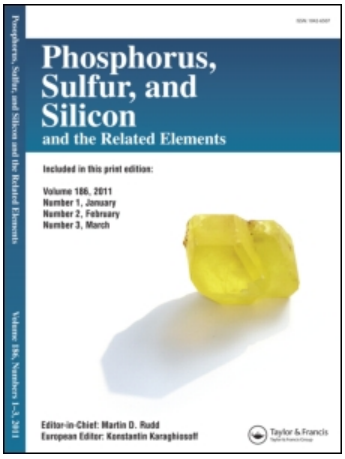

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Structural and Physicochemical Studies of $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$

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The crystal structure of a new organic cation cyclohexaphosphate, $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}.4H_2O$, is reported. It crystallizes in the triclinic system (space group P-1) with the following unit-cell parameters: $a = 9.628(8)$, $b = 12.801(9)$, $c = 19.528(6)$ Å, $\alpha = 78.60(4)^\circ$, $\beta = 83.00(5)^\circ$, $\beta = 89.98(4)^\circ$, $Z = 2$, and $V = 2341(3)Å^3$. The structure has been solved using direct methods and refined by least-squares analysis [$R_1 = 0.043$, $wR_2 = 0.108$]. The structure can be described as infinite anionic layers with composition of $[Li_2(P_6O_{18})(H_2O)_4]^{4-}$ and parallel to the ac plane. The organic groups are located in the accessible voids. The molecules are stabilized by O—H···O and N—H···O types of intermolecular hydrogen bonds in the unit cell in addition to Van der Waals forces.

Keywords Crystal structure; hybrid compound; infrared spectroscopy; thermogravimetric analysis; X-ray diffraction

INTRODUCTION

Research in the area of organic–inorganic hybrid materials has attracted much interest in recent years owing to the structural diversity of these compounds associated with their potential applications in areas such as catalysis, gas sorption/storage, pharmaceuticals, and emerging nanotechnologies.[1–3] Among them, organic phosphate materials still form a diverse and active field of research. This interest stems from their fascinating properties as well as great potential applications in many fields, such as magnetism, materials science, and nonlinear optics.[4] As a contribution to the study of this kind of materials, we report in this article the synthesis; crystal structure; IR, ATG, and DSC data of a new hybrid organic–inorganic compound, $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$.

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RESULTS AND DISCUSSION

Crystal Structure

The final atomic coordinates of all nonhydrogen atoms of the title compound and their U_{eq} temperature factors are given in the Table I. The hydrogen atoms were located but are omitted to shorten the table.

The atomic arrangement can be described by layers built of cyclohexaphosphate rings, $LiO_3(H_2O)$ tetrahedral, and water molecules and spreading parallel to the *ab* planes (Figure 1). Connection in these layers is established by OW-H···O hydrogen bonds. Figure 2 shows the stacking of the inorganic layer with the intercalated organic cations viewed along the [011] direction.

In this structure, we note the presence of two independent P_6O_{18} phosphoric rings, which are located around the inversion centers (0,1/2,0) and (1/2,0,0). They are built from $P(1)O_4$, $P(2)O_4$, and $P(3)O_4$ for the first one (I) and $P(4)O_4$, $P(5)O_4$, and $P(6)O_4$ for the second (II), their main interatomic distances and bond angles are given in Table II. The P–O distances and the O–P–O angles vary respectively from 1.463(2) to 1.601(2) Å and from 99.4(1) to 120.5(1)°. These values are in agreement with those commonly observed in other cyclohexaphosphates.[5–6]

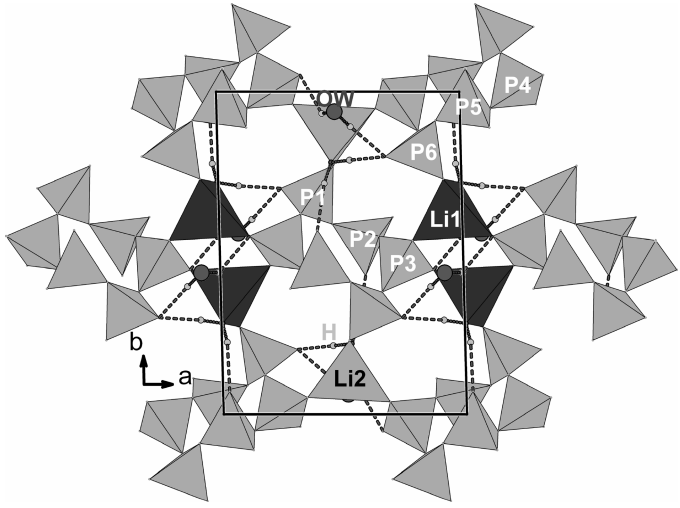

FIGURE 1 Projection of the anionic arrangement along the *c* axis. The phosphoric anion is given in a tetrahedral representation.

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

Atoms	x(σ)	y(σ)	z(σ)	Ueq.
P1	1.61838(9)	0.32151(7)	0.59963(6)	0.0211(3)
P2	1.38149(9)	0.45762(8)	0.63587(6)	0.0203(4)
P3	1.23759(9)	0.51733(8)	0.51394(6)	0.0228(4)
P4	1.25555(9)	1.01747(8)	0.51364(6)	0.0232(4)
P5	1.05172(9)	0.95793(7)	0.63565(6)	0.0200(4)
P6	0.83257(9)	0.82128(7)	0.59978(6)	0.0207(3)
OE11	1.7435(2)	0.2993(2)	0.63755(17)	0.0289(10)
OL23	1.3445(2)	0.4479(2)	0.55981(17)	0.0274(11)
OE23	1.1230(2)	0.5523(2)	0.56147(17)	0.0292(10)
OE21	1.5252(2)	0.2296(2)	0.59953(17)	0.0279(10)
OL13	1.6633(3)	0.3786(2)	0.52032(17)	0.0309(10)
OE13	1.2068(3)	0.4606(2)	0.45856(18)	0.0282(10)
OE22	1.4033(2)	0.57064(19)	0.64028(18)	0.0278(10)
OL12	1.5353(2)	0.4100(2)	0.63410(18)	0.0293(10)
OE12	1.2860(3)	0.3885(2)	0.69021(19)	0.0424(11)
OE26	0.6884(2)	0.7990(2)	0.63773(16)	0.0276(10)
OE16	0.9254(2)	0.7292(2)	0.59955(17)	0.0276(10)
OL45	1.1259(2)	0.9483(2)	0.55959(17)	0.0259(10)
OE14	1.3470(2)	1.0521(2)	0.56161(17)	0.0297(10)
OL46	0.8261(3)	0.8782(2)	0.52015(16)	0.0306(10)
OE24	1.3138(2)	0.9613(2)	0.45873(17)	0.0276(10)
OE15	1.1208(3)	0.8891(2)	0.68978(18)	0.0410(11)
OL56	0.8989(2)	0.9100(2)	0.63386(18)	0.0281(10)
OE25	1.0271(2)	1.0712(2)	0.64002(17)	0.0268(10)
Cl1	1.29737(16)	0.18222(19)	0.96191(12)	0.0912(8)
N1	1.7176(4)	0.0738(3)	0.6868(2)	0.0370(14)
C1	1.7556(4)	0.0569(5)	0.7591(3)	0.048(2)
C2	1.6419(4)	0.0885(4)	0.8099(3)	0.0408(18)
C3	1.5669(5)	0.0139(4)	0.8606(3)	0.053(2)
C4	1.4627(5)	0.0403(5)	0.9075(4)	0.067(3)
C5	1.4313(5)	0.1457(5)	0.9046(4)	0.051(2)
C6	1.5039(6)	0.2235(5)	0.8541(4)	0.060(2)
C7	1.6089(5)	0.1948(5)	0.8077(3)	0.053(2)
C8	1.2617(4)	0.1129(4)	0.7459(3)	0.0452(19)
Cl2	0.79541(15)	0.15575(17)	0.97158(10)	0.0822(7)
N2	1.2460(3)	0.1799(3)	0.6761(2)	0.0386(14)
C9	1.1416(4)	0.1230(4)	0.8006(3)	0.0351(16)
C10	1.0849(5)	0.0353(4)	0.8485(3)	0.0484(19)
C11	0.9784(5)	0.0429(5)	0.9007(3)	0.054(2)
C12	0.9277(5)	0.1413(5)	0.9059(3)	0.0459(19)
C13	0.9816(5)	0.2311(4)	0.8594(3)	0.058(2)
C14	1.0872(5)	0.2216(4)	0.8077(3)	0.050(2)
Cl3	0.97419(17)	0.68373(19)	0.96234(11)	0.0865(8)
N3	0.6894(4)	0.5730(3)	0.6873(2)	0.0366(14)

(Continued on next page)

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

Atoms	x(σ)	y(σ)	z(σ)	Ueq.
C15	0.6172(5)	0.5554(5)	0.7596(3)	0.050(2)
C16	0.7049(4)	0.5868(4)	0.8101(3)	0.041(2)
C17	0.7372(5)	0.6935(5)	0.8088(3)	0.056(2)
C18	0.8194(6)	0.7224(5)	0.8544(4)	0.062(2)
C19	0.8695(5)	0.6460(5)	0.9048(4)	0.052(2)
C20	0.8393(5)	0.5412(5)	0.9075(3)	0.059(2)
C21	0.7578(5)	0.5122(5)	0.8615(3)	0.055(2)
Cl4	1.46939(16)	0.65544(17)	0.97231(10)	0.0807(7)
N4	1.1669(4)	0.6805(3)	0.6757(2)	0.0363(13)
C22	1.1166(4)	0.6143(4)	0.7464(3)	0.0450(19)
C23	1.2087(4)	0.6241(4)	0.8006(3)	0.0353(17)
C24	1.2607(5)	0.7230(4)	0.8075(3)	0.052(2)
C25	1.3398(6)	0.7312(5)	0.8591(4)	0.061(2)
C26	1.3689(5)	0.6420(5)	0.9061(3)	0.048(2)
C27	1.3198(5)	0.5438(5)	0.9012(3)	0.051(2)
C28	1.2413(5)	0.5355(4)	0.8488(3)	0.0474(19)
Li1	0.9563(6)	0.6314(5)	0.5352(4)	0.025(2)
Li2	1.4738(6)	0.8683(5)	0.4658(4)	0.023(2)
O1W	1.4663(3)	0.7811(3)	0.55980(19)	0.0391(12)
O2W	0.9956(3)	0.7187(3)	0.44067(19)	0.0379(11)
O4W	0.9221(4)	0.4381(3)	0.6862(2)	0.0542(13)
O3W	1.4848(4)	-0.0621(3)	0.6864(2)	0.0543(14)

Estimated standard deviations are given in parentheses.

Two crystallographically independent lithium ions are found in this structure. They have a fourfold coordination involving, in each case, one water molecule and three external oxygens belonging to three ring anions (Figure 3). The Li-O distances and O-Li-O angles are comparable with those found in $Li_2K_4P_6O_{18}\cdot 2H_2O$.[7] The shortest Li–Li distance is found to be 8.058 Å.

Assuming the electric neutrality of the framework species, the four crystallographically independent organic groups, protonated as 4-$ClC_6H_4CH_2NH_3^+$, are linked into the infinite layers by means of the N–H$\cdots$O bonds and electrostatics forces. Selected distances and angles in these organic groups are given in Table III. All these distances and angles are in accordance with those observed in other organic phosphates.[8,9] All the phenyl rings of these groups are planar with an average rms deviation of 0.0067. The twisting of the -CH_2-NH_3^+ substituent with respect to the phenyl ring can be seen from the torsion angle ranging from 110.5(8) to 138.3(5)°.

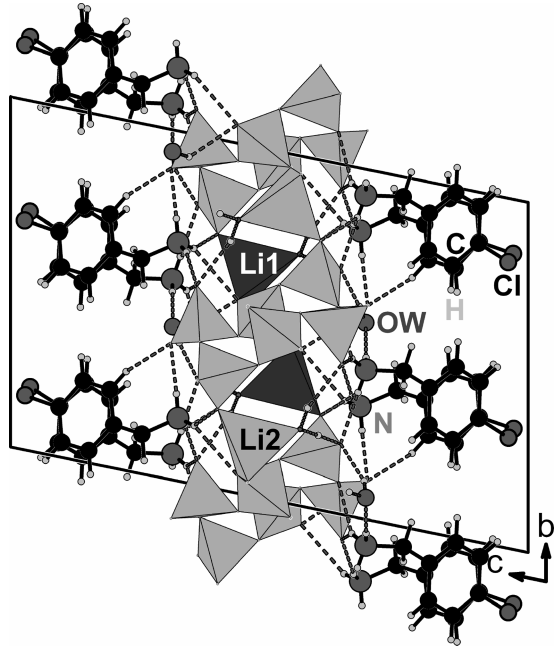

FIGURE 2 Projection of the structure of $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$, along the *a* axis. The phosphoric anion is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines.

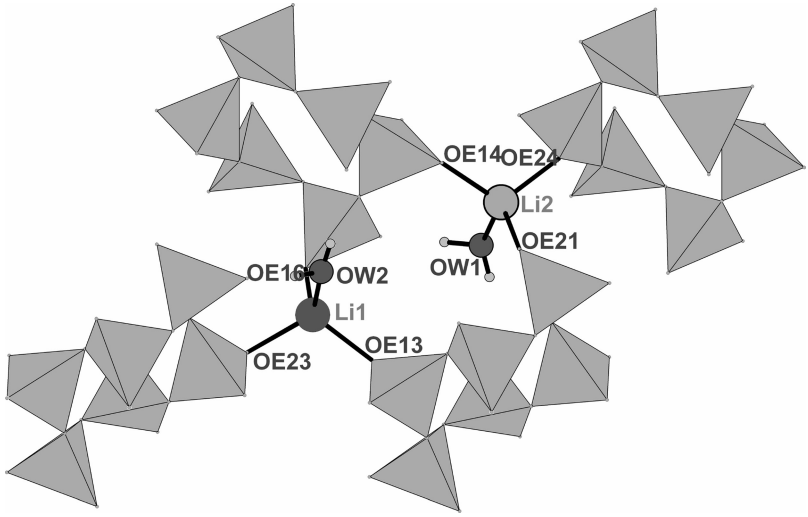

FIGURE 3 Coordination of the lithium atoms in $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$.

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in $P_6O_{18}^{6-}$ anions of [4-ClC$_6$H$_4$CH$_2$NH$_3$]4Li$_2$P$_6$O$_{18}$·4H$_2$O

The P(1)O_4 tetrahedron				
P(1)	OE11	OE12	OL12	OL13
OE11	1.488(3)	2.552(3)	2.565(4)	2.508(4)
OE12	117.06(15)	1.481(3)	2.503(5)	2.507(4)
OL12	105.42(19)	111.03(16)	1.596(3)	2.549(3)
OL13	110.55(15)	107.78(19)	104.27(16)	1.584(3)
The P(2)O_4 tetrahedron				
P(2)	OE21	OE22	OL12	OL23
OE21	1.465(3)	2.538(4)	2.436(4)	2.493(4)
OE22	119.7(2)	1.483(3)	2.436(4)	2.512(4)
OL12	109.56(17)	104.12(16)	1.600(3)	2.507(4)
OL23	109.59(19)	111.06(17)	101.01(19)	1.597(4)
The P(3)O_4 tetrahedron				
P(3)	OE31	OE32	OL23	OL13
OE31	1.474(4)	2.574(4)	2.549(4)	2.492(3)
OE32	120.81(17)	1.481(3)	2.518(3)	2.456(3)
OL23	108.16(18)	109.43(18)	1.600(2)	2.493(4)
OL34	110.01(17)	106.85(18)	99.48(14)	1.620(3)
The P(4)O_4 tetrahedron				
P(4)	OE41	OE42	OL45	OL13
OE41	1.488(4)	2.549(2)	2.530(5)	2.478(3)
OE42	120.59(17)	1.463(4)	2.506(3)	2.530(3)
OL34	109.19(18)	108.43(18)	1.600(3)	2.508(3)
OL45	106.66(18)	110.41(17)	99.50(14)	1.617(2)
The P(5)O_4 tetrahedron				
P(5)	OE51	OE52	OL45	OL56
OE51	1.463(3)	2.454(3)	2.531(3)	2.539(3)
OE52	119.8(2)	1.486(3)	2.481(3)	2.534(3)
OL45	109.57(18)	111.06(16)	1.596(4)	2.526(3)
OL56	109.70(17)	104.07(15)	100.83(19)	1.601(3)
The P(6)O_4 tetrahedron				
P(6)	OE61	OE62	OL46	OL56
OE61	1.487(3)	2.456(3)	2.527(3)	2.541(3)
OE62	116.98(15)	1.481(3)	2.468(3)	2.461(3)
OL16	110.57(15)	107.81(19)	1.585(3)	2.530(3)
OL56	104.18(16)	111.00(16)	105.59(19)	1.594(3)
P(1)-OL13-P(3)	131.6(2)	P(1)-P(2)-P(3)	107.9(2)	
P(1)-OL12-P(2)	136.8(2)	P(2)-P(1)-P(3)	95.80(2)	
P(2)-OL23-P(3)	128.0(2)	P(1)-P(3)-P(2)	115.4(2)	
P(4)-OL46-P(6)	131.3(2)	P(4)-P(5)-P(6)	108.0(2)	
P(4)-OL45-P(5)	128.0(2)	P(5)-P(4)-P(6)	115.3(2)	
P(5)-OL56-P(6)	137.1(2)	P(4)-P(6)-P(5)	95.62(2)	
P(1)-P(2)	2.872(2)	P(4)-P(5)	2.874(2)	
P(2)-P(3)	2.975(2)	P(5)-P(6)	2.972(2)	
P(3)-P(1)	2.922(2)	P(6)-P(4)	2.923(2)	

Estimated standard deviations are given in parentheses.

The crystal structure is stabilized by three types of hydrogen bonding (Table IV):

(i) The O(W)–H···O, which ensures the cohesion between anions in the layer. These interactions, including eight relatively long contacts, exhibit H···O distances ranging from 1.741 to 2.369 Å.
(ii) The N–H···O interactions, which are formed by 12 relatively weak contacts, since the H···O distances ranging from 1.890(2) to 2.507(2) Å link 4-chlorobenzylanilinium to the anionic layer.
(iii) One C—H···O hydrogen bond, with C—O distances 3.233(6)Å and C—H···O angle 156.00°.

Thermal Analysis

The combined TGA-DTA curves of the title compound are shown in Figure 4. The strong endothermic peak around 91°C is due to the loss of hydration water molecules. The calculated weight loss for this process is 6.37%, and the observed weight loss is 6.12%. After 143°C, a significant weight loss is observed for a series of weak ATD peaks. This can be interpreted by a decomposition of the P_6O_{18} ring and combustion of the

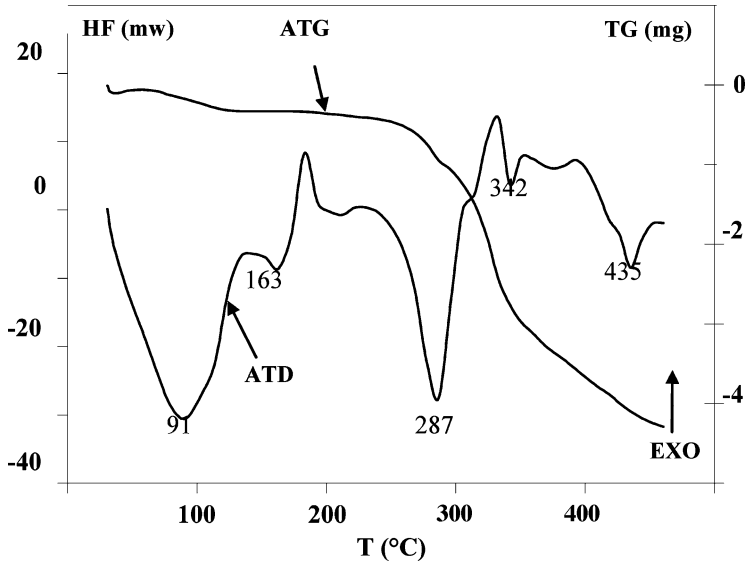

FIGURE 4 DTA and TGA thermograms of $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$ between room temperature and 500°C.

organic groups, which give polyphosphoric acids as viscous matter with a black residue of carbon.

IR Spectroscopy

Figure 5 shows the IR spectrum of [4-ClC$_6$H$_4$CH$_2$NH$_3$]$_4$Li$_2$P$_6$O$_{18}$·4H$_2$O between 4000 and 400 cm^{-1}. The absorption bands, in the range 4000–1350 cm^{-1} correspond to the O(N,C)–H stretching and bending vibrations of the water molecules and organic groups. The strong bands observed in the ranges 1350–1180, 1180–1060, 1060–960, and 850–660 cm^{-1} can be assigned to the stretching vibrations ν_{as}(OPO$^-$), ν_s(OPO$^-$), ν_{as}(POP), and ν_s(POP), respectively.[10] Nevertheless, special caution must be paid in attributing these bands because of their possible overlapping with ν(C–N) stretching vibration and δ(C–H) bending vibration bands. We note that the supplementary frequency in the ν_s(OPO) domain can be assigned to the stretching ν(C-C) vibrations. Frequencies below 660 cm^{-1}can be assigned to bending vibrations of P_6O_{18} ring.

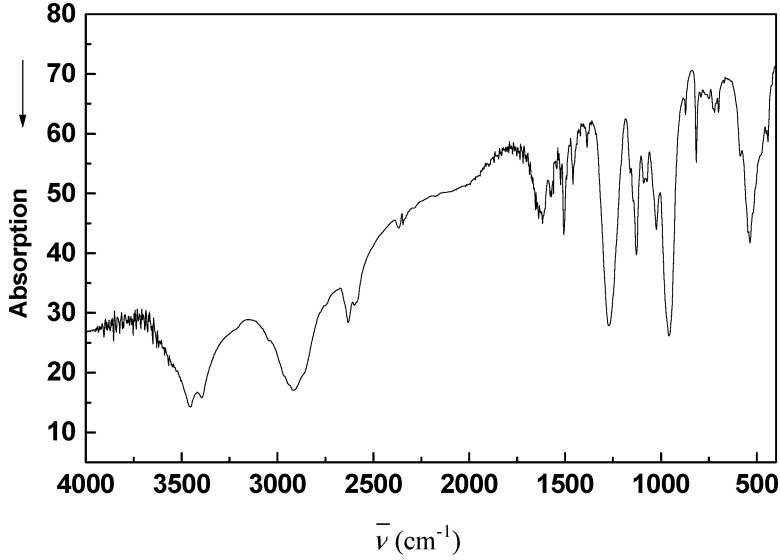

FIGURE 5 IR spectrum of [4-ClC$_6$H$_4$CH$_2$NH$_3$]$_4$Li$_2$P$_6$O$_{18}$·4H$_2$O in KBr pellet.

TABLE III Selected Bond Lengths (Å) and Bond Angles (°) in the Organic Groups of the $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$

(4-Cl(1)CH$_2$C$_6$ H$_4$N(1)H$_3$)$^+$					
C(7)-N1	1.477(7)	C(3)-C(4)	1.363(9)	C(6)-C(1)	1.373(9)
C(1)-C(2)	1.496(8)	C(4)-C(5)	1.375(9)	C(1)-C(7)	1.391(8)
C(2)-C(3)	1.366(6)	C(5)-C(6)	1.378(9)	Cl(1)-C(5)	1.728(7)
N1-C(1)-C(2)	112.3(4)	C(4)-C(5)-C(6)	119.9(6)	C(7)-C(2)-C(3)	117.4(5)
C(1)-C(2)-C(3)	121.2(5)	C(5)-C(6)-C(7)	119.4(6)	Cl(1)-C(5)-C(4)	119.2(5)
C(2)-C(3)-C(4)	122.5(6)	C(6)-C(7)-C(2)	121.3(5)	Cl(1)-C(5)-C(6)	120.9(5)
C(3)-C(4)-C(5)	119.5(5)	C(1)-C(2)-C(7)	121.4(4)		
(4-Cl(2)CH$_2$C$_6$ H$_4$N(2)H$_3$)$^+$					
C(8)-N2	1.483(6)	C(10)-C(11)	1.374(8)	C(13)-C(14)	1.366(8)
C(8)-C(9)	1.500(7)	C(11)-C(12)	1.368(9)	C(9)-C(14)	1.391(7)
C(9)-C(10)	1.376(6)	C(12)-C(13)	1.375(6)	Cl(2)-C(12)	1.731(6)
N2-C(8)-C(9)	112.5(4)	C(11)-C(12)-C(13)	120.7(6)	C(14)-C(9)-C(10)	117.0(5)
C(8)-C(9)-C(10)	121.2(5)	C(12)-C(13)-C(14)	119.4(5)	Cl(2)-C(12)-C(11)	120.8(4)
C(9)-C(10)-C(11)	122.3(5)	C(13)-C(14)-C(9)	121.7(4)	Cl(2)-C(12)-C(13)	118.5(5)
C(10)-C(11)-C(12)	118.9(4)	C(14)-C(9)-C(8)	121.8(4)		
(4-Cl(3)CH$_2$C$_6$H$_4$ N(3)H$_3$)$^+$					
C(15)-N3	1.471(7)	C(17)-C(18)	1.364(9)	C(20)-C(21)	1.365(9)
C(15)-C(16)	1.485(8)	C(18)-C(19)	1.375(7)	C(16)-C(21)	1.387(6)
C(16)-C(17)	1.396(9)	C(19)-C(20)	1.362(9)	Cl(3)-C(19)	1.733(7)
N3-C(15)-C(16)	112.7(4)	C(18)-C(19)-C(20)	119.5(7)	C(19)-C(20)-C(21)	120.4(5)
C(15)-C(16)-C(17)	121.6(5)	C(20)-C(21)-C(16)	122.0(6)	Cl(3)-C(19)-C(18)	120.8(5)
C(16)-C(17)-C(18)	121.7(5)	C(21)-C(16)-C(17)	116.3(6)	Cl(3)-C(19)-C(20)	119.7(6)
C(17)-C(18)-C(19)	120.2(6)	C(21)-C(16)-C(15)	122.1(5)		
(4-Cl(4)CH$_2$C$_6$H$_4$ N(4)H$_3$)$^+$					
C(22)-N4	1.495(6)	C(24)-C(25)	1.356(8)	C(27)-C(28)	1.365(8)
C(22)-C(23)	1.484(8)	C(25)-C(26)	1.368(7)	C(23)-C(28)	1.385(6)
C(23)-C(24)	1.399(8)	C(26)-C(27)	1.367(9)	Cl(4)-C(26)	1.741(6)
N4-C(22)-C(23)	113.1(4)	C(25)-C(26)-C(27)	120.6(6)	C(22)-C(23)-C(28)	121.0(5)
C(22)-C(23)-C(24)	121.8(4)	C(26)-C(27)-C(28)	119.3(5)	Cl(4)-C(26)-C(25)	118.9(5)
C(23)-C(24)-C(25)	121.1(4)	C(27)-C(28)-C(23)	121.8(5)	Cl(4)-C(26)-C(27)	120.5(4)
C(24)-C(25)-C(26)	120.0(6)	C(28)-C(23)-C(24)	117.1(5)		

EXPERIMENTAL

Synthesis of $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$

Crystals of the title compound were prepared by an acid/base reaction. An aqueous solution of cyclohexaphosphoric acid was first obtained by passing a solution of $Li_6P_6O_{18}$ (3.0 g, 4.8 mmol dissolved in 60 mL of water) through an ion exchange resin in its H-state (Amberlite IR 120). The lithium salt was prepared according to the procedure of Schulke and Kayser.[11] The obtained solution was immediately neutralized by adding an alcoholic solution of 4-chlorobenzylamine (2.35 mL, 19.2 mmol) dropwise. After several days of slow evaporation at room

TABLE IV Hydrogen-Bond Scheme in [4-ClC$_6$H$_4$CH$_2$NH$_3$]$_4$Li$_2$P$_6$O$_{18}$·4H$_2$O

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
N1-H1A···O3W	0.890	1.965	2.840(6)	167.20
N1-H1B···OL56	0.890	2.194	2.988(5)	148.20
N1-H1B···OE25	0.890	2.332	3.011(5)	133.02
N1-H1C···OE11	0.890	1.990	2.858(5)	164.71
N1-H1C···OE21	0.890	2.504	3.121(5)	126.90
N2-H2A···OE25	0.890	1.927	2.761(5)	155.39
N2-H2B···OE21	0.890	2.182	2.918(5)	139.67
N2-H2B···OE14	0.890	2.394	3.088(6)	134.95
N2-H2C···OE12	0.890	1.890	2.770(6)	169.33
N3-H3A···OE26	0.890	1.998	2.863(5)	163.67
N3-H3A···OE16	0.890	2.507	3.130(5)	127.52
N3-H3B···OL12	0.890	2.194	2.978(5)	146.61
N3-H3B···OE22	0.890	2.317	3.010(5)	134.76
N3-H3C···O4W	0.890	1.950	2.829(6)	169.06
N4-H4A···OE15	0.890	1.912	2.768(5)	160.62
N4-H4B···OE16	0.890	2.119	2.913(5)	148.15
N4-H4B···OE23	0.890	2.469	3.087(5)	126.96
N4-H4C···OE22	0.890	1.902	2.763(5)	162.38
O1W-H1W1···OE26	1.076	1.741	2.806(5)	169.25
O1W-H1W2···OE22	0.865	2.042	2.862(5)	158.03
O2W-H2W1···OE11	0.934	1.882	2.811(5)	172.53
O2W-H2W2···OE25	0.770	2.114	2.859(4)	162.76
O3W-H3W1···OE14	0.855	2.369	3.035(5)	135.12
O3W-H3W2···OE26	0.861	2.031	2.849(5)	158.31
O4W-H4W1···OE23	0.857	2.323	3.042(5)	141.66
O4W-H4W2···OE11	0.867	1.978	2.843(6)	174.88
C9-H9···OE41	0.930	2.360	3.233(6)	156.00

Estimated standard deviations are given in parentheses.

temperature, prismatic crystals appeared in the remaining solution with suitable dimensions for a crystallographic study. The lithium existence in [4-ClC$_6$H$_4$CH$_2$NH$_3$]$_4$Li$_2$P$_6$O$_{18}$.4H$_2$O resulted from an incomplete Li^+/H^+ exchange of $Li_6P_6O_{18}$ on the used resin.

Investigation Techniques

X-Ray Diffraction

The intensity data collection was performed using a Mach III Enraf-Nonius diffractometer operating at 296 K with wavelength Kα(Mo) = 0.7107 Å. The structures were solved by direct methods and refined by the full-matrix least-squares method on $F2$ using the SHELXL-97

TABLE V Crystal Data Measurement Conditions and Structure Determination of $[4\text{-}ClC_6H_4CH_2NH_3]_4Li_2P_6O_{18}\cdot 4H_2O$

Empirical Formula:	$C_{28}\ H_{44}Cl_4Li_2N_4O_{22}P_6$
Formula weight:	1130.17 (g mol^{-1})
Crystal system:	Triclinic
Space group:	P-1
a	9.628(8) (Å)
b	12.801(9) (Å)
c	19.528(6) (Å)
α	78.60(4)°
β	83.00(5)
γ	89.98(4)
Z	2
V	2341(3) ($Å^3$)
ρ-calc(g/cm^3)	1.603
F(0 0 0)	1160
μ(MoKα)	0.540 (mm^{-1})
Size (mm)	0.3*0.25*0.15
Index ranges	$-11 \leq h \leq 11$; $0 \leq k \leq 15$; $-5 \leq l \leq 22$
Independent reflections	5168
Refined parameters	632
Goodness-of-fit	1.045
R (anisotropic) ($I > 2\sigma(I)$)	0.0421
Rw (anisotropic)	0.1036

package.[12] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The maximum and minimum peaks on the final difference Fourier map correspond to 0.769 and -0.274 e/$Å^3$. The crystallographic data and structure determination parameters for the title compound are summarized in Table V.

Crystallographic data (CIF) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data center as supplementary publication No CCDC 665381.

Physical Measurements

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 was recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer Spectrum 1000 spectrophotometer using a sample dispersed in a spectroscopically pure KBr pellet.

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