CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

A Raman Study of Thallium(III) Chloride Complexes in Aqueous Solution

BY THOMAS G. SPIRO

Received November 25, 1964

Raman spectra of $TlCl^{+2}$, $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$ have been determined in aqueous solution. All four species exhibit a polarized band, at 327, 320, 313, and 305 cm.$^{-1}$, respectively, and for $TlCl_4^-$ an additional, depolarized band is observed at 81 cm.$^{-1}$. It is shown that at least one higher complex is formed, with a polarized band at 273 cm.$^{-1}$, and the data fit mass action expressions, in the concentrations of the species, for the equilibrium $TlCl_4^- + 2Cl^- = TlCl_6^{-3}$, with $K = 0.19 \pm 0.09\ M^{-2}$. No evidence could be found for polynuclear complex formation or for association between hydrogen ion and the complex anions. Indirect evidence indicates that aquo Tl^{+3} has a band around 445–455 cm.$^{-1}$ and that all of the coordinated waters which contribute to the Raman emission are replaced by the first two chlorides bound to Tl(III).

Introduction

Several studies of chloride complexes of thallium(III) have revealed a number of unusual properties for these species. They are among the most stable of metal chloride complexes, the standard free energy change on formation of the first complex in aqueous solution being close to 10 kcal./mole.[1,2] There occurs, however, a distinct break in the stability sequence after the second complex,[1,2] similar to, though less pronounced than, that found for the isoelectronic mercury(II) chloride complexes.[3] The maximum number of complexes formed has been a matter of controversy. Early reports of four[4a] and six[4b,c] successive complexes were based on silver chloride electrode measurements, which are of doubtful validity in the strongly oxidizing Tl(III) solutions.[1] Recent potentiometric studies, using the Tl(III)–Tl(I) couple, point to a maximum coordination number of four in solution.[1,2] However, solvent extraction data have been interpreted in terms of weak binding of a fifth chloride,[5] and chemical shifts of Tl^{205} nuclear magnetic resonance strongly indicate more than four chlorides per Tl(III) at high chloride concentrations.[6] The n.m.r. data have also been interpreted as showing $Tl_2Cl_9^{-3}$ to be a principal species. Both $Tl_2Cl_9^{-3}$ and $TlCl_6^{-3}$ units occur in crystals.[7,8]

Hydrolysis of Tl(III) is effectively suppressed by chloride ion,[9] the only mixed hydroxy complex formed in detectable amounts being $TlClOH^+$. Finally, the rate of homogeneous electron exchange between Tl(III) and Tl(I) is a peculiar function of chloride concentration.[10] Apparently the process is decelerated by formation of the first two chloride complexes of Tl(III), but strongly accelerated by addition of further chloride. Similar behavior has been noted for the rate of attainment of the equilibrium Tl(III)–Tl(I) potential at a platinum electrode.[2,9]

These findings suggest interesting structural relations between the various complexes, on which their vibrational spectra might be expected to throw some light. It was with a view toward this end that the present Raman study was undertaken.

Experimental

All solutions were prepared for Raman measurements by mixing together distilled water and varying proportions of three stock solutions: I, containing 0.96 *M* $Tl(ClO_4)_3$ and 2.56 *M* $HClO_4$; II, containing 1.39 *M* $TlCl_3$ and 3.15 *M* $HClO_4$; and III, containing 0.94 *M* $TlCl_3$, 10.3 *M* HCl, and 2.15 *M* $HClO_4$. Solution I was prepared by oxidizing $TlClO_4$ electrolytically in $HClO_4$.[11] Solution II was prepared by passing chlorine, generated from HCl and MnO_2, through a suspension of TlCl in $HClO_4$. Solution III was prepared from solution II by bubbling in gaseous HCl, generated from concentrated HCl by adding concentrated H_2SO_4. $TlClO_4$ and TlCl were both prepared from Tl_2CO_3 (K and K Laboratories) by reaction with an excess of $HClO_4$ and HCl, respectively, and recrystallized from water. For an auxiliary set of measurements to check the effect of acidity, a stock solution without $HClO_4$ and containing LiCl instead of HCl was used in place of solution III.

The presence of $HClO_4$ in the solutions, which is in any case necessary to prevent hydrolysis of Tl(III) at low chloride concentrations, provided a convenient internal standard for Raman intensity measurements.

The stock solutions were analyzed for Tl(III) by reducing with sulfite and titrating the resulting Tl(I) with KIO_3[11]; for chloride by AgCl precipitation; and for hydrogen ion by titration with standard base after Tl(III) interference was eliminated by H_2O_2 reduction for solution I or by addition of a large amount of NaCl for solution II (solution III contained sufficient chloride to mask Tl(III)).

In the main series of solutions Tl(III) was maintained between 0.83 and 0.95 *M* and perchlorate between 2.15 and 4.80 *M*, while chloride was varied between 0 and 13.1 *M*, the balance being made up with hydrogen ions. A number of measurements were also made on solutions in which Tl(III) was between two and three times as dilute as for the main series.

Raman spectra were recorded at 28 ± 1° with a Cary Model 81 Raman spectrophotometer using the 4358 Å. Hg line for excitation. Polarization of the Raman bands was determined with polaroid cylinders surrounding the sample tube. Intensity measurements of the bands arising from the complex species were always referred to the peak height of the (very sharp) A_1 band of ClO_4^- at 933 cm.$^{-1}$, recorded on the same spectrum,

---

[1] M. J. M. Woods, P. K. Gallagher, Z Z. Hugus, Jr., and E. L. King, *Inorg. Chem.*, **3**, 1313 (1964).

[2] S. Ahrland, I. Grenthe, L. Johansson, and B. Norén, *Acta Chem. Scand.*, **17**, 1567 (1963).

[3] L. G. Sillén, *ibid.*, **3**, 539 (1949).

[4] (a) R. Benoit, *Bull. soc. chim. France*, 518 (1949); (b) D. Peschanski and S. Valladas-Dubois, *ibid.*, 1170 (1956); (c) A. I. Busev, V. G. Tiptsova, and T. A. Sokolova, *Vestnick Moskov Univ. Khim.*, **11**, 6 (1960).

[5] D. L. Horrocks and A. F. Voigt, *J. Am. Chem. Soc.*, **79**, 2440 (1957).

[6] B. N. Figgis, *Trans. Faraday Soc.*, **55**, 1075 (1959).

[7] H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 1008 (1935).

[8] (a) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 199 (1935); (b) *ibid.*, **3**, 645 (1935).

[9] G. Biedermann and T. G. Spiro, *Acta Chem. Scand.*, in press.

[10] G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.*, **73**, 2442 (1951).

[11] G. Biedermann, *Arkiv Kemi*, **5**, 441 (1953).

the intensity ratio being normalized according to the concentration ratio of complex ions to perchlorate. This procedure leads to a dimensionless intensity scale which reflects the relative intensities of the complex ions, assuming that changes in solution composition affect scattering intensity equally for perchlorate and the complex ions. The estimated uncertainty in the intensity measurements is 5–10%.

Symbols and Terms

C_{Tl}	Analytical (molar) concentration of thallium(III)
R	Mole ratio of total chloride to total thallium(III)
P	Mole ratio of total perchlorate to total thallium(III)
I_ν	Pointwise intensity (height of Raman trace above the base line) at the frequency ν (in cm.$^{-1}$)
$I_{\int\nu}$	Integrated intensity of the band centered at ν
I_{M}	$I_\nu P/I_{933}$ $(R > 1)$[12] normalized (molar) intensity at ν $I_\nu P/RI_{933}$ $(R < 1)$ relative to the 933 cm.$^{-1}$ perchlorate peak height
(Cl)	Molar concentration of free (unbound) chloride
J_n	Normalized (molar) intensity arising from the species $\mathrm{TlCl}_n{}^{3-n}$ ($J_n(\nu)$ is the normalized spectrum of the species).

Results

(A) Chloride Complexes: General. When chloride is added to Tl(III) a polarized Raman band arises at 327 cm.$^{-1}$ and shifts to lower frequencies as R is increased. Representative spectra are shown in Figure 1. As R approaches 4 the peak, now at 305 cm.$^{-1}$, rapidly sharpens and gains intensity. Simultaneously another, depolarized peak grows at 81 cm.$^{-1}$. These peaks are also found at the same frequencies in the spectrum of an isopropyl ether extract of Tl(III) from 6 M HCl (Figure 2), in which it is known that thallium is associated with four chlorides,[5] so that the spectrum in aqueous solution must also arise from $\mathrm{TlCl_4^-}$. There are also two other very weak bands, at 145 and 167 cm.$^{-1}$ in the ether extract, whose origin is uncertain.

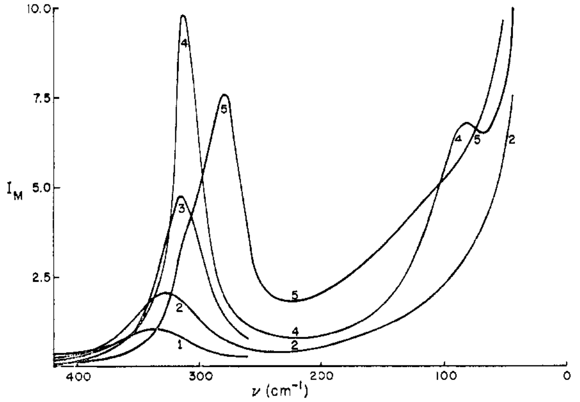

Figure 1.—Normalized Raman spectra of chloride–thallium mixtures, corresponding to the following values of R and C_{Tl} (M): 1: 1.00, 0.941; 2: 2.00, 0.940; 3: 2.97, 0.991; 4: 4.00, 0.860; 5: 13.92, 0.942.

With further addition of chloride the 305 and 81 cm.$^{-1}$ peaks continue to grow slightly until R = 4.5. After that they slowly recede and a new polarized peak grows at 273 cm.$^{-1}$. This peak, which must arise from a species containing more than four chlorides per thallium, is not saturated even when chloride reaches 13 M.

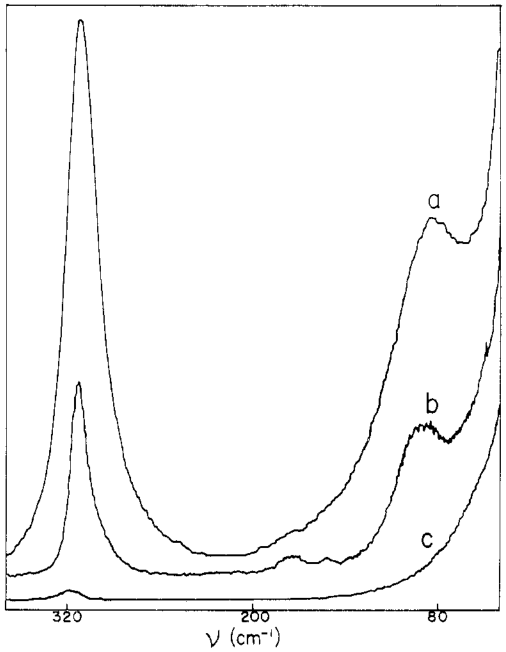

Figure 2.—Raman traces—Cary Model 81; lamp current 15 amp., RD3. (a) Aqueous solution with C_{Tl} = 0.87 M and R = 4.10; 10 cm.$^{-1}$ single slit, 2.2 × 100 amplification. (b) Isopropyl ether Tl(III) extract from 6 M HCl. (c) Pure isopropyl ether; 5 cm.$^{-1}$ single slit, 200 amplification.

Spectra were also recorded of solutions containing LiCl instead of HCl. Essentially the same pattern of peaks was observed. There is apparently no significant interaction of hydrogen ions with the complex anions.

It is clear that the shifts in frequency and intensity of the polarized band over the wide range of chloride concentration employed reflect varying contributions of a whole series of complexes. Unfortunately, the bands arising from the various complexes are too close together to be separated optically, so that their relative contributions cannot be assessed from the spectra alone. On the other hand, it is possible to bring the known solution chemistry of the thallium(III) chloride system to bear on the problem. In particular, because of the peculiar stability sequence of the complexes, it is possible to prepare the species $\mathrm{TlCl^{+2}}$, $\mathrm{TlCl_2^+}$, and $\mathrm{TlCl_4^-}$ almost quantitatively by proper adjustment of concentration. The spectra of the remaining species can be extracted from the data by application of the law of mass action. This procedure is reasonable for $\mathrm{TlCl_3}$, which exists in a narrow concentration range. For the weakly formed higher complex(es), whose composition is unknown, and whose formation requires large concentration changes, it is much more questionable; however, it leads to surprisingly straightforward results, as will be seen. The approach used in the present work is to treat the Raman data in the manner conventionally used for absorption spectrophotometry. A relation analogous to Beer's law is assumed, namely

---

(12) For $R > 1$, free thallium is negligible and the total concentration of complexes equals C_{Tl}, while for $R < 1$ free chloride is negligible and the total concentration of complexes equals the analytical chloride concentration.

$$I_{\text{M}} = \sum_{n=0} J_n(\text{TlCl}_n{}^{3-})/C_{\text{Tl}} \qquad (1)$$

where the intensity refers to the height of the Raman trace above the base line at a particular frequency. It is well established that the integrated intensity of a Raman band is proportional to the concentration of the scattering species (*cf.*, *e.g.*, ref. 13). Equation 1 implies a similar proportionality for the pointwise intensity and will hold as long as the band shape for each species remains constant over the range of measurements.

(B) **TlCl^{+2} and $\text{TlCl}_2{}^+$.**—Potentiometric studies have shown that the first two chlorides bind very strongly to Tl(III), and the binding of the third is much weaker.[1,2] Therefore, at $R = 2$ the formation of $\text{TlCl}_2{}^+$ is essentially quantitative; from the data of King, *et al.*, in 3 M HClO_4,[1] one calculates that 95% of the thallium is present in this form. Although the same stability quotients cannot be expected to apply exactly to the concentrated solutions of the present study, their relative values should remain similar, and, because of the great stability of $\text{TlCl}_2{}^+$, it represents almost all of the thallium present at $R = 2$ over a fairly wide range of quotients. It is therefore reasonable to assume that the spectrum at $R = 2$ represents the spectrum of $\text{TlCl}_2{}^+$. Furthermore, when thallium is in excess, essentially all the chloride is tied up as TlCl^{+2}, so that it is reasonable to assume that the spectrum at $R = 0.5$ represents the spectrum of TlCl^{+2}.

These spectra are shown in Figure 3, along with an intermediate spectrum, whose calculation permits a check on our assumptions. At $R = 1.5$, the formation of TlCl^{+2} should also be quantitative, in the sense that no Tl^{+3} is present, and the spectrum should be simply the mean of the spectra of $\text{TlCl}_2{}^+$ and TlCl^{+2}, *i.e.*

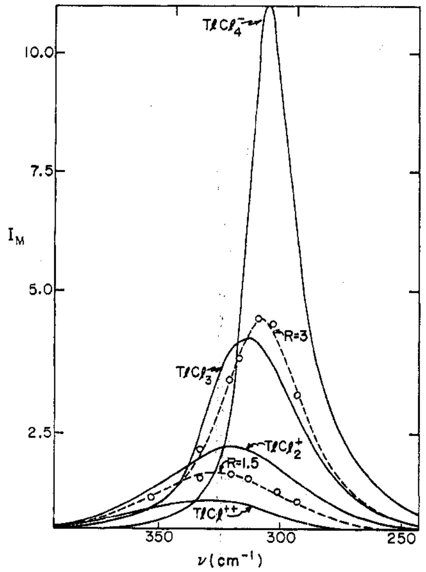

Figure 3.————, calculated spectra of the species indicated; – – – –, experimental curves at $R = 1.5$ and 3.0 compared with calculated points, O (see text).

$$I_{\text{M}} = {}^1/_2(J_2 + J_1)$$

The agreement between the measured spectrum and points calculated with the expression is indeed quite satisfactory.

(C) **TlCl_3 and $\text{TlCl}_4{}^-$.**—The binding of the third and fourth chloride to Tl(III) is moderately strong, but not quantitative. From the data of King, *et al.*,[1] one calculates that a 1 M solution of $\text{TlCl}_4{}^-$ should be 8.2% dissociated, while in the presence of 0.5 M free chloride the degree of dissociation should decrease to 1.3%. It is therefore not surprising that the $\text{TlCl}_4{}^-$ peaks should continue to increase in intensity between $R = 4$ and $R = 4.5$ (Figure 4). The increase is somewhat greater than the above numbers suggest, which indicates that the equilibrium quotient for the addition of chloride to TlCl_3 is somewhat lower in the concentrated solutions of the present study. Beyond $R = 4.5$, $\text{TlCl}_4{}^-$ is used up in further reaction with chloride. From the equilibrium quotient for this reaction, to be discussed below, it appears that at $R = 4.5$, only about 2.5% of the $\text{TlCl}_4{}^-$ is removed by this path. Consequently at $R = 4.5$ almost all of the Tl(III) is present in the form of $\text{TlCl}_4{}^-$.

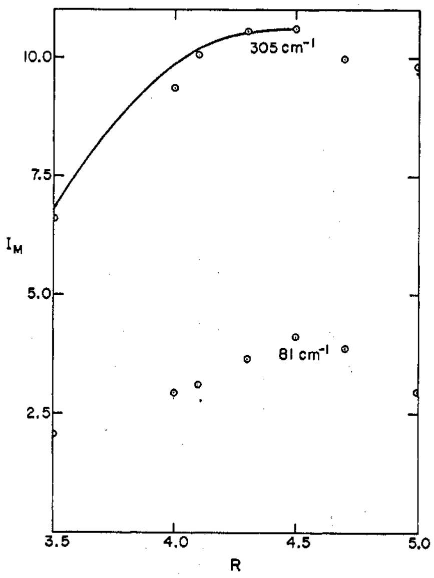

Figure 4.—Normalized intensities in the region $3.5 < R < 5.0$ at the $\text{TlCl}_4{}^-$ peak frequencies: O, experimental values; ————, calculated with the parameters $J_{4(305)} = 11.00$, $J_{3(305)} = 3.61$, $K_4 = 40$.

The species TlCl_3 disproportionates appreciably (56% in 3 M HClO_4) into $\text{TlCl}_2{}^+$ and $\text{TlCl}_4{}^-$. Its spectrum, $J_3(\nu)$, as well as the equilibrium quotient, K_{D}, for the disproportionation reaction $2\text{TlCl}_3 = \text{TlCl}_2{}^+ + \text{TlCl}_4{}^-$, was obtained by simultaneous analysis of the curves at $R = 2.5$ and $R = 3.0$, using the mass balances for these solutions (in which free chloride was assumed to be negligible) and eq. 1. Of the remaining parameters in the latter, J_2 was determined independently as described in the preceding section, and J_4 was taken from the intensity data at $R = 4.5$. The value of J_3 so obtained at 305 cm.$^{-1}$ was then used in a mass action expression to describe the peak intensities in the region $3.5 < R < 4.5$, a reasonable fit (Figure 4) being given with a quotient for the equilibrium, $TlCl_3 + Cl^- = TlCl_4{}^-$, $K_4 = 40$, and a $TlCl_4{}^-$ molar intensity $J_{4(305\ \mathrm{cm}^{-1})} = 11.00$. The latter value is 3.5% greater than the peak intensity at $R = 4.5$, and the spectrum of $TlCl_4{}^-$ was therefore obtained by increasing the value of $I_{M(R=4.5)}$ by this fraction at each frequency. The calculation of the spectrum and disproportionation quotient of $TlCl_3$ was then refined accordingly. A final check on these parameters was obtained by calculating several points in the spectrum of a solution with $R = 3$. They are compared with the experimental curve in Figure 3, which also shows the individual spectra of $TlCl_3$ and $TlCl_4{}^-$. The calculated disproportionation quotient for $TlCl_3$ is 0.11. It is interesting that, while for dilute thallium in 3 M $HClO_4$[1] both K_4 (148) and K_D (0.425) are larger than the present values, their ratio, which corresponds to K_3, the stepwise formation constant for $TlCl_3$, is practically the same in both cases. Thus it appears that $TlCl_4{}^-$, but not $TlCl_3$, is somewhat destabilized in concentrated solution.

(D) **Higher Complexes.**—As noted above, the Raman data definitely establish the formation of higher complexes since the addition of further chloride to solutions containing mainly $TlCl_4{}^-$ gives rise to an entirely new spectrum. However, the formation of the new species is quite weak, being incomplete even at very high chloride concentrations, and therefore the determination of their composition is not straightforward. A continuous variations study, successfully used, for example, to establish the highest halides of zinc(II) as $ZnX_4{}^-$,[13,14] cannot be performed in the present case because it is impossible to maintain the total of thallic and chloride concentrations constant in the range of significant formation of the higher species. When superimposed, the spectra above $R = 4.5$ appear to pass within experimental uncertainty of a common (isosbestic) point at 290 cm.$^{-1}$, which, in the light of eq. 1 (Beer's law behavior) implies, though it does not require, the existence of only one species in addition to $TlCl_4{}^-$.

Although the highly variable composition of the solutions would seem to preclude any assumption of constant activity coefficient factors, the dependence of intensity of both the 305 cm.$^{-1}$ $TlCl_4{}^-$ peak and the new 273 cm.$^{-1}$ peak on chloride concentration (see Table I) appeared to resemble simple mass action behavior, and it seemed worthwhile to attempt an equilibrium analysis in terms of the concentrations of the species. The technique (analogous to those employed in absorption spectrophotometry[15]) is to set up hypotheses as to the composition of the reaction products, and, from the resulting mass balances combined with eq. 1, to derive appropriate functions with which to test the experimental data.

Table I

Molar Intensities at 305 and 273 Cm.$^{-1}$ for Solutions Containing High Concentrations of Chloride

C_{Tl}, M	R	P	$I_{M(305)}$	$I_{M(273)}$
0.857	5.00	3.54	9.55	2.61
0.861	5.54	4.32	8.91	2.60
0.859	6.18	4.16	7.44	3.34
0.863	7.37	3.87	6.04	3.98
0.855	8.69	3.55	4.65	4.80
0.848	9.68	3.29	3.97	5.38
0.841	9.82	3.27	4.06	5.40
0.836	11.31	2.91	3.24	5.80
0.836	12.17	2.63	3.08	6.00
0.830	12.74	2.52	3.02	6.01
0.942	13.92	2.28	2.77	6.33

The simplest hypotheses are that either $TlCl_5{}^{-2}$ or $TlCl_6{}^{-3}$ is formed directly from $TlCl_4{}^-$. Appropriate test expressions are, in the first case

$$I_M = J_5 + K_5{}^{-1}(J_4 - I_M)(Cl^-)^{-1} \qquad (2)$$

and in the second

$$I_M = J_6 + K_6{}^{-1}(J_4 - I_M)(Cl^-)^{-2} \qquad (3)$$

K_5 and K_6 representing the equilibrium quotients for formation from $TlCl_4{}^-$ of $TlCl_5{}^{-2}$ and $TlCl_6{}^{+3}$, respectively. The free chloride concentration is first approximated with $C_{Tl}(R - 4)$ and then corrected by iteration, using preliminary values of the constants, in the formulas

$$(Cl^-) = C_{Tl}[(R - 4) - K_5(Cl^-)(1 + K_5(Cl^-))^{-1}] \qquad \text{for eq. 2}$$

and

$$(Cl^-) = C_{Tl}[(R - 4) - K_6(Cl^-)^2(1 + K_6(Cl^-)^2)^{-1}] \qquad \text{for eq. 3}$$

The constant, J_4, was determined independently, as described in the preceding section. In Figure 5, I_M is plotted against $(J_4 - I_M)(Cl^-)^{-1}$ (open symbols) and $(J_4 - I_M)(Cl^{-1})^{-2}$ (closed symbols) for the 305 cm.$^{-1}$ ($TlCl_4{}^-$) and 273 cm.$^{-1}$ ($TlCl_{n+4}{}^{-1-n}$) peaks. The plot for eq. 2 is clearly nonlinear, while the linearity of the plot for eq. 3 is quite satisfactory, although the K_6 values determined from the slopes are somewhat different for the two frequencies (0.23 at 305 cm.$^{-1}$ and 0.14 at 273 cm.$^{-1}$). Even if this analysis does not prove the formation of $TlCl_6{}^{-3}$, eq. 3 clearly provides a good extrapolation function to determine the molar intensities of the higher complex ($TlCl_{n+4}{}^{-1-n}$), whatever its composition; the intercepts provide $J_{n+4} = 2.25$ at 305 cm.$^{-1}$ and 6.75 at 273 cm.$^{-1}$. With these values, and those of J_4, it is possible, by combining the intensities at 305 and 273 cm.$^{-1}$, to calculate the fraction of thallium present as $TlCl_4{}^-$ and $TlCl_{n+4}{}^{-1-n}$. When this was done it was found that these two complexes accounted for the total thallium present within 8% for all solutions, so that, within the uncertainty of the measurements, there is no need to assume significant amounts of any other

---

(13) D. E. Irish, B. McCarroll, and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).

(14) W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

(15) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, Chapter 13.

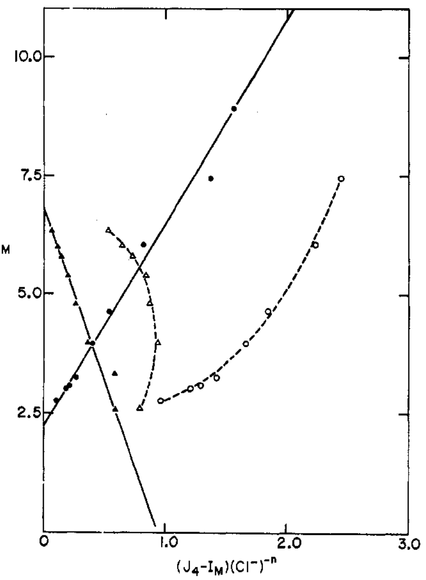

Figure 5.—Tests for mass action behavior in the formation of $TlCl_{4+n}^{-1-n}$, using - - - - eq. 2, $n = 1$, at 305 cm.$^{-1}$, ○, and 273 cm.$^{-1}$, △; and ——— eq. 3, $n = 2$, at 305 cm.$^{-1}$, ●, and 273 cm.$^{-1}$, ▲.

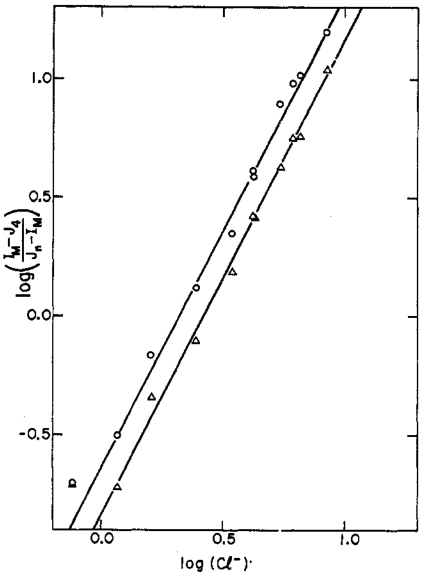

Figure 6.—Test for mass action behavior in the formation of $TlCl_{4+n}^{-1-n}$, using eq. 4 at 305 cm.$^{-1}$, ○, and 273 cm.$^{-1}$, △. Lines are drawn with slope (n) = 2.00.

species to describe the data. Finally, knowledge of the molar intensity of the unknown species permits a more rigorous test of mass action behavior because, for any equilibrium

$$TlCl_4^- + nCl^- = TlCl_{n+4}^{-1-n}$$

if

$$K_n = \frac{(TlCl_{n+4}^{-1-n})}{(TlCl_4^-)(Cl^-)^n}$$

then

$$\log \frac{(TlCl_{n+4}^{-1-n})}{(TlCl_4)} = \log K_n + n \log (Cl^-) \qquad (4)$$

so that a plot of the left side of eq. 4 against log (Cl⁻) must be linear, with an integral slope, n, representing the number of chlorides in excess of four in the unknown species. The ratio $(TlCl_{n+4}^{-1-n})/(TlCl_4^-)$ is obtainable from the intensity data alone, as $(I_M - J_{n+4})/(J_4 - I_M)$, without further assumptions. Its logarithm is plotted against the logarithm of the free chloride concentration (calculated as above) in Figure 6. The straight lines are drawn with slopes = 2.00 and intercepts corresponding to the quotients determined from eq. 3. The fit is excellent.[16] It appears therefore that the data are quite adequately described by the equilibrium $TlCl_4^- + 2Cl^- = TlCl_6^{-3}$, with the law of mass action applied to the *concentrations* of the species.

In situations of this kind, the variation in activity coefficients of the individual ionic species, which are in principle unobtainable, is sometimes taken into account by using instead the mean activity coefficient of one of the components of the mixture. In particular HCl is often substituted for chloride. Considering eq. 4, for example, one might assume that the ratio of activity coefficients for the anionic complexes remains constant and that in place of the concentration of chloride one should insert the activity of HCl. This quantity is of course not known for the complicated mixtures of the present study, but one might assume that it parallels roughly that of pure aqueous HCl. Between 1 and 10 *M* HCl, the latter quantity increases rather dramatically,[17] and the increase is more than proportional to the concentration. Therefore inclusion of a parallel set of values in eq. 4 would introduce in the plot of Figure 6 a negative curvature, which would violate the law of mass action since it would imply a decreasing number of chlorides bound to thallium with increasing chloride activity.

It is perhaps not altogether surprising that the equilibrium under consideration has little apparent relation to the activity coefficient of HCl, since at high concentrations variation in this quantity is apparently due to the effect of hydration of the ions,[18] which is undoubtedly more pronounced for H⁺ than for Cl⁻. Therefore in this region activity changes of HCl may be more reflective of those due to H⁺ than those due to Cl⁻.

In any case we are left with the conclusion that the data behave as if the activity coefficient quotient $f_{TlCl_6^{-3}}/f_{TlCl_4^-}f_{Cl^-}{}^2$ does not vary significantly over a wide range of HCl concentration. This constancy may result from cancellation of opposing trends in the enthalpy and entropy of the reaction with changing composition, a phenomenon observed by Nixon and Plane in the formation of $GaBr_4^-$.[19]

---

(16) That the lines are parallel, but not coincident, is due to the different equilibrium quotients that appear to apply to the two frequencies. They differ by 0.2 log unit, which is not unreasonable in view of the uncertainty of the intensity measurements.

(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 2nd Ed., 1959, pp. 491, 504.

(18) Reference 17, p. 238 ff.

(19) J. Nixon and R. A. Plane, *J. Am. Chem. Soc.*, **84**, 4445 (1962).

It should be noted that this analysis of the Raman data is not inconsistent with the recent potentiometric studies[1,2] which fail to show evidence of complexes containing more than four chlorides per thallium. These were limited to much lower chloride concentrations than those of the present work. Also with increasing chloride concentration the influence on the Tl(III)–Tl(I) electrode potential of Tl(I) complex formation becomes increasingly large and uncertain.

Solvent extraction data do provide evidence for the formation of higher species, as noted previously, since the extraction of $HTlCl_4$ into ether decreases somewhat with increasing chloride concentration.[5] Horrocks and Voigt fit their data adequately with a constant for the formation of $TlCl_5^{-2}$ from $TlCl_4^-$, but in view of the limited concentration range covered, it could probably be equally well fit on the basis of $TlCl_6^{-3}$ formation.

(E) **Polynuclear Species.**—The $Tl_2Cl_9^{-3}$ unit is found in crystals of $Cs_3Tl_2Cl_9$.[7,8a] Previous studies in dilute aqueous solution have shown the Tl(III) chloride complexes to be mononuclear, but Figgis has interpreted his n.m.r. data as implying the formation of $Tl_2Cl_9^{-3}$ in moderately concentrated (0.2–1.5 *M*) Tl(III) solutions.[6] His conclusion rests on a change in direction of the chemical shift of the Tl^{205} magnetic resonance at a chloride to thallium ratio of 4.5. It was shown above that a similar change in direction occurs in the molar Raman 305 cm.$^{-1}$ intensity at R = 4.5. It occurs because the addition of the fourth chloride to $TlCl_3$ is not quantitative at R = 4, while at much higher chloride concentrations $TlCl_4^-$ is removed by formation of a higher complex. The combination of these two reactions leads to a maximum concentration of $TlCl_4^-$ at about R = 4.5. The same effect serves to explain the peak in the n.m.r. chemical shift curve. The latter does not therefore establish the existence of $Tl_2Cl_9^{-3}$ in aqueous solution.

If polynuclear aggregates were formed, they would be expected to give rise to Raman bands at fairly low frequencies. Yet all of the observed Raman bands can be accounted for on the basis of successive mononuclear complex formation. In order to check this point, Raman spectra were obtained for a series of solutions with C_{Tl} = 0.3 *M*, considerably more dilute than in the main series. If equilibria occur between polynuclear and mononuclear complexes, they should be shifted toward the latter on dilution. It was found that the molar intensities were somewhat lower (~30%) in dilute solutions at the same free chloride concentration and that for $R < 2$ the band maximum shifted a few cm.$^{-1}$ to lower frequencies. However, the general pattern and sequence of appearance of the peaks was exactly the same for the dilute as for the concentrated solutions. Consequently the Raman data provide no evidence for the formation of polynuclear complexes.

(F) **Aquo Tl^{+3}.**—The spectrum of $Tl(ClO_4)_3$ in $HClO_4$ is at first glance identical with that of dilute $HClO_4$ or of perchlorate salts. An intense peak (933 cm.$^{-1}$), two weaker peaks (461 and 630 cm.$^{-1}$), and a broad band (1120 cm.$^{-1}$) all occur at the proper frequencies for tetrahedral perchlorate ion. There being no apparent distortion of the ClO_4^- structure, complex formation (except for possible ion pairing) between Tl^{+3} and ClO_4^- may be ruled out.[20a]

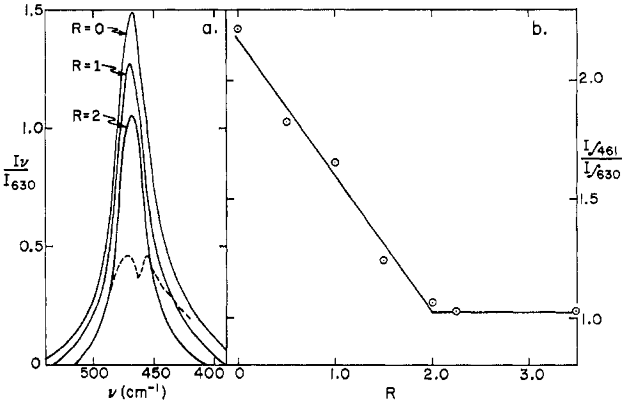

Figure 7.—Low-frequency perchlorate band showing enhancement for $R < 2$: (a) 461 cm.$^{-1}$ band normalized with respect to the perchlorate peak intensity at 630 cm.$^{-1}$ at R = 0, 1, and 2; – – – –, difference between spectra at R = 0 and R = 2. (b) Ratio of integrated intensities of 461 and 630 cm.$^{-1}$ bands as a function of R.

However, closer examination of the spectrum reveals that the 461 cm.$^{-1}$ peak is slightly skewed toward lower frequencies and is considerably more intense, relative to the 630 cm.$^{-1}$ peak, than it is in dilute $HClO_4$. Furthermore, it is partially polarized, and its intensity in perpendicular polarization, relative to that of the 630 cm.$^{-1}$ peak, is much closer to that found in $HClO_4$. A number of polyvalent metal ions give rise to polarized Raman bands in the 350–550 cm.$^{-1}$ region.[20b] It seems likely that the enhanced intensity and partial polarization of the 461 cm.$^{-1}$ peak arise from a polarized band of aquo Tl^{+3}, which it overlaps.

On addition of chloride, this intensity enhancement decreases. As shown in Figure 7, the ratio of integrated intensities of the 461 and 630 cm.$^{-1}$ bands decreases linearly with added chloride up to R = 2, whereafter it levels out and remains constant at about the $HClO_4$ value. Apparently, the coordinated water which gives rise to the aquo Tl^{+3} band is replaced by chloride. The fact that all of the intensity enhancement is eliminated by addition of two chlorides per thallium, and half of it by one, suggests that, of the water molecules bound to Tl^{+3}, half remain bound to $TlCl^{+2}$ and none are left bound to $TlCl_2^+$. Although for $Tl(H_2O)_m^{+3}$ m may on this basis be any even integer, it seems unlikely that each of the first two chlorides should displace more than one water molecule on coordination to thallium(III), *i.e.*, that $m > 2$. The simplest interpretation of the data is that only two water molecules are sufficiently strongly bound to Tl^{+3} to give rise to Raman emission. They may, of course, occur at equatorial positions of a distorted octahedron of water molecules, the four axial waters

---

(20) (a) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964); (b) *ibid.*, **3**, 768 (1964).

being much more weakly bound to Tl^{+3}.[21] Strong binding of only two waters by Tl^{+3} is also supported by hydrolysis data.[9] Thallic ion splits off two protons, $TlCl^{+2}$ only one, while $TlCl_2^+$ and higher complexes split off no protons prior to precipitation of Tl_2O_3.

In Figure 7a, the dotted curve is the difference between the spectra at $R = 0$ and $R = 2$ and should represent the spectrum of aquo Tl^{+3}. Its peak intensity appears to be between 445 and 455 cm.$^{-1}$. The extra peak at 461 cm.$^{-1}$ is probably only a remnant of the more intense ClO_4^- emission.

It is not out of the question that the intensity decrease on chloride addition is caused by some other mechanism. If, for example, chloride produces a strong distortion in the aquo Tl^{+3} symmetry, the Tl-O vibration might be strongly shifted and/or sufficiently broadened to be unobservable. It is not clear however why this effect should be linear to $R = 2$. It would seem more likely that the first chloride, producing the strongest distortion, should carry the greatest part of the effect.

Ideally, one would like to observe the Tl–O vibration unobscured by other species. Unfortunately it appears to be difficult to obtain Tl^{+3} in a medium which is noncomplexing and does not give Raman scattering in the region of interest. In preliminary experiments it was found that Tl^{+3} distorts the spectrum of NO_3^- severely. The spectrum of HSO_4^- does not appear to be much affected, but it has a peak in the region of interest. An attempt to obtain the spectrum of TlF_3 in aqueous HF solution was unsuccessful.

Structural Considerations.—The Raman peaks for the various complexes are summarized in Table II.

TABLE II

RAMAN BAND PARAMETERS FOR THALLIUM(III) SPECIES FOUND IN AQUEOUS SOLUTION

Species	Peak frequency, cm.$^{-1}$	Peak width at half-height, cm.$^{-1}$	Polarization[a]	Integrated intensity[b]
Aquo Tl^{+3}(?)	445–455	...	...	...
$TlCl^{+2}$	327	64	p	2.5
$TlCl_2^+$	320	62	p	6.1
$TlCl_3$	313	43	p	10.0
$TlCl_4^-$	305	25	p	17.6
	81	48	dp	9.2
$TlCl_6^{-3}$(?)	273	43	p	15.5

[a] p, polarized; dp, depolarized. [b] Relative to the A_1 (933 cm.$^{-1}$) peak of perchlorate.

The polarized, symmetric stretching band is the only one observable for all species except $TlCl_4^-$, which also shows a depolarized band at low frequency, probably arising from a bending mode of the complex. The $TlCl_4^-$ ion should have three Raman bands if square-planar, four if tetrahedral, and more than four if of lower symmetry. Failure of the theoretical number of bands to appear in solution spectra appears to be more the rule than the exception. Presumably the missing bands are either coincident with those that do appear or of too low intensity to be observed. However, Delwaulle[22] reported four tetrahedral Raman peaks for $TlBr_4^-$. Irish, *et al.*,[13] have invoked square-planar coordination for $ZnCl_4^{-2}$, arguing that the two tetrahedral bending modes observable in $ZnBr_4^{-2}$ and ZnI_4^{-2} should be even more clearly separated in tetrahedral $ZnCl_4^{-2}$, while in fact only one depolarized peak is observed. If this line of argument is valid, then $TlCl_4^-$ should also be square-planar. On the other hand, one of the bending modes might simply be of too low intensity to be observed, as suggested by Busey and Keller[23] for some tetrahedral oxy anions. Tetrahedral $TlCl_4^-$ has very recently been found in the crystalline state,[24] while both tetrahedral[25] and square-planar[26] crystal structures for $TlBr_4^-$ have been claimed. The issue as to the structure of T Cl_4^- in solution remains open

For the remaining species, the Raman spectra, containing only one band, provide no clue as to their structure. However, as Plane has noted,[27] the fact that the band occurs in the same frequency region, and that the peak frequency is a smooth function of the number of chlorides, at least up to four, implies that all of the complexes are reasonably symmetric. If one of them were not, the resulting contribution of the heavy thallium atom to the vibration frequency would shift its value considerably. Approximate symmetry could be provided by coordinated water molecules. Thus the ν_1 band parameters are consistent with successive replacement of water by chloride at tetrahedral or square-planar sites up to $TlCl_4^-$. On the other hand, if, as the preceding observations on the thallium–water interaction suggest, water is not bound firmly to species containing more than one chloride, then there must be structural rearrangement from linear $TlCl_2^+$ to trigonal $TlCl_3$ to either tetrahedral or square-planar $TlCl_4^-$. Structural change for these species is also suggested by unusual values for the heats and entropies of their formation.[1,28] Taken in their entirety, the Raman, thermodynamic,[1,28] and hydrolysis[9] data point to the following model of Tl(III) coordination by chloride. In perchlorate solution, Tl^{+3} is firmly bound to only two water molecules, which may be located at axial positions of a distorted octahedron of waters. These two are successively replaced by added chloride, leading to linear $TlCl_2^+$ (again possibly surrounded by four loosely bound waters in the equatorial plane). Addition of further chloride is energetically less favorable, requiring structural rearrangement to trigonal $TlCl_3$ and tetrahedral or square-planar $TlCl_4^-$. It should be emphasized, however, that the evidence for this model, though consistent, is entirely indirect insofar as structure is concerned.

---

[21] This type of structure, which is not uncommon for d^{10} ions, has been given a theoretical discussion by L. Orgel, *J. Chem. Soc.*, 4186 (1958).

[22] M. L. Delwaulle, *Compt. rend.*, **238**, 2522 (1954).

[23] R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 215 (1964).

[24] F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

[25] A. C. Hazell, *J. Chem. Soc.*, 3459 (1963).

[26] T. Watanable, Y. Sarto, R. Shiono, and M. Atoji, *Structure Rept.*, **11**, 393 (1947–48).

[27] R. A. Plane, private communication.

[28] I. Leden and T. Ryhl, *Acta Chem. Scand.*, **18**, 1196 (1964).

All of the ν_1 band parameters exhibit a sharp break—to lower frequency and intensity, and greater width—on adding more chloride to $TlCl_4^-$. The break in the stability sequence for the successive complexes is also pronounced. Most likely the product is octahedral $TlCl_6^{-3}$, in which the chlorides are, on the average, less tightly bound than in $TlCl_4^-$. Since addition of only one chloride would destabilize the $TlCl_4^-$ structure and the addition of one more would probably lead to a slight increase in stability, it is not surprising that $TlCl_5^{-2}$ does not appear to be an important species in aqueous solution.

Acknowledgments.—The author is grateful to Professors E. L. King and R. A. Plane for stimulating discussions concerning the results of this study, and to J. S. Kittelberger for assistance in obtaining the Raman spectra.

CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.
MURRAY HILL, NEW JERSEY

Pentacoordinated Molecules. V. The Preparation and Properties of $PClF_4$

BY RICHARD P. CARTER, JR., AND ROBERT R. HOLMES

Received January 12, 1965

Phosphorus monochlorotetrafluoride, $PClF_4$, the only previously unknown member of the series PCl_xF_{5-x}, was successfully prepared by the controlled low-temperature fluorination of the molecular form of PCl_2F_3 using SbF_3 as the fluorinating agent. Its characterization and some of its physical properties are reported.

The phosphorus(V) chlorofluorides have been the subject of a number of recent investigations[1]; however, the over-all correlation of structural information on these substances was hampered to a degree for lack of one member of the series, $PClF_4$. We now wish to report the successful synthesis and characterization of this member. It was obtained by the low-temperature fluorination of PCl_2F_3 using SbF_3 as the fluorinating agent.

Experimental

Preparation.—The apparatus consisted of a 100-ml. reaction flask containing a Teflon-coated stirring magnet. Attached to the flask was a swivel-type addition tube for adding solid SbF_3 (Columbia Organic Chemical Co.) and a reflux condenser with a dewar head suitable for use at low temperatures. The entire assembly was attached to the vacuum line through the connection at the upper part of the reflux condenser. A quartz spiral Bourdon pressure gauge and fractionation train also were essential parts of the vacuum system. The stopcock grease used was Kel-F.

The molecular form of PCl_2F_3 (approximately 6 ml.) was prepared *in vacuo* according to a modification[2] of a previous procedure[3] and transferred to the 100-ml. flask. Reaction was initiated by adding a small amount of SbF_3 through the addition tube. The head temperature was maintained at −95° (the vapor pressure of PCl_2F_3 at −95° is near zero) by means of a toluene slush bath. The temperature of the reaction flask was controlled at −40 to −50°. Reaction proceeded with the continued addition of SbF_3 causing pressure buildup in the reaction zone due to the formation of volatile products. To prevent the desired product, $PClF_4$, from being fluorinated further, a low pressure (about 25 mm.) was kept in the reaction zone by continuously bleeding off the product gases. This procedure was effective in limiting the formation of PF_5 to 1% or less of the total product. The addition of SbF_3 was completed during the first hour but the reaction continued very slowly. The reaction usually was terminated after 6 hr. Vacuum fractionation of the product through traps cooled to −123, −136, and −196° yielded a tensiometrically homogeneous sample after three or four recyclings. The yield of pure material is estimated at 20%.

At the end of 6 hr. the product is being evolved at about the same rate as was observed initially. Hence further yield may be realized on lengthening the collection time. Some solid does appear on the walls of the flask during the reaction, presumably solid modifications of the mixed halides[3] resulting from prolonged contact at temperatures considerably above −78°, but this action may be limited by maintaining the entire reaction assembly at −30 to −40°.

Results

Infrared Spectrum.—The gas phase spectrum of $PClF_4$ was recorded in the range 2000–400 cm.$^{-1}$ with a Perkin-Elmer Model 337 Grating Infracord and in the range 2000–250 cm.$^{-1}$ with a Perkin-Elmer Model 421 spectrophotometer. The former was calibrated with polystyrene and the latter with polystyrene and H_2O vapor. A 10-cm. gas cell fitted with KBr or CsI windows was used. Argon was mixed with the $PClF_4$ for some of the runs to minimize cell reaction and window attack.

After thorough conditioning of the cell with the $PClF_4$, reproducible spectra were obtained in the pressure region from 2 to 500 mm. Table I lists all but the very weak bands and serves to characterize the compound.

The bands at 993 and 1415 cm.$^{-1}$ are easily recognizable as POF_3 impurity bands while the line at 1026 cm.$^{-1}$ is in the region of an intense SiF_4 fundamental.[4] The POF_3 lines grow with time while the

---

[1] Previous paper: R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964), and references cited therein.

[2] R. R. Holmes and R. P. Carter, Jr., to be published.

[3] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[4] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).