inorganic compounds

Rare-earth site splitting in Sm$_3$MoO$_7$

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Trisamarium molybdenum heptaoxide, Sm$_3$MoO$_7$, is isomorphous with Ln$_3$MoO$_7$ (Ln = La and Pr). The crystal structure consists of chains of corner-linked MoO$_6$ octahedra running parallel to the b axis and separated from each other by seven- or eight-coordinate Sm–O polyhedra. In contrast to La$_3$MoO$_7$ and Pr$_3$MoO$_7$, a splitting of one Sm site into two positions is observed.

Comment

Metal oxides of general formula Ln$_3$$MO_7$, where M is a pentavalent 4d or 5d transition metal such as Nb, Mo, Ru, Ta, Re, Os or Ir, and Ln is a trivalent rare-earth metal, present an ordered double fluorite structure and crystallize in various orthorhombic space groups, such as $Pnma$, $Cmcm$, $C222_1$ or $P2_12_12_1$. The main structural feature of the Ln$_3$$MO_7$ compounds is the presence of isolated zigzag chains of $trans$-corner-linked MO$_6$ octahedra that are separated by seven- or eight-coordinate Ln–O polyhedra. Because of this quasi-one-dimensionality, La$_3$RuO$_7$, Ln$_3$OsO$_7$ (Ln = La, Pr, Nd, Sm, Eu and Gd; Lam *et al.*, 2002; Plaisier *et al.*, 2002; Gemmill *et al.*, 2005), Ln$_3$MoO$_7$ (Greedan *et al.*, 1997; Nishimine *et al.* 2005), Ln$_3$RuO$_7$ (Ln = La, Pr, Sm and Eu; Khalifah *et al.*, 2000; Wiss *et al.*, 2000; Harada & Hinatsu, 2001; Gemmill *et al.*, 2004), Ln$_3$ReO$_7$ (Ln = Pr, Nd, Sm, Gd, Tb and Dy; Wltschek *et al.*, 1996; Lam *et al.*, 2003; Hinatsu *et al.*, 2004) and Pr$_3$$MO_7$ (M = Nb and Ta; Vente *et al.*, 1994) have been extensively studied for their physical properties since peculiar magnetic and electronic properties are expected. We present here the crystal structure of Sm$_3$MoO$_7$. This compound was first synthesized as a powder sample by Prévost-Czeskleba (1987) and found to crystallize in the orthorhombic space group $Cmcm$ as Nd$_3$NbO$_7$ (Rossel, 1979). Our investigation on a single crystal indicates that Sm$_3$MoO$_7$ crystallizes in the noncentrosymmetric space group $P2_12_12_1$ as La$_3$MoO$_7$ (Greedan *et al.*, 1997) and Pr$_3$MoO$_7$ (Barrier & Gougeon, 2003). However, a partial disorder is observed at one rare-earth site, *i.e.* Sm1, in the title compound.

Perspective views of Sm$_3$MoO$_7$ along the b and c axes are shown in Figs. 1 and 2, respectively. The main structural feature of Sm$_3$MoO$_7$ is the occurrence of infinite single chains of tilted corner-linked MoO$_6$ octahedra running parallel to the b axis. These chains alternate with rows of edge-shared Sm1O$_7$ or Sm1$'$O$_8$ polyhedra to form slabs parallel to the ab plane. The slabs are separated by the Sm2 and Sm3 cations, which are both seven-coordinated by O atoms. The Mo—O distances within the MoO$_6$ octahedra (Fig. 3) range from 1.851 (3) to 2.088 (3) Å [1.861 (3)–2.098 (4) and 1.852 (4)–2.088 (5) Å in La$_3$MoO$_7$ and Pr$_3$MoO$_7$, respectively], with an average value of 1.966 Å compared with 1.981 and 1.974 Å in La$_3$MoO$_7$ and Pr$_3$MoO$_7$, respectively. Because of the octahedral tilt, the Mo—O5—Mo^{iv} angle [symmetry code: (iv) $-x + 1$, $y + \frac{1}{2}$,

Figure 1
A perspective view of Sm$_3$MoO$_7$ along the b axis. Displacement ellipsoids are drawn at the 97% probability level.

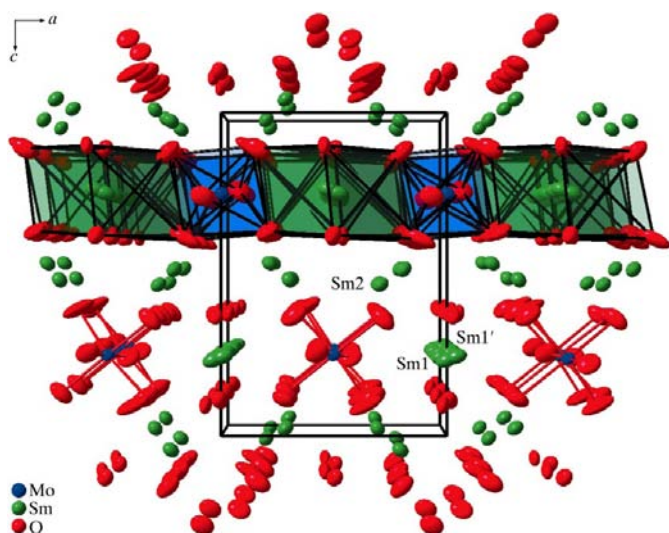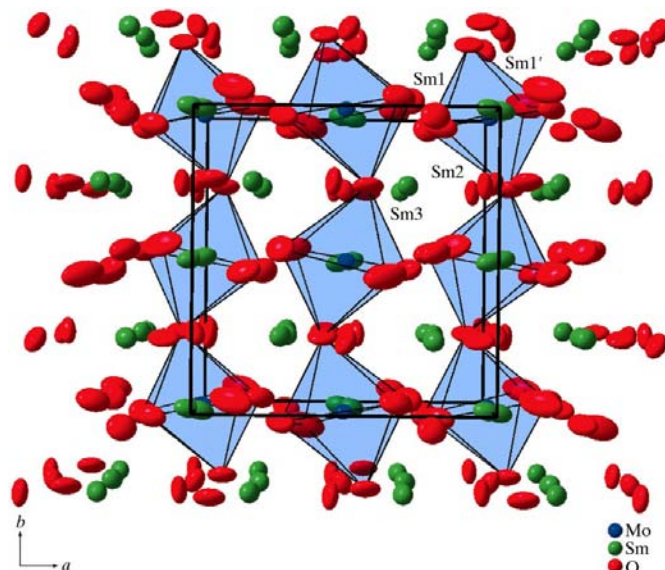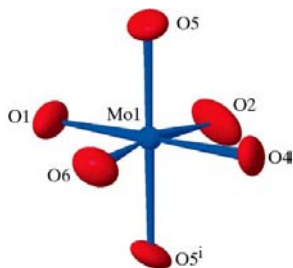**Figure 2**
A perspective view of Sm$_3$MoO$_7$ along the c axis. Displacement ellipsoids are drawn at the 97% probability level.

$-z + \frac{3}{2}$] along the chain differs significantly from 180°, with a value of 146.62 (14)°. The main difference with La$_3$MoO$_7$ and Pr$_3$MoO$_7$ concerns the Sm1 site, which is split into two independent parts, Sm1 and Sm1′. Atom Sm1, with 92.0 (3)% occupancy, has a coordination number of 7, with five short Sm—O bonds in the range 2.348 (3)–2.383 (3) Å and two long Sm—O bonds of 2.637 (3) and 2.637 (4) Å. This seven-coordination may be described as a bicapped square-based pyramid and corresponds to the rare-earth site 1 in La$_3$MoO$_7$ and Pr$_3$MoO$_7$. In contrast, atom Sm1′, with a site occupancy of 0.080 (3), has a coordination number of 8, with six Sm—O bonds distributed in the range 2.269 (6)–2.585 (6) Å and two others of length 2.969 (8) and 2.997 (8) Å. The six nearest O atoms form a highly distorted octahedron and the other two cap two faces. Atoms Sm2 and Sm3 are in distorted pentagonal bipyramidal configurations, with Sm—O distances in the ranges 2.273 (2)–2.642 (2) and 2.243 (3)–2.542 (2) Å, respectively.

The phenomenon of rare-earth site splitting has recently been observed for the related compounds Tb$_3$RuO$_7$ and Dy$_3$RuO$_7$ (Ishizawa, Suwa & Tateishi, 2007; Ishizawa, Suwa, Tateishi & Hester, 2007). Indeed, these compounds, which crystallize in the noncentrosymmetric space group $P2_1nb$ with a double b axis (a axis in Sm$_3$MoO$_7$), present two rare-earth atom sites (out of six crystallographically independent ones) that are split into two positions. As in the ruthenium compounds, the rare-earth sites that are split in the title compound are those that alternate with the MoO$_6$ chains. Our study shows clearly that such a partial disorder can exist with transition metals other than ruthenium in the Ln$_3$MO$_7$ series. Examination of various structures of the Ln$_3$MO$_7$ type shows that, in a number of them, the rare-earth metals that alternate with the MoO$_6$ chains present either equivalent isotropic displacement parameters that are, at least, double those of the other rare-earth atoms (Wltschek et al., 1996; Khalifah et al., 2000; Lam et al., 2003; Hinatsu et al., 2004; Gemmill et al., 2005) or large prolate anisotropic atomic displacement parameters (Barrier & Gougeon, 2003; Ishizawa et al., 2006). Finally, one can note that the rare-earth disorder seems to occur not only in the noncentrosymmetric space groups but also in the centrosymmetric ones, and it would be interesting to see if this partial structural disorder depends on the rare-earth atom size.

Figure 3
The numbering scheme of the MoO$_6$ octahedron. Displacement ellipsoids are drawn at the 97% probability level. The symmetry code is as in Table 1.

Experimental

Single crystals of Sm$_3$MoO$_7$ were prepared from a stoichiometric amount of Sm$_2$O$_3$, MoO$_3$ and Mo. Before use, the Mo powder was reduced under a hydrogen flow at 1273 K for 6 h and the rare-earth oxide was prefired at 1273 K overnight and left at 873 K. The initial mixture (ca 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low argon pressure using an arc welding system. The charge was heated at a rate of 300 K h^{-1} to 1973 K, at which temperature it was held for 10 min, then cooled at a rate of 100 K h^{-1} to 1373 K and finally furnace cooled.

Crystal data

Sm$_3$MoO$_7$	$V = 600.21$ (2) Å^3
$M_r = 658.99$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.4500$ (1) Å	$\mu = 30.94$ mm^{-1}
$b = 7.5460$ (1) Å	$T = 293$ (2) K
$c = 10.6766$ (2) Å	$0.19 \times 0.09 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	17049 measured reflections
Absorption correction: analytical	3719 independent reflections
(de Meulenaer & Tompa, 1965)	3438 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.037$, $T_{\max} = 0.367$	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{\max} = 1.94$ e Å^{-3}
$wR(F^2) = 0.042$	$\Delta\rho_{\min} = -3.05$ e Å^{-3}
$S = 1.05$	Absolute structure: Flack (1983),
3719 reflections	1593 Friedel pairs
107 parameters	Flack parameter: 0.491 (17)
1 restraint	

Table 1
Selected bond lengths (Å).

Mo1—O2	1.851 (3)	Sm1′—O4	2.585 (6)
Mo1—O6	1.913 (3)	Sm1′—O6	2.969 (8)
Mo1—O5	1.939 (2)	Sm1′—O2^{ii}	2.997 (8)
Mo1—O5^{i}	2.000 (2)	Sm2—O7^{iii}	2.273 (2)
Mo1—O1	2.002 (3)	Sm2—O7	2.313 (2)
Mo1—O4	2.088 (3)	Sm2—O4^{iv}	2.361 (3)
Sm1—O7^{ii}	2.348 (3)	Sm2—O1	2.385 (3)
Sm1—O4	2.376 (3)	Sm2—O2^{v}	2.438 (3)
Sm1—O7^{i}	2.378 (3)	Sm2—O6^{vi}	2.442 (3)
Sm1—O3^{ii}	2.382 (3)	Sm2—O5	2.642 (2)
Sm1—O3^{i}	2.383 (3)	Sm3—O3	2.243 (3)
Sm1—O1^{ii}	2.637 (3)	Sm3—O3^{vii}	2.272 (2)
Sm1—O6	2.637 (4)	Sm3—O4^{viii}	2.344 (3)
Sm1′—O7^{i}	2.269 (6)	Sm3—O1^{ix}	2.399 (3)
Sm1′—O3^{ii}	2.308 (6)	Sm3—O6^{iv}	2.465 (3)
Sm1′—O1^{ii}	2.420 (6)	Sm3—O2	2.498 (3)
Sm1′—O3^{i}	2.448 (6)	Sm3—O5	2.542 (2)
Sm1′—O7^{ii}	2.451 (6)		

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x - 1, y, z$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (vii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (ix) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$.

Systematic absences were only consistent with the noncentrosymmetric space group $P2_12_12_1$. The atomic coordinates of Pr, Mo and O from Pr$_3$MoO$_7$ (Barrier & Gougeon, 2003) were used as starting positions in the first stages of the refinement in the present study. The least-squares refinement with anisotropic atomic displacement parameters for all atoms yielded an R factor of 0.027 for 3438 reflections. At this stage, however, a relatively large residual electron-density peak of 8.1 e Å^{-3} was found at about 0.58 Å from atom Sm1. To model the electron density of the Sm1 site, it was necessary to split it into two independent sites, Sm1 and Sm1′, separated by 0.58 Å. The split pair Sm1/Sm1′ was constrained to have

inorganic compounds

the same anisotropic atomic displacement parameter in the later refinements. The site-occupation factors of atoms Sm1 and Sm1′ were first refined freely, leading to a sum of 1.001 (3). Consequently, the sum was constrained to be 1 in the final cycles of refinement. This split-atom model decreased the R factor to 0.022 and the residual electron density near the Sm1 and Sm1′ sites to 1.79 e Å^{-3}. An attempt to refine the structure in the space group $Pnma$, as suggested by $PLATON$ (Spek, 2003), was unsuccessful and led to an R factor of about 0.10. The Flack (1983) parameter refined to 0.491 (17), indicating that the crystal contained a mixture of the two absolute structures. The highest peak and the deepest hole in the final Fourier map are located 0.59 and 0.52 Å, respectively, from atom Sm2.

Data collection: $COLLECT$ (Nonius, 1998); cell refinement: $COLLECT$; data reduction: $EVALCCD$ (Duisenberg, 1998); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 1997); molecular graphics: $DIAMOND$ (Brandenburg, 2001); software used to prepare material for publication: $SHELXL97$.

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