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$NdMo_{7.7}O_{14}$ containing Mo_6, Mo_7 and Mo_8 clusters

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Nd–O) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.084
Data-to-parameter ratio = 23.4

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

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Neodymium molybdenum oxide, $NdMo_{7.7}O_{14}$, crystallizes in the orthorhombic space group *Aba*2. Its crystal structure derives from the $NdMo_8O_{14}$ type which contains bicapped 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 expected 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 constitute one of the most interesting families in reduced molybdenum oxide chemistry. Indeed, before the synthesis of the $RMo_{8-x}O_{14}$ compounds, the metal mono- and bicapping of a metallic octahedron never occurs in any solid-state materials whereas molecular inorganic chemistry provides several examples like $Os_7C(CO)_{21}$ (Eady *et al.*, 1977) and $Re_8C(CO)_{24}$(Ciani *et al.*, 1982). The latter species are richer in electrons than their isostructural solid-state analogues and their electron count is in agreement with the existing counting rules. Another interesting feature of the RMo_8O_{14} compounds results from the different crystalline forms in which they crystallize. 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 latter three compounds crystallize in the noncentrosymmetric space group *Aba*2. Their structures comprise only *cis*-edge-sharing bi-face-capped Mo_8 clusters. The other forms present 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 probability distribution of approximately 65 and 35%, respectively.

We present here the crystal structure of a new neodymium reduced molybdenum oxide $NdMo_{7.7}O_{14}$ that was synthesized by fused-salt electrolysis and presents, in contrast to the Nd phase prepared by solid-state reaction, a non-stoichiometry on the capping sites of the *cis*-edge-sharing bi-face-capped Mo_8

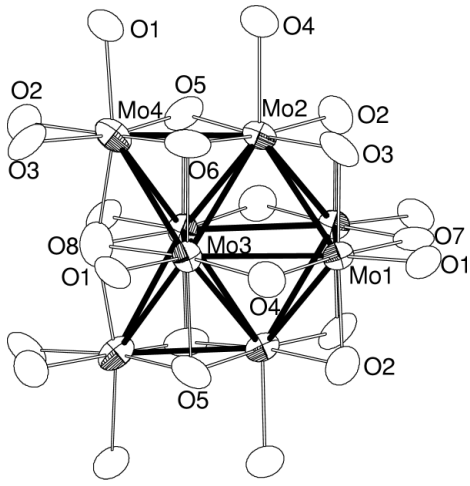

Figure 1
The *cis*-edge-sharing bi-face-capped Mo_8 cluster with its O-atom environment. Displacement ellipsoids are drawn at the 97% probability level.

cluster as previously observed with the compound $LaMo_{7.7}O_{14}$ also prepared by electrocrystallization.

The oxygen framework of $NdMo_{7.7}O_{14}$ derives from a packing of close-packed layers with sequence ABAC . . . along the *c* axis. While the B- ($y \simeq 0.25$) and C-type ($y \simeq 0.75$) layers are entirely occupied by O atoms, in the A-type layers ($y \simeq 0.0$ and 0.5) one quarter of the O atoms are missing or substituted by the Nd ions in an ordered way. Within the O network, 3/8 of the octahedral interstices are occupied by the Mo1, Mo2 and Mo3 atoms in an ordered way which form octahedral Mo_6 clusters and about one-tenth statistically by the Mo4 atoms that cap faces of the octahedral Mo_6 clusters. In $NdMo_{7.7}O_{14}$, the 85% occupancy of the capping Mo4 site results in the random co-existence of octahedral Mo_6 and monocapped octahedral Mo_7 clusters with the Mo_8 clusters since no satellite reflections were observed. It is interesting to note that, although $NdMo_{7.7}O_{14}$ and $LaMo_{7.7}O_{14}$ were obtained from melts with different compositions, the stoichiometry in molybdenum in both compounds is similar. The Mo—Mo distances within the Mo clusters, which range from 2.6274 (9) to 2.821 (1) Å, compare well with those found in $LaMo_{7.7}O_{14}$. Indeed, the greatest deviation observed is 0.01 Å. The average Mo—Mo distances in both molybdenum-deficient compounds are also similar, 2.725 and 2.724 Å for the Nd and La compounds, respectively. Compared with the fully stoichiometric molybdenum compound $NdMo_8O_{14}$, we observed significant differences that can reach 0.04 Å for the Mo2—Mo4 and Mo3—Mo4 distances. The mean Mo—Mo distance is also slightly higher at 2.730 Å. The shortest distance between Mo clusters that occurs in the *bc* plane is 3.0761 (8) Å, compared with 3.078 (1) and 3.068 (1) Å in $LaMo_{7.7}O_{14}$ and $NdMo_8O_{14}$, respectively. If we except the capping Mo4 atoms that are surrounded by six O atoms forming a distorted octahedron, the remaining ones are surrounded by five O atoms in a distorted square-based pyramidal environment. The Mo—O bond lengths vary from 1.931 (5) to 2.125 (6) Å in agreement with the 1.932 (6)–2.139 (8) Å range in $LaMo_{7.7}O_{14}$. For both compounds, the mean Mo—O distances calculated are 2.043 and 2.043 Å, respectively. For $NdMo_8O_{14}$, in which the Mo—O range from 1.97 (1) to 2.15 (1) Å, the average value is 2.050 Å. The Nd^{3+} ions lies away from the centre of a distorted cubo-octahedron with the seven nearest O atoms at distances varying between 2.391 (7) and 2.671 (5) Å, the remaining five at distances ranging from 3.048 (6) to 3.121 (5) Å.

Experimental

Single crystals of $NdMo_{7.7}O_{14}$ were obtained by the electrolysis of a melt formed at 1233 K from a mixture of Rb_2MoO_4, MoO_3 and Nd_2O_3 having 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 platinum spiral 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 grew 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 other elements than Nd, 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 the latter site.

Crystal data

$NdMo_{7.70}O_{14}$
M_r = 1106.98
Orthorhombic, *Aba*2
a = 9.1639 (2) Å
b = 9.9730 (2) Å
c = 11.1913 (2) Å
V = 1022.79 (4) $Å^3$
Z = 4
D_x = 7.189 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25665 reflections
θ = 1.0–37.8°
μ = 14.18 mm^{-1}
T = 293 (2) K
Irregular, black
0.09 × 0.06 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans (κ = 0) plus additional ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.247, T_{max} = 0.468
11 905 measured reflections
2556 independent reflections
2388 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 37.8°
$h = -15 \rightarrow 15$
$k = -17 \rightarrow 16$
$l = -19 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.11
2556 reflections
109 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 32.3150P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.83 e $Å^{-3}$
$\Delta\rho_{min}$ = −2.27 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00120 (8)
Absolute structure: Flack (1983), 1137 Friedel pairs
Flack parameter = −0.01 (2)

Table 1
Selected bond lengths (Å).

Nd—O7	2.391 (7)	Mo2—O6	2.025 (5)
Nd—O5^{i}	2.428 (5)	Mo2—O2^{xii}	2.026 (6)
Nd—O5^{ii}	2.428 (5)	Mo2—O3^{v}	2.055 (5)
Nd—O6^{iii}	2.531 (6)	Mo2—O5	2.067 (6)
Nd—O6^{iv}	2.531 (6)	Mo2—O4^{xiii}	2.119 (5)
Nd—O4^{v}	2.671 (5)	Mo2—Mo4^{vi}	2.6274 (9)
Nd—O4^{vi}	2.671 (5)	Mo2—Mo3^{vii}	2.7286 (7)
Nd—O2^{vii}	3.048 (6)	Mo2—Mo3	2.7886 (7)
Nd—O2	3.048 (6)	Mo3—O1^{viii}	2.021 (6)
Nd—O8	3.096 (8)	Mo3—O4^{xiv}	2.042 (5)
Nd—O3^{vii}	3.121 (5)	Mo3—O6^{vii}	2.082 (5)
Nd—O3	3.121 (5)	Mo3—O5	2.083 (5)
Mo1—O7	1.931 (5)	Mo3—O8	2.125 (6)
Mo1—O2^{i}	1.980 (5)	Mo3—Mo4^{v}	2.7261 (9)
Mo1—O3^{iv}	1.989 (5)	Mo3—Mo4^{vi}	2.7562 (8)
Mo1—O4^{viii}	2.047 (5)	Mo3—Mo3^{vii}	2.8209 (10)
Mo1—O1^{iv}	2.093 (6)	Mo4—O1^{xv}	2.005 (5)
Mo1—Mo1^{vii}	2.6758 (11)	Mo4—O8^{xv}	2.0123 (15)
Mo1—Mo2^{ix}	2.7086 (7)	Mo4—O6^{xv}	2.032 (6)
Mo1—Mo2^{x}	2.7223 (7)	Mo4—O5^{xv}	2.035 (6)
Mo1—Mo3^{ix}	2.7238 (8)	Mo4—O3^{xv}	2.059 (5)
Mo1—Mo4^{xi}	3.0761 (8)	Mo4—O2^{xv}	2.084 (6)

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

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, we allowed the site-occupancy factor of the Mo4 site to vary. The occupation factor converged thus to the value of 0.849 (4). Flack parameter (Flack, 1983) refinement indicated that a single-domain crystal was used in our study.

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

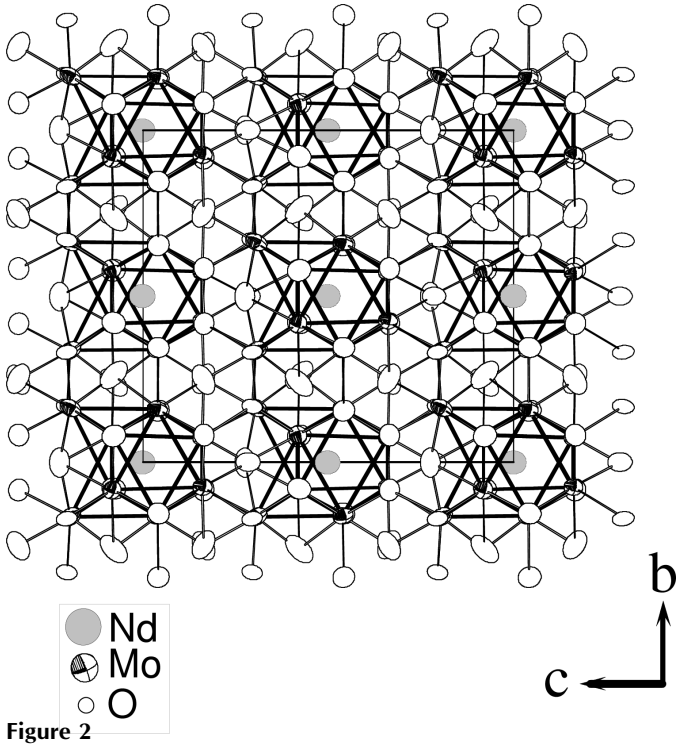

Figure 2
Projection of the $NdMo_{7.7}O_{14}$ structure on the *bc* plane.

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