Reactions of Di- and Trimethylplatinum(IV) Complexes with *N*-(Phosphonomethyl)glycine (Glyphosate) and Iminobis(methylenephosphonic acid). Crystal structures of Three Dimethylplatinum(IV) Complexes with *N*-(Phosphonomethyl)glycine Coordinated Facially

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Reaction of "*cis*-$[Pt(CH_3)_2(OD)_4]^{2-}$" with *N*-(phosphonomethyl)glycine (glyphosate, H_3impa) in D_2O at pD 11 gave a mixture of two isomers of $[Pt(CH_3)_2(OD)_2$(impa-*N*,*O*)$]^{3-}$ (N and either carboxylate O (O_c) or phosphonate O (O_p) trans to methyl). When the pH of a similar solution in H_2O was decreased to 3.4, and the solution was allowed to stand, crystals of $[Pt(CH_3)_2$(Himpa-*N*,O_c,O_p)$(H_2O)]\cdot H_2O$ deposited. The crystal structure was determined by X-ray diffraction: space group *Pbca*; a = 7.937(6), b = 10.484(2), c = 26.795(6) Å; Z = 8; R = 0.030, for 1418 reflections. The isomer was that with N and O_p trans to the methyl groups. When an alkaline solution (pD 10.5) was allowed to stand, the isomer of $[Pt(CH_3)_2(OD)$(impa-*N*,O_c,O_p)$]^{2-}$ with N and O_c trans to methyl formed. *fac*-$[PtBr(CH_3)_2(H_2O)_3]^+$ with glyphosate gave isomers of $[PtBr(CH_3)_2$(Himpa-*N*,O_c,O_p)$]^-$. At high pH, where coordinate phosphonate was deprotonated, the preferred isomer had N and O_c trans to methyl, while at low pH, where coordinated phosphonate was protonated, the preferred isomer had N and O_p trans to methyl. The crystal structure of the silver salt of the latter isomer, Ag[$PtBr(CH_3)_2$(Himpa)], was determined by X-ray diffraction: space group $Pna2_1$; a = 8.4009(9), b = 12.790(2), c = 10.467(2) Å; Z = 4; R = 0.022, 928 reflections. The silver ion was bound by bridging bromide and by three O atoms to give an approximately tetrahedral environment about the metal and a two-dimensional network structure. UV irradiation of a D_2O solution containing the isomers of $[PtBr(CH_3)_2$(impa)$]^{2-}$ with N trans to methyl gave the thermodynamically most stable isomer, with N trans to bromide and O_c, O_p trans to methyl. Acidification and addition of silver ion gave crystals of $Ag_3[PtBr(CH_3)_2$(Himpa)$][PtBr(CH_3)_2$(impa)$]\cdot 1.5H_2O$, whose structure was determined by X-ray diffraction: space group $P2_1/c$; a = 13.78(2), b = 14.523(4) Å, c = 14.38(2) Å; β = 118.33(5)°; Z = 4; R = 0.044. The two different anionic complex units form the basis of an extended ribbon structure, linked together through three independent silver ions by triply-bridging bromide ions and oxygen atoms from both carboxylate and phosphonate groups. Iminobis(methylenephosphonic acid) (H_4idmp) with *fac*-$[Pt(CH_3)_3(D_2O)_3]^+$ in D_2O at pD 5.5 gave a complex with the ligand coordinated tridentate, but broadening of peaks from ligand protons was interpreted in terms of a rapid process in which metal–oxygen bonds were ruptured. $[PtBr(CH_3)_2(D_2O)_3]^+$ with D_2idmp^{2-}, on long standing at pD 4, gave $[PtBr(CH_3)_2(D_2$idmp-*N*,*O*,*O*′$)]^-$. "*cis*-$[Pt(CH_3)_2(OD)_4]^{2-}$" with (methylimino)bis(methylenephosphonate) (midmp^{4-}) in D_2O at pD 12.5 gave $[Pt(CH_3)_2(OD)_2$(midmp-*N*,*O*)$]^{4-}$, but when the solution was acidified, the ligand dissociated. The relative instability of complexes with iminobis(methylenephosphonate) ligands coordinated tridentate may be due to steric interactions between phosphonate oxygen atoms and other ligands bound to the metal.

Introduction

N-(phosphonomethyl)glycine, or glyphosate, $^+H_2N(CH_2CO_2H)(CH_2PO_3H^-)$ (H_3impa)[2], is well-known as the active component of the herbicide "Roundup" or "Zero" (Monsanto). Studies of the coordination properties of this substance have included determinations of stability constants for a wide range of divalent and trivalent metal ions[3,4] and IR spectroscopic and X-ray powder diffraction studies of solid transition metal complexes.[5] Our multinuclear NMR study of platinum(II) complexes with glyphosate and related ligands[6] was the first in which discrete structures could be assigned to metal complexes in solution. The ligand was didentate (N,O_p or N,O_c) in most complexes and *mer* tridentate (N,O_p,O_c) in $[PtCl($impa$)]^{2-}$. No solids were isolated. Solid H_3impa has been characterized by single-crystal X-ray structure determinations, which clearly show that the zwitterion form $^+H_2N(CH_2CO_2H)(CH_2PO_3H^-)$ exists in the solid state.[7] The crystal structures of calcium complexes have also been determined, showing interaction only between oxygen atoms and the calcium ion.[8] The only transition metal complex whose crystal structure has been determined is Na[Cu(impa)]$\cdot 3.5H_2O$.[9] In this polymeric structure, the geometry about Cu^{2+} is a distorted square pyramid. In the basal "plane", the metal is coordinated by the nitrogen atom, carboxylate oxygen, and phosphonate oxygen of one impa^{3-} ligand (approximately meridional) and a monodentate phosphonate oxygen of an adjacent

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(2) As in our previous paper,[6] the abbreviation H_3impa is used to indicate that a methylenephosphonic acid ("mp") and acetic acid ("a") group are bound to an imino ("i") nitrogen atom. Subscripts will be used to distinguish oxygen of a phosphonate group (O_p) from oxygen of a carboxyl group (O_c). Other abbreviations used: H_4idmp = iminobis(methylenephosphonic acid); H_4midmp = (methylimino)bis(methylenephosphonic acid); H_2ida = iminodiacetic acid; Hgly = glycine.

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Cu(impa)⁻ unit. The apical bond is a weak bond (length 2.28(2) Å) from a phosphonate oxygen atom already bound more strongly (length 1.99(2) Å) to another copper ion.

The closely related ligand iminodiacetate (ida^{2-}) strongly prefers facial tridentate (*N,O,O'*) coordination,[10-12] although it will bind didentate (*N,O*) when only two coordination sites are available[12-14] and meridional tridentate (*N,O,O'*) when this geometry is forced by either the configuration of other ligands[15] or by a square planar geometry about the metal ion, as in Pd(II)[16] and Pt(II)[12] complexes. The preference for facial coordination is usually ascribed to strain in the C–N–C angle in the meridional isomer. The longer C–P and P–O bond lengths in one chelate ring of glyphosate complexes compared with C–C and C–O bond lengths in the iminodiacetate chelate rings may well decrease the angle strain in meridionally coordinated glyphosphate, but it would be expected that facial tridentate (N,O_c,O_p) coordination would remain a common coordination mode. It is surprising then, that no complex has yet been characterized in which this coordination mode has been shown to exist.

In trimethylplatinum(IV) complexes, the three methyl groups are always facial,[17] and because the methyl groups have high trans effect, the metal–ligand bonds trans to them are labile.[18] Trimethylplatinum(IV) complexes are therefore ideally suited for the formation of complexes with ligands which can coordinate facial tridentate. For example, reaction of *fac*-$[Pt(CH_3)_3(H_2O)_3]^+$ with iminodiacetate gives *fac*-$[Pt(CH_3)_3(ida\text{-}N,O,O')]^-$.[19] We therefore set out to study the reactions of *fac*-$[Pt(CH_3)_3(H_2O)_3]^+$ with glyphosate, in the hope of obtaining a well-characterized compound with the ligand coordinated facially.

In dimethylplatinum(IV) complexes, the methyl groups are always cis. Metal–ligand bonds trans to methyl are labile, and those cis to methyl are inert.[20-22] The interactions of the different donor atoms of the glyphosate ligand with these different coordination sites allows subtle differences between the coordination preferences of these donor atoms to be probed. We have recently described[23] the complexes of iminodiacetate with dimethylplatinum(IV).

Multinuclear NMR spectroscopy is very useful for characterizing these complexes in solution. Each distinct methyl group bound to platinum gives a singlet in ^1H or ^{13}C NMR spectra, with "satellites" from coupling with ^{195}Pt ($I = {}^1/_2$, 34% abundance). The values of $^2J(Pt–CH_3)$ provide a reliable guide to the identity of the donor atom trans to methyl,[19,24,25] while values of $^1J(Pt–C)$ are less useful, being affected to a greater degree by the ligands cis to methyl.[26-28] The shift of the carboxylate carbon nucleus provides a useful indication of coordination of the carboxylate group, as incorporation in a five-membered *N,O* chelate ring causes a characteristic deshielding.[29-31] The phosphonate ^{31}P chemical shift may be similarly used, as incorporation in a five-membered chelate ring causes a marked deshielding.[6,32]

Crystals suitable for X-ray diffraction were obtained of three compounds containing glyphosate complexes of dimethylplatinum(IV), and their structures are also discussed in this paper.

Some reactions of the related ligands iminobis(methylenephosphonic acid) (H_4idmp) and (methylimino)bis(methylenephosphonic acid) (H_4midmp) have also been included for comparison.

Experimental Section

Starting Materials. Literature methods were used to prepare $[\{Pt(CH_3)_3(\mu_3\text{-}I)\}_4]$[33] and thence $[\{Pt(CH_3)_3\}_2(SO_4)(H_2O)_4]$[34] (which, on dissolution in water, gives *fac*-$[Pt(CH_3)_3(H_2O)_3]_2(SO_4)$), $[\{PtBr_2(CH_3)_2\}_n]$,[35] $[\{Pt(CH_3)_2(OH)_2(H_2O)_{1.5}\}_n]$,[35] and solutions of *fac*-$[PtBr(CH_3)_2(H_2O)_3]NO_3$ in H_2O and *fac*-$[PtBr(CH_3)_2(D_2O)_3]NO_3$ in D_2O.[21,23] A solution of the commercial herbicide "Roundup" was donated by Monsanto Ltd. Solid H_3impa was obtained by acidifying this solution with concentrated HCl, and allowing the free acid to crystallize. The ligands H_4idmp and H_4midmp were prepared as previously described.[6]

NMR Spectra. The 400-MHz ^1H and 100.4-MHz ^{13}C NMR spectra were obtained with the use of a JEOL GX-400 spectrometer with a dual $^1H/^{13}C$ probe as previously described.[23] The 50.3-MHz ^{13}C NMR spectra were obtained with the use of a Bruker AC-200F spectrometer fitted with either a 5-mm quad $^{13}C/^1H/^{15}N/^{19}F$ probe or 10-mm broad band tunable probe, with internal deuterium lock. Approximately 14 000 pulses were used, 3-s apart, tilt 45°, width 12 000 Hz, and 32K data points. The 25.05-MHz ^{13}C and 40.3-MHz ^{31}P NMR spectra were recorded on a JEOL FX-100 spectrometer with a 10-mm broad band tunable probe, external ^7Li lock, and double precision mode as previously described.[36] ^{13}C shifts are reported relative to external tetramethylsilane, with internal dioxane taken as 67.73 ppm. ^1H shifts are reported relative to the methyl peak of internal sodium 3-(trimethylsilyl)propanesulfonate. ^{31}P shifts are referenced to 85% H_3PO_4 in a coaxial capillary. All ^{13}C and ^{31}P spectra were ^1H-decoupled, and all shifts are positive to lower shielding.

Other Techniques. UV irradiation experiments were carried out with the use of a 1-L Hanovia photochemical reactor as previously described.[23] IR spectra were recorded with the use of a Perkin-Elmer 1600 Series FT spectrometer, on pressed KBr disks. Routine pH measurements were made with the use of narrow range indicator papers supplied by Riedel-de-Haen or Merck. More accurate measurements were made with an Activon combination glass/reference electrode and a Jenco pH meter. Meter readings for D_2O solutions were converted to pD measurements by application of the correction[37]

$$pD = \text{meter reading} + 0.4 \quad (1)$$

Microanalyses were carried out either by the microanalytical service in this Department or by the Australian Microanalytical Service, Melbourne, Australia.

Preparation of Na[Pt(CH$_3$)$_3$(Himpa-*N,O$_c$,O$_p$*)] (Sodium Salt of 1a). $[\{Pt(CH_3)_3\}_2(SO_4)(H_2O)_4]$ (0.2073 g, 0.64 mmol Pt) was dissolved in 3 mL of water, and solid H_3impa (0.1090 g, 0.64 mmol) was added. Dilute NaOH solution was added to dissolve the glyphosate and to increase the pH to approximately 5.5. The solution was filtered, and the filtrate was taken to dryness in a stream of air. The residue was dried further over silica gel in a vacuum desiccator. The residue was extracted into dry methanol (5 × 1 mL). The methanol solution was filtered and then concentrated almost to dryness in a stream of air. Excess acetone was added to produce an oil, which, on trituration, became a white hygroscopic solid. The solid was dried in a vacuum desiccator over silica gel. The

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yield was 0.07 g (25%). The IR spectrum showed a strong peak from ν(C=O) at 1624 cm^{-1}. Anal. Calcd for $C_6H_{15}NNaO_5PPt$: C, 16.8; H, 3.5; N, 3.3. Found: C, 17.0; H, 3.9; N, 3.1.

Preparation of [Pt(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)(H$_2$O)]·H$_2$O (O$_c$ Trans to H$_2$O, 5a) (Compound A). [{Pt(CH$_3$)$_2$(OH)$_2$(H$_2$O)$_{1.5}$}$_n$] (0.0864 g, 0.30 mmol of Pt) and H$_3$impa (0.0561 g, 0.33 mmol) were suspended in 5 mL of water, and the mixture was warmed on a steam bath for 30 min and then filtered. The filtrate (pH approximately 3) was allowed to stand in the dark. After 1 week, a colorless crystalline solid had deposited, which was filtered off, washed with cold water, and dried in a vacuum desiccator over silica gel. The yield was 0.0291 g (24%). The IR spectrum showed a broad band from O–H stretching at 3400 cm^{-1}, a strong band from ν(C=O) at 1618 cm^{-1}, and a N–H stretching band at 3257 cm^{-1}. Anal. Calcd for $C_5H_{16}NO_7PPt$: C, 14.0; H, 3.8; N, 3.3. Found: C, 14.4; H, 3.6; N, 3.4.

Preparation of Ag[PtBr(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)] (O$_c$ Trans to Br, Silver Salt of 6a) (Compound B). A solution of 0.204 M *fac*-[PtBr(CH$_3$)$_2$(H$_2$O)$_3$]NO$_3$ (1 mL, 0.204 mmol) was added to solid H$_3$impa (0.0312 g, 0.185 mmol). The mixture was stirred while 1 M KOH solution was added dropwise until the solid dissolved, and the pH reached 3. The solution was warmed on a steam bath for 2 min and then filtered through a cotton wool plug into a small vial. An aqueous solution of AgNO$_3$ (0.0330 g, 0.194 mmol, in 1 mL) was added, and the vial was left to stand in the dark. Yellow crystals formed over several days as large aggregates with saw-tooth morphology (scratching the side of the vial caused precipitation of a fine yellow powder). Individual crystals were well-formed prisms with excellent diffraction characteristics. The IR spectrum showed a sharp peak from N–H stretching at 3248 cm^{-1} and a strong band from ν(C=O) at 1676 cm^{-1}. Anal. Calcd for $C_5H_{12}AgBrNO_5PPt$: C, 10.4; H, 2.1; N, 2.4. Found: C, 10.2; H, 2.0; N, 2.4.

Preparation of Ag$_3$[PtBr(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)][PtBr(CH$_3$)$_2$(impa-*N*,*O*$_c$,*O*$_p$)]·1.5H$_2$O (Silver Salt with Mixed Anions, 8a/b, Both with N Trans to Br) (Compound C). A solution containing the two isomers of [PtBr(CH$_3$)$_2$(impa-*N*,*O*$_c$,*O*$_p$)]$^{2-}$ with N trans to methyl (**6b** + **7b**) in D$_2$O at pD 6.5 in a 5-mm glass NMR tube was irradiated with a mercury lamp until isomerization to **8b** (N trans to Br) was complete (monitored by ^{1}H NMR). The pD of the solution was then adjusted to 2.7 with dilute D$_2$SO$_4$, and a large excess of AgNO$_3$ in aqueous solution was added. A white precipitate (Ag$_2$SO$_4$) immediately formed and was removed by centrifugation. The supernatant solution was allowed to stand for 1 week, during which time very pale yellow crystals deposited. The supernatant solution was removed by pipet. Its ^{1}H NMR spectrum did not show any peaks assignable to a platinum complex. The crystals were washed with a few drops of ^{1}H$_2$O and then dried in a vacuum desiccator over silica gel. The IR spectrum showed a strong band from ν(C=O) at 1618 cm^{-1}. Microanalysis of the bulk sample did not fit well with the overall composition present in the crystal examined, and it is likely that this material consisted of a mixture of silver salts of the anions **8a/b** in different protonation states. Anal. Calcd for $C_{10}H_{26}Ag_3Br_2N_2O_{11.5}P_2Pt_2$: C, 9.3; H, 2.0; N, 2.2. Found: C, 10.1; H, 2.2; N, 2.4.

Determination of Crystal Structures. For each of compounds A–C a crystal with almost equidimensions was mounted with epoxy resin on a glass fiber for data collection. X-ray data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å). Crystal data and other numerical details of structure determination and refinement are given in Table 1. Unit cell dimensions were obtained from the angle data for 25 reflections in the range 28° < 2θ < 32°. A maximum change of 0.3% (A), 1.9% (B), and 6.4% (C) in the intensities of three standard reflections monitored every 100 reflections during the respective data collection periods indicated negligible crystal decomposition. The structures were solved by the heavy-atom method of SHELXS 86[38] and refined by full-matrix least-squares (SHELX 76[39]). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the refinement at fixed calculated positions (d(C–H) = 1.08 Å) with isotropic U values set at 0.05 Å^2. Empirical absorption corrections were applied using the CAD-4 structure determination package.[40]

Table 1. Crystallographic Data for [Pt(CH$_3$)$_2$(Himpa)(H$_2$O)]·H$_2$O (Compound A), Ag[PtBr(CH$_3$)$_2$(Himpa)] (Compound B), and Ag$_3$[PtBr(CH$_3$)$_2$(Himpa)][PtBr(CH$_3$)$_2$(impa)]·1.5H$_2$O (Compound C)

	compd A	compd B	compd C
formula	$C_5H_{16}NO_7PPt$	$C_5H_{12}AgBrNO_5PPt$	$C_{10}H_{20}Ag_3Br_2N_2O_{11.5}P_2Pt_2$
fw	428.3	580.0	1287.8
cryst system	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	*Pna*2$_1$	*P*2$_1$/*c*
a (Å)	7.937(6)	8.4009(9)	13.78(2)
b (Å)	10.484(2)	12.790(2)	14.523(4)
c (Å)	26.795(6)	10.467(2)	14.38(2)
β (deg)			118.33(5)
V (Å^3)	2230(1)	1124.7(3)	2534(5)
Z	8	4	4
D_{calc} (g cm^{-3})	2.55	3.42	3.38
μ (cm^{-1})	134.0	186.7	166.8
T (K)	297	296	298
radiation	Mo Kα	Mo Kα	Mo Kα
λ (Å)	0.710 73	0.710 73	0.710 73
R	0.030	0.022	0.044
R_w	0.034	0.024	0.045

Literature values[41] were used for neutral atom scattering factors and for f' and f'' terms for anomalous dispersion. In compound **B**, a parallel refinement using the enantiomorphic coordinate set enabled the absolute configuration of the molecules in this crystal to be determined on the basis of a statistical significance test.

Determination of Acid Dissociation Constants for Coordinated Phosphonate Groups. When the pD of a D$_2$O solution containing one of the methylplatinum complexes with tridentate glyphosate was adjusted with dilute D$_2$SO$_4$ or KOH/D$_2$O, changes were observed in δ_H for the Pt–CH$_3$ groups due to deuteronation/dedeuteronation of the coordinted phosphonate group. These may be related to the acid dissociation constant K_a by the form of the Henderson–Hasselbach equation:[42]

$$pK_a\ (D_2O) = pD + \log\{(\delta - \delta_B)/(\delta_A - \delta)\} \quad (2)$$

where δ is the observed shift and δ_A and δ_B are the shifts in acid and base, respectively. A number of measurements of δ_H were made in the pD range where the shift was most sensitive to changes in pD (*e.g.*, 12 measurements for **6a/b**), pK_a values were calculated from each measurement, and these values were averaged.

Results

Selected NMR data are listed in Table 2, and selected bond lengths and angles for the dimethylplatinum glyphosate complexes in compounds A–C are listed in Table 3. Atomic coordinates for non-hydrogen atoms in these structures are given in Tables 4–6, respectively.

All ^{1}H and ^{13}C NMR spectra were consistent with the structures proposed below. The nonequivalent protons of the methylene group of the acetate arm of glyphosate in each complex gave an AB pattern. The weaker peaks from the AB part of the ABX spectrum arising from those isotopomers containing ^{195}Pt were sometimes also visible. The ^{13}C NMR spectra of these methylene carbon atoms, and of the adjacent carboxyl carbon, each gave a singlet, sometimes with resolvable coupling to ^{195}Pt. The methylene protons of the methylenephosphonate arm gave the AB part of an ABX spectrum (X = ^{31}P) superimposed on the AB part of an ABMX spectrum (M = ^{195}Pt). The ^{13}C spectrum of the methylene carbon atom adjacent to the phosphonate group appeared as a doublet (^1J(P–C) approximately 140 Hz), again, sometimes with observable satellites from platinum coupling.

Satellite peaks from Pt–CH$_3$ coupling in ^{1}H NMR spectra run at 400 MHz were often broadened, especially in complexes with hydroxo or aqua ligands cis to the methyl groups (*cf.*, iminodiacetate analogues[23]). This broadening can be attributed to rapid chemical shift anisotropy-induced relaxation of ^{195}Pt nuclei at

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(42) Edward, J. T.; Leane, J. B.; Wang, I. C. *Can. J. Chem.* **1962**, *40*, 1521.

Table 2. Selected NMR Data (in D_2O)

compd	structure	pD	^{1}H(Pt–CH_3) δ_H	^2J(Pt–CH_3) (Hz)	trans donor atom	δ_P	δ_C(carboxyl)
$[Pt(CH_3)_3$(Himpa-$N,O_c,O_p)]^-$ (partially deprotonated)	**1a/b**	6	0.78	69.0	N	33.8	186.6
			0.86	78.1	O_c		
			0.80	80.9	O_P		
$[Pt(CH_3)_2(OH)_2$(impa-$N,O_p)]^{3-}$	**2b**	11	1.37[a]	*b*		28.2[c]	178.7
			1.34[a]	*b*			
$[Pt(CH_3)_2(OH)_2$(impa-$N,O_c)]^{3-}$	**3b**	11	1.36[a]	*b*		13.8[d]	185.4
			1.32[a]	*b*			
$[Pt(CH_3)_2(OH)$(impa-$N,O_c,O_p)]^{2-}$	**4b**	9.4	1.43	68.4	N	30.4	188.8
			1.42	79.7	O_P		
	5b	9.4	1.56	*b*	N	39.1	185.9
			1.45	*b*	O_c		
$[Pt(CH_3)_2$(Himpa-$N,O_c,O_c)(H_2O)]$	**4a**	3.4				35.5	187.9
	5a	3.4				44.1	
$[Pt(CH_3)_2$(Himpa-$N,O_c)(H_2O)_2]$	**3a**	3.4				15.4	
$[Pt(CH_3)_2$(Himpa-$N,O_p)(H_2O)_2]$	**2a**	3.4				28.4	
$[PtBr(CH_3)_2$(Himpa-$N,O_c,O_p)]^-$	**6a**	2.0	1.65	66.8	N	35.4	188.2
			1.72	79.3	O_P		
	6a/b	5.7	1.62	67.1	N	33.9	188.6
			1.68	78.7	O_P		
	7a/b	5.7	1.61	66.5	N	39.2	184.4
			1.72	77.5	O_c		
$[PtBr(CH_3)_2$(impa-$N,O_c,O_p)]^{2-}$	**7b**	7.6	1.60	67.9	N	38.8	
			1.72	75.9	O_c		
	8b	7	1.60	74.5	O_c	29.1	
			1.51	75.4	O_p		
$[Pt(CH_3)_3$(Hidmp-$N,O,O')]^{2-}$	**9**	5.5	0.87	80.0	O_p	38.0	
			0.76	68.7	N		
$[PtBr(CH_3)_2(H_2$idmp-$N,O)(H_2O)]^-$	**12**	4	1.81[e]	*b*		34.0	
			1.78[e]	*b*		16	
	13	4	1.80[e]	*b*		32.9	
			1.73[e]	*b*		16	
$[PtBr(CH_3)_2(H_2$idmp-$N,O,O')]^-$	**11**	4	1.82	78.1	O_p	45.9[f]	
			1.67	65.3	N	39.0[g]	
$[PtBr(CH_3)_2(H_2$midmp-$N,O,O')]^-$	**14**	4				41.1[f]	
						32.9[g]	
$[Pt(CH_3)_2(OH)_2$(midmp)$]^{4-}$	**15**	12.5	1.45	*b*		13.9[h]	
			1.33	*b*		31.2[i]	

[a] Assignments for methyl peaks of **2b** and **3b** could be interchanged. [b] Satellite peaks too weak to allow measurement of J(Pt–CH_3). [c] J(Pt–P) = 17.1 Hz. [d] J(Pt–P) = 46.4 Hz. [e] Assignments for the methyl peaks of **12** and **13** could be interchanged. [f] Phosphonate trans to Br. [g] Phosphonate trans to CH_3. [h] J(Pt–P) = 42.7 Hz. [i] J(Pt–P) = 17.1 Hz.

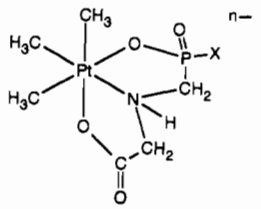
Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Platinum Complexes

	compd A complex **4a**	compd B complex **6a**	compd C[a] complex **8a**	compd C[a] complex **8b**
Bond Lengths				
Pt–O(1)(H_2O)	2.025(8)			
Pt–Br		2.442(1)	2.427(4)	2.450(4)
Pt–C(6)	2.01(1)	2.08(1)	2.02(2)	2.03(2)
Pt–C(7)	2.04(1)	2.04(1)	2.05(2)	2.04(2)
Pt–N(3)	2.216(8)	2.22(1)	2.06(1)	2.04(1)
Pt–O(51)[b]	1.998(7)	2.003(9)	2.17(1)	2.19(1)
Pt–O(11)[c]	2.222(6)	2.254(9)	2.223(9)	2.21(1)
P–O(11)	1.536(7)	1.521(9)	1.53(1)	1.57(1)
P–O(12)	1.571(7)	1.569(9)	1.47(1)	1.51(1)
P–O(13)	1.503(8)	1.477(9)	1.56(1)	1.50(1)
Bond Angles				
N(3)–Pt–O(51)	82.4(3)	81.2(4)	82.5(5)	82.0(5)
N(3)–Pt–O(11)	84.1(3)	84.0(4)	87.5(4)	87.7(4)
C(2)–N(3)–C(4)	113.6(8)	116.0(9)	113.0(12)	114.1(12)
O(11)–P–O(12)	106.5(4)	106.1(6)	115.4(6)	111.3(6)
O(11)–P–O(13)	114.2(4)	115.7(6)	109.5(6)	111.4(7)
O(12)–P–O(13)	111.5(4)	111.7(6)	113.1(7)	116.0(7)
O(11)–P–C(2)	107.5(4)	106.9(6)	104.9(6)	102.3(6)

[a] In figures and text, the labels for atoms in **8a** all have a final "2", and the labels for atoms in **8b** all have a final "1", which are omitted in this table. [b] Carboxylate. [c] Phosphonate.

high magnetic field strengths.[43] While ^{1}H spectra of most samples were run at 400 MHz to provide adequate dispersion, some spectra were also recorded at 100 MHz to allow accurate measurement of these coupling constants.

Reactions of Glyphosate with *fac*-$[Pt(CH_3)_3(H_2O)_3]^+$. Equimolar quantities of *fac*-$[Pt(CH_3)_3(D_2O)_3]^+$ and $Dimpa^{2-}$ were allowed to react in D_2O at pD 6. All NMR data were consistent with the formulation of the complex present as $[Pt(CH_3)_3$(Dimpa-$N,O_c,O_p)]^-$ (**1a**)in rapid equilibrium with $[Pt(CH_3)_3$(impa-$N,O_c,O_p)]^{2-}$ (**1b**). For example, the ^{1}H NMR spectrum showed three singlets of equal intensity, each with satellites from coupling with ^{195}Pt, from the Pt–CH_3 groups. The Pt–CH_3 coupling constants corresponded to methyl trans to N (69.0 Hz) and two O-donor groups (78.1, 80.9 Hz).[19,24,25] In the ^{31}P NMR spectrum, a sharp peak was observed at 33.8 ppm. This shift corresponds to a phosphonate group incorporated in a five-membered chelate ring.[6,32] In the ^{13}C NMR spectrum, the carboxylate carbon resonated at 186.6 ppm, characteristic of carboxylate in a five-membered chelate ring.[29–31]



1a X = OH, n = 1
1b X = O, n = 2

(43) Lallemand, J. Y.; Soulie, J.; Chottard, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Non-Hydrogen Atoms of Compound **A**, $[Pt(CH_3)_2(Himpa)(H_2O)]\cdot H_2O$

atom	*x*	*y*	*z*	*U*(eq)[a]
Pt(1)	1.01844(4)	0.22491(4)	0.15707(1)	0.0212(2)
P(1)	0.9177(3)	0.2640(2)	0.04443(9)	0.0247(8)
O(1)	1.2501(9)	0.1500(8)	0.1450(3)	0.034(3)
O(2)	0.2978(10)	0.0422(8)	0.0606(3)	0.041(3)
O(11)	1.0309(8)	0.3256(7)	0.0842(2)	0.032(2)
O(12)	0.7380(8)	0.3247(6)	0.0509(2)	0.0307(19)
O(13)	0.9812(9)	0.2788(8)	−0.0082(3)	0.036(3)
O(51)	0.7929(8)	0.3039(7)	0.1689(2)	0.031(2)
O(52)	0.5227(8)	0.2920(8)	0.1536(3)	0.042(3)
N(3)	0.8660(10)	0.0838(8)	0.1152(3)	0.027(3)
C(2)	0.8920(13)	0.1004(10)	0.0608(4)	0.032(3)
C(4)	0.6903(12)	0.1104(10)	0.1317(5)	0.035(3)
C(5)	0.6653(12)	0.2439(9)	0.1521(4)	0.026(3)
C(6)	1.0086(17)	0.1248(13)	0.2211(5)	0.041(4)
C(7)	1.1301(16)	0.3692(11)	0.1959(4)	0.037(4)

[a] *U*(eq) = one-third of the trace of the orthogonalized U.

Table 5. Atomic Coordinates and Thermal Parameters (Å²) for $Ag[Pt(CH_3)_2Br(Himpa)]$ (Compound **B**)

atom	*x*	*y*	*z*	*U*(eq)
Pt	0.23897(5)	0.06995(3)	1.000[a]	0.0169(2)
Ag	0.4300(1)	0.0806(1)	0.6161(2)	0.0369(6)
Br	0.4797(1)	0.0420(1)	0.8774(2)	0.0297(7)
C(6)	0.1963(17)	0.2109(10)	0.9077(16)	0.036(8)
C(7)	0.3581(14)	0.1557(10)	1.1341(13)	0.027(7)
P	0.1730(4)	−0.1691(3)	1.10532(3)	0.019(1)
O(11)	0.2838(11)	−0.0832(7)	1.1002(11)	0.027(5)
O(12)	0.0170(10)	−0.1592(7)	1.1347(10)	0.028(5)
O(13)	0.2383(10)	−0.2762(8)	1.0571(11)	0.033(5)
C(2)	0.1221(14)	−0.1377(9)	0.8892(12)	0.021(7)
N(3)	0.0796(12)	−0.0250(9)	0.8765(11)	0.025(6)
C(4)	−0.0870(16)	0.0048(11)	0.9177(13)	0.026(7)
C(5)	−0.0894(15)	0.0471(11)	1.0507(12)	0.020(6)
O(51)	−0.0370(10)	0.0854(6)	1.0999(10)	0.024(5)
O(52)	−0.2142(10)	0.0429(8)	1.1135(11)	0.031(5)

[a] Coordinated fixed.

The ^{13}C NMR spectrum showed three signals, each with satellites, from the carbon atoms of the methyl groups (−10.14 ppm, *J*(Pt–C) = 693 Hz; −13.51 ppm, *J*(Pt–C) = 754 Hz; −14.05, *J*(Pt–C) = 781 Hz). The Pt–C coupling constants allowed assignment of the resonance at −10.1 ppm to methyl trans to nitrogen. Both 25.05- and 50.3-MHz ^{13}C NMR spectra showed a splitting (2.8 Hz) in this signal (the splitting was not resolved in the 100.4-MHz spectrum because of increased line width). From the lack of field dependence, it is evident that the splitting must represent a coupling interaction, and the only possibility is a long-range ^{13}C–Pt–N–C–^{31}P coupling. An analogous 4-bond coupling, ^{15}N–Pt–N–C–^{31}P, has been observed in diammineplatinum(II) complexes with iminobis(methylenephosphonate).[6]

Addition of acid or base to produce **1a** or **1b**, respectively, caused changes in the ^1H NMR spectrum. The methyl group whose shift and Pt–CH_3 coupling constant were most sensitive to the change in pD was assigned as that trans to phosphonate oxygen. The value of pK_a (D_2O) was estimated as 6.2 ± 0.1.

Hydroxo- and Aquadimethylplatinum(IV) Complexes with Glyphosate. (Scheme 1). When solutions of "$[Pt(CH_3)_2(OD)_4]^{2-}$"[44] and $impa^{3-}$ in D_2O at pD 11 were mixed, the NMR spectra of the solution showed two sets of peaks of approximately equal intensity. The ^{31}P NMR spectrum showed a peak at 28.2 ppm corresponding to coordinated phosphonate and a peak at 13.8 ppm corresponding to uncoordinated phosphonate. The ^{13}C NMR spectrum showed a peak at 185.4 ppm, corresponding to coordinated carboxylate, and a peak at 178.7 ppm from uncoordinated carboxylate. These spectra may be interpreted in terms of the formation of the two isomers of $[Pt(CH_3)_2(OD)_2(impa\text{-}N,O)]^{3-}$ with the glyphosate ligand didentate trans to the methyl groups: *viz.*, $[Pt(CH_3)_2(OD)_2(impa\text{-}N,O_c)]^{3-}$ (**3b**) and $[Pt(CH_3)_2(OD)_2(impa\text{-}N,O_p)]^{3-}$ (**2b**). In the Pt–CH_3 region of the ^1H NMR spectrum, there were four peaks of equal intensity. The satellite peaks from coupling to ^{195}Pt were broad and overlapping, so no coupling constants were estimated. It was therefore difficult to assign these peaks to particular isomers.

At pD 11, there was little change in these spectra if the solution was heated or allowed to stand. In platinum(IV) complexes containing monodentate N-bound glycinate cis to Pt–OH (at an "inert" site), ring closure to give a complex of chelated glycinate does not readily occur,[45,46] and $[Pt(CH_3)_2(OH)_2(ida\text{-}N,O)]^{2-}$ does not form a complex with tridentate *N,O,O'*-iminodiacetate at high pH.[23] A decrease in pH in these systems allows some platinum–aqua complex to be present at equilibrium, so that chelate ring closure can occur. When the pD of the solution containing **2** and **3** was decreased to 9.4 by addition of D_2SO_4, new peaks slowly grew, corresponding to the isomers of $[Pt(CH_3)_2(OD)(impa\text{-}N,O_c,O_p)]^{2-}$, with glyphosate coordinated tridentate. One isomer was dominant (by a factor of approximately 4:1). This complex gave a ^{31}P NMR peak at 39.1 ppm and a carboxylate ^{13}C peak at 185.9 ppm. The lesser isomer gave a ^{31}P peak at 30.4 ppm and a carboxylate ^{13}C peak at 188.8 ppm. On the basis of comparisons of these shifts with those of phosphorus and carbon in the chelate rings of the complexes with didentate glyphosate, **2** and **3**, respectively, the major isomer was assigned as **5b**, with carboxylate and nitrogen trans to methyl, and the minor isomer as **4b**, with phosphonate and nitrogen trans to methyl.

Table 6. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Non-Hydrogen Atoms in Compound **C**, $Ag_3[PtBr(CH_3)_2(Himpa)][PtBr(CH_3)_2(impa)]\cdot 1.5H_2O$

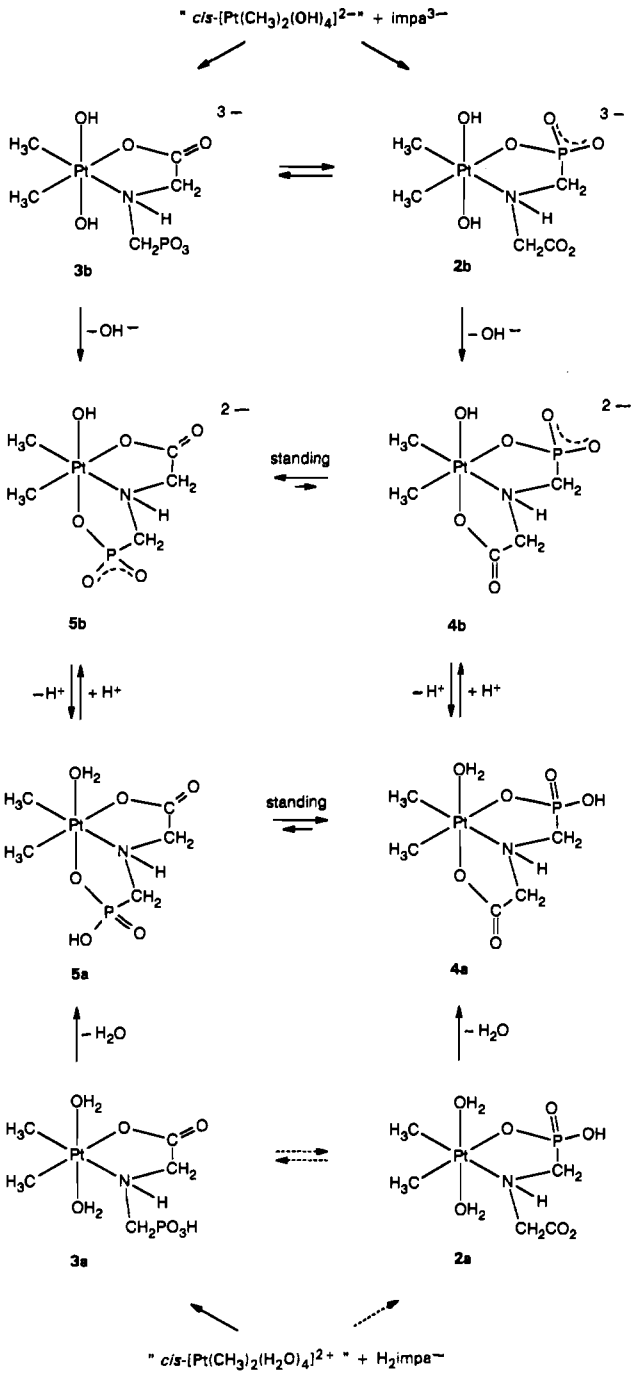
atom	*x*	*y*	*z*	*U*(eq)[a]
Pt(1)	0.20085(4)	0.33898(4)	0.62568(4)	0.0224(2)
Pt(2)	0.29376(4)	0.64407(4)	0.32815(4)	0.0197(2)
Ag(1)	−0.0869(1)	0.3942(1)	0.4459(1)	0.0527(5)
Ag(2)	0.3995(1)	0.4682(1)	0.5257(1)	0.0553(6)
Ag(3)	0.1368(1)	0.4848(1)	0.3945(1)	0.0512(5)
Br(1)	0.0923(1)	0.3126(1)	0.4352(1)	0.0339(5)
Br(2)	0.2793(1)	0.4786(1)	0.3019(1)	0.0368(5)
P(1)	0.3329(3)	0.5239(2)	0.6980(3)	0.024(1)
P(2)	0.4962(3)	0.7115(3)	0.5343(3)	0.024(1)
O(111)	0.2746(8)	0.4633(6)	0.5959(8)	0.028(3)
O(112)	0.4586(7)	0.6235(6)	0.4674(6)	0.022(3)
O(121)	0.2517(8)	0.5869(7)	0.7091(8)	0.033(4)
O(122)	0.6159(8)	0.7282(7)	0.5885(8)	0.033(3)
O(131)	0.4349(9)	0.5690(8)	0.706(1)	0.043(4)
O(132)	0.4445(9)	0.7148(7)	0.6103(9)	0.037(4)
O(511)	0.0764(8)	0.4293(7)	0.6319(8)	0.031(3)
O(512)	0.2188(9)	0.6411(7)	0.4310(8)	0.029(3)
O(521)	0.0380(9)	0.4891(8)	0.7519(9)	0.040(4)
O(522)	0.139(1)	0.7391(9)	0.492(1)	0.054(5)
N(31)	0.284(1)	0.3708(8)	0.7827(9)	0.027(4)
N(32)	0.310(1)	0.7819(8)	0.3656(9)	0.027(4)
C(21)	0.378(1)	0.437(1)	0.804(1)	0.029(5)
C(22)	0.428(1)	0.804(1)	0.443(1)	0.034(5)
C(41)	0.203(1)	0.406(1)	0.817(1)	0.036(5)
C(42)	0.233(1)	0.804(1)	0.443(1)	0.034(5)
C(51)	0.098(1)	0.447(1)	0.728(1)	0.028(5)
C(52)	0.194(1)	0.721(1)	0.450(1)	0.041(6)
C(61)	0.324(1)	0.258(1)	0.633(1)	0.042(6)
C(62)	0.363(1)	0.660(1)	0.233(1)	0.038(6)
C(71)	0.135(1)	0.226(1)	0.658(1)	0.043(6)
C(72)	0.142(1)	0.666(1)	0.200(1)	0.037(5)
O(100)	0.371(2)	0.264(1)	0.571(1)	0.088(7)
O(200)	0.893(3)	0.011(2)	0.523(2)	0.10(3)

[a] *U*(eq) = one-third of the trace of the orthogonalized U.

(44) For convenience, the complex mixture of species obtained in solution when $[\{Pt(CH_3)_2(OH)_2(H_2O)_{1.5}\}_n]$ dissolves in dilute alkali[27] will be designated "$[Pt(CH_3)_2(OH)_4]^{2-}$". Similarly, when it is dissolved in dilute acid, it will be designated "$[Pt(CH_3)_2(H_2O)_4]^{2+}$", even though some water molecules are probably deprotonated.

(45) Grinberg, A. A.; K'ang, Y. *Zh. Neorg. Khim.* **1962**, *7*, 2304.
(46) Agnew, N. H.; Appleton, T. G.; Hall, J. R. *Inorg. Chim. Acta* **1980**, *41*, 85.

Scheme 1



When more D_2SO_4 solution was added to decrease the pD of the solution to 3.4, the immediate reactions were deuteronation of coordinated OD^- and phosphonate groups. Chelate ring closure was now facile, and peaks due to complexes with glyphosate didentate, **2a** and **3a**, rapidly disappeared, so that the only ^{31}P NMR peaks present were soon those of the isomers of $[Pt(CH_3)_2(Dimpa\text{-}N,O_c,O_p)(D_2O)]$, **4a** and **5a** (shifted from those of the base forms **4b** and **5b**—see Table 2). The dominant isomer of the complex with glyphosate tridentate also changed, over several days, to that with phosphonate trans to methyl, **4a**. Colorless crystals of this compound deposited over several days (compound **A**), which analyzed (after washing with ^1H_2O) for $[Pt(CH_3)_2(Himpa)(H_2O)]\cdot H_2O$ and whose crystal structure confirmed the structure **4a** (see below).

Reaction of a D_2O solution of "$[Pt(CH_3)_2(D_2O)_4]^{2+}$" at pD 3.5 with H_3impa gave a solution whose ^{31}P NMR spectrum after a few minutes showed two peaks, apart from that due to free D_2impa^-: a peak due to $[Pt(CH_3)_2(Dimpa\text{-}N,O_c,O_p)(D_2O)]$ (isomer **4a**, with phosphonate trans to methyl) and a peak at 15.4 ppm assigned to $[Pt(CH_3)_2(Dimpa\text{-}N,O_c)(D_2O)_2]$ (**3a**), with didentate glyphosate coordinated through N and carboxylate O trans to methyl. After 2 h, only a peak due to **4a** was observed, and crystals of compound **A** began to deposit.

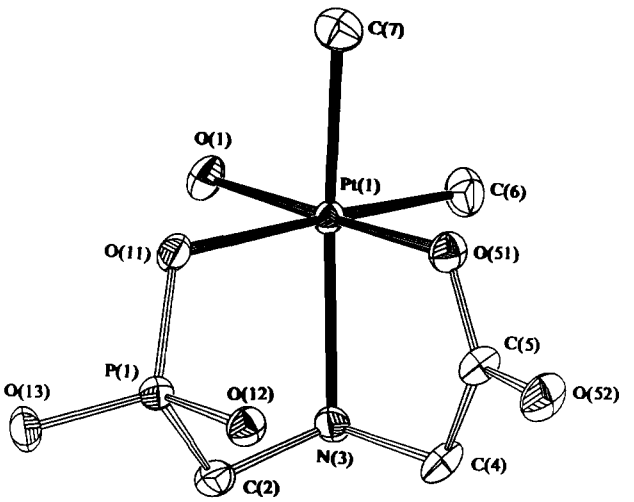


Figure 1. PLATON diagram showing the molecule of $[Pt(CH_3)_2(Himpa)(H_2O)]$ (**4a**) in compound **A**, with 30% probability ellipsoids. The structure of the anion $[PtBr(CH_3)_2(Himpa)]^-$ (**6a**) in compound **B** is similar, with Br replacing H_2O (O(1)).

These crystals were sparingly soluble only in water or acid but dissolved readily in base. The ^{31}P NMR spectrum of a solution in D_2O at pD 10.5, run immediately after dissolution, showed only the peak at 30.4 ppm, corresponding to $[Pt(CH_3)_2(OD)(impa\text{-}N,O_c,O_p)]^{2-}$ (isomer **4b**, with phosphonate trans to methyl). When the solution was allowed to stand, this peak slowly decreased, while that due to isomer **5b** slowly grew and eventually became dominant.

Description of the Structure of $[Pt(CH_3)_2(Himpa\text{-}N,O_c,O_p)(H_2O)]\cdot H_2O$, Compound A. The structure shows discrete molecules of $[Pt(CH_3)_2(Himpa\text{-}N,O_c,O_p)(H_2O)]$, with the expected octahedral geometry about the Pt atom, cis methyl groups, and glyphosate coordinated facial tridentate, with N and phosphonate oxygen trans to methyl groups (isomer **4a**). The structure of the complex, with atom labeling, is shown in Figure 1. Selected bond lengths and angles are given in Table 3. Internal bond lengths and angles within the glyphosate ligand are similar to those in solid H_3impa[7] and in glyphosate compounds whose structures have been determined.[8,9]

The P–O bond length to the coordinated oxygen O(11) is 1.536(7) Å. The remaining P–O bond lengths are quite different: P–O(12) = 1.571(7) Å and P–O(13) = 1.503(8) Å. This allows us to assign O(12) as the oxygen atom which carries the proton. These bond lengths are similar to the corresponding P–O bond lengths in solid glyphosate, in which the phosphonate group carries a single proton.[7]

The crystal structure is stabilized by a hydrogen-bonding network involving the coordinated water molecule O(1) (Figure 2). There is a single hydrogen bond between the lattice water, O(2), and coordinated water (O(1)–O(2) = 2.56(1) Å), while a bifurcated system links O(2) with the phosphonate O-atoms O(11) ($^3/_2 - x$, $^1/_2 + y$, z) (2.72(1) Å) and O(13) ($-^1/_2 + x$, $^1/_2 - y$, $-z$) (2.76(1) Å). The coordinated water also forms an intermolecular association with an uncoordinated carboxylate O-atom, $O(52)^1$ ($-1 + x$, y, $1 + z$) (O(1)–$O(52)^1$ = 2.63(1) Å).

Each molecule of **4a** is chiral, but both enantiomers are present in equal proportions in the unit cell of solid **A**.

Reactions of Glyphosate with *fac*-$[PtBr(CH_3)_2(H_2O)_3]^+$ (Scheme 2). When a solution of *fac*-$[PtBr(CH_3)_2(D_2O)_3]NO_3$ in D_2O was added to an equimolar quantity of H_3impa, and the pD of the solution was adjusted to 2.0, NMR spectra after several hours'

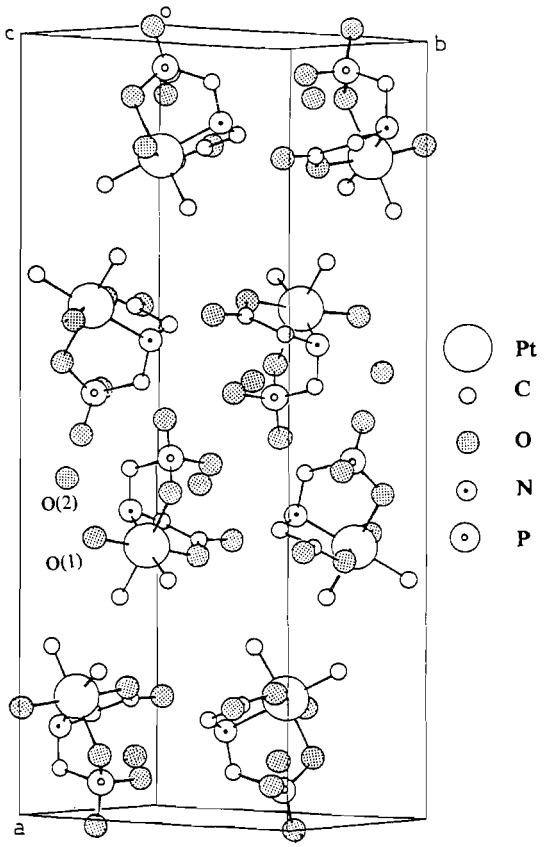
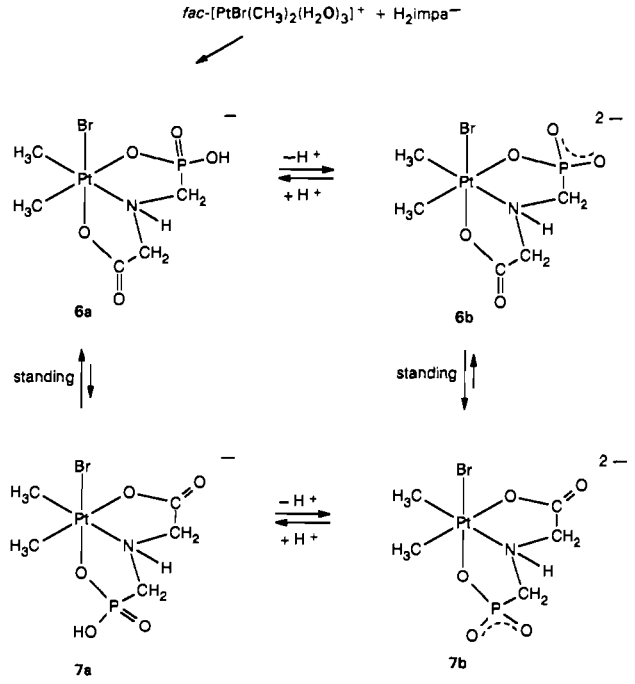


Figure 2. Packing diagram for $[Pt(CH_3)_2(Himpa)(H_2O)]\cdot H_2O$ (compound **A**).

Scheme 2



standing showed peaks due to the starting materials still predominant, but there were also additional peaks assignable to a complex $[PtBr(CH_3)_2(Dimpa\text{-}N,O_c,O_p)]^-$ with glyphosate coordinated tridentate. The ^1H NMR spectrum in the Pt–CH_3 region showed two singlets with satellites, with Pt–CH_3 coupling constants corresponding to methyl trans to nitrogen (66.8 Hz) and methyl trans to oxygen (79.3 Hz). The ^{31}P NMR spectrum showed a peak at 35.4 ppm, from phosphonate coordinated to a five-membered chelate ring, and the ^{13}C NMR spectrum a peak from carboxylate carbon at 188.2 ppm, from carboxylate in a five-membered ring. From detailed comparisons of these parameters with those for the compounds previously discussed (Table 2), isomer **6a** with phosphonate trans to methyl was more likely to be the species present than isomer **7a** with carboxylate trans to methyl.

It was noted that trace amounts of silver ion, present as an impurity in the solution of $[PtBr(CH_3)_2(D_2O)_3]NO_3$ (prepared by reaction of $[\{PtBr_2(CH_3)_2\}_n]$ with $AgNO_3$ in D_2O/acetone), caused pale yellow crystals to form from this solution. This led to the deliberate addition of $AgNO_3$ to give a solid which analyzed for $Ag[PtBr(CH_3)_2(Himpa)]$ (compound **B**). X-ray crystal structure determination confirmed that the anion was isomer **6a**. The solid was insoluble in water and dilute acids. When dilute alkali was added, the solid dissolved and $Ag_2O\cdot nH_2O$ precipitated. If dilute HNO_3 was added to this mixture, compound **B** again formed.

If $[PtBr(CH_3)_2(D_2O)_3]NO_3$ and H_3impa were mixed in D_2O, and the pD of the solution then increased to 5.7, ^1H NMR spectra of the resultant solutions were initially quite complex. The species formed under these conditions were probably isomers of $[PtBr(CH_3)_2(Dimpa)(D_2O)]^-$ in which glyphosate is coordinated didentate through nitrogen and one oxygen atom. There are four isomers of this complex, depending on whether carboxylate or phosphonate oxygen coordinates and then on the orientations of the groups bound to nitrogen with respect to the coordinated bromide ion. No attempt was made to assign the peaks in these spectra. However, if the solution was allowed to stand at this pD for 6 days, the ^1H NMR spectrum became much simpler. It now showed four singlets with satellites in the Pt–CH_3 region, of similar intensity, two with Pt–CH_3 coupling constants near 67 Hz corresponding to methyl trans to nitrogen and two with Pt–CH_3 coupling constants near 78 Hz corresponding to methyl trans to oxygen. The ^{31}P NMR spectrum showed two peaks of equal intensity (39.2, 33.9 ppm) each corresponding to phosphonate in a chelate ring, and the ^{13}C NMR spectrum showed two carboxylate peaks (188.6, 184.4 ppm) from coordinated carboxylate. The pD of this solution (5.7) was close to the pK_a for coordinated phosphonate. Subsequent experiments in which spectra were run rapidly when pD was changed allowed us to assign these sets of peaks to the two isomers, each partially deuteronated, of $[PtBr(CH_3)_2(impa\text{-}N,O_c,O_p)]^{2-}$ with nitrogen trans to methyl (**6a/b** and **7a/b**) as shown in Table 2.

If the pD of the solution was then further increased to 7.6, and the solution was allowed to stand for several days, ^1H, ^{13}C, and ^{31}P NMR spectra were all consistent with the presence in solution of a single isomer of $[PtBr(CH_3)_2(impa\text{-}N,O_c,O_p)]^{2-}$. Two singlets with satellites were observed for Pt–CH_3 groups in the ^1H NMR spectrum, corresponding to methyl groups trans to nitrogen and an oxygen donor. The ^{31}P NMR spectrum showed a peak at 38.8 ppm. Experiments in which spectra were run quickly after the solution pD was changed showed that these peaks were not due to the dedeuteronated form, **6b**, of the isomer with phosphonate and nitrogen trans to methyl. The complex in solution was therefore formulated as isomer **7b**, with carboxylate and nitrogen trans to methyl.

To summarize these results: At high pH, with the coordinated phosphonate group deprotonated, isomer **7b**, with carboxylate trans to methyl, is favored. At low pH, with the coordinated phosphonate group protonated, isomer **6a**, with phosphonate trans to methyl, is favored. At pH near the pK_a of coordinated phosphonate, where there will be partial deprotonation, the two isomers **6a/b** and **7a/b** are formed in similar amounts. These results parallel those for the relative preferences of isomers **4a/b** and **5a/b** for the aqua/hydroxo complexes discussed above.

The ^1H NMR spectra of solutions containing **6a/b** and **7a/b** were run at various pD values. The pK_a value in D_2O for **6a** was determined as 5.79 ± 0.05. When solutions of **7b** were acidified,

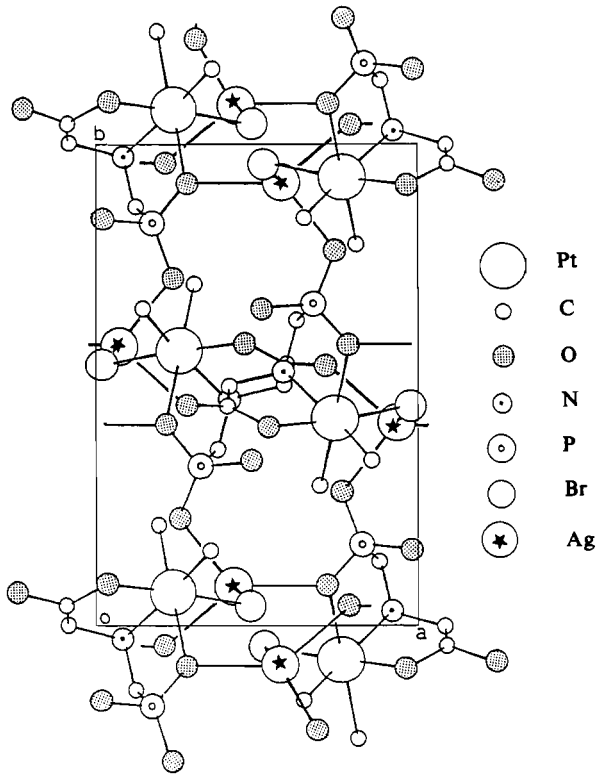


Figure 3. Packing in the cell of Ag[PtBr(CH$_3$)$_2$(Himpa)], compound **B**, viewed down *c*.

the rapid isomerization to **6a** prevented accurate determination of pK_a, but the spectra were consistent with a value slightly less than 5.

Description of the Structure of Ag[PtBr(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)] (Compound B). A packing diagram is given in Figure 3. Selected bond lengths and angles for the complex anion are given in Table 3. The structure determination confirmed that the isomer present was **6a**, with glyphosate coordinated tridentate through nitrogen and phosphonate O trans to methyl and through carboxylate O trans to bromide. The structure of this anionic complex is very similar to that of the neutral complex **4a** in compound **A**. There is again a significantly longer bond between phosphorus and O(12) (1.569(9) Å) than that with O(13) (1.477(9) Å), which allows O(12) to be identified as the atom carrying the proton.

The bromide ligand as well as being bound to platinum (Pt–Br = 2.422(1) Å) is also bonded to silver (Ag–Br = 2.810(2) Å) with a Pt–Br–Ag bridge angle of 111.5(1)°. This distance compares with 2.89 Å in the face-centered cubic AgBr structure[47] and with a range 2.690–2.861 Å in the more analogous series of bromo-bridged adducts LAgBr (L = 2-, 3-, 4-methylpyridine).[48] Completing a distorted tetrahedral stereochemistry about silver are three oxygen atoms from different glyphosate ligands: a carboxylate oxygen which is not also bound to platinum, O(52)^1 ($-x$, $-y$, $^1/_2 + z$) (Ag–O = 2.405(9) Å); a phosphonate oxygen atom which is not protonated and which is not bound to platinum, O(13)^2 ($^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$) (Ag–O = 2.394(9) Å); and a phosphonate oxygen also bound to platinum, O(11)^3 ($1 - x$, $-y$, $-^1/_2 + z$) (Ag–O = 2.410(9) Å). The angles about the silver atom range from 85.5(1) to 139.5(3)°. Bond lengths and angles about the silver atom are listed in Table 7. The result is a network structure which extends throughout the unit cell in two dimensions. Of the cations which were tried for the crystallization of a salt of the anion **6a**, silver ion was the only one which easily gave a well-defined crystalline product. It is important in stabilizing the present structure because of its interaction with oxygen atoms, as well as the bridging bromide ion. An additional advantage of silver as a counterion over sodium or potassium lies in its smaller size and common formation of four-coordinate, usually approximately tetrahedral, centers. This phenomenon has been previously observed in the group 15 metal tartrate complexes, $[\{Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4\}_n]$[49] and $[\{Ag_5As_4(C_4H_2O_6)_4(H_2O)_5\}_n]$-$A_n$ (A = NO_3^-, ClO_4^-),[50] in which four and five independent and different silver atoms respectively are disseminated throughout stable network polymers. These compounds are similar to compound **B** in being very dense and crystalline.

Table 7. Bond Lengths (Å) and Angles (deg) about Silver in Compound **B**[a]

Bond Lengths	
Ag–Br	2.819(2)
Ag–O(52)^1	2.405(9)
Ag–O(13)^2	2.394(9)
Ag–O(11)^3	2.410(9)
Bond Angles	
Br–Ag–O(52)^1	90.4(3)
Br–Ag–O(13)^2	118.2(3)
Br–Ag–O(11)^e	85.5(3)
O(52)^1–Ag–O(13)^2	93.1(3)
O(52)^1–Ag–O(11)^3	139.5(3)
O(13)^2–Ag–O(11)^3	124.1(3)

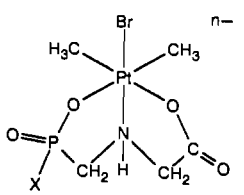
[a] Key for coordinates: (*1*) $-x$, $-y$, $-^1/_2 + z$; (*2*) $^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$; (*3*) $1 - x$, $-y$, $-^1/_2 + z$.

Photoisomerization Reactions. We have previously described the photoinduced isomerization of the isomer of [PtBr(CH$_3$)$_2$(ida-*N*,*O*,*O*′)]$^-$ with N trans to methyl to the isomer with N trans to Br.[23] When a solution containing isomers **6b** and **7b** of [PtBr(CH$_3$)$_2$(impa-*N*,*O*$_c$,*O*$_p$)]$^{2-}$ at pD 6.5 was irradiated with a mercury lamp for several minutes, an analogous isomerization occurred to isomer **8b**, with N trans to Br. The ^{1}H NMR spectrum in the Pt–CH$_3$ region showed two singlets with satellites, with both Pt–CH$_3$ coupling constants near 75 Hz (Table 2), corresponding to methyl trans to oxygen. The ^{31}P NMR spectrum showed a single peak at 29.1 ppm.

From the changes in the spectra when the pD of the solution was adjusted, pK_a for the coordinated phosphonate group in D_2O was estimated as 5.03 ± 0.03.

As with the iminodiacetate system,[23] photoisomerization of hydroxo complexes was less facile. Only limited reaction occurred over a long irradiatin period, and these reactions were not further investigated.

Structure of Ag$_3$[PtBr(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)][PtBr(CH$_3$)$_2$(impa-*N*,*O*$_c$,*O*$_p$)]·1.5H$_2$O (Compound C). A packing diagram is shown in Figure 4. The compound is the silver salt of the two anions [PtBr(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)]$^-$ (**8a**) and [PtBr(CH$_3$)$_2$-



8a X = OH, n = 1
8b X = O, n = 2

(impa-*N*,*O*$_c$,*O*$_p$)]$^{2-}$ (**8b**). Selected bond lengths and angles in the anionic complexes are given in Table 3. The two anions are distinct and may be assigned their respective protonation states

(47) Adams, D. M. *Inorganic solids-an Introduction to Concepts in Solid-state and Structural Chemistry*; Wiley: Chichester, U.K., 1981; p 106.
(48) Healy, P. C.; Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 111.
(49) Sagatys, D. S.; Smith, G.; Lynch, D. E.; Kennard, C. H. L. *J. Chem. Soc., Dalton Trans.* **1991**, 361.
(50) Bott, R. C.; Smith, G.; Sagatys, D. S.; Lynch, D. E., Kennard, C. H. L. *Aust. J. Chem.*, in press.

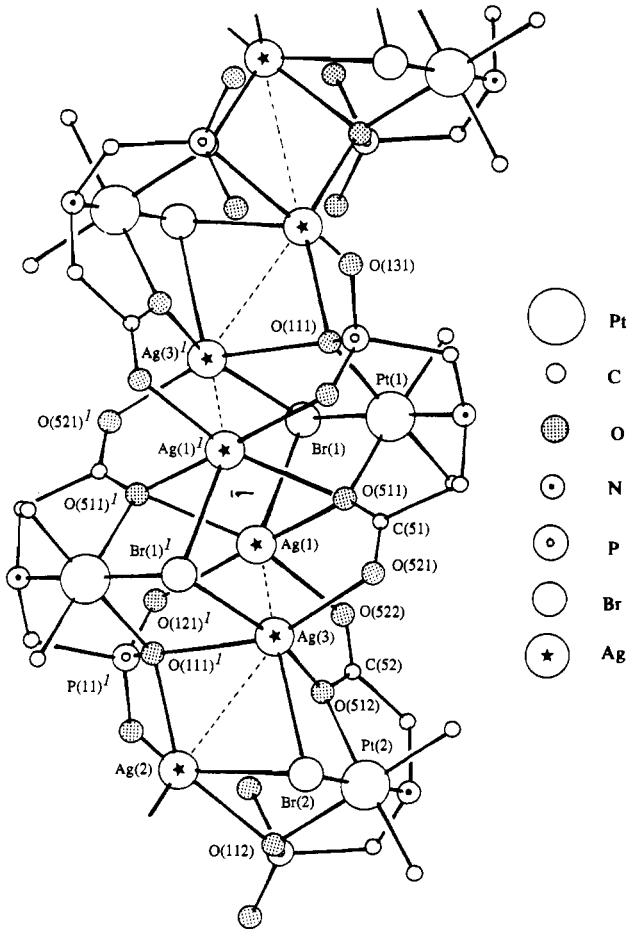


Figure 4. View of the extended network in $Ag_3[PtBr(CH_3)_2(Himpa)]$-$[PtBr(CH_3)_2(impa)]\cdot 1.5H_2O$, compound **C**. Dotted lines represent close Ag–Ag contacts.

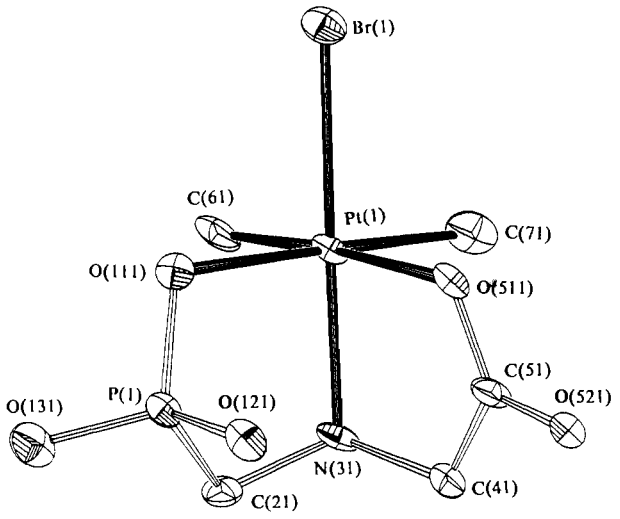


Figure 5. PLATON diagram showing the complex anion $[PtBr(CH_3)_2(impa)]^{2-}$ (**8b**) in compound **C**, with 30% probability ellipsoids. The other complex anion in compound **C**, $[PtBr(CH_3)_2(Himpa)]^-$ (**8a**), is very similar, except for the environment of the phosphorus atom.

by comparison of their P–O bond distances. For the complex anion containing Pt(1) and P(1), the P–O bond lengths to oxygen atoms not involved in platinum coordination are similar (P(1)–O(121) = 1.51(1) Å, P(1)–O(131) = 1.50(1) Å). This anion is therefore assigned as that in which the coordinated phosphonate is fully deprotonated (**8b**). The structure of this anion is shown in Figure 5. For the other complex anion, containing Pt(2) and P(2), the two P–O bond lengths are quite different (P(2)–O(122) = 1.47(1) Å, P(2)–O(132) = 1.56(1) Å), as was found above for the protonated phosphonate groups in compounds **A** and **B**. This allowed us to assign O(132) as the oxygen atom carrying the proton in **8a**.[51] The bond angles about P(2) are also quite different from those about P(1). Apart from these differences in the phosphonate groups, the structures of the two complex anions **8a/b** are very similar. The metal–ligand bond lengths are affected by the different trans influences of methyl and bromide (see Discussion); otherwise the binding of the glyphosate ligand is analogous to that in compounds **A** and **B**.

The two complex anions **8a,b** are bound together into a ribbon structure by the three independent silver ions, which have quite different environments. If the interactions with bromide ions and oxygen atoms (both carboxylate and phosphonate) are considered, each silver ion is five-coordinate. Ag(1) (bound to Br(1), O(511), $O(522)^I$, $O(121)^I$, $O(511)^I$) and Ag(2) (bound to Br(2), O(112), O(111), O(131), $O(112)^2$) are each in a distorted trigonal bipyramidal environment, while Ag(3) (bound to Br(2), $Br(1)^I$, O(512), O(521), and $O(111)^I$) has a distorted square pyramidal environment. Bond lengths and angles about each silver atom are given in Table 8. There are also relatively close contacts (3.2–3.3 Å) between pairs of silver ions: Ag(1)–Ag(3), Ag(2)–Ag(3), and Ag(2)–$Ag(2)^2$. Ag(1) and Ag(3) are bridged by two carboxylate groups (Ag(1)–O(511)–C(51)–O(521)–Ag(3) and Ag(1)–$O(522)^I$–C(52)–O(512)–Ag(3)) and one phosphonate group (Ag(1)–$O(121)^I$–$P(11)^I$–$O(111)^I$–Ag(3)). The planes of the coordinated carboxylate groups are at an angle of approximately 90°, in contrast to the planar arrangement typical of bis(carboxylate)-bridged dimers found in silver carboxylates.[52] Each bromide ion bridges between a Pt atom and two silver atoms (Br(1) is bound to Pt(1), Ag(1), and $Ag(3)^I$; Br(2) to Pt(2), Ag(2), and Ag(3)).

Reactions of Iminobis(methylenephosphonic acid) and (Methylimino)bis(methylenephosphonic acid) with Tri- and Dimethylplatinum(IV) Complexes. Equimolar quantities of *fac*-$[Pt(CH_3)_3(D_2O)_3]^+$ and H_4idmp were mixed in D_2O, and the pD was adjusted to 5.5 with NaOD solution. The ^{31}P NMR spectrum showed, in addition to a peak from the ligand, a relatively sharp peak at 38.0 ppm corresponding to phosphonate incorporated in a five-membered chelate ring. The ^1H NMR spectrum showed, in addition to the singlet with satellites from $[Pt(CH_3)_3(D_2O)_3]^+$, two singlets with satellites in the Pt–CH_3 region, with intensity ratio 2:1 (Figure 6b). The Pt–CH_3 coupling constants (80.0 and 68.7 Hz) were consistent with methyl groups trans to O and N, respectively. These data were as expected if the complex present contained the iminobis(methylenephosphonate) ligand coordinated N,O,O′-tridentate. However, the 400-MHz ^1H NMR spectrum showed a number of broad peaks between 3.0 and 3.2 ppm from the methylene protons (as well as a sharp doublet from the free ligand) (Figure 6b). The pD at which this spectrum was obtained (5.5) was close to the expected value for pK_a for coordinated phosphonate (see above). When the solution was made more acidic or more alkaline, apart from the expected changes from deuteronation/dedeuteronation, these peaks became broader (Figure 6). There was also extensive dissociation of the ligand in acidic solution (Figure 6a). In static complex $[Pt(CH_3)_3(D_2idmp\text{-}N,O,O^\wedge)]^-$ (**9**) the methylene protons would be expected to give an ABX pattern (X = ^{31}P) superimposed on ABMX (M = ^{195}Pt). As with $[Pt(CH_3)_3(impa\text{-}N,O_c,O_p)]^{2-}$ (**1b**), the peaks in this pattern would be expected to be sharp. As the

(51) In compounds **A** and **B**, O(12) and O(13) are labeled consistently, with regard to the orientation of the P–O bonds relative to the remainder of the tridentate ligand. In compound **C**, the oxygen atoms bound to P(1), O(121), and O(131), and those bound to P(2), O(122), and O(132), are labeled to retain this consistency, although the protonated O-atom in **C** is O(132) and in **A** and **B** is O(12).

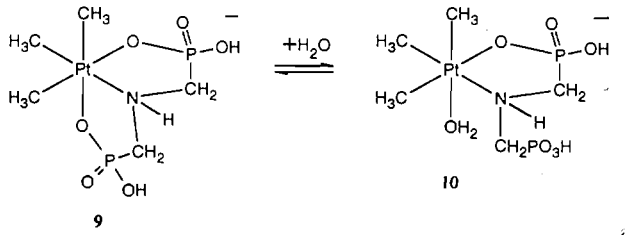
(52) (a) Charbonnier, F.; Faure, R.; Loiseleur, H. *Rev. Chim. Miner.* **1981**, *18*, 245. (b) Amiraslanov, I. R.; Usubaliev, B. T.; Nadzhafov, G. N.; Musaev, A. A.; Movsumov, E. M.; Mamedov, Kh. S. *Zh. Strukt. Khim.* **1980**, *21*, 112. (c) Mak, T. C. W.; Yip, W.-H.; Kennard, C. H. L.; Smith, G.; O'Reilly, E. J. *Aust. J. Chem.* **1986**, *39*, 541.

Table 8. Interatomic Distances (Å) and Angles (deg) about Silver Atoms in Compound C[a]

Distances					
Ag(1)–Br(1)	2.808(4)	Ag(2)–Br(2)	2.840(4)	Ag(3)–Br(1)^{1}	2.705(4)
Ag(1)–O(511)	2.60(1)	Ag(2)–O(111)	2.37(1)	Ag(3)–Br(2)	2.849(5)
Ag(1)–O(121)^{1}	2.32(1)	Ag(2)–O(112)	2.66(1)	Ag(3)–O(111)^{1}	2.62(1)
Ag(1)–O(522)	2.38(1)	Ag(2)–O(112)^{2}	2.33(1)	Ag(3)–O(512)	2.48(1)
Ag(1)–O(511)^{1}	2.83(1)	Ag(2)–O(131)	2.82(1)	Ag(3)–O(521)	2.36(1)
Ag(2)–Ag(2)^{2}	3.319(5)	Ag(1)–Ag(3)	3.214(5)	Ag(2)–Ag(3)	3.200(5)
Angles					
Br(1)–Ag(1)–O(511)	77.6(3)	Br(2)–Ag(2)–O(111)	109.4(3)	Br(1)^{1}–Ag(3)–Br(2)	110.40(9)
Br(1)–Ag(1)–O(121)^{1}	118.8(3)	Br(2)–Ag(2)–O(112)	72.51(18)	Br(1)^{1}–Ag(3)–O(111)^{1}	76.7(2)
Br(1)–Ag(1)–O(522)	96.2(4)	Br(2)–Ag(2)–O(112)^{2}	96.0(2)	Br(1)^{1}–Ag(3)–O(512)	158.2(3)
O(121)^{1}–Ag(1)–O(511)	159.7(4)	O(111)–Ag(2)–O(112)	123.4(3)	Br(1)^{1}–Ag(3)–O(521)	95.8(3)
O(511)–Ag(1)–O(522)	92.2(4)	O(111)–Ag(2)–O(112)^{2}	136.7(3)	Br(2)–Ag(3)–O(111)^{1}	102.4(3)
O(121)^{1}–Ag(1)–O(522)	97.2(5)	O(112)–Ag(2)–O(112)^{2}	97.0(3)	Br(2)–Ag(3)–O(512)	77.4(3)
Pt(1)–Br(1)–Ag(1)	87.63(8)	Pt(1)–Br(1)–Ag(3)^{1}	90.94(8)	Br(2)–Ag(3)–O(521)	95.8(3)
Ag(1)–Br(1)–Ag(3)^{1}	85.23(8)	Pt(2)–Br(2)–Ag(2)	85.15(8)	O(111)^{1}–Ag(3)–O(512)	81.8(3)
Pt(2)–Br(2)–Ag(3)	85.39(8)	Ag(2)–Br(2)–Ag(3)	68.45(8)	O(111)^{1}–Ag(3)–O(521)	154.5(4)
				O(512)–Ag(3)–O(521)	102.2(4)

[a] Key for coordinates: (*1*) x, $^1/_2 - y$, $^1/_2 + z$; (*2*) $1 - x$, $1 - y$, $1 - z$.

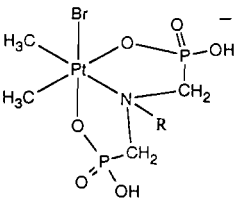
Pt–CH_3 peaks remained distinct, the process responsible for the methylene signal broadening did not involve any interchange of the environments of these methyl groups. A process which could be responsible is a rapid interconversion between **9** and a complex, **10**, with the ligand didentate and water coordinated (eq 3). If the



(3)

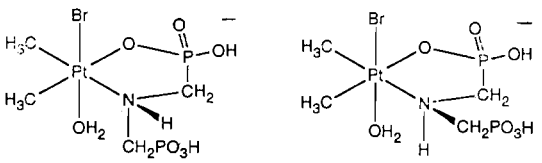
chemical shift differences between the methyl groups in **9** and **10** were small, but the differences in the methylene region more profound, the exchange reaction might be fast enough to allow coalescence of the methyl peaks from **9** and **10** but not to completely average the environments of the methylene protons. At higher and lower pD, the deuteronation state of **9** would, of course, change, and at high pD, OD^- would replace D_2O in the reaction. The ^{31}P NMR signal also broadened when the solution was made more acidic, or more alkaline, than 5.5 (Figure 6).

An equimolar quantity of H_4idmp was added to a solution of $[Pt(CH_3)_2Br(D_2O)_3](NO_3)$ in D_2O, and the pD of the solution was adjusted to 4.0 with dilute KOD solution. After the solution was allowed to stand for 4 days, the ^1H NMR spectrum still showed strong peaks from the starting materials, together with two weaker singlets with satellites in the Pt–CH_3 region. The Pt–CH_3 coupling constants, 65.3 and 78.1 Hz, corresponded to methyl groups trans to nitrogen and to an O-donor respectively. The ^{31}P NMR spectrum showed (in addition to a peak from the ligand) two peaks, at 45.9 and 39.0 ppm. The low shielding of both of these phosphorus nuclei indicated that each phosphonate group was part of a five-membered chelate ring. These peaks were therefore assigned to the isomer of $[PtBr(CH_3)_2(D_2idmp\text{-}N,O,O')]^-$ with N trans to methyl, **11**. From a comparison of the ^{31}P shifts with those for the isomers of $[PtBr(CH_3)_2(impa\text{-}N,O_c,O_p)]^{2-}$, the less shielded ^{31}P nucleus in **11** was assigned as that trans to bromide. There were much weaker peaks in these ^1H and ^{31}P spectra which were assigned to the isomers **12** and **13** of $[PtBr(CH_3)_2(D_2idmp\text{-}N,O)(D_2O)]^-$, in which the ligand was bound bidentate trans to the methyl groups (Table 2). In spectra run within 10 min of mixing, weak peaks from **12** to **13** were observed, with strong peaks from starting materials. In spectra run 24 h after mixing, peaks from **11**–**13** were of comparable intensities.



11 R = H

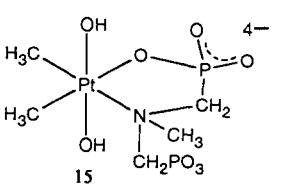
14 R = CH_3



12 **13**

In an analogous reaction between $[PtBr(CH_3)_2(D_2O)_3]^+$ and (methylimino)bis(methylenephosphonate) at pD 4, reaction occurred to a lesser extent than with the non-methylated ligand. The ^{31}P peaks of equal intensities that were observed 3 h after mixing were at 41.1 and 32.9 ppm, corresponding to a complex $[PtBr(CH_3)_2(D_2midmp\text{-}N,O,O')]^-$ (**14**). There were no peaks that could be assigned to complexes with the ligand N,O-didentate, analogous to **12** and **13**. A black solid (Pt metal?) slowly deposited on prolonged standing.

There was no reaction between "*cis*-$[Pt(CH_3)_2(D_2O)_4]^{2+}$" and an equimolar quantity of (methylimino)bis(methylenephosphonate) in acid solution (pD < 3). Above this pD value, a white precipitate of $[\{Pt(CH_3)_2(OD)_2\}_n \cdot mD_2O]$ formed, which did not dissolve completely until sufficient alkali was added to increase the pD to 12.5. The ^{31}P NMR spectrum of this solution showed a singlet from free midmp^{4-} and two singlets (with satellites) with equal intensities, at 31.2 ppm (J(Pt–P) 17.1 Hz) and at 13.9 ppm (J(Pt–P) 42.7 Hz), due to $[Pt(CH_3)_2(OD)_2(midmp\text{-}N,O)]^{4-}$ (**15**). The 400-MHz ^1H NMR spectrum showed peaks from $[\{Pt(CH_3)_2(OD)(\mu\text{-}OD)\}_2]^{2-}$ [27] and two additional singlets with broad satellites assigned to **15** (Table 2). There was no change in the spectrum when the solution was allowed to stand. When D_2SO_4 was added to decrease the pD of the solution to 3.5 quickly, no



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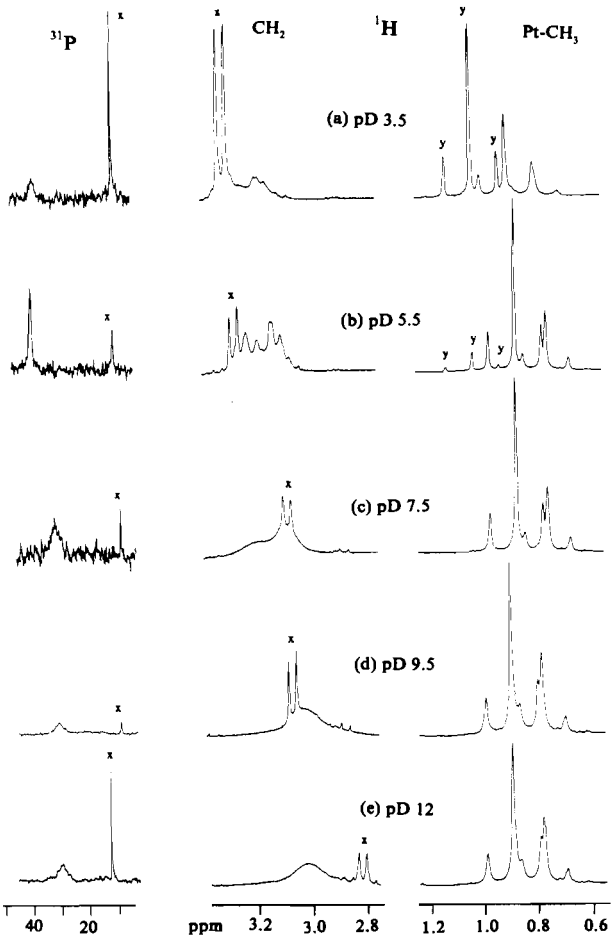


Figure 6. Effect of pD on the 400-MHz ^{1}H and 40.3-MHz ^{31}P NMR spectra of a D_2O solution prepared from D_2idmp^{2-} and *fac*-[Pt(CH$_3$)$_3$(D$_2$O)$_3$]$^+$. Key: x = peaks from free D_2idmp^{2-}; y = peaks from *fac*-[Pt(CH$_3$)$_3$(D$_2$O)$_3$]$^+$.

white precipitate formed during the addition, but the ^{1}H NMR spectrum showed only peaks from free ligand and "*cis*-[Pt(CH$_3$)$_2$(D$_2$O)$_4$]$^{2+}$.

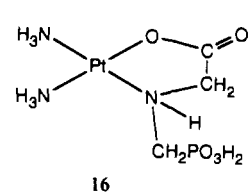
Discussion

Our results have shown that the facial tridentate coordination mode can be easily adopted by glyphosate when appropriate coordination sites are offered to the ligand. The bond angles within the glyphosate ligand are very similar to those of the uncoordinated species in the solid state.[7] However, the O–Pt–N "bite" angles are significantly less than 90°, which may indicate some strain as the ligand accommodates the requirements of the large platinum(IV) cation. The O$_c$–Pt–N angles all fall in the range 81.2–82.5°. The O$_p$–Pt–N angles for the two compounds with N and O$_p$ both trans to methyl (compounds **A** and **B**) are close to 84°. In each of the two anions in compound **C**, where N is trans to Br, this bite angle increases to 87.5°. This is probably a result of the shorter Pt–N bond in these anions (see discussion on trans influences below).

If the rule holds that the most stable isomer thermodynamically is the one in which ligands with the strongest trans influence are trans to those with the weakest trans influence,[53] the most stable isomer of a dimethylplatinum(IV) complex would be predicted to be that in which nitrogen is cis to methyl. With the iminodiacetate complexes, [PtBr(CH$_3$)$_2$(ida-*N*,*O*,*O*′)]$^-$, the isomer with N cis to methyl could be obtained easily only by a photoassisted isomerization of the isomer with N trans to methyl, but once it was formed, there was no reverse isomerization. The behavior of [PtBr(CH$_3$)$_2$(impa-*N*,*O*$_c$,*O*$_p$)]$^{2-}$ was similar, in that the isomer with N cis to methyl, **8b**, was formed irreversibly in a photo-assisted isomerization.

In the glyphosate complexes, there are two isomers with nitrogen trans to methyl, **6a/b** and **7a/b**. The kinetic barrier to formation of isomer **8a/b** from either of these isomers is high, since it involves migration of coordinated nitrogen from a labile site (trans to methyl) to an "inert" site (cis to methyl). The interconversion between **6a/b** and **7a/b** involves migration of more weakly bonding O-atoms between labile and inert sites and occurs more readily (on standing for several hours at ambient temperature). There are parallels in the interconversions of isomers of [PtBr(CH$_3$)$_2$(gly-*N*,*O*)(H$_2$O)][22,54] and [PtBr(CH$_3$)$_2$(gly)$_2$]$^-$.[46] From the results reported above, it is clear that in acid solution, where the coordinated phosphonate group is protonated, the more stable isomer is **6a**, with phosphonate trans to methyl, and in alkaline solution, where the coordinated phosphonate group is deprotonated, the more stable isomer is **7b**, with carboxylate trans to methyl. When the pH is close to pK_a for the coordinated phosphonate, both isomers are present. Similarly, the more stable isomer of [Pt(CH$_3$)$_2$(Himpa-*N*,*O*$_c$,*O*$_p$)(H$_2$O)] in acid solution is **4a**, with phosphonate trans to methyl, and the more stable isomer of [Pt(CH$_3$)$_2$(OH)(impa-*N*,*O*$_c$,*O*$_p$)]$^{2-}$ in alkaline solution is **5b**, with carboxylate trans to methyl. The methyl groups prefer to be trans to the weakest donor group available. Deprotonation of the phosphonate group increases the strength of the metal–oxygen(phosphonate) interaction, and carboxylate becomes the preferred ligand trans to methyl.

These results may be compared with those for diammineplatinum(II) complexes where there are only two coordination sites available for glyphosate coordination.[6] In this system, the choice is not which O-donor will coordinate trans to a high trans influence ligand but which O-donor will coordinate at all. We showed that, at low pH, where coordinated phosphonate would be protonated, the preferred complex is **16**,with carboxylate coordinated, while at high pH, where phosphonate would be fully deprotonated, the preferred complex is **17**, with phosphonate coordinated. In the light of these observations, it is, perhaps, surprising that there is no clear preference for one isomer, **2b** or **3b**, over the other for [Pt(CH$_3$)$_2$(OH)$_2$(impa-*N*,*O*)]$^{3-}$, where the ligand is also didentate. Perhaps intramolecular hydrogen bonding between the uncoordinated carboxylate or phosphonate and the axial hydroxide ligands also affects this equilibrium.



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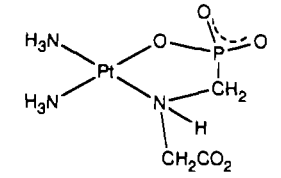

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For the diammineplatinum(II) complexes, ^{195}Pt–^{15}N coupling constants showed that the NMR trans influence series for the O-donor ligands is –OCO$^-$ > –OPO$_2^{2-}$ > –OPO$_2$H$^-$. From the Pt–CH$_3$ coupling constants listed in Table 2 (*e.g.*, in the trimethylplatinum(IV) complexes **1a/b** and in the dimethylplatinum(IV) complexes with the two O-donor groups trans to methyl, **8a/b**), the NMR trans influence series in the present compounds is similar. In comparing this order with the order of metal–ligand interaction obtained from the isomerization reactions discussed above (–OPO$_2^{2-}$ > –OCO$^-$ > –OPO$_2$H$^-$), it should be remembered that NMR coupling constants are dependent primarily on only one component of the metal–ligand bond, the metal *s*-character.[55,56]

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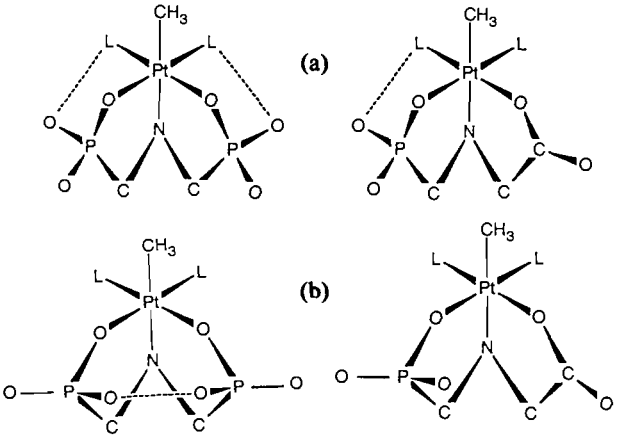

Figure 7. Potential steric interactions (dashed lines): (a) with adjacent ligands; (b) within the tridentate ligand for an iminobis(methylenephosphonate) ligand, compared with glyphosate.

In the structure of compound **C**, the differences between Pt–O bond lengths trans to methyl (Table 3) are not large enough to be very significant and may be affected by interactions with silver ions, but the order appears to be Pt–OCO– < Pt–OPO_2– < Pt–OPO_2H–.

The facial N,O,O′-tridentate coordination mode was clearly less stable for the imino- and (methylimino)bis(methylenephosphonate) ligands than for either iminodiacetate or glyphosate. From the discussion above, it seems unlikely that this would be due primarily to differences in the strength of binding of the different O-donor groups to the metal. The C–P and P–O bonds of the methylenephosphonate arm are longer than corresponding C–C and C–O bonds in an acetate arm, which would be more likely to decrease angle strain when the ligand coordinates tridentate. An important factor may be steric interactions between phosphonate oxygen atoms and adjacent ligands. In glyphosate complexes, the chelate rings can adopt conformations such that one noncoordinated phosphonate oxygen atom is well removed from adjacent ligands while the second does not interact too strongly with the uncoordinated carboxylate oxygen atom. In compound **B**, for example, the O(13)–Br distance is 4.48 Å, and the O(12)–O(52) distance is 3.24 Å. In a tridentate iminobis(methylenephosphonate) ligand, however, oxygen atoms from the two different phosphonate groups will interact strongly with one another if the chelate rings adopt conformations which minimize interactions with the adjacent ligands (Figure 7).

The major determinant of the Pt–N and Pt–O bond lengths is, as expected, the trans influence of the ligand trans to each bond. Thus, the Pt(1)–N(31) (2.04(1) Å) and Pt(2)–N(32) (2.06(1) Å) bond lengths trans to bromide in compound **C** are shorter than the Pt–N bond lengths trans to methyl in compound **A** (2.216(8) Å) and compound **B** (2.22(1) Å) (*cf.*, 2.20(2), 2.18(2) Å trans to methyl and 2.07(2) Å trans to carboxylate in two isomers of $[Pt(CH_3)_2(gly\text{-}N,O)_2]$[57,58]). The Pt–O(carboxylate) bond lengths trans to H_2O in compound **A** (1.998(7) Å) and trans to bromide in compound **B** (2.003(9) Å) are shorter than trans to methyl in compound **C** (Pt(1)–O(511) = 2.19(1) Å, Pt(2)–O(512) = 2.17(1) Å) (*cf.*, 1.99(2) Å trans to carboxylate,[57] 2.01(2) trans to N,[58] and 2.14(2) trans to methyl[58] in isomers of $[Pt(CH_3)_2(gly\text{-}N,O)_2]$). The Pt–C bond lengths all lie in the range 2.01–2.05 Å, similar to previously-determined values,[57–59] and Pt–Br bond lengths in the range 2.427–2.450 Å.

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Supplementary Material Available: Tables of full crystallographic data, all bond angles, anisotropic thermal parameters, and hydrogen atom coordinates, for each of compounds **A**–**C**, tables of additional NMR data, and Figure S1, showing the structure of the anion in compound **B** (20 pages). Ordering information is given on any current masthead page.

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