Table II

urethane	TLC R_f (SiO_2,Et_2O/hexane 1:2)	HPLC retention time, min
5	0.27 and 0.30	24.6–26.2
8	0.36	25.8–26.8
9	0.34	26.2–27.4
11	0.38	26.0–26.8
12	0.38	25.6–26.6
15	0.40	24.6–26.2

Table III

urethane	retention time, min: R	retention time, min: S	solvent	flow rate, mL/min
5	5.9	7.2	0.4% *i*-PrOH/0.1%HOAc/hexane	3.0
8	23.6	20.2	0.25% *i*-PrOH/hexane	1.0
9	42.2	46.2	0.25% *i*-PrOH/hexane	0.6
11	16.9	19.3	0.2% *i*-PrOH/hexane	2.0
12	186.6	172.4	0.18% *i*-PrOH/hexane	0.6
15	16.9	15.2	0.2% *i*-PrOH/hexane	1.5

11-HETE, respectively. Me-11- and Me-12-HETE: TLC, SiO_2, Et_2O/hexane 1:1, $R_f \sim 0.35$.

Me-14,15-EET to Me-15-HETE. Me-15-HETE was prepared as above from a mixture of carrier and radiolabeled Me-14,15-EET in 40% yield overall. Iodohydrins: TLC, SiO_2, Et_2O/hexane 1:1, $R_f \sim 0.42$ and 0.45, 1.5:1 ratio, respectively. Iodoacetates: TLC, SiO_2, Et_2O/hexane 1:2, $R_f \sim 0.38$. Me-15-HETE acetate and unreacted iodoacetate regioisomer were separated chromatographically: TLC, SiO_2, 1% $MeOH/CH_2Cl_2$, $R_f \sim 0.67$ and 0.69, respectively. NMR analysis revealed that the Me-15-HETE acetate was contaminated with an isomeric diene which was removed chromatographically after saponification and re-esterification (CH_2N_2). Me-15-HETE and isomeric diene: TLC, SiO_2, Et_2O/hexane 1:1, $R_f \sim 0.31$ and 0.27, respectively.

Me-HETE Urethanes: General Procedure. The Me-HETEs were derivatized with dehydroabietylisocyanate as described by Corey and Hashimoto[16] in 70–90% yield after TLC purification (SiO_2, Et_2O/hexane 1:2). The TLC products were further purified on a Waters μ-Bondapak C_{18} analytical column using a solvent program of isocratic 80% CH_3CN/19.9% H_2O/0.1% AcOH for 10 min and then a gradient over 20 min to 99.9% CH_3CN/0.1% HOAc at a flow rate of 2 mL/min.

The spectral data for Me-15-HETE urethane are representative of the urethane derivatives. NMR δ 0.84–2.20 (37 H, complex m), 2.36 (2 H, t, $J \sim 7$ Hz), 2.68–3.20 (8 H, m), 3.68 (3 H, s), 4.60–4.88 (1 H, m, C-15 methine), 5.16–5.80 (6 H, m), 5.96 (1 H, dd, $J \sim 10$, 10 Hz, C-12), 6.52 (1 H, dd, $J \sim 10$, 15 Hz, C-13), 6.82–7.22 (3 H, m, ArH); mass spec PCI (CH_4) *m/e* 646 (M + 1, 5%), 317 (75%), 286 (100%); high-resolution mass spec calcd for $C_{42}H_{32}NO_4$ 645.4757, found 645.4763.

Stereochemical Analysis. The purified diastereomeric urethane derivatives were resolved with baseline separation on a Waters μ-Porasil analytical column with UV monitoring (254 nm) with use of an isocratic solvent system.

Comparisons with Me-HETE urethane standards of known configuration were used to determine the absolute configuration of one side of the EET epoxide. Since the EETs are *cis*-epoxides, the configuration of the opposite side of the epoxide could be deduced.

Standards. 5-HETE derivatives were prepared and resolved by the method of Corey and Hashimoto.[16] Authentic 12(L)-HETE was purchased from New England Nuclear and 15(*S*)-HETE was obtained from an incubation of arachidonic acid with soybean lipoxidase.[17] Both were derivatized as described above. For analysis of the Me-8-HETE urethane, the sample was reduced (1 atm) over Pd/C in EtOH and compared wth the saturated urethane of methyl 8(*S*)-hydroxyeicosatrienoate prepared by incubation of homo-γ-linolenic acid with New Zealand White rabbit leukocytes.[18]

Acknowledgment. Financial support from the Kroc Foundation, Robert A. Welch Foundation (I-959), USPHS (NIGMS-16488), and NIH (2R01 AM 23091) is gratefully acknowledged.

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Phosphorus-31 NMR and Kinetic Studies of the Formation of Ortho-, Pyro-, and Triphosphato Complexes of *cis*-Dichlorodiammineplatinum(II)

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Abstract: The reactions of *cis*-dichlorodiammineplatinum(II) with pyro- and triphosphate follow biphasic kinetics over the temperature range 25–40 °C in 0.5 M $NaClO_4$ (pH 6.0–8.4). The initial step is a composite of aquation and monodentate phosphate complexation. The final step of the reaction is attributed to chelation by the phosphate ligands. The rate constants for aquation, monodenatate complexation, and chelation at 25 °C and pH 6.0 are 2.8×10^{-5} s^{-1}, 7.3×10^{-4} M^{-1} s^{-1}, and 2.9×10^{-5} s^{-1} for triphosphate and 2.9×10^{-5} s^{-1}, 1.4×10^{-3} M^{-1} s^{-1}, and 4.5×10^{-5} s^{-1} for pyrophosphate, respectively. The activation parameters (ΔH^*, kcal mol^{-1}, ΔS^*, cal deg^{-1} mol^{-1}) associated with the aquation, monodentate complexation, and chelation are 19.8, −14; 15.6, −20; and 11.8, −40 for triphosphate ion and 19.7, −14; 15.3, −21; and 11.5, −37 for pyrophosphate ion, respectively. Both monodentate and chelate complexes of pyro- and triphosphate were observed by phosphorus-31 NMR spectroscopy. The chemical shifts of coordinated phosphate groups of chelates are about 4–8 ppm downfield relative to the free phosphates while the monodentate phosphato complexes have smaller (2–3.5 ppm) coordination chemical shifts. The reaction of orthophosphate ion with *cis*-dichlorodiammineplatinum(II) at pH 6.0 in 0.5 M $NaClO_4$ yielded a blue species which has been characterized by formation kinetics, analytical data, redox titration, and ESR spectroscopy.

Many metal ions are known to form stable complexes with a variety of phosphate ligands.[2] Cobalt(III) complexes with phosphate ligands have been investigated in detail in this laboratory[3-5] and elsewhere.[6] Various binding modes of orthophosphate and polyphosphates have been reported. For example, triphosphate coordinates to cobalt(III) in both monodentate and bidentate fashions.[3-5] Two monodentate isomers containing triphosphate coordinated through the terminal phosphate group (the γ-isomer) and through the middle phosphate group (the β-isomer) have been isolated and characterized by X-ray crys-

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tallography and phosphorus-31 NMR spectroscopy.[5] Similarly, for complexes containing bidentate triphosphate, two isomers, coordinating through the two adjacent phosphate groups (the β,γ-isomer) and through the two terminal phosphate groups (the α,γ-isomer), have also been characterized.[3] Cobalt(III) complexes of other phosphate ligands such as pyrophosphate, orthophosphate, and phosphate esters are also known.[7]

Phosphate hydrolysis reactions of some polyphosphate complexes promoted by metal ions have been studied in order to gain mechanistic insight into the role of metal ions in phosphoryl-transfer reactions in biological systems. Such studies of metal ion promoted hydrolysis have been primarily limited to the octahedral complexes of cobalt(III) and chromium(III).[2,4,6] The metal ions cobalt(III) and chromium(III) are not known to participate in hydrolysis reactions in biological systems, and it remains to be determined whether phosphate hydrolysis follows a general mechanism irrespective of the metal ions used and their geometries. The choice of phosphato complexes of platinum(II) as model systems would introduce a square-planar coordination geometry. Platinum also carries the advantage, unlike Cr(III), of being diamagnetic so that phosphorus-31 NMR spectroscopy could be used to characterize the various hydrolyzed products as an aid to the understanding of the mechanism of hydrolysis. Until this study, neither the phosphato complexes of platinum(II) nor their NMR spectra have been known in detail, although a few phosphato complexes of platinum(II) are reported in the literature.[8]

Another important reason for exploring the coordination chemistry of platinum(II) phosphates is that several workers have suggested phosphate binding to platinum as the mode of interaction of DNA binding to *cis*-$Pt(NH_3)_2Cl_2$,[9] although recent studies suggest that such phosphate binding is unlikely.[10,11] Results from the study of phosphato complexes of platinum(II) may be relevant to studies aimed at determining the binding site of $Pt(NH_3)_2Cl_2$, and the complexes themselves might be effective as antitumor agents. Finally, many kinetic studies of *cis*-$Pt(NH_3)_2Cl_2$ have been carried out in phosphate buffers.[12] Clearly, a knowledge of the extent of phosphate coordination is important for the correct interpretation of the results of such studies. The kinetics of phosphate substitution onto platinum(II) have not been investigated, despite the numerous kinetic studies on the substitution reactions of platinum(II).[13] Here we report the phosphorus-31 NMR characterization and kinetic studies of ortho-, pyro- and triphosphate complexation with *cis*-$Pt(NH_3)_2Cl_2$. Subsequent papers will deal with platinum(II)-catalyzed hydrolysis of polyphosphates[14] and platinum nucleotide complexation.[15]

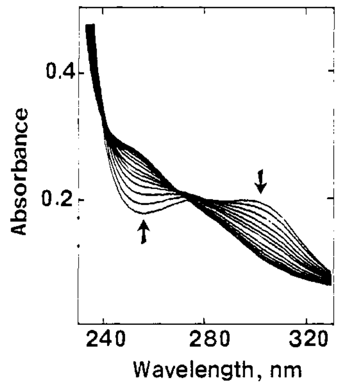

Figure 1. Ultraviolet spectral changes during the reaction between *cis*-dichlorodiammineplatinum(II) (1.75 mM) and triphosphate ion (20.5 mM) at 40 °C and pH 6.0 in 0.5 M $NaClO_4$. The successive spectra were recorded at 5, 36, 65, 95, 125, 155, 185, 245, 305, 425, 625, and 800 min.

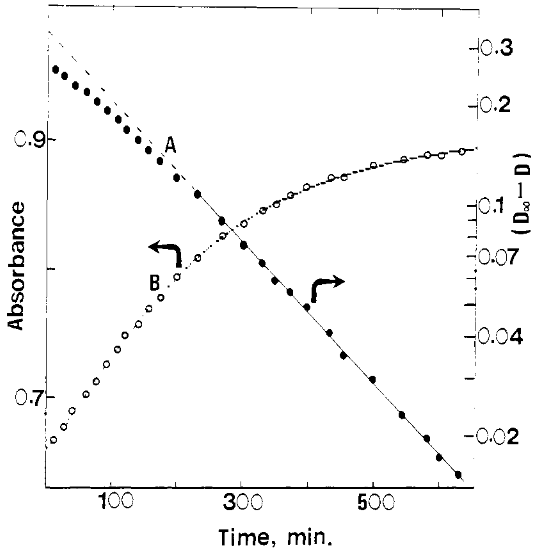

Figure 2. A typical absorbance-time profile and its first-order plot for the reaction of triphosphate ion (45.9 mM) *cis*-dichlorodiammineplatinum(II) (3.3 mM) at 40 °C, pH 6.0 in 0.5 M $NaClO_4$ (λ = 252 nm). (A) semilogarithmic plot of the absorbance changes vs. time; (B) open circles represent the observed absorbance-time profile, dotted line is the simulated profile using eq 3 with $k_1 = 2.85 \times 10^{-4}$ s^{-1}, $k_2 = 7.80 \times 10^{-5}$ s^{-1}, ϵ_A = 198 M^{-1} cm^{-1}, ϵ_I = 211 M^{-1} cm^{-1}, and D_∞ = 0.93 absorbance unit.

Experimental Section

Reagents. *cis*-Dichlorodiammineplatinum(II) was prepared from potassium hexachloroplatinate(IV) following a reported method.[16a] *cis*-Diaquodiammineplatinum(II) nitrate was prepared from the corresponding chloro complex by adding a stoichiometric amount of silver nitrate.[16b] Disodium hydrogen phosphate (Baker) was recrystallized from water and dried at 100 °C. Sodium salts of pyrophosphate (Baker analyzed reagent) and triphosphate (Fisher) were used without further purification. All other reagents were of analytical reagent grade and were used without further purification.

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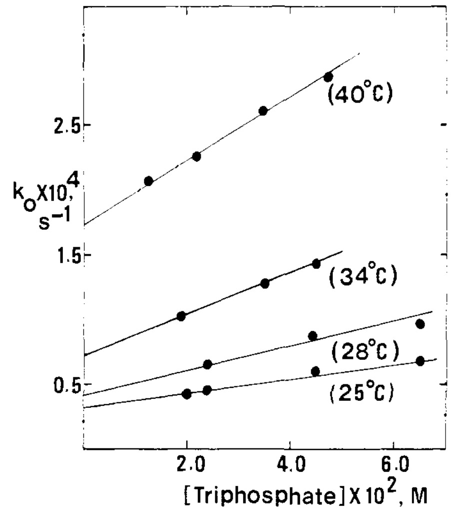

Figure 3. Variation of k_1 ($=k_0$) with triphosphate concentration at various temperatures. Values of k_s and k_y were evaluated by using linear least-squares fits of eq 4.

Instruments. A Cary-219 spectrophotometer was employed for kinetic studies. An Orion research digital pH meter with a combination electrode (Ag/AgCl) was used for pH measurements. Phosphorus-31 NMR studies were carried out at an observation frequency of 36.3 MHz on a JEOL FX 90 Q spectrometer, and all chemical shifts are reported with respect to an external reference of 85% phosphoric acid. Typical data acquisition conditions were as follows: 2000-Hz spectral width, 16 384 data points, 10-μs pulse width (40° pulse), 6-s pulse repetition rate, with complete proton decoupling. A line-broadening factor of 0.5 Hz was introduced to improve the signal to noise ratio during the Fourier transformation. EPR spectra were recorded on a Bruker ER-200D spectrometer operating at 9.1 GHz.

Kinetic Studies. Solutions of *cis*-$Pt(NH_3)_2Cl_2$ and phosphates were prepared by weighing out appropriate amounts of solid materials. The pH was adjusted to the desired values by adding the requisite amount of either 0.5 M $HClO_4$ or 0.5 M NaOH. Solutions of phosphates were thermostated for at least 10 min before use at a desired temperature. For *cis*-$Pt(NH_3)_2Cl_2$ solutions, only the solvent was thermostated in order to minimize the aquation reaction.

The kinetics of reactions of tri-, pyro-, and orthophosphate ions with *cis*-$Pt(NH_3)_2Cl_2$ were followed at two or more wavelengths under pseudo-first-order conditions using at least a 10-fold excess of phosphates over the platinum complex. The ionic strength was maintained at 0.5 M by using $NaClO_4$. The temperature was kept constant (±0.2 °C) by using a thermostated cell compartment.

The pseudo-first-order rate constant, k_0, was evaluated from the slope of the log ($D - D_\infty$) or log ($D_\infty - D$) vs. time plot, when such a plot was linear for at least four half-lives. First-order rate constants were also obtained for these consecutive first-order (or pseudo-first-order) reactions

$$\underset{\text{A}}{Pt(NH_3)_2Cl_2} + \underset{\text{B}}{\text{phosphate ligand}} \xrightarrow{k_1} \underset{\text{I}}{\text{intermediate}} \xrightarrow{k_2} \underset{\text{P}}{\text{product}} \quad (1)$$

Since the free phosphate ligands, B, do not adsorb at the wavelengths selected to monitor the reaction, the absorbance, D, at any time during the reaction is given by

$$D = \epsilon_A[A] + \epsilon_I[I] + \epsilon_P[P] \quad (2)$$

where ϵ_A, ϵ_I, and ϵ_P are the molar absorptivities of the platinum substrate, intermediate, and product. Combining this equation with rate expressions[17] from eq 2 yields

$$D = [A_0]\epsilon_A e^{-k_1 t} + \frac{[A_0]\epsilon_I k_1}{k_2 - k_1}\{e^{-k_1 t} - e^{-k_2 t}\} + \frac{D_\infty}{k_2 - k_1}\{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}\} + D_\infty \quad (3)$$

where $[A_0]$ is the initial concentration of the platinum substrate and D_∞ is the absorbance at infinite time. The rate constants k_1 and k_2 were evaluated from the fit of eq 3 using a nonlinear least-squares computer program.[18] The parameters, $[A_0]$, ϵ_A, and D_∞ were held constant, and initial estimates of the two rate constants were provided to the computer. These estimates were obtained from the biphasic plots as described in the literature.[19] Usually 3–5 iterations were required to simulate an absorbance–time profile that is within the precision of the experimental absorbance–time data. The reproducibility of the two rate constants is within 6%. Activation parameters were obtained from ln (k/T) vs. ($1/T$) plots.

Table I. Rate Constants for the Reaction of Inorganic Phosphates with *cis*-Dichlorodiammineplatinum(II),[a] I = 0.5 M $NaClO_4$, pH 6.0

T, °C	[phosphate] $\times 10^2$, M	$k_1 \times 10^5$, s^{-1}	$k_2 \times 10^5$, s^{-1}
	Reaction with Triphosphate Ion[b]		
25	2.02	4.34	3.21
	2.40	4.48	3.00
	4.54	5.97	3.13
	6.48	6.90	3.17
28	2.42	6.51	3.66
	4.40	8.80	3.51
	6.51	9.61	3.70
34	1.90	10.2	6.51
	3.53	12.8	6.20
	4.47	14.3	6.43
40	1.51	20.7	8.00
	2.24	22.5	8.12
	3.50	26.0	8.29
	4.59	28.4	7.78
	Reaction with Pyrophosphate Ion[b]		
25	1.78	5.52	4.29
	2.90	7.62	4.61
	5.40	10.1	4.43
30	1.92	12.1	5.78
	3.00	15.2	5.42
	4.16	15.9	5.69
	5.14	19.8	5.80
35	2.02	15.2	8.48
	3.61	22.1	8.66
	5.48	28.0	8.41
40	2.78	32.3	12.0
	4.43	39.2	11.1
	5.47	46.8	12.9
	Reaction with Orthophosphate Ion[b]		
40	2.31	34.3	
	4.39	40.3	
	4.83	42.2	

[a] $[Pt(NH_3)_2Cl_2]$ was within the range 1.5-3.5 mM. [b] Reference 23.

Stoichiometry of the Reaction of *cis*-Dichlorodiammineplatinum(II) with Pyro- and Triphosphate Anions. The stoichiometries of the reactions between the platinum substrate and pyro- and triphosphate were determined spectrophotometrically. A solution of *cis*-$Pt(NH_3)_2Cl_2$ (3.2 mM) was prepared at 0.5 M ionic strength maintained by $NaClO_4$, and the pH was adjusted to 6.0. Solutions of sodium pyrophosphate of various concentrations (0.2 to 35 mM) were also prepared at the same ionic strength and pH. Equal volumes of the platinum solution and each of 10 different pyrophosphate solutions were mixed and allowed to equilibrate at room temperature for 48 h. The absorbances at 302 and 252 nm were recorded for each of these mixtures. Plots of absorbance vs. molar ratio ([Pt]/[pyrophosphate]) show break points at molar ratio 1.00 ± 0.05 for both wavelengths.

A similar experiment for the reaction between the platinum substrate and triphosphate ion was also carried out. The stoichiometry of the reaction was found to be 1.0 ± 0.1.

Preparation of the (Orthophosphato)platinum Blue. *cis*-Dichlorodiammineplatinum(II) (0.1 g) was dissolved in aqueous $NaClO_4$ (0.2 M, 250 mL). The pH of the solution was adjusted to 6.0 by adding a few drops of NaOH solution (0.2 M). Disodium hydrogen phosphate (0.4

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[17] The rate equations and their solutions: $-d[A]/dt = k_1[A]$ or $[A] = [A_0]e^{-k_1t}$; $d[I]/dt = k_1[A] - k_2[I]$ or $[I] = (\epsilon_I[A_0]/(k_2 - k_1))\{e^{-k_1t} - e^{-k_2t}\}$; and $d[P]/dt = k_2[I]$ or $[P] = D_\infty\{1 - (k_2/(k_2 - k_1))e^{-k_1t} + (k_1/(k_2 - k_1))e^{-k_2t}\}$. For example, see ref 13, pp 20–23.

(18) Fits to eq 3 were accomplished by using the nonlinear least-squares program FIT kindly supplied by Professor Gilbert Gordon, Miami University. A description of the algorithm of the program is given in the Los Alamos publication LA-2367 and addenda. The original program includes the first two terms on the right hand side of eq 3, which assumes that the products are nonabsorbing species. The third term in eq 3 was added to include the absorbance of the products.

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Table II. Values of k_s and k_y for the Reaction of Inorganic Phosphates with *cis*-Dichlorodiammineplatinum(II), I = 0.5 M $NaClO_4$, pH 6.0

T, °C	$k_s \times 10^5$, s^{-1}	$k_y \times 10^4$, M^{-1} s^{-1}
Reaction with Triphosphate Ion[a]		
25	2.80	7.32
28	4.57	8.71
34	7.16	15.6
40	16.5	27.6
Reaction with Pyrophosphate Ion[a]		
25	2.91	14.0
30	6.63	24.2
35	7.58	36.0
40	17.0	51.0
Reaction with Orthophosphate Ion[a]		
40	16.5	58.5

[a] Reference 23.

Table III. Activation Parameters for the Various Rate Processes Associated with the Phosphate Complexation of *cis*-Dichlorodiammineplatinum(II), I = 0.5 M $NaClO_4$, pH 6.0

rate process	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
Reaction with Triphosphate Ion[a]		
k_s	19.8 ± 0.5	−14 ± 1
k_y	15.5 ± 0.4	−20 ± 2
k_2	11.8 ± 0.6	−40 ± 2
Reaction with Pyrophosphate Ion[a]		
k_s	19.7 ± 0.6	−14 ± 1
k_y	15.3 ± 0.4	−21 ± 1
k_2	11.5 ± 0.5	−37 ± 2

[a] Reference 23.

g) was added to this solution. The pH of the solution was again adjusted to 6.0 by adding $HClO_4$ (0.2 M), and the solution was incubated at 40 °C for 12 h. After about 3 h the solution turned blue and a small amount of precipitate appeared. No blue color was observed during 12 h when the reaction solution was maintained in a nitrogen atmosphere. The residue was filtered and ethanol was added to the blue filtrate. A blue precipitate was filtered, washed with ethanol (3 × 5 mL), and dried in vacuo over calcium sulfate. The yield was 0.04 g.

The phosphate content of the material was analyzed spectrophotometrically as phosphomolybdate following the method reported in the literature[20] and was found to be 28.3 ± 0.5%. The platinum content was analyzed gravimetrically[21] and was found to be 60 ± 1%. These values correspond to a Pt:PO_4 ratio of 1.03 ± 0.03.

Redox Titration. The oxidation state of the platinum complex was determined by titration with ceric nitrate. Since the solubility of the blue material was very low, a solid sample was dissolved in a known amount of standardized ceric solution and back-titrated with standard oxalic acid solution. Appearance of a faint yellow coloration was taken as the end point of the titration.

Results

Kinetics. The spectra of *cis*-dichlorodiammineplatinum(II) in 0.5 M $NaClO_4$ (pH 6.0) recorded at various time intervals in the wavelength region 330–230 nm exhibit isosbestic points at 284 and 240 nm. The absorbance maximum at 302 nm decreased while another increased at 260 nm. There were no further changes in absorbance after 4 h at 40 °C. From these absorbance changes the rate constant for the aquation reaction was computed to be 1.6 × 10^{-4} s^{-1} at 40 °C and 2.7 × 10^{-5} s^{-1} at 25 °C.

The spectral changes of *cis*-$Pt(NH_3)_2Cl_2$ in the presence of triphosphate at 40 °C at various time intervals are shown in Figure 1. In contrast to the observation for the aquation reaction, the change in absorbance for the reaction of triphosphate continued for 15 h. There was no absorbance change at 270 nm after about 3 h (a delayed isosbestic point). Similar spectral changes were observed for the reaction of pyrophosphate with *cis*-$Pt(NH_3)_2Cl_2$, where a delayed isosbestic point developed at 265 nm. The reaction of orthophosphate ion under identical experimental con-

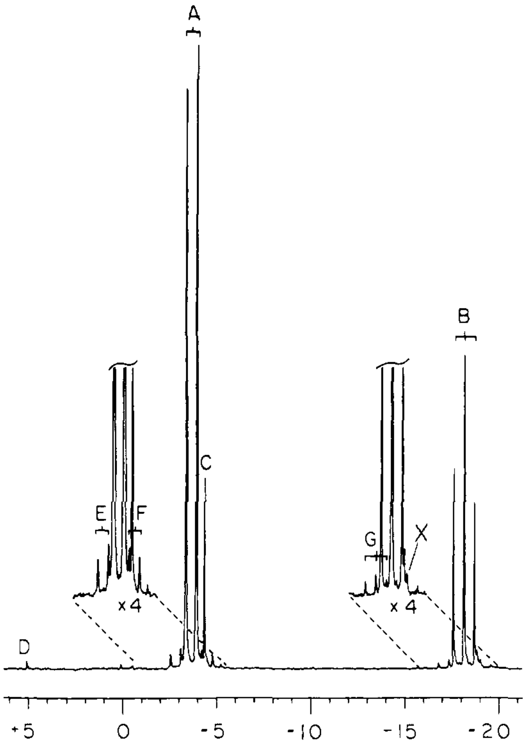

Figure 4. Ambient temperature 36.3-MHz phosphorus-31 NMR spectrum of the reaction mixture of *cis*-dichlorodiammineplatinum(II) (5 mM) and triphosphate anion (40 mM) at pH 8.0. The spectrum was recorded immediately after mixing the two reactants.

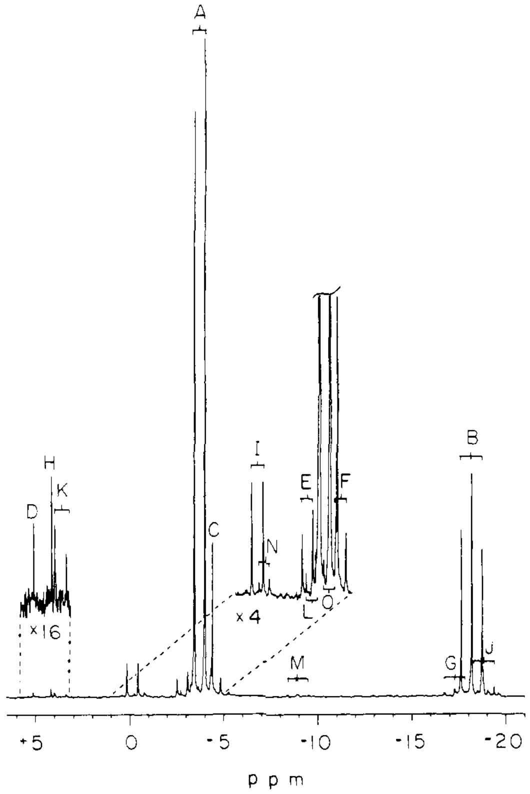

Figure 5. Ambient temperature 36.3-MHz phosphorus-31 NMR spectrum of the reaction mixture of *cis*-dichlorodiammineplatinum(II) and triphosphate ion at pH 8.0 after 24 h.

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(20) Chen, P. S.; Toribara, Y. T.; Warner, H. *Anal. Chem.* **1956**, *28*, 1756–1759.

(21) Vogel, A. I. "Quantitative Inorganic Analysis", 3rd ed.; Wiley: New York, 1961; pp 510–511.

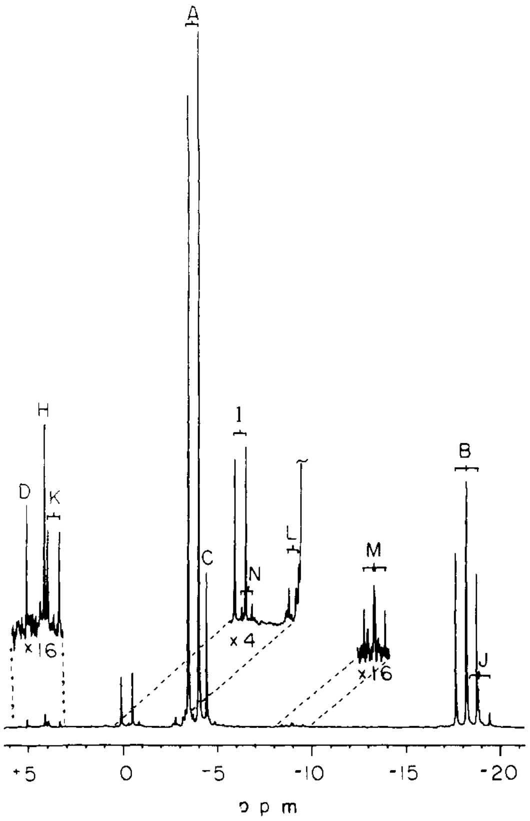
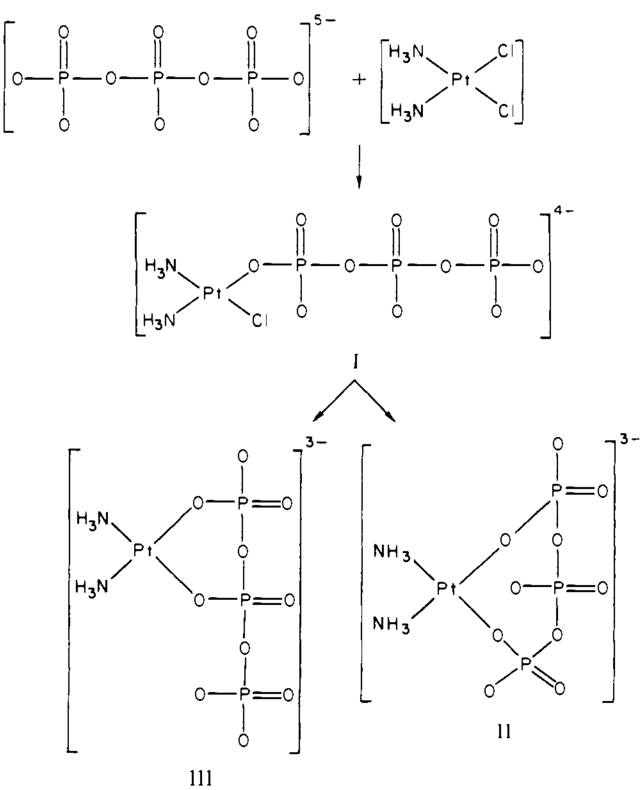


Figure 6. Ambient temperature 36.3-MHz phosphorus-31 NMR spectrum of the reaction mixture of *cis*-dichlorodiammineplatinum(II) and triphosphate ion at pH 8.0 after 48 h.

Scheme I



ditions is strikingly different. Although a delayed isosbestic point developed at 290 nm after about 3 h, the light yellow solution turned blue and a blue-black precipitate formed. The blue filtrate has absorption maxima at 620, 380, and 260 nm.

The kinetics of pyro- and triphosphate complex formation were followed at 302 and at 252 nm, corresponding to the decrease in absorbance of *cis*-$Pt(NH_3)_2Cl_2$ and increase in absorbance due to phosphate complexation, respectively. First-order plots of the data obtained at 302 or 252 nm for both pyro- and triphosphate complexation deviate from linearity within as little as 1 half-life. The data can be described by two consecutive first-order processes (Figure 2). The two rate constants k_1 and k_2 were evaluated from the fits to eq 3 as described earlier. When the reactions are followed at the wavelengths of the delayed isosbestic points for pyro-, tri-, and orthophosphate complexations at 265, 270, and 290 nm, respectively, the absorbance–time profile can adequately be described by a first-order process. The rate constant, k_0, obtained from these first-order plots for pyro- and triphosphate complexation at the delayed isosbestic wavelengths are the same within experimental error as k_1 obtained from the fit of consecutive reactions under identical experimental conditions, and hereafter will be represented as k_1. Due to the precipitation of a blue-black solid, the reaction of orthophosphate ion with the platinum substrate cannot be followed to completion spectrophotometrically. However, using the absorbance changes at 290 nm, the pseudo-first-order rate constant for initial orthophosphate complexation was evaluated.

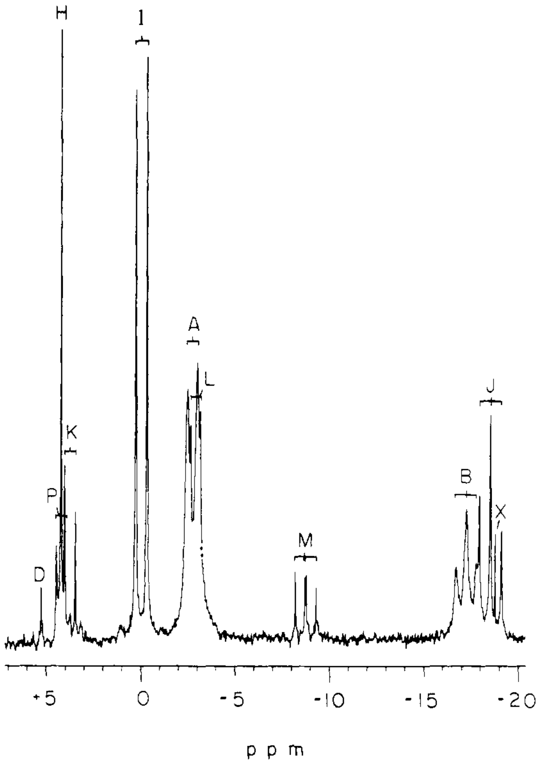


Figure 7. Ambient temperature 36.3-MHz phosphorus-31 NMR spectrum of the reaction of *cis*-diaquodiammineplatinum(II) dinitrate (40 mM) and triphosphate ion (50 mM) at pH 8.4 after 24 h. The positions of the doublets A and L have been shifted 0.8 and 0.2 ppm downfield relative to the corresponding doublets in the Figures 4–6 due to the change in pH from 8.0 to 8.4.

The pseudo-first-order rate constants, k_1, for the initial reaction[22] for all three phosphates follow the rate law

$$k_1 = k_s + k_y[\text{phosphate}] \qquad (4)$$

Values of k_s are the same, $1.6 \pm 0.1 \times 10^{-4}$ s^{-1}, for all the

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[22] Many authors (for example, Alcock, N. W.; Denton, D. J.; Moore, P. *Trans. Faraday Soc.* **1970**, *60*, 2210. Frost, A. A.; Pearson, R. G.; "Kinetics and Mechanism"; Wiley: New York, 1961; p 167) have concluded from their calculations that any rate profile dealing with the buildup and decay of an absorbing intermediate by first-order (or pseudo-first-order) processes can be described by two pairs of solutions having the same set of numerical values assigned to different rate constants. In the present case, the rate constant k_1 has been assigned to the formation of an intermediate as supported by the NMR data and activation parameters (see Discussion).

phosphates and the values of k_y are 2.8×10^{-3}, 5.1×10^{-3}, and 5.9×10^{-3} M^{-1} s^{-1} for tri-, pyro-, and orthophosphate complexation at 40 °C. A typical fit of eq 4 is shown in Figure 3. Table I lists all the pseudo-first-order rate constants determined at various phosphate concentrations, and the fitted values of k_s and k_y are tabulated in Table II. The rate constants, k_2, for the second consecutive reactions for pyro- and triphosphate complexations do not depend on the phosphate concentrations. The enthalpies and entropies of activation associated with these rate constants, k_s, k_y, and k_2, are listed in Table III.

NMR Spectra. Figure 4 shows the phosphorus-31 NMR spectrum of the reaction of triphosphate ion with *cis*-Pt(NH$_3$)$_2$Cl$_2$ at ambient temperature (~32 °C) recorded at zero time. Although the initial concentration of *cis*-Pt(NH$_3$)$_2$Cl$_2$ was small (5 mM) compared to the concentration of triphosphate (40 mM), the signals and coupling patterns of (phosphato)platinum(II) complexes thus formed are readily identified. In the absence of *cis*-Pt(NH$_3$)$_2$Cl$_2$, the NMR spectrum of free triphosphate ion contains a doublet (A) and a triplet (B) centered at −3.72 and −18.20 ppm (J = 20.4 Hz) together with impurities of pyrophosphate ion (C) at −4.40 ppm, orthophosphate ion (D) at 5.1 ppm, and an unknown species at −18.88 ppm. At the beginning of the reaction in the presence of *cis*-Pt(NH$_3$)$_2$Cl$_2$, two sets of doublets (E) at −2.85 (J = 20.5 Hz) and (F) at −4.50 ppm (J = 20.0 Hz) developed along with weaker signals (G) at −17.34 ppm. After 24 h (Figure 5) in addition to the above features, a doublet (I) at −0.17 ppm (J = 21.5 Hz), a shoulder on the downfield component of the triplet, and a signal at −19.42 ppm appeared. At the same time a pair of doublets at 3.68 (K) (J = 21.5 Hz), and −0.52 ppm (N) (J = 20.0 Hz), a doublet of doublets (M) centered at −8.90 ppm (J = 21.3 and 21.5 Hz), and a few smaller peaks near the doublet of the free triphosphate ion were observed. At the end of the reaction (see Figure 6), the two sets of doublets (E and F) which appeared at the beginning of the reaction have almost disappeared.

The analysis of the phosphorus-31 NMR spectra can be performed on the basis of observed splitting patterns and chemical shifts of chelate and monodentate triphosphato complexes of cobalt(III) whose molecular structures have been established from X-ray crystallographic measurements.[3,6] The appearance and disappearance of various peaks as shown in Figures 4–6 can readily be explained on the basis of Scheme I.

According to Scheme I, a monodentate triphosphato complex in which triphosphate is coordinated through a terminal phosphate group (the γ-triphosphato complex) is initially formed. The magnetic equivalency of the two terminal phosphate groups is lifted due to such coordination. The two sets of doublets in Figure 4 (E and F) are thus expected for the coordinated and free terminal phosphate groups of this monodentate complex. The weaker upfield signals (G) are most likely the doublet of doublets expected for the middle phosphate (β-phosphate) group, with the furthest upfield peak partially hidden under the triplet for free triphosphate ion. As the reaction continues, the γ-monodentate complex is converted to bidentate chelates. Two isomeric chelates are possible: the α,γ-isomer, in which the two terminal phosphate groups are coordinated, and the β,γ-isomer, in which two adjacent phosphate groups are coordinated. In the α,γ-isomer, two terminal phosphate groups are magnetically equivalent; however, because of coordination, their chemical shifts would be different from those of uncomplexed triphosphate ion. The doublet (I) and the partly masked triplet (J) in Figures 5 and 6 represent the α,γ-chelate (complex II in Scheme I). In the case of the β,γ-chelate, all three phosphate groups are magnetically nonequivalent. The chemical shifts of the coordinated β- and γ-phosphate groups are expected to be shifted in comparison with the chemical shift of the β- and γ-phosphate groups in free triphosphate ion. The doublet (K) and the doublet of doublets (M) (Figure 5 and 6) arise from the coordinated γ- and β-phosphate groups in the β,γ-chelate. The doublet for the uncomplexed α-phosphate group is expected to appear near the corresponding α-phosphate group of free triphosphate ion. Two smaller peaks (L) centered at −3.01 ppm represent the α-phosphate in the β,γ-isomer. The peak (H) at 4.15, the doublet (N) at −0.52 ppm, and the remaining small peaks (O) near the doublet of free triphosphate ion have been identified from a separate reaction between *cis*-Pt(NH$_3$)$_2$Cl$_2$ and pyrophosphate ion as being due to the formation of bidentate and monodentate pyrophosphato complexes.

In order to confirm the assignment of the various peaks for the α,γ- and β,γ-isomers formed using *cis*-Pt(NH$_3$)$_2$Cl$_2$ as a reactant, the phosphorus-31 NMR spectrum in Figure 7 was recorded of the reaction mixture of *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ and triphosphate ion at pH 8.4. Due to the higher solubility of the aquo complex than the chloro complex, phosphato complexes of platinum(II) are more easily distinguished in Figure 7 than in Figures 4–6. The same assignment applies: the doublet (I) and the triplet (J) arise from the α,γ-isomer, and the two doublets (K and L) and the doublet of doublets (M) are due to the β,γ-isomer.

The phosphorus-31 NMR spectrum at the end of the reaction between pyrophosophate ion and *cis*-Pt(NH$_3$)$_2$Cl$_2$ is shown in Figure 8. Apart from the signals of free pyrophosphate ion (C) at −4.4 ppm and an impurity of orthophosphate ion (D) at 5.1 ppm, the spectrum exhibits a singlet (H) at 4.15 ppm with two satellites (P) originating from splitting by the 33.7% abundant platinum-195 nucleus. This pattern is attributed to the final product of the reaction, a bidentate pyrophosphato complex. In addition to this chelate, two sets of doublets (N and O) resulting from a monodentate pyrophosphato complex appear initially and then nearly disappear as the monodentate complex is converted to the bidentate complex. Table IV lists the phosphorus-31 peak positions, their coupling patterns, and assignments.

Orthophosphate Platinum Blue. The blue species isolated from the reaction of orthophosphate ion and *cis*-Pt(NH$_3$)$_2$Cl$_2$ at pH 6.0 has a platinum to phosphate stoichiometric ratio of 1.03. Oxidation by ceric nitrate solution showed that 1.75 ± 0.05 mol of cerium(IV) per mol of platinum was necessary to oxidize both platinum(II) and platinum(III) to platinum(IV). Thus the average oxidation state of platinum atoms in the blue species is calculated to be +2.25. The partial oxidation of the starting platinum(II) to yield the (phosphato)platinum blue was achieved in nitrate and perchlorate media at pH values 4–6 in the presence of air. In the absence of electrochemical data of this blue species it would be speculative to conclude whether nitrate (perchlorate) and/or oxygen is responsible for this partial oxidation of platinum.

The blue species has absorption maxima at 620, 380, and 260 nm in 0.5 M NaClO$_4$. In both perchloric and nitric acids (0.1 M), the blue species slowly changes color from blue to purple to pale yellow within 3 days.

The pH-titration curve of the solid blue dissolved in 0.1 M NaNO$_3$ exhibits one inflection within the pH range 4.5–10.5 at 40 °C. A pK value of 6.5 was evaluated from the titration curve.

The EPR spectrum of the solid orthophosphate blue exhibits two main signals corresponding to $g_{\perp} = 2.35$ and $g_{\parallel} = 2.06$. These two signals are further split by platinum-195 nuclei ($I = {}^1/_2$) due to the nuclear hyperfine coupling interactions. The EPR spectra of (orthophosphate)- and other poly(phosphate)platinum blues will be discussed in detail elsewhere.[24]

Discussion

The magnitude of k_s (eq 4) is the same at constant temperature for all the three phosphates studied. The value of k_s, 1.60×10^{-4} s^{-1}, is in excellent agreement with the rate constant of aquation, 1.55×10^{-4} s^{-1}, measured under identical experimental conditions. Moreover, the enthalpies and entropies of activation, 19 kcal mol^{-1} and −14 cal deg^{-1} mol^{-1}, respectively, are in excellent agreement with the values of 20 kcal mol^{-1} and −14 cal deg^{-1} mol^{-1}, respectively, for the rate of aquation of *cis*-Pt(NH$_3$)$_2$Cl$_2$ reported

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[23] The pK values for triphosphoric acid are 0.5, 1.0, 2.0, 5.7, and 8.6; therefore at pH 6, the predominant species in solution would be HP$_3$O$_{10}^{4-}$. Similarly, at pH 6, the dominant species of orthophosphate and pyrophosphate ion are H$_2$PO$_4^-$ and H$_2$P$_2$O$_7^{2-}$.

[24] Bose, R. N.; Viola, R. E.; Cornelius, R. D., manuscript in preparation.

Table IV. Phosphorus-31 NMR Peak Positions and Their Assignments

species	peak position,[a] ppm	coupling constant,[b] Hz	assignments (phosphate)	coordination chemical shift,[c] ppm
P_3O_{10} ion[d]	−3.72 (A)	20.4 (d)	α, γ	
	−18.20 (B)	20.4 (t)	β	
PtP_3O_{10} (monodentate)	−2.85 (E)	20.5 (d)	γ (coordinated)	+0.87
	−4.50 (F)	20.0 (d)	α (uncoordinated)	−0.78
	−17.34[e] (G)		β (uncoordinated)	+0.86
PtP_3O_{10} (α,γ-chelate)	−0.17 (I)	21.5 (d)	α, γ (coordinated)	+4.18
	−18.82[e] (J)	21.5 (t)	β (uncoordinated)	−0.62
PtP_3O_{10} (β,γ-chelate)	3.68 (K)	21.5 (d)	γ (coordinated)	+8.03
	−3.01 (L)	21.3 (d)	α (uncoordinated)	+0.71
	−8.90 (M)	21.3, 21.5 (dd)	β (coordinated)	+8.30
P_2O_7 ion[d]	−4.40 (C)	(s)		
PtP_2O_7 (monodentate)	−0.52 (N)	20.0 (d)	coordinated	+3.88
	−3.98 (O)	20.0 (d)	uncoordinated	+0.42
PtP_2O_7 (chelate)	4.15 (H)	(s)		+8.55
PO_4 ion[d]	5.1 (D)	(s)	uncoordinated	

[a] Letters in parentheses refer to peaks in Figures 4–8. [b] s = singlet, d = doublet, dd = doublet of doublets, t = triplet. [c] Positive values are downfield. [d] pH 8.0; exact species depend upon p*K* values. [e] Partly masked.

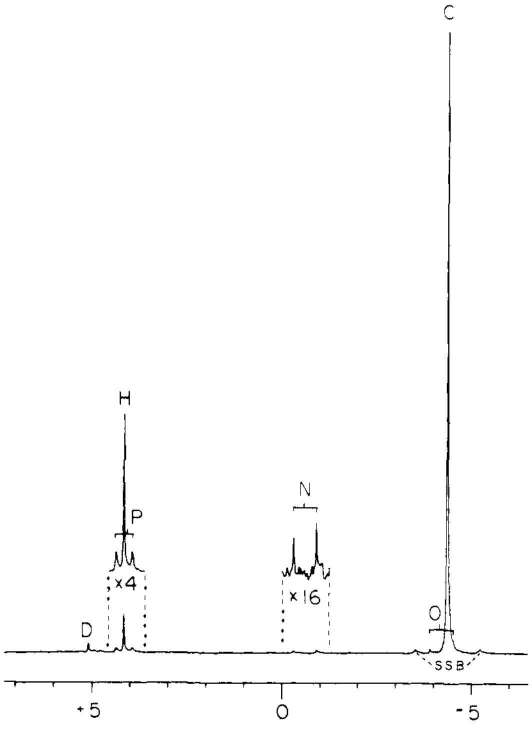

Figure 8. Ambient temperature 36.3-MHz phosphorus-31 NMR spectrum of the reaction mixture of *cis*-dichlorodiammineplatinum(II) (5 mM) and pyrophosphate ion (40 mM) at pH 8.0 after 48 h. SSB represents the spinning side bands.

by Reishus and Martin.[25] All of these results indicate that the first term, k_s, of the two-term rate law for initial phosphate complexation represents the rate of aquation of *cis*-$Pt(NH_3)_2Cl_2$. The second term of the rate law (eq 4), which exhibits a linear dependence on phosphate concentration, represents the direct reaction of phosphate ligands with *cis*-dichlorodiammineplatinum(II). These results are in accord with the established mechanism of substitution of platinum(II).[13] In addition to the two-term rate law for initial phosphate complexation, the kinetics exhibit a slower consecutive, first-order process. The phosphorus-31 NMR spectral data presented earlier support a mechanism in which formation of a monodentate complex is followed by conversion to a bidentate chelate. A mechanism consistent with our kinetic and NMR data is shown in Scheme II. This mechanism is applicable to both pyro- and triphosphate complexations. Since precipitation prevents the reaction of orthophosphate from being followed until completion, a detailed mechanism for the formation of (orthophosphato)platinum blue cannot be presented. However, since the initial orthophosphate complexation follows the same rate law as pyro- and triphosphate coordination, it is likely that a monodentate orthophosphate complex is initially formed with subsequent formation of a blue species.

According to Scheme II, k_2 represents the rate constant for the chelation step. The enthalpies and entropies of activation for the chelation reactions are 11.8 kcal mol^{-1} and −40 cal deg^{-1} mol^{-1} for triphosphate and 11.5 kcal mol^{-1} and −37 cal deg^{-1} mol^{-1} for pyrophosphate. These values are significantly different from aquation (20 kcal mol^{-1} and −14 cal deg^{-1} mol^{-1}) and from those for second-order processes for monodentate complexation reactions by nucleophiles toward any platinum(II) substrates (15 to 20 kcal mol^{-1} and −10 to −20 cal deg^{-1} mol^{-1}) so far reported in the literature.[15] Cattalini and co-workers[26] have found that the entropy of activation for reactions of $Pt(bpy)Cl_2$ (bpy = 2,2′-bipyridyl) with bidentate ligands such as ethylenediamine and ethylenetriamine is about −30 cal deg^{-1} mol^{-1}, in contrast to values for the monodentate complexation by similar amine ligands such as *n*-butylamine, pyridine, and substituted pyridines where entropies of activation have been computed to be near −18 cal deg^{-1} mol^{-1}. Although the monodentate complexation is the rate-limiting process in the reactions of $Pt(bpy)Cl_2$ with bidentate amine ligands, the $\Delta S^{\ddagger}$ is more negative than for purely monodentate coordination. This difference has been explained by considering a transition state as a compact trigonal bipyramid with a semichelated structure. In the present case the entropy of activation is even more negative. A possible explanation for this value could be that chelation itself is the rate-limiting process or that solvation of polyanionic platinum(II) phosphate intermediates is stronger than for the intermediates produced with the amine ligands.

Alternative explanations for the second step of the reaction due to the formation of either bis(polyphosphato) complexes or hydroxo-bridged species may be considered.[27] However, the results

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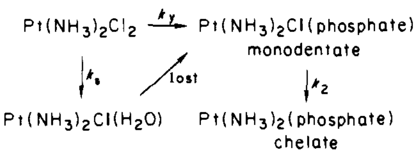
[25] Reishus, J. W.; Martin, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 2457–2461.

[26] Baracco, L.; Cattalini, L.; Coe, J. S.; Rotondo, E. *J. Chem. Soc. A* **1971**, 1800–1805.

[27] A competing reaction between a hydroxo-bridged dimer formation and the monodentate phosphate complexation with the transient aquated intermediate can also be ruled out. The concentration of $Pt(NH_3)_2(OH)Cl$ at pH 6.0 would be less than 10%[11] of the total platinum concentration. The hydroxo-bridged dimer formation has been reported to be second order with respect to the monohydroxo species for many platinum(II) amine complexes (for example, Rosenberg, B. *Biochimie* **1978**, *60*, 859–867. Gill, D. S.; Rosenberg, B. *J. Am. Chem. Soc.* **1982**, *104*, 4598–4604. Lim, M. C.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1911–1916). Assuming that the rate of dimer formation is as rapid as other aquoamine complexes of platinum(II), an upper limit of rate constant for dimer formation can be estimated as $<10^{-3}$ M^{-1} s^{-1}. The rate constant for monodentate triphosphate complex formation with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ is 1.2 × 10^{-2} M^{-1} s^{-1}[14] which is at least an order of magnitude greater than that for dimer formation.

Scheme II

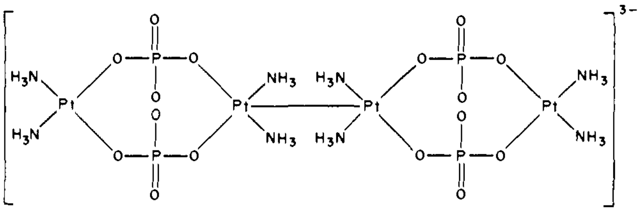


from the stoichiometric experiments suggest that the reactions of the phosphate ligands with the platinum substrate follow 1:1 stoichiometry. Morever, in the case of pyrophosphato complexation, a bis(pyrophosphato) complex would result in a doublet in the phosphorus-31 NMR spectra rather than the singlet observed in Figure 8. Also, after the reaction was allowed to proceed under the conditions used for kinetics a pyrophosphato chelate (dihydrogen pyrophosphato)diammineplatinate(II), was isolated and characterized.[15]

The phosphorus-31 NMR spectra show that both α,γ- and β,γ-chelate complexes are formed with triphosphate ion under our experimental conditions, with formation of the α,γ-complex being favored. From phosphorus-31 NMR intensities of these two chelated species a relative ratio of 10:1 (α,γ:β,γ) can be computed. In contrast, the reaction of diaquotetraaminecobalt(III) with triphosphate anion under similar conditions yielded β,γ-chelate as the dominant product with a very small amount of α,γ-isomer.[3] The equilibrium constant for the isomerization of β,γ-triphosphato)tetraamminecobalt(III) to the corresponding α,γ-isomer was found to be 0.1.[28] One factor contributing to the higher yield of α,γ over β,γ in the present case may be the larger size of platinum(II) over cobalt(III).

Monodentate coordination of the terminal phosphate of triphosphate results in a downfield shift of the phosphorus-31 spectrum of about 2 ppm compared to the free terminal phosphate. Chelation to either the β-phosphate or the other terminal phosphate group causes a further downfield shift of about 3 ppm for the coordinated terminal phosphate. Coordination of the terminal phosphate group causes a downfield shift of about 1 ppm in the free β-phosphate group. Chelation to the second terminal phosphate (α,γ-bidentate) results in a 2 ppm upfield shift of the β-phosphate. Chelation to the central phosphate (β,γ-bidentate) causes a 9 ppm downfield shift in the β-phosphate group. For the pyrophosphato complexes similar coordination shifts are observed. Monodentate coordination results in a 3.5 ppm downfield shift. Bidentate chelation causes a further 5 ppm downfield shift. These observed coordination shifts are comparable to the coordination chemical shifts observed for the (pyrophosphato)cobalt(III) complexes.[2a]

Orthophosphate ion forms a blue complex with *cis*-$Pt(NH_3)_2Cl_2$ while pyro- and triphosphate under identical experimental conditions do not yield similar complexes. The blue complex has a composition which reveals a 1:1 ratio of platinum to phosphate. A possible explanation for the formation of the (orthophosphato)platinum blue comes from our kinetic data which suggest that the formation of a monodentate orthophosphate complex is as rapid as pyrophosphato complexation. A chelation step to form a bidentate orthophosphate complex, however, would be unfavorable due to the large size of platinum(II) and the requirement for the formation of a four-membered chelate ring. Milburn et al. have found from their crystallographic studies that substantial ring strain is present in the four-membered chelate ring in the (orthophosphato)bis(ethylenediamine)cobalt(III) chelate.[6] Ring strain would be expected to be even larger in the platinum complex due to larger size of platinum(II). If coordination to a second platinum(II) species by the orthophosphate ligand is more favorable than chelation, a phosphato-bridged binuclear species would be formed. The analytical data showing a platinum to phosphate ratio of 1:1 are consistent with the formulation of a binuclear species where two phosphate groups bridge between two platinum atoms. Lippard and workers[29] have established that (uracil) and (α-pyridone)platinum blues are tetranuclear mixed-valence species in which two bridging dimers are held by a partial Pt–Pt axial bond. This partial metal–metal bond is accomplished by the removal of a $5d_{z^2}$ electron from one of the platinum(II) ions. A similar tetranuclear structure composed of two bridging phosphate dimers with partial oxidation can be suggested for the (orthophosphato)platinum blue. Therefore a suggested formulation for the (orthophosphato)platinum blue is shown as IV with one platinum out of every four platinum atoms being of +3 oxidation state, consistent with our redox titration data.



IV

Acknowledgment. This research was supported by National Science Foundation Grant No. CHE-8024043.

Registry No. *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1; $P_2O_7^{4-}$, 14000-31-8; $P_3O_{10}^{5-}$, 14127-68-5; PO_4^{3-}, 14265-44-2; Pt, 7440-06-4.

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(28) Reibenspies, J.; Cornelius, R. D. *Inorg. Chem.*, in press.

(29) Barton, K. J.; Caravan, C.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 7269–7277. Holis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2600–2604; **1983**, *22*, 2605–2614.