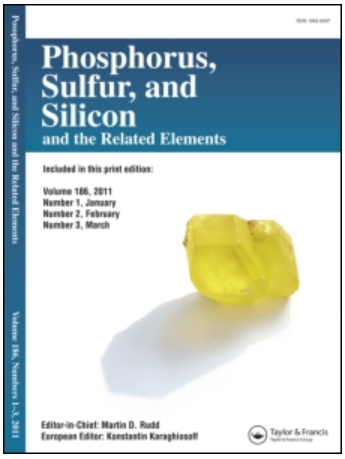

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Synthesis and Structure Characterization of Piperazine-1,4-diium Triphosphate

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SYNTHESIS AND STRUCTURE CHARACTERIZATION OF PIPERAZINE-1,4-DIIUM TRIPHOSPHATE

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$[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$, a new hydrate organic cation monohydrogeno-triphosphate, has been synthesized and characterized by X-ray diffraction, IR spectroscopy, mass angle spinning (MAS), NMR, and thermal analysis. The title compound crystallizes in a monoclinic unit cell with $a = 11.072(5)$, $b = 12.324(2)$, $c = 13.122(5)$ Å, $\beta = 93.85(5)^\circ$, $Z = 4$, $V = 1787(1)$ Å^3, and a noncentrosymmetric space group $P2_1$ (no. 4). Crystal structure is determined and refined to $R = 0.057$ using 4262 independent reflections. The atomic arrangement can be described as a typical layers organization. Layers built by $HP_3O_{10}^{4-}$ anions and water molecules are parallel to the (a, b) planes. Between these layers the piperazinium cations, which form hydrogen bonds with oxygen atoms of the triphosphate anion, are located.

Keywords: Crystal structure; NMR spectroscopy; triphosphate; X-ray diffraction

INTRODUCTION

Recently,[1] a molecular engineering strategy has been developed that aims at building very cohesive acentric crystalline structures for nonlinear optics based on the encapsulation of organic chromophores in inorganic host matrices. Short and multiple hydrogen-bonded networks observed in all these structures provide the crystalline materials with improved thermal, chemical, and mechanical stabilities compared with those observed in molecular compounds built up with the same chromophore. The main qualities required for nonlinear optical efficient crystal engineering are: high molecular first-order hyperpolarizability,

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optimal acentric packing[2] of nonlinear entities in the crystal structure, a wide range of spectral transparency (IR-UV), a high optical damage threshold, and easy crystal growth. In this work we report synthesis, crystal structure, thermal and infrared characteristics of a new hybrid organic inorganic compound, $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$.

RESULTS AND DISCUSSION

Crystal Structure

Structural determination shows that the title compound crystallizes in the monoclinic system with the noncentrosymmetric space group $P2_1$, which is confirmed by a positive second harmonic generation powder test observed on a sample illuminated by YAG Nd^{3+} laser radiation at 1.06 μm.

The final atomic coordinates of all nonhydrogen atoms of the title compound and their B equivalent temperature factors are given in Table I. Those of hydrogen atoms have also been determined but are not given to keep the table short.

The atomic arrangement of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$ can be described as typical inorganic layers, built by the $HP_3O_{10}^{4-}$ anions and the water molecules, parallel to the (a, b) planes, and centered at $z = 1/4$ and 3/4. Cohesion between these planes is established by H-bonds of the organic groups to assure a three-dimensional network. Figure 1 gives a

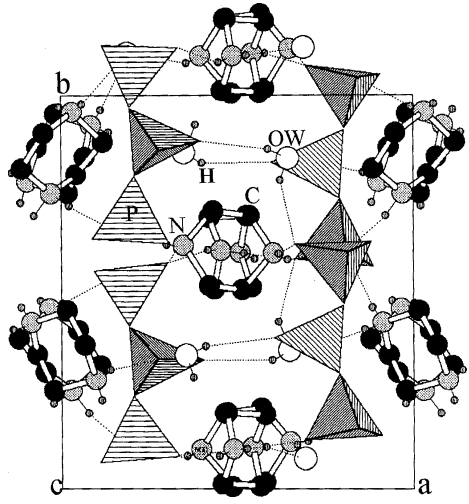

FIGURE 1 Projection of the structure of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$ along the c axis. The phosphoric anion is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines.

TABLE I Final Atomic Coordinates and $B_{eq.}$ ($Å^2$) for the Nonhydrogen Atoms

Atoms	x(σ)	y(σ)	z(σ)	Beq.
P(1)	−0.6915(2)	2.1729	0.5247(1)	2.07(4)
P(2)	−0.7824(2)	2.3762(2)	0.4560(2)	1.79(3)
P(3)	−0.7115(1)	2.5880(2)	0.51460(13)	1.78(3)
P(4)	−0.3095(2)	2.53233(9)	−0.0238(2)	1.90(3)
P(5)	−0.2170(2)	2.3285(2)	0.0461(2)	2.07(3)
P(6)	−0.2886(1)	2.1159(2)	−0.0150(1)	1.77(3)
O(1)	−0.6574(5)	2.1594(4)	0.6401(4)	2.74(10)
O(2)	−0.8059(4)	2.1212(5)	0.4814(4)	3.13(11)
O(3)	−0.5886(5)	2.1387(6)	0.4542(4)	4.9(2)
O(4)	−0.7102(6)	2.2979(5)	0.5264(4)	5.6(1)
O(5)	−0.8965(5)	2.3889(6)	0.4958(6)	5.3(1)
O(6)	−0.7797(5)	2.3605(5)	0.3369(4)	4.16(13)
O(7)	−0.6967(5)	2.4700(5)	0.4955(6)	4.8(2)
O(8)	−0.6850(4)	2.5999(5)	0.6356(3)	2.57(10)
O(9)	−0.8339(4)	2.6224(4)	0.4726(4)	2.57(10)
O(10)	−0.6132(4)	2.6278(6)	0.4495(4)	3.97(12)
O(11)	−0.4111(5)	2.5611(7)	0.0488(5)	5.0(2)
O(12)	−0.1927(4)	2.5751(4)	0.0186(5)	2.94(10)
O(13)	−0.3437(4)	2.5510(5)	−0.1436(4)	2.70(10)
O(14)	−0.3086(5)	2.4137(4)	−0.0019(6)	6.1(1)
O(15)	−0.2292(4)	2.3322(6)	0.1608(5)	4.35(13)
O(16)	−0.0925(5)	2.3338(7)	0.0022(6)	5.6(2)
O(17)	−0.2992(5)	2.2365(5)	0.0061(7)	5.4(2)
O(18)	−0.3892(5)	2.0652(5)	0.0436(5)	3.38(11)
O(19)	−0.1630(4)	2.0823(5)	0.0258(4)	3.08(11)
O(20)	−0.3117(4)	2.1021(4)	−0.1362(4)	2.21(9)
OW(1)	−0.8564(8)	1.8446(8)	0.4664(7)	8.7(3)
OW(2)	−1.1482(5)	2.8627(4)	0.0303(8)	7.0(2)
N(1)	−0.5374(12)	2.2941(10)	0.8311(10)	5.8(5)
N(2)	−0.4546(4)	2.4049(4)	0.6580(3)	1.89(7)
N(3)	−1.1547(3)	2.6204(4)	0.2390(3)	2.86(8)
N(4)	−0.8953(3)	2.6005(4)	0.2494(3)	2.81(8)
N(5)	−0.4786(10)	2.4508(10)	0.2886(11)	5.4(4)
N(6)	−0.5159(4)	2.2499(3)	0.2107(3)	1.55(6)
N(7)	−1.0394(9)	2.0158(9)	0.2933(8)	6.0(3)
N(8)	−0.9276(9)	2.1918(7)	0.2189(8)	6.9(2)
C(1)	−0.6154(7)	2.3894(6)	0.7844(6)	3.1(1)
C(2)	−0.5346(6)	2.4558(5)	0.7364(4)	1.66(10)
C(3)	−0.3864(6)	2.3237(7)	0.7128(6)	2.62(12)
C(4)	−0.4719(8)	2.2451(5)	0.7600(6)	2.84(13)
C(5)	−1.0795(7)	2.7093(7)	0.2591(7)	3.9(2)
C(6)	−0.9626(5)	2.6943(4)	0.2103(4)	1.96(9)
C(7)	−0.9838(8)	2.5083(7)	0.2108(9)	4.4(2)
C(8)	−1.0829(6)	2.5188(6)	0.2867(6)	3.12(13)
C(9)	−0.4306(5)	2.3633(6)	0.3533(6)	2.60(13)

(Continued on next page)

TABLE I Final Atomic Coordinates and $B_{eq.}$ ($Å^2$) for the Nonhydrogen Atoms *(Continued)*

Atoms	x(σ)	y(σ)	z(σ)	Beq.
C(10)	−0.5886(7)	2.4250(5)	0.2215(6)	2.32(13)
C(11)	−0.5684(7)	2.3403(7)	0.1478(5)	3.2(2)
C(12)	−0.4054(6)	2.2795(6)	0.2759(5)	1.93(11)
C(13)	−1.0278(7)	2.1970(7)	0.2864(7)	3.6(2)
C(14)	−1.0103(3)	2.1041(5)	0.3643(3)	2.58(8)
C(15)	−0.9405(7)	2.0076(6)	0.2112(7)	3.9(2)
C(16)	−0.9552(3)	2.1078(4)	0.1408(3)	2.27(7)

Estimated standard deviations are given in parenthese.

projection of this atomic arrangement along the c axis. The $HP_3O_{10}^{4-}$ group involved in these layers has no internal symmetry and is thus built by three independent tetrahedra. In this monoclinic cell, two crystallographically independent $HP_3O_{10}^{4-}$ groups coexist. The first one is built by $P(1)O_4$, $P(2)O_4$, and $P(3)O_4$, and the second by $P(4)O_4$, $P(5)O_4$, and $P(6)O_4$. The main interatomic distances (Å) and angles (°) in $HP_3O_{10}^{4-}$ anion are given in Table II. So, two distinct inorganic layers (HP_3O_{10}–H_2O) coexist in this crystalline structure. In these layers the $HP_3O_{10}^{4-}$ groups are strongly connected by H-bonds ($d_{O...O}$ = 2.430 Å and 2.421 Å) to form infinite chains. These chains are connected by hydrogen atoms of water molecules O(W) to form planer layers, between which are four crystallographically independent piperazinium cations $(C_4N_2H_{12})^{2+}$. These organic groups, anchored onto successive inorganic layers by N—H···O bonds, assure the three-dimentional network. The main geometrical features of the hydrogen bonds are described in Table III.

NMR Results

^{31}P MAS NMR spectrum presents six isotropic resonances at –23.8, −23.0, −11.1, −7.3, −6.5, and –3.4 ppm assigned to six crystallographically inequivalent sites of the phosphorus atoms in the structure with their corresponding satellite spinning side bonds at equal intervals. The obtained NMR results are in quite good agreement with the crystallographic study, which establishes a noncentrosymmetric structure of this material (Figure 2).

Thermal Analysis

The two curves corresponding to DTA and TGA analysis in open air are given in Figure 3. The DTA curve shows a succession of endothermic

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in $HP_3O_{10}^{4-}$ Anion

Tetrahedron P(1)O_4				
P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.458(9)	116.70(5)	111.20(5)	97.60(5)
O(E12)	2.520(1)	1.503(8)	107.50(6)	110.40(6)
O(E13)	2.477(13)	2.460(1)	1.544(10)	113.20(7)
O(L12)	2.346(2)	2.593(13)	2.630(2)	1.630(2)
Tetrahedron P(2)O_4				
P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1.535(2)	109.30(8)	115.00(6)	93.90(5)
O(E21)	2.390(2)	1.410(10)	116.30(6)	109.40(7)
O(E22)	2.546(2)	2.450(1)	1.484(9)	110.80(6)
O(L23)	2.460(2)	2.470(2)	2.550(1)	1.610(10)
Tetrahedron P(3)O_4				
P(3)	O(E31)	O(E32)	O(E33)	O(L23)
O(E31)	1.509(7)	115.20(5)	113.30(5)	103.50(6)
O(E32)	2.529(11)	1.487(8)	112.80(5)	110.30(5)
O(E33)	2.504(2)	2.4790(1)	1.489(9)	100.20(7)
O(L23)	2.420(1)	2.515(13)	2.350(2)	1.576(1)
Tetrahedron P(4)O_4				
P(4)	O(E41)	O(E42)	O(E43)	O(L43)
O(E41)	1.531(10)	111.10(6)	112.50(57)	98.00(7)
O(E42)	2.478(13)	1.474(8)	116.00(5)	108.60(5)
O(E43)	2.537(13)	2.539(11)	1.520(8)	108.80(6)
O(L43)	2.350(2)	2.481(11)	2.521(12)	1.580(8)
Tetrahedron P(5)O_4				
P(5)	O(L43)	O(E51)	O(E52)	O(L56)
O(L43)	1.596(8)	104.10(7)	113.90(7)	94.70(5)
O(E51)	2.390(1)	1.430(2)	120.00(6)	104.20(7)
O(E52)	2.610(2)	2.550(1)	1.515(92)	116.40(7)
O(L56)	2.330(12)	2.369(1)	2.620(2)	1.572(9)
Tetrahedron P(6)O_4				
P(6)	O(E61)	O(E62)	O(E63)	O(L56)
O(E61)	1.520(9)	113.70(6)	109.70(5)	106.80(6)
O(E62)	2.538(12)	1.512(8)	112.60(5)	108.00(6)
O(E63)	2.477(12)	2.514(10)	1.510(8)	105.50(6)
O(L56)	2.510(1)	2.525(13)	2.484(12)	1.609(10)

P(1)–P(2) = 2.957(9); P(2)–P(3) = 2.968(6); P(4)–P(5) = 2.974(7); P(5)–P(6) = 2.977(7); O(E13)–H(1) = 0.87; O(E41)–H(2) = 1.05; P(1)–O(E13)—H(1) = 98.3; P(4)–O(E41)—H(2) = 109.6.

Estimated standard deviations are given in parentheses.

peaks. The first one (99.6°C) corresponds to an elimination of the crystallization water molecule, well confirmed by the weight loss observed on TGA curve (% water experimental 4.53, calculated 4.9). After this dehydratation, organic entity of the anhydrous compound begins to

TABLE III Hydrogen Bond Scheme in $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$

O(N)—H···O	O(N)—H	H···O	O(N)—H···O	O(N)···O
O(E13)—H(1)···O(E63)	0.87	1.80	168.7	2.430
O(E41)—H(2)···O(E61)	1.05	1.85	165.3	2.421
N(1)—H(N11)···O(E11)	0.80	1.98	157.3	2.678
N(1)—H(N12)···O(E32)	0.88	1.85	168.5	2.619
N(2)—H(N21)···O(E21)	0.80	2.05	163.0	2.601
N(2)—H(N22)···O(E11)	0.82	2.11	147.2	2.750
N(3)—H(N31)···O(E13)	0.80	1.95	159.6	2.586
N(3)—H(N32)···O(E21)	0.92	1.90	167.5	2.975
N(4)—H(N41)···O(E31)	0.80	2.16	172.4	2.826
N(4)—H(N42)···O(E13)	0.80	2.07	178.0	2.776
N(5)—H(N51)···O(E32)	0.97	1.83	166.0	2.793
N(5)—H(N52)···O(E32)	0.83	1.84	163.8	2.793
N(6)—H(N61)···O(E32)	0.84	2.14	161.7	2.793
N(6)—H(N62)···O(E32)	0.80	2.26	154.3	2.793
N(7)—H(N71)···O(E32)	1.00	2.28	136.9	2.793
O(W1)—H(3)···O(E51)	0.87	2.14	130.7	2.775
O(W1)—H(4)···O(E42)	0.99	2.02	139.8	2.840
O(W2)—H(5)···O(E22)	0.98	2.15	129.8	2.880
O(W2)—H(6)···O(E33)	0.92	2.12	123.4	2.676

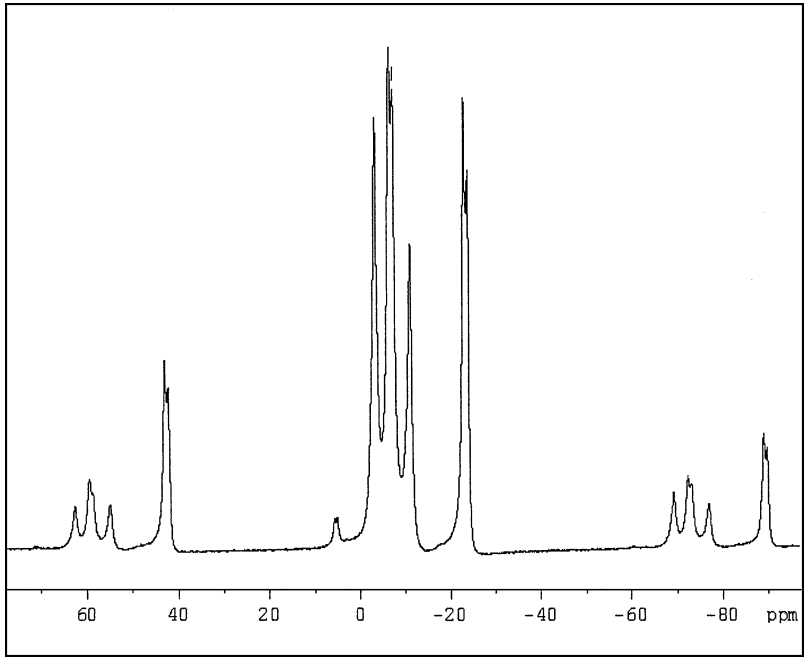

FIGURE 2 ^{31}P MAS–NMR spectrum of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$.

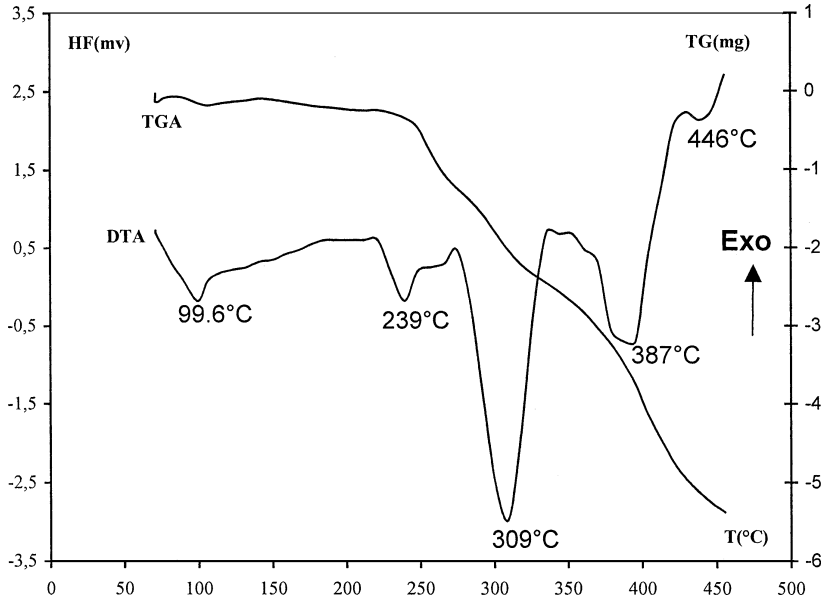

FIGURE 3 DTA and TGA curves of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$ between room temperature and 500°C.

decompose in a wide temperature range and forms volatile gas and a black residue of carbon in a viscous matter of polyphosphoric acid.

IR Spectroscopy

The infrared absorption spectrum of the title compound is shown in Figure 4. It exhibits absorption bands between 3500 and 1400 cm^{-1}, corresponding to the valency vibrations of the water molecules, the (νO—H) of P—OH groups and the $[C_4H_{12}N_2]^{2+}$ cations in molecular structure. The stretching vibrations of the PO_2 central groups are observed between 1100–1300 cm^{-1}. Those between 1200–950 cm^{-1} correspond to stretching vibrations of the PO_3 terminal groups, and those ranging from 975–650 cm^{-1} correspond to stretching POP modes.[3–5] The bending vibrations of PO_3 terminal groups are situated in the interval 600–400 cm^{-1}.

EXPERIMENTAL

Synthesis of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$

$[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$, is prepared by using ion exange resins. An aqueous solution of pentasodium triphosphate, $Na_5P_3O_{10}\cdot H_2O$,[6] is

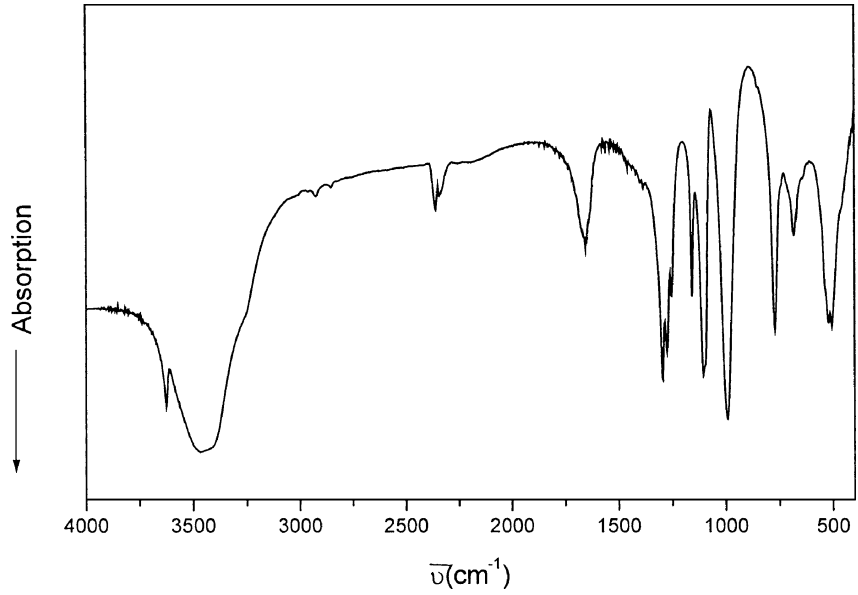

FIGURE 4 IR spectrum of $[C_4N_2H_{12}]_2HP_3O_{10}{\cdot}H_2O$ in KBr pellets.

passed through a column of Amberlite IR 120. The triphosphoric acid so obtained is immediately neutralized by an aqueous solution of the $C_4N_2H_{10}$ amine. To avoid any hydrolytic cleavage of the $P_3O_{10}^{5-}$ anion, this reaction must be run at a temperature close to 273 K. Larger single crystals are formed by slow and careful evaporation of aqueous solution.

Investigation Techniques

X-Ray Diffraction

A single crystal was used for X-ray measurements, with a MACH 3 Enraf Nonius diffractometer working at 296 K and the wavelength $K\alpha(Ag) = 0.5608$ Å. The structure was solved by direct methods using SIR92 program[7] and refined by full matrix least-squares techniques based on F using TeXsan.[8] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms position were located by difference-Fourier synthesis and not refined. The details of data collection, refinement, and crystallographic data are summarized in Table IV.

Crystallographic data (CIF) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 222553. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

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

Empirical formula	$C_8H_{27}N_4O_{11}P_3$
Formula weight	444.25
Crystal system	monoclinic
Space group	$P2_1$
a	11.072(5) (Å)
b	12.324(2) (Å)
c	13.122(5) (Å)
β	93.85(5)°
Z	4
V	1787(1) (Å^3)
ρ cal.	1.666 (g. cm^{-3})
F(000)	936
$\mu(AgK_\alpha)$	2.109 (cm^{-1})
Crystal size [mm]	0.80 × 0.50 × 0.40
Index ranges: ±h, k, l	$h_{max.} = 16$, $k_{max.} = 19$, $l_{max.} = 18$
Reflexions collected	6876
Independent reflexions	4262
R_{int}	0.050
Refined parameters	468
R [I > 3σ(I)]	0.057
$R_{(w)}$	0.058
Goodness of fit	2.07

Physical Measurements

^{31}P MAS–NMR spectrum were obtained on a solid-state high-resolution Bruker DSC-300 spectrometer operating at 121.51 MHz. The spinning rate was 10 kHz. The $\pi/2$ pulse was 4 μs, and the time interval between successive scans was 10 s. All measurements were carried out at room temperature with H_3PO_4 (85%) as an external standard reference.

Thermal analysis was performed using the multimodule 92 Setaram analyzer operating from room temperature up to 500°C at an average heating rate of 5°C/min.

IR spectrum were recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer Spectrum 1000 spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

CONCLUSION

In conclusion, structure of $[C_4N_2H_{12}]_2HP_3O_{10}\cdot H_2O$ was analyzed by X-ray and NMR techniques. Results from both studies are in good agreement and confirm the noncentrosymmetrical structure. This material,

which exhibits an uncommon richness in strong hydrogen bonds, is suitable for investigations of its optical properties.

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