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Amino Acid Complexes of Platinum(IV). III. Mono(glycinate) Complexes of *Cis*-dimethylplatinum(IV): Preparation and Isomerization, Exchange and Substitution Reactions

NEVILLE H. AGNEW, TREVOR G. APPLETON and JOHN R. HALL*

Department of Chemistry, University of Queensland, Brisbane, Qld., 4067, Australia

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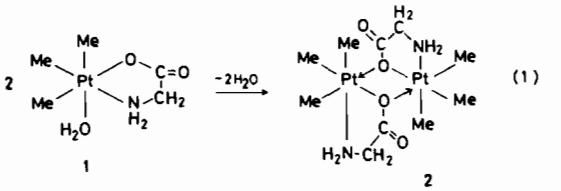
The three possible geometric isomers of $PtMe_2X(gly)H_2O$ (glyH = glycine) with X and the two methyl groups mutually cis *have been obtained in solution for X = Br, OH. For the isomer with both donor atoms of chelated glycinate* trans *to the methyl groups, $PtMe_2X(gly)(H_2O)$ precipitates from solution. For the other isomers, in which coordinated water is* trans *to methyl and labile, dimers, $[PtMe_2X(gly)]_2$, crystallize from solution. Reactions of these compounds with added NaOH, NaBr, and 3,5-lutidine have been studied, and found to be largely controlled by the high* trans *effect of the methyl ligands, but much slower reactions involving sites* cis *to the methyl groups also occur. The methyl groups always remain* cis. *Rapid exchange reactions have been studied by n.m.r.*

Introduction

Glycinate complexes of trimethylplatinum(IV) have been recently described [1]. In these compounds the three methyl groups are *facial*, and the remaining coordination sites are rendered labile by their high *trans* effect. A solution containing the mono-glycinate complex (1) may be obtained by mixing equimolar amounts of *fac*-$PtMe_3(H_2O)_3^+$ and sodium glycinate in aqueous solution. When a solution containing (1) is concentrated, or allowed to stand the labile water molecule is lost, and the dimer (2) crystallizes (reaction (1)). Related reactions occur with other bidentate amino acids [2].



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^{1}H n.m.r. is very useful in studying such compounds, since the Pt–CH_3 coupling constant (^{195}Pt, I = ½, 34% abundance) is very sensitive to the ligand *trans* to methyl (and almost unaffected by ligands *cis* to methyl) [3]. Typical coupling constant ranges in amino acid complexes of trimethylplatinum(IV) are 68–72 Hz for methyl *trans* to NH_2, 74–77 Hz for methyl *trans* to carboxylate O, and 78–82 Hz for methyl *trans* to water [1, 2]. $PtMe_3(gly)(H_2O)$ (1) and related compounds undergo rapid exchange reactions which are readily studied by n.m.r. [1, 2]. Related reactions probably occur with labile complexes of the first transition series, but are much less easily studied there.

In all known dimethylplatinum(IV) complexes the methyl groups are *cis*. Metal–ligand bonds *trans* to methyl are labile, while those *cis* to methyl are inert [4, 5], comparable to bonds in 'normal' complexes of platinum(IV) and -(II). It is thus possible to study, in the one series of compounds, the interaction of glycinate with both types of coordination site.

This paper describes the preparation, and the reactions in solution, of a number of dimethylplatinum(IV) mono(glycinate) complexes. The following paper discusses bis- and tris-(glycinate) complexes. A preliminary account of some of this work has been published [6].

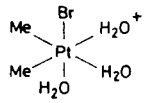
Starting Materials

A number of suitable dimethylplatinum(IV) starting materials are available, all derived from $[PtMe_2Br_2]_n$, which is itself insoluble in noncoordinating solvents [7]. Reaction of this compound with one equivalent of aqueous $AgNO_3$ solution gives, after removal of AgBr, a solution containing $PtMe_2Br(H_2O)_3^+$ (3) [4] (or, if the reaction is carried out in D_2O, $PtMe_2Br(D_2O)_3^+$). When neutral or anionic

†Part II, ref. 2.

*To whom correspondence should be addressed; no reprints available.

ligands are added to a solution of (3) rapid substitution occurs *trans* to methyl, with much slower reactions involving the coordination site *trans* to bromide (which itself tends to remain coordinated *cis* to the two methyl groups) [4]



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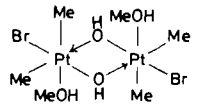

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Addition of NaOH to a solution of (3) causes precipitation of $[PtMe_2Br(OH)]_n$, which dissolves in methanol to give a solution containing $[PtMe_2Br(MeOH)(\mu\text{-}OH)]_2$ (4) [4].

The polymeric hydroxo compound, $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ may be obtained by reaction of $[PtMe_2Br_2]_n$ with concentrated NaOH solution, followed by neutralization [5, 8]. Unlike $[PtMe_2Br(OH)]_n$, this compound is insoluble in methanol, but it dissolves in alkali to give *cis*-$PtMe_2(OH)_4^{2-}$, and in acid to give *cis*-$PtMe_2(H_2O)_4^{2+}$ [5].

Results and Discussion

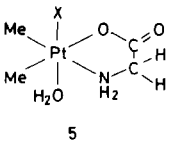
Because of the availability of the starting materials mentioned above, we have studied the two series of compounds $PtMe_2X(gly)(H_2O)$, X = Br and OH, and their derivatives. Apart from reactions in which the hydroxo group is protonated, most reactions of the two series of compounds are parallel. If X were another anionic ligand of low to moderate *trans* influence (*e.g.*, Cl, NCS), behaviour would be expected to be qualitatively similar to that when X = Br.

It will frequently be convenient to discuss compounds with X = Br and X = OH together. Where 'X' has been used in a text or scheme figure, it will be understood that the reference number with postscript 'a' refers to the compound with X = Br, and that with postscript 'b' to X = OH. Where no postscript is used, both compounds are meant.

There are five possible geometric isomers of $PtMe_2Br(gly)(H_2O)$ in which the two methyl groups are *cis*, (5a), (6a), (7a), (8), and (9). All have been obtained, at least in solution. Each of isomers (5a), (6a) and (7a) is the parent compound from which an extensive series of derivatives may be prepared. The other two isomers, (8), and (9), in which bromide is labilized by a *trans* methyl group, have no synthetic importance, and may be regarded as derivatives of $PtMe_2(OH)(gly)(H_2O)$ ((6b) and (7b) respectively).

Isomers of $PtMe_2(OH)(gly)(H_2O)$, (5b), (6b), and (7b), and many derivatives have also been obtained. The isomers of $PtMe_2(OH)(gly)(H_2O)$ analogous to (8) and (9) cannot be obtained, since water coordinated *cis* to methyl is more acidic than water coordinated *trans* to methyl.

For each of these geometric isomers, two enantiomers are possible.



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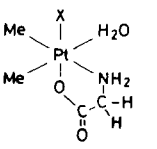

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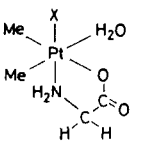

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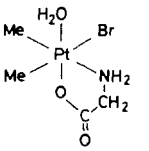

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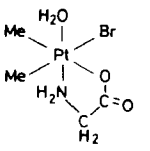

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Most of the reactions of these compounds $PtMe_2X(gly)(H_2O)$ are summarized in Schemes 1 (derivatives of (5)), 3 (derivatives of (6)), and 4 (derivatives of (7)). These three sets of reactions are discussed sequentially below.

Analytical data for new compounds isolated are given in Table I, and n.m.r. data in Table II.

Derivatives of $PtMe_2X(gly)(H_2O)$ (isomer (5)) Scheme 1)

Preparations of (5a) and (5b)

Addition of one equivalent of Na(gly) in D_2O to a dilute solution of $PtMe_2Br(D_2O)_3^+$ (3) gives a solution whose ^1H n.m.r. spectrum at 28 °C shows two sharp methyl peaks, each with 'satellites' from coupling to ^{195}Pt. The Pt–CH_3 coupling constants, 68.3 and 77.0 Hz, are similar to those observed for methyl groups *trans* to NH_2 and carboxylate O respectively in trimethylplatinum(IV) complexes. The structure of the compound is thus assigned as (5a), in which glycinate has displaced the two labile water molecules in (3).

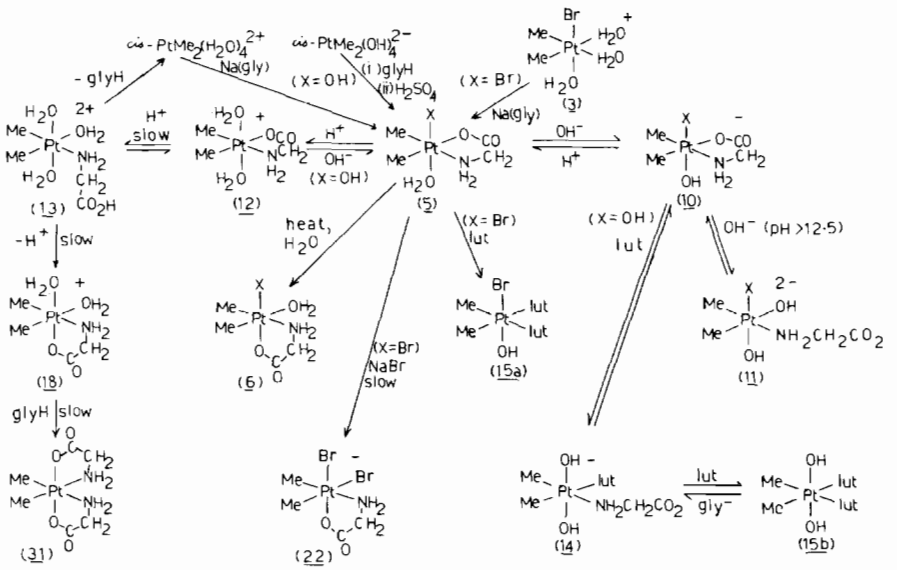
N-deuteration is instantaneous in D_2O for all of the complexes discussed here. The glycinate methylene protons of (5a) are non-equivalent. At 100 MHz, they show a slightly split peak with satellites, but at 270 MHz, a well-defined AB + ½(ABX) (X = ^{195}Pt) pattern is observed, and the coupling constants given in Table II may be determined. The low values of the Pt–N–C–H coupling constants (~11 Hz) are as expected for glycinate coordinated *trans* to methyl [1].

When concentrated aqueous solutions of the reactants are mixed, or if a dilute solution of (5a) is concentrated without heating, (5a) precipitates as a cream powder. The presence of a water molecule is indicated by analytical results (Table I). The IR spectrum shows two sharp bands at 3340 and 3260 cm^{-1},

TABLE 1. Analytical Data.[a]

Compound	Structure	C	H	N	Br	Mol Wt.[b]
$PtMe_2Br(gly)(H_2O)$	5a	12.1 (12.1)	3.1 (3.1)	3.7 (3.5)	20.0 (20.1)	291 (397)
$[PtMe_2Br(gly)]_2$	16a	12.9 (12.7)	2.9 (2.7)	3.8 (3.7)	20.5 (21.0)	349 (367)
$[PtMe_2Br(gly)]_2$	23a	13.0 (12.7)	2.8 (2.7)	3.6 (3.7)	20.9 (21.0)	326 (367)
$PtMe_2Br(gly)(H_2O)\cdot H_2O$	9	11.3 (11.6)	3.1 (3.2)	3.1 (3.4)	19.6 (19.3)	
$PtMe_2(OH)(gly)(H_2O)$	5b	14.4 (14.4)	4.0 (3.9)	4.5 (4.2)	–	
$[PtMe_2(OH)(gly)]_2$	16b	15.1 (15.2)	3.5 (3.5)	4.3 (4.4)	–	
$[PtMe_2(OH)(gly)]_2\cdot 2H_2O$	23b	14.4 (14.4)	4.0 (3.9)	4.3 (4.2)	–	
$PtMe_2(gly)(NO_3)(H_2O)\cdot \frac{1}{2}Me_2CO$	19	16.8 (16.2)	3.5 (3.7)	7.1 (6.9)	–	
$PtMe_2Br(gly)(lut)$	20a	26.7 (27.2)	4.2 (3.9)	5.6 (5.8)	16.7 (16.4)	
$PtMe_2Br(gly)(lut)$	29	27.8 (27.2)	4.1 (3.9)	5.9 (5.8)	15.6 (16.4)	

[a]Calculated values (%) in parentheses. [b]Measured in methanol. Calculated values are for monomeric units.



Scheme 1. Reactions of $PtMe_2X(gly)(H_2O)$, isomer (5) (X = Br, OH) (but = 3,5-lutidine).

assigned to ν(N–H), and a broad band at 2900 cm^{-1}, assigned to ν(O–H), overlapping the ν(C–H) peaks. These three bands shift on deuteration to 2490, 2410 and 2260 cm^{-1} respectively. Once it has precipitated, (5a) redissolves in water only sparingly, but it is soluble in methanol. An aqueous solution of (5a) is slightly acidic (pH ~ 5), owing to the acidity of the coordinated water molecule.

Addition of one equivalent of Na(gly) to an aqueous solution of *cis*-$PtMe_2(H_2O)_4^{2+}$ causes immediate precipitation of a white solid analysing for $PtMe_2(OH)(gly)(H_2O)$, which dissolves freely in acid or alkali, but is virtually insoluble in other common solvents. The same compound is obtained by reaction of a solution of *cis*-$PtMe_2(OH)_4^{2-}$ with glycine, followed by neutralization with dilute H_2SO_4. If the latter reaction is carried out in D_2O, but D_2SO_4 addition is stopped just before the precipitation point (pD ~ 7.5), the ^1H n.m.r. spectrum of the solution shows two sharp methyl peaks with satellites. The Pt–CH_3 coupling constants, 70.1 and 78.7 Hz, are consistent with methyl groups *trans* to glycinate N and O respectively, although the values are slightly higher than for the bromo analogue. This allows assignment of structure (5b) (at pD 7.5 in equilibrium with $PtMe_2(OD)_2(gly)^-$ (10b) – see below). The two methylene protons are equivalent, and, as expected, show a singlet with satellites.

The IR spectrum of (5b) shows a broad band centred at 3400 cm^{-1} which includes ν(O–H) and ν(N–H) bands.

Reactions of (5) with alkali

Both (5a) and (5b) are much more soluble in dilute alkali solution than in pure water, owing to the formation of anionic hydroxo complexes $PtMe_2$-

TABLE II. ^{1}H N.m.r. Data.[a]

Formula	Structure	Solvent[b]/pD	Temp. (°C)	Pt-CH_3			CH_2(gly)			Lutidine			
				Trans Ligand	δ	J(Pt-CH_3)	δ	J(PtNCH)	J(AB)	CH_3 δ	Hα δ	J(Pt-H_α)	Hβ δ
$PtMe_2Br(gly)(D_2O)$	5a	4.5	28[c]	N	1.53	68.3	3.88	~11	17.3				
				O(gly)	1.66	77.0	3.82	~10					
		CD_3OD	28	N	1.63	66.3	3.78	~10					
				O(gly)	1.67	74.0							
	6a	5	2.5[c]	N	1.60	67.0	d	d	d				
				D_2O	1.78	81.1							
	7a	5	2.5[c]	O(gly)	1.58	74.5	3.68[e]	31					
				D_2O	1.73	78.7							
	8	3.7	13	N	1.81	66.3	d	d	d				
				Br	1.93	73.3							
	9	4	1.5	O	1.72	72.7	d	d	d				
				Br	1.80	70.2							
$PtMe_2(OD)(gly)(D_2O)$	5b	7.2	28	N	1.34	70.1	3.81	9					
				O(gly)	1.47	78.2							
	6b	5	2.0[c]	N	1.44	68.0	3.75[e]	~8					
				D_2O	1.64	82.5							
	7b	6	1.5	O(gly)	1.35	75	3.62[e]	~27					
				D_2O	1.55	79.6							
$[PtMe_2(OD)(gly)]_2$	23b	6	1.5	μ-OD	1.71	75.0	3.51[e]	30.3					
				μ-OD	1.42	75.4							
$Na[PtMe_2Br(OD)(gly)]$	10a	11	28[c]	N	1.45	69.7	3.81[e]	10					
				O(gly)	1.58	78.0							
	17a	12	28	N	1.56	68.0	d	d					
				OD	1.35	70.8							
$Na[PtMe_2(OD)_2(gly)]$	10b	12	28	N	1.27	71.1	3.80	9					
				O(gly)	1.41	79.1							
	17b	12	28	N	1.39	70.3	d	d	d				
				OD	1.19	72.6							
$[PtMe_2(gly)(D_2O)_2]_2SO_4$	12	3.8	28	N	1.51	68.0	d	d					
				O(gly)	1.65	75.8							
	18	3.7	28	N	1.63	66.1	3.79	~19	~17				
				D_2O	1.83	79.8	3.78	~4					
	26	3.1	1.5	O(gly)	1.52	71.9	3.61[e]	36					
				D_2O	1.75	77.4							
$[PtMe_2(glyH)(D_2O)_3]SO_4$	13	3.8	28	N	1.78	72	d	d					
				D_2O	1.89	78							
$Na[PtMe_2Br_2(gly)]$	22	4	28	N	1.69	69.0	3.83[e]	12.2					
				Br	1.82	77.8							

	30	3.5	2	O(gly)[f] Br[f]	18.1 1.76	75 76	d	d					
$PtMe_2Br(gly)(lut)$	20a	$(CD_3)_2CO$	28	N(gly)[f] lut[f]	1.67 1.46	68.7 71.2	d	d		2.37	8.62	12	7.62
	29	CD_3OD	28	O lut	1.61 1.68	73.7 69.3	3.50 3.13	d	16.5	2.38	8.47	11	7.70
$[PtMe_2(gly)(lut)(D_2O)]_2SO_4$	21	4.5	28	N(gly)[f] lut[f]	1.53 1.62	68.2 70.4	d	d		2.39	8.24	9	7.77
$PtMe_2(OD)(gly)(lut)$	20b	9	28	N(gly)[f] lut[f]	1.43 1.50	69.7 71.5	3.72 3.32	8.5 10.0	17.5	2.38	8.24	9	7.74
$Na[PtMe_2(OD)_2(gly)(lut)]$	14	12	28	N(gly)[f] lut[f]	1.29 1.20	70.8 71.2	d	d		d	d	d	d
$PtMe_2(OD)_2(lut)_2$	15b	11.5	28	lut	1.43	70.6				2.27	8.08	9	7.69

[a]Chemical shifts in p.p.m. downfield form 3-trimethylsilylpropanesulfonate (TSS) in D_2O, downfield from tetramethylsilane (TMS) in other solvents. [b]Solvent is given if not D_2O. If solvent is D_2O, pD is given. [c]Spectrum run at both 100 and 270 MHz. [d]Pattern complex, not well resolved, or obscured by overlap with other peaks. [e]Methylene protons give singlet with satellites, although formally non-equivalent. [f]These assignments could be interchanged.

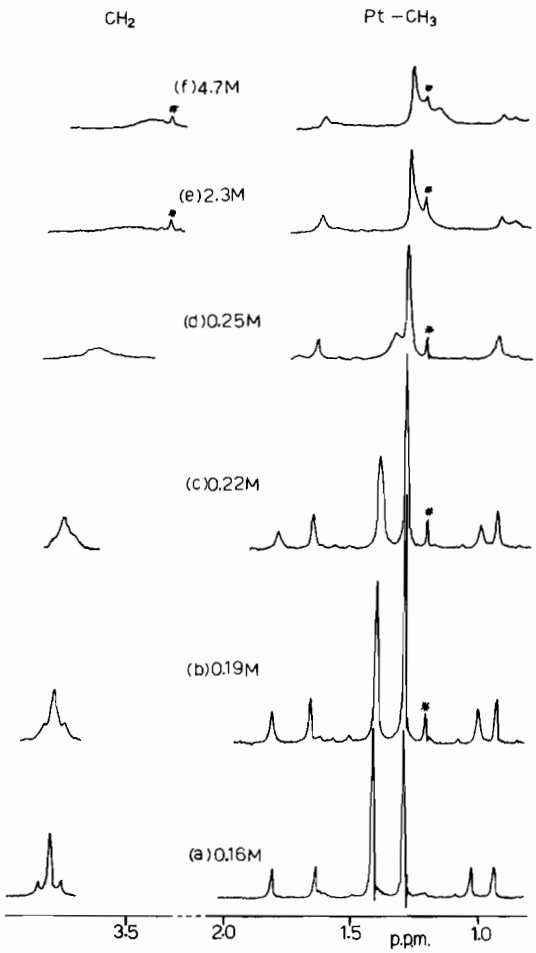


Fig. 1. 100 MHz ^1H n.m.r. spectraum of 0.14 *M* solutions of $PtMe_2(OH)(gly)(H_2O)$ (5b) in $NaOH/D_2O$ as a function of the initial concentration of NaOH (*i.e.*, ignoring OH^-/OD^- consumed in deprotonating (5b)). $*PtMe_2(OD)_2(gly)_2^{2-}$ impurity.

$X(OH)(gly)^-$ (10). Attempts to isolate these complexes always yielded extremely deliquescent materials. They were consequently studied only in solution.

When the pD of a solution of $PtMe_2X(gly)(D_2O)$ (5) is increased to ~11, the methyl peaks shift up to 0.08 p.p.m. to higher field as (5) depronates to (10), but the Pt–CH_3 coupling constants change little (Table II). No further change is observed in the spectrum up to pD ~ 12.5, but as a concentrated solution of NaOH in D_2O is added, the peak assigned to methyl *trans* to O broadens and shifts to higher field, while the peak due to methyl *trans* to NH_2 broadens and shifts only slightly. The changes are qualitatively similar for X = Br (10a) and X = OD (10b), and are illustrated for X = OD in Fig. 1.

These observations may be explained if the Pt–O-(gly) bond is being broken in concentrated alkali

solution, so that a rapid (on the n.m.r. time scale) equilibrium is set up between $PtMe_2X(OD)(gly)^-$ (10) (glycinate chelated) and $PtMe_2X(OD)_2(gly)^{2-}$ (11) (glycinate unidentate). The proportion of (11) in equilibrium with (10), and the rate of reaction of (10) with hydroxide, will increase as hydroxide concentration increases. The methyl chemical shifts will be weighted averages of those of (10) and (11). From the spectra it may be deduced that the chemical shifts for methyl *trans* to N are similar in (10) and (11), but the chemical shift for methyl *trans* to OD in (11) is significantly to higher field than that for methyl *trans* to glycinate O in (10).

The exchange between (10) and (11) does not make the two methyl groups equivalent. The mechanism is probably associative, involving hydroxide attack on coordinated carboxylate and *vice versa.*

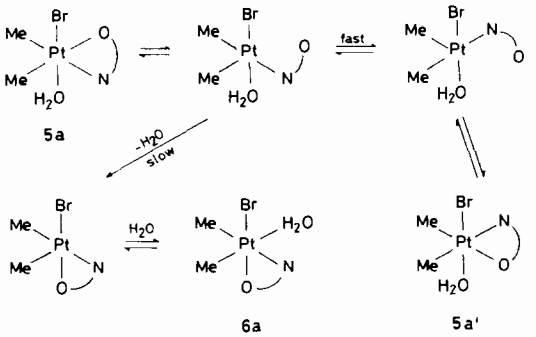
At very high hydroxide concentrations, the peak corresponding to methyl *trans* to O would be expected to begin to sharpen again, as the spectrum approached that of pure (11). The limit of hydroxide concentration imposed by viscosity broadening is reached before this point.

Spectra were also run near 0 °C, but showed only a slightly broader peak for methyl *trans* to O than at 28 °C.

The exchange between (10) in which glycinate is chelated, and (11), in which glycinate is unidentate, causes the initial sharp methylene singlet to broaden and shift to higher field in concentrated alkali solution.

Isomerization of (5)

$PtMe_2Br(gly)(H_2O)$ (5a) isomerizes to (6a) within a few minutes in aqueous solution at 60 °C. If the n.m.r. spectrum of (5a) is run quickly at 60 °C, the methyl peaks, sharp at 28 °C, are broadened, indicating that an exchange is beginning which makes the two methyl groups equivalent. Plausible mechanisms for this exchange between (5a) and (5a′), and for the much slower isomerization to (6a), are suggested in Scheme 2.



Scheme 2. Proposed mechanism for isomerization of (5a).

By contrast, $PtMe_2Br(OH)(gly)^-$ (10a) does not isomerize when heated in solution at high pH, but very slowly reacts to form $PtMe_2(OH)_2(gly)^-$ (10b). (10b) also does not isomerize when heated at pH $\geqslant$ 10, but at pH 7–8 slow rearrangement to (6b) (in equilibrium with deprotonated (17b)) does occur.

Reaction of $PtMe_2(OH)(gly)(H_2O)$ (5b) with acid

(5b) dissolves readily in dilute acid, but the n.m.r. spectrum of a D_2SO_4 solution (pD 3.8) shows that a number of species are present. Some peaks may be assigned to compounds which can be prepared from (6b) $PtMe_2(gly)(D_2O)_2^+$ (18) (Scheme 3) and $PtMe_2(gly)_2$ (31) (see following paper) and to *cis*-$PtMe_2(D_2O)_4^{2+}$. Using Pt–CH_3 coupling constants (Table II), two further sets of methyl peaks are assigned to $PtMe_2(gly)(D_2O)_2^+$ (12) and $PtMe_2(glyD)(D_2O)_3^{2+}$ (13). Peaks of (13) are slightly broadened, owing to an exchange analogous to reaction (2) (see below).

The composition of the solution depends on pD, and the time the solution has been allowed to stand. After several days, *cis*-$PtMe_2(D_2O)_4^{2+}$ and $PtMe_2(gly)_2$ (31) predominate.

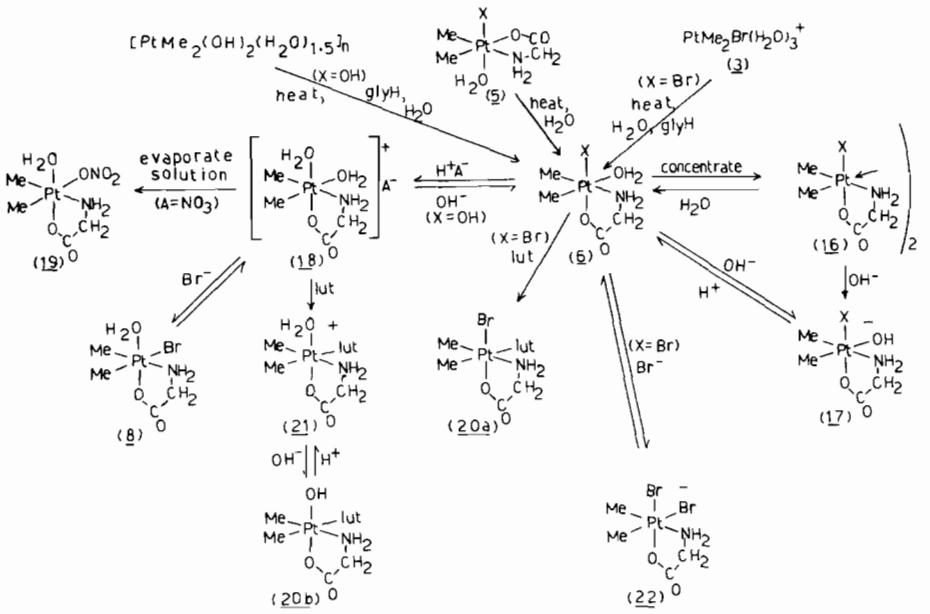
Reactions of (5) with lutidine

Since both labile coordination sites (*trans* to methyl) in (5) are occupied by chelated glycinate, this chelation must be disrupted if a substitution reaction is to occur. The coordinated water molecule in (5) is not displaced readily, since it occupies an inert site. That is, the labilizing effect of the *trans*-ligand over-rides the stabilizing effect of chelation. Even in non-organometallic complexes, where *trans* effect differences are less extreme, there are examples of cleavage of a Pt–O bond of chelated glycinate being preferred to displacement of coordinated H_2O [9].

When 3,5-lutidine (3,5-dimethylpyridine, abbreviated lut) is added to an aqueous solution of $PtMe_2Br(gly)(H_2O)$ (5a), the known compound [4], $PtMe_2Br(OH)(lut)_2$ (15a) immediately precipitates.

Since $PtMe_2(OH)(gly)(H_2O)$ (5b) is insoluble, lutidine was added to a solution of $PtMe_2(OD)_2(gly)^-$ (10b) in dilute NaOD solution. In this solution, a complex equilibrium is set up between (10b), $PtMe_2(OD)_2(gly)(lut)^-$ (14), and $PtMe_2(OD)_2(lut)_2$ (15b). Some of the glycinate released from formation of (15b) also reacts with $PtMe_2(OD)_2(gly)^-$ (10b) to give the bis(glycinate) complex $PtMe_2(OD)_2(gly)_2^{2-}$ (structure (34) in the following paper). When a large excess of lutidine is present, $PtMe_2(OD)_2(lut)_2$ (15b) predominates.

Since $PtMe_2(OH)_2(lut)_2$ (15b) has not previously been reported, it was obtained in solution independently by addition of lutidine to a solution of *cis*-$PtMe_2(OD)_4^{2-}$. The low value of J(Pt–N–C–H_α), 9 Hz, is consistent with coordination of lutidine *trans* to methyl [1, 3, 4]. Unlike the bromo analogue, (15a), this compound does not precipitate from



Scheme 3. Preparation and reactions of $PtMe_2X(gly)(H_2O)$, isomer (6) (X = Br, OH).

aqueous solution. The coordinated lutidine is extremely labile, and attempts to isolate (15b) led to loss of lutidine to give $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$.

Reaction of (5a) with bromide

When excess NaBr is added to a D_2O solution of $PtMe_2Br(gly)(D_2O)$ (5a), peaks due to $PtMe_2Br_2(gly)^-$ (22) (obtainable from (6a) – see Scheme 3 below) grow over a period of hours. The reaction occurs most readily near pD 4. At low pD ($\lesssim$3.3), appreciable quantities of *cis*-$PtMe_2Br_4^{2-}$ form (identified by n.m.r. [10]). At pD > 5.5, where (5a) is in equilibrium with $PtMe_2Br(OD)(gly)^-$ (10a), the reaction does not take place.

There is no observable reaction of $PtMe_2(OD)_2(gly)^-$ (10b) with bromide at pD $\geqslant$ 8.

Derivatives of $PtMe_2X(gly)(H_2O)$ (isomer (6) (Scheme 3)

Preparation of (6a), (6b), and the dimers $[PtMe_2X(gly)]_2$ (16)

As mentioned above, $PtMe_2Br(gly)(H_2O)$ (5a) isomerizes when heated in water. The product was identified as (6a) from its n.m.r. spectrum at 2.5 °C, which shows two methyl peaks, with $J(Pt–CH_3)$ 67.0 and 81.1 Hz, corresponding to methyl groups *trans* to NH_2– and water respectively.

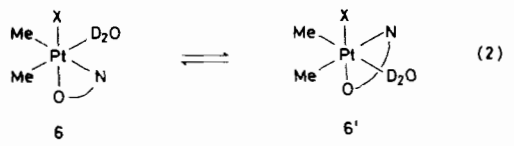
When a solution of (6a) is slowly concentrated, yellow crystals deposit, (16a), which analyse for $PtMe_2Br(gly)$. The IR spectrum shows sharp peaks at 3330 and 3250 cm^{-1} attributable to ν(N–H), but no ν(O–H) bands. The solid dissolves only sparingly in water to re-form (6a). It is very sparingly soluble in methanol. This prevents accurate molecular weight measurement, but it is monomeric in this solvent – probably as $PtMe_2Br(gly)(MeOH)$ (Table I) (*cf.* $[PtMe_3(L\text{-ala})]_2$ which is dimeric in acetone and monomeric in methanol [2]). (16a) may be formulated as a dimer with O-bridges, analogous to $[PtMe_3(gly)]_2$ (2) [1] or $[PtMe_3(L\text{-ala})]_2$ [2], but a bromo-bridged structure is also possible. Formation of (16a) from (6a) involves loss of the labile water molecule. A similar reaction does not occur for isomer (5a) because there the coordinated water molecule is not labile.

(16a) may be obtained more conveniently by heating an aqueous solution of $PtMe_2Br(H_2O)_3^+$ (3) and glycine, then evaporating off the solvent.

$PtMe_2(OH)(gly)(H_2O)$ (5b) dissolved in slightly alkaline solution rearranges only very slowly. Heating an aqueous suspension of $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ with one equivalent of glycine gives a compound (16b) formulated as $[PtMe_2(OH)(gly)]_2$, with either glycinate O or OH bridges. (16b) is only very sparingly soluble in water, to give $PtMe_2(OH)(gly)(H_2O)$ (5b), but is much more soluble in acid and alkali (see below). The IR spectrum of (16b) shows a moderately sharp band at 3450 cm^{-1} assigned to ν(O–H), and bands at 3290, 3250, and 3165 cm^{-1} assigned to ν(N–H).

Exchange reactions of (6) by n.m.r.

Each of (6a) and (6b) shows two sharp methyl peaks (with satellites) in its n.m.r. spectrum near 0 °C. As temperature is increased, the peaks broaden and coalesce, by 90° giving a sharp singlet with satellites. Thus, the two methyl peaks become equivalent as exchange reaction (2) becomes rapid on the n.m.r. time scale.



(2)

This reaction is analogous to the 'high temperature exchange' of $PtMe_3(gly)(H_2O)$ (1) [1, 2]. The probable mechanism involves dissociation of the labile water molecule *trans* to methyl, followed by migration of the N-atom in the five-coordinate intermediate. It is noteworthy that this exchange occurs without any alteration in the relative configuration of the two methyl groups, X (Br or OH), and glycinate O, since none of the other geometric isomers of $PtMe_2Br(gly)(H_2O)$, (5a), (7a), (8) and (9) interconverts rapidly with (6a). Reaction (2) is formally a racemization. Kinetics of this and related reactions will be reported elsewhere [11]. A similar rapid exchange does not occur for isomer (5), since there the coordinated water molecule is not labile.

Even at 2.5 °C, the glycinate methylene protons of (6a) have not 'frozen' into a well-defined AB + ½(ABX) (X = ^{195}Pt) pattern, but give a broad resonance. The methylene protons of (6b) would be expected to be non-equivalent at low temperature, but even at 270 MHz, 0 °C, only a singlet with satellites is observed.

Reactions of (6) with alkali

Addition of NaOH in D_2O to a solution of $PtMe_2X(gly)(D_2O)$ (6) gives a solution containing $PtMe_2X(OD)(gly)^-$ (17). A similar solution, but usually more concentrated, may be obtained by dissolving $[PtMe_2X(gly)]_2$ (16) in dilute NaOD solution. Each of (17a) and (17b) shows sharp methyl peaks in its n.m.r. spectrum at 28 °C, since exchange (2) is much slower when Pt–OD rather than Pt–OD_2 bonds must break. Values of $J(Pt–CH_3)$ *trans* to hydroxide (Table II) fall in the range 70–75 Hz found for methyl *trans* to hydroxide in monomeric trimethylplatinum(IV) compounds [12]. No change occurs when the spectrum is run in very concentrated alkali solution, in contrast to reactions of isomers (5) and (7), where Pt–O(gly) bonds *trans* to methyl are susceptible to hydroxide attack.

Reaction of $[PtMe_2(OH)(gly)]_2$ (16b) with dilute acid

(16b) dissolves readily in dilute H_2SO_4 or HNO_3 to give solutions containing $PtMe_2(gly)(H_2O)_2^+$ (18), which do not change significantly with time. At 28 °C in D_2SO_4 (pD 3.7) two sharp methyl peaks with satellites are observed. Pt–CH_3 coupling constants (Table II) correspond to methyl groups *trans* to NH_2 and H_2O. Since the peaks are sharp, exchange analogous to reaction (2) is relatively slow, but as the temperature is raised they broaden, and coalesce above 64 °C. The slower exchange compared with $PtMe_2(OD)(gly)(D_2O)$ (6b) is probably due to reduced lability of the water molecule *trans* to methyl in the cationic complex (*cf.* the reduced lability of coordinated water in *cis*-$Co(en)_2(H_2O)_2^{3+}$ compared with *cis*-$Co(en)_2(OH)(H_2O)^{2+}$ [13]).

The simplicity of protonation of (6b), where one end of the glycinate ligand (O) is 'anchored' by coordination to an inert site, contrasts with the complexity of the corresponding reaction of isomer (5b) (see above) where both ends of glycinate are bound to labile sites.

If the acid used is HNO_3, evaporation of the solution of $[PtMe_2(gly)(H_2O)_2]NO_3$ to dryness yields a solid which has been assigned structure (19), with coordinated nitrate. This compound in water is a weak electrolyte with a molar conductivity of 52.8 Ω^{-1} cm^2 mol^{-1} (for a 9.7 × 10^{-4} *M* solution). The molar conductivity of a 1:1 electrolyte (KCl) in water is 149.9 Ω^{-1} cm^2 mol^{-1} at infinite dilution. In acetone it is essentially a non-electrolyte with a molar conductivity of 10.1 Ω^{-1} cm^2 mol^{-1} (for a 4.7 × 10^{-3} *M* solution).

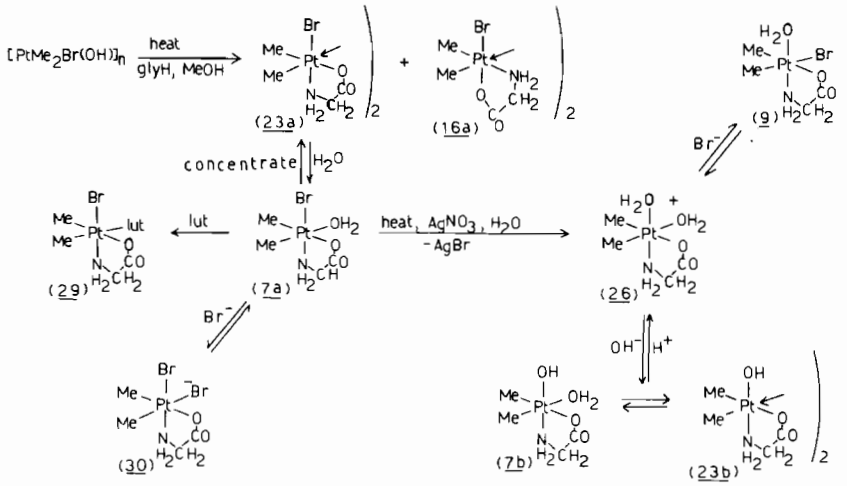
Reactions of (6) and derivatives with 3,5-lutidine

Unlike isomer (5), $PtMe_2X(gly)(H_2O)$ (6) has a labile water molecule (*trans* to methyl) which is readily displaced by neutral ligands. Addition of lutidine to an aqueous solution of (6a) causes immediate precipitation of a pale yellow compound, $PtMe_2Br(gly)(lut)$, which is soluble in acetone and methanol. Its n.m.r. spectrum in $(CD_3)_2CO$ (Table II) is entirely consistent with structure (20a). Since coordinated lutidine is less labile than water no rapid exchange analogous to reaction (2) occurs, and peaks are sharp (*cf.* $PtMe_3(gly)(lut)$ [1]).

Because of the low solubility of $[PtMe_2(OH)(gly)]_2$ (16b), it is convenient to dissolve it in acid, and add lutidine to the resultant solution of $PtMe_2(gly)(H_2O)_2^+$ (18). With one equivalent of lutidine, in D_2SO_4, $PtMe_2(gly)(D_2O)(lut)^+$ (21) is formed cleanly in solution. When pD is adjusted to ~9, peaks shift as $PtMe_2(OD)(gly)(lut)$ (20b) forms. The methylene protons of (20b) show a well-defined AB + ½(ABX) spectrum (X = ^{195}Pt). No precipitate forms. Attempts to isolate (20b) have been unsuccessful, because of very easy loss of lutidine. For example, when a concentrated aqueous solution of (20b) containing excess lutidine was left to evaporate at room temperature. $[PtMe_2(OH)(gly)]_2$ (16b) was obtained.

Reactions of (6) and derivatives with bromide

When a two-fold excess of NaBr is added to a solution of $PtMe_2(gly)(D_2O)_2^+$ (18) in dilute D_2SO_4, the n.m.r. spectrum at 28 °C shows two slightly broadened methyl peaks with satellites. At 2.5 °C,



Scheme 4. Preparation and reactions of $PtMe_2X(gly)(H_2O)$, isomer (7).

two sets of two methyl resonances are observed (intensity ratio 3:1) corresponding to $PtMe_2Br(gly)(D_2O)$ (8) and $PtMe_2(gly)(D_2O)_2^+$ (18) respectively. $J(Pt–CH_3)$ *trans* to bromide in (8) (73.3 Hz) is at the lower end of the range of values *trans* to bromide in monomeric trimethylplatinum(IV) complexes [3]. The methylene protons of (8) are formally non-equivalent, but at 100 MHz show a singlet with satellites. When the Br^-:Pt ratio is increased to 4:1, the peaks corresponding to $PtMe_2(gly)(D_2O)_2^+$ (18) become very weak compared with those from $PtMe_2Br(gly)(D_2O)$ (8).

The observation of two broadened methyl peaks at 28 °C shows that bromide exchange between (18) and (8) is relatively fast.

Although (8) is a non-electrolyte, it does not precipitate from concentrated aqueous solution. Attempts to separate it from excess NaBr after evaporation of an aqueous solution to dryness were unsuccessful. It showed no tendency to isomerize on prolonged standing in solution.

$[PtMe_2(OH)(gly)]_2$ (16b) does not dissolve in concentrated aqueous NaBr solution, but $[PtMe_2Br(gly)]_2$ (16a) does slowly dissolve to give $Na[PtMe_2Br_2(gly)]$ (22) in solution. Provided the ratio of added bromide to platinum is sufficiently large (>2:1), the n.m.r. spectrum at 28 °C shows two sharp methyl resonances with satellites. $Pt–CH_3$ coupling constants (Table II) are consistent with methyl groups *trans* to NH_2 and Br^-. Although the methylene protons are again formally non-equivalent, only a singlet with satellites is observed at 100 MHz. At lower ratios of added Br^-: Pt (~1:1), the methyl peaks are broad, indicating rapid bromide exchange between $PtMe_2Br_2(gly)^-$ (22) and $PtMe_2Br(gly)(D_2O)$ (6a).

Derivatives of $PtMe_2X(gly)(H_2O)$ (isomer (7)) (Scheme 4)

Preparation of $PtMe_2Br(gly)(H_2O)$ (7a) and $[PtMe_2Br(gly)]_2$ (23a)

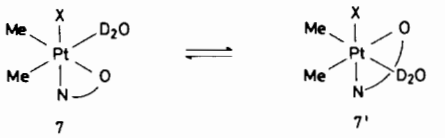
When a suspension of glycine in a methanol solution of $[PtMe_2Br(OH)]_n$ is heated, and the resultant solution is concentrated, a mixture of two isomers of $[PtMe_2Br(gly)]_2$ is obtained, yellow (16a) and a white compound (23a). These products may be separated by fractional crystallization from methanol. The white isomer (23a) dissolves sparingly in D_2O. The ^1H n.m.r. spectrum of the solution at 2.5 °C shows two singlets (slightly broadened – see below) with satellites in the methyl region. The $Pt–CH_3$ coupling constants, 74.5 and 78.7 Hz correspond to methyl groups *trans* to glycinate O and water respectively. Even at 0 °C, 270 MHz, the methylene protons show a singlet with satellites. The high value of $J(Pt–N–CH_2)$, 31 Hz, indicates that glycinate N is coordinated *cis* to methyl. The complex in solution is thus assigned structure (7a), and the solid, (23a), a dimeric structure with either glycinate O or bromide bridges.

Unlike $PtMe_2Br(gly)(H_2O)$ (5a) and $[PtMe_2Br(gly)]_2$ (16a) which show sharp $\nu(N–H)$ bands in their IR spectra, (23a) shows a broad band centred at 3160 cm^{-1}.

The formation of two different isomers of $[PtMe_2Br(gly)]_2$ from $[PtMe_2Br(MeOH)(\mu\text{-}OH)]_2$ (4) and glycine probably results from two competing reactions. Isomer (16a) is probably formed by glycinate displacement of methanol coordinated *trans* to methyl, while isomer (23a) is probably formed by reaction of Pt–OH with the acidic $^+NH_3$ group of zwitterionic glycine.

Exchange reaction of $PtMe_2Br(gly)(H_2O)$ (7a)

Above 2.5 °C, the methyl peaks of (7a) broaden and coalesce. By 28 °C, a broad singlet (with satellites) is observed, and this peak sharpens as temperature is increased further. These spectra indicate that exchange reaction (3) is rapid on the n.m.r. time scale. As with reaction (2), a mechanism involving dissociation of the labile water molecule is likely, but it is now the glycinate O-atom which migrates. This reaction is analogous to the 'low-temperature exchange' of $PtMe_3(gly)(H_2O)$ (1) [1, 2].



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Kinetics of this and related reactions will be discussed in a forthcoming publication [11].

Preparation of $[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ (23b)

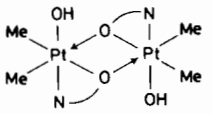
Attempts to prepare $PtMe_2(OH)(gly)(H_2O)$ (7b) or $[PtMe_2(OH)(gly)]_2$ (23b) directly from $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$, $PtMe_2(H_2O)_4^{2+}$, or $PtMe_2(OH)_4^{2-}$ were unsuccessful.

When an aqueous suspension of $[PtMe_2Br(gly)]_2$ (23a) is heated with two moles of silver nitrate for several hours, (23a) slowly dissolves and AgBr precipitates. If the pH is adjusted to 6.5 with NaOH solution, and the solution concentrated, colourless crystals slowly deposit which analyse for $PtMe_2(OH)(gly) \cdot H_2O$. Although the presence of water in the solid would allow it to be formulated as monomeric $PtMe_2(OH)(gly)(H_2O)$ (7b), n.m.r. spectra show that a dimeric species is present in aqueous solution (see below), and a dimeric structure with lattice water is more likely, $[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ (23b).

N.m.r. spectra of solutions of $[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ (23b) in D_2O and D_2SO_4

(23b), although still sparingly soluble in water, is much more soluble than either $PtMe_2(OH)(gly)(H_2O)$ (5b) or $[PtMe_2(OH)(gly)]_2$ (16b). The ^1H n.m.r. spectrum in D_2O (pD ~ 6) at 1.5 °C shows two sets of two methyl peaks (with satellites) (intensity ratio ~4:1) and two corresponding singlets with satellites in the glycinate methylene region. Both Pt–N–CH_2 coupling constants are in the vicinity of 30 Hz, indicating that glycinate N is *cis* to the methyl groups in both compounds. The Pt–CH_3 coupling constants for the less intense methyl resonances are 79.6 and 75 Hz, corresponding to methyl groups *trans* to water and glycinate O respectively. These peaks are assigned to the monomeric aqua complex, $PtMe_2(OD)(gly)(D_2O)$ (7b).

The Pt–CH_3 coupling constants for the more intense set of methyl resonances are 75.0 and 75.4 Hz. These values are consistent only with a dimeric structure, $[PtMe_2(OD)(gly)]_2$ (or a higher oligomer), but do not allow us to distinguish between a structure with bridging through glycinate O (24) and one with bridging hydroxide (25)



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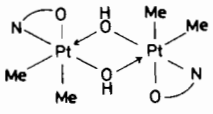

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If the pD is decreased by addition of D_2SO_4, peaks due to the monomeric complex grow at the expense of those due to the dimer. At pD 4.7, the two sets of n.m.r. peaks have nearly equal intensity. The peaks due to the dimer do not shift significantly, but the methyl peaks due to the monomeric species shift downfield, as would be expected if protonation to $PtMe_2(gly)(D_2O)_2^+$ (26) is occurring. No significant shift is observed for the methylene protons of the monomeric species, but as would be expected if OD is being replaced by the weaker ligand D_2O, J(Pt–N–CH_2) increases from ~27 to 36 Hz. There is no change in J(Pt–N–CH_2) for the dimer. By pD 4, peaks due to the dimer are very weak (~1/10 intensity of monomer peaks), and by pD 3 they have disappeared entirely. The Pt–CH_3 coupling constants *trans* to D_2O (77.4 Hz) and glycinate O (71.9 Hz) in $PtMe_2(gly)(D_2O)_2^+$ (26) are slightly below typical ranges.

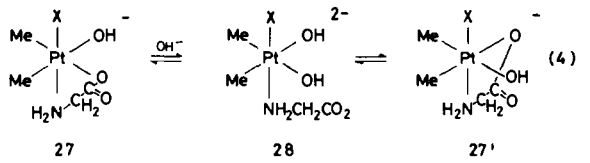
pK_b of coordinated hydroxide in structure (24) would not be expected to be very different from that in $PtMe_2(OH)(gly)(H_2O)$ (7b). The lack of any evidence for a protonated form of the dimer under conditions where (7b) is partially protonated to $PtMe_2(gly)(H_2O)_2^+$ (26) suggests that the dimer does not have structure (24). For the hydroxo-bridged structure, (25), protonation would, of course, destroy the dimeric structure, and this is consistent with the observed decrease in concentration of the dimer as pH decreases.

If a solution at pD 5, where approximately equal amounts of compound are in the monomeric and dimeric forms, is allowed to warm to 28 °C, the peaks due to the monomer broaden and begin to coalesce as reaction (3) occurs. The peaks due to the dimer remain sharp. However, as the temperature is raised further, these peaks also broaden, and coalesce with those from the monomer. By 65 °C all methyl peaks have coalesced into a broad singlet with satellites, which sharpens as temperature is raised further. The methylene resonances also coalesce. The changes in spectra are reversed on cooling.

N.m.r. spectra of $[PtMe_2X(gly)]_2$ (23) dissolved in alkaline solution

When NaOH is added to a D_2O solution of $PtMe_2Br(gly)(D_2O)$ (7a) or if $[PtMe_2Br(gly)]_2$ (23a) is dis-

solved in dilute NaOD solution, the methyl peaks give an extremely broad resonance, which does not sharpen significantly on cooling to 0 °C. The glycinate methylene protons give a relatively sharp central singlet with broadened satellites. This contrasts with the spectrum of $PtMe_2Br(OD)(gly)^-$ (17a), which shows two sharp methyl peaks (see above). The broad methyl resonance in this case arises because hydroxide may attack the Pt–O bond, causing exchange reaction (4) to occur.



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Reaction (4) is more complicated than the exchange between $PtMe_2X(OH)(gly)^-$ (10) and $PtMe_2X(OH)_2(gly)^-$ (11) discussed earlier, since, if reaction (4) became sufficiently fast, the two methyl groups would become equivalent.

When $[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ (23b) is dissolved in dilute NaOD solution (pD 12), the n.m.r. spectrum shows a broad singlet in the methyl region (width at half height 6 Hz), although it is much sharper than for the bromo compound. The methylene protons show a sharp singlet with satellites ($J(Pt–N–CH_2)$ 28.3 Hz). As well as (27b) and (28b), the dimer (25) may also be participating in the exchange.

Reaction of $PtMe_2Br(gly)(H_2O)$ (7a) with 3,5-lutidine

When lutidine is added to an aqueous solution of (7a), the labile water molecule is immediately displaced, and $PtMe_2Br(gly)(lut)$ (29) precipitates. Like isomer (20a), it is soluble in methanol, but unlike (20a), insoluble in acetone. Peaks in the n.m.r. spectrum in CD_3OD are sharp, and coupling constants (Table II) are consistent with structure (29).

Reaction of (7) and derivatives with bromide

When a five-fold excess of NaBr is added to a solution of $PtMe_2(gly)(D_2O)_2^+$ (26) at pD 3, the resultant spectrum at 2.5 °C shows only very weak peaks due to (26), and two sharp methyl peaks assigned to $PtMe_2Br(gly)(D_2O)$ (9). As with some other derivatives of (7b) (*e.g.*, (26)), the $Pt–CH_3$ coupling constant *trans* to Br (70.2 Hz) and glycinate O (72.7 Hz) are slightly lower than the usual range.

White crystals of solid $PtMe_2Br(gly)(H_2O) \cdot H_2O$ (9) slowly deposit from a cold concentrated solution. The I.R. spectrum shows a broad $\nu(O–H)$ peak at 3450 cm^{-1}. When the crystals are redissolved in dilute D_2SO_4 the n.m.r. spectrum at 2.5 °C shows peaks due to a mixture of $PtMe_2Br(gly)(D_2O)$ (9) and $PtMe_2(gly)(D_2O)_2^+$ (26) in the approximate ratio 5:2. At 28 °C, the peaks have broadened, as bromide exchange occurs.

$[PtMe_2Br(gly)]_2$ (23a) dissolves slowly in a dilute $NaBr/D_2SO_4$ solution, with gentle warming. At 2 °C, the n.m.r. spectrum of the solution shows two sets of two methyl peaks, slightly broadened, corresponding to $PtMe_2Br(gly)(D_2O)$ (7a) and $PtMe_2Br_2(gly)^-$ (30). The equilibrium in this case lies much more toward the aqua complex than for the isomeric compound (22). Even at a ratio of added bromide to platinum of 4:1, the proportion of bromo complex (30) to aqua complex (7a) is only approximately 2:1.

At 28 °C, exchange between (7a) and (30), together with reaction (3), makes all the methyl resonances coalesce to a broad singlet (with satellites).

Experimental

Instrumentation and Analyses

100 MHz ^1H n.m.r. spectra were run on a Jeol PS-100 spectrometer. 270 MHz spectra were run at the National NMR Centre, Canberra by Dr. A. J. Jones and associates. IR spectra were run on a Jasco IRA-2 spectrometer, as hexachlorobutadiene mulls between KBr plates. Molecular weights were measured using a Hewlett-Packard 302 Mechrolab High Temperature Vapour Pressure Osmometer. Microanalyses were performed by J. Kent and P. Nobbs of this department.

Materials

Platinum containing starting materials were prepared as described in references quoted in the Section, 'Starting Materials' above. Sodium glycinate was prepared as previously described [1], 3,5-lutidine was used as supplied by Aldrich.

Preparation of $PtMe_2Br(gly)(H_2O)$ (5a)

An aqueous solution of $[PtMe_2Br(H_2O)_3]NO_3$ (3) (10 ml containing 0.779 mmol) was concentrated on a rotary evaporator (bath temperature < 100 °C) to approx. 2.5 ml. The slightly cloudly solution was filtered, and to the combined filtrate and washings (6 ml) was added 0.0756 g sodium glycinate (0.779 mmol) in 1 ml water. The yellow solution was concentrated at room temperature over silica gel in a vacuum desiccator. Clusters of pale yellow crystals formed. These were washed with water, and dried under vacuum at 56 °C. Yield 0.217 g (55%).

Preparation of $PtMe_2(OH)(gly)(H_2O)$ (5b)

0.134 g $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ (0.467 mmol Pt) was suspended in 0.5 ml water, and 5 *M* H_2SO_4 was added dropwise with slight warming and stirring

until the solid dissolved. The solution was filtered, and 0.045 g sodium glycinate (0.47 mmol) in 2 ml water was added. A white precipitate formed initially, but redissolved on mixing. pH was adjusted to 4.8 with 1 *M* NaOH. A heavy precipitate formed, which was isolated by centrifugation, washed with water, and dried under vacuum at 56 °C. Yield 0.102 g (65%).

The same product may be obtained by dissolving $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ in 1 *M* NaOH, followed by addition of glycine, then dilute H_2SO_4 to adjust pH to ~8.5.

Preparation of $[PtMe_2Br(gly)]_2$ *(16a)*

To a solution of $[PtMe_2Br(H_2O)_3]NO_3$ (3) (5 ml containing 0.39 mmol) was added a solution of 0.060 glycine (0.80 mmol) in 3 ml water. The solution was evaporated on the steam bath to a yellow gum. 2 ml water was added, the mixture was warmed, then allowed to stand overnight. Small yellow rounded crystals formed. These were rinsed with a small volume of water, then acetone, and dried under vacuum at 110 °C. Yield 0.097 g (60%).

Preparation of $[PtMe_2(OH)(gly)]_2$ *(16b)*

A suspension of 0.0633 g $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ (0.221 mmol Pt) in a solution of 0.0166 g glycine (0.221 mmol) in 4 ml water was heated with stirring at 95–100 °C for three hours. During this time the starting material slowly dissolved, and product deposited on the side of the flask. 12 ml water was then added, and the mixture refluxed until all the product had dissolved. The slightly cloudy solution was filtered (porosity 4 sinter) and the filtrate was evaporated to dryness at ~50 °C. The white crystalline residue was washed twice with small volumes of hot water, then dried under vacuum at 110 °C. Yield 0.0721 g (97%).

Preparation of $[PtMe_2Br(gly)]_2$ *(23a)*

Reaction of $[PtMe_2Br(OH)]_n$ with glycine in methanol always gives a mixture of the isomers (16a) and (23a) of $[PtMe_2Br(gly)]_2$, although the relative amounts of the two products vary with reaction conditions. The procedure below gives the highest proportion of (23a) relative to (16a).

0.1974 g $[PtMe_2Br(OH)]_n$ (0.613 mmol Pt) was dissolved in 18 ml dry methanol, and 0.190 g glycine (2.45 mmol) was added. The mixture was refluxed, without stirring or crushing of the suspended glycine, by immersion of the flask in an oil bath maintained at a temperature less than 100 °C. The initial yellow colour of the solution faded. After three hours, the solution was allowed to cool, then filtered (porosity 4 sinter) from remaining glycine and traces of black material. When the fitrate was concentrated to approx. 8 ml, a heavy crop of white microcrystalline product formed, which was filtered off, and washed with a small volume of methanol. A second crop was obtained by concentrating the filtrate to approx. 3 ml. The supernatant solution was now pale yellow, and contained isomer (16a) as well as the desired product.

The two crops were united. This material, 0.09 g, which contained some glycine, was dissolved in 15 ml hot water. The solution was filtered, and the filtrate allowed to evaporate at room temperature in a vacuum desiccator until a white microcrystalline solid deposited. This material was isolated, and dried under vacuum at 56 °C for two hours. The product was isomerically pure and free from glycine. Yield 0.060 g (26%).

Preparation of $[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ *(23b)*

To $[PtMe_2Br(gly)]_2$ (23a) (0.1106 g, 0.1459 mmol Pt) was added 0.0991 g silver nitrate (0.5835 mmol) in 2 ml water. The mixture was heated at 90–100 °C with stirring for 16 hours. pH was then increased to 11.5, and the solution was centrifuged to remove AgBr and Ag_2O. The pH of the solution was adjusted to 6.5, and the solution was filtered. Slow concentration of the filtrate yielded clear crystals, which were recrystallized from water, then dried under vacuum at 56 °C for several hours, when the appearance of the crystals changed to an opaque white. Yield 0.070 g (80%).

Preparation of $PtMe_2(gly)(NO_3)(H_2O) \cdot \frac{1}{2}Me_2CO$ *(19)*

$[PtMe_2(OH)(gly)]_2$ (16b) (0.0304 g, 0.0961 mmol Pt) was treated with 1.34 ml 0.0708 *M* HNO_3 solution (*i.e.*, <1:1 molar ratio) with warming and stirring. After 1.5 hours the slight excess of undissolved dimer was filtered off, and the filtrate evaporated in a vacuum desiccator over silica gel. A clear glassy residue resulted. This was dissolved in acetone with warming and stirring, and the solution was filtered. Evaporation of the solvent yielded a white hygroscopic solid which after prolonged drying under vacuum at 56 °C still contained acetone, as evidenced by analytical results (Table I) and n.m.r. spectra. Yield 0.022 g (65%).

Preparation of $PtMe_2Br(gly)(H_2O) \cdot H_2O$ *(9)*

$[PtMe_2(OH)(gly)]_2 \cdot 2H_2O$ (23b) was dissolved in water and the pH adjusted to 3 with H_2SO_4. On addition of an excess of NaBr white crystals formed on standing at a low temperature. These were recrystallised from a small volume of water and vacuum dried at 56 °C for 3 hours.

Reaction of $PtMe_2Br(gly)(H_2O)$ *(5a) with 3,5-lutidine*

An aqueous solution (8 ml, containing 0.390 mmol) of (5a) was prepared by addition of sodium glycinate to a solution of $[PtMe_2Br(H_2O)_3]NO_3$ (3).

0.0835 g lutidine (0.779 mmol) in 6 ml water was added. An off-white precipitate formed immediately. The mixture was allowed to stand in the refrigerator for three hours. The solid was then filtered off, washed twice with water, and dried under vacuum at 110 °C. The product was shown, from IR and n.m.r. spectra, and C, H, N, and Br microanalyses, to be $PtMe_2Br(OH)(lut)_2$ (15a) [4]. Yield 0.021 g (50%).

The same product was obtained when only one equivalent of lutidine was used.

Preparation of $PtMe_2Br(gly)(lut)$ (20a)

$[PtMe_2Br(gly)]_2$ (16a) (0.0736 g, 0.1941 mmol Pt) was dissolved in 7 ml water (by stirring for 2.5 hours). The solution was filtered, and a slight excess of 3,5-lutidine in 1 ml water was added. The solution was allowed to stand overnight in the refrigerator during which time small clusters of white needles formed. The product was washed with water and dried under vacuum at 110 °C. Yield ~50%.

Preparation of $PtMe_2Br(gly)(lut)$ (29)

A solution of 0.0255 g $[PtMe_2Br(gly)]_2$ (23a) (0.0673 mmol Pt) in 3 ml water was treated as above. Yield 0.018 g (55%).

Preparation of n.m.r. samples

With the few exceptions noted in the discussion, where organic solvents were used, the solvent in all cases was D_2O, with conc. D_2SO_4 or 5 *M* NaOH in D_2O used to adjust pD when necessary. The low solubility of many of the compounds meant that dilute solutions often had to be used. Typically, sparingly soluble compounds were crushed under D_2O, and were allowed to stand with slight warming for several hours before the solution was filtered through a small plug of tissue paper into the n.m.r. tube.

Where protonation or deprotonation caused insoluble compounds to be converted into soluble ones, higher concentrations could be obtained. Typically, 20–30 mg of compound was suspended in 0.5 ml D_2O, and small amounts of $NaOH/D_2O$ or D_2SO_4 were added to effect dissolution. The solution was filtered into the tube.

Narrow range pH paper (Merck) was usually used to measure pD, and the value read from the calibration chart was taken as the pD value. In some cases, the value was checked using a small glass electrode supplied by Ionode immersed in the solution in an n.m.r. tube, and using the standard relation between pH reading and pD [14].

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