Synthesis and Crystal Structure of $K_6Mo_{10}O_{33}$

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A new potassium molybdenum oxide, $K_6Mo_{10}O_{33}$, was synthesized by solid state reaction from the appropriate quantities of pre-dried MoO_3 and K_2MoO_4, fired at around 650 °C for 2 d. The structure has been solved by using single crystal X-ray diffraction. The compound adopts the space group $P1$, with the lattice constants $a = 7.7100(5)$, $b = 11.9659(8)$, $c = 17.1321(12)$ Å, $\alpha = 86.42$ (10), $\beta = 77.18(10)$, $\gamma = 74.14(10)°$. The structure is built up of infinite chains of edge-sharing MoO_6 octahedra and groups of four MoO_6 octahedra forming Mo_4O_{17} units. These sub-units are connected together by common vertices.

Key words: Potassium, Molybdenum, Oxides, $K_6Mo_{10}O_{33}$, Structure Determination

Introduction

The family of alkali metal oxomolybdates is numerous and has been studied intensively. In most cases, the ratio of molybdenum to alkali metal is found to be less than one *e.g.* K_2MoO_4 [1, 2], Na_4MoO_5 [3] *etc.* Among the alkali metal oxomolybdates, only a few molybdenum rich compounds are known, namely, a three dimensional network of highly distorted edge-sharing MoO_6 octahedra in $Na_6Mo_{11}O_{36}$ [4], a molybdenum oxide cluster framework built from the condensation of three Mo_6O_{18} units in $K_3Mo_{14}O_{22}$ [5] and double strings of edge-sharing Mo_6 octahedra in KMo_4O_6 [6], a mixed valence compound in which the oxidation state of Mo is found to be +2 and +3. Other known molybdenum-rich alkali metal molybdates are $Na_2Mo_3O_6$ [7], $K_2Mo_7O_{20}$ [8] and $K_2Mo_8O_{16}$ [9]. The most common method of synthesizing such oxides involves the reaction between the molybdenum oxide and the hydroxide, nitrate, carbonate or the oxides of the corresponding alkali metals under the flow of argon or oxygen. Because of their interesting structural properties, preparation of new molybdenum rich compounds became an important task. Here we report the synthesis and structural characterization of a new potassium molybdate, $K_6Mo_{10}O_{33}$, which belongs to the category of molybdenum rich compounds. With respect to composition, the related phases of sodium and silver have been reported in the literature ($Ag_6Mo_{10}O_{33}$ [10] and $Na_6Mo_{10}O_{33}$ [11]).

Experimental Section

Synthesis

The new potassium molybdate, $K_6Mo_{10}O_{33}$, was prepared from MoO_3 (Merck 99.5 %) and K_2MoO_4 (Aldrich 99.5 %). A mixture containing stoichiometric amounts of the pre-dried reactants MoO_3 and K_2MoO_4 was thoroughly mixed, pressed to a pellet under 10^5 N, dried under vacuum (10^{-3} mbar) at 150 °C for 12 h, and placed under argon in a tightly closed steel container provided with a silver inlay. The reaction mixture was fired at 650 °C for 2 d and subsequently quenched to liquid nitrogen temperature.

Shiny needle-like crystals were discovered in the silver container. The shiny product was sealed and stored in glass ampoules under argon for further investigations. All the analyses have been performed in an atmosphere of dry argon.

X-Ray diffraction analyses

Powder diffraction analysis. The X-ray investigation on powder was performed on a STOE Stadi P diffractometer with Mo $K_{\alpha 1}$ radiation ($\lambda = 0.7103$ Å) at r. t. using a position sensitive detector and a curved germanium monochromator in Debye-Scherrer geometry. On comparing the measured X-ray pattern with the data base [12], no proper match was found.

Single crystal diffraction analysis. Single crystals of $K_6Mo_{10}O_{33}$ were selected in a glove box using a 0.1 mm glass capillary and were inserted into a 0.3 mm capillary which was then sealed under dry argon. Single crystal diffraction analysis was effected on a Bruker SMART-APEX CCD diffractometer. $K_6Mo_{10}O_{33}$ crystallizes in the triclinic

Table 1. Crystallographic data and structure refinement of $K_6Mo_{10}O_{33}$.

Empirical Formula	$K_6Mo_{10}O_{33}$
Crystal color and appearance	Black needles
Formula weight [g mol^{-1}]	3443.94
Crystal system	triclinic
Space group	$P1$ (No. 1)
a [Å]	7.7100(5)
b [Å]	11.9659(8)
c [Å]	17.1321(12)
α [deg]	86.42(10)
β [deg]	77.18(10)
γ [deg]	74.14(10)
Cell Volume [Å^3]	1482.46
Z	2
Density calc. [g · cm^{-3}]	3.8574
Absorption coefficient [mm^{-1}]	5.04
$F(000)$ [e]	1596
Temperature [K]	295
Diffractometer	Bruker SMART-APEX CCD
Monochromator	Graphite
λ (Mo K_α Radiation) [Å]	0.71073
$2\theta_{max}$	69.965
hkl range	$-12 \leq h \leq 12, -19 \leq k \leq 18, -26 \leq l \leq 27$
Reflections collected	22776
Independent reflections	20460
Method of the refinement	Full-matrix least-squares on F^2
Parameters refined	554
Flack Parameter	0.5092
R-Values	$R1 = 0.0676, wR2 = 0.1606$*

* Weight: $w = 1/(\sigma^2(F_0^2) + (0.0147 \times P)^2 + 76.19 \times P)$, where $P = (\max(F_0^2, 0) + 2 \times F_c^2)/3$.

crystal system. All reflections were indexed with the cell parameters $a = 7.7100(5)$, $b = 11.9659(8)$, $c = 17.1321(12)$ Å, $\alpha = 86.42(10)$, $\beta = 77.18(10)$, $\gamma = 74.14(10)°$. The structure was solved in the triclinic space groups $P1$ and $P\bar{1}$. However, after the complete refinement, the quality factors in the non-centrosymmetric space group ($R1 = 0.0681$, $wR2 = 0.1606$) were significantly lower than those in $P\bar{1}$ ($R1 = 0.0864$, $wR2 = 0.2217$). Selected X-ray crystallographic data of $K_6Mo_{10}O_{33}$, with the better solution in $P1$ are presented in Table 1. While all the atom parameters differ only slightly between both structure solutions, one significant structural change has been observed concerning the symmetrically created disorder of an oxygen atom, which will be explained in the discussion part.

Complete bond lengths and angles, co-ordinates and displacement parameters for $K_6Mo_{10}O_{33}$ have been deposited at Inorganic Crystal Structure Database. Supplementary data are available from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the registry number CSD-415961 (Filename – $K_6Mo_{10}O_{33}$ 293 K).

Thermal analysis

Thermogravimetric measurements were performed with a Netzsch STA 409, Selb, coupled with a quadrupole mass spectrometer. The container material for the thermal treatment (TGA and furnace) was of high purity Al_2O_3. The sample was heated at the rate of 10 °C min^{-1} in a corundum crucible under a flow of dry argon. It was observed that the sample decomposed at around 950 °C.

Results

Structure description and discussion

$K_6Mo_{10}O_{33}$ consists of sheets of MoO_6 octahedra in the crystallographic *ab* plane with K^+ ions connecting them. The sheets are built from infinite chains of edge-sharing octahedra (drawn with closed polyhedral faces) and groups of four octahedra (open polyhedra) as shown in Fig. 1.

The chains running parallel to [100] are formed by edge-sharing octahedra with a translational period of six different (and symmetry-independent) Mo centres. The MoO_6 octahedra are highly distorted. In all cases, the molybdenum atoms are displaced from their ideal positions in the centre of the octahedra, resulting in two short (Mo–O range from 1.647 to 1.802 Å), two medium (1.909 – 2.044 Å), and two long Mo–O distances (2.091 – 2.341 Å). Such coordinations are frequently observed in molybdenum oxides like, *e. g.,* MoO_3 [13], $K_2Mo_3O_{10}$ [14], $K_6Mo_7O_{24} \cdot 4 H_2O$ [15], or $Na_2Mo_2O_7$ [16].

The chains are linked in the second dimension by Mo_4O_{17} groups *via* common vertices. These units can
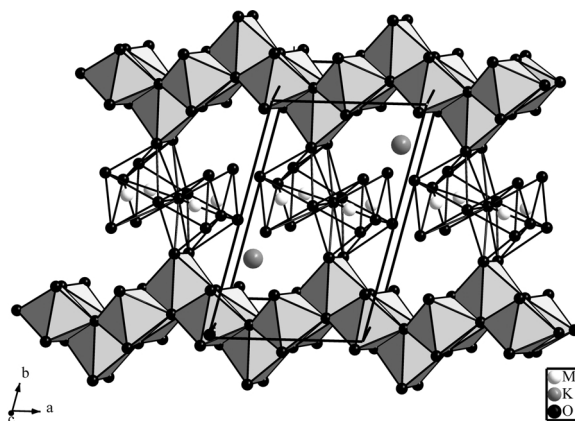

Fig. 1. Perspective view of the crystal structure of $K_6Mo_{10}O_{33}$ along [001]. Shown are infinite chains of edge-sharing octahedra (drawn with closed polyhedral faces) and groups of four octahedra (open polyhedra).

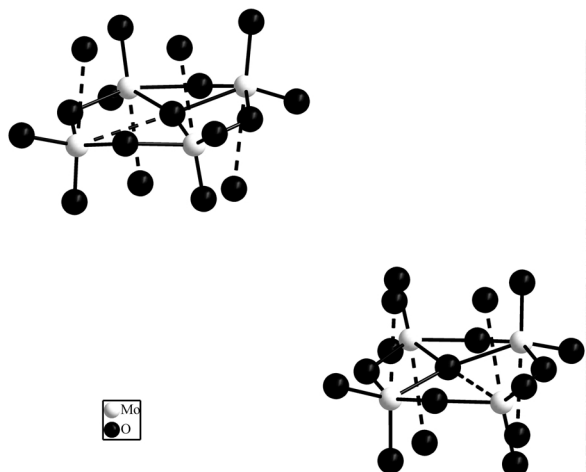Fig. 2. The two symmetrically independent Mo_4O_{17} groups of the structure solution in space group $P1$, dotted lines represent bonds longer than 2.64 Å.
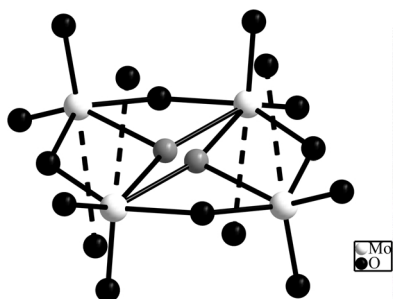

Fig. 3. Mo_4O_{17} group of the centrosymmetric structure solution (space group $P\bar{1}$). (Grey and black spheres: Oxygen atoms). Positions of grey oxygen atoms are half occupied; dotted lines represent bonds longer than 2.69 Å.

be described as four strongly distorted MoO_6 octahedra connected by common edges and altogether sharing one central oxygen atom as shown in Figs. 2 and 3. The molybdenum atoms are not forming a square, but a rhombus with angles of 78° and 102°. The dihedral angles are below 1°, resulting essentially in four coplanar molybdenum atoms.

Studying Fig. 1, one can expect to find an inversion centre in the crystal structure. As mentioned above, the main reason to exclude this symmetry element is a slight difference concerning the position of an oxygen atom. The relevant oxygen atom is placed in the middle of the Mo_4 rhomb, but is shifted away from the exact centre. The more remote molybdenum atom appears at the distances of 2.907 and 2.965 Å for both symmetrically independent individuals, respectively. In the centrosymmetric structure solution, the central oxygen
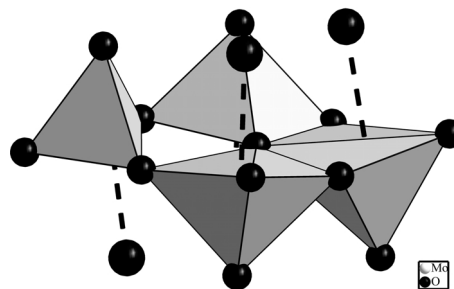

Fig. 4. Mo_4O_{17} groups in polyhedral representation in space group $P1$.

atom is created at two positions by the inversion centre (Fig. 3) with an occupation factor of 0.5 each, resulting in significantly higher R values after complete refinement and so this disorder seems to be an artifact of the symmetry element.

Another distortion is observed for the Mo coordination. Although the four molybdenum atoms of the Mo_4O_{17} groups are nearly in a common plane, they are displaced from the centre of the octahedra again. For each molybdenum atom, two short, two intermediate and two long Mo–O bonds were observed. But here, the larger distances are extremely long (bond lengths more than 2.645 Å are represented by dotted lines in Fig. 3). Due to the irregular and partially very large Mo–O distances in these Mo_4O_{17} units, the coordination polyhedra can be described as square pyramids and one tetrahedron instead of heavily distorted octahedra. In Fig. 4, the polyhedral representation of one Mo_4O_{17} unit is shown.

The potassium atoms shown in Fig. 1 are situated in the holes formed by the MoO_6 octahedra. The other potassium atom, in total eight of twelve over the whole unit cell, are spacing the sheets. These are coordinated by irregular polyhedra of oxygen atoms with K–O distances ranging continuously from 2.498 Å to higher values, such that no sharp gap between the first and the higher coordination spheres can be observed. If only K–O distances below 3.3 Å are taken into account, these coordination polyhedra around potassium atoms are built from 7 to 9 oxygen atoms each.

The crystal structure of $K_6Mo_{10}O_{33}$ shows significant similarities to the related phases reported earlier by Gatehouse *et al.* containing silver and sodium. The infinite chains are identical to those found in both related compounds, including the 2+2+2 MoO_6 coordination. Also the connection of these chains into

sheets of MoO_6 octahedra described here is found in the silver phase, $Ag_6Mo_{10}O_{33}$, with an identical connectivity pattern. Nevertheless, the stacking of the sheets is different which results in doubling of one crystallographic axis in the new compound described here.

Because of the disorder in the arrangement of oxygen atoms in the centrosymmetric space group ($P\bar{1}$), the structure has been solved in the non-centrosymmetric space group $P1$. Besides the close structural relationship of $Na_6Mo_{10}O_{33}$ and $Ag_6Mo_{10}O_{33}$, the synthetic conditions necessary to prepare the novel compound are close to those leading to $K_2Mo_3O_{10}$. Because of this, attempts to reproduce $K_6Mo_{10}O_{33}$ resulted in the neighboring phase, $K_2Mo_3O_{10}$.

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