bands at ~160 and 164 cm$^{-1}$, respectively. The latter would normally be obscured by the intense polarized bands at ~165 cm$^{-1}$. It is concluded that these *weak* bands are due to trace amounts of $TlCl_2I_2^-$ and $TlBr_2I_2^-$, respectively (see Table III). Since electronic absorption spectral measurements and X-ray powder photographs[1] give no evidence for significant contamination by these impurities, we conclude that the high intensity of the twin bands in the 170–145-cm$^{-1}$ region, both in the solid state and solution, rules out the possibility that either of them arises from impurities. The only remaining conclusion is that they result from combination or overtone vibrations, a possibility mentioned earlier. For the $TlCl_3I^-$ anion, a band at ~77 cm$^{-1}$ in the infrared spectrum[2] gives some support to this postulate since the first overtone of this band could account for the band doubling.

At this point it may be noted that Deacon, *et al.*,[3] have recently found that in the infrared spectra of $[(C_2H_5)_4N]_2ZnX_3Y$, where X = I when Y = Br and X = Br when Y = I, two $\nu$(Zn–Y) modes are observed although symmetry requires only one. No satisfactory explanation is yet available for this band doubling.

**Complex Anions $TlX_2Y_2^-$.**—A further increase in the complexity of the spectra of pseudo-tetrahedral $TlX_{4-n}Y_n^-$ should result as the symmetry is lowered from $C_{3v}$ to $C_{2v}$. In particular, four thallium–halogen stretching modes (symmetry $2A_1 + B_1 + B_2$) are predicted in both the infrared and Raman spectra. From the spectral data available for the $TlCl_2Br_2^-$, $TlCl_2I_2^-$, and $TlBr_2I_2^-$ anions (Tables I and III), this prediction is usually realized, although a clear resolution of the two $\nu$(Tl–X) and $\nu$(Tl–Y) modes is not always observed in the infrared spectra.

The Raman spectrum of $TlCl_2I_2^-$ (Table I) reveals bands at 152 and 133 cm$^{-1}$ which could be attributed to $TlI_4^-$ impurity, although the latter was not detected in the electronic absorption spectrum[1] of this sample. Polarization measurements revealed a broad depolarized band centered at ~157 cm$^{-1}$. This band envelope probably contains $\nu_d$(Tl–I) of $TlCl_2I_2^-$ (165 cm$^{-1}$) and $\nu_3$ of $TlI_4^-$ (154 cm$^{-1}$).

From the Raman spectrum of crystalline $(C_2H_5)_4NTlBr_2I_2$ it is uncertain whether the $A_1$ mode $\nu$(Tl–I) is at 146 or 138 cm$^{-1}$. This band doubling is similar to that described previously for $TlCl_3I^-$ and $TlBr_3I^-$.

No attempt has been made to assign in detail the five deformation modes of a $TlX_2Y_2^-$ molecule of $C_{2v}$ symmetry.

**Concluding Remarks.**—From the preceding section it has been shown that the products of stoichiometry $(C_2H_5)_4NTlX_{4-n}Y_n$, where $n$ = 1, 2, or 3, are pure phases and not mixtures of the appropriate $TlX_4^-$ and $TlY_4^-$ anions. Occasionally there is evidence, particularly from the Raman measurements, that the products contain trace amounts of other tetrahalothallate impurities. This incidentally reflects the difficulty of purifying the complexes by recrystallization, since all these salts have very similar solubility properties.

In agreement with the work of Deacon, *et al.*,[3] on the related mixed tetrahalozincate(II) anions, we conclude that the far-infrared spectra of such species, in contrast to their Raman spectra, are relatively unhelpful in unambiguously establishing their detailed stereochemistry, although such measurements can be used to confirm that the products are not mixtures of the component tetrahalometalates.

The origin of the "band doubling" observed for several of the tetrahalothallates remains obscure and it will be interesting if such effects can be detected in related systems.

Finally, while it is clear that $TlX_{4-n}Y_n^-$ can be stabilized in the solid state this need not be the case in solution. Thus it might have been anticipated that when $TlX_3Y^-$, for example, was dissolved in acetonitrile, equilibrium amounts of the species $TlX_2Y_2^-$, $TlX_4^-$, etc., would be formed. However, the very *close* similarity of the solid and solution Raman spectra gives no definite evidence for such equilibria in the systems investigated, so, if equilibria are established, they must favor the parent $TlX_{4-n}Y_n^-$ species which is dissolved. Also, the similarity of the solid and solution Raman spectra would seem to rule out the formation of significant amounts of polynuclear halide-bridged species such as $Tl_2X_{9-n}Y_n^{3-}$. However, these conclusions from the solution measurements cannot be regarded as entirely unambiguous.

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## The Lattice Parameters of a Series of Mixed Hexabromides

By B. W. Delf and M. A. Joynson

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The group of salts of the type $A_2SbX_6$ ($A^+ = NH_4^+$, $Rb^+$, or $Cs^+$; $X^- = Cl^-$ or $Br^-$) have been investigated by several workers[1,2] primarily in an attempt to see if the antimony is present in a tetravalent state or as a mixture of trivalent and pentavalent states and to explain the cause of the characteristic black color of these hexahalides in terms of the oxidation state(s). In general, these salts crystallize in a tetragonal, pseudo-cubic unit cell, and from the value of the axial ratio, $c/a$, a quantitative estimate of the deviation from cubic symmetry has been obtained.

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(1) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **232**, 193 (1937).

(2) A. Tovborg-Jensen and S. E. Rasmussen, *Acta Chem. Scand.*, **9**, 708 (1955).

(In an ideally cubic lattice $c/a = \sqrt{2} = 1.414$.) The structure of $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ has been reported to be a distorted $K_2PtCl_6$ structure.[3] The unit cell possesses tetragonal symmetry and may be described as two $K_2PtCl_6$-type cells stacked one above each other. The X-ray powder photographs of the $Sb^{III}Sb^{V}$ hexachloride and related compounds have been indexed in terms of a pure $K_2PtCl_6$ lattice with space group Fm3m—superlattice effects being observed for the $Bi^{III}Sb^{V}$ and $In^{III}Sb^{V}$ compounds.[4] A corresponding series of mixed valence hexabromides of the type $A_4M^{III}Sb^{V}Br_{12}$ ($A^+ = Rb^+$ or $Cs^+$; $M^{3+} = Sb^{3+}, Tl^{3+}, Bi^{3+}$, or $In^{3+}$) has been prepared,[5] and since these complexes displayed the intense black color characteristic of the hexahaloantimonates, it was decided to investigate their lattice parameters to see if they possessed crystal properties similar to those of compounds studied previously.

## Experimental Section

**General Preparation of Specimens.**—The specimens were prepared by the method described by Allen and Wood.[5] In order to produce uniform diffraction lines, it was necessary to grind each sample to a fine powder. The salts, however, were slightly unstable—the rate of decomposition increasing with decreasing particle size—and although the grinding operation was carried out in an atmosphere of nitrogen, a small amount of decomposition still occurred.

**X-Ray Investigation.**—The diffraction patterns of the various salts were recorded using a 5.73-cm radius de Wolff type of Guinier camera with Cu Kα radiation and a curved (quartz) crystal monochromator. For compounds which show slight deviation from cubic symmetry, certain of the lines of the diffraction patterns are split into two or more components. The high resolving power of the Guinier camera enabled very small amounts of cubic distortion to be detected while its somewhat limited range ($\theta = 0$–$45°$) was no restriction as no lines were observed outside this range with a Debye–Scherrer camera. The Guinier camera employed a septum technique and this allowed a simultaneous exposure of four specimens. The line positions were measured to an accuracy of ±0.01 mm with a linear comparator and any effects due to systematic errors were eliminated by the use of internal standard.

## Calculations

**Lattice Parameters.**—The lattice parameters were calculated using the analytical least-squares treatment of Cohen.[6] As the effect of the systematic errors had already been eliminated, the least-squares treatment merely served to minimize random errors. For a tetragonal system where there is no systematic error the normal equations take the form

$$A_0\sum\alpha_i^2 + C_0\Sigma\alpha_i\beta_i = \Sigma\alpha_i \sin^2\theta_i$$

$$A_0\sum\alpha_i\beta_i + C_0\Sigma\beta_i^2 = \Sigma\beta_i \sin^2\theta_i$$

using Cohen's nomenclature.

**Errors.**—The accuracies of the final lattice parameters were determined using the standard statistical methods of Jette and Foote.[7] The standard deviations were multiplied by a factor corresponding to a probability of 19 in 20 that the true values of the lattice parameters lay within the limits thus set. All of the computation was carried out on a Stantec Zebra computer and a value of 1.54176 Å was used for the wavelength of the Cu Kα radiation.

TABLE I

LATTICE PARAMETER DATA AT 21°

| Compound | c, Å | a, Å | c/a |
|---|---|---|---|
| $Rb_2SbBr_6$ | 10.830 | 7.565 | 1.432 ± 0.002 |
| $Rb_4TlSbBr_{12}$ | 10.679 | 7.560 | 1.413 ± 0.002 |
| $Rb_4BiSbBr_{12}$ | 10.883 | 7.588 | 1.434 ± 0.002 |
| $Rb_4InSbBr_{12}$ | 10.690 | 7.557 | 1.415 ± 0.002 |
| $Cs_2SbBr_6$ | 10.982 | 7.668 | 1.432 ± 0.002 |
| $Cs_4TlSbBr_{12}$ | 10.890 | 7.683 | 1.417 ± 0.002 |
| $Cs_4BiSbBr_{12}$ | 11.030 | 7.700 | 1.432 ± 0.002 |
| $Cs_4InSbBr_{12}$ | 10.850 | 7.672 | 1.414 ± 0.002 |

## Results and Discussion

The lattice parameters for the eight hexabromides investigated are listed in Table I. The axial ratios of $Rb_2SbBr_6$ and $Cs_2SbBr_6$ have been reported previously,[2] and good agreement with these values was obtained. Four of the complexes have $c/a$ ratios which are not significantly different from that for a perfectly cubic crystal while the remainder are tetragonal—each showing about 1.3% deviation from cubic symmetry. It is, of course, impossible to distinguish between a cubic crystal and a tetragonal one with an axial ratio which is equal to, or very nearly equal to, $\sqrt{2}$ from powder diffraction data alone. However, for the $Cs_4TlSbBr_{12}$ complex, slight broadening of certain lines in the diffraction pattern indicated that there might be a very small amount of cubic distortion present—as suggested by its $c/a$ value.

**Acknowledgments.**—The authors wish to express their appreciation to Dr. G. C. Allen for providing the compounds.

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# Vibrational Spectrum and Structure of Solid Diphosphine

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It has been tentatively concluded from a study of its infrared spectrum that gaseous diphosphine ($P_2H_4$) has a *gauche* structure.[1] Independently, the Raman spectrum of liquid diphosphine has also been interpreted on the basis of a *gauche* structure,[2] although subsequent work[3] has shown that the Raman spectrum could be

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