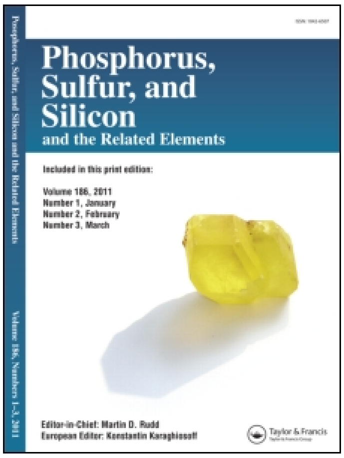

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A new cyclotetraphosphate of o-*ethylphenylammonium dihydrate* $[o\text{-}C_2H_5C_6H_4\text{-}NH_3]_4P_4O_{12}\cdot 2H_2O$ *is reported. This compound is monoclinic* $P2_1/a$ *with the following unit-cell parameters:* $a = 15.625(8)$, $b = 8.479(3)$, $c = 15.899(8)$ Å, $\beta = 111.46(4)^\circ$, $V = 1960(2)$ Å^3, $Z = 2$, *and* $D_x = 2.848$ g·cm^{-3}. *The structure has been determined and refined to* $R = 0.049$, *using 2860 independent reflections. The structure is built up by centrosymmetric* $P_4O_{12}^{4-}$ *anions, water molecules, and* $(C_8H_{12}N)^+$ *cations, which are held together into two-dimensional layers through (N,O)—H···O hydrogen bonds. Chemical preparation, characterization by RX diffraction, IR absorption, and thermal analysis, are described.*

Keywords Crystal structure; cyclotetraphosphate; IR spectroscopy; X-ray diffraction

INTRODUCTION

The condensed phosphates associated with organic cations are an attractive field of research due to their rich structural chemistry and their potential applications in catalysts, protonic conductors, and nonlinear optics, etc.[1–3] As a contribution to the study of this kind of materials, we report in the present work chemical preparation, crystallographic feature, thermal behavior, and IR analysis of a new *o*-ethylphenlammonium cyclotetraphosphate dihydrate $[o\text{-}C_2H_5C_6H_4NH_3]_4P_4O_{12}.2H_2O$, which results from the interaction

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Crystallographic data (CIF) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data center as the supplementary publication No. 262399. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK. E-mail: deposit@ccdc.cam.ac.uk

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between tetraphosphoric acid and an organic cation-containing donor center.

RESULTS AND DISCUSSION

Crystal Structure

The final atomic coordinates and their B_{eq} of all nonhydrogen atoms of $[o\text{-}C_2H_5C_6H_3NH_3]_4P_4O_{12}\cdot 2H_2O$ are reported in Table I. Those of hydrogen atoms have been determined too but are not given to shorten the table.

The atomic arrangement of $[o\text{-}C_2H_5C_6H_3NH_3]_4P_4O_{12}\cdot 2H_2O$ is shown in Figure 1. The structure consists of layers formed by cyclotetraphosphate anions, *o*-ethylanilinium cations, and water molecules connected via N–H$\cdots$O and O–H$\cdots$O hydrogen bonds. The main geometrical

TABLE I Final Atomic Coordinates and B_{eq}.(Å^2) for the Nonhydrogen Atoms. Estimated Standard Deviations are Given in Parentheses

Atoms	x (σ)	y (σ)	z (σ)	B (éq)
P(1)	0.37616(4)	0.35209(7)	−0.03422(5)	2.12(1)
P(2)	0.42196(4)	0.68741(7)	−0.01435(4)	2.00(1)
O(W)	0.1332(1)	0.5277(2)	−0.1002(1)	4.16(5)
O(E11)	0.32148(12)	0.3321(2)	0.02414(13)	3.17(4)
O(E12)	0.35068(11)	0.2517(2)	−0.11577(12)	2.81(4)
O(L12)	0.48136(10)	0.3246(2)	0.02786(11)	2.51(4)
O(L21)	0.37282(11)	0.5308(2)	−0.06594(11)	2.51(4)
O(E21)	0.37305(12)	0.8220(2)	−0.06991(12)	3.00(4)
O(E22)	0.43536(12)	0.6803(2)	0.08210(11)	2.93(4)
N(1)	0.0571(1)	0.5112(2)	0.1681(1)	2.59(5)
N(2)	0.3020(1)	0.5573(3)	0.1430(1)	2.72(5)
C(1)	0.0946(2)	0.5064(3)	0.2667(2)	2.29(5)
C(2)	0.0816(2)	0.3739(3)	0.3113(2)	3.04(6)
C(3)	0.1170(2)	0.3801(4)	0.4051(2)	4.51(8)
C(4)	0.1616(3)	0.5108(5)	0.4513(2)	5.05(9)
C(5)	0.1746(2)	0.6404(4)	0.4045(2)	4.31(8)
C(6)	0.1402(2)	0.6382(3)	0.3114(2)	3.05(6)
C(7)	0.0336(2)	0.2272(4)	0.2637(2)	4.19(8)
C(8)	0.0900(3)	0.0881(5)	0.2759(3)	7.40(1)
C(9)	0.3289(2)	0.5136(3)	0.2374(2)	2.25(5)
C(10)	0.3767(2)	0.6192(3)	0.3033(2)	3.13(6)
C(11)	0.4002(2)	0.5699(4)	0.3932(2)	4.36(8)
C(12)	0.3747(2)	0.4225(5)	0.4134(2)	4.71(9)
C(13)	0.3261(2)	0.3222(4)	0.3464(2)	4.26(8)
C(14)	0.3035(2)	0.3672(3)	0.2579(2)	3.39(7)
C(15)	0.4031(3)	0.7810(4)	0.2835(2)	5.09(9)
C(16)	0.3545(4)	0.9085(5)	0.3033(4)	10.3(2)

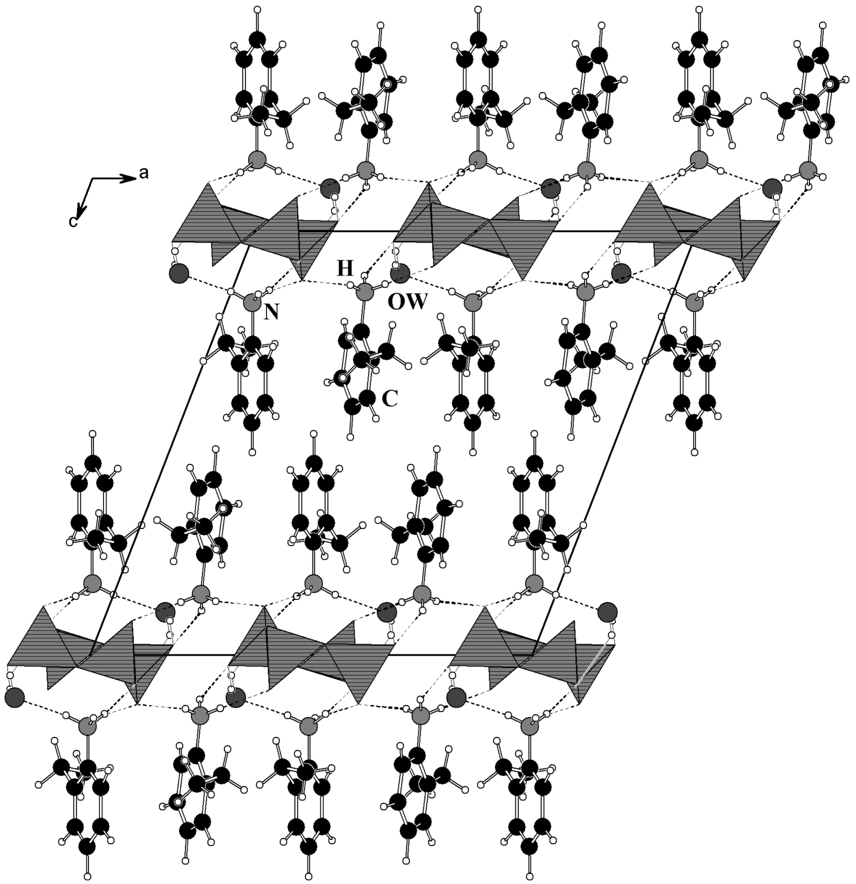

FIGURE 1 Projection of the full structure of [o-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot 2H_2O$ along the b direction. The phosphoric anions are given in the polyhedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by a dotted line.

features of hydrogen bonds are described in Table II. The stability of successive layers is performed by weak interactions from the organic cations. Inside this atomic arrangement, the phosphoric ring anion $P_4O_{12}^{4-}$ is localized around (0, 0, 0) and (1/2, 1/2, 0) inversion centers, and so it is centrosymmetrical and built up by only two independent PO_4 tetrahedra, P(1)O_4, and P(2)O_4. This ring is significantly distorted as shown by P—P—P angle values of 83.52(5) and 96.48(5)°. Nevertheless, these angle values are in good agreement with earlier results concerning P_4O_{12} groups having C_i local symmetry.[4,5] These $P_4O_{12}^{4-}$ ring anions, illustrated in Figure 2, are connected to water

TABLE II Hydrogen-Bond Scheme in [o-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot 2H_2O$

D—H···A	D—H(Å)	H···A(Å)	D···A(Å)	D—H···A(°)
O(W)-H(1W)···O(E21)	0.90	2.51	3.250(4)	139.7
O(W)-H(2W)···O(E11)	0.92	1.91	2.828(4)	170.3
N(1)-H(1N1)···O(E22)	1.02	1.73	2.729(4)	166.8
N(1)-H(2N1)···O(W)	0.88	1.93	2.786(4)	162.8
N(1)-H(3N1)···O(E12)	0.90	2.01	2.793(4)	143.9
N(2)-H(1N2)···O(E12)	0.77	2.05	2.800(4)	162.1
N(2)-H(2N2)···O(E21)	0.84	1.96	2.799(4)	173.3
N(2)-H(2N3)···O(E11)	0.85	2.02	2.780(4)	148.6

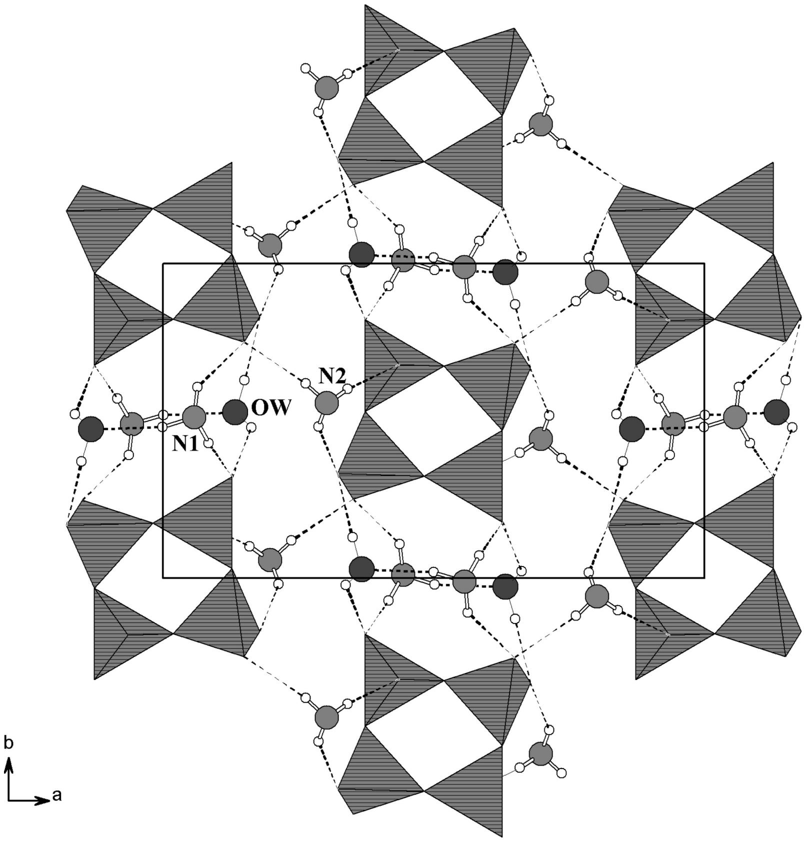

FIGURE 2 Projection along the c direction of an inorganic layer in the structure of [o-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot 2H_2O$. Carbon atoms are omitted for clarity.

molecules through O(W)–H···O(E) H-bonds with bond lengths of 1.990 and 2.544 Å, thus forming infinite ribbons extending along the b direction. Two of these ribbons are anchored [*o*-$(C_2H_5)C_6H_4$]N(1)H_3^+ groups with H-bonds N(1)H···O of length varying from 2.729(4) to 2.793(4) Å (Table II). These ribbons are themselves interconnected via H-bonds N(2)H···O originating from the [*o*-$(C_2H_5)C_6H_4$]N(2)H_3^+ groups, giving rise to thick layers spreading in the ($\vec{a}$,$\vec{b}$) planes. Thus, two crystallographically distinct *o*-ethylphenlammonium cations are involved in this atomic arrangement. One of the cations ensures the cohesion of the ribbon and the other cation joins them to participate to the intralayer cohesion. The principal geometrical features of [*o*-$(C_2H_5)C_6H_4NH_3^+$] are reported in Table III. They are in agreement with those observed for the same organic group associated with other phosphoric anions, such as $H_2P_2O_7^{2-}$ and $H_2P_3O_{10}^{3-}$.[6,7] The two phenyl rings are quite planar with mean deviations of ±0.0046 and ±0.0045 Å, respectively, and they could be considered parallels, with a dihedral angle of 0.93°. The conformation of the ethyl substituents in the two independent organic groups

TABLE III Selected Bond Lengths (Å) and Bond Angles (°) in the Organic Groups of the [*o*-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot 2H_2O$

	[*o*-$(C_2H_5)C_6H_4$]N(1)H_3^+		
N1–C1	1.461(4)	N1–C1–C2	119.8(3)
C1–C2	1.382(5)	N1–C1–C6	117.4(3)
C2–C3	1.389(5)	C1–C2–C3	116.4(4)
C3–C4	1.370(6)	C2–C3–C4	122.0(4)
C4–C5	1.382(6)	C3–C4–C5	120.1(4)
C5–C6	1.378(6)	C4–C5–C6	119.4(4)
C6–C1	1.375(5)	C5–C6–C1	119.4(4)
C7–C2	1.506(5)	C6–C1–C2	122.7(3)
C7–C8	1.443(7)	C7–C2– C3	120.0(4)
C7–C2–C1	123.6(3)		
C2–C7–C8	116.1(4)		
	[*o*-$(C_2H_5)C_6H_4$]N(2)H_3^+		
N2–C9	1.451(4)	N2–C9–C10	119.6(3)
C9–C10	1.373(5)	N2–C9–C14	118.5(3)
C10–C11	1.403(6)	C10–C9–C14	122.0(3)
C11–C12	1.384(7)	C9–C10–C11	116.7(4)
C12–C13	1.357(6)	C9–C10–C15	123.4(4)
C13–C14	1.373(6)	C11–C10–C15	119.8(4)
C14–C9	1.378(5)	C10–C11–C12	121.0(4)
C15– C9	1.499(6)	C11–C12–C13	120.6(4)
C15–C16	1.420(7)	C12–C13–C14	119.3(4)
C13–C14–C9	120.3(4)		
C10–C15–C16	116.1(4)		

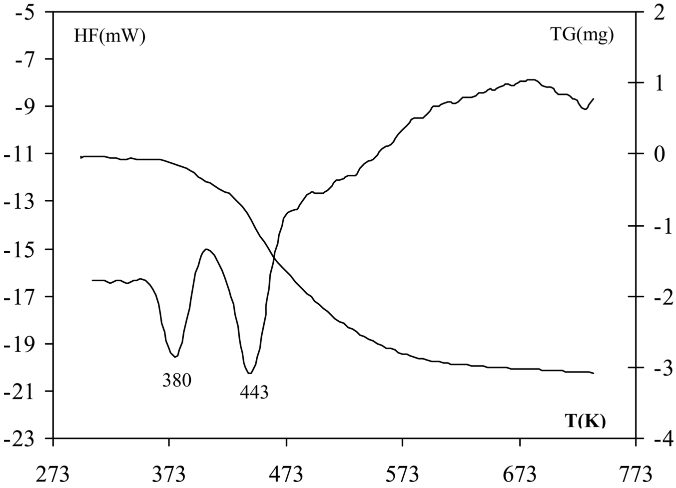

FIGURE 3 DTA and TGA curves of [o-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot2H_2O$ at a rising temperature.

lay are characterized by torsion angles of 113.1(5) and 108.4(6)°, respectively. Consequently, the ethyl groups lay out of the planes of their carrier phenyl rings.

Thermal Analysis

The DTA curve undertakes two endothermic peaks (Figure 3). The first one, at 380 K, corresponds to the departure of the two water molecules, because the corresponding weight loss obviously observed in the TGA curve is 4.13% (calculated is 4.28%). The second peak, at 443 K, followed by a series of small peaks in a wide temperature range for which an important weight loss is observed on a TGA curve, corresponds to the degradation of the title compound to give a polyphosphoric acid and a black residue of carbon.

IR Spectroscopy

The infrared absorption spectrum of [o-$C_2H_5C_6H_3NH_3]_4P_4O_{12}.2H_2O$ is depicted in Figure 4. It exhibits absorption bands between 4000–1370 cm^{-1} corresponding to the O(N,C)-H stretching and bending vibrations of water molecules and o-ethylphenlammonium groups. Those observed in the range of 1350–660 cm^{-1} correspond to asymmetric (as) and symmetric (s) stretching vibrations of atomic groups in $P_4O_{12}^{4-}$ ring.

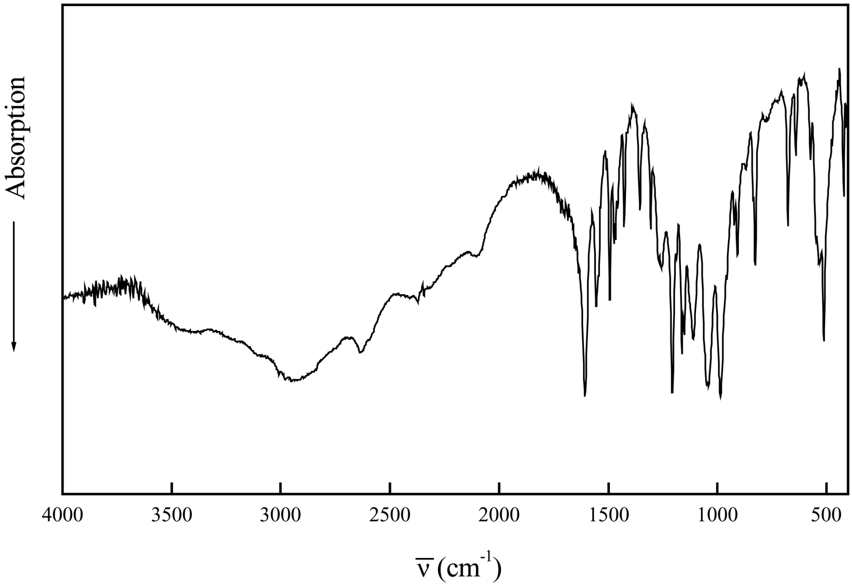

FIGURE 4 The IR spectrum of [*o*-$C_2H_5C_6H_4NH_3]_4P_4O_{12}\cdot 2H_2O$ in a KBr pellet.

Indeed, the stretching vibrations of ν_{as}(OPO) and ν_s(OPO) are observed in a range of 1350–1180 cm^{-1} and 1180–1060 cm^{-1}, respectively, while those ranging from 1060 to 950 cm^{-1} and 850 to 660 cm^{-1} correspond to ν_{as}(POP) and ν_s(POP), respectively. In assignment of these bands, a special caution must be paid because of their overlap with ν(C-N) and δ(C—H) vibrations. We note that the supplementary frequency in the ν_s(OPO) domain can be assigned to the stretching ν(C—C) vibrations.[8] Frequencies below 660 cm^{-1} can be assigned to bending vibrations of the P_4O_{12} ring.

EXPERIMENTAL PART

Synthesis of [o-$C_2H_5C_6H_3NH_3]_4P_4O_{12}\cdot 2H_2O$

Crystals of the title compound are prepared in two steps. In the first one, we prepare an aqueous solution of cyclotetraphosphoric acid by cold hydrolytic degradation of phosphorus P_4O_{10}, according to Eq. (1):

$$P_4O_{10} + 2H_2O \rightarrow H_4P_4O_{12} \qquad (1)$$

This process was carefully analyzed and optimized by Bell and colleagues[9] and by Thilo and Wicker.[10] In the second step, the obtained acidic solution was neutralized by adding dropwise the 2-ethyl aniline dissolved in ethanol. Schematically, the reaction is as follows:

$$4[o\text{-}C_2H_5C_6H_3NH_2]+H_4P_4O_{12}+2H_2O \rightarrow [o\text{-}C_2H_5C_6H_3NH_3]_4P_4O_{12}\cdot 2H_2O \quad (2)$$

After some days of slow evaporation, suitable single crystals appeared in the saturated solution. These crystals are well stablized in air under normal conditions of temperature and hygrometry.

Investigation Techniques

X-Ray Diffraction

For data collection a prismatic single crystal, 0.31 × 0.28 × 0.23 mm^3 was selected and mounted on an Enraf-Nonius Mach 3 four-circle diffractometer operating with $AgK\overline{\alpha}$ radiation. The intensities were corrected for the Lorentz–polarization factor and absorption. The structure was solved by direct method using the SIR92[11] program and refined by the full matrix least-squares techniques on F, using teXsan[12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by difference-Fourier synthesis and not refined. The details of data collection, refinement, and crystallographic data are summarized in Table IV.

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

Empirical formula	$C_{24}H_{52}N_4P_4O_{14}$
Formula weight	840.68
Crystal system	monoclinic
Space group	$P2_1/a$
a	15.625(8) (Å)
b	8.479(3) (Å)
c	15.899(8) (Å)
β	111.46(4)°
Z	2
V	1960(2) ($Å^3$)
$\rho_{cal.}$	1.424 ($g.cm^{-3}$)
F(000)	1776
$\mu(AgK\overline{\alpha})$	1.425 (cm^{-1})
Index range: ± h, k, l	$h_{max.} = 21$, $k_{max.} = 12$, $l_{max.} = 23$
Collected unique reflections ($R_{int} = 0.01$)	7416
Unique reflections included [$I > 4\,\sigma(I)$]	2860
Refined parameters	244
R	0.049
R(w)	0.055
Goodness of fit	1.870

Thermal Analysis

Thermal analysis was performed using a "multimodule 92 Setaram Analyzer" operating at r.t. up to 673 K in following argon at an average heating rate of 5 K/min for DTA and TGA.

Infrared Spectroscopy

The IR spectrum was recorded in a range of 4000 and 450 cm^{-1} with a "Spectrum 1000 Perkin-Elmer" spectrophotometer using a sample dispersed in a spectroscopically pure KBr pellet.

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