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DIMETHYLPLATINUM(IV) COMPOUNDS. IV. PREPARATION OF $[Pt(CH_3)_2Br(H_2O)_3]^+$ AND ITS REACTIONS WITH NEUTRAL AND UNINEGATIVE LIGANDS

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SUMMARY

Solutions containing the ion $[Pt(CH_3)_2Br(H_2O)_3]^+$ have been prepared by reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous Ag^+ and reactions of the ion with neutral (3,5-lutidine and N,N,N',N'-tetramethylethylenediamine) and uninegative (Br^-, Cl^-, I^-, OH^-, SCN^- and NO_2^-) ligands have been investigated by ^1H NMR and infrared spectra.

INTRODUCTION

In Part II [1] reactions of $[Pt(CH_3)_2Br_2]_n$ with a variety of neutral and uninegative ligands were studied. In general, reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous solutions containing excess uninegative ligands X resulted in displacement of both Br atoms, although with X=chloride ^1H NMR spectra indicated the intermediate formation of the monobromo species $[Pt(CH_3)_2BrCl_3]^{2-}$. Reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous $AgNO_3$ followed by treatment with chloride ions and pyridine produced the monobromo species $Pt(CH_3)_2BrClpy_2$ [1]. In the present study the reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous Ag^+ has been investigated in more detail and a number of monobromodimethylplatinum(IV) compounds have been synthesized and studied by ^1H NMR and infrared spectroscopy. Preliminary data have been reported previously [2].

RESULTS AND DISCUSSION

(i) Preparation and Properties of $[Pt(CH_3)_2Br(H_2O)_3]^+$.

$[Pt(CH_3)_2Br_2]_n$ reacts with a one mole ratio of aqueous $AgNO_3$ or $AgClO_4$ to give a yellow solution. ^1H NMR spectra have been used to monitor the reaction. The spectra indicate that after reaction for 5 minutes two separate dimethylplatinum(IV) species are present since two methyl platinum 'triplets' (^{195}Pt, $I=\frac{1}{2}$, 34% abundance) of unequal intensities are observed. On continued heating of the solution one of these species (τ 7.95, J 80.1 Hz) converts to the other (τ 8.04, J 76.3 Hz, Table 1) while AgBr precipitates from solution. As shown later, the initial species is probably $[Pt(CH_3)_2Br_2(H_2O)_2]$ with CH_3 *trans* to H_2O, while the final product is assumed to be predominantly $[Pt(CH_3)_2Br(H_2O)_3]^+$. Since the final solution is acidic ($pK_a \sim 5$) there is probably an equilibrium between the triaqua species and an hydroxo species, $[Pt(CH_3)_2BrOH(H_2O)_2]$ with OH *trans* to Br rather than CH_3 since aqua groups *trans* to CH_3 groups tend to undergo exchange rather than dissociate in methylplatinum(IV) systems [3,4]. Furthermore, as shown later, reactions of the triaqua species with ligands such as 3,5-lutidine or tetramethylethylenediamine yield species with an hydroxo group *trans* to Br. The Raman spectrum of an aqueous solution of the species is consistent with the formulation $[Pt(CH_3)_2Br(H_2O)_3]^+$ with peaks attributable to ν(Pt-Br) at 235 cm^{-1} and ν(Pt-C) at 590 cm^{-1}. The former peak is in the region usually associated with terminal Br atoms coordinated to platinum(IV) [5] and the latter peak is in the region associated with methyl groups *trans* to H_2O [6]. A Raman line at 1048 cm^{-1} is assigned to ν_{sym}(N-O) of ionic nitrate.

Attempts to isolate the compound were unsuccessful since evaporation of solutions containing this species gave a water-insoluble solid, while addition of solutions containing large anions failed to produce a precipitate. However, on neutralization of concentrated solutions of $[Pt(CH_3)_2Br(H_2O)_3]^+$ with NaOH solution a yellow precipitate analysing for $Pt(CH_3)_2BrOH$ was obtained and this undergoes many reactions analogous to those of $[Pt(CH_3)_2Br(H_2O)_3]^+$. Addition of acid to $[Pt(CH_3)_2BrOH]_n$ regenerates the $[Pt(CH_3)_2Br(H_2O)_3]^+$ ion.

$[Pt(CH_3)_2BrOH]_n$ is soluble in warm methanol and acetone, but unlike $[Pt(CH_3)_2Br_2]_n$ which dissolves in hot methanol to give a monomeric species containing coordinated solvent *trans* to CH_3, the former compound is dimeric in methanol, presumably due to incomplete breakdown of the initial polymer. The ^1H NMR spectrum of the compound in CD_3OH (Table 1) exhibits two non-equivalent methyl platinum triplets and is consistent with a dimeric structure of the type shown in Figure 1 (solvent = methanol). The high values for $^2J(^{195}Pt-CH_3)$ are indicative of oxygen-bonded groups *trans* to CH_3 [7].

The structure of $[Pt(CH_3)_2BrOH]_n$ is uncertain, but its behaviour in methanol solution suggests that if it is tetrameric as has been postulated for other compounds of the type $[Pt(CH_3)_2XY]_n$ [1] then it is the OH group rather than the Br atom which is functioning as the triply-bridging group. The infrared spectrum of $[Pt(CH_3)_2BrOH]_n$ is consistent with the presence of bridging OH groups (Table 2). Peaks attributable to $\nu(Pt-O)$ are present at 481, 373, 332 and 318 cm^{-1}. All of these are at lower frequency than that found for $\nu(Pt-O)$ for terminal OH in the compound

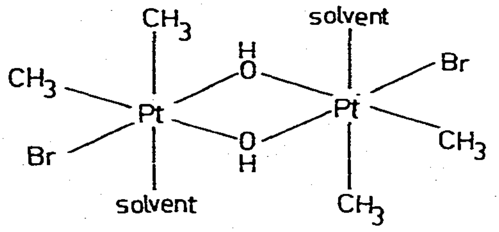
TABLE 1

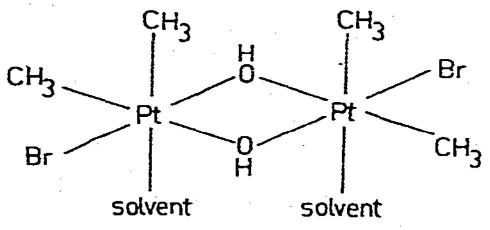
^1H NMR DATA FOR MONOBROMODIMETHYLPLATINUM(IV) COMPOUNDS

Compound	$\tau(Pt-CH_3)$	$^2J(^{195}Pt-CH_3)$		
In $CDCl_3$ solution				
			τ_{H_α}(Lut)	$J(Pt-N-C-H_\alpha)$
$Pt(CH_3)_2BrOHLut_2$	8.39	70.5	1.35	11.5
$Pt(CH_3)_2BrClLut_2$	8.05	69.0	1.46	13.0
$Pt(CH_3)_2BrILut_2$	7.76	71.3	1.39	13.0
$Pt(CH_3)_2Br(SCN)Lut_2$	8.20	69.2	1.65	12.5
$Pt(CH_3)_2Br(ONO)Lut_2$	8.01	69.8	1.68	12.0
$Pt(CH_3)_2Br(NO_2)Lut_2$	7.98	69.4	1.58	11.0

TABLE 1 (cont.)

Compound	τ(Pt-CH_2)	$^2J(^{195}Pt-CH_3)$	τ(N-CH_3)	J(Pt-NCH_3)
$Pt(CH_3)_2BrOH$Tetrameen	8.57	71.8	7.20,7.49	12.8,9.6
$Pt(CH_3)_2Br(ONO)$Tetrameen	8.18	70.5	7.20,7.62	14.0,8.5
$Pt(CH_3)_2Br(NO_2)$Tetrameen	8.20	71.2	7.18,7.28	14.4,11.0
In H_2O solution				
$[Pt(CH_3)_2Br(H_2O)_3]^+$	8.04	76.3		
$Pt(CH_3)_2Br_2(H_2O)_2$	7.95	80.1		
In NaOH solution				
$[Pt(CH_3)_2Br(OH)H_2O]_2$	8.02	76.6		
	8.43	76.6		
$[Pt(CH_3)_2Br(OH)_3]^{2-}$	8.62	74.5		
$[Pt(CH_3)_2(OH)_4]^{2-}$	8.79	76.5		
In NaCl solution				
$Pt(CH_3)_2BrCl(H_2O)_2$	8.02	78.2		
$[Pt(CH_3)_2BrCl_3]^{2-}$	7.96	77.1		
$[Pt(CH_3)_2Cl_4]^{2-}$	8.02	76.5		
In KSCN solution				
$[Pt(CH_3)_2Br(SCN)_2H_2O]^-$	8.00	66.8		
$[Pt(CH_3)_2Br(SCN)_3]^{2-}$	8.25	69.0		
$[Pt(CH_3)_2(SCN)_4]^{2-}$	8.49	69.8		
In $NaNO_2$ solution				
$[Pt(CH_3)_2Br(ONO)(NO_2)_2]^{2-}$	8.18	68.8		
$[Pt(CH_3)_2Br(NO_2)_3]^{2-}$	8.15	70.2		
$[Pt(CH_3)_2(NO_2)_4]^{2-}$	8.17	69.7		
In CD_3OH solution				
$[Pt(CH_3)_2Br(OH)CD_3OH]_2$	7.71	79.7		
	8.00	79.5		
$Pt(CH_3)_2Br_2(CD_3OH)_2$	7.97	80.7		

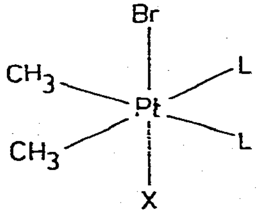




$Pt(CH_3)_2BrOHLut_2$ (542 cm^{-1}) (Table 2). Furthermore, peaks attributable to ν(Pt-Br) for terminal Br are found at 242 and 220 cm^{-1} (cf. 235 cm^{-1} in the Raman spectrum of $[Pt(CH_3)_2Br(H_2O)_3]^+$). Other bands attributable to OH vibrations are found at 3370, 940 and 740 cm^{-1}. The band at 3370 cm^{-1} assigned to ν(O-H) is broad, indicating hydrogen bonding, probably with the Br atoms. The other peaks are tentatively assigned to δ(Pt-O-H) modes. The peak at 740 cm^{-1} lies in the same region as that assigned to δ(Pt-O-H) in $[Pt(CH_3)_3OH]_4$ (722 cm^{-1}) [8].

(ii) Reactions of $[Pt(CH_3)_2Br(H_2O)_3]^+$

Addition of 3,5-lutidine (Lut) to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ immediately precipitates a yellow solid analysing for $Pt(CH_3)_2BrOHLut_2$.* The same compound is obtained by reaction of $[Pt(CH_3)_2BrOH]_n$ with lutidine. The compound has the structure shown in Figure 2 (L=Lut,



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* This may be contrasted with the trimethylplatinum(IV) system where addition of 3,5-lutidine to a solution of $[Pt(CH_3)_3(H_2O)_3]^+$ does not produce a precipitate, and ^1H NMR spectra indicate the presence of the species $[Pt(CH_3)_3Lut_n(H_2O)_{3-n}]^+$ (n = 1 - 3) similar to the pyridine system reported previously [9].

TABLE 2

INFRARED SPECTRA OF MONOBROMODIMETHYLPLATINUM(IV) COMPOUNDS

Compound	$\delta(CH_3)$	ν(Pt-C)	Ligand vibration	Assignment
$Pt(CH_3)_2BrOH$	1233m,1241m	581w	3370,br	ν(OH)
	1263m,1268sh		940m,br,740s,br	δ(Pt-O-H)
			481s,373s, 332s,318s	ν(Pt-O)
$Pt(CH_3)_2BrOHLut_2$	1228m,1274m	582w	3602w,sh	ν(OH)
			963s	δ(Pt-O-H)
			542s	ν(Pt-O)
$Pt(CH_3)_2BrSCNLut_2$	1233m		2118m	ν(C≡N)
			418w	ρ(SCN)
$Pt(CH_3)_2Br(ONO)Lut_2$	1229w	577vw	1511s	ν(N=O)
			960s	ν(N-O)
			828m	δ(ONO)
$Pt(CH_3)_2Br(NO_2)Lut_2$			1420s	ν_{asym}(N-O)
			1332s,1322s	ν_{sym}(N-O)
			828s,sh	$\delta(NO_2)$
			600m	$\rho(NO_2)$
$Pt(CH_3)_2BrOH$Tetrameen	1223m	590w	3522s,br	ν(OH)
			1054s,br	δ(Pt-O-H)
			550s	ν(Pt-O)
$Pt(CH_3)_2Br(ONO)$-Tetrameen	1224m	590w	1505s	ν(N=O)
			967s	ν(N-O)
			826s	δ(ONO)
$Pt(CH_3)_2Br(NO_2)$-Tetrameen	1228m		1420s	ν_{asym}(N-O)
			1322s	ν_{sym}(N-O)
			831s,sh	$\delta(NO_2)$
			595m	$\rho(NO_2)$

X=OH) since ^{1}H NMR spectra confirm that the methyl platinum groups are equivalent and *trans* to lutidine molecules ($^2J(^{195}Pt-CH_3)$ 71.4 Hz). It may be noted that no trimethylplatinum(IV) compound containing a terminal OH group has as yet been reported, the only known hydroxy compound in this system being $[Pt(CH_3)_3OH]_4$ which contains triply-bridging OH groups [10,11].

Addition of N,N,N',N'-tetramethylethylenediamine (Tetrameen) to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ precipitates a solid analysing for $Pt(CH_3)_2BrOH$ Tetrameen, which also contains methylplatinum groups *trans* to the N-donor ligand (J 71.8 Hz) (Table 1 ; Figure 2, L_2 = Tetrameen, X = OH). Two sets of N-methyl resonances for the Tetrameen ligand are observed, consistent with the presence of non-equivalent groups (OH and Br) above and below the plane of the two carbon and two nitrogen atoms bonded to platinum.

The infrared spectra of both $Pt(CH_3)_2BrOHLut_2$ and $Pt(CH_3)_2BrOH$-Tetrameen contain peaks characteristic of the OH group. The O-H stretching vibration appears in the spectrum of $Pt(CH_3)_2BrOHLut_2$ as a weak, sharp peak at 3600 cm^{-1}, while that in $Pt(CH_3)_2BrOH$ Tetrameen is much broader, more intense and appears at lower wavenumber (3522 cm^{-1}) presumably due to hydrogen bonding. A peak assignable to δ(Pt-O-H) is observed at 1054 cm^{-1} in the Tetrameen compound, which is in the region found for this vibration in $K_2[Pt(OH)_6]$ (1058, 1076 cm^{-1}) [12]. However, δ(Pt-O-H) in the Lut compound appears at 963 cm^{-1}. Peaks assignable to ν(Pt-O) are found at 542 and 550 cm^{-1} respectively in the Lut and Tetrameen complexes and these values are comparable with those found for this vibration in $K_2[Pt(OH)_6]$ (538, 515 cm^{-1}) [12].

Addition of approximately a one mole ratio of NaBr to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ produces a very broad methyl platinum triplet in the ^{1}H NMR spectrum which is apparently due to bromide/water exchange at sites *trans* to the methyl platinum groups. On allowing the solution to stand a sharp methyl platinum triplet (τ 7.94, J 79.8 Hz) increases in intensity at the expense of the original triplet. Chemical shift and coupling constant data confirm that the second species is the same as that found initially in the reaction of $[Pt(CH_3)_2Br_2]_n$ with $AgNO_3$ as noted earlier. On further standing, $[Pt(CH_3)_2Br_2]_n$ precipitates from solution and the methyl platinum triplet decreases in intensity. The magnitude of $^2J(^{195}Pt-CH_3)$ for this compound (79.8 Hz) suggests that the methyl groups are *trans* to a ligand of low *trans* influence, so that the compound is most probably $Pt(CH_3)_2Br_2(H_2O)_2$. Addition of Lut to solutions containing this species precipitates $Pt(CH_3)_2Br_2Lut_2$.(Figure 2, L = Lut, X = Br). Addition of excess NaBr to solutions containing $Pt(CH_3)_2Br_2(H_2O)_2$ causes a downfield shift of the methylplatinum protons and a decrease in coupling constant, indicating exchange between bromide and water *trans* to the methylplatinum groups. In saturated NaBr solution both τ and J approach the values reported for $[Pt(CH_3)_2Br_4]^{2-}$ [1] (Table 1).

When approximately a one mole ratio of NaCl is added to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ there is an initial slight broadening of the methyl platinum triplet due to chloride/water exchange *trans* to the methylplatinum groups. On allowing the solution to stand a sharp triplet grows at the expense of the first, but the formation of this species is much slower than for the bromide reaction. The formation of this triplet, which is attributed to $Pt(CH_3)_2BrCl(H_2O)_2$, is accelerated by heating the solution. Further addition of NaCl causes a decrease in the coupling constant and a shift of the triplet to lower field towards the values previously reported for the species $[Pt(CH_3)_2BrCl_3]^{2-}$ [1]. Addition of Lut to such solutions produces an immediate precipitate of $Pt(CH_3)_2BrClLut_2$. Prolonged heating of the concentrated chloride solutions of $[Pt(CH_3)_2BrCl_3]^{2-}$ results in formation of $[Pt(CH_3)_2Cl_4]^{2-}$ as reported previously [1].

In contrast to the slow displacement of the bromo group by chloride in the above reactions, addition of NaI to solutions of $[Pt(CH_3)_2Br(H_2O)_3]^+$ rapidly precipitates an orange-red solid which is probably a mixture of $[Pt(CH_3)_2BrI]_n$ and $[Pt(CH_3)_2I_2]_n$. Rapid addition of Lut to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ to which NaI has been added precipitates a mixture of $Pt(CH_3)_2BrILut_2$ and $Pt(CH_3)_2I_2Lut_2$ as confirmed by ^1H NMR.

On addition of approximately a one mole ratio of KSCN to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$, two broad methylplatinum triplets are initially observed in the ^1H NMR spectrum. One of these triplets (τ 8.00, J 66.8 Hz) decreases in intensity as solid $[Pt(CH_3)_2BrSCN]_n$ precipitates and is presumably either $[Pt(CH_3)_2Br(SCN)_2(H_2O)]^-$ or $[Pt(CH_3)_2BrOH(SCN)_2]^{2-}$ with thiocyanate groups *trans* to methyl. The mode of coordination of the thiocyanate groups is uncertain since $^2J(^{195}Pt\text{-}CH_3)$ values for CH_3 groups *trans* to N- and S-bonded thiocyanate have been found to be similar in methylplatinum(IV) systems [7]. The second methylplatinum triplet is presumably due to the ion $[Pt(CH_3)_2Br(SCN)_3]^{2-}$ since it increases in magnitude as more KSCN is added to the solution and the precipitate of $[Pt(CH_3)_2BrSCN]_n$ redissolves. On continued addition of KSCN there is only a slight chemical shift change (τ 8.22 to τ 8.25) and no coupling constant change in the triplet up to saturation. Heating solutions of $[Pt(CH_3)_2Br(SCN)_3]^{2-}$ containing a large excess of KSCN produces a new triplet (τ 8.49, J 69.8 Hz) which presumably is due to the formation of $[Pt(CH_3)_2(SCN)_4]^{2-}$.

The mode of bonding of the thiocyanate groups *trans* to CH_3 in both $[Pt(CH_3)_2Br(SCN)_3]^{2-}$ and $[Pt(CH_3)_2(SCN)_4]^{2-}$ is again uncertain, but the thiocyanate groups *cis* to the methyl groups in both compounds appear to be S-bonded since addition of Lut in each case produces a precipitate containing the S-bonded thiocyanate group (Figure 2, X = SCN). The infrared spectrum of $Pt(CH_3)_2(SCN)_2Lut_2$ has been reported previously [1]. The spectrum of $Pt(CH_3)_2Br(SCN)Lut_2$ contains bands assignable to ν(C≡N) at 2118 cm^{-1}, and ρ(SCN) at 418 cm^{-1} both of which lie in the range found for S-bonded thiocyanato complexes [13,14]. As was found for $Pt(CH_3)_2(SCN)_2Lut_2$, no peak attributable to δ(SCN) is observed. Addition of Tetrameen to solutions containing $[Pt(CH_3)_2Br(SCN)_3]^{2-}$ did not produce a precipitate.

When a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ is treated with $NaNO_2$ solution, an initial broad triplet in the NMR is replaced by a single sharp triplet (τ 8.18, J 68.8Hz). The magnitude of the coupling constant confirms that N-bonded nitro groups are in positions *trans* to the methyl groups since it lies in the same region as was found for N-bonded NO_2 in trimethylplatinum(IV) complexes (64-68 Hz) [7]. The position *trans* to the Br atom in this compound, however, must be occupied by a nitrito group since addition of Lut or Tetrameen to the solution precipitates the compounds $Pt(CH_3)_2Br(ONO)Lut_2$ and $Pt(CH_3)_2Br(ONO)$Tetrameen respectively (Figure 2, L_2 = 2Lut, Tetrameen, X = ONO)**. Evidence for the presence of O-bonded NO_2 comes from the infrared spectra of these compounds. Bands attributable to ν(N=O) and ν(N-O) are found at 1511 cm^{-1} and 960 cm^{-1} respectively in the Lut complex, and at 1505 and 967 cm^{-1} in the Tetrameen complex. These values are comparable to those found for the nitrito group in $[Pt(NH_3)_5(ONO)]^{3+}$ [15]. A band attributable to δ(ONO) appears as a broad peak at 828 cm^{-1} in the Lut complex and 826 cm^{-1} in the Tetrameen complex. No peak due to a rocking mode was observed in these spectra although they have been reported for other nitrito complexes. Both compounds are fairly stable both in the solid and in solution, but slowly change to the nitro isomer at ambient temperatures. Heating the compounds increases the rate of isomerization, and complete isomerization of the Lut complex occurs after 2 hours at 80°C.

The infrared spectra of both of the products $Pt(CH_3)_2Br(NO_2)Lut_2$ and $Pt(CH_3)_2Br(NO_2)$Tetrameen contain peaks characteristic of N-bonded NO_2. Thus ν_{sym}(N-O) and ν_{asym}(N-O) appear at 1420 and 1332, 1322 cm^{-1} respectively for the Lut complex and at 1420 and 1322 cm^{-1} respectively

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** In the trimethylplatinum(IV) system addition of $NaNO_2$ to a solution of $[Pt(CH_3)_3(H_2O)_3]^+$ produces the ion $[Pt(CH_3)_3(NO_2)_3]^{2-}$ [9]. The value of $^2J(^{195}Pt\text{-}CH_3)$ (70·9Hz) is consistent with N-bonded NO_2 groups. Addition of Lut to this solution produces $Pt(CH_3)_3Lut_2NO_2$ which also contains an N-bonded NO_2 group [7].

for the Tetrameen complex; peaks assignable to $\delta(NO_2)$ appear at 828 cm^{-1}(Lut) and 831 cm^{-1}(tetrameen); and peaks assignable to $\rho(NO_2)$ at 600 cm^{-1}(Lut) and 595 cm^{-1}(tetrameen). It may be noted that for each set of nitro and nitrito isomers, the peaks associated with $\delta(NO_2)$ and $\delta(ONO)$ appear at virtually the same wavenumber but in each case the $\delta(NO_2)$ peak is sharp while the $\delta(ONO)$ peak is quite broad.

It has been found in the formation of nitrito compounds from metal-hydroxo compounds, that a molecule of HNO_2 cleaves the O-H bond rather than the M-O bond [16]. The conditions for the present system (M-OH species in acid solution) are those which favour nitrito formation and a similar mechanism may be postulated here.

As was found for the Lut and Tetrameen derivatives, heating the solution of the ion $[Pt(CH_3)_2Br(ONO)(NO_2)_2]^{2-}$ for several minutes produces a new triplet (τ 8.15, J 70.2 Hz) in the NMR which is presumably due to the nitro isomer $[Pt(CH_3)_2Br(NO_2)_3]^{2-}$. Continued heating slowly converts this to a further species (τ 8.17, J 69.7 Hz) which is probably $[Pt(CH_3)_2(NO_2)_4]^{2-}$ since addition of Lut to this solution precipitates $Pt(CH_3)_2(NO_2)_2Lut_2$ as confirmed by its infrared spectrum [1].

Addition of NaOH to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ gives a broad triplet initially which is probably due to OH/water exchange *trans* to the methyl platinum groups. On allowing the solution to stand, two new triplets of equal intensity appear in the spectrum and $[Pt(CH_3)_2BrOH]_n$ precipitates from solution. The two triplets appear to be associated with the same species and probably arise from a dimeric compound of the type shown in Figure 1(a) or (b) (Solvent = H_2O). Continued addition of NaOH redissolves the precipitate of $[Pt(CH_3)_2BrOH]_n$ and decreases the intensity of the pair of triplets while a new triplet forms at τ 8.53 (J 74.5 Hz). This latter triplet is probably due to $[Pt(CH_3)_2Br(OH)_3]^{2-}$. Continued addition of NaOH causes a shift of this triplet to τ 8.62 while the coupling constant remains unchanged. Heating the solution produces a new triplet at τ 8.79 (J 76.5 Hz) which is probably due to $[Pt(CH_3)_2(OH)_4]^{2-}$. Addition of Lut to this latter species does not produce a precipitate.

Several features of the ^1H NMR spectra may be noted. All of the compounds $Pt(CH_3)_2BrXLut_2$ and $Pt(CH_3)_2BrXTetrameen$ have the structure shown in Figure 2 with Lut or Tetrameen(L_2) *trans* to methyl groups as confirmed both by the couplings $^2J(^{195}Pt\text{-}CH_3)$ for the methylplatinum groups and the couplings $^3J(^{195}Pt\text{-}N\text{-}C\text{-}H)$ for the N-donor ligands (Table 1) [1]. As has been found in other methylplatinum(IV) systems [7] the *cis* influence of the X group on $^2J(^{195}Pt\text{-}CH_3)$ in both sets of compounds is small, the variation being only 2Hz from X = OH to X = NO_2. The effect of X on the chemical shift values of the methylplatinum protons is consistent between both series and varies in order of decreasing τ : OH>SCN>Cl>ONO>NO_2>Br>I. A similar order holds for the series $Pt(CH_3)_3XL_2$ [7] and $Pt(CH_3)_2X_2L_2$ [1]. The chemical shift values and coupling constants for the compounds $Pt(CH_3)_2BrXLut_2$ in general lie at intermediate values between those for $Pt(CH_3)_2Br_2Lut_2$ and $Pt(CH_3)_2X_2Lut_2$ [1]. It may be noted that the effect of NO_2 and ONO groups in $Pt(CH_3)_2BrXLut_2$ is similar both with respect to chemical shifts and coupling constants. There is however, a more noticeable effect on these parameters for the H_α protons of the Lut molecules.

Each of the compounds $Pt(CH_3)_2BrXTetrameen$ exhibits two sets of N-methyl resonances, each with a different coupling constant (Table 1). One of these resonances remains at virtually the same chemical shift value as X is varied and may be assigned to the methyl groups lying nearest the Br atom while the other is due to the methyl groups near the X group. The coupling constants follow no regular pattern and probably result from slightly different conformations of the Tetrameen ligand produced by the varying size of the X-group.

EXPERIMENTAL

Analytical data for the compounds are listed in Table 3.

TABLE 3

ANALYTICAL DATA

Compound	Empirical formula	Analysis (calcd. (found)) (%)				
		C	H	N	Pt	Br
$Pt(CH_3)_2BrOH$	C_2H_7BrOPt	7.5	2.2	-	60.6	24.8
		(7.5)	(2.3)		(60.1)	(24.4)
$Pt(CH_3)_2BrOHLut_2$	$C_{16}H_{25}BrN_2OPt$	35.8	4.7	5.2	36.4	14.9
		(35.3)	(4.6)	(5.1)	(36.1)	(14.7)
$Pt(CH_3)_2BrClLut_2$	$C_{16}H_{24}BrClN_2Pt$	34.6	4.4	5.0	35.2	-
		(34.9)	(4.8)	(4.9)	(35.6)	-
$Pt(CH_3)_2BrSCNLut_2$	$C_{17}H_{24}BrN_3PtS$	35.4	4.2	7.3	33.8	13.8
		(35.3)	(4.2)	(7.0)	(33.4)	(13.8)
$Pt(CH_3)_2Br(ONO)Lut_2$	$C_{16}H_{24}BrN_3O_2Pt$	34.0	4.3	7.4	34.5	14.1
		(34.0)	(4.4)	(7.3)	(34.3)	(13.9)
$Pt(CH_3)_2Br(NO_2)Lut_2$	$C_{16}H_{24}BrN_3O_2Pt$	34.0	4.3	7.4	34.5	14.1
		(34.1)	(4.4)	(7.3)	(34.3)	(14.5)
$Pt(CH_3)_2BrOH$Tetrameen	$C_8H_{23}BrN_2OPt$	21.9	5.3	6.4	44.5	18.2
		(21.4)	(5.3)	(6.0)	(44.1)	(18.4)
$Pt(CH_3)_2BrCl$Tetrameen	$C_8H_{22}BrClN_2Pt$	21.0	4.9	6.1	42.7	
		(20.6)	(4.8)	(6.5)	(42.3)	
$Pt(CH_3)_2Br(ONO)$Tetrameen	$C_8H_{22}BrN_3O_2Pt$	20.6	4.8	9.0	41.7	17.1
		(20.8)	(4.8)	(9.3)	(42.0)	(17.0)
$Pt(CH_3)_2Br(NO_2)$Tetrameen	$C_8H_{22}BrN_3O_2Pt$	20.6	4.8	9.0	41.7	17.1
		(20.9)	(4.8)	(9.2)	(42.1)	(16.9)

Preparation of $[Pt(CH_3)_2Br(H_2O)_3]^+$

$[Pt(CH_3)_2Br_2]_n$ [1,2] (3.0 g) was suspended in aqueous $AgNO_3$ solution (1.32 g in 60 mls) and acetone (15 mls) added. The mixture was heated under reflux for 2.5 hours and the solution then filtered to remove AgBr. The resultant yellow solution was then heated until all acetone had been driven off. The resultant solution contained only a single methyl-platinum triplet in the NMR. The acidic solution presumed to contain the ion $[Pt(CH_3)_2Br(H_2O)_3]^+$ in equilibrium with $Pt(CH_3)_2BrOH(H_2O)_2$ was then used for the reactions noted below.

Preparation of $[Pt(CH_3)_2BrOH]_n$

A concentrated solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ was treated dropwise with NaOH solution (0.1M). Addition of base was continued until the pH of the solution was 7, at which time a permanent yellow precipitate had settled out. This was filtered off, washed with water and air-dried. The yield (based on $[Pt(CH_3)_2Br_2]_n$) was 70-80%.

Preparation of $[Pt(CH_3)_2BrOHL_2]$ (L_2 = 2Lut, Tetrameen)

Excess ligand L_2 was added to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$. The yellow solid which precipitated immediately was extracted into chloroform, the chloroform solution dried and concentrated to a small volume, and the product precipitated with pet. ether.

Preparation of $Pt(CH_3)_2BrCl\ Lut_2$

A solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ was treated with a large excess of NaCl solution and the resultant solution boiled for 30 minutes. Addition of Lut precipitated a yellow solid which was extracted into chloroform and crystallized from a chloroform-pet. ether mixture.

Preparation of $Pt(CH_3)_2BrSCN\ Lut_2$

Aqueous KSCN was added to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ and the yellow solution immediately deepened in colour. Addition of Lut precipitated a yellow solid which was extracted into chloroform and crystallized from chloroform-pet. ether. A similar reaction with Tetrameen failed to produce a precipitate. Extraction with chloroform in the latter reaction yielded only a small quantity of $Pt(CH_3)_2BrOH$ Tetrameen.

Preparation of $Pt(CH_3)_2BrONOL_2$ (L_2 = 2Lut, Tetrameen)

Excess $NaNO_2$ was added to a solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$. On addition of excess L_2 a pale yellow solid precipitated. This was filtered off, washed with water and air-dried.

Preparation of $Pt(CH_3)_2BrNO_2L_2$ (L_2 = 2Lut, Tetrameen)

$Pt(CH_3)_2BrONOL_2$ was heated in an oven at 100°C for two hours. Complete rearrangement to the nitro isomer was confirmed by ^1H NMR and infrared spectra.

Attempted Preparation of $Pt(CH_3)_2BrILut_2$

A solution of $[Pt(CH_3)_2Br(H_2O)_3]^+$ was treated in rapid succession with NaI and Lut. ^1H NMR spectra showed the yellow product contained two species, $Pt(CH_3)_2BrOHLut_2$ and a species intermediate between $Pt(CH_3)_2Br_2Lut_2$ and $Pt(CH_3)_2I_2Lut_2$ in both chemical shift and coupling constant. The latter is almost certainly $Pt(CH_3)_2BrILut_2$. If addition of Lut in the above reaction was delayed for several minutes, a mixture of $Pt(CH_3)_2BrILut_2$ and $Pt(CH_3)_2I_2Lut_2$ was obtained indicating rapid substitution of Br by I. Attempts to prepare pure $Pt(CH_3)_2BrILut_2$ were unsuccessful.

Reaction of $[Pt(CH_3)_2Br(H_2O)_3]^+$ with NaX (X = Br, Cl, OH, SCN, NO_2)

A sample of $[Pt(CH_3)_2Br(H_2O)_3]^+$ in an NMR tube was treated with approximately one mole of NaX and the ^1H NMR spectrum monitored. The species in solution were observed as the amount of added NaX was increased and/or the solution was heated. No attempt was made to isolate the anionic species in solution.

^1H NMR spectra were recorded in $CDCl_3$, CD_3OH and H_2O solution on a JEOL PS-100 spectrometer using sweep width 540 Hz and either TMS or DSS as reference. Chemical shifts are considered accurate to ±0.01 ppm and coupling constants to ±0.5 Hz.

Infrared spectra between 4000 and 200 cm^{-1} were recorded on a Perkin-Elmer 225 spectrometer as Nujol and hexachlorobutadiene mulls between CsI plates.

The Raman Spectrum of $[Pt(CH_3)_2Br(H_2O)_3]^+$ (ca. 2M) was recorded using a Cary 82 spectrometer and 80 mW of 657 nm from a CRL 52MG Ar/Kr laser.

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