Vibrational Spectroscopy at Very High Pressures. Part V.[1] Far-infrared Spectra of Inert Pair Hexahalogeno-complexes †

By **David M. Adams,* John D. Findlay, Michael C. Coles, and S. John Payne,** Department of Chemistry, The University, Leicester LE1 7RH

Far-i.r. spectra of salts of $[SeX_6]^{2-}$ (X = Cl or Br), and $[TeX_6]^{2-}$ (X = Cl, Br, or I), are reported for pressures up to 40 kbar. All observed bands show blue shifts but the most dramatic effects are exhibited by the ν_4 bending modes of the anions. For some compounds ν_4 is absent at ambient pressure but appears at increased pressure and exhibits a large blue shift, but other compounds which have ν_4 initially lose it at elevated pressure. These effects are accounted for on the basis of an anion–cation bonding scheme which allows a pressure-dependent delocalisation of inert-pair electrons throughout the lattice.

IN a recent report [2] on the pressure-sensitivity of the far-i.r. spectra of series of hexahalogeno-salts we showed that, in contrast to the behaviour of salts of $[PtCl_6]^{2-}$ and $[SnCl_6]^{2-}$, those of $[TeCl_6]^{2-}$ were abnormal. Specifically, ν_4 (T_{1u}, δ(TeCl)) is absent from room-pressure spectra but appears and suffers a substantial blue shift, with increase of pressure. This exceptional behaviour was attributed to the presence of an inert pair on tellurium. In the present paper we report a detailed investigation into the occurrence and origin of this effect.

Structures of the Complexes Used.—Not all the structures are cubic. The main reason for appearance of lower symmetry variants, either at ambient or at lower temperatures, seems to be the size of the cation relative to that of the complex anion. Thus, Rb^+ and Cs^+ salts are apparently always cubic at all temperatures for which *X*-ray data are available.[3,4] N.q.r. evidence supports this view for $Cs_2[TeX_6]$ (X = Br or I), showing only a single resonance.[5] Brown has shown [3] that for K^+ salts more efficient packing than in a cubic lattice is achieved if there is a slight reorientation of the $[TeCl_6]^{2-}$ and $[TeBr_6]^{2-}$ octahedra. Consequently $K_2[TeCl_6]$ is monoclinic. So also is $K_2[TeBr_6]$ and its n.q.r. spectrum accordingly shows a triplet; [5] $K_2[TeI_6]$ is just triclinic [3] and also exhibits an n.q.r. triplet.[5] Similarly, n.q.r. evidence [6] shows that $[NH_4]_2[SeCl_6]$, $Cs_2[SeBr_6]$, and $[NH_4]_2[SeBr_6]$ are cubic down to liquid nitrogen temperature but $K_2[SeBr_6]$ changes from cubic to lower symmetry below 240 K.

Far-i.r. Spectra at Ambient Pressure.—These structural differences are reflected in the room-temperature far-i.r. spectra particularly in the lattice mode region. Factor-group analysis of the bimolecular $P2_1/n$ cell of $K_2[TeBr_6]$ shows that none of the rotatory modes are i.r.-active but that $5A_u + 4B_u$ translatory modes (all i.r.-active) are expected. In addition, as shown by the

---

† No reprints available.

[1] Part IV, D. M. Adams and S. K. Sharma, *Chem. Phys. Letters*, 1975, **36**, 407.

[2] D. M. Adams and S. J. Payne, *J.C.S. Dalton*, 1974, 407.

[3] I. D. Brown, *Canad. J. Chem.*, 1964, **42**, 2758.

[4] A. K. Das and I. D. Brown, *Canad. J. Chem.*, 1966, **44**, 939.

[5] D. Nakamura, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 1962, **84**, 163.

[6] D. Nakamura, K. Ito, and M. Kubo, *Inorg. Chem.*, 1963, **2**, 61.

following correlation scheme, ν_6 (inactive in a cubic lattice) is now allowed.

$$\begin{array}{lll} O_h & C_i\ (\text{Site}) \xrightarrow{\times 2} & C_{2h}\ (\text{Factor group}) \\ \left.\begin{array}{ll} \nu_3 & T_{1u} \\ \nu_4 & T_{1u} \\ \nu_6 & T_{2u} \end{array}\right\} & 9A_u & 9A_u + 9B_u \end{array}$$

The spectra show two broad regions of absorption below 120 cm^{-1} at room temperature from which the components listed in Table 1 are gradually resolved by 120 K, in accord with the n.q.r. evidence, which shows that no phase change occurs in this range. An unambiguous assignment of these bands is impossible (single-crystal spectra would not help as the symmetry is too low) but we note that the complexity far exceeds what is found for cubic compounds. Comparison with earlier work,[7] which included calculations of ν_6 by use of a Urey–Bradley force field, shows (*a*) that the 52 cm^{-1} band is most probably associated mainly with ν_6, and (*b*) that ν_6 cannot be as high as 100 cm^{-1}. Hence the prominent and highly temperature- and pressure-sensitive bands *ca.* 100 cm^{-1} are due to ν_4 or to lattice modes, or to some admixture of them. The correlation shows that ν_3 should become a triplet; the spectra show evidence of structure in this region but none is clearly resolved even at 120 K.

TABLE 1

Frequencies (wavenumbers/cm^{-1}) of the i.r.-active modes of some inert-pair hexahalides, $A_2[MX_6]$, at room temperature (upper value) and at *ca.* 120 K (lower value)

	ν_3	ν_4	ν_L
$K_2[TeBr_6]$	199	105 [a]	76, 53 [c]
	203	113 [b]	78, 55
$Cs_2[TeBr_6]$	200		54
	205		56
$K_2[SeBr_6]$	231		82
	234		58, 86, 112
$Rb_2[SeBr_6]$	231	104	64
	233	106	66
$[NH_4]_2[SeBr_6]$	225	132	97
	231	130	97

[a] Possibly a lattice mode of the distorted structure; see text. [b] Band also loses intensity. [c] Further bands may be present.

TABLE 2

Pressure-dependencies of the i.r.-active vibrations of some inert pair hexahalides, $A_2[MX_6]$

	ν_3			ν_4			ν_L		
	0.001kbar	40kbar [a]	$\Delta\nu/\Delta P$ [b]	0.001kbar	40kbar [a]	$\Delta\nu/\Delta P$ [b]	0.001kbar	40kbar [a]	$\Delta\nu/\Delta P$ [b]
$K_2[TeCl_6]$ [k]	197	208	0.55						
$Rb_2[TeCl_6]$	262	278	0.80	148 [c]	159	1.10	65	85	1.00
$Cs_2[TeCl_6]$	256	265	0.45	135	164	1.45	66	82	0.80
$[NH_4]_2[TeCl_6]$	255	265	0.50	151	178 [c]	2.70	110	130	1.00
$[NMe_4]_2[TeCl_6]$	236	241	0.25				78	*d*	*d*
$[NBu_4]_2[TeCl_6]$	255	261	0.30						
$K_2[TeBr_6]$ [k]	200	208	0.40	105 [e]	125 [c]	2.00	77, 53	*f*	
$Rb_2[TeBr_6]$	201	212	0.55	107 [c]	115	0.80	54	72	0.90
$Cs_2[TeBr_6]]$	200	210	0.50	103 [c]	115	1.20	55	73	0.90
$[NH_4]_2[TeBr_6]$	195	205	0.50	125	147 [g]	1.40	82	91 [g]	0.60
$[NEt_4]_2[TeBr_6]$	176	184	0.40				63	*d*	*d*
$[PyH]_2[TeBr_6]$	174	179	0.25				60	*d*	*d*
$K_2[TeI_6]$ [l]	160	165	0.25	98 [e]	111 [c]	1.30	63	*d*	*d*
$Cs_2[TeI_6]$	159	167	0.40	88	96	0.40	45	58 [g]	0.85
$[NH_4]_2[TeI_6]$	158	168	0.50						
$[NEt_4]_2[TeI_6]$	157 [h]	164	0.35	100	107	0.35	55	66	0.55
$[PyH]_2[TeI_6]$	147	151	0.20	103	109 [i]	1.20	50	57 [g]	0.45
$Rb_2[SeCl_6]$	285	296	0.55	157	*d*	*d*	75	98	1.15
$Cs_2[SeCl_6]$	278	285	0.35	152	*d*	*d*	73	94	1.05
$[NH_4]_2[SeCl_6]$	*m*	*m*	*m*	*m*	*m*	*m*	132	152	1.00
$K_2[SeBr_6]$	231	239	0.40	132 [i]	147	1.00	82	98	0.80
$Rb_2[SeBr_6]$	232	243	0.55	103,[j] 87 [j]	*j*	*j*	63	80	0.85
$Cs_2[SeBr_6]$	225	232	0.35	102,[j] 87 [j]	*j*	*j*	63	77	0.70
$[NH_4]_2[SeBr_6]$	227	235	0.35	133	184	2.50	97	108	0.55

[a] Pressure at the centre of the anvil face. [b] Calc. from value of average pressure across anvil face. [c] At central pressure of 20 kbar. [d] This band lost intensity under pressure without shifting appreciably. [e] Possibly lattice mode of distorted structure; see text. [f] Shifts could not be measured accurately. [g] At central pressure 30 kbar. [h] ν_3 Is a triplet; position and shift of band at half height are given. [i] At central pressure of 10 kbar. [j] Very weak absorptions which disappear with increasing pressure. [k] Monoclinic at room temperature and pressure. [l] Just triclinic at room temperature. [m] At ambient pressure ν_3 and ν_4 are merged into one broad band, ν_L is a shoulder; at elevated pressure intensity in the region of ν_4 drops but the merged band shifts rapidly and ν_L separates clearly.

$K_2[SeBr_6]$ is reported to be cubic at room temperature [6] and in accord shows a single lattice mode although this is unusually broad. By 120 K several components can be resolved from it (Table 1).

Assignments of the spectra of the other compounds in this series are also shown in Table 1. As is well known, the i.r. spectra of most of the salts $M_2[TeX_6]$ and $M_2[SeX_6]$ are peculiar in having ν_3 of exceptional breadth and very weak or vanishingly weak ν_4. A few, however, ($Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$) show a fairly normal ν_4. From the foregoing *X*-ray, n.q.r., and vibrational evidence, it appears that ν_4 is absent or very weak only for compounds having the cubic structure, with the exception of $Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$ which we presume to be cubic in the absence of any *X*-ray or n.q.r. evidence.

At room temperature and pressure all the ammonium salts used by us are cubic.[5,6] In their far-i.r. spectra all

---

[7] D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), 1967, 2067.

show three bands and the lowest appears to be largely due to ν_L. We note that there is a considerable drop in ν_L from $[MCl_6]^{2-}$ to $[MBr_6]^{2-}$ to $[MI_6]^{2-}$ salts, probably due to weaker hydrogen bonding. [An equivalent effect is noted for $[NH_4]_2[MX_4]$ (M = Pd or Pt; X = Cl or Br).[8]]

Far-i.r. Spectra at High Pressures.—Results are shown in Table 2 and in Figures 1—4.

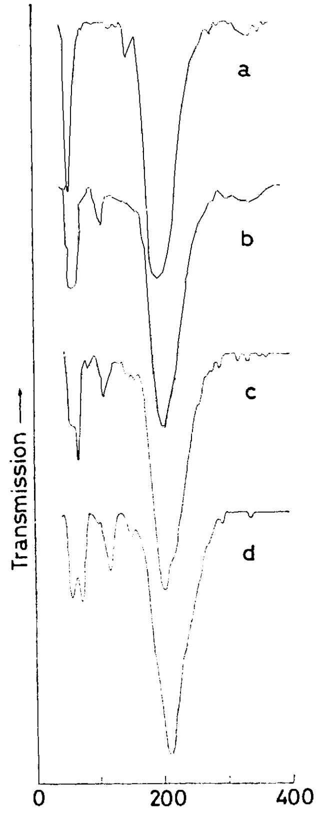

FIGURE 1 Far-i.r. spectra of $Cs_2[TeBr_6]$. a Ambient pressure, b 20, c 30, and d 40 kbar. Pressures given are those at anvil centres; where doublets are shown, the lower component is the residual due to material at ambient pressure

(*a*) *Cubic crystals with* A = *monatomic.* As already outlined above $Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$ show a prominent ν_4 band at room pressure, but the others of this group (*viz.* $K_2[SeBr_6]$, $Rb_2[TeCl_6]$, $Cs_2[TeCl_6]$, $Rb_2[TeBr_6]$, and $Cs_2[TeBr_6]$) do not show ν_4 except for $Rb_2[SeBr_6]$ and $Cs_2[SeBr_6]$ which have two very weak bands in positions consistent with ν_4. At elevated pressures two kinds of behaviour are exhibited, which correlate well with the room-pressure spectroscopic classification. (i) Taking $Cs_2[TeBr_6]$ as typical of its group, behaviour was observed as shown in Figure 1. Starting with a two-band spectrum (ν_L and ν_3), both suffered blue shifts with $\Delta\nu_i/\Delta P$ of 0.9 and 0.5 cm^{-1} kbar^{-1} respectively; a new band appeared in the ν_4 region (103 cm^{-1} at 10 kbar) and shifted rapidly with pressure, $\Delta\nu_i/\Delta P = 1.2$. At the highest pressure used (40 kbar at the anvil centres) the spectrum was similar to that exhibited by non-inert-pair hexahalides such as $K_2[PtCl_6]$.

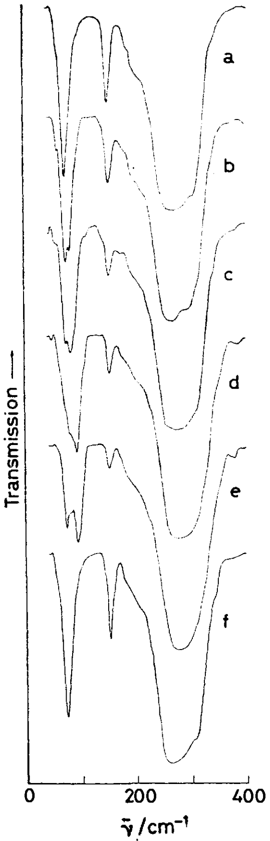

FIGURE 2 Far-i.r. spectra of $Cs_2[SeCl_6]$. a Ambient pressure; b 10, c 20, d 30, and e 40 kbar; f ambient pressure. Pressures given are those at anvil centres; where doublets are shown, the lower component is the residual due to material at ambient pressure

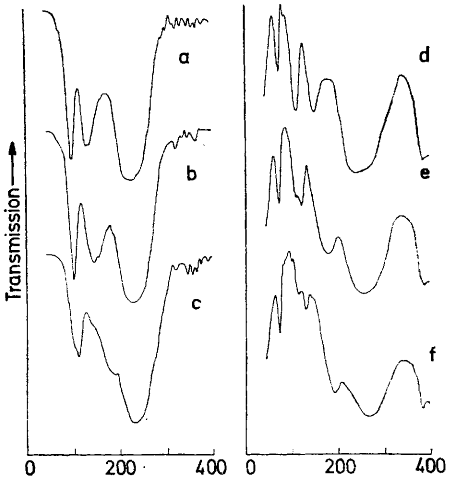

FIGURE 3 Far-i.r. spectra of $[NH_4]_2[SeBr_6]$ (a—c) and $[NH_4]_2[TeCl_6]$ (d—f) at ambient pressure (a and d), 20 kbar (b and e), and 40 kbar (c and f). Pressures given are those at anvil centres. The spectra of $[NH_4]_2[TeCl_6]$ are unratioed from the background and hence the 73 cm^{-1} band is due to polyethylene

---

[8] J. H. Fertel and C. H. Perry, *J. Phys. and Chem. Solids*, 1965, **26**, 1773.

(ii) For $Rb_2[SeCl_6]$ and $Cs_2[SeCl_6]$ (Figure 2) the prominent ν_4 rapidly lost intensity with increase of pressure but shifted very little in frequency: most of the intensity remaining at 40 kbar is due to residual unpressurised material at the diamond edges. We conclude that ν_4 vanishes at low applied pressures, after which the spectrum looks like that of $Cs_2[TeBr_6]$ at room pressure; ν_L and ν_3 show normal blue shifts. $Rb_2[SeBr_6]$ and $Cs_2[SeBr_6]$ appear also to belong to this class. They show two weak bands in the ν_4 region which cannot both be due to ν_4 (if, indeed, either is). Whatever their origin, these weak bands disappear quickly upon application of pressure, leaving ν_L and ν_3 which show normal blue shifts.

(iii) A final member of this set is $Cs_2[TeI_6]$. No structural information is available for this compound and we did not take an *X*-ray powder photograph as the kind of minor distortion shown by $K_2[TeI_6]$ would not be detectable other than by careful single-crystal study. However, if this were not cubic it would be the only non-cubic caesium salt in this series. $Cs_2[TeI_6]$ shows a normal three-band spectrum: ν_3, ν_4, and ν_L. All bands show normal blue shifts with no significant loss of intensity.

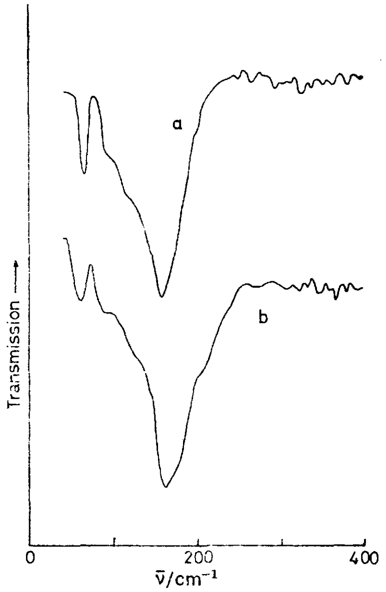

FIGURE 4 Far-i.r. spectra of $[NH_4]_2[TeI_6]$ at a, ambient pressure, and b, 40 kbar

(*b*) *Non-cubic crystals with* A = *monatomic.* $K_2[TeI_6]$ makes a link with section (*a*) (ii). It shows a normal three-band spectrum typical of a cubic hexahalide, although in fact it is only just triclinic ($\alpha = 90.0$, $\beta = 90.5$, $\gamma = 91.0°$). ν_3 shows a normal blue shift but the middle band, which we believe to be ν_4, loses intensity and shifts very rapidly, and ν_L behaves similarly but shifts less. At 40 kbar (at the anvil centres) ν_4 is too broad to be measured but there is clearly still absorption present. The spectrum at high pressure therefore bears a superficial resemblance to those of the cubic materials at room pressure.

$K_2[TeBr_6]$ is monoclinic: our assignment is given earlier. The most prominent feature is the very high pressure-sensitivity of the 105 cm^{-1} band which behaves like the 98 cm^{-1} band in $K_2[TeI_6]$, and has a very high $\Delta\nu/\Delta P$ value. The band at 53 cm^{-1} suffers a blue shift which brings it so close to the band at 80 cm^{-1} (room pressure) that it is not possible to say whether it continues to shift, or loses intensity.

$K_2[TeCl_6]$, as is well known, shows a ν_3 band of enormous width; this width is unchanged up to 40 kbar but there is a slight overall blue shift of *ca.* 10 cm^{-1}. No sign of ν_4 or ν_L was detected.

(*c*) *Ammonium salts.* N.q.r. evidence shows that $[NH_4]_2[TeCl_6]$, $[NH_4]_2[TeBr_6]$, and $[NH_4]_2[SeBr_6]$ are cubic at room temperature, but that $[NH_4]_2[TeI_6]$ is not.[5] No information is available for $[NH_4]_2[SeCl_6]$ but it is reasonable to presume that it also is cubic.

The chlorides and bromides are consistent in showing three-band spectra (ν_L, ν_4, and ν_3) in which ν_4 has intensity normal in comparison with non-inert-pair hexahalides. The effect of pressure was to impart a very substantial blue shift to ν_4 which results in it becoming entangled with the low-frequency wing of ν_3; ν_L and ν_3 show more modest and normal blue shifts. ν_4 appears not to lose intensity significantly, although it is difficult to be sure (see Figure 3).

$[NH_4]_2[TeI_6]$ is non-cubic and shows an asymmetric ν_3 band which might well resolve at lower temperature. If ν_4 is present, it is very weak and broad, and is certainly absent under high pressure (Figure 4).

(*d*) *Salts of organic cations.* There are no structural data for these compounds (Table 2). Their room-pressure spectra all showed a strong ν_3 band but this is narrower than ν_3 for the same anion combined with monatomic cations. For $[NR_4]_2[TeX_6]$ a lattice mode was found for R = Me or Et but not for R = Bu. The ν_3 modes for these complexes were very little affected by pressure, having $\Delta\nu/\Delta P \approx 0.4$ cm^{-1} kbar^{-1} or less, implying that any effect on the organic cation of the applied pressure was met by conformational adjustments. In the ν_4 regions some of these compounds showed very weak bands (see Table 2) but none of them gained or lost intensity with change of pressure.

DISCUSSION

From our earlier work,[2] which included only $Rb_2[TeCl_6]$ and $Cs_2[TeCl_6]$, it seemed that the appearance of ν_4 with increase of pressure was a characteristic of inert-pair systems. Our new results show that the situation is more complex and, as detailed above, is further complicated by the occurrence of non-cubic structures.

The Raman spectra of these materials are normal in comparison with those of other complex halides $A_2[MX_6]$, and so is the i.r.-active lattice mode ν_L. It is ν_3 and ν_4 which are abnormal in their behaviour; since these modes are distinguished from all other optically active ones in involving movement of the central metal atom

(Te or Se) the inert pair is clearly implicated. It is therefore important to identify the orbital(s) it occupies.

The *X*-ray and n.q.r. evidence is consistent in showing regular octahedral geometry at Te or Se; accordingly it has been suggested that the inert pair occupies a totally symmetric orbital on the metal.[9] Absence of quadrupole splitting in the tellurium-125 Mössbauer spectra [10] shows that these electrons exert no directional effect; hence they may be either in an *s* orbital or may contribute symmetrically to orbitals of directional character.

It would be of particular interest to know how ν_3 and ν_4 behave in solution at both ambient and elevated pressures. For various practical reasons we cannot do this experiment directly but a very good approximation is to take salts of large organic cations. Goggin and Mink [11] have recently shown that for a series of square-planar anions the frequencies of $[NBu_4]^+$ salts are essentially the same as those of their solutions in polar solvents. $[NBu_4]_2[TeCl_6]$ shows only a ν_3 band of moderate width ($\Delta\nu_{\frac{1}{2}} \approx 75$ cm^{-1}), with no sign of either ν_4 or ν_L. Absence of ν_L is not unexpected as there is precedent in the far-i.r. spectra of various tetrahalogenometallates with organic cations,[12] but absence of ν_4 suggests that the structure of $[TeCl_6]^{2-}$ in this salt is comparable with that in the Rb^+ and Cs^+ salts at ambient pressure. Under increased pressure ν_4 does not appear, implying that whatever mechanism is responsible for its development in the Rb^+ and Cs^+ salts cannot operate in $[NBu_4]^+$ which effectively isolates each anion within a hydrocarbon sheath. Behaviour of the other organic-cation salts broadly supports this view: ν_4 is either absent and fails to appear with applied pressure, or is weak and remains of approximately the same intensity under pressure, although for the smaller cations well-defined bands, ν_L, are also shown.

Taking this evidence, and that from the effects of pressure together with the observation that the ν_3 half-band widths and pressure shifts are dependent upon choice of monatomic cation for the salts $A_2[TeX_6]$ and $A_2[SeX_6]$, shows that the entire lattice must be considered in seeking an explanation for the distinctive behaviour of ν_3 and ν_4. Since any such cation–anion interaction must take place *via* the small (but cation-dependent) proportion of covalent bonding it is appropriate to couch a description in terms of band theory in the tight binding approximation. In the absence of quantitative calculations of energy levels we are limited to a qualitative explanation, the essential feature of which is a means of coupling the inert pair on Te or Se with the cations, and its subsequent modification by the application of pressure.

The σ bonds of $[TeX_6]^{2-}$ ions are constructed by use of $(5d)^2(5p)^3(ns)^1$ hybrids; if the inert pair is to participate (as it must) n will be 5, but $n = 6$ may also be mixed in, as there is no symmetry disqualification. These hybrids overlap with $(s + p_z)$-hybrids on X (z is taken as the Te–X direction) in appropriate combinations of A_{1g}, E_g, and T_{1u} symmetry: the $(s—p_z)$ components are available for overlap with cation ns levels to form a conduction band. Since the Mössbauer evidence is also consistent with an even distribution of inert pair density among directional orbitals we must also consider the possibility of $Te(d_\pi)$–$X(p_\pi)$ overlap as a means of transmitting the inert pair to the exterior of the anion since hybrids of this type can also combine with cation (ns) orbitals. The extent of inert-pair delocalisation into a conduction band by these means will clearly vary with the relative energies of the orbitals, depending upon the particular A, M(Te or Se), and X combination. Since the effect of pressure upon electronic levels is to decrease the energy spread of the manifold of levels,[13] the extent of inert-pair delocalisation will also be altered. For a few compounds (*e.g.* $Cs_2[TeBr_6]$, $Cs_2[SeBr_6]$), this was reflected in a slight darkening of the material under pressure (observed through a microscope) but for most there was no detectable change of colour.

The problem is now to link the behaviour of ν_4 with these changes in electronic structure. Two apparently contradictory types of behaviour were revealed in the pressure studies: (i) ν_4 was very weak or absent at ambient but developed intensity at elevated pressure (*e.g.* $Rb_2[TeCl_6]$, $Cs_2[TeCl_6]$, $K_2[SeBr_6]$); (ii) ν_4 was present at ambient pressure but rapidly vanished with applied stress (*e.g.* $Rb_2[SeCl_6]$, $Cs_2[SeCl_6]$).

The intensity of an i.r. absorption band is proportional to the square of the transition dipole moment between initial and final states. For ν_3 and ν_4 (both of T_{1u} symmetry) the forms of the first vibrationally excited states of the normal modes are well known and alone account for the magnitudes of the transition dipole moments (since $v = 0$ has A_{1g} symmetry). If ν_4 is vanishingly weak the implication is that the dipole moment associated with the $v = 1$ level of ν_4 is zero: the atom displacements are such that they inevitably require development of a dipole moment, but, since one is not present overall, this moment must be balanced by an equal and opposite moment which comes from dynamic rehybridisation involving the inert pair. The very high sensitivity of ν_4 to pressure, and the considerable widths of ν_3, both show that the lattice dynamics are highly anharmonic since both the pressure-dependence of phonons and oscillator damping are absent from harmonic theory; indeed the quadrupolar nature attributed to these modes further assists coupling to the lattice.

A high degree of delocalisation of the inert pair into the conduction levels removes the means of balancing the ν_4 mode atom-displacement dipole by an electronic one and allows development of normal intensity. Accordingly we account for the above classes of behaviour

---

[9] D. S. Urch, *J. Chem. Soc.*, 1964, 5775.

[10] T. C. Gibb, R. Greatrex, N. N. Greenwood, and A. C. Sarma, *J. Chem. Soc.* (*A*), 1970, 212.

[11] P. L. Goggin and J. Mink, *J.C.S. Dalton*, 1974, 1479.

[12] J. T. R. Dunsmuir and A. P. Lane, *J. Chem. Soc.* (*A*), 1971, 2781.

[13] H. G. Drickamer and C. W. Frank, ' Electronic Transitions and the High Pressure Chemistry and Physics of Solids,' Chapman and Hall, London, 1973.

(i) and (ii) as follows. (i) There is little delocalisation of the inert pair in the ambient pressure structure, but with increased pressure, the conduction band is lowered relative to the valence band thereby allowing greater delocalisation and hence development of intensity in ν_4. (ii) Exactly the reverse argument applies. The ultimate cause for this reversal of behaviour for some of the selenium complexes lies in the different relative energies of the A, Se, and X orbitals.

It follows from the foregoing argument that an isolated inert-pair complex ion should not show much intensity in ν_4; we note that ν_4 was absent for $[NBu_4]_2[TeCl_6]$. Similar behaviour is shown by XeF_6;[14] its electronic and spatial structures are still a matter for debate but it bears close resemblance to our situation. Xenon has a nonbonding pair of electrons, and the i.r. spectrum shows no ν_4.

In the salts with non-cubic structures it is reasonable to assume that anion–cation electronic coupling will be slightly modified, but that the foregoing mechanism will be broadly applicable.

EXPERIMENTAL

Far-i.r. spectra were recorded under pressure by use of the diamond anvil cell described elsewhere[15] in conjunction with a Beckmann RIIC FS 720 interferometer. No instrumental modification was necessary but a light pipe of length $2\frac{3}{4}$ in and diameter $1\frac{3}{16}$ in at the wide end was placed in front of the diamond anvil cell. The method of calibration of the cell was as described previously.

Compounds were, in general, prepared by standard methods. In the preparation of $[TeX_6]^{2-}$ salts, the starting material was TeO_2, which was dissolved in the appropriate halogen acid; addition of a solution of the appropriate halide AX caused immediate precipitation of the required complex.

Compounds of the type $A_2[SeBr_6]$ were prepared in a similar way; SeO_2 was dissolved in HBr and addition of a solution of the appropriate bromide ABr caused immediate precipitation of the complexes. Hexachloroselenate complexes were found to be much more difficult to prepare pure and the same method could not be used. Instead, SeO_2 was dissolved in water or dilute hydrochloric acid, and then HCl gas bubbled through the solution; a solution of the appropriate chloride ACl was then added and HCl gas passed through the mixed solutions for *ca.* 1 h. After lengths of time which varied for each cation, a yellow product $A_2[SeCl_6]$ was isolated. It is most important that these compounds are dried by passing a stream of dry HCl over them. Drying in a desiccator or in partial vacuum, or in an oven resulted in partial decomposition (especially for $K_2[SeCl_6)]$, which is readily monitored by a band *ca.* 924 cm^{-1} [ν(Se) 0] which is both i.r.- and Raman-active. The additional low-frequency bands thus introduced into i.r. and Raman spectra may account for the literature discrepancies on their spectra.

We thank the S.R.C. for a grant (to S. J. P.) and for other support.

[5/1084 *Received, 5th June*, 1975]

---

[14] H. Kim, H. H. Claassen, and E. Pearson, *Inorg. Chem.*, 1968, **7**, 616.

[15] D. M. Adams, K. Martin, and S. J. Payne, *Appl. Spectroscopy*, 1973, **27**, 377.