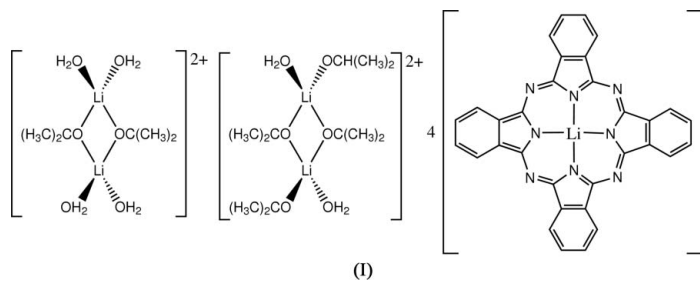


David A. Grossie,^{a*} William A. Feld,^a Lawrence Scanlon,^b Giselle Sandi^c and Zdzislaw Wawrzak^d^aDepartment of Chemistry, Wright State University, Dayton, Ohio 45435, USA, ^bAir Force Research Laboratory, Electrochemistry and Thermal Sciences Branch, PRPS, WPAFB, Ohio 45433, USA, ^cChemistry Division, Argonne National Laboratory, 9700 Cass Ave., Argonne, IL 40439, USA, and ^dDuPont–Northwestern–Dow Collaborative Access Team, Argonne National Laboratory, 9700 Cass Avenue, Argonne, IL 40439, USACorrespondence e-mail:
david.grossie@wright.edu**Key indicators**Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.049
 wR factor = 0.136
Data-to-parameter ratio = 17.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Di- μ -acetone- $\kappa^2\text{O}:\text{O}$ -bis[(acetone- κO)-aqualithium(I)] di- μ -acetone- $\kappa^2\text{O}:\text{O}$ -bis-[diaqualithium(I)] tetrakis[[phthalocyaninato(2-)- $\kappa^4\text{N},\text{N}',\text{N}'',\text{N}''''$]]lithiate(I)}**

The crystals of the title compound, $[\text{Li}_2(\text{C}_3\text{H}_6\text{O})_4(\text{H}_2\text{O})_2][\text{Li}_2(\text{C}_3\text{H}_6\text{O})_2(\text{H}_2\text{O})_4][\text{Li}(\text{C}_{32}\text{H}_{16}\text{N}_8)]_4$, were obtained by a recrystallization of dilithium phthalocyanine from an acetone/water/toluene solution. The title structure consists of two independent Li–phthalocyanine complexes along with acetone-bridged lithium dimers. The lithium dimers are located on inversion centers. The crystal structure is stabilized by a network of hydrogen bonds.

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Dilithium phthalocyanine (Li_2Pc) shows promise as a dielectric for lithium ion batteries. Experimental evidence indicates that the Li^{I} ions within the solid structure migrate in the presence of an electric field (Scanlon *et al.*, 2004). This suggests that Li_2Pc may have a solid structure which contains a continuous series of voids which act as Li^{I} ion-conducting channels. However, to date there have not been any successful single-crystal diffraction studies of Li_2Pc . As part of our effort to study the crystal structure of Li_2Pc , recrystallization of Li_2Pc from an acetone/water/toluene solution gave the title compound, (I).



The crystal structure of (I) is composed of four ionic units. The first unit is a phthalocyanine dianion (Pc) with the coordinated Li^{I} ion; this dianion is stacked in symmetry-related pairs. The inversion center relating this pair of fragments lies at the fractional coordinates $(\frac{1}{2}, 0, 0)$. The mean planes defined by Pc in this pair are separated by a distance of 3.38 (2) Å. The second unit is also a Pc with the coordinated Li^{II} ion. This second fragment is stacked in symmetry-related pairs. The inversion center relating the pairs of the second fragment is located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The mean planes defined by the symmetry-related pairs of Pc in this unit are separated by a distance of 3.062 (2) Å.

Each Li^{I} atom in units 1 and 2 shows square-planar coordination by the four N atoms of a Pc ligand. The Li–N distances are essentially the same in each of the units (Table 1). The slightly longer bond length in unit 1 is

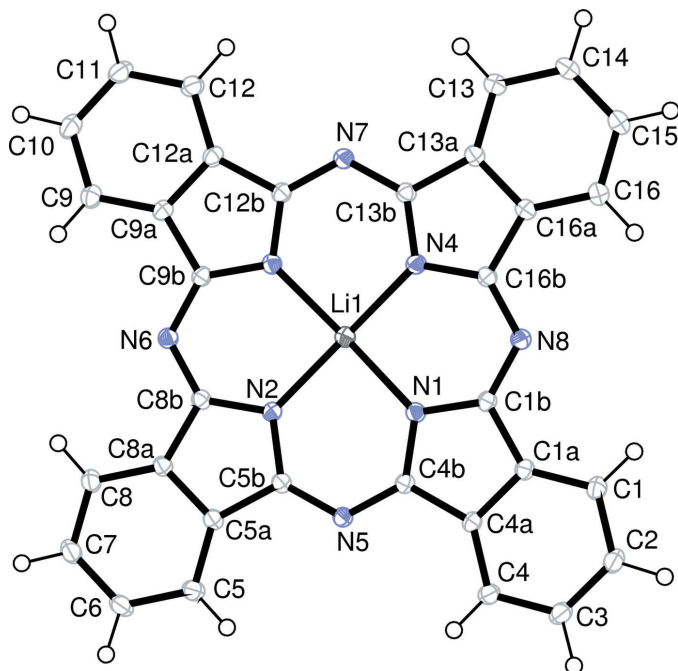


Figure 1
The anion containing Li1, which lies 0.396 (2) Å above the mean plane of the ring defined by all non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.

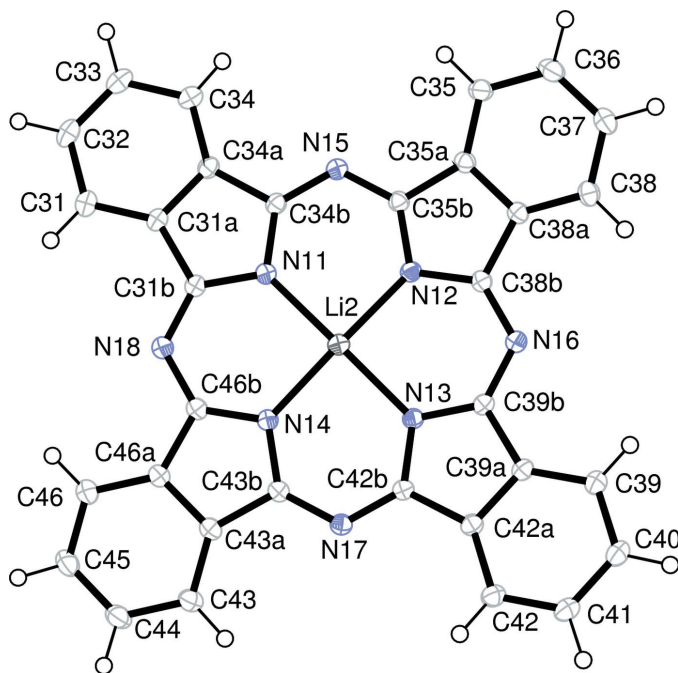


Figure 2
The anion containing Li2 which lies 0.121 (2) Å below the plane of the non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.

undoubtedly due to the weak interaction of Li1 with the atom N2¹ at a distance of 2.713 (2) Å [symmetry code: (i) 1 - x, 2 - y, -z]. Pairs of parallel Pc ligands lie at a dihedral angle of 72.93 (1)° to each other. With this manner of packing of LiPc complexes, open channels are created within the structure.

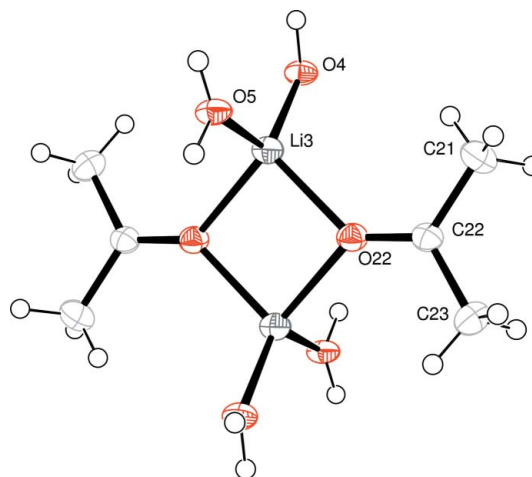


Figure 3
The cation containing Li3, an acetone-bridged tetrahedral dimer with two water ligands completing each coordination. Displacement ellipsoids are drawn at the 30% probability level.

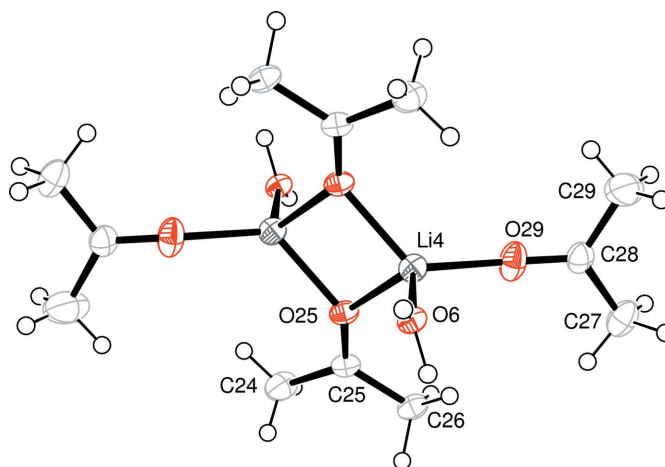


Figure 4
The cation containing Li4, an acetone-bridged tetrahedral dimer with water and acetone ligands completing each coordination. Displacement ellipsoids are drawn at the 30% probability level.

These channels are directed along the *a* axis of the unit cell, tangential to the *ab* and *ac* faces, and are occupied by the third and fourth units, which are cationic.

The third and fourth units, *viz.*, [Li₂(H₂O)₄[(CH₃)₂CO]₂]²⁺ and [Li₂(H₂O)₂[(CH₃)₂CO]₄]²⁺, lie on the inversion centers at (½, ½, 0) and (½, 0, ½), respectively. Although each of these dimers contains two Li^I ions bridged by two acetone molecules, the remaining two positions of the tetrahedral coordination are filled differently. Unit 3 fills the last two sites on each Li^I ion by water molecules, whereas unit 4 has one water and one acetone ligand filling the remaining coordination sites on each Li^I ion.

The four ionic units are held together through a network of hydrogen bonds between the anions and cations (Table 2).

Experimental

Dilithium phthalocyanine is commercially available from Sigma-Aldrich. Single crystals of (I) were obtained by recrystallization of

dilithium phthalocyanine from an acetone/toluene solution (3:1) over a period of 12 weeks.

Crystal data

$[\text{Li}_2(\text{C}_3\text{H}_6\text{O})_4(\text{H}_2\text{O})_2] \cdot$	$V = 3118.7 (3) \text{ \AA}^3$
$[\text{Li}_2(\text{C}_3\text{H}_6\text{O})_2(\text{H}_2\text{O})_4] \cdot$	$Z = 1$
$[\text{Li}(\text{C}_{32}\text{H}_{16}\text{N}_8)]_4$	$D_x = 1.364 \text{ Mg m}^{-3}$
$M_r = 2562.20$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 7231 reflections
$a = 12.8017 (6) \text{ \AA}$	$\theta = 2.2\text{--}30.5^\circ$
$b = 14.3637 (7) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 17.3859 (8) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 101.5838 (9)^\circ$	Block, purple
$\beta = 94.1351 (9)^\circ$	$0.45 \times 0.10 \times 0.08 \text{ mm}$
$\gamma = 92.3054 (9)^\circ$	

Data collection

Bruker SMART APEX CCD diffractometer	18798 independent reflections
ω scans	15504 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.019$
$T_{\text{min}} = 0.879$, $T_{\text{max}} = 0.993$	$\theta_{\text{max}} = 30.5^\circ$
37676 measured reflections	$h = -18 \rightarrow 18$
	$k = -20 \rightarrow 20$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 0.3984P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.136$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
18798 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
1105 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected bond lengths (\AA).

Li1—N1	1.994 (2)	Li3—O4	1.863 (2)
Li1—N2	1.991 (2)	Li3—O5	1.890 (2)
Li1—N2 ⁱ	2.713 (2)	Li3—O22	1.998 (2)
Li1—N3	1.973 (2)	Li3—O22 ⁱⁱ	2.002 (2)
Li1—N4	1.969 (2)	Li3—Li3 ⁱⁱⁱ	2.861 (4)
Li1—Li1 ⁱ	3.010 (4)	Li4—O6	1.880 (2)
Li2—N11	1.954 (2)	Li4—O25 ⁱⁱⁱ	1.981 (2)
Li2—N12	1.962 (2)	Li4—O25	1.986 (2)
Li2—N13	1.989 (2)	Li4—O28	1.895 (2)
Li2—N14	1.967 (2)	Li4—Li4 ⁱⁱⁱ	2.906 (4)
C35—C36	1.3913 (16)		

Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y + 2, -z + 1$.

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O4—H4C \cdots N5 ⁱⁱ	0.901 (19)	1.896 (19)	2.7241 (12)	151.9 (15)
O4—H4D \cdots N13	0.84 (2)	2.11 (2)	2.9279 (12)	165.8 (19)
O5—H5C \cdots N1 ⁱⁱ	0.84 (2)	2.32 (2)	3.1046 (13)	155.0 (17)
O5—H5D \cdots N17 ⁱⁱ	0.90 (2)	1.94 (2)	2.8239 (12)	171.3 (19)
O6—H6C \cdots N15 ^{iv}	0.90 (2)	2.08 (2)	2.9684 (13)	169.1 (17)
O6—H6D \cdots N7	0.95 (2)	1.90 (2)	2.8310 (12)	165.9 (18)

Symmetry codes: (ii) $-x + 1, -y + 1, -z$; (iv) $x, y + 1, z$.

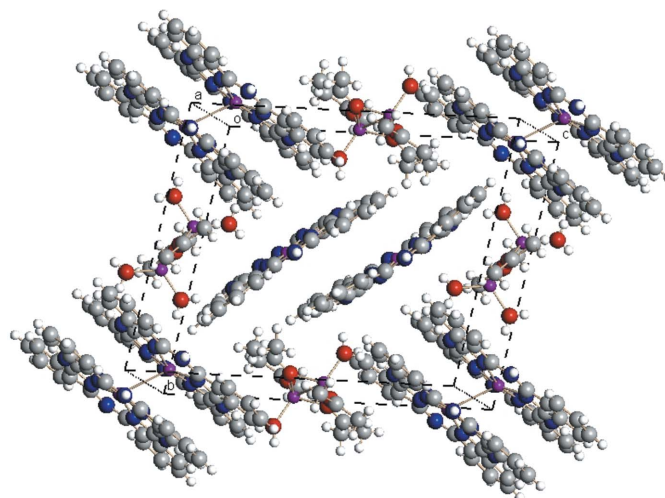


Figure 5

View of the crystal structure approximately down the a axis, showing the channels through the structure. The pairs of unit 1 (containing Li) are in the center of the drawing and the pairs of unit 2 are at each corner. Units 3 are on the right and left, while units 4 are top and bottom.

H atoms of the C29 methyl group were placed in calculated positions, with $\text{C—H} = 0.98 \text{ \AA}$, and torsion angles refined to fit the electron density, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H atoms were located in a difference Fourier map and refined with isotropic displacement parameters. The final range of refined C—H distances was $0.90\text{--}0.99 \text{ \AA}$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997), MERCURY (Bruno *et al.*, 2002) and OSCAIL (McArdle, 1995); software used to prepare material for publication: PLATON (Spek, 2003).

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