Stretching Vibrations of Planar Di-μ-halogeno-bisdihalogeno-palladate(II) and -platinate(II) Anions

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Raman and i.r. spectra of the anions $[M_2X_6]^{2-}$ (M = Pd or Pt; X = Cl, Br, or I) in solution are reported. Assignments of the stretching vibrations are proposed. The validity of the use of the descriptions 'terminal' and 'bridging' to differentiate vibrations in these and related systems is discussed.

WE have been interested in vibrations of binuclear complexes of platinum(II) and palladium(II) containing halogeno-, methylthio-, and dialkyl sulphido-bridging groups.[1-3] The simplest binuclear complexes of these metals are the halide anions $[M_2X_6]^{2-}$, and although i.r. spectra of their solid tetra-alkylammonium or tetraphenylarsonium salts have been reported[4] their Raman spectra have not. Since vibrations in ring systems have the complication of interdependence of bond length and angle changes, it seemed desirable to obtain more complete vibrational spectra. Compounds of related structure, $[Au_2Cl_6]$[5,6] and I_2Cl_6,[6] have been studied previously but only as solids and there is still some uncertainty about the assignments, even those of the stretching vibrations.

RESULTS

The salts are deeply coloured and this has prevented Raman spectra of the solids being obtained, except for $[Pt_2Cl_6]^{2-}$. In any case, depolarisation ratios provide a strong interpretational advantage when solutions are studied. For the sake of comparability, i.r. data should also be obtained from solutions. For the latter purpose ethanol-free chloroform is the most suitable solvent, but to avoid solvent interference dichloro- and dibromo-methane were also useful for the region of interest here. The $Pr^n{}_4N^+$ salts of these dimeric anions are insoluble in all these solvents. All the $Bu^n{}_4N^+$ salts are soluble in CH_2Cl_2 and CH_2Br_2, the solubility being higher where the anions contain the lighter halides. They do not dissolve significantly in $CHCl_3$ but the chlorides and bromides take up the solvent to form an oil which, unless it is in contact with the chloroform layer, tends to solidify; judging from the platinum(II) chloride system this state at room temperature is approximately $(Bu^n{}_4N)_2[Pt_2Cl_6],12CHCl_3$. The salts are quite soluble in mixtures of dichloromethane and

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chloroform. The salt $(Pn^n_4N)_2[Pd_2Cl_6]$ (Pn = pentyl) is extremely soluble in chloroform but the corresponding bromide behaves similarly to its $Bu^n_4N^+$ counterpart.

TABLE 1

Vibrational assignments (cm^{-1}) of the salts $(R_4N)_2[M_2X_6]$ (M = Pd or Pt; X = Cl, Br, or I) below 360 cm^{-1}

	$(Pn^n_4N)_2[Pd_2Cl_6]$		$(Pn^n_4N)_2[Pd_2Br_6]$		$(Bu^n_4N)_2[Pd_2I_6]$		$(Bu^n_4N)_2[Pt_2Cl_6]$		$(Bu^nN)_2[Pt_2Br_6]$		$(Pn^n_4N)_2[Pt_2I_6]$	
		Raman		Raman ^{a}		Raman ^{a}	Raman (solid)	Raman		Raman ^{b}		Raman ^{a}
A_g ν_1 MX str.		346(10) 0·1 ^{c}		262(2) 0·1		219(1) (p)	344vs	349(10) 0·1 ^{c}		241(5) 0·1		196(1) 0·5
ν_2 MX str.		302(10) 0·1 ^{c}		194(10) 0·1		143(10 (p)	319wm	316(4) 0·2 ^{c}		211(10) 0·1		160(10) 0·1
ν_3 in-plane def.		169(2) 0·2 ^{c}		115(4) 0·1				162(4) 0·4 ^{c}		116(2) 0·1		93(3) 0·1
ν_4 in-plane def.		119(7) 0·5 ^{c}		83(sh)				108(4) 0·4 ^{c}		84(sh)		*ca.* 60(sh)
B_{1g} ν_6 MX str.		328(2) (dp) ^{c}		253(0) (dp)			336m(sh)	333(1) (dp) ^{c}		238(2) (dp)		196(1)
ν_7 MX str.		265(2) (dp) ^{d}		173(3) (dp)		*ca.* 130(sh) (dp)	298wm	294(0?) ^{d}		193(6) (dp)		145(7) (dp)
Other bands		219(1) ^{e} (p) ^{c}		230(0) ^{e} (p) 218(0) ^{e} (p)			252m ^{e}					225(0) ^{e} (p) 219(0) ^{e} (p) 112(0) (p)
Lower limit		(90)		(65)		(115)	(180)	(90)		(75)		(55)
	I.r. (mull)	I.r.	I.r. (mull)	I.r.	I.r. (mull)	I.r.^{a}	I.r. (mull)	I.r.	I.r. (mull)	I.r.	I.r. (mull)	I.r.^{b}
B_{1u} ν_9 out-of plane def.	152m	156(1) ^{c}	113w	113(½) ^{b}	91w		157m 150m	158(1) ^{b}	107w			
B_{2u} ν_{12} MX str.	336vs	335(10) ^{d}	257vs	257(10) ^{a}	214vs	218(10)	330(sh)	330(sh) ^{a}	235vs	236(10) ^{d}	197s	196(10)
ν_{13} MX str.		262(sh) ^{d}	179w	178(0) ^{b}	133m		303wm (sh)	300(sh) ^{d}	188(sh)	192(0) ^{a}	148w	147(1)
B_{3u} ν_{16} MX str.	347(sh)	343(10) ^{d}	266s	264(8) ^{a}	220s	218(10)	338vs	341(10) ^{a}	238(sh)	239(sh) ^{d}	197s	196(10)
ν_{17} MX str.	301wm	297(2) ^{d}	193w	192(0) ^{b}	143m	140(sh)	316s	312(5) ^{a}	210w	210(0) ^{a}	157m	157(3)
Other bands	326(sh) *ca.* 162(sh) (?) 123vvw $<$50m, bd	*ca.* 166(sh) ^{c} 126(0) ^{e}			*ca.* 45bd		103m, bd *ca.* 61w, bd		116vvw 80w, bd 47wm, bd			
Lower limit	(50)	(80)	(50)	(90)	(40)	(130)	(40)	(120)	(40)	(130)	(50)	(90)

Semi-quantitative Raman peak heights are the sum of those observed from the two polarisation conditions relative to the strongest band = 10. Depolarisation ratios are given after intensities of most of the polarised bands (±0·05); dp = depolarised, p = polarised.

^{a} In CH_2Cl_2. ^{b} In CH_2Cl_2–$CHCl_3$. ^{c} In $CHCl_3$. ^{d} In CH_2Br_2. ^{e} Cation bands.

By using small-diameter cells, optimising the concentration, and using near-i.r. excitation where necessary, Raman spectra of all six anions were obtained. Only for the most deeply coloured, $[Pd_2I_6]^{2-}$, was the quality poor and even for this some of the stretching vibrations were located against the rising background of the solvent. The results are given in Table 1, together with i.r. spectra of the salts in solution and as mulls. In addition, i.r. spectra of mulls of the $Pr^n_4N^+$ salts and those $Bu^n_4N^+$ salts not reported in Table 1 were determined; these are not listed, but any band which did not show clear agreement between the different salts studied {*e.g.* the 103 cm^{-1} band of $(Bu^n_4N)_2[Pt_2Cl_6]$} has not been assigned specifically.

For a D_{2h} ion $[M_2X_6]^{2-}$, the two A_g and two B_{1g} stretching vibrations are Raman active whilst the two B_{2u} and two B_{3u} modes are i.r. active. The two vibrations of each symmetry species have previously been distinguished as 'terminal' and 'bridging' with the former having the higher frequency in each case. Such modes are depicted in Figure 1. The A_g modes differ from their B_{3u} counterparts only in the relative phase of motions about the two metal atoms and the same is true of B_{1g} and B_{3u}. For the bromo-anions a strong polarised Raman band above 240 cm^{-1}, which must be ν_1, revealed the related B_{1g} mode, ν_6, under the perpendicular polarisation condition. Two further Raman bonds separated by nearly 20 cm^{-1} were observed between 220 and 170 cm^{-1}, the higher-wavenumber one being polarised. In contrast to the assignment of A_g and B_{1g} modes, there is no absolute way of distinguishing between i.r.-active B_{2u} and B_{3u} species (the choice of Adams *et al.*[4] was presumably arbitrary). However, it is reasonable to assign them in the same order as their Raman-active counterparts when related pairs of vibrations are always within a few cm^{-1} of each other. The assignment is least certain for ν_{12} and ν_{16} of the ion $[Pt_2Br_6]^{2-}$, where the frequency separation is rather small.

For the chloride complexes, the four Raman bands were identified despite increased overlapping caused by the greater width of the bands. In the i.r. spectra, the lowest-energy stretching mode, ν_{13}, was at best observed as a weak shoulder and its position is not as accurately determined as that of other bands; the same applies to ν_{12} of the ion $[Pt_2Cl_6]^{2-}$.

Two bands were clearly located in the 130—160 cm^{-1} range for the iodide complexes. Only one band was found at higher wavenumbers and this was coincident between i.r.

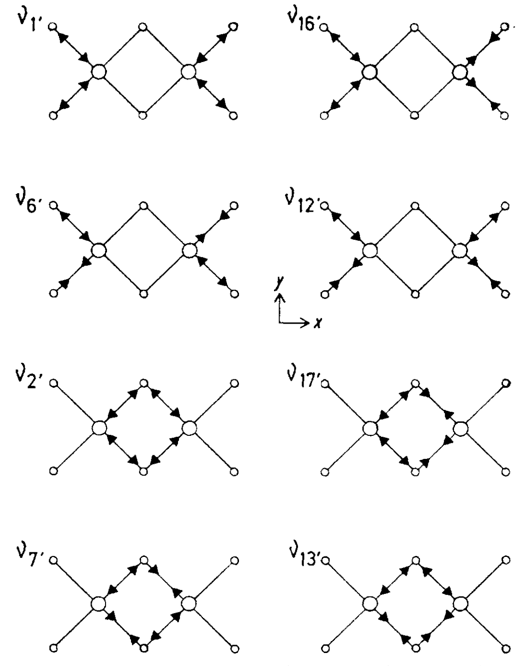

FIGURE 1 Representation of 'terminal' and 'bridging' bond-stretching vibrations of $[M_2X_6]^{2-}$ ions

and Raman spectra {no feature was observed corresponding to the strong i.r. absorption at 179 cm^{-1} reported by Adams *et al.*[4] for $(Et_4N)_2[Pt_2I_6]$}. It must be presumed that ν_1, ν_6, ν_{12}, and ν_{16} are coincident and it is noteworthy that in the ion $[Pt_2I_6]^{2-}$ the depolarisation ratio of the 196 cm^{-1} band was higher than that of ν_1 in the other species where ν_1 and ν_6 are not coincident.

In the deformation region, Raman spectra of the chloro-complexes showed two polarised bands clearly arising from the totally symmetric in-plane modes ν_3 and ν_4. For the bromides and $[Pt_2I_6]^{2-}$, the band corresponding to the higher wavenumber of these modes was clearly located and a lower-frequency shoulder was also indicated. In the main, only one i.r. feature clearly arising from a deformation mode of the anion was found. To judge from i.r. intensities of deformations of the ions $[MX_4]^{2-}$, the main contribution must arise from an out-of-plane mode[7] (B_{1u}, ν_9). The in-plane deformation (B_{3u}, ν_{18}) related to the Raman-active ν_3 probably has similar energy and may account for the weak feature sometimes observed near ν_9. Many of the bands assigned as deformations by Adams *et al.*[4] did not have counterparts in the present spectra.

DISCUSSION

Vibrational spectra of bridged complexes have commonly been discussed in terms of separate consideration of bridging and terminal bonds.[1,4,6] If, however, energies of stretching vibrations in planar $[M_2Br_6]^{2-}$ and $[MBr_4]^{2-}$ ions are compared, very close wavenumber correspondence is evident between what have been called ' bridging modes ' of the former[4] and A_{1g} and B_{1g} modes of the latter; ' terminal modes ' of $[M_2Br_6]^{2-}$ are just marginally higher than E_u modes of $[MBr_4]^{2-}$. This suggests alternative forms of the vibrations (Figure 2) which have equal contributions from terminal and bridging bonds and in which motions around any particular metal atom clearly resemble the normal modes of the ions $[MBr_4]^{2-}$. Observed intensities fit the latter descriptions. Raman-active vibrations of $[M_2Br_6]^{2-}$ ions related to Raman-active A_{1g} and B_{1g} vibrations of $[MBr_4]^{2-}$ are strong whilst their i.r. counterparts are weak, and the reverse is true of vibrations related to the i.r.-active E_u mode of $[MBr_4]^{2-}$. The situation does not seem to differ very greatly from those cases where an inactive mode of a free ion is rendered active by environmental effects, *e.g.* the observation of ν_1 of NO_3^- in the i.r. spectrum of solid KNO_3[8] or perturbation of spectra of $[GaBr_4]^-$ by R_3NH^+ ions in halogenated hydrocarbon solvents.[9] These relations between frequencies and intensities of monomeric and dimeric anions also apply to $[Pt_2I_6]^{2-}$ and $[PtI_4]^{2-}$, and $[Pd_2I_6]^{2-}$ has the same intensity distribution as $[Pt_2I_6]^{2-}$ (spectra of $[PdI_4]^{2-}$ could not be obtained). In a study of $[M_2X_6]^{2-}$ ions based on i.r.-active stretching frequencies, Adams *et al.*[4] found only very slight differences between bridging and terminal stretching force constants when X = Br and no difference for M = Pt, X = I, but they comment that terminal-bridge coupling is not important in the platinum case although it probably is in the palladium case. The present spectra do not give any reason to disagree with the implications of the force-constant conclusions, but the spectra strongly suggest that symmetry of vibrational movement all round the metal atom is more important than any distinction between terminal and bridging bonds for both palladium and platinum.

The chloride complexes present a somewhat different picture. In particular, the highest-shift Raman line (A_g) is now the most intense, ν_{17} has much greater i.r. intensity than in the bromo- or iodo-anions, and the lowest stretching frequencies occur below those of $[MCl_4]^{2-}$ in contrast to the bromo-anions. Such features might be expected of a species approximating more to the terminal–bridging description (Figure 1) and it is believed that there is more distinction between terminal and bridging bonds in the chloride dimers, as reflected in calculations of Adams *et al.*[4] Comparison between $[AuCl_4]^-$ and various assignments proposed for $[Au_2Cl_6]$[6,10,11] provide an even more extreme example of the behaviour exhibited by platinum(II) and palladium(II) chloride anions.

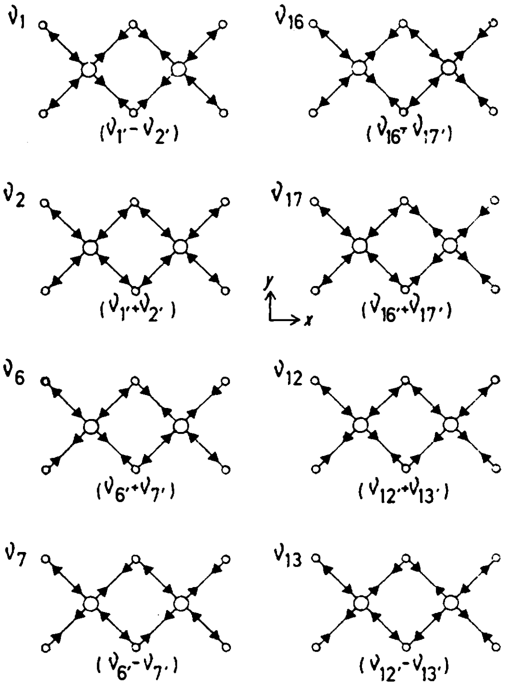

FIGURE 2 Representation of fully mixed terminal and bridging bond-stretching vibrations of $[M_2X_6]^{2-}$ ions (and relation to Figure 1)

Comparison of spectra of tetrahedrally co-ordinated dimers with their monomeric counterparts {*e.g.* $[Ga_2I_6]$[12] and $[GaI_4]^-$ (ref. 13)} suggests that descriptions related to those of Figure 2 may be as equally valid as terminal-bridging descriptions previously used for these vibrations. The descriptions ' terminal MX stretch ' and ' bridging MX (*trans* to X) stretch ' which were used[14] for *trans*-$[M_2X_4(L)_2]$ can, in a like manner, be reformulated as

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asymmetric and symmetric vibrations of the *trans*-$\mathrm{MX_2}$ group. Frequencies observed for the bromo- and iodo-complexes correlate well with those of the *trans*-$\mathrm{MX_2}$ unit in $[\mathrm{MX_3(L)}]^-$ or *trans*-$[\mathrm{MX_2(L)_2}]$, and bands related to the symmetric $\mathrm{MX_2}$ stretch [otherwise termed bridging MX (*trans* to X) stretches] are much more prominent in the Raman than the i.r. spectra. Again more deviation is shown by the chlorides.

It is interesting that the more closely spectra of the ions $[\mathrm{M_2X_6}]^{2-}$ resemble those of $[\mathrm{MX_4}]^{2-}$ the more difficult it becomes to obtain salts $(\mathrm{R_4N})_2[\mathrm{MX_4}]$,[7] further suggesting little difference in bond strength between terminal and bridging bonds in the iodides and bromides.

TABLE 2

Characterisation of salts

	Colour	M.p. (t/°C)	Analysis (%) [a] C	H	N
$(\mathrm{Bu^n_4N})_2[\mathrm{Pt_2Cl_6}]$	Pink-red	95—96	33·5 (33·35)	6·85 (6·65)	2·5 (2·6)
$(\mathrm{Bu^n_4N})_2[\mathrm{Pt_2Br_6}]$	Dark green	138—139	28·6 (28·35)	5·6 (5·35)	2·05 (2·05)
$(\mathrm{Pn^n_4N})_2[\mathrm{Pt_2I_6}]$	Green-black	78—82	27·3 (27·45)	5·0 (5·05)	1·7 (1·6)
$(\mathrm{Pn^n_4N})_2[\mathrm{Pd_2Cl_6}]$	Red-brown	79—80	46·65 (47·0)	8·4 (8·65)	2·75 (2·75)
$(\mathrm{Pn^n_4N})_2[\mathrm{Pd_2Br_6}]$	Deep red	101—102	37·1 (37·25)	7·0 (6·9)	2·15 (2·15)
$(\mathrm{Bu^n_4N})_2[\mathrm{Pd_2I_6}]$	Red-black	173—176	26·85 (26·35)	4·35 (4·95)	1·9 (1·9)

[a] Calculated values in parentheses.

EXPERIMENTAL

I.r. spectra were obtained as reported previously.[14] Raman spectra were excited with a Coherent Radiation Laboratories model 52G krypton-ion laser operating at 647·1 nm or, with special i.r. reflectors, at 676·4, 752·5, or 799·3 nm, and were recorded with a Coderg PHO spectrometer. The wavenumber accuracy of the results is $\pm 1\ \mathrm{cm^{-1}}$.

Preparation of the Salts.—The salts $(\mathrm{Bu^n_4N})_2[\mathrm{Pt_2X_6}]$ (X = Cl or Br) were prepared by methods similar to those reported for the $\mathrm{Pr^n_4N^+}$ salts,[15] but were recrystallised from acetone by addition of diethyl ether. In some preparations of the chloride it was found that decomposition to platinum occurred, but this was avoided by adding a few drops of hydrochloric acid to the aqueous reaction medium. The salts $(\mathrm{Pn^n_4N})_2[\mathrm{Pd_2X_6}]$ (X = Cl or Br) precipitated when aqueous $\mathrm{Pn^n_4NX}$ was added to aqueous $[\mathrm{PdX_4}]^{2-}$ and were recrystallised by adding diethyl ether to a dried dichloromethane solution of the salts followed by cooling in a refrigerator; in the case of X = Cl there is a tendency for the salt to separate as an oil. The salts $(\mathrm{Bu^n_4N})_2[\mathrm{Pd_2I_6}]$ and $(\mathrm{Pn^n_4N})_2[\mathrm{Pt_2I_6}]$ were precipitated from aqueous solutions of $[\mathrm{MCl_4}]^{2-}$ and excess of KI by slow addition of warm saturated aqueous solutions of $\mathrm{R_4NI}$; the complexes were recrystallised from dichloromethane by addition of diethyl ether. Analytical data are listed in Table 2.

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