Inorganica Chimica Acta, 30 (1978) L343–L345
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Isomerization, Exchange, and Ring-Closure Reactions of Glycinate Complexes of *Cis*-Dimethylplatinum(IV)

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

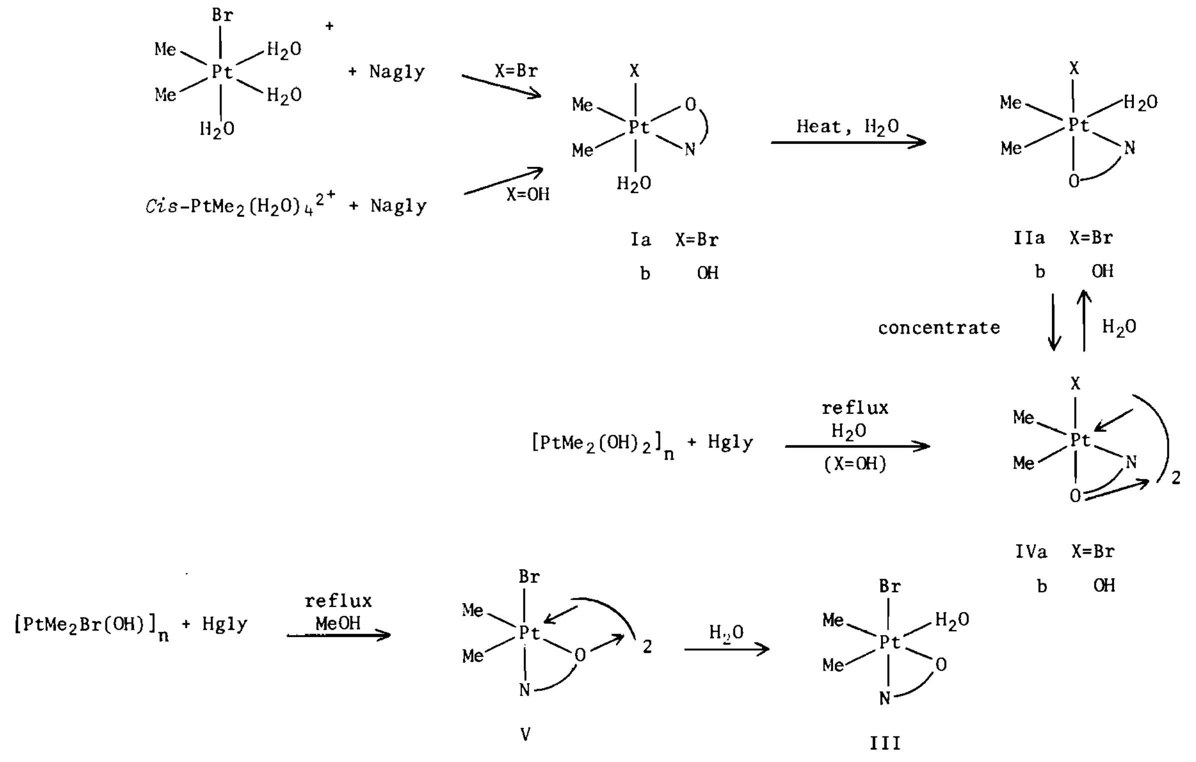
Department of Chemistry, University of Queensland, Brisbane, Australia 4067

Received August 11, 1978

There has been much interest in the coordination of amino acids to metal ions [1]. We have recently described the interactions between glycinate and *fac*-$PtMe_3(H_2O)_3^+$ [2]. In these trimethylplatinum(IV) complexes, all of the metal–ligand bonds *trans* to methyl are intermediate in lability between the bonds made by first transition series ions (*e.g.*, Cu^{2+}, Zn^{2+}) and the inert bonds of "normal" platinum complexes [3]. In *cis*-dimethylplatinum(IV) complexes both labile (*trans* to methyl) and inert (*cis* to methyl) coordination sites are present [4]. The interaction of glycinate with both types of coordination site may therefore be investigated in the one series of compounds.

Structural assignments presented here are based on the well-known dependence of Pt–CH_3 coupling constants on the nature of the ligand *trans* to methyl [5, 6]. Values *trans* to –NH_2, glycinate O, H_2O, and OH^- are ~69, ~76, ~81, and ~72 Hz respectively [2, 7].

. Three isomers of $PtMe_2Br(gly)(H_2O)$, (Ia), (IIa), and (III), have been obtained, as outlined in Scheme 1†. Initial coordination of glycinate *trans* to methyl is rapid, but reactions involving coordination sites *cis* to methyl usually require prolonged heating. Thus, when concentrated aqueous solutions of $PtMe_2Br(H_2O)_3^+$ [8] and sodium glycinate are mixed, cream, sparingly soluble $PtMe_2Br(gly)(H_2O)$ (isomer (Ia)) precipitates. When heated in water, (Ia) isomerizes to (IIa). When a solution of (IIa) is concentrated, the labile water molecule *trans* to methyl dissociates, and a yellow compound of empirical formula $PtMe_2Br(gly)$ crystallizes. This compound has been formulated as a dimer, (IVa), with oxygen bridges, analogous to $[PtMe_3(gly)]_2$ [2], but alternative structures with bridging bromide cannot be ruled out (similar comments apply to the related compounds (IVb) and (V) described below).



Scheme 1. Formation of isomers of $PtMe_2X(gly)(H_2O)$.

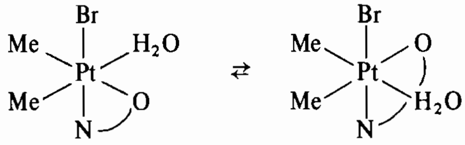
---

*To whom correspondence should be addressed.

†Abbreviations: glyH = glycine, $^+NH_3CH_2CO_2^-$; lut = 3,5-lutidine, $NC_5H_3(CH_3)_2$.

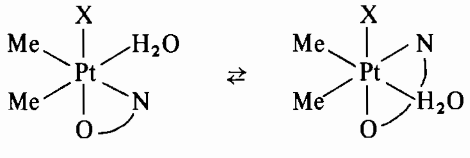
Heating a suspension of glycine in a methanol solution of $[PtMe_2Br(OH)]_n$ [8] gives a mixture of dimers (IVa) and (V), from which the colourless isomer, (V), less soluble in methanol, may be isolated. Since substitution reactions ususally give products with N *trans* to methyl, (V) is probably formed by reaction of a Pt–OH bond *cis* to methyl with the acidic $^+NH_3$ group of the amino acid. (V) dissolves sparingly in water to give the third isomer of $PtMe_2Br(gly)(H_2O)$, (III).

For (III) in D_2O, a rapid (on the NMR time-scale) exchange (1) makes the two Pt–Me groups equivalent. We propose that this reaction occurs by dissociation of the labile water molecule to give a square pyramidal intermediate, followed by migration of the glycinate O-atom to the vacant site (*cf.*, $PtMe_3(gly)(H_2O)$ [2]). Isomer (IIa) undergoes a similar exchange (2), but more slowly, since the more strongly bound N-atom must now migrate in the five-coordinate intermediate. No rapid exchange is observed for isomer (Ia), in which the Pt–H_2O bond is not labile.



III

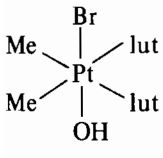
(1)



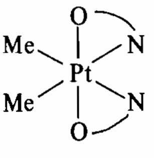
II

(2)

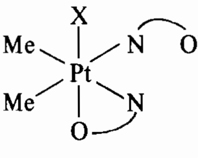
Lutidine displaces the labile water molecule from each of (IIa) and (III) to give the corresponding isomer of $PtMe_2Br(gly)(lut)$, but lutidine with (Ia) gives the known compound $PtMe_2Br(OH)(lut)_2$ (VI) [8]. The lutidine complexes are not fluxional.



VI



VII

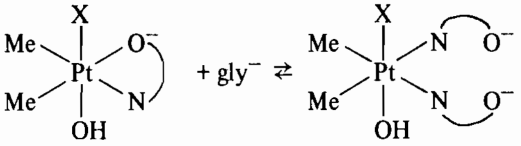


VIII a X = Br
b OH

Analogous hydroxo complexes have also been prepared (Scheme 1). White, sparingly-soluble $PtMe_2(OH)(gly)(H_2O)$ (Ib) precipitates when aqueous solutions of *cis*-$PtMe_2(H_2O)_4^{2+}$ [9] and sodium glycinate are mixed. When a solution is heated at pH ~6.5, (Ib) slowly isomerizes to (IIb) (which undergoes exchange reaction (2) at a comparable rate to (IIa)). The white dimer (IVb), which dissolves sparingly to give (IIb), may also be prepared directly by heating a suspension of $[PtMe_2(OH)_2(H_2O)_2]_n$ [9] in an aqueous glycine solution (glycine:Pt = 1:1). If the glycine/Pt ratio is increased to 2, the bis(chelate) complex $PtMe_2(gly)_2$ (VII) is obtained. As yet, the third isomer of $PtMe_2(OH)(gly)(H_2O)$, analogous to (III), or other isomers of $PtMe_2(gly)_2$ have not been prepared.

Addition of alkali to solutions of the aqua complexes causes deprotonation to the corresponding isomer of $PtMe_2X(OH)(gly)^-$. Since the Pt–OH bond is less labile than Pt–H_2O, the exchange reactions (1) and (2) become slower.

Addition of sodium glycinate solution to $PtMe_2X(gly)(H_2O)$ (II) gives quantitatively the mixed chelate-unidentate complex $PtMe_2X(gly)_2^-$ (VIII), but when sodium glycinate is added to a strongly alkaline (pH > 10) solution of isomer (I), equilibrium (3) is set up.



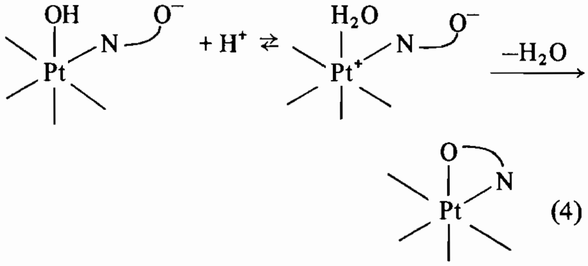
IX a X = Br
b OH

X a X = Br
b OH

(3)

No change occurs if this solution is heated for several hours at pH > 10. If pH is reduced to 6.5, equilibrium (3) is rapidly reversed, to give a mixture of $PtMe_2X(gly)(H_2O)$ (I) and glycine. If this solution is now heated, peaks due to $PtMe_2X(gly)_2^-$ (VIII) slowly grow in the NMR spectrum, but no $PtMe_2(gly)_2$ (VII) is formed. If the pH of a solution of $PtMe_2(OH)(gly)(H_2O)$ (Ib) and glycine is adjusted to ~4.5, and the solution is heated, $PtMe_2(gly)_2$ (VII) forms.

Thus, closure of the chelate ring occurs only under conditions where the appropriate Pt–OH group is protonated to Pt–H_2O^+ (*i.e.*, by reaction sequence (4)). These observations parallel those of Kukushkin and Gur'yanova [10] on ring closure in $PtCl(OH)(gly)_2(NH_3)_2$ and related complexes.



(4)

When a solution of $PtMe_2(gly)_2$ (VII) is heated at $pH \geqslant 9$, the chelate rings are cleaved to give a mixture of $PtMe_2(OH)_2(gly)_2^{2-}$ (Xb) and $PtMe_2(OH)(gly)_2^-$ (VIIIb).

These results indicate that hydroxide is able to compete quite effectively with glycinate O for coordination to Pt(IV) at high pH, in spite of the chelate effect, and provide chemical evidence in support of the spectroscopic data given elsewhere [7] for relatively strong covalent bonding of hydroxide to platinum.

Acknowledgement

We thank the Australian Research Grants Committee for supporting this project.

References

1 D. R. Williams, *Inorg. Chim. Acta Rev., 6,* 123 (1972).
2 T. G. Appleton, J. R. Hall and L. Lambert, *Inorg. Chim. Acta, 29,* 89 (1978).
3 G. E. Glass and R. S. Tobias, *J. Am. Chem. Soc., 89,* 6371 (1967).
4 J. R. Hall and G. A. Swile, *J. Organometal. Chem., 56,* 419 (1973).
5 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).
6 D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organometal Chem., 38,* 403 (1972).
7 N. H. Agnew, T. G. Appleton, R. G. Eggins, J. R. Hall and I. J. McMahon, to be submitted for publication.
8 J. R. Hall and G. A. Swile, *J. Organometal. Chem., 139,* 403 (1977).
9 J. R. Hall and G. A. Swile, *J. Organometal. Chem., 122,* C19 (1976).
10 Yu. N. Kukushin and G. P. Gur'yanova, *Zh. Neorg. Khim., 16,* 856 (1971).