Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.056$
$S = 1.184$
2180 reflections
48 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0136P)^2 + 0.4419P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.072$ e Å^{-3}
$\Delta\rho_{\min} = -0.804$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0038 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$U_{\rm iso}$ for H, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Mg	0	0	0	0.01306 (12)
Se	0.16547 (2)	0.18155 (3)	0.49075 (3)	0.01358 (4)
O1	0.28165 (13)	0.4209 (3)	0.4595 (3)	0.0225 (2)
O2	0.03231 (13)	0.2497 (3)	0.2852 (2)	0.0169 (2)
O3	0.06773 (15)	0.2828 (2)	0.7501 (2)	0.0187 (2)
H	0.038 (4)	0.425 (7)	0.725 (6)	0.041 (9)

Table 2. *Selected geometric parameters (Å, °)*

Mg—O1$^{\rm i}$	2.0366 (12)	Se—O1	1.6490 (13)
Mg—O1$^{\rm ii}$	2.0366 (12)	Se—O2	1.6906 (12)
Mg—O2	2.0738 (12)	Se—O3	1.7883 (12)
Mg—O2$^{\rm iii}$	2.0738 (12)	O3···O2$^{\rm vi}$	2.616 (2)
Mg—O3$^{\rm iv}$	2.1291 (13)	O3—H	0.80 (4)
Mg—O3$^{\rm v}$	2.1291 (13)	H···O2$^{\rm vi}$	1.82 (4)
O1—Se—O2	102.78 (7)	O2—Se—O3	97.17 (6)
O1—Se—O3	100.84 (7)	O3—H···O2$^{\rm vi}$	172 (4)

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

Lattice parameters were determined from X-ray Guinier powder photographs (Cu $K\alpha_1$ radiation, α-quartz as internal standard) using a Huber–Guinier system 600 and the refinement program *LSUCR* (Evans, Appleman & Handwerker, 1963). The atomic positions were obtained from a Patterson map (Se) and successive least-squares refinements and ΔF syntheses (Mg, O, H).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *LSUCR*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SDP* (B. A. Frenz & Associates Inc., 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971), *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BR1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$SmMo_8O_{14}$

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Abstract

The crystal structure of samarium octamolybdate is characterized by layers of *cis*-edge-sharing bi-face-capped octahedral Mo_8 clusters parallel to the *bc* plane of the orthorhombic unit cell. The arrangement of the O atoms is derived from the close-packing layer sequence *ABAC*. The Mo—Mo distances range from 2.5959 (5) to 2.8413 (6) Å within the Mo_8 clusters, with a mean value of 2.731 Å. The shortest Mo—Mo distance between the Mo_8 clusters within the same layer is 3.0672 (5) Å, and between clusters of adjacent layers 3.6342 (5) Å. The Mo—O distances lie between 1.949 (3) and 2.163 (3) Å (mean value 2.050 Å). The Sm^{3+} ion lies away from the centre of a distorted cuboctahedron with Sm—O distances ranging from 2.316 (4) to 3.159 (3) Å.

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Comment

The single-crystal structures of the first four members of the series of compounds $R\text{Mo}_8\text{O}_{14}$ (R = La, Ce, Pr, Nd) have been presented in recent papers. These compounds can be synthesized either by solid-state reaction for R = La, Ce, Pr, Nd (Kerihuel, Tortelier & Gougeon, 1996; Kerihuel & Gougeon, 1995*a*,*b*; Gougeon & McCarley, 1991) or by fused-salt electrolysis in the case of $\text{LaMo}_{8-x}\text{O}_{14}$ (x = 0.0 and 0.3) (Leligny, Ledésert, Labbé, Raveau & McCarroll, 1990; Leligny *et al.*, 1993). The main metallic building block in all these compounds is the bi-face-capped Mo_8 octahedron which exists in two of the three possible isomeric forms. To our knowledge, this cluster is the first example of geometric isomerism observed in reduced Mo compounds in solid-state chemistry. The simplest structures observed are those of $\text{LaMo}_{7.7}\text{O}_{14}$ (Leligny *et al.*, 1990) and $\text{NdMo}_8\text{O}_{14}$ (Gougeon & McCarley, 1991) where only the *cis*-edge-sharing isomeric form of the Mo_8 cluster is found. These two compounds crystallize in the space group *Aba*2 with the following parameters: a_{La} = 9.196 (1), b_{La} = 9.985 (1), c_{La} = 11.171 (1) Å; a_{Nd} = 9.209 (3), b_{Nd} = 10.008 (2), c_{Nd} = 11.143 (4) Å. In the $\text{LaMo}_8\text{O}_{14}$ compounds synthesized by solid-state reaction (Kerihuel *et al.*, 1996) and in $\text{CeMo}_8\text{O}_{14}$ (Kerihuel & Gougeon, 1995*a*), the *cis* isomer coexists in an ordered way in equal proportion with the *trans* bi-face-capped Mo_8 cluster. Both compounds crystallize in the orthorhombic space group *Pbcn* [a = 9.2065 (4), b = 11.1298 (9), c = 20.0264 (8) Å for $\text{LaMo}_8\text{O}_{14}$ and a = 9.1937 (7), b = 11.121 (1), c = 20.014 (1) Å for $\text{CeMo}_8\text{O}_{14}$]. The structure of the Pr member synthesized by solid-state reaction is also based on a mixture of *cis* and *trans* isomers but the ratio here is 2:1 (Kerihuel & Gougeon, 1995*b*). This compound crystallizes in the *Pbca* space group with the following unit cell parameters: a = 9.2037 (6), b = 11.114 (2), c = 30.012 (5) Å. Finally, a more complex structure is observed for the stoichiometric compound $\text{LaMo}_8\text{O}_{14}$ (Leligny *et al.*, 1993) obtained by fused-salt electrolysis. Indeed, this compound presents a one-dimensional commensurate modulation of wavevector $\underset{\circ}{q}^* = b^*/3$ [a = 11.129 (1), b = 10.000 (1), c = 9.218 (1) Å]. The structure that was solved in the superspace group $P^{C\underline{2c}a}_{111}$ consists of *cis*-edge-sharing and *trans* isomers with an average probability distribution of approximately 65 and 35%, respectively. We present here the crystal structure of the Sm member synthesized by high-temperature solid-state reaction.

The title compound is isostructural with $\text{LaMo}_{7.7}\text{O}_{14}$ and $\text{NdMo}_8\text{O}_{14}$ which are prepared by fused-salt electrolysis and solid-state reaction, respectively. Consequently, its structure is based on *cis*-edge-sharing bi-face-capped octahedral Mo_8 clusters arranged in layers parallel to the *bc* plane of the orthorhombic unit cell. The Mo_8 cluster is shown in Fig. 1 with its O-atom environment. Each Mo atom of the Mo_6 core is thus surrounded by five O atoms forming a distorted square pyramid and each of the capping Mo atoms by six O atoms in a distorted octahedron. The perspective view of the structure along the c axis (Fig. 2) clearly shows the layered arrangement of the Mo_8 clusters and O atoms parallel to the *bc* plane. The O-atom framework is similar to that previously described for all other $R\text{Mo}_8\text{O}_{14}$ forms and is derived from the close-packed layer sequence *ABAC*. While the *B* and *C* layers are entirely occupied by O atoms, the *A* layers are deficient with a quarter of the O atoms missing in an ordered way. The Sm^{3+} ions occupy half of these vacant O-atom sites and consequently are surrounded by six O atoms

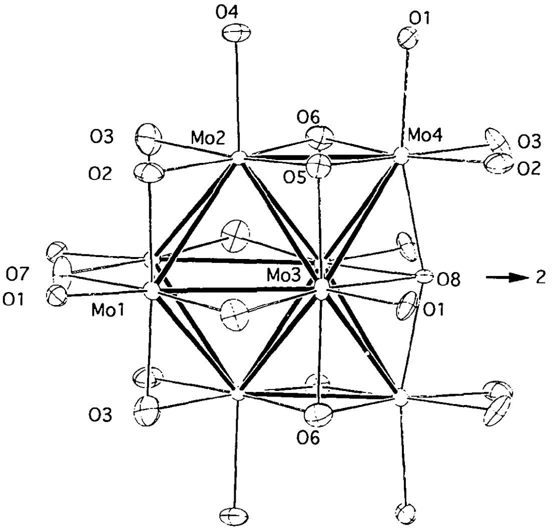

Fig. 1. The *cis*-edge-sharing bi-face-capped Mo_8 cluster with its O-atom environment. Displacement ellipsoids are plotted at the 95% probability level.

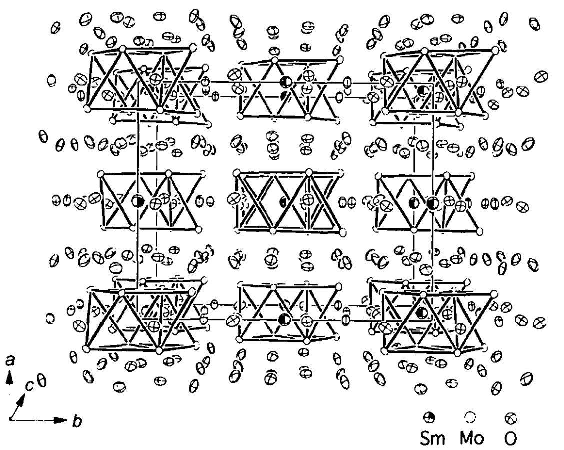

Fig. 2. Perspective view of the structure along the c axis. The Mo_8 clusters are emphasized by bold lines and displacement ellipsoids are plotted at the 95% probability level.

belonging to the *A*-type layers, three O atoms of the *B*-type layers and three O atoms of the *C*-type layers. Within the O-atom network, the Mo atoms occupy half of the octahedral interstices to create the Mo_8 clusters, the arrangement of which is shown in Fig. 2.

The Mo—Mo distances within the *cis*-edge-sharing bi-face-capped octahedral Mo_8 cluster range from 2.5959 (5) to 2.8413 (6) Å, with an average value of 2.731 Å. These values are similar to those determined for $NdMo_8O_{14}$ [2.590 (1)–2.848 (1) Å, mean value 2.731 Å]. The Mo—O distances vary between 1.949 (3) and 2.163 (3) Å, in agreement with the 1.97 (1)–2.15 (1) Å range found for $NdMo_8O_{14}$. The average Mo—O bond distances are equal to 2.050 Å for these two compounds. The shortest Mo—Mo intercluster distance, which occurs between the Mo1 and Mo4 atoms within the same layer, is 3.0672 (5) Å, and corresponds to that observed for $NdMo_8O_{14}$ [3.068 (1) Å]. On the other hand, the spacing between Mo_8 clusters of adjacent layers reaches 3.6342 (5) Å and does not change, in contrast to that observed in the other forms. The Sm^{3+} cation lies away from the centre of a distorted cuboctahedron with the seven nearest O atoms at distances varying between 2.316 (4) and 2.702 (3) Å and the remaining five at 3.071 (4) (× 3) and 3.159 (3) Å (× 2).

Experimental

Single crystals were obtained by heating a stoichiometric mixture (starting materials: Sm_2O_3, MoO_3 and Mo) in a sealed molybdenum crucible at about 2220 K for 15 min. The crucible was then cooled at a rate of 100 K h^{-1} to 1300 K and finally furnace-cooled to room temperature.

Crystal data

$SmMo_8O_{14}$
$M_r = 1141.87$
Orthorhombic
*Aba*2
$a = 9.1930 (4)$ Å
$b = 9.9973 (9)$ Å
$c = 11.1516 (8)$ Å
$V = 1024.89 (13)$ Å^3
$Z = 4$
$D_x = 7.318$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–32°$
$\mu = 13.588$ mm^{-1}
$T = 293 (2)$ K
Irregular
0.12 × 0.11 × 0.10 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.210$, $T_{max} = 0.257$
4257 measured reflections
2177 independent reflections

2078 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0262$
$\theta_{max} = 45°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 90 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.046$
$S = 1.285$
2177 reflections
108 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0118P)^2 + 4.2938P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.77$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00266 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.25 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sm	0	0	0.50218 (6)	0.00670 (5)
Mo1	0.12032 (3)	−0.07458 (3)	0.83730 (3)	0.00230 (4)
Mo2	0.12036 (3)	0.16105 (3)	−0.03946 (3)	0.00197 (4)
Mo3	0.12407 (3)	−0.08471 (3)	0.08047 (3)	0.00252 (4)
Mo4	0.12508 (3)	0.66408 (3)	0.69328 (3)	0.00251 (5)
O1	0.2405 (4)	0.3290 (3)	0.2020 (3)	0.0040 (4)
O2	0.2463 (4)	0.0809 (3)	0.3309 (3)	0.0058 (4)
O3	0.0123 (3)	0.2528 (3)	0.3325 (3)	0.0051 (4)
O4	0.2335 (3)	0.3443 (3)	0.9558 (3)	0.0050 (4)
O5	0.2672 (3)	0.0740 (3)	0.0754 (3)	0.0043 (4)
O6	−0.0111 (3)	0.2642 (3)	0.0749 (3)	0.0038 (3)
O7	0	0	0.7099 (4)	0.0051 (6)
O8	0	0	0.2268 (4)	0.0045 (5)

Table 2. *Selected bond lengths (Å)*

Sm—O7	2.316 (4)	Mo2—O4^{xiii}	2.107 (3)
Sm—O5^{i}	2.407 (3)	Mo2—Mo4^{vi}	2.5959 (5)
Sm—O5^{ii}	2.407 (3)	Mo2—Mo3^{vii}	2.7240 (4)
Sm—O6^{iii}	2.494 (3)	Mo2—Mo1^{xiii}	2.7272 (5)
Sm—O6^{iv}	2.494 (3)	Mo2—Mo1^{xiv}	2.7444 (4)
Sm—O4^{v}	2.702 (3)	Mo2—Mo3	2.7976 (5)
Sm—O4^{vi}	2.702 (3)	Mo3—O1^{viii}	2.032 (3)
Sm—O2^{vii}	3.071 (4)	Mo3—O4^{xv}	2.037 (3)
Sm—O2	3.071 (4)	Mo3—O5	2.062 (3)
Sm—O8	3.071 (4)	Mo3—O6^{vii}	2.074 (3)
Sm—O3^{vii}	3.159 (3)	Mo3—O8	2.163 (3)
Sm—O3	3.159 (3)	Mo3—Mo1^{xiii}	2.7138 (5)
Mo1—O7	1.949 (3)	Mo3—Mo2^{vii}	2.7240 (4)
Mo1—O2^{i}	1.981 (3)	Mo3—Mo4^{v}	2.7310 (5)
Mo1—O3^{iv}	1.992 (3)	Mo3—Mo4^{vi}	2.7873 (5)
Mo1—O4^{viii}	2.052 (3)	Mo3—Mo2	2.7976 (5)
Mo1—O1^{iv}	2.104 (3)	Mo3—Mo3^{vii}	2.8413 (6)
Mo1—Mo1^{vii}	2.6678 (6)	Mo4—O1^{xvi}	1.964 (3)
Mo1—Mo3^{ix}	2.7138 (5)	Mo4—O8^{xvi}	2.0378 (8)
Mo1—Mo2^{ix}	2.7272 (5)	Mo4—O5^{xvi}	2.060 (3)
Mo1—Mo2^{x}	2.7444 (4)	Mo4—O3^{xvi}	2.067 (3)
Mo1—Mo4^{xi}	3.0672 (5)	Mo4—O2^{xvi}	2.071 (3)
Mo2—O6	2.037 (3)	Mo4—O6^{xvi}	2.077 (3)
Mo2—O5	2.054 (3)	Mo4—Mo2^{xvi}	2.5959 (5)
Mo2—O2^{xii}	2.058 (3)	Mo4—Mo3^{iii}	2.7310 (5)
Mo2—O3^{v}	2.066 (3)	Mo4—Mo3^{xvi}	2.7873 (5)

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) $-x, -y, z - 1$; (xv) $\frac{1}{2} - x, y - \frac{1}{2}, z - 1$; (xvi) $x, \frac{1}{2} + y, \frac{1}{2} + z$.

Data were corrected for Lorentz and polarization effects. An absorption correction was applied using ψ scans of nine reflections (North, Phillips & Mathews, 1968). The atomic coordinates of Nd, Mo and O from the Nd analogue (Gougeon & McCarley, 1991) were used as starting positions for Sm, Mo and O in the present study. Refinements of the occupancy factors for the Sm and all of the Mo sites confirmed that they were fully occupied. Calculations were performed on a Digital Pentium Celebris 590 FP for *SHELXL*93 and on a Digital MicroVAX 3100 for the *MolEN* (Fair, 1990) programs.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DU1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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