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Supporting Document: Formation Mechanism of β - Li_3PS_4 through Decomposition of Complexes

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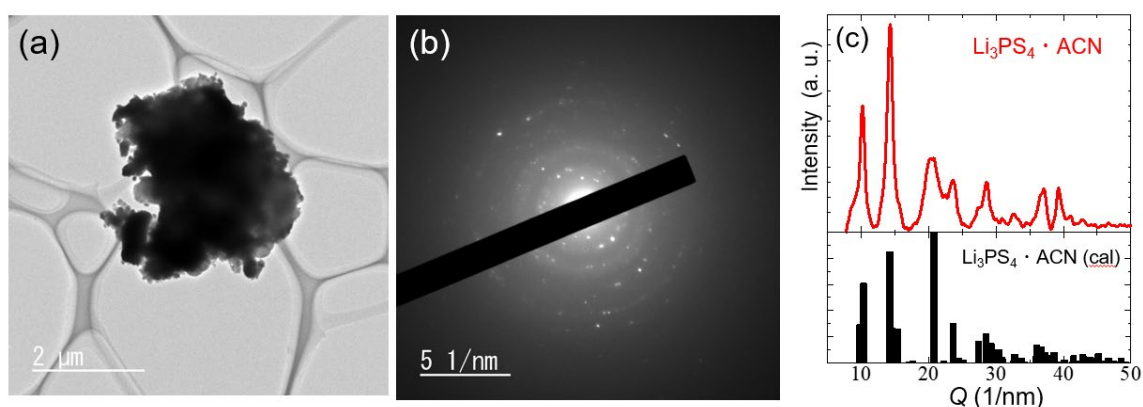


Figure S1 (a) Transmission electron microscopy (TEM) image and (b) corresponding electron diffraction pattern of $\text{Li}_3\text{PS}_4 \cdot \text{ACN}$. The $\text{Li}_3\text{PS}_4 \cdot \text{ACN}$ sample was thinned by crushing and dispersed on a carbon film. The sample was attached to a vacuum holder in an Ar-filled glove box to prevent air exposure. TEM observation was done using JEM-2100F (JEOL co. ltd.) (c) Radial averaged intensity profile along the scattering vector Q corresponding of the diffraction pattern (b). The positions of the experimental peaks match with those of simulated peaks (cal), demonstrating that the sample has the $\text{Li}_3\text{PS}_4 \cdot \text{ACN}$ structure determined by XRD analysis.

Rietveld Refinement of Li₃PS₄-ACN complex

The document described below was prepared by combination of RIETAN-FP,¹ ORFFE, lst2cif, and cif2pdf, which are included in the RIETAN-FP-VENUS package, developed by Dr. Fujio Izumi et al.² Two members of the VENUS system, VESTA³ and Dysnomia,⁴ are available for download from JP-Minerals.⁵

Table S1: Experimental conditions and analytical results

Compound	Li ₃ PS ₄ -ACN complex
Chemical formula	C ₂ Li ₃ NS ₄ P
M_r	218.085
Crystal system	Tetragonal
Space group	$P4_2/nbc$ (No. 133)
Hall symbol	−P 4ac 2b
Center of symmetry	An inversion center at the origin
$a/\text{\AA}$	8.5796(3)
$b/\text{\AA}$	8.5796(3)
$c/\text{\AA}$	12.7585(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	939.14(5)
Z	4
$D_x/\text{Mg m}^{-3}$	1.5424
$F(000)$	428.00
Radiation source	Synchrotron radiation
Wavelength, $\lambda/\text{\AA}$	0.496350
Goniometer	Debye–Scherrer geometry
$2\theta_{\min}/^\circ$	2.1000
$2\theta_{\max}/^\circ$	25.0140
$\Delta 2\theta/^\circ$	0.0060
Data points	3820
$d_{\min}/\text{\AA}$	1.14599
Refined parameters	33
Constraints	6
R_{wp}	0.03019
R_e	0.02148
$S = R_{\text{wp}}/R_e$	1.40549
R_p	0.02290
R_B	0.03918
R_{F^2}	0.07897
R_F	0.03023

Table S2: Fractional coordinates, isotropic atomic displacement parameters, and occupancies. mW denotes an integrated combination of the multiplicity and Wyckoff letter.

Site	mW	x	y	z	$U/\text{\AA}^2$	g
Li1	$16k$	0.489(9)	$-0.048(8)$	0.268(6)	0.038	0.5
Li2	$4a$	$3/4$	$3/4$	$1/2$	0.038	0.65(2)
Li3	$8e$	0	0	0	0.038	0.17(2)
P1	$4c$	$1/4$	$1/4$	$1/4$	0.009(2)	1
S1	$16k$	0.245(1)	0.0572(3)	0.3416(2)	0.024(1)	1
C1	$8i$	0.296(3)	$3/4$	$1/2$	0.019(4)	0.5
C2	$8i$	0.415(1)	$3/4$	$1/2$	0.019(4)	0.5
N1	$8i$	0.415(1)	$3/4$	$1/2$	0.019(4)	0.5

Table S3: Interatomic distances, l_{12} , between atoms 1 and 2, equivalent-position numbers (atoms2: n_2) and translations (atom 2: Δx_2 , Δy_2 , and Δz_2) along the a , b , and c axes

1	2	$l_{12}/\text{\AA}$	n_2	Δx_2	Δy_2	Δz_2
Li1	Li1	0.9(1)	8	0	0	0
Li1	S1	2.27(9)	11	0	0	0
Li1	S1	2.40(7)	13	0	0	0
Li1	S1	2.46(8)	1	0	0	0
Li1	P1	2.84(9)	11	0	0	0
Li1	S1	2.97(6)	8	0	0	0
Li1	Li3	3.00(8)	3	0	0	0
Li2	S1	2.612(3)	14	1	0	0
Li2	S1	2.612(3)	13	0	1	0
Li2	S1	2.612(3)	10	0	0	1
Li2	S1	2.612(3)	9	1	1	1
Li2	C2	2.870(8)	1	0	0	0
Li2	N1	2.8701(1)	1	0	0	0
Li2	C2	2.870(8)	2	1	1	0
Li2	N1	2.8701(1)	2	1	1	0
Li2	Li3	3.0333(1)	8	0	0	0
Li2	Li3	3.0333(1)	4	1	0	0
Li2	Li3	3.0333(1)	3	0	1	0
Li2	Li3	3.0333(1)	7	1	1	0
Li3	C2	2.264(3)	4	-1	0	-1
Li3	N1	2.2642(1)	4	-1	0	-1
Li3	C2	2.264(3)	12	1	-1	0
Li3	N1	2.2642(1)	12	1	-1	0
Li3	C1	2.77(2)	4	-1	0	-1
Li3	C1	2.77(2)	12	1	-1	0
Li3	S1	2.960(8)	7	0	0	0
Li3	S1	2.960(8)	15	0	0	-1
Li3	Li1	3.00(8)	12	0	-1	0
Li3	Li1	3.00(8)	4	0	0	-1
Li3	S1	3.017(9)	12	0	-1	0
Li3	S1	3.017(9)	4	0	0	-1
Li3	Li2	3.0333(1)	3	0	-1	-1
Li3	Li2	3.0333(1)	11	-1	1	0
P1	S1	2.025(2)	1	0	0	0
P1	S1	2.025(2)	2	0	0	0

1	2	$l_{12}/\text{\AA}$	n_2	Δx_2	Δy_2	Δz_2
P1	S1	2.025(2)	7	0	0	0
P1	S1	2.025(2)	8	0	0	0
P1	Li1	2.84(9)	13	-1	0	0
P1	Li1	2.84(9)	12	0	-1	0
P1	Li1	2.84(9)	14	1	0	0
P1	Li1	2.84(9)	11	0	1	0
S1	P1	2.025(2)	1	0	0	0
S1	Li1	2.27(9)	12	0	-1	0
S1	Li1	2.40(7)	13	-1	0	0
S1	Li1	2.46(8)	1	0	0	0
S1	Li2	2.612(3)	9	1	1	1
S1	Li3	2.960(8)	7	0	0	0
S1	Li1	2.97(6)	8	0	0	0
S1	Li3	3.017(9)	3	0	0	0
C1	C1	0.79(5)	2	0	1	0
C1	C2	1.02(3)	1	0	0	0
C1	N1	1.02(2)	1	0	0	0
C1	C2	1.82(2)	2	0	1	0
C1	N1	1.82(2)	2	0	1	0
C1	Li3	2.77(2)	8	0	0	0
C1	Li3	2.77(2)	3	0	1	0
C2	C1	1.02(3)	1	0	0	0
C2	C1	1.82(2)	2	0	1	0
C2	Li3	2.264(3)	8	0	0	0
C2	Li3	2.264(3)	3	0	1	0
C2	C2	2.84(2)	2	0	1	0
C2	N1	2.84(2)	2	0	1	0
C2	Li2	2.870(8)	1	0	0	0
N1	C1	1.02(2)	1	0	0	0
N1	C1	1.82(2)	2	0	1	0
N1	Li3	2.2642(1)	8	0	0	0
N1	Li3	2.2642(1)	3	0	1	0
N1	C2	2.84(2)	2	0	1	0
N1	N1	2.8394(1)	2	0	1	0
N1	Li2	2.8701(1)	1	0	0	0

Table S4: Bond angles, ϕ_{123} , for atoms 1, 2, and 3 with atom 2 as the apex, equivalent-position numbers (atom 1: n_1 ; atom 3: n_3), and translations (atom 1: Δx_1 , Δy_1 , Δz_1 ; atom 3: Δx_3 , Δy_3 , Δz_3) along the a , b , and c axes

1	2	3	$\phi_{123}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
Li1	Li1	S1	88(8)	8	0	0	0	11	0	0	0
Li1	Li1	S1	71(7)	8	0	0	0	13	0	0	0
Li1	Li1	S1	119(2)	8	0	0	0	1	0	0	0
Li1	Li1	P1	81(1)	8	0	0	0	11	0	0	0
Li1	Li1	S1	46(3)	8	0	0	0	8	0	0	0
Li1	Li1	Li3	114.9(5)	8	0	0	0	3	0	0	0
S1	Li1	S1	89(3)	11	0	0	0	13	0	0	0
S1	Li1	S1	137(3)	11	0	0	0	1	0	0	0
S1	Li1	P1	45(2)	11	0	0	0	11	0	0	0
S1	Li1	S1	113(3)	11	0	0	0	8	0	0	0
S1	Li1	Li3	135(3)	11	0	0	0	3	0	0	0
S1	Li1	S1	130(4)	13	0	0	0	1	0	0	0
S1	Li1	P1	44(1)	13	0	0	0	11	0	0	0
S1	Li1	S1	110(2)	13	0	0	0	8	0	0	0
S1	Li1	Li3	65(2)	13	0	0	0	3	0	0	0
S1	Li1	P1	157(3)	1	0	0	0	11	0	0	0
S1	Li1	S1	75(2)	1	0	0	0	8	0	0	0
S1	Li1	Li3	66(2)	1	0	0	0	3	0	0	0
P1	Li1	S1	127(2)	11	0	0	0	8	0	0	0
P1	Li1	Li3	98(2)	11	0	0	0	3	0	0	0
S1	Li1	Li3	110(2)	8	0	0	0	3	0	0	0
S1	Li2	S1	78.6(1)	14	1	0	0	13	0	1	0
S1	Li2	S1	101.4(1)	14	1	0	0	10	0	0	1
S1	Li2	S1	178.3(5)	14	1	0	0	9	1	1	1
S1	Li2	C2	90.9(3)	14	1	0	0	1	0	0	0
S1	Li2	N1	90.9(3)	14	1	0	0	1	0	0	0
S1	Li2	C2	89.1(3)	14	1	0	0	2	1	1	0
S1	Li2	N1	89.1(3)	14	1	0	0	2	1	1	0
S1	Li2	Li3	64.1(2)	14	1	0	0	8	0	0	0
S1	Li2	Li3	62.7(2)	14	1	0	0	4	1	0	0
S1	Li2	Li3	117.3(2)	14	1	0	0	3	0	1	0
S1	Li2	Li3	115.9(2)	14	1	0	0	7	1	1	0
S1	Li2	S1	178.3(5)	13	0	1	0	10	0	0	1
S1	Li2	S1	101.4(1)	13	0	1	0	9	1	1	1

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
S1	Li2	C2	89.1(3)	13	0	1	0	1	0	0	0
S1	Li2	N1	89.1(3)	13	0	1	0	1	0	0	0
S1	Li2	C2	90.9(3)	13	0	1	0	2	1	1	0
S1	Li2	N1	90.9(3)	13	0	1	0	2	1	1	0
S1	Li2	Li3	115.9(2)	13	0	1	0	8	0	0	0
S1	Li2	Li3	117.3(2)	13	0	1	0	4	1	0	0
S1	Li2	Li3	62.7(2)	13	0	1	0	3	0	1	0
S1	Li2	Li3	64.1(2)	13	0	1	0	7	1	1	0
S1	Li2	S1	78.6(1)	10	0	0	1	9	1	1	1
S1	Li2	C2	89.1(3)	10	0	0	1	1	0	0	0
S1	Li2	N1	89.1(3)	10	0	0	1	1	0	0	0
S1	Li2	C2	90.9(3)	10	0	0	1	2	1	1	0
S1	Li2	N1	90.9(3)	10	0	0	1	2	1	1	0
S1	Li2	Li3	62.7(2)	10	0	0	1	8	0	0	0
S1	Li2	Li3	64.1(2)	10	0	0	1	4	1	0	0
S1	Li2	Li3	115.9(2)	10	0	0	1	3	0	1	0
S1	Li2	Li3	117.3(2)	10	0	0	1	7	1	1	0
S1	Li2	C2	90.9(3)	9	1	1	1	1	0	0	0
S1	Li2	N1	90.9(3)	9	1	1	1	1	0	0	0
S1	Li2	C2	89.1(3)	9	1	1	1	2	1	1	0
S1	Li2	N1	89.1(3)	9	1	1	1	2	1	1	0
S1	Li2	Li3	117.3(2)	9	1	1	1	8	0	0	0
S1	Li2	Li3	115.9(2)	9	1	1	1	4	1	0	0
S1	Li2	Li3	64.1(2)	9	1	1	1	3	0	1	0
S1	Li2	Li3	62.7(2)	9	1	1	1	7	1	1	0
C2	Li2	N1	0	1	0	0	0	1	0	0	0
C2	Li2	C2	180	1	0	0	0	2	1	1	0
C2	Li2	N1	180	1	0	0	0	2	1	1	0
C2	Li2	Li3	45	1	0	0	0	8	0	0	0
C2	Li2	Li3	135	1	0	0	0	4	1	0	0
C2	Li2	Li3	45	1	0	0	0	3	0	1	0
C2	Li2	Li3	135	1	0	0	0	7	1	1	0
N1	Li2	C2	180	1	0	0	0	2	1	1	0
N1	Li2	N1	180	1	0	0	0	2	1	1	0
N1	Li2	Li3	45	1	0	0	0	8	0	0	0
N1	Li2	Li3	135	1	0	0	0	4	1	0	0

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
N1	Li2	Li3	45	1	0	0	0	3	0	1	0
N1	Li2	Li3	135	1	0	0	0	7	1	1	0
C2	Li2	N1	0	2	1	1	0	2	1	1	0
C2	Li2	Li3	135	2	1	1	0	8	0	0	0
C2	Li2	Li3	45	2	1	1	0	4	1	0	0
C2	Li2	Li3	135	2	1	1	0	3	0	1	0
C2	Li2	Li3	45	2	1	1	0	7	1	1	0
N1	Li2	Li3	135	2	1	1	0	8	0	0	0
N1	Li2	Li3	45	2	1	1	0	4	1	0	0
N1	Li2	Li3	135	2	1	1	0	3	0	1	0
N1	Li2	Li3	45	2	1	1	0	7	1	1	0
Li3	Li2	Li3	90	8	0	0	0	4	1	0	0
Li3	Li2	Li3	90	8	0	0	0	3	0	1	0
Li3	Li2	Li3	180	8	0	0	0	7	1	1	0
Li3	Li2	Li3	180	4	1	0	0	3	0	1	0
Li3	Li2	Li3	90	4	1	0	0	7	1	1	0
Li3	Li2	Li3	90	3	0	1	0	7	1	1	0
C2	Li3	N1	0	4	-1	0	-1	4	-1	0	-1
C2	Li3	C2	180.0000(1)	4	-1	0	-1	12	1	-1	0
C2	Li3	N1	180.0000(1)	4	-1	0	-1	12	1	-1	0
C2	Li3	C1	20.5(5)	4	-1	0	-1	4	-1	0	-1
C2	Li3	C1	159.5(5)	4	-1	0	-1	12	1	-1	0
C2	Li3	S1	85.9(2)	4	-1	0	-1	7	0	0	0
C2	Li3	S1	94.1(2)	4	-1	0	-1	15	0	0	-1
C2	Li3	Li1	98(1)	4	-1	0	-1	12	0	-1	0
C2	Li3	Li1	82(1)	4	-1	0	-1	4	0	0	-1
C2	Li3	S1	94.5(2)	4	-1	0	-1	12	0	-1	0
C2	Li3	S1	85.5(2)	4	-1	0	-1	4	0	0	-1
C2	Li3	Li2	63.7(2)	4	-1	0	-1	3	0	-1	-1
C2	Li3	Li2	116.3(2)	4	-1	0	-1	11	-1	1	0
N1	Li3	C2	180.0000(1)	4	-1	0	-1	12	1	-1	0
N1	Li3	N1	180.0000(1)	4	-1	0	-1	12	1	-1	0
N1	Li3	C1	20.5(4)	4	-1	0	-1	4	-1	0	-1
N1	Li3	C1	159.5(4)	4	-1	0	-1	12	1	-1	0
N1	Li3	S1	85.95(8)	4	-1	0	-1	7	0	0	0
N1	Li3	S1	94.05(8)	4	-1	0	-1	15	0	0	-1

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
N1	Li3	Li1	98(1)	4	-1	0	-1	12	0	-1	0
N1	Li3	Li1	82(1)	4	-1	0	-1	4	0	0	-1
N1	Li3	S1	94.46(6)	4	-1	0	-1	12	0	-1	0
N1	Li3	S1	85.54(6)	4	-1	0	-1	4	0	0	-1
N1	Li3	Li2	63.6804	4	-1	0	-1	3	0	-1	-1
N1	Li3	Li2	116.3196	4	-1	0	-1	11	-1	1	0
C2	Li3	N1	0	12	1	-1	0	12	1	-1	0
C2	Li3	C1	159.5(5)	12	1	-1	0	4	-1	0	-1
C2	Li3	C1	20.5(5)	12	1	-1	0	12	1	-1	0
C2	Li3	S1	94.1(2)	12	1	-1	0	7	0	0	0
C2	Li3	S1	85.9(2)	12	1	-1	0	15	0	0	-1
C2	Li3	Li1	82(1)	12	1	-1	0	12	0	-1	0
C2	Li3	Li1	98(1)	12	1	-1	0	4	0	0	-1
C2	Li3	S1	85.5(2)	12	1	-1	0	12	0	-1	0
C2	Li3	S1	94.5(2)	12	1	-1	0	4	0	0	-1
C2	Li3	Li2	116.3(2)	12	1	-1	0	3	0	-1	-1
C2	Li3	Li2	63.7(2)	12	1	-1	0	11	-1	1	0
N1	Li3	C1	159.5(4)	12	1	-1	0	4	-1	0	-1
N1	Li3	C1	20.5(4)	12	1	-1	0	12	1	-1	0
N1	Li3	S1	94.05(8)	12	1	-1	0	7	0	0	0
N1	Li3	S1	85.95(8)	12	1	-1	0	15	0	0	-1
N1	Li3	Li1	82(1)	12	1	-1	0	12	0	-1	0
N1	Li3	Li1	98(1)	12	1	-1	0	4	0	0	-1
N1	Li3	S1	85.54(6)	12	1	-1	0	12	0	-1	0
N1	Li3	S1	94.46(6)	12	1	-1	0	4	0	0	-1
N1	Li3	Li2	116.3196	12	1	-1	0	3	0	-1	-1
N1	Li3	Li2	63.6804	12	1	-1	0	11	-1	1	0
C1	Li3	C1	180.0000(1)	4	-1	0	-1	12	1	-1	0
C1	Li3	S1	71.3(3)	4	-1	0	-1	7	0	0	0
C1	Li3	S1	108.7(3)	4	-1	0	-1	15	0	0	-1
C1	Li3	Li1	97.3(9)	4	-1	0	-1	12	0	-1	0
C1	Li3	Li1	82.7(9)	4	-1	0	-1	4	0	0	-1
C1	Li3	S1	109.4(3)	4	-1	0	-1	12	0	-1	0
C1	Li3	S1	70.6(3)	4	-1	0	-1	4	0	0	-1
C1	Li3	Li2	84.2(4)	4	-1	0	-1	3	0	-1	-1
C1	Li3	Li2	95.8(4)	4	-1	0	-1	11	-1	1	0

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
C1	Li3	S1	108.7(3)	12	1	-1	0	7	0	0	0
C1	Li3	S1	71.3(3)	12	1	-1	0	15	0	0	-1
C1	Li3	Li1	82.7(9)	12	1	-1	0	12	0	-1	0
C1	Li3	Li1	97.3(9)	12	1	-1	0	4	0	0	-1
C1	Li3	S1	70.6(3)	12	1	-1	0	12	0	-1	0
C1	Li3	S1	109.4(3)	12	1	-1	0	4	0	0	-1
C1	Li3	Li2	95.8(4)	12	1	-1	0	3	0	-1	-1
C1	Li3	Li2	84.2(4)	12	1	-1	0	11	-1	1	0
S1	Li3	Li1	47(1)	7	0	0	0	12	0	-1	0
S1	Li3	Li1	133(1)	7	0	0	0	4	0	0	-1
S1	Li3	S1	94.84(8)	7	0	0	0	12	0	-1	0
S1	Li3	S1	85.16(8)	7	0	0	0	4	0	0	-1
S1	Li3	Li2	128.33(8)	7	0	0	0	3	0	-1	-1
S1	Li3	Li2	51.67(8)	7	0	0	0	11	-1	1	0
S1	Li3	Li1	133(1)	15	0	0	-1	12	0	-1	0
S1	Li3	Li1	47(1)	15	0	0	-1	4	0	0	-1
S1	Li3	S1	85.16(8)	15	0	0	-1	12	0	-1	0
S1	Li3	S1	94.84(8)	15	0	0	-1	4	0	0	-1
S1	Li3	Li2	51.67(8)	15	0	0	-1	3	0	-1	-1
S1	Li3	Li2	128.33(8)	15	0	0	-1	11	-1	1	0
Li1	Li3	S1	48(2)	12	0	-1	0	12	0	-1	0
Li1	Li3	S1	132(2)	12	0	-1	0	4	0	0	-1
Li1	Li3	Li2	94(2)	12	0	-1	0	3	0	-1	-1
Li1	Li3	Li2	86(2)	12	0	-1	0	11	-1	1	0
Li1	Li3	S1	132(2)	4	0	0	-1	12	0	-1	0
Li1	Li3	S1	48(2)	4	0	0	-1	4	0	0	-1
Li1	Li3	Li2	86(2)	4	0	0	-1	3	0	-1	-1
Li1	Li3	Li2	94(2)	4	0	0	-1	11	-1	1	0
S1	Li3	S1	180.0000(1)	12	0	-1	0	4	0	0	-1
S1	Li3	Li2	51.16(9)	12	0	-1	0	3	0	-1	-1
S1	Li3	Li2	128.84(9)	12	0	-1	0	11	-1	1	0
S1	Li3	Li2	128.84(9)	4	0	0	-1	3	0	-1	-1
S1	Li3	Li2	51.16(9)	4	0	0	-1	11	-1	1	0
Li2	Li3	Li2	180	3	0	-1	-1	11	-1	1	0
S1	P1	S1	109.6(2)	1	0	0	0	2	0	0	0
S1	P1	S1	107.5(6)	1	0	0	0	7	0	0	0

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
S1	P1	S1	111.4(6)	1	0	0	0	8	0	0	0
S1	P1	Li1	56(1)	1	0	0	0	13	-1	0	0
S1	P1	Li1	52(1)	1	0	0	0	12	0	-1	0
S1	P1	Li1	118(1)	1	0	0	0	14	1	0	0
S1	P1	Li1	135(1)	1	0	0	0	11	0	1	0
S1	P1	S1	111.4(6)	2	0	0	0	7	0	0	0
S1	P1	S1	107.5(6)	2	0	0	0	8	0	0	0
S1	P1	Li1	118(1)	2	0	0	0	13	-1	0	0
S1	P1	Li1	135(1)	2	0	0	0	12	0	-1	0
S1	P1	Li1	56(1)	2	0	0	0	14	1	0	0
S1	P1	Li1	52(1)	2	0	0	0	11	0	1	0
S1	P1	S1	109.6(2)	7	0	0	0	8	0	0	0
S1	P1	Li1	52(1)	7	0	0	0	13	-1	0	0
S1	P1	Li1	56(1)	7	0	0	0	12	0	-1	0
S1	P1	Li1	135(1)	7	0	0	0	14	1	0	0
S1	P1	Li1	118(1)	7	0	0	0	11	0	1	0
S1	P1	Li1	135(1)	8	0	0	0	13	-1	0	0
S1	P1	Li1	118(1)	8	0	0	0	12	0	-1	0
S1	P1	Li1	52(1)	8	0	0	0	14	1	0	0
S1	P1	Li1	56(1)	8	0	0	0	11	0	1	0
Li1	P1	Li1	17(2)	13	-1	0	0	12	0	-1	0
Li1	P1	Li1	171(3)	13	-1	0	0	14	1	0	0
Li1	P1	Li1	165(2)	13	-1	0	0	11	0	1	0
Li1	P1	Li1	165(2)	12	0	-1	0	14	1	0	0
Li1	P1	Li1	171(3)	12	0	-1	0	11	0	1	0
Li1	P1	Li1	17(2)	14	1	0	0	11	0	1	0
P1	S1	Li1	83(2)	1	0	0	0	12	0	-1	0
P1	S1	Li1	79(2)	1	0	0	0	13	-1	0	0
P1	S1	Li1	94(1)	1	0	0	0	1	0	0	0
P1	S1	Li2	85.92(8)	1	0	0	0	9	1	1	1
P1	S1	Li3	122.9(4)	1	0	0	0	7	0	0	0
P1	S1	Li1	80(2)	1	0	0	0	8	0	0	0
P1	S1	Li3	120.3(4)	1	0	0	0	3	0	0	0
Li1	S1	Li1	21(3)	12	0	-1	0	13	-1	0	0
Li1	S1	Li1	108(2)	12	0	-1	0	1	0	0	0
Li1	S1	Li2	131(1)	12	0	-1	0	9	1	1	1

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
Li1	S1	Li3	81(2)	12	0	-1	0	7	0	0	0
Li1	S1	Li1	109(3)	12	0	-1	0	8	0	0	0
Li1	S1	Li3	155(2)	12	0	-1	0	3	0	0	0
Li1	S1	Li1	128(3)	13	-1	0	0	1	0	0	0
Li1	S1	Li2	110(1)	13	-1	0	0	9	1	1	1
Li1	S1	Li3	67(2)	13	-1	0	0	7	0	0	0
Li1	S1	Li1	127.9(9)	13	-1	0	0	8	0	0	0
Li1	S1	Li3	157(2)	13	-1	0	0	3	0	0	0
Li1	S1	Li2	121(2)	1	0	0	0	9	1	1	1
Li1	S1	Li3	143(1)	1	0	0	0	7	0	0	0
Li1	S1	Li1	14(2)	1	0	0	0	8	0	0	0
Li1	S1	Li3	65(2)	1	0	0	0	3	0	0	0
Li2	S1	Li3	65.6(1)	9	1	1	1	7	0	0	0
Li2	S1	Li1	116(1)	9	1	1	1	8	0	0	0
Li2	S1	Li3	64.7(1)	9	1	1	1	3	0	0	0
Li3	S1	Li1	157(2)	7	0	0	0	8	0	0	0
Li3	S1	Li3	91.74(7)	7	0	0	0	3	0	0	0
Li1	S1	Li3	70(2)	8	0	0	0	3	0	0	0
C1	C1	Li3	129.2(4)	2	0	1	0	8	0	0	0
C1	C1	Li3	129.2(4)	2	0	1	0	3	0	1	0
C2	C1	N1	0	1	0	0	0	1	0	0	0
C2	C1	C2	180	1	0	0	0	2	0	1	0
C2	C1	N1	180	1	0	0	0	2	0	1	0
C2	C1	Li3	50.8(4)	1	0	0	0	8	0	0	0
C2	C1	Li3	50.8(4)	1	0	0	0	3	0	1	0
N1	C1	C2	180	1	0	0	0	2	0	1	0
N1	C1	N1	180	1	0	0	0	2	0	1	0
N1	C1	Li3	50.8(4)	1	0	0	0	8	0	0	0
N1	C1	Li3	50.8(4)	1	0	0	0	3	0	1	0
C2	C1	N1	0	2	0	1	0	2	0	1	0
C2	C1	Li3	129.2(4)	2	0	1	0	8	0	0	0
C2	C1	Li3	129.2(4)	2	0	1	0	3	0	1	0
N1	C1	Li3	129.2(4)	2	0	1	0	8	0	0	0
N1	C1	Li3	129.2(4)	2	0	1	0	3	0	1	0
Li3	C1	Li3	101.6(8)	8	0	0	0	3	0	1	0
C1	C2	C1	0	1	0	0	0	2	0	1	0

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
C1	C2	Li3	108.7(2)	1	0	0	0	8	0	0	0
C1	C2	Li3	108.7(2)	1	0	0	0	3	0	1	0
C1	C2	C2	0.0000(1)	1	0	0	0	2	0	1	0
C1	C2	N1	0.0000(1)	1	0	0	0	2	0	1	0
C1	C2	Li3	108.7(2)	2	0	1	0	8	0	0	0
C1	C2	Li3	108.7(2)	2	0	1	0	3	0	1	0
C1	C2	C2	0.0000(1)	2	0	1	0	2	0	1	0
C1	C2	N1	0.0000(1)	2	0	1	0	2	0	1	0
Li3	C2	Li3	142.6(4)	8	0	0	0	3	0	1	0
Li3	C2	C2	108.7(2)	8	0	0	0	2	0	1	0
Li3	C2	N1	108.7(2)	8	0	0	0	2	0	1	0
Li3	C2	Li2	71.3(2)	8	0	0	0	1	0	0	0
Li3	C2	C2	108.7(2)	3	0	1	0	2	0	1	0
Li3	C2	N1	108.7(2)	3	0	1	0	2	0	1	0
Li3	C2	Li2	71.3(2)	3	0	1	0	1	0	0	0
C2	C2	N1	0	2	0	1	0	2	0	1	0
C2	C2	Li2	180	2	0	1	0	1	0	0	0
N1	C2	Li2	180	2	0	1	0	1	0	0	0
C1	N1	C1	0	1	0	0	0	2	0	1	0
C1	N1	Li3	108.6804	1	0	0	0	8	0	0	0
C1	N1	Li3	108.6804	1	0	0	0	3	0	1	0
C1	N1	C2	0.0000(1)	1	0	0	0	2	0	1	0
C1	N1	N1	0.0000(1)	1	0	0	0	2	0	1	0
C1	N1	Li3	108.6804	2	0	1	0	8	0	0	0
C1	N1	Li3	108.6804	2	0	1	0	3	0	1	0
C1	N1	C2	0.0000(1)	2	0	1	0	2	0	1	0
C1	N1	N1	0.0000(1)	2	0	1	0	2	0	1	0
C1	N1	Li2	180	2	0	1	0	1	0	0	0
Li3	N1	Li3	142.6392	8	0	0	0	3	0	1	0
Li3	N1	C2	108.7(2)	8	0	0	0	2	0	1	0
Li3	N1	N1	108.6804	8	0	0	0	2	0	1	0
Li3	N1	Li2	71.3196	8	0	0	0	1	0	0	0
Li3	N1	C2	108.7(2)	3	0	1	0	2	0	1	0
Li3	N1	N1	108.6804	3	0	1	0	2	0	1	0
Li3	N1	Li2	71.3196	3	0	1	0	1	0	0	0
C2	N1	N1	0	2	0	1	0	2	0	1	0

1	2	3	$\phi_{12}/^\circ$	n_1	Δx_1	Δy_1	Δz_1	n_3	Δx_3	Δy_3	Δz_3
C2	N1	Li2	180	2	0	1	0	1	0	0	0
N1	N1	Li2	180	2	0	1	0	1	0	0	0

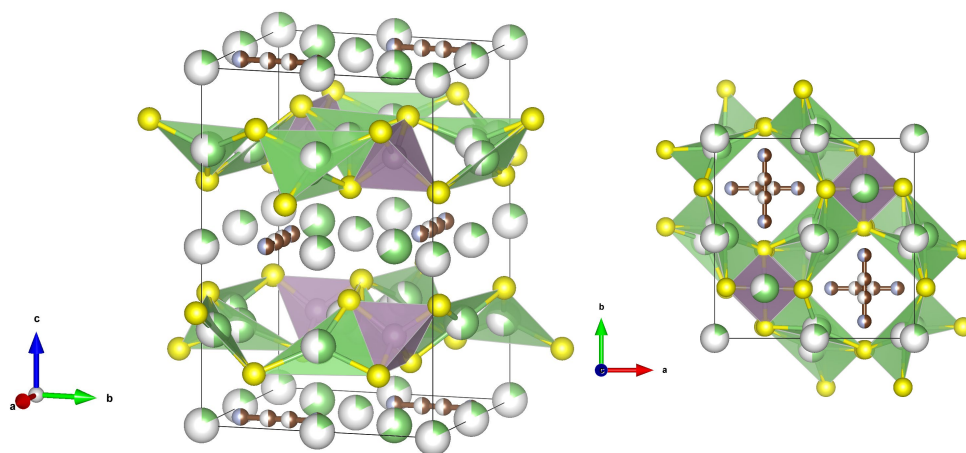


Figure S2: Crystal structure of $\text{Li}_3\text{PS}_4\text{-ACN}$ complex drawn with VESTA

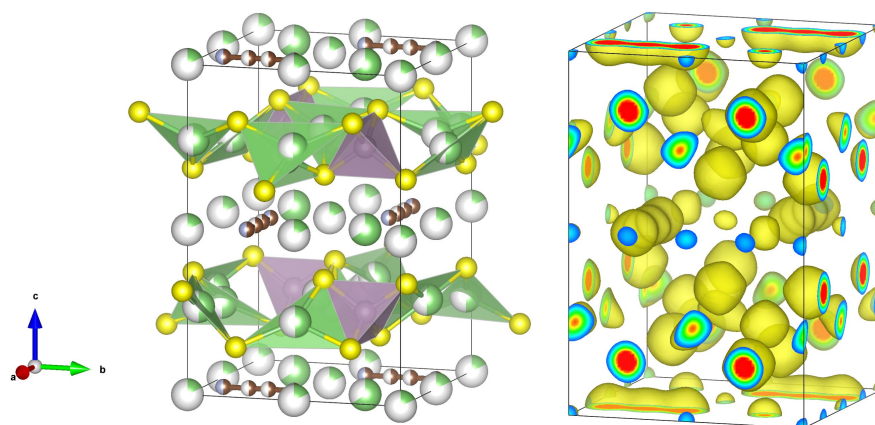


Figure S3: Electron-density distribution in $\text{Li}_3\text{PS}_4\text{-ACN}$ complex with an electron-density level of $0.6 \text{ } \text{\AA}^{-3}$

Table S5: Coordinates of general equivalent positions. Equivalent-position numbers, n , are used in the tables of the geometrical parameters

n	
1	x, y, z
2	$-x + 1/2, -y + 1/2, z$
3	$-y + 1/2, x, z + 1/2$
4	$y, -x + 1/2, z + 1/2$
5	$-x + 1/2, y, -z$
6	$x, -y + 1/2, -z$
7	$y, x, -z + 1/2$
8	$-y + 1/2, -x + 1/2, -z + 1/2$
9	$-x, -y, -z$
10	$x + 1/2, y + 1/2, -z$
11	$y + 1/2, -x, -z + 1/2$
12	$-y, x + 1/2, -z + 1/2$
13	$x + 1/2, -y, z$
14	$-x, y + 1/2, z$
15	$-y, -x, z + 1/2$
16	$y + 1/2, x + 1/2, z + 1/2$

Table S6: Information about possible reflections. I_o is the observed integrated intensity, $I_o(\text{rel}) = 100I_o/I_o(\text{max})$, and H is the full width at half maximum.

No.	h	k	l	$2\theta/^\circ$	$d/\text{\AA}$	I_o	$I_o(\text{rel})$	$ F $	$H/^\circ$
1	0	0	2	4.459	6.37925	—	—	91.1651	0.04526
2	1	1	0	4.689	6.06668	—	—	98.0096	0.02518
3	1	1	2	6.473	4.39614	9.14367	80.64	115.7611	0.04808
4	2	0	0	6.633	4.28979	2.81272	24.81	92.5905	0.03514
5	2	0	1	6.998	4.06610	2.81522	24.83	67.4443	0.04321
6	2	1	1	7.746	3.67435	0.12121	1.07	9.4404	0.04642
7	2	0	2	7.995	3.55977	—	—	16.0168	0.05309
8	2	1	2	8.658	3.28799	—	—	2.0129	0.05564
9	0	0	4	8.925	3.18963	—	—	9.0216	0.06705
10	2	2	0	9.386	3.03334	—	—	80.8462	0.04931
11	2	0	3	9.427	3.02019	—	—	186.4229	0.06362
12	2	1	3	9.995	2.84883	—	—	1.6722	0.06578
13	1	1	4	10.086	2.82320	—	—	26.1472	0.07075
14	2	2	2	10.396	2.73942	—	—	3.6613	0.06297
15	3	1	0	10.497	2.71310	—	—	2.5933	0.05503
16	3	1	1	10.732	2.65376	—	—	83.7583	0.06030
17	2	0	4	11.128	2.55962	0.32656	2.88	39.2086	0.07456
18	3	1	2	11.410	2.49668	0.21079	1.86	22.2857	0.06752
19	2	1	4	11.614	2.45279	0.00000	0.00	0.3091	0.07645
20	3	2	1	12.180	2.33921	0.00023	0.00	0.7793	0.06736
21	3	1	3	12.458	2.28729	2.11844	18.68	71.5531	0.07609
22	3	2	2	12.782	2.22949	0.01043	0.09	5.1292	0.07390
23	2	2	4	12.966	2.19807	2.90967	25.66	124.4704	0.08201
24	2	0	5	12.996	2.19305	0.03209	0.28	13.0886	0.08585
25	4	0	0	13.289	2.14489	—	—	148.4057	0.06945
26	0	0	6	13.405	2.12642	—	—	138.2657	0.09116
27	2	1	5	13.415	2.12474	—	—	3.2043	0.08755
28	4	0	1	13.476	2.11521	—	—	11.5259	0.07377
29	3	2	3	13.728	2.07659	—	—	2.7844	0.08182
30	3	1	4	13.794	2.06660	—	—	63.6965	0.08559
31	4	1	1	13.881	2.05372	—	—	1.2220	0.07580
32	4	0	2	14.023	2.03305	—	—	56.9866	0.07981
33	3	3	0	14.099	2.02223	—	—	69.4087	0.07365
34	1	1	6	14.208	2.00672	—	—	7.5916	0.09433
35	4	1	2	14.414	1.97827	—	—	10.2375	0.08170

No.	h	k	l	$2\theta/^\circ$	$d/\text{\AA}$	I_o	$I_o(\text{rel})$	$ F $	$H/^\circ$
36	3	3	2	14.794	1.92769	—	—	36.2217	0.08355
37	4	2	0	14.866	1.91845	—	—	17.0142	0.07763
38	4	0	3	14.892	1.91511	—	—	80.1502	0.08723
39	3	2	4	14.953	1.90727	—	—	2.8895	0.09076
40	2	0	6	14.970	1.90520	—	—	5.3371	0.09745
41	4	2	1	15.034	1.89712	—	—	35.3944	0.08158
42	4	1	3	15.260	1.86911	0.00374	0.03	4.0417	0.08897
43	2	1	6	15.336	1.85989	0.00193	0.02	2.9298	0.09899
44	3	1	5	15.346	1.85877	0.36477	3.22	40.2145	0.09577
45	4	2	2	15.527	1.83717	—	—	15.8081	0.08713
46	4	0	4	16.030	1.77989	—	—	7.6212	0.09571
47	4	2	3	16.317	1.74876	—	—	53.4917	0.09402
48	4	1	4	16.374	1.74278	—	—	8.9915	0.09731
49	2	2	6	16.389	1.74120	—	—	127.7342	0.10353
50	3	2	5	16.398	1.74027	—	—	3.7480	0.10047
51	3	3	4	16.711	1.70790	—	—	122.2404	0.09889
52	4	3	1	16.783	1.70060	—	—	3.9190	0.09046
53	5	1	0	16.964	1.68259	—	—	101.5720	0.08856
54	2	0	7	17.016	1.67751	—	—	68.0640	0.10934
55	3	1	6	17.055	1.67363	—	—	62.8898	0.10648
56	5	1	1	17.112	1.66815	—	—	16.7657	0.09214
57	4	3	2	17.228	1.65702	—	—	0.6577	0.09556
58	2	1	7	17.340	1.64633	—	—	1.4177	0.11075
59	4	2	4	17.365	1.64399	—	—	48.9486	0.10199
60	4	0	5	17.387	1.64189	—	—	2.4701	0.10502
61	5	1	2	17.548	1.62695	—	—	74.4581	0.09717
62	4	1	5	17.706	1.61263	—	—	7.1040	0.10649
63	0	0	8	17.905	1.59481	—	—	55.7749	0.11618
64	4	3	3	17.945	1.59127	—	—	4.3595	0.10194
65	3	2	6	18.010	1.58557	—	—	3.2541	0.11079
66	5	2	1	18.064	1.58091	—	—	6.3170	0.09702
67	5	1	3	18.254	1.56459	—	—	39.5231	0.10346
68	5	2	2	18.479	1.54571	—	—	6.1841	0.10185
69	1	1	8	18.519	1.54241	—	—	12.4537	0.11885
70	4	2	5	18.628	1.53341	—	—	16.1255	0.11083
71	4	4	0	18.836	1.51667	—	—	46.2025	0.09837

No.	h	k	l	$2\theta/^\circ$	$d/\text{\AA}$	I_o	$I_o(\text{rel})$	$ F $	$H/^\circ$
72	3	1	7	18.882	1.51294	—	—	67.8983	0.11762
73	4	3	4	18.905	1.51113	—	—	0.6106	0.10941
74	4	0	6	18.918	1.51009	—	—	38.8286	0.11499
75	2	0	8	19.113	1.49485	—	—	36.9055	0.12148
76	5	2	3	19.151	1.49194	—	—	1.3147	0.10791
77	5	1	4	19.199	1.48822	—	—	28.8580	0.11084
78	4	1	6	19.212	1.48723	—	—	0.6856	0.11636
79	4	4	2	19.366	1.47554	—	—	40.6595	0.10634
80	2	1	8	19.404	1.47267	—	—	4.1051	0.12278
81	5	3	0	19.421	1.47139	—	—	41.7450	0.10144
82	3	3	6	19.501	1.46538	—	—	105.2425	0.11772
83	5	3	1	19.551	1.46170	—	—	64.8051	0.10469
84	3	2	7	19.752	1.44695	—	—	2.3322	0.12162
85	5	3	2	19.936	1.43374	—	—	29.4838	0.10925
86	6	0	0	19.990	1.42993	—	—	129.2923	0.10444
87	5	2	4	20.055	1.42528	—	—	5.1885	0.11504
88	4	2	6	20.068	1.42442	—	—	59.7461	0.12040
89	4	3	5	20.075	1.42391	—	—	9.6591	0.11777
90	6	0	1	20.116	1.42103	—	—	7.7194	0.10762
91	2	2	8	20.252	1.41160	—	—	43.8172	0.12663
92	5	1	5	20.352	1.40470	—	—	5.3581	0.11912
93	6	1	1	20.393	1.40193	—	—	10.3318	0.10906
94	6	0	2	20.491	1.39531	—	—	39.4122	0.11208
95	5	3	3	20.562	1.39051	—	—	84.4081	0.11499
96	4	0	7	20.586	1.38891	—	—	18.7663	0.12551
97	6	1	2	20.763	1.37721	—	—	5.3980	0.11348
98	3	1	8	20.799	1.37487	—	—	32.8176	0.12915
99	4	1	7	20.857	1.37106	—	—	4.3140	0.12679
100	4	4	4	20.878	1.36971	—	—	20.2882	0.11912
101	6	2	0	21.083	1.35655	—	—	30.6233	0.11021
102	6	0	3	21.101	1.35537	—	—	24.1426	0.11772
103	5	2	5	21.164	1.35141	—	—	2.4239	0.12309
104	6	2	1	21.203	1.34895	—	—	27.0866	0.11328
105	2	0	9	21.250	1.34602	—	—	90.6707	0.13387
106	6	1	3	21.366	1.33877	—	—	0.4528	0.11906
107	5	3	4	21.410	1.33608	—	—	30.3196	0.12178

No.	h	k	l	$2\theta/^\circ$	$d/\text{\AA}$	I_o	$I_o(\text{rel})$	$ F $	$H/^\circ$
108	4	3	6	21.421	1.33536	—	—	2.8234	0.12690
109	5	4	1	21.467	1.33258	—	—	10.0659	0.11466
110	2	1	9	21.513	1.32975	—	—	2.4538	0.13508
111	6	2	2	21.560	1.32688	—	—	16.6754	0.11758
112	3	2	8	21.594	1.32479	—	—	5.8937	0.13286
113	4	2	7	21.651	1.32138	—	—	34.1505	0.13056
114	5	1	6	21.682	1.31948	—	—	25.7769	0.12817
115	5	4	2	21.819	1.31129	—	—	5.9200	0.11892
116	6	0	4	21.929	1.30481	—	—	5.8065	0.12438
117	6	2	3	22.142	1.29240	—	—	67.7187	0.12301
118	6	1	4	22.184	1.28998	—	—	3.0221	0.12567
119	4	0	8	22.363	1.27981	—	—	35.3511	0.13650
120	5	4	3	22.395	1.27798	—	—	1.4025	0.12431
121	0	0	10	22.433	1.27585	—	—	88.6234	0.14191
122	5	2	6	22.448	1.27502	—	—	0.4906	0.13191
123	5	3	5	22.455	1.27466	—	—	31.3802	0.12948
124	6	3	1	22.491	1.27259	—	—	2.6039	0.12003
125	4	1	8	22.614	1.26580	—	—	3.4579	0.13770
126	3	1	9	22.784	1.25644	—	—	39.9930	0.14102
127	6	3	2	22.829	1.25401	—	—	5.7579	0.12416
128	3	3	8	22.862	1.25225	—	—	47.1642	0.13889
129	4	3	7	22.915	1.24936	—	—	5.8176	0.13667
130	1	1	10	22.931	1.24854	—	—	65.7673	0.14422
131	6	2	4	22.934	1.24834	—	—	42.9569	0.12946
132	6	0	5	22.951	1.24742	—	—	0.2380	0.13196
133	5	1	7	23.160	1.23632	—	—	19.3352	0.13787
134	5	4	4	23.179	1.23533	—	—	5.1979	0.13071
135	4	4	6	23.190	1.23477	—	—	18.5836	0.13558
136	6	1	5	23.196	1.23444	—	—	6.7770	0.13319
137	4	2	8	23.350	1.22639	—	—	25.4658	0.14124
138	6	3	3	23.381	1.22478	—	—	1.9157	0.12938
139	2	0	10	23.418	1.22291	—	—	24.0330	0.14650

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