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Supplementary information

A layered oxalatophosphate framework as cathode material for Li-ion batteries

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Controlled synthesis of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$

The title compound, $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$ has been synthesized by systematically varying different synthetic parameters such as molar ratio, reaction temperature and reaction time. However, isolation of the pure product could only be achieved when the reported reaction conditions are maintained. The effects of various parameters on the synthesis of the compound are described below in detail.

Effect of molar ratio of the reactants:

In these types of oxalatophosphate materials, the anionic part (in this case $[(VO)_2(C_2O_4)(HPO_4)_2]^{2-}$) are held together with the help of large organic amine cations or alkali metal cations. However, in our study smaller Li^+ cation has been used to synthesize a lithium containing oxalatophosphate for the first time. Because of the smaller size of Li^+ cation and its high hydration energy, the compound does not precipitate out easily at lower concentraions of LiOH. Increase in the concentration of LiOH resulted in the isolation of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$. However, $LiVOPO_4\cdot 2H_2O$ was also formed as impurity at large LiOH concentrations (Fig. S1). When the LiOH concentration was further increased to 10 mmol, $LiVOPO_4\cdot 2H_2O$ was formed as the exclusive product. Therefore, 5 mmol of LiOH was used in the synthesis which resulted in the precipitation of pure phase of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$. In addition, there was not any observable effect in the concentration of H_3PO_4 except at very high concentrations, where formation of the desired product is not favoured.

Effect of temperature

The reaction was carried out at different temperatures to obtain the compound in pure phase. At low temperatures around 120^oC, the formation of compound is favoured. At higher temperatures incorporation of organic moiety (oxalate) in the compound is unlikely.

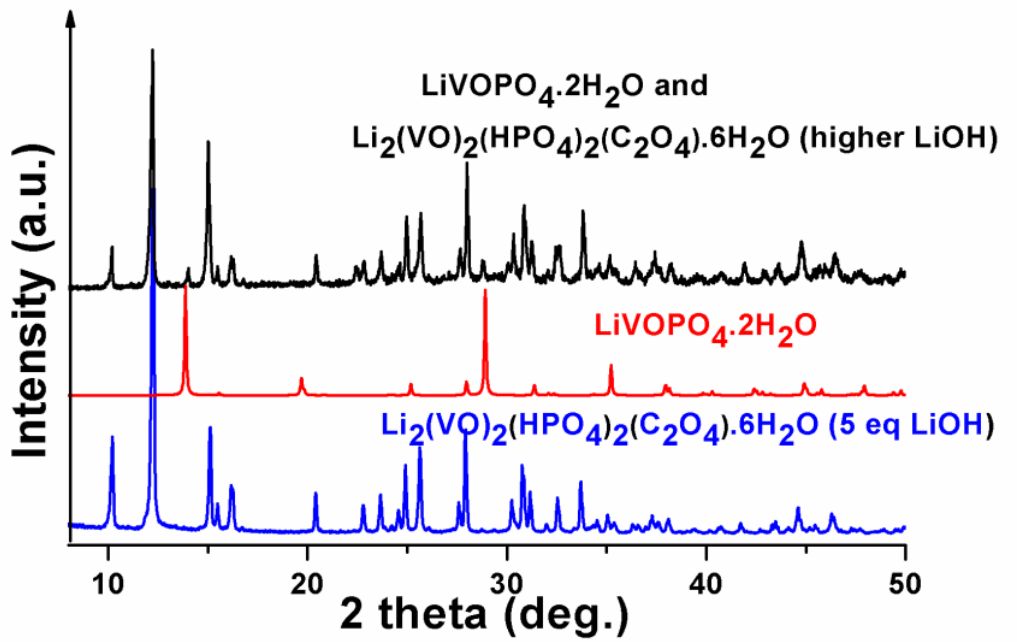

Fig. S1. PXRD patterns of (a) pure $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$ when 5 eq. of LiOH was used for synthesis, (b) $LiVOPO_4\cdot 2H_2O$ and (c) mixture of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$ and $LiVOPO_4\cdot 2H_2O$ when higher concentrations of LiOH was used in the synthesis

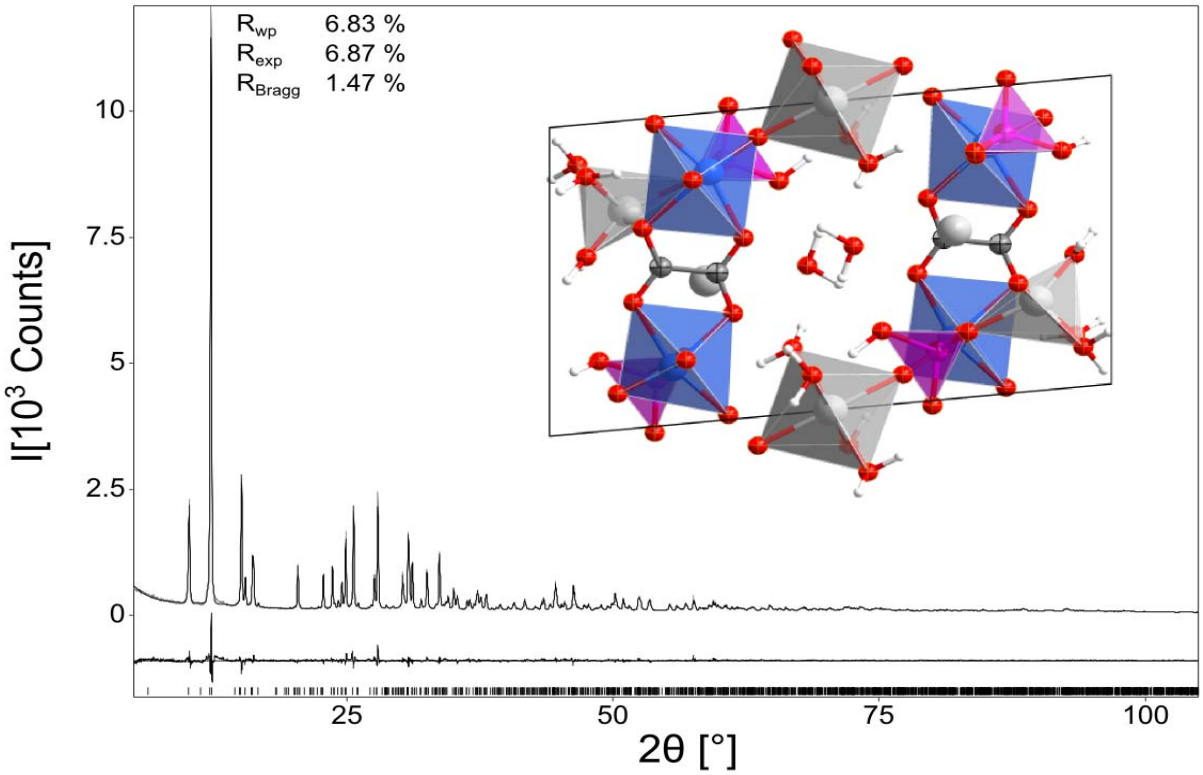

Fig. S2. Rietveld refinement of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$

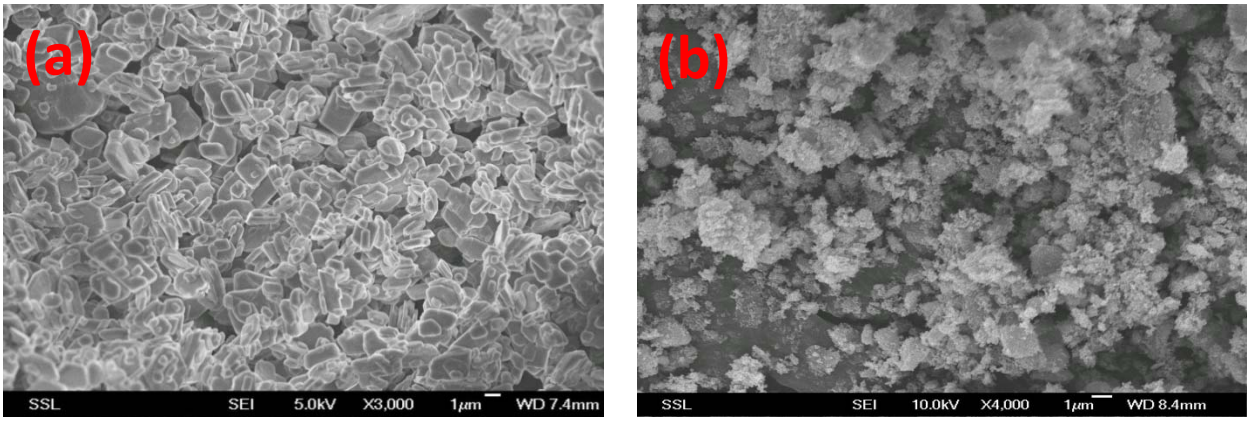

Fig. S3. Scanning electron micrographs of (a) as synthesized and (b) ball-milled $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$

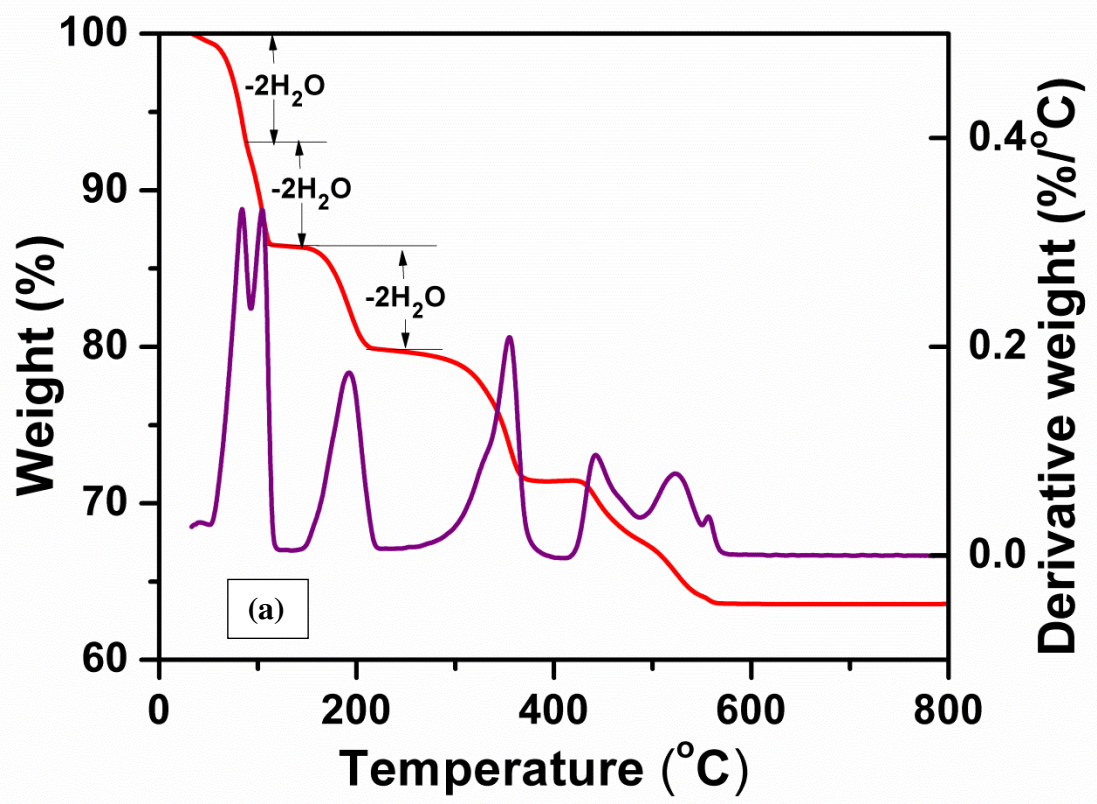

Fig. S4. TGA-DTG of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$ in N_2 flow at a heating rate of $5^oC\ min^{-1}$. TGA curve is shown in red and the derivative weight loss curve is shown in purple.

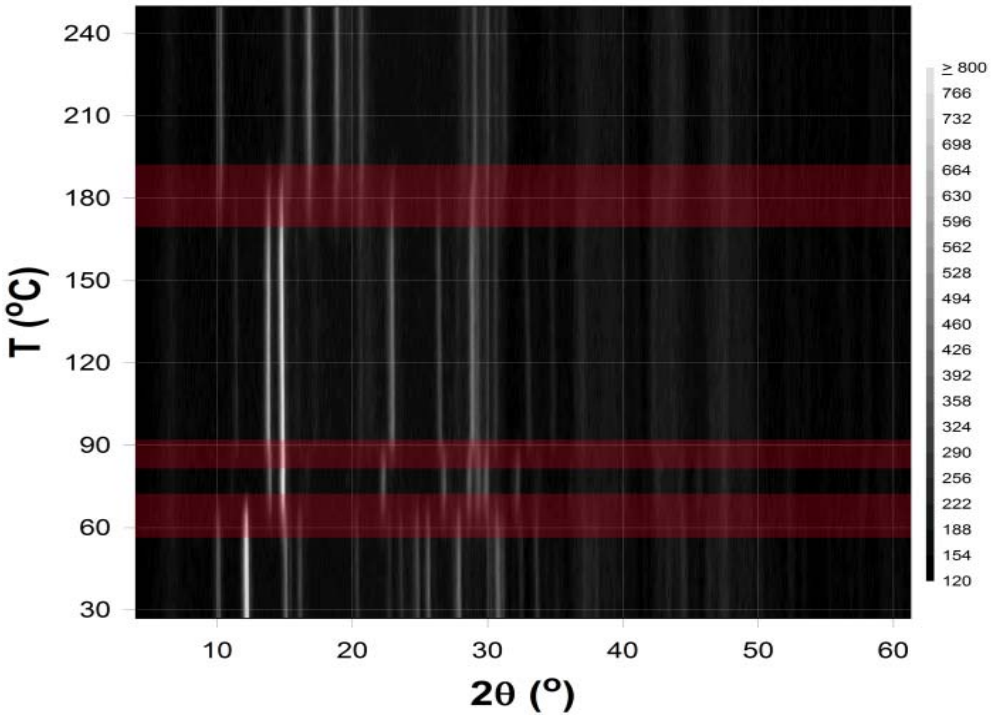

Fig.S5. Temperature dependant PXRD pattern of $Li_2(VO)_2(HPO_4)_2(C_2O_4)\cdot 6H_2O$ from RT to 250°C with intervals of 5 °C recorded in helium atmosphere

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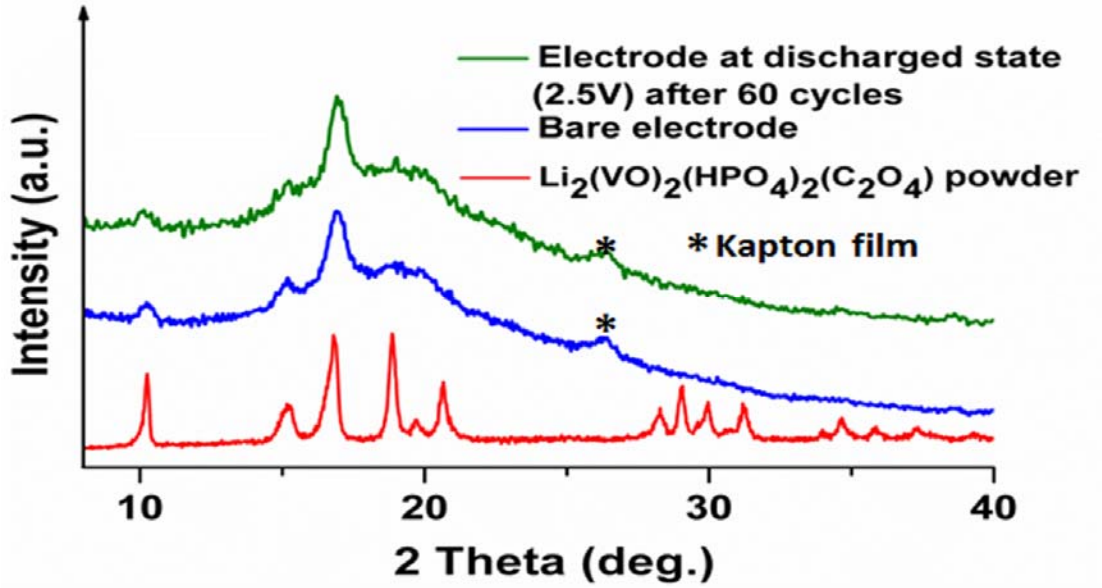

Fig. S6. PXRD patterns of bare electrode and cycled electrode at discharged state (after 60 cycles)

Table S1: EIS fitting results of $Li_2[(VO)_2(C_2O_4)(HPO_4)_2]$ at various voltages for 1st and 6th cycles

Voltage	$R_{(sf+ct)}$ (±5 Ω)	$CPE_{(sf+dl)}$ (±3 µF)	α (±0.02)	R_b (±5 Ω)	CPE_b (±3 mF)	C_i (F)
1st charge cycle						
2.6 V	209	28	0.83	-	-	0.02
3.0 V	208	27	0.83	-	-	0.07
3.5 V	144	31	0.80	-	-	3.94
3.7 V	100	34	0.79	-	-	0.04
3.9 V	74	32	0.80	-	-	0.22
4.0 V	81	40	0.76	-	-	1.07
4.1 V	84	41	0.76	-	-	0.64
4.3 V	97	41	0.76	-	-	0.58
4.5 V	112	41	0.76	-	-	0.19
1st discharge cycle						
4.3 V	123	44	0.75	-	-	0.66
4.1 V	125	39	0.77	-	-	0.55
4.0 V	125	31	0.79	-	-	0.75
3.9 V	124	28	0.81	-	-	2.01
3.7 V	132	33	0.78	-	-	6.08
3.6 V	138	35	0.77	-	-	1.03
3.5 V	145	32	0.79	-	-	0.35
3.4 V	154	31	0.79	-	-	0.16
3.0 V	171	31	0.79	-	-	0.05
2.5 V	212	31	0.78	-	-	0.09
6th charge cycle						
3.0 V	128	22	0.83	-	-	0.03
3.5 V	134	23	0.82	-	-	0.06
3.7 V	114	22	0.82	-	-	0.24
3.9 V	96	23	0.81	-	-	1.13
4.0 V	95	25	0.81	-	-	4.22
4.1 V	94	27	0.80	-	-	1.68
4.3 V	97	33	0.78	-	-	0.58
4.4 V	100	34	0.78	-	-	0.27
4.5 V	101	33	0.78	-	-	0.15
6th discharge cycle						
4.3 V	108	36	0.77	-	-	0.18
4.1 V	112	35	0.76	-	-	0.51
4.0 V	116	34	0.78	-	-	4.04
3.9 V	119	31	0.79	-	-	2.42
3.8 V	123	26	0.81	-	-	1.58
3.7 V	142	27	0.81	29	32	-
3.6 V	180	28	0.79	71	9	-
3.4 V	416	32	0.77	-	-	0.20
3.0 V	425	30	0.77	-	-	0.04

Table S2: Lattice and refinement parameters of Dilithium Bis(vanadylhydrogenphosphate) Oxalate Hexaydrate

Compound name	**Dilithium Bis(vanadylhydrogenphosphate) Oxalate Hexahydrate**
Formula sum	$Li_2[(VO)_2(C_2O_4)(HPO_4)_2]\cdot 6H_2O$
Formula weight	535.84 g/mol
Crystal system	triclinic
Space-group	P -1 (2)
Cell parameters	a 6.4133(0) Å
	b 9.2173(1) Å
	c 14.6206(0) Å
	α 95.0157(11)°
	β 91.7967(17)°
	γ 107.7622(2)°
Cell volume	818.38(0) $Å^3$
Z	2
Calc. density	2.17433 g/cm^3
R_{wp}	6.83 %
R_{exp}	6.87 %
R_{Bragg}	1.47%
Pearson code	aP85
Formula type	NOPQR10...
Wyckoff sequence	i42b

Table S3: Atomic Parameters of $Li_2[(VO)_2(C_2O_4)(HPO_4)_2]\cdot 6H_2O$

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	B_{iso} [Å^2]
V1	2i	1	0.07627(26)	0.19209(2)	0.28353(36)	1.1141(97)
V2	2i	1	0.42122(77)	0.81421(13)	0.21974(15)	1.1141(97)
Li1	1b	1	0	0	½	0.1*
Li2	2i	1	0.10269(77)	0.45563(60)	-0.2792(15)	0.1*
Li3	2i	0.5	0.76241(72)	0.2923(49)	0.1337(14)	0.1*
C1	2i	1	0.2372(14)	0.4860(4)	0.19774(11)	0.819(81)
C2	2i	1	0.2651(15)	0.52144(53)	0.29829(11)	0.819(81)
O1	2i	1	0.1404(18)	0.35392(47)	0.16573(17)	0.780(10)
O2	2i	1	0.29732(88)	0.59139(27)	0.14909(7)	0.780(10)
O3	2i	1	0.1927(19)	0.41540(68)	0.34547(15)	0.780(10)
O4	2i	1	0.3501(10)	0.65687(49)	0.32664(5)	0.780(10)
P1	2i	1	1.06798(44)	0.15475(49)	-0.18994(9)	1.024(29)
O5	2i	1	1.09422(72)	0.22876(26)	-0.08860(19)	0.780(10)
O6	2i	1	0.89561(47)	0.2054(15)	-0.24308(27)	0.780(10)
O7	2i	1	1.27767(45)	0.21790(14)	-0.24111(16)	0.780(10)
O8	2i	1	1.0010(18)	-0.01996(18)	-0.18735(35)	0.780(10)
H8	2i	1	1.1952(15)	0.20205(33)	-0.04421(25)	0.780(10)
P2	2i	1	-0.42258(11)	0.15759(69)	1.30900(3)	1.024(29)
O9	2i	1	-0.21697(88)	0.21296(70)	1.25418(83)	0.780(10)
O10	2i	1	-0.6059(12)	0.2068(10)	1.26306(53)	0.780(10)
O11	2i	1	-0.49440(72)	-0.01548(82)	1.31828(23)	0.780(10)
O12	2i	1	-0.3615(20)	0.24128(12)	1.40795(1)	0.780(10)
H12	2i	1	-0.3760(32)	0.17634(12)	1.46017(8)	0.780(10)
O13	2i	1	0.02647(81)	1.09300(14)	0.3710(27)	0.780(10)
O14	2i	1	0.45208(29)	0.8827(11)	0.12144(57)	0.780(10)
O15	2i	1	0.4209(32)	0.17019(57)	0.06455(32)	0.780(10)
H15A	2i	1	0.3373(32)	0.17088(57)	0.11918(32)	0.780(10)
H15B	2i	1	0.3422(32)	0.20888(57)	0.01910(32)	0.780(10)
O16	2i	1	0.9505(14)	0.21180(14)	-0.43274(25)	0.780(10)
H16A	2i	1	0.8870(14)	0.17169(14)	-0.37677(25)	0.780(10)
H16B	2i	1	0.8623(14)	0.27613(14)	-0.44969(24)	0.780(10)
O17	2i	1	0.8098(25)	0.1293(16)	0.04967(54)	0.780(10)
H17A	2i	1	0.6955(25)	0.0475(16)	0.01353(54)	0.780(10)
H17B	2i	1	0.9170(25)	0.1687(16)	0.00472(53)	0.780(10)
O18	2i	1	1.33701(97)	0.11843(69)	-0.46765(25)	0.780(10)
H18A	2i	1	1.40541(97)	0.20917(69)	-0.42466(25)	0.780(10)
H18B	2i	1	1.35489(97)	0.03471(69)	-0.43484(24)	0.780(10)
O19	2i	1	0.7505(16)	0.4304(14)	0.06532(37)	0.780(10)
H19A	2i	1	0.9065(16)	0.4596(14)	0.05411(37)	0.780(10)
H19B	2i	1	0.6973(16)	0.5005(14)	0.03180(37)	0.780(10)
O20	2i	1	0.72458(90)	0.5247(17)	0.45875(43)	0.780(10)
H20A	2i	1	0.74816(89)	0.5939(17)	0.51526(43)	0.780(10)
H20B	2i	1	0.65277(89)	0.4243(17)	0.47911(43)	0.780(10)

* The B_{iso} for Lithium refined to the minimum value allowed in the refinement.