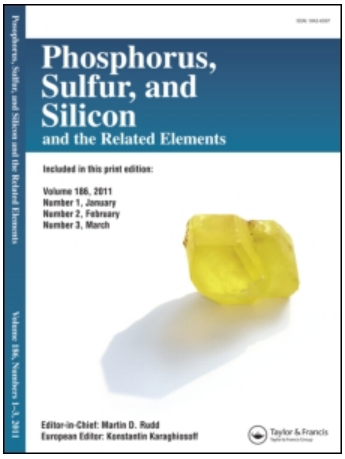

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Synthesis and Characterization of $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7\cdot 6H_2O$

A. Selmi[a]; S. Akriche[a]; M. Rzaigui[a]
[a] Laboratoire de Chimie des Matériaux, Faculté des Sciences, Zarzouna, Bizerte, Tunisie

To cite this Article Selmi, A. , Akriche, S. and Rzaigui, M.(2006) 'The Synthesis and Characterization of $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7\cdot 6H_2O$', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 9, 2201 — 2211
To link to this Article: DOI: 10.1080/10426500600614642
URL: http://dx.doi.org/10.1080/10426500600614642

Phosphorus, Sulfur, and Silicon, 181:2201–2211, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600614642

Taylor & Francis
Taylor & Francis Group

The Synthesis and Characterization of $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$

A. Selmi
S. Akriche
M. Rzaigui
Laboratoire de Chimie des Matériaux, Faculté des Sciences, Zarzouna, Bizerte, Tunisie

Inorganic–organic hybrid compounds exhibit interesting properties in several application areas. In this regard, chemical preparation and characterization by X-ray diffraction, thermal analysis, and IR spectroscopy are given for a new organic cation diphosphate $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$. *This later crystallizes in a C2/c unit cell with* $a = 38.238(6)\text{Å}$, $b = 6.453(1)\text{Å}$, $c = 16.942(7)\text{Å}$; $\beta = 97.60(4)^\circ$; $Z = 4$; *and* $V = 4144(2)\text{Å}^3$ *and* $D_x = 1.377\ g{\cdot}cm^{-3}$. *Its crystal structure has been determinated and refined to* $R = 0.044$, *using 7978 independent reflections. This atomic arrangement consists of inorganic layers built up from* $P_2O_7^{4-}$ *anions and water molecules. On these layers, which are parallel to the (b, c) planes, the* $(4\text{-}CH_3OC_6H_4CH_2NH_3)^+$ *cations are anchored through multiple hydrogen bonds.*

Keywords Crystal structure; diphosphate; infrared spectroscopy; thermal analysis; X-ray diffraction

INTRODUCTION

A large number of diphosphates with mineral cations have been synthesized, but a limited number of organic cation diphosphates has been characterized.[1] Thus, the elaboration and characterization of new compounds of this family have essentially double aims:

1. to diversify types of links (electrostatic, H-bonds, and Van Der Waals interactions) in the crystal in order to have particularly original configurations.
2. the possibility of elaborating new interesting compounds, which could have important properties on the practical plan.[2,3] In the present work, we report the synthesis, structural study,

Received November 14, 2005; accepted December 30, 2005.
Address correspondence to S. Akriche, Laboratoire de Chimie des Matériaux, Faculté des Sciences, Zarzouna, 7021 Bizerte, Tunisie. E-mail: samah.akriche@fsb.rnu.tn

and IR analysis of a new organic cation diphosphate, [4-$CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$.

RESULTS AND DISCUSSION

Crystal Structure

The atomic arrangement could be described by layers of diphosphate anions and water molecules, which are developed around the x = n/2 planes. The organic cations are anchored through multiple H-bonds between these layers (Figure 1). The final atomic coordinates of this structure are given in Table I.

The diphosphate group consists of two symmetric tetrahedra PO_4 with the bridging oxygen atom O(L) located on the twofold axis. So the anion $P_2O_7^{4-}$ has a binary internal symmetry and built of only one independent PO_4 tetrahedron. This later with two organic groups and three water molecules forms the asymmetric unit.

The P_2O_7 groups are interconnected by hydrogen bonds originating from the water molecules O(W2) and O(W3) to form corrugated ribbons extending along the c-axis, with a period of two $[P_2O_7(H_2O)_4]^{4-}$ units. Two successive rows are linked by hydrogen bonds from the remaining O(W1) water molecule, so as to build two-dimensional layers of formula $[P_2O_7(H_2O)_6]_n^{4n-}$, which is parallel to the (b, c) planes (Figure 2). The organic groups are located between these layers by establishing hydrogen bonds to contribute in the stability and the cohesion of the three-dimensional network.

In this atomic arrangement, there are multiple hydrogen bonds originating from the three water molecules and the NH_3^+ and CH_3O groups of the organic cations, as it is shown in Table II. Only 6 of them originate from the water molecules. It is worth noticing that the three independent water molecules do not have the same neighboring environment. Indeed, the O(W2) water molecule has a tetrahedral coordination since it accepts two hydrogen bonds, one from N(2)—H(3) and the other from O(W3)—H(1), while the two other water molecules O(W1) and O(W3) have a trigonal coordination where they accept one hydrogen bond from the hydrogen atom of the NH_3^+ groups.

Among the 6 hydrogen bonds involving the hydrogen atoms of $N(1)H_3^+$ and $N(2)H_3^+$ groups, two of them, which are implying the two external oxygen atoms O(E2) and O(E3) of the diphosphate group, are medium. The four other hydrogen bonds with D···A distances grater than 2.75 Å are relatively weak.

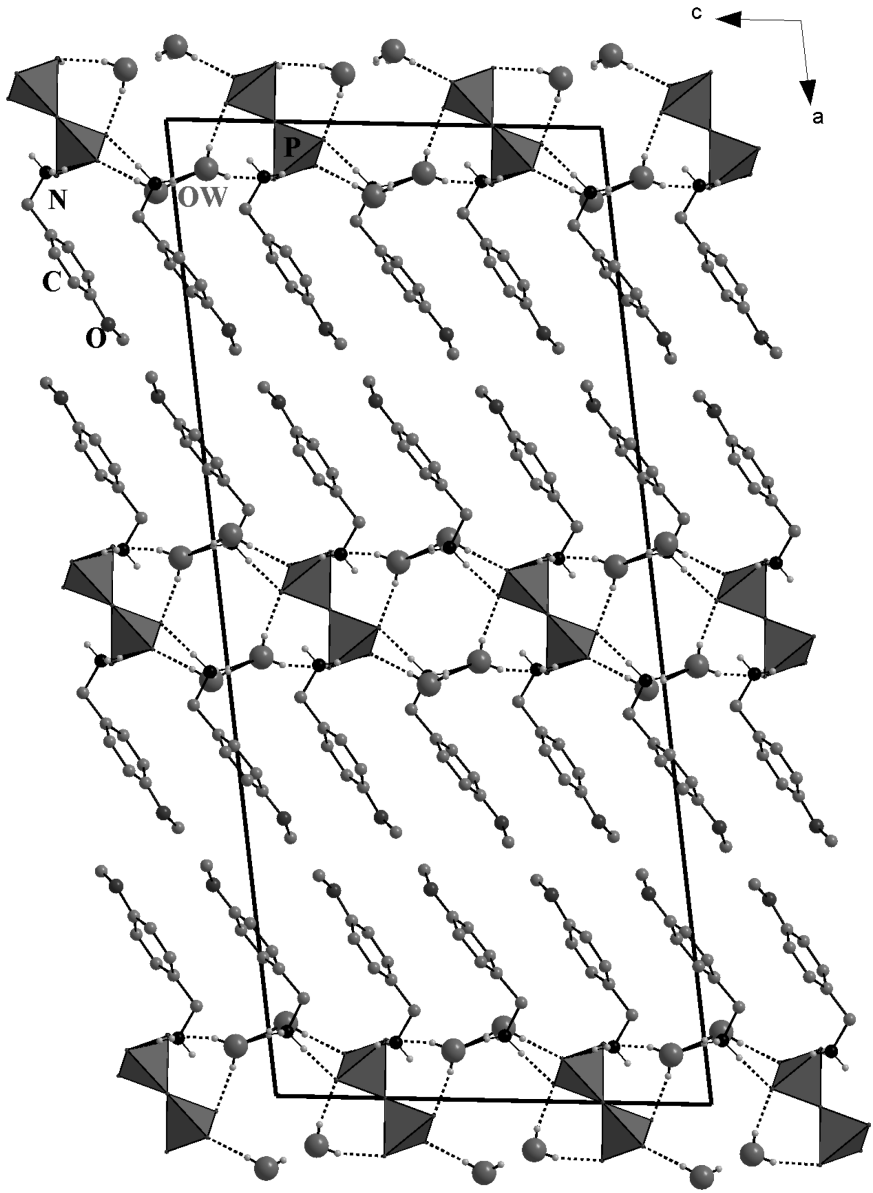

FIGURE 1 The arrangement of [4-$CH_3OC_6H_4CH_2NH_3$]$_4P_2O_7$·6H_2O in projection along the *b* axis. P_2O_7 groups are represented by tetrahedral representation. Hydrogen bonds are indicated by dotted lines.

TABLE I Final Atomic Coordinates and $B_{éq}$ for the Non–Hydrogen Atoms. Esds are Given in Parentheses

Atoms	x (σ)	y (σ)	z (σ)	Béq · (Å^2)
P(1)	0.468023(12)	0.99064(8)	0.79497(3)	2.197(8)
O(E1)	0.45598(3)	0.7937(2)	0.83109(7)	2.87(3)
O(E2)	0.44041(3)	1.0824(2)	0.73347(8)	3.06(3)
O(L)	0.5000	0.9096(3)	0.7500	2.66(4)
O(E3)	0.48256(3)	1.1459(2)	0.85710(8)	3.19(3)
O(W1)	0.51095(4)	0.5515(3)	0.90293(12)	6.27(5)
O(W2)	0.55015(4)	1.0609(2)	0.91985(8)	3.66(3)
O(W3)	0.42528(4)	0.6641(2)	0.95869(9)	3.54(3)
O(N1)	0.28809(4)	0.5017(3)	0.81393(12)	6.71(5)
O(N2)	0.28478(4)	0.8269(3)	0.59001(10)	5.70(4)
N(1)	0.44282(5)	0.5017(3)	0.71053(10)	3.53(4)
N(2)	0.43380(4)	0.7643(3)	0.45827(10)	3.06(4)
C(1)	0.40965(7)	0.5588(4)	0.66001(13)	4.31(6)
C(2)	0.37843(6)	0.5450(3)	0.70501(12)	3.65(5)
C(3)	0.36678(6)	0.7156(4)	0.74167(14)	4.40(6)
C(4)	0.33703(7)	0.7084(4)	0.78001(16)	5.03(6)
C(5)	0.31858(6)	0.5260(4)	0.78077(14)	4.83(6)
C(6)	0.33051(7)	0.3524(4)	0.74593(16)	4.94(6)
C(7)	0.36019(6)	0.3620(4)	0.70882(14)	4.35(6)
C(8)	0.27304(9)	0.6824(7)	0.8440(2)	8.25(10)
C(9)	0.39932(6)	0.8186(4)	0.41164(13)	3.77(5)
C(10)	0.36941(5)	0.8135(3)	0.46092(12)	3.26(5)
C(11)	0.35832(6)	0.9934(4)	0.49409(15)	4.57(5)
C(12)	0.33053(6)	0.9904(4)	0.53755(16)	4.96(6)
C(13)	0.31278(5)	0.8103(4)	0.54758(13)	4.00(5)
C(14)	0.32343(6)	0.6304(4)	0.51564(14)	4.13(5)
C(15)	0.35175(6)	0.6347(4)	0.47229(13)	3.88(5)
C(16)	0.26516(7)	0.6468(6)	0.60012(18)	6.47(8)

The main geometrical features of the different entities are assigned in Table III. The average values of the basic parameters, the P—O distances, and O—P—O angles of the diphosphate group are 1.533 Å and 109.35°. The condensed parameters and P—P distance is 3.047(2) Å, and the P—O—P angle 142.1(2)°. All these distances and angles are quite similar to those measured in the diphosphate anion with the C_2 internal symmetry.[4–6]

The calculated average value of the distortion indices[7] corresponding to the different angles and distances in the independent PO_4 tetrahedron, DI(PO) = 0.0258, DI(OPO) = 0.0297, and ID(OO) = 0.0094 show an above distortion of the P—O distances compared to O—O distances. The PO_4 tetrahedron is thus described by a regular oxygen atom

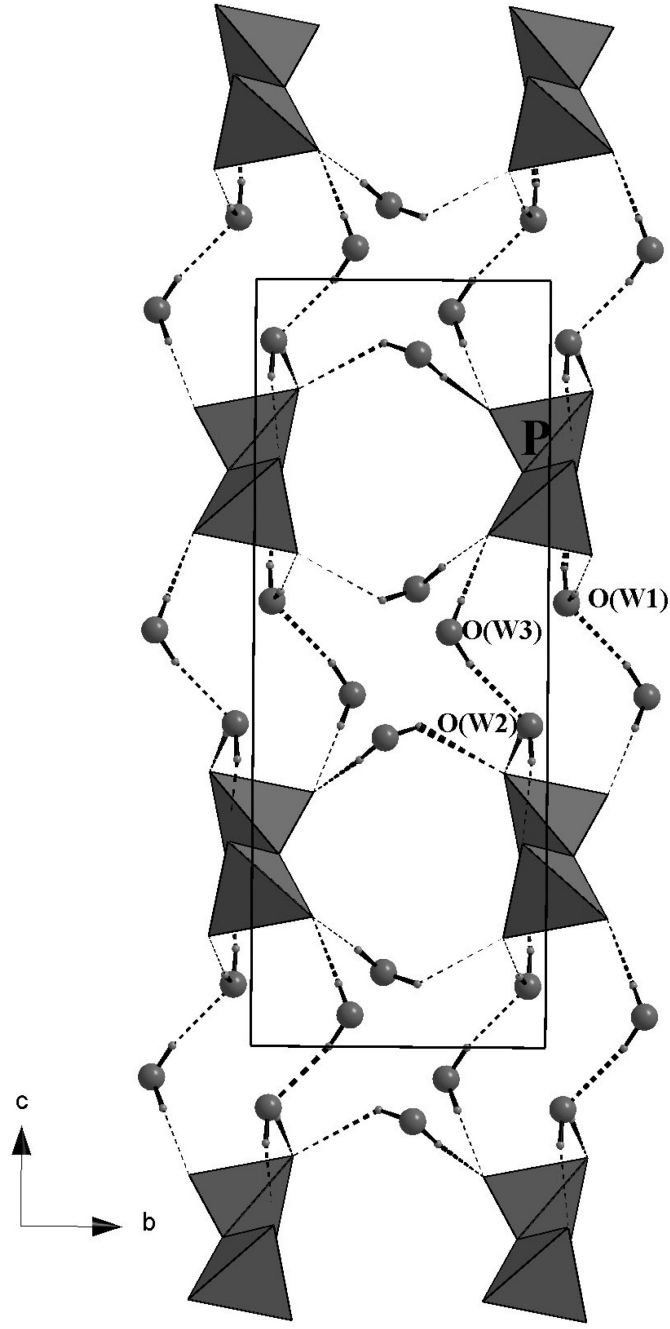

FIGURE 2 Projection along the *a* axis of the inorganic layer in the structure of [4-$CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$.

TABLE II Hydrogen-Bond Scheme in $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$

D—H···A	D···A(Å)	D—H(Å)	H···A(Å)	D—H···A(°)
O(W1)-H(1w1)···O(E3)	2.769(3)	0.96(2)	1.82(2)	171(2)
O(W1)-H(2W1)···O(E1)	2.900(3)	0.91(3)	2.19(3)	134(2)
O(W2)-H(1W2)···O(E3)	2.717(2)	0.85(4)	1.88(4)	167(4)
O(W2)-H(2W2)···O(E2)	2.673(3)	0.87(3)	1.83(3)	161(2)
O(W3)-H(1W3)···O(W2)	2.785(3)	0.86(3)	1.94(3)	168(3)
O(W3)-H(2W3)···O(E1)	2.724(2)	0.88(3)	1.84(3)	176(2)
N1-H(1N1)···O(W1)	2.797(3)	0.84(2)	1.97(2)	167(2)
N1-H(2N1)···O(E2)	2.737(3)	0.94(3)	1.81(3)	169(2)
N1-H(3N1)···O(E1)	2.775(3)	0.88(2)	1.91(3)	168(2)
N2-H(1N2)···O(E3)	2.756(3)	0.95(2)	1.81(2)	174(2)
N2-H(2N2)···O(W3)	2.784(3)	1.01(3)	1.83(3)	157(3)
N2-H(3N2)···O(W2)	2.823(3)	0.88(2)	1.96(2)	168(2)

arrangement with the phosphorus atom slightly shifted from the gravity center of PO_4 (δ P = 0.074).

The interatomic distances N—C and C—C and angles N—C—C, C—C—C, and C—C—O range respectively from 1.365 Å to 1.502(4) Å and 111.8(2)° to 124.8(3)°. They are comparable to those observed in other organic cation diphosphates.[8] The two arene rings (A_1: C_2—C_7, A_2: C_{10}—C_{15}) of the two independent organic cations are slightly deviated with respectively mean plane deviations of 0.0092°and 0.0042°, but they do not have a similar orientation since they form a dihedral angle of 5.32° between A_1 and A_2.

Infrared Spectroscopy

The infrared spectrum of $4\text{-}(CH_3O)C_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$ is recorded in the range 4000–400 cm^{-1} (Figure 3). This diphosphate, which crystallizes in the monoclinic system C2/c (C^6_{2h}), exhibits 4 P_2O_7 groups per unit cell. The P_2O_7 group with a bent geometry (P—O—P = 142.1(2)°) has a binary internal symmetry C_2.

Theoretical vibrational studies of X_2O_7 (X = P; S; Si) groups with an ideal D_{3h} symmetry[9] show 21 normal modes of vibration of the free ion group, given by the following representation: $\Gamma(\text{vib}) = 3A'_1 + 4E' + A''_1 + 3A''_2 + 3E''$.

The correlation between free ion group D_{3h}, the site group C_2, and the factor group C_{2h} show 21 × 2 modes active in Raman (11Ag + 10Bg) and in IR (11Au + 10Bu). The 21 modes that are active in IR of the P_2O_7 group with a bent configuration are distributed in 6 stretching modes and 11 bending modes for the PO_3 terminal groups and 2 stretching

TABLE III Main Interatomic Distances (Å) and Bond angles (°) in the Inorganic and Organic Entities of the $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$. Esd Are Given in Parentheses

P(1)	O(E1)	O(E2)	O(E3)	O(L)
		The PO_4 Tetrahedron		
O(E1)	1.509(2)	2.510(2)	2.505(3)	2.427(2)
O(E2)	112.88(9)	1.503(2)	2.502(2)	2.519(2)
O(E3)	112.42(9)	112.52(10)	1.505(2)	2.527(2)
O(L)	102.10(10)	107.91(8)	108.28(8)	1.611(1)
P—P = 3.047(2)Å		P—O(L)—P = 142.1(2)°		
		$[4\text{-}(CH_3O)C_6H_4CH_2N(1)H_3]^+$ group		
C(1)-N(1)	1.480(3)	N(1)-C(1)-C(2)		111.7(2)
C(1)-C(2)	1.502(4)	C(1)-C(2)-C(3)		120.8(3)
C(2)-C(3)	1.367(4)	C(2)-C(3)-C(4)		121.6(3)
C(2)-C(7)	1.378(4)	C(3)-C(4)-C(5)		119.2(3)
C(3)-C(4)	1.383(4)	C(4)-C(5)-C(6)		119.7(3)
C(4)-C(5)	1.373(4)	C(4)-C(5)-O(N1)		124.6(3)
C(5)-C(6)	1.372(4)	C(6)-C(5)-O(N1)		115.7(3)
C(5)-O(N1)	1.368(3)	C(5)-O(N1)-C(8)		117.4(3)
C(6)-C(7)	1.370(4)	C(5)-C(6)-C(7)		120.2(3)
O(N1)-C(8)	1.424(5)	C(6)-C(7)-C(2)		121.1(3)
		C(7)-C(2)-C(1)		121.1(3)
		$[4\text{-}(CH_3O)C_6H_4CH_2N(2)H_3]^+$ group		
C(9)-N(2)	1.487(3)	N(2)-C(9)-C(10)		112.7(2)
C(9)-C(10)	1.503(4)	C(9)-C(10)-C(11)		120.3(2)
C(10)-C(11)	1.381(4)	C(10)-C(11)-C(12)		120.6(3)
C(11)-C(12)	1.371(4)	C(11)-C(12)-C(13)		120.8(3)
C(12)-C(13)	1.367(4)	C(13)-C(14)-C(15)		119.2(3)
C(13)-C(14)	1.366(4)	C(12)-C(13)-C(14)		119.6(3)
C(14)-C(15)	1.387(4)	C(15)-C(10)-C(11)		118.0(2)
C(15)-C(10)	1.363(4)	C(15)-C(10)-C(9)		121.6(2)
C(13)-O(N2)	1.370(3)	C(12)-C(13)-O(N2)		115.7(3)
O(N2)-C(16)	1.406(4)	C(14)-C(13)-O(N2)		124.7(3)
		C(13)-O(N2)-C(16)		117.8(3)

modes and 2 bending modes for the POP bridge group. According to the literature, the bridge POP stretching vibration lays at wave numbers lower than the PO_3 stretching ones.[10] In fact, the bands observed between 1116 and 1023 cm^{-1} are attributed to the stretching symmetric and asymmetric modes of the POP group. Those ranging from 1292 to 1081 cm^{-1} and from 600 to 400 cm^{-1} correspond respectively to asymmetric stretching and bending modes of the terminal PO_3 group [11]. In the domain 600–400 cm^{-1}, the number of observed vibrational modes is less than the one predicted by factor group analysis; apparently some of the bands are overlapped or too weak to be observed.

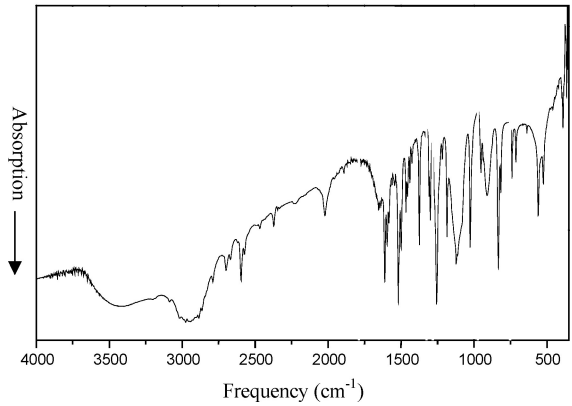

FIGURE 3 The IR spectrum of $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$.

Supplementary bands in the domain of the POP bridge group and PO_3 terminal group are attributed to the stretching modes of C(O,N)—C and those bending of C_{aryl}—H and C=C.[12] The wide bands, between 3400–2800 cm^{-1}, are attributed to the bending vibrations of $-NH_3^+$ $-CH_3$ $-CH_2$ and O(W)—H groups of the organic and water molecules.

Thermal Analysis

The DTA and TGA curves are given for the $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$ (Figure 4). The DTA curve shows two endothermic peaks at

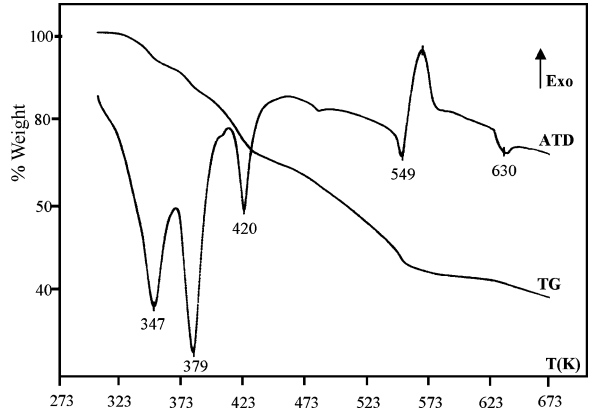

FIGURE 4 DTA and TGA curves of $[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$ at a rising temperature.

347 and 379 K, which correspond to the departure of 6 water molecules well confirmed by the weight loss observed in the TGA curve (% experimental, 13.23%; calculated, 12.94%). The series of peaks that appear in a wide temperature range (400–673 K) can be assigned to the degradation of the obtained anhydrous compound since this phenomenon is accompanied by a significant weight loss observed on the TGA curve and gives a viscous substance contaminated by a residue of black carbon.

EXPERIMENTAL

Chemical Preparation

$[4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7{\cdot}6H_2O$ was prepared by slowly adding 1.2 mL of pure 4-methoxybenzylamine (d = 1.05) diluted in 3 mL of ethanol, to 20 mL of a diphosphoric acid solution containing 2.25 mmol of $H_4P_2O_7$. Schematically, the products reacted according to the following equation:

$$4\,(4\text{-}CH_3OC_6H_4CH_2NH_2) + H_4P_2O_7 + 6H_2O \longrightarrow [4\text{-}CH_3OC_6H_4CH_2NH_3]_4P_2O_7 \cdot 6H_2O \quad (1)$$

In order to avoid hydrolysis of the diphosphoric acid, the reaction in Eq. (1) should be performed at a low temperature. Prismatic crystals of the title compound grew as the water evaporated over the course of a few days.

The diphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_4P_2O_7.10H_2O$ (0.05 g/mL) passed through an ion-exchange resin (Amberlite IR 120).

This compound has been studied using different techniques with the experimental conditions described in the following section.

Investigation Techniques

X-Ray Diffraction

X-ray intensity data was collected on a Mach3 Enraf-Nonius diffractometer operating with silver radiation (AgK$\bar{\alpha}$ = 0.5608 Å). The unit cell dimensions were measured and refined using a set of 25 reflections with $7^\circ < \theta g\ 10^\circ$. The X-ray diffraction study showed that the space group was centro-symmetric C2/c. The crystal structure was solved using the direct method with the program SIR92[13] and refined on F by the full-matrix least-squares method using the teXsan[14] program. All non–hydrogen atoms were refined with anisotropic thermal parameters. The final cycle of the least-squares refinement, including 369 parameters,

TABLE IV Crystal Data and Experimental Parameters Used for the Intensity Measurements

Empirical formula	$[4\text{-}CH_3OC_6H_4CH_2NH_3]_4\ P_2O_7{\cdot}6H_2O$
Formula weight	834.79
Crystal system	Monoclinic
Space group	C2/c
a	38.238(6)
b	6.453(1)
c	16.942(7) Å
β	97.60(4)°
Z	4
V	4143.7(2) $Å^3$
ρ_{cal}	1.338 $g{\cdot}cm^{-3}$
F(000)	1784
μ (AgK$\overline{\alpha}$)	1.008 cm^{-1}
Measurement area: ±h, k, l	$h_{max} = 56$, $k_{max} = 9$, $l_{max} = 25$
Collected unique reflections (Rint = 0.03)	7978
Unique reflections included [$I > 3\sigma(I)$]	2692 with
Refined parameters	369
R	0.044
Rw	0.047
Goodness of fit	1.39

lead to reliability factors R = 0.044 and wR = 0.047. The crystal data, the parameters used for X-ray data collection, and the structure determination results are reported in Table IV.

Crystallographic data (CIF) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 275117. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, U (Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

Thermal Analysis

Thermal analysis was performed using the multimodule 92 Setaram' analyzer operating from r.t up to 673 k in following argon at an average heating rate of 5 k/min for DTA and TGA.

Infrared Spectroscopy

Infrared spectrum was recorded using a Perkin-Elmer Spectrum 1000 spectrophotometer. The sample was dispersed in a KBr pellet and the scanning was performed in the 4000–400 cm^{-1} spectral domain.

REFERENCES

[1] M. T. Averbuch-Pouchot and A. Durif, *Topics in Phosphate Chemistry*, (World Scientific Publication, 1996).
[2] J. Pecaut, Y. Le Fur, and R. Masse, *Acta. Cryst*, **B49,** 535 (1993).
[3] R. Ittyachan and P. Sagayaraj, *J. Crytal Growth*, **243,** 356 (2002).
[4] M. T. Averbuch-Pouchot and A. Durif, *Eur. J. Solid State Inorg. Chem.*, **29,** 993 (1992).
[5] S. Kamoun, A. Jouini, and A. Daoud, *J. Solid State Chem.*, **99,** 18 (1992).
[6] M. Charfi and A. Jouini, *Acta Cryst*, **C53,** 463 (1997).
[7] W. Baur, *Acta Cryst.*, **B30,** 1195 (1974).
[8] H. Hemissi, S. Abid, and M. Rzaigui, *Z. Kristallogr.*, **NCS 220,** 265 (2005).
[9] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, (New York: John Wiley, 1963).
[10] M. Harcharras, A. Ennaciri, A. Rulmont, and B. Gilbert, *Spectrochim. Acta*, **A53,** 345 (1997).
[11] M. Harcharras, A. Ennaciri, H. Assaaoudi, G. Mattei, V. D'orazio, and A. G. G. Moliterni, *J. Solid State Chem.*, **172,** 160 (2003).
[12] R. M. Silverstein, G. C. Bassler,and T. C. Morrill *Spectrometric Identification of Organic Compounds*, 3rd ed., (Wiley, New York, 1974).
[13] A. Altomare, M. Cscarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst*, **26,** 343 (1993).
[14] teXsan for Windows (version 1.03), Molecular Structure Corporation, Single Crystal, Structure Analysis Software, The Woodlands, TX (1997).