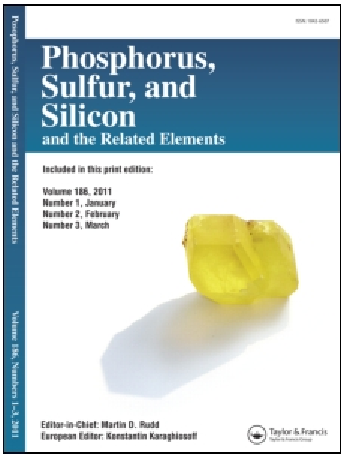


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Structural Characterization of an Adduct Cyclotetraphosphate

Z. Aloui[a]; S. Abid[a]; M. Rzaigui[a]
[a] Laboratoire de Chimie des Matériaux, Faculté des Sciences, Zarzouna, Bizerte, Tunisia

To cite this Article Aloui, Z. , Abid, S. and Rzaigui, M.(2007) 'Synthesis and Structural Characterization of an Adduct Cyclotetraphosphate', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 11, 2637 — 2646

To link to this Article: DOI: 10.1080/10426500701518130

URL: http://dx.doi.org/10.1080/10426500701518130

Phosphorus, Sulfur, and Silicon, 182:2637–2646, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701518130

Synthesis and Structural Characterization of an Adduct Cyclotetraphosphate

Z. Aloui
S. Abid
M. Rzaigui
Laboratoire de Chimie des Matériaux, Faculté des Sciences, Zarzouna, Bizerte, Tunisia

Few adduct monophosphates are identified and characterized whereas adduct cyclotetraphosphates remains uninvestigated. Their richness into H-bonds constitutes one of the explanatory factors of their peculiar physicochemical properties. In this article, crystals of a new adduct compound, the 4-Methoxybenzylammonium cyclotetraphosphate monophosphoric acid dihydrate $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$*, have been prepared and characterized by X-ray diffraction, thermal behavior, and IR analysis. This compound is triclinic* $P\bar{1}$ *with the following unit-cell dimensions:* $a = 8.115(7)$, $b = 9.997(2)$, $c = 15.180(9)$ Å, $\alpha = 94.36(3)$, $\beta = 104.30(5)$, $\gamma = 92.73(3)^\circ$, $V = 1187.0\ (1)$ Å^3*, and* $Z = 1$*. Crystal structure has been determined and refined to* $R = 0.035$ *using 5219 independent reflexions. This structure can be described as inorganic layers parallel to the ab planes, built up of* P_4O_{12} *rings,* H_3PO_4 *monophosphoric acid and water molecules. Between these layers the 4-methoxybenzylammonium cations are located.*

Keywords Crystal structure; cyclotetraphosphate; infrared spectroscopy; thermal analysis.

INTRODUCTION

The design, synthesis and structural characterization of hybrid materials, for which many applications can be predicted, through the assembly of organic and inorganic building blocks, are a highly visible in research areas.[1] The construction of such organic-inorganic hybrid compounds has established new areas of research in the chemistry of materials that is based upon a bridge between organic and inorganic chemistry and is useful in order to obtain multifunctional materials which exhibit coexistence of solid-state magnetic, electric and/or optical properties.[2] As a

Received March 24, 2007; accepted May 4, 2007

Address correspondence to S. Abid, Laboratoire de Chimie des Matériaux, Faculté des Sciences, 7021 Zarzouna, Bizerte, Tunisia. E-mail: sonia.abid@fsb.rnu.tn

contribution to the elaboration of these hybrid compounds, we report in the present investigation synthesis, crystal structure, thermal behavior, and results of a spectroscopy study of the first organic-inorganic hybrid adduct compound $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$.

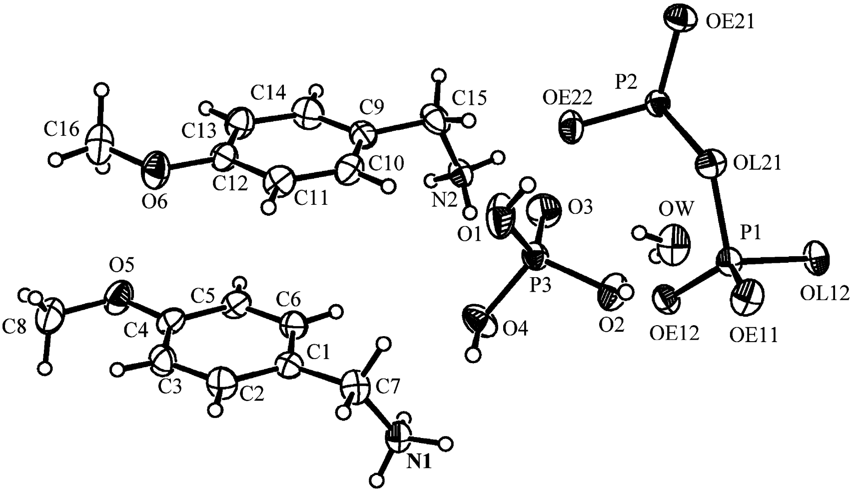
RESULTS AND DISCUSSION

X-ray Crystal Structure

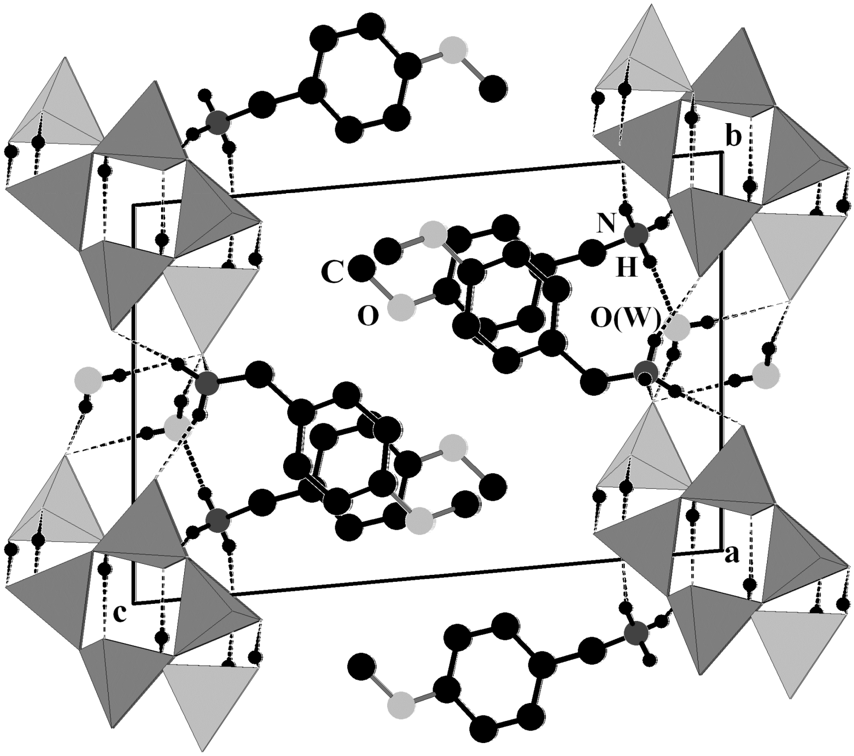
An ORTEP drawing (Figure 1) shows the asymmetric unit of molecular structure containing two independent PO_4 tetrahedral, H_3PO_4 molecule, two crystallographically distinct organic groups 4-methoxybenzylammonium, and one water molecule.

The atomic arrangement of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$ can be described as layers of the inorganic entities parallel to the ab planes. Between these inorganic layers are located the organic groups forming H-bonds (Figure 2). Inside such a layer, the $(P_4O_{12})^{4-}$ ring anion alternates with the H_3PO_4 groups to form, via strong H-bonds ribbons running along the [100] direction. These ribbons are themselves linked by the water molecules OW through H-bonds to form a thick inorganic layer parallel to the ab planes.

The cyclic anion $(P_4O_{12})^{4-}$ is formed by four PO_4 tetrahedra sharing oxygen corners. It is centrosymmetrical with –1 internal symmetry and exhibits only two independent PO_4 tetrahedra. The main interatomic



SCHEME 1 ORTEP drawing of the asymmetric unit cell of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$. Probability 45%.



SCHEME 2 Projection along the a axis of the atomic arrangement of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$. The phosphoric anion is given in polyhedral representation. Hydrogen bonds are denoted by dotted lines.

distances and bond angles for the two independent tetrahedra are given in Table I; this ring anion presents a strong distortion as shown by the P-P-P angle values of 82.17(4) and 97.38(4)°. This distortion is comparable with that observed in $C_{10}H_{28}N_4P_4O_{12}.4H_2O$,[3] which shows the greatest distortion for the same angles P-P-P (80.24(5)–99.76(5)°) measured up to now. Furthermore, the P-O-P angle (131.98(7)–135.59(7)°) has an average of 133.785°, while the average value of the P-P (2.924(1)–2.962(2) Å) distances is 2.943 Å, correspond also to values generally observed in this ring.[4]

The monophosphoric acid molecule is connected to the external oxygen atoms of $(P_4O_{12})^{4-}$ anions through strong hydrogen bonds type O-H…OE to form a ribbon. This molecule is characterized by the P-O, O-O distances and HO-P-O, HO-P-OH angles (Table I). Their values are in agreement with those observed in other adduct monophosphate compounds.[5]

TABLE I Main Interatomic Distances (Å) and Bond Angles (°) in the Inorganic Entities of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$

		P(1)O_4 tetrahedron			
P(1)	OE11	OE12	OL12	OL21	
OE11	**1.470(1)**	2.552(2)	2.455(2)	2.483(2)	
OE12	119.84(6)	**1.480(2)**	2.534(3)	2.541(3)	
OL12	106.12(6)	110.63(7)	**1.601(2)**	2.464(2)	
OL21	107.43(7)	110.65(8)	100.32(8)	**1.608(2)**	
		P(2)O_4 tetrahedron			
P(2)	OE21	OE22	OL12	OL21	
OE21	**1.487(2)**	2.550(3)	2.543(2)	2.456(2)	
OE22	118.99(6)	**1.472(2)**	2.443(2)	2.530(2)	
OL12	110.95(7)	105.35(7)	**1.598(1)**	2.507(1)	
OL21	105.77(7)	111.22(7)	103.57(6)	**1.592(1)**	
P1-P2	2.924(1)	P1-P2-P1	82.17(4)	P2-OL21-P1	131.98(7)
P2-P1	2.962(2)	P2-P1-P2	97.83(4)	P2-OL12-P1	135.59(7)
		P(3)O_4 tetrahedron			
P(3)	O(1)	O(2)	O(3)	O(4)	
O(1)	**1.525(2)**	2.496(2)	2.552(2)	2.448(2)	
O(2)	109.09(8)	**1.539(1)**	2.463(2)	2.499(3)	
O(3)	116.69(9)	109.68(8)	**1.473(2)**	2.437(2)	
O(4)	105.53(9)	108.02(9)	107.44(8)	**1.550(2)**	
O(1) — H(4)	0.80(2)	H(3) — O(4) — P(3)	112.3(2)		
O(2) — H(5)	0.71(2)	H(4) — O(1) — P(3)	117.9(2)		
O(4) — H(3)	0.90(2)	H(5) — O(2) — P(3)	118.7(2)		

Estimated standard deviations are given in parentheses.

The two independent organic groups are located in the space delimited by successive inorganic layers to achieve the charge neutrality. Interatomic bond lengths and angles of these groups spread within the respective ranges of 1.371(2)–1.498(2) Å and 105.2(2) – 124.6(2)° (Table II). These values are almost similar to those obtained in other organic phosphates associated to the same organic groups.[6] Their phenyl rings are planar, with a mean plane deviation of 0.0033 Å and are parallel with a dihedral angle of 0.59°. The inter planer distance between the aryl rings is 3.78 Å, indicating the existence of $\pi - \pi$ interactions,[7] in addition to the Van der Waals ones.

The water molecules, H_3PO_4 monophosphoric acid molecule, and 4-methoxybenzylammonium cations participate in the H-bonding scheme (Table III). Three types of hydrogen bonds occur in this atomic arrangement:

1) OH...OE involving 3 short contacts with H...O distances, in the range 1.71(2) to 1.86(2) Å, perform the cohesion between P_4O_{12} rings to form a ribbon;

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in Organic Groups of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$

$C_8H_{12}ON(1)^+$			
N1-C7	1.487(3)	N1-C7-C1	112.0(1)
C7-C1	1.498(2)	C7-C1-C2	121.0(2)
C1-C2	1.374(2)	C7-C1-C6	120.9(2)
C2-C3	1.379(3)	C1-C2-C3	121.7(2)
C3-C4	1.375(2)	C2-C3-C4	119.5(2)
C4-C5	1.381(2)	C3-C4-C5	119.6(2)
C4-O12	1.363(2)	C3-C4-O12	124.5(2)
C5-C6	1.371(2)	C4-C5-C6	120.2(2)
C6-C1	1.385(2)	C5-C6-C1	121.0(2)
C8-O12	1.416(3)	C5-C4-O12	115.9(2)
		C4-O12-C8	117.4(2)
		C6-C1-C2	118.0(2)
		H1N1-N1-H2N1	105.3(2)
		H1N1-N1-H3N1	110.6(2)
		H2N1-N1-H3N1	105.2(2)
$C_8H_{12}ON(2)^+$			
N2-C15	1.496(3)	N2-C15-C9	111.9(2)
C15-C9	1.496(3)	C15-C9-C10	122.1(2)
C16-O13	1.413(3)	C15-C9-C14	119.9(2)
C9-C10	1.384(2)	C9-C10-C11	121.0(2)
C9-C14	1.372(3)	C10-C11-C12	120.0(2)
C10-C11	1.373(3)	C11-C12-C13	119.7(2)
C11-C12	1.383(2)	C11-C12-O13	115.7(2)
C12-C13	1.374(2)	C12-C13-C14	119.4(2)
C12-O13	1.362(2)	C13-C14-C9	121.9(2)
C13-C14	1.377(3)	C13-C12-O13	124.6(2)
		C14-C9-C10	118.0(2)
		C12-O13-C16	117.7(2)
		H1N2-N2-H2N2	109.1(2)
		H1N2-N2-H3N2	108.1(2)
		H2N2-N1-H3N2	110.7(2)

Estimated standard deviations are given in parentheses.

2) OW-H...O including 2 relatively weak contacts with H...O distances ranging from 2.13(2) to 2.26(3) Å, connect the different ribbons to form a layer; and
3) N-H...O bonds are formed by 6 relatively weak contacts, since the H...O distances ranging from 1.91(2) to 2.06(2) Å connect the organic cation and inorganic layers.

These different interactions (hydrogen bonds, Van der Waals, π-π stacking, and electrostatic between organic cations and phosphate

TABLE III Bond Lengths (Å) and Bond Angles (°) in the Hydrogen Bonding Scheme of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$

D-H. . . A	D-H (Å)	H. . . A (Å)	D...A (Å)	D-H. . . A (°)
O(1)-H4....OE22	0.80(2)	1.72(2)	2.498(3)	162(2)
O(2)-H5...OE12	0.71(2)	1.86(2)	2.560(2)	175(2)
O(4)-H3. . . OE21	0.90(2)	1.71(2)	2.594(2)	169(2)
O(W)-H1W. . . O3	0.78(2)	2.13(2)	2.903(3)	174(2)
O(W)-H2W...O3	0.84(3)	2.26(3)	2.903(9)	159(2)
N1-H1N1. . . OE11	0.95(2)	1.94(2)	2.882(3)	169(2)
N1-H2N1...OE11	0.83(2)	2.00(2)	2.767(2)	151(2)
N1-H3N1....O3	0.93(2)	1.91(2)	2.832(3)	170(2)
N2-H1N1...OW	0.89(2)	1.94(2)	2.822(2)	171(2)
N2-H2N2. . . OE21	0.88(2)	2.02(2)	2.874(2)	165(2)
N2-H3N2. . . OE12	0.86(2)	2.06(2)	2.870(3)	155(2)
	H1W-O(W)-H2W		102.5(2)	

Estimated standard deviations are given in parentheses.

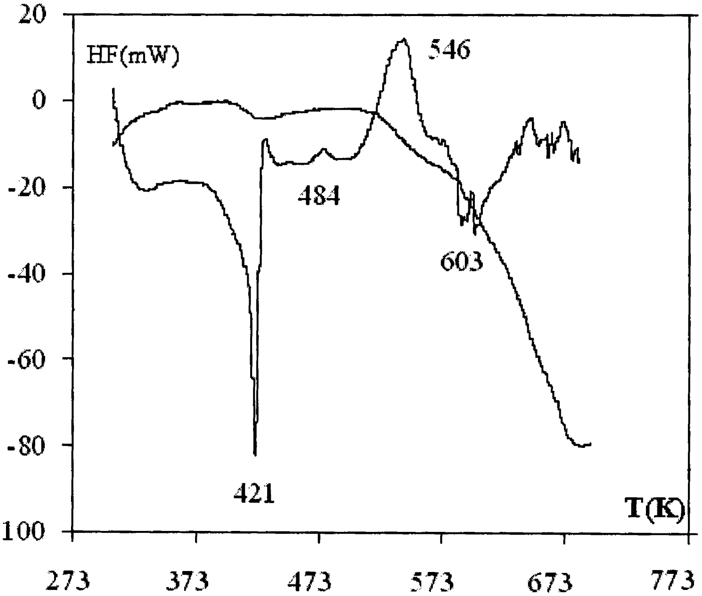
anions) contribute to the cohesion and the stability of the three-dimensional network.

Thermal Behavior

The two curves corresponding to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are given in Figure 3. The DTA curve shows that the cyclotetraphosphate undergoes a series of thermal phenomenous. The first one, at 421 K is accompanied with a weight loss obviously observed by TGA. From the latter, we deduce a departure of the crystallization H_2O molecule (weight loss calculated: 3.27%, experimental: 3.00%). The exothermic peak at 484 K, without weight loss on the TGA curve, can be assigned to the crystallization of anhydrous phase. The last peaks between 523 and 673 K could be assigned to a degradation of the crystallized phase which is confirmed by a significant weight loss (TGA curve). This degradation gives a viscous substance of polyphosphoric acids contaminated with a carbon black deposit.

IR Spectroscopy

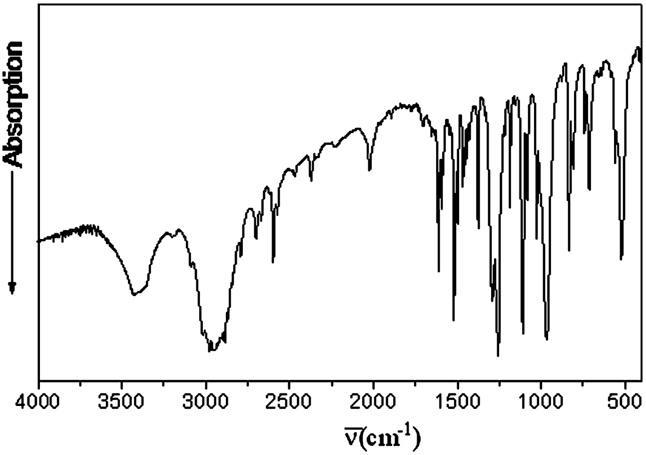
The bands observed in the infrared spectrum (Figure 4) of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$ are tentatively assigned according to the literature. The $(P_4O_{12})^{4-}$ anion exhibits almost all the characteristic bands observed in similar compounds [8–10]. Indeed, the



SCHEME 3 DTA and TGA thermograms of the title compound at rising temperature.

stretching vibrations $\nu_{as}(OPO^-)$, $\nu_s(OPO^-)$, $\nu_{as}(POP)$ and $\nu_s(POP)$ are, respectively, observed in the range 1350–1180, 1180–1060, 1060–950 , and 850–660 cm^{-1}. Those below 660 cm^{-1} correspond to bending of the P_4O_{12} ring. Various valences and bending vibration bands whose number and positions, between 1200 and 350 cm^{-1}, are both characteristic of a monophosphate.[11] The PO_4 tetrahedra gives in IR two stretching vibrations, ν_s and ν_{as}, respectively, symmetric and asymmetric bands, which are observed in the 1200–1000 cm^{-1} and 1000–800 cm^{-1} ranges. The two bending vibrations δ_s and δ_{as} of the PO_4 tetrahedra are located in the 750–500 cm^{-1} and 500–350 cm^{-1} ranges.

For the organic cations, the high wavenumber part (3400–2800 cm^{-1}) corresponds to stretching vibrations of NH_3, CH_2, OH and aromatic C-H.[12,13] Symmetric and asymmetric bending vibrations of NH_3, C-C stretching vibrations of the aromatic ring and OH-bending vibrations appear in the range 1650–1400 cm^{-1}. The 1400–1090 cm^{-1} range corresponds to C-N, C-O-C vibrations and δ (C_{ary}-H) in plane bending mode of the aromatic ring but $\delta(C_{ar}$-H) out of plane appear in 900–675 cm^{-1} range.[14]



SCHEME 4 IR spectra of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$.

EXPERIMENTAL

Synthesis of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$

Single crystals of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$ have been prepared by slowly adding cyclotetraphosphoric acid (8.2 mmol) to an ethanolic solution of 4-methoxybenzylamine (21.38 mmol in 10 mL of ethanol). This acid is freshly prepared by adding a stoechiometric amount of phosphorus pentoxyde (2 g, 16.4 mmol) to ice water kept at low temperature. Schematically, the produced reactions are:

$$2P_4O_{10}+4H_2O \rightarrow 2H_4P_4O_{12}, \quad \text{and}$$

$$8[C_8H_{11}NO] + 3H_4P_4O_{12} + 8H_2O \rightarrow$$

$$2[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O. \qquad (1)$$

The obtained solution was then slowly evaporated. After some days 0.5 g (yield: 67%) of stable crystals with suitable dimensions for a crystallographic study. These crystals are stable in air under normal conditions of temperature and hygrometry.

3.2 Investigation Techniques

3.2.1 X- ray Diffraction

A single crystal of the title compound was selected with a polarizing microscope and measured by a Mach3 Enraf– Nonius diffractometer operating with silver radiation ($AgK\bar{\alpha} = 0.5608'$) for a structural determination. The structure was solved using the direct methods and refined by a full–matrix least–squares technique.[15] 8737 reflections were collected and omission of intensity with $I > 3\sigma$ (I_{obs}) give 5219 observed reflections employed for analysis. The non–hydrogen atoms were refined with anisotropic thermal parameters. The parameters used for X-ray data collection, crystal structure determination, and final 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 CCDC 637244 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).

3.2.2.Physical Measurements

The IR spectrum was recorded in the range 4000–400 $cm^{-1}$with a "Perkin-Elmer Spectrum 1000" spectrophotometer, using samples dispersed in spectroscopically pure KBr pellet.

TABLE IV Crystal Data, Intensity Measurements and Refined Parameters of $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$

Empirical formula	$[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$
Formula weight	1098.65
Crystal system	Triclinic
Space group	$P\bar{1}$
a	8.115(7) (Å)
b	9.997(2) (Å)
c	15.180(9) (Å)
α	94.36(3)°
β	104.30(5)°
γ	92.73(3)°
Z	1
V	1187.0(**??**) $Å^3$
$\rho_{cal.}$	1.537 (g. cm^{-3})
F(000)	574
$\mu(AgK_\alpha)$	1.71 (cm^{-1})
Crystal size [mm]	0.60 × 0.50 × 0.20
Index ranges: ±h, ±k, l	$h_{max.} = 11$, $k_{max.} = 15$, $l_{max.} = 22$
Reflexions collected	8737
Independent reflexions	8462
R_{int}	0.018
Refined parameters	423
R [$I > 3\sigma(I)$]	0.035
$R_{(w)}$	0.038
Goodness of fit	1.8

Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operating from room temperature up to 673 K at an average heating rate of 3 K. min^{-1} in argon.

CONCLUSION

In this article, the first adduct cyclotetraphosphate $[C_8H_{12}NO]_4P_4O_{12}(H_3PO_4)_2.2H_2O$ is reported and characterized by X-ray diffraction, thermal behavior, and IR analysis. The packing of this hybrid compound shows moderate interlocking between the phosphate groups and the organic entities by a multidirectional hydrogen-bonding network and π-π interactions. Such interactions are known to exist in many systems of biological importance. We think that other adduct cyclotetraphosphates are possible to be synthesized under appropriate conditions. Further experiments should carried out to determine the influence of the main reaction parameters (temperature, pH, and concentration) in the synthesis of new adduct cyclotetraphosphate.

REFERENCES

[1] J. P. Hargmann, D. Hargmann, and J. Zubieta, *Angew. Chem. Int. Ed.,* **38,** 2638 (1999).

[2] F. Costantino, S. Midollini, A. Orlandini, and L. Sorace, Inorg. *Chem. Commun.,* **9,** 591 (2006).

[3] E. H. Soumhi, I. Saadoune, and A. Driss, *J. Solid State Chem.,* **156,** 364 (2001).

[4] M. T. Averbuch-Pouchot, and A. Durif, *Topics in Phosphate Chemistry* (World Scientific, New York, 1996).

[5] J. Zaccaro, M. Bagieu-Beucher, A. Ibanez, and R. Masse, *J. Solid State Chem.*, **124,** 8 (1996).

[6] H. Hemissi, S. Abid and M. Rzaigui, *Z. Kristallogr.*, **220,** 265 (2005).

[7] S. Chang-Wei, W. Chi-Phi, C. Jhy-Der, L. Lin-Shu, and W. Ju-Chun, *Inorg. Chem. Commun.*, **5,** 215 (2002).

[8] E. H. Soumhi, I. Saadoune, A. Driss, and T. Jouini, *J. Solid State Chem.,***144,** 318 (1999).

[9] Z. Aloui, S. Abid, and M. Rzaigui, *Mater Res Bull.*, **37,** 697 (2002).

[10] G. Foumakoye, R. Cahay, and P. Tarte, *Spectrochim Acta.*, **46A,** 1245 (1990).

[11] S. Kamoun, M. Kamoun, A. Daoud, and F. Romain, *Spectrochim. Acta.,* **47A,** 1051 (1991).

[12] Z. Aloui, S. Abid, and M. Rzaigui, *Mater Res Bull.*, **40,** 2056 (2005).

[13] B. Stuart, *Modern Infrared Spectroscopy* (John Wiley and Sons Ltd, Chichester, UK, 1996).

[14] R. M. Silverstein, G. C. Bassler, and T. C. Morill *Spectrometric Identification of Organic Compounds* (John Wiley and Sons, Inc.: New York, 1974), 3rd ed.

[15] texsan for Windows, version 1.03, Molecular Structure Corporation, Single Crystal, Structure Analysis Software, Version 1.03, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA (1997).