that it is a fluoro complex rather than an oxyfluoro complex since the line appears in the Ta–F stretch region rather than the Ta–O stretch region. As NH_4F is added, the TaF_6^- ion concentration decreases as the TaF_7^{2-} ion concentration increases and the line at 673 cm^{-1} disappears. In the spectra of solutions 11-D and E a line appears in the tantalum–oxygen stretch region around 880 cm^{-1}. Although this line is most likely due to a $TaOF_6^{3-}$ or $TaOF_5^{2-}$ ion, we cannot identify the ion from this line alone in two solutions.

In Table III a comparison is given of the species tantalum forms under conditions similar to those studied for niobium. It is apparent that the oxyfluoride of niobium is very stable since it is found at high HF concentrations (in fact, $NbOF_5^{2-}$ was detectable in 19 *M* HF solutions). On the other hand, the oxyfluoride of tantalum disappears at HF concentrations in the 0.1 *M* range leaving only fluorotantalates. Another notable difference is that all of the tantalum solutions we studied contained the TaF_7^{2-} ion whereas none of the niobium solutions contained the NbF_7^{2-} ion. The niobium study included K:Nb ratios of 2 only, so it may be that higher ratios would lead to formation of NbF_7^{2-}. Indeed, Fordyce and Baum[20] found NbF_7^{2-} to be the predominant species in KF:LiF melts containing Nb(V). Nonetheless, it is clear that tantalum forms the TaF_7^{2-} ion much more readily than niobium forms the NbF_7^{2-} ion.

[20] J. S. Fordyce and R. L. Baum, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13–17, 1965.

Contribution from the Chemistry Department,
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Infrared and Nuclear Magnetic Resonance Spectra of Hydroxytrimethylplatinum(IV)

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An nmr method for determining the structure of tetrameric hydroxytrimethylplatinum by analyzing the hydroxylic proton resonance is reported. Mixed polymers of hydroxytrimethylplatinum and iodotrimethylplatinum have been detected in the nmr spectra, and interesting changes have been observed in J_{Pt-C-H_3}. Both infrared and nmr evidence for hydrogen bonding of the hydroxylic proton have been obtained. A more complete infrared spectrum is reported in which all of the Pt–O and Pt–C vibration modes are identified. The unsymmetric CH_3 deformation frequency is apparently split by Fermi resonance with an overtone of the Pt–O stretching frequency.

Trimethylplatinum derivatives have been known for many years[1,2] but have still not been fully characterized. Chlorotrimethylplatinum was found to be tetrameric in benzene solution and was shown by single-crystal X-ray analysis[3] to have the structure shown in Figure 1.

Although one can reasonably assume that this structural unit is preserved in solution and that other tetrameric trimethylplatinum derivatives will have a similar structure, a direct determination of the structure in solution seemed most desirable. Proton magnetic resonance of the hydroxy derivative was measured in the hope that the environment of the hydroxylic proton could be determined as well as evaluating the properties of the hydroxyl group in this environment.

Experimental Section

Preparation of Compounds.—Iodotrimethylplatinum was prepared by the method of Foss and Gibson[4] as well as by a modification of this method in which a methyllithium–lithium iodide mixture in diethyl ether was substituted for methylmagnesium iodide. This modification more than doubled the yield (55% based on *cis*-dipyridinetetrachloroplatinum(IV)). The method of Gel'man and Ivanova[2] was also employed with excellent results (66% yield based on sodium hexachloroplatinate). In all syntheses the product was extracted into benzene, dried over sodium sulfate, and recrystallized four times from benzene.

Trimethylplatinum sulfate was prepared by the method of Pope and Peachey.[1]

Hydroxytrimethylplatinum was prepared by adding 0.8 g of freshly precipitated silver hydroxide to 0.2172 g of iodotrimethylplatinum in 50 ml of acetone and 50 ml of benzene. This mixture was refluxed with stirring for 45 hr, then stirred for an additional 11 hr at room temperature. The colorless filtrate yielded a solid which was recrystallized three times to give 0.1258 g of impure hydroxytrimethylplatinum. Integration of the methyl peak intensities in the nmr spectrum indicated a 5% impurity of iodotrimethylplatinum.

A much better synthesis was devised by reaction of ionic, water-soluble trimethylplatinum sulfate to form covalent, water-insoluble hydroxytrimethylplatinum. A 2-ml quantity of a saturated barium hydroxide solution was added to 80.3 mg (0.261 mmole) of trimethylplatinum sulfate dissolved in 3 ml of water. After standing for 24 hr, the mixture was filtered, and the residue was washed with water and acetone (to remove unreacted trimethylplatinum sulfate and barium hydroxide). The remaining residue was boiled in 10 ml of benzene and filtered, and 56.6 mg (0.220 mmole) of hydroxytrimethylplatinum (84%) was crystallized from the filtrate. The sample was analyzed for per cent platinum by thermally decomposing the sample under hydriodic

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[1] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **95**, 571 (1909).

[2] O. M. Ivanova and A. D. Gel'man, *Zh. Neorgan. Khim.*, **3**, 1334 (1958).

[3] R. E. Rundle and J. K. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).

[4] M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 299 (1951).

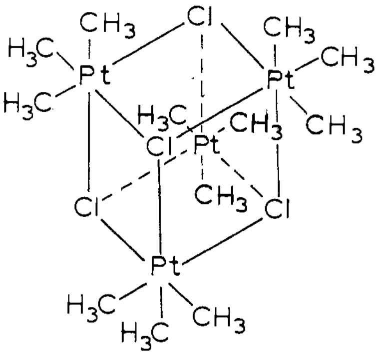

Figure 1.—Structure of chlorotrimethylplatinum.

acid followed by heating at 900° to constant weight. *Anal.* Calcd for $C_3H_{10}Pt$: Pt, 75.85. Found: Pt, 75.7.

A very poor method of synthesis, but one which produced interesting intermediates, consisted of refluxing a saturated dry ether solution of iodotrimethylplatinum with sodium hydroxide for 4 days. The ether was evaporated off, and the residue was extracted several times with benzene. The product was crystallized twice from benzene and finally dissolved in benzene for nmr analysis.

Molecular Weight Measurement.—Molecular weight data for pure hydroxytrimethylplatinum were obtained using a Mechrolab Inc. vapor pressure osmometer, Model 301A. Samples were dried in an Abderhalden drier at 50° over phosphorus pentoxide with a trace of paraffin added. Dry carbon tetrachloride was used as the solvent. *Anal.* Calcd for $[C_3H_{10}OPt]_4$: 1029 g/mole. Found: 1025 ± 10 g/mole.

Infrared and Nmr Spectra—Infrared spectra were obtained with a Beckman IR-10 grating spectrophotometer calibrated with indene and polystyrene and a Perkin-Elmer 221 with sodium chloride optics calibrated with water and carbon dioxide vapors and checked with polystyrene. The reported data were reproducible to 5 cm^{-1} above 2000 cm^{-1} and to 3 cm^{-1} below 2000 cm^{-1}. All spectral data reported were obtained as KBr pellets or as mulls between cesium bromide plates.

Nuclear magnetic resonance spectra were measured on a Varian Associates Model A-60 spectrometer by Mr. Francis McDonald of the U. S. Bureau of Mines Petroleum Research Center at Laramie, Wyo. The large spectrum in Figure 2 was obtained with the A-60 spectrometer coupled to a CAT-1024 spectrum integrator set at a sweep width of 100 cps for 25.0-sec readout of 50 scans.

The samples were usually saturated benzene or chloroform solutions. Chemical shifts were measured with respect to tetramethylsilane although the solvent or the methyl protons in iodotrimethylplatinum were commonly used as references. The values of chemical shifts and coupling constants reported are based on several determinations for each compound. The τ values, $10-\delta$, where δ is the chemical shift in ppm relative to tetramethylsilane, are precise to ±0.01; the coupling constants are accurate to 0.5 cps.

Results

Nmr Results.—The only platinum nuclide with a spin is ^{195}Pt ($I = {}^1/_2$) with an isotopic abundance of 33.8%. Trimethylplatinum derivatives thus exhibit a methyl resonance consisting of an unsplit central peak plus a doublet,[5] the latter having 33.8% of the total area of the three peaks.

The hydroxylic protons of hydroxytrimethylplatinum appear at a τ value of 11.52 with a somewhat more complex structure (Figure 2 inset). If one considers a structure similar to that shown in Figure 1 with hydroxyl groups replacing chloride, it is seen that the hydroxyl group may exist in environments in which 0, 1, 2, or 3 of the platinum atoms to which it is bonded through oxygen may have a spin. Four different signal shapes are thus possible from which the net peak intensities may be calculated assuming the same *Pt*–O–*H* coupling constant for all platinum atoms. This calculation and the observed intensities are presented in Table I.

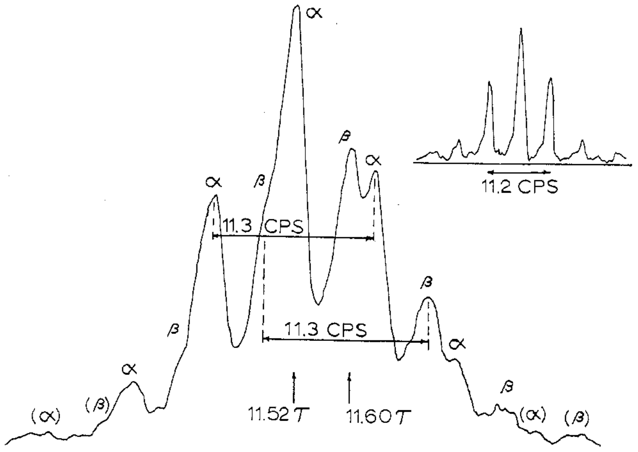

Figure 2.—Nmr spectra of the hydrolytic protons of hydroxytrimethylplatinum and of a dried sample showing the appearance of a new multiplet (β) superimposed on the original multiplet (α).

TABLE I

SPIN–SPIN SPLITTING PROBABILITIES FOR OH PROTONS SPLIT BY PLATINUM IN HYDROXYTRIMETHYLPLATINUM TETRAMER

No. of the 3 Pt atoms having a spin	Probability of arrangement	Peak intensities of arrangement
0	0.2901	1
1	0.4444	1:1
2	0.2268	1:2:1
3	0.0384	1:3:3:1

Net calculated and observed peak intensities (per cent)

	Center peak	First pair	Second pair	Third pair
Calcd	40.35	47.32	11.34	0.96
Obsd (±1%)	41	48	10	1

The large spectrum in Figure 2 represents the hydroxylic protons of a sample of hydroxytrimethylplatinum that had been dried for the molecular weight determination. The sample was dissolved in dry benzene, and its spectrum was recorded immediately. Two "five"-peak (actually seven-peak) multiplets are observed superimposed on one another. These sets are designated α, the same set as in the inset, and β, shifted 5 cps to higher field. No change is observed in the *Pt*–O–*H* coupling constant, which is 11.3 cps in both cases. Only one methyl resonance signal was observed. The peak at a τ value of 11.52 (α) is attributed to a hydrogen-bonded species whereas the peak with a τ value of 11.60 (β) is assigned to nonhydrogen-bonded hydroxylic protons. The area under both hydroxylic proton peaks was 10% of the total area of the spectrum.

The reaction of iodotrimethylplatinum with sodium

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(5) J. A. S. Smith, *J. Chem. Soc.*, 4736 (1962).

hydroxide–ether gave a product whose nmr spectrum consisted of four distinct methyl multiplets, two of which were those of hydroxy- and iodotrimethylplatinum. In addition to the OH resonance of hydroxytrimethylplatinum, an unresolved peak at a τ value of 11.32 was present. Upon standing several weeks, the two new methyl peaks and the new hydroxyl peak disappeared, leaving only a mixture of hydroxy- and iodotrimethylplatinum. In this incomplete reaction one can assume that 0, 1, 2, 3, and finally 4 hydroxyl groups will replace iodide in the tetrameric structure. Examining these five structures, one can see four environments for methyl groups bonded to platinum, $(CH_3)_3PtI_{3,2,1,0}(OH)_{0,1,2,3}$, giving rise to four observed peaks for all possible combinations of iodide and hydroxyl groups. The nmr data for these environments are presented in Table II.

TABLE II

NMR DATA FOR METHYLPLATINUM ENVIRONMENTS

Environment	τ	$J_{^{195}Pt-C-H_3}$, cps
$(CH_3)_3PtI_3$	8.27	77.5
$(CH_3)_3PtI_2OH$	9.07	75.5
$(CH_3)_3PtI(OH)_2$	9.32	86.0
$(CH_3)_3Pt(OH)_3$	9.15	78.8

Infrared Spectra.—The infrared spectrum of hydroxytrimethylplatinum has been reported by Hoechstetter[6] but is reported here since we observed different frequencies and additional bands. In the light of this information and the Raman study of trimethylplatinum sulfate in aqueous solution by Clegg and Hall,[7] the band positions have been reassigned. Table III lists the absorption frequencies observed for hydroxytrimethylplatinum with literature data included for comparison. The assignments are largely based on the study of Clegg and Hall.

TABLE III

INFRARED SPECTRUM OF HYDROXYTRIMETHYLPLATINUM (CM^{-1})

Lit values[6]	Our values	Assignments	Raman data for $[(CH_3)_3Pt(OH_2)_3]^{+}$ [7]
	365 vs	Pt–O def	. . .
	382 wsh	Pt–O def	. . .
	570 vwsh	Pt–C sym str	600
	590 w	Pt–C unsym str	. . .
719 vs[a]	721 vs	Pt–O str	. . .
858 msh	854 msh	CH_3 rock	. . .
873 m	877 m	CH_3 rock	882
	1160 w	Unidentified combination	1143, 1194
1238 vs	1248 vs	CH_3 nontotally sym def	1250
1271 m	1280 w	CH_3 sym def	1290
	1344 wsh	CH_3 sym def	1329
1368 m	1381 msh	Overtone of 721-cm^{-1}	
1399 m	1411 m	and CH_3 unsym def	1427
1410 m	1427 msh	Fermi resonance	. . .
2778 s	2805 w	CH sym str	2823
2865 s	2899 s	CH sym str	2909
2941 s	2959 s	CH unsym str	2978
3559 s	3584 s	OH str	

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder.

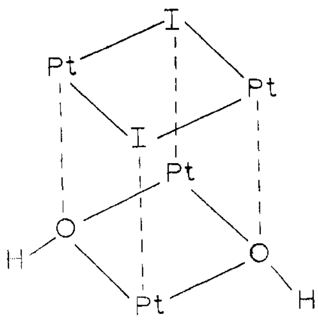

Figure 3.—Multicentered bonds of $[(CH_3)PtI]_2[(CH_3)_3PtOH]_2$.

Discussion

The hydroxylic proton resonance of tetrameric hydroxytrimethylplatinum clearly demonstrates that the structure of this molecule in solution is the same as the structure shown in Figure 1 with hydroxide substituted for chloride. All hydroxylic protons must also be equidistant from the three nearest platinum atoms since only one *Pt*–O–*H* coupling constant is observed. The three lone pairs on the hydroxyl group are thus equivalently used in bonding.

The very high field of the hydroxylic proton resonance signal may be due to inductive effects, but recent studies[8] indicate that paramagnetic shielding from the Pt 5d electrons may be an important contributing factor. Decreasing positive chemical shift with increasing distance from the platinum atoms would thus be consistent with our assigning the peak at a τ value of 11.52 to the hydrogen-bonded hydroxylic protons (*i.e.*, they would be pulled away from the platinum atoms by the oxygen in water).

Since hydroxy- and iodotrimethylplatinum have rather similar Pt–C–H_3 coupling constants, it is interesting that the intermediate compounds (Table II) have coupling constants that are out of this range. Figure 3 is a model of the intermediate having both $(CH_3)_3PtI_2OH$ and $(CH_3)_3PtI(OH)_2$ environments. The methyl groups are not shown. It is obvious that in this structure the Pt–O bonds will be longer than those in hydroxytrimethylplatinum and that the Pt–I bonds will be shorter than those in iodotrimethylplatinum (iodide being a much larger ion). This change should manifest itself by causing more p character (or more correctly, less s character) to be in the Pt–O bonds[9] and thus correspondingly more s character in the Pt–C bonds for those platinum atoms bonded to two oxygen atoms. This increased s character will result in a larger Pt–C–H_3 coupling constant.[10] Conversely, more s character in the Pt–I bond will induce less s character in the Pt–C bonds causing a smaller Pt–C–H_3 coupling constant. The arrangement in Figure 3 actually may be considered as two dimers held together by weaker bonds (dashed lines). A disproportionation mechanism

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(6) M. N. Hoechstetter, *J. Mol. Spectry.*, **13**, 407 (1964).

(7) D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, **21**, 357 (1965).

(8) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 4583 (1964).

(9) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p 200.

(10) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).

to form hydroxy- and iodotrimethylplatinum tetramers thus becomes plausible. This reasoning is applicable to the other two intermediates if one considers distortions in the central "cubic" arrangement.

The infrared spectrum of hydroxytrimethylplatinum was found to be rather different from that reported by Hoechstetter.[6] Adams, Chatt, and Shaw[11] have reported Pt–C stretching frequencies in alkylplatinum(II) complexes in the region 500–600 cm^{-1}, and Gel'man[12] has reported the Pt–C stretching frequency in iodotrimethylplatinum at 562 cm^{-1}. Hoechstetter asserts that he did not see the slightest indication of Gel'man's Pt–C band in a series of trimethylplatinum derivatives. We, on the other hand, have observed two bands in hydroxytrimethylplatinum and also in the iodo, bromo, and chloro derivatives.[13] The reason for this disagreement must be that we used much thicker samples and a more sensitive instrument in this region.

The hydroxyl group bonded to three platinum atoms has local C_{3v} symmetry and should be expected to have four normal Pt–O modes of vibration.[14] The band at 365 cm^{-1} is assigned to the Pt–O deformation frequencies (although the weak shoulder at 382 cm^{-1} may be the unsymmetric Pt–O deformation).

The band at 721 cm^{-1} represents both symmetric and unsymmetric Pt–O stretching frequencies which often appear as one intense band.[14] This band has an overtone at 1411 cm^{-1}. The whole series of tetrameric trimethylplatinum derivatives have unsymmetric CH deformation bands in the region 1410–1420 cm^{-1},[6,13] while the aquated trimethylplatinum cation has this band at 1427 cm^{-1}.[7] Under high resolution we observed three definite bands in this region. A logical explanation for this is that the overtone of the unsymmetric Pt–O stretching frequency is in Fermi resonance with the unsymmetric CH deformation frequency, generating the bands at 1427 and 1381 cm^{-1}. The overtone of the symmetric Pt–O stretching frequency cannot take part in Fermi resonance and appears at 1411 cm^{-1}.

Clegg and Hall assigned their 1143-cm^{-1} band as a combination band of the Pt–C_3 skeletal deformation and CH_3 rocking frequencies ($259 + 882 = 1141$) and their 1194-cm^{-1} band as an overtone of the Pt–C stretching frequency ($2 \times 600 = 1200$). Since we were not able to make a choice among these overtones and combinations, the band at 1160 cm^{-1} is labeled an unidentified combination.

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(12) A. D. Gel'man, L. A. Gribov, F. A. Zakharova, and M. N. Orlova, *Zh. Neorgan. Khim.*, **5**, 987 (1960).

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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High Resolution Mass Spectroscopic Studies of Metal Chelates

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The mass spectra of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone complexes of copper(II), zinc(II), and iron(III) ions are presented. The spectra provide valuable information, including molecular weights, metal:ligand ratios, and relative stabilities of ion fragments. The possibility of rearrangements due to radical transfer processes is depicted.

Introduction

Mass spectrometry has been used extensively over the past few years in studies of large organic molecules,[2,3] but its applicability to the investigation of transition metal complexes has yet to be firmly established. With the advent of highly efficient direct evaporation inlet systems, the problems with low volatility and thermal instability which are encountered frequently when dealing with metal complexes have to some extent been overcome. To date, only a few metal chelates have been studied by mass spectrometry, *e.g.*, metalloporphyrins,[4] a chromium complex of acetylacetone,[5] and several ferrocene derivatives.[6–8] Shannon[9] has also described in some detail the ionization and fragmentation processes in a number of inorganic complexes. Most of these compounds have, however, been of moderate volatility or of considerable thermal stability (as in the case of the metalloporphyrins). We wish to

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