

VIBRATIONAL SPECTRA OF CHLORO-, BROMO- AND IODOTRIMETHYLPLATINUM(IV)

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SUMMARY

The infrared spectra from 4000 to 30 cm^{-1} and the Raman spectra of chloro-, bromo- and iodotrimethylplatinum(IV) in the solid state have been recorded and qualitative assignments made. Very strong Raman lines at 581, 574 and 560 cm^{-1} are assigned to Pt-C stretching vibrations in the three compounds respectively. Coincident infrared bands are observed but with very low intensity. A weak Raman line at 272 cm^{-1} in the spectrum of the chloro compound is assigned to $\nu(\text{Pt}-\text{Cl})$ but Raman features attributable to Pt-Br and Pt-I stretching modes could not be detected in the other compounds. The far-infrared spectra of the compounds showed distinct trends due to the changing halo group.

INTRODUCTION

Various reports on the infrared spectra of the halotrimethylplatinum(IV) compounds have been published. Hoechstetter¹ studied the compounds and their deuterio analogues. Gribov *et al.*² have reported the spectrum of the iodo compound and Smith³ has published the C-H stretching frequencies of a chloroform solution of the same compound. Kettle⁴ commented on the spectrum of $[\text{PtCl}(\text{CH}_3)_3]_4$. Binns *et al.*⁵ have reported far-infrared spectra of the chloro and iodo compounds. Some disagreement has been expressed concerning the appearance of absorption bands ascribable to Pt-C stretching modes. Our absorption spectra cover the range from 4000 cm^{-1} to 30 cm^{-1} and we report Raman studies for the first time. Raman spectra clearly indicate the Pt-C stretching modes.

EXPERIMENTAL

Iodotrimethylplatinum(IV) was prepared by the method of Clegg and Hall⁶.

Chlorotrimethylplatinum(IV) was prepared as a white precipitate by adding an aqueous solution of potassium chloride to an aqueous solution of trimethylplatinum(IV) sulphate⁷. The precipitate was filtered off and washed with water. (Found: C, 13.0; H, 3.2; Cl, 12.9; Pt, 70.8. $\text{C}_3\text{H}_9\text{ClPt}$ calcd.: C, 13.1; H, 3.3; Cl, 12.9; Pt, 70.5%.)

Bromotrimethylplatinum(IV) was prepared in a similar manner to the chloro compound using KBr (Found: C, 11.4; H, 2.8; Br, 25.0; Pt, 60.5. $\text{C}_3\text{H}_9\text{BrPt}$ calcd.:

C, 11.3; H, 2.8; Br, 24.9; Pt, 60.8%.) The molecular weight of the substance in benzene solution (0.007 molal) was determined with an Hewlett-Packard Model 302 vapour pressure osmometer. Found 1254 ± 65 , calcd. for $[\text{PtBr}(\text{CH}_3)_3]_4$ 1281.

Raman spectra were obtained using a Perkin-Elmer LR-1 Spectrometer (He/Ne; 8 mw at 6328 Å) from crystals grown by slow evaporation of solutions of various organic solvents. Frequencies are considered accurate to $\pm 3 \text{ cm}^{-1}$.

Infrared spectra were recorded on a Perkin-Elmer Model 225 Spectrometer as Nujol and hexachlorobutadiene mulls, CsI and KBr pressed discs and as polythene dispersions. Frequencies are considered accurate to $\pm 2 \text{ cm}^{-1}$. Far-infrared spectra of the compounds in Nujol were recorded between 400 and 30 cm^{-1} on an Hitachi FIS-3 Spectrophotometer.

RESULTS AND DISCUSSION

Infrared and Raman spectra of the compounds are set out in Table 1. For interpretation of spectra of the solid state a factor group analysis based on the space group of each compound should be made. Structure studies have been carried out on the chloro and iodo compounds only and these have been shown to consist of tetrameric units. The bromo compound is tetrameric in benzene and we assume that in the solid state it has a structure similar to the other members of the series. In the case of the chloro compound the tetramer (see Fig. 1) is made up of two interpenetrating tetrahedra, one composed of four $(\text{CH}_3)_3\text{Pt}$ groups, the other of four chloro groups. On the basis of point group symmetry (T_d) the number of active fundamentals for a

TABLE I

INFRARED AND RAMAN FREQUENCIES (cm^{-1}) FOR HALOTRIMETHYLPLATINUM(IV) COMPOUNDS IN THE SOLID STATE

w = weak, m = medium, s = strong, v = very, b = broad, sh = sharp, sd = shoulder.

$[\text{PtCl}(\text{CH}_3)_3]_4$		$[\text{PtBr}(\text{CH}_3)_3]_4$		$[\text{PtI}(\text{CH}_3)_3]_4$		Assignment
Infrared	Raman	Infrared	Raman	Infrared	Raman	
2985 m, sd	2993 w					
2964 m, sh	2976 w, b	2980 m, sh	2979 w, b	2971 m, sh	2978 w, b	$\nu(\text{C-H})$
2900 s, sh	2901 m, sh	2907 s, sh	2901 m, sh	2899 s, sh	2900 m, sh	$\nu(\text{C-H})$
2797 w, sh		2802 w, sh		2798 w, sh		$2 \times \delta_{\text{asym}}(\text{CH}_3)$
1411 m, b	1416 w, b	1418 m, b	1421 w, b	1416 m, b	1422 w, b	$\delta_{\text{asym}}(\text{CH}_3)$
1271 m, sh	1272 m, sh	1267 s, sh	1272 m, sh	1260 s, sh	1264 m, sh	$\delta_{\text{sym}}(\text{CH}_3)$
1234 s, sh	1236 m, sh	1230 s, sh	1230 m, sh	1224 s, sh	1222 m, sh	$\delta_{\text{sym}}(\text{CH}_3)$
877 w	878 w	875 w	870 w	859 w	868 w	$\rho(\text{CH}_3)$
580 vw	581 vs, sh	573 vw	574 vs, sh	559 vw	560 vs, sh	$\nu(\text{Pt-C})$
331 w						?
270 w	272 w, b					$\nu(\text{Pt-Cl})$
240 w, sd	238 w, b	218 w	249 m, b	241 vw, b	261 m, b	$\delta(\text{PtC}_3)$
216 s, sh		176 s, sh		164 w		} $\nu(\text{Pt-X})$
		152 s, sh		122 s, sh		
170 w		120 w, sd		92 s, sh		
136 m		106 s, sh				} $\delta(\text{Pt}_4\text{X}_4)$
108 w						
	76 w		66 w		60 w	

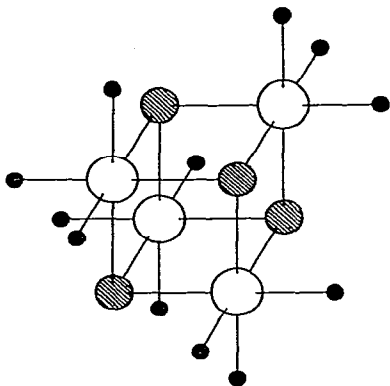


Fig. 1. Structure of $[\text{PtCl}(\text{CH}_3)_3]_4$. $\circ = \text{Pt}$; $\ominus = \text{Cl}$; $\bullet = \text{CH}_3$.

tetramer is 101. Although some degeneracy is expected, the number of observed frequencies for any one compound is about 25, and therefore only a qualitative assignment of modes is attempted. These are included in Table 1.

An examination of the spectra illustrated in Fig. 2 reveals a close similarity in the region where the methyl group vibrations are expected to occur, *i.e.* $3000\text{--}800\text{ cm}^{-1}$. The effect of a change in the halogen atom is more evident from the differences exhibited by the compounds in the region illustrated in Fig. 3.

The pattern of the three bands in the C–H stretching region is a common feature of the infrared spectra. The two bands of higher frequency are assigned to C–H stretching and they have counterparts in the Raman spectra. A shoulder appears on the high frequency side of the absorption at 2964 cm^{-1} in the infrared spectrum of the chloro compound and there is a corresponding Raman shift of 2993 cm^{-1} , but there are no similar features in the spectra of the other compounds. The absorption at ca. 2800 cm^{-1} , common to the infrared spectra, for which no corresponding Raman shift is observed, is assigned to the overtone of the asymmetric methyl deformation at about 1415 cm^{-1} .

In the range of $1270\text{--}1220\text{ cm}^{-1}$, all spectra show pairs of sharp absorption bands assignable to symmetric deformations of the methyl groups. The members of a pair show a regular variation in their relative intensity through the series (see Fig. 2). The corresponding Raman lines show a less pronounced trend in the reverse direction.

Methyl rocking vibrations normally occur for methyl–metal compounds in the frequency region $900\text{--}700\text{ cm}^{-1}$. The infrared and Raman spectra each contain a feature at about 870 cm^{-1} ascribable to this kind of mode.

Very strong Raman lines ranging from 581 to 560 cm^{-1} in the series of spectra are attributed to Pt–C stretching modes. The corresponding infrared bands are very weak and have escaped detection in some earlier studies. The trend in the frequency values, which increase in the order iodo, bromo to the chloro compound, cannot be a function of the changing mass of the halo group since the moiety against which the Pt–C bonds is vibrating is so heavy. More likely the trend in the infrared frequencies, for example, from 559 cm^{-1} (iodo) to 580 cm^{-1} (chloro) and further to 590 cm^{-1} (hydroxo)^{8,9} is the result of an electronic (bonding) change, due to the *trans* influence of the halogen atoms.

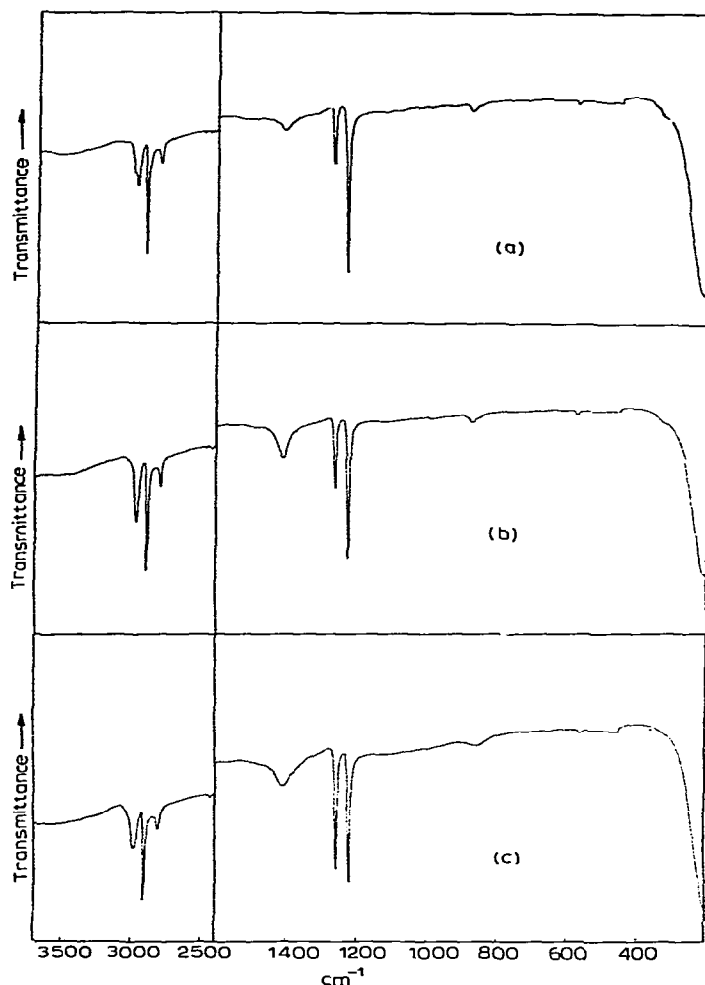


Fig. 2. Infrared spectra of (a) chloro-, (b) bromo- and (c) iodotrimethylplatinum(IV).

Plots of the sym-deformation frequencies of the methyl groups *vs.* the Pt-C stretching frequencies for the complexes $[\text{PtX}(\text{CH}_3)_3]_4$, X=I, Br, Cl and OH, are linear as has been observed¹⁰ for Pt^{II} alkyls, and the values rise in the direction of increasing electronegativity of the X group. Sheppard¹¹ has reported that the symmetric methyl deformation frequency of CH_3X increased linearly with increasing electronegativity of atoms X in the same row of the periodic classification. The variation in the methyl deformation frequency may be the result of non-bonded repulsive interaction between the group X and the hydrogen atoms of the methyl groups, which requires the inclusion of a cross-term in the potential energy function. Support for this possibility is the correlation between methyl deformation frequency and Pt-X distance¹²⁻¹⁴ as illustrated in Fig. 4. The vibrational data predict that the Pt-Br bond distance lies about 2.62 to 2.65 Å. An estimated value for the Pt-Br distance is 2.63 Å, which is obtained from the sum of the covalent radii for Br and Pt, where the latter was calculated using the known Pt-X distance for $[\text{PtX}(\text{CH}_3)_3]_4$, X=OH, Cl and I, and the covalent radius for X.