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Amino Acid Complexes of Platinum(IV). V. A Dimethylplatinum(IV) Complex containing Deprotonated Glycinate as an Amido-Bridging Ligand, $[PtMe_2(OH)(\mu\text{-}NHCH_2CO_2)]_2^{2-}$

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Heating $PtMe_2Br(OH)(gly)^-$ (N trans to Br; glyH = $NH_3^+CH_2CO_2^-$) in alkali gives a solution containing $[PtMe_2(OH)(\mu\text{-}NHCH_2CO_2)]_2^{2-}$, in which deprotonated glycinate acts as an amide-bridging ligand. The complex has been characterized in solution by ^1H, ^{13}C, and ^{195}Pt NMR spectra. When the solution is acidified, rapid protonation of Pt–OH to Pt–OH_2 occurs, followed by slow decomposition to $PtMe_2(gly)(H_2O)_2^+$ (N trans to H_2O).

Introduction

We have recently described the preparation of isomers (1)–(3) of $PtMe_2X(gly)(H_2O)$ (X = Br, OH)‡ [1].

Because of the lability of coordination sites *trans* to methyl, isomers (1) and (2) may be prepared without difficulty from $PtMe_2X(H_2O)_3^+$ and glycinate [1]. Isomer (3) would be expected to be the most stable thermodynamically (with the ligands of lowest trans influence, the O-donors, *trans* to the ligands of highest trans influence [2]) but these compounds may be prepared only with difficulty. Isomer (3a) (X = Br) was obtained from reaction of $[PtMe_2Br(OH)]_n$ and glycine in methanol only after a tedious fractional crystallization. The corresponding hydroxo-compound, (3b), could not be obtained directly from $[PtMe_2(OH)_2(H_2O)_{1.5}]_n$ and glycinate, and was eventually prepared from (3a) by prolonged reaction with silver nitrate (Scheme 1). NMR spectra show that (3b) is in equilibrium with the hydroxo-bridged dimer (4b) in aqueous solution.

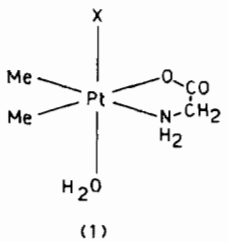
In one attempt to find an improved preparation for (3b), $[PtMe_2Br(gly)]_2$ (4a) was heated with sodium hydroxide in D_2O in an NMR tube. The ^1H NMR spectrum of the resultant solution showed that the product of this reaction was not $PtMe_2(OD)_2(gly)^-$ (6b) [1], but a species previously unknown. Attempts to isolate this compound were unsuccessful (see below), so characterization rests mainly on ^1H and ^{13}C NMR data, given below. From these data, structure (7b) (Scheme 2) was assigned.

The ^1H NMR spectrum at pD 11.5 shows two sharp methyl signals at 1.34 and 0.77 p.p.m. from 3-trimethylsilylpropane-1-sulfonate (TSS), each with 'satellites' from coupling with ^{195}Pt (I = ½, 34% abundance), $^2J_{Pt-CH_3}$ 79.3 and 64.6 Hz respectively. Pt–CH_3 coupling constants are sensitive primarily to the nature of the ligand *trans* to the methyl group [3]. A value of 79.3 Hz is at the high end of the range of couplings (74–79 Hz) for methyl *trans* to carboxylate O in amino acid complexes [1, 4, 5]. A value of 64.6 Hz is slightly lower than the typical range (66–71 Hz) for methyl *trans* to N of chelated glycinate [1, 4, 5], and would be consistent with a methyl group *trans* to an amido N-atom, as in (7b).

† Part IV, reference 5.

*Author to whom correspondence should be addressed; no reprints available.

‡Where 'X' is used in a text or scheme figure, the reference number with postscript 'a' will refer to the compound with X = Br, and that with postscript 'b' to X = OH. Where no postscript is used, both compounds are meant.



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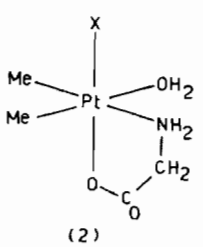

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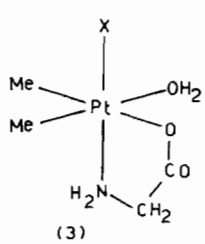

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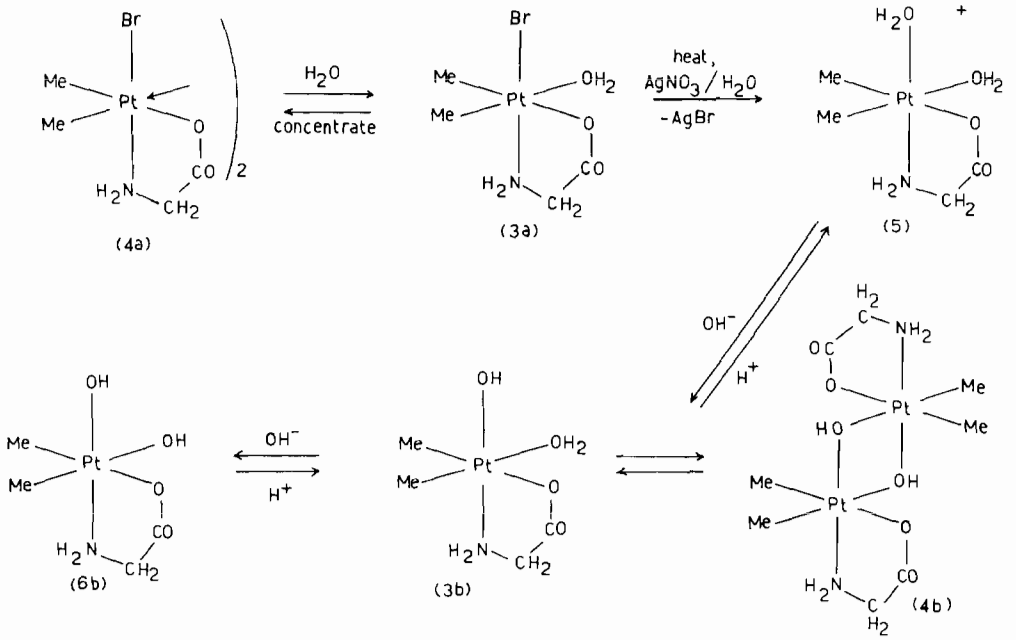


Scheme 1. Preparation of $PtMe_2(OH)(gly)(H_2O)$ (isomer (3b)).

Under the reaction conditions in D_2O, the methylene protons tend to exchange with solvent deuterium, so that signals due to these protons were not observed.

To provide a sample for ^{13}C measurement in which the methylene group was protonated rather than deuterated, the reaction was carried out in H_2O. The ^{13}C spectrum was run with the instrument internally locked on D_2O in an insert. Shifts were measured relative to the methyl resonance of TSS.

In the methyl region of the ^1H-decoupled ^{13}C spectrum there are two main peaks, as expected. One of these is a singlet (δ = 8.54 p.p.m.) with satellites ($^1J_{Pt-C}$ 712.9 Hz). This would correspond to methyl *trans* to carboxylate O. The other methyl group gives a singlet (δ – 5.89 p.p.m.) with *two* sets of satellites, with coupling constants 618.2 Hz ($^1J_{Pt-C}$) and 10.7 Hz ($^3J_{Pt-N-Pt-C}$). Coupling of this C-atom to two platinum nuclei is not possible in a monomeric structure. In tetramers $[PtMe_3(\mu_3\text{-}Z)]_4$, for Z = OH, SCH_3, $^{195}Pt-Z-Pt-^{13}C$ coupling is observed when the three bonds in the coupling path are nearly coplanar [6]. In (7b) the Pt–N–Pt–C path is planar for the methyl group *trans* to N, but not for the methyl group *trans* to O.

In the methylene region, the ^1H-decoupled spectrum shows a singlet (55.83 p.p.m.), again with two sets of satellites ($^2J_{Pt-N-C}$ 25.4, 11.4 Hz). This indicates that the methylene C-atom is within a few bonds of two Pt-atoms, as in (7b). A structure analogous to (4b), with hydroxo bridges and simple chelated glycinate, can therefore be excluded. In the ^1H-coupled spectrum, the central resonance is split into a doublet of doublets by coupling to two (non-equivalent) H-atoms ($^1J_{C-H}$ 133, 142 Hz).

In the carbonyl region, the ^1H decoupled spectrum shows a singlet at 191.94 p.p.m. without resolved platinum coupling. In the ^1H-coupled spectrum, a doublet of doublets is observed, $^nJ_{CH}$ 8.8, 5.9 and 3.9 Hz. If the two larger couplings are assigned to $^2J_{C-C-H}$ with the protons of the adjacent methylene group, the remaining coupling, 3.9 Hz, must be assigned to $^3J_{C-C-N-H}$.

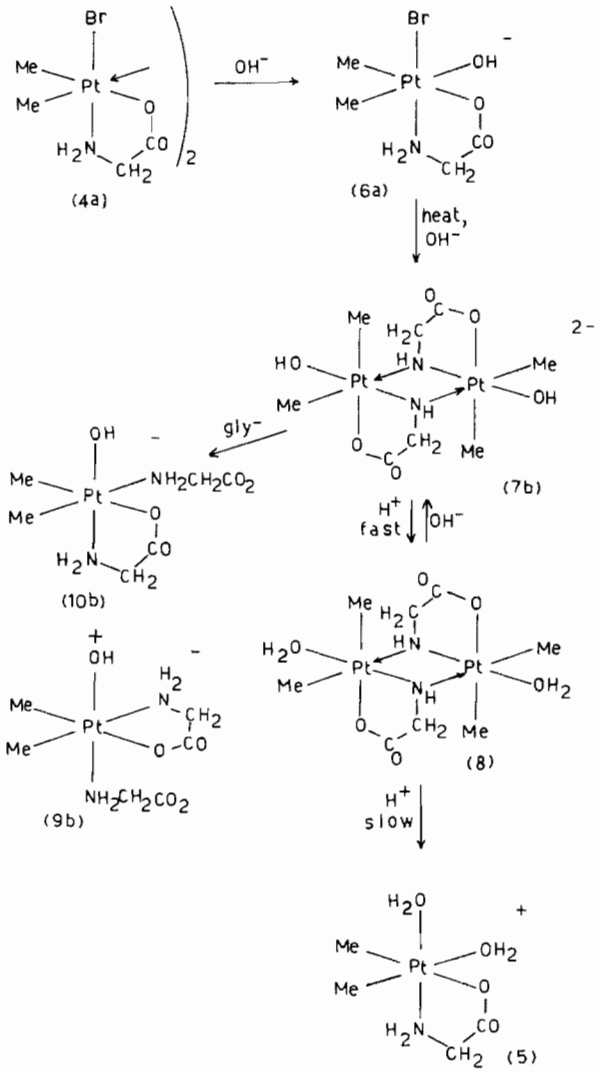
Unless precautions are taken to exclude atmospheric carbon dioxide during the reaction, a peak due to carbonate ion also appears at 170.62 p.p.m.

The ^{195}Pt NMR spectrum shows one peak –698.4 p.p.m. from Na_2PtCl_6 in water. This is consistent with the presence of only one type of Pt-atom in the dimer. The peak is broad, (width at half height 61 Hz), presumably owing to partial decoupling from ^{14}N.

If sodium glycinate is added to a solution of the compound in D_2O, the NMR spectrum corresponds to a mixture of the two isomers of $PtMe_2(OH)(gly)_2^-$, (9b) and (10b) (obtainable from (3b) and glycinate) [5]. This shows that coordinated bromide has been replaced by hydroxide in the course of the initial reaction.

Only structure (7b), in which two Pt-atoms and two deprotonated glycinate N-atoms form a four membered ring, is consistent with all these data.

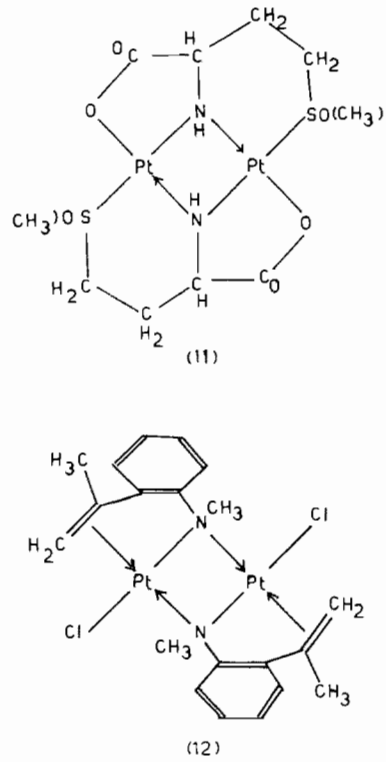
X-ray crystallography has shown the presence of a double amide bridge in the platinum(II) compounds (11) [7] and (12) [8]. Platinum(I) compounds $[Pt\{PPh_3\}_3(\mu\text{-}N{=}NH)]_2$ and $[Pt\{PPh_3\}_2(\mu\text{-}NH_2)]_2$



Scheme 2. Formation and Reactions of $[PtMe_2(OH)(\mu\text{-}NHCH_2CO_2)]_2^{2-}$ (7b).

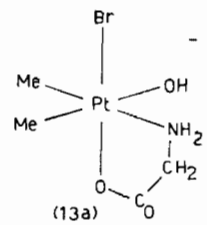
are formed in the hydrazine reduction of *cis*-$PtCl_2\{PPh_3\}_2$ [9]. A much less symmetric Cu_2N_2 bridge has been reported for a copper(II) peptide complex [10]. To our knowledge, (7b) is the first reported platinum(IV) complex with an amido bridge. A doubly bridging N-atom does, however, occur in $[PtMe_3(NCS)]_4$ [11, 12], and a triply-bridging N-atom is present in $[PtMe_3(N_3)]_4$ [13].

(7b) is stable indefinitely in alkaline solution. If pD is adjusted to 5 with D_2SO_4, the methyl peaks shift (methyl *trans* to N, δ 1.04 p.p.m., $^2J_{Pt-CH_3}$ 63.8 Hz; methyl *trans* to carboxylate O, δ 1.54 p.p.m., $^2J_{Pt-CH_3}$ 75.8 Hz), corresponding to formation of the neutral compound, (8). Over a period of hours, peaks due to (8) decrease in intensity, while peaks corresponding to $PtMe_2(gly)(D_2O)_2^+$ (5) and $[PtMe_2(\mu\text{-}OD)(gly)]_2$ (4b) grow.



All attempts to precipitate (7b) from concentrated aqueous solution were unsuccessful. Among the potential precipitants tried were $[NR_4]X$ (R = Me, Et, n-Bu; X = Cl, Br), $[Ph_4P]Cl$, $[Pt(en)_2]Cl_2$ (en = 1,2-diaminoethane), *trans*-$[Pt(en)_2Cl_2]Cl_2$ (which is slowly reduced in the reaction medium to $[Pt(en)_2]Cl_2$). Neutralization of a concentrated alkaline solution of (7b) did not cause (8) to precipitate. Concentration (in an air stream or vacuum desiccator) of a solution at pH < 8 always led to formation of $[PtMe_2(\mu\text{-}OH)(gly)]_2$ (4b).

Formation of (7b) from $PtMe_2Br(OH)(gly)^-$ (6a) would be facilitated by the inertness of the Pt–N bond *cis* to methyl and the lability of the Pt–OH bond *trans* to methyl. These conditions are not sufficient to guarantee formation of a μ-amido compound. $PtMe_2(OH)_2(gly)^-$ (6b) does not react under comparable conditions to give (7b), presumably owing to a complex interplay of steric and electronic factors. If the reaction of (6a) is closely monitored, transient NMR peaks are observed which are probably due to the bromo analogue, $[PtMe_2Br(\mu\text{-}NHCH_2CO_2)]_2^{2-}$ (7a).



Extensive decomposition occurs when $PtMe_2Br(OH)(gly)^-$ (isomer (13a), with N *trans* to methyl, derived from (2a)) is heated at pH 12.5.

Experimental

Preparation of an Aqueous Solution of $[PtMe_2(OH)(\mu\text{-}NHCH_2CO_2)]_2^{2-}$

$[PtMe_2Br(gly)]_2$ (4a) was prepared as previously described [1], and recrystallized from water to ensure the absence of free glycine. 0.1176 g (0.310 mmol Pt) was stirred with 4 ml water for two hours with gentle warming. Much of the solid dissolved, although some residue remained. A 5 *M* sodium hydroxide solution was added dropwise with stirring until pH (as measured by narrow-range pH paper) reached 12.5. The clear solution was heated under nitrogen from room temperature to 85 °C over 1.5 hours, by which time pH had dropped to 12. During subsequent heating at 85–90 °C, pH was maintained at 12.5–12.8 by addition of small volumes of 5 *M* sodium hydroxide solution. The reaction was monitored by ^1H NMR, using the $Pt-CH_3$ peaks which are sufficiently upfield from the H_2O signal to be observed in aqueous solution. Reaction was complete after 16 hours.

It is important that the pH not be too high (not greater than 12.5) during the initial stages of heating, as decomposition with deposition of platinum metal occurs readily. Once initiated, the decomposition is autocatalytic; glycinate is released into solution, and the major platinum-containing products are then $PtMe_2(OH)(gly)_2^-$ (9b) + (10b) and, eventually, $PtMe_2(OH)(gly)_3^{2-}$.

Bromide ion could be removed from solution by reducing pH to 7, and adding a slight excess of silver nitrate solution. In this case precipitated silver bromide was removed by centrifugation. Increase of pH to 10–11 caused excess silver ion to be precipitated as silver oxide, which was also removed by centrifugation. These operations had no effect on the ^1H NMR spectrum.

Instrumentation

^1H NMR spectra were run on a Jeol PS-100 instrument, and ^{13}C and ^{195}Pt spectra on a Jeol FX-100 instrument, using a multinuclear 10 mm tunable probe. ^{13}C spectra were run at 25.5 MHz with 16 K data points on double precision mode, spectrum width 8 KHz and 13.000 scans. ^{195}Pt spectra were run at 21.36 MHz as previously described [6], with ^1H-broad-band decoupling.

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