

Raman Spectra of a Series of Square Planar Anions

OVER the past 10 years a number of reports have appeared in the literature on the infra-red spectra of square planar co-ordination compounds. Interest has been demonstrated in the exact whereabouts, in terms of frequency, of absorption bands associated primarily with stretching vibrations of metal-halogen bonds. A number of attempts have been made to estimate force constants for the metal ligand bonds in simple cases. A careful consideration of species with formula $[MX_4]^{n-}$ and trans $[MX_2Y_2]$, where M is a metal such as platinum(II), palladium(II) or gold(III), X is a halogen and Y is a donor system such as ammonia, a thio-ether or a phosphine, can provide a large amount of information particularly if the symmetric stretching modes of vibration are identified. Unfortunately, these modes are inactive in infra-red spectroscopy, and although they can be analysed by Raman spectroscopy, it is extremely difficult to obtain scattering data on deeply coloured materials such as these. The only reliable Raman spectra of compounds of this type is that due to Stammreich and Forneris¹, who report three lines for each of the three anions, $PtCl_4^{2-}$, $AuCl_4^-$ and $AuBr_4^-$ using aqueous solutions and exciting the spectra with yellow, red or near-infra-red sources, as appropriate. An attempt which I made to obtain a spectrum from a solution of potassium tetrabromoplatinate by exciting the spectrum with an electrodeless rubidium arc was unsatisfactory; two indistinct features were observed near $\Delta\nu = 190$ and 120 cm^{-1} .

Recently, there has been considerable activity in the application of lasers to Raman spectroscopy and two commercial instruments using helium-neon sources have been announced. One of these, by the Perkin-Elmer Corporation, uses a fairly conventional method of excitation in that the sample is illuminated and viewed at right angles. In the second instrument, the Cary 81 laser Raman spectrometer of the Applied Physics Corporation, the sample is placed against the plane surface of a hemispherical lens and illuminated normally by the laser. Reflected and scattered light is collected by the lens and projected into the pre-slit optics of the instrument. It was this latter instrument which was used in these experiments. The application of the Cary 81 laser instrument to the problem of obtaining spectra from small liquid samples has been described at a number of spectroscopic conferences, but it now seems that it is possible to obtain good Raman spectra from almost opaque solids. Compounds of the type K_nMX_4 (where M is gold(III), palladium(II) or platinum(II), and X is Cl, Br or I) were examined, and, with the exception of potassium tetraiodopalladate, all gave excellent spectra, even though many of them are jet black or dark brown powders. The Raman bands observed are given in Table 1.

Table 1

Complex anion	$\nu_{1A_{1g}}$	ν_2	ν_4	$(4\pi^2 \nu_{A_{1g}}^2 M_x)$ (mdynes/Å)
Au Cl_4^- (soln.)	(347)	(324)	(171)	2.5
Au Br_4^- (soln.)	(212)	(196)	(102)	2.2
Au Br_4^-	214	196	102	2.2
Au I_4^-	148	110	75	0.7
Pt Cl_4^{2-} (soln.)	(335)	(304)	(164)	2.3
Pt Cl_4^{2-}	333	306	196	2.3
Pt Br_4^{2-}	205	190	125	2.0
Pt I_4^{2-}	140	125	-	0.5
Pd Cl_4^{2-}	310	275	198	1.9
Pd Br_4^{2-}	187	167	125	1.6

All frequency values are here expressed in wavenumbers and were determined on pelleted solid samples. Solution results are bracketed and are due to Stammreich and Forneris (ref. 1).

Two bands were observed with all these compounds and with most three. For the compounds where Stammreich and Forneris have reported solution spectra, the agreement seems excellent, except with potassium tetrachloroplatinate. A D_{4h} anion of this type will give three bands in the infra-red region as a result of out-of-plane

bending $A_{2u}(\nu_3)$, of plane stretching $E_u(\nu_6)$, and of asymmetric bending $E_u(\nu_7)$ modes. It will also give three bands in the Raman spectrum owing to A_{1g} fully symmetric $M-X$ stretching (ν_1), to asymmetric stretching $B_{2g}(\nu_2)$, and to symmetric $X-M-X$ bending $B_{1g}(\nu_4)$ modes. One mode, ν_5 , a B_{2u} class out-of-plane twisting, is non-active. The mode numbering is that suggested by Nakamoto² with the exceptions that ν_2 is of the B_{2g} class and ν_4 is from B_{1g} . Of the three Raman active fundamentals ν_1 and ν_2 will be of higher frequency than ν_4 . The A_{1g} class vibration will, of course, be polarized and Stammreich and Forneris indeed observed that the highest frequency band was in fact polarized in their spectra of the $AuCl_4^-$ and ICl_4^- ions. They duly assigned this band to the symmetric stretching mode. Unfortunately, polarization measurements on the solid complexes gave no meaningful results except with potassium tetraiodoaurate when the highest frequency line was, in fact, strongly polarized. It is worth noting that on this occasion the sample was very finely divided and thus random orientation of the ions in the laser beam may have been achieved. It has been accepted, therefore, that the highest frequency line always results from the A_{1g} mode, that ν_2 follows it at lower frequency, and that ν_4 is closest to the exciting line.

An estimate of the $M-X$ stretching force constant can be obtained by calculating the value of the parameter $(4\pi^2 \nu_{A_{1g}}^2 M_x)$, where $\nu_{A_{1g}}$ is the frequency of the A_{1g} mode and M_x the atomic mass of the halogen. This, of course, is not in any way a useful force constant because it ignores halogen-halogen and other forms of non-bonded interaction. It is of interest to note, however, that as X increases in atomic weight, the value falls and that when M is varied the values decrease in the order gold(III) > platinum(II) > palladium(II). This order is paralleled by chemical reactivity which increases from gold to palladium and also with increasing atomic weight of the halogen atom. This trend has been previously noted in connexion with ammine complexes of platinum and palladium³.

A study of the far infra-red spectra of these complexes is being completed by Dr. Clive Perry and his colleagues at the Massachusetts Institute of Technology and it is intended in a later publication to present more meaningful values of the force constants using all the available data.

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¹ Stammreich, H., and Forneris, R., *Spectrochim. Acta*, **16**, 363 (1960).

² Nakamoto, K., *Infra-red Spectra of Inorganic and Coordination Compounds*, 113 (Wiley, New York, 1963).

³ Hendra, P. J., and Sadasivan, N., *Spectrochim. Acta*, **21**, 1271 (1965).

High Intensity Triboluminescence in Europium Tetrakis (Dibenzoylmethide)-triethylammonium

THE emission of light which accompanies mechanical deformation or fracture of certain crystalline compounds is designated as triboluminescence. Stranski *et al.*^{1,2} investigated some 1,700 organic and inorganic substances and found 356 of them to exhibit triboluminescence. Special impact mechanisms and complete darkness are required to observe the triboluminescent emission from all previously reported triboluminescent materials. In addition, a number of these compounds showed detectable triboluminescence only in a small range of environmental gas pressure and low temperature. Triboluminescence