

# Crystal Structure of Fibrillar Potassium Trimolybdate $K_2Mo_2O_{10} \cdot 3H_2O$ by Direct Method/Powder Diffraction Package

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The crystal structure of polycrystalline fibrillar potassium trimolybdate  $K_2Mo_2O_{10} \cdot 3H_2O$  has been solved *ab initio* by a default run of the direct method and powder diffraction program package POWSIM. The structure was refined by the Rietveld method with final discrepancy factors  $R_F = 7.7$  and  $R_{wp} = 15.1\%$ . All nonhydrogen atoms were located. The structure consists of polymeric chains of Mo-O polyhedra parallel to the *c* axis. The space group is *Cmcm* (63),  $a = 13.663(1)$  Å,  $b = 12.050(2)$  Å,  $c = 7.6337(6)$  Å, and  $Z = 4$ . © 1995 Academic Press, Inc.

## INTRODUCTION

The fibrillar crystals due to the small diameter of the fibers (about 0.1–1 μm) can be investigated only by powder diffraction methods. The direct method and powder diffraction program package POWSIM (1) has been recently successfully applied to solve an unknown structure of a fibrillar silver trimolybdate (2). Due to the small size of the fibrillar crystals, diffraction lines were broad and weak; as a result, the Rietveld refinement of the structure model was very difficult. A powder sample with much better particle statistics has been selected for potassium trimolybdate hydrate, which can be prepared from an acidified solution of  $K_2MoO_4$  (3). The fibrillar crystals are stable in air and produce a diffraction pattern without an amorphous hump or significant line broadening. The lattice parameters and probable space group for this compound have been published already with a partial description of its diffraction pattern (3) and are also listed in the JCPDS file under Card No. 32-815. No information about its structure is present in the literature including the Inorganic Crystal Structure Database. The structure of anhydrous potassium trimolybdate, obtained by melting a mixture of  $MoO_3$  and  $K_2CO_3$  has been determined by a single crystal method (4, 5), the lattice parameters

and crystallographic system being, however, completely different.

## DATA COLLECTION AND SPACE GROUP DETERMINATION

The sample, prepared according to a published procedure (3), was grounded under alcohol and loaded into a specimen holder from the back to avoid texture. Details of the data collection are presented in Table 1. Since refinement of the lattice parameters in the suggested space group (3) was not satisfactory, indexing and space group determination were performed again. Initial pattern decomposition, indexing, and lattice constants refinement was performed using the PC powder diffraction program package PROSZKI (6). Even though similar values of lattice parameters were determined, careful examination of *hkl* indices of single and overlapping lines indicated the space group *Cmcm* (63) to be the most probable. All but one (1.5% of intensity) line can be indexed in this space group; the suspicious line cannot be indexed in the related space groups without extinctions either. This line can be explained as "unknown isopoly-molybdates" impurities since in sodium trimolybdate, crystallized by a similar procedure, the same line is observed. The list of *d* values and their *hkl* indices and intensities is given in Table 2.

## INTENSITIES OF REFLECTIONS, STRUCTURE SOLUTION, AND REFINEMENT

The procedures and the organization of the POWSIM system have been extensively described in the original papers (1); in the present work, the default values of the required parameters are used. Initial values of back-

TABLE 1  
Details of Data Collection and Structure Refinement for  
 $K_2Mo_3O_{10} \cdot 3H_2O$

Diffractometer	PW3710 Philips X'pert
Radiation	CuK $\alpha$ , filtered
2 $\theta$ range	6–96
Step scan increment	0.02°
Count time (sec/step)	14 sec
Standard peak: <i>hkl</i> , 2 $\theta$	110, 9.78
<i>R</i> for standard peak (%)	1.1
Space group	<i>Cmcm</i> (63)
<i>a</i> (Å)	13.663 (1)
<i>b</i> (Å)	12.050 (2)
<i>c</i> (Å)	7.6337 (6)
<i>V</i> (Å <sup>3</sup> )	1256.7 (2)
Number of observations	4128
Number of reflections	338
Number of structural parameters refined	26
Number of profile parameters refined	9
<i>R<sub>F</sub></i>	7.7
<i>R<sub>wp</sub></i>	15.1
<i>R<sub>exp</sub></i>	6.7
Max. shift/error	0.3

ground polynomial coefficients and peak shape parameters were obtained using results from the PC version of the NEWPEAK program (7), incorporated into the PROSZKI system (6). The diffraction pattern was decomposed for single and overlapping intensities by the LSQPROF program, with an *R* value of 2.01%. Assuming 0.5 of half-width as a separation limit, 77 nonoverlapping reflections were found, that is, 22% of the total number of possible reflections. Respectively 63, 59, and 29 reflections have normalized structure factor values *E* greater than 0.1, 0.2, and 1.0. In the two initial runs of the DOREES program the weight of the Patterson estimation was set to 0. In the next steps all weights were equal to 1.0. After 4 cycles of intensity estimation procedure file of single reflections contained 181 reflections. In this case the |*E*'s of 143, 138, and 59 were greater than 0.1, 0.2, and 1.0, respectively. At this time the structure solution program SIMPEL88 was run. All reflections with *E* greater than or equal to 1.0 were used in the calculations and given a phase for the *E*-map, in which the Mo and K atoms were easily recognized. The structure was further refined by the Rietveld method using the PC version of the XRS-82 (8). After refinement of the heavy atom positions all oxygen atoms were found on a difference Fourier map. Structure was refined initially without any constraint on bond length or angles. In this case, however, one molybdenum–oxygen bond distance was too long. Thus, two soft-constraint limiting bond distances for two terminal oxygen atoms were introduced (weight of soft geometrical constraint was 1.34% of that of the diffraction data only) and as a result the geometry of MoO<sub>6</sub> octahedra was improved. All temperature factors

TABLE 2  
Fibrillar Potassium Trimolybdate Observed  
Diffraction Lines Their *hkl* Indices and Intensity

<i>d</i> <sub>obs</sub>	<i>d</i> <sub>cal</sub>	<i>h k l</i>	<i>I</i> / <i>I</i> <sub>max</sub> (%)
9.039	9.037	1 1 0	100
6.833	6.831	2 0 0	2
6.027	6.025	0 2 0	10
5.833	5.832	1 1 1	10
4.732	4.729	0 2 1	11
4.261	4.260	3 1 0	6
3.889	3.888	2 2 1	4
3.721	3.720	3 1 1	14
3.515	3.516	1 1 2	11
3.331	3.332	2 0 2	4
3.224	3.224	0 2 2	27
3.013	3.012, 3.012	0 4 0, 3 3 0	33
2.972	2.971	4 2 0	25
2.843	2.843	3 1 2	18
2.802	2.802, 2.802	3 3 1, 0 4 1	5
2.769	2.769	4 2 1	3
2.712	2.712	1 3 2	9
2.546	2.545	4 0 2	5
2.449	2.449	1 1 3	2
2.373	2.373	1 5 0	2
2.344	2.344, 2.345	0 2 3, 4 2 2	5
2.260	2.259, 2.259	4 4 0, 5 3 0	19
2.185	2.185, 2.185	5 1 2, 3 1 3	2
2.167	2.166, 2.164	4 4 1, 5 3 1	3
2.053	2.052, 2.052	3 5 1, 6 2 1	4
2.029	2.015		2 i
2.010	2.008	0 6 0	3
1.9446	1.9442, 1.9442	4 4 2, 5 3 2	
	1.9439, 1.9439	0 4 3, 3 3 3	5
1.9275	1.9267, 1.9267	2 6 0, 7 1 0	4
1.9088	1.9084	0 0 4	7
1.8682	1.8682, 1.8681	2 6 1, 7 1 1	6
1.8604	1.8600, 1.8600	3 5 2, 6 2 2	7
1.8082	1.8074	5 5 0	2
1.7675	1.7672	6 4 1	1
1.7590	1.7588, 1.7580	5 5 1, 2 2 4	2
1.7341 b	1.7356, 1.7312	1 5 3, 4 6 0	1
1.7097 b	1.7102, 1.7079	1 3 4, 1 7 0	
	1.7079	8 0 0	3
1.6902	1.6895, 1.6894	4 4 3, 5 3 3	1
1.6440	1.6431	8 2 0	1
1.6350	1.6335, 1.6333	5 5 2, 3 5 3	
	1.6333	6 2 3	2
1.6132	1.6121, 1.6121	0 4 4, 3 3 4	5
1.6074	1.6063, 1.6058	8 2 1, 4 2 4	4
1.5955	1.5949	7 3 2	4
1.5771	1.5766, 1.5764	4 6 2, 0 6 3	5
1.5178	1.5168	7 5 0	2
1.5085 b	1.5092, 1.5062	8 2 2, 0 8 0	
	1.5062	6 6 0	2
1.4865 b	1.4872, 1.4857	1 5 4, 8 4 0	2
1.4768	1.4777, 1.4777	9 1 1, 0 8 1	
	1.4777	6 6 1	1
1.4590	1.4583, 1.4579	8 4 1, 4 4 4	4
1.4012	1.4011, 1.4011	0 8 2, 6 6 2	
	1.4011	9 1 2	1
1.3840	1.3845, 1.3834	8 4 2, 0 6 4	2
1.3802	1.3803	8 2 3	1

Note: The letter i refers to an impurity line and b refers to a broad diffuse line.

TABLE 3  
List of Atomic Parameters

Atom	X	Y	Z	U
K	0.803(2)	0.311(4)	0.75	0.03(1)
Mo(1)	0.	0.171(2)	0.25	0.005(7)
Mo(2)	0.134(1)	0.	0.5	0.006(4)
O(1)	0.231(3)	0.106(4)	-0.037(7)	-0.01(2)
O(2)	0.117(7)	-0.003(9)	0.25	0.03(3)
O(3)	0.	0.140(8)	0.01(1)	0.03(4)
O(4)	0.094(5)	0.273(6)	0.25	0.12(6)
Ow(5)	0.5	0.22(1)	0.25	0.01(4)
Ow(6)	0.090(6)	0.516(9)	0.25	0.06(5)

Note. Ow indicates the O of H<sub>2</sub>O.

TABLE 4  
Selected Interatomic Distances

Mo(1) octahedron		Mo(2) octahedron	
Mo(1)-O(4) 2×	1.78 (7)	Mo(2)-O(1) 2×	1.86 (5)
Mo(1)-O(3) 2×	1.85 (9)	Mo(2)-O(2) 2×	1.92 (1)
Mo(1)-O(2) 2×	2.64 (11)	Mo(2)-O(3) 2×	2.49 (7)
Mo-Mo			
Mo(1)-Mo(2) 4×	3.35 (2)	Mo(2)-Mo(2)	3.67 (2)
		Mo(2)-Mo(1) 2×	3.35 (2)
K-O			
K-Ow(6)	2.54 (11)	K-Ow(5)	2.72 (4)
K-O(1) 2×	2.61 (6)	K-O(4)	3.03 (8)
K-O(1) 2×	2.99 (7)	K-O(2)	3.45 (11)

but one oxygen atom was refined to positive values. However, the esd for the oxygen temperature factors are high and their values seem to be not very reliable. In special runs the presence of the preferred orientations and site occupancy factors for heavy atoms were tested. No preferred orientation nor partial occupancy could be detected. The difference pattern was carefully examined but no indication for a change of space group could be found.

The final atomic parameters and most important interatomic distances are listed in Tables 3 and 4. The observed calculated and difference pattern for the investigated compound are presented in Fig. 1.

### STRUCTURE DESCRIPTION AND DISCUSSION

The projection of the structure in a polyhedral representation is presented in Figs. 2A and 2B. The structure consists of infinite zigzag chains of distorted edge- and vertex-shared MoO<sub>6</sub> octahedra parallel to the *c* axis. Pairs of octahedra joined by an edge create Mo<sub>2</sub>O<sub>10</sub> units. Each unit shares four vertices with adjacent units and form infinite ribbons with formula Mo<sub>2</sub>O<sub>8</sub> to which MoO<sub>6</sub> octahedra are attached alternately to both sides of this ribbon, forming chains with the formula Mo<sub>3</sub>O<sub>10</sub> (Fig. 2B). The distortions present in MoO<sub>6</sub> octahedra are reflected by the bond-length dispersion, the Mo-O distances being between 1.78–2.64 for one type of molybde-

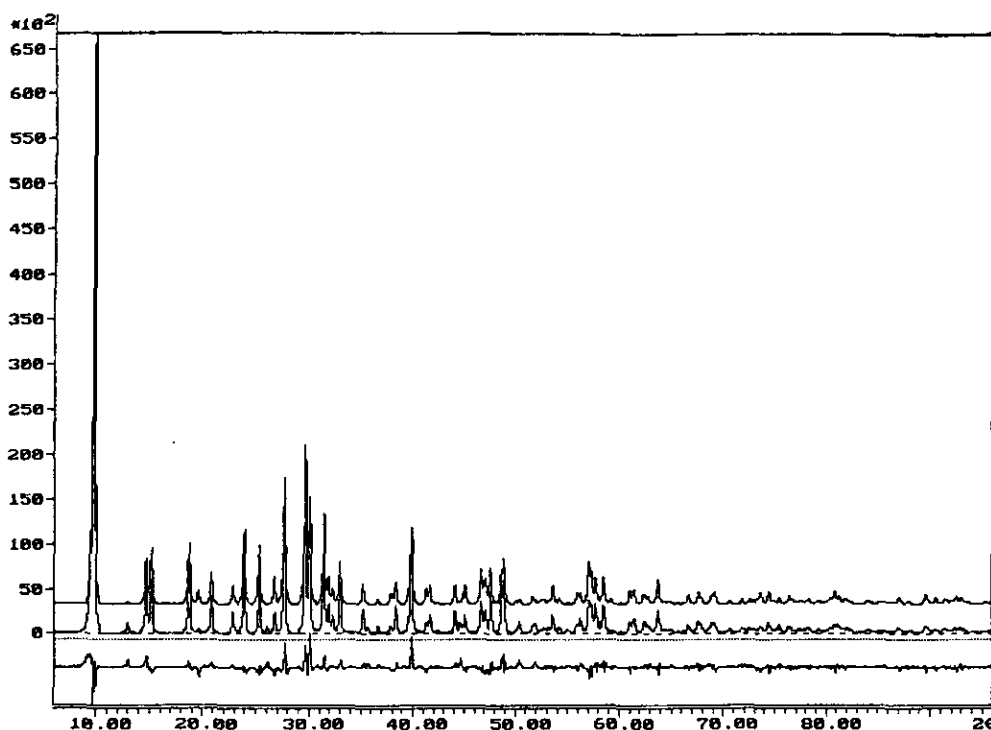


FIG. 1. Observed (middle), calculated (upper), and difference (lower) profiles for the Rietveld refinement of K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub> · 3H<sub>2</sub>O.

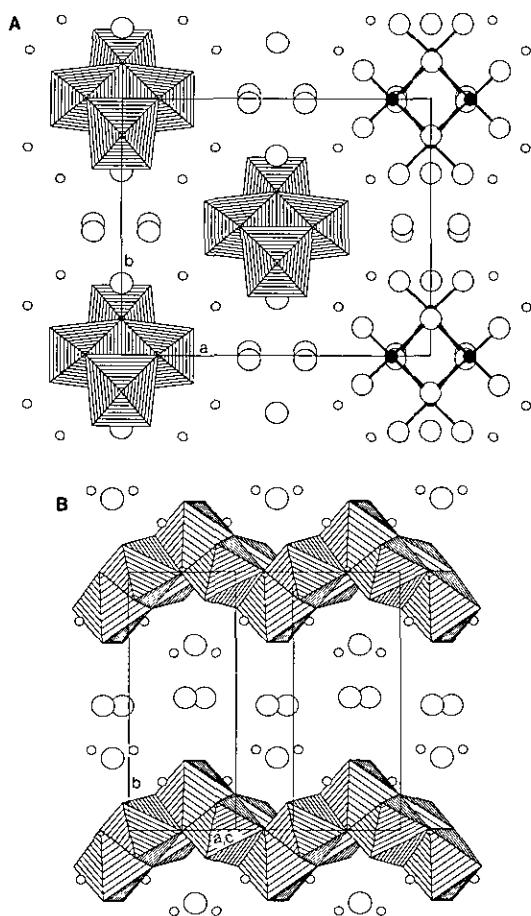


FIG. 2. The structure of  $K_2Mo_3O_{10} \cdot 3H_2O$ : (A) projection along the  $c$  axis (left part of figure in polyhedral representation); (B) linkage of the octahedra in  $Mo_3O_{10}^{4-}$  chains. The large, small, and black circles represent oxygen, potassium, and molybdenum atoms, respectively.

num atoms and 1.86–2.49 for the other. Distortions present in this structure are rather prominent but they are smaller than those in the cases of ammonium tetramolybdate (9) for which the structures were determined by the single crystal method. As in most structures built up from  $MoO_6$  octahedra there are two short, two intermediate, and two long Mo–O distances. The shortest Mo–O distances are observed for the terminal bonds; these bonds are in *cis* position. It is interesting that the infinite Mo–O chain obeys the general rules formulated by Porai-Koshits for nonpolymeric structures built up from  $MeO_6$  octahedra (10). Adjacent chains have no common oxygen atoms and are held together by potassium ions and water molecules. The potassium ions occupy interchain positions in irregular eightfold coordination with K–O distances varying from 2.54 to 3.45 Å. The same type of molybdenum–oxygen chains were found in hydrated trimolybdates of rubidium, ammonium, and silver (11, 12, 2). The crystal structure of anhydrous  $K_2Mo_3O_{10}$ , pro-

duced by fusion of  $K_2CO_3$  and  $MoO_3$ , is also known (4). The  $K_2Mo_3O_{10}$  crystallizes in space group  $C2/c$  that is the nonisomorphic subgroup of  $Cmcm$  (space group of hydrated salt). In both structures exist molybdenum–oxygen infinite zigzag chains lying parallel to the needle axis; the Mo–O polyhedra and their arrangement are different in each structure, though. The structure of anhydrous salt contains distorted  $MoO_6$  octahedra and  $MoO_5$  square pyramids (trigonal bipyramids). The square pyramids occur in double  $Mo_2O_8$  units, in which the pyramids are joined by an edge with apices directed oppositely to one another. In the chain each octahedron is surrounded by two pyramidal units. Comparing structures of both potassium trimolybdates it should be stated that the hydrated compound crystallizes in the space group of higher symmetry and possesses different types of Mo–O chain built up of only one type of coordination polyhedra.

## CONCLUSIONS

The crystal structure of fibrillar potassium trimolybdate was solved by the powder diffraction method. It is significant to note that applied methods allow one to solve moderately complicated structures (about 10 atoms) in a default mode.

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