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4,9-Diazonia-1,12-dodecanediammonium Dilithium *cyclo*-Hexaphosphate Tetrahydrate

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Abstract

In $(C_{10}H_{30}N_4)[Li_2(P_6O_{18})].4H_2O$, the $[P_6O_{18}]^{6-}$ anion is located around the twofold axis. Two Li cations, in regular tetrahedral environments, are connected to the phosphoric anion by short Li—P bonds of 3.074 (4) Å. An isolated eight-membered complex ring anion $[Li_2(P_6O_{18})(H_2O)_4]^{4-}$ of symmetry 2 is then formed. Hydrogen bonds from the water molecules link these anions in successive layers parallel to the *bc* plane. The cohesion between these layers is a result of hydrogen bonds from the long chain tetracation, $[NH_3(CH_2)_3NH_2(CH_2)_4NH_2(CH_2)_3NH_3]^{4+}$.

Comment

The present investigation is part of a systematic study of organic cation derivatives of cyclohexaphosphates. Some results involving small organic molecules have been reported previously (Durif & Averbuch-Pouchot, 1990; Averbuch-Pouchot & Durif, 1991). In this work, we describe the crystal structure of the title compound. Its preparation, main crystallographic features and physico-chemical properties will be described elsewhere (Gharbi & Jouini, 1996). Fig. 1 shows a projection of the atomic arrangement along the *a* axis. For clarity, only half the contents of the cell is represented. This atomic arrangement can be described as a stacking of isolated eight-membered $[Li_2(P_6O_{18})(H_2O)_4]^{4-}$ ring anions interconnected in a two-dimensional way *via* hydrogen-bonded water molecules. The average planes of the layers are located at $x = 0.25$ and $x = 0.75$. The P—P and P—Li distances in the ring anion formed by one P_6O_{18} phosphoric group and two LiO_4 tetrahedra are similar. The ring anions are located around the twofold axis, so have internal symmetry 2 and consequently comprise only four tetrahedra: three independent PO_4 and one LiO_4. The cohesion between successive layers is the result of the relatively strong hydrogen bonds (Blessing, 1986; Brown, 1976) from the organic tetracation. The geometric features observed in the title compound are quite similar to those reported previously for condensed phosphates with organic cations (Gharbi & Jouini, 1995). It should be noted that the organic cation is the first long chain, so far, to be observed with condensed phosphate anions.

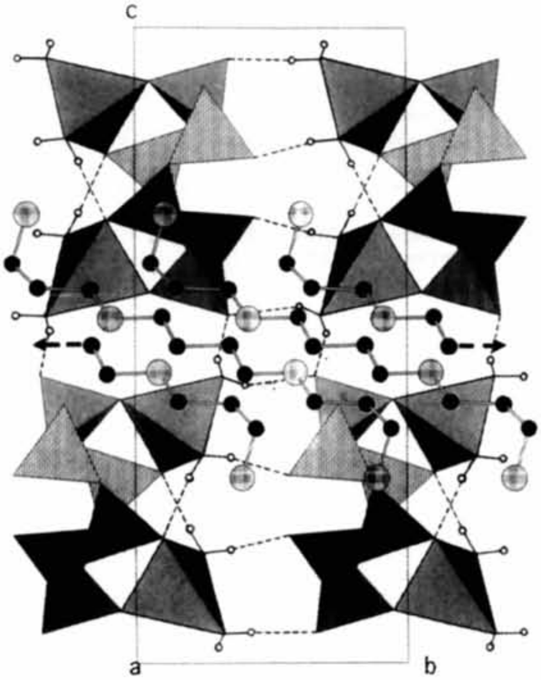

Fig. 1. Projection along the [100] direction of the ring anions $[Li_2P_6O_{18}(H_2O)_4]^{4-}$, in polyhedral representation, located at $x = 0.25$. The large shaded circles represent N atoms, black circles C atoms and the small circles water-molecule H atoms. Hydrogen bonds in the layer are denoted by full and dashed lines.

Experimental

The title compound was prepared as described by Gharbi & Jouini (1996).

Crystal data

$(C_{10}H_{30}N_4)[Li_2(P_6O_{18})].$-
$4H_2O$
$M_r = 766.14$
Monoclinic
$C2/c$
$a = 21.040\ (2)$ Å
$b = 7.936\ (2)$ Å
$c = 20.444\ (2)$ Å
$\beta = 116.440\ (10)°$
$V = 3056.5\ (9)$ Å^3
$Z = 4$
$D_x = 1.665$ Mg m^{-3}
$D_m = 1.556$ Mg m^{-3}
D_m measured by pycnometry (toluene)

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–16°$
$\mu = 0.445$ mm^{-1}
$T = 293\ (2)$ K
Multifaced prism
$0.24 \times 0.22 \times 0.15$ mm
Colourless

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Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2776 measured reflections
2691 independent reflections
2196 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0115$
$\theta_{\rm max} = 24.98°$
$h = -24 \rightarrow 22$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 24$
2 standard reflections
frequency: 120 min
intensity decay: 0.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0326$
$wR(F^2) = 0.1092$
$S = 0.906$
2691 reflections
276 parameters
H-atom parameters refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 3.771P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.330$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.434$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0011 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P(1)	0.48409 (3)	0.28137 (7)	0.10477 (3)	0.0138 (2)
P(2)	0.61289 (3)	0.42963 (8)	0.21920 (3)	0.0178 (2)
P(3)	0.61333 (3)	0.20929 (7)	0.33528 (3)	0.0149 (2)
O(*E*11)	0.47648 (9)	0.1601 (2)	0.04704 (9)	0.0232 (4)
O(*E*12)	0.44990 (8)	0.4480 (2)	0.08348 (9)	0.0213 (4)
O(*L*12)	0.56790 (8)	0.2991 (2)	0.15616 (8)	0.0189 (4)
O(*E*21)	0.58180 (10)	0.6015 (2)	0.19861 (9)	0.0259 (4)
O(*L*23)	0.59718 (10)	0.3747 (2)	0.28574 (9)	0.0242 (4)
O(*E*31)	0.67032 (9)	0.2476 (2)	0.40913 (9)	0.0248 (4)
O(*L*13)	0.46042 (8)	0.1901 (2)	0.16077 (9)	0.0201 (4)
O(*E*320	0.62183 (10)	0.0605 (2)	0.29646 (9)	0.0261 (4)
O(*E*22)	0.68779 (9)	0.4032 (3)	0.23641 (10)	0.0382 (5)
O(*W*1)	0.45975 (12)	−0.1806 (3)	0.04590 (12)	0.0322 (5)
Li	0.4779 (2)	0.6640 (5)	0.1245 (2)	0.0268 (9)
O(*W*2)	0.4251 (2)	0.7501 (3)	0.17312 (14)	0.0499 (7)
N(1)	0.29925 (11)	0.4123 (2)	−0.04206 (11)	0.0173 (4)
N(2)	0.83232 (12)	0.3887 (3)	0.29243 (12)	0.0232 (5)
C(1)	0.74459 (15)	0.6547 (3)	0.49889 (15)	0.0268 (6)
C(2)	0.29172 (14)	0.5997 (3)	−0.04469 (15)	0.0239 (5)
C(3)	0.33105 (13)	0.3406 (3)	−0.08812 (13)	0.0212 (5)
C(4)	0.32200 (13)	0.1502 (3)	−0.09139 (13)	0.0206 (5)
C(5)	0.64090 (14)	−0.0586 (3)	0.12983 (15)	0.0268 (6)

Table 2. *Selected geometric parameters (Å, °)*

P(1)O$_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1.476 (2)	118.9 (1)	106.1 (1)	108.5 (1)
O(*E*12)	2.542 (2)	1.475 (2)	111.3 (1)	110.4 (1)
O(*L*12)	2.464 (2)	2.546 (2)	1.607 (2)	99.9 (1)
O(L13)	2.505 (2)	2.534 (2)	2.462 (2)	1.610 (2)

P(2)O$_4$ tetrahedron

P(2)	O(*E*21)	O(*E*22)	O(*L*12)	O(*L*23)
O(*E*21)	1.490 (2)	119.2 (1)	109.8 (1)	105.0 (1)
O(*E*22)	2.552 (3)	1.469 (2)	106.8 (1)	111.3 (1)
O(*L*12)	2.525 (2)	2.460 (2)	1.595 (2)	103.7 (1)
O(*L*23)	2.450 (2)	2.533 (3)	2.511 (2)	1.597 (6)

P(3)O$_4$ tetrahedron

P(3)	O(*E*31)	O(*E*32)	O(*L*13)	O(*L*23)
O(*E*31)	1.482 (2)	118.3 (1)	109.4 (1)	108.9 (1)
O(*E*32)	2.541 (2)	1.478 (2)	107.7 (1)	111.0 (1)
O(*L*13)	2.513 (2)	2.483 (2)	1.597 (2)	100.0 (1)
O(*L*23)	2.509 (2)	2.537 (2)	2.448 (2)	1.599 (2)

P(1)—P(2)	2.925 (1)	P(2)—P(3)	2.944 (1)
P(1)—P(3)	2.875 (1)	P(2)—Li	3.221 (1)
P(1)—Li	3.074 (4)		

P(2)—P(1)—P(3)	108.76 (3)	P(1)—P(2)—P(3)	94.30 (3)
P(1)—P(3)—P(2)	118.58 (3)	P(1)—O(L12)—P(2)	132.0 (1)
P(2)—O(L23)—P(3)	134.2 (1)	P(1)—O(L13)—P(3)'	127.5 (1)

LiO$_4$ tetrahedron

Li—O(*E*12)	1.884 (5)	Li—O(*W*1)	1.924 (5)
Li—O(*E*21)	2.090 (5)	Li—O(*W*2)	1.918 (5)

[NH$_3$(CH$_2$)$_3$NH$_2$(CH$_2$)$_4$(CH$_2$)$_3$NH$_3$] group

C(1)—C(1)	1.528 (5)	C(3)—C(4)	1.521 (3)
C(1)—C(2)	1.512 (3)	C(4)—C(5)	1.517 (3)
C(2)—N(1)	1.494 (3)	C(5)—N(2)	1.490 (3)
N(1)—C(3)	1.490 (3)		

C(1)—C(1)—C(2)	112.1 (3)	N(1)—C(3)—C(4)	108.9 (2)
C(1)—C(2)—N(1)	109.9 (2)	C(3)—C(4)—C(5)	114.5 (2)
C(1)—N(1)—C(3)	115.3 (2)	C(4)—C(5)—N(2)	112.4 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H(1N1)···O(*E31*)$^{\rm i}$	0.90 (4)	2.06 (4)	2.820 (3)	141 (3)
N1—H(2N1)···O(*E*31)$^{\rm ii}$	0.90 (4)	1.85 (4)	2.748 (3)	176 (3)
N2—H(1N2)···O(*E*22)	0.92 (3)	1.83 (4)	2.733 (3)	166 (3)
N2—H(2N2)···O(*E*21)$^{\rm iii}$	0.84 (4)	2.09 (4)	2.863 (3)	154 (3)
N2—H(3N2)···O(*E*32)$^{\rm iv}$	0.89 (3)	1.88 (3)	2.766 (3)	172 (3)
O(*W*1)—H(1*W*1)···O(*E*11)$^{\rm v}$	0.70 (4)	2.10 (4)	2.776 (3)	163 (4)
O(*W*1)—H(2*W*1)···O(*E*11)	0.87 (5)	1.89 (5)	2.725 (3)	161 (4)
O(*W*2)—H(1*W*2)···O(*E*32)$^{\rm vi}$	0.84 (5)	2.03 (5)	2.824 (3)	157 (4)
O(*W*2)—H(2*W*2)···O(*E*21)$^{\rm i}$	0.88 (5)	2.06 (5)	2.937 (3)	175 (4)
H(1*W*1)—O(*W*1)···H(2*W*1)				105 (4)
H(1*W*2)—O(*W*2)···H(2*W*2)				104 (4)

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$; (v) $1 - x, -y, -z$; (vi) $1 - x, 1 + y, \frac{1}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium Phthalimide

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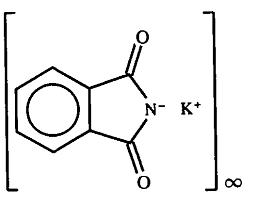
Abstract

Potassium phthalimide, $K^+.C_8H_4NO_2^-$, a widely used reagent for the preparation of anthranilic acid *via* Hofmann degradation or primary alkylamines *via* the Gabriel synthesis, crystallizes in polar layers of potassium cations coordinated by five O and three N centres alternating with apolar layers of stacked benzene subunits.

Comment

Potassium phthalimide, (I), is an industrial product prepared on a technical scale, *e.g.* as a precursor of anthranilic acid (*Ullmann's Encyclopedia of Industrial Chemistry*, 1992) or for the selective preparation of primary amines *via* the Gabriel synthesis (Gibson & Bradshaw, 1968; Gabriel, 1887). Neither its crystal structure nor crystal structures of other alkaline salts of phthalimide have been reported previously.



(I)

The potassium salt crystallizes in space group $P2_1/n$ with one molecular anion and one potassium cation in the asymmetric unit (Fig. 1). The cations are arranged in layers perpendicular to the *b* axis (Fig. 2) and within a layer are surrounded by four potassium neighbours, with K···K distances between 3.841 (1) and 4.120 (1) Å. The coordination sphere of the cation consists of five carbonyl O centres, with contact distances between 2.683 (2) and 3.086 (2) Å, and three N centres, with contact distances ranging from 2.935 (2) to 3.199 (2) Å. The molecular anions are stacked along the *a* axis almost perpendicular to their plane, with an interplanar distance of about 3.4 Å. The offset between the centroids of their benzene rings is about 1.76 Å and al-

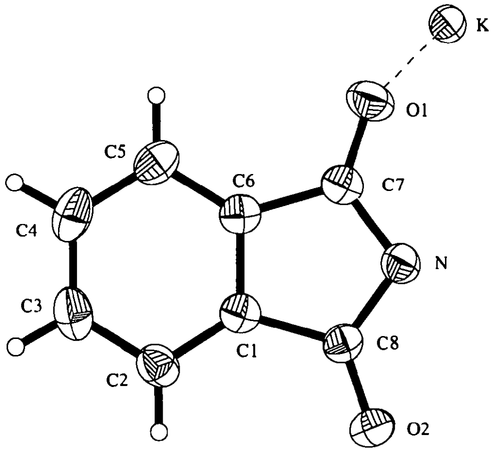


Fig. 1. View of both the anisotropic displacement ellipsoids for the non-H atoms of (I), plotted at the 50% probability level, and the numbering scheme for the asymmetric unit.

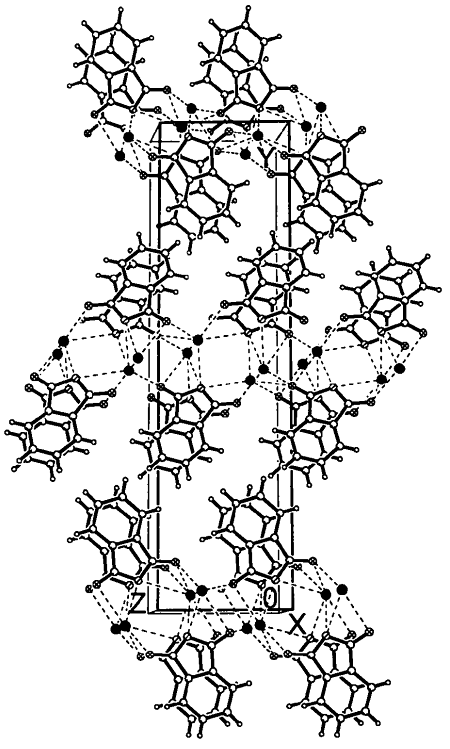


Fig. 2. The crystal packing viewed almost along the *a* axis.

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