Spectroscopy at Very High Pressures. Part II.[1] Far-infrared Spectra of Some Complex Chlorides $M^I_2MCl_6$

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Far-i.r. absorption spectra of some hexachlorometallates, $M^I_2MCl_6$, have been studied at average pressures up to 20 kbar by use of a new design of diamond anvil cell. No simple pattern of behaviour emerged although the ν_4, δ(ClMCl), mode is generally much more pressure-sensitive than the corresponding ν_3, ν(M–Cl). Lattice modes usually have $d\nu/dP \approx 1{\cdot}0$ kbar cm^{-1}, but exceptions were found. For $(NH_4)_2[PtCl_6]$ and $(NH_4)_2[SnCl_6]$ ν_4 and ν_L are in Fermi resonance which can be pressure-scanned to reveal different apparent sensitivities of ν_4 and ν_L; the results are analysed to obtain true shifts. Finally, in hexachlorotellurates the vanishingly weak ν_4 gained intensity dramatically as pressure was applied; a possible mechanism is discussed.

VERY little systematic study has been devoted to the effects of high pressure on the vibrational spectra of inorganic complexes. We report an investigation into the pressure-dependence of the far-i.r. spectra of complex halides of the type $M^I_2MCl_6$. These compounds all have three i.r.-active T_{1u} modes and provide a particularly simple series with several variables. Their i.r.-actives modes are: ν_3, ν(M–Cl); ν_4, δ(M–Cl); and a lattice mode, ν_L, in the factor group O_h.

The only published high-pressure work on these

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

compounds is Ferraro's report [2] on K_2PtCl_6 and K_2PdCl_6. He found that ν_L is more sensitive than ν_3 or ν_4, having $d\nu/dP$ (in cm^{-1} $kbar^{-1}$) of 0·76 compared with 0·62 (ν_3) and 0·60 (ν_4). Our work considerably widens the number of examples and is in conflict with Ferraro's conclusions in some respects.

EXPERIMENTAL

A new design [1] of diamond anvil cell was used. I.r. spectra were recorded with a Beckman-R.I.I.C. 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 smaller of the two opposed anvils was of area 0·00089 in^2.

TABLE 1

I.r. frequencies/cm^{-1} for some transition-metal complex hexahalides at ambient pressure and at 20 kbar

	ν_3			ν_4			ν_L		
Pressure/kbar	0	20	$\Delta\nu$	0	20	$\Delta\nu$	0	20	$\Delta\nu$
K_2PtCl_6	345	352	7	187	203	16	88	106	18
Rb_2PtCl_6	342	350	8	187	207	20	78	98	20
Cs_2PtCl_6	332	339	7	186	208	22	70	88	18
Tl_2PtCl_6	335	347	12	181	191	10	49	61	12
$(NH_4)_2PtCl_6$	340	350	10	201 [a]	235 [a]	34	135 [a]	152 [a]	17 [a]
K_2PtBr_6	244	263	19	82 [b]	94 [b]	12 [b]			
K_2PtI_6	184	185	1						
K_2PdCl_6	357	370	13	*c*			95	115	20
K_2ReCl_6	330	340	10	177	183	6	86	100	14
K_2OsCl_6	329	342	13	178	190	12	85	105	20
K_2IrCl_6	336	345	9	184	192	8	88	105	17

[a] In Fermi resonance; see text. [b] Probably ν_4 and ν_L. [c] Not observed.

TABLE 2

I.r. frequencies/cm^{-1} for some complex hexachlorides of d^0 ions at ambient pressure and at 20 kbar

	ν_3			ν_4			ν_L		
Pressure/kbar	0	20	$\Delta\nu$	0	20	$\Delta\nu$	0	20	$\Delta\nu$
K_2SnCl_6	320	340	20	172	186	14	81	107	26
Rb_2SnCl_6	313	325	12	172	179	7	68	91	23
Cs_2SnCl_6	308	320	12	171	181	10	67	92	25
$(NH_4)_2SnCl_6$	317	325	8	180 [a]	200 [a]	20	125 [a]	132 [a]	7
$(NEt_4)_2SnCl_6$	295	308	13	162	194	32			
Rb_2PbCl_6	281	301	20	140	153	13	60	81	21
$(NH_4)_2PbCl_6$	277	277	0	*b*			*b*		
$(NMe_4)_2PbCl_6$	263	267	4	143	143	0			
$RbTeCl_6$	262	278	16	137	159	22	65	85	20
Cs_2TeCl_6	256	265	9	135	164	29	66	82	16
$(NEt_4)_2CeCl_6$	262	276	14	121	*c*	>20			
$(NEt_4)_2ZrCl_6$	304	312	8	152	170	18	76	84	8
$(NEt_4)_2HfCl_6$	274	285	11	145	*c*	>20			

[a] In Fermi resonance; see text. [b] Very broad envelope; see text. [c] At 20 kbar this band is considerably shifted and broadened.

It is known that the pressure distribution across the anvil faces in a diamond anvil cell is approximately parabolic.[3] A calibration line established by observation of the established phase changes in KCl, KBr, HgI_2, TlBr, AgI, and CuBr was close to the theoretical line for the cell calculated from force/area values, *provided that* the applied pressure was such that the phase change only affected a small area of material at the centre of the field of view. Increasing the applied pressure caused the phase boundary to travel across the entire diamond face. The values which we quote are ' average applied pressure ' figures, *i.e.*, half the pressure at the centre of the diamond faces. It is the average of all the pressure values across the face. We note that Ferraro uses force/area values; [4] his quoted pressures should be divided by two for comparison with ours (1 kbar $\equiv$ 10^8 N m^{-2}).

RESULTS

The data are in Tables 1 and 2. In general a series of spectra at increasing pressure were recorded and showed progressive changes. We list only the shift observed at 20 kbar. After each run pressure on the sample was released and a final spectrum recorded; in every case this was identical with the initial spectrum at ambient pressure. Measurement of the shifts is not always simple. When they are large and the bands are narrow there is no ambiguity as it is then possible to see a small residual band due to material at ambient pressure which has been extruded and is lying on the face of the larger diamond. This residual band is not resolved from that due to material under high pressure when the shifts are small, or when the shifts are large and the bands are broad. In these cases we have measured the band frequency at half height but this certainly leads to an underestimate of the shift. For clearly resolved bands, plots of pressure against frequency are approximately linear.

Alkali-metal Salts.—The three bands in the $[PtCl_6]^{2-}$ series spectra are sharp and shifts can be measured accurately (Figure 1). For M^I = K, Rb, or Cs the pressure-dependences

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[2] J. R. Ferraro, *J. Chem. Phys.*, 1970, **53**, 117.

[3] E. R. Lippincott and H. C. Duecker, *Science*, 1964, **144**, 1119.

[4] C. Postmus, J. R. Ferraro, and S. S. Mitra, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 55.

of ν_4 and ν_L do not differ greatly, and both are considerably larger than that for ν_3. This result, which was substantiated in some tens of experiments for each compound, is at variance with Ferraro's report [2] which shows ν_3 and ν_4 to have similar pressure-dependences. If shifts are expressed as a percentage of the ambient pressure frequency, *viz.* 100 $\Delta\nu/\nu$, then the invariable order of pressure-dependence is $\nu_L > \nu_4 > \nu_3$. Our results for K_2PdCl_6 agree with Ferraro's within experimental error.

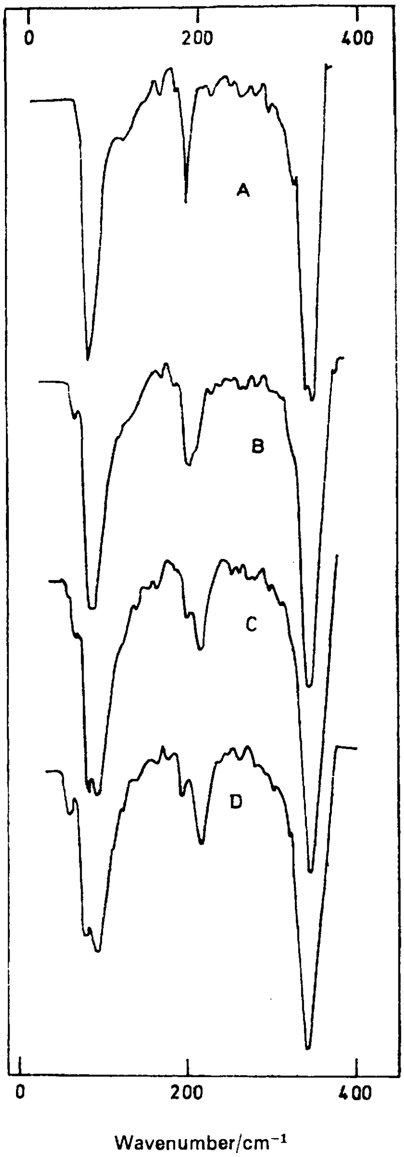

FIGURE 1 Far-i.r. spectra of Cs_2PtCl_6 at high pressures. Where doublets are shown, the lower component is the residual due to material at ambient pressure; A, Ambient pressure; B, 10 kbar; C, 15 kbar; and D, 20 kbar

K_2PtBr_6 and K_2PtI_6 were used to test the idea that the pressure-dependence is simply related to the actual frequency of the internal vibration. ν_3 for the bromide fits this suggestion, being very sensitive in comparison with that of K_2PtCl_6, but ν_3 for K_2PtI_6 showed no significant shift to 20 kbar. Extension of the series along the third-row metals showed that ν_3 and ν_4 for M = Re, Os, and Ir shift roughly equal amounts (although $\Delta\nu$ for $\nu_4 > \nu_3$ when expressed as a percentage), and that ν_L is again the most sensitive mode.

In the hexachlorostannate series with M^I = K, Rb, or Cs ν_L again suffers the greatest shift but for the potassium salt ν_3 is also very sensitive and Rb_2PbCl_6 behaves similarly. In contrast to the hexachloroplatinates, for the hexachlorostannates increasing pressure results in considerable loss of intensity of ν_L relative to ν_3 and ν_4.

Tetraethylammonium Salts.—We have examined four Et_4N^+ salts $[MCl_6]^{2-}$ where M = Zr, Hf, Sn, or Ce. Although ν_3 and ν_4 were readily observed there was little evidence of absorption due to a lattice mode, except for the $[ZrCl_6]^{2-}$ salt which showed a broad and oddly shaped band centred at *ca.* 76 cm^{-1} and which was not very pressure sensitive. Absence of ν_L is probably associated with disorder of cation arrangement, giving a density of states distribution rather than a discrete lattice mode. The significant observation is that ν_4 is exceptionally sensitive; although for the Hf and Ce salts increasing pressure so broadened the band that the shift could not be measured accurately. ν_4 of $(Et_4N)_2[SnCl_6]$ has $d\nu/dP = 1{\cdot}5$, the largest observed in this work.

Ammonium Salts.—In $(NH_4)_2[PtCl_6]$ ν_4 is both abnormally high and exceptionally pressure-sensitive with $d\nu/dP = 1{\cdot}7$, but ν_L is no more sensitive than for the others of this series. This appears to be an example of a Fermi doublet which can be pressure-scanned. ν_4 for $M^I{}_2[PtCl_6]$ salts is relatively insensitive to cation so that an unperturbed value of 185 cm^{-1} is reasonable. Since NH_4^+ is of low mass, ν_L for the compound will be high; indeed its position may be estimated by considering it as a diatomic cubic lattice with frequency $\nu_L = (1/2\pi)\sqrt{(3k/\mu)}$ with the same anion–cation force constant as K_2PtCl_6. This yields ν_L = 130 cm^{-1}, somewhat lower than the true value but clear indication that it is sufficiently close to ν_4 to be in Fermi resonance with it. Thus, under pressure both ν_4 and ν_L will *rise*; if ν_L is more pressure-sensitive than ν_4 the gap between them will start to narrow, only to be widened by more effective Fermi resonance. The same increased resonance will raise ν_4 even more than pressure alone giving it an abnormally high $d\nu/dP$, whilst ν_L has a lower value of $d\nu/dP$ than it would have done in the absence of Fermi resonance because the resonance interaction acts in the opposite sense to the pressure. From the observed frequencies together with the assumed position of ν_4 (185 cm^{-1}) the unperturbed ν_L is found [5] to be 151 cm^{-1}. On the further assumption that ν_4 will have the same pressure-dependence as in K_2PtCl_6, the shifts of ν_4 and ν_L, corrected for Fermi resonance, are 17 and 33 cm^{-1} respectively.

A similar effect is seen in $(NH_4)_2[SnCl_6]$ which also has ν_4 higher than expected by comparison with others of the series. In this case, ν_4 is lower than in the platinum salt and greater resonance interaction with ν_L is expected. The Fermi interaction now almost balances the tendency of pressure to raise ν_L, resulting in a very small shift of only 7 cm^{-1}, and $d\nu/dP = 0{\cdot}35$. ν_4 in $[PbCl_6]^{2-}$ salts is *ca.* 140 cm^{-1}, so close to the ' unperturbed ' value of ν_L in its ammonium salt that there is very strong resonance interaction resulting in a broad absorption envelope in which no detail can be distinguished. The lower-frequency edge is raised by *ca.* 1 cm^{-1} kbar^{-1} but the higher edge is insensitive. It is possible that $\nu_L > \nu_4$ in this case.

Hexachlorotellurates.—The i.r. spectra of $M^I{}_2[TeCl_6]$ salts are known to be odd and this is attributed to the presence of the non-bonding electron pair.[6] ν_3 is abnormally broad [7] and ν_4 is nearly vanishingly weak. Shifts of ν_3 and ν_L for M^I = Rb or Cs are comparable with those for other metals. The surprising observation is that with increase of pressure ν_4 actually *gains* intensity, and then suffers a rather substantial shift (Figure 2).

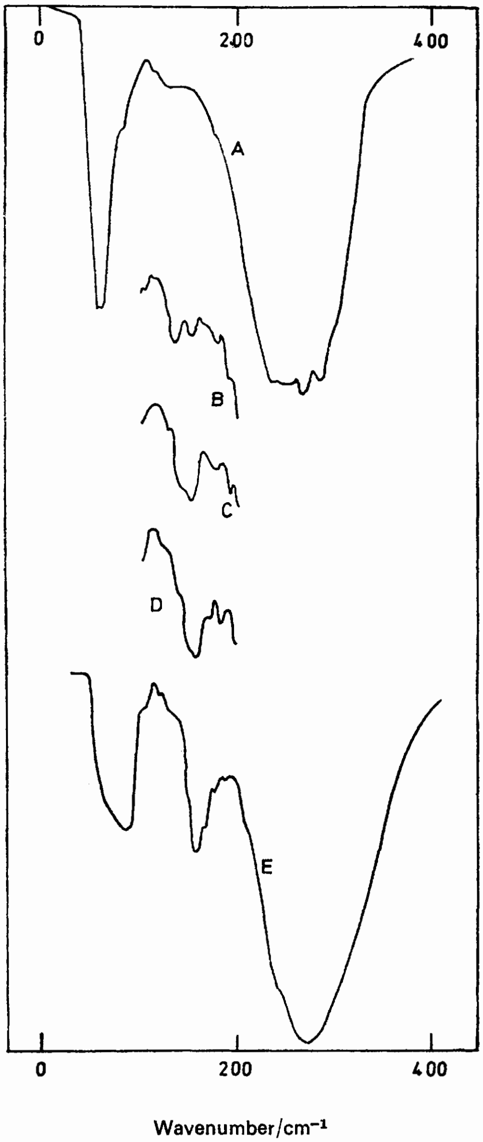

FIGURE 2 Far-i.r. spectra of Rb_2TeCl_6 at ambient pressure and at 20 kbar with (insert) detail of development of intensity in ν_4 with increase of pressure; A, ambient pressure; B, 5 kbar; C, 10 kbar; D, 15 kbar; and E, 20 kbar

DISCUSSION

If pressure-induced shifts of vibrational frequency are expressed as percentages of the unperturbed value then the order of increasing pressure-sensitivity is $\nu_3 < \nu_4 < \nu_L$. Beyond this, no simple relation between shift and chemical composition emerges.

The most dramatic effect noted, the increase of intensity of ν_4 for the hexachlorotellurates, can be accounted for qualitatively as follows. The prime effect of increasing pressure on a material is to compress the energy-level manifold and to alter the relative energies of the levels. Consequently a measure of rehydridisation will result. In the hexachlorotellurates the inert pair is believed to occupy an orbital of spherical symmetry.[8] We suggest that at ambient pressure dynamic rehybridisation accompanies the ν_4 (T_{1u}) bending mode and that this results in the inert pair acquiring some directional character; it is further suggested that the electric moment associated with the semi-directional inert pair is in opposition to that associated with the change of nuclear positions during ν_4, thereby resulting in very low observed intensity. However, with increase of pressure the different relative energy levels now allow a permanent rehybridisation which effectively locks the inert pair in one orientation, although this will not be apparent as a distortion observable by *X*-ray diffraction owing to orientational averaging. In this new configuration the electric moments are no longer opposed and ν_4 develops intensity. In support of this suggestion we note the delicate balance between the development or non-development of directional character throughout the structural chemistry of those elements showing a pronounced inert-pair effect (Pb^{II}, Sn^{II}, Bi^{III}, Te^{IV}). The suggestion that this balance can be affected by the application of pressure seems reasonable.

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[3/1936 *Received*, 20*th September*, 1973]

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[5] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, New York, 1945, p. 215.

[6] J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968, 808; D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), 1967, 2067.

[7] D. M. Adams and M. H. Lloyd, *J. Chem. Soc.* (*A*), 1971, 878.

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