Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

Crystal and Molecular Structures of Two (Cyclophosphazene)platinum Compounds: $[N_4P_4(CH_3)_8]Pt^{II}Cl_2{\cdot}CH_3CN$ and $[H_2N_4P_4(CH_3)_8]^{2+}PtCl_4^{2-}$

JOHN P. O'BRIEN, ROBERT W. ALLEN, and HARRY R. ALLCOCK*

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The antitumor agents *cis*-dichloro(octamethylcyclotetraphosphazene-*N,N''*)platinum(II)–acetonitrile (compound **1**) and the related salt, *N,N''*-dihydro(octamethylcyclotetraphosphazenium) tetrachloroplatinate (compound **2**), have been subjected to X-ray structure analysis. Crystals of **1** were orthorhombic, with the space group $P2_1mn$ and with $a = 10.328$ (6) Å, $b = 11.439$ (6) Å, $c = 9.050$ (3) Å, and $Z = 2$. The structure was refined by full-matrix least-squares methods to a final $R_1 = 0.048$. The eight-membered phosphazene ring in **1** is puckered into a saddle conformation and is coordinated to platinum through two antipodal nitrogen atoms. The ring–platinum binding appears to be by a composite of σ-bonding and π-type interactions. Crystals of compound **2** were monoclinic, with the space group $P2_1/c$ and with $a = 14.911$ (2) Å, $b = 12.177$ (2) Å, $c = 11.760$ (7) Å, $\beta = 94.94$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and was refined by full-matrix least-squares methods to $R_1 = 0.041$ and $R_2 = 0.052$. The eight-membered phosphazene ring in **2** is protonated at two antipodal nitrogen atoms and is puckered into a distorted chair conformation. The tetrachloroplatinate dianion forms a hydrogen-bonded bridge between parallel sets of phosphazene rings via the protonated nitrogen atoms. The coordination of ring nitrogen atoms to platinum or hydrogen in **1** or **2** causes a lengthening of the P–N bonds that flank the coordination site.

The syntheses of the first platinum complexes of cyclic and high polymeric phosphazenes were described in an earlier paper.[1] These compounds are of general interest because of their anticancer activity and because they constitute model systems for a new class of polymer-bound transition-metal complexes. In earlier papers[1,2] we discussed the synthesis and molecular structure of the complex $[N_4P_4(NHCH_3)_8]Pt^{II}Cl_2$ formed from octakis(methylamino)cyclotetraphosphazene, $[NP(NHCH_3)_2]_4$, and showed that the coordination occurs between platinum and the *ring* nitrogen atoms rather than those of the methylamino substituent groups. This complex also exhibited an unusual ring geometry, and it was of interest to determine if these characteristics were typical of other related species.

In this paper we describe the mode of coordination and ring geometry of two related complexes based on the phosphazene cyclic tetramer $[NP(CH_3)_2]_4$. The two compounds are $[N_4P_4(CH_3)_8]Pt^{II}Cl_2{\cdot}CH_3CN$ (**1**), prepared by the reaction of $[NP(CH_3)_2]_4$ with platinum dichloride in benzene solution,[1] and a salt, $[H_2N_4P_4(CH_3)_8]^{2+}PtCl_4^{2-}$ (**2**), prepared by the reaction of $[NP(CH_2)_2]_4$ with potassium tetrachloroplatinate, K_2PtCl_4, in aqueous hydrochloric acid.

These compounds were studied for the following reasons. By contrast with complexes formed from $[NP(NHCH_3)_2]_4$, the compound $[NP(CH_3)_2]_4$ does not possess potential metal- or proton-binding sites in the substituent group structure. Moreover, $[NP(CH_3)_2]_4$ is a model compound for a new class of high polymers currently being synthesized. Comparisons between a diprotonated form of $[NP(CH_3)_2]_4$ and a direct metal-coordinated analogue were expected to provide information about the response of the cyclophosphazene skeleton to different coordinated species in the absence and presence of chelation effects.

Experimental Section

Synthesis and Isolation of Crystals. Compounds **1** and **2** were prepared by the methods described previously.[1] After purification of **1** from the crude reaction mixture with the use of column chromatography, crystallographically suitable crystals were obtained by slow evaporation of solvent from a solution in acetonitrile during a period of several days. The rapid deterioration of the crystals after drying in air suggested the presence of included solvent molecules. Subsequent density and unit-cell measurements indicated that the molecular formula was $N_4P_4(CH_3)_8PtCl_2{\cdot}CH_3CN$, a solvent-included form. Single crystals of **2** suitable for X-ray examination were grown from a dilute solution in 0.1 N hydrochloric acid by slow recrystallization over a period of 24 h.

Collection and Reduction of X-ray Data for Compound 1. A transparent, yellow, rectangular crystal of **1** (0.40 × 0.50 × 0.30 mm) was mounted on a glass fiber with epoxy cement. The fiber and crystal were then sealed inside a glass capillary tube and this assembly was mounted on a eucentric goniometer head for space group determination by photographic methods. Precession photographs using nickel-filtered X radiation ($\lambda(K\alpha)$ 1.542 Å) indicated that the crystal was orthorhombic (Laue symmetry *mm*), with the *k* direction along the spindle axis. Systematic absences were observed for $hk0$, $h + k \neq 2n$, for $0k0$, $k \neq 2n$, and for $h00$, $h \neq 2n$. These absences led to four possible choices for the space group: $Pmmn$, $P2_1mn$, $Pm2_1n$, and $P2_12_12$.

A second, smaller crystal of size 0.10 × 0.12 × 0.16 mm was mounted as before and was transferred to an Enraf-Nonius CAD-4 diffractometer controlled by a PDP8/a computer. Twenty-two reflections were located and centered by using the Enraf-Nonius program SEARCH with the use of molybdenum X radiation from a graphite monochromator. Unit cell dimensions, as calculated from a least-squares refinement of the 2θ values for these 22 well-centered reflections, were as follows: $a = 10.328$ (6), $b = 11.439$ (6), $c = 9.050$ (3) Å; $V = 1069.1$ (7) Å^3; $d_m = 1.890$ g cm^{-3} (by flotation in bromoform–carbon tetrachloride mixtures); $Z = 2$, $d_c = 1.886$ g cm^{-3}; mol wt 607.25. The linear absorption coefficient was calculated to be 74.482 cm^{-1} for molybdenum radiation.

Intensity data were collected at 20 °C by using a θ–2θ scan mode for all reflections for which $0.5 \leq 2\theta \leq 60°$. Scan widths were calculated from $SW = A + B \tan\theta$ where A is estimated from the mosaic character of the crystal, and B accounts for the increase in the width of the peak due to the $K\alpha_1$ and $K\alpha_2$ splitting. The values chosen for A and B were 0.45 and 0.35, respectively. The scan angle was increased by 25% on each side for taking background intensity measurements. The net intensities (I) were found by the formula $I = CTS - 2(BGR + BGL)$ where CTS is the total number of counts and BGR and BGL are the right and left background counts, respectively. Reflection data were automatically rejected by the computer if, for a rapid prescan, the ratio $\sigma(I)/I < 3$. Three standard reflections were measured every 3 h, and the intensities did not exhibit any systematic trend throughout the data collection. The data were then corrected for Lorentz and polarization effects. Of 2338 intensities measured, 1991 had $I > 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics. Only those reflections for which $I > 3\sigma(I)$ and $(\sin\theta)/\lambda \leq 0.66$ (1263) were used in the subsequent refinement.

Collection and Reduction of X-ray Data for Compound 2. A clear, red crystal of **2** with dimensions 0.24 × 0.16 × 0.08 mm was mounted on a glass fiber with epoxy cement. The crystal and fiber were then mounted on a eucentric goniometer head, and precession photographs were taken by using nickel-filtered copper X radiation ($K\alpha = 1.542$ Å). Zero-level photographs indicated that the crystal was monoclinic (Laue symmetry $2/m$) with the *a* direction along the spindle axis. Systematic absences were observed for $h0l$ with $l \neq 2n$ and for $0k0$ with $k \neq 2n$. These extinctions led to a choice of $P2_1/c$ for the space

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[N_4P_4(CH_3)_8]PtCl_2 \cdot CH_3CN$ (**1**)

atom	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Pt	0.5449 (1)	0.5000 (0)	0.81635 (9)	3.3 (5)	5.5 (5)	5.4 (7)	0.0 (0)	1.5 (3)	0.0 (0)
Cl(1)	0.6022 (7)	0.5000 (0)	0.0655 (8)	6.7 (6)	14.0 (9)	7.2 (7)	0.0 (0)	−6.0 (1)	0.0 (0)
Cl(2)	0.7703 (7)	0.5000 (0)	0.7559 (9)	4.5 (6)	14.2 (9)	10.9 (9)	0.0 (0)	0.0 (1)	0.0 (0)
P(1)	0.4444 (4)	0.3686 (4)	0.5545 (5)	5.0 (4)	5.4 (3)	5.9 (5)	−0.3 (7)	2.2 (8)	−1.7 (8)
P(2)	0.2982 (4)	0.3693 (4)	0.8220 (5)	5.1 (4)	5.9 (3)	5.2 (4)	−1.9 (7)	0.1 (8)	−0.4 (8)
N(1)	0.505 (2)	0.500 (0)	0.597 (2)	1.0 (1)	16.0 (3)	5.0 (2)	0.0 (0)	−1.0 (3)	0.0 (0)
N(2)	0.330 (2)	0.325 (2)	0.659 (2)	7.0 (1)	9.0 (1)	4.0 (1)	−5.0 (3)	4.0 (3)	−3.0 (3)
N(3)	0.354 (2)	0.500 (0)	0.864 (2)	2.0 (1)	5.0 (1)	8.0 (2)	0.0 (0)	3.0 (3)	0.0 (0)
N(4)	0.562 (9)	0.000 (0)	0.789 (4)	42.0 (8)	9.0 (2)	18.0 (4)	0.0 (0)	−29.0 (13)	0.0 (0)
C(11)	0.581 (2)	0.273 (2)	0.565 (2)	7.0 (2)	8.0 (2)	15.0 (3)	6.0 (3)	5.0 (4)	6.0 (4)
C(12)	0.395 (2)	0.360 (2)	0.367 (2)	9.0 (2)	9.0 (2)	7.0 (2)	−5.0 (4)	2.0 (4)	−1.0 (4)
C(21)	0.130 (2)	0.354 (3)	0.854 (3)	8.0 (2)	17.0 (3)	16.0 (3)	−9.0 (4)	13.0 (4)	2.0 (6)
C(22)	0.367 (3)	0.272 (2)	0.956 (2)	17.0 (3)	6.0 (2)	9.0 (2)	−2.0 (4)	−9.0 (5)	2.0 (4)
C(3)	0.477 (5)	0.000 (0)	0.724 (4)	22.0 (6)	7.0 (3)	9.0 (4)	0.0 (0)	1.0 (9)	0.0 (0)
C(4)	0.347 (4)	0.000 (0)	0.656 (5)	10.0 (4)	17.0 (5)	18.0 (6)	0.0 (0)	4.0 (9)	0.0 (0)

group. A second, smaller crystal, with dimensions 0.12 × 0.08 × 0.12 mm and with rectangular faces, was mounted as before and was transferred to the diffractometer. Molybdenum X radiation reflected from a graphite monochromator was again used. Twenty-five reflections were located and centered by using the program SEARCH. The unit cell dimensions, as calculated for least-squares refinement of the 2θ values for 25 well-centered reflections, were as follows: $a = 14.911$ (2), $b = 12.177$ (2), $c = 11.760$ (7) Å; $\beta = 94.94$ (2)°; $V = 2127.3$ Å^3; $d_m = 2.05$ g cm^{-3} (by flotation in bromoform–carbon tetrachloride mixtures); $Z = 4$, $d_c = 2.00$ g cm^{-3}; mol wt 639.12. The linear absorption coefficient was calculated to be 77.30 cm^{-1} for molybdenum radiation.

Intensity data were collected at 20 °C by using a θ–2θ scan mode for all reflections for which $3 < 2\theta < 60°$. Scan widths were calculated as described before. The background intensity measurements, net intensities (I), rejection criteria, and standard reflection techniques were as described for **1**. The data were corrected for Lorentz and polarization effects. Of the 2758 intensities measured, 1857 had $I > 3\sigma(I)$ where $\sigma(I)$ was based on counting statistics. Only those reflections for which $I > 3\sigma(I)$ and $(\sin\theta)/\lambda \leq 0.66$ (1805) were used in the subsequent refinement.

Solution and Refinement (General). The atomic scattering factors as tabulated by Cromer and Waber[3] were used for all atoms, and the anomalous dispersion factors $\Delta f'$ and $\Delta f''$ were those of Cromer.[4] The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F_o)^2$. The residuals R_1 and R_2 are expressed by $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Computations were carried out on a PDP 11/34 computer by using the Enraf-Nonius structure determination package and on an IBM 370/168 computer at The Pennsylvania State University. Additional programs used were FIXUP (for generating idealized hydrogen atom positions) and ORTEP (for perspective and stereoscopic drawings).

Solution and Refinement for Compound 1. A three-dimensional Patterson map revealed the position of the platinum atom. Attempts to refine with platinum in the centric space group *Pmmn* indicated a lower symmetry space group, and attempts were then made to refine the structure in each of the three acentric space groups $P2_1mn$, $Pm2_1n$ and $P2_12_12$. After positioning of the platinum atom in each space group as required by symmetry, subsequent difference Fourier maps revealed that space group $P2_1mn$ yielded a model which was acceptable chemically. Two cycles of least-squares refinement based on platinum alone gave $R_1 = 0.255$. A second difference Fourier synthesis gave the location of the phosphorus and chlorine atoms. Three additional cycles of least-squares refinement based on these five atoms gave $R_1 = 0.136$. At this point, another difference map was generated which clearly revealed the positions of the nitrogen atoms in the phosphazene ring. Refinement through three more cycles gave $R_1 = 0.112$. A difference Fourier map was then used to locate the carbon atoms attached to phosphorus. Refinement through three more cycles lowered R_1 to 0.097. Another difference map was generated, and the carbon and nitrogen atoms of the acetonitrile molecule were located. Three additional cycles of least-squares refinement on these 15 atoms lowered R_1 to 0.089. At this point, with all nonhydrogen atoms positioned, the thermal parameters were changed to anisotropic, and refinement through six additional cycles of least squares gave $R_1 = 0.051$. A final difference Fourier map was then generated to locate the hydrogen atoms. One hydrogen atom was selected for each carbon atom bound to phosphorus, and an idealized model, with a C–H distance of 1.00 Å and tetrahedral angles at carbon, was used to generate the positions of the other two hydrogen atoms for each methyl group. The isotropic thermal parameters for all hydrogen atoms were fixed at 4.0 Å^2, and refinement through four cycles of least squares followed by repositioning gave a final $R_1 = 0.048$ and $R_2 = 0.062$. The relatively high thermal parameters on the solvent molecule atoms indicated that the acetonitrile molecule is rather loosely held, and attempts to locate the methyl hydrogen atoms on this molecule were not successful. No absorption correction was applied to the data.

Table II. Idealized Hydrogen Atom Positions for $[N_4P_4(CH_3)_8]PtCl_2 \cdot CH_3CN$ (**1**)[a]

atom	x	y	z
H(111)	0.551	0.192	0.593
H(112)	0.624	0.269	0.466
H(113)	0.642	0.302	0.641
H(121)	0.318	0.411	0.351
H(122)	0.467	0.386	0.302
H(123)	0.371	0.277	0.342
H(211)	0.081	0.407	0.787
H(212)	0.103	0.271	0.833
H(213)	0.110	0.373	0.959
H(221)	0.460	0.256	0.930
H(222)	0.361	0.307	0.056
H(223)	0.318	0.196	0.954

[a] All B values are 4.00 A^2.

Table IV. Bond Distances (Å) and Angles (deg) in the Platinum Unit of **1** and the Acetonitrile Molecule

Platinum Unit			
Pt–Cl(1)	2.331 (4)	Cl(1)–Pt–Cl(2)	88.5 (2)
Pt–Cl(2)	2.391 (4)	N(1)–Pt–N(3)	90.5 (5)
Pt–N(1)	2.026 (12)	N(1)–Pt–Cl(2)	88.6 (4)
Pt–N(3)	2.023 (10)	N(3)–Pt–Cl(1)	92.4 (4)
		N(1)–Pt–Cl(1)	177.1 (4)
		N(3)–Pt–Cl(2)	179.1 (4)
		Pt–N(1)–P(1)	107.6 (4)
		Pt–N(3)–P(2)	106.9 (4)
Acetonitrile Molecule			
C(3)–C(4)	1.475 (40)	C(4)–C(3)–N(4)	171.2 (34)
C(3)–N(4)	1.058 (60)		

The refined values of the atomic positional and anisotropic thermal parameters are given in Table I. The idealized hydrogen atom positions and isotropic thermal parameters appear in Table II. Table III, a table of the observed and calculated structure factor amplitudes of the 1263 nonequivalent observed reflections, is given as supplementary material. Bond distances and angles for **1** are shown in Tables IV and V.

Solution and Refinement for Compound 2. A three-dimensional Patterson map revealed the position of the platinum atom at the special position 0, 0, 0. Three cycles of least-squares refinement with two platinum atoms on the special positions at half-occupancy gave $R_1 = 0.354$. A difference Fourier synthesis gave the location of the chlorine and phosphorus atoms. Four cycles of least-squares refinement

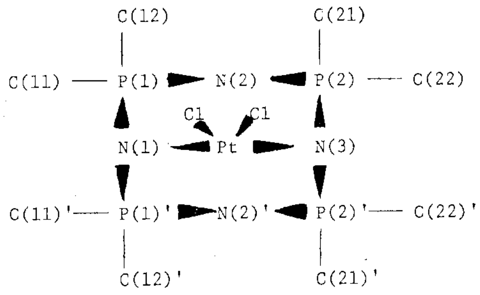
Table V. Bond Distances (Å) and Angles (deg) in the Cyclophosphazene Unit of 1

Ring Distances			
P(1)-N(1)	1.672 (6)	P(2)-N(2)	1.591 (8)
P(1)-N(2)	1.596 (8)	P(2)-N(3)	1.645 (6)
Ring Angles			
N(1)-P(1)-N(2)	114.9 (6)	P(1)-N(2)-P(2)	127.0 (6)
N(2)-P(2)-N(3)	115.6 (6)	P(2)-N(3)-P(2)′	130.7 (8)
P(1)-N(1)-P(1)′	128.0 (7)		
Exocyclic Distances			
P(1)-C(11)	1.787 (11)	P(2)-C(21)	1.771 (13)
P(1)-C(12)	1.772 (11)	P(2)-C(22)	1.795 (12)
Exocyclic Angles			
C(11)-P(1)-C(12)	104.0 (6)	C(21)-P(2)-C(22)	102.6 (8)

gave $R_1 = 0.145$. A second difference Fourier map revealed the positions of the nitrogen atoms and seven of the eight carbon atoms. Refinement through three cycles of least squares for these 21 atoms gave an $R_1 = 0.083$. The final carbon atom was located by a third difference Fourier map, and the data were subjected to two additional cycles of least-squares refinement to give $R_1 = 0.073$. At this point, with all nonhydrogen atoms positioned, the thermal parameters were changed to anisotropic, and refinement through six additional cycles of least-squares gave $R_1 = 0.044$ and $R_2 = 0.057$. A final difference Fourier map was then generated to locate the hydrogen atoms. One hydrogen atom was selected for each carbon atom, and an idealized model, with a C–H distance of 1.00 Å and tetrahedral angles at carbon, was used to generate the positions of the other two hydrogen atoms for each methyl group. The isotropic thermal parameters for all hydrogen atoms were set at 4.0 Å^2, and refinement through three cycles of least squares followed by repositioning gave a final $R_1 = 0.041$ and $R_2 = 0.052$. The location of the hydrogen atoms connected to the nitrogen atoms could not be deduced from the final difference map, and, hence, they were not included in the structure. No absorption correction was applied. The refined values of the atomic positional and anisotropic thermal parameters are given in Table VI. The idealized hydrogen atom positions and isotropic thermal parameters appear in Table VII. Table VIII, a table of the observed and calculated structure factor amplitudes of the 1805 nonequivalent observed reflections, is given as supplementary material. Tables IX–XI list bond distances and angles and the unweighted least-squares planes for **2**.

Results and Discussion

Overall Structure of Compound 1. It is emphasized that, because of the lack of an absorption correction to the intensity data, the bond length and bond angle values do not have the precision needed to support or dispute bonding arguments based on minor fluctuations in bond distances or angles. Hence, only those gross structural features that are unambiguously obvious from the data will be discussed in this and the following sections. The bond lengths and bond angles for the cyclotetraphosphazene unit are given in Table V.



1

Figure 1. Atom designations and general coordination linkage in compound **1**.

Each platinum in **1** is coordinated to two transannular nitrogen atoms on the phosphazene ring and to two chlorine ligands. The structure of the molecule is shown along with the atom designations in Figure 1, and a stereoview is given in Figure 2. Figure 3 illustrates the coordination geometry about platinum. The carbon and nitrogen atoms of the acetonitrile molecule are all more than 3.6 Å away from the atoms of the metal–phosphazene complex. These data, together with the experimentally observed high thermal parameters for these atoms, indicate that the acetonitrile unit is rather loosely held and that it functions as a space filler in the lattice.

The phosphazene ring in **1** is puckered into a saddle conformation in which two skeletal nitrogen atoms (N(1) and N(3)) project upward toward the platinum atom from a plane defined by the four phosphorus atoms. The P–N bonds flanking the coordinated nitrogen atoms are definitely longer (mean value 1.66 Å) than those at the uncoordinated positions (mean value 1.59 Å).

The platinum atom in **1** is coordinated to two chlorine ligands and to the two nitrogen atoms from the phosphazene ring. The platinum has an essentially cis square-planar coordination geometry with the angles about platinum summing to 360.0 (5)° (Table IV). The mean Pt–Cl bond length of 2.36 Å is similar to that found in *cis*-$Pt^{II}(NH_3)_2Cl_2$ (2.33 Å)[5]

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for 2

atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.00339 (5)	0.00299 (5)	0.00540 (6)	0.0008 (2)	0.00076 (9)	−0.0009 (2)
Pt(2)	0.5000 (0)	0.5000 (0)	0.0000 (0)	0.00399 (5)	0.00371 (5)	0.00346 (5)	0.0005 (2)	0.00045 (8)	0.0007 (2)
Cl(1)	0.1511 (4)	−0.0297 (5)	0.0475 (6)	0.0036 (3)	0.0070 (5)	0.0133 (6)	0.0017 (6)	−0.0003 (7)	0.0039 (8)
Cl(2)	0.0363 (4)	0.4114 (5)	0.3361 (4)	0.0064 (3)	0.0054 (4)	0.0067 (4)	−0.0011 (6)	0.0031 (6)	−0.0011 (7)
Cl(3)	0.4420 (5)	0.3362 (5)	0.0575 (5)	0.0083 (4)	0.0054 (4)	0.0104 (5)	−0.0029 (7)	0.0051 (8)	0.0042 (8)
Cl(4)	0.3664 (5)	0.9179 (5)	0.5373 (6)	0.0059 (4)	0.0089 (5)	0.0112 (5)	−0.0054 (7)	0.0055 (7)	−0.0052 (9)
P(1)	0.1078 (4)	0.1151 (4)	0.4820 (4)	0.0038 (3)	0.0045 (3)	0.0051 (4)	−0.0007 (6)	0.0015 (5)	0.0015 (6)
P(2)	0.0945 (4)	0.6211 (4)	0.0440 (4)	0.0038 (3)	0.0033 (3)	0.0049 (3)	−0.0010 (5)	−0.0003 (5)	−0.0014 (6)
P(3)	0.3842 (3)	0.5037 (6)	0.3926 (4)	0.0031 (2)	0.0044 (3)	0.0044 (3)	−0.0008 (8)	0.0001 (4)	0.0012 (9)
P(4)	0.4193 (3)	0.0048 (6)	0.1452 (4)	0.0033 (2)	0.0046 (3)	0.0041 (3)	−0.0010 (8)	0.0010 (4)	0.0008 (8)
N(1)	0.098 (1)	0.493 (1)	0.050 (1)	0.0059 (9)	0.0025 (9)	0.007 (1)	0.001 (2)	0.001 (2)	−0.003 (3)
N(2)	−0.009 (1)	0.668 (1)	0.061 (2)	0.0043 (10)	0.0050 (13)	0.009 (2)	−0.002 (2)	0.002 (2)	−0.000 (2)
N(3)	0.473 (1)	0.484 (2)	0.318 (1)	0.0036 (9)	0.0134 (20)	0.003 (1)	0.000 (3)	0.001 (2)	0.002 (3)
N(4)	0.401 (1)	0.038 (1)	0.014 (1)	0.0046 (10)	0.0036 (10)	0.004 (1)	0.000 (2)	0.001 (2)	−0.002 (2)
C(11)	0.174 (2)	0.286 (2)	0.060 (3)	0.012 (2)	0.004 (2)	0.023 (3)	0.007 (3)	−0.025 (4)	−0.008 (4)
C(12)	0.166 (2)	0.102 (2)	0.361 (2)	0.010 (2)	0.011 (2)	0.014 (2)	0.002 (4)	0.015 (3)	0.011 (4)
C(21)	0.159 (2)	0.681 (2)	0.161 (2)	0.005 (1)	0.005 (1)	0.007 (2)	0.001 (2)	−0.002 (2)	−0.004 (3)
C(22)	0.134 (2)	0.822 (2)	0.420 (2)	0.009 (2)	0.007 (2)	0.007 (2)	0.007 (3)	0.005 (3)	0.001 (3)
C(31)	0.299 (1)	0.425 (2)	0.317 (2)	0.003 (1)	0.006 (2)	0.006 (2)	−0.002 (2)	0.001 (2)	−0.002 (3)
C(32)	0.349 (2)	0.645 (2)	0.384 (2)	0.008 (2)	0.004 (2)	0.011 (2)	0.000 (3)	−0.004 (3)	0.004 (3)
C(41)	0.378 (2)	0.111 (2)	0.230 (2)	0.008 (2)	0.007 (2)	0.005 (2)	0.005 (3)	0.003 (3)	0.001 (3)
C(42)	0.365 (2)	0.882 (2)	0.186 (2)	0.008 (2)	0.009 (2)	0.007 (2)	−0.005 (3)	0.000 (3)	0.004 (3)

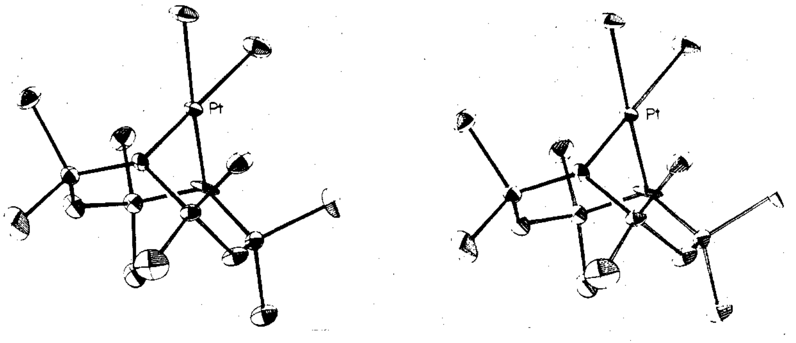


Figure 2. Stereoview of the $[N_4P_4(CH_3)_8]PtCl_2$ molecule (**1**).

Table VII. Idealized Hydrogen Atom Positions for **2**[a]

atom	*x*	*y*	*z*
H(111)	0.2369	0.2022	0.5669
H(112)	0.1570	0.2918	0.5362
H(113)	0.1540	0.2132	0.6483
H(121)	0.1909	0.1752	0.3407
H(122)	0.2153	0.0479	0.3744
H(123)	0.1229	0.0765	0.2951
H(211)	0.1441	0.6455	0.2337
H(212)	0.2246	0.6714	0.1519
H(213)	0.1451	0.7617	0.1645
H(221)	0.1337	0.7372	0.4210
H(222)	0.0927	0.8420	0.3471
H(223)	0.1962	0.8453	0.4051
H(311)	0.2406	0.4372	0.3507
H(312)	0.2932	0.4480	0.2351
H(313)	0.3153	0.3454	0.3224
H(321)	0.3942	0.6920	0.4295
H(322)	0.3452	0.6699	0.3019
H(323)	0.2889	0.6535	0.4138
H(411)	0.4228	0.1716	0.2397
H(412)	0.3200	0.1406	0.1913
H(413)	0.3658	0.0812	0.3065
H(421)	0.3748	−0.1266	0.2711
H(422)	0.2996	−0.1134	0.1626
H(423)	0.3919	−0.1824	0.1486

[a] All *B* values are 4.00 Å^2.

Table IX. Bond Distances (Å) and Angles (deg) in the Tetrachloroplatinate Unit of **2**

Pt(1)-Cl(1)	2.302 (3)	Pt(2)-Cl(3)	2.300 (2)
Pt(1)-Cl(2)	2.315 (2)	Pt(2)-Cl(4)	2.305 (3)
Cl(1)-Pt(1)-Cl(2)	88.9 (1)	Cl(3)-Pt(2)-Cl(4)	88.1 (1)

Table X. Bond Distances (Å) and Angles (deg) in the Cyclophosphazene Units of **2**

Ring Distances			
P(1)-N(1)	1.557 (8)	P(3)-N(3)	1.664 (7)
P(1)-N(2)	1.643 (8)	P(3)-N(4)	1.514 (6)
P(2)-N(1)	1.562 (9)	P(4)-N(3)	1.653 (7)
P(2)-N(2)	1.682 (8)	P(4)-N(4)	1.597 (6)
Ring Angles			
N(1)-P(1)-N(2)	111.8 (4)	N(3)-P(3)-N(4)	112.1 (4)
P(1)-N(1)-P(2)	145.3 (5)	P(3)-N(3)-P(4)	129.6 (4)
N(1)-P(2)-N(2)	111.0 (4)	N(3)-P(4)-N(4)	112.0 (4)
P(1)-N(2)-P(2)	129.5 (5)	P(3)-N(4)-P(4)	145.9 (5)
Exocyclic Distances			
P(1)-C(11)	1.807 (11)	P(3)-C(31)	1.766 (8)
P(1)-C(12)	1.741 (11)	P(3)-C(32)	1.806 (10)
P(2)-C(21)	1.770 (9)	P(4)-C(41)	1.782 (10)
P(2)-C(22)	1.829 (10)	P(4)-C(42)	1.781 (11)
Exocyclic Angles			
C(11)-P(1)-C(12)	104.7 (7)	C(31)-P(3)-C(32)	107.3 (5)
C(21)-P(2)-C(22)	106.9 (5)	C(41)-P(4)-C(42)	105.7 (5)

and in $Pt^{II}(NH_2CH_2CH_2NH_2)Cl_2$ (2.29 Å).[6] The mean Pt–N bond length of 2.03 Å compares well with corresponding

Table XI. Unweighted Least-Squares Planes[a] for **2**

constants	atoms[b]	dist from plane, Å
	Plane 1	
	P(1)	0.083
A = 0.1920	P(2)	0.222
B = −0.3026	N(1)	0.310
C = 0.9336	N(2)	0.094
D = 5.5692	P(1)′	−0.083
	P(2)′	−0.222
	N(1)′	−0.310
	N(2)′	−0.094
	Plane 2	
	P(3)	−0.249
A = −0.1104	P(4)	−0.053
B = 0.9936	N(3)	−0.126
C = 0.0245	N(4)	−0.310
D = 5.1368	P(3)′	0.249
	P(4)′	0.053
	N(3)′	0.126
	N(4)′	0.310

[a] The equation of the plane is of the form $AX + BY + CZ - D = 0$, where *A*, *B*, *C*, and *D* are constants and *X*, *Y*, and *Z* are orthogonalized coordinates. [b] The atoms P(1)′-P(4)′ and N(1)′-N(4)′ were generated by symmetry.

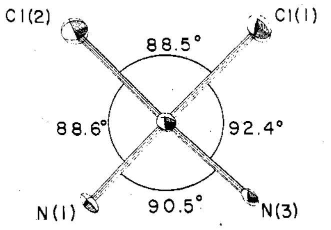


Figure 3. Coordination geometry about platinum in compound **1**.

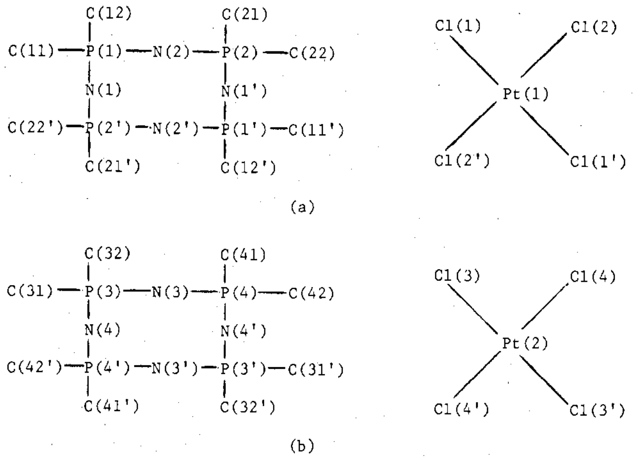


Figure 4. Diagram showing the atom designations for the two crystallographically distinct molecules of **2** in the unit cell: (a) the mean plane of the ring is nearly parallel with the 001 plane; (b) the mean plane of the ring is nearly parallel to the 010 plane.

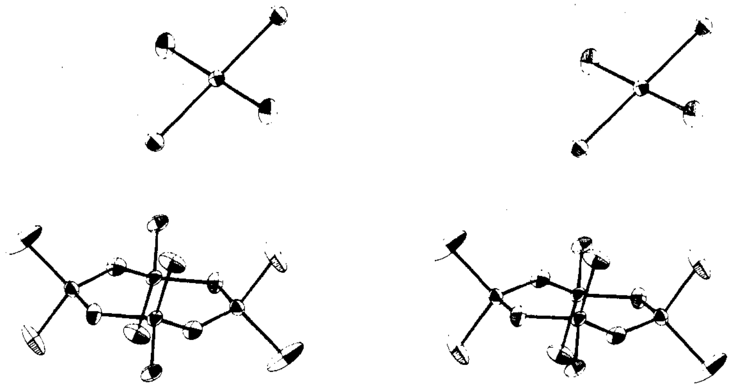


Figure 5. Stereoview of the $[H_2N_4P_4(CH_3)_8]^{2+}PtCl_4^{2-}$ complex. The molecule is the one defined by (a) in Figure 4.

average values of 2.01 and 2.08 Å found in *cis*-$Pt^{II}(NH_3)_2Cl_2$[5] and $Pt^{II}(NH_2CH_2CH_2NH_2)Cl_2$,[6] respectively.

General Structure of Compound 2. Atom designations and a stereoview of the structure are shown in Figures 4 and 5. Each molecular unit consists of two discrete ions, a diprotonated cyclotetraphosphazene cation, $[H_2N_4P_4(CH_3)_8]^{2+}$, and a square-planar tetrachloroplatinate dianion, $[PtCl_4]^{2-}$. The tetrameric phosphazene rings occupy a distorted chair conformation. The solid-state structure is stabilized by hydrogen-bonding interactions with chlorine atoms, and the tetrachloroplatinate units link adjacent pairs of parallel phosphazene units via hydrogen bonding to diametrically opposite chlorine atoms. The unit cell contains two crystallographically distinct phosphazene rings, one being nearly parallel to the 001 plane (P(1), P(2), N(1), N(2)) and the other (P(3), P(4), N(3), N(4)) lying approximately parallel to the 010 plane. Each ring has C_i symmetry, a feature which is not uncommon in cyclic phosphazenes because of the high symmetry available to symmetrically substituted rings.

The $PtCl_4^{2-}$ anions also have C_i symmetry because platinum is located at the special positions in the space group. The Pt–Cl bond distances (Table IX) are between 2.302 (3) and 2.315 (3) Å, values that are comparable with a mean value of 2.34 Å for $PtCl_4^{2-}$ in Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$.[7] The Cl–Pt–Cl angles for adjacent chlorine atoms do not deviate more than 1.9° from the perpendicular, thus indicating only a very slight distortion from a square-planar arrangement.

Again, the lack of an absorption correction to the data for **2** precludes a detailed theoretical analysis of the bond angle and bond length data for the phosphazene ring (Table X). However, the following structural features are unambiguous.

Each phosphazene ring appears to be protonated at two antipodal ring nitrogen atoms. The protons themselves were not detected, but their presence was inferred from the long P–N bond lengths (mean value 1.66 Å) flanking these sites. This behavior is in agreement with the results described in the literature for other protonated phosphazene rings: $[HN_3P_3(N(CH_3)_2)_6]_2CoCl_4$, 1.68 Å;[8] $N_4P_4(CH_3)_6(CH_3CH_2)_2{\cdot}2HCl$, 1.67 Å;[9] $[HN_4P_4(CH_3)_8]CuCl_3$, 1.67 Å;[10] $[H_2N_5P_5(CH_3)_{10}]CuCl_4{\cdot}H_2O$, 1.67 Å;[11] $[HN_3P_3(N(CH_3)_2)_6]_2Mo_6O_{19}$, 1.67 Å.[12] These longer bond lengths (compared to 1.60 Å in $[NP(CH_3)_2]_4$[13]) are probably a consequence of the localization of the lone-pair electrons on nitrogen following binding of the proton. Bond lengthening may result from the unavailability of these electrons for participation in the p_π–d_π bonding with the adjacent phosphorus atoms.[14] The P–N bonds in compound **2** that flank the unprotonated nitrogen atoms are considerably shorter (mean value 1.56 Å).

Coordination Characteristics in Compounds 1 and 2. For compound **1**, interatomic vectors drawn from platinum to the planes formed by P(1)–N(1)–P(1)′ or P(2)–N(3)–P(2)′ form angles of 46.4 and 46.0°, respectively, a geometry which does not place the nitrogen sp^2 orbitals into the correct orientation

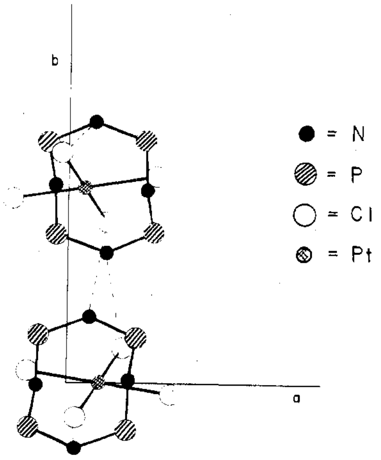


Figure 6. View of the contents of half the unit cell in the *c* direction. The dotted lines show probable N^+–H···Cl^- hydrogen-bonding interactions.

for σ-bond formation with platinum. In this respect, the structure of $[N_4P_4(CH_3)_8]PtCl_2$ differs from those of $[N_4P_4(N(CH_3)_2)_8]W(CO)_4$,[15] $[N_6P_6(N(CH_3)_2)_{12}CoCl^+]_2CoCl_6^{2-}{\cdot}2CHCl_3$,[16] $[N_6P_6(N(CH_3)_2)_{12}CuCl]^+CuCl_2^-$,[17] and $[HN_4P_4(CH_3)_8]^{2+}CuCl_3^{2-}$,[10] where the coordination geometry is in the plane of the nearby ring atoms and clearly involves the use of a radially oriented sp^2 lone-pair orbital on nitrogen. In this respect, the structure of **1** more closely resembles that of $[N_4P_4(NHCH_3)_8]PtCl_2$.[2] The unusual coordination geometry in these two compounds must be a consequence of the constraints imposed by the puckered, chelating cyclotetraphosphazene ring. Nevertheless, it implies that the coordination geometry has been modified by rehybridization toward an sp^3 arrangement at nitrogen. The Pt–N(1)–P(1) and Pt–N(3)–P(2) bond angles in $[N_4P_4(CH_3)_8]PtCl_2$ of 107.6 and 106.9° are close to tetrahedral. However, the P–N–P angles at the coordination sites are 128.0°, and this represents only a small contraction from the P–N–P angle of 132° in $[NP(CH_3)_2]_4$. Hence, it is assumed that the platinum atom in **1** is partly coordinated to the π electrons of the phosphazene ring.

An unexpected feature of the structure of compound **2** is the coordination of the anion to the cation by hydrogen bonding (Figure 6). The interatomic contact distance between N(2) and Cl(2) is 3.236 (8) Å. This is shorter than the sum of the van der Waals radii and is within the range for a N^+–H···Cl^- hydrogen bond. The P(1)–N(2)–Cl(2) and P(2)–N(2)–Cl(2) angles are 110° and 120°, respectively, which orients the proton (presumably bonded to the lone pair in an sp^2 orbital) into the correct geometry for participation in hydrogen bonding. All the other nonbonding contacts between the tetrachloroplatinate dianion and ring I (P(1), P(2), N(1), N(2)) are greater than 3.6 Å. The distance between Cl(3) and N(3) is 3.535 (8) Å. This is a longer distance than expected for hydrogen bonding, but the P(3)–N(3)–Cl(3) and P(4)–N(3)–Cl(3) angles of 119 and 111° suggest that the geometry is suitable for hydrogen-bond formation. The next closest intermolecular contacts for ring II are Cl(3)–N(4), 3.710 (7) Å, and Pt(2)–N(3), 3.796 (6) Å.

The three main conclusions derived from this work are as follows. (1) The formation of a transannular chelation bridge between the cyclophosphazene ring and platinum in compound **1** appears to be favored by the square-planar characteristics of platinum and the potential for π bonding between the phosphazene ring and the metal. (2) The cyclotetraphosphazene ring is exceedingly flexible and can accommodate a wide range of different puckered structures according to the demands of coordination or crystal-packing forces. (3) Coordination by a ring nitrogen atom to a proton or the metal causes a lengthening of the P–N bonds that flank the coordination site. This latter factor now appears to be a general characteristic of a wide range of cyclophosphazenes.[2,8–12,15,17–19]

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Registry No. **1**, 70368-91-1; **2**, 61735-18-0.

Supplementary Material Available: Tables III and VIII listing structure factor amplitudes for $[N_4P_4(CH_3)_8]Pt^{II}Cl_2{\cdot}CH_3CN$ and $[H_2N_4P_4(CH_3)_8]^{2+}PtCl_4^{2-}$ (22 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Molecular Science, University of Warwick, Coventry CV4 7AL, United Kingdom,
the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071,
and I.B.M. Research Laboratory, San Jose, California 91193

Synthesis and Structure of 3,7-Diphenyl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1*,*5*-S^{IV})tetrazadiarsocine and 3,7-Dimesityl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1*,*5*-S^{IV})tetrazadiarsocine, $As_2S_2N_4C_{12}H_{10}$ and $As_2S_2N_4C_{18}H_{22}$

N. W. ALCOCK,[1a] E. M. HOLT,*[1b] J. KUYPER,[1c] J. J. MAYERLE,[1c] and G. B. STREET[1c]

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The crystal data for the title compounds are as follows. $As_2S_2N_4C_{18}H_{22}$: triclinic, $P\bar{1}$, at −100 °C; $a = 7.390$ (2), $b = 8.089$ (2), $c = 18.235$ (5) Å; $\alpha = 86.63$ (2), $\beta = 106.16$ (2), $\gamma = 98.89$ (2)°; $V = 1034.1$ (5) Å^3; $Z = 2$; $D_c = 1.63$ g cm^{-3}; μ(Mo Kα) 36.15 cm^{-1}; $R = 6.3\%$ for 2764 reflections. $As_2S_2N_4C_{12}H_{10}$: orthorhombic, *Pnma*, at −100 °C; $a = 21.288$ (4), $b = 28.581$ (6), $c = 7.532$ (1) Å; $V = 4582.8$ (4) Å^3; $Z = 12$; $D_c = 1.84$ g cm^{-3}; μ(Mo Kα) 48.68 cm^{-1}; $R = 5.7\%$ for 2718 reflections. In each material, the $As_2S_2N_4$ group exists as a boat-shaped ring with arsenic atoms at prow and helm, joined by two –N–S–N chains. The four nitrogen atoms are coplanar. Each arsenic is also bonded to a phenyl or mesityl group. While the ring is conformationally similar to the S_4N_4 cage, cross-ring As–As or S–S interactions may be considered minimal. Attempts to prepare polymers analogous to $(SN)_x$, either by thermal splitting of the title compounds or by reaction of arylarsenic dichloride with sulfur diimides, have been unsuccessful.

Introduction

The solid-state polymerization of S_2N_2 by thermal splitting of S_4N_4 leads to the superconducting polymer $(SN)_x$.[2] Bromination of $(SN)_x$ has been shown to give rise to $SNBr_{0.4}$, an intercalation compound of $(SN)_x$.[3] This same compound can be prepared by the direct polymerization of solid S_4N_4 in the presence of bromine vapor. Similar polymers can be envisaged in which sulfurs are replaced by isoelectronic aryl arsenic groups.

In this paper, we report the preparation and single-crystal X-ray structures of two possible precursors to $(RAsNSN)_x$: 3,7-diphenyl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1*,*5*-S^{IV})tetrazadiarsocine and 3,7-dimesityl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1*,*5*-S^{IV})tetrazadiarsocine.

Experimental Section

General Methods. Phenylarsenic dichloride was obtained commercially and the mesitylarsenic dichloride was prepared by reaction of mesitylmagnesium bromide with $AsCl_3$ in ether. Vacuum distillation of the resulting mixed mesitylarsenic chloride and bromide followed by hydrolysis gave the corresponding dihydroxide, which was then treated with concentrated HCl to give mesitylarsenic dichloride, which was purified by vacuum distillation. ^1H NMR spectra (Table I) were

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