X-RAY STRUCTURAL STUDY OF THE DOUBLE MOLYBDATE KY(MoO$_{4}$)$_{2}$

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Abstract

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X-RAY STRUCTURAL STUDY OF THE DOUBLE MOLYBDATE $KY(MoO_4)_2$

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Work in recent years has shown that among double molybdates and tungstates there are many compounds with as yet unknown types of crystal structures. A preliminary study has been carried out of one of them, $KY(MoO_4)_2$, obtained by crystallization from solution in a melt.* It was noted that the crystals possess perfect cleavage, which distinguishes them among analogous compounds. From their growth forms and from X-ray data they were assigned to the class D_{2h} of the rhombic system, with the space group $Pbna$ determined unambiguously. In the present study, for the convenience of further work, we adopted another—tabular—setting of the space group $D_{2h}^{14} = Pbcn$: $a = 5.07$; $b = 18.23$; $c = 7.95$ Å ($z = 4$).

On a Weissenberg-type equi-inclination X-ray goniometer, using Mo K_α radiation, seven layer-line photographs $hk0$, $0kl$—$5kl$ were taken and evaluated from the intensity-blackening marks. After introducing corrections for polarization and the angular factor (no absorption correction was introduced), about 700 values of F_{hkl} were obtained, which constituted the experimental material for subsequent work.

The coordinates of the heavy atoms Y, Mo, K and some information about the oxygen atoms were obtained from the $hk0$-, $0kl$- and $1kl$-projections of the Patterson function. Analysis of these projections led to the conclusion that the heavy atoms, and probably also the light atoms, are arranged with respect to the coordinate x on four equally spaced levels. Of the three types of fourfold special positions of the group D_{2h}^{14} ([1]), the positions on the twofold axis proved most suitable for Y and K; for Y the coordinate $y \approx 0$, and for K $y \approx 1/4$. The coordinates of the Mo atom, located in a general position, were established both from the Mo—Mo maxima and from the Mo—Y maxima, which "tied" the Mo coordinates to a single origin. The relatively short Y—Y distance in a chain parallel to the c axis (~ 4 Å) suggested the existence of common elements (vertices, edges) in neighboring Y-polyhedra; at the same time, the Mo—Mo distances had a lower limit of 3.70 Å, which in previously studied structures ([2], [3]) usually corresponds to isolated Mo-polyhedra. The latter circumstance makes coordination 4 most probable for Mo, and this, in turn, already greatly facilitates the search

Figure 1

Figure 1: Figure 1

for the four basic oxygen atoms. Their preliminary coordinates were established in accordance with the positions of the remaining maxima of the Patterson function, and also from geometrical and crystal-chemical considerations.

The structural model was refined by the least-squares method ([4]), first by zones of reflections F_{0kl} and F_{hk0} (final values of the R-factors 11.5 and 15.7%, respectively), and then by the three-dimensional set of amplitudes (R_{hkl} 11.4%).

* A description of the compound will be published in the journal *Inorganic Materials*.

The coordinates of the basis atoms, the isotropic temperature corrections (B_j), and the standard deviations for these quantities are given in Table 1.

The principal interatomic distances, given in Table 2, provide an idea of the coordination of the cations in the structure. Thus, in the nearest environment of Mo^{6+}, four neighbors are undoubtedly distinguished, the interatomic distances to which fall within rather narrow limits characteristic of tetrahedral coordination of Mo. At the same time one can also note the emerging tendency for two adjacent tetrahedra to condense into pairs of pentagonal bipyramids (the distance to the fifth oxygen is 2.33 Å). It is known that in molybdates and tungstates having Mo (W) coordination 5 or 6, the cation–anion distances vary within rather wide limits, so that in determining the coordination number one cannot formally use only this criterion. In $CoMoO_4$, for example, four Mo–O distances are less than 1.98 Å, and two are greater than 2.31 Å ([5]); in $CdWO_4$, four W–O distances are less than 1.87 Å, two are 2.22 Å ([6]), etc. An indirect indication in favor of including an oxygen atom in the coordination polyhedron of Mo or W may be the observed effect, in these compounds, of shortening of the common edges of the polyhedra. In our case, the inclusion of a fifth oxygen atom in the coordination of Mo leads to the formation of pairs of pentagonal bipyramids with a common edge of 2.69 Å, while the O–O distances in the MoO_4 tetrahedron are all somewhat larger: 2.75–3.12 Å. Evidence in favor of isolated polyhedra—tetrahedra—is the relatively large distance between the Mo cations (Table 2). Indeed, the Mo–Mo distance in two adjacent pentagonal bipyramids in

Fig. 1. yz-projection of the structure of $KY(MoO_4)_2$. K atoms located at heights $x = 0$ and $x = 1/2$ are shown by different circles

Table 1

	x	σ_x	y	σ_y	z	σ_z	B	σ_B
Mo	0.5229	0.0005	0.1013	0.0001	−0.0161	0.0003	0.68	0.03
Y	0	–	0.0064	0.0002	0.25	–	1.02	0.06

Figure 2 and Figure 3 diagrams

Figure 2: Figure 2 and Figure 3 diagrams

	x	σ_x	y	σ_y	z	σ_z	B	σ_B
K	0.50	–	0.2696	0.0005	0.25	–	1.49	0.15
O_1	0.726	0.005	0.100	0.001	0.159	0.003	0.87	0.31
O_2	0.747	0.005	0.095	0.001	−0.187	0.003	0.85	0.35
O_3	0.252	0.004	0.035	0.001	0.004	0.003	0.61	0.27
O_4	0.398	0.005	0.189	0.001	−0.028	0.004	1.32	0.36

$K_2Mo_3O_{10}$ is only about 3.22 Å ([7]), while between W cations in $Eu_2(WO_4)_3$ it is about 3.3 Å ([2]). On the basis of this, and also of the strong differentiation of the Mo–O distances, in the subsequent description coordination 4 was taken for Mo.

On a general view of the structure (Fig. 1), one must first note the ribbons of edge-sharing Y octahedra, elongated

Fig. 2. Wall composed of ribbons of Y octahedra (dotted hatching), joined by Mo tetrahedra

Fig. 3. Wall of K decahedra. The positions of the K atoms forming a hexagonal net are shown by circles

along the c axis. Two Y octahedra related by the translation $a = 5.07$ Å are separated by an empty octahedron, to four lateral edges of which the edges of four Mo tetrahedra adjoin (Fig. 2). Each Mo tetrahedron, joining two translationally identical ribbons of Y octahedra, also binds the vertices of two polyhedra neighboring along the ribbon.

As a whole, the radical $[Y(MoO_4)_2]^-$ forms a porous wall parallel to the xz plane. The wall passing through the middle of the cell ($y \approx 1/2$) is displaced with respect to neighboring walls by $^1/_2a$. The connection between neighboring walls is effected only by K ions (Fig. 1), which explains the perfect cleavage along the xz plane observed in the crystal. The less perfect cleavage along the xy plane observed in the crystal apparently passes through the Y and K cations.

Table 2

Interatomic distances in Å in the structure of $KY(MoO_4)_2$

Mo tetrahedron (five-vertex polyhedron)				Y polyhedron	
Mo $-O_1$	1.73	O_1 $-O_2$	2.75	Y $-O_1$	2.32 (2)
Mo $-O_2$	1.77	O_1 $-O_3$	2.95	Y $-O_2$	2.30 (2)
Mo $-O_3$	1.83	O_1 $-O_4$	2.75	Y $-O_3$	2.40 (2)
Mo $-O_4$	1.71	O_3 $-O_4$	2.90	Y $-O_3'$	2.50 (2)
(Mo $-O_2'$	2.33)	O_2 $-O_3$	3.13		
		O_2 $-O_4$	2.76	O $-$O	2.74 (2); 2.76 (1); 2.78 (2);
		(O_2' $-O_4$	2.93)	O $-$O	2.79 (2); 2.86 (2); 2.93 (2);
		(O_2' $-O_3$	2.75)	O $-$O	3.13 (1); 3.16 (1); 3.17 (2).
		(O_2' $-O_2$	2.69)		
K polyhedron					
K $-O_4$	2.71 (2)			Mo $-$Mo	3.71; 3.73; 4.22
K $-O_4'$	2.79 (2)			Mo $-$Y	3.63; 3.65; 3.81
K $-O_2$	2.83 (2)			Mo $-$K	3.73; 3.85
K $-O_1$	3.38 (2)			Y $-$Y	3.98
K $-O_4''$	3.61 (2)				

The walls of the Y and Mo polyhedra alternate in the direction of the c axis with continuous walls of K decahedra, joined by common edges (Fig. 3). The centers of the polyhedra are marked in the figure by circles, and it is readily seen that the K ions, lying approximately in one plane, form an almost hexagonal network. This may provide an explanation for the trigonal shape of the plates that sometimes form during crystallization.

A comparative crystal-chemical analysis of this compound will be continued.

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