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Amino Acid Complexes of Platinum(IV). IV. Bis- and Tris-(Glycinate) Complexes of *Cis*-dimethylplatinum(IV): Chelate Ring Closure and Cleavage Reactions†

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Reactions of sodium glycinate with the three isomers of $PtMe_2X(gly)(H_2O)$ having the two methyl groups and X mutually cis *have been studied (X = Br, OH; glyH = glycine). Bis-(glycinate) complexes $PtMe_2X(OH)(gly)_2^{2-}$ (two unidentate N-bound glycinates) or $PtMe_2X(gly)_2^-$ (one chelated and one unidentate glycinate) and tris-(glycinate) complexes $PtMe_2X(gly)_3^{2-}$ (three unidentate glycinates) are formed according to the rules:*

(i) water coordinated trans *to methyl is readily displaced by glycinate N.*

(ii) if excess glycinate is used, glycinate O coordinated trans *to methyl in a chelate ring may be displaced by glycinate N.*

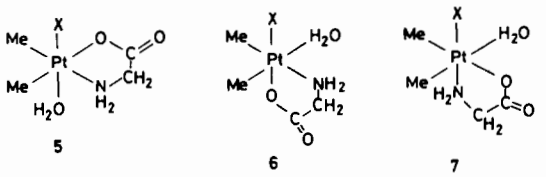
(iii) groups coordinated cis *to methyl are not displaced at room temperature.*

When X = OH, ring closure to an isomer of $PtMe_2(gly)_2$ does not occur in alkaline solution. Two of the three possible isomers of $PtMe_2(gly)_2$ with methyl groups cis *(viz., the isomer with both N-atoms* trans *to methyl, and the isomer with one N-atom* trans *to methyl) may be obtained by reaction of the appropriate isomer of $PtMe_2(gly)(H_2O)_2^+$ with glycine in acid solution. The third isomer of $PtMe_2(gly)_2$, with both N-atoms* cis *to methyl, is slowly formed by isomerization of the other isomers.*

Glycinate O coordinated trans *to methyl in isomers of $PtMe_2(gly)_2$ is susceptible to attack by hydroxide or glycinate N.*

Introduction

In part III, we reported the preparation of the isomers (5), (6), and (7) of $PtMe_2X(gly)(H_2O)$ (glyH = glycine, X = Br and OH), and, for (6) and (7), the dimers $[PtMe_2X(gly)]_2$ (16) and (23) formed after loss of the labile water molecule**.



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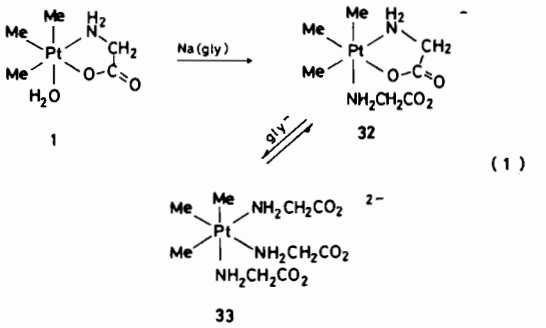
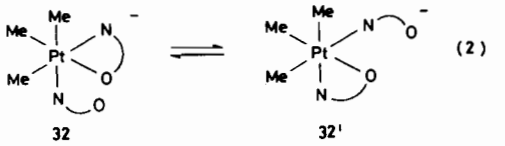
In this paper we report the reactions of these compounds with sodium glycinate, and the preparation and properties of the three isomers of $PtMe_2(gly)_2$ with methyl groups *cis*. A preliminary account of some of this work has been published [1].

In the trimethylplatinum (IV) system [2], $PtMe_3(gly)(H_2O)$ (1) reacts with glycinate to give the bis-(glycinate) complex $PtMe_3(gly)_2^-$ (32), and, with excess, the tris-(glycinate) complex $PtMe_3(gly)_3^{2-}$ (33).



(1)

For (32), the exchange reaction (2) is rapid on the n.m.r. time scale at higher temperature.



(2)

Results and Discussion

N.M.R. data for new compounds are given in Table I.

†Part III. Preceding Paper (page 000 of this issue).

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**To facilitate reference to part III, numbers used there will be retained in this paper. Numbers for compounds introduced in this paper will begin with (32). As in part III, postscript 'a' refers to X = Br and 'b' to X = OH.

TABLE I. ^{1}H N.M.R. Data[a].

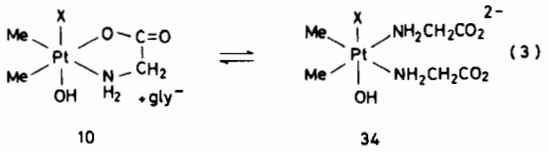
Formula	Structure	pD	Pt–CH_3			CH_2(gly)		
			Trans Ligand	δ	J(Pt–CH_3)	δ	J(PtNCH)	J(AB)
$PtMe_2(gly)_2$	31	~7	N	1.48	69.7	3.74	11.1(av.)	
	39[d]	~7	N	1.40	65.1	3.78[b]	9.7(av.)	
			O	1.37	74.0			
						3.64[c]	21.8	17.2
						3.58[c]	43.6	17.2
	41	~7	O	1.35	73.3	3.75	26.6(av.)	
$Na[PtMe_2Br(gly)_2]$	35a[d]	12	N[e]	1.42	66.6	3.78[e]	g	18
			N[f]	1.39	67.3	3.63[e]	g	18
						3.35[f]	12.1	17.3
						3.23[f]	12.1	17.3
	36a[h]	10	N(γ)	1.40	67.3	g	g	
			O(α)	1.48	74.5			
	37a[h]	10	N(δ)	1.40	67.3	g	g	
			O(β)	1.43	74.0			
$Na[PtMe_2(OD)(gly)_2]$	35b[d]	12	N[e]	1.34	69.5	3.75[e]	g	17.3
			N[f]	1.28	71.0	3.65[e]		17.3
						3.34[f]	g	17.3
						3.20[f]		17.3
	36b[h]	12	N(γ)	1.21	67.6	g	g	
			O(α)	1.29	75.8			
	37b[h]	12	N(δ)	1.21	67.6	g	g	
			O(β)	1.23	76			
	40[i]	12.5	N[j]	1.32	66	g	g	
			OD[j]	1.09	67			
$Na_2[PtMe_2Br(OD)(gly)_2]$	34a[d]	11	N	1.36	69.9	3.37	9.7(av.)	
$Na_2[PtMe_2(OD)_2(gly)_2]$	34b	12	N	1.19	71.4	3.30	8	
$Na_2[PtMe_2Br(gly)_3]$	38a	12	N	1.28	67.2	g	g	
$Na_2[PtMe_2(OD)(gly)_3]$	38b	12	N	1.13	67.8	g	g	
$Na[PtMe_2(gly)_3]$	44[d]	11	N[e]	1.28	65.2	g	g	
			N[f]	1.24	66.9			
	45	10.5	N	1.23	64.9	3.50[b]	15.0(av.)	
			O	1.13	71.0	3.73[k]	25.0(av.)	
						3.39[l]	~25	

[a]Chemical shifts in p.p.m. downfield from 3-trimethylsilylpropanesulfonate (TSS); coupling constants in Hz. All spectra in D_2O solutions. [b]Attached to N *trans* to methyl. [c]Attached to N *cis* to methyl. [d]Spectrum run at 270 and 100 MHz. [e]Chelated glycinate. [f]Unidentate glycinate. [g]Spectrum complex, or peaks obscured. [h]Assignment tentative; see text. [i]Peaks moderately broad. [j]Assignments could be reversed. [k]Broad singlet; chelated glycinate N-coordinated *cis* to methyl. [l]Broad singlet; unidentate glycinate N-coordinated *cis* to methyl.

Reactions of Isomers of $PtMe_2X(gly)(H_2O)$ or $[PtMe_2X(gly)]_2$ (X = Br, OH) with Sodium Glycinate

Reaction of $PtMe_2X(gly)(H_2O)$ (isomer (5)) with Na(gly)

As mentioned in part III, $PtMe_2X(gly)(H_2O)$ (5) deprotonates at high pH to $PtMe_2X(OH)(gly)^-$ (10). When Na(gly) is added to a D_2O solution of (10) at pD > 10, an equilibrium is set up between (10) and $PtMe_2X(OD)(gly)_2^{2-}$ (34). Only at very high glycinate concentration does (34) predominate. As pD is decreased by addition of D_2SO_4, the proportion of (34) relative to (10) plus (5) decreases until, by pD ~ 7, only a trace of (34) remains.



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The cleavage by glycinate of the Pt–O(gly) bond *trans* to methyl rather than Pt–OH *cis* to methyl, may be compared with the reactions of (5a) and (5b) with lutidine (Scheme 1 in part III).

The ^{1}H n.m.r. spectrum of D_2O of each of (34a) (X = Br) and (34b) (X = OD) shows a singlet with 'satellites' in the methyl region. J(Pt-CH_3) in each case is near 70 Hz (Table I), characteristic of methyl *trans* to glycinate N.

The methylene protons of $PtMe_2(OD)_2(gly)_2^{2-}$ (34b) are equivalent, but those of $PtMe_2Br(OD)(gly)_2^{2-}$ (34a) are formally non-equivalent. Nevertheless, at both 100 and 270 MHz the methylene protons of each compound give a singlet with satellites. Values of J(Pt-N-CH_2) (<10 Hz) are consistent with glycinate N-bound *trans* to methyl.

A solution containing (34b) in equilibrium with (10b) and glycinate is unaffected by prolonged heating at pD > 10. Similar treatment of (34a) causes slow replacement of bromide by hydroxide.

Reactions of $PtMe_2X(gly)(H_2O)$ (isomer (6)) and derivatives with Na(gly) (Scheme 1)

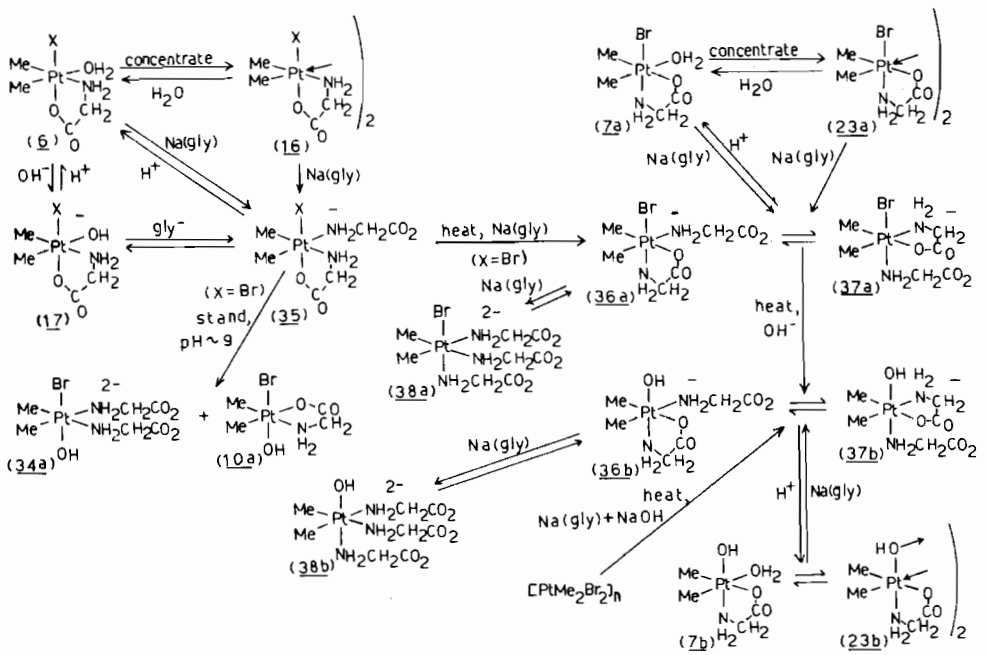
Solid $[PtMe_2X(gly)]_2$ (16), $PtMe_2X(gly)(H_2O)$ (6) in solution, and $PtMe_2X(OH)(gly)^-$ (17) in solution, all react nearly quantitatively with one equivalent of Na(gly) to give a solution of $Na[PtMe_2X(gly)_2]$ (35) in which one glycinate ligand is chelated and one is unidentate, N-bound. Attempts to isolate these compounds gave extremely deliquescent materials which were not further characterized. In strongly alkaline solution, the proportion of $PtMe_2X(OH)(gly)^-$ (17) in equilibrium with (35) increases.

Each of (35a and b) shows two sharp methyl peaks in its n.m.r. spectrum at 28° and at 80 °C. There is therefore no rapid intramolecular exchange between unidentate and bidentate glycinate, analogous to reaction (2) for $PtMe_3(gly)_2^-$ (32). Such an exchange would not be expected for (35), where the O-atom of the chelated glycinate occupies an inert site *cis* to methyl.

Addition of excess Na(gly) at room temperature does not cause formation of a tris-(glycinate)complex, analogous to $PtMe_3(gly)_3^{2-}$ (33), as an inert Pt–O bond would have to be broken. As discussed below, heating a solution of (35a) with Na(gly) does cause isomerization to (36a) plus (37a), probably *via* $PtMe_2Br(gly)_3^{2-}$ (38a).

The assignments of the methyl peaks given in Table I are based on the assumption that J(Pt-CH_3) *trans* to N of unidentate glycinate will be slightly greater than *trans* to N of chelated glycinate (*cf.* $PtMe_2Br(gly)_3^{2-}$ (38a).

For each of (35a) and (35b), the methylene protons give two AB + ½(ABX) patterns (X = ^{195}Pt), more clearly observed at 270 MHz than at 100 MHz. The assignments in Table I are based on the observation that methylene protons of unidentate glycinate usually resonate to higher field (nearer free ligand) than those of chelated glycinate.



Scheme 1. Reactions of isomers (6) and (7) of $PtMe_2X(gly)(H_2O)$ (and derivatives) with glycinate.

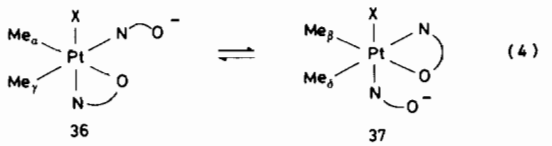
When D_2SO_4 is added to a D_2O solution of $PtMe_2X(gly)_2^-$ (35), $PtMe_2X(gly)(D_2O)$ (6) is formed in solution at pD $\lesssim$ 5.5. At pD ~ 4, $[PtMe_2X(gly)]_2$ (16) precipitates.

A sample of $PtMe_2Br(gly)_2^-$ (35a) which was allowed to stand for several months at pD ~ 9 was converted into an equilibrium mixture of $PtMe_2Br(OD)(gly)^-$ (10a) and $PtMe_2Br(OD)(gly)_2^{2-}$ (34a) (*i.e.*, the chelate ring was cleaved).

Reactions of $PtMe_2X(gly)(H_2O)$ (isomer (7)) and derivatives with Na(gly) (Scheme 1)

When Na(gly) is added to a D_2O solution of $PtMe_2Br(gly)(D_2O)$ (7a), or a D_2O suspension of $[PtMe_2Br(gly)]_2$ (23a), the n.m.r. spectrum of the resultant solution shows that a number of species are present. When there is a large excess of Na(gly) present, one methyl peak (with satellites) becomes dominant. $J(Pt\text{-}CH_3)$, 67.2 Hz, corresponds to methyl *trans* to glycinate N, and this peak has been assigned to $PtMe_2Br(gly)_3^{2-}$ (38a), analogous to $PtMe_3(gly)_3^{2-}$ (33) (reaction (1)). The presence of a large excess of free glycinate prevents observation of the free methylene resonances.

At ratios of added glycinate: Pt less than ~2:1, only a trace of $PtMe_2Br(gly)_3^{2-}$ (38a) is present, and at 28 °C three methyl peaks are observed, with approximate relative intensities 1:2:3 (Fig. 1(a)). The $Pt\text{-}CH_3$ coupling constants, 74.5 (A), 74.0 (B), and 67.3 (C) Hz correspond to methyl groups *trans* to O(gly), O(gly), and N(gly) respectively. These peaks may be assigned to the two isomers of $PtMe_2Br(gly)_2^-$, (36a) and (37a), in equilibrium, with the peaks due to methyl *trans* to N in the two species (γ and δ) accidentally coincident at C.



(4)

The methylene protons of each of (36a) and (37a) would be expected to give two sets (AB + ½ABX) patterns (X = ^{195}Pt). The region shows a multiplicity of peaks which defy detailed analysis. Two singlets with satellites may be discerned, P($J(Pt\text{-}N\text{-}CH_2)$ 32 Hz) and Q ($J(Pt\text{-}N\text{-}CH_2)$ 13 Hz), which may be due to 'accidental' equivalence of some of the methylene protons.

An unequivocal assignment of the methyl peaks *trans* to O in the two isomers cannot be made. On steric grounds, (36a), in which unidentate glycinate is *cis* to the bulky bromide ligand, would be expected to be less stable than (37a), in which unidentate glycinate is *trans* to bromide. If this is so, the least intense of the methyl peaks, A, would be assigned to

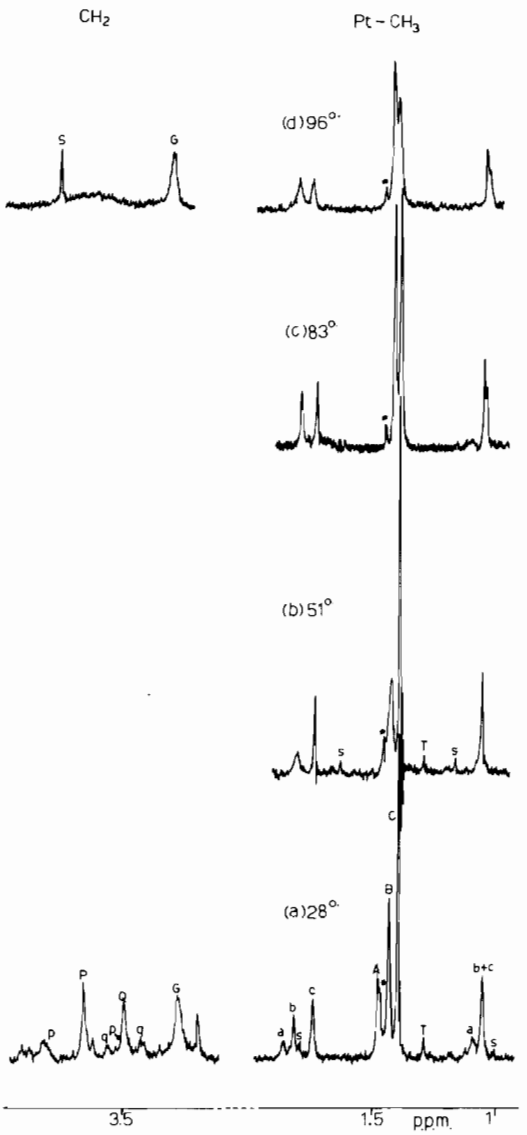


Fig. 1. Variable-temperature 100 MHz ^1H n.m.r. spectra of $PtMe_2Br(gly)_2^-$ ((36a) + (37a)) in D_2O. T, $PtMe_2Br(gly)_3^{2-}$ (38a); G, free glycinate; s spinning side band ($Pt\text{-}CH_3$), S spinning side band (HDO), * impurity. For other labels, see text.

Me_α of (36a), and peak B would be assigned to Me_β of (37a). For convenience, these assignments will be used in the following discussion, but the argument is unaffected if they are reversed.

Since separate signals are observed for (36a) and (37a) at 28 °C, reaction (4) is slow at this temperature. Changes in the n.m.r. spectrum as temperature is increased, and reaction (4) becomes more rapid, are illustrated in Fig. 1. If reaction (4) is sufficiently fast, Me_α in (36a) becomes equivalent to Me_β in (37a), and Me_γ in (36a) becomes equivalent to Me_δ in (37a). Consequently, as temperature increases, peaks A(Me_α) and B(Me_β) broaden and coalesce, while peak C,

where resonances from Me_γ and Me_δ are already coincident, remains sharp. By 83 °C, there are two sharp singlets with satellites in the methyl region (Fig. 1(c)). Reaction (4) is analogous to the intramolecular exchange reaction (2) observed for $PtMe_2(gly)_2^-$ (32), but is significantly slower. At still higher temperatures, the peaks begin to broaden (Fig. 1(d)), probably due to an intermolecular glycinate exchange *via* $PtMe_2Br(gly)_3^{2-}$ (38a), which makes the two methyl groups equivalent (*cf.* behaviour at high temperatures of $PtMe_3(gly)_2^-$ (32) and related compounds [2, 3]).

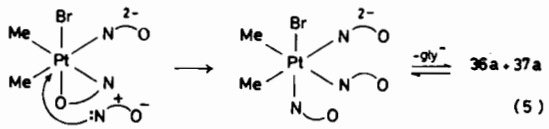
If reaction (4) became sufficiently fast without commencement of intermolecular glycinate exchange, the methylene region would, in principle, be expected to show two overlapping (AB + ½ABX) patterns (X = ^{195}Pt). However, at the highest temperature used, only a broad featureless peak is observed.

Addition of Na(gly) to a solution of $[PtMe_2(OH)(gly)]_2$ (23b) gives the hydroxo analogues, $PtMe_2(OH)(gly)_2^-$ (36a) and (37b), and, with excess glycinate, $PtMe_2(OH)(gly)_3^{2-}$ (38b). The overall pattern in the methyl region of the n.m.r. spectrum in D_2O is similar to that for the bromo analogues, except that the peaks are shifted to higher field. Once again, the peaks due to methyl *trans* to N in the two isomers (Me_γ and Me_δ) are coincident. In contrast with the bromo compounds, the more deshielded of the methyl groups *trans* to O gives a more intense peak than that from the more shielded group (intensity ratio ~ 2:1). If the chemical shifts for the two isomers (36) and (37) are in the same order for X = Br and X = OH, this suggests that isomer (36b) is favoured over isomer (37b). This might be expected on steric grounds, since in (36b) unidentate glycinate is *cis* to hydroxide which is less bulky than bromide. In addition, there is the possibility of intramolecular H-bonding between the OH group and the uncoordinated carboxylate group.

The variable temperature n.m.r. spectra are qualitatively similar to those of the bromo analogues.

The same mixture of isomers of $PtMe_2(OD)(gly)_2^-$ ((36b) plus (37b)) may be obtained by heating a NaOD solution (pD ≥ 12) of $PtMe_2Br(gly)_2^-$ ((36a) plus (37a)) at 60 °C for twenty minutes.

An unusual isomerization reaction occurs when a sample of $PtMe_2Br(gly)_2^-$ (isomer (35a), with both N-atoms *trans* to methyl) is heated at ≥ 60 °C in the presence of one equivalent of sodium glycinate. A mixture of isomers (36a) and (37a) is formed cleanly. Since the reaction proceeds best in the presence of significant amounts of free glycinate, we may postulate a reaction mechanism involving glycinate attack on the Pt–O bond *trans* to bromide (reaction (5)) (attack on a Pt–N bond *trans* to methyl is more likely, but this would merely cause an exchange between unidentate coordinated glycinate and free glycinate, with no net chemical reaction). The tris-(glycinate)complex (38a) formed by this reaction dissociates at low glycinate concentrations to a mixture of (36a) and (37a) (see above).



35a 38a (5)

In the absence of added glycinate, the isomerization of (35a) is slower, but some free glycinate is always in equilibrium with (35a) and $PtMe_2Br(OH)(gly)^-$ (17a), which catalyses the reaction. There is no tendency for the reverse reaction (conversion of (36a) plus (37a) to (35a)) to occur, so that (35a) appears to be the least stable of the three isomers of $PtMe_2Br(gly)_2^-$. This is in accordance with the general rule that the thermodynamically most stable isomer tends to be that in which ligands of highest *trans* influence are *trans* to ligands of least *trans* influence [4]. In these compounds, the trans influence order is Me > N > Br ~ O.

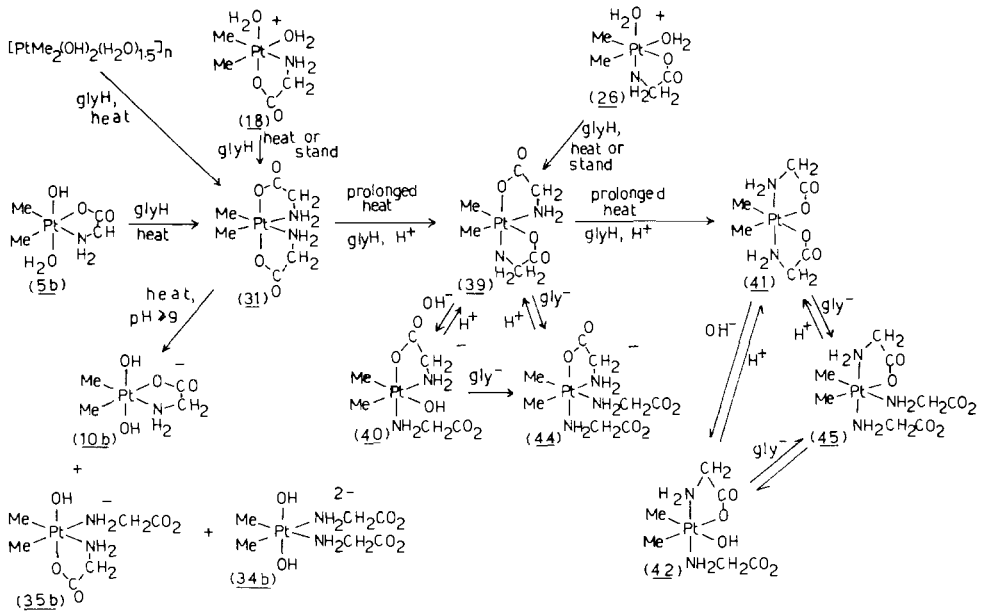
When $PtMe_2(OD)(gly)_2^-$ (35b) is heated in D_2O with sodium glycinate, two competing reactions occur, both very slow. The major reaction is alkaline cleavage of the chelate ring to give $PtMe_2(OD)_2(gly)^-$ (10b) in equilibrium with $PtMe_2(OD)_2(gly)_2^{2-}$ (34b). The minor product (about one third of the reaction) is an equilibrium mixture of isomers (36b) and (37b) of $PtMe_2(OD)(gly)_2^-$. The much lower reactivity of $PtMe_2(OD)(gly)_2^-$ (35b) compared with $PtMe_2Br(gly)_2^-$ (35a) may be due in part to the higher trans effect of bromide relative to hydroxide.

Since, as mentioned above, $PtMe_2Br(gly)_2^-$ ((36a) + (37a)) is hydrolysed in strong alkali to $PtMe_2(OH)(gly)_2^-$ ((36b) + (37b)), a mixture of (36b) and (37b) may be obtained directly by heating $PtMe_2Br(gly)_2^-$ (35a) in a strongly alkaline sodium glycinate solution. A similar solution may be obtained directly by heating $[PtMe_2Br_2]_n$ with Na(gly) in alkaline solution.

Bis(chelate) Complexes, $PtMe_2(gly)_2$ (Scheme 2)

Formation and Isomerization of Complexes $PtMe_2(gly)_2$

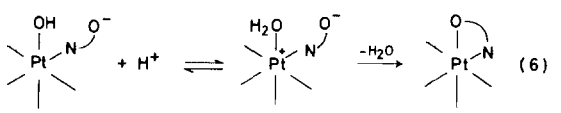
When $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ is heated in aqueous suspension with two equivalents of glycine, colourless crystals of $PtMe_2(gly)_2 \cdot H_2O$ (isomer (31)) are obtained. This isomer contains two chelated glycinate ligands with N *trans* to methyl. It is moderately water-soluble. Its n.m.r. spectrum in D_2O shows only one methyl peak with satellites (J(Pt-CH_3) 69.7 Hz). The glycinate methylene protons are non-equivalent. They give a slightly broadened singlet with satellites at 100 MHz; at 270 MHz, a definite splitting is observed, but the pattern is not sufficiently well resolved to be analysed in detail. The spectrum is unchanged in NaOD solution. The same



Scheme 2. Preparation and reactions of isomers of $PtMe_2(gly)_2$.

compound may be obtained by heating any of $[PtMe_2(OH)(gly)]_2$ (16b) $PtMe_2(gly)(H_2O)_2^+$ (18 or $PtMe_2(OH)(gly)(H_2O)$ (5b) with glycine in water (pH ~ 4.5).

By contrast with this facile ring closure under acidic conditions, $PtMe_2(OH)_2(gly)_2^{2-}$ (34b), which contains two unidentate glycinate ligands *cis* to hydroxide, may be heated indefinitely at high pH (≥9) without any ring closure occurring. If pH is reduced to 4.5, and the solution is heated, $PtMe_2(gly)_2$ (31) forms within a few minutes. Thus, the inert Pt–OH group does not react with carboxylate of unidentate N-bound glycinate until it is protonated to the more labile $Pt–OH_2$ (reaction sequence (6)).



The glycinate chelate ring is thermodynamically unstable at high pH. If $PtMe_2(gly)_2$ (31) is heated in D_2O at pD ≥ 9 for several hours the resultant solution contains $PtMe_2(OD)(gly)_2^-$ (35b), $PtMe_2(OD)_2(gly)_2^{2-}$ (34b), and $PtMe_2(OD)_2(gly)^-$ (10b).

An unsymmetrical isomer of $PtMe_2(gly)_2$, (39), in which one N-atom is *trans* to methyl, and the other N-atom is *trans* to glycinate O, is formed by a similar ring closure when $PtMe_2(gly)(H_2O)_2^+$ (26) is allowed to stand several days in solution with glycine at pH ~ 4. The reaction is faster if the solution is heated. Again, there is no tendency for the isomers of $PtMe_2(OH)(gly)_2^-$, (36b) and (37b), to undergo ring-closure reactions under alkaline conditions.

Like isomer (31), (39) crystallizes from water as a hydrate, $PtMe_2(gly)_2 \cdot H_2O$. It is more soluble in water than (31). Its n.m.r. spectrum in D_2O shows two narrowly separated methyl resonances, each with satellites. The Pt-CH_3 coupling constants are 65.1 (*trans* to N and 74.0 Hz (*trans* to O)*. The glycinate methylene region would be expected to show two overlapping (AB + ½ABX) patterns (X = ^{195}Pt). At 100 MHz, a singlet with satellites is observed for the methylene protons attached to N *trans* to methyl. At 270 MHz the peak is definitely split, but J(AB) cannot be determined. The protons of the other glycinate ligand (N *cis* to methyl) give a well-defined AB + ½(ABX) pattern (especially at 270 MHz) from which the coupling constants given in Table II may be calculated. The Pt-N-C-H coupling constants, 21.8 and 43.6 Hz, are quite different, which indicates that there is a strongly preferred conformation for this chelate ring [2, 5, 6].

As pD is increased to ~10 by addition of NaOD solution, little change occurs in the spectrum, but at pD 12, the methyl groups give a very broad singlet. By pD 12.5, two new broad methyl peaks are present, which sharpen as pD is increased to ~13.5. Pt-CH_3 coupling constants are 66.2 and 67.3 Hz. The changes are reversed on addition of D_2SO_4**. The species present in the strongly alkaline solution may be

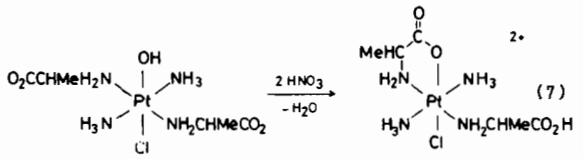
*It appears to be general for isomers (39) and (41) of $PtMe_2(gly)_2$ and their derivatives that Pt-CH_3 coupling constants are slightly lower than the usual ranges for di- and trimethylplatinum (IV) compounds given in Part III.

**Chemical shifts of the methyl resonances are affected slightly by sulfate ion concentration.

assigned as $PtMe_2(OD)(gly)_2^-$ (40). At pD between 10 and 13, both $PtMe_2(gly)_2$ (39) and $PtMe_2(OD)(gly)_2$ (40) are present, and interconverting rapidly on the n.m.r. time scale, giving the broad peaks observed.

The exchange between (39) and (40) may be compared with those discussed in Part III between $PtMe_2X(OH)(gly)^-$ (10) and $PtMe_2X(OH)_2(gly)^{2-}$ (11), and between $PtMe_2X(OH)(gly)^-$ (27) and $PtMe_2X(OH)_2(gly)^{2-}$ (28). For these reactions occurring at a *labile* site, there is no high kinetic barrier to either cleavage of the glycinate chelate ring by hydroxide, or the reverse reaction, ring closure by displacement of hydroxide by the carboxylate group. At sufficiently high concentrations, the equilibrium lies toward the hydroxo complex.

Similar conclusions about the relative facility of ring closure and ring stability under acid conditions, have been reached for non-organometallic Pt(IV) complexes from consideration of reaction (7) and related reactions [7–10].



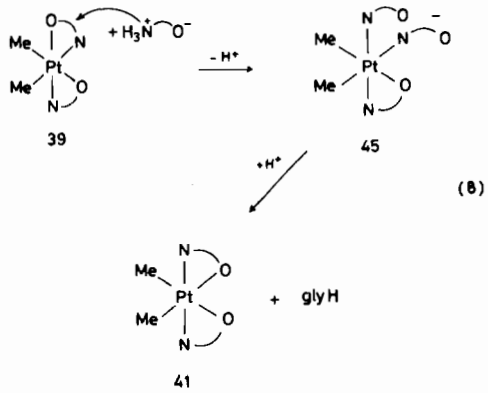
(7)

Reactions analogous to (6) and (7) with other metals have been little studied, in part because of difficulties in obtaining stable complexes with N-bound unidentate glycinate coordinated *cis* to OH^- or H_2O. Ring closure of *cis*-$Co(en)_2(OH)(gly)^+$ to $Co(en)_2(gly)^{2+}$ has been noted, but not studied in detail [11]. However, it has been found that ring closure to give $Co(en)_2(C_2O_4)^+$ is much faster in acid solution (from $Co(en)_2(C_2O_4)(H_2O)^+$) than in alkaline solution (from $Co(en)_2(C_2O_4)(OH)$) [12].

If $PtMe_2(gly)_2$ (39) is heated with glycine in D_2O at pD 3.2 at 100 °C, a new singlet with satellites slowly grows in the methyl region. The reaction is essentially complete after four weeks. $J(Pt\text{-}CH_3)$ for this new species in 73.3 Hz. It has been assigned as the symmetrical isomer of $PtMe_2(gly)_2$ with both glycinate O-atoms *trans* to methyl, (41). The glycinate methylene protons would be expected to be non-equivalent, but give a singlet with satellites at 100 MHz. $J(Pt\text{-}N\text{-}CH_2)$, 26.6 Hz, is as expected for a compound with N *cis* to methyl. No trace of isomer (31) is obtained in this reaction.

The same reaction may be carried out in a much shorter time (4 days) in a Carius tube at 130 °C. A small amount of $Pt(gly)_2$ (mixture of *cis* and *trans* isomers) is formed as a by-product at this higher temperature, presumably by reductive elimination of ethane.

The reaction is even slower in the absence of added glycine (a trace of glycine would always be present in equilibrium with $PtMe_2(gly)_2$ (39) and $PtMe_2(gly)(H_2O)_2^+$ (26)). A plausible mechanism for the reaction involves glycine N-attack at the carboxylate O-atom coordinated *cis* to methyl (reaction (8)). The tris(glycinate) complex (46) is known to react with acid to give $PtMe_2(gly)_2$ (41) (see below).



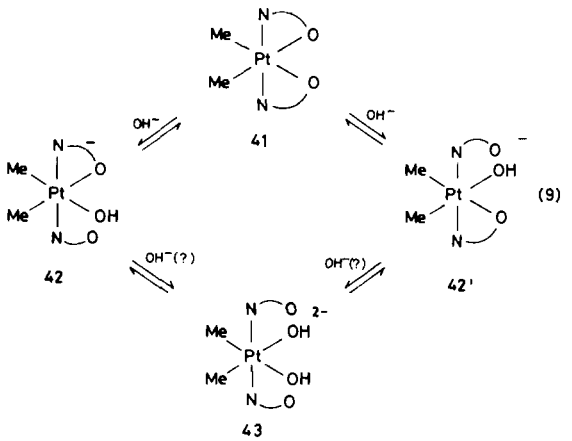
The nucleophilicity of glycinate N will, of course, be greatest in alkaline solution, but the Pt–O bond is then subject to base hydrolysis and the resultant Pt–OH group is not attacked by glycinate. If the pH is too low, $PtMe_2(gly)(H_2O)_2^+$ (26) is formed. Optimum pH for the reaction is consequently ~3.2.

$PtMe_2(gly)_2$ (31) undergoes a similar isomerization reaction on prolonged heating (4–6 weeks at 100 °C) with glycine at pH 3.2. Isomer (39) is formed, then (41), the concentration of (39) going through a maximum. The reaction is not reversible, so that (41) appears to be the most stable thermodynamically of the three isomers of $PtMe_2(gly)_2$. This is in accord with the general rule that, in the absence of severe steric constraints and strong solvation preferences, the most stable isomer is one in which ligands of highest *trans* influence (methyl) are *trans* to ligands of lowest *trans* influence (O) [4]. A similar isomerization occurs for the salicylaldehydato complexes, $PtMe_2(sal)_2$ [13].

Isomerization of (31) to (41) is much faster at higher temperatures in a Carius tube (*e.g.*, two days at 150 °C), but much more $Pt(gly)_2$ is formed than in the corresponding reaction starting from (39). It is not surprising that ethane eliminates more readily from isomer (31) than from (39) or (41). The trans influence of glycinate N is significantly higher than that of glycinate O, and it has been shown [14] that cleavage of $Pt(IV)\text{–}CH_3$ bonds in reductive elimination reactions occurs more readily when ligands of high *trans* influence are *trans* to methyl.

The mechanism for the glycine-catalysed isomerization of (31) to (39) will be similar to that for isomerization of (39) to (41) (reaction (8)), involving attack by glycine N on a Pt–O bond *cis* to methyl to give $PtMe_2(gly)_3^-$ (44) which decomposes to $PtMe_2(gly)_2$ (39).

No change occurs in the n.m.r. spectrum of $PtMe_2(gly)_2$ (41) on addition of $NaOH/D_2O$ up to pD ~ 11. At higher pD, both the methyl and methylene peaks broaden (to ~5 Hz width), but there is no significant shift. This may be attributed to the rapid exchange reaction (9) between $PtMe_2(gly)_2$ (41) and $PtMe_2(OD)(gly)_2^-$ (42) (and, perhaps at high base concentrations, $PtMe_2(OD)_2(gly)_2^{2-}$ (43)).



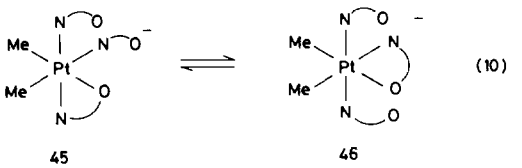
Since it is very difficult to remove all traces of glycine from samples of $PtMe_2(gly)_2$ (41), n.m.r. spectra at high pD usually show weak peaks due to $PtMe_2(gly)_3^-$ (45). As well, all spectra at high pD show a weak pair of $Pt-CH_3$ peaks (δ 1.21, 1.22 p.p.m., $J(Pt-CH_3)$ 64, 72 Hz respectively) which is not affected by addition of excess glycinate. The species responsible for these peaks is not known.

Reactions of isomers of $PtMe_2(gly)_2$ with sodium glycinate

From the reactions of excess glycinate with isomers of $PtMe_2X(gly)(H_2O)$ discussed above it is apparent that *trans* to methyl Pt–O bonds of chelated glycinate are susceptible to glycinate attack while Pt–N bonds are not. It is thus not surprising that $PtMe_2(gly)_2$ (31), in which N-atoms are *trans* to methyl, does not react with sodium glycinate at room temperature.

$PtMe_2(gly)_2$ (39) with excess Na(gly) gives $Na[PtMe_2(gly)_3]$ (44) in solution. Its n.m.r. spectrum in D_2O shows two sharp methyl peaks with satellites. The $Pt-CH_3$ coupling constants, 65.2 and 66.9 Hz, are assigned to methyl groups *trans* to N of chelated and unidentate glycinate respectively. The glycinate region of the spectrum would be expected to show three overlapping AB + ½(ABX) patterns (X = ^{195}Pt), and is complex.

When Na(gly) is added to a D_2O solution of $PtMe_2(gly)_2$ (41), the n.m.r. spectrum at 28 °C shows two sharp methyl peaks with satellites (as well as peaks due to residual (41)). $Pt-CH_3$ coupling constants are 64.9 and 71.0 Hz. These peaks are assigned to methyl groups *trans* to N and O respectively in a tris(glycinate) complex, $PtMe_2(gly)_3^-$. In the methylene region, as well as a peak due to free glycinate, there is a moderately sharp singlet with satellites (δ 3.50 p.p.m., $J(Pt-N-CH_2)$ 15.1 Hz) corresponding to glycinate N-coordinated *trans* to methyl, and two broad singlets with satellites (δ 3.73 p.p.m., $J(Pt-N-CH_2)$ 25 Hz; δ 3.39 p.p.m., $J(Pt-N-CH_2)$ 25 Hz) corresponding to glycinate peaks *cis* to methyl. This allows the structure of the complex to be assigned as (45), rather than (46).



No peaks assignable to (46) are observed. However, as the temperature of the solution is raised, the peak due to methyl *trans* to O broadens. Peaks due to methyl *trans* to N in (45) and $PtMe_2(gly)_2$ (41) remain sharp. This indicates that exchange reaction (10), involving small amounts of isomer (46) is becoming rapid on the n.m.r. time scale (*cf.* reactions (2), (4)). Since the peak due to methyl *trans* to N is unaffected by the exchange, chemical shifts for this methyl group must be near coincident for (45) and (46). The chemical shift difference for methyl *trans* to O must be much larger. In an exchange of nuclei between unequally populated sites, the peak from the minor site broadens before that from the major site. Thus, the peak due to methyl *trans* to O in (46) is probably broad between 0 °C and 28 °C, which would make it difficult to observe.

At high temperatures the proportion of $PtMe_2(gly)_3^-$ in equilibrium with $PtMe_2(gly)_2$ (41) decreases. A similar observation was made for $PtMe_3(gly)_3^{2-}$ (33) in equilibrium with $[PtMe_3(gly)_2^-$ (32) [2].

With a large excess of Na(gly) present, there are no peaks attributable to a tetrakis(glycinate) species, $PtMe_2(gly)_4^{2-}$. Formation of this complex is probably hindered sterically.

Experimental

Instrumentation and preparation of n.m.r. samples were as described in Part III.

Preparation of $PtMe_2(gly)_2 \cdot H_2O$ (Isomer (31))

To $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ (0.1993 g, 0.6964 mmol Pt) was added glycine (0.2614 g, 3.48 mmol) in 10 ml water. The mixture was stirred and heated at 80–90 °C for 16 hours, during which time the hydroxo complex dissolved. The colourless solution was filtered, then evaporated to dryness. Recrystal-

lization of the white solid from water gave large clear laths. The crystals were dried under vacuum at 56 °C for several hours, when their appearance changed to opaque white. Yield was 0.153 g (60%) $PtMe_2(gly)_2 \cdot H_2O$. *Anal.* Calc. for $C_6H_{16}N_2O_5Pt$: C 18.4; H 4.1; N 7.2. Found: C 18.5; H 4.1; N 7.3.

Preparation of $PtMe_2(gly)_2 \cdot H_2O$ (Isomer (39))

Method 1

0.1392 g glycine (1.854 mmol) in 10 ml water was added to a mixture of isomers (16a) and (23a) of $[PtMe_2Br(gly)]_2$ (see part III) (0.616 g, 1.625 mmol Pt). The pH was adjusted to ~12.5 with 1 *M* NaOH solution and the suspension was stirred. The platinum compound slowly dissolved. The solution was then heated with stirring for 16 hours at 55 °C, during which time the pH decreased to ~12 and the initial pale yellow colour faded somewhat. The pH was then increased to ~12.8, and the temperature raised to 85–90 °C for 3 hours. The discoloured solution (containing $PtMe_2(OH)(gly)^-_2$ ((36b) + (37b))) (with some insoluble precipitate) was cooled, and the pH was adjusted to 6.5 with dilute H_2SO_4. 0.2760 g $AgNO_3$ (1.625 mmol) in 2 ml water was added. The mixture was stirred for one hour, then centrifuged to remove AgBr and other insoluble material. The solution was evaporated to dryness at pH 6.5 in a vacuum desiccator over silica gel. The residue of product, Na_2SO_4, and excess glycine was extracted three times with small volumes of boiling methanol. The methanol solution was filtered, and evaporated to yield a clear colourless gum which dissolved readily in cold water. Slow evaporation of the aqueous solution over several days in a vacuum desiccator over silica gel gave clear rod-like crystals, which were dried under vacuum at 56 °C for several hours. Yield of $PtMe_2(gly)_2 \cdot H_2O$ (39) was 0.0192 g (30%). *Anal.* Calc. for $C_6H_{16}N_2O_5Pt$: C 18.4; H 4.1; N 7.2. Found: C 18.3; H 4.3; N 7.1.

Method 2

To $[PtMe_2Br_2]_n$ [15] (1.00 g, 2.598 mmol Pt) was added glycine (0.42 g, 20.8 mmol) water (20 ml) and NaOH (1 g, 25 mmol). The mixture was heated with stirring at 90–100 °C for 16 hours. The resultant discoloured solution was adjusted to pH 6 with dilute H_2SO_4, then evaporated to dryness. The residue was extracted with boiling methanol. The methanol solution was evaporated to dryness and the residue was dissolved in water and treated with 0.880 g $AgNO_3$ (5.20 mmol) AgBr was removed by centrifugation, and the solution was evaporated to dryness, with slight warming, in a stream of air. The residue was extracted with hot methanol, and the solution evaporated. The product was obtained as outlined for Method 1. Yield after two recrystallizations from water 0.288 g (28%).

Preparation of $PtMe_2(gly)_2$ (Isomer (41))

Method 1 – from isomer (39)

0.2875 g $PtMe_2(gly)_2 \cdot H_2O$ (39) (0.7347 mmol) was dissolved in 3.5 ml water. 0.1103 g glycine (1.47 mmol) was added and the pH was adjusted to 3.2 with 0.5 *M* H_2SO_4. The solution was heated in a sealed glass tube at 130 °C for 86 hours. The tube was opened and the solution filtered to remove a small amount of insoluble material. The filtrate was evaporated to dryness under a stream of air. The residue was redissolved in water, and the solution was filtered to remove a small amount of insoluble crystalline material identified by analysis as $Pt(gly)_2 \cdot H_2O$. The reddish brown colour of the filtrate was removed using activated charcoal. The colourless solution was then evaporated to dryness in a stream of air, and dried under vacuum at 56 °C for 3 hours.

This residue consisted mainly of $PtMe_2(gly)_2$ (41) and glycine, with a small amount of residual (39) (n.m.r.). It was extracted four times with 4 ml boiling methanol. The residue contained very little product (n.m.r.). On evaporation of the methanol extract to half its original volume, a precipitate formed which also contained only a trace of product. The filtrate was evaporated in a stream of air to a mobile oil, which solidified on drying at 56 °C under vacuum.

This material was dissolved in water, and pH increased to 6.5 with dilute NaOH solution. Slow evaporation in a vacuum desiccator over silica gel resulted in formation of small coulourless crystals of product from a syrupy mother liquor. The product is very water-soluble, and was recrystallized from water by slow evaporation as above. Yield of $PtMe_2(gly)_2$ (41), after drying at 56 °C under vacuum was 0.053 g (17.6 %). *Anal.* Calc. for $C_6H_{14}N_2O_4Pt$: C 19.3; H 3.8; N 7.5. Found: C 19.5; H 4.0; N 7.2.

Method 2

A similar preparation using $PtMe_2(gly)_2 \cdot H_2O$ (31), which can be more easily prepared than (39), and a three-fold excess of glycine at pH 3.2–3.5 at 150 °C for 47 hours gave essentially complete isomerization, but decomposition was more extensive and a larger amount of $Pt(gly)_2 \cdot H_2O$ formed.

The reaction may be carried out at 100 °C, without significant decomposition or side reactions, but 4–6 weeks is required.

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