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NOTE

VIBRATIONAL SPECTRUM OF HYDROXYTRIMETHYLPLATINUM(IV)

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INTRODUCTION

Two accounts of the infrared spectrum of tetrameric hydroxytrimethylplatinum(IV) have been reported[1,2]. There was some disagreement about the number of bands observed and their frequencies. We have recorded the Raman spectra of $[PtOH(CH_3)_3]_4$ and $[PtOD(CH_3)_3]_4$ and extended the infrared work. It appears that the previous assignments[1,2] of strong absorption bands at *ca.* 720 cm^{-1} and 365 cm^{-1} to Pt–O stretching and Pt_4O_4 deformation vibrations respectively are incorrect.

EXPERIMENTAL

Hydroxytrimethylplatinum(IV) was prepared by precipitation from an aqueous solution[3] of $[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$ using dilute NaOH solution. (Found: C, 14.1; H, 3.9; Pt, 76.0. $C_3H_{10}OPt$ calcd.: C, 14.0; H, 3.9; Pt, 75.9%.) The deuterio analogue (>80% OD) was prepared by mixing D_2O solutions of $[Pt(CH_3)_3]_2SO_4 \cdot 4\,D_2O$ and NaOD under dry N_2.

Infrared spectra were run on KBr discs, Nujol and hexachlorobutadiene mulls between KBr discs and polythene plates and also on dispersions of the compounds in polythene film[4] using a Perkin–Elmer Model 225 Spectrometer. A far-infrared spectrum of $[PtOH(CH_3)_3]_4$ in Nujol was recorded between 400 and 30 cm^{-1} on an Hitachi FIS-3 Spectrophotometer.

Raman spectra were recorded with a Perkin–Elmer LR-1 Spectrometer with a He/Ne gas laser (6328 Å) as source. The best spectra were obtained from crystals grown slowly from chloroform.

RESULTS AND DISCUSSION

X-ray[5,6] and neutron diffraction[7] studies have shown tetrameric hydroxytrimethylplatinum(IV) to have a structure similar to that of the well-known chlorotrimethylplatinum(IV)[8]. The structure corresponds to two interpenetrating tetrahedra, one consisting of four OH groups, the other of four $Pt(CH_3)_3$ groups. The NMR spectrum[2] is consistent with this arrangement. The point group for an isolated tetra-

TABLE 1

INFRARED AND RAMAN FREQUENCIES (CM^{-1}) FOR $[PtOH(CH_3)_3]_4$ AND $[PtOD(CH_3)_3]_4$ IN THE SOLID STATE[a]

$[PtOH(CH_3)_3]_4$ (infrared)	$[PtOH(CH_3)_3]_4$ (Raman)	$[PtOD(CH_3)_3]_4$ (infrared)	$[PtOD(CH_3)_3]_4$ (Raman)	Approximate description of mode
3598 sh,s[a]	3595 w	(3596 sh,w)[b]		ν(O–H)
2957 sh,s	2965 b,w	2958 sh,s	2961 b,w	ν(C–H)
2898 sh,s	2895 sh,m	2897 sh,s	2896 sh,m	ν(C–H)
2801 b,m		2803 b,m		ν(C–H) or $2\times\delta_{asym.}(CH_3)$
		2654 sh,s	2648 sh,m	ν(O–D)
1423 b,m	1427 w	1423 b,m	1427 w	$\delta_{asym.}(CH_3)$
1408 b,m	1408 w	1409 b,m	1404 w	
1380 b,m	1376 w	1384 sh,w		
1279 sh,w	1280 w	1279 sh,w	1278 w	$\delta_{sym.}(CH_3)$
1243 sh,s	1243 m	1244 sh,s	1242 m	
877 w	876 vw	873 w	874 vw	$\rho(CH_3)$
854 w		851 w		$\rho(CH_3)$
722 sh,s	716 sd	(~715 vw)[b]		δ(Pt–O–H)
	700 m			
590 sh,vw	595 sh,vs	593 sh,w	590 sh,vs	ν(Pt–C)
		559 sh,s	[c]	δ(Pt–O–D)
394 vw				ν(Pt–OH)
368 sh,s	360 m			
		358 vw		ν(Pt–OD)
		340 sh,s	333 m	
245 w	250 m	249 w	249 m	$\delta(PtC_3)$
147 w				$\delta(Pt_4O_4)$
126 w				
	102 w		100 w	$\delta(Pt_4O_4)$

[a] w = weak, m = medium, s = strong, v = very, b = broad, sh = sharp, sd = shoulder. [b] Residual absorption due to –OH compound. [c] Masked by laser line.

mer is T_d and the crystal space group has been established[7] as $I_{\bar{4}3m}(T_d^3)$★. Assignment of frequencies for the solid state should be based on a factor group analysis, but since the number of normal modes far exceeds the number of observed frequencies [*e.g.*, for one tetramer, $\Gamma = 10A_1(R) + 5A_2(ia) + 15E(R) + 19F_1(ia) + 24F_2(R, ir)$] a systematic analysis is not attempted. Infrared and Raman results obtained in the present work are listed in Table 1 together with a qualitative description of the types of modes.

The assignment of frequencies to vibrational modes of the methyl group is straightforward and the assignments in Table 1 are in accord with the conclusions of Morgan *et al.*[2]. The infrared O–H stretching frequency at 3598 cm^{-1} falls to 2654 cm^{-1} on deuteration and the observed ratio, $\nu(OH)/\nu(OD)$ (= 1.36), is close to the value calculated from Hooke's Law. The corresponding Raman shifts are 3595 cm^{-1} and 2648 cm^{-1}.

We find on substitution of deuterium for the hydroxyl proton that, as expected,

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★ This space group contains two equivalent sites of T_d symmetry corresponding to the two tetramer units found per unit cell.

the spectral features attributed to methyl group vibrations are practically unaffected. However, a strong infrared band at 722 cm^{-1} in the –OH compound is absent from the spectrum of the –OD compound which contains in turn a strong band at 559 cm^{-1}. The low intensity Raman lines at 716 cm^{-1} and 700 cm^{-1} are missing from the spectrum of the deuterio compound but no feature corresponding to the infrared absorption at 559 cm^{-1} could be detected because this region is masked by a laser line (*ca.* 540 cm^{-1}).

Infrared bands at 590 cm^{-1} and 593 cm^{-1} in the spectra of the two compounds are attributed to Pt–C stretching. The strongest lines in the Raman spectra have shifts of 595 cm^{-1} and 590 cm^{-1} and these are assigned to Pt–C stretching also. The infrared bands at 394 cm^{-1} and 368 cm^{-1} undergo a small shift on deuteration of the hydroxyl group to 358 cm^{-1} and 340 cm^{-1}. The corresponding Raman line at 360 cm^{-1} shifts to 333 cm^{-1}. Other features in the Raman spectrum appear to be unaffected by deuteration.

The skeletal vibrations which are expected to be most sensitive to deuteration of the OH group are Pt–O–H bending and Pt–OH stretching. The shift of the infrared band at 722 cm^{-1} to 559 cm^{-1} (ratio = 1.3) on deuteration, indicates that the corresponding vibration directly involves motion of the hydrogen nucleus. This feature is therefore ascribed to Pt–O–H bending in preference to Pt–O stretching as previously assigned[1,2]. Maltese and Orville-Thomas[9] have assigned bands at 1076 cm^{-1} and 1058 cm^{-1} in the infrared spectrum of $K_2[Pt(OH)_6]$ to Pt–O–H bending and on deuteration these bands shift to 804 cm^{-1}. It is claimed[10] that X–O–H bending frequencies decrease as the ionic character of the X–O bond increases. The lower value (722 cm^{-1}) for $[PtOH(CH_3)_3]_4$ *versus* 1076–1058 cm^{-1} for $K_2[Pt(OH)_6]$ suggests greater ionic character for the Pt–O bond in the former compound. This point is referred to later in the discussion.

We assign the infrared bands at 394 cm^{-1} and 368 cm^{-1} and the Raman shift of 360 cm^{-1} for the –OH compound to Pt–O stretching modes. The 20–30 cm^{-1} decrease on deuteration is consistent with the increased mass effect. The assignment differs from earlier workers'[1,2], but is supported by the interpretation of the Raman spectrum[3] of the aquated trimethylplatinum(IV) ion, shown to be $[Pt(CH_3)_3(H_2O)_3]^+$ by Glass and Tobias[11]. In this case 357 cm^{-1} was assigned to Pt–O stretching. The values suggest that in spite of the compact network of oxygen and platinum atoms in the Pt_4O_4 skeleton of the tetramer, the Pt–O bonds are as flexible as those in the open C_3PtO_3 skeleton of the triaquo species. The frequencies are lower than the values assigned for Pt–O stretching in $K_2[Pt(OH)_6]$, *viz.*, 515, 538 cm^{-1}, but the decrease is due to the effect which the methyl groups have in weakening the bonds *trans* to them. The bond weakening influence occurs in the complex ion $[Pt(CH_3)_3(NH_3)_3]^+$, whose aqueous solutions are alkaline due to the dissociation of NH_3 groups. Also the Pt–N symmetric stretching frequency is 390 cm^{-1}, which is correspondingly lower than 569 cm^{-1}, found[12] for $[Pt(NH_3)_6]^{4+}$. We consider that the relatively low values for the Pt–O–H bending and Pt–O stretching frequencies, together with the low intensity of the 360 cm^{-1} line in the Raman spectrum of $[PtOH(CH_3)_3]_4$, are indicative of considerable ionic character in the Pt–O bonds.

The Raman lines at 250 cm^{-1} and 249 cm^{-1} in the –OH and –OD compounds respectively (245 and 249 cm^{-1} in the infrared) are attributed to PtC_3 deformation vibrations which were assigned 271 cm^{-1} and 259 cm^{-1} in the Raman spectra of the

TABLE 2

RAMAN FREQUENCIES FOR THE C_3PtX_3 GROUPING ($X=O$, N) IN VARIOUS COMPLEXES

Complex	$\delta(PtN_3)$	$\delta(PtC_3)$	$\nu(PtO)$	$\nu(PtN)$	$\nu(PtC)$
$[PtOH(CH_3)_3]_4$		250	360		595
$[PtOD(CH_3)_3]_4$		249	333		590
$[Pt(CH_3)_3(H_2O)_3]^+$		259	357		600
$[Pt(CH_3)_3(D_2O)_3]^+$		259	345		599
$[Pt(CH_3)_3(NH_3)_3]^+$	201	271		390	584
$[Pt(CH_3)_3(ND_3)_3]^+$	180	266		364	585

triammine[12] and triaquo[3] ions respectively. Skeletal frequencies for the C_3PtX_3 grouping ($X=O$ and N) are summarised in Table 2.

The far-infrared spectrum of $[PtOH(CH_3)_3]_4$ contains bands at 147 and 126 cm^{-1} which are tentatively ascribed to deformations of the Pt_4O_4 skeleton. Alternative assignments would be to lattice vibrations (although the frequencies appear high for this type of mode) or to methyl torsions. The 102 cm^{-1} Raman line (100 cm^{-1} in the deuterated compound) is attributed to a Pt_4O_4 deformation mode since lattice modes are Raman forbidden for cubic space groups. Absence of strong Raman lines from the low frequency region suggests that metal–metal bonding does not occur to a significant extent. Intense Raman lines which occur about 60–130 cm^{-1} in polynuclear hydroxy complexes of Bi^{III} and Pb^{II} have been attributed by Maroni and Spiro[13] to metal–metal interaction.

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