of $[NP(CH_3)_2]_4$ (0.30 g, 1 $\times$ 10^{-3} mol) in 0.1 M hydrochloric acid (25 mL). An immediate, light red precipitate formed. The precipitate was filtered off, washed several times with acetone–water mixtures, and then dried under vacuum. Anal. Calcd for $C_8H_{26}N_4Cl_4P_4Pt$: C, 15.04; H, 4.07; N, 8.77; Cl, 22.20; P, 30.97; Pt, 18.95. Found: C, 15.04; H, 4.24; N, 9.02; Cl, 22.15; P, 30.54; Pt (by difference), 19.01.

References and Notes

(1) This paper is part 30 in a series on phosphorus–nitrogen compounds. A preliminary communication on this work appeared in *J. Chem. Soc., Chem. Commun.*, 717 (1976).
(2) Part 29 by R. W. Allen and H. R. Allcock, *Macromolecules*, **9**, 956 (1976).
(3) B. Rosenberg, L. Van Camp, J. E. Trosko, and V. H. Mansour, *Nature (London)*, **222**, 385 (1969).
(4) B. J. Leonard, *Nature (London)*, **234**, 43 (1971).
(5) For recent reviews on phosphazene chemistry see (a) H. R. Allcock, "Phosphorus–Nitrogen Compounds", Academic Press, New York, N.Y., 1972; (b) H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972).
(6) H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem.*, **11**, 2584 (1972).
(7) The details of this x-ray structure determination will be found in R. W. Allen, J. O'Brien, and H. R. Allcock, *J. Am. Chem. Soc.*, following paper in this issue.
(8) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 875 (1963).
(9) D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 4464 (1964).
(10) Tests performed at the National Institutes of Health.
(11) These tests were performed by Dr. Iris H. Hall, Division of Medicinal Chemistry, University of North Carolina. The test data will be described in more detail in a later publication.
(12) K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **83**, 2608 (1961).
(13) H. R. Allcock and D. B. Patterson, *Inorg. Chem.*, **16**, 197 (1977).
(14) G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, **7**, 239 (1963).
(15) This procedure resembles one described by J. Dyson (Ph.D. Thesis, 1964, Victoria University of Manchester, pp 93–94) for the reaction of PdCl_2 with $[NP(CH_3)_2]_4$.

Crystal and Molecular Structure of a Platinum–Cyclophosphazene Complex: cis-Dichloro[octa-(methylamino)cyclotetraphosphazene-N,N″]platinum(II)[1,2]

Robert W. Allen, John P. O'Brien, and Harry R. Allcock*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received August 27, 1976

Abstract: The compound, $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$, is both an antitumor agent and a model compound for the analogous polymeric derivative, $(PtCl_2)_x[NP(NHCH_3)_2]_n$. The x-ray structure of $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$ has revealed a unique form of bonding in which a square planar platinum atom is bonded to two antipodal *skeletal* nitrogen atoms of the saddle-shaped cyclotetraphosphazene ring. The orientation of the phosphazene ring relative to the platinum atom cannot be explained solely by σ-coordinate bonding or by a π-type interaction. The crystals are monoclinic with the space group $P2_1/n$, and with $a =$ 10.34 (2), $b =$ 15.61 (4), $c =$ 14.32 (4) Å, $\beta=$ 92.36 (18)°, $Z =$ 4. The Pt–N bond distances are 2.026 (16) and 2.081 (15) Å and the Pt–Cl bond distances are 2.304 (5) and 2.300 (6) Å. The N–Pt–N angle is 87.0 (6)° and the Cl–Pt–Cl angle is 92.9 (2)°. Within the cyclotetraphosphazene unit the P–N bonds flanking the Pt–N units are longer (1.61–1.64 (2) Å) than those at a greater distance from the coordination site (1.57–1.61 (2) Å). The skeletal P–N–P bond angle is marginally wider (128.8 (10)°) at the coordination sites than at the uncoordinated locations (122.2–127.8°). The bonding implications of these results are discussed.

The synthesis of the first platinum-phosphazene complexes was described in the preceding paper.[2] Several of these compounds have shown activity in preliminary anticancer screening tests, and particular interest was focused on the noncrystalline high polymeric derivative, $(PtCl_2)_x$-$[NP(NHCH_3)_2]_n$. The analogous complex containing a cyclotetraphosphazene ligand, $PtCl_2[N_4P_4(NHCH_3)_8]$, is itself active as an antitumor agent. Moreover, this compound crystallizes readily and was found to be suitable for x-ray analysis. It was anticipated that the structural information derived from the cyclotetraphosphazene adduct could be used to understand the binding characteristics of the phosphazene high polymer.

Apart from the biomedical implications of this work and the relationship of it to the anticancer activity of platinum compounds in general,[3,4] considerable fundamental interest revolves around the mode of binding of metal atoms to phosphazene rings. Relatively few metal complexes of cyclophosphazenes have been synthesized.[5-14] In most (if not all) of these, the metal–ring binding involves a σ-type donation of lone pair electrons from ring nitrogen atoms to the metal. Thus, it was anticipated that the structure solution of

$PtCl_2[N_4P_4(NHCH_3)_8]$ might provide an added insight into the behavior of phosphazenes as coordinate ligands.

Crystallographic Section

Synthesis of cis-Dichloro[octa(methylamino)cyclotetraphosphazene-N,N'']platinum(II). The compound, $PtCl_2[N_4P_4(NHCH_3)_8]$, was prepared by the reaction of octa(methylamino)cyclotetraphosphazene, $[NP(NHCH_3)_2]_4$, with potassium tetrachloroplatinate, K_2PtCl_4, in chloroform solution as described in the preceding paper.[2]

Collection and Reduction of X-Ray Data. Single crystals suitable for x-ray diffraction examination were grown from acetone solution over several weeks. A clear yellow crystal, 0.24 $\times$ 0.16 $\times$ 0.08 mm, was chosen and mounted on a eucentric goniometer head. Precession photographs with nickel-filtered copper x radiation ($K\alpha = 1.542$ Å) indicated that the crystal was monoclinic (Laue symmetry $2/m$) with the $h0h$ direction along the spindle axis. Systematic absences were observed for $0k0$ with $k \neq 2n$ and for $h0l$ with $h + l \neq 2n$. These absences led to a choice of a space group as $P2_1/n$. The crystal was transferred to a Syntex four-circle, computer-controlled diffractometer. Ten reflections were centered with molybdenum

Table I. Refined Positional and Thermal Parameters for $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$

Atom	10^3x	10^3y	10^3z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Pt	139.03 (7)	262.58 (6)	236.34 (6)	5.33 (7)	3.15 (6)	1.85 (6)	0.24 (5)	−1.03 (4)	−0.05 (4)
Cl (1)	343.9 (5)	278.8 (4)	303.2 (4)	6.6 (5)	5.0 (4)	3.3 (4)	−0.6 (3)	−2.4 (3)	0.1 (1)
Cl(2)	60.1 (5)	203.9 (4)	369.8 (4)	7.2 (5)	6.6 (4)	2.5 (4)	0.6 (3)	0.2 (3)	0.3 (3)
P (1)	220.3 (4)	232.5 (4)	41.8 (4)	4.7 (5)	3.9 (4)	2.2 (4)	−0.3 (3)	−0.2 (3)	−0.2 (3)
P (3)	142.6 (5)	404.8 (4)	97.9 (4)	6.2 (5)	2.8 (4)	3.2 (4)	−0.1 (3)	−0.9 (3)	0.0 (3)
P (5)	−100.7 (5)	343.2 (4)	143.9 (4)	5.8 (5)	3.5 (4)	2.4 (4)	0.2 (3)	−1.1 (3)	0.2 (3)
P (7)	−23.0 (5)	168.2 (4)	94.1 (4)	5.4 (5)	3.1 (4)	2.5 (4)	−0.5 (3)	−0.9 (3)	−0.1 (3)
N (2)	205 (1)	311 (1)	116 (1)	7 (2)	3 (1)	3 (1)	−0.9 (9)	−3 (1)	0.0 (8)
N (4)	−13 (2)	407 (1)	88 (1)	8 (2)	3 (1)	4 (1)	1 (1)	0 (1)	1.1 (8)
N (6)	−40 (1)	249 (1)	166 (1)	9 (2)	2 (1)	2 (1)	0 (1)	−2.2 (9)	0.5 (8)
N (8)	98 (1)	174 (1)	29 (1)	7 (2)	4 (1)	4 (1)	2 (1)	0 (1)	−1.3 (8)
N (11)	352 (1)	183 (1)	84 (1)	6 (2)	4 (1)	4 (1)	0 (1)	−1 (1)	−0.2 (8)
N (12)	259 (1)	259 (1)	−62 (1)	7 (2)	5 (1)	3 (1)	−1 (1)	0 (1)	0.5 (9)
N (31)	202 (2)	459 (1)	186 (1)	13 (2)	2 (1)	4 (1)	−1 (1)	−2 (1)	−0.2 (9)
N(32)	194 (1)	448 (1)	4 (1)	4 (2)	7 (1)	2 (1)	−1 (1)	1.1 (9)	1.8 (9)
N(51)	−136 (2)	337 (1)	247 (1)	9 (2)	3 (1)	3 (1)	2 (1)	−1 (1)	−1.2 (8)
N(52)	−237 (1)	341 (1)	84 (1)	5 (2)	3 (1)	4 (1)	−0.1 (9)	−2 (1)	1.5 (8)
N(71)	−25 (2)	88 (1)	166 (1)	11 (2)	1 (1)	5 (1)	0 (1)	−2 (1)	0 (1)
N(72)	−148 (1)	155 (1)	23 (1)	4 (2)	6 (1)	2 (1)	−1 (1)	0.2 (9)	−0.2 (8)
C (11)	382 (2)	97 (2)	50 (2)	7 (3)	6 (2)	8 (2)	2 (2)	2 (2)	−1 (2)
C(12)	168 (2)	284 (2)	−136 (1)	10 (2)	9 (2)	0 (2)	0 (2)	−1 (1)	1 (1)
C(31)	173 (2)	548 (2)	198 (2)	11 (3)	1 (2)	9 (2)	−1 (2)	−1 (2)	−1 (1)
C(32)	328 (2)	468 (2)	−6 (2)	8 (2)	5 (2)	7 (2)	1 (1)	0 (2)	2 (1)
C(51)	−171 (2)	461 (2)	268 (2)	12 (3)	5 (2)	6 (2)	1 (2)	1 (2)	−1 (1)
C(52)	−363 (2)	324 (2)	124 (2)	7 (2)	7 (2)	6 (2)	−1 (2)	−1 (2)	1 (1)
C(71)	14 (3)	3 (2)	136 (2)	16 (4)	3 (2)	5 (2)	1 (2)	1 (2)	0 (1)
C(72)	−273 (2)	124 (2)	47 (2)	4 (2)	9 (2)	6 (2)	−2 (1)	0 (1)	0 (1)

x radiation, zirconium filtered in the incident beam ($K\alpha$ = 0.7107 Å). Unit-cell dimensions as calculated by a least-squares refinement with the 2θ values for these centered reflections were a = 10.34 (2), b = 15.61 (4), c = 14.32 (4) Å, and β = 92.36° (18), V = 2314.1 Å^3, d_m = 1.93 g cm^{-3} (by flotation in bromoform–carbon tetrachloride mixtures), Z = 4, d_c = 1.97 g cm^{-3}, and molecular weight (I) = 686.25. The linear absorption coefficient, μ, for Mo $K\alpha$ was 69.0 cm^{-1}.

Intensity data were collected with zirconium-filtered molybdenum x radiation and with a θ–2θ scan mode. The scan width varied linearly from 2.0° at a 2θ of 5.0° to 2.5° at a 2θ of 120.0°. The scan rate was fixed at 1°/min. Each background intensity was measured for one-half the total scan time at the beginning and end of the scan range. After every 25 reflections two check reflections were measured to serve as standards. Data were collected for the planes hkl and $hk\bar{l}$. A total of 2541 nonstandard reflections were measured.

The net intensities were found by the formula I = [CTS − ($B_1 + B_2$)] where CTS is the total scan count, and B_1 and B_2 were the background counts. The intensities were scaled to the check reflections. The standard deviation for the corrected intensity, $\sigma(I)$, where $\sigma(I)$ = [CTS + ($B_1 + B_2$)]$^{1/2}$, was based on counting statistics. No absorption correction was made to the data. Corrections for Lorentz and polarization effects were applied to the data, and the observed structure factors were determined. The value for σ used in the refinement was determined as follows: F < 11$\sigma(F)$, σ = 1.2; F > 200$\sigma(F)$, σ = 1.1; otherwise, σ = 1.0. Equivalent reflections ($0kl$ and $0k\bar{l}$) were averaged. Of the 2431 unique reflections measured, 1753 had I > 3$\sigma(I)$ and were used in the subsequent refinement.

Solution and Refinement of the Structure. The atomic scattering factors as tabulated by Cromer and Waber[15] were used for all nonhydrogen atoms, and those calculated from quantum mechanics were used for the hydrogen atoms.[16] Anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for Pt, P, and Cl were those of Cromer.[17] The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with w = 1/σ^2. The residuals R_1 and R_2 are expressed by R_1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The map of

the three-dimensional Patterson function was used to locate the position of the platinum atom. Three cycles of refinement of the positional and isotropic thermal parameters of this atom gave R_1 = 0.31. A Fourier synthesis revealed the location of two chlorine atoms and the four phosphorus atoms of the phosphazene ring. Refinement through four cycles based on these seven atoms lowered R_1 to 0.180. A difference Fourier revealed the location of the four endocyclic nitrogen atoms and the eight exocyclic nitrogen atoms of the methylamino substituents. Three more cycles of refinement of the positional and thermal parameters of these 19 atoms lowered R_1 to 0.122. Another difference Fourier synthesis revealed electron density at positions that were attributable to the eight methylamino carbon atoms. Placement of these additional atoms into the model and refinement through three cycles yielded R_1 = 0.086. At this point, with all nonhydrogen atoms positioned, anomalous dispersion was introduced and thermal parameters were changed to anisotropic. Four cycles with anisotropic thermal parameters for all nonhydrogen atoms gave R_1 = 0.053 and R_2 = 0.066.

A difference Fourier map was then generated to locate the hydrogen atoms. Hydrogen atom positions were approximated by analysis of the difference map. An idealized model with a C–H and N–H distance of 1.00 Å and with a tetrahedral geometry at the carbon and nitrogen atoms was used to position the hydrogen atoms in the model. The isotropic thermal parameters for the amino hydrogen atoms were fixed at a value of 1.0 Å^2 greater than the equivalent isotropic thermal parameter of the nitrogen atoms to which they were attached. The isotropic thermal parameters for the methyl hydrogen atoms were set equal to the equivalent isotropic thermal parameter of the carbon atoms to which they were bound. Three cycles of refinement of all nonhydrogen atoms and repositioning of hydrogen atoms to idealized positions gave a final R_1 = 0.049 and R_2 = 0.060.

The refined values of the atomic positional and anisotropic thermal parameters for all nonhydrogen atoms are given in Table I. The idealized hydrogen atom positions and isotropic thermal parameters appear in Table II. Table III, a table of
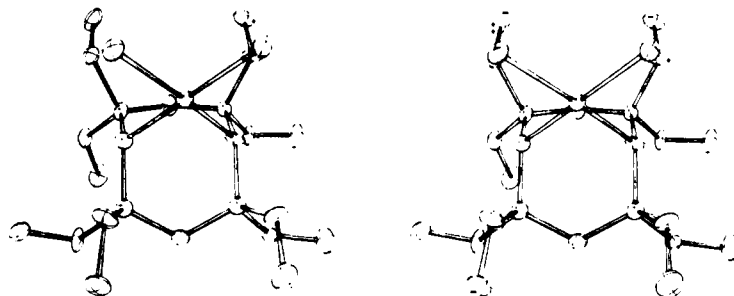
Figure 1. Stereoscopic view of the molecular structure of $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$.
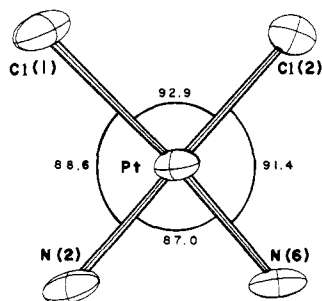
Figure 2. Orientation of the ligands around platinum in $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$.

the observed and calculated structure factor amplitudes for the 1753 nonequivalent observed reflections, appears in the microfilm or microfiche editions.

Computations were carried out on an IBM 370/168 computer at The Pennsylvania State University. Programs used were SFLS5A (for structure factor calculations and least-squares refinement), FORDAP (for Fourier summations), and ORTEP (for stereoscopic drawings).

Results and Discussion

General Structure of the Molecule. The x-ray determination of $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$ indicates that the molecule consists of a platinum metal atom coordinated to two antipodal nitrogen atoms of the phosphazene ring and to two chloride ligands. The structure of this molecule is shown in structure I and in a stereoscopic view in Figure 1.
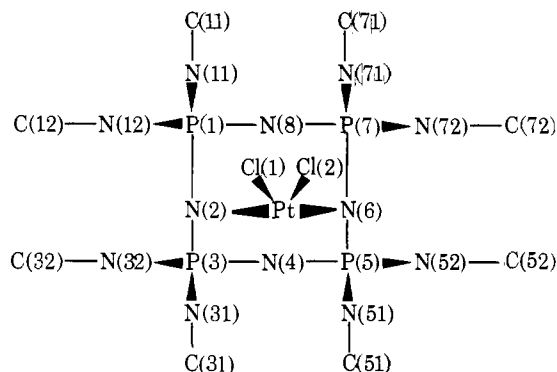
I

The platinum atom is coordinated through the nitrogen atoms of the phosphazene ring rather than to the exocyclic nitrogen atoms of the methylamino group. This observation is consistent with the general belief that, in aminophosphazenes, the endocyclic nitrogen atoms are the most basic sites[18-20] and the site of coordination to metal atoms in other complexes.[5-11] The coordinated nitrogen atoms are located at opposite sides of the ring at positions N(2) and N(6).

Table II. Idealized Hydrogen Atom Positions

Atom	10^3x	10^3y	10^3z	B, Å²
H(111)	359	183	154	4.30
H(112)	458	100	9	5.22
H(113)	403	59	104	5.22
H(114)	305	74	13	5.22
H(121)	323	302	−56	4.38
H(122)	86	304	−108	4.54
H(123)	150	235	−178	4.54
H(124)	205	332	−172	4.54
H(311)	183	428	245	4.67
H(312)	235	583	162	4.62
H(313)	83	560	173	4.62
H(314)	180	563	265	4.62
H(321)	140	499	−16	4.33
H(322)	347	525	22	4.43
H(323)	347	468	−74	4.43
H(324)	382	423	27	4.43
H(511)	−68	357	293	3.87
H(512)	−265	469	255	4.88
H(513)	−149	473	335	4.88
H(514)	−122	502	228	4.88
H(521)	−244	391	41	4.01
H(522)	−393	378	156	5.07
H(523)	−355	276	169	5.07
H(524)	−427	310	72	5.07
H(711)	25	104	224	4.42
H(712)	−49	−19	87	4.63
H(713)	15	−37	191	4.63
H(714)	102	5	111	4.63
H(721)	−124	129	−38	3.93
H(722)	−325	173	68	4.98
H(723)	−316	97	−9	4.98
H(724)	−262	81	98	4.98

Coordination about Platinum. The platinum atom is coordinated to two cis chlorine atoms and two nitrogen atoms of the phosphazene ring, as shown in Figure 2. The bond angles about the platinum atom indicate that the complex is only slightly distorted from square planar. Thus, the coordination about platinum is similar to that in cis-$Pt^{II}(NH_3)_2Cl_2$.

The bond lengths are also consistent with those found in other platinum complexes. The mean Pt–Cl bond length of 2.302 Å (Table IV) is similar to those found in cis-Pt^{II}-$(NH_3)_2Cl_2$ (2.33 Å)[21] and in $Pt^{II}(NH_2CH_2CH_2NH_2)Cl_2$ (2.29 Å).[22] The mean Pt–N bond length of 2.053 Å is similar to that found in amine complexes of platinum such as: cis-$Pt^{II}(NH_3)_2Cl_2$ (2.01 Å)[21] and $Pt^{II}(NH_2CH_2CH_2NH_2)Cl_2$ (2.08 Å).[22]

Structure of the Cyclotetraphosphazene Unit. The bond angles and bond distances for the octa(methylamino)cyclotetraphosphazene component of the molecule are given in Table V. The atom designations for the molecule correspond to those shown in structure I. The coordination to the platinum metal atom by the ring nitrogen atoms undoubtedly affects the structure of the phosphazene ring. No x-ray structure is

Table IV. Bond Distances and Angles in the Platinum Unit

Atoms	Distance, Å	Atoms	Angle, deg
Pt-Cl(1)	2.304 (5)	Cl(1)-Pt-Cl(2)	92.9 (2)
Pt-Cl(2)	2.300 (6)	N(2)-Pt-N(6)	87.0 (6)
Pt-N(2)	2.026 (16)	N(2)-Pt-Cl(1)	88.6 (4)
Pt-N(6)	2.081 (15)	N(6)-Pt-Cl(2)	91.4 (5)
		N(2)-Pt-Cl(2)	178.0 (5)
		N(6)-Pt-Cl(1)	175.5 (4)
		Pt-N(2)-P(1)	108.4 (9)
		Pt-N(2)-P(3)	109.4 (8)
		Pt-N(6)-P(5)	109.4 (9)
		Pt-N(6)-P(7)	105.6 (8)

Table V. Bond Distances and Angles in the Cyclophosphazene Unit

Atoms	Distance, Å	Atoms	Angle, deg
Ring Distances		**Ring Angles**	
P(1)-N(2)	1.64 (2)	N(8)-P(1)-N(2)	114.5 (9)
P(1)-N(8)	1.57 (2)	P(1)-N(2)-P(3)	128.6 (10)
P(3)-N(2)	1.61 (2)	N(2)-P(3)-N(4)	115.0 (9)
P(3)-N(4)	1.61 (2)	P(3)-N(4)-P(5)	122.2 (11)
P(5)-N(4)	1.59 (2)	N(4)-P(5)-N(6)	115.8 (9)
P(5)-N(6)	1.63 (2)	P(5)-N(6)-P(7)	128.8 (10)
P(7)-N(6)	1.64 (2)	N(6)-P(7)-N(8)	115.5 (9)
P(7)-N(8)	1.59 (2)	P(7)-N(8)-P(1)	127.8 (12)
Exocyclic Distances		**Exocyclic Angles**	
P(1)-N(11)	1.66 (2)	N(11)-P(1)-N(12)	102.8 (9)
P(1)-N(12)	1.61 (2)	N(31-P(3)-N(32)	107.6 (10)
P(3)-N(31)	1.63 (2)	N(51)-P(5)-N(52)	105.5 (9)
P(3)-N(32)	1.62 (2)	N(71)-P(7)-N(72)	105.5 (10)
P(5)-N(51)	1.63 (2)	N(11)-P(1)-N(2)	102.2 (9)
P(5)-N(52)	162 (2)	N(11)-P(11)-N(8)	114.8 (10)
P(7)-N(71)	1.62 (2)	N(12)-P(1)-N(2)	116.2 (10)
P(7)-N(72)	1.63 (2)	N(12)-P(1)-N(8)	105.9 (9)
N(11)-C(11)	1.47 (4)	N(31)-P(3)-N(2)	102.2 (10)
N(12)-C(12)	1.44 (3)	N(31)-P(3)-N(4)	114.0 (10)
N(31)-C(31)	1.43 (4)	N(32)-P(3)-N(2)	111.9 (9)
N(32)-C(32)	1.43 (3)	N(32)-P(3)-N(4)	106.0 (9)
N(51)-C(51)	1.41 (4)	N(51)-P(5)-N(4)	114.6 (10)
N(52)-C(52)	1.47 (3)	N(51)-P(5)-N(6)	102.7 (9)
N(71)-C(71)	1.46 (4)	N(52)-P(5)-N(4)	104.2 (9)
N(72)-C(72)	1.43 (3)	N(52)-P(5)-N(6)	113.9 (9)
		N(71)-P(7)-N(6)	101.2 (9)
		N(71)-P(7)-N(8)	116.5 (10)
		N(72)-P(7)-N(6)	113.1 (9)
		N(72)-P(7)-N(8)	105.0 (9)
		P(1)-N(11)-C(11)	119 (1)
		P(1)-N(12)-C(12)	124 (1)
		P(3)-N(31)-C(31)	121 (2)
		P(3)-N(32)-C(32)	122 (1)
		P(5)-N(51)-C(51)	125 (2)
		P(5)-N(52)-C(52)	124 (2)
		P(7)-N(71)-C(71)	120 (2)
		P(7)-N(72)-C(72)	126 (1)

available for the uncoordinated [NP(NHCH₃)₂]₄, but comparisons with other cyclophosphazene structures are instructive.[23]

The phosphazene ring is puckered into a saddle conformation. Atoms N(2) and N(6) are positioned above a plane defined by the four phosphorus atoms, while atoms N(4) and N(8) lie below this plane. This saddle conformation has been observed for only two other cyclotetraphosphazenes.[24,25] The ring conformation in the compound reported here undoubtedly reflects the constraints imposed by the metal complex formation.

Complex formation with platinum also affects the bond lengths and bond angles of the cyclophosphazene ligand. A number of previous structural studies have shown that protonation[19,20,26] or coordination of a metal atom[5-11] to the nitrogen of a phosphazene ring increases the length of the P–N bonds flanking that nitrogen atom. This lengthening has been attributed[5,6,10,19,20] to a decrease in the amount of π character in the skeletal bonds. Consistent with this postulate, the mean P–N bond length of 1.63 Å for the coordinated nitrogen atoms in $PtCl_2[N_4P_4(NHCH_3)_8]$ is lengthened relative to the other P–N endocyclic distances (mean value = 1.59 Å). All the ring angles at nitrogen are narrower than those in the cyclic tetrameric phosphazenes studied to date. The P–N–P ring bond angles are marginally wider (128.6°) at the coordinated sites than at the uncoordinated positions (122.2, 127°). This contrasts with the situation found in $[N_4P_4(CH_3)_6(C_2H_5)_2H_2]^{2+}$ and $W(CO)_4[N_4P_4(NMe_2)_8]$, where the bond angles at the coordinated nitrogen atoms are narrower (by 13 and 15°, respectively) than at the uncoordinated sites.[5,26]

The exocyclic P–N bond lengths (mean = 1.63 Å) are comparable to the 1.66 and 1.68 Å values found in other aminophosphazene structures.[5,25] The exocyclic N–P–N angles have a mean value of 105.4 Å compared to 103.8° and 104° in other aminophosphazene molecules.[5,25]

Nature of the Bonding in $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$. The study of metal complexes of phosphazenes provides a means for understanding the bonding within the phosphazene ring and the mode of coordination by the cyclophosphazene to the metal atom. Previous studies with metal carbonyl complexes, such as $Mo(CO)_3[N_4P_4(CH_3)_8]$ and $W(CO)_3[N_4P_4(CH_3)_8]$,[12] suggested that the metal may be complexed with the π system of the phosphazene. The x-ray structure of the molybdenum adduct showed the metal atom to be within bonding distance of five of the ring atoms, but the structure was considered too approximate to unequivocally confirm that the compound was a π complex.[14] In other phosphazene complexes with metal atoms, such as $[N_6P_6(N(CH_3)_2)_{12}CuCl]^+$, $[N_6P_6(N(CH_3)_2)_{12}CoCl]^+$, $N_4P_4(CH_3)_8HCuCl_3$, and $W(CO)_4[N_4P_4(N(CH_3)_2)_8]$, the coordination has been explained by utilization of the lone pair of electrons in an sp² orbital of the endocyclic nitrogen atom of the cyclophosphazene.[5-11] Such coordination explains why the P–N bond lengths to the coordinated nitrogen are increased relative to

those of the uncoordinated nitrogen atoms, since the lone pair electrons no longer participate in the π system of the phosphazene ring.

In a π complex, the metal atom is expected to be situated over a segment of the ring, approximately perpendicular to the plane defined by the P–N–P unit which makes up the nearby π system, and approximately equidistant from both the phosphorus and nitrogen atoms. If the metal is bonded through the nitrogen sp² lone pair, the metal atom should be coplanar with the plane formed by the P–N–P unit. However, in $Pt^{II}Cl_2(N_4P_4(NHCH_3)_8]$, an interatomic vector from the coordinated nitrogen atom to the platinum atom makes an angle of 41–44° with respect to the plane defined by the P–N–P unit. Thus, the bonding of metal to ligand does not fall clearly into either the pure π or pure lone pair binding category. An argument can be made for localization of four electrons into two sp³ orbitals on the nitrogen atom. One pair would form the platinum–nitrogen bond, and the other electrons would constitute a lone pair capable of an interaction with the phosphazene π system. Although this scheme rationalizes the nonplanarity of platinum with respect to the P–N–P unit and the lengthening of the P–N bonds, it does not explain why the P–N–P bond angle is 128.7° rather than close to a tetrahedral angle expected for sp³ hybridization. Thus, the evidence suggests the possibility that partial stabilization of the complex is achieved by π-bond formation.

Relationship of the Structure of $PtCl_2[N_4P_4(NHCH_3)_8]$ to

Other Phosphazene–Platinum Derivatives. Although the structures of high polymeric $(PtCl_2)_x[NP(NHCH_3)_2]_n$ and $PtCl_2[N_4P_4(CH_3)_8]$ have not been obtained by x-ray diffraction techniques, their structure can tentatively be deduced by analogy. Thus, $PtCl_2[N_4P_4(CH_3)_8]$ is expected to contain a square planar cis platinum unit bonded to the skeletal ring nitrogen atoms. A similar situation is envisaged for $(PtCl_2)_x[NP(NHCH_3)_2]_n$. However, in this case the average number of phosphazene repeat units in the polymeric loop between the coordinated nitrogen atoms is at present unknown. This cis configuration at platinum appears to be retained in view of spectral evidence and the anticancer activity of the complex.[2]

Supplementary Material Available: Table III, a listing of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This paper is part 31 in a series on phosphorus–nitrogen compounds.
(2) Part 30 in this series by H. R. Allcock, R. W. Allen, and J. P. O'Brien, *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) B. Rosenberg, L. Van Camp, J. E. Trosko, and V. H. Mansour, *Nature (London)*, **222**, 385 (1969).
(4) A. J. Thomson, R. J. P. Williams, and S. Reslova, *Struct. Bonding (Berlin)*,
11, 1 (1972).
(5) H. P. Calhoun, N. C. Paddock, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2708 (1973).
(6) W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 1482 (1971).
(7) W. C. Marsh, N. L. Paddock, C. J. Steward, and J. Trotter, *Chem. Commun.*, 1190 (1970).
(8) W. Harrison, N. L. Paddock, J. Trotter, and J. N. Wingfield, *J. Chem. Soc., Chem. Commun.*, 23 (1972).
(9) W. Harrison and J. Trotter. *J. Chem. Soc., Dalton Trans.*, 61 (1973).
(10) H. P. Calhoun, N. L. Paddock, and J. N. Wingfield, *Can. J. Chem.*, **53**, 1765 (1975).
11) J. Trotter and S. H. Whitlow, *J. Chem. Soc. A*, 455 (1970).
(12) N. L. Paddock, T. N. Rangunathan, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 1578 (1972).
(13) N. K. Hota and R. O. Harris, *J. Chem. Soc., Chem. Commun.*, 407 (1972).
(14) F. A. Cotton, G. A. Rusholme, and A. Shaver, *J. Coord. Chem.*, 99 (1973).
(15) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(16) K. Lonsdale, Ed., "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, pp 202–203.
(17) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(18) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 875 (1963).
(19) A. MacDonald and J. Trotter, *Can. J. Chem.*, **52**, 734 (1974).
(20) H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, **12**, 2963 (1973).
(21) G. H. W. Milburn and M. R. Trutter, *J. Chem. Soc. A*, 1609 (1966).
(22) J. Iball, M. MacDougall, and S. Scrimgeour, *Acta Crystallogr., Sect. B*, **31**, 1672 (1975).
(23) H. R. Allcock, "Phosphorus–Nitrogen Compounds", Academic Press, New York, N.Y., 1972, Appendix I; *Chem. Rev.*, **72**, 315 (1972).
(24) M. W. Dougill, *J. Chem. Soc.*, 5471 (1961).
(25) G. J. Bullen, *J. Chem. Soc.*, 3193 (1962).
(26) H. P. Calhoun, R. T. Oakley, N. L. Paddock, and J. Trotter, *Can. J. Chem.*, **53**, 2413 (1975).

Hydration and Dehydration of Phosphoric Acid Derivatives: Free Energies of Formation of the Pentacoordinate Intermediates for Phosphate Ester Hydrolysis and of Monomeric Metaphosphate

J. Peter Guthrie[1]

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada. Received August 24, 1976

Abstract: The heat of hydrolysis for pentaethoxyphosphorane is -17.75 ± 0.45 kcal mol^{-1} for the process: $P(OEt)_5(l) + H_2O(l) = PO(OEt)_3(aq) + 2EtOH(aq)$. From this may be derived the free energies of formation in aqueous solution of $P(OEt)_n(OH)_{5-n}$ (n, $\Delta G_f°$ (kcal/mol^{-1})): 5, -232 ± 3; 4, -249 ± 3; 3, -266 ± 3; 2, -281 ± 3; 1, -298 ± 3; 0, -314 ± 3). These permit the calculation of the free energy changes for the addition of water to phosphoric acid and its esters. Comparison with the results of earlier kinetic studies reveals surprisingly high barriers to breakdown of the pentacoordinate intermediates in phosphoryl transfer reactions. A kinetic argument leads to a value for the free energy of dehydration of orthophosphoric acid to monomeric metaphosphoric acid in aqueous solution of 32 ± 2 kcal mol^{-1}. These data permit comparison of the behavior of orthophosphate derivates toward addition and elimination. The intrinsic barrier for addition of hydroxide ion to phosphate esters is much greater than for the analogous addition to carbonyl compounds.

Despite their considerable interest to organic and biochemistry, the study of the mechanisms of phosphoryl group reactions has lagged behind that of acyl group reactions. In part this is due to the slowness of many phosphoryl transfer reactions; in part it is due to the greater mechanistic versatility of phosphoric acid derivatives relative to carboxylic acid derivatives.[2] Simple alkyl esters of phosphoric acid may undergo hydrolysis by nucleophilic attack at phosphorus, nucleophilic attack at carbon, or elimination of alcohol to give a transient metaphosphate intermediate.[2] By contrast simple esters of carboxylic acids ordinarily react by nucleophilic attack at the carbonyl[3] and only rarely by attack at the ester carbon[3] or by elimination to give a ketene intermediate.[4] For reactions of carboxylate esters by the usual mechanism, nucleophilic attack

at carbonyl carbon, the tetrahedral intermediate which is normally postulated, has well known and quite stable (in the absence of acid) alkyl derivatives in the ortho esters. By contrast the analogues of the intermediates for reaction by nucleophilic attack at phosphoryl phosphorus, the pentaalkoxyphosphoranes, have only recently been prepared, and are usually rather reactive.[5]

Recently it was shown that the free energy levels of the intermediates in acyl transfer reactions could be evaluated by determining the free energy level in aqueous solution of the ortho ester analogue of the intermediate and making use of the fact that ΔG for the reaction

$$C-OH + CH_3OH \rightleftharpoons C-OCH_3 + H_2O$$