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Nuclear Magnetic Resonance Investigation of the Hydrogen Peroxide Oxidation of Platinum(II) Complexes. Crystal and Molecular Structures of Sodium *trans*-Dihydroxobis(malonato)platinate(IV) Hexahydrate and Sodium *trans*-Dihydroxobis(oxalato)platinate(IV) Hexahydrate

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Nuclear magnetic resonance techniques utilizing ^{195}Pt and ^{13}C have been employed to study the formation of dihydroxo platinum(IV) compounds in the hydrogen peroxide oxidation of Pt(II) complexes. The *trans*-dihydroxo isomer is the exclusive kinetic product for oxalato, malonato, and chloro complexes. Isotopic labeling experiments with $H_2{}^{18}O$ demonstrate that one hydroxo ligand originates from hydrogen peroxide, while the trans hydroxo ligand originates from water. Hydrogen peroxide oxidation in methanol or ethanol results in the formation of *trans*-hydroxomethoxo- and *trans*-hydroxoethoxoplatinum(IV) complexes, respectively. The structure of sodium *trans*-dihydroxobis(malonato)platinate(IV) hexahydrate has been determined by X-ray crystallography: $P\bar{1}$, $a = 6.648(1)$ Å, $b = 8.234(1)$ Å, $c = 9.065(1)$ Å, $\alpha = 63.82(1)°$, $\beta = 70.67(1)°$, $\gamma = 71.78(1)°$, $V = 412.0(1)$ Å^3, $Z = 1$, $R = 0.0308$, $R_w = 0.0300$. The structure of sodium *trans*-dihydroxobis(oxalato)platinate(IV) hexahydrate has also been determined by X-ray crystallography: *Cmca*, $a = 15.562(2)$ Å, $b = 7.200(1)$ Å, $c = 13.840(1)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1550.9(3)$ Å^3, $Z = 4$, $R = 0.0509$, $R_w = 0.0492$.

Introduction

Hydrogen peroxide is a widely studied oxidizing agent for inorganic complexes. A number of different mechanisms have been observed. The hydrogen peroxide oxidation of Pt(II) complexes to Pt(IV) complexes has been utilized in many important aspects of platinum chemistry such as the formation of mixed valence linear chain complexes[1-3] and the synthesis of Pt(IV) antitumor drugs.[4-7] Several crystal structures as well as ^{15}N and ^{195}Pt nuclear magnetic resonance (NMR) studies indicate that hydrogen peroxide oxidation of Pt(II) complexes leads to *trans*-dihydroxo Pt(IV) complexes.[4-8] While one-electron oxidation involving hydroxyl radicals occurs with many metals, a one-step two-electron oxidation has been suggested in the oxidation of $[Pt(NH_3)_4]^{2+}$ by hydrogen peroxide.[9] Mechanistic studies with $H_2{}^{18}O$ solvent support the formation of an oxidant to Pt bond early in the transition state for the oxidation reaction of $[PtCl_4]^{2-}$ by $[MnO_4]^{2-}$.[10,11]

^{195}Pt NMR is a sensitive probe for the environment of the Pt nucleus.[12] Elding has observed that coordinated $H_2{}^{18}O$ shifts ^{195}Pt NMR resonances 0.5–1.0 ppm from the corresponding resonance when $H_2{}^{16}O$ is bound. Elding has used the ^{18}O isotopic shifts to study the reaction mechanism for Cl_2 oxidation of Pt(II) complexes and to determine water exchange rates for Pt(II) complexes.[13,14] Herein, we have extended ^{18}O labeling approaches to the study of the mechanism and product distribution for the hydrogen peroxide oxidation of a variety of Pt(II) complexes.

Experimental Section

Starting Materials. Oxalic (OxH_2), malonic ($MalH_2$), and 2-methylmalonic acids ($MmalH_2$) (Aldrich) and $K_2[PtCl_4]$ (**18**) (Johnson Matthey) were used as supplied. $[Pt(Ox)_2]^{2-}$ (**1**), $[Pt(Mal)_2]^{2-}$ (**4**), and *syn*- and *anti*-$[Pt(Mmal)_2]^{2-}$ (**7**, **8**) were also prepared as previously described.[15,16]

Preparations. Potassium and Sodium *trans*-Dihydroxobis(oxalato)platinate(IV) (2). The potassium salt was prepared essentially as first reported by Werner and more recently by Preetz.[17,18] Two equivalents of a 30% aqueous solution of H_2O_2 (0.047 g, 0.4 mmol) were added to an aqueous solution of $K_2[Pt(Ox)_2]\cdot 2H_2O$ (0.100 g, 0.2 mmol) (**1**), and the solution was heated at 50 °C for 15 min. ^{195}Pt and ^{13}C NMR show greater than 95% conversion of **1** to *trans*-$[Pt(OH)_2(Ox)_2]^{2-}$ (**2**). Vapor diffusion of acetone into an aqueous solution gave green crystals of $K_2[trans\text{-}Pt(OH)_2(Ox)_2]\cdot xH_2O$ (**2**) for X-ray crystallography. The sodium salt of **2** was prepared by ion exchange of an aqueous solution of the potassium salt over Dowex 50W-X8 in the sodium form. Vapor diffusion of acetone into an aqueous solution of **2** in the sodium form gave yellow crystals of $Na_2[trans\text{-}Pt(OH)_2(Ox)_2]\cdot 6H_2O$ (**2**).

Potassium *cis*-Dihydroxobis(oxalato)platinate(IV) (3). An aqueous solution of *trans*-$[Pt(OH)_2(Ox)_2]^{2-}$ (**2**) was heated at 70 °C for 14 days. ^{195}Pt NMR showed the solution to be a 80/20 cis/trans mixture. Diffusion of acetone into an aqueous solution gave yellow crystals of two types. Plate shaped crystals were shown to be $K_2[cis\text{-}Pt(OH)_2(Ox)_2]\cdot xH_2O$ (**3**) by X-ray crystallography.

Sodium *trans*-Dihydroxobis(malonato)platinate(IV) Hexahydrate (5). The sodium salt was prepared by the same method as for **1** first described by Preetz.[19] ^{195}Pt and ^{13}C NMR showed greater than 95% conversion of **4** to the $[trans\text{-}Pt(OH)_2(Mal)_2]^{2-}$. Sodium $[trans\text{-}Pt(OH)_2(Mal)_2]^{2-}$ was recrystallized from aqueous solutions as green yellow needles of $Na_2[trans\text{-}Pt(OH)_2(Mal)_2]\cdot 6H_2O$ (**5**) for X-ray crystallography.

Sodium Dichloro(oxalato)platinate(II) (16). A modification of our earlier method was used for the synthesis of dichloro(oxalato)platinate(II).[16] K_2PtCl_4 (**18**) was heated at 50 °C with 10 mol equiv of K_2Ox

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Table I. Crystallographic Data

Sodium *trans*-Dihydroxobis(oxalato)platinate(IV) Hexahydrate	
$a = 15.562\ (2)$ Å	fw = 559.25
$b = 7.200(1)$ Å	space group *Cmca*
$c = 13.840(1)$ Å	$T = 24$ °C
$\alpha = \beta = \gamma = 90°$	$\lambda = 0.710\ 69$ Å (Mo Kα)
$V = 1550.9(3)$ Å^3	$\rho_{calcd} = 2.39$ g cm^{-3}
$Z = 4$	$\mu = 92.7$ cm^{-1} (Mo Kα)
$R(F_o) = 0.0509$	transm factor range = 0.044–0.224
$R_w(F_o) = 0.0492$	
Sodium *trans*-Dihydroxobis(malonato)platinate(IV) Hexahydrate	
$a = 6.648(1)$ Å	fw = 587.3
$b = 8.234(1)$ Å	space group $P\bar{1}$
$c = 9.065(1)$ Å	$T = 24$ °C
$\alpha = 63.82(1)°$	$\lambda = 0.710\ 69$ Å (Mo Kα)
$\beta = 70.67(1)°$	$\rho_{calcd} = 2.37$ g cm^{-3}
$\gamma = 71.78(1)°$	$\mu = 87.3$ cm^{-1} (Mo Kα)
$V = 412.0(1)$ Å^3	transm factor range = 0.290–0.575
$Z = 1$	$R_w(F_o) = 0.0300$
$R(F_o) = 0.0308$	

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) with Standard Deviations for $Na_2[\textit{trans}\text{-}Pt(OH)_2(C_2O_4)_2]\cdot 6H_2O$

atom	x/a	y/b	z/c	U_{eq}[a]
Pt	0.5	0.5	0.5	0.0161(1)
O(1)	0.5849(3)	0.5850(7)	0.5981(4)	0.023(2)
C	0.5506(5)	0.651(1)	0.6762(6)	0.025(2)
O(2)	0.5899(5)	0.708(1)	0.7446(5)	0.040(2)
O(3)	0.5	0.754(1)	0.4427(6)	0.024(2)
O(4)[b]	0.7481(4)	0.930(1)	0.6351(5)	0.038(2)
O(5)[b]	0.6228(8)	0.0	0.5	0.042(3)
Na[b]	0.75	0.691(1)	0.75	0.036(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] The sodium ion and water oxygen atoms are not shown in Figure 5.

Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) with Standard Deviations for $Na_2[\textit{trans}\text{-}Pt(OH)_2(C_3H_2O_4)_2]\cdot 6H_2O$

atom	x/a	y/b	z/c	U_{eq}[a]
Pt	0.5	0.5	0.5	0.0171(2)
O(1)	0.6139(4)	0.3771(3)	0.3353(3)	0.025(1)
O(2)	0.6201(4)	0.7256(3)	0.3458(3)	0.025(1)
O(3)	0.7475(6)	0.3746(4)	0.0824(4)	0.039(1)
O(4)	0.7321(6)	0.9255(4)	0.0970(4)	0.035(1)
C(1)	0.6714(6)	0.4642(5)	0.1738(4)	0.024(1)
C(2)	0.6349(8)	0.6718(5)	0.0971(5)	0.032(1)
C(3)	0.6676(6)	0.7803(4)	0.1826(4)	0.023(1)
O(5)	0.7804(4)	0.3818(4)	0.5728(3)	0.026(1)
Na[b]	0.7047(3)	0.0512(2)	0.3122(2)	0.032(1)
O(6)[b]	0.0905(5)	–0.0186(4)	0.2525(4)	0.034(1)
O(7)[b]	0.6835(5)	–0.1021(4)	0.6116(4)	0.035(1)
O(8)[b]	0.1061(5)	0.4697(5)	0.2642(4)	0.036(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] The sodium ions and water oxygen atoms are not shown in Figure 6.

for 24 h. The solution was cooled to 5 °C in a refrigerator and $K_2[Pt(Ox)_2]\cdot 2H_2O$ (**1**) was separated by centrifugation as a yellow solid. Two mole equivalents of tetra-*n*-butylammonium nitrate, $(TBA)NO_3$ were added as a solid to the supernate containing **16** and the solution was extracted five times with 5 mL of CH_2Cl_2. Ion exchange of a 70% H_2O/30% CH_3OH solution of the TBA salt of **16** over Dowex 50W-X8 in the sodium form gave $Na_2[Pt(Ox)Cl_2]\cdot xH_2O$ (**16**) as an orange/red solid. ^{195}Pt NMR spectra show less than 5% contribution from $[PtCl_4]^{2-}$ (**2**) and $[Pt(Ox)_2]^{2-}$ (**1**).

NMR Spectroscopy. ^{195}Pt and ^{13}C spectra were recorded on Bruker WM250, AC300, and AM500 spectrometers as previously described.[16] Chemical shifts for ^{195}Pt were measured relative to an external standard of 0.1 M $Na_2[PtCl_6]$ = 0 ppm. Isotopically shifted ^{195}Pt resonances were measured on the AM500. ^{13}C and ^{1}H spectra were measured and corrected to tetramethylsilane with an internal reference of dioxane (^{13}C = 67.73 ppm, ^{1}H = 3.53 ppm) in water or $CDCl_3$ (^{13}C = 77.0 ppm, ^{1}H = 7.24 ppm) in chloroform.

Structure Determinations and Refinements

For both structures, unit cell dimensions were obtained by least-squares refinement using 25 centered reflections for which $20° < 2\theta < 30°$ (graphite-monochromatized Mo Kα radiation). Intensity data were collected with a Nicolet R3mE four-circle diffractometer. Three check reflections, monitored every 100 reflections, showed less than 3% loss of intensity for **2** and **5** during the course of data collection. All non-hydrogen atoms were refined anisotropically by block-cascade least-squares minimizing $\sum w\Delta^2$. The weighting scheme used was $w = k(\sigma^2(F_o) + gF_o{}^2)^{-1}$ where $g = 0.002$ for **2** and $g = 0.0004$ for **5**. Absorption corrections were calculated by Gaussian integration using crystal dimensions between indexed crystal faces. Atomic scattering factors, including terms for anomalous scattering, were taken from ref 20.

$Na_2[\textit{trans}\text{-}Pt(OH)_2(C_2O_4)_2]\cdot 6H_2O$ (2). A yellow plate shaped hexagonal crystal (approximately 0.16 × 0.44 × 0.66 mm) was mounted on a glass fiber for crystallographic data collection. Intensity data for the orthorhombic unit cell $(+h,+k,+l)$ were collected. Crystallographic data for this compound appear in Table I.

Data reduction[21] gave 1671 unique reflections in the range $3° < 2\theta < 75°$, of which 1078 with $I > 3\sigma(I)$ were used for structure refinement. The volume of the orthorhombic unit cell indicated four formula units. Systematic absences indicated the space group to be *Cmca*, No. 64. A Patterson synthesis was consistent with placement of the platinum atom on a 2/*m* site. All other non-hydrogen positions were located from difference syntheses. Hydrogen atom positions could not be located on difference maps. Because several hydrogen bonding schemes are possible for the complex, calculated coordinates were not used for hydrogen positions and hydrogens were not included in the structure refinement. Five reflections in the data set showed significant extinction and were excluded during final refinement. Final difference maps showed only the usual ripple near the platinum position. Atom coordinates are given in Table II.

$Na_2[\textit{trans}\text{-}Pt(OH)_2(C_3H_2O_4)_2]\cdot 6H_2O$ (5). A yellow-green, needle-shaped crystal (approximately 0.07 × 0.11 × 0.44 mm) was mounted on a glass fiber for crystallographic data collection. Intensity data for the triclinic unit cell $(\pm h,\pm k,+l)$ were collected. Crystallographic data for this compound appear in Table I. Data reduction, as described above gave 3630 unique reflections in the range $3° < 2\theta < 70°$, of which 3581 with $I > 3\sigma(I)$ were used for structure refinement. The volume of the triclinic unit cell was appropriate for one formula unit. A Patterson synthesis did not reveal any non-origin peak of sufficient relative magnitude for a platinum–platinum vector, confirming the indication from the unit cell volume. Placement of the platinum atom on the inversion center in the centric space group led to successful structure solution and refinement. The positions of all other atoms including reasonable hydrogen positions were located by difference synthesis. Water and hydroxyl hydrogen positions were refined with distance constraints; calculated positions were used for the malonato hydrogens. A common isotropic hydrogen thermal parameter was refined, $U_H = 0.054(6)$ Å^2. Seven reflections in the data set showed significant extinction and were excluded during final refinement. The refinement did not converge in the acentric space group. Final difference maps showed only the usual ripple near the platinum position. Atom coordinates are given in Table III.

$K_2[\textit{trans}\text{-}Pt(OH)_2(C_2O_4)_2]\cdot xH_2O$ and $K_2[\textit{cis}\text{-}Pt(OH)_2(C_2O_4)_2]\cdot xH_2O$. Single crystals were obtained and crystallographic data accumulated as described above. The trans complex crystallized with a tetragonal unit cell, space group I4/m, No. 87: $a = b = 12.209(1)$ Å, $c = 13.077(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1949.1(5)$ Å^3, $Z = 4$. The structure was solved and refined but exhibited disorder and partial occupancy of the potassium and lattice waters over several sites. Refinement of the structure (R = 0.058, R_w = 0.058) indicated that the anionic complex is identical to that of the well ordered sodium salt. The cis complex crystallized in the triclinic space group $R3c$, No. 167: $a = b = 17.582\ (2)$ Å, $c = 47.414\ (8)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$ (hexagonal axis), $V = 12694\ (4)$ Å^3, $Z = 36$. This structure also showed disorder and partial occupancy of the potassium and lattice water sites. The anionic complex has cis stereochemistry and the structure was refined to $R = 0.071$, $R_w = 0.068$. Details

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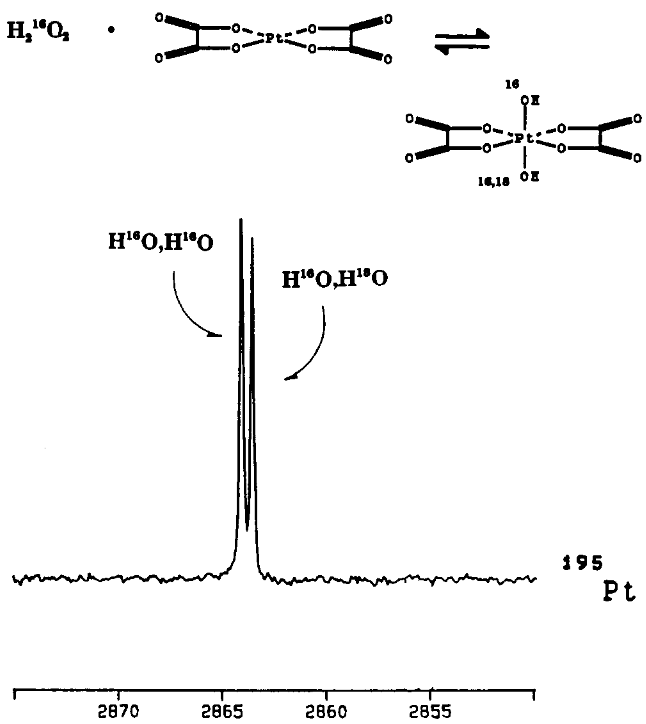

Figure 1. ^{195}Pt NMR spectrum of *trans*-dihydroxobis(oxalato)platinate(IV) formed in the reaction of $K_2[Pt(Ox)_2]\cdot 2H_2O$ with $H_2{}^{16}O_2$ in 50% $H_2{}^{16}O$/50% $H_2{}^{18}O$. The two resonances arise from two isotopomeric complexes which are formed in the oxidation.

of the refined structures of the two potassium salts will not be presented because of the disorder of the potassium and water sites.

Results and Discussion

Nuclear Magnetic Resonance Studies. H_2O_2 Oxidation of $[Pt(Ox)_2]^{2-}$ (1). When 30% H_2O_2 is added to an aqueous solution of $[Pt(Ox)_2]^{2-}$ (**1**) the ^{195}Pt NMR resonance for **1** at –525 ppm diminishes over 30 minutes at room temperature. It is replaced by a single new resonance at 2873 ppm in the ^{195}Pt NMR spectrum, and a single new resonance is observed in the ^{13}C NMR spectrum at 167.1 ppm. The large shift in the ^{195}Pt NMR spectrum is consistent with the oxidation of **1** to a Pt(IV) complex with six oxygen ligands.[12] The new resonance is 400 ppm upfield from the resonance for $[Pt(OH)_6]^{2-}$.[22] Such an upfield shift is in agreement with chemical shifts observed for Pt(II) complexes with this type of bidentate ligand.[16] The resonance at 2873 ppm is assigned to *trans*-$[Pt(OH)_2(Ox)_2]^{2-}$ (**2**) since the cis complex should have two ^{13}C resonances. Vapor diffusion of acetone into an aqueous solution of the sodium or potassium salt at pH = 5.0 gives green/yellow crystals. X-ray crystallography shows the anionic complex to be *trans*-$[Pt(OH)_2(Ox)_2]^{2-}$ (**2**) (vida infra).

When **1** is dissolved in 50% $H_2{}^{16}O$/50% $H_2{}^{18}O$ and oxidized by a 30% aqueous solution of $H_2{}^{16}O_2$ the ^{195}Pt NMR resonance for **2** is observed to be two peaks separated by 0.52 ppm, as illustrated in Figure 1. The resonances arise from two of three possible $^{16}O/^{18}O$ isotopically labeled forms of complex **2**. The lowest field resonance is **2** where both hydroxo ligands are ^{16}OH. For the second resonance, one hydroxo ligand is ^{16}OH and the other is ^{18}OH. The substitution of a heavier isotope causes an upfield shift of the ^{195}Pt resonance.[12–14,23] The ratio of the two observed isotopomeric resonances depends solely upon the ratio of $H_2{}^{16}O$ and $H_2{}^{18}O$ present in the solvent. The ^{13}C NMR spectrum of ^{18}O isotopically labeled **2** is a single resonance at 167.1 ppm. The single resonance observed in the ^{13}C spectrum shows that the isotopic shift in the ^{195}Pt spectrum is not the result of isotopic exchange of oxygen on the oxalato ligand, a process which occurs more slowly (vida infra).[24,25] ^{195}Pt NMR spectra taken over several weeks show that the isotopic ratio of the two resonances remains unchanged. Exchange of coordinated OH of **2** is slow in this pH range. If significant OH exchange did occur, the ratio of the two resonances would change and a resonance corresponding to the $^{18}O,^{18}O$ complex would be observed.

Table IV. ^{195}Pt NMR Data

complex[g]	no.	δ_{Pt} (ppm)	isotope shift (ppm)
$[Pt(Ox)_2]^{2-}$ [a]	**1**	–520	
[*trans*-$Pt(OH)_2(Ox)_2]^{2-}$	**2**	2873	0.52[e]
[*cis*-$Pt(OH)_2(Ox)_2]^{2-}$	**3**	2847	0.52[e]
$[Pt(Mal)_2]^{2-}$ [a]	**4**	–562	
[*trans*-$Pt(OH)_2(Mal)_2]^{2-}$	**5**	3153	0.55[e]
[*cis*-$Pt(OH)_2(Mal)_2]^{2-}$	**6**	3158	0.55[e]
[*syn*-$Pt(Mmal)_2]^{2-}$ [a]	**7**	–608	
[*anti*-$Pt(Mmal)_2]^{2-}$ [a]	**8**	–600	
[*anti-trans*-$Pt(OH)_2(Mmal)_2]^{2-}$	**9**	3140	0.56[e]
[*syn-trans*-$Pt(OH)_2(Mmal)_2]^{2-}$	**10**	3120	0.57[e]
[*cis*-$Pt(OH)_2(Mmal)_2]^{2-}$ [b]	**11**	3104	0.72[e]
[*cis*-$Pt(OH)_2(Mmal)_2]^{2-}$ [b]	**13**	3071	0.73[e]
[*trans*-$Pt(OH)(OMe)(Ox)_2]^{2-}$ [c]	**14**	2774	
[*trans*-$Pt(OH)(OEt)(Ox)_2]^{2-}$ [c]	**15**	2800	
$[PtCl_2(Ox)]^{2-}$ [a]	**16**	–1005	
[*cis,trans*-$PtCl_2(OH)_2(Ox)]^{2-}$	**17**	2050	0.69[e] 0.20[f]
$[PtCl_4]^{2-}$ [d]	**18**	–1624	
[*trans*-$Pt(OH)_2Cl_4]^{2-}$ [d]	**19**	1247	0.67[e] 0.19[f]

[a] Chemical shifts reported in ref 16. [b] Absolute conformation of methyl is not established. [c] Tetra-*n*-butylammonium salts in $CDCl_3$. [d] Chemical shift reported in ref 12. [e] $^{16}O/^{18}O$ isotopic shift. [f] $^{35}Cl/^{37}Cl$ isotopic shift. [g] Ox = oxalato, Mal = malonato, Mmal = 2-methylmalonato.

Table V. ^{13}C NMR Data

complex	no.	δ (ppm) C=O	δ (ppm) CH/CH_2	δ (ppm) CH_3
[*trans*-$Pt(OH)_2(Ox)_2]^{2-}$	**2**	167.11		
[*cis*-$Pt(OH)_2(Ox)_2]^{2-}$	**3**	167.33 168.11		
[*trans*-$Pt(OH)_2(Mal)_2]^{2-}$	**5**	177.95	46.96	
[*cis*-$Pt(OH)_2(Mal)_2]^{2-}$	**6**	168.11 167.33	48.34 47.02	
[*anti-trans*-$Pt(OH)_2(Mmal)_2]^{2-}$	**7**	179.36	48.63	13.71
[*syn-trans*-$Pt(OH)_2(Mmal)_2]^{2-}$	**8**	179.89	49.08	14.11
[*trans*-$Pt(OH)(OMe)(Ox)_2]^{2-}$ [a]	**14**	165.90		56.63
[*trans*-$Pt(OH)(OEth)(Ox)_2]^{2-}$ [a]	**15**	166.00	63.34	18.56
[*cis,trans*-$PtCl_2(OH)_2(Ox)]^{2-}$	**17**	167.68		

[a] Tetra-*n*-butylammonium salts in $CDCl_3$.

The absence of a resonance for a species with two ^{18}OH ligands indicates that the mechanism begins with the addition of $H_2{}^{16}O_2$ to an axial position of the Pt(II) square. This is followed by electron transfer which occurs in either a one-step two-electron transfer, or by two one-electron transfer steps where the second electron transfer occurs more rapidly than structural rearrangement of the Pt(III) intermediate. After the rate determining step, the trans axial site of the Pt(IV) is coordinated by either an $H_2{}^{16}O$ or an $H_2{}^{18}O$ from the solvent. The retention of the ^{16}OH from hydrogen peroxide shows the electron transfer occurs after the hydrogen peroxide oxygen enters the inner coordination sphere of the Pt(II). The exclusively trans product shows that the oxidation occurs via a square bottom pyramidal intermediate.

The axial site trans to hydrogen peroxide addition can be occupied by other solvents with oxygen donating ligands. Hydrogen peroxide oxidation of $(TBA)_2[Pt(Ox)_2]$ in methanol results in the disappearance of the resonance for **1** and the appearance of a new resonance at 2774 ppm in the ^{195}Pt NMR

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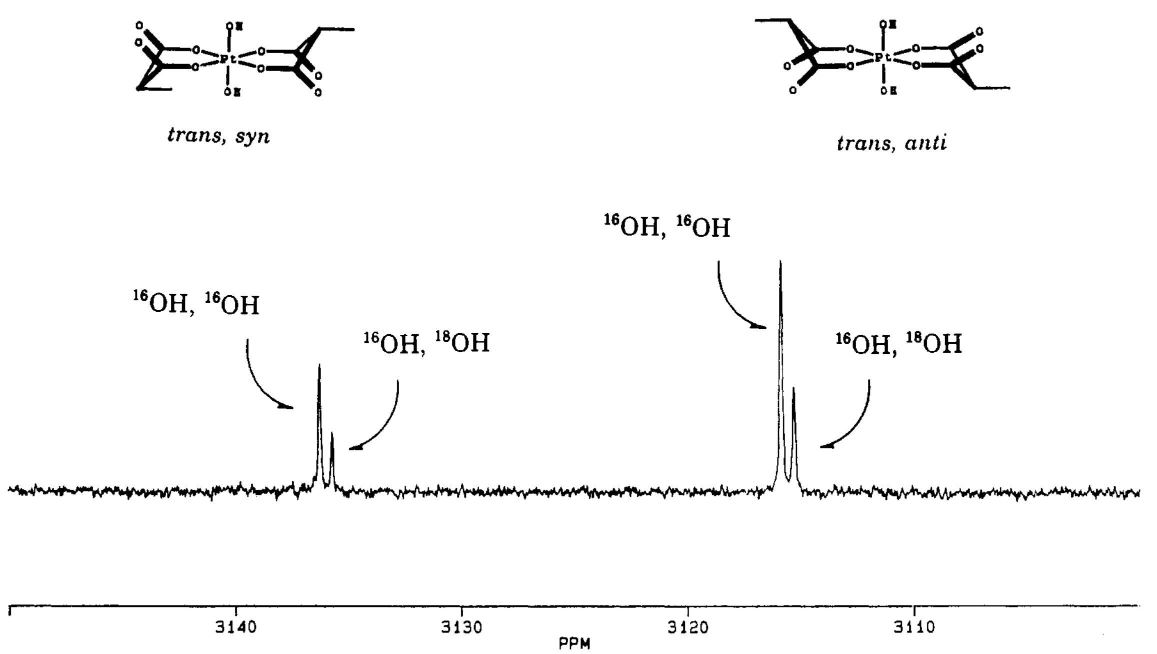

Figure 2. ^{195}Pt NMR spectrum of *syn*- and *anti*-*trans*-dihydroxobis(2-methylmalonato)platinate(IV) formed from the reaction of *syn*- and *anti*-[Pt(2-methylmalonato)$_2$]$^{2-}$ with $H_2{}^{16}O_2$ in 60% $H_2{}^{16}O$/40% $H_2{}^{18}O$.

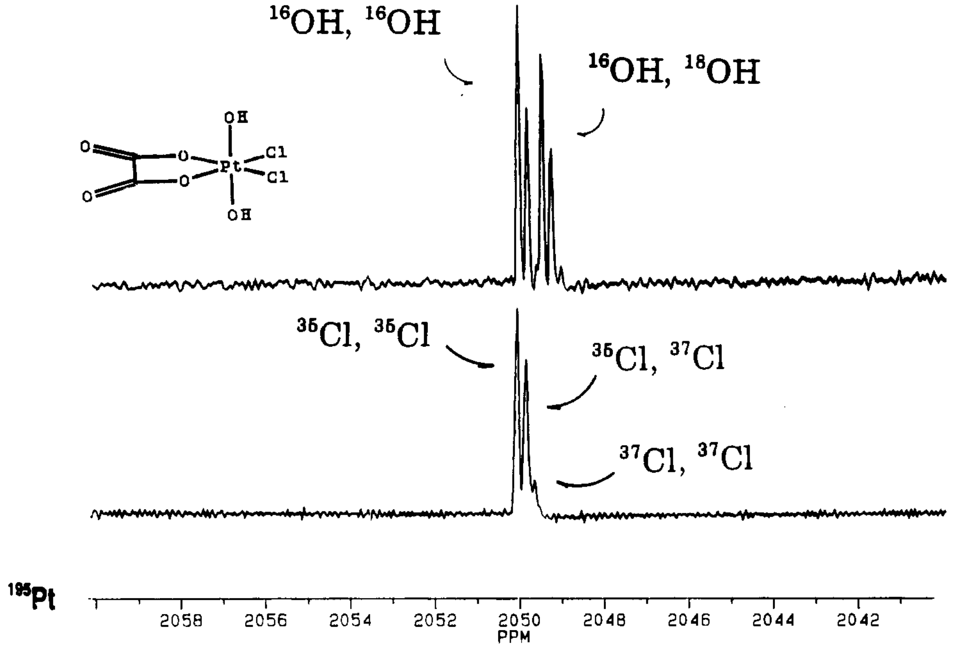

Figure 3. ^{195}Pt NMR spectra of *cis*-dichloro-*trans*-dihydroxo(oxalato)platinate(IV) formed in the reaction of $Na_2[PtCl_2(oxalato)]$ with H_2O_2: lower, $H_2{}^{16}O_2$ reaction in $H_2{}^{16}O$ showing the chlorine isotopomers; upper, $H_2{}^{16}O_2$ reaction in 50% $H_2{}^{16}O$/50% $H_2{}^{18}O$ showing the chlorine and oxygen isotopomers.

spectrum. The ^{1}H spectrum shows a new resonance at 2.93 ppm with a spin coupling of 23.6Hz to ^{195}Pt. The ^{13}C spectrum also shows a new resonance at 56.6 ppm, and a single resonance is observed in the carboxyl region at 165.9 ppm. Positive ion mass spectrometry by fast atom bombardment (FAB) shows a molecular ion peak at m/z = 903 for $(TBA)_2[Pt(Ox)_2(OH)(OMe)H]^+$. The predominant peak is at m/z = 1145 corresponding to $(TBA)_3[Pt(Ox)_2(OH)(OMe)]^+$. The new complex is assigned to *trans*-$[Pt(OH)(OMe)(Ox)_2]^{2-}$ (**14**). Oxidation in 50% methanol/50% H_2O results in the formation of an equal mixture of **2** and **14**. The lack of a solvent dependence on the product ratio supports the formation of a hydrogen peroxide to Pt bond formation before the trans axial position is coordinated by solvent. If solvent coordination occurred first, we would expect to see a distribution of products that should favor water coordination since water is expected to be the better ligand. H_2O_2 oxidation of **1** in ethanol results in the appearance of a new resonance in the ^{195}Pt NMR spectrum at 2800 ppm. The ^{1}H spectrum shows two new resonances at 0.98 ppm (CH_3) and 3.30 ppm (CH_2). The ^{13}C NMR spectrum shows new resonances at 18.56 ppm (CH_3), 63.34 ppm (CH_2), and a single resonance is observed in the carboxyl region at 165.9 ppm. These new resonances are assigned to the formation of *trans*-$[Pt(OH)(OEt)(Ox)_2]^{2-}$ (**15**). The NMR data for **14** and **15** are summarized in Tables IV and V.

Monaghan and Puddephatt have reported that dimethyl(bipyridyl)platinum(II), and the corresponding phenanthroline complex, react with alcohols to form alkoxyhydroxoplatinum(IV) complexes analogous to **14** and **15**.[26] Unlike the compounds they reported, our complexes hydrolyze slowly in 0.1 M $HClO_4$. In

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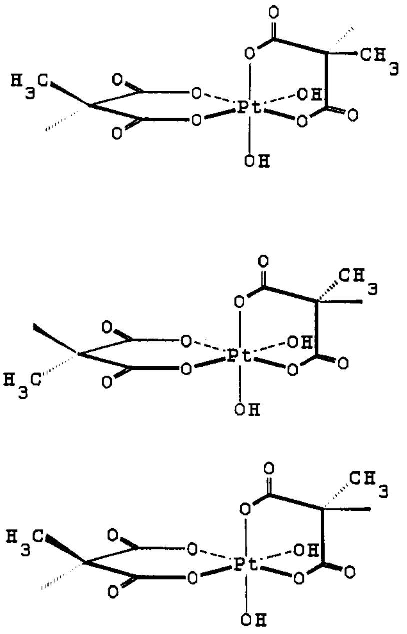
[26] Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

Chart I. Three Diastereomers of *cis*-Dihydroxobis(2-methylmalonato)platinate(IV)



endo, endo

exo, exo

endo, exo

neutral solution our complexes undergo a slow isomerization reaction, presumably converting slowly from trans to cis geometry (vida infra).

When solutions of the *trans*-dihydroxo complex, **2**, are heated at 70 °C for 24 h or kept at room temperature for several weeks, new resonances are observed in the ^{195}Pt and ^{13}C NMR spectra. A single new resonance is observed at 2847 ppm in the ^{195}Pt spectra. The proximity of this resonance to that of **2** suggests a species with six oxygen ligands and one or more bidentate ligands. The ^{13}C spectrum shows the appearance of new resonances of equal intensity at 167.33 and 168.11 ppm. These resonances are consistent with carboxylato carbon atoms in different symmetry environments, as expected for a *cis*-dihydroxobis(oxalato)platinate(IV) complex. Vapor diffusion of acetone into a solution of this species produced crystals for X-ray diffraction. Crystallography shows the anionic unit to be *cis*-dihyroxobis(oxalato)platinate(IV) (**3**). The new ^{195}Pt and ^{13}C NMR resonances are assigned to *cis*-$[Pt(OH)_2(Ox)_2]^{2-}$ (**3**).

Trans–cis isomerization for dihydroxo Pt(IV) complexes has been observed in the recrystallization of the all *trans* complex $[PtCl_2(OH)_2(NH_3)_2]$.[4] Trans–cis isomerization is also consistent with the NMR spectra changes reported for the compounds formed when diammine(1,1-cyclobutanedicarboxylato)platinum(II) or diammine(ethylmalonato)platinum(II) are oxidized by hydrogen peroxide.[7] Changes in the ^{13}C and ^{195}Pt chemical shifts and ^{195}Pt–^{14}N coupling constants can be interpreted to indicate *trans* to cis isomerization as reported herein rather than a change in oxidation mechanism, as was suggested.[7]

H_2O_2 Oxidation of $[Pt(Mal)_2]^{2-}$. When 30% H_2O_2 is added to an aqueous solution of $[Pt(Mal)_2]^{2-}$ (**4**), its ^{195}Pt NMR resonance is replaced by a single peak at 3153 ppm and new resonances are observed in the ^{13}C NMR spectrum at 178.0 ppm (C=O) and 47.0 ppm (CH_2). The chemical shift of the ^{195}Pt NMR resonance is again consistent with oxidation to a Pt(IV) species with six oxygen ligands. The 150 ppm upfield shift of this resonance from $[Pt(OH)_6]^{2-}$ is less than observed in the corresponding oxalato complex, **2**, and is also less than the shift observed for the Pt(II) species, **4**, upon chelate ring formation.[16] Recrystallization of the sodium salt from a pH = 5.0 solution gives green-yellow crystals. X-ray crystallography shows the complex to be $Na_2[$*trans*$\text{-}Pt(OH)_2(Mal)_2]\cdot 6H_2O$ (**5**). Hydrogen peroxide oxidation with $H_2{}^{16}O_2$ in 70% $H_2{}^{16}O$/30% $H_2{}^{18}O$ results in two isotopically shifted ^{195}Pt resonances, and the oxidation mechanism is the same as suggested above for **1**.

When solutions of **5** are heated at 70 °C for 24 h or kept at room temperature for several weeks, new resonances are observed in the ^{195}Pt and ^{13}C NMR spectra. A single new resonance is observed at 3158 ppm in the ^{195}Pt spectra. The proximity of this resonance to **5** once again suggests a species with six oxygen ligands and one or more bidentate ligands. The ^{13}C spectrum shows the appearance of new resonances of equal intensity at 167.33 and 168.11 ppm in the carboxyl region, and a new resonance at 48.34 ppm in the methylene region. These resonances are consistent with isomerization of **5** to form *cis*-dihyroxobis(malonato)platinate(IV) complex (**6**).

H_2O_2 Oxidation of *syn*- and *anti*-$[Pt(Mmal)_2]^{2-}$ (7, 8). When 30% H_2O_2 is added to an aqueous solution of *anti*- (**7**) and

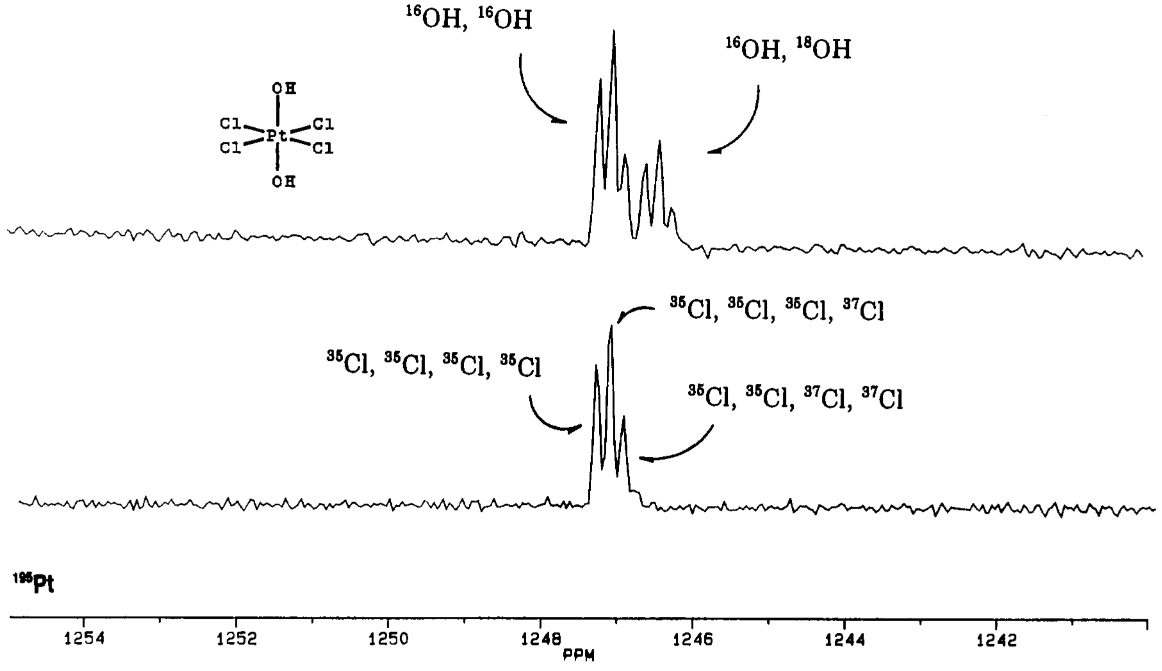


Figure 4. ^{195}Pt NMR spectrum of *trans*-dihydroxotetrachloroplatinate(IV) formed in the reaction of $K_2[PtCl_4]$ with $H_2{}^{16}O_2$: lower, $H_2{}^{16}O_2$ reaction in $H_2{}^{16}O$ showing the chlorine isotopomers; upper, $H_2{}^{16}O_2$ reaction in 60% $H_2{}^{16}O$/40% $H_2{}^{18}O$ showing the chlorine and oxygen isotopomers.

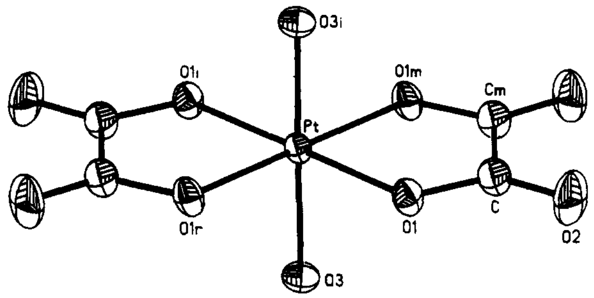


Figure 5. Thermal ellipsoid plot of *trans*-$[Pt(OH)_2(C_2O_4)_2]^{2-}$ showing 50% probability ellipsoids and numbering scheme for the structure.

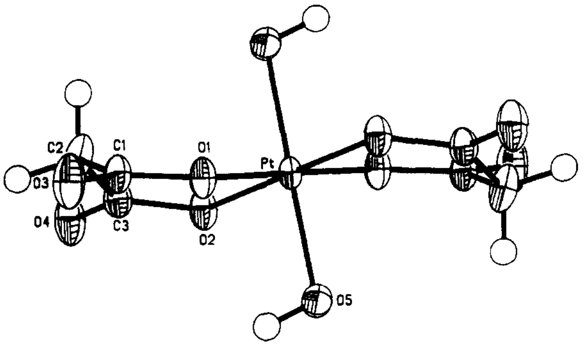


Figure 6. Thermal ellipsoid plot of *trans*-$[Pt(OH)_2(C_3H_2O_4)_2]^{2-}$ showing 50% probability ellipsoids and numbering scheme for the structure.

Table VI. Bond Lengths (Å) and Angles (deg) with Standard Deviations for All Non-Hydrogen Atoms of Na_2[*trans*-$Pt(OH)_2(C_2O_4)]\cdot 6H_2O$

	Bond Lengths		
Pt–O(1)	1.991(5)	O(1)–C	1.297(9)
Pt–O(3)	1.992(7)	C–C	1.57(2)
C–O(2)	1.20(1)		
	Bond Angles		
O(1)–Pt–O(1m)	83.1(3)	O(1)–C–O(2)	125.0(8)
O(1)–Pt–O(1r)	96.9(3)	O(1)–C–Cm	114.3(3)
O(1)–Pt–O(3)	89.4(2)	O(2)–C–Cm	120.7(5)
O(1)–Pt–O(3i)	90.6(2)	Pt–O(1)–C	114.1(5)
O(3)–Pt–O(3i)	180.0	O(1)–Pt–O(1i)	180.0

Table VII. Bond Lengths (Å) and Angles (deg) with Standard Deviations for Na_2[*trans*-$Pt(OH)_2(C_3H_2O_4)_2]\cdot 6H_2O$

	Bond Lengths		
Pt–P(1)	1.983(3)	Pt–O(2)	1.985(3)
Pt–O(5)	1.993(3)	O(1)–C(1)	1.295(4)
O(2)–C(3)	1.298(4)	O(3)–C(1)	1.232(6)
O(4)–C(3)	1.224(5)	C(1)–C(2)	1.506(5)
C(2)–C(3)	1.514(7)		
	Bond Angles		
O(1)–Pt–O(2)	95.0(1)	O(1)–Pt–O(5)	87.4(1)
O(2)–Pt–O(5)	89.2(1)	Pt–O(1)–C(1)	123.6(3)
Pt–O(2)–C(3)	123.6(3)	O(1)–C(1)–O(3)	118.7(3)
O(1)–C(1)–C(2)	121.1(4)	O(3)–C(1)–C(2)	120.1(3)
C(1)–C(2)–C(3)	121.2(4)	O(2)–C(3)–O(4)	119.2(4)
O(2)–C(3)–C(2)	121.0(3)	O(4)–C(3)–C(2)	119.7(3)
Pt–O(5)–H(5)	108(3)	H(6a)–O(6)–H(6b)	99(6)
H(7a)–O(7)–H(7b)	108(7)	H(8a)–O(8)–H(8b)	100(6)

syn-$[Pt(Mmal)_2]^{2-}$ (**8**), where **7** is the predominant species, the ^{195}Pt NMR resonances are replaced by peaks at 3120 (**9**) (dominant) and 3140 ppm (**10**). The ca. 150 ppm upfield shift of these resonances from $[Pt(OH)_6]^{2-}$ is less than would be predicted from analogous comparisons among Pt(II) complexes, but it is consistent with the upfield shift for **5** and **6**. It appears that the malonato six membered chelate ring system causes less of a shift in the Pt(IV) complexes than in the malonato chelated Pt(II) complexes.[16] Two sets of resonances of different intensity are observed for the methyl, methylene, and carboxyl carbons in the ^{13}C NMR spectrum, consistent with the formation of the two different *trans*-dihydroxo Pt(IV) isomers. These resonances are assigned by their relative intensities to ***anti-trans***-$[Pt(OH)_2(Mmal)_2]^{2-}$ (**9**) (dominant), and ***syn-trans***-$[Pt(OH)_2(Mmal)_2]^{2-}$ (**10**). Isotopic labeling experiments with $H_2{}^{18}O$ are shown in Figure 2. Oxidation of **7** and **8** with $H_2{}^{16}O_2$ in 60% $H_2{}^{16}O$/40% $H_2{}^{18}O$ gives results analogous to those observed for **1** and **4** and so the mechanism for H_2O_2 oxidation is the same.

When solutions of **9** and **10** are heated at 70 °C for 24 h or kept at room temperature for several weeks, new resonances are observed in the ^{195}Pt and ^{13}C NMR spectra. The new resonances are observed at 3106, 3102 and 3073 ppm in the ^{195}Pt spectra. The proximity of these resonances to **9** and **10** again suggests species with six oxygen ligands and one or more bidentate ligands. The ^{13}C spectrum shows the appearance of four new resonances in both the methyl and methylene regions, and the appearance of eight new resonances in the carboxyl region. These resonances are consistent with isomerization to form three isomers of *cis*-dihyroxobis(2-methylmalonato)platinate(IV) (**11–13**). The structural differences among the isomers are most simply visualized if the 2-methylmalonato ligands are constrained to a planar chelate ring conformation as shown in Chart I. Depending on how the methyl groups are placed on each of the 2-carbon atoms, cis complexes are formed with methyl groups as close as possible to one another, as far away from one another as possible, or at an intermediate distance from one another. The Pt is the common fusion point for the two chelate rings in the cis isomers, and the nomenclature for the cis complexes is taken from the commonly used terms of exo and endo faces. The endo face is less than 180° between chelate rings, and the exo face is greater than 180° between chelate rings. These three isomers can be called endo,endo, exo,exo, and endo,exo, respectively, and are illustrated in Chart I. The endo,endo and the exo,exo complexes have C_2 symmetry and should have a single methyl resonance while the endo,exo isomer has C_1 symmetry and should have two methyl resonances; however, we do not have sufficient spectroscopic evidence to assign the resonances for **11–13** to the three cis isomers.

H_2O_2 Oxidation of $[PtCl_2(Ox)]^{2-}$. When 30% H_2O_2 is added to an aqueous solution of $[PtCl_2(Ox)]^{2-}$ (**16**), the ^{195}Pt NMR resonance for **16** at −1005 ppm is replaced by a single resonance at 2050 ppm in the ^{195}Pt NMR spectrum, and a single new resonance is observed in the ^{13}C NMR spectrum at 167.7 ppm. These resonances are assigned to *cis,trans*-$[PtCl_2(OH)_2(Ox)]^{2-}$ (**17**). The large shift in the ^{195}Pt spectrum is consistent with oxidation to Pt(IV). The resonance for **17** is 310 ppm to higher shielding than *cis*-$[PtCl_2(OH)_4]^{2-}$.[12] Similar upfield shifts are observed when five membered bidentate chelate rings form in Pt(II) complexes.[16] The high resolution ^{195}Pt NMR spectrum in Figure 3 shows three peaks due to different isotopic contributions from ^{35}Cl and ^{37}Cl in the ratio 1:0.64:0.10.[23] This confirms that only two chloro ligands are bound to the Pt. Isotopic labeling experiments with 50% $H_2{}^{16}O$/50% $H_2{}^{18}O$ shows the oxidation to follow the same mechanism as described above for **1**, **4**, **7**, and **8**. The high resolution ^{195}Pt NMR spectrum of 50% ^{18}O labeled **17** is also shown in Figure 3. As before, two separate ^{195}Pt resonances are observed, one for the ^{16}O complex and one for the $^{16}O,^{18}O$ species. Each of these resonances is divided in to three additional peaks by the chlorine isotopes present, as described above.

H_2O_2 Oxidation of $[PtCl_4]^{2-}$. *trans*-$[Pt(OH)_2Cl_4]^{2-}$ has been characterized as the product from oxidation of $[PtCl_4]^{2-}$ with H_2O_2.[27] Isotopic labeling experiments with 60% $H_2{}^{16}O$/40% $H_2{}^{18}O$ yields two ^{195}Pt resonances in proportion to the ^{18}O content of the solvent. This shows the mechanism for H_2O_2 oxidation to be the same as described above for **1**, **4**, **7**, **8**, and **16**. The high

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(27) Cox, L. E.; Peters, D. G. *Inorg. Chem.* **1970**, *9*, 1927.

resolution ^{195}Pt NMR spectrum in Figure 4 shows two sets of three peaks due to $H_2{}^{18}O$ incorporation and ^{35}Cl and ^{37}Cl isotopic contributions in the ratio 0.78:1.0:0.48 for each group of resonances.[23] Further chlorine isotopomers were not observed due to their low natural abundance, but the ratio of the resonances observed is consistent with the presence of four chloro ligands bound to ^{195}Pt.

A summary of all NMR data appears in Tables IV and V.

Crystallographic Studies. $Na_2[$*trans*$\text{-}Pt(OH)_2(C_2O_4)_2]\cdot 6H_2O$ (2). The structure of the anionic complex of **2** is shown in Figure 5 and bond distances and angles are in Table VI. The bond lengths and angles for the Pt(IV) complex are not statistically different from the Pt(II) complex $K_2[Pt(Ox)_2]\cdot 2H_2O$.[28]

$Na_2[$*trans*$\text{-}Pt(OH)_2(C_3H_2O_4)_2]\cdot 6H_2O$ (5). The structure of **5** is shown in Figure 6. Bond distances and angles are in Table VII. Bond length and bond angle determinations are in agreement with crystallographic studies for Pt(II) and Pt(IV) malonato complexes.[7,16,29,30] The malonato ligand is in a boat conformation as is the case with all other malonato complexes of platinum. Both crystal structures feature extensive hydrogen bonding networks involving the anionic complexes and the lattice waters.

Summary

The mechanism for hydrogen peroxide oxidation for several Pt(II) complexes has been established by ^{195}Pt and ^{13}C NMR spectroscopies. The rate determining step is electron transfer in hydrogen peroxide coordinated Pt(II) complex. Oxidation is a two-electron process or two sufficiently rapid one-electron steps that exclusively *trans*-dihydroxoplatinum(IV) complexes are formed. One hydroxo ligand originates from hydrogen peroxide, and the other hydroxo ligand originates from solvent. Oxidation in nonaqueous oxygen donating solvents results in the formation of *trans*-hydroxo(solvent)platinum(IV) complexes.

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Supplementary Material Available: Listings of crystal data and structure refinement parameters, anisotropic thermal parameters, H atom coordinates, and lattice water contacts and packing diagrams (3 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors are available from E.H.A.

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