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CRYSTALLINE STRUCTURE OF IRON MOLYBDATE

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The compound $Fe_2(MoO_4)_3$ is the active component of oxide iron-molybdenum catalysts (^{1}). 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—$R\mathrm{MeO}_4$ ($R = \mathrm{Ca, Ba, Pb, Me} = \mathrm{Mo, W}$) and $R_2(\mathrm{MeO}_4)_3$ ($R = \mathrm{Bi, La, Ce, Eu}$)—have a scheelite-type structure; in the latter case the two cations are distributed statistically over three positions ($^{2-7}$). Structures are also known for tungstates with a small cation $R = \mathrm{Mg, Mn, Co, Fe, Ni}$ (structural type $MgWO_4$ (^{2})). It has recently been shown that the molybdates of these metals are no longer isostructural with the analogous tungstates (^{8}). The structures

Table 1

Coordinates of the basis atoms in the structure of iron molybdate

	Mo_1	Mo_2	Mo_3	Mo_4	Mo_5	Mo_6	Fe_1	Fe_2	Fe_3	Fe_4
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
σ_x	0,002	0,001	0,001	0,001	0,001	0,001	0,002	0,002	0,002	0,002
σ_y	0,005	0,003	0,002	0,005	0,003	0,003	0,005	0,004	0,005	0,004
σ_z	0,002	0,001	0,001	0,001	0,001	0,001	0,002	0,002	0,002	0,002
σ_B	0,161	0,183	0,186	0,200	0,199	0,183	0,311	0,330	0,325	0,332

	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	O_{11}	O_{12}
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 $Fe_2(MoO_4)_3$ in projection onto the xz plane

Figure 1: Fig. 1. Structure of $Fe_2(MoO_4)_3$ in projection onto the xz plane

	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	O_{11}	O_{12}
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
σ_x	0,007	0,007	0,007	0,008	0,007	0,007	–	0,007	0,007	0,007	0,007	0,007
σ_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
σ_z	0,008	0,008	0,008	0,008	0,008	0,008	–	0,008	0,008	0,008	0,008	0,008

	O_{13}	O_{14}	O_{15}	O_{16}	O_{17}	O_{18}	O_{19}	O_{20}	O_{21}	O_{22}	O_{23}	O_{24}
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
σ_x	–	0,007	0,007	–	0,007	–	–	0,007	–	–	0,007	0,006
σ_y	–	–	0,015	–	0,016	0,015	0,016	0,015	0,016	0,015	0,016	0,016
σ_z	–	–	–	0,008	0,008	–	0,008	–	–	–	0,008	–

* Unrefined coordinates.

compounds $R_2(MeO_4)_3$ with a small cation R, to which iron molybdate also belongs, have not been described in the literature.

Single crystals of $Fe_2(MoO_4)_3$, synthesized under hydrothermal conditions, were kindly provided by P. V. Klevtsov (^{12}). Earlier (^{9}) we established that iron molybdate has a monoclinic elementary cell with parameters $a = 15.5$; $b = 9.2$; $c = 18.1$ Å, $\beta = 125°$, in which 8 molecules of $Fe_2(MoO_4)_3$ are accommodated. The space group was determined unambiguously as C_{2h}^5—$P\,2_1/a$. 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 $Fe_2(MoO_4)_3$ 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 (^{11}), 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 (^{10})

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 $Fe_2(MoO_4)_3$ 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 Fe^{3+} and Mo^{6+} play the principal role in the construction of the structure, determining the low packing density of O^{2-} ions (22 Å^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): $\angle Fe_1O_4Mo_1$ 156° (3.40); $\angle Fe_1O_{11}Mo_5$ 180° (3.70); $\angle Fe_1O_{13}Mo_1$ 150° (3.40); $\angle Fe_1O_{14}Mo_1$ 167° (3.70); $\angle Fe_1O_{15}Mo_6$ 180° (3.60); $\angle Fe_1O_{17}Mo_3$ 175° (3.35); $\angle Fe_3O_1Mo_4$ 134° (3.32); $\angle Fe_3O_2Mo_4$ 135° (3.45); $\angle Fe_3O_3Mo_3$ 134° (3.35); $\angle Fe_3O_4Mo_5$ 151° (3.50); $\angle Fe_3O_5Mo_6$ 150° (3.65); $\angle Fe_4O_{18}Mo_6$ 145° (3.60); $\angle Fe_4O_{19}Mo_6$ 135° (3.60); $\angle Fe_4O_{20}Mo_5$ 156° (3.50); $\angle Fe_4O_{21}Mo_1$ 175° (3.60); $\angle Fe_4O_{22}Mo_1$ 165° (3.55); $\angle Fe_4O_{24}Mo_5$ 137° (3.30); $\angle Fe_2O_6Mo_3$ 180° (3.60); $\angle Fe_2O_7Mo_6$ 153° (3.62); $\angle Fe_2O_8Mo_2$ 140° (3.60); $\angle Fe_2O_9Mo_4$ 145° (3.40); $\angle Fe_2O_{10}Mo_4$ 128° (3.30); $\angle Fe_2O_{12}Mo_2$ 180° (3.70).

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

Mo_1-tetrahedron. Mo_1—O_{13} 1.64, Mo_1—O_{14} 1.85, Mo_1—O_{21} 1.79, Mo_1—O_{22} 1.68; O—O 2.51-3.19.

Mo_2-tetrahedron. Mo_2—O_8 1.95, Mo_2—O_{11} 1.75, Mo_2—O_{12} 1.63, Mo_2—O_{16} 1.62; O—O 2.65-3.05.

Mo_3-tetrahedron. Mo_3—O_3 1.70, Mo_3—O_6 1.75, Mo_3—O_{17} 1.61, Mo_3—O_{19} 1.62; O—O 2.52-2.91.

Mo_4-tetrahedron. Mo_4—O_1 1.95, Mo_4—O_2 1.90, Mo_4—O_9 1.61, Mo_4—O_{10} 1.87; O—O 2.75-2.95.

Mo_5-tetrahedron. Mo_5—O_4 1.61, Mo_5—O_{20} 1.67, Mo_5—O_{23} 1.72, Mo_5—O_{24} 1.87; O—O 2.56-2.89.

Mo_6-tetrahedron. Mo_6—O_5 1.87, Mo_6—O_{15} 1.75, Mo_6—O_{18} 1.85, Mo_6—O_{19} 1.75; O—O 2.62-3.05.

Fe_1-octahedron. Fe_1—O_{13} 1.95, Fe_1—O_{14} 2.30, Fe_1—O_{15} 1.80, Fe_1—O_{16} 1.89, Fe_1—O_{17} 1.77, Fe_1—O_{23} 2.00; O—O 2.55-3.45.

Fe_2-octahedron. Fe_2—O_6 1.80, Fe_3—O_8 1.95, Fe_2—O_9 1.75, Fe_2—O_{10} 2.10, Fe_2—O_{12} 2.12, Fe_2—O_{19} 2.01; O—O 2.62-3.05.

Fe_3-octahedron. Fe_3—O_1 2.02, Fe_3—O_2 1.80, Fe_3—O_3 1.91, Fe_3—O_4 2.05, Fe_3—O_5 1.85, Fe_3—O_{11} 1.85; O—O 2.50-3.10.

Fe_4-octahedron. Fe_4—O_{18} 2.10, Fe_4—O_{19} 2.25, Fe_4—O_{20} 1.85; Fe_4—O_{21} 1.90, Fe_4—O_{22} 2.10, Fe_4—O_{24} 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.

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