The Crystal Structure of $LiMoO_2AsO_4$

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The previously unknown compound $LiMoO_2AsO_4$ has been prepared and its crystal structure has been derived on the basis of three-dimensional X-ray diffractometer data registered with $CuK\alpha$-radiation. The dimensions of the orthorhombic unit cell ($Pn2_1a$) which contains four formula units are:

$$a = 9.3792 \pm 5\text{Å}$$
$$b = 8.9114 \pm 4\text{Å}$$
$$c = 4.9043 \pm 2\text{Å}$$

Least squares refinement was carried out to a final R-value of 3.95 %. The structure is built up of MoO_6-octahedra interconnected by AsO_4-tetrahedra. The lithium atoms are octahedrally surrounded by oxygen atoms.

In connection with X-ray studies performed at this Institute [1,2] on the relationship between materials in a vitreous and in a crystalline state, the crystal structures of $AMoO_2PO_4$ ($A = $ Na and Ag) [3,4] have been determined, and the glass,[1] formed upon melting and subsequent quenching of $NaMoO_2PO_4$, has been studied. The structural analogies often displayed by phosphorus (V) and arsenic (V) made it of interest to find out whether corresponding crystalline phases, and similar tendencies to glass-formation exist in preparations of the general composition $A_2O - 2MO_3 - As_2O_5$ ($A = $ Li, Na, K, Rb, Cs, or Ag, and $M = $ Mo or W).[2]

EXPERIMENTAL

The system $Li_2O - MoO_3 - As_2O_5$ was investigated by the present author, and glasses of different compositions were prepared at 1100°C. The glass preparations (colours ranging from brownish to light green) could, with one exception, be transformed into crystalline material (a number of different phases were formed) by heat-treatment at $550 - 600$°C for 12 h.

$Li_2O \cdot 2MoO_3 \cdot As_2O_5$ was prepared by heating of an intimate mixture of lithium carbonate (Baker's Analyzed, J. T. Baker Chem. Co.), molybdenum trioxide (Analytical Reagent, Mallinckrodt Chem. Works), and arsenic pentoxide (Reagent, Matheson, Coleman and Bell) in a ratio 1:2:1 (a slight excess of As_2O_5 was added) followed by quenching of the melt. The glassy product was then subjected to heat-treatment for 12 h, which resulted in formation of small colourless crystal plates.

The loss of weight upon melting of the mixture indicated that only CO_2 and a minute amount of As_2O_5 were volatilized. No loss of weight was observed during the heat-treatment. Also, the Guinier photograph showed only one single phase to be present, and therefore the composition given above was assumed to be that of the crystals.

CRYSTAL DATA AND X-RAY DATA COLLECTING

Rotation and Weissenberg photographs of a single crystal showed the Laue-symmetry to be *mmm*. Refined values for the cell-dimensions were calculated from a Guinier photograph taken with strictly monochromatized $CuK\alpha_1$-radiation ($\lambda = 1.54056$ Å) and with potassium chloride ($a = 6.29288$ Å)

Table 1. Guinier powder pattern of $LiMoO_2AsO_4$.

h k l	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I obs	h k l	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I obs
2 0 0	2694	2697	vf	1 3 2	17270	17266	m
0 2 0	2990	2988	vs	3 2 2	18902	18926	m
1 0 1	3148	3141	vw	2 3 2	19284	19289	m
0 1 1	3218	3214	vs	5 0 1		19328	
2 1 0	3439	3445	s	4 3 1	19983	19983	m
1 1 1	3891	3888	vs	5 1 1	20062	20075	m
2 0 1	5167	5164	vs	3 4 1	20494	20491	m
2 2 0	5692	5686	vs	0 5 1	21147	21145	m
2 1 1	5917	5911	vs	2 5 0	21382	21376	m
1 2 1	6131	6129	vs	4 1 2		21406	
2 2 1	8153	8153	m	1 5 1	21813	21819	s
3 0 1	8535	8537	m	0 4 2		21821	
0 3 1	9195	9191	s	5 2 1	22330	22317	vf
3 1 1	9278	9284	m	1 4 2	22497	22496	s
2 3 0	9419	9422	s	3 3 2	22653	22662	s
1 3 1	9861	9865	w	4 4 0	22737	22745	w
0 0 2		9867		0 1 3	22957	22949	s
1 0 2	10541	10542	w	1 1 3	23631	23623	m
4 0 0	10802	10791	w	4 2 2		23647	
1 1 2	11283	11289	vs	2 5 1	23844	23843	m
3 2 1	11525	11525	m	2 4 2	24506	24519	vvf
4 1 0		11538		2 0 3	24888	24899	m
2 3 1	11886	11889	m	6 1 0	25039	25028	vf
2 0 2	12572	12565	m	4 4 1	25207	25212	m
0 2 2	12843	12856	vw	2 1 3	25641	25647	m
2 1 2	13318	13312	vw	1 2 3	25870	25865	m
1 2 2	13535	13530	vs	5 3 1	26056	26053	m
4 2 0	13779	13780	w	5 0 2	26727	26729	m
4 1 1	14003	14005	vw	6 0 1		26748	
2 4 0	14654	14652	m	0 6 0	26898	26897	vs
1 4 1	15089	15095	vs	3 5 1	27205	27215	vf
2 2 2	15547	15554	vw	2 2 3	27843	27888	w
4 2 1	16245	16247	m	3 4 2	27894	27892	m
3 1 2	16675	16684	m	3 0 3	28286	28272	w
2 4 1	17129	17119	m	0 3 3	28934	28926	vs

as an internal standard (*cf.* Table 1). The dimensions of the orthorhombic unit cell are as follows:

$$a = 9.3792 \pm 5 \text{ Å}$$
$$b = 8.9114 \pm 4 \text{ Å}$$
$$c = 4.9043 \pm 2 \text{ Å}$$

The value 4.35 g/cm³ for the density found from the apparent loss of weight in carbon tetrachloride indicates that there are four formula units in the cell. The calculated density, assuming the weighed-in composition and four formula units in the cell, is 4.43 g/cm³.

The reflections systematically absent are:

$$0kl \text{ for } k+l \neq 2n$$
$$hk0 \text{ for } h \neq 2n$$

This is characteristic of the space groups $Pn2_1a$ and $Pnma$.

Integrated intensities for the X-ray reflections from the selected crystal were obtained by means of a manual General Electric Single-crystal diffractometer, equipped with a scintillation counter with pulse height discrimination and Ni-filtered CuK-radiation.

The $\theta - 2\theta$-scan technique [6] was used with a preset time of 40 sec and a scan interval of 1.30 degrees. The background intensity was calculated as the average of the background intensities at each end of the scan interval. The intensities of 293 reflections within the $0 \leq \sin^2\theta \leq 0.70$ range in the unique eighth of the reciprocal lattice were collected. Only four reflections had to be considered "unobservable", apart from systematically absent reflections.

The approximate size of the crystal used in gathering the diffractometer data was 0.008 mm in the direction of the a-axis, 0.048 mm in the direction of the b-axis, and 0.072 mm in the direction of the c-axis. The net intensities were corrected for Lorentz polarization and absorption effects. In the calculation of absorption-factors, a linear absorption coefficient [7] with the value $\mu = 376.7$ cm⁻¹ was used. For different reflections, the transmission factors varied from 0.18 to 0.74.

STRUCTURE DETERMINATION AND REFINEMENT

The Patterson sections and projections calculated showed clearly, considering the possible vectors between Mo and As, that the space group $Pnma$ had to be dismissed as a possibility. Space group $Pn2_1a$ was then tried, and the following parameters were derived for Mo and As in the four-fold position 4(a):

$$x,y,z; \quad -x,\tfrac{1}{2}+y, \quad -z; \quad \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{2}+z; \quad \tfrac{1}{2}+x,y,\tfrac{1}{2}-z;$$

	x	y	z
Mo	0.158	0.000	0.111
As	0.052	0.323	0.402

A refinement of the coordinates thus obtained, by the method of least squares, yielded an R-value of 14.5 %. The refined coordinates were used in computing a three-dimensional Fourier synthesis $\varrho(x,y,z)$. Through three

successive calculations, the six oxygen atoms were located in 4(a) with the approximate coordinates:

	x	y	z
O(1)	0.01	0.15	0.25
O(2)	0.49	0.47	0.30
O(3)	0.23	0.32	0.46
O(4)	0.25	0.13	0.92
O(5)	0.47	0.33	0.78
O(6)	0.24	0.51	0.90

These parameters were then refined, with anomalous dispersion correction [8] applied to the data, and equal weights for all structure factors. Also, the atomic scattering curves [9] for un-ionized atoms were used. The structure was refined to an unweighted R-value of 7.7 %.

Anomalous scattering leads to the breakdown of Friedel's law for crystals, in which the atoms are not related by a centre of symmetry. The chosen spacegroup $Pn2_1a$ is non-enantiomorphous; however, optical activity may occur. In this spacegroup there is one polar axis, namely the y-axis.

It can be shown that changing the sign of the imaginary part of the anomalous dispersion correction produces the same effect on the calculations as changing the sign of all the hkl-indices.

As only one eighth of the reciprocal lattice was measured, two least squares refinements with the same set of starting parameters (use was made of aniso-tropic temperature factors for Mo and As) were performed to determine the orientation. The refinement in which the appropriate sign was chosen should give the lower R-value; the significance can be ascertained by Hamilton's R-factor test.[10]

The first choice of sign, used above, gives a weighted R-value, $R_1 = 8.97$ %, and the second, $R_2 = 8.37$ %. Suppose that the first choice is correct. According to Hamilton, this is a one-dimensional problem (no change in the number of parameters) with 251 degrees of freedom (the number of observations minus the number of parameters varied). The ratio $R_1/R_2 = 1.072$ should now be compared with $R_{1,251,\alpha}$ at a desired level of significance. The tables given by Hamilton include only $1 - 120$ degrees of freedom, but extrapolation according to the expression

$$R_{b,N_1,\alpha} \simeq 1 \pm \frac{120}{N_1}(R_{b,120,\alpha} - 1)$$

(where b is the dimension of the problem, N_1 the degrees of freedom, and α the desired level of significance) yields $R_{1,251,0.005} = 1.016$.

Since the R_1/R_2-ratio greatly exceeds the test value, the hypothesis can be rejected at the 0.005 level. This also holds true if the unweighted values of R are used. The value found for the $R_1/R_2 = 1.059$ in that case. Consequently, the second set of calculations shows that the sign of the anomalous dispersion correction or the signs of the positional parameters on the polar axis should be changed.

The significance of the calculations is further substantiated by the fact that the standard deviations of 41 out of the 42 parameters are smaller than in the first case (*cf.* Table 2).

Table 2. Positional and thermal parameters with estimated standard deviations. A comparison between the two calculations. II = neg. anomalous dispersion correction. I = pos. anomalous dispersion correction.

Atom		x	y	z	B
Mo	II	0.16040 ± 15	0.0	0.11042 ± 26	—
Mo	I	0.16039 ± 16	0.0	0.11041 ± 28	—
As	II	0.05106 ± 24	0.31926 ± 41	0.40094 ± 34	—
As	I	0.05110 ± 26	0.32328 ± 45	0.40097 ± 37	—
O(1)	II	0.01515 ± 148	0.15556 ± 171	0.24273 ± 298	0.880 ± 0.300
O(1)	I	0.01583 ± 153	0.16212 ± 177	0.24472 ± 313	0.580 ± 0.295
O(2)	II	0.49729 ± 133	0.46261 ± 142	0.29366 ± 228	0.177 ± 0.231
O(2)	I	0.49725 ± 148	0.46918 ± 159	0.29502 ± 252	0.311 ± 0.252
O(3)	II	0.23283 ± 160	0.32480 ± 184	0.45139 ± 332	0.190 ± 0.299
O(3)	I	0.23230 ± 174	0.32965 ± 202	0.45129 ± 361	1.215 ± 0.321
O(4)	II	0.24993 ± 200	0.12994 ± 195	0.92152 ± 333	0.998 ± 0.323
O(4)	I	0.24944 ± 214	0.13665 ± 207	0.92236 ± 351	0.947 ± 0.347
O(5)	II	0.47668 ± 129	0.32966 ± 184	0.78550 ± 295	0.507 ± 0.278
O(5)	I	0.47703 ± 147	0.33477 ± 211	0.78583 ± 345	0.802 ± 0.308
O(6)	II	0.24276 ± 173	0.50177 ± 228	0.90262 ± 265	1.166 ± 0.330
O(6)	I	0.24247 ± 187	0.51115 ± 231	0.90177 ± 284	1.106 ± 0.357

For Mo and As the following anisotropic temperature parameters with standard deviations results. The anisotropic temperature factor

$$T = \exp\{-[h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23}]\}.$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo II	20 ± 25	249 ± 31	178 ± 92	37 ± 43	60 ± 40	92 ± 78
Mo I	17 ± 27	252 ± 34	172 ± 100	37 ± 46	42 ± 43	90 ± 86
As II	35 ± 30	245 ± 42	341 ± 102	-24 ± 52	75 ± 60	-128 ± 128
As I	37 ± 33	197 ± 45	332 ± 110	-25 ± 55	80 ± 65	-158 ± 136

The anisotropic temperature parameters are all multiplied by 10^5.

The significance of the anisotropic temperature factors of Mo and As can also be probed by means of Hamilton's *R*-test. The dimension of the problem is $42 - 32 = 10$, and the number of degrees of freedom the same as above.

Unweighted: $R_2/R_1 = 7.71/6.09 = 1.26$. Weighted: $R_2/R_1 = 9.56/8.37 = 1.15$. These values exceed a test value, $R_{10.251,0.005} = 1.051$, which shows that the introduction of anisotropy was justified.

As a test for possible extinction effects, the 31 strongest reflections were given zero weight in a least squares refinement. This caused the R-value to decrease to 4.8 % and produced shifts in some parameters, larger than their standard deviations. For this reason, a correction was made for isotropic secondary extinction according to the expression derived by Zachariasen.[11]

A c-value $= (8.82 \pm 1.2) \times 10^{-5}$ was derived from the 18 reflections with the highest $I_{obs}\beta(2\theta)$-values. The extinction correction resulted in an R-value of 4.3 %. At this stage an attempt was made to find the position of the lithium atom. To that end, a three-dimensional difference Fourier synthesis was calculated. The resulting map indicated that lithium might be situated in a four-fold position $4(a)$, with the approximate parameters: $x = 0.38$, $y = 0.15$, and $z = 0.60$. A final least squares refinement yielded an unweighted R-value of 3.95 %. Thus, the inclusion of lithium in the model proved to be significant. The final structural parameters and the normalized weight analysis are given in Tables 3 and 4, resp. The observed and calculated structure factors are listed in Table 5.

Table 3. Final positional and thermal parameters with their estimated standard deviations.

Atom	x	y	z	B
Mo	0.1606 ± 1	0.0	0.1107 ± 2	—
As	0.0513 ± 2	0.6802 ± 3	0.4005 ± 3	—
O(1)	0.0144 ± 11	0.8445 ± 11	0.2439 ± 21	1.08 ± 21
O(2)	0.4968 ± 10	0.5359 ± 11	0.2944 ± 16	0.77 ± 17
O(3)	0.2329 ± 11	0.6745 ± 14	0.4474 ± 22	1.30 ± 20
O(4)	0.2482 ± 14	0.8687 ± 13	0.9204 ± 23	1.34 ± 23
O(5)	0.4761 ± 9	0.6717 ± 14	0.7873 ± 21	1.06 ± 19
O(6)	0.2458 ± 12	0.4963 ± 16	0.9035 ± 18	1.56 ± 23
Li	0.387 ± 6	0.848 ± 7	0.592 ± 8	4.65 ± 1.20

Anisotropic temperature factors

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	10 ± 2	28 ± 2	52 ± 6	2 ± 3	1 ± 3	2 ± 6
As	13 ± 2	25 ± 3	58 ± 7	1 ± 3	3 ± 4	-3 ± 9

The anisotropic temperature parameters are all multiplied by 10^4.

Root mean square displacement in Å

Atom	Rmsd 1	Rmsd 2	Rmsd 3
Mo	0.063	0.073	0.102
As	0.068	0.085	0.100

Table 4. Weight analysis. w = weighting function. $\Delta = |F_o| - |F_c|$.

F_o-interval	No. of refl.	$w\Delta^2$ normalized	sin$^2\theta$-interval	No. of refl.	$w\Delta^2$ normalized
0.0 — 16.8	29	0.6158	0.0 — 0.3945	35	0.4424
16.8 — 22.7	29	0.9009	0.3945 — 0.4971	29	0.4350
22.7 — 28.7	29	0.6450	0.4971 — 0.5690	33	1.5915
28.7 — 35.7	30	0.9864	0.5690 — 0.6263	26	0.5896
35.7 — 45.4	29	0.9994	0.6263 — 0.6746	32	1.1160
45.4 — 58.5	28	1.2083	0.6746 — 0.7169	31	1.2164
58.5 — 69.7	30	1.1856	0.7169 — 0.7547	26	1.0322
69.7 — 82.5	29	1.0879	0.7547 — 0.7891	30	1.4631
82.5 — 101.9	29	0.4438	0.7891 — 0.8207	32	1.4065
101.9 — 213.1	30	1.8973	0.8207 — 0.8500	18	0.3830

Weights were calculated according to Hughes with $h = 4.0$ and $F_{o,\text{min}} = 5.80$.

Table 5.

H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL
C	0	2	29.54	32.39	7	1	1	78.25	76.81	5	3	2	26.53	26.72	6	5	1	61.45	56.14
C	0	4	107.45	126.46	7	1	2	51.74	52.41	5	3	3	53.61	51.04	6	5	2	28.68	28.55
C	0	2	20.52	21.43	7	1	3	37.83	37.53	5	3	4	11.36	1C.15	6	5	3	65.67	66.15
1	0	2	27.09	28.55	8	1	1	66.75	87.68	6	3	C	26.31	35.11	7	5	1	80.64	79.14
1	0	2	8.66	5.67	8	1	1	25.82	25.12	6	3	1	12.59	13.54	7	5	2	3C.C1	29.27
1	C	5	15.40	15.54	8	1	2	8.C4	7.50	6	3	2	3C.37	3C.59	8	5	C	65.57	62.96
2	C	C	27.61	27.65	8	1	3	45.31	44.45	6	3	3	44.42	44.24	8	5	1	29.C2	26.6C
2	C	1	178.72	136.11	9	1	1	25.07	26.82	7	3	1	29.40	28.61	0	6	C	213.15	236.16
2	0	2	65.68	72.93	9	1	2	1C1.8C	104.24	7	3	2	96.82	93.52	0	6	2	25.25	26.11
2	C	3	114.85	126.41	10	1	1	41.24	4C.62	7	3	3	15.55	16.23	1	6	1	21.23	24.18
2	0	4	20.89	21.66	0	2	C	13C.37	12C.66	8	3	C	54.83	95.38	1	6	2	43.40	35.61
2	C	5	15.85	17.58	0	2	2	18.82	15.45	8	3	2	48.CC	46.28	1	6	4	10.37	4.85
3	0	1	136.42	143.37	0	2	4	68.61	65.31	8	3	2	30.24	29.31	2	6	C	35.75	34.74
3	0	2	14.35	14.90	1	2	1	138.62	136.56	9	3	1	5.31	5.23	2	6	1	69.63	83.71
3	0	3	61.95	6C.56	1	2	2	1C6.61	108.64	0	4	C	121.C2	122.53	2	6	2	28.C7	28.55
3	0	5	96.68	101.12	1	2	3	59.53	58.15	0	4	2	46.18	44.63	2	6	2	57.56	91.C7
4	C	C	66.27	62.32	1	2	4	34.44	33.31	0	4	4	84.78	85.65	2	6	4	15.51	15.45
4	C	1	7.5C	8.08	1	2	5	69.92	67.33	1	4	1	1C6.C4	103.4C	3	6	1	1C1.67	96.47
4	C	2	21.47	22.36	2	2	C	145.85	145.78	1	4	2	103.38	95.64	3	6	2	25.3C	24.53
4	C	3	8.45	6.88	2	2	1	54.CC	54.34	1	4	3	51.61	45.72	3	6	3	53.72	45.21
4	C	4	45.43	44.23	2	2	2	23.92	23.C5	1	4	4	35.42	35.C4	4	6	C	33.44	32.83
5	C	1	23.66	24.85	2	2	3	61.49	61.53	2	4	C	81.56	75.64	4	6	1	19.16	17.CC
5	C	2	191.13	205.6C	2	2	4	74.67	75.32	2	4	1	6C.58	59.62	4	6	2	12.98	12.6C
5	C	3	22.29	22.26	2	2	5	24.76	23.47	2	4	2	19.82	16.51	4	6	3	24.76	25.58
5	C	4	72.53	74.35	3	2	1	5C.14	5C.2C	2	4	3	72.64	71.37	5	6	2	142.54	14C.16
6	C	C	49.77	7C.13	3	2	2	32.62	31.1C	2	4	4	6C.23	57.57	5	6	3	14.55	14.C6
6	C	1	42.16	42.31	3	2	3	3C.72	31.15	3	4	1	62.46	75.52	6	6	C	59.57	55.68
6	C	2	35.94	36.45	4	2	C	82.C7	83.36	3	4	2	61.66	55.19	6	6	2	21.37	2C.54
5	C	3	31.C8	31.18	4	2	1	1C2.32	1C3.C5	3	4	3	42.18	4C.15	7	6	1	74.65	65.77
6	0	4	33.13	34.19	4	2	2	16.35	16.43	4	4	C	84.37	82.25	7	6	2	26.5C	24.47
7	C	1	95.82	95.83	4	2	3	55.84	104.37	4	4	1	64.65	61.52	8	6	C	31.36	31.65
7	C	2	26.76	26.57	4	2	4	46.33	46.5C	4	4	2	25.12	25.34	0	7	1	85.46	83.23
7	C	3	41.13	4C.36	5	2	1	37.52	36.92	4	4	3	84.17	83.C4	0	7	2	62.62	77.C6
8	C	C	25.76	27.37	5	2	2	76.73	76.C5	4	4	4	42.CC	42.C5	1	7	1	67.82	64.35
8	C	1	84.52	86.58	5	2	3	21.94	22.11	5	4	2	32.55	31.76	1	7	2	66.45	55.8C
8	C	2	23.C9	24.4C	5	2	4	21.55	21.41	5	4	2	54.45	94.53	2	7	C	3C.15	26.2C
8	C	3	77.68	78.58	6	2	C	116.C7	115.72	5	4	3	2C.28	15.67	2	7	2	89.24	85.25
9	C	1	12.30	12.75	6	2	1	65.57	63.63	5	4	4	33.31	33.14	2	7	1	35.54	33.78
5	C	2	6.61	5.08	6	2	2	20.16	2C.88	6	4	C	111.3C	1C5.72	2	7	2	15.C4	16.71
1C	C	C	112.7C	114.75	6	2	3	65.13	66.C1	6	4	1	54.23	52.64	2	7	2	46.26	41.C4
10	C	1	15.34	2C.16	6	2	4	72.46	71.83	6	4	2	22.66	22.51	3	7	1	29.77	27.99
0	1	1	50.75	85.99	7	2	2	43.72	43.66	6	4	3	58.73	56.C2	3	7	2	82.21	78.41
C	1	3	76.82	77.88	7	2	2	1C1.74	103.75	7	4	1	5C.2C	46.47	3	7	3	17.C8	15.27
0	1	5	27.5C	27.53	7	2	3	29.19	29.23	7	4	2	79.3C	77.15	4	7	C	65.97	75.31
1	1	1	117.30	116.81	8	2	C	57.10	54.35	7	4	3	28.32	26.3C	4	7	1	33.23	31.27
1	1	2	110.42	113.81	8	2	1	38.87	38.35	8	4	C	54.85	53.33	4	7	2	21.84	21.62
1	1	2	38.55	38.42	8	2	2	14.52	13.85	8	4	1	45.36	42.65	4	7	2	48.8C	47.C1
1	1	4	66.58	65.75	8	2	3	58.46	57.94	8	4	2	4.53	5.13	5	7	1	64.74	75.35
1	1	5	66.40	65.97	9	2	2	30.C5	3C.25	9	5	1	67.77	67.15	5	7	2	23.C1	24.61
2	1	C	115.34	117.C1	0	3	1	1C8.67	108.64	0	5	1	48.51	45.C5	6	7	C	45.13	51.C3
2	1	1	79.34	81.36	0	3	3	179.47	221.51	0	5	3	5C.41	47.CC	6	7	1	23.C2	24.61
2	1	2	18.65	18.54	1	3	1	22.7C	22.54	1	5	1	77.48	75.CC	0	8	C	36.16	39.33
2	1	2	80.63	83.17	1	3	1	17.62	16.76	1	5	2	1C9.32	1C6.C5	6	8	2	5.85	6.17
2	1	4	58.56	6C.97	1	3	2	25.71	26.66	1	5	2	36.78	34.41	1	8	1	67.75	75.36
2	1	5	20.44	19.C1	1	3	2	40.86	35.67	1	5	3	53.C8	5C.24	1	8	2	61.11	65.68
3	1	1	63.77	66.78	1	3	4	18.41	17.59	2	5	C	66.24	63.25	2	8	C	80.77	94.75
3	1	2	1C2.52	108.9C	1	3	4	30.42	29.86	2	5	1	65.22	63.65	2	8	2	22.60	23.67
3	1	2	26.51	26.51	2	3	1	174.55	173.65	2	5	2	1C.15	5.32	2	8	2	12.54	13.55
3	1	4	25.54	25.23	2	3	1	76.17	72.65	2	5	4	37.55	42.77	3	8	1	31.73	34.67
3	1	5	52.65	53.64	2	3	2	44.97	44.52	3	5	1	69.48	66.C6	3	8	2	51.57	57.14
4	1	C	141.45	141.7C	2	3	3	19.61	2C.44	3	5	2	72.53	7C.33	4	8	C	51.37	57.2C
4	1	1	57.C2	57.C2	2	3	4	1C1.94	101.2C	3	5	3	23.79	22.52	4	8	2	58.51	64.4C
4	1	2	36.65	37.66	3	3	1	4.31	4.C5	3	5	4	11.85	1C.58	4	8	2	6.14	5.C3
4	1	2	62.55	62.08	3	3	2	147.76	146.55	4	5	C	130.12	125.74	C	5	1	56.74	61.C6
4	1	4	91.90	94.62	3	3	2	12.14	12.77	4	5	1	38.72	37.23	1	9	1	2e.C7	2e.5C
5	1	1	72.92	74.25	3	3	3	45.58	44.32	4	5	2	37.54	31.2C	2	5	C	47.C8	85.C7
5	1	2	28.85	27.45	4	3	1	31.62	3C.C6	4	5	3	52.48	5C.23	2	5	1	13.47	14.54
5	1	2	35.67	4C.17	4	3	1	56.67	54.57	4	5	4	85.43	86.45					
5	1	4	22.66	21.87	4	3	2	16.93	17.13	5	5	1	43.C2	4C.21					
6	1	C	50.70	89.57	4	3	3	19.17	2C.2C	5	5	2	25.1C	23.62					
6	1	1	67.76	67.21	4	3	3	1C.90	1C.61	5	5	3	27.57	27.15					
6	1	2	35.75	36.C2	5	3	1	167.18	167.81	6	5	C	83.65	79.17					
6	1	3	84.3C	85.64															
6	1	4	54.07	52.4C															

Finally, a least squares refinement was performed, using the final positional and thermal parameters but again switching the sign of the imaginary component of the anomalous dispersion correction. This resulted in an unweighted R-value of 4.41 % and some changes of the positional parameters, most noticeable along the polar axis. The changes in the y-coordinates were as follows:

Atom	Pos. anom. A (3.95)	Neg. anom. B (4.41)	Δ	σ (3.95)
As	0.680186	0.676438	0.003748	0.000280
O(1)	0.844488	0.838511	0.005977	0.001106
O(2)	0.535910	0.529683	0.006227	0.001077
O(3)	0.674542	0.669199	0.005343	0.001378
O(4)	0.868693	0.862213	0.006480	0.001325
O(5)	0.671722	0.666947	0.004775	0.001353
O(6)	0.496307	0.488047	0.008360	0.001570
Li	0.847589	0.836197	0.011392	0.006409

This has of cause a certain effect on the interatomic distances, which is most noticeable on the AsO_4-tetrahedron (distances in Å).

	A (3.95)	B (4.41)
As − O(2)	$1.681 \pm\ 9$	1.702 ± 11
As − O(5)	1.688 ± 10	1.689 ± 12
As − O(1)	1.689 ± 10	1.665 ± 11
As − O(3)	1.720 ± 11	1.717 ± 12

Although the average arsenic-oxygen distance in both cases is 1.69 Å, which already is a short distance compared with the values reported in the literature,[15-17] we here have a case where one distance is 1.665 ± 11 Å. This also indicates that the right choice has been made in case A.

The calculations were performed on the computers IBM 1800 and IBM 360/75 with the programs listed in Table 10.

DISCUSSION

The structure consists of MoO_6-octahedra connected to four different AsO_1-tetrahedra; each AsO_4-tetrahedron is connected to four different MoO_6-octahedra, thus forming a three-dimensional network. Parallel to the c-axis run tunnels, which can be looked upon as stretches of octahedral holes. In these holes, lithium is situated. The building principle of the crystals might be expressed by the formula $LiMoO_2AsO_4$.

All the inter-atomic distances are of normal lengths (cf. Tables 6 and 7). Notable is the grouping of the Mo − O distances into two long, two intermediate, and two short bonds, which is also the case in other hexavalent molybdenum compounds, e.g. disodium dimolybdate,[12] molybdenum trioxide,[13] dipotassium trimolybdate,[14] $NaMoO_2PO_4$,[3] and $AgMoO_2PO_4$.[4]

There is no doubt as to the coordination number of any of the metal atoms since, in each case, the distances between the metal atom and the coordinating oxygen atoms lie grouped about an average value; all other metal − oxygen
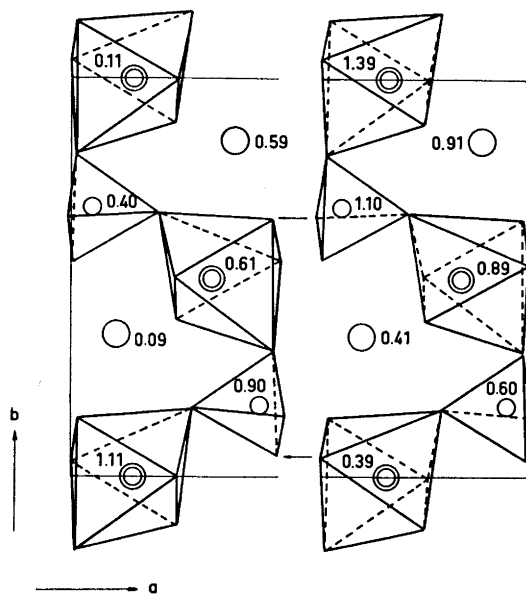
Fig. 1. The structure of LiMoO$_2$AsO$_4$ viewed along [001] showing the links in the b-direction between AsO$_4$-tetrahedra and MoO$_6$-octahedra. The arrows indicate where the sequences of polyhedra are linked together in the a-direction. Small circles denote As. Large circles denote Li. Double concentric circles denote Mo.
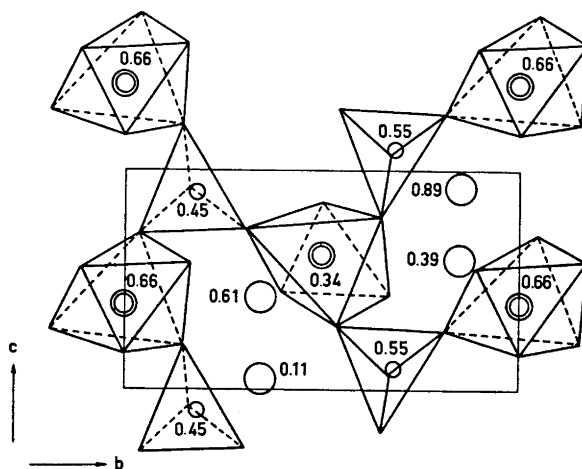

Fig. 2. The structure of LiMoO$_2$AsO$_4$ viewed along [100] showing the links between AsO$_4$-tetrahedra and MoO$_6$-octahedra in the bc-plane. The symbols are the same as in Fig. 1.

Table 6. Metal−oxygen distances (in Å) with standard deviations (± σ).

Mo−O(6)	1.683 ± 10	Li−O(5)	2.02 ± 6	As−O(2)	1.681 ± 9
Mo−O(4)	1.707 ± 12	Li−O(1)	2.04 ± 4	As−O(5)	1.688 ± 10
Mo−O(3)	2.014 ± 12	Li−O(6)	2.04 ± 5	As−O(1)	1.689 ± 10
Mo−O(1)	2.056 ± 10	Li−O(4)	2.08 ± 5	As−O(3)	1.720 ± 11
Mo−O(2)	2.165 ± 9	Li−O(2)	2.08 ± 6		
Mo−O(5)	2.176 ± 11	Li−O(3)	2.23 ± 6		

Oxygen−oxygen distances.

O(1)−O(4)	2.715 ± 16	O(3)−O(4)	2.734 ± 17
O(1)−O(3)	2.737 ± 15	O(3)−O(5)	2.738 ± 14
O(1)−O(6)	2.739 ± 16	O(3)−O(6)	2.746 ± 16
O(1)−O(2)	2.761 ± 14	O(3)−O(5)	2.825 ± 14
O(1)−O(2)	2.789 ± 13		
O(1)−O(5)	2.790 ± 15	O(4)−O(6)	2.629 ± 15
		O(4)−O(6)	2.799 ± 15
O(2)−O(5)	2.710 ± 13	O(4)−O(5)	2.842 ± 16
O(2)−O(5)	2.773 ± 13		
O(2)−O(6)	2.788 ± 14	O(5)−O(6)	2.726 ± 16
O(2)−O(3)	2.800 ± 14	O(5)−O(4)	2.842 ± 16
O(2)−O(4)	2.807 ± 16		

Table 7. Interatomic angles with standard deviations (± σ).

O(1)−Mo−O(3)	167.8 ± 4
O(4)−Mo−O(5)	169.4 ± 5
O(2)−Mo−O(6)	165.8 ± 5
O(4)−Mo−O(6)	101.7 ± 6
O(1)−Li−O(4)	174.7 ± 3.0
O(3)−Li−O(2)	170.0 ± 2.8
O(5)−Li−O(6)	166.7 ± 3.0
O(1)−As−O(2)	110.0 ± 5
O(1)−As−O(3)	106.8 ± 6
O(1)−As−O(5)	111.4 ± 6
O(2)−As−O(3)	110.8 ± 5
O(2)−As−O(5)	110.8 ± 5
O(3)−As−O(5)	106.9 ± 5

Table 8. Molybdenum−oxygen distances (in Å) and the angle between molybdenum and its two nearest neighbors.

NaMoO₂PO₄		AgMoO₂PO₄		MoO₃	LiMoO₂AsO₄	Na₂Mo₂O₇	
MoI	MoII	MoI	MoII			octa-hedron	tetra-hedron
1.78	1.87	1.76	1.73	1.67	1.68	1.68	1.71
1.78	1.97	1.80	1.79	1.73	1.71	1.68	1.75
1.97	1.92	2.02	2.00	1.95	2.01	1.90	1.78
1.98	1.96	2.00	2.07	1.95	2.06	1.90	
1.91	2.17	2.11	2.20	2.25	2.17	2.27	
2.04	2.09	2.19	2.15	2.33	2.18	2.27	
Angle:							
100.49	105.29	104	102	103.6	101.7	104	
"Oxygen volume":							
19.14 Å³		19.12 Å³		16.91 Å³	17.08 Å³	22.28 Å³	

In NaMoO₂PO₅ the angle is the one between the two first listed distances, in octahedron MoII.

distances are very much larger. The shortest oxygen — oxygen distance in the coordination octahedron around molybdenum is 2.63 ± 2 Å, viz. between the two oxygens which are not coordinated to As. The angle within this "MoO$_2$"-group in the structure is 101.7°. This deviation from the 90° and 180° angles, which characterizes the regular octahedron, is noted in several of the compounds listed above. A comparison is given in Table 8.

LiMoO$_2$AsO$_4$ is not isostructural with the two compounds NaMoO$_2$PO$_4$ and AgMoO$_2$PO$_4$, despite the similarity in composition. One obvious reason for this is that an AsO$_4$-tetrahedron requires more space than does a PO$_4$-tetrahedron; also, lithium is a smaller cation than sodium and silver.

The AsO$_4$-tetrahedron can be regarded as quite undistorted (*cf.* Table 6), and the As — O distances (average value = 1.69 Å) are somewhat shorter than mentioned in the Tables of Interatomic Distances [15] and in the International Tables,[7] which both give the value 1.75 ± 5 Å. However, the preliminary values for As — O distances in W$_2$O$_3$(AsO$_4$)$_2$[16] are in excellent agreement with the values found in the present investigation. These values are also consistent with the average value of 1.69 Å, found in As$_2$O$_5 \cdot 5/3$H$_2$O.[17]

The "oxygen volume", V_{cell}/n_0 is 17.08 Å³, which indicates a fairly close-packed oxygen arrangement. Corresponding values for structures with small cations in a close-packed framework usually lie within the range 16.0 — 16.5 Å³.

The coordination around lithium is a somewhat distorted octahedral arrangement, with one oxygen further away from the metal than the rest. Both four-fold and six-fold coordination has been suggested for lithium. The six-fold coordination is well documented in the literature, and in this case, there is no doubt of the six-coordination, with five distances equal to 2.05 ± 5 Å and one equal to 2.23 ± 6 Å. A comparison with other Li — O distances (six-coordination) is given in Table 9.

A further discussion of the structure will be given later.

Table 9. Lithium — oxygen distances found in other compounds (in Å).

LiMnPO$_4$[18]	LiCuCl$_3 \cdot$2H$_2$O [19]	LiNbO$_3$[20]	LiIO$_3$[21]
$2 - 2.224 \pm 10$	$2 - 2.04 \pm 3$	$3 - 2.068 \pm 11$	$2 - 1.962 \pm 38$
$2 - 2.113 \pm 9$	$2 - 2.14 \pm 2$	$3 - 2.238 \pm 23$	$4 - 2.151 \pm 43$
$2 - 2.160 \pm 7$	$2 - 2.22 \pm 3$		

Table 10.

Programs used on IBM 1800	Author
Pirum [22] LS-refinement of cell dimensions	Werner, P.-E.
ABSG [23] Absorption, LP-correction and correction factors for sec. extinction	Werner, P.-E. and Leijonmark, M.
Programs used on IBM 360/75	
LALS [24] LS-refinement, full matrix including anisotropic temperature factors	Gantzel, Sparks and Trueblood, modified by Brandt and Nord for IBM 360/75
DRF Fourier synthesis, structure factor calculations	Allan Zalkin, Berkeley, Cal. modified by Nord and Brandt for IBM 360/75

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