

Crystal Structure of the Phosphorus Oxynitride P_4ON_6

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The *ab initio* crystal structure determination of the phosphorus oxynitride P_4ON_6 has been performed by the X-ray powder diffraction technique (space group $Pn\bar{m}$; $a = 6.8424(1)\text{Å}$, $b = 6.0714(2)\text{Å}$, $c = 6.8176(1)\text{Å}$, $Z = 2$; $R_{\text{Bragg}} = 4.8\%$, $Gof = 1.35$) A structure refinement of neutron data incorporating anisotropic temperature coefficients for oxygen and nitrogen reduces the R_{Bragg} -factor down to 2.2% ($Gof = 1.35$). P atoms are more or less rigid at room temperature. Significant oxygen/nitrogen exchange was observed for one of the symmetrically different N sites ($9 \pm 5\%$). A remarkable modulation of the diffuse background reflects considerable disorder in the structure not analyzed so far. The structure is formed by PON_3 and PN_4 tetrahedra. PN_4 tetrahedra are linked in pairs via a joint edge, which is a unique phenomenon among inorganic phosphorus–nitrogen compounds. © 1995 Academic Press, Inc.

INTRODUCTION

The description of the novel modification of phosphorus nitride P_3N_5 , referred to the tetragonal system, has been published in (1, 2). More detailed studies have shown that the synthesized compound contains oxygen and represents a phosphorus oxynitride with the empirical formula P_4ON_6 ($PON \cdot P_3N_5$) (3). It has to be pointed out that the oxynitride P_4ON_6 is of particular interest among crystalline compounds of the series PON – $PON \cdot xP_3N_5$ – P_4ON_6 – P_3N_5 , because its physicochemical properties differ essentially from those of other compounds (3). Crystal structure determination of a number of related inorganic phosphorus–nitrogen compounds by the powder diffraction technique has been reported: PON , MPN_2 (M -H, Li, Na) (3), $M_3P_6N_{11}$ (M -Na, K) (4), $M_4P_6N_{12}S$ (M -Cd, Zn, Mg, Mn, Fe, Co) (5) and Mg_2PN_3 (6). Recently physicochemical properties of P_4ON_6 were analyzed and attempts were made to predict some structural features of this compound (7). The aim of the present work was structure determination of P_4ON_6 by

X-ray and neutron powder diffraction techniques. The neutron work was performed in part to detect some interchange of oxygen and nitrogen on their sites, if any, which cannot be decided from X-ray data.

EXPERIMENTAL

The phosphorus oxynitride P_4ON_6 was prepared by the reaction of crystalline PON with ammonia (3):



To perform the synthesis the compacted sample of PON was heated in a quartz tube in a slow gaseous ammonia flow at a temperature of about 850°C for 30 hr. P_4ON_6 was obtained as a compact powder of white or light orange color. It contained (%) 54.9 P; 38.0 N; 6.9 O. Calculated for P_4ON_6 (%): 55.33 P; 37.53 N; 7.14 O.

Strong absorption bands in the infrared spectrum of P_4ON_6 , observed in the vicinities of the bands 1440 – 1325 , 1100 – 900 , 800 , and 680 cm^{-1} , can be assigned to the excitations of various phosphorus–nitrogen and phosphorus–oxygen bonds. Absence of absorption bands in the range 3400 – 3000 cm^{-1} indicates that synthesized oxynitride does not contain NH groups.

X-ray diffraction measurements were carried out with a DRON-3 X-ray powder diffractometer: $CrK\alpha$ radiation, flat, thick powder sample, step scanning mode with step width of 0.02° between 25 and 162° . A so-called two stage data processing and interpretation strategy was initially applied, using the POWDER (8) program package for the peak position and integrated intensity determination and SHELX-76 program package (9) for the structure solution and first stages of refinement. Final refinement, however, was done by the DBWS program (10).

Neutron measurements were carried out at the instrument MAN1 of the FRM reactor in München/Garching Germany. A wavelength of 1.075 Å was used. Refine-

ment was done with a local version of the same DBWS program (11). An impression of the quality of the final fit is given in Fig. 1.

Indexing

The indexing of powder diffraction data demonstrates that P_4ON_6 has an orthorhombic unit cell with the following lattice parameters: $a = 6.8424(1)\text{\AA}$, $b = 6.0714(2)\text{\AA}$, $c = 6.8176(1)\text{\AA}$, $Z = 2$, $V = 283\text{\AA}^3$ (12). The reliability of unit cell and indexing is characterized by the figure of merit $M_{20} = 172$. A systematic extinction of Ok_l reflections with $k + 1$ odd and hOl reflections with $h + l$ odd is observed; consequently, the crystals can be referred to one of the two space groups—centrosymmetrical $Pn\bar{1}m$ or noncentrosymmetrical $Pnn2$.

Structure Solution and Description

After processing of the X-ray powder diffraction pattern the array of 76 integrated intensities of the diffraction maxima was obtained: 70 of them corresponded to the individual reflections, 6 were a sums of two overlapping independent reflections. In order to obtain an initial set of structural amplitudes, the intensities were divided assuming the equality of $|F|$ values for all the components. Further, at each alteration of model, a redistribution of intensity proportional to the calculated structural

TABLE 1
Refinement Results of P_4ON_6 X-Ray Powder Data in Space Group $Pn\bar{1}m$

Atom	Site	x/a	y/b	z/c	$B, \text{\AA}^2$
P(1)	4(g)	0.8617(3)	0.2056(4)	0	0.45(6)
P(2)	4(f)	0	0.5	0.3122(4)	0.21(5)
O	2(a)	0	0	0	3.54(24)
N(1)	4(g)	0.6414(10)	0.1068(9)	0	0.21(14)
N(2)	8(h)	0.1176(6)	0.6794(8)	0.2038(6)	0.63(11)

$a = 6.8424(1) \text{\AA}$ $b = 6.0714(2) \text{\AA}$ $c = 6.8176(1) \text{\AA}$
 $R_{\text{Bragg}} = 4.8\%$ $\text{Gof} = R_{\text{wp}}/R_{\text{exp}} = 10.93/8.08 = 1.35$

Note. Estimated standard deviations are given in parentheses.

amplitudes of the overlapping peaks was performed as described in (13). The analysis of the Patterson function made if possible to find the fourfold position of phosphorus atoms in the unit cell, and from the results of Fourier syntheses and refinement of parameters by the least-squares method the remaining positions of phosphorus, oxygen, and nitrogen atoms could be estimated. Final refinement was done by the DBWS program (10). Thus, the refined structure shows that P_4ON_6 corresponds to the space group $Pn\bar{1}m$ with two formula units in the unit cell, $R_{\text{Bragg}} = 4.8\%$, $\text{Gof} = 1.35$. The positional parameters are given in Table 1.

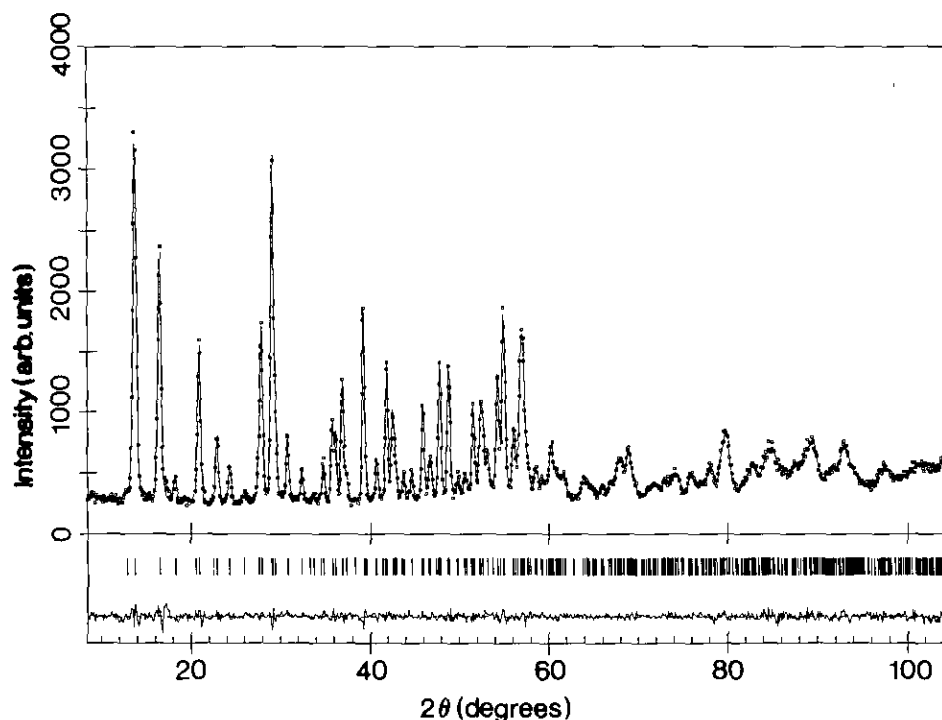


FIG. 1. Neutron measurement: refinement of the data with anisotropic temperature coefficients (see text). Note the remarkable difference curve (bottom) reflecting the excellent fit.

TABLE 2
Refinement Results of P₄ON₆ Neutron Powder Data in Space Group *Pnmm*

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²
P(1)	4(g)	0.8614(8)	0.2054(8)	0	0.04(7)
P(2)	4(f)	0	0.5	0.3136(7)	-0.03(7)
O	2(a)	0	0	0	*3.03
N(1)	4(g)	0.6353(5)	0.1014(4)	0	*0.26
N(2)	8(h)	0.1190(4)	0.6766(3)	0.2012(3)	*1.17

occupancy N(2) on O - site = O, on N(2) - site = 9(5)%
occupancy N(1) on O: not significant
a = 6.8229(6) Å *b* = 6.0541(4) Å *c* = 6.7970(5) Å
*R*_{Bragg} = 0.022 Gof = *R*_{wp}/*R*_{exp} = 4.59/3.41 = 1.35

Note. Estimated standard deviations are given in parentheses. An asterisk indicates equivalent isotropic displacement parameters calculated from $\langle u^2 \rangle = \sum \beta_{ii} a_i^2$ as derived from Table 3.

Within the limits of 1–4 esd's of the X-ray results the positional parameters are the same as found by the refinement of the neutron data (cf. Tables 2, 3).

According to the calculated data the three-dimensional structure of P₄ON₆ is built up from two types of tetrahedra: P(1)ON₃ and P(2)N₄. Each P(1)ON₃ tetrahedron contains one bridging oxygen atom, one three-coordinated nitrogen atom N(1), and two two-coordinated N(2) atoms, but P(2)N₄ tetrahedron contain two N(1) and two N(2) atoms. These results entirely correspond to the preliminary calculation of the number of three-coordinated nitrogen atoms in the structure of the phosphorus oxynitride P₄ON₆ (7).

In contrast to the structure of Na₃P₆N₁₁ (4), where three-coordinated nitrogen atoms connect three tetrahedra of one type via vertices, in the structure of P₄ON₆ the three-coordinated N(1) atom belongs simultaneously to one P(1)ON₃ and two P(2)N₄ tetrahedra. Moreover, in the structure of phosphorus oxynitride, P₄ON₆, the P(2)N₄ tetrahedra are linked in pairs via the joint edge N(1)–N(1). Such a union of tetrahedra is a rare phenomenon for tetrahedral compounds, but it is really unknown for the structures of inorganic compounds (phosphazenes, phosphates, silicates) of period III elements.

TABLE 3
Anisotropic Displacement Parameters of P₄ON₆ as Refined from Neutron Powder Data

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0.004(2)	0.009(3)	0.038(4)	0.005(2)	0	0
N(1)	0.0007(6)	0.0031(8)	0.0010(7)	-0.0006(6)	0	0
N(2)	0.0056(5)	0.0128(7)	0.0033(5)	-0.0049(7)	-0.0010(5)	0.0046(4)

Note. The corresponding temperature factor is defined as $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

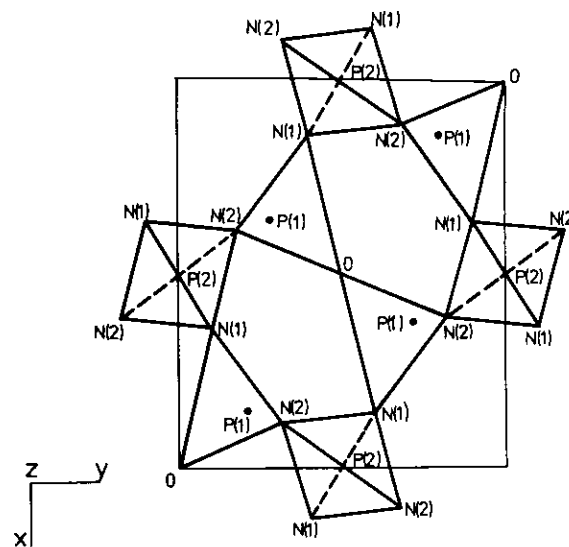


FIG. 2. Projection of PN₄ and PON₃ tetrahedra onto the plane (001) in the structure of P₄ON₆.

The P(1)ON₃ tetrahedra in turn are bound in pairs via the oxygen bridging atoms, and thus the structure of P₄ON₆ is formed by five-membered rings, consisting of three P(1)ON₃ tetrahedra and two P(2)N₄ tetrahedra (Figs. 2, 3). The interatomic distances and bond angles in P₄ON₆ are shown in Table 4.

The average P–N distance—1.62 Å in P(2)N₄ tetrahedra—is characteristic for the phosphorus–nitrogen compounds and corresponds to the sum of effective ionic

TABLE 4
Interatomic Distances (Å) and Bond Angles (°)

P(1)ON ₃ tetrahedron		P(2)N ₄ tetrahedron	
P(1)–O	1.567(7)	2 × P(2)–N(1)	1.688(13)
P(1)–N(1)	1.671(20)	2 × P(2)–N(2)	1.549(14)
2 × P(1)–N(2)	1.553(14)		
O–N(1)	2.570(18)	N(1)–N(1)	2.224(35)
2 × O–N(2)	2.530(14)	2 × N(1)–N(2)	2.648(19)
2 × N(1)–N(2)	2.554(20)	2 × N(1)–N(2)	2.718(18)
N(2)–N(2)	2.743(28)	N(2)–N(2)	2.693(27)
O–P(1)–N(1)	105.0(7)	N(1)–P(2)–N(1)	82.4(9)
2 × O–P(1)–N(2)	108.4(5)	2 × N(1)–P(2)–N(2)	109.7(8)
2 × N(1)–P(1)–N(2)	104.7(6)	2 × N(1)–P(2)–N(2)	114.1(8)
N(2)–P(1)–N(2)	124.0(10)	N(2)–P(2)–N(2)	120.7(11)

Bond angles between tetrahedra	
P(1)–O–P(1)	180.0(0)
P(1)–N(1)–P(2)	130.2(5)
P(2)–N(1)–P(2)	97.6(9)
P(1)–N(2)–P(2)	143.3(10)

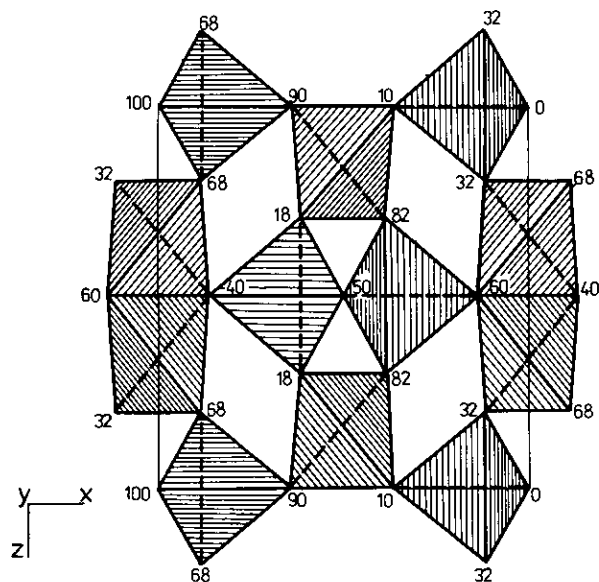


FIG. 3. Projection of PN_4 and PON_3 tetrahedra onto the plane (010) in the structure of P_4ON_6 . Numbers indicate heights in units of one-hundredth on the projection axis, y .

radii (14). However, in the interior, of the $\text{P}(2)\text{N}_4$ tetrahedron the bond lengths differ significantly: $\text{P}(2)\text{-N}(1) = 1.69\text{\AA}$ and $\text{P}(2)\text{-N}(2) = 1.55\text{\AA}$, respectively, for three- and two-coordinated nitrogen atoms. This indicates the low degree of delocalization of the π -electrons. An analo-

gous prolongation of the P-N bond for the three-coordinated nitrogen atom ($\sim 1.7\text{\AA}$) has also been established in the structure of $\text{Na}_3\text{P}_6\text{N}_{11}$ (4).

In the $\text{P}(1)\text{ON}_3$ tetrahedra the general regularity is preserved—the bond with the three-coordinated nitrogen atom $\text{P}(1)\text{-N}(1)$ is longer, but $\text{P}(1)\text{-O}$ and $\text{P}(1)\text{-N}(2)$ bonds are shorter by $\sim 0.1\text{\AA}$. The presence of the more electronegative oxygen atom in $\text{P}(1)\text{ON}_3$ tetrahedra causes contraction of the adjacent phosphorus–nitrogen bonds. It is in good agreement with the conclusions of Allcock (15) that the shortest P-N bonds in phosphazenes are the compounds with the most electronegative substituents.

A more detailed discussion can be related to the anisotropic refinement of the neutron data. The B -values of the P -atoms do not differ from zero significantly; i.e., there is neither considerable displacement disorder, nor remarkable dynamical fluctuation of the P atom. Relatively high B values were found for oxygen and $\text{N}(2)$ atoms, but not for $\text{N}(1)$. Anisotropic coefficients of both O and $\text{N}(2)$ reveal significant anisotropy (Table 3).

Remarkably, O and $\text{N}(2)$ sites are also affected by a significant exchange of atomic species (compare Table 2). With other words, there is some chemical disorder. Presumably this disorder is also reflected by the considerable modulation of the diffuse background (Fig. 4). A further discussion of disorder in this compound is beyond the scope of this paper.

There is a simple relationship between constants a_1 and

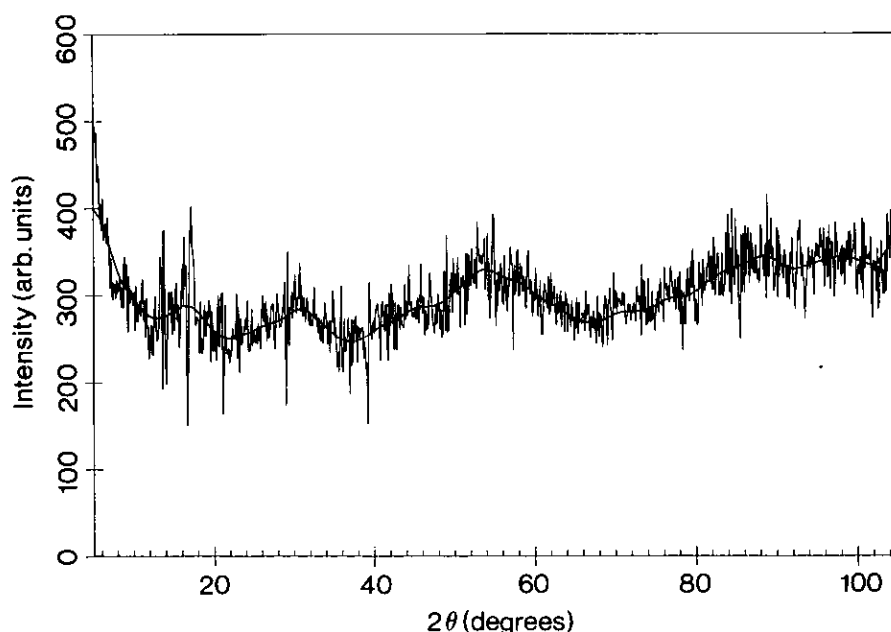


FIG. 4. Background of the neutron diagram. Note the remarkable humps indicating further disorder not analyzed so far.

c_t of the tetragonal PON structure and constants a_r , b_r , and c_r of orthorhombic P₄ON₆ structure:

$$c_t \cong c_r, \sqrt{2} a_t \cong \frac{a_r + b_r}{2}.$$

Furthermore, the spatial arrangement of phosphorus atoms in both oxynitride structures exhibits strong similarities and it seems to be reasonable to speak of some sort of genetic relationship between both structures. On the other hand, it should be mentioned that linkage of the basic structural units (tetrahedra), as described above, considerably differs from that in other phosphorus–nitrogen compounds known up to now. Evidently this is a reason for the different physicochemical properties of P₄ON₆ in comparison with those of the other phosphorus oxynitrides and nitride P₃N₅.

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