On the Structures of the Thallium(III) Chloride Complexes in Solution. I. Evidence for Tetrahedral TlCl$_4^-$ and Octahedral TlCl$_6^{3-}$ Species in Aqueous Solution

JULIUS GLASER

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

The structures of the TlCl$_4^-$ and the TlCl$_6^{3-}$ complexes have been determined from X-ray diffraction measurements on concentrated aqueous solutions of thallium(III) (0.9 M – 2.7 M) and chloride (6.2 M – 12.3 M). The TlCl complex is tetrahedral with a Tl–Cl distance of 2.43(1) Å and a Cl–Cl distance of 3.96(3) Å. The TlCl$_6^{3-}$ complex is octahedral with a Tl–Cl distance of 2.59(1) Å and a Cl–Cl distance of 3.69(6) Å. There is no evidence that polynuclear species are present in the investigated solutions. These results are in agreement with Raman spectra for solutions and for solids containing discrete thallium(III) chloride complexes.
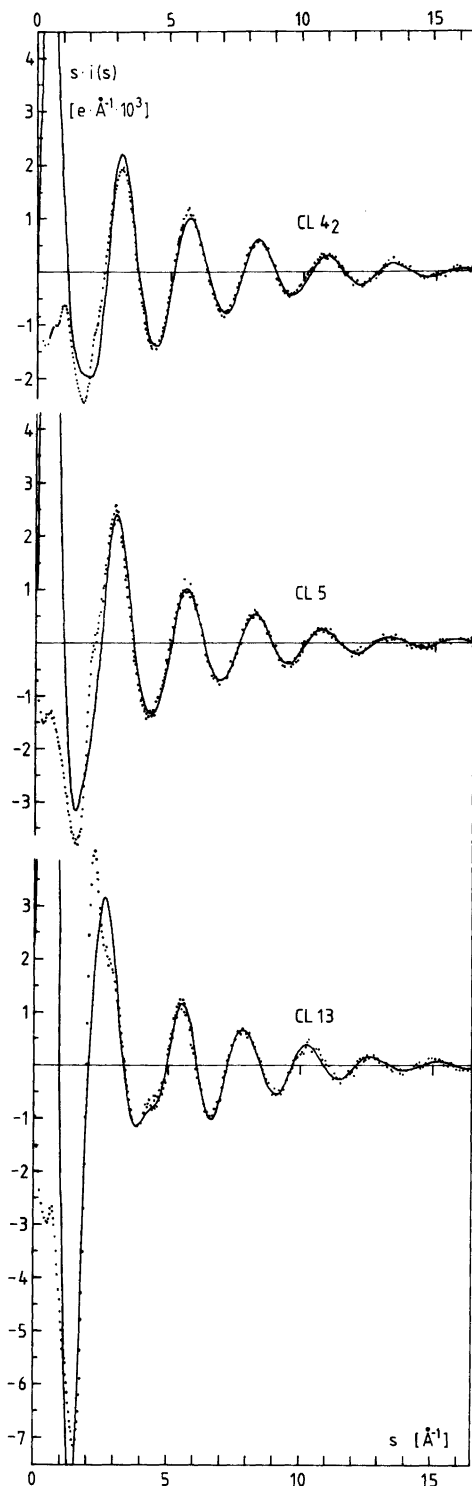
The complexes formed between Tl^{3+} and Cl$^-$ in aqueous solution are among the strongest metal ion-chloride complexes known.[1] They have been the subject of several studies,[2] and some of their properties have been elucidated. The stability constants[3-5] and the enthalpies of formation[3,6] can be explained assuming the TlCl$_n^{3-n}$ species (n = 0,1,2,3,4) to be present in dilute aqueous solutions. The existence of higher complexes (n > 4) has, however, for a long time been a matter of controversy.[2] Ultraviolet spectra[7] indicate the existence of the fifth complex, TlCl$_5^{2-}$, with the formation constant K_5 = [TlCl$_5^{2-}$]/[TlCl$_4^-$][Cl$^-$]) = 0.8(2) M^{-1}. Extraction measurements have also been interpreted in terms of weak bonding of the fifth chloride ligand (K_5 = 0.3 M^{-1}),[8] although other workers using the same method found no evidence for complexes higher than TlCl$_4^-$.[9]

In concentrated aqueous solutions clear evidence for at least one higher species, possibly octahedral TlCl$_6^{3-}$, was found by Spiro[10] and Davies[11] from

Raman spectra. Tl NMR spectra also indicate the formation of complexes with more than four chlorides per thallium.[12,13] Figgis[12] claimed that the most stable species at higher chloride concentrations is Tl$_2$Cl$_9^{3-}$, a structural unit previously found to be present in the crystal structure of Cs$_3$Tl$_2$Cl$_9$.[14] Very little is known about the structures of the Tl^{3+} halide complexes formed in aqueous solution. The only information existing on this subject is inferred from vibrational spectra, where the interpretation of the data is difficult and ambiguous, particularly when two or three complexes coexist.[2,10,15]

In the solid state, several discrete thallium(III) chloride species have been found. In TlCl$_3$ · 4H$_2$O,[16] as well as in TlCl$_3$(C$_6$H$_4$N$_2$O)$_2$,[17] a trigonal bipyramidal complex, TlCl$_3$O$_2$, exists, with the thallium atom 0.072(3) Å off the plane of the three chlorides. In tetrachlorothallates(III), the only discrete T(III) unit found is the TlCl$_4^-$ tetrahedron.[18-21] The existence of the higher complexes, TlCl$_5^{2-}$ and TlCl$_6^{3-}$, in the solid state is also evident.[22-24,24-28] The TlCl$_5^{2-}$ unit has a distorted square-pyramidal geometry in [N(C$_2$H$_5$)$_4$]$_2$TlCl$_5$,[29] but in salts obtained from aqueous solutions, such as Cs$_2$TlCl$_5$(H$_2$O) or Rb$_2$TlCl$_5$·H$_2$O, a water molecule coordinates to TlCl$_5^{2-}$ and thus completes the octahedral geometry.[22-24] In hexachlorothallates, octahedral TlCl$_6^{3-}$ units have been found.[24-28] Polynuclear complexes have also been found in the solid state.[14,24] Tl$_2$Cl$_9^{3-}$ (see above) is composed of two TlCl$_6$ octahedra sharing one face,[14] and Tl$_2$Cl$_{10}^{4-}$ contains two octahedra sharing one edge.[24]

In order to elucidate the structures of the thallium(III) halide complexes in solution, a series of

Fig. 1. The experimental reduced intensity curves, multiplied by s, for the investigated solutions ($\cdots$). The *solid lines* are calculated for the interactions shown in Fig. 2, including the $Cl-(H_2O)$ and the long $Tl-(H_2O)$ contributions.

investigations has been started. The distribution of Tl(III) among the different TlX_n^{3-n} species ($X = Cl, Br$) in dilute and concentrated aqueous solutions have been determined by the ^{205}Tl NMR method.[30] The highest ligand number is proved to be six for the Tl(III) chloride system and is probably the same for the $TlBr_n^{3-n}$ complexes, but the stability constant is much lower in the latter case.

Accurate bond lengths within the different $TlX_n(H_2O)_m^{3-n}$ complexes have been derived from crystal structures, *e.g.* Refs. 16b, 21, 27. These give plausible models for the complexes existing in solution. Finally, X-ray diffraction measurements and Raman spectra have been recorded for concentrated aqueous solutions. The first part, dealing with thallium(III) aqua- and bromide complexes, was presented in the preceding paper.[31] In the present article, the structures of the $TlCl_4^-$ and $TlCl_6^{3-}$ complexes are elucidated.

EXPERIMENTAL

The solutions were prepared and analyzed as described previously.[32] The compositions of the solutions investigated by X-ray diffraction are given in Table 1. The $\theta-\theta$ diffractometer was used in the same way as previously.[33] The scattered radiation ($\lambda_{MoK\alpha} = 0.7107$ Å) was monochromatized by a focusing LiF crystal and measured by a scintillation counter as a function of the scattering angle. The intensities were collected at discrete points at intervals of $0.1°$ for $1.5° < \theta < 20°$ and of $0.25°$ for $20° < \theta < 70°$, which corresponds to $0.3 \text{ Å}^{-1} < s = (4\pi \sin \theta)/\lambda < 16.7 \text{ Å}^{-1}$. Typically, 10^5 counts were collected for each point. A complete data collection was performed twice for each solution in order to eliminate any long-term experimental drift. Raman spectra were collected on a Cary 82 and a Coderg T 800 laser source spectrophotometer.

DATA TREATMENT AND RESULTS

The data processing was performed as described in the preceding paper.[31] The curves were calculated for a stoichiometric unit of volume containing one Tl atom.
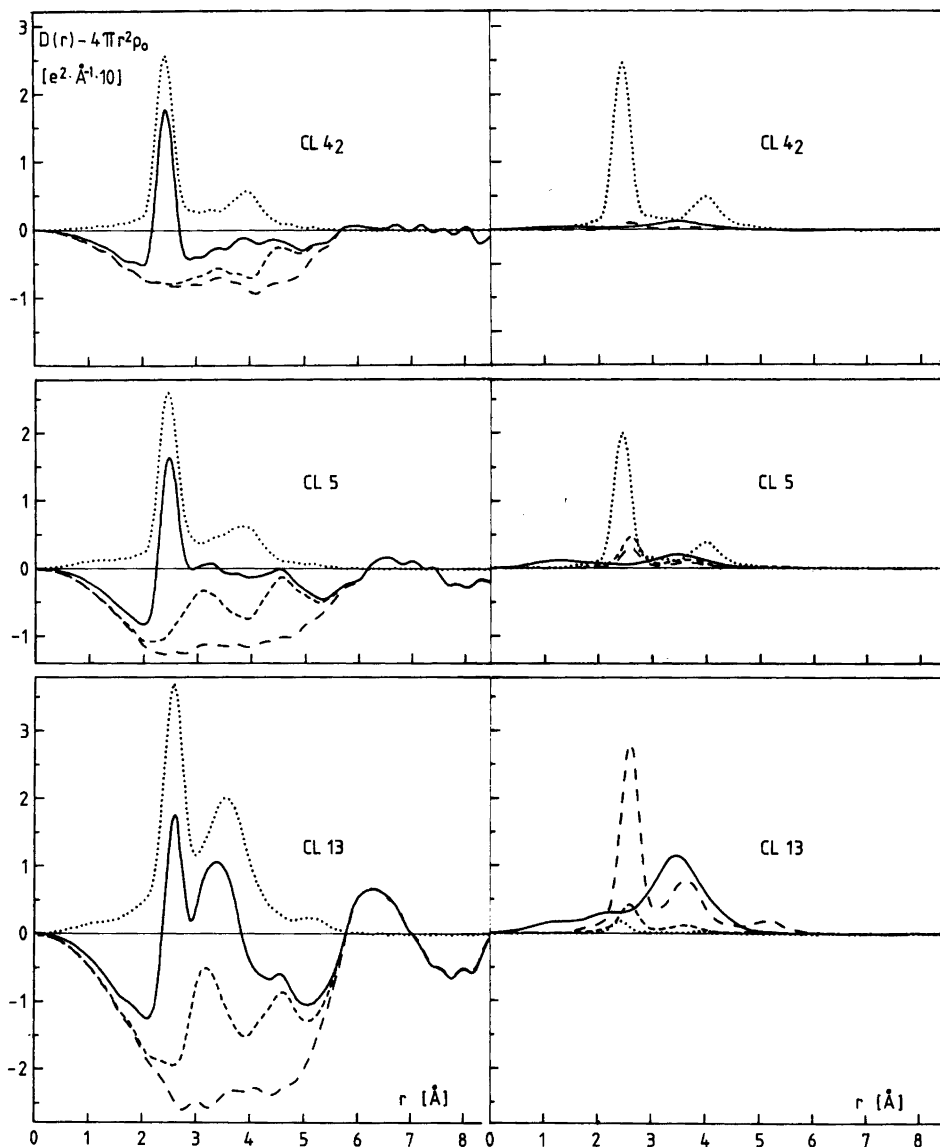
Fig. 2. Comparison between the experimental radial distribution functions, $D(r) - 4\pi r^2 \rho_o$, and the peak shapes calculated for the nearest neighbour interactions. The curves to the right show the peak shapes calculated for the following interactions: —, sums of the "background" contacts O−H and Li(H$_2$O)$_4^+$; ···, the tetrahedral TlCl$_4^-$ complex; ---, the octahedral TlCl$_5$(H$_2$O)$^{2-}$ complex; − − −, the octahedral TlCl$_6^{3-}$ complex. The curves to the left represent: —, the experimental $D(r) - 4\pi r^2 \rho_o$ functions; ···, the sums of the peak shapes shown in the figures to the right; ---, the differences between the experimental and the calculated curves; − − −, the differences between the experimental and the calculated curves when also the Cl−H$_2$O and the long Tl−H$_2$O interactions are taken into account.

Table 1. Compositions (in mol/l) of the solutions investigated by X-ray diffraction. The concentrations of the $TlCl_n^{3-n}$ complexes have been calculated using the stability constants in Ref. 30, determined for similar total Tl concentrations.

Solution	Tl	Cl	Li	H_2O	Ratio Cl/Tl	$TlCl_4^-$	$TlCl_5^{2-}$	$TlCl_6^{3-}$
CL5	1.29	6.23	2.36	48	4.8	0.99	0.20	0.10
CL13	0.92	12.3	9.54	42	13.4	0.06	0.13	0.73
CL4$_2$	2.65	10.87	2.92	41	4.1	2.57	–	0.08

The experimental reduced intensity values, multiplied by s, for the investigated solutions, are given in Fig. 1. The radial distribution functions (RDF's) $D(r) - 4\pi r^2 \rho_0$, (ρ_0 is the average scattering power per stoichiometric volume[34]) obtained through Fourier inversion of the reduced experimental intensities,[34] are shown in Fig. 2.

Parameters for intramolecular interactions were obtained by a least-squares refinement procedure,[34] using different ranges of s in order to reduce the influence of systematic errors in different parts of the intensity curves. The refined parameters were: the distance, r, the mean-square variation in the distance, l^2, and the number of distances per Tl atom, n. The refinements were performed in different ways: (I) At first, only the Tl – Cl interactions (r_{Tl-Cl}, l^2_{Tl-Cl} and n_{Tl-Cl}) were refined, without any assumptions about the existing complexes, using the high

angle region of the intensity curves. The results are given in Table 2a. (II) Next, the minor $TlCl_n^{3-n}$ complexes were included with distances found in the appropriate crystal structures.[21,22,27] The concentrations were calculated using the stability constants from Ref. 30 (*c.f.* Table 1) and the Tl – Cl contributions within the major species were refined. Finally, the Cl – Cl interactions were also refined.

The results from all the calculations under point (II) are given in Table 2b. For the solution CL5, the Cl – Cl interactions contribute too little to the intensity curve and consequently could not be refined.

Raman frequencies for some aqueous solutions of Tl(III) and Cl$^-$, as well as for several solid compounds containing discrete $TlCl_n^{3-n}$ complexes, are presented in Table 3.

Table 2. Results of least-squares refinements (r_{pq} is the distance in Ångström units between atoms "p" and "q"; n is the number of distances per Tl atom; and l^2 the mean-square variation of the distance, in Å^2). Only the parameters for which the estimated standard deviations are given were refined. The standard deviations are those obtained in the least-squares procedure, but they were increased in order to account for the variation of the parameters when different s-ranges were used in the refinements.

a. Tl – Cl interactions only (no other complexes included).

Solution	r_{Tl-Cl}	l^2_{Tl-Cl}	n_{Tl-Cl}
CL5	2.458(3)	0.011(2)	4.2(5)
CL13	2.568(3)	0.011(2)	5(1)
CL4	2.436(2)	0.009(1)	4.2(5)

b. Tl – Cl and Cl – Cl interactions within the dominating complex (the minor Tl(III) complexes included with constant parameter values).

Solution	The dominating complex	r_{Tl-Cl}	l^2_{Tl-Cl}	n_{Tl-Cl}	r_{Cl-Cl}	l^2_{Cl-Cl}	n_{Cl-Cl}	r_{Cl-Cl}/r_{Tl-Cl}
CL5	$TlCl_4^-$	2.446(2)	0.010(1)	4.6(6)	–	–	–	–
CL13	$TlCl_6^{3-}$	2.590(3)	0.009(2)	5.5(7)	3.69(6)	0.04	13(2)	1.42
CL4$_2$	$TlCl_4^-$	2.433(1)	0.009(1)	4.2(3)	3.96(3)	0.04	5(1)	1.63

Table 3. Raman band frequencies for aqueous solutions of Tl(III) and Cl⁻. (1 M $TlCl_{4.1}$ means $[Tl(III)] =$ 1 M; $[Cl^-]_{tot}/[Tl(III)] = 4.1$). The concentrations of the dominating Tl(III) species are given in percent of the total thallium content according to the stability constants in Ref. 30. Data for some solid compounds with known structures, containing discrete Tl(III)−Cl⁻ complexes, are given for comparison (the weakest peaks are omitted). The following abbreviations are used: s = strong, m = medium, w = weak, sh = shoulder, br = broad.

	Dominating complex	Frequencies in cm^{-1}	Ref.
Solutions			
A. 1 M $TlCl_{4.1}$	97 % $TlCl_4^-$	305 s, ~81 w, br	10
B. 2.7 M $TlCl_{4.1}$ ("CL4₂")	97 % $TlCl_4^-$	303 s, ~78 w, br	This work
C. 1.3 M $TlCl_{4.8}$ ("CL5")	77 % $TlCl_4^-$	302 s, 260−285 sh, ~120 sh, ~90 w, br	"
D. 2.7 M $TlCl_{4.8}$	72 % $TlCl_4^-$	303 s, 260−290 sh, ~120 sh, ~85 w, br	"
E. 2.5 M $TlCl_{6.4}$	79 % $TlCl_6^{3-}$	275 s, ~110 w, br	"
F. 0.9 M $TlCl_{13.4}$ ("CL13")	79 % $TlCl_6^{3-}$	270 s, ~120 m, br	"
Solid			
$[As(C_6H_5)_4]TlCl_4$		312 s, 296 w, 78, 60	10
$MTCl_4$ (M = K,Rb,Tl(I),NH₄)		300(±3) s, 289(±5) w, 125(±7) m, 96(±1) m	24 This work
$Rb_2TlCl_5(H_2O)$		294 s, ~249 w, ~143 m	24
$(NH_4)_2TlCl_5(H_2O)$		286 s, ~194 m, ~169 m	"
$Cs_2TlCl_5(H_2O)$		264 s, 152 m, 131 m	This work
$M_3TlCl_6 \cdot nH_2O$ (M = Na,Tl(I),Co(NH₃)₆,NH₄)		270(±7) s, 116(±24) m	24,39 This work
$Cs_3Tl_2Cl_9$		285 s, 260 w, 229 w, 155 w, 130 m, 108 m	40 This work

DISCUSSION

Intramolecular interactions. For all the investigated solutions the first prominent peak in the RDF's occurs at about 2.5 Å, a value close to the Tl−Cl distance found in several crystal structures.[17−28] Thus, it can be identified as representing the Tl−Cl interactions within the different thallium(III) chloride species. The Tl−Cl distances, refined without any assumptions concerning the complexes present in the solutions (Table 2a), increase noticeably from 2.436(2) Å for the CL4₂ solution to 2.568(3) Å for CL13 solution. The number of such distances per Tl atom could not be determined very precisely because of the low scattering power of the Cl atoms. Nevertheless, these results of the X-ray

scattering measurements given in Table 2a are consistent with the formation of higher $TlCl_n^{3-n}$ (n > 4) complexes predicted by the stability constants determined for the same concentrations using Tl−NMR.[30] Thus, it seemed reasonable to include the minor $TlCl_n^{3-n}$ species (*cf.* Table 1) when refining the parameters of the dominant complex (Table 2b). The results for the CL4 solution provide the structure of the $TlCl_4^-$ complex: the ratio r_{Cl-Cl}/r_{Tl-Cl} is equal to 1.63, to be compared with the theoretical value for a tetrahedron, $\sqrt{2}/(\sqrt{3}/2) = 1.633$. The numbers of the Tl−Cl and the Cl−Cl interactions, 4 and 6, respectively, are also consistent with those expected for a tetrahedron.

The parameters determined for the Cl13 solution are in agreement with an octahedral $TlCl_6^{3-}$ complex: the ratio $r_{Cl-Cl}/r_{Tl-Cl} = 1.42$ can be compared with the theoretical value, $\sqrt{2} = 1.414$, and the frequencies, n_{Tl-Cl} and n_{Cl-Cl}, are not significantly different from the expected ones, 6 and 12, respectively. A comparison of the peak shapes, calculated on the basis of the parameter values in Table 2b for the $TlCl_n^{3-n}$ complexes and of the previously reported values for the "background" interactions $(O-H$ and $Li(H_2O)_4^+)$,[35] with the observed $D(r) - 4\pi r^2 \rho_0$ functions is given in Fig. 2. Raman spectra reported by Spiro,[10] Davies[11] and in the present work (see Table 3) are consistent with the conclusion reached on the basis of the X-ray diffraction and the NMR[30] results. For the solutions where the $TlCl_4^-$ complex dominates ($TlCl_{4.1}$ and $TlCl_{4.8}$ in Table 3) the major peak is observed at about 303 cm^{-1} (v_1) and a minor, broad band occurs at $80-90$ cm^{-1} (v_4), in agreement with the Raman spectra of seversl solid tetrahalothallates containing discrete tetrahedral $TlCl_4^-$ units.[15,24] Similar v_1 and v_4 frequencies were observed for solutions of $[NBu_4]$-$TlCl_4$ in several non-coordinating solvents,[36] where, presumably, a tetrahedral $TlCl_4^-$ complex is present. Furthermore, infrared spectra for the $CL4_2$ solution and for a 0.2 M solution of $[NBu_4]TlCl_4$ in CH_2Br_2 are very similar to each other, with the dominating peak at 293 cm^{-1} (v_3) and a minor, broader peak at about 100 cm^{-1} (v_4),[37] i.e. essentially the same as the IR spectrum for the solid $KTlCl_4(s)$, containing tetrahedral $TlCl_4^-$ units.[21]

When the ratio $R_{Cl} = [Cl^-]_{tot}/[Tl(III)]$ increases above 4.1, the major peak becomes broader and its centre moves towards lower frequencies. For $[Tl(III)] \approx 1$ M, it reaches the frequency of ~ 270 cm^{-1} at $R_{Cl} \approx 9$ and does not shift upon further addition of chloride up to $R_{Cl} \approx 13$,[11] whereas the intensity of the peak increases continuously.[10] For the CL13 solution, in addition, a very broad peak centered at ~ 120 cm^{-1} arises. Thus, the spectrum of the CL13 solution shows the same major frequencies as those observed in the Raman spectra of several crystalline hexachlorothallates containing octahedral $TlCl_6^{3-}$ species (cf. Table 3). Such changes in the spectra for the solutions with $R_{Cl} > 4$ are nicely explained by the distribution of the complexes according to the stability constants for 1 M solutions.[30] For R_{Cl} values between 4 and 6 the concentration of the $TlCl_4^-$ complex decreases, whereas the concentrations of the higher species increase. For $6 < R_{Cl} < 8$ the concentrations of the

$TlCl_4^-$, $TlCl_5^{2-}$ and $TlCl_6^{3-}$ complexes are all of the same order of magnitude and no species dominates. Finally, for $R_{Cl} \approx 9$, about 60 % of the total thallium is present as $TlCl_6^{3-}$ and the concentration of this complex increases upon further addition of chloride, reaching about 80 % of the total thallium for $R_{Cl} \approx 14$, where the solubility limit is reached.

The spectra for the solutions C and D are very similar to each other (see Table 3). The same is true for the solutions E and F. This gives no support for the assumption of Figgis[12] that $Tl_2Cl_9^{3-}$ dominates for $R_{Cl} > 4.5$, since formation of polynuclear complexes should be more pronounced for the more concentrated solutions and thus alter the spectral patterns.

It is of interest to compare the distances determined for the $TlCl_4^-$ and the $TlCl_6^{3-}$ units in solution with the accurate values obtained for the same complexes in the solid state. The $Tl-Cl$ distance of 2.433(1) Å and the $Cl-Cl$ distance of 3.96(3) Å calculated for the $CL4_2$ solution (Table 2b) can be compared with the values 2.433(3) Å and 3.98 Å (average), respectively, determined for the tetrahedral $TlCl_4^-$ in the crystal structure of $KTlCl_4$.[21,*] For the CL5 solution the $Tl-Cl$ distance is about 0.01 Å longer, but this slight increase may not be significant. Because of the high relative and absolute concentrations of the $TlCl_4^-$ complex in the $CL4_2$ solution as compared with that in CL5 (cf. Table 1), the value of 2.433 Å is more reliable.

The distances $r_{Tl-Cl} = 2.590(3)$ Å and $r_{Cl-Cl} = 3.69(6)$ Å found for the $TlCl_6^{3-}$ complex in solution are not significantly different from the values 2.593(3) Å and 3.68 Å, respectively, for the crystal structure of $Na_3TlCl_6 \cdot 12H_2O$.[27,*]

Finally, it may be noted that the results in Table 2a are not consistent with the dominance of the $Tl_2Cl_9^{3-}$ complex[12] (see above) in the solutions investigated. The high scattering power of the thallium atoms would result, if the $Tl_2Cl_9^{3-}$ complex reached any considerable concentration, in a dominating $Tl-Tl$ peak at ~ 3.6 Å[14] in the RDF's. For the $CL4_2$ and CL5 solutions, there are no peaks at this distance. For the CL13 solution, the broad peak centered at 3.4 Å can be satisfactorily explained by

---

*The distances in the crystal structures have been corrected for thermal motion,[38] assuming "riding" motion for the $Tl-Cl$ distances and independent motion for the Cl $-Cl$ distances. Note that an uncorrected distance for the atoms "p" and "q", r_{pq}, is obtained as $|\langle \mathbf{r}_q \rangle - \langle \mathbf{r}_p \rangle|$ in a crystal structure, but as $|\langle \mathbf{r}_q - \mathbf{r}_p \rangle|$ in a solution ($\mathbf{r}$ denotes a vector and the brackets mean values).

the Cl−Cl interactions in the $TlCl_6^{3-}$ complex and the generally accepted[35] "background" interactions (tetrahedral $Li(H_2O)_4^+$ species and Cl−H_2O distances). Moreover, in this type of complexes, $M_2Cl_9^{3-}$, the M−Cl distances are ~0.2 Å shorter for the terminal chlorine atoms than for the bridging ones, at least in the solid state.[14,24] If this property is retained in solution, as may be expected, it would lead to a significant increase of the mean-square variation of the Tl−Cl distance, l^2, in Table 2a. Such an increase in l^2 would also be expected if, for instance, two of the Tl−Cl bonds in $TlCl_6^{2-}$ were appreciably shorter than the remaining ones. Apparently, the $TlCl_6^{3-}$ octahedron is regular.

Intermolecular interactions. In the difference curves (Fig. 2, left side, short dashes) between the experimental RDF's and the peak shapes calculated for the intramolecular interactions, as described above, there remain broad maxima centered at ~3.2 and ~4.6 Å. In this region, several types of intermolecular interactions can be expected, e.g. H_2O-H_2O (−2.8 Å), Cl−H_2O (3.2 Å)[35] and distances between the Tl atom and the molecules in its second coordination sphere.

Close-packing of water molecules around the $TlCl_n^{3-n}$ complexes, as assumed in the preceding paper for the $TlBr_4^-$ complex,[31] is less probable in the present case because of the higher tendency of the chloride ions to participate in hydrogen bonds. Such a model would lead to Tl−H_2O distances slightly shorter than 4.0 Å, which are not present in the difference curves (Fig. 2).

In the crystal structure of the water-rich compound, $Na_3TlCl_6 \cdot 12H_2O$, three water molecules are hydrogen bonded to each of the chlorines within the $TlCl_6^{3-}$ octahedra, leading to 12 Tl−H_2O distances between 4.47 and 4.79 Å.[27] Similarly, it was assumed that in solution water molecules are arranged around the $TlCl_n^{3-n}$ complexes at the Tl−H_2O distances of ~4.55 Å, which also leads to several Cl−H_2O distances at ~3.2 Å. In addition to the generally accepted tetrahedral $Li(H_2O)_4^+$ unit,[35] already included in the calculated peak shapes (see above), the free chloride ions were also assumed to be in contact with water molecules (~3.2 Å).[35] The difference curves between the experimental RDF's and the peak shapes, where the Tl−H_2O and Cl−H_2O intermolecular interactions (described above) were also included in the calculations, are shown in Fig. 2 (long dashes). The agreement in the high angle region between experimental $s \cdot i(s)$ values and the theoretical curves calculated

for the same model (Fig. 1) finally confirms the conclusions drawn above concerning the structures of the complexes.

REFERENCES

1. Smith, R. M. and Martell, A. E. *Critical Stability Constants*, Plenum, New York 1977, Vol. 4.
2. Lee, A. G. *The Chemistry of Thallium*, Elsevier, Amsterdam 1971 and references therein.
3. Woods, M. J. M., Gallagher, P. K., Hugus, Z. Z. and King, E. L. *Inorg. Chem. 3* (1964) 1313.
4. a. Ahrland, S., Grenthe, I., Johansson, L. and Norén, B. *Acta Chem. Scand. 17* (1963) 1567; b. Ahrland, S. and Johansson, L. *Acta Chem. Scand. 18* (1964) 212.
5. Biedermann, G. and Spiro, T. G. *Chem. Scr. 1* (1971) 155.
6. Leden, I. and Ryhl, T. *Acta Chem. Scand. 18* (1964) 1196.
7. Schmidt, K. J. *J. Inorg. Nucl. Chem. 32* (1970) 3549.
8. Horrocks, D. L. and Voigt, A. F. *J. Am. Chem. Soc. 79* (1957) 2440.
9. Nord, G. and Ulstrup, J. *Acta Chem. Scand. 18* (1964) 307.
10. Spiro, T. G. *Inorg. Chem. 4* (1965) 731.
11. Davies, E. D. and Long, D. A. *J. Chem. Soc. A* (1968) 2050.
12. Figgis, B. N. *Trans. Faraday Soc. 55* (1959) 1075.
13. Freeman, R., Gasser, R. P. H. and Richards, R. E. *Mol. Phys. 2* (1959) 301.
14. a. Powell, H. M. and Wells, A. F. *J. Chem. Soc.* (1935) 1008; b. Hoard, J. L. and Goldstein, L. *J. Chem. Phys. 3* (1935) 199.
15. a. Spiro, T. G. *Inorg. Chem. 4* (1965) 1290; b. *Ibid. 6* (1967) 569.
16. a. Zvonkova, Z. V. *Zh. Fiz. Khim. 30* (1956) 340; b. Glaser, J. *Acta Chem. Scand. A 33* (1979) 789.
17. Gutiérrez-Puebla, E., Vegas, A. and Garcia-Blanco, S. *Acta Crystallogr. B 36* (1980) 145.
18. Hazell, A. C. *J. Chem. Soc.* (1963) 3459.
19. Thiele, G. *Z. Naturforsch. Teil B 34* (1979) 1512.
20. Brodersen, K., Rath, J. and Thiele, G. *Z. Anorg. Allg. Chem. 394* (1972) 13.
21. Glaser, J. *Acta Chem. Scand. A 34* (1980) 75.

22. Rath, H. J. *Thesis*, Univ. Erlangen-Nürnberg, Erlangen 1972.
23. Watanabe, T. and Atoji, M. *J. Am. Chem. Soc. 72* (1950) 3819.
24. Grunwald, B. *Thesis*, Univ. Erlangen-Nürnberg, Erlangen 1977.
25. Linhard, M., Manthey, W. and Plieth, K. *Z. Electrochem. 57* (1953) 862.
26. Watanabe, T., Atoji, M. and Okazaki, Ch. *Acta Crystallogr. 3* (1950) 405.
27. Glaser, J. *Acta Chem. Scand. A 34* (1980) 141.
28. Böhme, R., Rath, J., Grunwald, B. and Thiele, G. *Z. Naturforsch. Teil B 35* (1980) 1366.
29. Joy, G., Gaughan, A. P., Wharf, I., Shriver, D. F. and Dougherty, J. P. *Inorg. Chem. 14* (1975) 1795.
30. Glaser, J. and Henriksson, U. *J. Am. Chem. Soc. 103* (1981) 6642.
31. Glaser, J. and Johansson, G. *Acta Chem. Scand. A 36* (1982) 125.
32. Glaser, J. *Thesis*, Royal Institute of Technology, Stockholm 1981.
33. Johansson, G. *Acta Chem. Scand. 20* (1966) 553.
34. Johansson, G. and Sandström, M. *Chem. Scr. 4* (1973) 195.
35. a. Palinkas, G., Radnai, T. and Hajdu, F. *Z. Naturforsch. Teil A 35* (1980) 107; b. Narten, A. H. Vaslov, F. and Levy, H. A. *J. Chem. Phys. 58* (1973) 5017.
36. Andrews, P. S., Badger, P. E. R., Goggin, P. L., Hurst, N. W. and Rattray, A. J. M. *J. Chem. Research.* (M) (1978) 1401.
37. Goggin, P. L. *et al. To be published.*
38. a. Busing, W. R. and Levy, H. A. *Acta Crystallogr. 17* (1964) 142; b. Busing, W. R., Martin, K. O. and Levy, M. A. *Function and Error Program*, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge 1965.
39. Barrowcliffe, T., Beattie, I. R., Day, P. and Livingstone, K. *J. Chem. Soc. A* (1967) 1810.
40. Beattie, I. R., Gilson, T. R. and Ozin, G. A. *J. Chem. Soc. A* (1968) 2765.