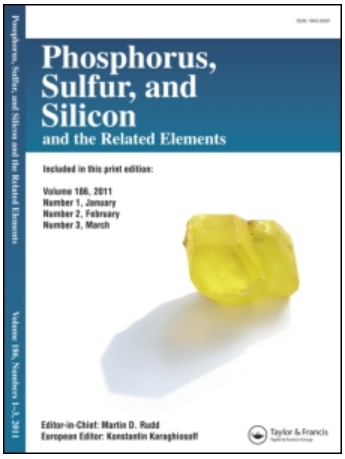

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Synthesis and Characterization of a New Cyclotriphosphate $[C_8H_{11}NH_3]_3P_3O_9 \cdot 3H_2O$

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Among the various categories of phosphates, the number of organic cation cyclotriphosphates remains limited. In this work, we report the chemical preparation, crystal structure, thermal analysis, and spectroscopic investigations of a new cyclotriphosphate $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$. *It is characterized by X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance, and thermal analysis. This compound is a triclinic* $P\bar{1}$ *unit cell with the following parameters:* $a = 13.949(4), b = 9.867(3), c = 14.180(2)\text{Å}, \alpha = 92.22(2), \beta = 119.27(2), \gamma = 85.10(10)^\circ, V = 1696.1(8)\text{Å}^3$, *and* $Z = 2$. *Its structure has been determined and refined to* $R = 0.041$ *and* $R_w = 0.062$, *using 4527 independent reflections. The atomic arrangement can be described by corrugated thick layers built by* $[P_3O_9]^{3-}$ *anions, ammonium groups, and water molecules. The organic entities are located between these layers. H-bonds connecting the different species play an important role in the tridimensionnal network cohesion. This compound is also characterized by infrared spectroscopy, nuclear magnetic resonance, and thermal analysis.*

Keywords Chemical synthesis; crystal structure; infrared spectroscopy; X-ray diffraction

INTRODUCTION

Phosphates have attracted considerable interest in recent years because of many practical and potential uses in various fields, such us catalysts, protonic conductors, biomaterials research, and linear optics.[1–3] After the chemical preparation of $Na_3P_3O_9$,[17] several inorganic cation cyclotriphosphates have been characterized, whereas the number of organic cation cyclotriphosphate compounds remain limited in phosphate

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bibliography compared to other cyclophosphates $[P_nO_{3n}]^{n-}$ where $n > 3$. In the present investigation, we report the synthesis and crystal structure of a hybrid cyclotriphosphate $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ and its characterization by different techniques.

RESULTS AND DISCUSSION

Structural Description

All data concerning the experimental parameters used for the structure determination as well as their final results are gathered in Table I. Final atomic coordinates of non-hydrogen atoms of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ and their B_{eq} are reported in Table II. Those of hydrogen atoms have been determined too but not given to shorten the Table.

An ORTEP drawing of the asymmetric unit $[C_8H_{11}NH_3]_3P_3O_9 \cdot 3H_2O$ is shown in Figure 1. Three chemical species are present in the asymmetric unit: a $[P_3O_9]^{3-}$ ring anion, three independent

TABLE I Crystal Data and Experimental Parameters Used for the Intensity Data Collection. Procedure and Final Results of the Structure Determination

Empirical Formula	$C_{24}H_{48}N_3O_{12}P_3$
Formula weight	663.58
Crystal system	Triclinic
Space group	: $P\bar{1}$
a	13.949(4) (Å)
b	9.867(3) (Å)
c	14.180(2) (Å)
α	92.22 (2)
β	119.27(2)
γ	85.10(10)
Z	2
V	1696.1(8) (Å^3)
ρcal.	1.299 (g cm^{-3})
F(000)	708
$\mu(AgK_\alpha)$	2.340 (cm^{-1})
Crystal size (mm)	0.65 × 0.30 × 0.20
Index ranges: ± h, k, l	$h_{max.} = 16$, $k_{max.} = 11$, $l_{max.} = 16$
Reflexions collected	6207
Independent reflexions	5943
R_{int}	0.001
Refined parameters	379
R [I > 1.75σ (I)]	0.0411
R(w)	0.0620
Goodness of fit	1.790

TABLE II Final Atomic Coordinates and B_{eq}.(Å^2) for the Non-Hydrogen Atoms in $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$

Atoms	x (σ)	y (σ)	z (σ)	Beq.(Å^2)
P(1)	0.35746(4)	0.17116(5)	−0.43301(4)	2.121(10)
P(2)	0.40635(4)	0.15659(4)	−0.20993(3)	2.139(9)
P(3)	0.20709(3)	0.31288(4)	−0.36696(4)	2.095(9)
O(E11)	0.3364(1)	0.0290(2)	−0.46413(12)	4.15(4)
O(E12)	0.40455(11)	0.2514(2)	−0.48391(10)	3.20(3)
O(L12)	0.43477(9)	0.18414(13)	−0.30391(10)	2.41(3)
O(E21)	0.47694(11)	0.2379(1)	−0.11556(10)	3.14(3)
O(E22)	0.40538(13)	0.00990(13)	−0.19440(12)	3.56(3)
O(L23)	0.28087(10)	0.2191(1)	−0.26278(10)	2.90(3)
O(E31)	0.24035(13)	0.4541(1)	−0.3420(1)	4.37(4)
O(E32)	0.09059(10)	0.2890(2)	−0.40923(11)	3.38(3)
O(L13)	0.24524(10)	0.2501(2)	−0.44977(10)	3.31(3)
O(W1)	0.2412(2)	−0.1201(3)	−0.3710(2)	7.84(6)
O(W2)	0.3959(2)	0.5359(2)	−0.4169(2)	6.58(6)
O(W3)	0.4407(2)	0.5234(2)	−0.1673(2)	7.54(5)
N(1)	−0.10247(13)	0.3070(2)	−0.61076(12)	2.58(3)
N(2)	0.60896(12)	0.2294(2)	−0.47869(13)	2.63(3)
N(3)	0.47850(12)	0.2255(2)	0.08477(12)	2.47(3)
C(1)	−0.2586(2)	0.2724(3)	−0.8865(2)	4.30(5)
C(2)	−0.1767(2)	0.2779(2)	−0.8026(2)	3.21(4)
C(3)	−0.0033(2)	0.3920(2)	−0.6968(2)	3.32(4)
C(4)	0.0433(2)	0.3619(3)	−0.7736(2)	4.45(6)
C(5)	0.1088(2)	0.2242(3)	−0.7492(2)	4.59(6)
C(6)	0.0375(2)	0.1127(3)	−0.7536(2)	4.30(5)
C(7)	−0.0073(2)	0.1400(2)	−0.6761(2)	3.30(4)
C(8)	−0.0734(2)	0.2790(2)	−0.6986(1)	2.47(4)
C(9)	0.8877(2)	0.2483(3)	−0.3674(2)	3.93(5)
C(10)	0.8038(2)	0.2449(2)	−0.3667(2)	2.97(4)
C(11)	0.6995(2)	0.2441(2)	−0.3641(2)	2.50(4)
C(12)	0.7004(2)	0.1227(2)	−0.2996(2)	3.20(4)
C(13)	0.7802(2)	0.1390(3)	−0.1795(2)	5.13(6)
C(14)	0.7534(3)	0.2718(4)	−0.1370(2)	6.05(8)
C(15)	0.7546(2)	0.3920(3)	−0.2005(2)	5.30(6)
C(16)	0.6742(2)	0.3780(2)	−0.3197(2)	3.99(5)
C(17)	0.3701(2)	0.2342(3)	0.2570(2)	4.20(5)
C(18)	0.3674(2)	0.2333(2)	0.1726(2)	3.00(4)
C(19)	0.3622(2)	0.2305(2)	0.0656(1)	2.51(4)
C(20)	0.3010(2)	0.3602(2)	0.0008(2)	3.44(4)
C(21)	0.1781(2)	0.3652(3)	−0.0358(2)	4.69(6)
C(22)	0.1273(2)	0.2377(4)	−0.1018(2)	5.77(7)
C(23)	0.1866(2)	0.1113(3)	−0.0344(2)	4.81(6)
C(24)	0.3096(2)	0.1025(2)	0.0031(2)	3.45(4)

Estimated standard deviations are given in parentheses. $B_{eq} = 4/3 \sum_i \sum_j \mathbf{a}_i.\mathbf{a}_j \beta ij$.

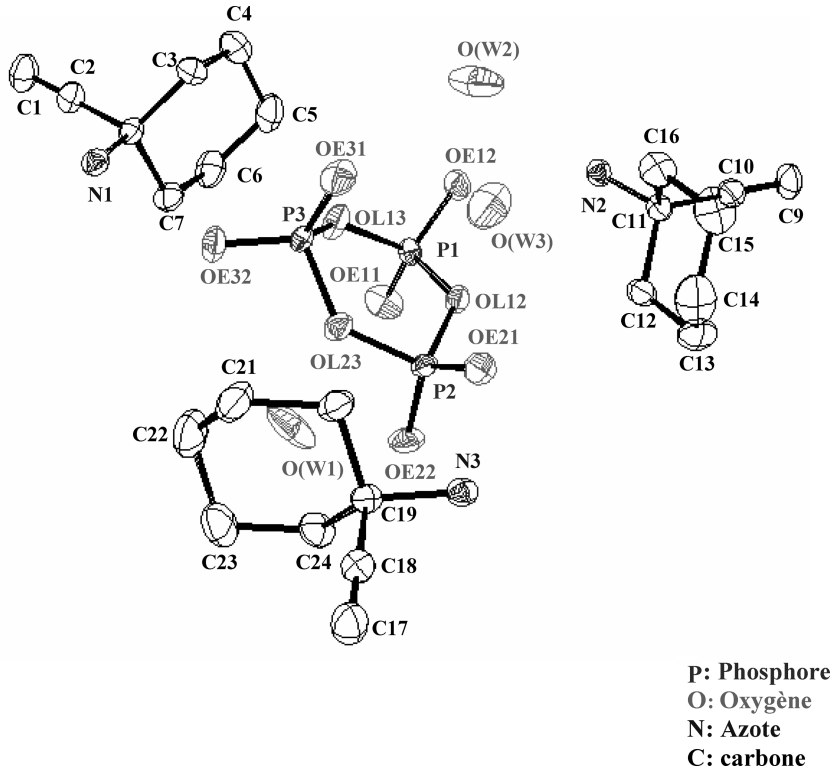


FIGURE 1 An ORTEP drawing of the asymmetric unit of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$, representing atoms as 30% probability ellipsoids and H atoms as spheres of arbitrary radius.

1-ethynylcyclohexanammonium cations, and three water molecules. All atoms that form these entities occupy general positions.

The atomic arrangement is characterized by the existence of infinite corrugated thick layers, which are built by P_3O_9 rings, water molecules, and $[NH_3]^+$ groups, parallel to the (a,b) planes at z = ½. The organic molecules are located in the space 14.180 Å delimited by the inorganic layers (Figure 2).

As is always the case in triclinic compounds, the triphosphoric ring anions $[P_3O_9]^{3-}$ have no internal symmetry. Three independent PO_4 tetrahedra, $P(1)O_4$, $P(2)O_4$, and $P(3)O_4$, which are linked by three O(L) atoms, form the P_3O_9 group. The main geometric features of this group (Table III) are the P–P distances, the P–P–P and P–O–P angles. The values of P–O–P angles (128.5(3) and 132.6(2)°) and P–P distances (2.898(4) and 2.920(2) Å) are comparable to those generally measured

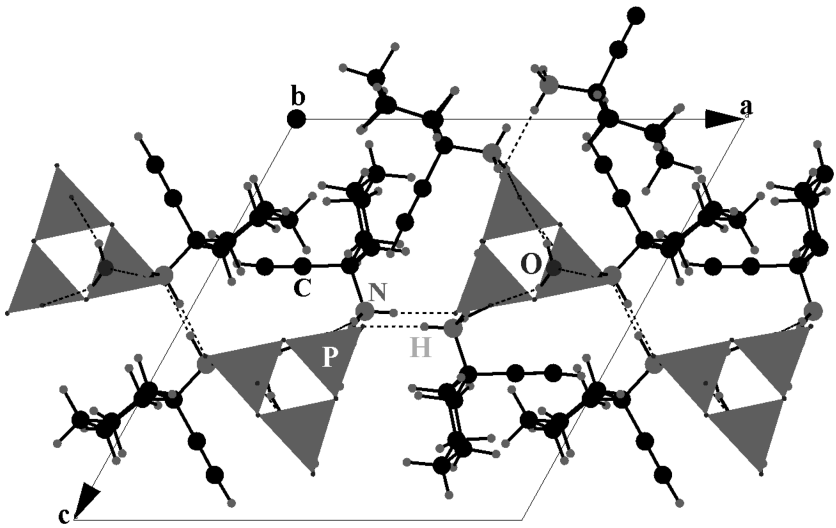


FIGURE 2 The projection along the b axis of the $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ structure. The phosphoric anions are given in a polyhedral representation.

in these types of condensed phosphates.[4] The detailed geometry of the $[P_3O_9]^{3-}$ ring shows that the P–O(E) distances are significantly shorter [1.464(5) to 1.482(8) Å] with an average 1.472 Å than the P–O(L) distances [1.595(4) to 1.614(2) Å] with an average 1.601 Å. This significant difference between the P–O(L) and P–O(E) distances gives the PO_4 tetrahedron described by a regular tetrahedral oxygen atoms arrangement with the phosphorus atom slightly shifted from the gravity center.

Inside the unit cell, three crystallographically independent water molecules (OW1, OW2, and OW3) coexist. These latters are assembled with $[P_3O_9]^{3-}$ ring anions through hydrogen bonds O(W)-H...O(E) to give a repetitive $(H_6P_3O_{12})^{3-}$ unit and to contribute to the layer cohesion. The O...O distances and O–H...O angles spread in the range from 2.795(3) to 2.940(3) Å and 151.0 to 175.0°, respectively (Table IV).

In this structure, three independent $[C_8H_{11}NH_3]^+$ cationic groups coexist, compensating the negative charge of the $[P_3O_9]^{3-}$ ring anions and performing the electric neutrality of the total complex. These organic cations are anchored onto successive corrugated layers through H-bonds involving the hydrogen atoms of the $-NH_3$ groups, water molecules, and some external oxygen atoms of the P_3O_9 groups (Figure 2) with N(H)...O(E,W) distances varying between 2.702(3) and 2.808(3) Å and H(N)...O(E,W) distances ranging between 1.69 Å and 1.95 Å. These hydrogen bonds participate in the cohesion of the

TABLE III Main Interatomic Distances (Å) and Bond Angles (°) in the $[P_3O_9]^{3-}$ Anion of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$

The $P(1)O_4$ Tetrahedron				
P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1.464(5)	2.480(2)	2.548(2)	2.480(2)
O(E12)	119.8(4)	1.476(6)	2.483(3)	2.496(3)
O(L12)	110.8(6)	106.9(5)	1.614(2)	2.480(12)
O(L13)	108.2(2)	108.5(4)	101.1(2)	1.598(13)
The $P(2)O_4$ Tetrahedron				
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	1.472(2)	2.530(2)	2.484(3)	2.519(4)
O(E22)	118.4(6)	1.475(2)	2.547(5)	2.470(3)
O(L12)	107.6(4)	111.6(3)	1.603(2)	2.480(6)
O(L23)	109.9(4)	106.7(10)	101.3(2)	1.604(2)
The $P(3)O_4$ Tetrahedron				
P(3)	O(E31)	O(E32)	O(L13)	O(L23)
O(E31)	1.482(8)	2.540(2)	2.496(3)	2.512(10)
O(E32)	118.7(10)	1.469(5)	2.487(6)	2.498(3)
O(L13)	108.4(3)	108.5(4)	1.595(4)	2.474(3)
O(L23)	109.3(4)	109.0(5)	101.6(6)	1.597(11)
P(1)–P(2)		2.898(4)	P(2)–P(1)–P(3)	60.2(4)
P(1)–P(3)		2.920(2)	P(1)–P(2)–P(3)	60.3(10)
P(2)–P(3)		2.920(2)	P(1)–P(3)–P(2)	59.5(5)
P(1)–O(L12)–P(2)		128.5(3)	P(1)–O(L13)–P(3)	132.6(2)
P(2)–O(L23)–P(3)		131.7(5)		

Estimated standard deviations are given in parentheses.

three-dimensional network (Table IV). The mean value of C—C bond lengths of the cyclohexyl group is 1.525 Å and corresponds to single bonds. Furthermore, the bond lengths of C1–C2, C9–C10, and C17–C18 and the three angles C(1)–C(2)–C(8), C(9)–C(10)–C(11), and C(17)–C(18)–C(19) are 1.183(4), 1.178(4), and 1.179(4) Å and 177.7(7), 178.4(3), and 178.9(3)° respectively, clearly indicating the existence of three triple bonds. The N–C distance and N–C–C angle spread from 1.496(4) to 1.505(3) Å and 107.4(2) to 108.4(8)°, respectively (Table V).

IR Spectroscopic Study

The infrared absorption spectrum (Figure 3) of the title compound $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ shows bands corresponding to the vibrations of 1-ethynylcyclohexanammonium cation, the $[P_3O_9]^{3-}$ ring anion, and water molecules. It exhibits broad bands between 3500–2500 and 1650–1350 cm^{-1}, corresponding respectively, to stretching ($\nu_{OH} + \nu_{NH3} + \nu_{CH2}$) and bending ($\delta_{OH} + \delta_{NH3} + \delta_{CH2}$) modes of the water molecules

TABLE IV Main Geometrical Features of the Hydrogen-Bond Scheme in $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$

D—H...A	D—H(Å)	H...A(Å)	D...A(Å)	D—H...A(Å)
O(W1)-H(1W1)...O(E11)	0.97	1.92	2.807(3)	151.0
O(W1)-H(2W1)...O(E22)	0.87	1.94	2.795(3)	166.2
O(W2)-H(1W2)...O(E12)	1.04	1.89	2.940(3)	175.0
O(W2)-H(2W2)...O(W3)	1.02	2.29	3.285(5)	161.8
O(W3)-H(1W3)...O(E31)	0.92	1.89	2.801(3)	172.5
O(W3)-H(2W3)...O(E21)	0.86	2.06	2.878(3)	160.3
N(1)-H(1N1)...O(E31)	0.92	1.89	2.790(3)	168.8
N(1)-H(2N1)...O(W1)	1.02	1.69	2.702(3)	170.6
N(1)-H(3N1)...O(E32)	1.01	1.80	2.808(3)	176.4
N(2)-H(1N2)...O(E12)	0.89	1.92	2.806(3)	176.6
N(2)-H(2N2)...O(W2)	1.03	1.77	2.775(3)	164.8
N(2)-H(3N2)...O(E11)	0.96	1.85	2.802(3)	171.6
N(3)-H(1N3)...O(E21)	0.89	1.95	2.837(3)	174.3
N(3)-H(2N3)...O(E22)	1.01	1.76	2.758(3)	167.5
N(3)-H(3N3)...O(W3)	0.91	1.89	2.782(3)	165.5
H(1W1)–O(W1)–H(2W1)	99.0	H(1N1)–N(1)–H(2N1)		108.1
H(1W2)–O(W2)–H(2W2)	106.5	H(1N1)–N(1)–H(3N1)		104.2
H(1W3)–O(W3)–H(2W3)	103.4	H(2N1)–N(1)–H(3N1)		110.0
H(1N2)–N(2)–H(2N2)	108.3	H(1N3)–N(3)–H(2N3)		106.3
H(1N2)–N(2)–H(3N2)	112.2	H(1N3)–N(3)–H(3N3)		103.0
H(2N2)–N(2)–H(3N2)	112.0	H(2N3)–N(3)–H(3N3)		109.3

and $[C_8H_{11}NH_3]^+$ of the compound. The line at 3280 cm^{-1} can be assigned to the stretching vibration ν(C—H) of the acetylenic group, and the band at 2115 cm^{-1} corresponds to the stretching mode ν(C≡C). Absorptions in the range 1400–1200 cm^{-1} correspond to the valency vibrations of the C—N and C—C bands.[5] Between 1300–650 cm^{-1}, various valence and bending vibration bands are both characteristic of a phosphoric ring anion.[6] In these types of anions, vibrations of the groups take place at relatively high frequencies, $1200 < \nu_{as}(PO_2) < 1300$ cm^{-1} and $1050 < \nu_s(PO_2) < 1200$ cm^{-1}, and those corresponding to the P–O–P groups constitute a broad band ν_{as} at about 983 cm^{-1} and a doublet ν_s between 800 and 700 cm^{-1}. Symmetric and asymmetric bands below 650 cm^{-1} are attributed to bending modes δ_s and δ_{as} of the $[P_3O_9]^{3-}$ ring anion.[7]

NMR Spectroscopy

The ^{31}P MAS NMR spectrum reported in Figure 4a displays only one peak at −26.8 ppm with two side bands, which are separated with

TABLE V Selected Bond Lengths (Å) and Bond Angles (°) in the Organic Groups of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$

$[C_8H_{14}N(1)]^+$ Group					
N1–C8	1.496(4)	C1–C2	1.183(4)	C2–C8	1.475(4)
C3–C8	1.537(13)	C3–C4	1.526(5)	C4–C5	1.520(2)
C5–C6	1.560(1)	C6–C7	1.513(5)	C7–C8	1.540(2)
N1–C8–C2	108.2(3)	C1–C2–C8	177.7(3)	C8–C3–C4	111.9(2)
N1–C8–C3	108.1(2)	C3–C4–C5	111.4(3)	C4–C5–C6	110.1(3)
N1–C8–C7	108.3(3)	C5–C6–C7	111.8(3)	C6–C7–C8	111.3(4)
C7–C8–C2	110.8(8)	C7–C8–C3	110.3(3)		
$[C_8H_{14}N(2)]^+$ Group					
N2–C11	1.505(4)	C11–C10	1.474(4)	C10–C9	1.178(4)
C11–C12	1.530(4)	C12–C13	1.523(5)	C13–C14	1.515(8)
C14–C15	1.522(6)	C15–C16	1.514(5)	C11–C16	1.529(6)
N2–C11–C12	107.5(7)	C9–C10–C11	178.4(3)	C11–C12–C13	110.8(7)
N2–C11–C10	107.4(2)	C12–C13–C14	111.2(8)	C14–C15– C16	110.8(7)
N2–C11–C16	108.0(8)	C15–C16–C11	111.0(8)	C16–C11–C10	111.1(9)
C16–C11–C12	110.9(3)	C13–C14–C15	110.8(3)		
$[C_8H_{14}N(3)]^+$ Group					
N3–C19	1.505(3)	C18–C19	1.482(4)	C17–C18	1.179(4)
C19–C20	1.532(13)	C20–C21	1.526(4)	C21–C22	1.541(12)
C22–C23	1.515(13)	C23–C24	1.522(5)	C24–C19	1.536(11)
N3–C19–C18	107.7(2)	C17–C18–C19	178.9(3)	C19–C20–C21	111.4(9)
N3–C19–C20	107.4(8)	C20–C21–C22	110.7(9)	C21–C22–C23	109.7(3)
N3–C19–C24	108.4(8)	C22–C23–C24	111.8(9)	C23–C24–C19	111.2(9)
C24–C19–C18	110.4(2)	C24–C19–C20	111.5(2)		

Estimated standard deviations are given in parentheses.

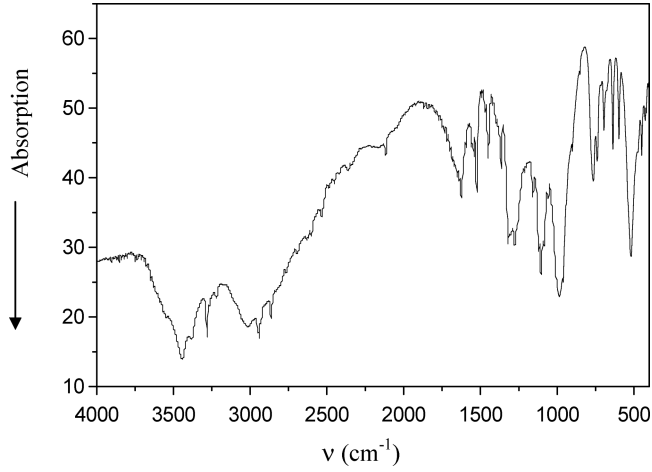


FIGURE 3 IR spectrum of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$.

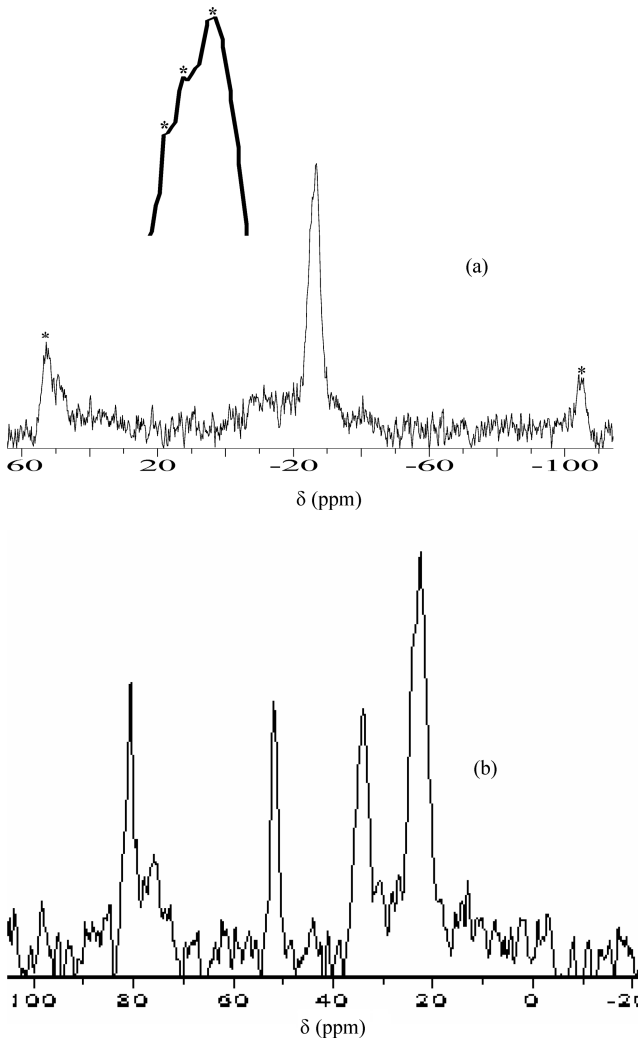
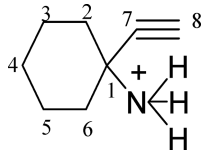


FIGURE 4 (a) ^{31}P and (b) ^{13}C CP-MAS-NMR spectra of $[C_8H_{11}NH_3]_3$-$P_3O_9{\cdot}3H_2O$.

the same frequency interval as the sample spinning frequencies. In order to distinguish the isotropic line from the side bands, we performed two measurements using different spinning frequencies. This isotropic chemical shift value σ_{iso} is higher than those corresponding to monophosphates (10/−5 ppm) or diphosphates (−5/−20 ppm) of alkali or alkaline earth cations[8–14] and similar is to those obtained previously

in polyphosphates, indicating that σ_{iso} values are mainly defined by the tetrahedral condensation of phosphates. The presence of a very large single NMR peak ($\Delta\nu_{1/2} = 607.5$ ppm) with two shoulders in the spectrum proves that the environments of the three crystallographic phosphorus sites are very close.

The ^{13}C CP MAS spectrum (Figure 4b) of the synthesized cyclotriphosphate displays four different signals. The carbon atoms of the organic group are labelled as depicted in Scheme 1.



SCHEME 1

The most important peak at -22.5 ppm ($\Delta\nu_{1/2} = 283.1$ ppm) with a shoulder is related to the secondary C_2, C_3, C_4, C_5, and C_6 carbon atoms of the cyclohexyl ring. The second peak at -33.9 ppm is assigned to the quaternary C_1 carbon atom. The two other signals are attributed to the acetylenic C_7 ($\delta_{C7} = 80.7$ ppm) and C_8 ($\delta_{C8} = 51.8$ ppm) carbon atoms.

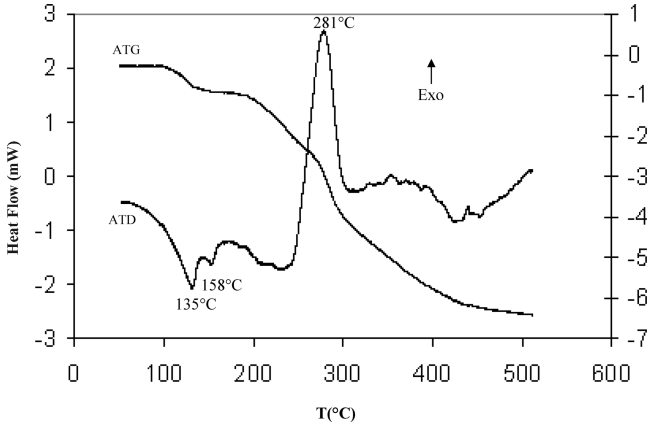


FIGURE 5 DTA and TGA curves of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ at a rising temperature.

Thermal Analysis

The two curves corresponding to DTA and TGA analysis in open air are given in Figure 5. The DTA curve shows that the cyclotriphosphate $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$ undertakes at about 135 and 158°C two endothermic peaks, which correspond to a departure of the three water molecules well confirmed by the weight loss observed in the TGA thermogram (% water experimental, 8.13; calculated, 8.20). This total dehydration leads to the anhydrous phosphate. The other series of peaks beginning at 190°C and accompanied by an important weight loss in a wide temperature range [186, 512°C] correspond to a degradation of the obtained anhydrous compound leading to a mixture of polyphosphoric acids with a black deposit of carbon.

EXPERIMENTAL

Synthesis of $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$

The title compound, $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$, was prepared in two steps. In the first one, we prepare the sodium cyclotriphosphate from NH_2PO_4 by the Thilo and Grunze process.[15] In the second one, (7.51 g, 24.51 mmoles) of the salt $Na_3P_3O_9$ are passed through an ion-exchange resin Amberlite IR 120 to prepare the cyclotriphosphoric acid $H_3P_3O_9$. The fresh, obtained acidic solution is immediately neutralized with (9.06 g, 73.53 mmoles) of 1-ethynyl-cyclohexanamine in an alcoholic solution according to Eq. (1).

$$3[C_8H_{11}NH_2] + H_3P_3O_9 + 3H_2O \longrightarrow [C_8H_{11}NH_3]_3P_3O_9 \cdot 3H_2O \qquad (1)$$

The obtained solution is slowly evaporated at r.t. until crystallization occurs (4.4 g, 6.63 mmoles), and colorless crystals are then obtained (reaction yield 26.9%).

Investigation Thechniques

X-Ray Diffraction

For data collection, a parallelipedic single crystal, with $0.65 \times 0.30 \times 0.20$ mm^3, was selected and mounted on an Enraf-Nonius Mach 3 four-circle diffractometer. The intensities were corrected for the Lorentz-polarization factor. The structure was solved by a direct method using the SIR92[16] program and refined by full-matrix least-squares techniques on F, using teXsan software.[17] The hydrogen atoms positions were located by difference-Fourier synthesis and not refined. All non-hydrogen atoms were refined anisotropically.

CIF for the structure reported in this article has been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 602093. 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).

Physical Measurements

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 121.51 MHz for ^{31}P with a classical 4-mm probehead allowing spinning rates up to 10 kHz. ^{13}C NMR chemical shifts are given relative to tetramethylsilane, and ^{31}P ones are given relative to 85% H_3PO_4 (external references precision 0.5 ppm). Phosphorous spectra were recorded under classical MAS conditions both with or without cross-polarization, while the carbon ones were recorded only by the use of cross-polarization from protons (contact time 5 ms).

The infrared spectrum was recorded on a spectrum 1000 Perkin Elmer spectrometer in the 4000–400 cm^{-1} region using samples dispersed in spectroscopically pure KBr pellets.

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

CONCLUSION

Compared to other phosphates, cyclotriphosphate compounds remain limited in bibliography. The use of $C_8H_{11}NH_3$ as an organic-structure directing agent leads to a new cyclotriphosphate of the chemical formula $[C_8H_{11}NH_3]_3P_3O_9{\cdot}3H_2O$. The atomic arrangement consists of infinite corrugated thick layers built by P_3O_9 rings, water molecules, and $[NH_3]^+$ groups. The structure is stabilized by strong hydrogen bondings with the organic entity and water molecules. Solid-state ^{31}P and ^{13}C MAS-NMR spectroscopies are in accordance with the X-ray structure. When heated, this cyclotriphosphate loses its three crystallization water molecules between 135 and 158°C. The degradation of the organic entity, observed in the temperature range [186, 512°C], is confirmed by the obtained carbon black residue at the end of the experience.

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