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The Crystal and Molecular Structure of trans-Diamminebis(*N*-methylimidazole)platinum(II) Chloride Dihydrate, trans-[Pt(NH₃)₂(N₂C₄H₆)₂]Cl₂·2H₂O¹

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The crystal structure of *trans*-diamminebis(*N*-methylimidazole)platinum(II) chloride dihydrate, *trans*-[Pt(NH₃)₂(N₂C₄H₆)₂]Cl₂·2H₂O, has been determined by three-dimensional X-ray methods. The compound crystallized in a monoclinic system of space group *P*2₁/*c*, with *a* = 7.423 (1), *b* = 13.512 (2), *c* = 8.562 (2) Å, β = 104.30 (5)°, *Z* = 2, *d*_{measd} = 2.00 (3), and *d*_{calcd} = 1.99 g/cm³ at 25°. A total of 456 observed intensities were obtained by counter methods using Mo Kα (λ 0.71069 Å) radiation. The platinum atoms occupy special positions (inversion centers) in the unit cell; the complex cations are square planar and the potential axial coordination sites are vacant with the nearest atoms being ring carbons 3.04 (3) Å away. The imidazole rings are planar to within experimental error. With the exception of the ammonia ligands and water molecule all nonhydrogen atoms lie in the plane which closely approximates the [102] plane. The crystal is stabilized by a hydrogen-bonding system involving NH···O, NH···Cl, and OH···Cl interactions. The final full-matrix least-squares refinement resulted in an unweighted *R* value of 0.049.

Introduction

As part of our program of structural determinations⁴ in support of photochemical and polarized single-crystal spectral studies involving square-planar complexes, we have determined the crystal and molecular structure of the *trans*-[Pt(NH₃)₂(N₂C₄H₆)₂]Cl₂·2H₂O.

In addition to our interest in this compound as a potential candidate for spectroscopic studies, we have observed a relatively facile solid-state photochemical reaction in which the ammonia ligands of either geometric isomer of the title compound are displaced by chloride ions to yield *trans*-Pt(C₄H₆N₂)₂Cl₂. We were interested in determining the extent of reorganization (displacement, hydrogen-bond breaking, etc.) which was required in this process. Further, while imidazole and imidazole derivatives are common donor groups in biologically important coordination compounds, relatively few structural studies of simple imidazole complexes have been performed.⁵

Experimental Section

trans-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O was prepared by treating 1.0 g of *trans*-Pt(NH₃)₂Cl₂ with 0.55 g of 1-methylimidazole (MIM) in 20 ml of H₂O at 80°. After the reaction had completed (0.5 hr), a small amount of decolorizing carbon was introduced into the yellow solution, the mixture was heated for 20 min, then cooled in an ice bath, filtered, and washed with a small amount of H₂O. The colorless solution was added to 600 ml of acetone and then cooled in an ice bath for 1 hr to yield the flaky white compound. *Anal.* Calcd for [Pt(MIM)₂(NH₃)₂]Cl₂·2H₂O: Pt, 39.03; C, 20.21; H, 4.43; N, 16.80. Found: Pt, 39.70; C, 20.78; H, 4.51; N, 16.38. Single crystals were obtained by vapor diffusion of acetone into an aqueous solution of the compound.

A crystal with dimensions of 0.04 × 0.13 × 0.20 mm in the [010], [001], and [100] directions was mounted with *a** approximately parallel to the φ axis and was investigated using a GE quarter-circle manually operated XRD-5 diffractometer system. The Mo Kα beam (λ 0.71069 Å) was filtered with 1-mil zirconium

foil. The unit cell parameters at 23° are *a* = 7.423 (1), *b* = 13.512 (2), *c* = 8.562 (2) Å, β = 104.30 (5)°, as determined by a least-squares refinement⁶ of the setting angles of 14 carefully centered reflections. The estimated error is the estimated deviation from this least-squares analysis.

The crystal density, obtained by flotation in a mixture of 1,3-dibromopropane and 1,2-dibromethane, was 2.00 (3) g cm⁻³ which agrees with the calculated density of 1.99 g cm⁻³ for two molecules per unit cell. The crystal belongs to the monoclinic system and the systematic absences (*h*0*l*, *l* odd; 0*k*0, *k* odd) imply the centrosymmetric space group *P*2₁/*c* (*C*_{2h}⁵; no. 14). The Pt atoms occupy special positions (inversion centers) in the unit cell and all other atoms are in general fourfold positions.

Intensity data were collected for 2θ ≤ 45° using the above-mentioned diffractometer system. Each reflection was scanned at a scan speed of 2°/min with a takeoff angle of 3°. All peaks with 2θ < 40° were scanned 2.5° in 2θ and stationary-crystal, stationary-counter background readings were taken for 10 sec at each end of the scans. Peaks with 40° ≤ 2θ < 45° were rather broad and they were scanned 3.0° in 2θ and background readings were taken for 40 sec at each end of the scans. A total of 1108 reflections were scanned. Of these, 456 reflections⁷ were found to have intensities greater than two standard deviations. These latter reflections were used for the structure determination and refinement. The standard deviations were calculated by σ_{*I*} = (S + BT² + 0.0016I²)^{1/2} where *S* is the total scan count, *B* is the sum of the background counts, *T* is scan time per total background time, and *I* = *S* - *BT*. Some of the reflections had background readings differing by more than twice the calculated σ. For these reflections the standard deviations were set equal to the deviation of the background readings from the mean background value. The linear absorption coefficient of this compound is rather large (95.22 cm⁻¹ for Mo Kα). Consequently, the 456 reflections with intensities greater than two standard deviations were corrected for absorption using the program DEAR.⁸ A 4 × 10 × 10 summation was employed. Transmission factors varied from 0.37 to 0.69. Atomic scattering factors for neutral atoms were calculated using the analytical coefficients given by Cromer and Waber.⁹ Real and imaginary anomalous dispersion corrections¹⁰ were made for Pt and Cl.

A three-dimensional Patterson map revealed the positions of

(6) A. Foust, program ANGSET, University of Wisconsin, 1969.

(7) A table of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St. N.W., Washington, D. C. 20036, by referring to code number INORG-72-1117. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(8) A general absorption program from the University of Wisconsin which utilizes the method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(9) D. T. Cromer and J. T. Waber, private communication, Los Alamos Scientific Laboratory.

(10) Values obtained from D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(1) Support by National Science Foundation Grant GP-17520 is gratefully acknowledged.

(2) Public Health Service Fellow, 1969-1971.

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(4) J. S. Anderson, J. W. Carmichael, and A. W. Cordes, *Inorg. Chem.*, **9**, 143 (1970).

(5) A. Santoro, A. D. Mighell, M. Zocchi, and V. W. Reimann, *Acta Crystallogr.*, **25**, 842 (1969); K. S. Lundberg, *ibid.*, **21**, 901 (1968); S. Martinez-Carrera, *ibid.*, **20**, 783 (1968); C. K. Prout and T. J. Wiseman, *J. Chem. Soc.*, 497 (1964).

TABLE I
ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS
FOR *trans*-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Pt	0	0	0	
Cl	0.385 (1)	0.111 (6)	-0.247 (1)	
O	0.302 (3)	0.176 (2)	0.375 (3)	6.8 (6)
N3 ^b	0.270 (3)	0.048 (1)	0.091 (3)	3.7 (6)
N1	-0.097 (3)	0.128 (2)	0.063 (3)	3.0 (5)
N2	-0.143 (3)	0.286 (2)	0.085 (3)	3.7 (5)
C1	-0.049 (3)	0.222 (2)	0.031 (3)	2.1 (6)
C2	-0.236 (4)	0.145 (2)	0.142 (3)	3.4 (7)
C3	-0.266 (4)	0.238 (3)	0.161 (4)	4.8 (8)
C4 ^b	-0.129 (5)	0.398 (3)	0.065 (5)	7.2 (10)
H1 ^c	0.053	0.231	-0.029	4.0
H2 ^c	-0.284	0.090	0.170	4.0
H3 ^c	-0.364	0.274	0.215	4.0

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b N3 is the ammonia nitrogen and C4 is the methyl carbon. ^c H1, H2, and H3 are the hydrogens bonded to C1, C2, and C3, respectively. Hydrogen atom positions were not refined.

the platinum, chlorine, and the imidazole ring atoms and a three-dimensional Fourier map revealed the ammonia nitrogen and the water oxygen atoms. Full-matrix, least-squares refinement with isotropic temperature factors for all atoms led to an unweighted residual R_1 ($\sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.065. A similar refinement with anisotropic temperature factors for Pt and Cl yielded $R_1 = 0.049$ and a weighted residual R_2 ($[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma$) of 0.052. When all atoms were refined with anisotropic temperature factors, $R_1 = 0.046$ and $R_2 = 0.048$. At this point a difference Fourier of the special plane defined by the imidazole rings revealed the positions of the three ring hydrogens. Inclusion of these hydrogen atoms with isotropic temperature factors of $B = 4.0$ in the structure factor calculations did not affect the residuals. Application of Hamilton's R factor ratio test¹¹ showed the use of anisotropic thermal motions for carbon, nitrogen, and oxygen was not significant at the 75% confidence level. Consequently, the structural parameters reported here are

TABLE II
ANISOTROPIC THERMAL PARAMETERS FOR PLATINUM AND
CHLORINE IN *trans*-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O^{a,b}

	10 ⁴ β (1,1)	10 ⁴ β (2,2)	10 ⁴ β (3,3)	10 ⁴ β (1,2)	10 ⁴ β (1,3)	10 ⁴ β (2,3)
Pt	127 (4)	29 (1)	120 (3)	-26 (7)	46 (2)	-2 (6)
Cl	234 (23)	52 (6)	177 (17)	-6 (10)	63 (15)	17 (9)

^a Numbers in parentheses are estimated standard deviations in the least significant digit. ^b The anisotropic temperature factor is in the form of $\exp\{-[\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + 2\beta(1,2)hk + 2\beta(1,3)hl + 2\beta(2,3)kl]\}$.

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å) OF
PLATINUM AND CHLORINE IN
trans-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O

	Min	Intermed	Max
Pt	0.124	0.196	0.213
Cl	0.203	0.248	0.259

from the refinement with only Pt and Cl having anisotropic thermal motion.

A final inspection of the $\Delta f/\sigma$ values did not show any apparent dependence on θ or F values, and a final difference Fourier map showed no peak >2.0 e/Å³ except for a small region around the Pt atom. On the final cycle of least-squares refinement the maximum shifts were 0.09 σ .

Description of the Structure

The crystal packing is such that, with the exception of the ammonia ligands and the waters of hydration, all nonhydrogen atoms lie within 0.04 Å of a plane (approximately [102]) yielding a layered arrangement which does not conform with the planes of the in-

dividual cations. The oxygen atoms are only 0.46 Å from this plane (see Table VI). Extensive hydrogen bonding (see below) within and between these densely packed planes plays a major role in stabilizing the crystalline lattice.

The bond distances and angles in the Pt(NH₃)₂-(MIM)₂²⁺ cation are listed in Table IV along with

TABLE IV
DISTANCE AND ANGLES FOR
trans-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O^a

Atoms	Distance, Å	Atoms	Angle, deg
Pt-N3	2.07 (3)	N1-Pt-N3	90.3 (9)
Pt-N1	2.01 (2)	Pt-N1-C1	128.1 (18)
N1-C1	1.36 (4)	Pt-N1-C2	129.1 (20)
N1-C2	1.38 (4)	C1-N1-C2	102.7 (23)
C2-C3	1.30 (5)	N1-C2-C3	112.8 (18)
N2-C3	1.41 (4)	C2-C3-N2	103.7 (33)
N2-C1	1.27 (4)	C3-N2-C1	109.2 (27)
N2-C4	1.53 (5)	N2-C1-N1	111.5 (21)
Av ring C-H	0.99 (7)	C1-N2-C4	125.5 (19)
		C3-N2-C4	125.2 (21)

Nonbonded Contacts			
C1-N3	3.32 (2)	C1-N3-Pt	100.7 (3)
O-N3	2.95 (3)	O-N3-Pt	111.7 (8)
O-N1	3.52 (3)		
Pt-C1	3.04 (3)		
Pt-C2	3.07 (3)		
O-Cl ^b	3.17 (3)		
N3 ^c -Cl ^b	3.35 (2)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b The coordinates of the chlorine atom are ($x, 0.5 - y, 0.5 + z$) with respect to those reported. ^c The coordinates of the N3 atom are ($1.0 - x, 0.5 + y, 0.5 - z$) with respect to those reported.

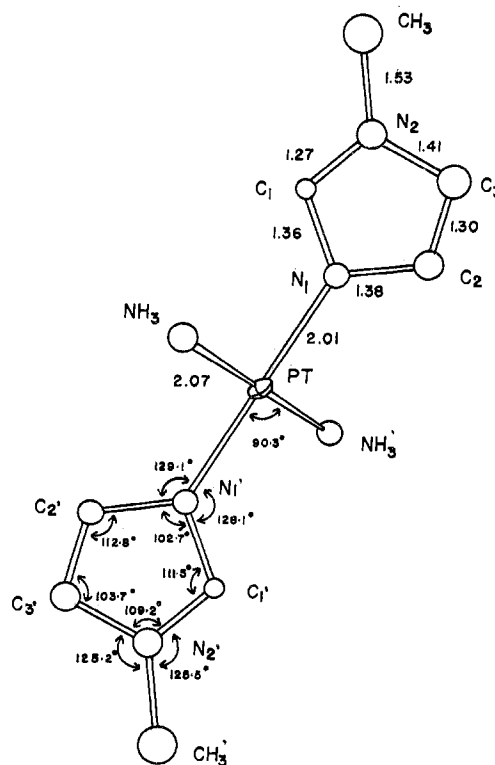


Figure 1.—The bond distances and angles in *trans*-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O.

their estimated standard deviations. The four ligating nitrogen atoms form a regular square-planar array about the platinum atoms (see Table VI). The N1-

Pt-N₃ (CH₃NC₃H₃N-Pt-NH₃) bond angle is 90.30°. The potential axial coordination sites of the planar cations are vacant, with the nearest atoms being imidazole ring carbons at a distance of 3.04 Å. The nearest probable donor groups, the chloride ions and the water molecules, are 4.22 and 4.18 Å away, respectively. The platinum to nitrogen distances are slightly longer for Pt-NH₃ (2.07 (3) Å) and shorter for Pt-C₄N₂H₆ (2.01 (2) Å) than the 2.05-Å distance usually observed for platinum(II) complexes¹² which may indicate some π bonding character to the ring-to-platinum bonds. Alternatively, the difference might be associated with difference in hybridization at the donor atoms. However, it is apparent that these chemically reasonable descriptions are probably not warranted by the data and the metal-ligand bonds are best considered to be predominantly σ interactions. The results of this investigation indicate that the square-planar cations of trans-[Pt(NH₃)₂(MIM)₂]Cl₂·2H₂O can be treated as an "oriented gas" in subsequent spectroscopic investigations. The angles made by the various Pt-N bonds with the crystal axes are given in Table V.

TABLE V
ANGLES MADE BY Pt-N BONDS WITH THE CRYSTAL AXES^a

	a	b	c
Pt-N ₃	28.9 (6)	71.6 (6)	82.1 (6)
Pt-N ₁	115.3 (6)	30.1 (6)	68.9 (6)
Pt-N ₃ ^b	28.9 (6)	108.4 (6)	82.1 (6)
Pt-N ₁ ^b	115.3 (6)	149.9 (6)	68.9 (6)

^a All angles are measured from positive axes. ^b The atomic coordinates are (x, 0.5 - y, 0.5 + z) with respect to those reported in Table I.

The N-methylimidazole rings are essentially planar (see Table VI) with none of the nonhydrogen atoms displaced from the plane by more than 0.02 Å. The

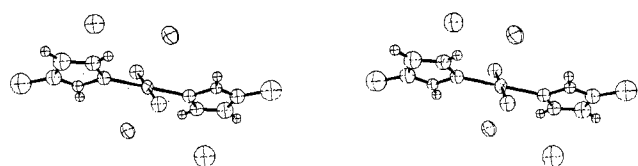


Figure 2.—ORTEP stereodiagram of trans-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O.

heterocyclic ring is not coplanar with the PtN₄ plane, the dihedral angle being 49.2°. From the data in Table VI it can be seen that the best plane through the heterocyclic ring is not identical with the most densely packed plane; however, these two planes intersect at an angle of only 1.5°. A number of structural investigations of imidazole complexes have been reported⁶ and the general features of the rings of this study resemble those of previous investigations. In general, the higher uncertainties in this study, due to the dominance of the scattering power of platinum, obviate any detailed comparison. The distance between imidazole rings (ca. 4 Å) is sufficiently great to preclude strong van der Waals interactions between rings in consecutive layers.

Hydrogen bonding plays a considerable role in stabilizing the crystal lattice of [Pt(NH₃)₂(MIM)₂]Cl₂·2H₂O. Each of the ammonia hydrogens is involved

(12) G. A. Kukina, Zh. Strukt. Khim., 3, 474 (1962).

TABLE VI
DISTANCES FROM THE ATOMS TO THE LEAST-SQUARES PLANES^{a-c}

Atoms	Distance, Å	Atoms	Distance, Å
(1) C ₄ N ₂ H ₆ Plane Equation: -0.4927x - 0.0239y - 0.8699z - 0.0833 = 0			
N1	0.00	C2	0.02
N2	-0.02	C3	-0.02
Cl	-0.01	C4	0.02
(2) PtClON ₂ C ₄ Plane Equation: -0.5138x - 0.0150y - 0.8578z - 0.0136 = 0			
Pt	0.01	Cl	-0.04
Cl	0.01	C2	0.03
O ^c	-0.46	C3	0.01
N1	-0.03	C4	0.03
N2	-0.02		

(3) PtN₄ Plane Equation: 0.2308x + 0.3879y - 0.8924z = 0

^a The plane equations are in orthogonalized coordinates.

^b The dihedral angle between plane 1 and plane 3 is 49.2°.

^c The coordinates of this atom are (-x, -y, -z) with respect to those reported in Table I.

as the donor in three hydrogen bonds, two to Cl⁻ ions and one to water of crystallization. The water molecule functions as a hydrogen-bond donor to one of the chloride ions completing a three-dimensional network of hydrogen bonds both within and between the layers of the crystal.

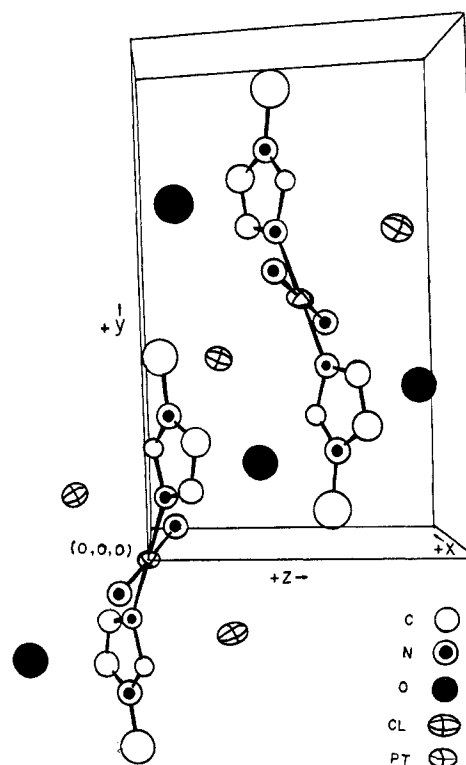


Figure 3.—The crystal packing of trans-[Pt(N₂C₄H₆)₂(NH₃)₂]Cl₂·2H₂O.

Examination of the packing of the crystal indicates a convenient path for the photochemical production of trans-Pt(C₄N₂H₆)₂Cl₂ is available with only a small amount of motion of the leaving and entering groups required. Attempts to obtain similar structural information concerning the cis isomer have been unsuccessful due to difficulties encountered in obtaining good crystals. The thermal path for the isomerization

of square-planar complexes in solution involves the generation of a five-coordinate adduct which is proposed to be a labile configuration.¹³ Isomerization can be effected photochemically in solution *via* an excited state postulated to be a triplet state of tetrahedral geometry. However, in solution both thermal and photochemical substitution reactions studied to date precede with retention of initial geometry.¹⁴ It is

(13) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).

(14) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 377; V. Balzani and V. Carasiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 247 ff.

possible that the production of *trans*-Pt(MIM)₂Cl₂ from *cis*-[Pt(NH₃)₂(MIM)₂]Cl₂ is a two-stage process in which isomerization and substitution are not concurrent. When structural studies of the product molecule now underway are complete, it may be possible to clarify this aspect of the solid-state chemistry of these square-planar complexes.

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Phosphonitrilic Compounds. XIII.¹ The Structure and Properties of Poly(difluorophosphazene)²

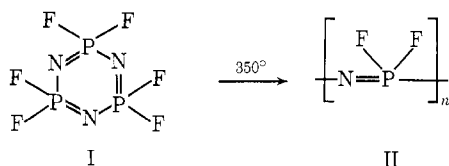
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X-Ray diffraction investigation of oriented fibers of high molecular weight poly(difluorophosphazene), (NPF₂)_n, revealed the presence of two molecular conformers. Conformer A, with a chain repeating distance of 6.49 Å, was detected at temperatures between +25 and -36°. Conformer B, observed near -56°, showed a fiber (*c*) axis repeat of 4.86 Å. An orthorhombic unit cell (space group *Cmc*2₁) was assigned with *a* = 8.69 Å and *b* = 5.38 Å. Structure factor calculations for conformer B indicated a *cis,trans*-planar chain conformation, with P-N = 1.52 Å, P-F = 1.47 Å, F-P-F = 95°, N-P-N ≈ 119°, and P-N-P ≈ 136°. The low-temperature flexibility and high-temperature depolymerization of this polymer were also studied.

Results and Discussion

Poly(difluorophosphazene) (II) was first reported by Seel and Langer³ as a product formed by the high-temperature polymerization of hexafluorocyclotriphosphazene (I). In view of the developing interest in



phosphazene high polymers, this compound is of structural importance, since it contains a minimum number of atoms per monomer unit and provides a basis for the analysis of the more complex organo-substituted derivatives.

We have undertaken an X-ray crystallographic examination of this compound with a view to determining the structure and chain conformation. Additional descriptive data have been obtained by ¹⁹F nmr, differential thermal analysis, and depolymerization experiments.

Description of the Polymer.—Poly(difluorophosphazene) was prepared by the high-pressure, thermal polymerization of hexafluorocyclotriphosphazene (see

Experimental Section). The polymer was a pale amber, rubbery elastomer. When exposed to atmospheric moisture it degraded rapidly with a loss of elasticity and formation of phosphoric and hydrofluoric acids. The polymer was insoluble in common organic solvents, but it swelled in hexadecafluoro-*n*-heptane in a manner characteristic of a lightly cross-linked polymer. The elemental analysis and infrared spectra were consistent with structure II (see Experimental Section).

The ¹⁹F nmr spectrum of the swelled polymer consisted of a doublet at +70.5 ppm (relative to CFCl₃) due to spin-spin coupling with ³¹P. No fine structure from coupling with nearby PF₂ units was observed. The chemical shift value was in good agreement with the values of +71.9 and +72.3 ppm reported for (NPF₂)₃ and (NPF₂)₄, respectively.⁴

The measured coupling constant *J*_{PF} of 878 cps for II was comparable to the values of 868 cps reported for (NPF₂)₃ and (NPF₂)₄.⁴ The sharp doublet spectrum of solid II persisted at temperatures between +20 and -60°, and it must be assumed that conformational averaging of the fluorine environments takes place even at -60°. Thus, the barriers to internal rotation are small.

Restriction of backbone torsional motion normally occurs below the glass transition temperature (*T*_g) of a polymer. Thermomechanical measurements indicated that poly(difluorophosphazene) changes from a rubber

(1) Part XII: H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, **94**, 119 (1972).

(2) A preliminary report of this work has appeared: H. R. Allcock, G. Konopski, R. L. Kugel, and E. G. Stroh, *J. Chem. Soc. D*, 985 (1970).

(3) F. Seel and J. Langer, *Z. Anorg. Allg. Chem.*, **295**, 317 (1958).

(4) T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc. A*, 2324 (1970).