of the above alternatives is the best since, in each case, there seems good reasons for *not* accepting any particular assignment of the 12,750 cm.$^{-1}$ absorption.

On dissolving this complex (or $K_2MnF_5\cdot H_2O$) in 40% hydrofluoric acid it is thought that a MnF_6^{3-} complex ion is formed.[21] Recently it has been demonstrated[22] that in <6 *M* perchloric acid solutions containing Mn(III) and a large excess of Mn(II) the ion $Mn(H_2O)_5OH^{2+}$ exists. Furthermore, when free fluoride ion is added, it has been suggested[23] that a complex $Mn(H_2O)_5F^{2+}$ is formed.

In the present experiments (in 40% HF with and without excess F^-) the spectrum has been found to be very sensitive to the $Mn(III)/F^-$ ratio in the solutions, thus agreeing with the previous reports.[21,23] The spectrum shown in Figure 2 is that observed when a large excess of fluoride ion is present, and the absorbing species is thought to be anionic,[21] and, from the correspondence between solution and crystal, both in terms of energy and intensity, we consider the absorbing complex to be MnF_6^{3-}. We cannot, however, rule out complexes of the type $MnF_x(H_2O)_y^{3-x}$ where $x \geq 4$ and $y \leq 2$.

Under normal circumstances the MnF_6^{3-} units in solution should have a regular octahedral configuration, but since the ground state is $^5E_g(O_h)$ a large Jahn–Teller distortion may be anticipated. The correspondence between the crystal and the solution spectrum, Figure 2, indicates that if a single absorbing species is present then it exists in a conformation that is as distorted as that seen in the crystal.

Presently we prefer to think that single MnF_6^{3-} units exist in the solution and that the assignments discussed for the crystal may be transferred directly to the solution spectrum. Even if the actual assignments, especially with regard to the 12,750 cm.$^{-1}$ absorption, are in doubt, the correspondence between the spectrum of the tetragonally distorted ammonium pentafluoromanganate and that of the solution must be considered as strong evidence for a distorted ground-state conformation, perhaps of a Jahn–Teller origin for the complex in solution.

Acknowledgments.—It is a pleasure to thank Professors N. S. Bayliss and C. J. Ballhausen for helpful discussions. The author is grateful to the Commonwealth Scientific and Industrial Research Organization for financial support in the form of a senior Postgraduate Studentship.

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Raman Spectra of Crystalline Chlorothallates

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Raman spectra have been obtained for a series of crystalline compounds containing the complex anions $TlCl_6^{-3}$, $TlCl_5^{-2}$, $Tl_2Cl_9^{-3}$, and $TlCl_4^-$. Comparison with solution spectra leads to the conclusion that addition of chloride to aqueous $TlCl_4^-$ involves a tetrahedral–octahedral transition, although both structures are somewhat distorted by water.

Introduction

Raman spectra of chloride complexes of thallium(III) have recently been determined in aqueous solution.[1] The solution data raise some questions about the structures of the complexes which seemed worth exploring further through investigation of crystalline materials containing these species. A number of chlorothallate salts can be prepared and several crystal structures have been determined. Thus, $K_3TlCl_6\cdot 2H_2O$ contains $TlCl_6^{-3}$ octahedra,[2] while $Cs_2TlCl_5\cdot H_2O$ contains square pyramidal $TlCl_5^{-2}$,[3] with a water molecule occupying the sixth octahedral position. In $Cs_3Tl_2Cl_9$, on the other hand, the complex consists of two octahedra fused at a face.[4] The tetrachloro complex in crystalline $(C_6H_5)_4AsTlCl_4$ is tetrahedral.[5] Raman spectra arising from these structural units are presented in this work and their implications for the structures of chlorothallates formed in solution are discussed.

Experimental

The crystalline compounds of known structure were prepared following the methods of the investigators who determined the structure. Thus $K_3TlCl_6\cdot 2H_2O$[2] and $Cs_3Tl_2Cl_9$[4] were prepared according to Hoard and Goldstein, $Cs_2TlCl_5\cdot H_2O$ according to Watanabe and Atoji,[3] and $(C_6H_5)_4AsTlCl_4$ according to Cotton, *et al.*[5] In addition, $K_2TlCl_5\cdot 2H_2O$ and the pyridinium salt of $TlCl_4^-$, $(C_5H_5NH)TlCl_4$, were prepared according to Meyer,[6] and $(CH_3)_4NTlCl_4$ was prepared according to Cotton, *et al.*[5] In all cases the method consisted of adding a proper amount of a solution containing the appropriate chloride salt to a solution of

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[1] T. G. Spiro, *Inorg. Chem.*, **4**, 731 (1965).

[2] J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 645 (1935).

[3] T. Watanabe and M. Atoji, *J. Am. Chem. Soc.*, **72**, 3819 (1950).

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

[6] R. J. Meyer, *Z. anorg. Chem.*, **24**, 321 (1900).

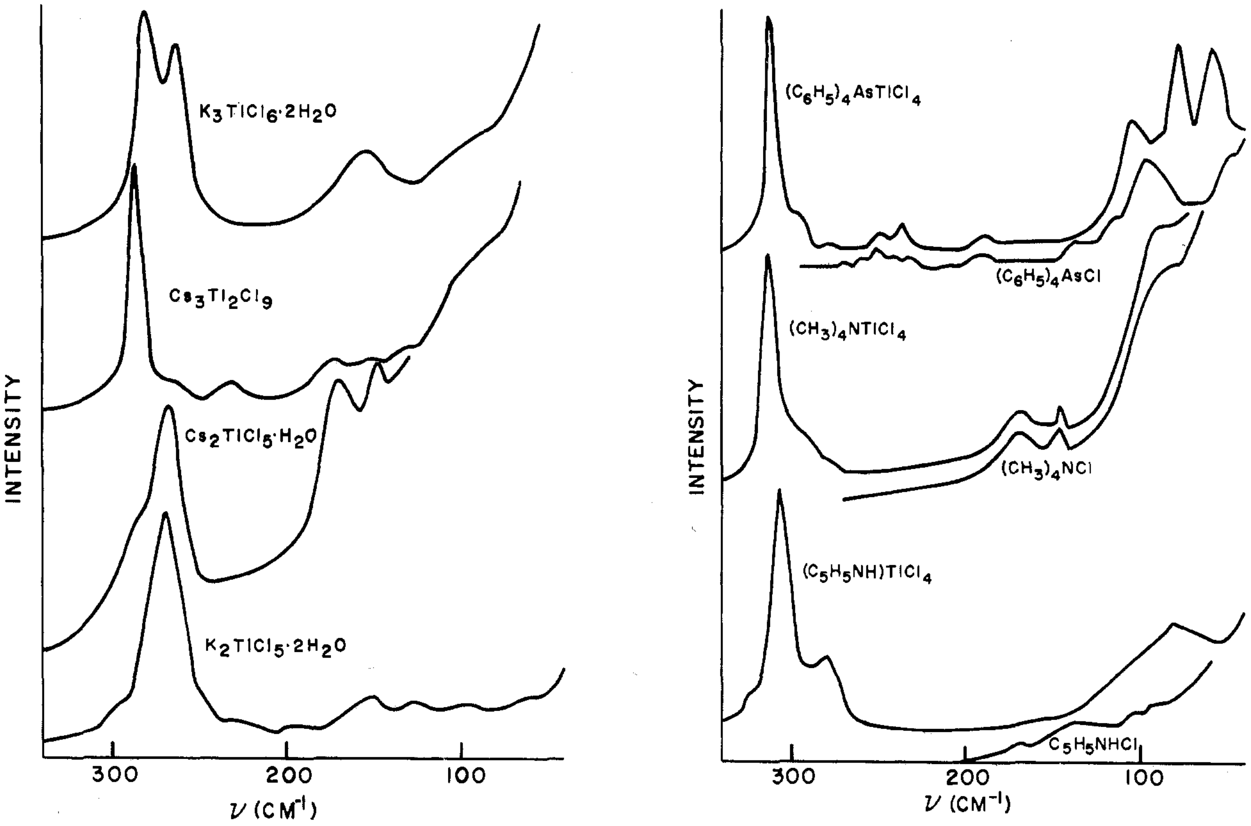

Figure 1.—Raman spectra of crystalline chlorothallate powders. Cary Model 81; lamp current 15 amp., RD3. Amplification and slit width (SS = single slit, DS = double slit) as follows for the individual spectra.

Sample	Amplification	Slit width, cm.$^{-1}$
$K_3TlCl_6 \cdot 2H_2O$ and $Cs_3Tl_2Cl_9$	3 × 1000	8 SS (<220 cm.$^{-1}$) 4 DS (>220 cm.$^{-1}$)
$Cs_2TlCl_5 \cdot H_2O$	2.8 × 1000	5 SS
$K_2TlCl_5 \cdot 2H_2O$	1000	2 SS

Sample	Amplification	Silt width, cm.$^{-1}$
$(C_6H_5)_4AsTlCl_4$	1000	3 SS
$(CH_3)_4NTlCl_4$	1000	3 SS
$(C_5H_5NH)TlCl_4$	1.4 × 1000	3 SS

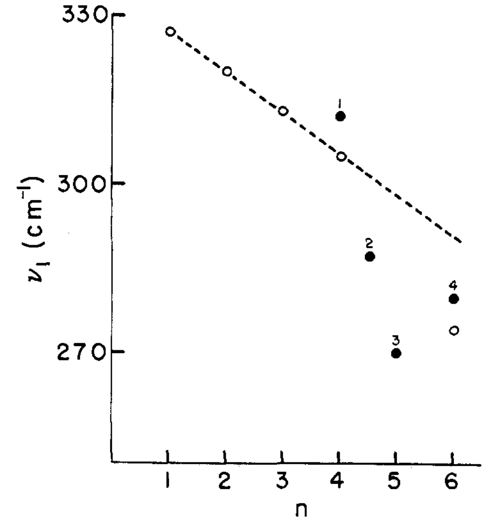

Figure 2.—ν_1 frequency as a function of number of chlorides per thallium(III): O, aqueous complexes; ●, crystalline chlorothallates: 1, $(C_6H_5)_4AsTlCl_4$; 2, $Cs_3Tl_2Cl_9$; 3, $Cs_2TlCl_5 \cdot H_2O$; 4, $K_3TlCl_6 \cdot 2H_2O$.

thallic chloride and recrystallizing the resulting precipitate, when possible. Thallic chloride solution was prepared by bubbling chlorine through a suspension of thallous chloride, under reflux. The solvent was water in all cases except $(C_6H_5)_4AsTlCl_4$, for which acetonitrile was used.

Raman spectra, at 28 ± 1°, were obtained with a Cary Model 81 Raman spectrophotometer, using the 4358 Å. mercury line for excitation. The compounds were ground in a mortar and tapped into a conical sample holder, constructed on the design of Busey and Keller.[7] Excellent spectra were obtained with this sample cell.

Results and Discussion

The spectra are reproduced in Figure 1. For systems involving complex cations, spectra of the cation chlorides are also shown, to aid in distinguishing the features due to the cation from those due to the chlorothallate anions. For convenience in comparison, all chlorothallate spectra are plotted to give about the same intensity for the most intense peak. However, the actual intensity, and particularly the background scattering, varied a good deal from one sample to another. Weak bands were observed for all solid samples at about 100, 145, and 170 cm.$^{-1}$ and are considered to be part of the background. The prominence of these features in a given spectrum depends on the relative intensity of Raman and background scattering and on the proximity of Raman bands. The spectral features attributable to the chlorothallate complexes are summarized in Table I.

$K_3TlCl_6 \cdot 2H_2O$.—According to Hoard and Goldstein[2]

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(7) R. H. Busey and O. L. Keller, *J. Chem. Phys.*, **41**, 215 (1964).

TABLE I

RAMAN FREQUENCIES AND ASSIGNMENTS

Compound	Chlorothallate symmetry	Frequency, cm.$^{-1}$	Description^a	Assignment
$K_3TlCl_6 \cdot 2H_2O$	O_h	280	s, sh	ν_1 (A_{1g})
		262	s, sh	ν_2 (E_g)
		155	s, b	ν_5 (F_{2g})
$Cs_2TlCl_5 \cdot H_2O$	C_{4v}	270	s, sh	ν_1 (A_1)
$K_2TlCl_5 \cdot 2H_2O$	C_{4v} (?)	270	s, sh	ν_1 (A_1)
		300	w, b	
		230	vw, b	
		194	vw, b	
		152	w, b	
		126	w, b	
$Cs_3Tl_2Cl_9$	D_{3h}	287	s, v sh	ν_1 (A_1)
		264	w, b	
		232	w, b	
$(C_6H_5)_4AsTlCl_4$	T_d	312	s, v sh	ν_1 (A_1)
		296	w, b	ν_3 (F_2)
		78	s, sh	ν_2 (E)
		60	s, b	ν_4 (F_2)
$(CH_3)_4NTlCl_4$	T_d (?)	312	s, v sh	ν_1 (A_1)
		294	w, b	ν_3 (F_2)
$(C_5H_5NH)TlCl_4$ (H_2O)	T_d (?)	326	w, sh	
		306	s, sh	ν_1 (A_1)
		279	m, b	ν_3 (F_2)
		80	s, vb	ν_2,ν_4 (E, F_2)

^{a} w, weak; m, medium; s, strong; v, very; sh, sharp; b, broad.

$K_3TlCl_6 \cdot 2H_2O$ contains discrete $TlCl_6^{-3}$ octahedra. These should give rise to three Raman-active vibrations. The Raman spectrum indeed shows three strong bands, at 280, 262, and 155 cm.$^{-1}$. These are assigned to the A_{1g} symmetric stretch, the E_g asymmetric stretch, and the F_{2g} bending modes, respectively.

The $TlCl_6^{-3}$ Raman spectrum is of interest in relation to the anomalous spectra of $PdCl_6^{-2}$, $PtCl_6^{-2}$, and $PtBr_6^{-2}$, studied in solution by Woodward and Creighton.[8] For these octahedral species the ν_1 (A_{1g}) and ν_2 (E_g) bands are much closer together ($\delta = (\nu_1 - \nu_2)/\nu_1 = 0.07$–$0.08$) than for $SnCl_6^{-2}$ and $SnBr_6^{-2}$ ($\delta = 0.25$–0.26). Furthermore, ν_2 is more intense than ν_1 for the former species, whereas it is much less intense for the tin complexes and also for other octahedral complexes which have been measured.[8] Woodward and Creighton suggest that these anomalies may relate to the six nonbonding d electrons of Pt(IV) and Pd(IV). However, the $TlCl_6^{-3}$ spectrum resembles those of the platinum and palladium complexes more than those of the tin species ($\delta = 0.064$ and the ν_2 intensity is only slightly lower than that of ν_1), even though Tl(III) and Sn(IV) have formally similar electronic structures (d^{10}). These subtle effects may be sensitive to the environment of the species, which is very different in the crystals of the present work than in the solutions studied by Woodward and Creighton. On the other hand, in aqueous solution the separation of the ν_1 and ν_2 bands of $TlCl_6^{-3}$ apparently does not increase toward the $SnCl_6^{-2}$ value, but, on the contrary, becomes unobservable, only one broad band appearing in the spectrum (*vide infra*).

$Cs_2TlCl_5 \cdot H_2O$ and $K_2TlCl_5 \cdot 2H_2O$.—Watanabe and Atoji[3] report that $Cs_2TlCl_5 \cdot H_2O$ is isomorphous with $(NH_4)_2FeCl_5 \cdot H_2O$ and $(NH_4)_2InCl_5 \cdot H_2O$, and $TlCl_5^{-2}$ in this material is therefore presumably square pyramidal, the sixth octahedral position being occupied by a water molecule. Meyer[6] prepared $K_2TlCl_5 \cdot 2H_2O$ long ago, but its crystal structure has apparently not been determined. Both solids show a single intense band, at 270 cm.$^{-1}$, and therefore probably contain essentially isostructural anions, for which this band no doubt corresponds to the A_1 symmetric stretching mode. The potassium salt also gives rise to weak Raman emission at 300, 230, 194, 152, and 126 cm.$^{-1}$ (whose observation is made possible by the exceptionally low background scattering of this sample). For square-pyramidal $TlCl_5^{-2}$, four Raman bands in addition to the A_1 band are expected, and splittings may arise from crystal forces. The cesium salt gave high background scattering and a consequently poor quality spectrum. Also it appears to be difficult to prepare free from another component, probably $Cs_3Tl_2Cl_9$, which causes a bulge, varying in prominence from one preparation to another, on the high-frequency side of the A_1 band.

$Cs_3Tl_2Cl_9$.—This material was shown by Hoard and Goldstein[4] to contain $Tl_2Cl_9^{-3}$ units which are equivalent to two $TlCl_6^{-3}$ octahedra fused at a face. Its Raman spectrum contains a single intense band at 287 cm.$^{-1}$, which must correspond to the A_1 vibration of the complex and is at slightly higher frequency than that of $TlCl_6^{-3}$. It is reasonable that the "breathing" vibrations should be similar in both the monomeric and dimeric octahedral species. On the other hand, the remaining features of the $TlCl_6^{-3}$ spectrum are missing in that of $Tl_2Cl_9^{-3}$; one would indeed expect that binding three chlorides to another thallium, as in $Tl_2Cl_9^{-3}$, would destroy the purely octahedral asymmetric stretching and bending modes. Weak Raman emissions from $Cs_3Tl_2Cl_9$ occur at 264 and 232 cm.$^{-1}$.

Compounds Containing $TlCl_4^-$.—Cotton, *et al.*,[5] have shown that $(C_6H_5)_4AsTlCl_4$ is isomorphous with $(C_6H_5)_4AsFeCl_4$ and therefore contains tetrahedral $TlCl_4^-$. Its Raman spectrum indeed shows a very well-defined tetrahedral pattern. The four expected bands, ν_1 (A_1), ν_3 (F_2), ν_2 (E), and ν_4 (F_2), show up clearly at 312, 298, 78, and 60 cm.$^{-1}$, respectively. The remaining features of the spectrum are due to $(C_6H_5)_4As^+$. The tetramethylammonium salt has a very similar spectrum, but the low-frequency bands are masked by intense scattering, apparently due to $(CH_3)_4N^+$.

On the other hand, the spectrum of $(C_5H_5NH)TlCl_4$ is somewhat different. The ν_1 band is shifted slightly to 306 cm.$^{-1}$ and has a small shoulder at 326 cm.$^{-1}$. The ν_3 band is shifted to 279 cm.$^{-1}$, and there is now only one broad band, at 80 cm.$^{-1}$, in the bending region. This material turned out to be very difficult to dry, and the spectrum was actually run on an aqueous slush of the crystals. The spectrum in fact closely resembles that of aqueous $TlCl_4^-$, except that the shoulder at 326 cm.$^{-1}$ is missing in the latter and the ν_3 band cannot be

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(8) L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, **17**, 594 (1961).

observed (although the ν_1 band is somewhat skewed to lower frequencies—see Figure 2 of ref. 1).

Consequences for Solution Structure.—The aqueous solution study[1] established that the first four species formed by successive addition of chloride to Tl^{+3} (aq.) each gave rise to a polarized (ν_1) band, whose frequency shifted smoothly from 327 cm.$^{-1}$ for $TlCl^+$ to 305 cm.$^{-1}$ for $TlCl_4^-$. For $TlCl_4^-$ an additional depolarized band was observed at 81 cm.$^{-1}$. Since only these two bands were observable, the question was left open whether aqueous $TlCl_4^-$ has the expected tetrahedral structure, as in $(C_6H_5)_4AsTlCl_4$, or is perhaps octahedrally coordinated, with two waters bound in addition to the four chlorides. The present work shows that the Raman spectrum of $(C_6H_5)_4AsTlCl_4$ differs significantly from that of aqueous $TlCl_4^-$. However, the following consideration makes the assumption of octahedral coordination for the aqueous species implausible. As noted above, the decrease in ν_1 frequency on adding chloride to Tl^{+3} (aq.) is a smooth (in fact linear) function of chloride number up to $TlCl_4^-$. If this species is octahedrally coordinated, then further replacement of the remaining waters by chloride should continue the smooth trend in ν_1. In fact, there is an abrupt break to lower frequencies when more than four chlorides are bound to thallium in the crystals. The effect is illustrated in Figure 2. If, then, $TlCl_4^-$ underwent a change from tetrahedral to octahedral coordination on going from the crystalline $(C_6H_5)_4As-TlCl_4$ to the aqueous solution, one would expect a much greater lowering of the ν_1 frequency than the observed 7 cm.$^{-1}$. It seems likely, therefore, that aqueous $TlCl_4^-$ is still essentially tetrahedral and that the tetrahedral–octahedral transition occurs only on coordination of further chloride. The alteration in solution of the tetrahedral spectral pattern for $TlCl_4^-$ could be due to hydrogen-bonded interaction of water with the coordinated chlorides. Such an interaction would be expected to have little effect on the symmetric stretching vibration, but a large effect on the bending modes, as indeed is observed.

The solution work also demonstrated the existence at high chloride concentrations of a complex with more than four chlorides per thallium, which has a polarized band at 273 cm.$^{-1}$. Analysis of the Raman intensities in terms of the law of mass action pointed clearly to this species being $TlCl_6^{-3}$. It was hoped that this identification could be tested by comparison of solution and crystal spectra. The 273 cm.$^{-1}$ solution band is coincident with the center of gravity of the ν_1 and ν_2 bands of $K_3TlCl_6 \cdot 2H_2O$. Thus the solution spectrum could well be accounted for on the basis of broadening and merging of these two bands under the influence of water on $TlCl_6^{-3}$. (There is also a broad scattering region in the solution spectrum that overlaps the ν_5 band of $K_3TlCl_6 \cdot 2H_2O$.) On the other hand, the solution band could arise from $TlCl_5^{-2}$, its ν_1 frequency shifted upward slightly from the crystal value, 270 cm.$^{-1}$. Even $Tl_2Cl_9^{-3}$ (ν_1 = 287 cm.$^{-1}$) cannot be ruled out at least as a contributor to the solution spectrum. In this ambiguous situation we are forced back to the mass action analysis of the solution data, which indicate that $TlCl_5^{-2}$ and $Tl_2Cl_9^{-3}$ do not form in significant concentration in solution. In support of this inference there is an argument based on the energetics of successive complex formation, which was suggested in ref. 1 and is strengthened by the present crystal spectra. From the sharp drop in ν_1 frequency (Figure 2) on adding chloride to $TlCl_4^-$, it is clear that the tetrahedral–octahedral transition is energetically unfavorable. It is reasonable to expect that the high chloride activity needed in solution to produce this change would favor the species with the highest chloride to thallium ratio, namely $TlCl_6^{-3}$. Destabilization of complexes of intermediate composition accompanying structural change has been observed in other systems.[9] The fact that the ν_1 frequency of $TlCl_5^{-2}$ is actually *lower* than that of $TlCl_6^{-3}$ implies that the Tl–Cl bonds are definitely weaker in the former species. For $Tl_2Cl_9^{-3}$, although the ν_1 frequency is slightly higher than that of $TlCl_6^{-3}$, it is still much lower than that of $TlCl_4^-$. Stabilization of this species could occur through Tl–Tl interaction, but the crystallographic data[4] provide no evidence for this. It seems most likely that formation of $TlCl_5^{-2}$ and $Tl_2Cl_9^{-3}$ occurs primarily during the precipitation process and is due to the specific crystal forces in their respective salts.

Acknowledgments.—The crystalline chlorothallates were prepared by Mrs. Judith Lee. This work was supported in part by the National Science Foundation, under Grant GP 3404.

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(9) F. J. C. Rossotti, "The Thermodynamics of Metal Ion Complex Formation in Solution," in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp. 38, 39.