Inorganica Chimica Acta, 29 (1978) 89–99

Amino Acid Complexes of Platinum(IV). I. Trimethylplatinum(IV) Complexes with Glycinate, Iminodiacetate, N-Methyliminodiacetate, Nitrilotriacetate, and Ethylenediamine-tetraacetate

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Received October 24, 1977

Reaction between $PtMe_3(H_2O)_3^+$ and sodium glycinate gives a series of glycinato complexes, $PtMe_3(gly)(H_2O)$, $[PtMe_3(gly)]_2$, $PtMe_3(gly)_2^-$ and $PtMe_3(gly)_3^{2-}$. Variable-temperature PMR has been used to study rapid intramolecular exchange reactions in $PtMe_3(gly)(D_2O)$ and $PtMe_3(gly)_2^-$ in D_2O. Iminodiacetate, N-Methyliminodiacetate, and nitrilotriacetate act as tridentate ligands, coordinating through the N- and two O-atoms. The most stable EDTA complex is $(Me_3Pt)_2(EDTA)^{2-}$, in which each Pt-atom is coordinated to one N and two O-atoms of bridging EDTA.

Introduction

The trimethylplatinum(IV) system is ideally suited for the study of interactions between heavy metal ions and molecules of biological interest, such as amino acids. The geometry of the compounds formed is well-defined, being invariably octahedral, with a very strong preference for the *fac* configuration of the three methyl groups [1]. The remaining coordination sites are rendered relatively labile by the high *trans* effect of the methyl ligand. Whereas the typical platinum(IV) starting material, $PtCl_6^{2-}$, reacts only slowly with glycinate to give insoluble products [2], $PtMe_3(H_2O)_3^+$ reacts rapidly to give a range of products amenable to NMR study. The donor atom *trans* to a particular methyl group can usually be identified from the value of $^2J(Pt-CH_3)$ [3] (^{195}Pt, I = ½, 34% abundance). Coupling constants to ^{195}Pt from nuclei within the organic ligand can also provide information on binding site and ligand conformation.

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Results and Discussion

Analytical data for compounds isolated are given in Table I, and spectroscopic data in Table II.

Monoglycinate Complexes

When equimolar amounts of $PtMe_3(H_2O)_3^+$ (as the sulphate) and Nagly* are mixed in aqueous solution, or if sodium hydroxide is added to a solution of $PtMe_3(H_2O)_3^+$ and glycine, a white precipitate of $[PtMe_3(OH)]_4$ immediately forms (known to occur when base is added to $PtMe_3(H_2O)_3^+$ [4]). However, most of the platinum remains in solution as $PtMe_3$-

*Abbreviations: Hgly = glycine, $NH_3^+CH_2CO_2^-$; H_2IDA = iminodiacetic acid, $HN(CH_2COOH)_2$; H_2MIDA = N-methyliminodiacetic acid, $CH_3N(CH_2COOH)_2$; H_3NTA = nitrilotriacetic acid, $N(CH_2COOH)_3$; H_4EDTA = ethylenediamine-N,N,N',N'-tetraacetic acid, $(HOOCCH_2)_2N(CH_2)_2N(CH_2COOH)_2$; lut = 3,5-lutidine (3,5-dimethylpyridine), C_7H_9N.

TABLE I. Analytical Data[a].

Compound	Structure	C	H	N	Pt
$[PtMe_3(gly)]_2$	IV	19.3(19.1)	4.2(4.2)	4.7(4.5)	62.4(62.1)
$PtMe_3(gly)(lut)$	V	34.0(34.4)	5.2(4.8)	6.7(6.7)	47.0(46.5)
$Na[PtMe_3(gly)_2]$[b]	VI	19.7(20.4)	4.4(4.2)	6.8(6.8)	
$Na[PtMe_3(IDA)]$	X	21.5(21.3)	3.7(3.6)	3.9(3.6)	
$Na[PtMe_3(MIDA)]$	XI	23.4(23.5)	4.2(4.0)	3.3(3.4)	
$Na[PtMe_3(HNTA)]\cdot H_2O$	XII	23.3(23.0)	4.1(3.9)	3.3(3.0)	
$Na[PtMe_3)_2(EDTA)]$	XV	23.2(23.6)	3.7(3.7)	3.8(3.4)	

[a]Calculated values (%) in parentheses. [b]Extremely deliquescent.

TABLE II. Spectroscopic Data.

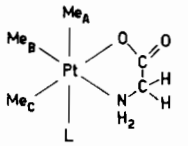
Compound	Structure	PMR Spectra[a]									IR Spectra	
		Temp. (°C)	Pt–CH_3			N–CH_2				Other Resonances	ν(C=O) (cm^{-1})	ν(NH) or ν(ND) (cm^{-1})
			Trans Group	δ p.p.m.	^2J(Pt–CH_3) Hz	Assignment[b]	δ p.p.m.	^3J(Pt–N–C–H) Hz	J_{AB} Hz			
$PtMe_3(gly)(H_2O)$	I	1.5	D_2O(A)	0.92	81.4		3.76	11.7	~17		[c]	[c]
			O(gly) (C)	0.87	76.9		3.68	9.6				
			N(B)	0.74	67.4							
		28					3.72	10.5				
$[PtMe_3(gly)]_2$[l]	IV			[d]			[d]				1609 1579	3345 3254
$[PtMe_3(gly)]_2$[e] (N-deuterated)	IV										1601 1561	2514 2398
$PtMe_3(gly)(lut)$[fg]	V	28	O(C)	0.87	75.9		3.56	12.0	16.9	δNH_2 4.2 p.p.m.[h]	1626	3217 3137
			N(A)[i] (lut)	0.86	70.0		3.16	11.6		lutidine δCH_3 2.37 p.p.m. δH_α 8.25 p.p.m., J(Pt–N–H_α) 11.2 Hz δH_γ 7.65 p.p.m.		
			N(B)[i] (gly)	0.70	68.0							
$PtMe_3(gly)(lut)$ (N-deuterated)	V										1597	2414 2310
$Na[PtMe_3(gly)_2]$	VI	1.5	O(B)	0.72	78.3	H_A	3.78	16.4	17.3		1585[j]	3334
			N(C) (chelate)	0.63	68.8	H_B	3.58	5.9				3236 3144
			N(A) (uni-dentate)	0.59	70.0	Unidentate gly	3.27	11.4				
$Na_2[PtMe_3(gly)_3]$	IX	28	N	0.54	68.8		3.26	12.8			[c]	[c]
$Na[PtMe_3(IDA)]$	X	28	N	0.83	69.6	H_A	3.98	~3	17.5		1600	3328
			O	0.82	78.7	H_B	3.55	19.2				
$Na[PtMe_3(MIDA)]$	XI	28	N	0.93	69.1	H_A	3.76	~3	17.2	N–CH_3 δ 2.70 p.p.m. ^3J(Pt–N–CH_3) 17.3 Hz	1620	
			O	0.79	76.6	H_B	3.69	19.4				

TABLE II. Continued

$Na[PtMe_3(HNTA)]$ $\cdot H_2O$	XII	1.5	N	1.04	71.5	H_B	4.15	~15			1748 (free)
			O	0.77	76.6	H_A	3.99	⩽3		16.8	1629 (bound)
						Free Acetate	3.95	6.8			
$Na_2[(PtMe_3)_2(EDTA)]$	XV	28	N	1.04	71.2	H_A	3.90	⩽3	$N-CH_2CH_2-N$		1620
			O	0.83	76.8	H_B	3.75	15.7	δ 3.32 p.p.m.	16.5	
$Na[PtMe_3(H_2EDTA)]$	XIII	28	N	1.04	71		k		k		c
			O	0.78	77						

[a] In D_2O, chemical shifts p.p.m. downfield from DSS, unless otherwise specified. [b] See text figures. [c] Obtained only in solution. [d] Spectrum in D_2O identical with dilute solution $PtMe_3(gly)(D_2O)$. [e] $\delta(NH_2)$ 1546 cm^{-1}. [f] NMR in CD_3OD, chem. shifts relative to TMS. [g] $\delta(NH_2)$ 1587 cm^{-1}. [h] In freshly-prepared solution. [i] These assignments could be reversed. [j] See text. [k] Methylene region complex, and overlaps with (XV) and H_4EDTA.

$(gly)(H_2O)$ (I). Small amounts of free glycine and $PtMe_3(H_2O)_3^+$ or $PtMe_3(gly)_2^-$ are also usually present.



I L = H_2O or D_2O

V L = lut

When the reaction is carried out in D_2O, the PMR spectrum at 1.5 °C of the filtrate shows three peaks in the Pt–CH_3 region, each with "satellites" from coupling to ^{195}Pt (Figure 1(a)). The Pt–CH_3 coupling constants, 81.4, 76.9, and 67.4 Hz, are as expected for methyl groups *trans* to water (A), glycinate O(C) and glycinate N(B) respectively (*cf.* $^2J(Pt-CH_3)$ *trans* to Z in $PtMe_3(bipy)Z$; Z = H_2O, 82 Hz; Z = $CH_3CO_2^-$, 74 Hz; Z = $EtNH_2$, 70 Hz) [3].

By 28 °C, the methyl resonances A and C (*trans* to O) have collapsed to a singlet, but methyl resonance B (*trans* to N) remains unchanged (Figure 1(b)). The exchange reaction (1) is thus fast (on the NMR time-scale) at this temperature.

Ia Ib (1)

As the temperature is increased further, the methyl peaks broaden (Figure 1(c)), then coalesce into a singlet (Figure 1(d)) as all three methyl groups become equivalent.

In (I), the glycinate methylene protons would be expected to be non-equivalent at low temperatures, when exchange reaction (1) is slow, and equivalent at higher temperatures. In D_2O, the $-NH_2$ group rapidly deuterates to $-ND_2$, so the methylene region of the spectrum is not complicated by HNCH coupling. At 28 °C, the methylene protons give a slightly broadened singlet, with "satellites" from platinum coupling (10.5 Hz) (Figure 1(b)). Little further change occurs in this pattern up to 95 °C. At 1.5 °C, the methylene protons give an AB pattern superimposed on the AB part of an ABX spectrum (half the intensity of the AB pattern; X = ^{195}Pt). Because of the small chemical shift difference between the protons, the outer lines of the AB quartets cannot be observed, and J_{AB} cannot be obtained directly from the spectrum. However, if it is assumed that $J_{AB} \approx 17$ Hz (*cf.*, J_{AB} for methylene protons in the complexes discussed below) the spectrum may be satisfactorily analysed to give the chemical shifts and coupling constants reported in Table II.

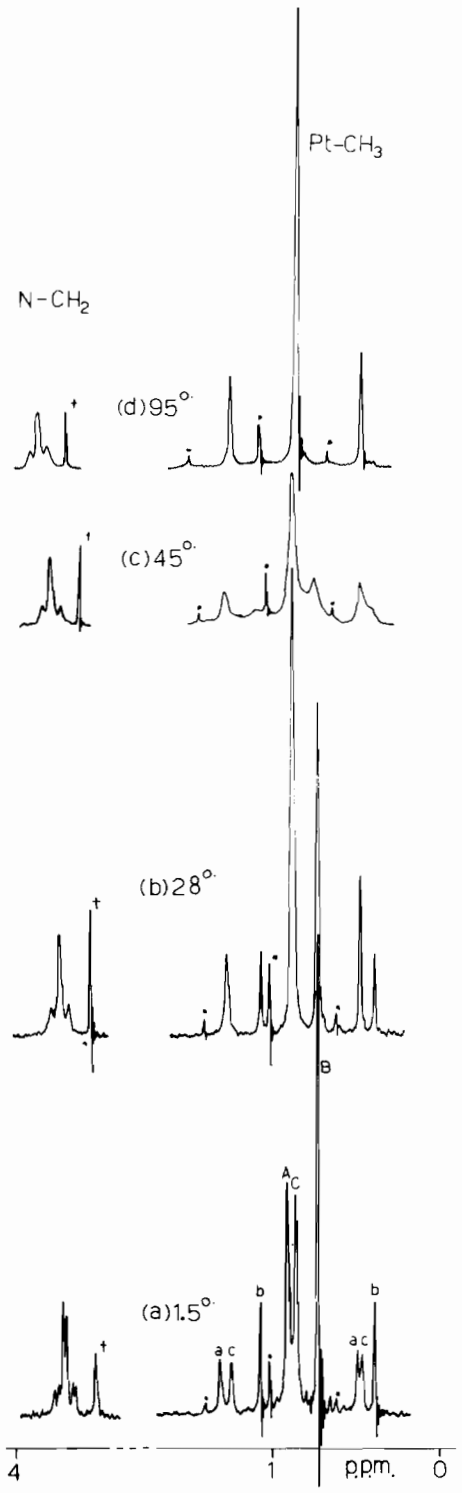


Figure 1. Variable-temperature 100 MHz PMR spectra of $PtMe_3(gly)(D_2O)$ (I) in D_2O (amplitude not constant). *$PtMe_3(D_2O)_3^+$, † free glycine.

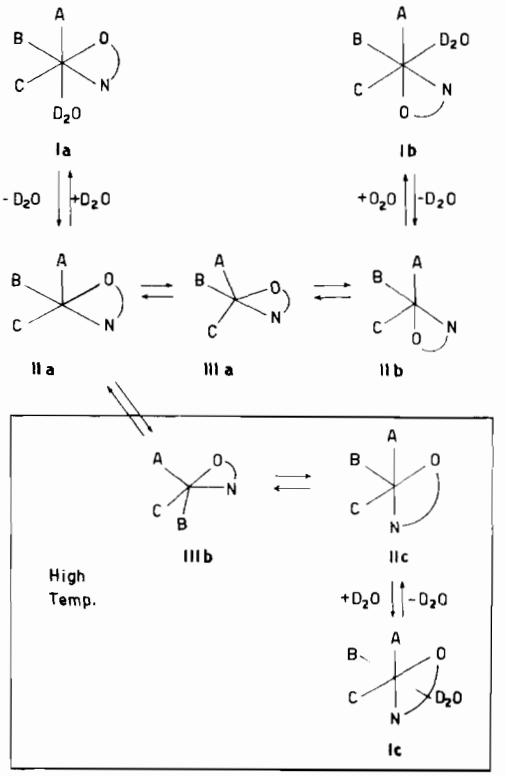
The Pt–N–C–H coupling constants are expected to show a Karplus-type dependence on ϕ, the dihedral angle between the planes PtNC and NCH [5–7]. That is,

$$|^3J(Pt\text{–}N\text{–}C\text{–}H)| \approx K\cos^2\phi + C \qquad (2)$$

where K and C are constants. Since the two Pt–N–C–H coupling constants in (I), 11.7 and 9.6 Hz, differ only slightly, there is no strong preference for a particular conformation where one C–H bond is close to equatorial ($\phi \approx 180°$). A strong conformational preference would not be expected, as the "axial" substituents on the metal, CH_3 and D_2O, do not differ greatly in steric bulk.

When spectra are run of mixtures of $PtMe_3(gly)(D_2O)$ (I) and $PtMe_3(D_2O)_3^+$, the methyl peak of the latter species remains sharp, and is unaffected by the presence of the glycinate complex. Together with the observation that Pt–CH_3 and Pt–N–C–H couplings in (I) are maintained up to 95 °C, this indicates that there is no rapid intermolecular exchange of glycinate ligand.

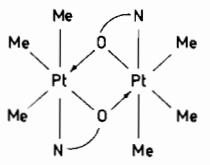
Rapid intramolecular exchange reactions have been previously studied by NMR for $PtMe_3(bipy)(H_2O)^+$ [8] and $[PtMe_3(\beta\text{-diketonate})]_2$ [9]. In each case, all three methyl groups become equivalent at high temperatures, and the reactions are postulated to proceed *via* five-coordinate intermediates. For the exchange reactions of (I) the most likely intermediate is $PtMe_3(gly)$ (II), formed by dissociation of coordinated water. Possible mechanisms for the two exchange reactions are given in Scheme 1.



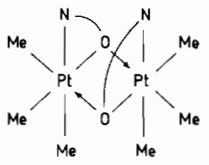
SCHEME 1. Possible Mechanism for Intramolecular Exchange Reactions in $PtMe_3(gly)(D_2O)$.

In the low-temperature exchange reaction (1), the glycinate O-atom migrates to the vacant site in a square pyramidal complex (IIa → IIb) *via* the trigonal bipyramid (IIIa). The activation energy for this migration will include a component from Pt–O bond weakening as the O-atom traverses regions where metal σ-orbitals are less accessible. Since the Pt–N bond is stronger than Pt–O, the activation energy will be greater for the corresponding N-migration (IIa → IIIb → IIc). Consequently the exchange (Ia ⇌ Ib) occurs at lower temperatures than (Ia ⇌ Ic).

If a solution of $PtMe_3(gly)(H_2O)$ (I) is allowed to stand, or is concentrated to small volume, a white solid crystallizes which analyses for $PtMe_3(gly)$ (Table I), and whose IR spectrum shows no peaks attributable to water. This compound is formulated as the oxygen-bridged dimer (IV) (probably a mixture of isomers a and b), similar to trimethylplatinum(IV) 8-hydroxyquinolate [10].



IV a



IV b

The compound is only sparingly soluble in water. Its NMR spectrum in D_2O corresponds with that of a dilute solution of $PtMe_3(gly)(D_2O)$ (I). It is too insoluble in common organic solvents to allow molecular weight or NMR measurements to be carried out. The analogous alanine complex, $[PtMe_3(ala)]_2$, is quite soluble in acetone, and has been shown to be dimeric (a mixture of isomers corresponding to (IVa) and (IVb)) in that solvent [11].

The IR spectrum of $[PtMe_3(NH_2CH_2CO_2)]_2$ (IV) shows three bands in the region 1500–1700 cm^{-1}, at 1546, 1579, and 1609 cm^{-1}. The band at 1546 cm^{-1} has shifted in the spectrum of $[PtMe_3(ND_2CH_2CO_2)]_2$, and so is assigned to $\delta(NH_2)$. The bands at 1579 and 1609 cm^{-1} shift only slightly, and must arise mainly from $\nu(C{=}O)$.

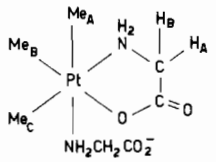
The oxygen bridges of (IV) are readily cleaved by 3,5-lutidine to give $PtMe_3(gly)(lut)$ (V), whose PMR spectrum in CD_3OD shows three Pt–CH_3 resonances, with coupling constants 75.9, 70.0, and 68.0 Hz corresponding to methyl groups *trans* to glycinate O(C), lutidine (A), and glycinate NH_2 (B) respectively. The small difference between the two values of $^2J(Pt{-}CH_3)$ *trans* to the two different N-donors does not allow the above assignment to be made with certainty, but it is more consistent with the known range of $^2J(Pt{-}CH_3)$ *trans* to substituted pyridines [3] and glycinate N (other compounds described in this paper) than the alternative assignment. In a freshly prepared solution of (V) in CD_3OD, the $-NH_2$ protons give a broad resonance at ~4.2 p.p.m., and the methylene proton pattern is complex, owing to the presence of HNCH coupling. If the solution is allowed to stand for several days, the amino protons exchange with solvent deuterium, and the methylene protons show the usual AB + ½ABX pattern. Once again, the two Pt–N–C–H coupling constants are very similar (12.0 and 11.6 Hz), indicating that there is no strong conformational preference for the amino acid chelate ring.

When free glycine is added to an aqueous solution of $PtMe_3(H_2O)_3^+$ the equilibrium (3) is set up. At room temperature, several hours are required before equilibrium is reached, and a large excess (~20:1) of glycine is required before all $PtMe_3(H_2O)_3^+$ reacts. Only a trace of $PtMe_3(gly)_2^-$ is observed. The dimer (IV) does not precipitate from these solutions on standing.

$$PtMe_3(H_2O)_3^+ + Hgly \rightleftharpoons PtMe_3(gly)(H_2O) + 2H_2O + H^+ \quad (3)$$

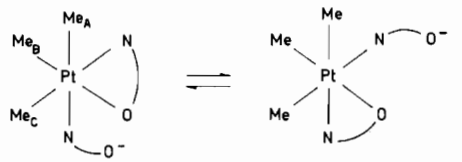
Bis(glycinate) Complex

If two mol sodium glycinate are added to one mol $PtMe_3(H_2O)_3^+$ in aqueous solution, the major species in the filtrate after removal of $[PtMe_3(OH)]_4$ is $PtMe_3(gly)_2^-$ (VI), with glycine and $PtMe_3(gly)(H_2O)$ (I) or $PtMe_3(gly)_3^{2-}$ as impurities.



VI

In D_2O at 1.5 °C, three distinct methyl resonances are observed (Figure 2(a)) with Pt–CH_3 coupling constants 78.3, 68.8, and 70.0 Hz corresponding to methyl groups *trans* to O(B), N(chelated glycinate)-(C), and N(unidentate glycinate)(A) respectively (assuming that Pt–N bonding is slightly stronger when glycinate is chelated). By 28 °C, the two resonances corresponding to methyl groups *trans* to N (A and C) have collapsed to a singlet (Figure 2(b)) indicating that exchange reaction (4) is occurring.



(4)

VI a VI b

The reaction may be associative, with concerted breaking of one Pt–O bond as a new Pt–O bond forms, or dissociative, *via* five-coordinate $Pt^+Me_3(ND_2CH_2CO_2^-)_2$. This exchange reaction may be

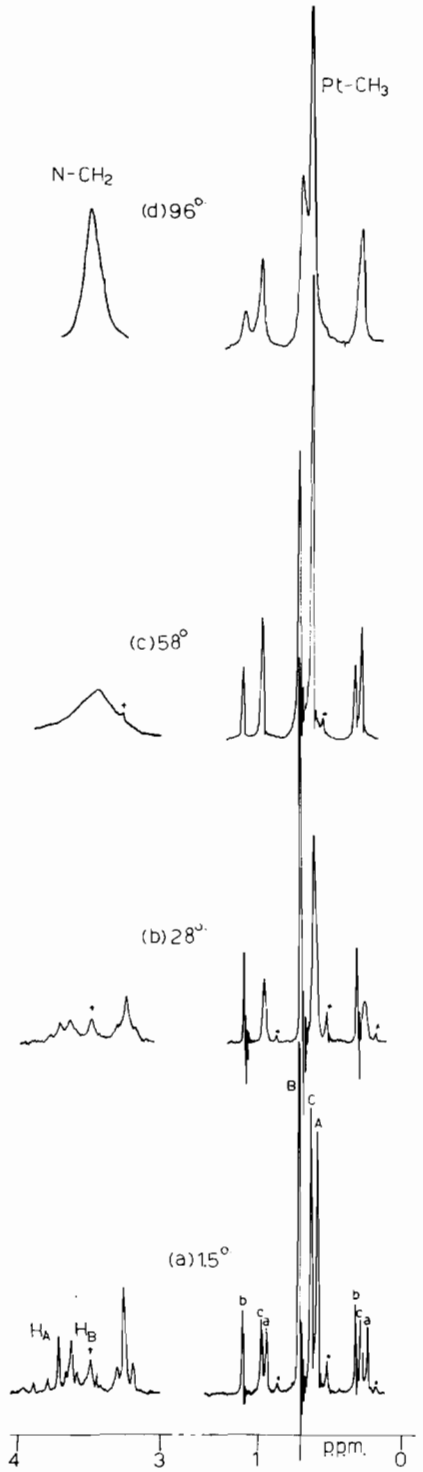
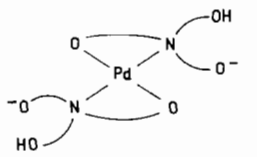
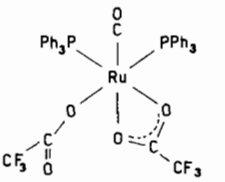


Figure 2. Variable-temperature 100 MHz PMR spectra of $Na[PtMe_3(gly)_2]$ (VI) in D_2O. * $Na_2[PtMe_3(gly)_3]$, † free glycine.

compared with that between coordinated and uncoordinated acetate groups in $Pd(HNTA)_2^{2-}$ (VII) [12] and the exchange between chelated and unidentate trifluoroacetate in $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (VII) [13].



VII



VIII

The two methyl resonances continue to sharpen to ~60 °C (Figure 2(c)), then begin to broaden again. At the highest temperature attainable, 96 °C, the peaks are clearly in the process of collapsing together (Figure 2(d)), so that at some hypothetical higher temperature all three methyl groups would become equivalent. This exchange may be intramolecular, by rearrangement of five-coordinate $Pt^*Me_3(ND_2CH_2CO_2^-)_2$, or by breaking of Pt–N as well as Pt–O bonds in a higher-temperature associative mechanism. Alternatively, intermolecular glycinate exchange between $PtMe_3(gly)_2^-$ and traces of $PtMe_3(gly)_3^{2-}$ may be involved since this intermolecular exchange is known to occur at 96 °C (see below).

At 1.5 °C, separate resonances are observed for methylene protons of chelated and unidentate glycinate ligands (Figure 2(a)). The resonance for unidentate glycinate is a singlet with satellites ($J(Pt–N–CH_2)$ 11 Hz). The methylene protons of the chelated glycinate give a well-defined AB + ½ABX pattern (X = ^{195}Pt). Since $^3J(Pt–N–C–H_A)$ (16.4 Hz) is greater in magnitude than $^3J(Pt–N–C–H_B)$ (5.9 Hz), from equation (2), $\cos^2\phi_A$ is greater than $\cos^2\phi_B$. If the flexible amino acid chelate ring [14] bends away from the bulky unidentate glycinate substituent on the metal, the assignment of H_A ("equatorial") and H_B ("axial") is as indicated in structure (VI).

If the exchange reaction (4) is sufficiently fast, all the methylene protons are expected to become equivalent. As the temperature is increased, the separate methylene peaks begin to broaden (Figure 2(b)) and by 96 °C have coalesced to a broad singlet (Figure 2(d)).

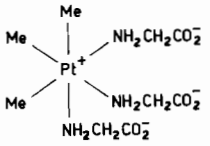
In the spectra of mixtures of $PtMe_3(gly)(D_2O)$ (I) and $PtMe_3(gly)_2^-$ (VI), separate sets of peaks for the two species are observed at all temperatures. There is no rapid intermolecular exchange between them.

The solution of $Na[PtMe_3(gly)_2]$ obtained as above by mixing aqueous solutions of $(PtMe_3)_2SO_4$ and sodium glycinate also contains sodium sulphate. A solution free from this contaminant may be obtained by reaction of sodium glycinate with an aqueous suspension of $[PtMe_3(gly)]_2$ (IV). When this solution is evaporated to dryness, and the residue triturated under acetone, $Na[PtMe_3(gly)_2]$ (VI) is obtained as a very deliquescent white solid. In the

region 1500–1700 cm^{-1}, its IR spectrum shows only one strong broad band (at 1585 cm^{-1}) whose envelope presumably contains the two ν(C–O) bands expected in this region, as well as $\delta(NH_2)$.

Tris(glycinate) Complex

When excess sodium glycinate is added to a solution of $Na[PtMe_3(gly)_2]$ (VI) in D_2O, an additional Pt–CH_3 peak with satellites (^2J(Pt–CH_3) 68.8 Hz) is observed, attributable to $Na_2[PtMe_3(gly)_3]$ (IX). The methylene protons give a singlet with satellites (^3J(Pt–N–CH_2) 12.8 Hz) partly obscured by the peak due to uncoordinated glycinate.



IX

As the temperature is increased, the equilibrium (5) shifts toward the left. At 80–100 °C, the methyl peak of $PtMe_3(gly)_3^{2-}$ broadens and coalesces with the more intense peaks from $PtMe_3(gly)_2^-$. Glycinate exchange between the two species thus becomes rapid at higher temperatures.

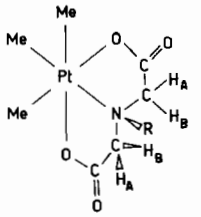
$$PtMe_3(gly)_2^- + gly^- \rightleftarrows PtMe_3(gly)_3^{2-} \quad (5)$$
VI IX

Iminodiacetate Complex

When $PtMe_3(H_2O)_3^+$ (as the sulphate), iminodiacetic acid, and sodium hydroxide are mixed in aqueous solution in the molar ratio 1:1:2, a small amount of $[PtMe_3(OH)]_4$ precipitates, leaving a solution containing $Na[PtMe_3(IDA)]$ and sodium sulphate. After evaporation of the solution to dryness, the complex may be separated from the sodium sulphate residue by extraction with methanol.

NMR studies (*e.g.*, $Co(IDA)_2^-$ [15], $Rh(IDA)_2^-$ [16]) and X-ray crystallography ($Ni(IDA)_2^{2-}$ [17]) have shown that the tridentate iminodiacetate ligand prefers to coordinate *facially*, although the *meridional* configuration may be forced on it by the bonding requirements of the metal (*e.g.*, Pd(II) [18], Pt(II) [19]) or of other ligands (*e.g., trans mer* Co(dien)(IDA)$^+$ [20]). Given the preferred *fac* geometry of trimethylplatinum(IV) complexes, it is not surprising that the structure of $PtMe_3(IDA)^-$, from NMR, is (X).

In the platinum–methyl region, two barely resolved peaks are observed, intensity ratio 1:2, with ^2J(Pt–CH_3) 69.6 and 78.7 Hz, corresponding to methyl groups *trans* to N and O respectively. The methylene region shows a well-defined AB + ½ABX spectrum. In agreement with assignments for Co(III) [15] and Rh(III) [16] complexes with *facially* coordinated IDA, the lower-field resonance is assigned to H_A (*cis* to N–H or N–D) in structure (X). Platinum coupling to this proton (~3 Hz) is much less than that to H_B (19.2 Hz). Thus $\cos^2\phi_A$ is much less than $\cos^2\phi_B$ in the time-averaged ring conformation. Models indicate that the chelate rings in iminodiacetate complexes have some flexibility. The conformations of the individual chelate rings in $Li_2[Ni(IDA)_2]\cdot 4H_2O$ and $Cs_2[Ni(IDA)_2]\cdot 4H_2O$ do differ significantly [17]. The dihedral angles between the planes NiNC and NCH, calculated from the crystal data, range from 69.5° to 88.1° for H_A (average over four independent values 79.0°) and from 137.6° to 150.4° for H_B (average 142.1°). The condition that $\cos^2\phi_B \gg \cos^2\phi_A$ holds over this range of conformations.



X R = H or D
XI R = Me
XII R = $-CH_2COOH$
XIII R = $-CH_2CH_2N(CH_2COOH)_2$

In the platinum(II) complex, $Pt(IDA)Cl^-$, where the ligand coordinates *mer*, the methylene proton *cis* to N–D (corresponding to our H_A) occurs to higher field, and has a greater coupling constant to ^{195}Pt, than the other methylene proton [19].

At higher temperatures (95 °C), the methyl–platinum peaks begin to broaden and coalesce, presumably owing to rapid rearrangement in a five-coordinate intermediate formed by breaking one of the Pt–O bonds. However, the rate of this exchange reaction is not sufficiently fast to have much effect on the methylene proton peaks, since the chemical shift difference between H_A and H_B is much greater than that between the Pt–CH_3 peaks.

N-Methyliminodiacetate Complex

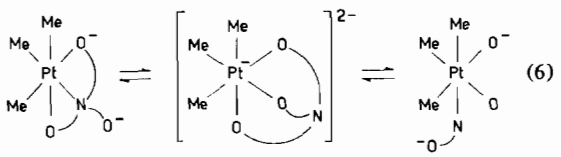
In the PMR spectrum of $Na[PtMe_3(MIDA)]$ (XI), the chemical shift difference between the platinum–methyl resonances is much greater than in the IDA complex. As found for Co(III) [15] and Rh(III) [16] complexes with *facially* coordinated ligands, the chemical shift difference between the non-equivalent methylene protons is less for the MIDA than for the IDA complex. The Pt–N–C–H coupling constants, and hence the ring conformations, are similar in the two compounds.

Nitrilotriacetate Complex

Reaction of $PtMe_3(H_2O)_3^+$ (as the sulphate), nitrilotriacetic acid (H_3NTA), and sodium hydroxide in the molar ratio 1:1:2 gives a solution containing $Na[PtMe_3(HNTA)]$ and Na_2SO_4. The complex as a monohydrate may be isolated by evaporation to dryness followed by methanol extraction. Since the PMR spectrum at 1.5 °C shows two platinum methyl peaks, intensity ratio 1:2, with $^2J(Pt-CH_3)$ corresponding to methyl groups *trans* to N and O respectively, the ligand coordinates through the N-atom and two O-atoms, as in structure (XII). Similar coordination of nitrilotriacetate has been found in $H[M(HNTA)_2]$ (M = Co, Rh; NMR) [16] and $K_4[Ni(NTA)_2]$ (X-ray crystallography) [21].

In the methylene region, the usual AB + ½ABX pattern from the coordinated acetate groups overlaps with a singlet with satellites ($J(Pt-N-CH_2)$ 6.8 Hz) from the uncoordinated acetate group. The order of chemical shifts of H_A and H_B (as labelled in structure (XII)) is reversed from that in the IDA, MIDA, and EDTA complexes.

As the temperature is raised, both sets of peaks begin to broaden and coalesce. By 95 °C, the methyl peaks give a singlet with satellites, and the methylene signals have also coalesced to a broad singlet with platinum coupling just resolved ($J(Pt-N-CH_2)$ ~9 Hz). At 28 °C, the spectrum is only slightly broader than at 1.5 °C, but if NaOD solution is added to increase pD above the initial value, 2.3, the spectrum broadens significantly. As well, the methylene peak of the uncoordinated acetate group moves upfield. When pD ≈ 5, this peak, much broadened, appears ~0.3 p.p.m. upfield from its original position. A similar shift, without the broadening, is observed when pD of a solution of $Co(DNTA)_2^-$ is increased [16]. No further change occurs in the spectrum of $PtMe_3(DNTA)^-$ as the pD is increased beyond ~5. Thus, deprotonation of the uncoordinated acetate group increases the rate of the exchange reaction, but additional base has no effect. This suggests that the exchange rate is determined by a step involving nucleophilic attack on platinum by the O-atom of the uncoordinated acetate group. Since the three methyl groups become equivalent simultaneously with the methylene protons, the Pt–N bond does not remain unaffected while the acetate groups exchange. A possible mechanism for the exchange reaction consistent with the NMR evidence is reaction (6), *via* an intermediate (XIV) in which the nitrilotriacetate ligand coordinates symmetrically through three O-atoms.

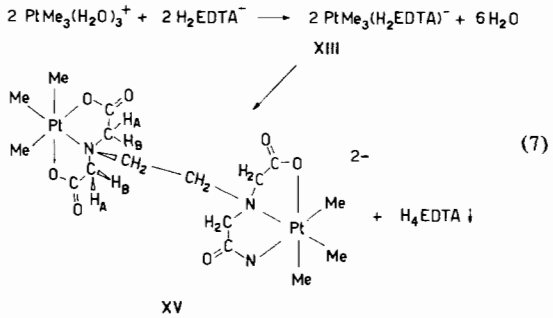


XIV (6)

Like $H[M(HNTA)_2]$ (M = Co, Rh) [16], $Na[PtMe_3(HNTA)]\cdot H_2O$ shows two distinct bands in the $\nu(C{=}O)$ region in its IR spectrum, at 1748 and 1629 cm^{-1}, corresponding to the free –COOH group and $Pt-O_2C-$ group respectively.

EDTA Complexes

When $PtMe_3(H_2O)_3^+$ and $Na_2[H_2EDTA]$ are mixed in aqueous solution in equimolar amounts, the resultant solution contains a mixture of $Na[PtMe_3(H_2EDTA)]$ (XIII) and $Na_2[(PtMe_3)_2(EDTA)]$ (XV). If the solution is allowed to stand, or is concentrated, colourless crystals of H_4EDTA precipitate, as (XV) is formed at the expense of (XIII) (Reaction (7)).



XIII XV (7)

Even if sufficient sodium hydroxide is added to completely deprotonate all the EDTA carboxylate groups, the major species in solution are $Na_2[(PtMe_3)_2(EDTA)]$ (XV) and $Na_4[EDTA]$. The compound (XV) may be prepared more rationally by mixing in aqueous solution $PtMe_3(H_2O)_3^+$ (as the sulphate), $Na_2[H_2EDTA]$, and NaOH in the molar ratio 2:1:2. After the small amount of precipitated $[PtMe_3(OH)]_4$ is removed by filtration, the filtrate is evaporated to dryness and the product extracted with methanol from the sodium sulphate residue. However prepared, the compound is usually contaminated with a small amount (<5%) of $Na[PtMe_3(H_2EDTA)]$ (XIII).

The PMR spectrum of $Na_2[(PtMe_3)_2(EDTA)]$ is consistent only with structure (XV). The platinum–methyl region shows two peaks (intensity ratio 1:2) with $Pt-CH_3$ coupling constants corresponding to methyl groups *trans* to N and O respectively. The $N-CH_2CH_2-N$ protons give a broad singlet whose envelope presumably includes peaks arising from $Pt-N-CH_2$ and $Pt-N-C-CH_2$ coupling. At 100 MHz, the acetate methylene proton resonances are not well-resolved, but the 270 MHz spectrum is easily analysed to give the values in Table II. Again, $J(Pt-N-C-H_A)$ (15.7 Hz) is much greater than $J(Pt-N-C-H_B)$ (<3 Hz). Except for minor chemical shift changes, the spectrum is unchanged up to 95 °C.

To confirm the structure (XV), the ^{13}C NMR spectrum at 67.09 MHz was also obtained. The platinum–methyl groups give resonances at 8.05 and 10.16 p.p.m. upfield from DSS, with Pt–C coupling

constants 688 Hz (*trans* N) and 762 Hz (*trans* O) respectively. Consistent with the proposed structure, only three resonances are observed for the EDTA C-atoms (all without resolved Pt-coupling): N–C–C–N, 55.74 p.p.m. downfield from DSS, acetate N–C, 65.36 p.p.m., and carboxylate C, 184.38 p.p.m.

A similar bridging EDTA ligand has been shown by X-ray crystallography to be present in $Na_4[(O_3Mo)_2(EDTA)]\cdot 8H_2O$ [22].

Since platinum(IV) usually prefers to coordinate to N-donors over O-donors (as shown by the structures of the glycinate complexes above), EDTA might have been expected to coordinate to the three remaining sites in a trimethylplatinum complex through two N-atoms and one O-atom. The preference for the *facial* N, 2(O) coordination actually found in these compounds probably results from a lower angle strain for this configuration.

Experimental

Instrumentation and Analyses

100 MHz PMR spectra were run on a Jeol PS-100 spectrometer. 270 MHz PMR and the ^{13}C spectra were run at the National NMR Centre, Canberra. Chemical shifts are reported in p.p.m. downfield from internal sodium 3-trimethylsilylpropane sulphonate (DSS).

IR spectra were run on a Jasco IRA-2 spectrometer, as nujol or hexachlorobutadiene mulls between KBr plates.

C, H, and N microanalyses were performed by J. Kent and P. Nobbs in this department. Pt analyses on non-electrolytes were by ignition, after treatment with iodine.

Materials

$(PtMe_3)_2SO_4\cdot 4H_2O$ was prepared by the literature method [23]. Other chemicals were obtained from the following suppliers: glycine, nitrilotriacetic acid, ethylenediaminetetraacetic acid, disodium salt, BDH; iminodiacetic acid, Fluka; N-methyliminodiacetic acid, 3,5-lutidine, Aldrich. Sodium glycinate was obtained by mixing equimolar amounts of glycine and sodium hydroxide in aqueous solution, followed by evaporation and drying in a vacuum desiccator over conc. H_2SO_4.

Preparation of a Sample Containing $PtMe_3(gly)(D_2O)$ (I) for NMR

The following is typical of the procedure used when solutions were prepared for running NMR spectra of species not isolated as solids.

0.5 ml D_2O was added to a mixture of 0.0593 g $(PtMe_3)_2SO_4\cdot 4H_2O$ (0.183 mmol Me_3Pt^+) and 0.0188 g sodium glycinate (0.194 mmol) and the mixture was shaken. The white precipitate of $[PtMe_3(OH)]_4$ was filtered off by passing the solution through a cotton wool plug into an NMR tube. The spectrum of the solution showed it to contain $PtMe_3(gly)(D_2O)$, together with small amounts of free glycine and $Na[PtMe_3(gly)_2]$.

Preparation of $[PtMe_3(gly)]_2$ (IV)

A solution of 0.1582 g sodium glycinate (1.630 mmol) in 5 ml water was added dropwise, with stirring, to a solution of 0.5214 g $(PtMe_3)_2SO_4\cdot 4H_2O$ (1.618 mmol $PtMe_3^+$) in 6 ml water. A white precipitate formed, which was filtered off, washed with water, and dried. Its PMR spectrum in $CDCl_3$ was identical with that of $[PtMe_3(OH)]_4$ [10, 24]. Yield 0.0555 g, 13.4%. The filtrate and washings were concentrated on the steam bath until a white solid began to form (~3 ml). The mixture was cooled in ice, the solid filtered onto a sintered glass funnel, washed with cold water, and air-dried. Yield 0.3511 g (69.5%).

The product is very sparingly soluble in water and methanol, and insoluble in acetone.

Preparation of $PtMe_3(gly)(lut)$ (V)

0.1356 g $[PtMe_3(gly)]_2$ (IV) (0.432 mmol monomer) was suspended in 25 ml methanol. 0.05 ml 3,5-lutidine (0.440 mmol) was added, and the stirred mixture was briefly heated under reflux, to give a colourless solution. The solution was evaporated to dryness to give a white solid which was washed with chloroform. Yield of crude product was 0.1393 g (77.0%).

A portion of the product was recrystallized by dissolving it in methanol, reducing the volume, and adding acetone. The compound was filtered off, washed with acetone, and dried under vacuum.

$PtMe_3(gly)(lut)$ is very soluble in methanol and dimethyl sulphoxide, but insoluble in acetone, chloroform, and water.

Preparation of $Na[PtMe_3(gly)_2]$ (VI)

0.1162 g $[PtMe_3(gly)]_2$ (IV) (0.370 mmol monomer) was suspended in a solution of 0.0353 g sodium glycinate (0.364 mmol) in 20 ml water. The stirred mixture was heated for fifteen minutes, until the solid dissolved, then cooled and filtered. The resultant solution was evaporated to an oil, which on trituration under acetone gave a white solid, which was dried at 110 °C under vacuum. $Na[PtMe_3(gly)_2]$ is extremely deliquescent. Analytical results are less reliable than for other compounds described here, since, even in a controlled humidity environment, the sample rapidly absorbed moisture during weighing. Yield based on $[PtMe_3(gly)]_2$ 85%.

Preparation of $Na[PtMe_3(IDA)]$ (X)

0.1968 g $(PtMe_3)_2SO_4\cdot 4H_2O$ (0.608 mmol $PtMe_3^+$) and 0.0844 g iminodiacetic acid (0.634 mmol) were

dissolved in 10 ml water. A solution of 0.053 g NaOH (1.33 mmol) in 3 ml water was added dropwise, with stirring. The precipitated $[PtMe_3(OH)]_4$ was filtered off, and the filtrate was evaporated to dryness on a steam bath. The resultant solid was ground, and repeatedly extracted with 10 ml portions of hot methanol (total volume approx. 150 ml). The methanol solution was filtered from the sodium sulphate residue, then evaporated to dryness. The white crystalline product was washed with acetone, and dried at 110 °C in a drying pistol over silica gel. Yield was 0.1468 g, 61.4%.

The product $Na[PtMe_3(IDA)]$ is very soluble in water, sparingly soluble in methanol, and insoluble in acetone. It slowly absorbs moisture on exposure to the atmosphere.

Preparation of $Na[PtMe_3(MIDA)]$ (XI)

0.2025 g $(PtMe_3)_2SO_4 \cdot 4H_2O$ (0.625 mmol $PtMe_3^+$) and 0.0970 g N-methyliminodiacetic acid (0.655 mmol) were dissolved in 4 ml water, and 0.05 g NaOH (1.25 mmol) in 3 ml water was added dropwise, with stirring. The filtrate after removal of $[PtMe_3(OH)]_4$ was evaporated to dryness, the complex was extracted with approx. 30 ml methanol, and the methanol solution, after sodium sulphate had been filtered off, was evaporated to dryness. The crude product was dissolved in 5 ml methanol, the solution was filtered, and diethyl ether was added to the filtrate to reprecipitate the product. Since the NMR spectrum still revealed the presence of impurities, the compound was again dissolved in 5 ml methanol. Acetone was added, and the mixture warmed briefly to give colourless crystals, which were filtered off, washed with acetone, and dried under vacuum. Yield of pure $Na[PtMe_3(MIDA)]$ was 32.6%.

The compound is very soluble in water and methanol, insoluble in acetone and ether. It is slightly hygroscopic.

Preparation of $Na[PtMe_3(HNTA)]$ (XII)

0.1900 g $(PtMe_3)_2SO_4 \cdot 4H_2O$ (0.586 mmol $PtMe_3^+$) and 0.1217 g nitrilotriacetic acid (0.637 mmol) were dissolved in 5 ml water, and 0.051 g NaOH (1.27 mmol) in 5 ml water was added. The solution remained clear. It was evaporated to dryness, and the product extracted from the sodium sulphate residue with 30 ml methanol. The methanol solution was evaporated to dryness to yield a white solid, which was dissolved in 5 ml methanol, and reprecipitated by addition of diethyl ether. Even after prolonged heating at 110 °C under vacuum, the product contained lattice water, as evidenced by analytical results and IR spectra.

Yield $Na[PtMe_3(HNTA)] \cdot H_2O$ 0.2116 g (76.8%). The compound is soluble in water and methanol, insoluble in acetone and ether.

Preparation of $Na_2[(PtMe_3)_2(EDTA)]$ (XV)

Method A

0.3076 g $(PtMe_3)_2SO_4 \cdot 4H_2O$ (0.949 mmol $PtMe_3^+$) and 0.1796 g $Na_2[H_2EDTA] \cdot 2H_2O$ (0.483 mmol) were mixed in 10 ml water, and 0.039 g NaOH, (0.975 mmol) in 5 ml water was added dropwise with stirring. A small quantity of $[PtMe_3(OH)]_4$ precipitated, and was filtered off. The filtrate was evaporated to dryness, ground, and extracted with methanol in a Soxhlet extractor for 3 days. Evaporation of the methanol solution to dryness gave $Na_2[(PtMe_3)_2(EDTA)]$ as a white crystalline solid, which was dried at 110 °C in a drying pistol. The PMR spectrum of this product showed it to contain a trace (~3%) of $Na[PtMe_3(H_2EDTA)]$ (XIII). Yield 0.2576 g (66.7%).

The product is soluble in water, very sparingly soluble in methanol, and insoluble in acetone. It is slightly hygroscopic.

Method B

0.2110 g $(PtMe_3)_2SO_4 \cdot 4H_2O$ (0.652 mmol $PtMe_3^+$) was dissolved in 3 ml water, and 0.2433 g $Na_2[H_2EDTA] \cdot 2H_2O$ (0.654 mmol) in 4 ml water was added. The solution remained clear. It was evaporated to 5 ml, and allowed to stand near 0 °C. Colourless crystals of H_4EDTA deposited, identified by IR spectrum and C, H, N analysis. The solution was decanted from the crystals, which were washed with 2 ml cold water. The combined solution was evaporated to dryness, and the product extracted and dried as above. Yield 0.1207 g, 45.5%. Product obtained by this method tended to contain more $Na[PtMe_3(H_2EDTA)]$ (XIII) as an impurity (~5%) than that prepared by method A.

Acknowledgements

We thank M. L. McEniery and I. McMahon for assistance in the initial stages of this work.

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