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DI- AND TRIMETHYLPLATINUM(IV) COMPLEXES WITH ASPARTATE: SOME SUBTLE EFFECTS OF CHELATE RING SIZE*

TREVOR G. APPLETON,† JOHN R. HALL, TREVOR G. JONES and JACQUELINE A. SINKINSON

Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia

Abstract—The complex Na[$PtMe_3$(asp-N,αO,βO)] (H_2asp = aspartic acid) was obtained as a solid from reaction of $[PtMe_3]_2(SO_4)\cdot 4H_2O$ with aspartate. In D_2O, the interchange between this complex with aspartate tridentate and $[PtMe_3(D_2O)$(asp-N,αO)$]^-$ was rapid on the NMR time-scale. *Fac*-$[PtMe_2Br(D_2O)_3]^+$ with D_2asp at pD 2.5 gave the two isomers of [$PtMe_2Br$(Dasp-N,αO)(D_2O)] with the chelate ring *trans* to the methyl groups. With standing at pD 5–6, the two isomers of $[PtMe_2Br$(asp-N,αO,βO)$]^-$ with N *trans* to methyl were formed, initially in similar proportions. With long standing, the isomer with N and β-carboxylate *trans* to methyl predominated. When the pD was decreased to 3, this isomer was in equilibrium with a complex in which water replaced β-carboxylate. UV irradiation of a solution containing the two isomers of $[PtMe_2Br$(asp-N,αO,βO)$]^-$ with N *trans* to methyl caused formation of the isomer with N *trans* to bromide.

A common coordination mode for aspartate (asp^{2-}) is *facial* tridentate, through N and an O atom from each carboxylate group. This mode is adopted when three *facial* coordination sites are available, as, for example, in the cobalt(III) complexes $[Co(asp)(NH_3)_3]^+$, $[Co(asp)(dien)]^+$ and $[Co(L\text{-}asp)_2]^-$.[1,2] Another common coordination mode which is adopted for square planar platinum(II) complexes is bidentate, through nitrogen and a carboxylate oxygen atom.[3–5] In all complexes characterized with aspartate bidentate, the oxygen atom involved in chelation has always been from the α-carboxylate group. This has been ascribed to the greater stability of the five-membered N,αO-chelate ring compared with the six-membered N,βO-ring.[5] In complexes in which aspartate is bound tridentate (N,αO,βO), significant differences in the properties of the M—αO and M—βO bonds might be expected, but there has been little experimental evidence for such differences to date. For example, X-ray crystal structure determinations for Co^{III} and Ni^{II} complexes have not shown significant differences between M—αO and M—βO bond lengths.[6,7]

The methyl groups in trimethylplatinum(IV) complexes are always *fac*, so that the remaining three coordination sites are ideally suited for coordination of a *fac*-tridentate ligand, as, for example, in complexes with iminodiacetate (ida^{2-}), $[PtMe_3$(ida-N,O,O′)$]^-$[8] and glyphosate (N-phosphonomethylglycine, $Himpa^{2-}$), $[PtMe_3$(Himpa-N, O, O′)$]^-$.[9] The Pt—CH_3 coupling constants (^{195}Pt, $I = 1/2$, 34% abundance) are very sensitive to the ligand *trans* to methyl,[8,10] and can, for example, discriminate between the different O-donors in the glyphosate complex.[9] These coupling constants would also be expected to be sensitive to any differences in platinum binding by the O-atoms of α- and β-carboxylate groups of aspartate. The coordination sites *trans* to methyl are rendered labile by the high *trans* effect of the ligands,[11] so that fluxional processes may often be observed by

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† Author to whom correspondence should be addressed.

NMR.[8,12–16] $[PtMe_3]_4SO_4 \cdot 4H_2O$, which gives *fac*-$[PtMe_3(H_2O)_3]^+$ (**1**) when dissolved in water, is a convenient starting material.

For dimethylplatinum(IV) complexes derived from *fac*-$[PtMe_2X(H_2O)_3]^+$ (**2**), the two coordination sites *trans* to methyl are labile, while that *cis* to methyl is inert.[17,18] When X = Br, the coordination site *cis* to methyl may be photochemically labilized.[19,20] This allows the reactions of the ligand donor atoms with the different types of coordination site to be studied. We have previously reported the reactions of dimethylplatinum(IV) complexes with glycinate,[13,18,21,22] iminodiacetate[20] and glyphosate.[9]

EXPERIMENTAL

Starting materials

Literature methods were used to prepare $[\{PtMe_3I\}_4]$[23] and thence $[PtMe_3]_2SO_4 \cdot 4H_2O$,[24] $[\{PtMe_2Br_2\}_n]$[25] and a solution of *fac*-$[PtMe_2Br(D_2O)_3]NO_3$ in D_2O.[17] L-Aspartic acid was used as supplied by Light & Co.

Instrumentation

^1H (400 MHz) and ^{13}C (100.4 MHz) NMR spectra were obtained using a JEOL JNM GX400 spectrometer as previously described.[9,20] Spectra were run with internal lock in D_2O. ^1H shifts are referenced relative to the methyl peak of sodium 3-trimethylsilylpropanesulfonate (TSS) and ^{13}C spectra to internal dioxane, taken as 67.73 ppm relative to external TMS.[26] Shifts to lower nuclear shielding are positive. ^{13}C spectra were ^1H decoupled.

IR spectra were recorded on KBr discs with a Perkin–Elmer 1720X FT spectrometer.

Approximate measurements of pD were made using narrow-range indicator strips supplied by Riedel-de-Haan. More accurate measurements were made using a TPS digital pH meter equipped with a combination glass/reference electrode, with the addition of 0.4 to convert meter readings to pD values.[27]

UV irradiation experiments were carried out as previously described.[20]

Preparation of $Na[PtMe_3(asp)]$

To a solution of $[PtMe_3]_2SO_4 \cdot 4H_2O$ (0.1029 g, 0.317 mmol $PtMe_3^+$) and aspartic acid (0.0416 g, 0.317 mmol) in water (30 cm^3) was added dropwise with stirring a solution of sodium hydroxide (0.0253 g, 0.633 mmol) in water (30 cm^3). Dilute solutions were used to minimize formation of insoluble $[\{PtMe_3(OH)\}_4]$. The pH of the solution when addition was complete was approximately 5. The solution was filtered, then taken to dryness in a stream of air. The resultant solid was extracted with hot A.R. methanol, and the filtered methanol solution was taken to dryness in a stream of air, then dried in a vacuum desiccator over silica gel, to give 0.10 g (82% yield) of the product as a hygroscopic white glassy solid. Microanalysis was carried out by the service in this Department: Found: C, 21.0; H, 4.0; N, 3.2. Calc. for $C_7H_{14}NNaO_4Pt$: C, 21.3; H, 3.6; N, 3.6%.

Solutions for NMR study of trimethylplatinum aspartate complexes

A bulk solution of $[PtMe_3]_2SO_4 \cdot 4H_2O$ (0.0994 g, 0.307 mmol $PtMe_3^+$) and aspartic acid (0.0404 g, 0.308 mmol) in D_2O (4 cm^2) was heated in a sealed sample tube in a boiling water bath for 30 min and then allowed to cool. Aliquots (0.4 cm^3) were removed from this solution, and to each a measured volume of a standard solution of NaOH in D_2O (0.260 mmol cm^{-3}) was added, to produce solutions with nominal mole ratios of $[PtMe_3(D_2O)_3]^+ : H_2asp : NaOH$ equal to $1 : 1 : x$, with x varied. Solutions with alkali added became slightly cloudy, owing to precipitation of a small amount of $[\{PtMe_3(OD)\}_4]$. This precipitation made the precise ratios uncertain. Solutions were filtered into NMR tubes. Spectra did not change with time.

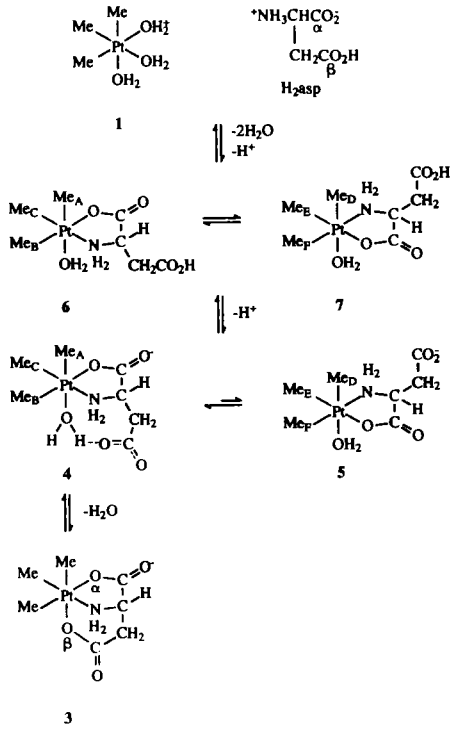
Solutions for NMR study of dimethylplatinum aspartate complexes

A solution of $[PtMe_2Br(D_2O)_3]NO_3$ (0.81 mmol) and aspartic acid (0.084 g, 0.63 mmol) in D_2O (4 cm^3) was prepared. The pD was adjusted to the desired value (measured with a pH meter) by the addition of a 0.5 M solution of KOH in D_2O. Some precipitation of $[\{PtMe_2Br(OH)\}_n]$ usually occurred. An aliquot was filtered into an NMR tube, and an NMR spectrum was run.

RESULTS

Preparation and properties of $Na[PtMe_3(asp)]$

Solid $Na[PtMe_3(asp)]$ was prepared by a method analogous to that previously used for $Na[PtMe_3(ida)]$.[8] Its IR spectrum showed an intense broad band at 1598 cm^{-1} assignable to coordinated carboxylate.[28] There was no band above 1700 cm^{-1}, as would be expected if a protonated carboxyl group (—COOH) were present.[28] This was consistent with the presence in the solid state of a complex anion **3**



Scheme 1.

(Scheme 1) in which aspartate is bound tridentate through N, α-carboxylate and β-carboxylate.

The methyl region of the ^{1}H NMR spectrum of a solution of this solid in D_2O at 298 K is shown in Fig. 1, which shows three sharp singlets with satellites from coupling to ^{195}Pt. For one of these, labelled C, at 0.70 ppm, ^2J(Pt—CH_3) was 67.8 Hz, corresponding to a methyl group *trans* to an amine nitrogen.[8,10] For the two remaining resonances, A [0.92 ppm, ^2J(Pt—CH_3) 81.2 Hz] and B [0.88 ppm, ^2J(Pt—CH_3) 79.4 Hz], the Pt—CH_3 coupling constants corresponded to methyl *trans* to O-donor ligands.[8,10] If this were the only part of the spectrum available, it could be interpreted in terms of a static structure **3**, with peak C from methyl *trans* to N, peak B from methyl *trans* to α-carboxylate, and peak A, with the largest Pt—CH_3 coupling constant, from methyl *trans* to β-carboxylate. However, the spectrum of the aspartate protons was inconsistent with this interpretation. These showed a number of broadened peaks at 298 K. In the methine region [Fig. 2(b)], there were two broad singlets, as well as a sharp quartet from a small amount of free ligand. The variable-temperature spectra in this region shown in Fig. 2 are complicated by the large temperature dependence of the chemical shifts, but it is clear that the two distinct methine resonances observed at lower temperatures

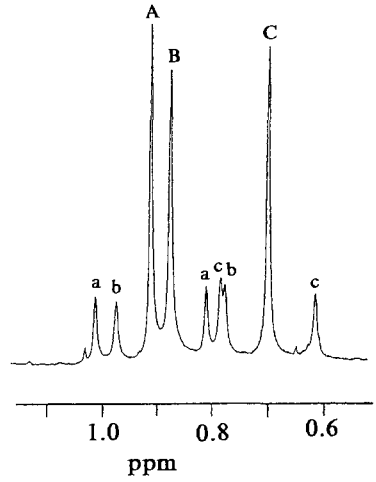


Fig. 1. Methyl region of the 400 MHz ^{1}H NMR spectrum at 298 K of a solution of Na[$PtMe_3$(asp)] in D_2O. For labels, see text. Satellite peaks from coupling with ^{195}Pt are indicated by lower case letters.

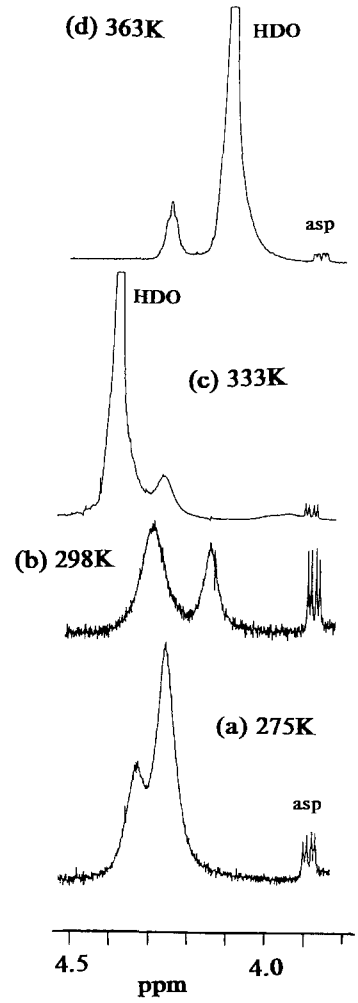


Fig. 2. Variable-temperature 400 MHz ^{1}H NMR spectra in the methine region of a solution of Na[$PtMe_3$(asp)] in D_2O. Peaks due to free aspartate are labelled "asp". Spectrum amplitude is not constant.

coalesce at higher temperature. At 363 K, the triplet structure was beginning to appear in the peak [Fig. 2(d)], and the methylene signals had the appearance of a broad doublet (not shown). There was therefore a process which interconverted methine protons in two different environments which was slow enough at 298 K and below to allow two distinct signals to be observed (although not slow enough by 275 K to allow any structure to be observed from coupling to the methylene protons). Since the resonance from free aspartate remained sharp [only slightly broadened at 363 K, Fig. 2(d)], the process did not involve intermolecular exchange between bound and coordinated aspartate. The spectra may be explained if the six-membered ring of **3** was opening, with replacement of the Pt—O (β-carboxylate) bond by coordinated water to give **4** (Scheme 1; in structural diagrams, "H" is used to denote either ^1H or ^2H). This would require that the chemical shift difference between each methyl signal in **3** and the corresponding signal in **4** be small enough that coalescence had occurred at 298 K. Indeed, there was no broadening or splitting of the methyl peaks down to 275 K. We have proposed that an analogous reaction occurs with $[PtMe_3(H_2idmp)]^-$, where H_4idmp = iminobis(methylenephosphonic acid).[9]

The temperature dependence of the methine proton chemical shifts was probably related to changes in populations of conformations as the temperature changed. It appears likely that the peak from **4**, with its free β-carboxylate group, would be affected more than that from **3**. If this is so, δ_H for **4** increased by approximately 0.16 ppm between 298 and 275 K, and the proportion of **4** relative to **3** decreased significantly.

At 363 K, the methyl peaks had coalesced into a broad singlet. This required another reaction in addition to the interconversion of **3** and **4** to become important at higher temperatures, a movement of the aspartate N and O_α donor atoms between the different coordination sites. Such reactions have previously been observed at high temperatures for $[PtMe_3(gly\text{-}N,O)(H_2O)]$[8] and $[PtMe_3(\alpha ala\text{-}N,O)(H_2O)]$[12] [Hgly = glycine, H($\alpha$ala) = α-alanine].

The 100.4 MHz ^{13}C NMR spectrum at 298 K showed a single set of peaks, but all were broad. Methyl *trans* to N gave a peak at −7.9 ppm [^1J(Pt—C) 691 Hz], methyl *trans* to α-carboxylate a peak at −14.95 ppm [^1J(Pt—C) 750 Hz] and methyl *trans* to β-carboxylate/H_2O −15.00 ppm [^1J(Pt—C) 775 Hz]. Platinum couplings were not resolved for the remaining C atoms: methine (56.1 ppm), methylene (40.1 ppm), α-carboxylate (186.4 ppm) and β-carboxylate (178.4 ppm). The α-carboxylate C atom was easily assigned on the basis of its low nuclear shielding, characteristic of carboxylate carbon in a five-membered chelate ring.[5,29–31]

Addition of alkali to solutions of $[PtMe_3(D_2O)_3]^+$ (**1**) *with aspartic acid* (*Scheme* 1).

^1H NMR spectra were run on a series of solutions in D_2O with ratios of $[PtMe_3(D_2O)_3]^+$ (**1**) : H_2asp : NaOH of 1 : 1 : x, where x varied from 0 to 2. The methyl regions of these spectra (298 K) are shown in Fig. 3. As expected, the spectrum with $x = 2$ was the same as that for the D_2O solution of solid Na[$PtMe_3$(asp)] (Fig. 1). The spectra from

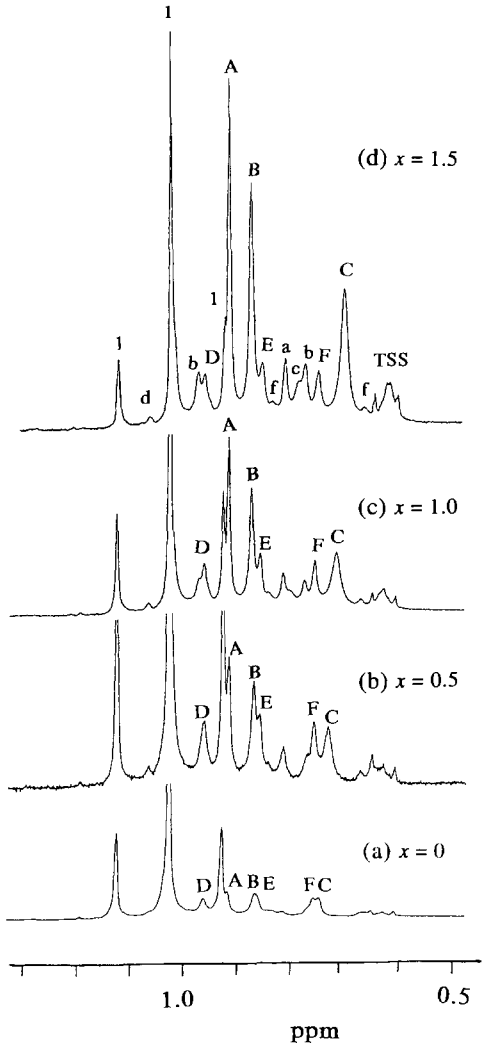


Fig. 3. 400 MHz ^1H NMR spectra of D_2O solutions prepared from $[PtMe_3(D_2O)_3]^+$ (**1**), aspartic acid, and NaOH in mole ratios 1 : 1 : x. Spectrum (a) ($x = 0$) was run at 275 K, others at 298 K. Peaks labelled "1" are from $[PtMe_3(D_2O)_3]^+$. A complex multiplet from TSS is also present. See text for other labels. Satellite peaks from coupling with ^{195}Pt are indicated by lower case letters.

solutions with $x < 2$ showed a strong singlet with satellites from $[PtMe_3(D_2O)_3]^+$ (**1**), increasing in intensity as x decreased. With $x = 1.5$, the β-carboxylate group of **4** would be expected to be partially deuteronated to form **6**, and the proportion of complex **3** with tridentate aspartate would be expected to be less than with $x = 2$. Comparison of the spectrum with $x = 1.5$ [Fig. 3(d)] with that for $x = 2$ (Fig. 1) showed that peak C from methyl *trans* to N was broadened, and peak B from methyl *trans* to α-carboxylate broadened to a lesser extent. These two methyl groups are *cis* to D_2O/β-carboxylate, and their chemical shifts were more affected by these changes than that of methyl group A *trans* to D_2O/β-carboxylate. For $x = 0$, broadening due to reactions in which donor atoms migrate between coordination sites was severe at 298 K, and the spectrum in Fig. 3(a) was run at 275 K to allow resolution of all the peaks.

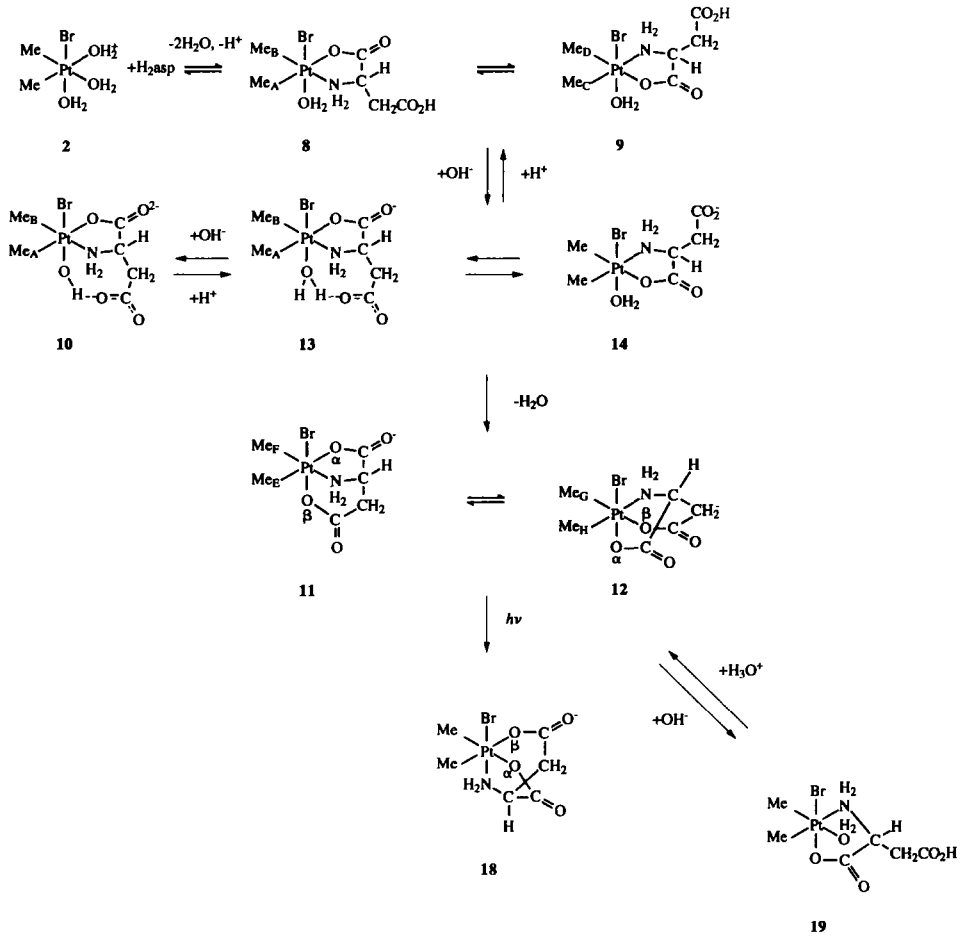
An additional set of methyl peaks, labelled D, E and F, was also present. These were assigned to the isomer **5** and its deuterated form **7**. Isomers **4** and **5** may be considered as diastereomers with the same configuration about the asymmetric carbon in L-aspartate, and enantiometric configurations at the metal centre. Spectra of analogous diastereomers have been previously observed, for example, for $[PtMe_3(\alpha ala\text{-}N,O)(H_2O)]$.[12] As x decreased, the intensities of peaks D, E, F, relative to A, B, C, increased, until, with $x = 0$, the two sets of peaks had comparable intensities. That is, there was no preference for diastereomer **6** over **7**. When the β-carboxylate group was only partially deuteronated, the methyl peaks from the complex with aspartate tridentate (**3**), with the metal configuration forced, appeared together with those for the aqua complex **4**. As well, **4** might be favoured by hydrogen bonding between the bound water molecule and the uncoordinated β-carboxylate group (as shown in Scheme 1). No analogous hydrogen bonding would be possible in **5**. Such hydrogen bonding would become less important when this carboxylate group was deuteronated.

Reactions of $[PtMe_2Br(D_2O)_3]^+$ (**2**) *with aspartic acid* (*Scheme* 2)

An equimolar amount of aspartic acid was added to a solution of $[PtMe_2Br(D_2O)_3]^+$ in D_2O (solution pD 2.5) and the 400 MHz ^1H NMR spectrum obtained within 30 min. The major peaks in the spectrum were from unreacted $[PtMe_2Br(D_2O)_3]^+$ (**2**) and aspartic acid, but there were two sets of weak methyl peaks [Fig. 4(a)]: A (1.75 ppm) and B (1.64 ppm), approximately twice as intense as C (1.76 ppm) and D (1.66 ppm). There were two corresponding sets of aspartate resonances. The methine protons gave broad triplets [Fig. 4(b)], and the methylene protons broad doublets. These peaks were assigned to the two isomers, **8** and **9**, in which aspartate is bound bidentate through N and α-carboxylate *trans* to the methyl groups. The water molecules bound *trans* to methyl in **2** are labilized by the high *trans* effect of the methyl groups, so that substitution occurred initially at these sites. An analogous reaction occurred with glycinate.[18]

The pD of this solution was then increased to 8, by slow addition of a solution of KOH in D_2O. Significant quantities of $[\{PtMe_2Br(OD)\}_n]$ precipitated, and were filtered off. The methyl region of the spectrum showed two singlets with satellites as the only significant peaks (Fig. 5). Peak A [1.58 ppm, $^2J(Pt—CH_3)$ 77.8 Hz] corresponded to methyl *trans* to carboxylate, and peak B [1.44 ppm, $^2J(Pt—CH_3)$ 68.7 Hz] to methyl *trans* to N. In spectra run at intermediate pD (where other reactions also occurred—see below), it was clear that these peaks corresponded to peaks A and B from **8** with shifts due to dedeuteronation to **13** and **10**, and that peaks C and D from **9** decreased markedly in intensity as pD increased. At pD 8, the peaks could be assigned to only one isomer of $[PtMe_2Br(OD)(asp\text{-}N,\alpha O)]^{2-}$, which we propose was **10**, which may be stabilized by intramolecular hydrogen bonding between hydroxide and carboxylate, as depicted. Due to the removal of platinum species from solution by precipitation of $[\{PtMe_2Br(OD)\}_n]$, excess free aspartate was present, whose peaks obscured those from **10**. No peaks assignable to complexes with aspartate tridentate were observed on standing. This is consistent with our previous observations with glycinate[22] and iminodiacetate[20] complexes, that Pt—OH groups at an inert site are not readily displaced by carboxylate at high pH to allow chelate ring closure. With long standing, $[\{PtMe_2Br(OD)\}_n]$ slowly precipitated.

A fresh solution of $[PtMe_2Br(D_2O)_3]^+$ (**2**) and aspartic acid in D_2O was prepared, and KOH/D_2O was added to increase the pD to 3.2. No solid precipitated at this stage. The solution was allowed to stand for 30 min, then more KOH/D_2O was added to increase the pD further, to 5.4. Only a very small amount of $[\{PtMe_2Br(OD)\}_n]$ precipitated. This solid was filtered off, and the ^1H NMR spectrum was run within 30 min. The methyl region of the spectrum is shown in Fig. 6. Two relatively weak peaks were recognized as from methyl groups A and B in **13**. The remaining peaks were four singlets with satellites. From comparisons of intensities in many spectra obtained under different conditions, it was evident that two peaks, E [1.79 ppm, $^2J(Pt—CH_3)$ 78.7 Hz] and F [1.59 ppm,



Scheme 2.

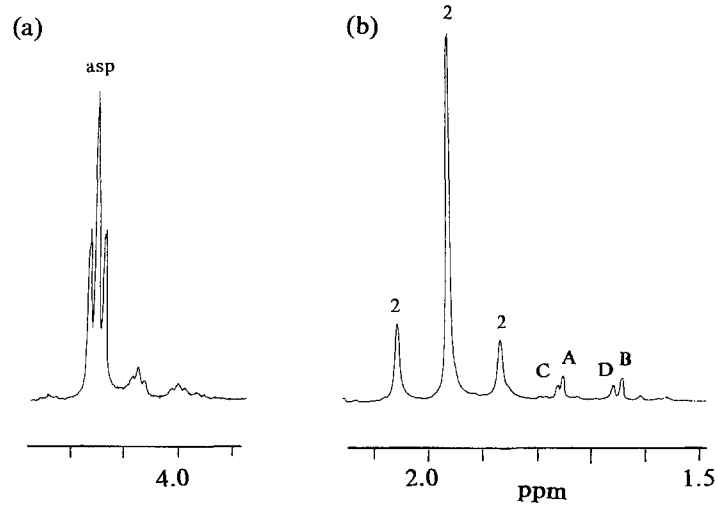


Fig. 4. 400 MHz ^{1}H NMR spectrum at 298 K of a solution obtained by mixing equimolar quantities of $[PtMe_2Br(D_2O)_3]NO_3$ and aspartic acid in D_2O: (a) methine region (peaks from free aspartic acid are labelled "asp"); (b) methyl region (peaks from $[PtMe_2Br(D_2O)_3]^+$ are labelled "2"; see text for other labels).

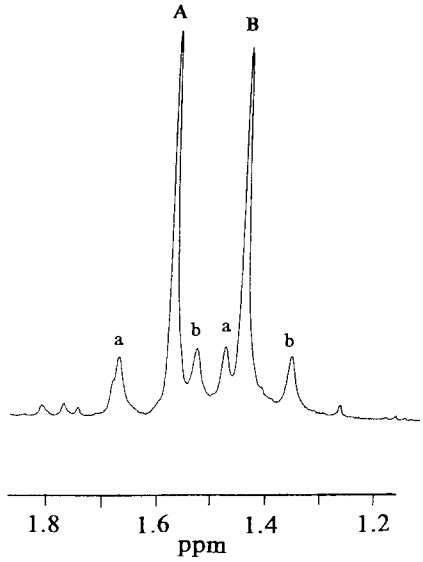


Fig. 5. Methyl region of the 400 MHz ^{1}H NMR spectrum (298 K) of a solution of $[PtMe_2Br(OD)(asp\text{-}N,\alpha O)]^{2-}$ (**10**) at pD 8 obtained by addition of KOH/D_2O to a solution of $[PtMe_2Br(D_2O)_3]NO_3$ and aspartic acid. See text for labels. Satellite peaks are indicated by lower case letters.

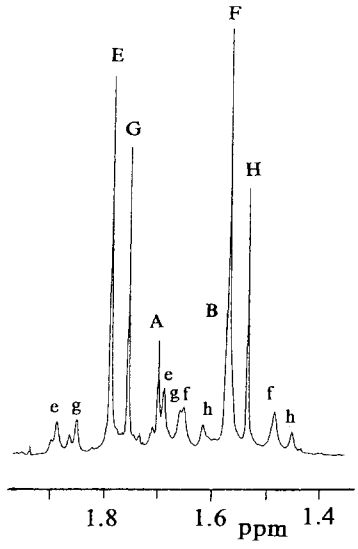
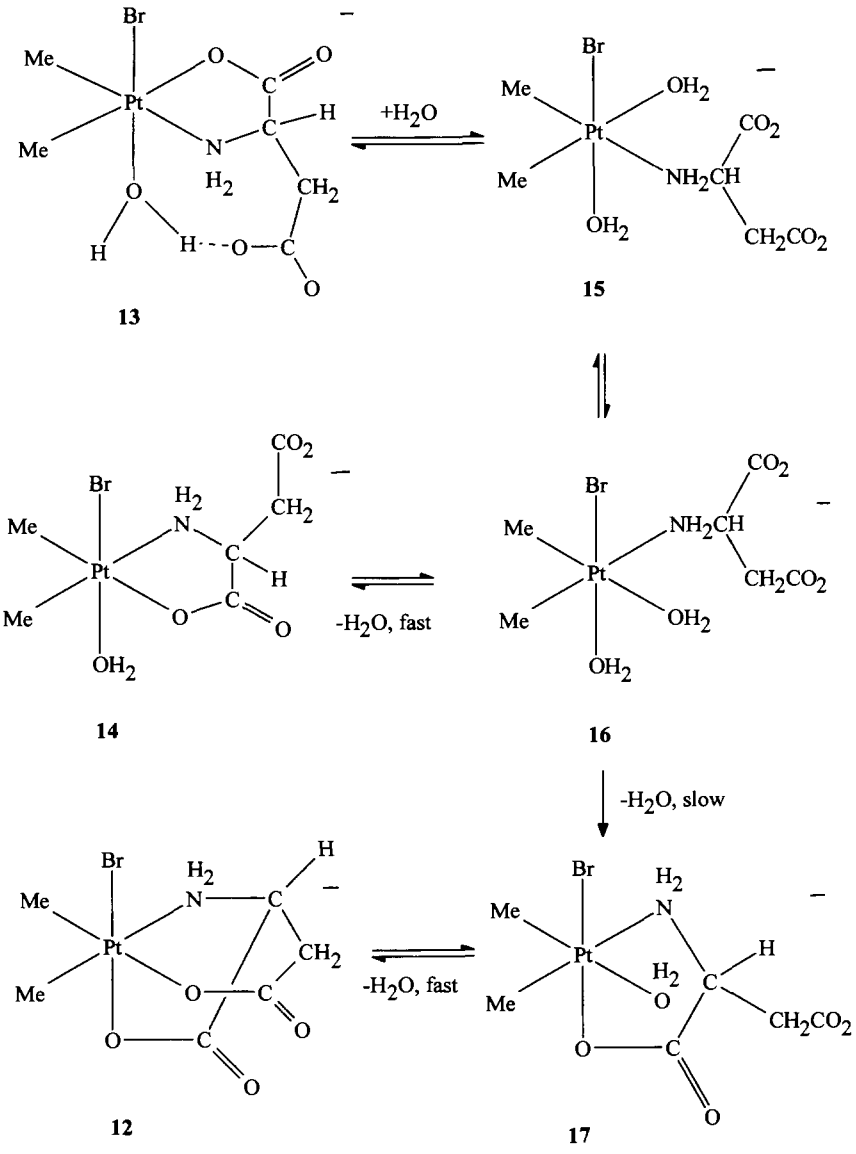


Fig. 6. Methyl region of the 400 MHz ^{1}H NMR spectrum (298 K) of a solution at pD 5.4 obtained by addition of KOH/D_2O to a D_2O solution of $[PtMe_2Br(D_2O)_3]NO_3$ and aspartic acid, after standing. See text for labels. Satellite peaks are indicated by lower case letters.

$^2J(Pt—CH_3)$ 65.9 Hz] were from one compound, and the remaining two peaks, G [1.76 ppm, $^2J(Pt—CH_3)$ 76.6 Hz] and H [1.54 ppm, $^2J(Pt—CH_3)$ 64.7 Hz] were from a second compound. The Pt—CH_3 coupling constants indicated that peaks F and H were from methyl groups *trans* to nitrogen, and peaks E and G *trans* to carboxylate O atoms. The chemical shifts for all of these peaks were not affected by changes in pD of the solution, so that these species were unlikely to contain aqua or hydroxo ligands. For glycinate[22] and iminodiacete[20] complexes, chelate ring closure occurred readily in mildly acidic solution. These four methyl peaks were therefore assigned to isomers of $[PtMe_2Br(asp\text{-}N,\alpha O,\beta O)]^-$ with aspartate tridentate. There are two isomers possible with aspartate N *trans* to methyl, **11** and **12**. The Pt—CH_3 coupling constant for peak G was smaller than that for peak F. On the basis that the Pt—CH_3 coupling constant *trans* to α-carboxylate in a five-membered ring would be smaller than in an analogous compound *trans* to β-carboxylate in a six-membered ring, peaks G and H were assigned to isomer **11**, in which the five-membered N,αO-chelate ring was *trans* to the methyl groups. Peaks E and F were therefore assigned to isomer **12**. With this assignment, the methyl group *trans* to amine nitrogen in a five-membered ring (peak F from **11**) also showed a smaller Pt—CH_3 coupling constant than the methyl group *trans* to amine nitrogen in a six-membered ring (peak H from **12**).

A 100.4 MHz ^{13}C NMR spectrum was obtained for a solution containing **11** and **12** in approximately equal amounts. Satellite peaks from coupling to ^{195}Pt were too weak to be observed, but four methyl peaks and two sets of ligand peaks were observed. It was not possible to assign the peaks to a specific isomer, **11** or **12**: Pt—CH_3 −3.20, −5.32, −5.80, −9.32 ppm; methylene C 39.5, 39.3 ppm; methine C 56.3, 53.0 ppm; α-carboxylate 187.7, 187.2 ppm; β-carboxylate 177.3, 176.1 ppm.

It is clear that isomers **11** and **12** were formed initially in comparable amounts. Isomer **11** would be easily formed by ring closure from the aqua complex **8** (or the form with β-carboxylate dedeuteronated, **13**). Isomer **12** cannot be formed directly from an aqua complex with N and αO both *trans* to methyl. A possible mechanism for formation of **12** is outlined in Scheme 3. Cleavage of the Pt—αO bond of **13** gives a complex **15** with aspartate bound monodentate through N. Migration of nitrogen to the second labile site gives **16**. Closure of the five-membered ring by coordination of α-carboxylate to the site *trans* to methyl gives **14**, by a fast but reversible reaction. A much slower but less easily reversed reaction would involve ring closure by coordination of α-carboxylate to the "inert site" *trans* to bromide, to give **17**, with subsequent rapid coordination of β-carboxylate to the labile *trans* to methyl to give **12**. Although the concentration of **16** at any instant would be very much less than that of **13**, conversion of **16** to **17** requires closure of a five-membered chelate ring, for which the rate constant would be



Scheme 3.

expected to be larger than for comparable closure of a six-membered ring, in conversion of **13** to **11**.[30,32]

When the solution was allowed to stand with pD between 5 and 6, the peaks A and B from **13** disappeared, and there was a slow increase in the proportion of isomer **12** of $[PtMe_2Br(asp)]^-$ relative to **11**. After 2 weeks [Fig. 7(a)], peaks E and F from **12** were five times as intense as peaks G and H from **11**. From the rule[33] that the most stable isomer will be that in which ligands with the strongest trans influence are *trans* to those with weakest *trans* influence, the most stable isomer would be expected to be **18**, with N *trans* to bromide. With the kinetic barrier to formation of **18** too high in the absence of UV irradiation (see below), isomer **12**, with β-carboxylate *trans* to methyl, will be slightly more stable than isomer **11** with α-carboxylate *trans* to methyl, and predominates at equilibrium. The slow isomerization of **11** to **12** probably involves initial cleavage of one of the Pt—O bonds, followed by a redistribution of aspartate donor atoms among the available coordination sites.

When the pD of a solution containing isomer **12**, with β-carboxylate *trans* to methyl, was decreased to 3 by the addition of a dilute D_2SO_4, two new peaks were present in the methyl region of the ^1H NMR spectrum. At this pD value, their intensity was two thirds that of peaks E and F from **12**. From spectra run at various pD values in this vicinity, it was clear that these peaks grew at the expense of E and F when pD was lowered, and that this was

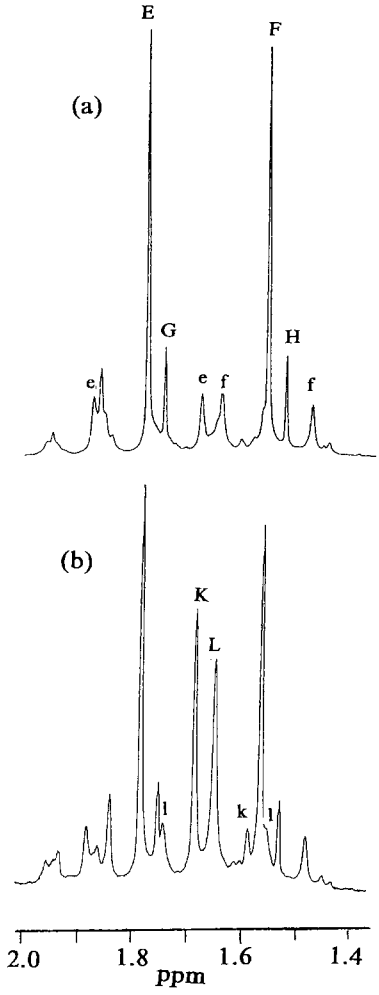


Fig. 7. Methyl region of the 400 MHz ^{1}H NMR spectrum (298 K) in D_2O of (a) an equilibrium mixture of the isomers **12** and **11** of $[PtMe_2Br(asp)]^-$, after 2 weeks at pD 6, and (b) the solution from (a) after 20 min UV irradiation. See text for labels. Satellite peaks are indicated by lower case letters.

reversed when pD was increased again. One of these peaks [1.60 ppm, ^2J(Pt—CH_3) 66.5 Hz] corresponded to methyl *trans* to amine. For the other peak (1.85 ppm), the Pt—CH_3 coupling constant, 81.2 Hz, was larger than usually observed for methyl *trans* to carboxylate, but was within the range for methyl *trans* to water.[18,22] These peaks were therefore assigned to the aqua complex **19**, formed by cleavage of the Pt—βO bond of **12**, with deuteration of β-carboxylate. There was no detectable analogous reaction involving cleavage of the Pt—αO bond of isomer **11**. The interconversion between **12** and **19**, while facile, was not fast on the NMR time-scale, as was the similar interconversion between the trimethylplatinum complexes **3** and **4**.

UV irradiation of $[PtMe_2Br(asp)]^-$ *(isomers* **11** *and* **12**)

In none of the spectra discussed above were there any NMR peaks observed assignable to the isomer of $[PtMe_2Br(asp)]^-$, which would be expected to be the most stable (**18**), with N *trans* to bromide. No such peaks were apparent when a solution containing **11** and **12** was heated for several hours in a water bath maintained at 90–95°C.

The solution whose ^{1}H NMR spectrum is shown in Fig. 7(a) (containing **11** and **12**, with **12** in excess, at pD 6) was irradiated with a mercury lamp for 20 min. The ^{1}H NMR spectrum of the resultant solution is shown in Fig. 7(b). Two new singlets with satellites were present, K [1.69 ppm, ^2J(Pt—CH_3) 76.9 Hz] and L [1.65 ppm, ^2J(Pt—CH_3) 75.7 Hz]. These two Pt—CH_3 coupling constants would both correspond to methyl *trans* to carboxylate, as expected for **18**. Since the Pt—CH_3 coupling constant for K was slightly larger than that for L, peak K was assigned to the methyl group *trans* to β-carboxylate. Analogous reactions in which the isomer with N *trans* to bromide is formed under UV irradiation occur with dimethylbromoplatinum(IV) complexes of iminodiacetate[20] and glyphosate.[9]

A solution was subjected to prolonged irradiation in an attempt to obtain a solution containing **18** as the only species present in significant concentration, but this led to extensive decomposition and formation of a black residue.

SUMMARY

Differences between behaviour of chelated α- *and* β-*carboxylate groups*

The tendency for bidentate aspartate to bind through N and α-carboxylate has been previously well documented,[3–5] and our spectra may all be interpreted in terms of formation of similar five-membered rings in complexes such as **8** and **9**. When aspartate is tridentate with both α- and β-carboxylate bound, the greater stability of the five-membered N,αO-chelate ring compared with the six-membered N,βO-chelate ring causes a number of subtle differences to be observed in the behaviour of the different Pt—O bonds. Pt—CH_3 coupling constants *trans* to β-carboxylate are consistently slightly larger than *trans* to α-carboxylate. The weaker bonding of β-carboxylate relative to α- makes $[PtMe_2Br(asp)]^-$ with β-carboxylate *trans* to methyl, isomer **12**, more stable thermodynamically than isomer **11**, with α-carboxylate *trans* to methyl. Isomer **12**, with β-carboxylate at the labile site *trans*

to methyl, is in equilibrium with the aqua complex **19** in acid solution, but the Pt—αO bond of isomer **11** does not react similarly. When water cleaves a Pt—O bond of $[PtMe_3(asp)]^-$ (**3**), it appears likely that it is the bond to β-carboxylate which is selectively broken to form **4**.

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REFERENCES

1. J. I. Legg and D. W. Cooke, *J. Am. Chem. Soc.* 1967, **89**, 6854.
2. S. Yamada, J. Hidaka and B. E. Douglas, *Inorg. Chem.* 1971, **10**, 2187.
3. L. M. Volshtein and L. S. Anokhova, *Zh. Neorg. Khim.* 1959, **4**, 1734.
4. L. M. Volshtein and L. S. Anokhova, *Zh. Neorg. Khim.* 1961, **6**, 300.
5. T. G. Appleton, J. R. Hall, D. W. Neale and C. S. M. Thompson, *Inorg. Chem.* 1990, **29**, 3985.
6. L. P. Battaglia, A. B. Corradi, L. Antolini, G. Marcotrigiano, L. Menabue and G. G. Pellacani, *J. Am. Chem. Soc.* 1982, **104**, 2407.
7. I. Oonishi, S. Sato and Y. Saito, *Acta Cryst.* 1975, **B31**, 1318.
8. T. G. Appleton, J. R. Hall and L. Lambert, *Inorg. Chim. Acta* 1978, **29**, 89.
9. T. G. Appleton, K. A. Byriel, J. R. Hall, C. H. L. Kennard, D. E. Lynch, J. A. Sinkinson and G. Smith, *Inorg. Chem.* 1994, **33**, 444.
10. D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organomet. Chem.* 1972, **38**, 403.
11. G. E. Glass, W. B. Schwabacher and R. S. Tobias, *Inorg. Chem.* 1968, **7**, 2471.
12. T. G. Appleton, J. R. Hall and T. G. Jones, *Inorg. Chim. Acta* 1979, **32**, 127.
13. T. G. Appleton, J. R. Hall, N. S. Ham, F. W. Hess and M. A. Williams, *Aust. J. Chem.* 1983, **36**, 673.
14. E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.* 1984, **32**, 1.
15. E. W. Abel, D. Ellis, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.* 1992, 3497.
16. E. W. Abel, E. S. Blackwall, P. J. Heard, K. G. Orrell, V. Sik, M. B. Hursthouse, M. A. Mazid and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.* 1994, 445.
17. J. R. Hall and G. A. Swile, *J. Organomet. Chem.* 1977, **139**, 403.
18. N. H. Agnew, T. G. Appleton and J. R. Hall, *Inorg. Chim. Acta* 1980, **41**, 71.
19. T. G. Appleton, J. R. Hall and M. A. Williams, *Aust. J. Chem.* 1987, **40**, 1565.
20. T. G. Appleton, R. D. Berry, J. R. Hall and J. A. Sinkinson, *Inorg. Chem.* 1991, **30**, 3860.
21. N. H. Agnew, T. G. Appleton and J. R. Hall, *Inorg. Chim. Acta* 1978, **30**, L343.
22. N. H. Agnew, T. G. Appleton and J. R. Hall, *Inorg. Chim. Acta* 1980, **41**, 85.
23. D. E. Clegg and J. R. Hall, *Inorg. Synth.* 1967, **10**, 71.
24. O. M. Ivanova and A. D. Gel'man, *Zh. Neorg. Khim.* 1958, **3**, 1334.
25. J. R. Hall, D. A. Hirons and G. A. Swile, *Inorg. Synth.* 1980, **20**, 185.
26. J. E. Sarneski, J. L. Suprenant, F. K. Molen and C. N. Reilley, *Analyt. Chem.* 1975, **47**, 2116.
27. P. K. Glasoe and F. A. Long, *J. Phys. Chem.* 1960, **64**, 188.
28. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn, p. 308. Wiley-Interscience, New York (1978).
29. O. W. Howarth, P. Moore and N. Winterton, *J. Chem. Soc., Dalton Trans.* 1974, 2271.
30. T. G. Appleton, J. R. Hall and S. F. Ralph. *Aust. J. Chem.* 1986, **39**, 1347.
31. T. G. Appleton, J. R. Hall and P. D. Prenzler, *Inorg. Chem.* 1989, **28**, 815.
32. L. M. Volshtein, L. F. Krylova and N. S. Slyudkina, *Zh. Neorg. Khim.* 1978, **23**, 108.
33. T. G. Appleton, H. C. Clark and L. E. Manzer, *J. Organomet. Chem.* 1974, **65**, 275.