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Raman and Infrared Spectra of Crystalline Halothallates

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Raman and far-infrared spectra have been obtained for a number of crystalline hexa- and tetrahalothallates. For the hexachloro and hexabromo salts, all vibrational frequencies expected for the octahedral complexes have been observed and assigned. The spectra of the tetrahalothallates are most consistent with a tetrahedral structure for TlX_4^- ($X = Cl, Br,$ and I) even for some salts of $TlBr_4^-$ ($Cs^+, Rb^+,$ and K^+) for which square-planar coordination has previously been reported.

Introduction

Recently, Raman spectra were reported for a number of crystalline chlorothallates of known structure,¹ with a view toward elucidating the structure of thallium(III) chloride complexes in solution.² In the present work Raman studies are extended to crystalline bromo- and iodothallates. In addition, infrared spectra are reported for the various halothallates.

The main focus of this investigation is on the structural relations among the thallium(III) halide complexes. A fair amount of X-ray and spectroscopic evidence is now available on this subject. X-Ray studies have shown that $TlCl_6^{3-}$ is octahedral in its potassium salt³ and that $TlCl_4^-$ is tetrahedral in its tetraphenylarsonium salt.⁴ Raman spectra¹ are in full accord with these structures and indicate that they are retained in solution as well. In the bromide system, $TlBr_6^{3-}$ is known to be octahedral in its rubidium³ and $Co(NH_3)^{3+5}$ salts, and solution Raman spectra indicate a tetrahedral structure for $TlBr_4^-$.⁶ In crystals, however, the structure of $TlBr_4^-$ would appear to be somewhat variable. It is reported to be tetrahedral in $TlTlBr_4$,⁷ but square-planar in $CsTlBr_4$ and also in $RbTlBr_4 \cdot H_2O$, with a water coordinated above the square plane, and in $KTlBr_4 \cdot H_2O$ and $NH_4TlBr_4 \cdot 2H_2O$, with waters coordinated above and below the plane.^{5,8,9} A full account of the square-planar structures does not appear to have been published, however. Salts of TlI_4^- can be prepared.^{4,10} Very recently alkali metal salts of composition $MTlI_4 \cdot 2H_2O$ ($M = NH_4, K, Rb,$ or Cs) have been reported to be isomorphous with $KTlBr_4 \cdot 2H_2O$ and $NH_4TlBr_4 \cdot 2H_2O$ on the basis of X-ray powder patterns,¹¹ and the iodine nuclear quadrupole resonance was interpreted accordingly. Higher iodo complexes are unknown.

A major conclusion of this study is that the reported square-planar coordination of $TlBr_4^-$ is inconsistent with its vibrational spectrum. All of the tetrahalothallates appear to be normally tetrahedral.

Experimental Section

The preparation of the chloride complexes was described previously.¹ The bromothallates were crystallized from appropriate mixtures of aqueous solutions of thallic bromide and the required bromide salt (cesium, rubidium, or potassium) according to Pratt.¹⁰ The thallic salt was prepared by allowing thallic and thallic bromides to react, as described by Hazell.⁷ Tetra-(*n*-butyl) tetraiodothallate, $(n-C_4H_9)_4NTlI_4$, was prepared by halide exchange in the manner of Cotton, *et al.*⁴ Attempts were made to prepare alkali metal tetraiodothallates, which have been reported,^{10,11} but the residues obtained always appeared to contain free iodine, and they were not used further.

Since the bromo- and iodothallates are all colored (yellow to red), their Raman spectra could not be obtained with the conventional mercury arc exciting radiation. Good-quality spectra on polycrystalline samples were obtained, however, on a Cary Model 81 Raman spectrophotometer equipped with a helium-neon laser source (6328 Å) made available through the courtesy Cary Instruments, Monrovia, Calif. For infrared work the crystals were milled in Nujol and placed on polyethylene windows. Spectra above 190 cm^{-1} were scanned with a Beckman IR-12 infrared spectrophotometer, and those between 40 and 220 cm^{-1} , with an RIIC FS-520 interferometer.¹²

Results

The Raman spectra are traced in Figure 1. Raman and infrared band frequencies are tabulated in Table I for TlX_6^{3-} species and in Table II for TlX_4^- species. The infrared bands are fairly broad, and their maxima are uncertain by $\sim \pm 5\text{ cm}^{-1}$. For the bands below 140 cm^{-1} they are uncertain by as much as 10 cm^{-1} . Assignments are made on the basis of Raman intensities, and by reference to band orderings for analogous compounds.¹³ In some cases splittings attributable to lowered site symmetry are used, as noted below.

Discussion

TlX_6^{3-} Species.—The Raman spectrum of $Rb_3TlBr_6 \cdot 8/7H_2O$ contains the three bands expected for octahedral species, as well as a weak band at 49 cm^{-1} , probably due to a lattice mode. As in the case of $K_2TlCl_6 \cdot H_2O$,¹ the two stretching bands (ν_1 and ν_2) are unusually close together and are of comparable intensity.

For octahedral species two infrared bands are ex-

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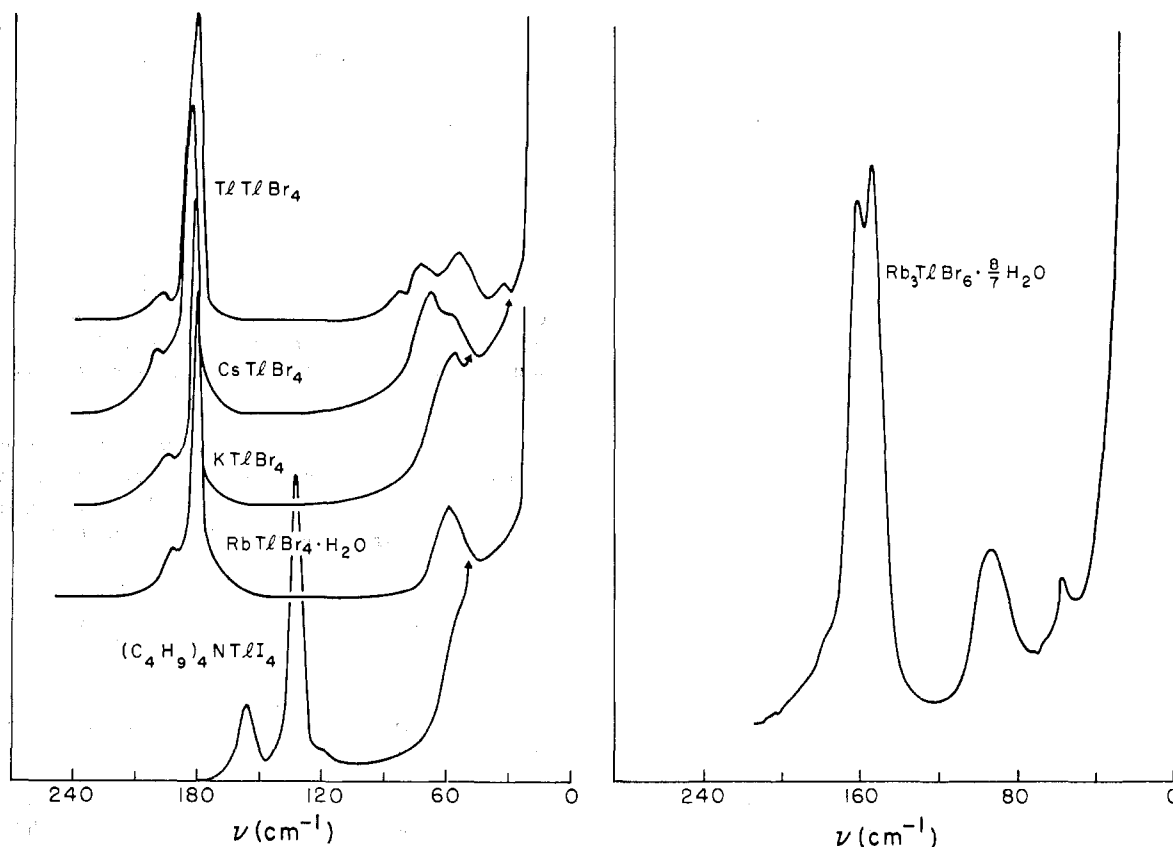


Figure 1.—Raman spectra of halothallate crystalline powders. Cary Model 81 with 50-mw Ne-He laser source; RD5. All samples were run as pellets, except for $(n\text{-C}_4\text{H}_9)_4\text{NTlI}_4$ which was packed in a 0.5-mm i.d. Suprasil capillary tube. Sensitivity and slit width (cm^{-1}), respectively, for the individual spectra are: TlTlBr_4 , 5, 2; CsTlBr_4 , 2.4, 3; KTlBr_4 , 2, 3; $\text{RbTlBr}_4 \cdot \text{H}_2\text{O}$, 9, 2; $(n\text{-C}_4\text{H}_9)_4\text{NTlI}_4$, 10, 2.5; $\text{Rb}_3\text{TlBr}_6 \cdot \frac{8}{7}\text{H}_2\text{O}$, 10, 3.

TABLE I
VIBRATIONAL FREQUENCIES (cm^{-1}) OF HEXAHALOTHALLATES^a

Assignment (O_h)	$\text{K}_3\text{TlCl}_6 \cdot \text{H}_2\text{O}$	$\text{Rb}_3\text{TlBr}_6 \cdot \frac{8}{7}\text{H}_2\text{O}$
ν_1 (A_{1g})	280 R ^b	161 R
ν_2 (E_g)	262 R ^b	153 R
ν_3 (F_{1u})	294 I	195, 190 sh, I
ν_4 (F_{1u})	246, 222 I	156, 134 I
ν_5 (F_{2g})	155 R ^b	95 R
ν_6 (F_{2u})	~136 I	~80 I
Lattice		57 R

^a R, observed in the Raman; I, observed in the infrared; sh, shoulder. ^b From ref 1.

pected, both of F_{1u} symmetry. The greater complexity of the actual spectra of $\text{Rb}_3\text{TlBr}_6 \cdot \frac{8}{7}\text{H}_2\text{O}$ and $\text{K}_3\text{TlCl}_6 \cdot \text{H}_2\text{O}$ (see Table I) may be understood on the basis of the lowered site symmetry, C_i , of the complexes in the crystals.³ The F_{1u} modes should both be split. Actually the highest frequency (ν_3) band appears to be little affected, although a shoulder at 190 cm^{-1} is observed on the 195-cm^{-1} TlBr_6^{3-} band. However, in the region where ν_4 is expected, two bands, separated by about 25 cm^{-1} , appear for both compounds.

Also the inactive F_{2u} mode should split and become infrared active. The lowest frequency absorptions may arise in this way. The F -matrix elements for the F_{2g} (ν_5) and F_{2u} (ν_6) modes of an octahedral XY_6 molecule are identical on the assumption of a Urey-Bradley force field, and nearly so for a generalized valence force

TABLE II
VIBRATIONAL FREQUENCIES (cm^{-1}) OF TETRAHALOTHALLATES^a

Compd	Assignment (T_d)					Lat- tice
	ν_1 (A_1)	ν_2 (E)	ν_3 (F_2)	ν_4 (F_2)		
$(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$ R ^b	312	60	296			78
TlTlBr_4	I	306 sh	296, 278 sh			~88
	R	182	56	198		74, 84, 34
CsTlBr_4	I	186 sh	200			~72
	R	184	58	201		69
$\text{RbTlBr}_4 \cdot \text{H}_2\text{O}$	I	186 sh	205			~74
	R	180	59	193		59
KTlBr_4	I	186 sh	200			~64
	R	182	58	196		58
$(n\text{-C}_4\text{H}_9)_4\text{NTlI}_4$	I		203			~53
	R	133	...	156		...
	I		152			~56

^a R, observed in the Raman; I, observed in the infrared; sh, shoulder. ^b From ref 1.

field.¹⁴ The G -matrix elements, on the other hand, differ by a factor of 2. Thus, it is expected that $\nu_3/\nu_6 \approx \sqrt{2}$. On this basis ν_6 is predicted at 110 cm^{-1} for TlCl_6^{3-} (observed 136 cm^{-1}) and at 68 cm^{-1} for TlBr_6^{3-} (observed 80 cm^{-1}). Actually in a series of hexafluorides for which all fundamental frequencies¹⁵ have been determined, ν_5/ν_6 ranges between 1.1 and 1.6. The observed low-frequency bands could, therefore, reasonably arise from F_{2u} . However, they are very broad and may contain lattice modes as well.

(14) See ref 13, p 264 ff.

(15) See ref 3, p 119.

TIX₄⁻ Species.—The Raman spectrum of TlBr₄⁻ in its thallos salt is entirely consistent with the tetrahedral structure reported by Hazell.⁷ The sharp, strong band at 182⁻¹ is clearly the symmetric stretching mode, ν_1 (A₁), of the complex, and the weaker band at 198 cm⁻¹ must then be the asymmetric stretching mode, ν_3 (F₂). There are two well-resolved bands of moderate intensity at low frequency, 56 and 74 cm⁻¹, which may be assigned to the two expected bending modes, ν_2 (E) and ν_4 (F₂), respectively. Two weak bands also appear on either side of this pair. Most likely, these arise from lattice vibrations, which should have appreciable Raman intensities for this compound, since the lattice cations are the highly polarizable Tl⁺. The triply degenerate modes, ν_3 and ν_4 , should also be active in the infrared, and indeed the infrared spectrum shows two strong bands centered at 200 and 72 cm⁻¹. There is also a shoulder at 186 cm⁻¹ which probably arises from ν_1 , rendered infrared-active by crystal forces.

If TlBr₄⁻ is square-planar in its cesium salt, as previously reported,⁸ it should have a vibrational spectrum markedly different from that found for the thallos salt. Three Raman bands are expected, instead of four, and their frequencies should be substantially different from those observed in the tetrahedral spectrum. Three infrared bands are expected, instead of two, and none of them should be coincident with the Raman bands. In fact, however, the spectra are substantially the same for CsTlBr₄ as TlTlBr₄. The Raman spectrum shows a sharp spike at 184 cm⁻¹ and a weak band at 201 cm⁻¹. In the bending region two bands are still apparent, although they have moved toward one another from the TlTlBr₄ frequencies. The infrared spectrum shows two strong bands, coincident with the Raman bands assignable to ν_3 and ν_4 , and a shoulder at 178 cm⁻¹ which probably arises from ν_1 . The vibrational features are therefore consistent with a tetrahedral structure, and not with a square-planar one.

The same can be said for RbTlBr₄·H₂O and KTI-Br₄.^{16,17} All of the vibrational features of these two compounds are virtually identical with those of the thallos and cesium salts, except in the bending region, where now only one Raman band is observed, at frequencies intermediate between the two bending modes of TlTlBr₄. Probably the most telling evidence against a change to square-planar geometry is that the Raman-active asymmetric stretching band continues to lie at a higher frequency than the symmetric stretching band (whose intensity makes its identification unmistakable). For square-planar XY₄ molecules these two modes, ν_2 (B_{1g}) and ν_1 (A_{1g}), have the same *G*-matrix

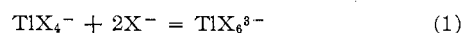
element, and the *F*-matrix element differs only in an interaction constant.¹⁴ To have $\nu_2 > \nu_1$ would require a negative interaction constant between adjacent bonds in the valence force field or a negative nonbonded interaction in the Urey-Bradley field, both of which are physically implausible. The observed order of the stretching modes is reasonable only for a tetrahedral structure. As to the failure to observe two tetrahedral bending modes, the most likely explanation is accidental coincidence. Since the two modes begin to merge as Tl⁺ is replaced by Cs⁺ in the crystals, it is not unreasonable to suppose that they overlap completely on substitution of Rb⁺ or K⁺. It is expected that interactions of the lattice cations with the complex anions will affect the bending modes more than the stretching modes.

The Raman spectrum of tetrahedral TlCl₄⁻ in its tetraphenylarsonium salt has been given previously.¹ Its vibrational features are included in Table II for comparison with the other tetrahalothallates. Part of its infrared spectrum has been reported by Johnson and Walton,¹⁸ who found three bands in the ν_3 region and ascribed them to a total lifting of the degeneracy of the triply degenerate mode in the crystals. In the present study the three components were confirmed, but it seems at least equally plausible to assign the 306-cm⁻¹ shoulder to the ν_1 mode, which appears at 312 cm⁻¹ in the Raman. The remaining weak shoulder at 278 cm⁻¹ may still be due to splitting of the ν_3 mode.

The Raman spectrum of (*n*-C₄H₉)₄NII₄ shows a sharp, strong band at 133 cm⁻¹, clearly the symmetric stretching mode, ν_1 . The weaker band observed at 156 cm⁻¹ must arise from the asymmetric stretching mode, and its position higher than ν_1 indicates that II₄⁻ is tetrahedral, on the basis of the argument given above. This assignment is corroborated by the appearance of the same band in the infrared, at 152 cm⁻¹. The bending region is obscured by the exciting radiation in the Raman, but a strong infrared absorption at about 56 cm⁻¹ may arise from ν_4 of the tetrahedral complex.

In summary, one may reasonably infer from the Raman and infrared evidence that the tetrahalothallate ions, TIX₄⁻, are all tetrahedral in a variety of their salts, including some for which square-planar structures have previously been reported. The X-ray data on the alkali metal salts of TlBr₄⁻ should clearly be reevaluated.

The reaction



therefore appears to involve a tetrahedral to octahedral transition for bromide as well as chloride. The probable involvement of this stereochemical change in the thermodynamics of reaction 1 has been discussed^{1,2} for the thallic chloride system. Here the free energy change for reaction 1 is quite unfavorable,² even though it is highly favorable for the binding of the first

(16) There is some question about the composition of the potassium salt. Meyer¹⁷ reported crystals of composition KTI-Br₄·2H₂O, which however were rather unstable in air, giving off bromine readily. Presumably it was on these crystals that the X-ray work⁸ was performed. On the other hand, Pratt¹⁹ lists the anhydrous salt, KTI-Br₄. In the present work it was found quite difficult to obtain any crystals free of coprecipitated KBr, and the sample used was in fact somewhat contaminated from this source. (The far-infrared spectrum contained a band of moderate intensity at 113 cm⁻¹ due to KBr.) The spectra are reported nevertheless to show that TlBr₄⁻ is apparently identical structurally when precipitated with K⁺ as in crystals with other cations.

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four chlorides^{19,20} to Tl^{3+} . In the bromide system ΔF is even more favorable for the binding of the first four bromides.²⁰ No equilibrium data are available for the addition of bromide to $TlBr_4^-$, but the synthesis of the rubidium salt of $TlBr_6^{3-}$ requires a considerably greater halide excess than is the case for any of a number of alkali metal $TlCl_6^{3-}$ salts.¹⁰ It seems likely therefore that ΔF for reaction 1 is more unfavorable for bromide than for chloride. No compounds of TlI_6^{3-} are known. Apparently even very high iodide concentrations lead only to the formation of TlI_4^- salts.¹⁰ Although $Tl(III)$ is a typical class B metal²¹

(soft acid²²), in that the aquo cation binds bromide more strongly than chloride (iodide binding has not been measured because of its ready oxidation by Tl^{3+}), it appears to act as a class A metal (hard acid) with respect to reaction 1. This behavior is readily understood if all of the aqueous TlX_4^- ions are indeed tetrahedral. Steric repulsion with increasing ligand size increases much more rapidly in octahedral (or square-planar) than in tetrahedral complexes, and this could overcome the opposite trend of $Tl(III)$ affinity for the halides.

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The Dipole Moments of Boron and Carbon Brominated Carboranes

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In agreement with theoretical considerations and earlier experimental evidence, dipole moment measurements of selectively substituted *o*- and *m*-carborane derivatives established that in the polar icosahedra of *o*- $B_{10}H_{10}C_2H_2$ and *m*- $B_{10}H_{10}C_2H_2$ the carbon atoms and the borons adjacent to them constitute the positive pole.

Introduction

During recent years, the icosahedral carboranes [dicarbaclododecaboranes(12)] were discovered²⁻⁵ and their chemistry has developed.⁶ Structural elucidation of the three forms of this organoborane nucleus, which were identified as *ortho*, *meta*, and *para* isomers⁷ with regard to the position of the nuclear carbon atoms, was established particularly by ¹¹B nmr spectroscopy.⁸⁻¹¹ Subsequently, conclusive proof of the *ortho* configuration was obtained *via* X-ray diffraction studies.^{12,13}

The dipole moments of all three isomers in benzene solution have recently been reported.¹⁴ The polarity decreases from the *ortho* through the *meta* form and becomes zero in the *para* configuration, as could be expected due to the change of distribution of the two carbon atoms in the framework. The direction of the dipole moment, however, remained undefined. From purely atomic considerations, such as electronegativity, the direction of the dipole moment in the cage would be expected to be in the direction of the carbon atoms. However, in these electron-deficient cage structures the carbon and boron atoms are hexacoordinated and their calculated charge distributions^{15,16} indicate the direction to be exactly opposite.

This was substantiated by recent X-ray diffraction studies¹⁷ on B-brominated *o*-carborane derivatives¹⁸ which indicated that electrophilic substitution of *o*-carborane occurs first at the 9,12 boron atoms opposite the carbon atoms, thus demonstrating that these borons are the sites of highest electron density.

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