Solid-state Effects and the Vibrational Spectra of Hexahalogeno-stannates(IV) and -tellurates(IV)

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The vibrational spectra of the mixed phases $A_2[(Sn,Te)X_6]$ (A = NH_4, K, Rb, or Cs; X = Cl or Br) are compared with those of the parent hexahalogeno-stannates(IV) and -tellurates(IV). The low intensity of the T_{1u} bending mode (ν_4) in the spectra of the Te-containing compounds is explained in terms of solid-state effects arising from direct population of delocalised valence-shell bands by the Te^{IV} non-bonding electrons.

THERE have been several previous studies [1-9] of the vibrational spectra of compounds $A_2[M^{IV}X_6]$ (M^{IV} = Sn, Se, or Te; X = Cl, Br, or I). Where the compound has the cubic $K_2[PtCl_6]$ structure, with the A, M, and X atoms on the T_d, O_h, and C_{4v} sites, respectively, of the space group O_h^5 ($Fm3m$) the observed i.r. spectra display the three modes of T_{1u} symmetry predicted by factor-group analysis. The Raman spectrum should contain ($1A_{1g} + 1E_g + 2T_{2g}$) modes, of which one (T_{2g}) is external and two are inactive ($T_{1g} + T_{2u}$). Of the 25 compounds studied in this work, four have been previously reported as having structures which are lower-symmetry variants of the $K_2[PtCl_6]$ arrangement, *i.e.* $K_2[SnBr_6]$,[10,11] $K_2[TeCl_6]$,[12] $K_2[TeBr_6]$,[13,14] and $K_2[TeI_6]$.[14] In addition, the compounds $Rb_2[SeCl_6]$ and $Co_2[SeCl_6]$, previously reported [12] as being isostructural with $K_2[PtCl_6]$, are shown in this work to have a less symmetrical structure. All six of these compounds display additional bands in their vibrational spectra.

We have also studied the mixed phases $A_2[(Sn,Te)X_6]$ (A = NH_4, K, Rb, or Cs; X = Cl or Br) and this work, together with ^{119}Sn Mössbauer and u.v.-reflectance studies, has led to a mechanism for the reduction in intensity of the T_{1u} bending mode (ν_4) which is somewhat different to that recently suggested by Adams and Payne.[9]

RESULTS AND DISCUSSION

(a) *Deviations from the Selection Rules for the* $K_2[PtCl_6]$ *Structure.*—Tables 1 and 2 give the observed vibrational spectra of the compounds $A_2[MX_6]$ and the mixed phases $A_2[(Sn,Te)X_6]$ respectively. The ^{119}Sn Mössbauer data for the mixed phases are in Table 3, together with parameters for related compounds. These data show that

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the Sn environments in the mixed phases are similar to those in the hexahalogenostannates(IV). The spectra listed in Table 1 show few differences, either in observation or assignment, with corresponding results obtained by previous workers. The most striking difference is the observation of several additional bands in the spectra of the hexabromostannates, though on structural grounds only $K_2[SnBr_6]$ should display these. The latter has been shown to be tetragonal;[10,11] the suggested space group is D_4^2 ($P42_1$) with $Z = 2$. In this structure the Sn atoms are on sites of C_4 symmetry. The K atoms occupy two sets of positions of D_2 symmetry, and the Br atoms are on four C_4 sites plus eight general positions. The selection rules for this structure are $\Gamma = 6A_1 + 5B_1 + 3B_2(\text{Raman}) + 16E(\text{i.r., Raman}) + 8A_2(\text{i.r.})$, but the observed spectrum is much less complicated than that predicted on this basis. In fact the only noticeable differences between the spectrum of $K_2[SnBr_6]$ and those of other, cubic, hexabromostannates involves the splitting of the T_{1u} and T_{2g} bending modes in the spectrum of the

TABLE 1

Vibrational spectra (cm^{-1}) of compounds $A_2[MX_6]$ [a]

Mode	ν_1	ν_2	ν_3	ν_4	ν_5	ν_L		Others	
Symmetry class and activity	A_{1g}(Raman)	E_g(Raman)	T_{1u}(I.r.)	T_{1u}(I.r.)	T_{2g}(Raman)	T_{1u}(I.r.)	T_{2g}(Raman)	I.r.	Raman
$[NH_4]_2[SnCl_6]$	321	240	320	180	176	127			
$K_2[SnCl_6]$	324	246	325	175	172	84			
$Rb_2[SnCl_6]$	320	242	322	173	170	71			
$Cs_2[SnCl_6]$	312	234	314	173	171	69			
$[NH_4]_2[SnBr_6]$	190	142	222	124	120	103	94	290	286, 196
$K_2[SnBr_6]$	192	146	223	137, 123	110, 86	79	64	288	288, 198, 170
$Rb_2[SnBr_6]$	190	142	224	119	107	60	62	290	287, 197, 166
$Cs_2[SnBr_6]$	184	136	221	118	108	60	62	285	282, 192, 160
$Cs_2[SnI_6]$			168	85		48			
$[NH_4]_2[TeCl_6]$	300	248	252	150	140	111			
$K_2[TeCl_6]$	296	250	280, 244, 216	158, 148, 142	142	88, 70			
$Rb_2[TeCl_6]$	297	250	252	*b*	140	64			
$Cs_2[TeCl_6]$	288	246	252	*b*	141	66			
$[NH_4]_2[TeBr_6]$	178	154	199	118	81	84			
$K_2[TeBr_6]$	176	162	198	104	100, 88 (78)	77	(78)		
$Rb_2[TeBr_6]$	178	153	202	*b*	88	56			
$Cs_2[TeBr_6]$	174	150	200	*b*	90	57			
$[NH_4]_2[TeI_6]$			164	*c*		65			
$K_2[TeI_6]$			162	95		64			
$Rb_2[TeI_6]$			167	*b*		50			
$Cs_2[TeI_6]$			166	*b*		46			
$Rb_2[SeCl_6]$			294 (300) [d] 275 (272)	176, 157, 125		75			
$Cs_2[SeCl_6]$			296 (297), 265 (267)	204, 152		73			
$Rb_2[SeBr_6]$			233	140		65			
$Cs_2[SeBr_6]$			226	102		64			

[a] The assignment of the frequencies between ν_4 and ν_L is to some extent arbitrary. [b] Too weak to be observed (see text). [c] Greenwood and Straughan [1] observed bands at 82 and 92 cm^{-1} but we did not find either of these. [d] Values in parentheses obtained on a Perkin-Elmer 457 spectrometer as Nujol mulls between CsI plates.

TABLE 2

Vibrational spectra (cm^{-1}) of $A_2[(Sn,Te)X_6]$

Mode	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(T_{1u})$	$\nu_4(T_{1u})$	$\nu_5(T_{2g})$	Lattice (T_{1u})
X = Cl,						
A = NH_4	319	260	318	180	174	128
	298	245	268, 248		138	
K	325	248	326	176	174	84
	300	240	274, 248		140	
Rb	321	256	320	176	171	89
	300	240	264, 250		141	
Cs	309	248	312	172	170	67
	289	240	264, 246		140	
X = Br,						
A = NH_4	190	160	202vbd	130	85	84
	182					
K	190	160	220	120,		
	180		198	95	105, 90, 80	77
Rb	190	160	210	116	106	58
	180		198		90	
Cs	188	157	215	116	109	
	178		194		95	58

For each mode the first and second lines are assigned as due to the SnX_6 and TeX_6 co-ordination polyhedra respectively.

TABLE 3

Mössbauer parameters ($mm\ s^{-1}$) for $A_2[(Sn,Te)X_6]$

	$\delta \pm 0.03\ mm\ s^{-1}$		
	a	*b*	$\Gamma \pm 0.03\ mm\ s^{-1}$
X = Cl, A = NH_4	0.48	0.48	0.85
K	0.46	0.45	1.08
Rb	0.46	0.43	0.82
Cs	0.51	0.45	0.80
X = Br, A = NH_4	0.84	0.80	0.82
K	0.84	0.75	0.84
Rb	0.82		0.78
Cs	0.84		0.75

[a] Relative to $BaSnO_3$. [b] For corresponding hexahalogenostannates(IV).

potassium salt. Apart from these all the hexabromostannate spectra contain four extra bands in the Raman (except for the ammonium salt which has three) and one in the i.r. spectrum. The lowest-frequency Raman-active mode in these spectra has a mass dependence which suggests that it is an external mode. If so, it belongs to T_{2g} and such a mode, in combination with the T_{1u} stretch, could account for the extra band near 290 cm^{-1} in these spectra, since $T_{1u} \times T_{2g} = A_{2u} + E_u + T_{1u} + T_{2u}$, of which the T_{1u} component is active under O_h symmetry. The remaining Raman bands may also be accounted for as binary combinations; the bands at *ca.* 280, 190, and 170 cm^{-1} are fitted by $2\nu_2$ ($E_g \times E_g \rightarrow A_{1g} + E_g$), $\nu_2 + \nu_L$ ($E_g \times T_{2g} \rightarrow T_{2g}$), and $\nu_5 + \nu_L$ ($T_{2g} \times T_{2g} \rightarrow E_g + T_{2g}$) respectively. Only the Raman-active components are given; the others are inactive. All other departures from the selection rules for the $K_2[PtCl_6]$ structures can be accounted for in terms of the known structures, except for those shown by $Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$. We were able to obtain only the i.r. spectra of these compounds and these show splitting of both ν_3 and ν_4. This, together with our *X*-ray powder data (listed in the Experimental section), shows that these compounds do not have the cubic $K_2[PtCl_6]$ structure suggested by Engel.[12]

(b) *The Intensity of the* T_{1u} *Bending Mode* (ν_4).—The abnormally low intensity of this mode in hexahalogenotellurates was first noted by Creighton and Green,[5] though they did not propose an explanation. In a recent study of pressure effects on the vibrational spectra of some hexahalogenometallates Adams and Payne[9] invoked a mechanism involving dynamic rehybridisation whereby the lone pair acquires some directional character with a moment opposing that due to the change in nuclear positions which occurs during the ν_4 mode. Our observations of the intensity of ν_4 in $A_2[SnX_6]$, $A_2[TeX_6]$, and $A_2[(Sn,Te)X_6]$ confirm that the lone pair is involved in the lowering of the intensity of ν_4 in the halogenotellurates, but we suggest another possible mechanism which does not involve rehybridisation.

Previous ^{125}Te Mössbauer studies on hexachloro- and hexabromo-tellurates by Gibb *et al.*[15] show that there is no quadrupole splitting; a splitting should be observed if the non-bonding electrons have directional character.

We studied the relative intensities (I_{43}) of ν_4 and ν_3 of the hexachloro- and hexabromo-stannates and -tellurates (Table 4). As is to be expected if the non-bonding electrons are involved in reducing the intensity of ν_4, I_{43} is high for the tin and much lower for the tellurium compounds. For the (Sn,Te) bromide compounds the value of I_{43} is near or below the mean value for the corresponding Sn and Te compounds, but, for the (Sn,Te) chloride compounds, the value of I_{43} is greater than the mean value for the individual Sn and Te compounds. This suggests that the mechanism whereby the intensity of ν_4 is lowered is more effective in the bromides than in the chlorides. We have previously shown[16,17] that there is a considerable amount of evidence to support the suggestion that the directional effects of lone-pair orbitals in ions with an ns^2 outer electronic configuration can be eliminated if the electron density in the orbitals can be reduced by direct population of delocalised, non-valence-shell, solid-state bands. The effects of direct population of this type include the development of colour and electrical conductivity and the presence of high-symmetry environments, as found in the hexahalogenotellurates(IV). The available evidence suggests that population of low-energy solid-state bands by the non-bonding electron pairs is the main reason for the suppression of directional lone-pair effects, rather than population of a non-bonding a_{1g} orbital. The latter hypothesis[18] explains the high-symmetry environments but not the physical properties of the compounds of the elements in question. We now consider the interpretation of the spectra, taking into account the existence of populated, delocalised, solid-state bands.

TABLE 4

Relative intensities (I_{43})[a] of ν_4 and ν_3 in $A_2[MX_6]$[b]

	Chloride complexes			Bromide complexes		
M / A	Sn	Te	(Sn,Te)	Sn	Te	(Sn,Te)
NH_4	0.71	0.07	0.77	0.46	0.11	0.13
Rb	0.59	0.00	0.53	0.28	0.00	0.14
Cs	0.58	0.00	0.32	0.25	0.00	0.13

[a] Mean of three values over a four-fold range of concentration (3—12 mg per 300 mg of wax). No values differed from the mean by more than 10% of the mean. The potassium salts were excluded as they are not isostructural with the others and display splittings of the i.r.-active bands.

TABLE 5

Wavelength (nm) of the absorption edge in the reflectance spectra of $A_2[MX_6]$

	Chloride complexes			Bromide complexes		
M / A	Sn	Te	(Sn,Te)	Sn	Te	(Sn,Te)
NH_4	320	480	454	444	568	557
Rb	301	478	446	428	543	546
Cs	293	463	457	424	546	542

Our reflectance measurements in the u.v. and visible region of the spectrum show absorption edges which appear to arise from transitions causing the non-valence-shell band, consisting of the halogen d_{xz}, d_{yz}, and d_{xy} orbitals, to become populated. As Table 5 shows, the positions of the absorption edges demonstrate that this transition requires more energy for the chlorides than for the bromides; therefore these orbitals will be less strongly populated. Consequently interaction between the

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non-bonding electrons on the central metal atom and the electrons in the halide band will be greater in the bromide than in the chloride compounds.

(c) *Assignments of the Vibrational Spectra.*—For those compounds with the $K_2[PtCl_6]$ structure the only differences in assignment among previous studies involves the identification of the T_{1u} bending and lattice modes. Labonville *et al.*[8] carried out an extensive set of normal-co-ordinate calculations for the internal modes of octahedral species, and in all cases force constants were fitted under the assumption that the bending mode lies above the lattice mode. Not all other workers agree with this assignment. In an attempt to clarify this situation we carried out a normal-co-ordinate analysis for $A_2[MX_6]$ with the $K_2[PtCl_6]$ structure, including the T_{1u} and T_{2g} lattice modes. We assumed the most regular geometry for the structure, which is that with the parameter u, specifying the X atom positions, equal to 0.25. This simplifying assumption is justifiable, since in all the compounds where its value has been determined it lies between 0.23 and 0.25.[19]

For each compound with the $K_2[PtCl_6]$ structure whose i.r. spectrum we have obtained, except the hexaiodotellurates, we calculated the elements F_{11}, F_{21}, F_{22}, and F_{33} of the force-constant matrix. A similar calculation has been made for $M_2[PtCl_6]$ by Hiraishi and Shimanouchi [20] (M = K, Rb, or Cs) and here also the G.V.F.F. constants calculated are those corresponding to ours. This is reasonable, since, because of the small values of the off-diagonal G matrix elements between the lattice and internal modes, the coupling between them must be very slight. Gans [21] showed that the extent of coupling between two modes ν_i and ν_j depends not on the frequency separation but on the magnitude of the term $G_{ij}{}^2F_{ii}F_{jj}$. The result of this condition, for the systems being studied, is that neither the potential-energy distribution nor the eigenvalues are sensitive to the size of the interaction force constants between the internal and lattice modes. The converse, of course, is the case with respect to the two internal modes, between which the G matrix element is large. We conclude from our calculations that, where ν_4 and ν_L are both observed, ν_4 lies above ν_L for all compounds except $[NH_4]_2[TeBr_6]$.

EXPERIMENTAL

The hexahalogenometallates(IV) were prepared by standard methods. The mixed hexahalogenometallates(IV) were prepared by dissolving TeO_2 in concentrated HCl containing $SnCl_4$ or 50% HBr containing $SnBr_4$, and adding a saturated aqueous solution of the appropriate alkali-metal halide.

To characterise the hexahalogenometallates(IV), X-ray powder data were obtained with a Phillips 11.64 cm camera using Cu-K_α radiation. The powder data for the mixed hexahalogenometallates with the $K_2[PtCl_6]$ structure were indexed in the same way as the simple hexahalogeno-stannates and -tellurates, giving cell edge lengths intermediate between those of the parent compounds. There was no evidence for precipitation of mixtures of the parent compounds. The powder data showed that $K_2[(Sn,Te)Br_6]$ did not have the $K_2[PtCl_6]$ structure; calculated d spacings (visually estimated intensities) were 5.99(s), 5.19(s), 3.66(w), 2.77(m), 2.59(vs), 2.38(m), 2.31(m), 2.12(w), 2.04(vw), 2.00(w), 1.86(m), 1.76(w), 1.73(w), 1.68(w), and 1.51(w) Å. Similarly, $Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$ do not have the $K_2[PtCl_6]$ structure: for $Rb_2[SeCl_6]$ 5.63(s), 3.70(w), 3.45(s), 3.23(m), 3.05(vw), 2.94(w), 2.83(s), 2.72(s), 2.60(w), 2.25(vw), 1.86(ms), 1.66(vw), 1.62(vw), 1.55(w), and 1.48(m); for $Cs_2[SeCl_6]$ 5.79(s), 5.02(m), 4.09(w), 4.03(w), 3.62(w), 3.56(vs), 3.39(m), 3.19(vw), 3.03(w), 2.91(vs), 2.86(m), 2.70(m), 2.62(m), 2.51(w), 2.40(vs), 2.25(m), 2.12(w), 2.05(s), 1.78(s), 1.75(w), 1.70(w), 1.68(w), 1.65(w), 1.60(m), 1.57(w), and 1.52(m) Å.

Mössbauer spectra were recorded with a $BaSnO_3$ source and the absorber at 80 K. The apparatus has been previously described.[22] I.r. data were obtained using a Beckmann–RIIC FS-720-EL Fourier spectrometer, the materials being studied as dispersions in paraffin-wax discs. Raman spectra were recorded with a Cary 81 spectrometer, using Kr 5 682 Å excitation.

We thank the S.R.C. for a grant for Mössbauer studies, P.C.M.U., Harwell, for the far-i.r. spectra, and U.L.I.R.S. at Imperial College for the laser-Raman spectra.

[4/2356 *Received*, 11*th November*, 1974]

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