(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.

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Vibrational Spectrum and Structure of Solid Diphosphine

BY STEPHEN G. FRANKISS

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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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satisfactorily assigned to a *trans* structure. Comparison between the infrared and Raman data is difficult since they were determined from diphosphine in different physical states, and so it seemed worthwhile obtaining its infrared and Raman spectra in at least one state in order to obtain more evidence about its structure. Since preliminary X-ray measurements on polycrystalline diphosphine have been reported[1] and since the recent use of lasers as sources in Raman spectroscopy has facilitated the recording of Raman spectra of unstable compounds as solids at low temperatures,[4] the examination of the vibrational spectrum of solid diphosphine seemed timely. From this work it is tentatively concluded that diphosphine has a *trans* structure in the solid state.

Experimental Section

Diphosphine was prepared by Nixon's procedure.[1] Since it is light sensitive, decomposes fairly rapidly above −30°, and decomposes slowly when distilled *in vacuo*, its purity was not determined. Its infrared spectrum was measured from 33 to 4000 cm^{-1} with Beckman IR-9 and IR-11 grating spectrophotometers, the solid sample being held at about 100°K in a conventional low-temperature cell. Its Raman spectrum was obtained with a Cary Model 81 spectrophotometer using 6328-Å excitation from a Spectra-Physics 125 He–Ne laser. The sample was studied as a solid at about 140°K in a specially designed, evacuated, low-temperature cell which is described elsewhere.[4] The solid samples were, in general, not annealed because of the thermal instability of diphosphine. The sharp spectral bands observed and the appearance of the compound, however, strongly indicated that the samples studied were polycrystalline.

Results and Discussion

The Raman and infrared spectra of crystalline diphosphine are given in Table I. Frequencies of typical bands should be accurate to ±1 cm^{-1} in the infrared spectrum and to ±2 cm^{-1} in the Raman spectrum. The reported infrared spectrum agrees well with Nixon's results,[1] the only discrepancies being that we did not observe his 975-cm^{-1} band (which may be due to phosphine), and several weak bands were observed that he did not report.

The proton resonance spectrum of liquid diphosphine has shown that it has a H_2PPH_2 type of structure.[5] Thus the similarity between the Raman spectrum of the liquid[3] and that of the solid shows that the solid also has an H_2PPH_2 structure, which may have a *cis, trans,* or *gauche* conformation depending on whether the azimuthal angle of rotation of one PH_2 group relative to the other is 0, 180°, or some intermediate angle, respectively. The spectroscopic activity of these three models has been summarized in earlier papers.[6,7] For isolated diphosphine having a *gauche* structure all 12 fundamentals are expected to be both infrared and Raman active, while for the *cis* structure only 9 fundamentals are active in both spectra; however, for the *trans* structure, which is centrosymmetric, the rule of mutual exclusion should apply.

Table I

Raman and Infrared Spectra of Solid Diphosphine

Raman		Infrared		
cm^{-1}	I^a	cm^{-1}	I^a	Assignment
62	w			lattice bands
80	s			
		169	w	ν_7, impurity?
437	vs			ν_4
		615	vw	?
		628	s	ν_{12}
		644	s	
		781	w	ν_6
878	vw			ν_9
1043	w			ν_2
1056	w			
		1052	m, sh	ν_{11}
		1054	s	
		1066	w	628 + 437 = 1065
		1078	w	644 + 437 = 1081
		1214	vw	781 + 437 = 1218
		1518	vw	644 + 878 = 1522
		2093	vw	1052 + 1043 = 2095
		2201	vw	2283 − 80 = 2203
2271	m			ν_1, ν_3
2292	m			
		2283	s	ν_5, ν_{10}
		2299	s	
		2307	m	?
		2365		2283 + 80 = 2363
		2454	vw	2292 + 169 = 2461
		3314	vw	2271 + 1052 = 3323
		3331	vw	2292 + 1052 = 3344

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder.

Nixon has tentatively concluded from X-ray diffraction measurements[1] that polycrystalline diphosphine has space group C_2^1 or C_s^1, with two molecules per unit cell having site symmetry C_1. If this result is accepted, then all 12 molecular fundamentals are expected to have 2 components in the crystal, and the resultant 24 modes are both infrared and Raman active. Examination of the observed spectrum in Table I shows a marked lack of coincidences between infrared and Raman bands. No weak infrared bands coincident with the Raman bands were observed, even though thick samples were studied. Only the Raman 1056-cm^{-1} band and the infrared 1054-cm^{-1} band are coincidental to within experimental error. These two bands do not necessarily come from the same transition, however, since the two PH_2 scissors are expected to be near 1050 cm^{-1}. This apparent mutual exclusion appears inconsistent with Nixon's reported low site symmetry. It suggests that P_2H_4 has a *trans* structure in the solid state.

If the vibrational spectrum of the solid is assigned on the basis of C_{2h} molecular symmetry, then the infrared doublets near 630 and 1050 cm^{-1} and the Raman doublet near 1050 cm^{-1} must be attributed to factor group (fg) splitting of molecular fundamentals. The observed splittings (3–16 cm^{-1}) are somewhat larger than typical fg splittings in organic compounds, which are usually less than 10 cm^{-1}. However, the recently reported fg splittings of over 30 cm^{-1} in methylammonium halides[8] suggest that the postulated fg split-

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TABLE II

FUNDAMENTAL VIBRATIONS OF DIPHOSPHINE

	Solid			Vapor[d]		
Schematic description	C_{2h} species	No.	Cm^{-1}	C_2 species	No.	Cm^{-1}
PH str	a_g	1	2281[a]	a	2	2312
PH_2 scissors		2	1049		3	*e*
PH_2 wag		3	(653)[b]		5	743
PP str		4	437		6	*e*
PH str	a_u	5	2296[a]		1	2312
PH_2 twist		6	781		4	792
PH_2 rock (torsion)		7	(169)[c]		7	*e*
PH str	b_g	8	2281[a]	b	9	2312
PH_2 twist		9	878		11	827
PH str	b_u	10	2296[a]		8	2312
PH_2 scissors		11	1053[a]		10	1081
PH_2 wag		12	636[a]		12	633

[a] Mean of doublet. [b] From liquid diphosphine.[2,3] [c] Possible impurity band. [d] Wave numbers from ref 1. [e] Not reported.

tings in diphosphine are not unreasonable. Further evidence suggesting that the Raman doublet 1056 and 1043 cm^{-1} can be attributed to fg splitting is that only one band (1070 cm^{-1}) was reported in this region in the Raman spectrum of the liquid.[2] We tentatively attribute the doublets near 2200 cm^{-1} to fg splitting, although they may well arise from separate molecular fundamentals.

The 878-cm^{-1} Raman band in the solid shifts to 856 cm^{-1} in the liquid,[2] and it appears to correlate with the 827-cm^{-1} infrared band in the gas. It therefore appears that the three bands originate from a similar fundamental, which provides strong evidence that the effective symmetry of P_2H_4 in the gas is lower than C_{2h}. The large gas–solid shift of this band, with the solid at higher frequency, supports the possibility of a *gauche–trans* change of structure on condensation.

A vibrational assignment of the solid on the basis of C_{2h} symmetry is given in Table I, and fundamentals of the solid and vapor are *tentatively* summarized in Table II. The deformation fundamentals are assigned by analogy with the well-established fundamentals of N_2H_4,[9] so that their frequencies decrease along the series: PH_2 scissors > PH_2 twist > PH_2 wag. This results in different assignments of ν_3, ν_6, and ν_{12} in the solid from those proposed by Nixon,[1] which do not appear compatible with the *trans* structure in the solid. The assignment of 169 cm^{-1} to the torsion ν_7 is somewhat uncertain since Baudler and Schmidt have reported the presence of an impurity band near here in the Raman spectrum of the liquid.[2,3]

In conclusion, it is interesting to note that *trans* structures have been proposed for $P_2H_4(s)$, P_2I_4,[7,10] P_2Cl_4,[6] and P_2F_4,[11] in contrast to the *gauche* structures reported for $P_2H_4(g)$[1] and N_2H_4,[12,13] while N_2F_4 has been reported to consist of both *trans* and *gauche* isomers.[14]

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On the Preparation of Perchloryl Fluoride by Acid Solvolysis of Perchlorates in Fluorinated Solvents

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Perchloryl fluoride, ClO_3F, has been prepared by the action of elemental fluorine on potassium perchlorate,[1] by the electrolysis of sodium perchlorate in anhydrous hydrofluoric acid,[2] and by reactions of various metal perchlorates with fluorinated Lewis acid–solvent systems (HSO_3F,[3] SbF_5,[4] or mixtures thereof[4]). Although the Lewis acid–perchlorate processes for ClO_3F synthesis are claimed in the patent literature,[3,4] details of the technique are insufficient to test the validity of the mechanism advanced by Woolf to explain the reaction of perchlorates with fluorosulfonic acid. The present study, in which the ClO_3F yields and reaction temperatures were shown to correlate with Lewis acid strength of the medium, suggests an underlying mechanism involving solvolysis similar to that proposed by Woolf.

Experimental Section

Solutions of $KClO_4$ in anhydrous HF were prepared in tubes made of polychlorotrifluoroethylene closed with Swagelok-fitted Teflon valves for connection to a Monel Metal vacuum line. Weighed quantities of the anhydrous perchlorate salt were transferred into the tube in a plastic dry bag under an atmosphere of dry nitrogen. Anhydrous HF was distilled into the tube and the resulting solution then treated with an excess of AsF_5, SbF_5, or BF_3 condensed into the tube at −196°. The reaction mixture was warmed slowly to 20° and samples of vapor were withdrawn successively into a gas infrared cell (Monel Metal with AgCl windows) connected into a section of the vacuum manifold of known volume. No attempts were made in this study to isolate the ClO_3F produced; instead, yields were based on measurements of the vapors above the reaction mixture. The spectra of the vapors from the reaction mixtures containing AsF_5 and SbF_5 showed only ClO_3F and HF. These vapors could easily be separated, if desired, by passage

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