Stability and Reactivity of Dihydroxobis(trimethylphosphine)platinum(II), an Intermediate Species for the Synthesis of a Variety of Water-Soluble Phosphine Complexes

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(Received July 2, 1992)

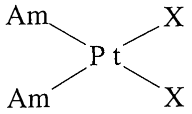
A dihydroxoplatinum(II) compound, *cis*-[Pt(OH)$_2$(PMe$_3$)$_2$]·nH$_2$O (Me=methyl, n=2—3; **1**), has been characterized by ^{31}P, ^{195}Pt, ^{13}C, and ^{1}H NMR spectroscopy. The thermal stability of **1** was examined. The presence of several water molecules is required for the stabilization of **1**. The solution equilibria and the reaction of **1** with aqueous hydrogen peroxide were observed by ^{31}P NMR spectroscopy. The neutralization of **1** with several dicarboxylic acids afforded water-soluble phosphine complexes in quantitative yields. Exposure of **1** toward air gives the carbonatoplatinum(II), *cis*-[Pt(CO$_3$)(PMe$_3$)$_2$]·2H$_2$O. Its crystal structure determination has revealed that the carbonate anion forms four-membered ring with a platinum atom.

Metal-phosphine complexes have been used due to their versatility in reaction chemistry. Their catalytic properties have found several applications, not only in industrial processes,[1] but also in laboratory syntheses, i.e., asymmetric hydrogenation or carbon–carbon bond formation.[2] Those types of reactions have so far been carried out mainly in organic solvents, because of the oleophilic nature of the phosphine ligands. A judicious choice of an aqueous medium may open the possibility of phase-transfer catalysts, solvent extraction or medicinal applications. To overcome the inherent low solubility into an aqueous solvent, a chemical modification of the phosphine ligands has been devised. The catalytic reactivities of their metal complexes were tested regarding synthetic applications.[3,4] In spite of these trials, there have been very few cases of water-soluble phosphine complexes to date.[3—5]

The discovery of the anticancer drug *cisplatin, cis*-diamminedichloroplatinum(II),[6] aroused great interest in the aqueous chemistry of diammineplatinum(II) complexes.[7,8] Successive efforts have been made to exploite new agents, the so-called "*second* or *third generation drugs*".[9] As the result of a synthetic pursuit, a huge number of water-soluble square planar diammineplatinum(II) is now accumulating (Fig. 1a).[9]

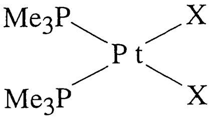
In 1986, an elegant method using the anion-exchange resin was reported regarding the preparation of diammineplatinum(II) complexes.[10] The quantitative formation of dihydroxo *cis*-diammineplatinum(II) species was proposed as a synthetic intermediate.[10] In our study, the method was very effective for the syntheses of several types of amminecomplexes.[11]

Our current objective is to explore and to develop a new aqueous chemistry of phosphine complexes. We report here on the successful use of the anion-exchange method[11] for a series of the water-soluble phosphineplatinum(II) complexes, such as [Pt(ox)(PMe$_3$)$_2$] (**2a**) and [Pt(cbdca)(PMe$_3$)$_2$]·H$_2$O (**2b**) (where ox: oxalate, cbdca: 1,1-cyclobutanedicarboxylate, Fig. 1b).



(a) L=Am, Antitumor ammine complexes.

2Am=2NH$_3$, 2X=2Cl; *cisplatin.*
2Am=2NH$_3$, 2X=cbdca; *carboplatin.*
2Am=*R, R*-dach, 2X=ox; *l*-OHP.



(b) L=PMe$_3$, Trimethylphosphine analogue.

Fig. 1. Square planar platinum(II) complexes *cis*-PtX$_2$L$_2$.

An intermediate species of this method, dihydroxobis(trimethylphosphine)platinum(II), has been isolated, and the stability surveyed in a simple fashion. The solution equilibria and reaction with aqueous hydrogen peroxide have also been investigated. A preliminary communication concerning this work has already appeared.[12]

Experimental

Spectroscopic Measurement. Infrared spectra were recorded on a Hitachi I-3000 infrared spectrometer over the range 4000—250 cm^{-1} as Nujol mulls or KBr pellets. The solution spectrum was recorded in 0.1 mm KRS-5 cells. Fourier transform NMR spectra were recorded on a JEOL FX 90Q (^{1}H 89.6 MHz, ^{31}P 36.3 MHz, ^{195}Pt 19.2 MHz) or a Bruker AM 500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometer. The ^{31}P, ^{195}Pt, or ^{13}C NMR mesurement was carried out by broad-band noise decoupling of the hydrogen nuclei (^{1}H). Chemical shifts (δ, positive toward down field) are given in ppm and are referenced to external standards; to tetramethyl-

Table 1. ^{31}P, ^{195}Pt, ^{13}C, and ^{1}H NMR Parameters[a,b] (in ppm) of Phosphine Complexes

Compound	Nucleus				Solvent	Ref.
	^{31}P	^{195}Pt	^{13}C	^{1}H		
cis-$[\mathrm{Pt(OH)_2(PMe_3)_2}]\cdot n\mathrm{H_2O}$ (**1**)	−31.37 (s, $^{1}J_{\mathrm{PtP}}$=3320)	−4107 (t)	16.45 (m, $\lvert ^{1}J_{\mathrm{CP}}+^{3}J_{\mathrm{CP}}\rvert$=43)[c]	1.52 (m, $\lvert ^{2}J_{\mathrm{HP}}+^{4}J_{\mathrm{HP}}\rvert$=11.2),[c] 4.74[d]	$\mathrm{D_2O}$	This work
	−31.30 (s, $^{1}J_{\mathrm{PtP}}$=3254)	−4043 (t)		1.57 (m, $\lvert ^{2}J_{\mathrm{HP}}+^{4}J_{\mathrm{HP}}\rvert$=10.8),[c] 2.40[d]	$\mathrm{CD_2Cl_2}$	This work
cis-$[\mathrm{Pt(NO_3)_2(PMe_3)_2}]$ (**3**)	−25.31 (s, $^{1}J_{\mathrm{PtP}}$=3745)	−4346 (t)			$\mathrm{D_2O}$	This work
	−25.25 (s, $^{1}J_{\mathrm{PtP}}$=3742)	−4348 (t)			$\mathrm{D_2O}$	5
	−29.48 (s, $^{1}J_{\mathrm{PtP}}$=3765)			1.67 (m, $\lvert ^{2}J_{\mathrm{HP}}+^{4}J_{\mathrm{HP}}\rvert$=11.4)[c]	$\mathrm{CD_2Cl_2}$	This work
	−24.9 (s, $^{1}J_{\mathrm{PtP}}$=3738)				DMSO-d_6	5
$[\mathrm{Pt(ox)(PMe_3)_2}]$ (**2a**)	−26.72 (s, $^{1}J_{\mathrm{PtP}}$=3577)	−4334 (t)	15.54 (m, $\lvert ^{1}J_{\mathrm{CP}}+^{3}J_{\mathrm{CP}}\rvert$=45),[c] 170.25[e]	1.69 (m, $\lvert ^{2}J_{\mathrm{HP}}+^{4}J_{\mathrm{HP}}\rvert$=12.2)[c]	$\mathrm{D_2O}$	This work
	−27.8 (s, $^{1}J_{\mathrm{PtP}}$=3546)				$\mathrm{C_6D_6}$/MeOH	13
$[\mathrm{Pt(cbdca)(PMe_3)_2}]\cdot\mathrm{H_2O}$ (**2b**)	−27.12 (s, $^{1}J_{\mathrm{PtP}}$=3586)	−4263 (t)	15.41 (m, $\lvert ^{1}J_{\mathrm{CP}}+^{3}J_{\mathrm{CP}}\rvert$=42),[c] 17.67[f] ($\mathrm{C_5}$), 33.01[f] ($\mathrm{C_4}$, $\mathrm{C_6}$), 58.29[f] ($\mathrm{C_3}$), 163.19[f] ($\mathrm{C_1}$, $\mathrm{C_2}$)	1.66 (18H, m, $\lvert ^{2}J_{\mathrm{HP}}+^{4}J_{\mathrm{HP}}\rvert$=12.0),[c] 1.81 (2H, q, $\mathrm{CH_2}$), 2.65 (4H, t, $\mathrm{CH_2}$)	$\mathrm{D_2O}$	This work
$[\mathrm{Pt(CO_3)(PMe_3)_2}]\cdot 2\mathrm{H_2O}$ (**2c**)	−27.80 (s, $^{1}J_{\mathrm{PtP}}$=3511), −25.64 (s, $^{1}J_{\mathrm{PtP}}$=3396)		15.16 (m, $\lvert ^{1}J_{\mathrm{CP}}+^{3}J_{\mathrm{CP}}\rvert$=45),[c] 15.96 (m, $\lvert ^{1}J_{\mathrm{CP}}+^{3}J_{\mathrm{CP}}\rvert$=45)[c] g)		$\mathrm{D_2O}$	This work
	−31.30 (s, $^{1}J_{\mathrm{PtP}}$=3440), −24.70 (s, $^{1}J_{\mathrm{PtP}}$=3481)				$\mathrm{CDCl_3}$	This work
cis-$[\{\mathrm{Pt(PMe_3)_2}\}_2(\mu\text{-}\mathrm{OH})_2](\mathrm{NO_3})_2$ (**4**)	−25.64 (s, $^{1}J_{\mathrm{PtP}}$=3401)	−3921 (t)			$\mathrm{D_2O}$	This work
	−25.58 ($^{1}J_{\mathrm{PtP}}$=3398)	−3920			$\mathrm{D_2O}$	5

a) The coupling pattern and the coupling constants in Hz in parentheses. b) Abbr. s=singlet flanked by satellites, t=tripplet, q=quartet, m=multiplet. c) Parameters due to the trimethylphosphine group ($\mathrm{X_3AA'X'_3}$ or $\mathrm{X_9AA'X'_9}$ system, respectively. See Ref. 14). d) A broad singlet due to the water molecules and the OH anion. e) Parameters due to the oxalato group. f) Parameters due to the 1,1-cyclobutanedicarboxylate group. $\mathrm{C_1}$ and $\mathrm{C_2}$: carboxyl carbon; $\mathrm{C_3}$: quaternary carbon; $\mathrm{C_4}$ and $\mathrm{C_6}$: methylene carbon next to $\mathrm{C_3}$; $\mathrm{C_5}$: methylene carbon. See Ref. 15. g) Signals due to carbonato group were not observed.

Table 2. Infrared Band Assignments[a—c] of Phosphine Platinum(II) Complexes

Compound	2b	2c	3	4
Medium	KBr	Nujol or KBr	Nujol	Nujol or KBr
	3428	3460	1504	3400—3100
	vs, br H_2O	vs, br H_2O	sh, $\nu_a(NO_2)$	vs, br H_2O
	1630—1560	1670	1482	1626
	vs, br H_2O, (C=O)	vs, br H_2O	sh, $\nu_a(NO_2)$	s, br H_2O
	1346	1646	1262	1368
	vs, ν(C-O)	vs, br H_2O	vs, $\nu_s(NO_2)$	vs, ν_d(NO)
	1332	1608[d]	1002	1042
	vs, ν(C-O)	vs, ν(C=O)	m, ν(NO)	m, δ(PtO-H)
	Δ_1[f]$\approx$250	1606[e]	804	834
		vs, ν(C=O)	m, $\delta(NO_2)$	m, $\pi(NO_3)$
		1234	710	510
		s, ν(C-O)+δ(O-C=O)	w, $\rho(NO_2)$	vs, stretching vibrations of the $P_2PtO_2PtP_2$ skelton
		1008	Δ_2[g]$\approx$230	452
		m, ν(C-O)		m, stretching vibrations of the $P_2PtO_2PtP_2$ skelton
		826		
		m, π		

a) Infrared band assignments other than that of trimethylphosphine group. b) Band positions in cm^{-1}. c) IR-intensities; vs=very strong, s=strong, m=medium, w=weak, sh=shoulder, br=broad. d) Recorded as KBr pellet. e) Recorded as Nujol mull. f) Δ_1=difference between two frequencies; ν(C=O) and ν(C-O). g) Δ_2=difference between two frequencies; $\nu_a(NO_2)$ and $\nu_s(NO_2)$.

silane (in CD_2Cl_2) for ^1H spectra recorded in CD_2Cl_2 and to sodium 3-(trimethylsilyl)propanesulfonate (in D_2O) for ^1H spectra recorded in D_2O; to 85% H_3PO_4 for ^{31}P spectra; to Na_2PtCl_6 (saturated D_2O solution) for ^{195}Pt spectra recorded in D_2O and to Na_2PtCl_6 (saturated H_2O solution) for ^{195}Pt spectra recorded in CD_2Cl_2 or $CDCl_3$; to sodium 3-(trimethylsilyl)propanesulfonate (in D_2O) for ^{13}C NMR spectra recorded in D_2O. The ^{31}P, ^{195}Pt, ^{13}C, and ^1H NMR parameters are given in Table 1, and infrared data concerning the phosphine complexes are listed in Table 2. In addition to the above-mentioned spectroscopic measurements, the pH of a solution was measured using a TOA pH meter (HM-5ES).

Starting Material. Trimethylphosphine was purchased from Aldrich Chemical Company and used as received. The complex *cis*-dichlorobis(trimethylphosphine)platinum(II), *cis*-$[PtCl_2(PMe_3)_2]$, was prepared by a slight modification of a method from the literature.[16] The solution of $AgNO_3 \cdot PMe_3$[16] (28.70 g; 0.1167 mol) in H_2O (120 ml) was added dropwise to a solution of K_2PtCl_4 (23.22 g; 0.05595 mol) in H_2O (300 ml) in 6 h. The reaction mixture was stirred for 0.5 h. The resultant product was filtered and extracted with dichloromethane (3×150 ml), which was evaporated in vacuo to give a mixture of *cis*- and *trans*-$[PtCl_2(PMe_3)_2]$. The yield was 17.0 g (73 %). A mixture of two isomers was dissolved in a minimum amount of dichloromethane. The addition of a trace amount of trimethylphosphine to this solution converted the mixture into a pure *cis* isomer.[17] (Found: C, 17.18; H, 4.17; Cl, 17.66%, ^{31}P NMR ($CDCl_3$) δ=−24.70 (s, $^1J_{PtP}$= 3479)). The compound *cis*-dinitratobis(trimethylphosphine)platinum(II), *cis*-$[Pt(NO_3)_2(PMe_3)_2]$ (**3**), was prepared according to a method from the literature.[5] Crystals suitable for X-ray structural analysis were obtained by recrystallization from a dichloromethane solution. (Found: C, 15.34; H, 3.78; N, 6.02%).

Dihydroxo *cis*-Bis(trimethylphosphine)platinum(II) Hydrate; *cis*-$[Pt(OH)_2(PMe_3)_2] \cdot nH_2O$ (n=2—3) (1). Compound **3** (1.89 g; 4.01 mmol) was dissolved in H_2O (150 ml); the solution was then passed through a column packed with an anion-exchange resin (DIAION SA10AOH, 160 ml). An additional amount of water (400 ml) was passed through the column. The resultant eluate was evaporated in vacuo under thermal control by a water bath (temperature<5 °C). A very hygroscopic white powder **1** was obtained in a quantitative yield. Found: C, 16.62; H, 5.51%. Calcd for $C_6H_{20}O_2P_2Pt \cdot 2.5H_2O$: C, 16.9; H, 5.91%.

(Oxalato-*O*,*O′*)bis(trimethylphosphine)platinum(II); $[Pt(ox)(PMe_3)_2]$ (2a). An aqueous solution (400 ml) of **1** (5 mmol) was obtained as described in the above procedure. To this solution was added $H_2ox \cdot 2H_2O$ (6.30 g; 5 mmol) in water (100 ml). The resultant solution was condensed in vacuo until a highly crystalline solid **2a** was deposited. The yield was quantitative. Crystals suitable for an X-ray structural analysis were obtained by recrystallization from an aqueous solution. Found: C, 22.09; H, 4.06%. Calcd for $C_8H_{18}O_4P_2Pt$: C, 22.07; H, 4.17%.

(1,1-Cyclobutanedicarboxylato-*O*,*O′*)bis(trimethylphosphine)platinum(II) Monohydrate; $[Pt(cbdca)(PMe_3)_2] \cdot H_2O$ (2b). 1,1-cyclobutanedicarboxylic acid was purchased from WAKO Chemicals. The procedure mentioned above was applied to the preparation of **2b**. The compound was isolated as a white powder in quantitative yield. Crystals suitable for an X-ray structural analysis were obtained by recrystallization from a cyclohexanol solution. The compound was also soluble in ethanol; attempts to obtain single crystals of **2b** from an ethanol solution, however, were not successful. Found: C, 28.32; H, 5.03%. Calcd for $C_{12}H_{24}O_4P_2Pt \cdot H_2O$: C, 28.41; H, 5.17%.

(Carbonato-*O,O′*)bis(trimethylphosphine)platinum(II) Dihydrate; *cis*-[Pt(CO$_3$)(PMe$_3$)$_2$]·2H$_2$O (2c). Compound **2c** was obtained as follows. Dihydroxy compound **1** was exposed to air for several days, until the color turned black. The coloration indicated a partial decomposition of **1**. The product was dissolved in chloroform and the insoluble material was filtered off. The solution was slowly evaporated to give brown transparent block crystals, on which an X-ray structural analysis was carried out. Several attempts to recrystallize **2c** from a chloroform solution were unsuccessful. Found: C, 19.02; H, 4.73%. Caled for $C_7H_{18}O_3P_2Pt \cdot 2H_2O$: C, 18.97; H, 5.00%.

Di-*μ*-hydroxo-tetrakis(trimethylphosphine)diplatinum(II) Dinitrate; *cis*-[{Pt(PMe$_3$)$_2$}$_2$(*μ*-OH)$_2$](NO$_3$)$_2$ (4). To an aqueous solution (500 ml) of **1** (6.37 mmol) was added the aqueous nitric acid (56.3 ml; 6.37 mmol; 0.1131 N). The resultant solution was evaporated in vacuo to give **4** in quantitative yield. (Found: C, 16.91; H, 4.33; N, 3.37%).

X-Ray Structure Determination. Crystal structure determinations of **2a**, **2b**, **2c** or **3** were carried out. For **2a**, **2b**, or **3**, the X-ray diffraction intensities were collected on a Rigaku AFC-5R diffractmeter using graphite-monochromatized Mo *Kα* (λ=0.71069 Å) radiation and a 12 kW rotating anode generator. Details concerning an X-ray structure analysis of **2a**, **2b** or **3** will be described to *Acta Crystallogr., Sect. C.*[18] For **2c**, the X-ray diffraction intensities were collected on a Rigaku AFC-6 diffractmeter using graphite-monochromatized Mo *Kα* (λ=0.71069 Å) radiation (45 kV, 25 mA). The density of the crystals was determined by a flotation method in a 1,2-dibromoethane/hexane mixture. The crystal gradually became yellow during exposure to X-rays. Lorentz-polarization, absorption, and decay corrections were applied. Three representative reflections monitored every 147 reflections were declined by 11%. The structure was solved by the direct method. Anisotropic thermal parameters were applied for Pt and P atoms. The one PMe$_3$ ligand is disordered. Two sets of trimethyl-carbon atoms were located for PMe$_3$. The occupancy factors for these sets were refined to 59.278% (C1—C3) and 40.722% (C1A—C3A), respectively. The carbon atoms of C1A-C3A have been omitted for clarity in Fig. 8 and Fig. 9a. The refinement was performed by performing a full-matrix least-squares fit on F with $w=1/\sigma(F_o)^2$. H atoms were not included. Secondary extinction was applied (2.49838×10^{-7}). The scattering factors were from International Tables for X-ray Crystallography.[19] All calculations were performed using SHELXS-76, SHELXS-86, and ANYBLK[20] on an mips RS 3230. The positional parameters and U_{eq} are given in Table 3. The crystallographic data are summarized in Table 4. A table of the anistropic thermal parameters (for Pt and P), a listing of the observed and calculated structure factors, the full bond distances and the angles data are deposited as Document No. 9047 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 3. Atomic Parameters (×10000) and Isotropic Temperature Factors (×1000) for **2c**

Atom	x	y	z	U_{eq} [a]
Pt [b]	6107(2)	10633(3)	12798(3)	200(2)
P1	1882(1)	825(2)	1268(3)	31(1)
P2	586(2)	1914(2)	−265(2)	30(1)
O1	−576(4)	1095(5)	1716(5)	31(2)
O2	334(4)	460(5)	2768(6)	39(2)
O3	−885(4)	437(6)	3428(6)	47(2)
O4	938(5)	−802(6)	4408(7)	51(2)
O5	−1794(5)	2576(7)	1491(8)	72(3)
C1	2288(16)	−193(21)	569(33)	47(8)
C1A	2188(17)	−93(21)	174(31)	15(8)
C2	2211(13)	612(30)	762(25)	15(8)
C2A	2187(14)	245(26)	2507(24)	11(8)
C3	2549(15)	799(21)	1098(24)	28(7)
C3A	2496(20)	2004(27)	980(28)	13(8)
C4	−418(6)	1895(8)	−915(9)	38(3)
C5	813(7)	3284(9)	−12(11)	58(4)
C6	1217(6)	1553(8)	−1408(10)	45(3)
C7	−471(8)	682(9)	2695(11)	50(4)

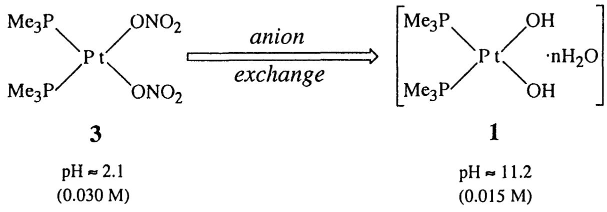
a) $U_{eq}=1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i \cdot \boldsymbol{a}_j$. b) Atomic parameters (×100000) and isotropic temperature factors (×10000).

Table 4. Crystallographic Data for **2c**

Formula	$C_7H_{18}O_3P_2Pt \cdot 2H_2O$
Formula weight	443.27
Crystal system	Orthorhombic
Space group	*Pbca*
Z	8
a/Å	17.249(3)
b/Å	13.497(5)
c/Å	12.210(3)
V/Å	2843(1)
D_x/g cm^{-3}	2.071
D_m/g cm^{-3}	2.06
μ(Mo $K\alpha$)/cm^{-1}	101.9
Range of transmittance (for Absorption correction)	0.6416—0.9431
F(000)	1696
T/K	298
Crystal size/mm	0.40×0.25×0.25
No. Ref. used in cell dimentions	24
(θ range/°)	($18<2\theta<24$)
Mode	2θ-ω
Range of measurement/°	$2.00<2\theta<60.00$ ($0\leq h\leq 24$, $0\leq k\leq 19$, $0\leq l\leq 17$)
Scan rate (° min^{-1} in ω)	4
No. Ref. Measured	4167
No. Ref. Observed	2321 ($F_o>4\sigma(F_o)$)
No. of variable	90
$R(wR)$	0.068 (0.058)
S	3.796
$(\Delta\sigma)_{max}$	0.01
$\Delta\rho$/eÅ^{-3}	2.3

Results and Discussion

An Intermediate of the Anion-exchange Method. When an aqueous solution of compound **3** was passed through a column packed with the anion exchange resin (DIAION SA10AOH), the eluate showed a high pH. The solution was evaporated in vacuo to give a very hygroscopic white powder. The ^{31}P or ^{195}Pt NMR measurement (in D$_2$O) showed only a set of signals,[21] of which both the shift value and the coupling constant differed from those of known complexes,[5] such as a nitrate **3** and a dimer **4**. The ^{13}C NMR again confirmed the *cis* geometry of the phosphine ligands. It is thus assumed that dihydroxobis(trimethylphosphine)-



Scheme 1. Formation of **1** and pH value before and after anion-exchange.

platinum(II) species is formed in solution.[22] (Scheme 1)

Elemental analysis and infrared data (Nujol mull) suggest that powder sample **1** contained a certain amount of water. Its ^{1}H NMR spectrum was also recorded in either a D_2O or a CD_2Cl_2 solution. Each spectrum gave a multiplet due to trimethylphosphine ligands and a broad singlet. The spectral intensity of the broad signal suggests that **1** has several water molecules (n=2—3), except for hydroxy protons. The ^{31}P, ^{195}Pt, ^{13}C, and ^{1}H NMR parameters are summarized in Table 1.

The thermal stability of **1** was examined in a simple fashion. The white powder **1** scarcely showed any coloration at room temperature (15—20 °C) under a nitrogen atmosphere for at least 1 week, but turned dark brown upon desiccation at a higher temperature (40—50 °C). An enforced removal of water molecules might cause the decomposition of **1**. These observations indicate that several water molecules are essential for the stabilization of dihydroxobis(trimethylphosphine)-platinum(II).

The solution-stability of the compound has also been checked. Although **1** dissolves in CD_2Cl_2 to initially give a yellow solution, the color turns black within 30 min, and a black material is precipitated. After 2 months, the material was filtered off by a sintered-glass filter (G4). The ^{31}P NMR spectrum of the filtrate showed two singlets; one was a singlet symmetrically flanked by ^{195}Pt satellites; the other was a simple singlet.[23] They had almost equal intensities. The former is characteristic of trimethylphosphine bound to a platinum atom,[21] and the latter is considered to be due to trimethylphosphine oxide (Me_3PO).[24] The result indicates that the dihydroxo species tends to decompose in CD_2Cl_2. In a D_2O solution, however, the color did not show any change for at least 1 week. After further standing, the solution gradually darkened. The ^{31}P NMR measurement was carried out according to a similar procedure as that in the case of the CD_2Cl_2 solvent; only a sole signal due to the dihydroxo species, however, was observed. The experiment was carried out either in an inert atmosphere or under air. The same result was obtained under both conditions. Therefore, it is not O_2 gas that brings about a decomposition of the dihydroxo species; it is inferred that water is a preferable solvent to dichloromethane, as far as the solution-stability of the dihydroxo species is concerned. The polarity of the solvent might affect the stability of the dihydroxo species.

The acid-base equilibria in an aqueous solution were surveyed qualitatively by ^{31}P NMR spectroscopy. About 0.1 mmol of **1** was dissolved in D_2O (1.0 ml), to which some equivalents of aqueous nitric acid (0.1131 equiv) were added (in a molar ratio; 2:1, 1:1, or 1:2 respectively). A ^{31}P NMR measurement (after 28 h) identified three main solution-species, referenced to those of authentic samples; nitrate **3**, dimer **4**, and dihydroxide **1**. The representative spectra and the proposed scheme are shown in Fig. 2

Other researchers have reported that the addition of NaOH to the aqueous solution of **3** forms **4**.[5] An extension of their experiment to a higher pH region has been attained by this work. Compound **4** (0.1 mmol) was dissolved in D_2O (1.0 ml), to which some equivalents of NaOD/D_2O were added[25] (in a molar ratio; 4:1, 2:1, or 1:1 respectively); the ^{31}P NMR spectrum was then measured (after 24 h). The reaction scheme is proposed in Fig. 3.

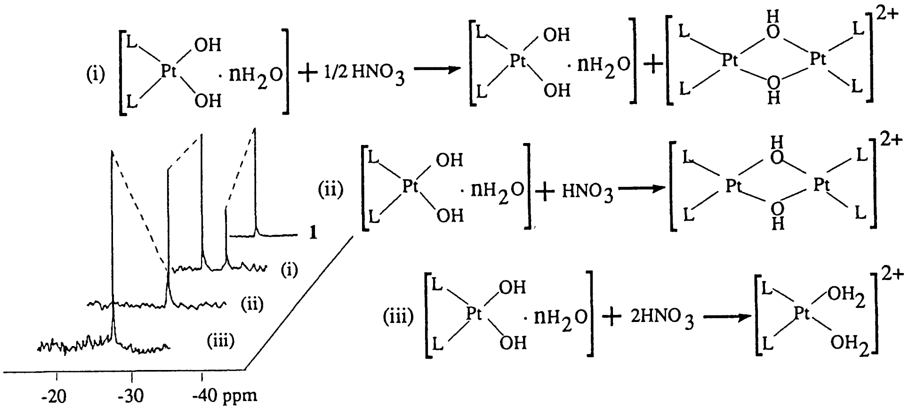


Fig. 2. The change of ^{31}P NMR spectra with equivalent amounts of nitric acid (satellites are omitted for clarity) and the proposed scheme. L=PMe_3.

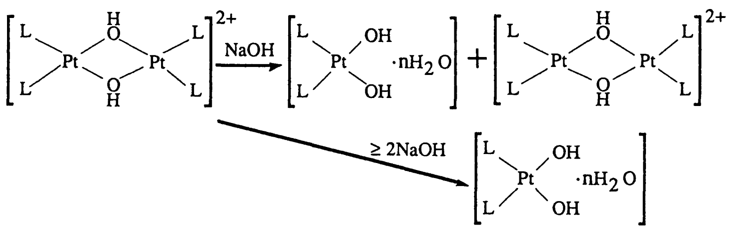


Fig. 3. Addition of sodium hydroxide to the dimer **4**.

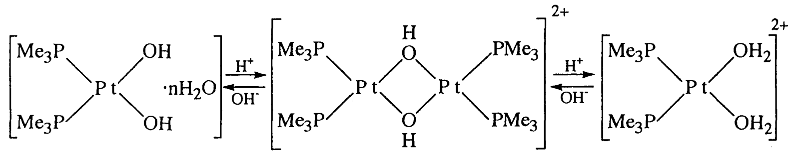
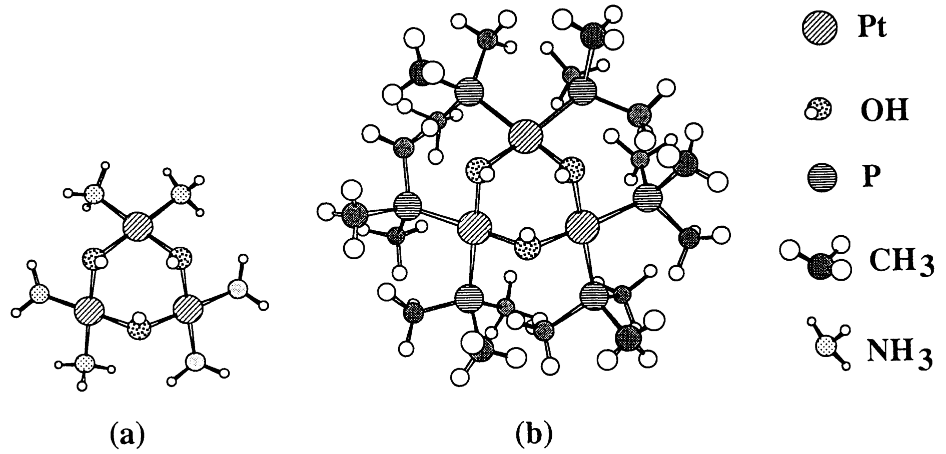


Fig. 4. Equilibria in aqueous solution (^{31}P NMR).



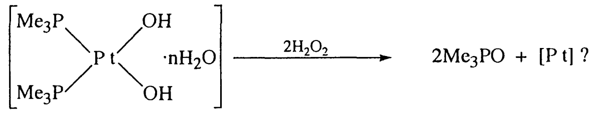
(a) **(b)**

Fig. 5. Visual images of trimers.

Thus, the overall equilibria are shown in Fig. 4.

The acid-base equilibria seem to be different from those of ammine complexes.[8] In the ammine-platinum system, the formation of the hydroxo-bridged trimer is well known.[26] The corresponding trimethylphosphine trimer has so far not been isolated by our trials, and has not so far been detected by ^{31}P NMR spectroscopy. A heavy steric congestion of the phosphine ligands around the platinum atom might hinder formation of the trimer. Figures 5a and 5b shows the visual image of diammine trimer, *cis*-$[\{Pt(NH_3)_2\}_3(\mu\text{-}OH)_3]^{3+}$ and bis(trimethylphosphine) trimer, *cis*-$[\{Pt(PMe_3)_2\}_3(\mu\text{-}OH)_3]^{3+}$, respectively.

The reaction of **1** with hydrogen peroxide was also qualitatively traced by ^{31}P NMR spectroscopy. About 0.1 mmol of **1** was dissolved in D_2O (0.8 ml), to which aqueous hydrogen peroxide (ca. 0.460 M) was added (in a molar ratio; 4:2, 2:2, or 1:2 respectively). As the original colorless solution turned light orange within 1 h, the ^{31}P NMR spectrum was measured (after 80 h). A new singlet due to trimethylphosphine oxide (Me_3PO)[27,28] appeared (52.90 ppm) along with an increase in the amount of H_2O_2. The ^{195}Pt NMR spectrum showed a singlet[29] when two equivalents of H_2O_2 were added to the D_2O solution. Unfortunately, at the present stage, we have no strong evidence to define the platinum chemical species and oxidation state. The reaction is represented in Scheme 2.



Scheme 2. Addition of H_2O_2 to **1** (^{31}P NMR).

Kurosawa's group reported that the reaction of a dimer, *cis*-$[\{Pt(PR_3)_2\}(\mu\text{-}OH)_2](BF_4)_2$ (where PR_3=PPh_3, $P(p\text{-}tol)_3$, $P(p\text{-}C_6H_4Cl)_3$ or $1/2Ph_2PCH_2CH_2PPh_2$) with H_2O_2, gave a novel μ-peroxo-platinum(II) complex, $[\{Pt(PR_3)_2\}_2(\mu\text{-}OO)(\mu\text{-}OH)](BF_4)$.[30] The reaction pattern in an organic solvent (CD_2Cl_2) represents a great contrast to this work; our reaction proceeds in a straightforward way until phosphine ligands are released (as phosphine oxide) in an aqueous solution, while in an organic solvent the μ-peroxide dimer seems to be stable. The presence of H^+ in an aqueous solution might be the key factor to explain the difference.

Syntheses of the Water-Soluble Phosphine Complexes. Facile Synthetic Method via Dihydroxobis(trimethylphosphine)platinum(II). The trimethylphosphine analogues (**2a** or **2b**) of *l*-OHP or *carboplatin*,[9] were prepared in a quantitative yield without any anion-contamination. Both compounds are stable to air and are soluble in water. Compound **2b** is very soluble in water, as compared with **2a**. The presence of water molecules as hydrate might cause such a slight difference. The molecular structures of [Pt(ox)$(PMe_3)_2$] (**2a**) and [Pt(cbdca)$(PMe_3)_2$]$\cdot H_2O$ (**2b**) are shown in Figs. 6 and 7, respectively.[18] As shown by these examples, a wide variety of water-soluble phosphine platinum(II) complexes could be prepared by a simple neutralization with inorganic and/or organic acids. (Scheme 3)

When **1** was exposed to air, it reacted with atmospheric CO_2 gas and formed carbonatoplatinum(II) (**2c**). This event might be attributed to the inherent preference of a base **1** to a weak acid, HCO_3^- or CO_3^{2-}. The compound is also stable and readily soluble in water, chloroform or dichloromethane. The molecular structure of **2c** is shown in Fig. 8. The compound crystallizes in the orthorhombic system, the *Pbca* space group. An X-ray structural analysis revealed that the geometry of the Pt(II) coordination sphere is essentially square-planar, and that the carbonate ligand constitutes a four-membered ring, together with a platinum atom. The

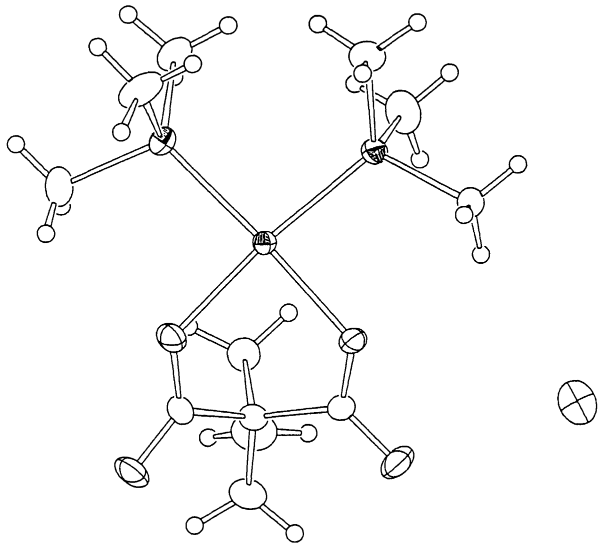


Fig. 7. Molecular structure of **2b**, [Pt(cbdca)$(PMe_3)_2$]$\cdot H_2O$.

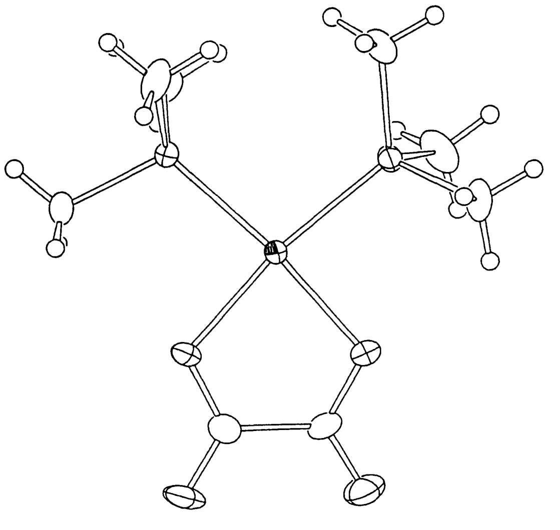


Fig. 6. Molecular structure of **2a**, [Pt(ox)$(PMe_3)_2$].

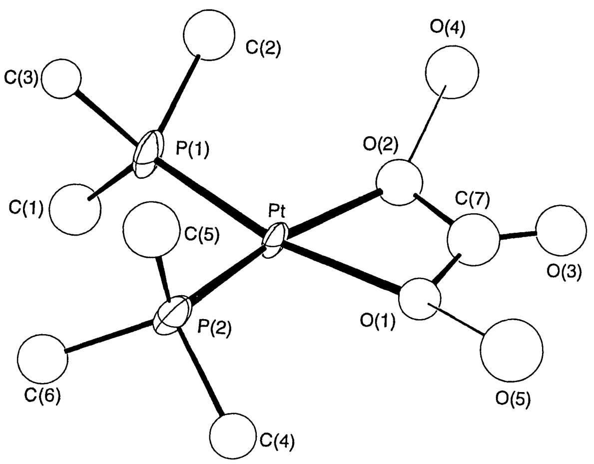
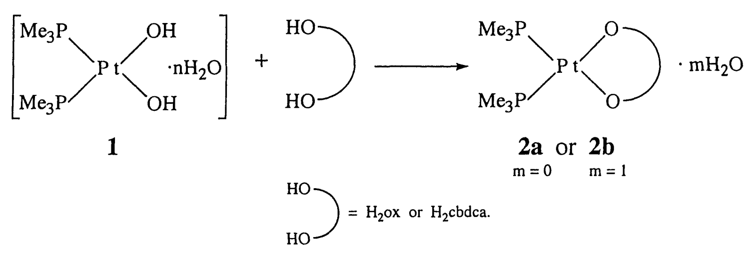


Fig. 8. Molecular structure of **2c**, [Pt$(CO_3)(PMe_3)_2$]$\cdot 2H_2O$, with atomic numbering. Thermal ellipsoids are drawn at the 50% probability level for Pt and P atoms.



Scheme 3. Synthetic procedure to phosphine complex.

other characteristics of the molecular structure are understandable, compared with those of a triphenylphosphine analogue, carbonatobis(triphenylphosphine)platinum(II) tetrahydrofuran solvate (**2c′**).[31] The selected bond distances and angles for both **2c** and **2c′** are listed in Table 5. The P(1)–Pt–P(2) angle of **2c** has a relatively small value, in fulfillment of the steric requirement due to trimethylphosphine; the O(1)–Pt–O(2) angle, however, is 63.9(3)°, which is similar to the observed value of **2c′**. Both compounds have a planar carbonate group. The observed Pt–O(1) distance of **2c** is longer than the Pt–O(2) distance, although the two Pt–O distances of **2c′** are almost equal. The difference in the Pt–O distances might be related to hydrogen bonding between the water molecules and the carbonate group: between O(1) and O(5), or between O(2) and O(4). The hydrogen bonding between O(3) and O(4^{i}) might cause the dissimilarity between the two O–C–O angles in the carbonate group; i.e., between O(1)–C(7)–O(3) and O(2)–C(7)–O(3).

The unit cell of **2c** is shown in Fig. 9a. The crystal lattice contains water molecules in spite of crystallization from a chloroform solution. The carbonate anion and the water molecules (O(1)–O(5)) form the one-dimensional infinite hydrogen-bond along the *C*-axis (Fig. 9b). The network comprises the 8- and 10-membered rings that are fused alternately in a row (Fig. 9c). All of the 10-membered rings are twisted clockwise and counterclockwise by turns along the axis.

Table 5. Selected Bond Distances (Å) and Angles (°) for **2c** and **2c′**

	2c	**2c′**
Pt–P(1)	2.216(4)	2.254(2)
Pt–P(2)	2.209(3)	2.228(1)
Pt–O(1)	2.116(7)	2.047(5)
Pt–O(2)	2.047(7)	2.053(3)
C(7)–O(1)	1.333(15)	1.315(6)
C(7)–O(2)	1.423(15)	1.358(8)
C(7)–O(3)	1.192(15)	1.201(7)
P(1)–Pt–P(2)	95.09(12)	99.25(5)
O(1)–Pt–O(2)	63.9(3)	64.5(2)
O(1)–C(7)–O(3)	135.1(12)	125.7(7)
O(2)–C(7)–O(3)	118.7(11)	124.7(5)
O(1)–C(7)–O(2)	106.1(10)	109.8(5)
O(1)–O(5)	2.912(7)	
O(2)–O(4)	2.827(7)	
O(3)–O(4^{i})[a]	2.690(8)	
O(4)–O(5^{ii})[a]	2.859(8)	

a) Symmetry code: (i) $-x$, $-y$, $-z$, (ii) $-x$, $y+1/2$, $-z+1/2$.

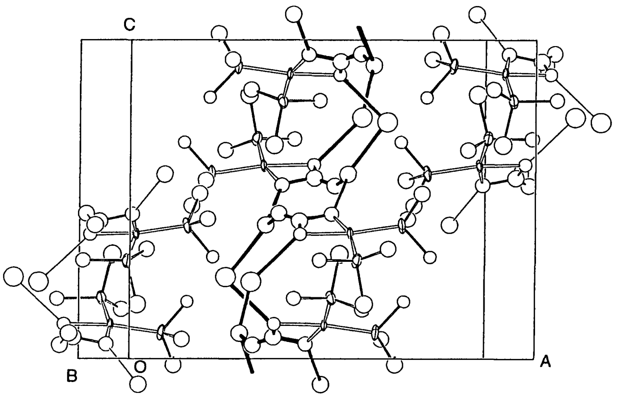


Fig. 9a. Unit cell of **2c**, $[Pt(CO_3)(PMe_3)_2]\cdot 2H_2O$. Thermal ellipsoids are drawn at the 50% probability level for Pt and P atoms.

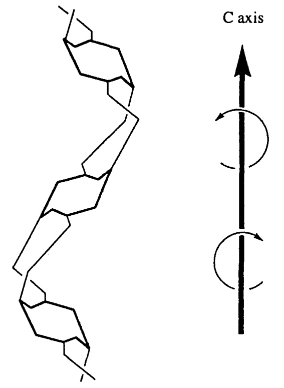


Fig. 9b. Schematic view of the one-dimensional infinite hydrogen-bond of the carbonate anion and the water molecules.

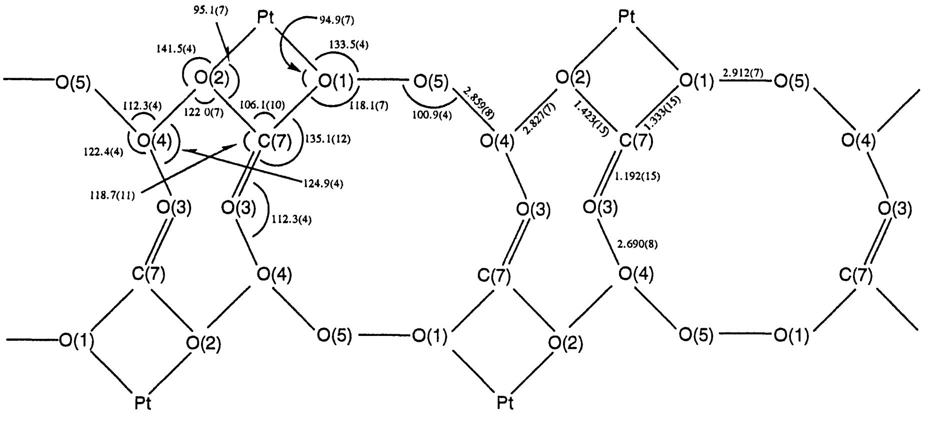


Fig. 9c. Bond distances and angles of the network.

The entire structure is not a double helical, but might be represented as a "waved-ribbon".

Because the positions of the H atoms have not been determined by an X-ray structural analysis, the H–O–H angle has not been determined. However, as far as the O atoms are concerned, it seems likely that the O(4) atom has a 3 coordination number, and is almost planar; the O(5) atom has a 2 coordination number. The coordination-environment of the O(4) atom belongs to a novel type, which might be attributed to the crystal packing of the molecules. The O(1)–O(5)–O(4^{ii}) angle has a similar value to the H–O–H angle (104.5°)[32] of liquid H_2O.

X-Ray structural determinations of **2a**,[18], **2b**,[18] and **3**[18] have also been carried out. The structures of these complexes exhibit essentially a square-planar coordination geometry. A comparison of the molecular structures of **2a**,[18], **2b**,[18] **2c**, **3**,[18] (Fig. 10) or **4**[5] has established a structural feature of the "*cis*-$(Me_3P)_2Pt$" unit. The average value of the Pt–P distances is substantially the same, and there is no dramatic influence exerted by a series of O-donor ligands (Table 6). The mean Pt–P distance of the dichloride complex, however, is slightly longer: 2.248±0.007 Å.[33] The bond lengthening is ascribable to a rule that the trans influence of the chloride ligand is stronger than those of O-donor ligands.[34] The P–Pt–P angles for a series of complexes, **2**—**4**, again show similar values, although a slight deviation is noticeable for the angle of **2a**.

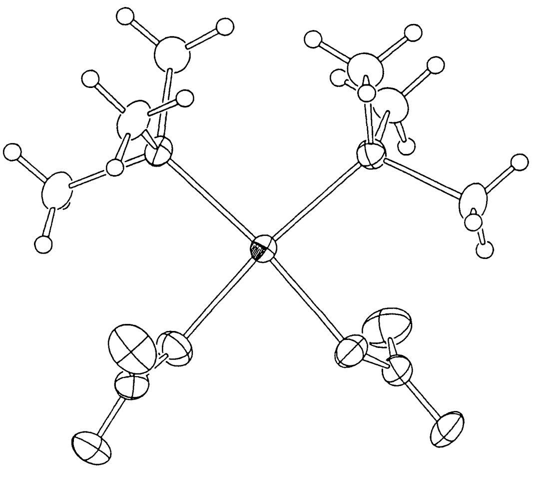


Fig. 10. Molecular structure of **3**, *cis*-$[Pt(NO_3)_2(PMe_3)_2]$.

Table 6. The Average Value of P–Pt–P Angles (°) and Pt–P Distances (Å) for a Series of Bis(trimethylphosphine)platinum(II) Complexes

Compound	P–Pt–P	Pt–P	Ref.
3	94.9(1)	2.231(3)	18
2a	97.27(9)	2.215(2)	18
2b	95.13(6)	2.222(2)	18
4	95.4(1)	2.230(4)	5

Spectroscopic Properties. Spectroscopic properties of trimethylphosphine complexes **1**—**4** are discussed regarding their molecular structures.

The infrared spectra of **2b**, **2c**, **3**, and **4** were measured (Table 2) just as the spectrum of compound **1**. The assignment of the infrared bands due to trimethylphophine ligands had already been made on the basis of normal coordinate analyses by other researchers.[35]

In the solid state, compounds **3** and **4** showed the characteristic absorption bands of the nitrate groups. The patterns were distinctly different from each other. It is well known that an ionic nitrate (point group D_{3h}) gives rise to four fundamental absorption frequencies, while a linked nitrate (C_{2v} or C_s for unidentate nitrate) exhibits six fundamental vibrations.

Three NO stretching bands of **3** showed the characteristics of the unidentate nitrate group:[36] $\nu_a(NO_2)$, $\nu_s(NO_2)$, and $\nu(NO)$. In general, separation of the two highest-frequency bands (Δ_2) is larger for bidentate than that for unidentate coordination.[36] The observed absorption frequencies of **3** were close to the reported values of the unidentate coordination.[37] The possibility of a free or bidentate nitrate group was thus ruled out. The two nitrate groups may link to platinum(II) in a unidentate fashion. Our X-ray structural analysis of **3** confirmd this estimation.

A strong band occured at 1368 cm^{-1} for the spectra of **4**. It was assigned to $\nu_d(NO)$ of free nitrate. An additional band appeared at 1042 cm^{-1}, which is close to the frequency of the PtO–H bending vibration for the ammine analogue, tetraammine-di-μ-hydroxo-diplatinum(II) dinitrate.[38] No band characteristics of unidentate or bidentate nitrate group appeared. Thus, nitrate seems to be free nitrates. The deduction from infrared measurement agrees well with the result of an X-ray structural determination.[5] The stretching vibrations of the $N_2PtO_2PtN_2$ skeleton were assigned to a diammine analogue.[38] In the region lower than these stretching bands, two distinctive bands were observed (Table 2). Judging from the dimer structure elucidated from an X-ray structural analysis, the bands are tentatively assignable to $P_2PtO_2PtP_2$ skeletal stretching.

Substantial differences in the coupling constants, $^1J_{PtP}$, were found among the NMR spectra of complexes **1**—**4**.

It must be emphasized that the $^1J_{PtP}$ of **2a** or **2b** differs significantly from those of **1** and **3**. As reported by an Italian group, the nitrate ligands of **3** are replaced with water molecules in an aqueous solution.[5] Thus, it is not likely that aquation or hydroxylation occurs on **2a** or **2b**; i.e., even in an aqueous solution, oxalate or the 1,1-cyclobutanedicarboxylate ligand may link to the platinum atom, thus forming a chelate ring. The similarity of $^1J_{PtP}$ for **2a** and **2b** indicates that the coordination-environment around platinum resembles each other.

The infrared spectrum of **2b** showed two strong bands, ν(C=O) and ν(C–O), in addition to the absorption bands due to lattice water (Table 2). The overlap of the stretching ν(C=O) and the HOH bending mode precluded measuring accurate wavenumbers for ν(C=O). The spectrum, however, exhibits the Δ_1 value (Table 2), which is much greater than the data observed for bidentate carboxylate or ionic carboxylate complexes.[36] The result led us to the conclusion that the two carboxylate groups are unidentate. An X-ray structural analysis[18] supports our speculation.

Trogler et al. reported the assignment of infrared data on **2a**.[13] An estimation of the molecular structure from their data again agreed well with our result concerning the X-ray structural analysis.

The infrared spectra of **2c** (Nujol mull or KBr disk) indicated that the carbonate group is bidentate (Fig. 11). The result of an X-ray structure analysis verified the bidentate coordination and the local symmetry (C_{2v}) of the carbonate ligand. The infrared spectrum was also recorded in a chloroform solution. Although the low concentration prevented us from measuring the spectrum with high resolution, the signal corresponding to ν(C=O) definitely dissapeared, nevertheless. Generally speaking, as far as the two highest frequency bands are concerned, unidentate coordination gives rise to a smaller separation than does the bidentate type; such a smaller separation may be explained by a reduction to C_s symmetry.[36] The observed spectral feature leads to the idea that the symmetry of the carbonate group in the solid state changed into another in a chloroform solution. Thus, the chemical structure of the solution-species would be different from the molecular structure in the crystals.

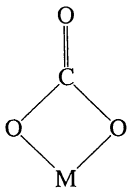


Fig. 11. Bidentate coordination of carbonate group.

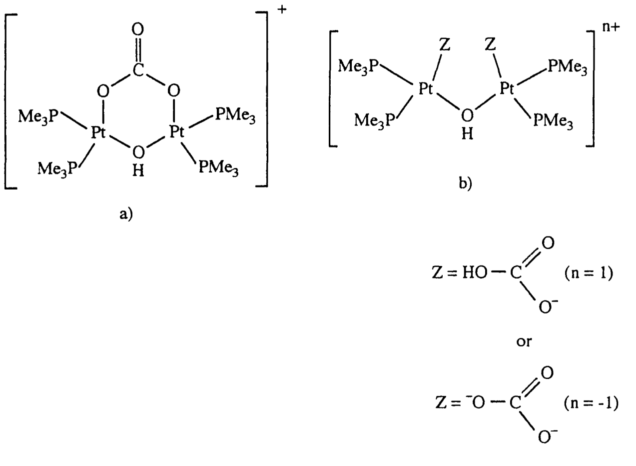


Fig. 12. Two possible structures of solution-species for **2c** in aqueous solution.

The ^{31}P NMR spectrum of **2c** in D_2O solution showed two singlets, both of them were symmetrically flanked by ^{195}Pt satellites (Table 1). The coupling constant of each singlet was smaller than that of **3** in the D_2O solution. The reduction in the *s* character of Pt–P bonding means that the ligands other than the water molecules linked to platinum(II) in an aqueous solution. The several anionic ligands would be the strong candidates, for instance OH^-, CO_3^{2-}, and HCO_3^-. Of the observed two singlets, the lower shielded signal had both the coupling constant and the chemical shift close to the data for **4** but far from the observed values of **1** or **3**. The NMR data of the higher shielded signal were quite different from the values of **1**, **3**, or **4**, and were rather close to those of **2a** or **2b**. Judging from these characteristics, two potentially possible structures are proposed as the solution species of **2c** (Fig. 12a or 12b).

Finally, the ^{31}P NMR data concerning a series of *cis*-bis(trimethylphosphine)platinum(II) compounds are listed in Table 7, including the literature values. The coupling constants, $^1J_{\mathrm{PtP}}$, have a fairly good correlation with the donor atom trans to the phophine ligands. A noticeable trend is depicted in Fig. 13, in which a considerable separation can be seen between the N and O donor groups. Thus, in solution chemistry , the coupling constant, $^1J_{\mathrm{PtP}}$, may be useful for the discrimination of the N donor from the O donor ligand.

The moiety of "*cis*-$Pt(PMe_3)_2$" is a good spin system for polynuclear NMR spectroscopy and, hence, provides much information concerning the solution species, as demonstrated in this paper. In particular, highly

Table 7. The Value of Coupling Constant, $^1J_{\mathrm{PtP}}$, for the Complexes, *cis*-$Pt(PMe_3)_2A_2$

Donor element bound to platinum(II)	A	$^1J_{\mathrm{PtP}}$ [a]	Ref.
H	H^-	1875	39)
C	$Me_3CCH_2^-$	1605	40)
	Me^-	1790	41)
	$Me_3SiCH_2^-$	1945.1	42)
	$CH_2{=}CHSiMe_2CH_2^-$	1976	43)
N	OSN^-	3029	44)
	(N_3-mbi)[b,c]	3145	
	(N_7-dGuo)[b,c]	3276	
	SCN^-	3333	45)
O	$1/2((CF_3)_4C_2O_2^{2-})$	3414	46)
P	PMe_3[d]	2230	47)
S	$1/2(O_2C_2S_2^{2-})$	2890	48)
	$1/2(CS_3^{2-})$	2971	49)
Se	$1/2(SCSe_2^{2-})$	2985	49)

a) The coupling constant in Hz. b) The compound was prepared in the course of our research. Elemental analysis satisfies the molecular formula, *cis*-$[Pt(PMe_3)_2(N_3\text{-mbi})_2](NO_3)_2$ or *cis*-$[Pt(PMe_3)_2(N_7\text{-dGuo})_2]Cl_2$. c) mbi; 1-methylbenzimidazole, dGuo; deoxyguanosine. d) $[Pt(PMe_3)_4](BF_4)_2$.

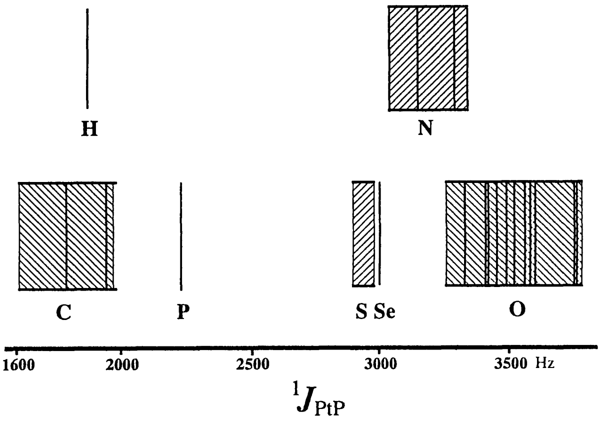


Fig. 13. Plot of $^1J_{PtP}$ for a series of bis(trimethylphosphine)platinum(II) complexes. Each upright line represents the observed value of $^1J_{PtP}$ for each compound listed in Table 1 and 7.

water-soluble compounds **1** or **3** would serve as useful spin-markers for the identification of platinum-linkage sites to water-soluble polymers, such as natural proteins. An extension to the biological system is under way in our laboratory.

This work was supported in part by a Grant-in-Aid for Scientific Research No. 04453043 from the Ministry of Education, Science and Culture, to which our thanks are due.

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21) ^{195}Pt, I=1/2, 34% abundance. The ^{31}P NMR spectra for the complexes (**1**—**4**) show a singlet with "satellites" from ^{195}Pt-^{31}P coupling, with each satellite ca. one-fourth the intensity of the center peak.

22) We have also carried out the characterization of dihydroxodiammineplatinum(II) compound, *cis*-$[Pt(OH)_2(NH_3)_2]\cdot nH_2O$ in a similar procedure as described in text. Anal. Found: H, 3.78; N, 9.55%. Calcd for $H_8N_2O_2Pt\cdot 1.5H_2O$: H, 3.82; N, 9.65. For *cis*-$[Pt(OH)_2(^{15}NH_3)_2]\cdot nH_2O$; ^{15}N NMR ($H_2O$) $\delta=-77.34$ (s, $^1J_{PtN}$=297 Hz), ^{195}Pt NMR (H_2O) $\delta=-1571$ (t, $^1J_{PtN}$=299 Hz).

23) ^{31}P NMR (CD_2Cl_2) $\delta=-24.63$ (s, $^1J_{PtP}$=3481 Hz), 37.69 (s).

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