Vibrational Spectra of Square-planar Tetrahalogeno-gold(III), -palladium(II), and -platinum(II) Anions in Solution

By **Peter L. Goggin,*** Inorganic Chemistry Department, The University, Bristol BS8 1TS
Janos Mink, Institute of Isotopes, The Hungarian Academy of Sciences, Budapest, Hungary

I.r. and Raman spectra of the salts $R_4N[AuX_4]$ [R = Bu^n or Pn^n(n-pentyl), X = Cl or Br] and $(R_4N)_2[MX_4]$ (R = Bu^n or Pn^n; M = Pd, X = Cl; M = Pt, X = Cl or Br) in solution are reported, together with the i.r. spectrum of a solid containing $(Bu^n_4N)_2[PdBr_4]$ and Raman spectra of aqueous solutions containing the above anions and $[PtI_4]^{2-}$. Studies of the solvent dependence of the Raman frequencies of $[AuCl_4]^-$ and the cation dependence of vibrational frequencies of solid $R_4N[AuCl_4]$ (R = Me, Et, Pr^n, Bu^n, or Pn^n) have also been made. The inactive B_{2u} mode has been deduced as 112 cm^{-1} from a study of the combination bands of solid $Cs[AuCl_4]$. The most consistent sets of vibrational frequencies have been used to recalculate force constants.

THERE have been a number of investigations of vibrational spectra of square-planar anions $[MX_4]^{n-}$ (M = Pd, Pt, or Au; X = Cl, Br, or I; n = 1 or 2).[1-8] Because all the work has been with alkali-metal or ammonium salts, i.r. spectra were only measured for solids. This also applies to Raman results,[6] except that spectra of aqueous solutions of the ions $[AuCl_4]^-$, $[AuBr_4]^-$, $[PtCl_4]^{2-}$, and $[PtBr_4]^{2-}$ have been reported.[1,7] Vibrational energies of solid salts of these ions show a marked dependence on the cation [3-5] and (for $K_2[PtCl_4]$) differ from those for aqueous solution,[7] which suggests that they do not correspond well with the frequencies of the 'free ion.' Because these anions are important reference points for the study of vibrational spectra of square-planar complexes in general, we regarded it as important to obtain i.r. and Raman results free from the complications of the solid state. Here we present studies which lead to the best-obtainable set of vibrational energies which we have then used to calculate a revised set of force constants.

RESULTS

Regarding the MX bonds as defining the x and y axes, vibrations of the ions $[MX_4]^{n-}$ are: (Raman active) A_{1g} (stretching, ν_1), B_{1g} (stretching, ν_3), B_{2g} (in-plane deformation, ν_4); (i.r. active) E_u (stretching, ν_6), E_u (in-plane deformation, ν_7), A_{2u} (out-of-plane deformation, ν_2); and (inactive) B_{2u} (out-of-plane deformation, ν_5).

Raman Spectra of Aqueous Solutions (*Table* 1).—We have remeasured spectra of aqueous $K_2[PtCl_4]$, $Na[AuCl_4]$, and $K[AuBr_4]$ and in the case of the first two salts notice slight differences from previous reports.[1,7] In contrast to the previous study,[7] we observed all three fundamentals of the ion $[PtBr_4]^{2-}$. The anion $[PtI_4]^{2-}$ was prepared *in situ* by addition of excess of NaI to aqueous $K_2[PtCl_4]$. Weak features extra to those expected for $[PtI_4]^{2-}$ were observed, but as none correspond to PtCl stretching vibrations or to intense bands of the ion $[Pt_2I_6]^{2-}$,[9] we are confident that the spectrum reported is correctly assigned. The spectrum of commercially obtained $Na_2[PdCl_4]$ in water is not solely that of the ion $[PdCl_4]^{2-}$ since two polarised bands at 303vs and 335m cm^{-1} were observed. Addition of a few drops of concentrated hydrochloric acid eliminated the higher-frequency band to leave the three bands expected for the ion $[PdCl_4]^{2-}$; a similar situation arises with $K_2[PdBr_4]$. When excess of NaI was added to aqueous $Na_2[PdCl_4]$, a black deposit slowly formed and ultimately most of the colour disappeared from the solution; thus no spectrum of $[PdI_4]^{2-}$ could be obtained, if indeed such a species is ever formed in solution.

TABLE 1

Raman shifts (cm^{-1}) of planar $[MX_4]^{n-}$ ions in aqueous media *

	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$
ν_1 A_{1g}	330(10) 0·1	208(10) 0·15	155(10) 0·15
ν_3 B_{1g}	312(2) (dp)	194(4) (dp)	142(5) (dp)
ν_4 B_{2g}	171(2) (dp)	106(2) (dp)	85(2) (dp)
Others			132(2) 108(0)

	$[PdCl_4]^{2-}$	$[PdBr_4]^{2-}$	$[AuCl_4]^-$	$[AuBr_4]^-$
ν_1 A_{1g}	303(10) 0·1	188(10) 0·1	348(10) 0·1	215(10) 0·1
ν_3 B_{1g}	275(1) (dp)	172(2) (dp)	325(4) (dp)	197(4) (dp)
ν_4 B_{2g}	164(1) (dp)	102(1) (dp)	172(2) (dp)	104(2) (dp)

* Peak heights, relative to ν_1 = 10, are given in parentheses after the wavenumbers and are for total height scattered (= sum under the two polarisation conditions). Depolarisation ratios (±0·05) are given after the intensities, dp = depolarised (0·75).

Vibrational Spectra of $(R_4N)_n[MX_4]$.—One reason why so little far-i.r. solution data (particularly below 200 cm^{-1}) has been published for ionic species is that there are very few solvents suitable for the purpose. By using cations with very long alkyl chains Kelly and Good [10] obtained results for benzene solutions of species produced *in situ*. Cations with shorter alkyl chains make the isolation of pure solids much easier and the most suitable solvent in these cases is ethanol-free chloroform. (The Figure shows far-i.r. spectra of a number of solvents.) Adequate solubility was obtained by using $Bu^n_4N^+$ and $Pn^n_4N^+$ counter-ions for $[MX_4]^{2-}$ and $[AuX_4]^-$ respectively and this allowed a satisfactory study of $[PtCl_4]^{2-}$, $[PtBr_4]^{2-}$, $[PdCl_4]^{2-}$, $[AuCl_4]^-$, and $[AuBr_4]^-$.

When the salt $(Bu^n_4N)_2[Pd_2Br_6]$ was fused with a slight excess of Bu^n_4NBr and allowed to resolidify the i.r. spectrum was changed, stretching bands associated with $[Pd_2Br_6]^{2-}$ having disappeared and been replaced by a single stretching band at 243 cm^{-1} consistent with formation of $[PdBr_4]^{2-}$.

---

[1] H. Stammreich and R. Forneris, *Spectrochim. Acta*, 1960, **16**, 363.

[2] A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, 1964, **3**, 1775.

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

[4] J. Hiraishi and T. Shimanouchi, *Spectrochim. Acta*, 1966, **22**, 1483.

[5] C. H. Perry, D. P. Athans, E. F. Young, J. R. Durig, and B. R. Mitchell, *Spectrochim. Acta*, 1967, **A23**, 1137.

[6] P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1298.

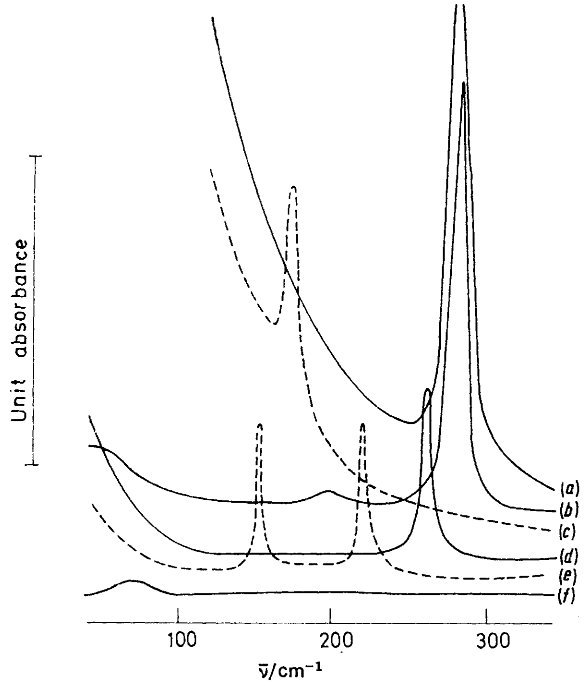
[7] P. J. Hendra, *Spectrochim. Acta*, 1967, **A23**, 2871.

[8] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1969, 2998.

[9] P. L. Goggin, following paper.

[10] D. A. Kelly and M. L. Good, *Spectrochim. Acta*, 1972, **A28**, 1529.

However, in organic solvents spectra showed that the reaction was reversed, so our observations on this complex were confined to the solid state. To assess how closely frequencies from this solid can be regarded as a reasonable approximation to solution values we made a corresponding platinum bromide phase and no i.r. feature of this solid differed by more than 2 cm^{-1} from those of authentic $(Bu^n{}_4N)_2[PtBr_4]$ in solution. Fusion of salts $(Bu^n{}_4N)_2[M_2I_6]$ with $Bu^n{}_4NI$ did not result in bridge rupture. The observations and assignments are collected together in Table 2. In a number of cases, to avoid masking of vibrations of the anion, it was necessary to use more than one solvent and elsewhere it proved more convenient to do so. To assess the validity of accepting data from different solvents we measured Raman spectra for the ion $[AuCl_4]^-$ in $CHCl_3$, CH_2Br_2, CH_2Cl_2, and Me_2CO. The frequencies in $CHCl_3$ were practically identical with those in water, and over the range of solvents the total wavenumber spreads were (A_{1g}) 1·7, (B_{1g}) 0·9, and (B_{2g}) 3·6 cm^{-1}.



I.r. spectra (absorbance, 0·5 mm thickness) of (*a*) dichloromethane, (*b*) thionyl chloride, (*c*) dibromomethane, (*d*) chloroform (ethanol-free), (*e*) bromoform, and (*f*) benzene

The only aspect of assignment which requires comment concerns ν_2 and ν_7. Adams and Newton[8] have shown unambiguously from single-crystal studies that for the salt $K_2[PtCl_4]$ ν_2 is at lower energy. For all these complex anions, two bands are observed in the appropriate range. In the solid R_4N^+ ($R = Bu^n$ or Pn^n) salts, and in solution, the higher-wavenumber mode is much less intense and in one case it is split into two components in the solid, perhaps further indicating its doubly degenerate nature. We regard intensity criteria as a reliable guide for this assignment. In the case of the ion $[AuBr_4]^-$, ν_7 was observed as a distinct shoulder to high wavenumber of ν_2, but in $[PtBr_4]^{2-}$ it was less pronounced and in solution was a mere broadening on the high-wavenumber side. The solid phase containing $[PdBr_4]^{2-}$ had the less-intense band at lower energy than the stronger one; it appears to be the only example of ν_7 being lower than ν_2.

It would be helpful (*e.g.* for cases like $[PdBr_4]^{2-}$ above) if above a particular size of cation, solid-state frequencies could be regarded as a reliable indication of ' free-ion ' frequencies (the cation effectively providing a solution environment). We studied a series of $R_4N[AuCl_4]$ salts in the solid state and the results are listed in Table 3 together with those for $Cs[AuCl_4]$. For the R_4N^+ salts, there was no regular frequency dependence on alkyl chain length, but frequencies observed for such solids were generally closer to solution values than are those of alkali-metal salts. The results for solid $Pr^n{}_4N$ and $Bu^n{}_4N$ salts approximate quite well to spectra of their solutions.

The Inactive Fundamental, B_{2u} (ν_5).—It is, in principle, possible to deduce the energy of the ν_5,B_{2u} mode from a study of overtones or combinations and this should be easiest for the ion $[AuCl_4]^-$ which has the widest wavenumber spread in the observed fundamentals. We were unable to detect any such features in the Raman spectrum of a concentrated solution of $Na[AuCl_4]$ because, on increasing amplification, wings of the intense fundamental bands swamped the region of interest before any new features could be observed. The i.r. spectrum should only allow observation of one binary combination involving ν_5 ($\nu_5,B_{2u} + \nu_3,B_{1g} = A_{2u}$), and since calculations suggest that ν_5 should be the lowest-energy deformation mode this combination falls in a region which should be free from confusion with any other binary transition. An ordinate-expanded spectrum of a very thick mull of $Cs[AuCl_4]$ showed a number of weak broad features in the 400—700 cm^{-1} region, namely {in cm^{-1} (approximate relative intensity) [possible assignments]}: 675(10) [$\nu_6,E_u + \nu_3,B_{1g} = 677$]; 535(10) [$\nu_6,E_u + \nu_4,B_{2g} = 533$; $\nu_7,E_u + \nu_1,A_{1g} = 517, 528$]; 500(2) [$\nu_7,E_u + \nu_3,B_{1g} = 489, 500$; $\nu_2,A_{1u} + \nu_1,A_{1g} = 503$]; and 435(1) [$\nu_5,B_{2u} + \nu_3,B_{1g}$]. The last value leads to an ' energy ' of 112 cm^{-1} for B_{2u}.

Attempts to obtain additional confirmation of the above from tetra-alkylammonium salts were unsuccessful because bands due to the cations tended to dominate the region of interest at the sample thickness necessary for these studies. Other species for which the $B_{2u} + B_{1g}$ combination should be sufficiently above ν_6 for detection are caesium salts of $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$. In samples of these we found an exceedingly broad band at *ca.* 370 cm^{-1} of uncertain origin which prevented the desired observations. (We were also unable to overcome a slight Christiansen-filter problem in thick mulls of these two salts.)

Force-constant Calculations.—Necessarily, even the more extensive of the previous force-field studies on these square-planar anions have relied on solid-state data for alkali-metal salts[6,11] or on a combination of the same solid-state i.r. and aqueous-solution Raman data.[4] Because our observed frequencies differed markedly from those used previously, we have re-examined the force-field problem.

The internal co-ordinates we used were: *r*, MX bond; α, XMX in-plane angle; and β, XMX out-of-plane angle. The *G*-matrix calculation and force-constant refinement procedure used programs previously described.[12,13] The

---

[11] M. Tranquille and M. T. Forel, *J. Chim. phys.*, 1971, **68**, 471.

[12] J. Mink, L. M. Mink, and Yu A. Pentin, *Zhur. priklad. Spektroskopii*, 1968, **9**, 129.

[13] J. Mink, L. M. Mink, and Yu A. Pentin, *Vestnik Moscov. Univ.*, 1971, **3**, 285.

valence force constants used were: f_r, bond stretching; f_{rr}, stretch–stretch (*cis*-bonds) interaction; $f_{rr'}$, stretch–stretch (*trans*-bonds) interaction; f_α, in-plane bending; $f_{r\alpha}$, stretch–bend (adjacent in-plane angle) interaction; $f_{\alpha r'}$, stretch–bend (non-adjacent in-plane angle) interaction; $f_{\alpha\alpha}$, bend–bend (adjacent in-plane angles) interaction; $f_{\alpha\alpha'}$, bend–bend (non-adjacent in-plane angles) interaction; f_β, out-of-plane bending; and $f_{\beta\beta}$, bend–bend (out-of-plane angles) interaction. Where possible, the frequencies used were solution values from Table 2. For $[PdBr_4]^{2-}$, aqueous-solution Raman data and i.r. data from solid '$(Bu^n{}_4N)_2[PdBr_4]$' were employed. For $[PtI_4]^{2-}$, aqueous-solution Raman data and the i.r. frequency ν_6 of solid [6] $K_2[PtI_4]$ were used and, because of the similarity in energy of ν_2, ν_4, and ν_7 in the bromides, we assumed ν_2 and ν_7 to be the same as ν_4.

TABLE 2

Vibrational fundamentals (cm^{-1}) of $[MX_4]^{n-}$ as tetra-alkylammonium salts

	$(Bu^n{}_4N)_2[PdCl_4]$	$(Bu^n{}_4N)_2[PdBr_4]$	$(Bu^n{}_4N)_2[PtCl_4]$	$(Bu^n{}_4N)_2[PtBr_4]$	$(Pn^n{}_4N)[AuCl_4]$ Raman		$(Pn^n{}_4N)[AuBr_4]$ Raman	
	Raman		Raman [a]	Raman [a]	(solid)	*a*	(solid)	*a*
ν_1 A_{1g}	300(10) 0·1 [a]		328(10) 0·1	205(10) 0·1	345vs	349(10) 0·1	213vs	214(10) 0·1
ν_3 B_{1g}	270(1) (dp) [b]		305(3) (dp)	192(5) (dp)	322s	325(3) (dp)	195vs	196(3) (dp)
ν_4 B_{2g}	176(3) (dp) [a]		173(4) (dp)	113(3) (dp)	175s	172(3) (dp)	110ms	106(2) (dp)
Other bands					356w(sh) 215w, bd			
Lower limit	(100)		(90)	(80)	(55)	(70)	(70)	(80)

	$(Bu^n{}_4N)_2[PdCl_4]$ I.r. (mull)	*a*	$(Bu^n{}_4N)_2[PdBr_4]$ I.r. (mull)	$(Bu^n{}_4N)_2[PtCl_4]$ I.r. (mull)	*a*	$(Bu^n{}_4N)_2[PtBr_4]$ I.r. (mull)	*a*	$(Pn^n{}_4N)[AuCl_4]$ I.r. (mull)		$(Pn^n{}_4N)[AuBr_4]$ I.r. (mull)	*a*
ν_6 E_u	317vs	321(10)	243vs	325m 309vvs	313(10)	225vvs	227(10)	356vs	361(10) [c]	250vs	252(10)
ν_7 E_u	167w(sh)	*ca.* 161(sh)	104w	167w	165(0)	112(sh)	*ca.* 112(sh)	170w	166(0) [a]	108vw	106(1)
ν_2 A_{2u}	150m	150(1)	114wm	147m	147(1)	104ms	105(1)	141s	142(3) [a]	99m	99(2)
Other bands	75wm, bd		65wm, bd			201vvw 88m		77m		76m	
Lower limit	(50)	(110)	(50)	(40)	(80)	(40)	(80)	(40)	(70)	(40)	(70)

Raman peak heights are the sum of those observed under the two polarisation conditions. Solutions in *a* chloroform, *b* acetone, and *c* dichloromethane.

TABLE 3

Cation dependence of solid-state vibrational spectra of tetrachloroaurate(III) salts (below 400 cm^{-1})

I.r.	Cs^+	Me_4N^+	Et_4N^+	$Pr^n{}_4N^+$	$Bu^n{}_4N^+$	$Pn^n{}_4N^+$
ν_6 E_u		*ca.* 362(sh)			*ca.* 361(sh)	
	354vs	356·5vs	357·5vs	360vs	358vs	356vs
ν_7 E_u	177w	174w	173w	170w	167w	170w
	166w		166w			
ν_2 A_{2u}	152m	147s	149s	141s	143s	141s
Lattice and other bands		80s	96w	128w	107w, bd	77m
		66s	75w	61s	76w	
		319vw	*ca.* 56ms	326vvw	69w	
Limit of study	(80)	(40)	(40)	(40)	(40)	(40)
Raman						
ν_1 A_{1g}	351vs	352·4vs	350·2vs	350·1vs	348·0vs	345·2vs
ν_3 B_{1g}	323s	322·7s	325·9s	325·6s	324·7s	321·6s
ν_4 B_{2g}	179s	171·4s	172·4m	173·7s	168·2s	174·8s
			168·3m(sh)			
Lattice and other bands		*ca.* 56w(sh)	88m, bd	84w(sh)	362·0wm	356w(sh)
		34·9s	58·5m	305·9w	*ca.* 256vw, bd	218w, bd
		ca. 371w(sh)	42·4ms		*ca.* 154vw	
			358wm(sh)			
Limit of study	(90)	(14)	(30)	(60)	(60)	(55)

For in-plane modes, the F matrix (in symmetry-coordinate representation) has, after the necessary removal of redundant contributions, six different entries to be determined. F_{11}, F_{33}, and F_{44} are readily obtained from the relation $F_{ii} = \lambda_{exp}/G_{ii}$, but F_{66}, F_{67}, and F_{77} are interdependent and, because there are only five observable in-plane frequencies, the problem cannot be solved without further assumptions. Recently Tranquille and Forel [11] applied Torkington's method [14] of constructing ellipses relating to diagonal and off-diagonal terms. They used a plot of F_{77} against F_{67} to find the minimum value of the former which they then accepted as its correct value. It is not certain that this leads to appropriate values for these two force constants [15] but it does at least lay down a criterion for comparability between different studies; it is also worth noting that a ±50% change in F_{67} from the value corresponding to the minimum value of F_{77} has only a 4% effect on F_{77} in the most variable of the examples studied here. These assumptions allowed us to evaluate stretching and stretch–stretch interaction valence force constants explicitly.

Since we had only one experimental frequency to determine two out-of-plane bending force constants, we assumed $f_{\beta\beta}$ to be zero in order to give a value to f_β and to calculate the energy of the inactive mode. In the case of the ion $[AuCl_4]^-$, this gave 108 cm^{-1} for ν_5 which agrees well with 112 cm^{-1} derived from the combination vibration observed for $Cs[AuCl_4]$. (The agreement is probably

---

[14] P. Torkington, *J. Chem. Phys.*, 1949, **17**, 357.

[15] W. Sawodny, *J. Mol. Spectroscopy*, 1969, **30**, 56.

TABLE 4

Force constants of square-planar anions

	$[PdCl_4]^{2-}$	$[PdBr_4]^{2-}$	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$	$[AuCl_4]^{-}$	$[AuBr_4]^{-}$	Units
(*a*) In symmetry-co-ordinate representation								
A_{1g}, $F_{11} = f_r + 2f_{rr} + f_{rr'}$	$1{\cdot}88_0$	$1{\cdot}66_4$	$2{\cdot}24_7$	$1{\cdot}97_9$	$1{\cdot}79_6$	$2{\cdot}54_4$	$2{\cdot}15_6$	*a*
A_{2u}, $F_{22} = r^2(f_\beta + f_{\beta\beta})$	$0{\cdot}53_3$	$0{\cdot}44_0$	$0{\cdot}71_0$	$0{\cdot}56_2$	$0{\cdot}46_9$	$0{\cdot}71_7$	$0{\cdot}58_1$	*b*
B_{1g}, $F_{33} = f_r - 2f_{rr} + f_{rr'}$	$1{\cdot}52_3$	$1{\cdot}39_3$	$1{\cdot}94_3$	$1{\cdot}73_6$	$1{\cdot}50_8$	$2{\cdot}20_6$	$1{\cdot}80_9$	*a*
B_{2g}, $F_{44} = r^2(f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'})$	$0{\cdot}85_6$	$0{\cdot}70_5$	$0{\cdot}84_9$	$0{\cdot}85_9$	$0{\cdot}89_2$	$0{\cdot}90_5$	$0{\cdot}87_3$	*a*
B_{2u}, $F_{55} = r^2(f_\beta - f_{\beta\beta})$	$0{\cdot}53_3$	$0{\cdot}44_0$	$0{\cdot}71_0$	$0{\cdot}56_2$	$0{\cdot}46_9$	$0{\cdot}71_7$	$0{\cdot}58_1$	*b*
E_u, $F_{66} = f_r - f_{rr'}$	$1{\cdot}36_6$	$1{\cdot}22_8$	$1{\cdot}53_3$	$1{\cdot}41_8$	$1{\cdot}16_0$	$2{\cdot}03_8$	$1{\cdot}72_2$	*a*
$F_{67} = 2^{1/2}r(f_{r\alpha} - f_{r\alpha'})$	$0{\cdot}27_5$	$0{\cdot}32_7$	$0{\cdot}20_0$	$0{\cdot}31_3$	$0{\cdot}35_0$	$0{\cdot}22_5$	$0{\cdot}29_3$	*c*
$F_{77} = r^2(f_\alpha - f_{\alpha\alpha'})$	$1{\cdot}02_0$	$0{\cdot}91_6$	$1{\cdot}23_4$	$1{\cdot}16_3$	$1{\cdot}13_5$	$1{\cdot}33_3$	$1{\cdot}20_7$	*b*
(*b*) In internal-co-ordinate representation								
f_r	$1{\cdot}53_4$	$1{\cdot}37_8$	$1{\cdot}81_4$	$1{\cdot}63_7$	$1{\cdot}40_6$	$2{\cdot}20_6$	$1{\cdot}85_2$	*a*
f_{rr}	$0{\cdot}08_9$	$0{\cdot}06_8$	$0{\cdot}07_6$	$0{\cdot}06_1$	$0{\cdot}07_2$	$0{\cdot}08_5$	$0{\cdot}08_7$	*a*
$f_{rr'}$	$0{\cdot}16_8$	$0{\cdot}15_0$	$0{\cdot}28_1$	$0{\cdot}22_0$	$0{\cdot}24_6$	$0{\cdot}16_8$	$0{\cdot}13_0$	*a*
$f_{r\alpha} - f_{r\alpha'}$	$0{\cdot}08_5$	$0{\cdot}09_6$	$0{\cdot}06_1$	$0{\cdot}09_3$	$0{\cdot}09_6$	$0{\cdot}06_6$	$0{\cdot}08_1$	*a*
$f_\alpha - f_{\alpha\alpha'}$	$0{\cdot}19_3$	$0{\cdot}15_9$	$0{\cdot}22_7$	$0{\cdot}20_4$	$0{\cdot}17_2$	$0{\cdot}22_8$	$0{\cdot}18_3$	*a*
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	$0{\cdot}01_6$	$0{\cdot}01_8$	$0{\cdot}03_5$	$0{\cdot}02_7$	$0{\cdot}01_8$	$0{\cdot}03_7$	$0{\cdot}02_5$	*a*
f_β	$0{\cdot}10_1$	$0{\cdot}07_6$	$0{\cdot}13_1$	$0{\cdot}09_3$	$0{\cdot}07_1$	$0{\cdot}12_2$	$0{\cdot}08_8$	*a*
Calculated value of ν_5 (cm^{-1})	98	57	112	65	45	108	61	
Interatomic distance (pm)	229·9	240	233	239	257	242	257	

[a] 10^2 N m^{-1}. [b] 10^{-18} N m rad^{-2}. [c] 10^{-8} N rad^{-1}.

better still since deformation frequencies of solid $Cs[AuCl_4]$ are marginally higher than those in solution.) This suggests that our estimates for this mode are probably quite good for all the other cases. The results presented in Table 4 reproduced the observed frequencies.

DISCUSSION

Wavenumber differences between published data for solid potassium or rubidium salts and the solutions studied here are listed in Table 5. Nearly all the frequencies are lower in solution but the effect is much more pronounced for deformations than it is for stretching vibrations. From previous i.r. studies[4] it has been suggested that the particular sensitivity of deformation modes to the counter cation is due to their coupling with lattice modes of the same symmetry. However, since the B_{2g} mode shows similar dependency between solid and solution when there is no B_{2g} lattice mode for such coupling, this must certainly not be the complete explanation.

TABLE 5

Wavenumber differences (cm^{-1}) between solid [5-7] potassium or rubidium * salts and R_4N^+ salts in solution

Anion	ν_1 A_{1g}	ν_2 A_{2u}	ν_3 B_{1g}	ν_4 B_{2g}	ν_6 E_u	ν_7 E_u
$[PtCl_4]^{2-}$	5	28	1	23	8	26
$[PtBr_4]^{2-}$	0	13	−2	12	5	23
$[PdCl_4]^{2-}$	10	16 *	5	22	15	32
$[PdBr_4]^{2-}$ †	4	16	−7	23	17	36
$[AuCl_4]^-$	2	2 *	1	14	4 *	7 *
$[AuBr_4]^-$	0	1 *	0	−2	0 *	0 *

* From rubidium salts for which the differences are probably less than those from potassium salts. † Solution values refer to aqueous $K_2[PdBr_4]$ (Raman) and solid '$(Bu_4N)_2[PdBr_4]$' (i.r.)

Crystal structures of the platinum and palladium salts[16,17] are such that the alkali-metal ions are above and below the interbond angles of the complex anion. Thus the cations may directly affect the field in which the halide ions vibrate and especially changes in MX_2 angles. In $K_2[MX_4]$ salts, ν_2 and ν_7 are generally quoted as being of comparable intensity but the latter is clearly much more intense in solution. Frequencies of the gold anions are much less sensitive to their environment, but the crystal structures of these salts have not been studied.

The force constants calculated here show some consistent relations. Stretching force constants follow the order $f_r \gg f_{rr'} > f_{rr}$. The greater value of the *trans*- than the *cis*-interaction constant is in keeping with the well known importance of the *trans*-influence in square-planar chemistry. Between corresponding chlorides and bromides the direction and approximate size of any change is comparable in the three sets of ions (with two minor exceptions, both between small quantities). Such consistency has not been apparent in previous work. It is not surprising that our values of $f_\alpha - f_{\alpha\alpha'}$ and f_β are much lower than those reported previously in view of the much lower deformation frequencies used in our calculations. The stretching force constants are relatively much less sensitive to the deformation frequencies used, which means that useful approximate stretching force constants for comparison between related species may be calculated even if the deformation assignments are not accurately known.

EXPERIMENTAL

I.r. and Raman spectra were determined as previously outlined[18] except that extensive use was made of 752·5 nm excitation from a krypton-ion laser (C.R.L. model 52G) fitted with i.r. mirrors. The wavenumber accuracy is ±1 cm^{-1}, apart from Tables 3 and 4 where Raman shifts are accurate to ±0·5 cm^{-1} and corresponding shifts are consistent to ±0·2 cm^{-1}.

Commercially available salts were used for the aqueous solutions except for solutions of $Na_2[PtBr_4]$ which were prepared by stirring platinum(II) bromide with sodium bromide in water for 24 h. The salt $Cs[AuCl_4]$ was precipitated from an aqueous solution of $Na[AuCl_4]$ on ad-

---

[16] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.

[17] W. Theilaker, *Z. anorg. Chem.*, 1937, **234**, 161.

[18] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1972, 1298.

dition of caesium chloride and was recrystallised from hot water.

Preparation of Tetra-alkylammonium Salts.—Complexes $R_4N[AuX_4]$ (X = Cl or Br) were precipitated from aqueous solutions of $Na[AuCl_4]$ or $K[AuBr_4]$ by addition of aqueous solutions of R_4NX. Salts with R = Et or Pr^n were recrystallised from acetone and those with R = Bu^n or Pn^n crystallised from dichloromethane solutions on addition of diethyl ether. The salts $(Bu^n_4N)_2[PtX_4]$ were prepared by addition of an excess of a saturated aqueous solution of Bu^n_4NX to a saturated aqueous solution of $K_2[PtCl_4]$ or an aqueous solution of $Na_2[PtBr_4]$ respectively. The resulting precipitates were washed with water and dried in air before recrystallisation from acetone by adding diethyl ether until the onset of a slight turbidity, followed by storing in a refrigerator overnight. The salt $(Bu^n_4N)_2$-$[PdCl_4]$ was prepared by stirring $(Bu^n_4N)_2[Pd_2Cl_6]$ with a slight excess of Bu^n_4NCl in acetone and crystallised on addition of diethyl ether. Characterising data for the salts are listed in Table 6.

TABLE 6

Characterisation of salts

			Analyses (%) Found (Calc.)			
	Colour	M.p. (t/°C)	C	H	N	X
$(Bu^n_4N)_2[PtCl_4]$	Orange-red	143—144	46·9 (46·75)	9·15 (8·85)	3·4 (3·4)	17·45 (17·25)
$(Bu^n_4N)_2[PtBr_4]$	Red-brown	128—129	38·4 (38·45)	7·15 (7·25)	2·75 (2·8)	
$(Bu^n_4N)_2[PdCl_4]$	Red-brown	145	52·3 (52·4)	10·0 (9·9)	3·85 (3·8)	19·25 (19·35)
$Me_4N[AuCl_4]$	Yellow	358 (decomp.)	11·65 (11·65)	2·95 (2·95)	3·35 (3·4)	34·05 (34·35)
$Et_4N[AuCl_4]$	Yellow	270—271 (decomp.)	20·55 (20·5)	4·25 (4·3)	2·9 (3·0)	30·3 (30·25)
$Pr^n_4N[AuCl_4]$	Yellow	197—198	27·85 (27·45)	5·4 (5·35)	2·65 (2·65)	26·5 (27·0)
$Bu^n_4N[AuCl_4]$	Yellow	164—165	33·05 (33·05)	6·45 (6·25)	2·75 (2·4)	24·1 (24·4)
$Pn^n_4N[AuCl_4]$	Yellow	141—143	37·4 (37·7)	6·95 (6·95)	2·2 (2·2)	23·15 (22·25)
$Pn^n_4N[AuBr_4]$	Deep red	126—127	29·5 (29·45)	5·65 (5·45)	1·85 (1·7)	

We thank the S.R.C. for a grant to purchase the Raman equipment, and the Institute of Isotopes of the Hungarian Academy of Sciences, Budapest, for leave of absence (to J. M.).

[4/072 *Received*, 16*th January*, 1974]