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γ -Mo₄O₁₁

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Abstract

The space group of the title compound, tetramolybdenum undecaoxide, has been confirmed to be *Pna2*₁. Three out of the four Mo atoms are each coordinated by six O atoms to form MoO₆ octahedra. The remaining Mo atom is coordinated by four O atoms to form an MoO₄ tetrahedron. In the crystal, all the octahedra share their corner O atoms to form stacked quasi-two-dimensional layers which are connected by the tetrahedra.

Comment

The transport, structure and charge-density-wave (CDW) properties of γ -phase molybdenum oxide, *i.e.* γ -Mo₄O₁₁, have been extensively studied (Schlenker, 1989; Kihlborg, 1959; Koyano *et al.*, 1988; Inoue *et al.*, 1988; Gao *et al.*, 1995, 1996). However, this structure has been assigned different space groups, *Pnma* and *Pna2*₁, based on consideration of the packing and powder diffraction data, respectively (Wyckoff, 1967; JCPDS, card 5–337; Ghedira *et al.*, 1985; Magresi, 1948). To resolve this space-group ambiguity, a single-crystal structure determination was carried out.

The space group of γ -Mo₄O₁₁ has been confirmed to be *Pna2*₁. In the crystal, Mo atoms Mo1, Mo2 and Mo3 are each coordinated by six O atoms to form MoO₆ octahedra and the remaining Mo4 atoms are each coordinated by four O atoms to form MoO₄

tetrahedra. The coordination and the bond lengths are as shown in Fig. 1 and Table 1, respectively. The octahedra share their corners to form stacked quasi-two-dimensional layers which are interconnected by MoO₄ tetrahedra through mutual sharing of the O1, O4, O6 and O7 atoms. The minimum and maximum Mo—O bond lengths are 1.702(4) (Mo4—O6) and 2.117(4) Å (Mo3—O6), respectively, which are close to reported values (Orpen *et al.*, 1989). The axial O—Mo—O angles in the octahedra vary from 161.09(13) to 176.4(2)° for O11—Mo3—O4 and O3—Mo1—O5, respectively. Similarly, the bond angles in the tetrahedra range from 108.5(2) (O6—Mo4—O1 and O1—Mo4—O7) to 113.1(2)° (O4—Mo4—O7).

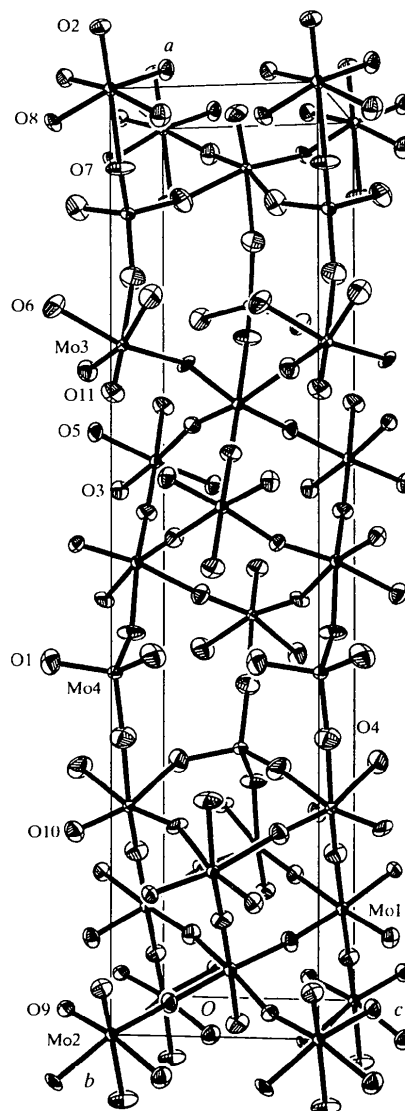


Fig. 1. The structure of the title compound showing 90% probability displacement ellipsoids. For clarity, some of the atoms are marked at symmetry-related positions. The origin of the coordinates is shifted to the Mo2 atom site.

Experimental

Crystals of the title compound was grown over a period of a week by a chemical-vapour-transport technique from a mixture of MoO₂:MoO₃ powders in a 1:3 ratio using a two-zone furnace. A quartz ampoule (about 15 cm long and 1.2 cm in diameter) packed with the powders and I₂ as a carrier gas (at 5 mg cm⁻³) was placed in the temperature region $T_L = 948$ and $T_H = 1008$ K. The crystals grown were plate-like, with surfaces parallel to *bc* planes (Koyano *et al.*, 1988; Inoue *et al.*, 1988).

Crystal data

Mo ₄ O ₁₁	Mo <i>K</i> α radiation
$M_r = 559.76$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 7459 reflections
$Pna2_1$	$a = 24.0723 (5) \text{ \AA}$
$a = 24.0723 (5) \text{ \AA}$	$b = 6.6483 (1) \text{ \AA}$
$b = 6.6483 (1) \text{ \AA}$	$c = 5.3569 (1) \text{ \AA}$
$c = 5.3569 (1) \text{ \AA}$	$V = 857.32 (3) \text{ \AA}^3$
$V = 857.32 (3) \text{ \AA}^3$	$Z = 4$
$Z = 4$	$D_x = 4.337 \text{ Mg m}^{-3}$
$D_x = 4.337 \text{ Mg m}^{-3}$	D_m not measured
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	2236 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.050$
Absorption correction: empirical using <i>SADABS</i> (Sheldrick, 1996)	$\theta_{\text{max}} = 29.99^\circ$
$T_{\text{min}} = 0.454$, $T_{\text{max}} = 0.891$	$h = 0 \rightarrow 33$
6465 measured reflections	$k = 0 \rightarrow 9$
2267 independent reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 3.995 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{\text{min}} = -2.633 \text{ e \AA}^{-3}$
$wR(F^2) = 0.093$	Extinction correction: <i>SHELXTL</i> (Siemens, 1996a)
$S = 1.293$	Extinction coefficient: 0.0303 (11)
2267 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
138 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.6933P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = -0.001$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Mo1—O3 ⁱ	1.837 (5)	Mo2—O7	2.066 (3)
Mo1—O3	1.847 (5)	Mo3—O10 ^v	1.725 (4)
Mo1—O2	1.888 (2)	Mo3—O8 ^v	1.731 (3)
Mo1—O5	1.951 (4)	Mo3—O11 ^{vi}	1.749 (3)
Mo1—O9	1.956 (4)	Mo3—O4	2.040 (3)
Mo1—O11	1.961 (3)	Mo3—O1 ^{vii}	2.081 (4)
Mo2—O5 ⁱⁱ	1.763 (4)	Mo3—O6	2.117 (4)
Mo2—O9 ⁱⁱⁱ	1.771 (4)	Mo4—O6 ^v	1.702 (4)
Mo2—O2	1.795 (2)	Mo4—O1 ^v	1.725 (4)
Mo2—O10	2.042 (4)	Mo4—O4	1.734 (3)
Mo2—O8	2.043 (3)	Mo4—O7	1.742 (3)

O3 ⁱ —Mo1—O3	93.57 (2)	O9 ⁱⁱⁱ —Mo2—O7	92.0 (2)
O3 ⁱ —Mo1—O2	94.7 (2)	O2—Mo2—O7	164.57 (12)
O3—Mo1—O2	95.3 (2)	O10—Mo2—O7	80.0 (2)
O3 ⁱ —Mo1—O5	176.4 (2)	O8—Mo2—O7	81.61 (13)
O3—Mo1—O5	88.7 (2)	O10 ^{iv} —Mo3—O8 ^v	101.4 (2)
O2—Mo1—O5	87.9 (2)	O10 ^{iv} —Mo3—O11 ^{vi}	100.0 (2)
O3 ⁱ —Mo1—O9	89.5 (2)	O8 ^v —Mo3—O11 ^{vi}	99.9 (2)
O3—Mo1—O9	175.5 (2)	O10 ^{iv} —Mo3—O4	93.0 (2)
O2—Mo1—O9	87.8 (2)	O8 ^v —Mo3—O4	90.9 (2)
O5—Mo1—O9	88.06 (14)	O11 ^{vi} —Mo3—O4	161.09 (13)
O3 ⁱ —Mo1—O11	88.0 (2)	O10 ^{iv} —Mo3—O1 ^{vii}	163.4 (2)
O3—Mo1—O11	87.2 (2)	O8 ^v —Mo3—O1 ^{vii}	87.3 (2)
O2—Mo1—O11	176.21 (11)	O11 ^{vi} —Mo3—O1 ^{vii}	86.6 (2)
O5—Mo1—O11	89.3 (2)	O4—Mo3—O1 ^{vii}	77.4 (2)
O9—Mo1—O11	89.5 (2)	O10 ^{iv} —Mo3—O6	87.3 (2)
O5 ⁱⁱ —Mo2—O9 ⁱⁱⁱ	97.53 (15)	O8 ^v —Mo3—O6	167.0 (2)
O5 ⁱⁱ —Mo2—O2	97.6 (2)	O11 ^{vi} —Mo3—O6	87.9 (2)
O9 ⁱⁱⁱ —Mo2—O2	98.7 (2)	O4—Mo3—O6	79.0 (2)
O5 ⁱⁱ —Mo2—O10	87.4 (2)	O1 ^{vii} —Mo3—O6	77.7 (2)
O9 ⁱⁱⁱ —Mo2—O10	170.8 (2)	O6 ^v —Mo4—O1 ^v	108.5 (2)
O2—Mo2—O10	88.3 (2)	O6 ^v —Mo4—O4	109.1 (2)
O5 ⁱⁱ —Mo2—O8	169.5 (2)	O1 ^v —Mo4—O4	108.6 (2)
O9 ⁱⁱⁱ —Mo2—O8	90.9 (2)	O6 ^v —Mo4—O7	109.0 (2)
O2—Mo2—O8	87.1 (2)	O1 ^v —Mo4—O7	108.5 (2)
O10—Mo2—O8	83.4 (2)	O4—Mo4—O7	113.1 (2)
O5 ⁱⁱ —Mo2—O7	91.9 (2)		

Symmetry codes: (i) $-x, -y, \frac{1}{2} + z$; (ii) $-x, 1 - y, \frac{1}{2} + z$; (iii) $-x, 1 - y, z - \frac{1}{2}$; (iv) $-\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (v) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (vii) $x, y, 1 + z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -35° . Coverage of the unique set was over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible. The largest peak in the difference map (3.995 e \AA^{-3}) is at (0.0569, 0.1633, 0.3951), 0.68 Å from the Mo1 atom, and the largest hole ($-2.633 \text{ e \AA}^{-3}$) is at $(-0.2972, 0.7066, -0.1049)$, 1.61 Å from the O6 atom. The structure can also be solved in space group *Pnma*. However, the refinement yielded high *R* values ($wR2 = 0.1776$ and $R1 = 0.0701$ for 1363 observed reflections) and large s.u.'s for bond lengths.

Data collection: *SMART* (Siemens, 1996b). Cell refinement: *SAINT* (Siemens, 1996c). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996a). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1071). Services for accessing these data are described at the back of the journal.

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RbMoO₂AsO₄

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Abstract

The title compound, rubidium molybdenyl arsenate, consists of AsO₄ tetrahedra and MoO₆ octahedra sharing corners to form a three-dimensional framework containing large tunnels, parallel to $[\bar{1}10]$, where the Rb⁺ ions are located. It is shown that in the series AMoO₂XO₄ (A = Na, K, Rb; X = P, As), the only isotypic compounds are KMoO₂PO₄ and RbMoO₂AsO₄ in which the ratio of atomic radii [$r(K)/r(P) = r(Rb)/r(As)$] remains constant.

Commentaire

Dans le but de trouver de nouveaux matériaux à charpente ouverte formée d'octaèdres et de tétraèdres,

nous poursuivons l'exploration du diagramme Rb–Mo–As–O dans lequel nous avons précédemment mis en évidence le composé en couches Rb₂MoO₂As₂O₇ (Zid *et al.*, 1998). Une nouvelle phase, RbMoO₂AsO₄, a été caractérisée dans ce diagramme. Elle est formée par une charpente anionique tridimensionnelle, MoO₂AsO₄, constituée d'octaèdres MoO₆ et des tétraèdres AsO₄ partageant des sommets. On peut la décomposer en chaînes (MoAsO₈)_n parallèles à la direction $[\bar{1}10]$, reliés entre elles par les ponts mixtes Mo—O—As. Elles délimitent des tunnels où logent les cations Rb⁺ (Fig. 1). Le caractère ouvert de cette structure est mis en évidence dans la projection selon $[\bar{1}10]$, où se manifestent des cycles à huit polyèdres constituant la section de larges canaux, communiquant selon la direction [001], par des fenêtres formées par des cycles à quatre polyèdres.

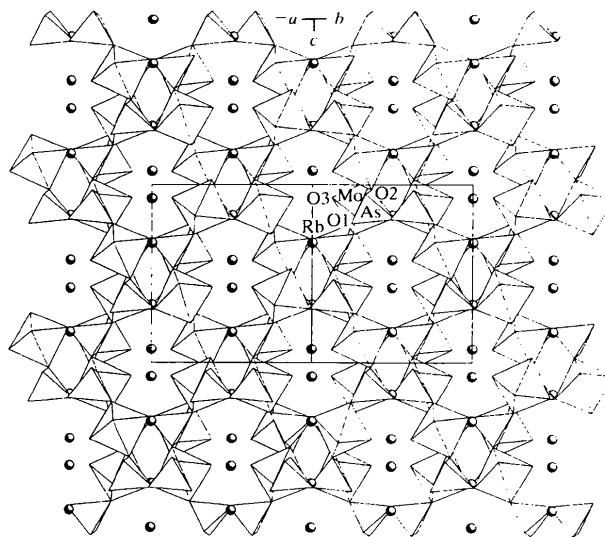


Fig. 1. Projection de la structure de RbMoO₂AsO₄ selon $[\bar{1}10]$.

Les distances As—O, Mo—O et Rb—O (Tableau 1) sont en bon accord avec le nombre et la nature des liaisons formés dans les polyèdres AsO₄, MoO₆ et RbO₈. Elles sont conformes à celles rencontrées dans d'autres molybdényl arsénates (Zid & Jouini, 1996a,b,c; Zid *et al.*, 1998). En effet, le calcul des forces de valence (Brown & Altermatt, 1985; Brese & O'Keefe, 1991) de ces liaisons confirment les valeurs de charges des ions As (+5,096), Mo (+5,023) et Rb (+1,028) attendues dans la structure.

L'examen de la série de composés de formulation analogue: NaMoO₂PO₄ (Kierkegaard, 1962), KMoO₂PO₄ (Peascoe & Clearfield, 1991), NaMoO₂-