BRIEF COMMUNICATION

New Refinement of the Crystal Structure of o-P$_2$O$_5$

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The crystal structure of o-modification of diphosphorus pentaoxide was refined at 295 K. It consists of a network of [PO$_4$] tetrahedra linked by three common apices. Moreover, this o-modification of P$_2$O$_5$ is also found to crystallize in the orthorhombic system with the space group *Fdd*2 and the lattice parameters $a = 16.314(2)$ Å, $b = 8.115(3)$ Å, $c = 5.265(9)$ Å, $Z = 8$, and $D_{calc} = 2.705$ (g · cm^{-3}). The main value of the P–O length is estimated to be 1.543 Å. As expected, the nonbridging P–O bonds, equal to 1.445 Å, are shorter than the bridging ones which average 1.582 Å. The structure parameters are refined to a final R of 0.0351 (wR = 0.0643) for 550 independent reflections [$I > 3\sigma(I)$]. © 1996 Academic Press

I. INTRODUCTION

Investigation of the title compound is part of a large program of research devoted to the structural approach of various ternary phosphate glasses (1–7). As a matter of fact, all the glass forming regions of the ternary systems examined expand inside the ternary diagrams starting from the composition P$_2$O$_5$ (3). Furthermore, former infrared and Raman studies have shown that the evolution of the glass structure within vitreous domains can be regarded as resulting from the depolymerization of the three-dimension network of pure vitreous P$_2$O$_5$, in proportion to the modifying oxide incorporated: Na$_2$O, CuO, Ln_2O$_3$ (Ln = rare earth), etc. (1–13). In addition, it is well known that access to the local structure of glass materials is based, on the one hand, according to Zachariasen theory, on the closeness of crystalline and vitreous states of the same chemical composition and, on the other hand, on the similarity of the vibrational spectra of both states (3, 14). Therefore, the structural determination of all varieties of the

diphosphorus pentaoxide, a basic forming oxide for almost all phosphate glasses, appears essential for a complete vibrational study to be exploited for a better structural understanding of such vitreous compounds.

After the analysis of the structural results found in the literature, it could now be established that under normal conditions of temperature and pressure, three different forms of crystalline P$_2$O$_5$ are so far isolated (3, 15):

(a) The metastable hexagonal variety, known as the h-form, is made of discrete P$_4$O$_{10}$ molecules. It crystallizes with the space group $R3c$ and the rhombohedral lattice parameters $a = 7.44$ Å and $\alpha = 87°$. The first structure, reported by de Decker and MacGillavry, was recently refined by Jansen and Lüer who obtained more accurate X-ray crystallographical data (16, 17).

(b) The stable orthorhombic variety is named form III by Cruickshank who refined the structure initially solved by MacGillavry *et al.* (18–20). A new refinement of this structure, denominated hereinafter o'-P$_2$O$_5$, was recently published by Stachel *et al.* (21).

(c) A second orthorhombic form, whose structure was solved by de Decker, has the space group *Fdd*2 and the lattice parameters (22) $a = 16.3$ Å, $b = 8.14$ Å, and $c = 5.26$ Å.

The purpose of the present work is to report the new refinement of the structure of the last form (henceforth labeled o-P$_2$O$_5$), and it was undertaken in order to get more precise interatomic distances and angles to be used for a sound vibrational study of both crystalline and vitreous phosphates including pure P$_2$O$_5$. Furthermore, among all known allotrops of the diphosphorus pentaoxide, the structure of o-P$_2$O$_5$ is hitherto the least accurate (15–23).

II. EXPERIMENTAL

(a) *Crystal Growth*

The pulverulent h-P$_2$O$_5$ form was used as starting material for the growth of single crystals of the title compound,

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TABLE 1
Crystal Data and Structure Refinement Parameters of o-P_2O_5

Chemical formula	P_2O_5 (o-form)
Crystal system	Orthorhombic
Space group	$Fdd2$
Cell dimensions	
a (Å)	16.314(2)
b (Å)	8.115(3)
c (Å)	5.265(9)
Cell volume (Å^3)	697.18
Z	8
$D_{calc.}$ (g · cm^{-3})	2.705
Crystal color	transparent
Data collection	
Equipment	Enraf–Nonius CAD4
λ [Mo$K\alpha$ (graphite monochromator)]	0.7107 Å
Temperature (K)	295
Scan mode	$\omega - 2\Theta$
Scan width (°)	1.2
Θ range (°)	$2\Theta < 90°$
Recording reciprocal space	$-32 \leq h \leq +32;$
	$-15 \leq k \leq +15;$
	$0 \leq l \leq 10$
No. of reflections measured	3085
No. of reflections [$I > 3\sigma(I)$]	1866
No. of independent reflections	566
μ(cm^{-1}) for λ Mo$K\alpha$ = 0.7107 Å	11.3
Transmission factor range	0.83–1.00
Merging R factor	0.037
Refinement	
No. of parameters refined	33
$R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$	0.035
$wR2 = [\Sigma w(I_o - I_c)^2/\Sigma wI_o^2]^{1/2}$	0.064
with $w = [1/(\sigma F_o^2)] + (0.0334P)^2$	
$P = (\max F_o^2 + 2F_c^2)/3$	

according to the procedure reported by Hill *et al.* (23). Owing to the peculiar hygroscopic character of the diphosphorus pentaoxide, all samples were manipulated in a dried glove box. A platinum tube was filled with powder of h-P_2O_5 and then inserted into a quartz pipe of about 1 cm diameter and 20 cm length. The silica tube was then sealed off under vacuum and heated in a temperature gradient for 4 days. The upper part of the silica ampoule was

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic (U_{eq}) Displacement Parameters for o-P_2O_5

Atoms	x	y	z	U_{eq} (Å)^2
P	0.17477(3)	0.16940(6)	0	0.00695(11)
O (1)	0.19398(11)	0.08499(22)	0.23409(40)	0.01573(27)
O (2)	0.11341(9)	0.31958(17)	0.02563(40)	0.01016(30)
O (3)	1/4	1/4	0.85663(48)	0.01013(36)

TABLE 3
Anisotropic Temperature Factors^a $U_{ij} \times 10^4$ for o-P_2O_5

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	66(1)	61(2)	82(2)	−6(2)	1(2)	−2(2)
O$_1$	184(6)	161(6)	127(7)	52(7)	−29(7)	21(6)
O$_2$	106(5)	86(5)	113(8)	−35(6)	−3(5)	32(4)
O$_3$	72(7)	124(8)	109(9)	0	0	−26(6)

^{a} The subfractional coefficients relate to the expression $\tau = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

kept at 380°C while its bottom was maintained at 480°C. Due to the high rate of sublimation of h-P_2O_5, at high temperature, single crystals appeared as dentrites at the colder part of the tube, 2 days after the calcination started. After the heat treatment for the desired time, the ampoule was quenched to room temperature and opened inside the dry box. Selected single crystals were then immersed in paraffin oil for their continuous conservation.

(b) *Data Collection and Structure Determination*

A random reflection search performed on an Enraf–Nonius CAD4 four-circle diffractometer confirmed the unit cell with the lattice parameters given in Table 1. Intensity data collection was performed in this cell, with graphite monochromated (Mo$K\alpha$) radiation, a scintillation counter, and a pulse-height discriminator. Intensities were corrected for Lorentz and polarization effects. Empirical absorption correction was made on the basis of psi-scan data. Intensity collection conditions are reported in Table 1. Calculations were performed using SHELX86 and SHELXL93 programs (24, 25). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography (26). The

TABLE 4
Selected Interatomic Distances (Å) and Bond Angles (°) for o-P_2O_5

P–O (1) = 1.445 (2)	
P–O (2) = 1.562 (2)	
P–O (2′) = 1.583 (1)	
P–O (3) = 1.582 (1)	
⟨P(1)–O⟩ = 1.547	
O (1)–P–O (2) = 119.08(10)	P–O (2)–P = 135.72(13)
O (1)–P–O (2′) = 115.44(10)	P–O (3)–P = 123.01(16)
O (1)–P–O (3) = 115.77(10)	
O (2)–P–O(3) = 99.36(10)	
O (2)–P–O (2′) = 102.22(7)	
O (2′)–P–O (3) = 102.29(7)	
⟨O–P–O⟩ = 109.02	
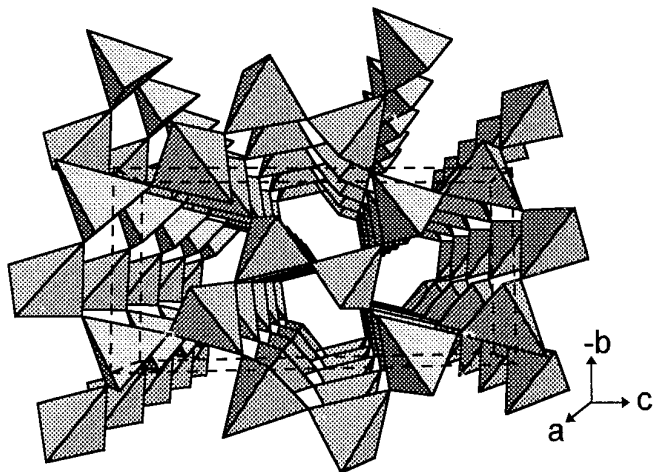
FIG. 1.   Three-dimensional view of o-P_2O_5 structure.

FIG. 2.   Connexion of adjacent helices through one common [PO₄] tetrahedron.

structure was determined by interpretation of the Patterson map, with the help of the automatic procedure included in the SHELX86 program. The phosphorous atom was then located and oxygen atoms were found in subsequent difference Fourier maps, using the SHELXL93 program. The final conventional reliability factors are $R1 = 0.035$ (based on F_o) and $wR2 = 0.064$ (based on F_o^2), including anisotropic thermal motions for all atoms. Atomic positions, thermal parameters, and selected atomic distances are listed in Tables 2, 3, and 4, respectively. The list of the structure factors may be obtained on request from the authors (J.D.).
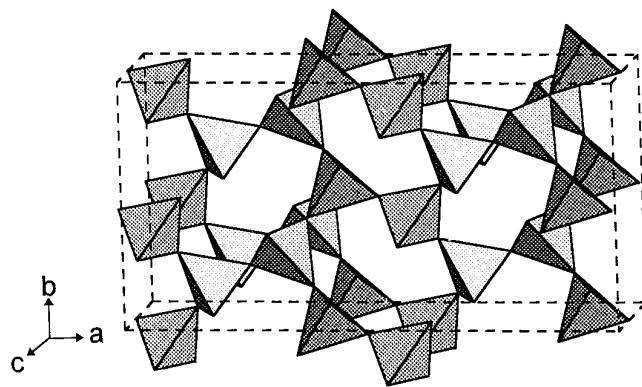
III. RESULTS AND DISCUSSION

A three-dimensional view of o-P_2O_5 is given in Fig. 1. It could be regarded as made of helices of [PO₄] tetrahedra running along [001]. Each [PO₄] tetrahedron shares three apices with three adjacent helices as clearly shown in Fig. 2.

The results of our refinements show that the main framework of P_2O_5 structure (o-form), resolved by de Decker, is totally identical to o-P_2O_5 reported in the present work (22). Nevertheless, the crystal data given here are more accurate. As a matter of fact, e.s.d.'s are lowered by at least two orders of magnitude for the lattice parameters and by one for the atomic coordinates. Furthermore, it is to be noticed that interatomic distances are more regular

TABLE 5
Bond Lengths Measured for the Known Varieties of Diphosphorous Pentaoxide

Variety	Bridging P–O bond length (Å)	Nonbridging P–O bond length (Å)	References
h-P_2O_5	P(1)–O = 1.588(3) × 3 P(2)–O = 1.597(3) 1.590(2) 1.589(2)	1.434(4) 1.431(3)	17
o′-P_2O_5	P(1)–O = 1.566(3) 1.568(3) 1.568(3) P(2)–O = 1.573(2) 1.573(2) 1.574(3)	1.452(3) 1.437(3)	21
o-P_2O_5	P–O = 1.562(2) 1.583(1) 1.582(1)	1.445(2)	this work
g-P_2O_5 (molecular gaseous)	P–O = 1.562	1.429	27

than those found by de Decker. For example, the shortest and the longest P–O bonds given by de Decker are equal to 1.61 and 1.39 Å, respectively, while equivalent distances found in the present work correspond to 1.582 and 1.445 Å. Since the shortest and the longest phosphorus–oxygen distances are related to nonbridging and bridging P–O bonds, respectively, it could be assumed that there is less difference between the chemical bond strengths within the tetrahedra [PO_4] identified in our refinement than between identical bonds reported by de Decker (22). However, the bond length seem to be equivalent in the three forms, h-, o'-, and o-P_2O_5, according to the most recent structural results given in Table 5. Furthermore, both bridging and nonbridging P–O bonds are shorter in gaseous molecular diphosphorous pentaoxide, labeled g-P_2O_5 (Table 5).

A close examination of the P–O bond lengths within the three crystalline varieties of P_2O_5 (Table 5) shows that:

—the bridging P–O bond length is least uniform in o-P_2O_5 (its average value is intermediate between those of h-P_2O_5 and o'-P_2O_5);

—the nonbridging P–O bond length is intermediate between nonbridging P(1)–O and P(2)–O of o'-P_2O_5; and

—the chemical bond strengths are not fully identical in all varieties of P_2O_5.

Therefore some shift is to be expected for the frequencies of the corresponding vibrational modes. These results might be fruitful for a better understanding of the vibrational spectroscopy of crystalline and vitreous P_2O_5.

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