H_2O$.[31,38] But, as only 2 of 14 thallium atoms are coordinated in this way, it was not possible to obtain the shift for the fifth complex. In fact, no resonance was found for this compound, probably because of the extreme broadening of the line.

Solutions. Three series of solutions were investigated. Within each series, the total thallium concentration was kept constant (0.05, 1.0, and 2.6 M), and the halide concentration was varied.

In the 0.05 M solutions, the ionic medium was exactly the same as in ref 10 and 11 (3 M $HClO_4$ + 1 M $NaClO_4$) in order to maintain the validity of the equilibrium constants. In the 1.0 M

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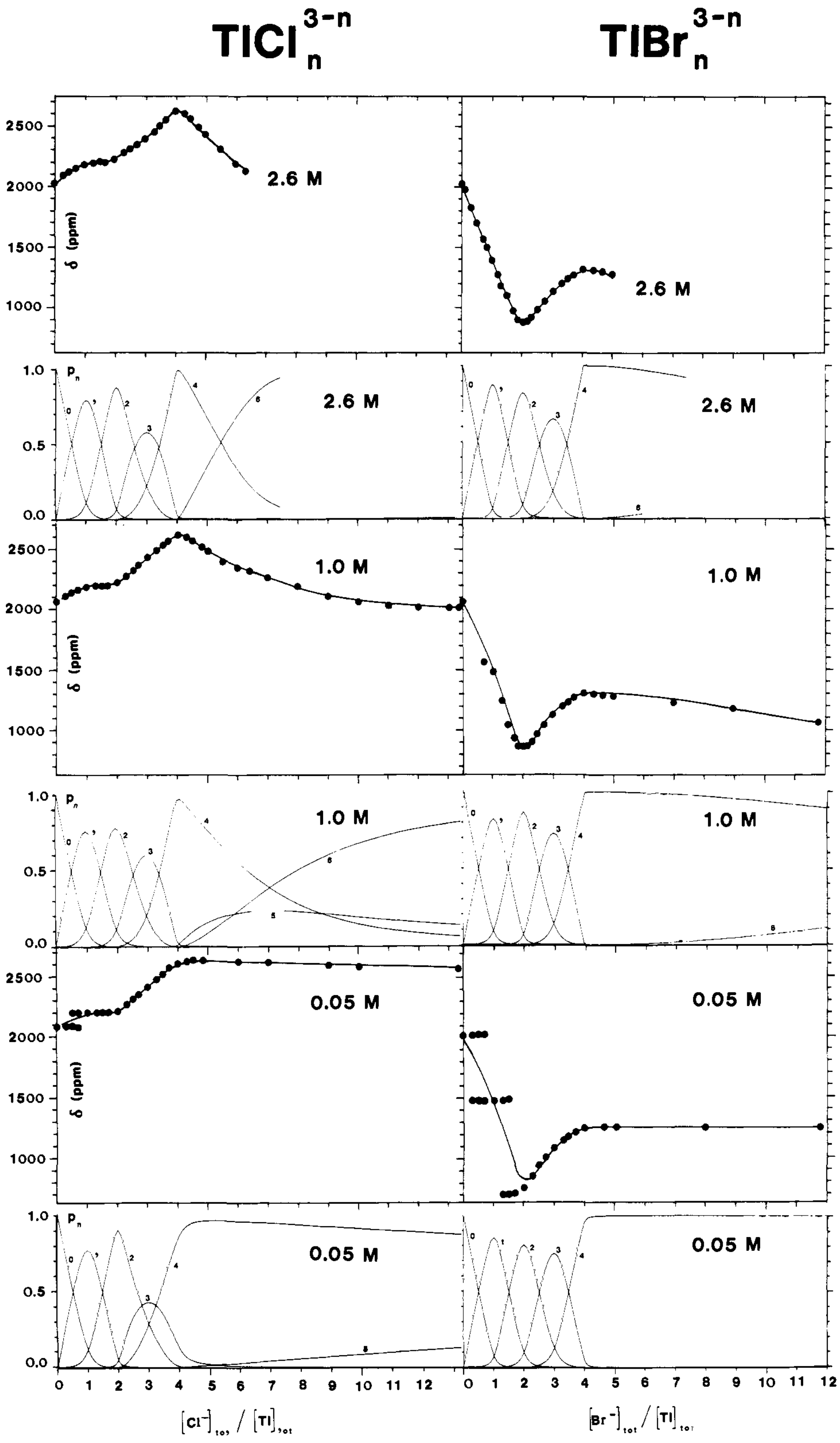

Figure 1. ^{205}Tl chemical shifts from aqueous solutions of Tl(III) as functions of $R_X = [X^-]_{tot}/[Tl]_{tot}$ (X = Cl, Br). ● indicates experimental points, full lines are calculated from eq 1 by using the stability constants and chemical shifts for individual complexes given in Table III. The fraction of Tl(III) present as TlX_n^{3-n}, calculated by using the same stability constants, is also shown. Separate signals for the different complexes were observed for the R_X values for which two experimental points are marked in the figure.

solutions, the sum $[H^+]_{tot} + [Li^+]_{tot} = 3.0$ M was kept constant for $R = [X^-]_{tot}/[Tl]_{tot} \leq 6.0$. For [Tl(III)] = 2.6 M, no ionic medium was used (moreover, $[Tl]_{tot}$ was ~15% lower for $R \leq 1$). These conditions were chosen since the concentrated solutions should have exactly the same composition as those investigated by X-ray diffraction.[21,31]

The measured chemical shifts are shown in Figure 1. Some additional shifts are presented in Table II. For the 0.05 M solutions separate signals were observed for the species Tl^{3+}, $TlCl^{2+}$, $TlBr^{2+}$, and $TlBr_2^+$, showing that the rate of exchange between these complexes is slow on a time scale defined by the difference between their chemical shifts. The signals are, however,

Table III. Calculated ^{205}Tl Chemical Shifts[a] and Stability Constants (Recalculated to 25 °C) for the TlX_n^{3-n} Complexes[b]

	$[Tl]_{tot} = 0.05$ M, $[NaClO_4] = 1$ M, $[HClO_4] = 3$ M	$[Tl]_{tot} = 1.0$ M, $[HClO_4] + [Li^+] = 3$ M	$[Tl]_{tot} = 2.6$ M	solids	$[Tl]_{tot} \leqslant 0.05$ M[c] $[NaClO_4] = 1$ M $[HClO_4] = 3$ M
			X = Cl		
δ_0	2086 (±1)	2075 (4)	2048 (15)	2175 (±30)	
δ_1	2198 (±4)	2209 (4)	2194 (9)		
δ_2	2201 (2)	2183 (5)	2220 (10)		
δ_3	2412 (5)	2457 (9)	2357 (12)	2051 (±35)	
δ_4	2645 (2)	2630 (3)	2649 (6)	2716 (±30)	
δ_5				2022 (±20)	
δ_6				1972 (±25)	
β_1		$1.5 (4) \times 10^{7}$	$3 (1) \times 10^{7}$		$2.9 (\pm 0.3) \times 10^{7}$
β_2	$1.9 (5) \times 10^{13}$	$0.6 (2) \times 10^{13}$	$1.8 (6) \times 10^{13}$		$1.8 (\pm 0.2) \times 10^{13}$
β_3	$3.6 (5) \times 10^{16}$	$5.0 (7) \times 10^{16}$	$6.8 (9) \times 10^{16}$		$4.5 (\pm 0.5) \times 10^{16}$
β_4	$3.1 (1) \times 10^{19}$	$4.8 (2) \times 10^{19}$	$3.8 (3) \times 10^{19}$		$2.8 (\pm 0.4) \times 10^{19}$
β_5	$1.0 (3) \times 10^{19}$	$1.4 (2) \times 10^{19}$			$<0.2 \times 10^{19}$
β_6		$1.1 (2) \times 10^{19}$	$2.9 (3) \times 10^{19}$		
			X = Br		
δ_0	2086 (±1)	2061 (±1)	2026 (10)	2175 (±30)	
δ_1	1538 (±3)		1388 (6)		
δ_2	766 (±3)	790 (13)	783 (6)		
δ_3	1184 (5)	1164 (12)	1182 (12)	1098 (±50)	
δ_4	1318 (2)	1311 (11)	1314 (8)	1262 (±55)	
δ_5					
δ_6				−1271 (±70)	
β_1			$3.7 (5) \times 10^{9}$		$3.2 (\pm 0.1) \times 10^{9}$
β_2		$12 (1) \times 10^{16}$	$7.2 (6) \times 10^{16}$		$7.5 (\pm 0.5) \times 10^{16}$
β_3	$2.6 (4) \times 10^{22}$	$2.6 (5) \times 10^{22}$	$1.7 (4) \times 10^{22}$		$2.2 (\pm 0.3) \times 10^{22}$
β_4	$2.6 (6) \times 10^{26}$	$2.0 (5) \times 10^{26}$	$3.0 (5) \times 10^{26}$		$2.9 (\pm 0.2) \times 10^{26}$
β_5					$<1.1 \times 10^{26}$
β_6	$(8 (1) \times 10^{24})$	$(4 (1) \times 10^{23})$	$(4 (1) \times 10^{23})$		

[a] The shifts are given in ppm toward higher frequency with respect to Tl^+(aq) at infinite dilution. [b] The stability constants, β_n:s, are calculated for the reaction $Tl^{3+} + nX^- \rightleftarrows TlX_n^{3-n}$. For the least-squares refined parameters the standard deviations (in the last digit) are given in parentheses. For the remaining parameters maximum random errors are given. [c] From ref 10.

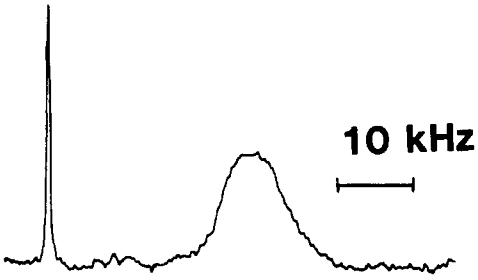

Figure 2. 51.9 MHz ^{205}Tl spectrum from $TlCl_3 \cdot 4H_2O$(s) in the presence of some mother liquor.

still broadened due to the exchange. When the total thallium concentration is increased, the lines become further broadened and finally coalesce to a single average signal for the exchanging species. This clearly shows that the rate of exchange increases with increasing total thallium concentration. The great difference between the chemical shifts for the different species gives rise to very broad signals (up to ~50 kHz) for intermediate exchange rates.

Data Treatment

In the 50 mM solutions the chemical shifts for the species Tl^{3+}, $TlCl^{2+}$, $TlBr^{2+}$, and $TlBr_2^+$ were determined directly from the recorded spectra. For the solutions where the rate of exchange is fast, the parameters in eq 1 were fitted to the experimental data in Figure 1 by using the program SPEFO.[39] The species $Tl_2Cl_9^{3-}$ and $Tl_2Br_9^{3-}$, which were proposed by Figgis[6] to dominate in concentrated solutions with high halide/thallium ratios, were not included in the least-squares refinements since recent X-ray investigations of the thallium(III) halide systems show unambiguously that no polynuclear species are present to any great extent in these solutions.[21,31] The parameters $p_n^i = [TlX_n^{3-n}]/[Tl]_{tot}$ can be determined if the stability constants for the different complexes are known. This method was applied earlier for zinc(II)[22] and cadmium(II)[23,24] halide complexes. The results of the least-squares refinements are presented in Table III. The standard deviations given are those calculated by the program and do not include all possible systematic errors.

Different values of stability constants for the chloride complexes (n = 1–4) can be found in the literature: (a) Ahrland et al.[10,11] (in 3 M $HClO_4$ + 1 M $NaClO_4$); (b) Woods et al.[12] (in 3 M $HClO_4$); (c) Kul'ba et al.[16] (in 3 M $LiClO_4$); (d) Biedermann et al.[20] (in 3 M $NaClO_4$). For the 0.05 M chloride solutions the values of the stability constants were fixed and the δ_n:*s* were refined for n = 1–4. Only the data for $1.5 \leq R_{Cl} \leq 4.8$ were used in the refinements in order to avoid the contribution from the fifth complex (for $R_{Cl} < 1.5$ separate signals were observed for the individual complexes, vide supra). The number of measurements per determined parameter were five in these refinements. The chemical shifts obtained were not significantly different for the four sets of stability constants as far as δ_1, δ_2, and δ_3 are concerned, whereas δ_4 in the set a was ~50 ppm lower than in sets b, c, and d. Also, the shifts obtained for the three latter sets of constants had 2–3 times higher standard deviations than in the refinement a. Finally, the least-squares sums for the calculations b, c, and d were 4–6 times higher than for a.

This result is expected since the ionic medium used in the present work was exactly the same as in a. The influence of the different concentration and type of the ionic medium on the stability constants can certainly not be neglected. The effect of increasing the ionic strength and/or the concentration of the hydrogen ion on the formation of the $TlCl_n^{3-n}$ species can be seen in ref 12, where the stability constants in 0.5 M $HClO_4$ and 3 M $HClO_4$ were determined. The influence of replacing $NaClO_4$ by $HClO_4$ at constant ionic strength is also of great importance, as

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shown by Heistand and Clearfield in their spectrophotometric study[40] of the reaction

$$Fe(H_2O)_x^{3+} + Cl^- \rightleftarrows FeCl(H_2O)_{x-1}^{2+} + H_2O$$

However, the replacement of $LiClO_4$ by $HClO_4$ did not affect the stability constant to such a great extent. In fact, the effect of different ionic media on the stability constants for the $TlCl_n^{3-n}$ species could be calculated by use of the semiempirical specific interaction theory,[41] showing that the differences in the values of the constants in ref 10, 16, and 20 are almost completely due to the influence of the ionic media.[31] The general aspects of the medium effect and its relationship to the different methods of studying complex formation equilibria will be the subject of a separate communication.[42]

For the concentrated solutions no stability constants are known and the only way to estimate the complex distribution is to determine the δ_n:*s* and the stability constants simultaneously from eq 1. In these refinements the number of measurements per determined parameter was only about half of the number used in the refinements described above. This is reflected in the rather high standard deviations in the determined stability constants in Table III. However, for the concentrated solutions the systematic errors due to the variation of the ionic strength are probably greater than the uncertainties introduced by the low number of measurements/parameter. The use of stability constants based on concentrations and not activities in the concentrated solutions, where the ionic strength varies, is of course a rather serious limitation, but it was thought that a rough estimation of the stability constants is better than no information at all.

For each data set, the data were treated in two steps. (1) $R \leq 4$, where the concentration of higher complexes ($n > 4$) was negligible; the parameters for the first five complexes ($n = 0$–4) could be refined. (2) All the data were used in the refinement, but some or all parameters for the lower complexes were kept constant at the values from step 1.

In some cases, when all the parameters could not be refined simultaneously, they were refined in subgroups, in different combinations, until no further change was obtained. The standard deviations given in Table III were increased to account for the variation of the parameters during the different refinements.

However, it should be emphasized that in the least-squares refinements the experimental points close to the domination regions of the different TlX_n^{3-n} complexes are weighted up as a consequence of the calculation procedure used. Thus the standard deviations in the stability constants for the concentrated solutions are valid only in these regions and are probably much higher outside the domination areas as a result of the dependence of the stability constants on the ionic strength.

The reliability of the simultaneous determination of stability constants and chemical shifts for the different species can be tested for the 50 mM solutions. It is seen from the results in Table III that our stability constants agree with those of Ahrland et al.[10,11] within the standard deviations. The situation is in fact quite favorable for the thallium(III) halide complexes since (1) each TlX_n^{3-n} complex has a predominance region for some halide to thallium ratio (cf. distribution curves in Figure 1, calculated by the HALTAFALL program[25]), (2) the chemical shift range for the TlX_n^{3-n} complexes in aqueous solutions is very wide, almost 2000 ppm, and the shifts can be determined quite accurately, and (3) the high NMR sensitivity of ^{205}Tl makes it possible to record the spectra at a low total thallium concentration, 50 mM, where the results can be compared with accurate stability constants.[10,11] The method has, however, some limitations. When several complexes exist in solution, the change of the ionic strength (in the concentrated solutions) may alter the distribution of the complexes and/or the δ_n:*s*. The two effects may be difficult to separate. For the solutions where the chemical shifts for the individual complexes could be measured directly due to the slow exchange, the dependence of δ_n on ionic strength was studied. Some of the results are presented in Table IV.

Table IV. Dependence of the Chemical Shifts[a] for the Individual Complexes (δ_n) on the Ionic Strength (I) and the Hydrogen Ion Concentration of the Solution

solution composition	$[H^+]$, mol·L^{-1}	I, mol·L^{-1}	complex	δ_n
0.05 M $TlCl_{0.5}(ClO_4)_{2.5}$	3	4	Tl^{3+}	2077
			$TlCl^{2+}$	2195
0.05 M $TlCl_{0.5}(ClO_4)_{2.5}$	3	7	Tl^{3+}	2069
			$TlCl^{2+}$	2190
0.05 M $TlBr_{0.5}(ClO_4)_{2.5}$	3	4	Tl^{3+}	2084
			$TlBr^{2+}$	1539
0.05 M $TlBr_{0.5}(ClO_4)_{2.5}$	3	7	Tl^{3+}	2067
			$TlBr^{2+}$	1513
0.05 M $TlBr_{1.5}(ClO_4)_{1.5}$	3	4	$TlBr^{2+}$	1535
			$TlBr_2^+$	767
0.05 M $TlBr_{1.5}(ClO_4)_{1.5}$	3	7	$TlBr^{2+}$	1502
			$TlBr_2^+$	747
0.05 M $Li_{1.5}TlCl_{4.5}$	3	4	$TlCl_4^-$	2634
1.0 M $Li_{1.0}TlCl_{4.0}$	2	3	$TlCl_4^-$	2625
2.6 M $Li_{1.0}TlCl_{4.0}$	0	2.6	$TlCl_4^-$	2624
0.05 M $Li_{1.6}TlBr_{4.6}$	3	4	$TlBr_4^-$	1317
1.0 M $Li_{1.0}TlBr_{4.0}$	2	3	$TlBr_4^-$	1317
2.7 M $Li_{1.0}TlBr_{4.0}$	0	2.7	$TlBr_4^-$	1319

[a] The shifts are given in ppm toward higher frequency with respect to Tl^+(aq) at infinite dilution.

The peaks from the complexes with $n = 0$, 1 and 2 are, however, rather broad (1–2 kHz). Hence, the uncertainty in the determined shifts can be estimated to approximately ±7 ppm. As can be seen, the shifts for Tl^{3+}, $TlBr^{2+}$, and $TlBr_2^+$ show a small, but probably significant, change to lower frequency when the ionic strength is increased from 4 to 7 M. For the $TlBr_4^-$ species, which accounts for more than 99% of the total thallium in solutions where $R_{Br} \gtrsim 4$, there is no significant change in the shift when the ionic media is varied. The same conclusion is probably valid for $TlCl_4^-$, which accounts for ~95% of the total thallium present for $R_{Cl} \gtrsim 4$.

For $n = 5$ and 6 the complexes are comparatively weak, and it was not possible to obtain the δ_n:*s* from the refinements since there is a strong correlation between the shifts and the stability constants. Therefore, for an estimation of the stability constants β_5 and β_6, the shifts from corresponding solid compounds were used. This procedure is reasonable because of the good agreement between the shifts from aqueous solutions and solids found for CdX_4^- (X = Cl, Br, I) and for most of the Tl(III) complexes (vide infra).

For the chlorides, both the fifth and the sixth complexes in the solid state are well-known and the structures established. For the bromides, only the sixth complex is known in the solid state. Thus, in order to use the solution data for $R_{Br} = [Br^-]_{tot}/[Tl]_{tot} > 4$, it was necessary to assume that only the sixth complex is formed and to use the shift for $TlBr_6^{3-}$ from the solid state. This assumption may be plausible (at least for the concentrated solutions) when one takes into account that the fifth complex does not occur at all in the solid state, whereas the sixth complex can be found in several salts which can be precipitated from aqueous solutions. The great width of the signal from the solid salt is not a serious problem for the estimation of the stability constant for $TlBr_6^{3-}$ since the difference between $\delta_{TlBr_4^-}$ and $\delta_{TlBr_6^{3-}}$ is ~2500 ppm.

It is important to point out that the accuracy of our measurements for $R_X > 4$ is better than ~0.2 ppm for all the investigated solutions. The differences between the experimental values and the shifts calculated by using an improper model are 2 orders of magnitude higher than the experimental accuracy.

For all the data sets (Cl, Br), the reported stability constants for the fifth and sixth complexes do not change by more than two standard deviations when δ_5 and δ_6 are changed by the highest possible error in their determined values (i.e., 30 ppm for the

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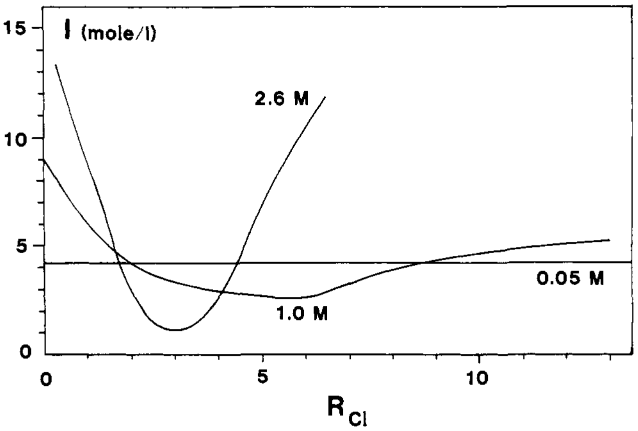

Figure 3. The variation of the ionic strength with $R_{Cl} = [Cl^-]_{tot}/[Tl]_{tot}$ for the different total thallium concentrations.

chloride compounds and 70 ppm for the hexabromide).

The 0.05 M Solutions. Separate lines were observed for the different complexes for $[Cl^-]_{tot}/[Tl]_{tot} < 1$ and for $[Br^-]_{tot}/[Tl]_{tot} < 2$. Thus, $\delta_{TlCl^{2+}}$, $\delta_{TlBr^{2+}}$, and $\delta_{TlBr_2^+}$ could be measured directly. The remaining shifts and stability constants were obtained by least-squares refinements of the data for higher halide/$[Tl]_{tot}$ ratios.

The 1 M Solutions. The lines for the bromide system for $R_{Br} \leq 2$ are very broad and were not used in the refinements. Therefore, it was not possible to determine β_1 and δ_1. The number of experimental points per determined parameter decreased, resulting in high standard deviations for δ_2, δ_3, δ_4, and probably a less reliable value of β_2. The chloride system behaved well, and accordingly relatively low standard deviations were obtained (except for β_3 and δ_3, which are discussed below).

The 2.6 M Solutions. The limited solubility in both systems did not permit the investigation to be extended beyond $R_{Cl} = 6.4$ and $R_{Br} = 5.0$. The ionic strength in the solutions varies strongly, as shown in Figure 3. Consequently, as the shifts are somewhat sensitive to this variation, the standard deviations in the δ_n:s are higher. For the chloride solutions, β_1 is not very well determined, since the dependence of δ^{obsd} on R_{Cl} is weak in this region.

Discussion

Chemical Shifts. The agreement between the δ_n:s for the different thallium concentrations is surprisingly good (with two exceptions discussed below), indicating that the assumption of their independence of ionic strength is reasonable. This fact can be understood if no change occurs in the structures of the complexes, when the ionic medium is changed. The comparison with corresponding solids with known structures may provide some additional information.

The chemical shift difference (~100 ppm) between $\delta_{Tl(aq)^{3+}}$ in the solid and in solution (cf. Table III) is certainly significant. In $Tl(ClO_4)_3 \cdot 6H_2O$, a regular octahedral $Tl(H_2O)_6^{3+}$ unit has been found.[32] In this salt, the water molecules are probably oriented trigonally (i.e., the negative sides of the dipoles point toward Tl^{3+}) because of the packing in the crystal. This would also be in agreement with the fact that small three-charged metal ions are often coordinated in this way.[43] Each $Tl(H_2O)_6^{3+}$ octahedron is surrounded by 14 perchlorate groups. In aqueous solutions of this salt, on the other hand, the situation is partially changed. As shown in the recent X-ray diffraction investigation of thallic perchlorate solutions in water,[21] such solutions contain regular octhedral $Tl(H_2O)_6^{3+}$ units with the Tl–O distance not significantly different from the distance in the solid. However, in the solutions the concentration of free water is much higher than $[ClO_4^-]$. The water molecules also have a greater ability than the perchlorate ions to participate in hydrogen bonds. Therefore, the second coordination sphere around the $Tl(H_2O)_6^{3+}$ octahedron probably consists mostly of water molecules. Furthermore, these solutions were prepared by using an excess of acid, in order to avoid precipitation of Tl_2O_3. The high concentration of $[H^+]$ and the good accessibility of water molecules make it possible for some of the water molecules in $Tl(H_2O)_6^{3+}$ to be tetrahedrally oriented (i.e., pointing toward the metal ion with one-electron pair, accepting a hydrogen bond from another water molecule, and donating two hydrogens bonds).

As seen in Table II, two rather narrow peaks are observed from the mother liquor in contact with $Tl(ClO_4)_3\ 6H_2O(s)$. The signals disappear when perchloric acid is added. These signals may originate from hydrolysis complexes present in the mother liquor. The existence of such species in dilute aqueous solutions was established by Biedermann.[33] Further discussion of these complexes is outside the scope of this work.

The shift for $TlBr^{2+}$ in the 2.6 M solutions is 150 ppm lower than that in the dilute solutions. Even though the peaks from the concentrated solutions are very broad in this region and the ionic strength varies a lot, this difference may still be an indication of some change in geometry of the complex.

The crystal structures of $TlX_3 \cdot 4H_2O$ (X = Cl, Br) contain trigonal-bipyramidal $TlX_3(H_2O)_2$ units with the water molecules in the apex positions and the thallium a little off the plane of the three halides.[44,45] The chemical shifts for the $TlBr_3$ complex in solution agrees rather well with the shift for the solid compound, indicating that the geometry of the $TlBr_3$ species is approximately the same in both phases. Still, there is a difference of ~90 ppm between the shifts in the solid and in the solutions which may be due to a small change in the position of Tl in the complex (more or less off the plane of the bromides) or may only reflect some difference in the second coordination sphere (e.g., different hydration).

For the $TlCl_3$ complex the situation is quite different. First, there is a surprisingly large difference (~300–400 ppm) between the shifts for the trigonal bipyramid in the solid state and for the complex in the solution. Second, δ_{TlCl_3} changes significantly with the total thallium concentration (cf. Table III). This indicates that $TlCl_3$ in aqueous solution is not a trigonal bipyramid, but probably a tetrahedron, $TlCl_3(H_2O)$. Such a tetrahedral geometry has been found for $HgX_3(H_2O)^-$ (X = Br, I) in aqueous solutions.[46a] Another possibility is a coexistence of the trigonal bipyramid and the tetrahedron, as found for HgX_3 (X = Cl, Br) in various organic solvents.[46b]

The shifts of the fourth complexes in solids are very close to those calculated for the solutions, as these species are tetrahedral in both phases.[21,31,47-50]

X-ray powder photographs show that the compounds $Cs_3Tl_2Cl_9$ and $Cs_3Tl_2Br_9$ are not isomorphous. $Cs_3Tl_2Cl_9$ is known to contain $Tl_2Cl_9^{3-}$ units (two $TlCl_6$ octahedra sharing one face),[51,68] and its chemical shift is rather close to that of other salts containing the $TlCl_6^{3-}$ complex. The shift of $Cs_3Tl_2Br_9$ is very close to that of the octahedral $TlBr_6^{3-}$. Thus, it is probable that $Cs_3Tl_2Br_9$ contains a $Tl_2Br_9^{3-}$ unit of the same type as found in $Cs_3Tl_2Cl_9$.

It is noteworthy that the ^{205}Tl shifts for TlI_4^- (both in the solid and in CH_2Cl_2 solution), $Cs_3Tl_2Br_9(s)$, and $Co(NH_3)_6TlBr_6(s)$ fall in the region −1200 to −1800 ppm where no Tl shifts were reported before.[52]

The shift from the solid $[N(C_4H_9)_4]TlI_4$ differs almost 200 ppm from the shift of this salt in dichloromethane solution. This difference is experimentally significant and may be due to the different degree of distortion of the TlI_4^- unit in the two phases

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Table V. Chemical Shifts for Various MX^{m-n} Complexes (M = Zn(II), Cd(II), Tl(III); X = Cl, Br, I) in Aqueous Solutions and in Some Solids[h]

	$MX^{(m-1)+}$	$MX_2{}^{(m-2)+}$	$MX_3{}^{(m-3)+}$	$MX_4{}^{(m-4)+}$	$MX_5{}^{(m-5)+}$	$MX_6{}^{(m-6)+}$	ref
X = Cl							
Zn	30	295	119	253			22
Cd	89	114	292	495	188[a]	162[b]	24
Cd	63	98	282				23
Tl	112	115	326 -35[g]	559	-64[c]	-114[d]	
X = Br							
Zn	10	511	(-230)	136			22
Cd	72	75	365	379			24
Cd	62	83	186	399			23
Tl	-548	-1320	-902	-768		-3357[e]	
X = I							
Cd	47	(57)	140	71			24
Cd	46	(47)	122	71			23
Tl				-3646[f]			

[a] $[Co(NH_3)_6]CdCl_5$. [b] $[Co(en)_3]_2[CdCl_6]Cl_2 \cdot 2H_2O$. [c] $Cs_2TlCl_5 \cdot H_2O$. [d] $Na_3TlCl_6 \cdot 12H_2O$. [e] $[Co(NH_3)_6]TlBr_6$. [f] $[NBu_4]TlI_4$. [g] $TlCl_3 \cdot 4H_2O$. [h] Shifts are given in ppm toward higher frequency from $M(aq)^{m+}$.

and to the fact that the second coordination sphere is not exactly the same. This is in agreement with the fact that tetrahedral TlI_4^- has been found in the solution on the basis of vibrational spectra[2,30] and X-ray diffraction data[53] and that slightly distorted tetrahedral TlI_4^- has been found in the solid state.[53,54]

The correlation between the chemical shift of the metal nucleus and the geometry of the halide complexes of the d^{10} ions Zn^{2+} and Cd^{2+} was discussed by Maciel et al.,[22,24] who found that the octahedral complexes are more shielded than the complexes with tetrahedral structure. The shifts for the thallium(III) chloride and bromide complexes determined in this work make it possible to extend this discussion. It would be of great interest to include ^{199}Hg shifts for the mercury(II)halide complexes. However, no such investigation was found in the literature.

The chemical shifts of some halide complexes of the d^{10} ions Zn^{2+}, Cd^{2+}, and Tl^{3+} are given in Table V. The structures of the halide complexes in aqueous solutions are probably approximately the same for Zn(II), Cd(II), and Tl(III), at least as far as the octahedral $M(H_2O)_6{}^{m+}$, $MX(H_2O)_5{}^{(m-1)+}$, $MX_6{}^{(m-6)+}$, and the tetrahedral $MX_4{}^{(m-4)+}$ are concerned.[21,31,55-58] The $MX_2(H_2O)_4{}^{(m-2)+}$ species are probably octahedral for Cd[59,60] and Tl,[21] but ZnX_2 may be different. Certainly, Raman spectra[61] were interpreted in terms of octahedral $ZnX_2(H_2O)_4$, but the unusually high values of $\Delta S_2°$[62] may indicate that these complexes are not octahedral.

Trigonal-bipyramidal geometry was proposed for $ZnCl_3^-$, $ZnBr_3^-$ (Raman spectra[61]), $CdCl_3^-$, and CdI_3^- (vibrational spectra[59]). However, pyramidal $CdBr_3^-$ is invoked from another Raman study.[60] In any case, the high entropy values for the formation of the CdX_3^- species[62] indicate that the octahedral symmetry is lost when the third cadmium halide complexes are formed. The $TlBr_3(H_2O)_2$ complex has an essentially trigonal-bipyramidal geometry (both in the solid and in solution), as shown by X-ray diffraction results[45,21] and by similar values of δ_{TlBr_3} in the solid and in the solution (Table III). The configuration of $TlCl_3$ in solution is not trigonal bipyramidal but probably approximately tetrahedral (vide supra).

From the data in Table V, some common features can be observed. For complexes with the same geometry, the shielding of the metal nucleus increases in the order Cl^-, Br^-, I^-, i.e., with increasing atomic weight and polarizability and with decreasing electronegativity of the halide. The big shifts to lower frequency for TlI_4^-, $Tl_2Br_9{}^{3-}$, and $TlBr_6{}^{3-}$ do probably contain considerable contribution from the "heavy-atom effect" caused by the high value of the spin-orbit coupling constant for bromine and iodine.[69] There are two exceptions to this pattern: ZnX_2 (X = Cl, Br) and $CdBr_3$ in ref 24.

As pointed out by Maciel et al.,[22] the measurements on the Zn solutions were performed at $[Zn]_{tot} = 0.5$ M, whereas the stability constants used are not necessarily valid for $[Zn]_{tot} > 0.1$ M. Moreover, the species $ZnCl^+$, $ZnBr_2$, and $ZnBr_3^-$ are never present in the solution to any great extent (at most $\simeq 15\%$ of the total zinc concentration). This can lead to some systematic errors in the obtained shifts. On the other hand, if the ^{67}Zn shifts for these species are of the correct order of magnitude, the difference in their changes can be the result of the fact that Zn(II) is a hard acceptor, whereas Cd(II) and Tl(III) are soft.[63]

The values of $\delta_{CdBr_3^-}$ in ref 23 and 24 are quite different. The different ionic strengths used (4.5 and 3.0 M, respectively) in these investigations cannot be responsible for this discrepancy. As pointed out previously,[22,23] the values of the shifts derived for the complexes are only as good as the equilibrium constants used if the latter are kept constant during the least-squares procedure, as is the case for ref 22–24. Thus, the discrepancy is probably caused by the use of different sets of equilibrium constants.

The shifts for the thallium(III) chloride complexes follow the same pattern as those for $CdX_n{}^{(2-n)+}$ (X = Cl, Br, I). The octahedral complexes are more shielded than the tetrahedral. The $MX_3{}^{(m-3)+}$ complexes have intermediate shielding. Furthermore, the difference between the different octahedral complexes is small, and especially the species with $n = 1$ and 2 are almost equally shielded. The ZnX_2 complexes are, on the other hand, considerably less shielded than ZnX^+ which indicates that they have lost the octahedral symmetry. At first sight, the shifts for the thallium(III) bromide complexes seem to behave differently. The tetrahedral $TlBr_4^-$ is, for example, considerably more shielded than the octahedral $Tl(H_2O)_6{}^{3+}$. However, this pattern may be rationalized as follows. For the four octahedral $TlBr_n(H_2O)_{6-n}{}^{(3-n)+}$

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complexes (n = 0, 1, 2, and 6), the increase in the shielding when one water molecule is substituted by a bromide is very large and almost constant (~600 ppm). It can now be seen that the tetrahedral $TlBr_4^-$ is about 1600 ppm less shielded than a hypothetical octahedral $TlBr_4(H_2O)_2^-$ complex (which would be ~2400 ppm more shielded than $Tl(H_2O)_6^{3+}$). If seen this way, the proposed difference in shielding between octahedral and tetrahedral complexes[24] is also valid for the Tl(III)–Br^- system. A comparison with mercury(II) halide complexes (which have similar values of the stability constants, the enthalpy and the entropy of formation[62]) could reveal whether this is a more general behavior.

Stability Constants. For the first four bromide complexes there is apparently no significant difference, if the standard deviations are taken into account, between the stability constants obtained for the different total thallium concentrations. The constants are also in good agreement with those given by Ahrland et al.[10,11] The existence of at least one higher complex ($n > 4$) seems to be significant. For $[Tl]_{tot}$ = 0.05 M the ^{205}Tl shift in concentrated HBr solution is 1169 ppm, i.e., ~150 ppm below the value of $\delta_{TlBr_4^-}$. In 1 M solutions, the corresponding decrease is from 1331 to 1086 ppm, i.e., 225 ppm. It is improbable that $\delta_{TlBr_4^-}$, which does not change significantly between the different ionic media investigated (cf. Table IV), should change to this great extent and account for the observed shift. However, it was not possible to determine which of the complexes $TlBr_5^{2-}$ and $TlBr_6^{3-}$ is formed. In any case, the values of β_6 are very low, in fact much lower than the detection limit given in ref 10. For $[Tl]_{tot}$ = 1.0 M and the highest value of R_{Br} = 11.8, only 10% of the thallium is present as $TlBr_6^{3-}$, according to the stability constants in Table III. The dominating complex is $TlBr_4^-$ even at very high bromide concentrations. No values for the stability constants for the higher bromide complexes in aqueous solutions were found in the literature.

For the first four chloride complexes in the 0.05 M solutions, good agreement is obtained with the data of Ahrland et al. In 1.0 M solutions, the $TlCl^{2+}$ and $TlCl_2^+$ complexes are somewhat weaker, β_3 is unchanged, and β_4 is slightly higher. In 2.6 M solutions, β_3 is slightly higher than for the dilute solutions, the other constants being unchanged. However, all the variation of the stability constants for $n \leq 4$ falls within the limit of ±3 standard deviations from the values of ref 10.

The existence of higher chloride complexes is evident, but the calculated stability constants should be seen as rough estimates only, as the shifts from solids were used. Thus, in 0.05 M solutions the value of K_5 = 0.3 (1) M^{-1} is not significantly higher than the detection limit given by Ahrland et al.[10,11] It is also in agreement with K_5 = 0.8 (2) M^{-1} obtained by spectrophotometric measurements[19] and K_5 = 0.3 M^{-1} calculated from extraction data.[5]

In 1 M solutions, both $TlCl_5^{2-}$ and $TlCl_6^{3-}$ occur, with formation constants K_5 = 0.6 M^{-1} and $K_{4,6}$ = 0.2 M^{-2}. Using Raman spectra from approximately 1 M solutions (containing ~2 M $HClO_4$), Spiro[15] claimed that $TlCl_6^{3-}$ is formed ($K_{4,6}$ = 0.2 M^{-2}) and that for solutions with $R \geq 5$, $TlCl_4^-$ and $TlCl_6^{3-}$ accounted for 92–100% of the total thallium concentration. The lower limit of our K_5 = 0.2 M^{-1} gives 15% of the total thallium present as $TlCl_5^{2-}$.

In 2.6 M solutions only $TlCl_6^{3-}$ occurs, with $K_{4,6}$ = 0.8 M^{-2}. It may be noted that the formation constants of $TlCl_5^{2-}$ and $TlCl_6^{3-}$ are rather low for all three ionic media. However, a gradual change from only $TlCl_5^{2-}$ in 0.05 M, through both species in 1 M, to $TlCl_6^{3-}$ solely in the 2.6 M solutions can be observed. This is understandable if one takes into account that the ratio $[H_2O]/[Cl^-]_{free}$ varies from 475 to 7 between the 0.05 and the 2.6 M solutions. Even if the chloride is a strong complexing agent for Tl(III) and strives to substitute the H_2O molecules in the first coordination sphere of the metal ion, the equilibrium $H_2O + TlCl_6^{3-} \rightleftarrows TlCl_5(H_2O)^{2-} + Cl^-$ can be shifted to the right if a sufficient amount of water compared to $[Cl^-]_{free}$ is present.

Concluding Remarks

NMR spectroscopy is very suitable for studying the coordination chemistry of Tl(III). It is possible to obtain information about the stability of the complexes, changes in geometry, and the kinetics of ligand exchange. If the chemical shift is measured at a sufficient number of points, the stability constants can be determined with an accuracy comparable to that obtained from emf studies. As far as formation of weak complexes is concerned, the NMR method is even more sensitive. A comparison of the chemical shifts for the different complexes in solution with the shifts from solid salts with known structure is of great value since it makes it possible to obtain structural information about the complexes in solution.

Note Added in Proof. A recent paper by McGarvey[70] presents some results of direct relevance to our investigation. (1) The chemical shifts for the $InCl_5^{2-}$ and for the $InCl_6^{3-}$ species show the same pattern as that observed for $TlCl_5^{2-}$ and $TlCl_6^{3-}$. (2) The chemical shift of the compound InI_3, which has the iodine-bridged structure $I_2InI_2InI_2$ in nondonor solvents, is close to the shift of the InI_4^- ion. As pointed out, the formal charge apparently has little effect on the resonance frequency, given that both InI_4^- and In_2I_6 involve In(III) tetrahedrally bonded to iodine. This fact supports our conclusion about the probable structure of $Cs_3Tl_2Br_6$(s). (3) There is no change in the chemical shift or in the line width for the acetonitrile solution of $[(C_6H_5)_4P)]InI_4$, when a threefold excess of $[(C_6H_5)_4P]I$ is added. This is in agreement with the fact that the maximum coordination number for the InI_n^{3-n} complexes is four. These results also show that changes in the second coordination sphere, due to the addition of excess halide, do not influence the ^{115}In chemical shift. Our conclusion on the existence of $TlBr_n^{3-n}$ species with $n > 4$ can be seen in this light. Moreover, weak complex formation of $InBr_n^{3-n}$ ($n > 4$) is suggested in acetonitrile, whereas both $InCl_5^{2-}$ and $InCl_6^{3-}$ are formed, showing the same trend as the corresponding thallium(III) species.

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