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Abstract

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CRYSTAL STRUCTURE OF BASIC Li,Cd MOLYBDATE LiCd

$$MoO_4$$

OH

Transparent, slightly yellowish crystals of the double Li,Cd molybdate were obtained by hydrothermal synthesis at the Institute for the Synthesis of Mineral Raw Materials. With a specific gravity of 4.26 g/cm^3 and parameters of the monoclinic cell (RKOP camera)

$$a = 7.91 \pm 0.1; \quad b = 5.95 \pm 0.2; \quad c = 9.77 \pm 0.1 \text{ Å}; \quad \beta = 107°30' \pm 30'$$

chemical analysis (Institute of Crystallography, Academy of Sciences of the USSR) gives the material content of the cell as

$$\mathrm{Li_{3.22}Cd_4[MoO_4]_4 \cdot (OH)_{3.92}(H_2O)_{0.65}}.$$

Table 1 gives the interplanar spacings calculated from a powder photograph on a URS-50I diffractometer with a scintillation counter (Cu radiation, Ni filter).

Table 1

LiCd

$$MoO_4$$

OH. Interplanar spacings

No. p.p.	d/n	I	No. p.p.	d/n	I
1	9.368	49	21	2.240	23
2	4.632	46	22	2.184	9
3	4.470	34	23	2.149	11
4	3.808	26	24	2.014	7
5	3.654	62	25	1.975	22

No. p.p.	d/n	I	No. p.p.	d/n	I
6	3.466	8	26	1.919	26
7	3.255	100	27	1.883	21
8	3.186	95	28	1.816	33
9	3.136	56	29	1.785	48
10	3.058	36	30	1.735	12
11	2.834	73	31	1.704	38
12	2.797	59	32	1.673	58
13	2.766	69	33	1.616	24
14	2.695	13	34	1.598	13
15	2.624	25	35	1.560	9
16	2.556	28	36	1.528	30
17	2.488	32	37	1.519	19
18	2.396	23	38	1.504	23
19	2.348	17	39	1.435	8
20	2.327	13	40	1.385	17

Preliminary structural indications were also obtained from the data of thermal analysis and infrared spectroscopy. The thermogram (recorded and interpreted by G. O. Pilyan, IGEM, Academy of Sciences of the USSR) showed the presence of hydroxyl groups in the structure and the absence of H_2O particles. The fixed amount, 3.7% OH, agrees with the chemical analysis. The diffuse form of the thermal effect in differential thermal analysis indicates a statistical distribution of the deficiency. Infrared absorption spectra taken (by I. I. Plyusnina) at the Department of Crystallography of Moscow University first of all confirmed, in agreement with the formula given above, tetrahedral coordination of Mo (absorption maxima 840 and 786 cm^{-1} in the NaCl-prism region). Bands at 1160, 1097 cm^{-1} in the same region make it possible to speak of fourfold (tetrahedral) coordination of Li atoms, and, finally, the absorption maximum at 3430 cm^{-1} is usually attributed to stretching vibrations of OH^- (hydrogen bond). Bands of molecular H_2O are absent.

If the constant deficiency in the chemical analyses of Be and Li is taken into account, these results make it possible to accept as the number of chemical units in the cell

$$Z = 4 \text{ units of } LiCd[MoO_4]OH.$$

For the crystal-structure analysis, two series of X-ray goniometric scans were recorded (Mo radiation, owing to the low quality of the reflections, $\max \sin\vartheta/\lambda = 0.73$ Å^{-1}): five layer lines along the b axis and two along c. From the systematic extinctions, the centrosymmetric Fedorov group was determined fairly unambiguously as

$$C_{2h}^5 = P2_1/a.$$

The intensities were estimated visually on a $2^{0,25}$ scale of blackening marks.

In solving the structure by the heavy-atom method, Patterson projections and, subsequently, projections and the three-dimensional distribution of electron density were used. To localize the O atoms, three-dimensional difference syntheses of electron density were required. The final averaged coordinates of all atoms are given in Table 2. The origin of the coordinates is at the center of symmetry on the common O–O edge of two Cd octahedra.

The interatomic distances corresponding to the refined coordinates are given in Table 3*. The discrepancy factor is $R = 16\%$.

The Cd atoms in the structure of $LiCd[MoO_4]OH$ occupy the centers of octahedra somewhat flattened along the pseudo-fourfold axis, i.e., they have four longer equatorial distances of 2.31–2.45 Å and two shortened ones, 2.23–2.24 Å. It is of interest to note that the octahedral coordination of Cd in the double molybdate separates it from $Cd[MoO_4]$ with the scheelite structural type $CaWO_4$, i.e., with Cd in eightfold coordination (1), and, conversely, the double molybdate approaches $CdWO_4$, which crystallizes in the wolframite type (2), i.e., with Cd in octahedra; moreover these octahedra (both in the tungstate and in the double molybdate) are joined by common edges into rocking columns extending along the axis $b = 5.95$ Å. Mo orthotetrahedra adjoin the columns on both sides through common vertices.

Table 2

$LiCd[MoO_4]OH$. Coordinates of the basis atoms

	x/a	y/b	z/c
Cd	0.061	0.735	0.122
Mo	0.315	0.078	0.963
(Li)	0.422	0.602	0.173
O I	0.435	0.925	0.120
O II	0.355	0.378	0.971
O III	0.285	0.571	0.235
O IV	0.146	0.410	0.515
O V	0.107	0.930	0.374

Table 3

$LiCd[MoO_4]OH$. Interatomic distances

Mo tetrahedron	Cd octahedron	Cd octahedron
Mo–O_I 1.69	Cd–O_{III} 2.37	O_{III}–O_V 3.04
Mo–O_{II} 1.83	Cd–O_V 2.23	O_{III}–O_V 3.75
Mo–O_{III} 1.75	Cd–O_V 2.45	O_{III}–O_V 3.06
Mo–O_{IV} 1.82	Cd–O_V 2.38	O_{III}–O_V 3.70
Mean 1.77 Å	Cd–O_{IV} 2.24	O_V–O_V 3.82
O_I–O_{II} 2.96	Cd–O_{IV} 2.31	O_V–O_{IV} 3.32
O_I–O_{III} 2.75	Mean 2.33 Å	O_V–O_{IV} 3.13
O_I–O_{IV} 2.87		O_V–O_V 3.40
O_{II}–O_{III} 3.10		O_V–O_{IV} 3.06
O_{II}–O_{IV} 2.77		O_V–O_{IV} 3.11
O_{III}–O_{IV} 2.88		O_V–O_{IV} 3.28
Mean 2.89 Å		O_{IV}–O_{IV} 2.99
		Mean 3.30 Å

The Li atoms, since they account for only 2.2% of the scattering matter, almost do not appear on the electron-density maps; nevertheless, their positions are clearly established from an unexpected analogy of the structure of the basic molybdate $LiCd[MoO_4]OH$ with the structure of the basic zinc silicate, hutchinsonite $Zn_2Mn[SiO_4](OH)_2$ (3), from the "molecule" of which, leaving aside for the moment the qualitative difference, one cation in a tetrahedron (Zn) and one anion OH are thrown out.

These two structures in projection along the short axis b are shown in Figs. 1A and 1B; in both, in addition to the "economic" cells (with an angle β close to 90°) appearing in the original articles on hutchinsonite and above in the present work for the double molybdate, elongated cells are also indicated (for the double molybdate $a' = a = 7.91$, $b' = b = 5.95$, $c' = (2a + c) = 15.90$ Å; $\beta = 144°06'$), with the aid of which the basic structural principle of both structures appears more clearly: two layers (along the axis $a = 7.71$ Å directed obliquely to them) of the densest hexagonal packing of anions, of length (along the new axis c') of 6 O–O edges in hutchinsonite and only 5 O–O edges in the double molybdate. In the six and, respectively, five

* All calculations were carried out at the Computing Center of Moscow University.

the outer edges are the ridges of the end octahedra in the Mn-column of hutchinsonite and the Cd-column in the molybdate. Along the obliquely running axis a, in each successive layer of the packing these ends are shifted by one edge, and the columns represented by them become the steps of an infinitely wide staircase (Fig. 2). The space between the staircases, corresponding to five and four

Fig. 1. Comparison, in the xz projection, of the structures of hutchinsonite (A) and Li, Cd molybdate (B). In both projections, along the axis c, the cells

Fig. 1. Comparison, in the xz projection, of the structures of hutchinsonite (A) and Li,Cd molybdate (B).

Figure 1: Fig. 1. Comparison, in the xz projection, of the structures of hutchinsonite (A) and Li,Cd molybdate (B).

Fig. 2

Figure 2: Fig. 2

are bounded by "staircases" of occupied octahedra. In the tetrahedral material between the staircases, the light tetrahedra are the ends of the metachains $[Zn_2O_6]_\infty$ in A and $[Li_2O_6]_\infty$ in B. The solid black ones are the encrusting Si-tetrahedra in A and Mo-tetrahedra in B.

edges, is filled by Zn- and Si-tetrahedra in hutchinsonite, and by Mo- and Li-tetrahedra in the double molybdate.

Immediately adjacent to the rocking columns of occupied octahedra (with only one common vertex) are Zn-tetrahedra in hutchinsonite and Mo-tetrahedra in the double molybdate. One step farther (from the column of octahedra) in hutchinsonite we encounter a Zn-tetrahedron, likewise an end tetrahedron in the metachain $[Zn_2O_6]_\infty$, extending along the axis $b = 2_1$ parallel to the column of octahedra. The metachains are encrusted by Si-orthotetrahedra. The pecul—

···of these chains is also that at each of their steps along the axis 2_1 ($\| b$) the Zn tetrahedra are doubled, and the second Zn tetrahedron is precisely the one that directly adjoins the column of Mn octahedra. This is shown in Fig. 2, where it is also seen that the second halves, the second tetrahedra, of the chain $[Zn_2O_6]_\infty$ are located at another level of the closest packing, and the "additional" Zn tetrahedron is already linked with the left-hand swinging column of Mn octahedra. The chains are polar along the axis $2_1 = b$, but in alternating layers of the closest packing they alternately change their polarity, being reflected with a shift in the glide plane a. The chains nearest to the axis (2_1)

Fig. 2. Hodgkinsonite (**A**) and Li,Cd molybdate (**B**). Arrangement in a two-layer closest packing of the basic metachains (light tetrahedra) $[Zn_2O_6]_\infty$ in (**A**) and $[Li_2O_6]_\infty$ in (**B**). Solid black: the incrusting Si tetrahedra in (**A**) and Mo tetrahedra in (**B**).

Zn tetrahedra are linked only with one another, with the Zn_2 tetrahedron, and with their own Zn tetrahedra. To the latter, however, there immediately adjoin two Si from different metachains, and thus the tetrahedra Zn_1, Zn_2, and Si are tied into a thick two-dimensional net clamped between walls of Mn octahedra. In the double molybdate $LiCd[MoO_4]OH$, the metachains $[Zn_2O_6]_\infty$ are entirely excluded, but the "second" Zn tetrahedra remain in place and are replaced by Mo tetrahedra. At the same time, the previously incrusting Si tetrahedra come closer together and join into a metachain which, after replacement of Si by Li,

acquires the form $[Li_2O_6]$, while the former Zn_2, and now Mo, tetrahedra incrust the "basic" chain $[Li_2O_6]_\infty$.

We have before us a new example of the manifestation of the "anion" (anion-forming) function of lithium, which was emphasized by one of the authors in analyzing the structure of the garnet-like F analogue of cryolithionite $Na_3Al_2Li_3F_{12}$. The less certain Li coordinates are given (in Table 2) in parentheses. The Li–O distances (1.92–2.07 Å) agree well, even with respect to their scatter, with those usually cited ([5]).

The valence balance makes the atoms O_V undoubted hydroxyls, since they form the common edges of Cd octahedra, and in addition only three Cd octahedra meet at each O ($3 \cdot 2/6 = 1$). However, the Cd octahedron has one more common edge with a neighboring Cd, and since Mo tetrahedra are also attached to its ends, the corresponding O_{IV} no longer include H. At the anion O_{III}, besides one Cd octahedron, Mo and Li also meet. Nevertheless each Cd also has a third OH vertex, likewise O_V; this is the one by which the Cd octahedron abuts against the common edge of two neighboring Cd. The strain in the balance at those O atoms (O_I) at which 1Mo, 1Cd, and 1Li meet ($\Sigma = 2\frac{1}{4}$) lengthens the Li–O distance to 2.07 Å.

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Note: Figure translations are in progress. See original paper for figures.