

# CRYSTALLINE STRUCTURE OF IRON MOLYBDATE

L. M. Plyasova, R. F. Klevtsova, S. V. Borisov, L. M. Kefeli

1966

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196601.83406>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

## Abstract

## Full Text

UDC 549.76

## CRYSTALLOGRAPHY

L. M. PLYASOVA, R. F. KLEVTSOVA, S. V. BORISOV, L. M. KEFELI

# CRYSTALLINE STRUCTURE OF IRON MOLYBDATE

(Presented by Academician N. V. Belov, 20 XI 1965)

The compound  $\text{Fe}_2(\text{MoO}_4)_3$  is the active component of oxide iron-molybdenum catalysts <sup>(1)</sup>. Among the molybdates and tungstates of divalent and trivalent metals described in the literature one may encounter compounds of analogous composition but with strongly differing structure and, conversely, a difference in composition is not necessarily accompanied by dissimilarity of structure. Thus, compounds with a large cation  $R\text{—}R\text{MeO}_4$  ( $R = \text{Ca, Ba, Pb, Me} = \text{Mo, W}$ ) and  $R_2(\text{MeO}_4)_3$  ( $R = \text{Bi, La, Ce, Eu}$ )—have a scheelite-type structure; in the latter case the two cations are distributed statistically over three positions <sup>(2–7)</sup>. Structures are also known for tungstates with a small cation  $R = \text{Mg, Mn, Co, Fe, Ni}$  (structural type  $\text{MgWO}_4$  <sup>(2)</sup>). It has recently been shown that the molybdates of these metals are no longer isostructural with the analogous tungstates <sup>(8)</sup>. The structures

**Table 1**

Coordinates of the basis atoms in the structure of iron molybdate

|            | Mo <sub>1</sub> | Mo <sub>2</sub> | Mo <sub>3</sub> | Mo <sub>4</sub> | Mo <sub>5</sub> | Mo <sub>6</sub> | Fe <sub>1</sub> | Fe <sub>2</sub> | Fe <sub>3</sub> | Fe <sub>4</sub> |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $x/a$      | 0,997           | 0,351           | 0,150           | 0,008           | 0,142           | 0,362           | 0,374           | 0,392           | 0,115           | 0,126           |
| $y/b$      | 0,249           | 0,116           | 0,130           | 0,749           | 0,625           | 0,613           | 0,963           | 0,477           | 0,473           | 0,962           |
| $z/c$      | 0,502           | 0,128           | 0,275           | 0,030           | 0,376           | 0,227           | 0,307           | 0,065           | 0,188           | 0,449           |
| $B$        | 0,214           | 0,147           | 0,506           | 0,427           | 0,432           | 0,205           | 0,124           | 0,513           | 0,314           | 0,572           |
| $\sigma_x$ | 0,002           | 0,001           | 0,001           | 0,001           | 0,001           | 0,001           | 0,002           | 0,002           | 0,002           | 0,002           |
| $\sigma_y$ | 0,005           | 0,003           | 0,002           | 0,005           | 0,003           | 0,003           | 0,005           | 0,004           | 0,005           | 0,004           |
| $\sigma_z$ | 0,002           | 0,001           | 0,001           | 0,001           | 0,001           | 0,001           | 0,002           | 0,002           | 0,002           | 0,002           |
| $\sigma_B$ | 0,161           | 0,183           | 0,186           | 0,200           | 0,199           | 0,183           | 0,311           | 0,330           | 0,325           | 0,332           |

  

|       | O <sub>1</sub> | O <sub>2</sub> | O <sub>3</sub> | O <sub>4</sub> | O <sub>5</sub> | O <sub>6</sub> | O <sub>7</sub> | O <sub>8</sub> | O <sub>9</sub> | O <sub>10</sub> | O <sub>11</sub> | O <sub>12</sub> |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|
| $x/a$ | 0,078          | 0,047          | 0,184          | 0,173          | 0,260          | 0,020          | 0,342*0,330    | 0,413          | 0,403          | 0,476           | 0,261           |                 |
| $y/b$ | 0,377          | 0,632          | 0,292          | 0,545          | 0,480          | 0,077          | 0,616          | 0,316          | 0,617          | 0,322           | 0,099           | 0,025           |

Fig. 1. Structure of  $\text{Fe}_2(\text{MoO}_4)_3$  in projection onto the  $xz$  plane

Figure 1: Fig. 1. Structure of  $\text{Fe}_2(\text{MoO}_4)_3$  in projection onto the  $xz$  plane

|            | O <sub>1</sub> | O <sub>2</sub> | O <sub>3</sub> | O <sub>4</sub> | O <sub>5</sub> | O <sub>6</sub> | O <sub>7</sub> | O <sub>8</sub> | O <sub>9</sub> | O <sub>10</sub> | O <sub>11</sub> | O <sub>12</sub> |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|
| $z/c$      | 0,071          | 0,121          | 0,252          | 0,314          | 0,217          | 0,167          | 0,125*         | 0,081          | 0,018          | 0,947           | 0,145           | 0,044           |
| $B$        | 0,500          | 0,500          | 0,500          | 0,500          | 0,500          | 0,500          | 0,500          | 0,500          | 0,500          | 0,500           | 0,500           | 0,500           |
| $\sigma_x$ | 0,007          | 0,007          | 0,007          | 0,008          | 0,007          | 0,007          | —              | 0,007          | 0,007          | 0,007           | 0,007           | 0,007           |
| $\sigma_y$ | 0,016          | 0,016          | 0,015          | 0,016          | 0,014          | 0,016          | 0,015          | 0,016          | 0,016          | 0,016           | 0,015           | 0,015           |
| $\sigma_z$ | 0,008          | 0,008          | 0,008          | 0,008          | 0,008          | 0,008          | —              | 0,008          | 0,008          | 0,008           | 0,008           | 0,008           |

  

|            | O <sub>13</sub> | O <sub>14</sub> | O <sub>15</sub> | O <sub>16</sub> | O <sub>17</sub> | O <sub>18</sub> | O <sub>19</sub> | O <sub>20</sub> | O <sub>21</sub> | O <sub>22</sub> | O <sub>23</sub> | O <sub>24</sub> |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $x/a$      | 0,409*          | 0,429           | 0,346           | 0,371*          | 0,255           | 0,476*          | 0,108*          | 0,157           | 0,083*          | 0,112*          | 0,027           | 0,228           |
| $y/b$      | 0,811*          | 0,200*          | 0,801           | 0,066*          | 0,043           | 0,555           | 0,119           | 0,802           | 0,133           | 0,837           | 0,566           | 0,517           |
| $z/c$      | 0,401*          | 0,380*          | 0,237*          | 0,220           | 0,298           | 0,355*          | 0,335           | 0,404*          | 0,491*          | 0,533*          | 0,376           | 0,483*          |
| $B$        | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           | 0,500           |
| $\sigma_x$ | —               | 0,007           | 0,007           | —               | 0,007           | —               | —               | 0,007           | —               | —               | 0,007           | 0,006           |
| $\sigma_y$ | —               | —               | 0,015           | —               | 0,016           | 0,015           | 0,016           | 0,015           | 0,016           | 0,015           | 0,016           | 0,016           |
| $\sigma_z$ | —               | —               | —               | 0,008           | 0,008           | —               | 0,008           | —               | —               | —               | 0,008           | —               |

\* Unrefined coordinates.

compounds  $R_2(\text{MeO}_4)_3$  with a small cation  $R$ , to which iron molybdate also belongs, have not been described in the literature.

Single crystals of  $\text{Fe}_2(\text{MoO}_4)_3$ , synthesized under hydrothermal conditions, were kindly provided by P. V. Klevtsov<sup>(12)</sup>. Earlier<sup>(9)</sup> we established that iron molybdate has a monoclinic elementary cell with parameters  $a = 15.5$ ;  $b = 9.2$ ;  $c = 18.1$  Å,  $\beta = 125^\circ$ , in which 8 molecules of  $\text{Fe}_2(\text{MoO}_4)_3$  are accommodated. The space group was determined unambiguously as  $C_{2h}^5 - P2_1/a$ . The experimental material for the present study was obtained with Mo radiation: 11 Weissenberg layer photographs about the  $b$  axis ( $h0l$ )—( $h.10.l$ ) and 3 about the  $c$  axis ( $hk0$ ), ( $hk2$ ), ( $hk4$ ). The intensities of the reflections were estimated visually from blackening standards with a step of  $\sqrt[4]{2}$ , corrected for the Lorentz and angular factors, and brought to a single scale. From 2470 values of  $F_{hkl}^2$  with  $\sin \theta/\lambda < 0.8$ , a three-dimensional Patterson function was calculated on a large computer (program by F. A. Brusentsev).

**Fig. 1.** Structure of  $\text{Fe}_2(\text{MoO}_4)_3$  in projection onto the  $xz$  plane

A careful analysis of this function, taking into account the relationships in the arrangement of interaction peaks characteristic of this space group<sup>(11)</sup>, led to the unambiguous determination of the coordinates of all 10 heavy atoms (6Mo and 4Fe). After their preliminary refinement by the least-squares method<sup>(10)</sup>

Fig. 2

Figure 2: Fig. 2

for the zone of reflections  $F_{h0l}$  (227 amplitudes), the discrepancy coefficient  $R_{h0l}$  decreased from 64 to 47.9%, and, with the addition of 238 amplitudes  $F_{hk2}$ , to 34.1%.

The position of the heavy atoms in the structure suggested the further course: each Mo atom had as its nearest neighbors 4 iron atoms, and each Fe atom had 6 Mo atoms located, to a first approximation, at the vertices of an octahedron. Thus, tetrahedral coordination for the former and octahedral coordination for the latter can be obtained if the oxygen atoms are placed on the straight lines connecting neighboring Fe and Mo atoms. The initial variant of the light atoms reduced  $R_{h0l}$  somewhat (to 46.8%), with subsequent refinement by least squares to 41.2%. Inclusion in the refinement of 238 reflections  $F_{hk2}$  lowered  $R$  to 28.5%.

The process of mathematical refinement of the structural model was duplicated by constructing Fourier syntheses of projections of the electron density  $\sigma(xz)$  and  $\sigma_{\text{theor}}(xz)$ , as well as by a geometrical analysis based on crystal-chemical considerations. A somewhat modified variant of the coordinates obtained as a result of this analysis led to stable refinement of the positions of most of the oxygen atoms. At the final stage the refinement was carried out over 600 reflections of the types  $F_{h0l}$ ,  $F_{hk0}$ , and  $F_{hk2}$ . Table 1 gives

final atomic coordinates and isotropic temperature parameters  $B$ ;  $R = 20\%$ .

A strong pseudoperiodicity of the structure ( $c' = c/2$ ) (9) proved to be an obstacle to further refinement of the light atoms. It facilitated the first stage—the finding of the structure model, reducing the number of coordinate parameters to be determined—but noticeably lowered the effectiveness of the least-squares method in the refinement. The predominance of reflections with  $l = 2n$  leads to the fact that the  $z$ -coordinates of the atoms, especially the light ones, require further refinement using an expanded set of amplitudes.

**Fig. 2.** Shaded Fe octahedra—the first layer of the fragment outlined by a dashed line in Fig. 1

The structure of  $\text{Fe}_2(\text{MoO}_4)_3$  is built of Fe octahedra and Mo tetrahedra joined by vertices (Fig. 1). All oxygen atoms have two nearest neighbors: 1 Fe and 1 Mo, and thus the rule of electrostatic valences is exactly satisfied:  $(3/6)\text{Fe} + (6/4)\text{Mo} = 2$ . It also follows from this that each Fe octahedron is connected by vertices with 6 Mo tetrahedra, and each Mo tetrahedron with 4 Fe octahedra. In Fig. 2 an increment of the structure is shown—two layers of octahedra and two layers of tetrahedra connecting them—in the direction perpendicular to the  $c$  axis. Apparently, the highly charged cations  $\text{Fe}^{3+}$  and  $\text{Mo}^{6+}$  play the principal role in the construction of the structure, determining the low packing density of  $\text{O}^{2-}$  ions ( $22 \text{ \AA}^3$  per 1 oxygen atom) and the large Fe—O—Mo angles.

The Fe—O—Mo angles and the corresponding Fe—Mo distances (in angstroms):  
 $\angle \text{Fe}_1\text{O}_4\text{Mo}_1$   $156^\circ$  (3.40);  $\angle \text{Fe}_1\text{O}_{11}\text{Mo}_5$   $180^\circ$  (3.70);  $\angle \text{Fe}_1\text{O}_{13}\text{Mo}_1$   $150^\circ$  (3.40);  
 $\angle \text{Fe}_1\text{O}_{14}\text{Mo}_1$   $167^\circ$  (3.70);  $\angle \text{Fe}_1\text{O}_{15}\text{Mo}_6$   $180^\circ$  (3.60);  $\angle \text{Fe}_1\text{O}_{17}\text{Mo}_3$   $175^\circ$  (3.35);  
 $\angle \text{Fe}_3\text{O}_1\text{Mo}_4$   $134^\circ$  (3.32);  $\angle \text{Fe}_3\text{O}_2\text{Mo}_4$   $135^\circ$  (3.45);  $\angle \text{Fe}_3\text{O}_3\text{Mo}_3$   $134^\circ$  (3.35);  
 $\angle \text{Fe}_3\text{O}_4\text{Mo}_5$   $151^\circ$  (3.50);  $\angle \text{Fe}_3\text{O}_5\text{Mo}_6$   $150^\circ$  (3.65);  $\angle \text{Fe}_4\text{O}_{18}\text{Mo}_6$   $145^\circ$  (3.60);  
 $\angle \text{Fe}_4\text{O}_{19}\text{Mo}_6$   $135^\circ$  (3.60);  $\angle \text{Fe}_4\text{O}_{20}\text{Mo}_5$   $156^\circ$  (3.50);  $\angle \text{Fe}_4\text{O}_{21}\text{Mo}_1$   $175^\circ$  (3.60);  
 $\angle \text{Fe}_4\text{O}_{22}\text{Mo}_1$   $165^\circ$  (3.55);  $\angle \text{Fe}_4\text{O}_{24}\text{Mo}_5$   $137^\circ$  (3.30);  $\angle \text{Fe}_2\text{O}_6\text{Mo}_3$   $180^\circ$  (3.60);  
 $\angle \text{Fe}_2\text{O}_7\text{Mo}_6$   $153^\circ$  (3.62);  $\angle \text{Fe}_2\text{O}_8\text{Mo}_2$   $140^\circ$  (3.60);  $\angle \text{Fe}_2\text{O}_9\text{Mo}_4$   $145^\circ$  (3.40);  
 $\angle \text{Fe}_2\text{O}_{10}\text{Mo}_4$   $128^\circ$  (3.30);  $\angle \text{Fe}_2\text{O}_{12}\text{Mo}_2$   $180^\circ$  (3.70).

The principal interatomic distances in the coordination polyhedra have the following values (in angstroms):

Mo<sub>1</sub>-tetrahedron. Mo<sub>1</sub>—O<sub>13</sub> 1.64, Mo<sub>1</sub>—O<sub>14</sub> 1.85, Mo<sub>1</sub>—O<sub>21</sub> 1.79, Mo<sub>1</sub>—O<sub>22</sub> 1.68; O—O 2.51–3.19.

Mo<sub>2</sub>-tetrahedron. Mo<sub>2</sub>—O<sub>8</sub> 1.95, Mo<sub>2</sub>—O<sub>11</sub> 1.75, Mo<sub>2</sub>—O<sub>12</sub> 1.63, Mo<sub>2</sub>—O<sub>16</sub> 1.62; O—O 2.65–3.05.

Mo<sub>3</sub>-tetrahedron. Mo<sub>3</sub>—O<sub>3</sub> 1.70, Mo<sub>3</sub>—O<sub>6</sub> 1.75, Mo<sub>3</sub>—O<sub>17</sub> 1.61, Mo<sub>3</sub>—O<sub>19</sub> 1.62; O—O 2.52–2.91.

Mo<sub>4</sub>-tetrahedron. Mo<sub>4</sub>—O<sub>1</sub> 1.95, Mo<sub>4</sub>—O<sub>2</sub> 1.90, Mo<sub>4</sub>—O<sub>9</sub> 1.61, Mo<sub>4</sub>—O<sub>10</sub> 1.87; O—O 2.75–2.95.

Mo<sub>5</sub>-tetrahedron. Mo<sub>5</sub>—O<sub>4</sub> 1.61, Mo<sub>5</sub>—O<sub>20</sub> 1.67, Mo<sub>5</sub>—O<sub>23</sub> 1.72, Mo<sub>5</sub>—O<sub>24</sub> 1.87; O—O 2.56–2.89.

Mo<sub>6</sub>-tetrahedron. Mo<sub>6</sub>—O<sub>5</sub> 1.87, Mo<sub>6</sub>—O<sub>15</sub> 1.75, Mo<sub>6</sub>—O<sub>18</sub> 1.85, Mo<sub>6</sub>—O<sub>19</sub> 1.75; O—O 2.62–3.05.

Fe<sub>1</sub>-octahedron. Fe<sub>1</sub>—O<sub>13</sub> 1.95, Fe<sub>1</sub>—O<sub>14</sub> 2.30, Fe<sub>1</sub>—O<sub>15</sub> 1.80, Fe<sub>1</sub>—O<sub>16</sub> 1.89, Fe<sub>1</sub>—O<sub>17</sub> 1.77, Fe<sub>1</sub>—O<sub>23</sub> 2.00; O—O 2.55–3.45.

Fe<sub>2</sub>-octahedron. Fe<sub>2</sub>—O<sub>6</sub> 1.80, Fe<sub>3</sub>—O<sub>8</sub> 1.95, Fe<sub>2</sub>—O<sub>9</sub> 1.75, Fe<sub>2</sub>—O<sub>10</sub> 2.10, Fe<sub>2</sub>—O<sub>12</sub> 2.12, Fe<sub>2</sub>—O<sub>19</sub> 2.01; O—O 2.62–3.05.

Fe<sub>3</sub>-octahedron. Fe<sub>3</sub>—O<sub>1</sub> 2.02, Fe<sub>3</sub>—O<sub>2</sub> 1.80, Fe<sub>3</sub>—O<sub>3</sub> 1.91, Fe<sub>3</sub>—O<sub>4</sub> 2.05, Fe<sub>3</sub>—O<sub>5</sub> 1.85, Fe<sub>3</sub>—O<sub>11</sub> 1.85; O—O 2.50–3.10.

Fe<sub>4</sub>-octahedron. Fe<sub>4</sub>—O<sub>18</sub> 2.10, Fe<sub>4</sub>—O<sub>19</sub> 2.25, Fe<sub>4</sub>—O<sub>20</sub> 1.85; Fe<sub>4</sub>—O<sub>21</sub> 1.90, Fe<sub>4</sub>—O<sub>22</sub> 2.10, Fe<sub>4</sub>—O<sub>24</sub> 1.95; O—O 2.65–3.15.

The accuracy of the determination of the distances is insufficient for conclusions about the character of the chemical bond in this compound, but the general features of the structure indicate that it is covalent to a significant degree.

Institute of Catalysis  
 Siberian Branch of the Academy of Sciences of the USSR

Institute of Inorganic Chemistry  
 Siberian Branch of the Academy of Sciences of the USSR

Received  
1 XI 1965

## REFERENCES

1. G. K. Boreskov, G. D. Kolovertov et al., *Methods for the Study of Catalysts and Catalytic Reactions*, 2, Novosibirsk, 1965, p. 428.
2. E. K. Broch, *Strukturber.*, 2, 1937, S. 451.
3. J. B. Nelson, M. Kee, *Nature*, 157, 753 (1946).
4. D. H. Templeton, A. Zalkin, *Acta crystallogr.*, 16, 762 (1963).
5. K. M. Mextie, E. R. C. T. A. Milodov et al., *DAN*, 162, No. 3, 563 (1965).
6. L. Sillen, A. Nylander, *Ark. Kemi Min. Geol.*, A, 17, No. 1 (1943).
7. R. W. G. Wyckoff, *Crystal Structures*, 8, N. Y., 1951, p. 91.
8. G. W. Smith, *Acta crystallogr.*, 15, 1054 (1962).
9. P. V. Klevtsov, R. F. Klevtsova et al., *Izv. AN SSSR, Neorganich. mater.*, 1, 66, 918 (1965).
10. F. A. Brusentsev, *Crystallography*, 8, 10 (1963).
11. S. V. Borisov, *Crystallography*, 9, 5, 603 (1964).
12. P. V. Klevtsov, *Crystallography*, 3, 445 (1965).

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

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*