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^{1}H NMR EVIDENCE FOR MIXED TETRAMERS OF IODO- AND HYDROXO-TRIMETHYLPLATINUM(IV)

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SUMMARY

^{1}H NMR spectra of the product obtained from reaction between $[Pt(CH_3)_3]_2SO_4 \cdot 4\ H_2O$ and an aqueous mixture of sodium iodide and sodium hydroxide have yielded evidence for tetramers containing both iodo and hydroxo bridging groups in the same framework.

INTRODUCTION

Crystal structure determinations of $[PtI(CH_3)_3]_4$[1] and $[PtOH(CH_3)_3]_4$[2,3] have shown both compounds to consist of tetrameric units involving three-way bridging of I and OH respectively (Fig. 1a, e). In 1966, Morgan *et al.*[4] reported that reaction between $[PtI(CH_3)_3]_4$ and NaOH in dry ether gave not only the anticipated $[PtOH(CH_3)_3]_4$ but also intermediate compounds which were considered to be tetramers containing both I and OH in the one framework. They cited as evidence for such species the NMR spectrum of the reaction product, which showed four distinct methyl–platinum triplets (^{195}Pt, $I=\frac{1}{2}$, 34% abundance), two due to $[PtI(CH_3)_3]_4$ and $[PtOH(CH_3)_3]_4$, the other two arising from the intermediates. There are three possible "mixed" species, *viz.*, $[\{PtI(CH_3)_3\}_3\{PtOH(CH_3)_3\}]$, $[\{PtI(CH_3)_3\}_2\{PtOH(CH_3)_3\}_2]$, and $[\{PtI(CH_3)_3\}\{PtOH(CH_3)_3\}_3]$, Fig. 1b, c, d, which, for convenience, may be abbreviated to I_3OH, $I_2(OH)_2$, and $I(OH)_3$ respectively.

RESULTS AND DISCUSSION

Morgan *et al.*[4] considered that for the five possible species (Fig. 1) there were only four non-equivalent environments for methyl protons, *viz.*, where the three methyl groups on the one platinum atom are *trans* to three iodo groups, $(CH_3)_3PtI_3$, two iodo groups and one hydroxo group, $(CH_3)_3PtI_2OH$, one iodo group and two hydroxo groups, $(CH_3)_3PtI(OH)_2$, and three hydroxo groups, $(CH_3)_3Pt(OH)_3$, and that each environment gave rise to one triplet in the NMR spectrum.

Such an interpretation neglects several factors which may operate to produce inequivalence of methyl resonances:

(*i*). The chemical shifts and coupling constants of methylplatinum protons have been found in a number of systems[5-7] to depend markedly on the nature of the atoms in

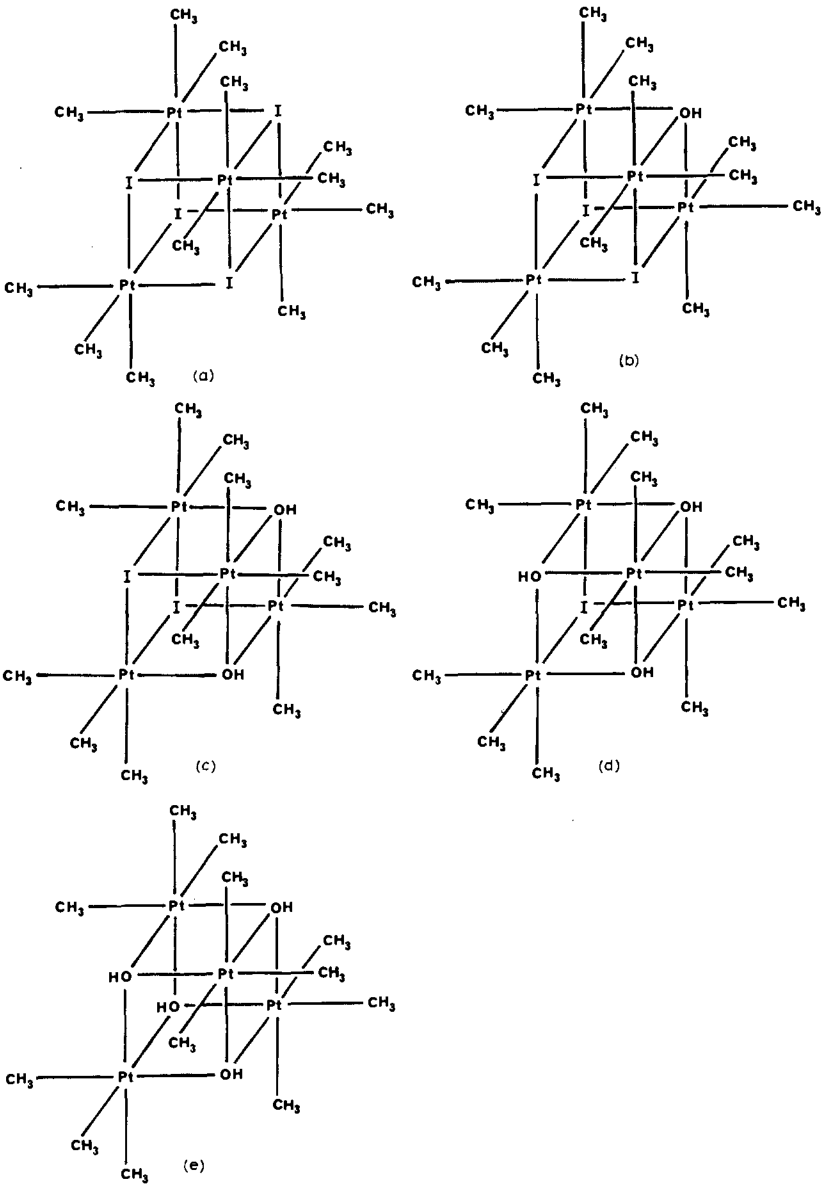

Fig. 1.

the *trans* positions. Thus methyl groups *trans* to I would be expected to be non-equivalent to those *trans* to OH. Consequently the three CH_3 groups on the one Pt atom could not be treated as an equivalent set.

(*ii*). There may be some dependence of coupling constants and chemical shifts on the nature of groups in the *cis* positions, although this *cis* influence has been found to be much smaller than the *trans* influence in other trimethylplatinum(IV) systems[7]. If this influence is important, then, for example, groups *trans* to I and *cis* to two I atoms

TABLE 1

METHYL GROUP ENVIRONMENTS FOR HYDROXO–IODO TETRAMERS

Tetramer	*No. of CH_3 groups per tetramer in the various environments*					
	$I_tI_cI_c$	$I_tI_cOH_c$	$OH_tI_cI_c$	$I_tOH_cOH_c$	$OH_tOH_cI_c$	$OH_tOH_cOH_c$
I_4	12					
I_3OH	3	6	3			
$I_2(OH)_2$		4	2	2	4	
$I(OH)_3$				3	6	3
$(OH)_4$						12

($I_tI_cI_c$) would be non-equivalent to those *trans* to I and *cis* to OH and I ($I_tOH_cI_c$). If factors (*i*) and (*ii*) are operating in this system a total of six triplets would be observed, corresponding to the environments in Table 1.

(*iii*). Changes in bond lengths and angles necessitated by the introduction of both I and OH in a tetramer as compared with those of the parent compounds $[PtI(CH_3)_3]_4$ and $[PtOH(CH_3)_3]_4$ may produce differences in both chemical shifts and coupling constants of protons of methyl groups *trans* and *cis* to the same atoms but in different tetramers. Differences in the geometry of the mixed species compared with the parent tetramers might well be significant since the Pt–I (2.8 Å) and Pt–O (2.2 Å) bond distances in the parent compounds are substantially different. Thus, for example, the protons in the structural environment $I_tI_cI_c$ in tetramer I_4 may have different chemical shifts and coupling constants from the protons in the same environment in tetramer I_3OH (Table 1). If factors (*i*), (*ii*), and (*iii*) are in operation, a total of twelve triplets would be predicted as shown in Table 1.

In view of the above possibilities it seemed desirable to reexamine this system. It was found that a much more convenient method of preparation of mixed tetramers than that of Morgan *et al.*[4] involved the reaction of $[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$ with an aqueous mixture of sodium iodide and sodium hydroxide.

The NMR spectra of the reaction products were recorded in a number of solvents such as $CDCl_3$, benzene, and tetrachloroethylene. In each case, a number of peaks in addition to those assignable to $[PtI(CH_3)_3]_4$ and $[PtOH(CH_3)_3]_4$ were observed, although the peaks due to the parent compounds were invariably the most intense. The number of peaks observed varied from solvent to solvent, but in benzene as many as eleven triplets (or components thereof) could be distinguished. The spectrum of a benzene solution of the product obtained using a sodium iodide to sodium hydroxide ratio of 2/1 appears in Fig. 2.

The number of peaks observed tended to confirm that all three factors noted above were in operation, so that a total of twelve triplets would be expected. Reference to Table 1 shows that the intensities of a number of these peaks should be related. Thus for each of the tetramers I_3OH and $I(OH)_3$ three triplets in the intensity ratio of 1/1/2 should be observed, while for $I_2(OH)_2$ four triplets in the ratio of 1/1/2/2 would be anticipated. The intensities of triplets from different tetramers would be unrelated. By examining the products from a number of reactions using different ratios of NaI to NaOH which gave a variation in relative intensities of peaks from different tetramers, the assignment of bands to particular tetramers was facilitated.

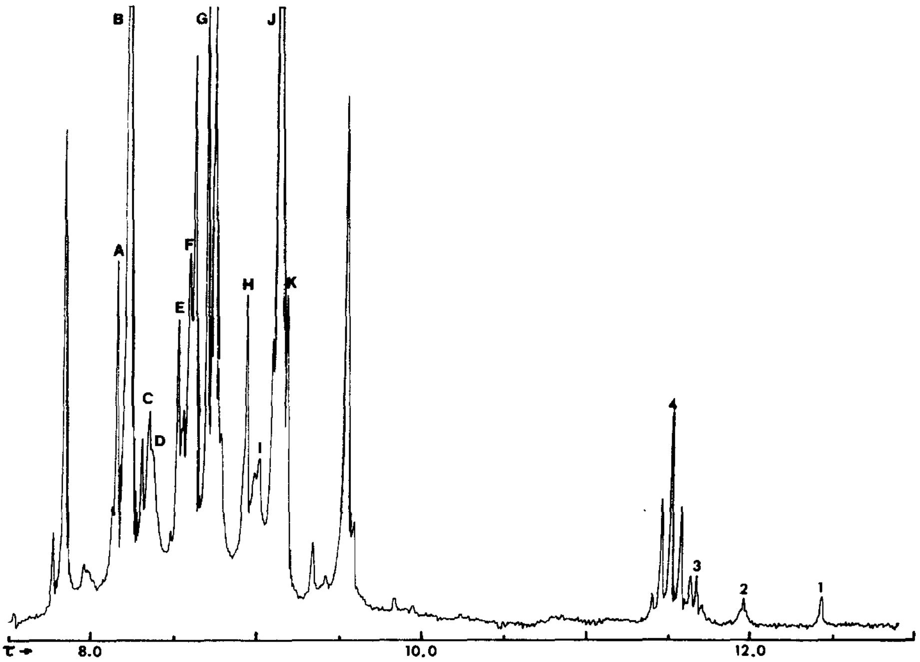

Fig. 2. ^{1}H NMR spectrum of mixed tetramers of iodo- and hydroxo-trimethylplatinum(IV) in benzene.

TABLE 2

^{1}H NMR DATA FOR THE TETRAMERS $[\{PtI(CH_3)_3\}_n\{PtOH(CH_3)_3\}_{4-n}]$[a]

Peak	*τ*	*J*	*Tetramer*	*Environment*
A	8.18	77.0	I_3OH	$I_tI_cOH_c$
B	8.26	77.2	I_4	$I_tI_cI_c$
C	8.36	77.5	I_3OH or $I_2(OH)_2$	$OH_tI_cI_c$
D	8.39	77.5	$I_2(OH)_2$ or I_3OH	$OH_tI_cI_c$
E	8.54	78.0	$I_2(OH)_2$	$I_tI_cOH_c$?
F	8.61	77.8	$I_2(OH)_2$	$OH_tOH_cI_c$?
G	8.71	78.0	$I(OH)_3$	$OH_tOH_cI_c$
H	8.95	78.2	$I(OH)_3$	$I_tOH_cOH_c$
I	9.02	78.5	$I_2(OH)_2$?	$I_tOH_cOH_c$?
J	9.14	78.5	$(OH)_4$	$OH_tOH_cOH_c$
K	9.18	78.7	$I(OH)_3$	$OH_tOH_cOH_c$
4	11.52	11.2	$(OH)_4$	
3	11.67	6.0	$I(OH)_3$	
2	11.96	3.4	$I_2(OH)_2$	
1	12.43		I_3OH	

[a] Spectrum recorded in benzene at 34° C.

The qualitative relative intensities and the coupling constants of peaks assignable to each tetramer aided in the assignment of peaks to actual environments.

Table 2 lists the observed peaks and the tentative assignments which have been made. Peaks B and J (Fig. 2) were readily assignable from chemical shifts and coupling constants to the parent species $[PtI(CH_3)_3]_4$ and $[PtOH(CH_3)_3]_4$ respectively. The more intense peaks from each of the mixed tetramers were fairly readily assigned. Table 1 indicates one such peak for each of I_3OH and $I(OH)_3$, and two equally intense peaks for $I_2(OH)_2$. Peaks E and F appeared to be of equal intensity in a range of mixtures and were assigned to $I_2(OH)_2$. Peaks A and G were assigned to the most intense peaks from I_3OH and $I(OH)_3$ respectively. Peaks H and K seemed to have intensities related to that of G and in the correct ratio, and were assigned to environments $I_tOH_cOH_c$ and $OH_tOH_cOH_c$ respectively in the tetramer $I(OH)_3$ on the basis of coupling constants. The other peaks, C, D and I were difficult to interpret satisfactorily. However, C was tentatively assigned to environment $OH_tI_cI_c$ in one of the tetramers I_3OH or $I_2(OH)_2$ and D to the same environment in the other tetramer. Peak I might be from environment $I_tOH_cOH_c$ in $I_2(OH)_2$. Unlabelled peaks in Fig. 1 were all accounted for as satellites to principal resonances.

Reference to Table 2 indicates that in most cases peaks assigned to similar environments in different tetramers have similar chemical shifts. However, one exception to this is the difference between peaks A and E which were both assigned to environment $I_tI_cOH_c$. In general, chemical shifts appeared to depend on the nature of the *cis* groups, moving to higher field as the number of *cis* oxygens increased.

It was reported[4] that coupling constants of protons in the mixed tetramers lay substantially outside those of the parent compounds. This has not been substantiated in the present work, where all coupling constants were similar to those of the parent tetramers (77.2 Hz for $[PtI(CH_3)_3]_4$, 78.5 for $[PtOH(CH_3)_3]_4$).

The OH proton absorption of $[PtOH(CH_3)_3]_4$ was observed at τ 11.52 by Morgan *et al.*, as a seven line multiplet in agreement with theory[4]. As shown in Fig. 2, the mixture obtained exhibited 4 separate multiplets attributable to OH protons. The major peak at τ 11.52 was attributed to the OH proton of $[PtOH(CH_3)_3]_4$. The three remaining peaks may be assigned to the OH protons in the mixed species, each of which should give rise to one multiplet for the OH proton. Since the methylplatinum spectrum indicated that the amounts of the mixed tetramers present decreased in the order $I(OH)_3 > I_2(OH)_2 > I_3OH$, the peaks at τ 11.67, 11.96 and 12.43 have been assigned to $I(OH)_3$, $I_2(OH)_2$ and I_3OH respectively on the basis of their relative intensities.

The most significant feature of these resonances was the variation in $^2J(^{195}Pt-OH)$ from tetramer to tetramer. For $[Pt(OH)(CH_3)_3]_4$ the value was 11.2 Hz as found previously[4], but this coupling decreased regularly to < 2 Hz for I_3OH (Table 2). Since the magnitude of a coupling constant is dependent on the degree of *s*-character in the bonds through which the coupling acts, such a decrease may indicate less *s*-character in the Pt–O bonds of the mixed tetramers compared with that in $[Pt(OH)(CH_3)_3]_4$. This is probably the result of a lengthening of the Pt–O bonds and changes in bond angles at the Pt and O atoms in the mixed tetramers due to the presence of the larger I atoms in the tetrameric framework.

The chemical shifts of the OH protons (τ 11.52–12.43) were of interest. For $[Pt(OH)(CH_3)_3]_4$, paramagnetic shielding from the 5*d* electrons of the three adjacent

Pt atoms was suggested as a possible factor[4] responsible for the upfield shifts. Such a mechanism would predict higher field chemical shift values with decreasing distance of the proton from the Pt nuclei. If such a factor is operating, it follows that the proton of the OH group in I_3OH (τ 12.43) is nearest the Pt atoms and therefore that the effect due to lengthening of the Pt–O bonds is more than compensated by the opening out of the Pt–O–Pt angles.

The hydroxo–iodo system studied above was the most useful of a number of mixed tetrameric systems investigated because the chemical shift values of the parents were sufficiently well separated to allow observation of a majority of peaks due to mixed tetramers. However, the coupling constant variations were too small to allow any inferences to be made as to the relative magnitudes of *trans* and *cis* influences in these molecules. Preliminary investigations of mixed systems such as iodo–chloro and bromo–chloro also revealed evidence for mixed tetramers, but the resonances tended to overlap.

The infrared spectrum of the hydroxo–iodo tetramer system (solid state) showed several features of interest. The ν(Pt–C) and asymmetric CH_3 deformation regions were broad and structureless, but the O–H stretching and symmetric CH_3 deformation regions showed features beyond those for the parent compounds. In the O–H stretching region four peaks were observed, at frequencies of 3600, 3588, 3574 and 3532 cm^{-1}. The peak at 3600 cm^{-1} was the most intense and was assigned to ν(O–H) for $[PtOH(CH_3)_3]_4$[8]. The other tetramers $I(OH)_3$, $I_2(OH)_2$ and $I_3(OH)$, Fig. 1, have local symmetries of C_{3v}, C_{2v} and C_{3v} respectively, so that two infrared active bands would be expected for $I(OH)_3$, two for $I_2(OH)_2$, and one for $I_3(OH)$. However, one of the vibrations in $I(OH)_3$ is doubly degenerate, so that solid state effects may produce some splitting of the corresponding peak, and a total of 6 bands from these three species is possible. It is difficult to assign the observed peaks to particular vibrations, but the peak at 3532 cm^{-1} may be due to the O–H stretching vibration in I_3OH.

The symmetric methyl deformation region had in addition to peaks attributable to the parent compounds (1224 and 1260 cm^{-1} for $[PtI(CH_3)_3]_4$[9], 1242 and 1277 cm^{-1} for $[PtOH(CH_3)_3]_4$[8]) a peak at 1268 cm^{-1} and small shoulders at 1238 and 1226 cm^{-1} attributable to methyl vibrations in the mixed tetramers.

EXPERIMENTAL

$[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$ (0.1 g) was dissolved in water (5 ml) and an aqueous solution of a mixture of NaOH and NaI in the appropriate ratio added. The white solid which precipitated immediately was filtered, washed with water and air-dried. Best results were obtained using 2/1 ratios of NaI/NaOH.

^1H NMR spectra

^1H NMR spectra were recorded on a JEOL MH 100 MHz spectrometer on sweep width 540. Spin–spin coupling constants are considered accurate to ±0.5 Hz and τ values to ±0.01 ppm.

Infrared spectra

IR spectra were recorded on a Perkin Elmer 457 Spectrometer as Nujol and hexachlorobutadiene mulls.

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REFERENCES

1 G. Donnay, L. B. Coleman, N. G. Krieghoff and D. O. Cowan, *Acta Crystallogr., Sect. B*, 24 (1968) 157.
2 T. G. Spiro, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 7 (1968) 2165.
3 H. S. Preston, J. C. Mills and C. H. L. Kennard, *J. Organometal. Chem.*, 14 (1968) 447.
4 G. L. Morgan, R. D. Rennick and C. C. Soong, *Inorg. Chem.*, 5 (1966) 372.
5 K. Kite, J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., A*, (1966) 1744.
6 D. E. Clegg and J. R. Hall, *Austr. J. Chem.*, 20 (1967) 2025.
7 D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organometal. Chem.*, 38 (1972) 403.
8 D. E. Clegg and J. R. Hall, *J. Organometal. Chem.*, 17 (1969) 175.
9 D. E. Clegg and J. R. Hall, *J. Organometal. Chem.*, 22 (1970) 491.