Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A STUDY OF SOME AMINE, PYRIDINE AND 3,5-LUTIDINE COMPLEXES OF TRIMETHYLPLATINUM(IV)

J. R. HALL and G. A. SWILE
Chemistry Department, University of Queensland, Brisbane, Queensland 4067 (Australia)

(Received March 16th, 1972)

SUMMARY

The reactions of trimethylplatinum(IV) compounds with a number of amines have been examined. With ammonia and methylamine, tris- and mono(amine) species have been obtained, but no bis(amine) species apart from $[Pt(CH_3)_3(NH_3)_2I]$. With ethylamine the bis(amine) species is formed with excess ligand. The ^1H NMR spectra of $[Pt(CH_3)_3LI]_2$ (L=pyridine, 3,5-lutidine*) exhibit evidence for two isomers in solution and an equilibrium of these compounds with $[Pt(CH_3)_3L_2I]$ and $[Pt(CH_3)_3I]_4$.

INTRODUCTION

A number of amine complexes of trimethylplatinum(IV) have been reported. The compounds $[Pt(CH_3)_3(NH_3)_3]X$ (where X=Cl, Br and I) were first prepared by Ivanova and Gel'man[1]. The iodide and chloride complexes have since been studied by various spectroscopic techniques[2-4] and are well characterized. The methylamine complex $[Pt(CH_3)_3(CH_3NH_2)_3]I$ has also been investigated[4,5]. However, amine complexes of trimethylplatinum containing fewer than three amine groups have been examined to a lesser extent. The compound $[Pt(CH_3)_3(NH_3)_2I]$ (characterised by platinum analysis only) was reported by Pope and Peachey[6] to result from the reaction between aqueous ammonia and $[Pt(CH_3)_3I]_4$ in ethanol/benzene solution. Ivanova and Gel'man[1] claimed that the same compound could be prepared by careful thermal decomposition of $[Pt(CH_3)_3(NH_3)_3]I$, but characterized it by a molecular weight determination only. Reaction of this compound with either one mole, or with an excess, of pyridine was reported to yield the compound $[Pt(CH_3)_3PyNH_3I]$[1].

The pyridine derivatives of iodotrimethylplatinum(IV) have been well characterized. Addition of excess pyridine to $[Pt(CH_3)_3I]_4$ yielded the compound $[Pt(CH_3)_3Py_2I]$[7,8]. Reaction of one mole of pyridine with $[Pt(CH_3)_3I]_4$ or treatment of $[Pt(CH_3)_3Py_2I]$ with dilute acid gave the dimeric species $[Pt(CH_3)_3PyI]_2$[9]. Both have been examined by NMR[10], and $[Pt(CH_3)_3Py_2I]$ also by infrared spectroscopy[2].

The present paper deals with a more extensive study of amine derivatives of trimethylplatinum(IV) and investigates several features of the NMR spectra of $[Pt(CH_3)_3Py_2I]$, $[Pt(CH_3)_3PyI]_2$, and their 3,5-lutidine analogues.

---

* 3,5-Dimethylpyridine.

RESULTS

The compounds $[Pt(CH_3)_3(NH_3)_3]X$ and $[Pt(CH_3)_3(CH_3NH_2)_3]X$ (where $X=Cl$ and I) were prepared without difficulty by literature methods. Attempts to prepare the compound $[Pt(CH_3)_3(NH_3)_2I]$ by chemical means, however, proved unsuccessful. Pope and Peachey[6] reported that reaction between aqueous ammonia and $[Pt(CH_3)_3I]_4$ was difficult, and their preparative conditions did not indicate the mole ratio of ammonia used. In the present investigation, reaction of $[Pt(CH_3)_3I]_4$ in ethanol/benzene with excess aqueous ammonia was found to yield the compound $[Pt(CH_3)_3(NH_3)_3]I$. With a two mole ratio of ammonia to $[Pt(CH_3)_3I]_4$, a mixture of the compounds $[Pt(CH_3)_3(NH_3)_3]I$ and $[Pt(CH_3)_3NH_3I]_2$ was invariably obtained. The latter compound is probably dimeric with bridging iodine atoms analogous to the compound $[Pt(CH_3)_3PyI]_2$[9].

Reaction of an aqueous solution of $[Pt(CH_3)_3(NH_3)_3]I$ with one mole of $HClO_4$ yielded a product consisting predominantly of $[Pt(CH_3)_3I]_4$ as indicated by its infrared spectrum, which included only very weak N–H stretching bands.

Similar results were observed for the corresponding methylamine system, where a mixture of $[Pt(CH_3)_3(CH_3NH_2)_3]I$ and $[Pt(CH_3)_3(CH_3NH_2)I]_2$ was obtained by reaction of $[Pt(CH_3)_3I]_4$ with a two mole ratio of methylamine, and the compound $[Pt(CH_3)_3(CH_3NH_2)I]_2$ precipitated on addition of one mole of $HClO_4$ to $[Pt(CH_3)_3(CH_3NH_2)_3]I$.

The compounds $[Pt(CH_3)_3(NH_3)_3]I$ and $[Pt(CH_3)_3(CH_3NH_2)_3]I$ were examined by the thermogravimetric technique. Figure 1 shows the thermogravimetric analysis curves as a function of temperature.

The compound $[Pt(CH_3)_3(NH_3)_3]I$ lost one mole of ammonia above 76° to form $[Pt(CH_3)_3(NH_3)_2I]$ (calcd. weight loss for one mole ammonia 4.1%; found, 3.6%). This compound lost further ammonia almost immediately on continued heating to yield $[Pt(CH_3)_3NH_3I]_2$ (calcd. weight loss for 2 moles ammonia 8.2%; found 7.6%) and finally $[Pt(CH_3)_3I]_4$ (calcd. 12.2%; found 11.6%) by 165°. On the other hand, $[Pt(CH_3)_3(CH_3NH_2)_3]I$ showed no evidence for formation of an intermediate compound of stoichiometry $[Pt(CH_3)_3(CH_3NH_2)_2I]$ on heating, since loss of CH_3NH_2 occurred at a steady rate until the compound $[Pt(CH_3)_3(CH_3NH_2)I]_2$ was formed (calcd. 13.5%; found 13.3%). Continued heating resulted in the formation of $[Pt(CH_3)_3I]_4$ at 188° (calcd. 20.2%; found 20.0%). All loss of ammonia or methylamine in these compounds proceeded endothermally.

The compound $[Pt(CH_3)_3(NH_3)_3]Cl$ has been observed to be much more stable than the corresponding iodide[1], being stable indefinitely in the solid state. We have found that addition of one mole of $HClO_4$ to an aqueous solution of $[Pt(CH_3)_3(NH_3)_3]Cl$ did not give an immediate precipitate as was found for the iodide. Indeed, boiling this solution for several hours resulted in only a slight cloudiness. On concentration of the solution, a water-insoluble product was obtained but analytical figures and infrared spectra indicated the compound was mainly $[Pt(CH_3)_3Cl]_4$. Addition of excess $HClO_4$, however, produced an immediate precipitate of $[Pt(CH_3)_3Cl]_4$. Similar observations were made for the corresponding methylamine compound.

Thermogravimetric analyses of both $[Pt(CH_3)_3(NH_3)_3]Cl$ and $[Pt(CH_3)_3(CH_3NH_2)_3]Cl$ indicated that the compounds behaved similarly to $[Pt(CH_3)_3(CH_3NH_2)_3]I$ (Fig. 1). Loss of amine occurred steadily up to an amount correspond-

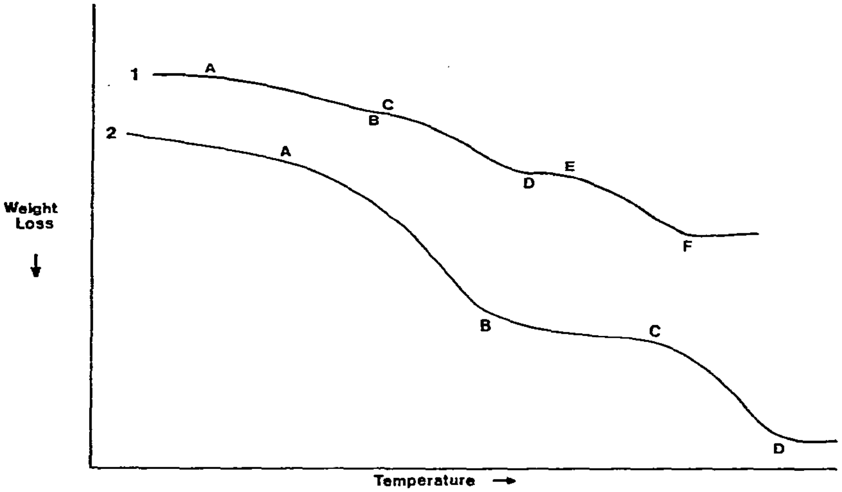

Fig. 1. TGA curves for trimethylplatinum(IV) amine complexes.

Curve	*Compound*	*Temp. (°C)*					
		A	*B*	*C*	*D*	*E*	*F*
1	$[Pt(CH_3)_3(NH_3)_3]I$	76	110	112	135	142	165
2	$[Pt(CH_3)_3(CH_3NH_2)_3]I$	86	132	163	188		
2	$[Pt(CH_3)_3(NH_3)_3]Cl$	94	145	173	203		
2	$[Pt(CH_3)_3(CH_3NH_2)_3]Cl$	99	150	180	205		

ing to two molecules per molecule of compound, and the product at this stage, $[Pt(CH_3)_3(amine)Cl]_2$ remained stable for some time before decomposing to $[Pt(CH_3)_3Cl]_4$. The methylamine complexes were only slightly more stable thermally than the ammine complexes (Fig. 1).

Ammonia and methylamine were apparently unique in forming tris(amine) compounds. Addition of excess ethylamine to $[Pt(CH_3)_3I]_4$ gave $[Pt(CH_3)_3(EtNH_2)_2I]$ as the only product, and experiments with dimethylamine and higher aliphatic amines indicated similar results.

Reaction of $[Pt(CH_3)_3I]_4$ with excess pyridine gave $[Pt(CH_3)_3Py_2I]$ as reported by Lile and Menzies[8]. With excess 3,5-lutidine the compound $[Pt(CH_3)_3Lut_2I]$ was formed. The ^1H NMR spectral data for these compounds appear in Table 1.

As noted by Foss and Gibson[9], treatment of a solution of $[Pt(CH_3)_3Py_2I]$ with one mole of dilute acid gave the dimer $[Pt(CH_3)_3PyI]_2$. This latter compound was reported[9] to be unaffected by dilute acids. We have found, however, that dilute acids reacted quite readily with $[Pt(CH_3)_3PyI]_2$ to yield $[Pt(CH_3)_3I]_4$. Indeed, use of more than one mole of acid in the preparation of $[Pt(CH_3)_3PyI]_2$ led to decreased yields and some contamination with $[Pt(CH_3)_3I]_4$.

The NMR spectrum of $[Pt(CH_3)_3PyI]_2$ proved interesting. Morgan *et al.*[10] reported that the spectrum of $[Pt(CH_3)_3PyI]_2$ in the mixture obtained by addition of pyridine to $[Pt(CH_3)_3I]_4$ in benzene contained two sets of triplets in the intensity ratio

TABLE 1

^{1}H NMR SPECTRA OF PYRIDINE AND LUTIDINE COMPLEXES OF TRIMETHYLPLATINUM(IV) IN $CDCl_3$

Peak	τ^a	J^b	*Trans ligand*	*Compound*	*Lutidine peaks*		
					$\tau(CH_3)$	$\tau(H_\alpha)$	$\tau(H_\gamma)$
	8.49	70.7		$[Pt(CH_3)_3Py_2I]$			
	8.79	69.5					
	8.53	71.2		$[Pt(CH_3)_3Lut_2I]$	7.71	1.60	2.54
	8.82	70.7					
$[Pt(CH_3)_3PyI]_2$ (*equilibrium mixture, Fig. 2*)							
A	8.00	71.6	Py	*cis*-$[Pt(CH_3)_3PyI]_2$			
B	8.27	77.5	I	$[PtI(CH_3)_3]_4$[c]			
C	8.49	70.4	Py	$[Pt(CH_3)_3Py_2I]$			
D	8.62	70.8	Py	*trans*-$[Pt(CH_3)_3PyI]_2$			
E	8.70	75.5	I	*cis*- and *trans*-$[Pt(CH_3)_3PyI]_2$			
F	8.79	69.6	I	$[Pt(CH_3)_3Py_2I]$			
$[Pt(CH_3)_3LutI]_2$ (*equilibrium mixture, Fig. 4*)							
A	8.01	71.6	Lut	*cis*-$[Pt(CH_3)_3LutI]_2$	7.82	1.74	2.73
B	8.25	77.4	I	$[PtI(CH_3)_3]_4$ [c]			
C	8.52	70.5	Lut	$[Pt(CH_3)_3Lut_2I]$	7.71	1.58	2.56
D	8.56	71.0	Lut	*trans*-$[Pt(CH_3)_3LutI]_2$	7.61	1.27	2.56
E	8.69	75.4	I	*trans*-$[Pt(CH_3)_3LutI]_2$			
F	8.82	70.3	I	$[Pt(CH_3)_3Lut_2I]$			
G	8.74	75.5	I	*cis*-$[Pt(CH_3)_3LutI]_2$			

[a] $\tau(PtCH_3)$. [b] $^2J(^{195}Pt{-}CH_3)$. [c] In $CDCl_3$, τ 8.25 and $^2J(^{195}Pt{-}CH_3)$ 77.7 Hz.

of 2/1. We have recorded the spectrum of $[Pt(CH_3)_3PyI]_2$, obtained by reaction of $[Pt(CH_3)_3Py_2I]$ with a one mole ratio of $HClO_4$, in both benzene and $CDCl_3$. The spectra in both $CDCl_3$ and benzene however were far more complex than the simple 2/1 ratio expected and a discussion of this appears later. A similar complex spectrum was obtained for $[Pt(CH_3)_3LutI]_2$ prepared by reaction of $[Pt(CH_3)_3Lut_2I]$ with a one mole ratio of $HClO_4$.

Ivanova and Gel'man[1] reported that the compound $[Pt(CH_3)_3(NH_3)_2I]$ reacted with pyridine to give $[Pt(CH_3)_3PyNH_3I]$ irrespective of whether the pyridine was in a one mole ratio or in excess. We have attempted without success to prepare this compound by reaction of pyridine with $[Pt(CH_3)_3(NH_3)_2I]$ or $[Pt(CH_3)_3NH_3I]_2$.

Reaction of $[Pt(CH_3)_3NH_3)_2I]$ with excess pyridine gave a product whose infrared spectrum was identical with the spectrum of $[Pt(CH_3)_3Py_2I]$[2]. The product of reaction of $[Pt(CH_3)_3NH_3I]_2$ with two moles of pyridine gave an infrared spectrum identical with that of an authentic sample of $[Pt(CH_3)_3PyI]_2$ with no evidence for N–H stretching bands. The infrared spectrum of the product of the reaction of $[Pt(CH_3)_3(CH_3NH_2)I]_2$ with two moles of pyridine in the cold contained bands due to pyridine as well as weak N–H stretching bands due to methylamine, but the latter bands disappeared rapidly on standing. The resultant spectrum agreed well with that of an authentic sample of $[Pt(CH_3)_3PyI]_2$. When an excess of pyridine was used, $[Pt(CH_3)_3Py_2I]$ was obtained, as identified by its infrared spectrum.

DISCUSSION

As noted in the experimental section, all attempts to prepare the compounds $[Pt(CH_3)_3(NH_3)_2I]$ and $[Pt(CH_3)_3(CH_3NH_2)_2I]$ by chemical methods led to the formation of $[Pt(CH_3)_3L_3]I$ or $[Pt(CH_3)_3LI]_2$ ($L = NH_3, CH_3NH_2$). The compound $[Pt(CH_3)_3(NH_3)_2I]$ reported by Pope and Peachy[6] from the action of ammonia on $[Pt(CH_3)_3I]_4$ was characterized only by a platinum analysis, and it is possible that the product obtained was an equimolar mixture of $[Pt(CH_3)_3(NH_3)_3]I$ and $[Pt(CH_3)_3NH_3I]_2$. Its solubility in a variety of solvents does add support to this conjecture, since $[Pt(CH_3)_3(NH_3)_3]I$ is water soluble and $[Pt(CH_3)_3NH_3I]_2$ is soluble in organic solvents such as chloroform and benzene.

The thermal decomposition of $[Pt(CH_3)_3(CH_3NH_2)_3]I$ tends to rule out the formation of the intermediate species $[Pt(CH_3)_3(CH_3NH_2)_2I]$ and supports the evidence from chemical reactions. On the other hand, the compound $[Pt(CH_3)_3(NH_3)_2I]$ does appear to have some stability as indicated by the thermogram of $[Pt(CH_3)_3(NH_3)_3]I$ (Fig. 1). It is possible to prepare the compound by carefully heating the triammine, as observed by Ivanova and Gel'man[1]. The inability to obtain this compound by action of ammonia on $[Pt(CH_3)_3I]_4$ or by action of $HClO_4$ on $[Pt(CH_3)_3(NH_3)_3]I$ in aqueous solution must therefore be unrelated to any instability at room temperature.

The stability of the dimeric species $[Pt(CH_3)_3NH_3I]_2$ and $[Pt(CH_3)_3(CH_3NH_2)I]_2$ has been well established. These compounds are the products of reactions both of amine with $[Pt(CH_3)_3I]_4$ and of $HClO_4$ with $[Pt(CH_3)_3(\text{amine})_3]I$, and TGA indicates they are fairly stable species.

All evidence obtained for the amine and methylaminechloro species indicates that as for the methylamine iodo system, no compound of the type $[Pt(CH_3)_3(\text{amine})_2Cl]$ can be isolated, although the dimers $[Pt(CH_3)_3NH_3Cl]_2$ and $[Pt(CH_3)_3(CH_3NH_2)Cl]_2$ are both quite stable entities.

The results indicate that for the ammonia and methylamine systems, the compounds $[Pt(CH_3)_3L_2X]$ are not readily prepared by chemical means, although complexes of the type $[Pt(CH_3)_3L_3]X$ ($X = Cl$ or I) are isolable. Other amines do give $[Pt(CH_3)_3L_2X]$ readily, but species of the type $[Pt(CH_3)_3L_3]X$ are not isolable, presumably due to steric effects from these ligands.

The existence of the compound $[Pt(CH_3)_3PyNH_3I]$[1] appears doubtful in view of the fact that the ammine groups in $[Pt(CH_3)_3NH_3I]_2$ were lost quite readily at room temperature on reaction with two moles of pyridine. It seems even more doubtful that such a compound could exist when excess pyridine was used[1], since in the present work, pyridine readily displaced ammine groups from both $[Pt(CH_3)_3(NH_3)_2I]$ and $[Pt(CH_3)_3NH_3I]_2$ to yield $[Pt(CH_3)_3Py_2I]$. Indeed, heating $[Pt(CH_3)_3(NH_3)_3]I$ with excess pyridine also produced $[Pt(CH_3)_3Py_2I]$.

The ^1H NMR spectra of the compounds $[Pt(CH_3)_3Py_2I]$ and $[Pt(CH_3)_3Lut_2I]$ in $CDCl_3$ consist of two platinum-methyl triplets in the intensity ratio of 2/1, and with different coupling constants as predicted from the theory of *trans* influences[4,11,12], if the compounds are monomeric. $[Pt(CH_3)_3Py_2I]$ in benzene has been reported variously to be monomeric[1] and to have a concentration-dependent molecular weight due to dissociation into $[Pt(CH_3)_3PyI]_2$ and pyridine[9]. The PMR spectrum of the compound $[Pt(CH_3)_3Py_2I]$ in benzene indicated that no dissociation occurred with increasing dilution[11], while in nitrobenzene, evidence for rapid exchange of pyridine groups was obtained only above 60°. The observation of coupling between the α-protons on pyridine or lutidine and ^{195}Pt in the $CDCl_3$ spectra confirmed that no exchange of ligands was occurring at 34°.

The PMR spectrum of a solution of $[Pt(CH_3)_3PyI]_2$ in $CDCl_3$ initially contained three sets of platinum-methyl triplets. However, if the solution was heated before recording the spectrum, or the solution was allowed to stand at room temperature, three further sets of triplets appeared. The spectrum of the solution on standing is shown in Fig. 2.

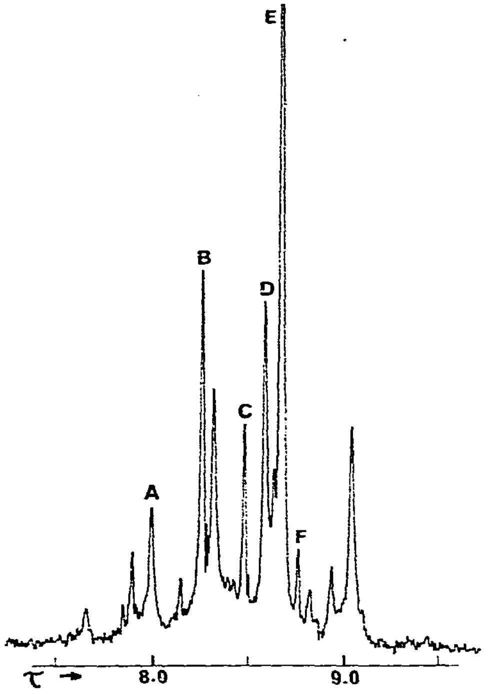

Fig. 2. ^1H NMR spectrum of $[Pt(CH_3)_3PyI]_2$ in $CDCl_3$ on standing.

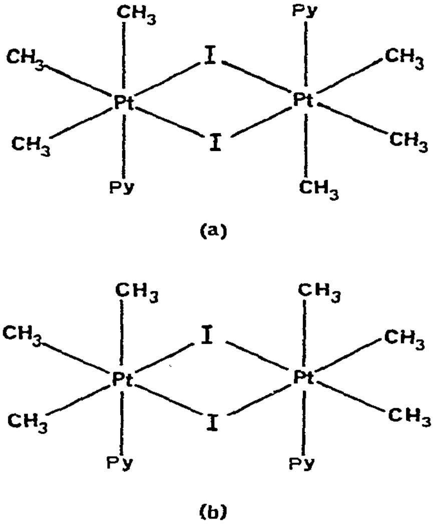

Fig. 3

Two isomers are possible for $[Pt(CH_3)_3PyI]_2$ as shown in Fig. 3., and peaks A, D, and E, which were present originally are assigned to the isomers. In theory, *four* peaks are predicted, with two sets in the ratio 2/1 each. Reference to Fig. 3, however, shows that for both isomers the environment of the methyl peaks *trans* to bridging iodide would be almost identical so that little, if any, difference in chemical shifts and coupling constants would be expected. Indeed, for $[Pt(CH_3)_3PyI]_2$, the peaks are apparently superimposed (peak E) at τ 8.70 with the same coupling constant (75.5 Hz). On the other hand, the methyl groups *trans* to pyridine would be expected to have markedly different chemical shifts for the two isomers, since the shielding effect of the heteroaromatic ring would be significant for isomer (a) and insignificant for isomer (b) (*cis*-isomer). Thus the peak at higher field (D) (τ 8.62) may readily be assigned to isomer (a) and that at much lower field (A) (τ 8.00) to isomer (b). From the relative intensities, the *trans* isomer is favoured by about 2/1.

Peaks B, C and F, which appeared on allowing the solution to stand, are in the ratio of 3/2/1, and may be readily assigned to $[Pt(CH_3)_3I]_4$ (B) and $[Pt(CH_3)_3Py_2I]$ (C and F) on the basis of chemical shifts and coupling constants (see Table 1). Apparently in $CDCl_3$ solution, the following disproportionation reaction was set up:

$$4\,[Pt(CH_3)_3PyI]_2 \rightleftarrows 4\,[Pt(CH_3)_3Py_2I]+[Pt(CH_3)_3I]_4$$

The spectrum in Fig. 2 represents the equilibrium position of this reaction, and it is clear that the compound $[Pt(CH_3)_3PyI]_2$ is favoured. As would be expected if such an equilibrium exists, an equimolar mixture of $[Pt(CH_3)_3I]_4$ and $[Pt(CH_3)_3Py_2I]$ on standing in $CDCl_3$ gave a spectrum similar to that in Fig. 2. The spectrum in benzene showed only very weak peaks due to the *cis*-isomer of $[Pt(CH_3)_3PyI]_2$ and to disproportionation products. Hence both disproportionation and isomeric distribution are influenced by solvent.

A similar situation appears to exist for the compound $[Pt(CH_3)_3LutI]_2$. The spectrum of $[Pt(CH_3)_3LutI]_2$ in $CDCl_3$ on standing is shown in Fig. 4. As for $[Pt(CH_3)_3PyI]_2$, two isomers are present, although for this compound the methyl groups *trans* to bridging I groups for the two isomers have slightly different chemical shifts (E and G at σ 8.69 and 8.74 respectively). The two peaks A (τ 8.01) and D (τ8.56)

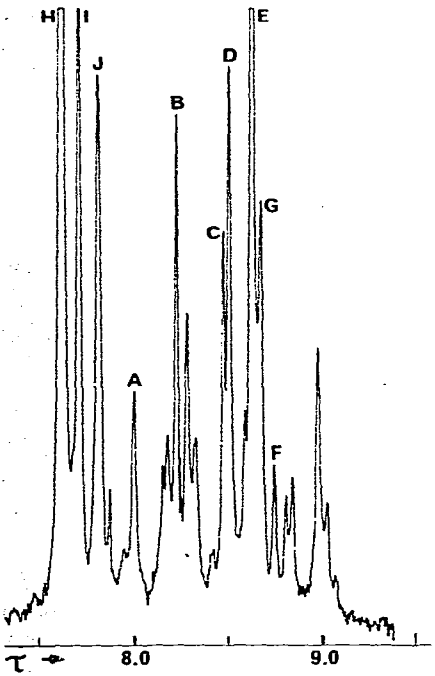

Fig. 4. ¹H NMR spectrum of $[Pt(CH_3)_3LutI]_2$ in $CDCl_3$ on standing.

are related to E and G respectively. As for the corresponding pyridine species, peaks A and G may be assigned to the *cis* isomer (b) and peaks D and E to the *trans* isomer (a). Again as for]$Pt(CH_3)_3PyI]_2$, the isomers are in the approximate ratio of 2/1 (*trans*/*cis*). Peaks B, C and F are assigned to the species $[Pt(CH_3)_3I]_4$ (B) and $[Pt(CH_3)_3Lut_2I]$ (C and F), so that disproportionation occurred for this compound also.

The methyl proton resonances of the lutidine ligands can also be rationalized in terms of the shielding effects of the ring systems. Thus peaks H, I, and J, all due to the methyl ligands on the lutidine groups, may be readily assigned to the species $[Pt(CH_3)_3LutI]_2$ (*trans* isomer), $[Pt(CH_3)_3Lut_2I]$ and $[Pt(CH_3)_3LutI]_2$ (*cis* isomer) respectively due to the increasing interaction of lutidine groups on neighbouring lutidine groups in this series, with resultant upfield shift of the τ values. A similar effect occurred in the resonances of the α-protons on the lutidine molecules and the same order of chemical shifts was found (Table 1). For all three α-proton resonances, a coupling of $\approx$ 14 Hz between ^{195}Pt and the α-protons was observed, so that no exchange of lutidine groups occurred in either of the isomers of $[Pt(CH_3)_3LutI]_2$ at 34°. For the γ-protons, only two resonances were observed, so that apparently the γ-protons in both $[Pt(CH_3)_3LutI]_2$ (*trans*) and $[Pt(CH_3)_3Lut_2I]$ absorbed in the same region, while that for $[Pt(CH_3)_3LutI]_2$ (*cis*) occurred at a higher field.

EXPERIMENTAL

Trimethyltriammineplatinum(IV) iodide

The compound was prepared by a similar method to that of Ivanova and Gel'man[1]. Gaseous ammonia was bubbled through a solution of iodotrimethylplatinum(IV) in chloroform. After several minutes colourless plates of the product were precipitated. These were filtered off, washed with chloroform and air-dried. Yield 95%. (Found: C, 8.7; H, 4.4; I, 30.6; N, 9.9; Pt, 46.5. $C_3H_{18}IN_3Pt$ calcd.: C, 8.6; H, 4.3; I, 30.3; N, 10.0; Pt, 46.6%.)

Trimethyltris(methylamine)platinum(IV) iodide

The compound was prepared either by an analogous method to the triammine species using gaseous methylamine, or by treating $[Pt(CH_3)_3I]_4$ with an ethanolic methylamine solution until dissolution occurred, concentrating the solution and precipitating the product with chloroform. Yield 95%. (Found: C, 15.9; H, 5.4; I, 27.2; N, 8.7; Pt, 42.4. $C_6H_{24}IN_3Pt$ calcd.: C, 15.6; H, 5.2; I, 27.6; N, 9.1; Pt, 42.2%.)

Trimethyltriammineplatinum(IV) chloride

The compound was prepared similarly to the corresponding iodide, using $[Pt(CH_3)_3Cl]_4$ as starting material. Yield 95%. (Found: C, 11.2; H, 5.5; Cl, 11.2; N, 12.6; Pt, 59.7. $C_3H_{18}ClN_3Pt$ calcd.: C, 11.0; H, 5.5; Cl, 10.9; N, 12.9; Pt, 59.7%.)

Iododiamminetrimethylplatinum(IV)

$[Pt(CH_3)_3(NH_3)_3]I$ (10 mg) was heated at 95° on a thermal balance until a weight loss equivalent to one mole of NH_3 per mole of compound was observed. (Found: C, 9.4; H, 3.6; I, 31.2; N, 6.9. $C_3H_{15}IN_2Pt$ calcd.: C, 9.0; H, 3.8; I, 31.6; N, 7.0%.)

Attempted preparation of $[Pt(CH_3)_3(NH_3)_2I]$ *by chemical means*

(i). Reaction of $[Pt(CH_3)_3(NH_3)_3]I$ *with* $HClO_4$. $[Pt(CH_3)_3(NH_3)_3]I$ (0.2 g) in water (5 ml) was treated with 1 mole of dilute perchloric acid (0.2 *M*). There was an immediate white precipitate which was filtered off, washed with water, and air-dried. An infrared spectrum of this solid showed the presence of an appreciable proportion of $[Pt(CH_3)_3I]_4$ and a small amount of ammine species since weak N–H stretching bands were observed. Addition of a second mole of $HClO_4$ to the filtrate gave further solid which was almost completely $[Pt(CH_3)_3I]_4$. More $[Pt(CH_3)_3I]_4$ precipitated after addition of a third mole of $HClO_4$ to the filtrate.

(ii). Reaction of $[Pt(CH_3)_3I]_4$ *with a 2 mole ratio of ammonia*. Yellow $[Pt(CH_3)_3I]_4$ (1.6 g) was suspended in a mixture of benzene (8 ml) and ethanol (8 ml), and a two mole ratio of an aqueous ammonia (11 *M*) solution added. The solid dissolved over a 10 min period, giving a pale yellow solution. This was evaporated to dryness in a vacuum desiccator, and the residue extracted with hot chloroform, in which about half of the material dissolved. An infrared spectrum of the residue was identical with that for an authentic sample of $[Pt(CH_3)_3(NH_3)_3]I$.

The filtrate from the extraction was evaporated in a vacuum desiccator, and the residue extracted with acetone in which $[Pt(CH_3)_3I]_4$ is insoluble. Addition of n-hexane to the acetone solution precipitated almost colourless plates of a compound analysing for $Pt(CH_3)_3NH_3I$ (yield 0.5 g).

The compound is moderately soluble in benzene and acetone, insoluble in water and decomposes on standing to $[Pt(CH_3)_3I]_4$. (Found: C, 9.6; H, 3.2; N, 4.2; Pt, 50.9. $C_3H_{12}INPt$ calcd.: C, 9.4; H, 3.1; N, 3.6; Pt, 50.8%.)

Attempted preparation of $[Pt(CH_3)_3(CH_3NH_2)_2I]$ *by chemical means*

(i). Reaction of $[Pt(CH_3)_3(CH_3NH_2)_3]I$ *with* $HClO_4$. $[Pt(CH_3)_3(CH_3NH_2)_3]I$ (0.2 g) in water (5 ml) was treated with 1 mole of dilute perchloric acid (0.2 *M*). A white solid precipitated immediately and was filtered off, washed with water, and air-dried (yield 0.07 g). (Found: C, 12.1; H, 3.6; I, 31.8; N, 3.6; Pt, 48.6. $C_4H_{14}INPt$ calcd.: C, 12.1; H, 3.5; I, 31.9; N, 3.5; Pt, 49.0%.) Addition of a second mole of $HClO_4$ to the filtrate produced more of the same compound.

(ii). Reaction of $[Pt(CH_3)_3I]_4$ *with a 40% ethanolic methylamine solution*. This gave a mixture of $[Pt(CH_3)_3(CH_3NH_2)_3]I$, and a solid with an infrared spectrum identical to that of $[Pt(CH_3)_3(CH_3NH_2)I]_2$.

Attempted preparation of $[Pt(CH_3)_3(NH_3)_2Cl]$

(i) Reaction of $[Pt(CH_3)_3Cl]_4$ *with a 2 mole ratio of* NH_3. The same procedure was used as for the corresponding iodo compound. The product analysed for less than two ammonia groups per molecule.

(ii). Reaction of $[Pt(CH_3)_3(NH_3)_3]Cl$ *with* $HClO_4$. The procedure was the same as that for the corresponding iodide. There was no immediate precipitate as for the iodide, and continued refluxing of the solution for several hours produced no precipitate. Analysis and infrared spectra of the products obtained by evaporation of such reaction mixtures indicated a predominance of $[Pt(CH_3)_3Cl]_4$ in the samples.

Iodotrimethylbis(ethylamine)platinum(IV)

Iodotrimethylplatinum(IV) (0.1 g) was dissolved in chloroform (5 ml) and excess ethylamine added. The resultant solution was concentrated to a small volume and the product precipitated with n-hexane. Yield 90%. (Found: C, 18.3; H, 5.0; I, 28.1; N, 6.0; Pt, 43.0. $C_7H_{23}IN_2Pt$ calcd.: C, 18.4; H, 5.1; I, 27.8; N, 6.1; Pt, 42.7%.)

Iodotrimethylbis(pyridine)platinum(IV)

The compound was prepared by the method of Lile and Menzies[8]. (Found: C, 29.8; H, 3.8; I, 23.9; N, 5.2; Pt, 37.2. $C_3H_{19}IN_2Pt$ calcd.: C, 29.7; H, 3.6; I, 24.2; N, 5.3; Pt, 37.1%.)

Iodotrimethyl(pyridine)platinum(IV)

Iodotrimethylbis(pyridine)platinum(IV) (0.2 g) was dissolved in a minimum of acetone, and a one mole ratio of 0.2 *M* $HClO_4$ added. The solution was allowed to stand for several minutes and the precipitate which formed was filtered off, washed with a small volume of cold chloroform, and air-dried. Yield 70%. (Found: C, 21.7; H, 3.2; I, 28.8; N, 2.9; Pt, 43.6. $C_8H_{14}INPt$ calcd.: C, 21.5; H, 3.2; I, 28.4; N, 3.1; Pt, 43.7%.)

Iodotrimethylbis(lutidine)platinum(IV)

Iodotrimethylplatinum(IV) (0.2 g) was dissolved in chloroform (10 ml) and excess 3,5-lutidine added. The solution was concentrated to a small volume and n-hexane added to precipitate the product as pale yellow crystals. Yield 90%. (Found: C, 34.8; H, 4.7; I, 22.0; N, 4.7; Pt, 33.3. $C_{17}H_{27}IN_2Pt$ calcd.: C, 35.1; H, 4.7; I, 21.8; N, 4.8; Pt, 33.5%.)

Iodotrimethyl(lutidine)platinum(IV)

The compound was prepared from $[Pt(CH_3)_3Lut_2I]$ by a similar procedure to the preparation of $[Pt(CH_3)_3PyI]_2$. Yield 75%. (Found: C, 25.5; H, 3.8; I, 26.5; N, 2.9; Pt, 41.0. $C_{10}H_{18}INPt$ calcd.: C, 25.3; H, 3.8; I, 26.8; N, 2.9; Pt, 41.1%.)

Nuclear magnetic resonance spectra of the bis(pyridine) and bis(lutidine) compounds

These were recorded at 60 MHz on a Varian A60 spectrometer at a sample temperature of $34 \pm 2°$. The complexes were studied in saturated or near-saturated solutions on sweep width of 500 Hz using tert-butanol as internal reference. τ values were obtained using τ(t-BuOH) = 8.72 ppm for $CDCl_3$. Spin–spin coupling constants are considered accurate to ±0.5 Hz and τ values to ±0.01 ppm. The spectra of the pyridine and lutidine dimers were also recorded at 100 MHz using a Jeol MH100 spectrometer on a sweep width of 540 Hz and TMS as internal standard. Coupling constants are accurate to ±0.5 Hz and τ values to ±0.01 ppm.

Thermogravimetric analyses

These were carried out using a Rigaku TG-DTA Model M8075 standard temperature type instrument. Heating rate was 10°/min.

ACKNOWLEDGEMENTS

We thank Mr. E. J. O'Reilly of the Queensland Institute of Technology for the use of and assistance in running the Rigaku equipment. One of us (G.A.S.) acknowledges the award of a Commonwealth Post-Graduate Scholarship.

REFERENCES

1 O. M. Ivanova and A. D. Gel'man, *Zh. Neorg. Khim.*, 3 (1958) 1334.
2 M. N. Hoechstetter, *J. Mol. Spectrosc.*, 13 (1964) 407.
3 D. E. Clegg and J. R. Hall, *Spectrochim. Acta, Part A*, 23 (1967) 263.
4 D. E. Clegg and J. R. Hall, *Aust. J. Chem.*, 20 (1967) 2025.
5 D. E. Clegg, Ph. D. Thesis, University of Queensland, 1970.
6 W. J. Pope and S. J. Peachey, *J. Chem. Soc.* (*Trans.*), 95 (1909) 571.
7 A. D. Gel'man and E. A. Gorushkina, *Dokl. Akad. Nauk SSSR*, 57 (1947) 259.
8 W. J. Lile and R. C. Menzies, *J. Chem. Soc.*, (1949) 1168.
9 M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, (1951) 299.
10 J. M. Homan, J. M. Kawamoto and G. L. Morgan, *Inorg. Chem.*, 9 (1970) 2533.
11 D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organometal. Chem.*, 38 (1972) 403.
12 K. Kite, J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, (1966) 1744.