Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

The cluster compound $PrMo_{7.6}O_{14}$

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Received 2 December 2002
Accepted 12 December 2002
Online 7 February 2003

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mo–O) = 0.001 Å
R factor = 0.041
wR factor = 0.093
Data-to-parameter ratio = 23.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Praseodymium molybdenum oxide, $PrMo_{7.6}O_{14}$, is isostructural with $LaMo_{7.7}O_{14}$ and $NdMo_{7.7}O_{14}$. Their crystal structures derive from the $NdMo_8O_{14}$ type, which contains *cis*-edge-sharing bi-face-capped octahedral Mo_8 clusters. Because of the non-stoichiometry on the capping Mo sites and the absence of satellite reflections, Mo_6, Mo_7 and Mo_8 clusters are believed to co-exist randomly.

Comment

The $RMo_{8-x}O_{14}$ (R = La, Ce, Pr, Nd, Sm; $x = 0$ or $x \simeq 0.3$) compounds containing bicapped Mo_8 clusters crystallize in four different crystalline forms, depending on the rare earth element and the synthetic method. The first crystalline form was observed with the compounds $LaMo_{7.7}O_{14}$ (Leligny *et al.*, 1990), $NdMo_8O_{14}$ (Gougeon & McCarley, 1991) and $SmMo_8O_{14}$ (Tortelier & Gougeon, 1997), obtained by fused-salt electrolysis (La compound) and by high-temperature solid-state reaction (Nd and Sm compounds), respectively. The crystal structures of the latter three compounds consist only of *cis*-edge-sharing bi-face-capped octahedral Mo_8 clusters. The other forms exist as well-ordered mixtures of *cis*-edge-sharing and *trans* bi-face-capped Mo_8 clusters. Thus, in the La and Ce compounds (Kerihuel & Gougeon, 1995*a*; Kerihuel *et al.*, 1996), obtained by high-temperature solid-state reaction, the two isomeric forms of the Mo_8 cluster are in equal proportion, while they are in the ratio 2:1 in $PrMo_8O_{14}$ (Kerihuel & Gougeon, 1995*b*). Finally, a modulated form was also discovered with the synthesis of the stoichiometric compound $LaMo_8O_{14}$ by fused-salt electrolysis (Leligny *et al.*, 1993). The crystal structure of the latter compound is more complex due to a one-dimensional commensurate modulation of wave vector $q^* = b^*/3$. The structure consists of *cis*-edge-sharing and *trans* bi-face-capped Mo_8 clusters with an average

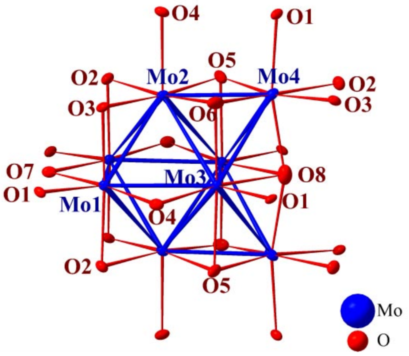

Figure 1
The *cis*-edge-sharing bi-face-capped Mo_8 cluster, with its O-atom environment. Displacement ellipsoids are drawn at the 97% probability level.

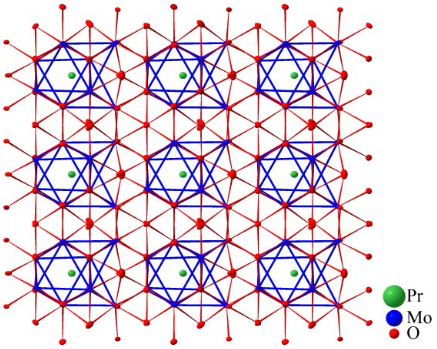

Figure 2
Projection of the $PrMo_{7.6}O_{14}$ structure on the *bc* plane.

probability distribution of approximately 65 and 35%, respectively. We present here the crystal structure of a new praseodymium reduced molybdenum oxide, $PrMo_{7.6}O_{14}$, that was synthesized by fused-salt electrolysis and exhibits, in contrast to the Pr phase prepared by solid-state reaction, a non-stoichiometry on the capping sites of the *cis*-edge-sharing bi-face-capped Mo_8 cluster, as previously observed with the compounds $LaMo_{7.7}O_{14}$ and $NdMo_{7.7}O_{14}$ (Barrier & Gougeon, 2001), also prepared by electrocrystallization. Because of the non-stoichiometry on the capping Mo sites and the absence of satellite reflections, Mo_6, Mo_7 and Mo_8 clusters are believed to co-exist randomly. A view of the *cis*-edge-sharing bi-face-capped Mo_8 cluster with its oxygen environment is shown in Fig. 1, and the projection of the crystal structure is shown in Fig. 2. The Mo—Mo distances within the Mo clusters range from 2.638 (1) to 2.814 (1) Å, while the shortest distance between clusters is 3.076 (1) Å. The Mo—O distances vary between 1.933 (6) and 2.124 (5) Å. All these Mo—Mo and Mo—O distances are in agreement with those reported previously for $LaMo_{7.7}O_{14}$ (Leligny *et al.*, 1990) and $NdMo_{7.7}O_{14}$ (Barrier & Gougeon, 2001). The Pr^{3+} ions are shifted away from the center of a distorted cubo-octahedron, with the seven nearest O atoms at distances ranging from 2.405 (8) to 2.661 (5) Å, and the other five at distances ranging between 3.038 (7) and 3.106 (6) Å.

Experimental

Single crystals of $PrMo_{7.6}O_{14}$ were obtained by the electrolysis of a melt formed at 1233 K from a mixture of Rb_2MoO_4, MoO_3 and Pr_6O_{11} in the molar ratio 8.4:5:1. The electrolysis was carried out in air using an alumina crucible. The anode was a platinum foil with a surface area of about 1 cm^2 and the cathode a 10-turn spiral of platinum made from a 0.4 mm diameter wire. At the end of the run, the electrodes were raised above the melt to allow them to cool rapidly to room temperature. Crystals, which grow on the cathode in the form of black irregular plates, were obtained by applying a constant current of 40 mA for 12 h. Single crystals were separated from the matrix and the cathode by repeated and alternate washings in hot dilute solutions of potassium carbonate and hydrochloric acid. Qualitative microanalyses of the crystals thus obtained, using a Jeol JSM-35 CF scanning electron microscope equipped with a Tracor energy-dispersive-type X-ray spectrometer, did not reveal elements other than Pr, Mo and O. This precludes the possibility of an element lighter than molybdenum on the capping site, Mo4, that could lead to a deficiency in electrons on this site.

The atomic coordinates of Nd, Mo and O from $NdMo_8O_{14}$ (Gougeon & McCarley, 1991) were used as starting positions in the first stages of the refinement in the present study. During the refinements, the equivalent isotropic atomic displacement parameter of the Mo4 atom being greater than that of the other Mo atoms, the site-occupancy factor of the Mo4 site was allowed to vary. The occupation factor thus converged to a value of 0.811 (4). Flack (1983) parameter refinement indicated that a single-domain crystal was used in the study.

Crystal data

$PrMo_{7.6}O_{14}$
$M_r = 1095.97$
Orthorhombic, *Aba*2
$a = 9.1611\ (4)$ Å
$b = 9.9709\ (9)$ Å
$c = 11.1916\ (8)$ Å
$V = 1022.29\ (13)$ Å^3
$Z = 4$
$D_x = 7.121$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 995 reflections
$\theta = 1.0\text{–}37.8°$
$\mu = 13.78$ mm^{-1}
$T = 293\ (2)$ K
Irregular, black
0.06 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans ($\kappa = 0$) + additional ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.403$, $T_{max} = 0.508$
11 744 measured reflections
2540 independent reflections
2249 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 37.9°$
$h = -15 \rightarrow 15$
$k = -17 \rightarrow 16$
$l = -19 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.093$
$S = 1.10$
2540 reflections
108 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 22.8476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.97$ e Å^{-3}
$\Delta\rho_{min} = -2.37$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00076 (8)
Absolute structure: Flack (1983), 1118 Friedel pairs
Flack parameter = −0.01 (3)

Table 1
Selected interatomic distances (Å).

Pr—O7	2.405 (8)	Mo2—O2^{xii}	2.018 (7)
Pr—O5^{i}	2.443 (6)	Mo2—O6	2.031 (6)
Pr—O5^{ii}	2.443 (6)	Mo2—O3^{vi}	2.043 (6)
Pr—O6^{iii}	2.552 (6)	Mo2—O5	2.064 (6)
Pr—O6^{iv}	2.552 (6)	Mo2—O4^{xiii}	2.124 (5)
Pr—O4^{v}	2.661 (5)	Mo2—Mo4^{v}	2.6384 (11)
Pr—O4^{vi}	2.661 (5)	Mo2—Mo3^{vii}	2.7306 (8)
Pr—O2	3.038 (7)	Mo2—Mo3	2.7864 (8)
Pr—O2^{vii}	3.038 (7)	Mo3—O1^{viii}	2.027 (6)
Pr—O8	3.088 (10)	Mo3—O4^{xiv}	2.040 (6)
Pr—O3	3.106 (6)	Mo3—O6^{vii}	2.077 (6)
Pr—O3^{vii}	3.106 (6)	Mo3—O5	2.090 (5)
Mo1—O7	1.933 (6)	Mo3—O8	2.116 (7)
Mo1—O2^{i}	1.988 (6)	Mo3—Mo4^{vi}	2.7254 (11)
Mo1—O3^{iv}	1.992 (6)	Mo3—Mo4^{v}	2.7499 (10)
Mo1—O4^{viii}	2.051 (6)	Mo3—Mo3^{vii}	2.8141 (11)
Mo1—O1^{iv}	2.078 (6)	Mo4—O8^{xv}	2.0066 (18)
Mo1—Mo1^{vii}	2.6784 (12)	Mo4—O1^{xv}	2.012 (5)
Mo1—Mo2^{ix}	2.7031 (8)	Mo4—O6^{xv}	2.017 (7)
Mo1—Mo2^{x}	2.7163 (8)	Mo4—O5^{xv}	2.026 (7)
Mo1—Mo3^{ix}	2.7244 (9)	Mo4—O3^{xv}	2.063 (6)
Mo1—Mo4^{xi}	3.0761 (10)	Mo4—O2^{xv}	2.077 (6)

Symmetry codes: (i) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $-x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $x, y-\frac{1}{2}, z-\frac{1}{2}$; (v) $x, y-\frac{1}{2}, \frac{1}{2}+z$; (vi) $-x, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $-x, -y, z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (ix) $x, y, z-1$; (x) $-x, -y, z-1$; (xi) $x, y-1, z$; (xii) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (xiii) $x, y, 1+z$; (xiv) $\frac{1}{2}-x, y-\frac{1}{2}, 1+z$; (xv) $x, \frac{1}{2}+y, z-\frac{1}{2}$.

The maximum and minimum electron-density peaks are located 1.22 Å from O5 and 0.65 Å from Mo2, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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