O54	0.496 (1)	0.210 (2)	0.820 (3)	0.07 (1)
O55	0.508 (2)	0.095 (3)	1.029 (5)	0.17 (2)
O56	0.573 (2)	0.073 (3)	0.838 (4)	0.13 (2)
O57	0.486 (2)	0.051 (4)	0.833 (5)	0.24 (3)

Table 2. *Bond lengths* (Å)

W0—O1	1.75 (2)	W5—O34	1.98 (2)
W0—O4	1.89 (2)	W5—O31	2.30 (2)
W0—O5	1.89 (2)	W6—O19	1.73 (2)
W0—O2	1.95 (2)	W6—O23	1.80 (2)
W0—O3	1.97 (2)	W6—O30	1.89 (3)
W0—O14	2.26 (2)	W6—O32	1.92 (2)
W1—O6	1.74 (2)	W6—O27	1.93 (2)
W1—O15	1.80 (2)	W6—O31	2.29 (2)
W1—O2	1.97 (2)	W7—O24	1.76 (2)
W1—O10	1.97 (2)	W7—O20	1.77 (2)
W1—O13	2.00 (2)	W7—O28	1.95 (2)
W1—O14	2.35 (2)	W7—O27	1.97 (2)
W2—O7	1.77 (2)	W7—O33	2.02 (2)
W2—O16	1.78 (2)	W7—O31	2.27 (3)
W2—O11	1.97 (2)	W8—O25	1.77 (3)
W2—O10	1.98 (2)	W8—O21	1.78 (2)
W2—O3	2.03 (2)	W8—O28	1.94 (2)
W2—O14	2.24 (2)	W8—O29	1.95 (3)
W3—O8	1.77 (2)	W8—O34	2.02 (2)
W3—O17	1.78 (2)	W8—O31	2.35 (2)
W3—O11	1.91 (2)	W9—O26	1.71 (2)
W3—O4	1.92 (2)	W9—O22	1.78 (2)
W3—O12	2.00 (2)	W9—O35	1.94 (2)
W3—O14	2.28 (2)	W9—O29	1.96 (2)
W4—O9	1.77 (2)	W9—O30	1.98 (2)
W4—O18	1.78 (2)	W9—O31	2.36 (3)
W4—O5	1.91 (2)	Gd—O16	2.37 (2)
W4—O12	1.95 (2)	Gd—O21	2.39 (2)
W4—O13	1.97 (2)	Gd—O15	2.41 (2)
W4—O14	2.35 (2)	Gd—O22	2.42 (2)
W5—O36	1.76 (2)	Gd—O17	2.45 (2)
W5—O33	1.93 (2)	Gd—O20	2.47 (2)
W5—O35	1.95 (2)	Gd—O18	2.47 (2)
W5—O32	1.98 (2)	Gd—O19	2.49 (2)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71225 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1055]

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Structure of $La_5Mo_{32}O_{54}$ Containing *trans* Bicapped Mo_8 Octahedral Clusters and Tricluster Mo_7–Mo_{10}–Mo_7 Chain Fragments

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Abstract

The crystal structure of $La_5Mo_{32}O_{54}$ contains the new *trans*-face bicapped Mo_8 cluster and a novel Mo_{24} tricluster chain fragment composed of one Mo_{10} and two Mo_7 clusters. The Mo_8 and Mo_{24} clusters are connected by bridging O atoms and are arranged in layers parallel to the *ac* plane. The three crystallographically distinct La^{3+} ions have coordination numbers of 11 or 12 with an environment in each case based on a distorted cubo-octahedron.

Comment

The present work constitutes part of our program in search of new reduced molybdenum oxides in combination with the rare-earth elements. Up to now, this study has led to the synthesis of six new structure types by solid-state reaction: $La_4Mo_2O_{11}$ (Gall & Gougeon, 1992) including isolated Mo_2 dimers, RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm) (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Gougeon & McCarley, 1991) comprising Mo_8 clusters, $R_{16}Mo_{21}O_{56}$ (R = La, Ce, Pr, Nd) (Gall & Gougeon, 1993) showing isolated Mo_{10} clusters, RMo_5O_8 (R = La, Ce, Pr, Nd, Sm, Eu, Gd) (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Gougeon, Gall & Sergent, 1991; Gall, 1990) containing chains of bioctahedral Mo_{10} clusters, $R_4Mo_4O_{11}$ (R = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) (Gougeon, Gall & McCarley, 1991*a*) characterized by infinite chains of *trans*-edge-shared Mo_6 octahedra, and $R_4Mo_{18}O_{32}$ (R = Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) (Gougeon, Gall & McCarley, 1991*b*) which contains three kinds of infinite Mo chains, *i.e.* linear chains with alternate short and long Mo—Mo distances, chains of *trans*-edge-shared rhomboidal Mo_4 clusters and chains of *trans*-edge-shared octahedral Mo_6 clusters. We

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present here the crystal structure of $La_5Mo_{32}O_{54}$ characterized by two novel Mo cluster types.

The basic building blocks of $La_5Mo_{32}O_{54}$ are the new Mo_8 cluster and the novel Mo_{24} tricluster chain fragment, shown in Fig. 1 with their oxygen environments. These cluster units also share some of their O atoms so that the clusters are arranged in layers parallel to the *ac* plane (Fig. 2). The La^{3+} ions occupy voids in these layers between the Mo clusters. The centrosymmetrical Mo_8 cluster is formed by capping two opposite faces of an Mo_6 octahedron. It constitutes the second example of the Mo_8-type cluster found in reduced molybdenum oxides. Indeed, the first example, which corresponds to the *cis*-edge-shared form, has recently been observed in the series RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm) (Leligny *et al.*, 1990; Gougeon & McCarley, 1991). The Mo—Mo distances within the *trans*-bicapped Mo_8 cluster range from 2.5728 (9) to 2.7777 (8) Å. The average value is 2.705 Å and is slightly shorter than that observed for the *cis*-edge-shared Mo_8 cluster occurring in $NdMo_8O_{14}$ (2.731 Å). With the exception of the two capping Mo atoms, which are surrounded by six O atoms forming a distorted octahedron, the other Mo atoms are bonded to five O atoms in an approximately square-pyramidal symmetry. The Mo—O distances range from 2.019 (5) to 2.148 (5) Å with an average of 2.069 Å (2.050 Å for the *cis*-edge-shared form).

The second novel feature of the title compound is the occurrence of the unexpected chain-like $Mo_{24}O_{60}$ cluster unit. Its Mo core consists of one Mo_{10} and two Mo_7 clusters strongly linked through an Mo—Mo bond of 2.7688 (9) Å [Mo(11)—Mo(12)] and four weaker bonds of 2.9916 (9) [Mo(10)—Mo(12)], 3.0053 (9) [Mo(9)—Mo(12)], 3.0373 (9) [Mo(11)—Mo(13)] and 3.0637 (9) Å [Mo(11)—Mo(14)] according to the sequence Mo_7–Mo_{10}–Mo_7. This intercluster linkage is identical to that encountered between the Mo_6 clusters in $BaMo_6O_{10}$ (Lii, Wang & Wang, 1988) and between the Mo_{10} clusters in MMo_5O_8. The Mo_7 cluster is new to reduced molybdenum oxides and is formed by capping one face of a distorted octahedron. In the chain fragment, the two Mo_7 clusters are related through an inversion point which lies at the center of the Mo_{10} cluster. The latter is similar to that previously found in the $Ce_{16}Mo_{21}O_{56}$ (Gall & Gougeon, 1993) and MMo_5O_8 compounds and consists of two distorted Mo_6 octahedra sharing an edge. Within the Mo_7 cluster, the Mo—Mo distances lie between 2.5561 (9) and 2.7925 (8) Å with the average value of 2.710 Å close to that found for the Mo_8 cluster. As in the latter cluster, the capping Mo atom of the Mo_7 cluster is surrounded by six O atoms forming a distorted octahedron and the remaining six Mo atoms are surrounded by five O atoms in an approximately square-pyramidal geometry. The Mo—O bond lengths vary from 1.957 (5) to 2.140 (5) Å (average 2.059 Å). Within the Mo_{10} cluster, the Mo—Mo distances range from 2.5879 (9) to 2.838 (1) Å, slightly longer than in $Ce_{16}Mo_{21}O_{56}$ and MMo_5O_8 (*ca* 2.60 2.83 Å). The average Mo—Mo distance of 2.740 Å is similar to that calculated for the MMo_5O_8 compounds containing divalent cations [2.736 Å in $CaMo_5O_8$, 2.742 Å in $SrMo_5O_8$ and 2.740 Å in $EuMo_5O_8$ (Gall, 1990)]. The Mo—O dis-

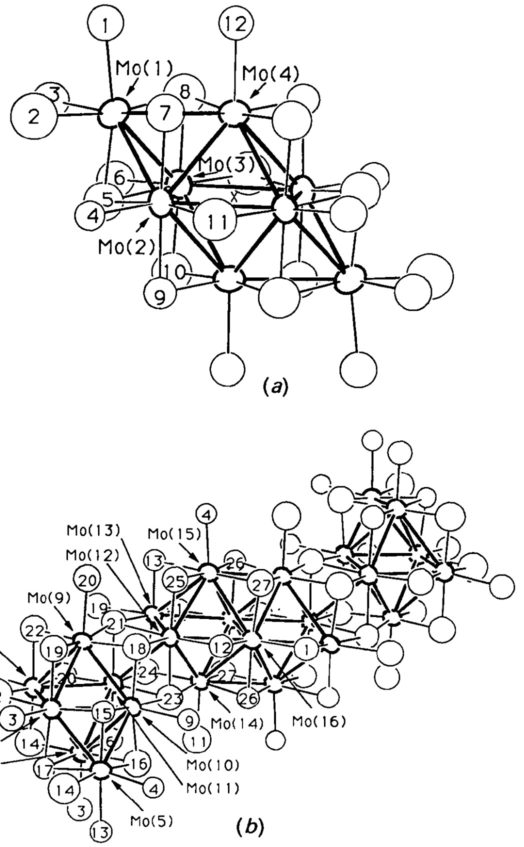

Fig. 1. (*a*) The *trans* bi-face Mo_8 cluster, and (*b*), the tricluster Mo_7–Mo_{10}–Mo_7 chain fragment with their oxygen environments. An inversion center lies at the center of the Mo_8 cluster and at the middle of the Mo(16)—Mo(16) bonds in the tricluster chain fragment.

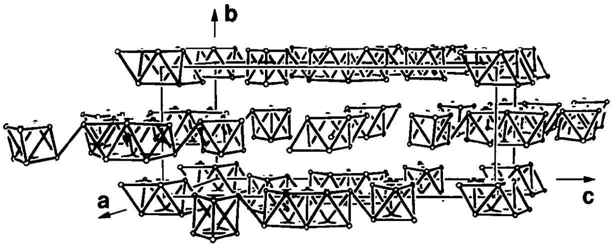

Fig. 2. The arrangement of the Mo_8 clusters and tricluster Mo_7–Mo_{10}–Mo_7 chain fragments within the unit cell.

tances spread over a wide range, 1.919 (5)–2.160 (5) Å, with an average value of 2.064 Å which also corresponds to that found in the $M\mathrm{Mo}_5\mathrm{O}_8$ compounds where $M = \mathrm{Ca}^{2+}$ (2.064 Å), Sr^{2+} (2.064 Å) and Eu^{2+} (2.063 Å) (Gall, 1990). The shortest Mo—Mo intercluster distance is 3.1317 (9) Å and occurs between the Mo_8 clusters and the chain-like Mo_7–Mo_{10}–Mo_7 clusters belonging to the same layer. On the other hand, the spacing between clusters of adjacent layers is as long as 3.580 (1) Å. Consequently, although the structure is three-dimensional overall, it can be considered to be two-dimensional with respect to the Mo network.

The La(1) and La(2) cations are each bonded to 12 O atoms forming a distorted cubo-octahedron. However, the distortion is less pronounced for the La(1) site, located around an inversion center, than for the La(2) site on a general position. For these two sites, the La(1)—O and La(2)—O distances range from 2.572 (5) to 2.748 (5) Å and from 2.477 (5) to 3.206 (5) Å, respectively. La(3) is surrounded by 11 O atoms at distances from 2.405 (5) to 3.142 (5) Å. Its environment can be viewed as a highly distorted cubo-octahedron with one vertex removed.

By using the bond-length–bond-strength formula (Brown & Wu, 1976) for the Mo—O bonds [$s = (d_{\mathrm{Mo—O}}/1.882)^{-6.0}$], the valence of each independent Mo atom was determined as follows: Mo(1) +3.25, Mo(2) +2.90, Mo(3) +2.94, Mo(4) +2.89, Mo(5) +3.38, Mo(6) +2.91, Mo(7) +3.16, Mo(8) +2.92, Mo(9) +3.16, Mo(10) +2.96, Mo(11) +2.70, Mo(12) +2.68, Mo(13) +3.24, Mo(14) +2.88, Mo(15) +2.83 and Mo(16) +2.38. From these values, we can deduce an average Mo oxidation state of +2.99 for the Mo_8 cluster and +3.03 and +2.80 for the Mo_7 and Mo_{10} clusters, respectively (+2.94 for the Mo_{24} chain fragment). The calculated valence of molybdenum in $\mathrm{La}_5\mathrm{Mo}_{32}\mathrm{O}_{54}$ is +2.95 which is in good agreement with that based on the stoichiometry, +2.91. A similar calculation for the La ions [$s = (d_{\mathrm{La—O}}/2.167)^{-6.5}$] leads to +2.95, +2.85 and +2.90 for La(1), La(2) and La(3), respectively. These values are consistent with the expected value of +3 as well as with those observed in other reduced molybdenum oxides containing La^{3+} ions [+2.90 in $\mathrm{LaMo}_{7.7}\mathrm{O}_{14}$ (Leligny *et al.*, 1990), +2.89 in $\mathrm{La}_2\mathrm{Mo}_2\mathrm{O}_7$ (Moini, Subramanian, Clearfield, Di Salvo & McCarroll, 1987) and +2.89 in $\mathrm{LaMo}_5\mathrm{O}_8$ (Gall, 1990)].

Isostructural compounds are also formed with Ce, Pr and Nd as the ternary element.

Experimental

Crystal data

$\mathrm{La}_5\mathrm{Mo}_{32}\mathrm{O}_{54}$
$M_r = 4628.60$
Monoclinic
$P2_1/c$
$a = 10.176$ (1) Å
$b = 9.1471$ (5) Å
$c = 22.910$ (3) Å
$\beta = 105.14$ (7)°
$V = 2058.6$ (4) Å^3
$Z = 2$
$D_x = 7.467$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$30°$
$\mu = 14.37$ mm^{-1}
$T = 295$ K
Irregular
0.16 × 0.12 × 0.12 mm
Black

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.9093$, $T_{\max} = 1.1609$
6637 measured reflections
5465 independent reflections

4316 observed reflections [$I > 2\sigma(I)$]
$R_{\mathrm{int}} = 0.053$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -31 \rightarrow 31$
3 standard reflections
frequency: 90 min
intensity variation: −0.1%

Refinement

Refinement on F
Final $R = 0.028$
$wR = 0.040$
$S = 1.260$
4316 reflections
278 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 1.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 2.6 (1) $\times 10^{-8}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\mathrm{eq}} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
La(1)	0.000	0.000	0.500	0.429 (9)
La(2)	0.23563 (4)	0.99573 (5)	0.20684 (2)	0.551 (7)
La(3)	0.47747 (4)	0.00421 (5)	0.08013 (2)	0.457 (7)
Mo(1)	0.84545 (6)	0.12041 (7)	0.09661 (3)	0.230 (9)
Mo(2)	0.91273 (6)	0.61754 (7)	0.55194 (3)	0.20 (1)
Mo(3)	0.07866 (6)	0.12426 (7)	0.06822 (3)	0.200 (9)
Mo(4)	0.15784 (6)	0.87818 (7)	0.02131 (3)	0.215 (9)
Mo(5)	0.93556 (6)	0.87715 (7)	0.67717 (3)	0.221 (9)
Mo(6)	0.15687 (6)	0.87692 (7)	0.76698 (7)	0.211 (9)
Mo(7)	0.31909 (6)	0.12015 (7)	0.78766 (3)	0.21 (1)
Mo(8)	0.91969 (6)	0.87855 (7)	0.30322 (3)	0.22 (1)
Mo(9)	0.40510 (6)	0.87814 (7)	0.74164 (3)	0.210 (9)
Mo(10)	0.83671 (6)	0.12185 (7)	0.35039 (3)	0.193 (9)
Mo(11)	0.66710 (6)	0.88513 (7)	0.32978 (3)	0.198 (9)
Mo(12)	0.42476 (6)	0.88458 (7)	0.61304 (3)	0.197 (9)
Mo(13)	0.59461 (6)	0.11286 (7)	0.62998 (3)	0.197 (9)
Mo(14)	0.34696 (6)	0.12760 (7)	0.53835 (3)	0.191 (9)
Mo(15)	0.34008 (6)	0.13345 (7)	0.42466 (3)	0.216 (9)
Mo(16)	0.41420 (6)	0.87524 (7)	0.49081 (3)	0.203 (9)
O(1)	0.3337 (5)	0.7562 (6)	0.9173 (2)	0.35 (7)
O(2)	0.2512 (5)	0.9965 (6)	0.8447 (2)	0.57 (8)
O(3)	0.0813 (5)	0.7601 (6)	0.8263 (2)	0.37 (7)
O(4)	0.8335 (5)	0.7480 (6)	0.1038 (2)	0.25 (7)
O(5)	0.0170 (5)	0.9936 (6)	0.1277 (2)	0.41 (7)
O(6)	0.1736 (5)	0.2595 (6)	0.6488 (2)	0.35 (7)
O(7)	0.2715 (5)	0.4989 (6)	0.4757 (2)	0.40 (7)
O(8)	0.0783 (5)	0.7686 (6)	0.4548 (2)	0.44 (8)
O(9)	0.9234 (5)	0.2607 (6)	0.9286 (2)	0.27 (7)

O(10)	0.2535 (5)	0.4986 (6)	0.5965 (2)	0.44 (7)
O(11)	0.8336 (5)	0.7405 (6)	0.9816 (2)	0.49 (8)
O(12)	0.3404 (5)	0.7414 (6)	0.5458 (2)	0.31 (7)
O(13)	0.2471 (5)	0.0098 (6)	0.3479 (2)	0.28 (7)
O(14)	0.8349 (5)	0.7396 (6)	0.2311 (2)	0.52 (8)
O(15)	0.0952 (5)	0.7705 (6)	0.1992 (2)	0.27 (7)
O(16)	0.9977 (5)	0.9913 (6)	0.3824 (2)	0.46 (7)
O(17)	0.0132 (5)	0.9914 (6)	0.2477 (2)	0.27 (7)
O(18)	0.3374 (5)	0.7509 (6)	0.1685 (2)	0.44 (8)
O(19)	0.3256 (5)	0.7384 (6)	0.7886 (2)	0.41 (8)
O(20)	0.4112 (5)	0.2471 (6)	0.2395 (2)	0.43 (7)
O(21)	0.5218 (5)	0.9987 (6)	0.6946 (2)	0.37 (7)
O(22)	0.4951 (5)	−0.0002 (6)	0.8108 (2)	0.45 (7)
O(23)	0.7586 (5)	0.9964 (6)	0.4114 (2)	0.41 (7)
O(24)	0.5726 (5)	0.7457 (6)	0.8831 (2)	0.46 (7)
O(25)	0.5812 (5)	0.7633 (6)	0.1320 (3)	0.38 (7)
O(26)	0.2401 (5)	0.9979 (6)	0.4706 (2)	0.32 (7)
O(27)	0.5661 (5)	0.7816 (6)	0.0055 (2)	0.38 (8)

Table 2. *Selected bond distances* (Å)

Mo_8 cluster			
Mo(1)—Mo(2)	2.5728 (9)	Mo(2)—O(4)	2.019 (5)
Mo(1)—Mo(3)	2.6196 (9)	Mo(2)—O(5)	2.051 (5)
Mo(1)—Mo(4)	2.6930 (9)	Mo(2)—O(11)	2.063 (5)
Mo(1)—Mo(6)	3.1317 (9)†	Mo(2)—O(9)	2.075 (5)
Mo(2)—Mo(4)	2.7380 (9)	Mo(2)—O(7)	2.105 (5)
Mo(2)—Mo(3)	2.7484 (9)	Mo(3)—O(5)	2.031 (5)
Mo(2)—Mo(4)	2.7621 (8)	Mo(3)—O(8)	2.033 (5)
Mo(2)—Mo(3)	2.7777 (8)	Mo(3)—O(11)	2.039 (5)
Mo(3)—Mo(4)	2.7061 (9)	Mo(3)—O(10)	2.060 (5)
Mo(3)—Mo(4)	2.7243 (9)	Mo(3)—O(6)	2.131 (5)
Mo(1)—O(3)	2.045 (5)	Mo(4)—O(9)	2.027 (5)
Mo(1)—O(5)	2.061 (5)	Mo(4)—O(8)	2.033 (5)
Mo(1)—O(8)	2.075 (5)	Mo(4)—O(10)	2.076 (5)
Mo(1)—O(7)	2.089 (5)	Mo(4)—O(7)	2.080 (5)
Mo(1)—O(1)	2.097 (5)	Mo(4)—O(12)	2.101 (5)
Mo(1)—O(2)	2.148 (5)		
Mo_{24} tricluster			
(*a*) Mo_7 subcluster			
Mo(5)—Mo(10)	2.5561 (9)	Mo(6)—O(17)	2.062 (5)
Mo(5)—Mo(6)	2.6240 (8)	Mo(6)—O(19)	2.087 (5)
Mo(5)—Mo(8)	2.6494 (9)	Mo(6)—O(2)	2.096 (5)
Mo(5)—Mo(15)	3.1468 (9)‡	Mo(7)—O(2)	1.983 (5)
Mo(6)—Mo(10)	2.7068 (9)	Mo(7)—O(14)	1.984 (5)
Mo(6)—Mo(9)	2.7357 (9)	Mo(7)—O(20)	2.027 (5)
Mo(6)—Mo(7)	2.7369 (9)	Mo(7)—O(22)	2.050 (5)
Mo(6)—Mo(8)	2.7463 (9)	Mo(7)—O(25)	2.140 (5)
Mo(7)—Mo(9)	2.6945 (9)	Mo(8)—O(3)	2.034 (5)
Mo(7)—Mo(11)	2.7313 (9)	Mo(8)—O(17)	2.055 (5)
Mo(7)—Mo(8)	2.7564 (9)	Mo(8)—O(16)	2.058 (5)
Mo(8)—Mo(10)	2.7037 (9)	Mo(8)—O(6)	2.061 (5)
Mo(8)—Mo(11)	2.7925 (8)	Mo(8)—O(14)	2.084 (5)
Mo(9)—Mo(11)	2.6978 (9)	Mo(9)—O(22)	1.957 (5)
Mo(9)—Mo(10)	2.7913 (9)	Mo(9)—O(19)	1.975 (5)
Mo(9)—Mo(12)	3.0053 (9)§	Mo(9)—O(18)	2.017 (5)
Mo(10)—Mo(11)	2.7322 (9)	Mo(9)—O(21)	2.111 (5)
Mo(10)—Mo(12)	2.9916 (9)§	Mo(9)—O(20)	2.139 (5)
Mo(11)—Mo(12)	2.7688 (9)§	Mo(10)—O(16)	2.005 (5)
Mo(11)—Mo(13)	3.0373 (9)§	Mo(10)—O(15)	2.007 (5)
Mo(11)—Mo(14)	3.0637 (9)§	Mo(10)—O(18)	2.078 (5)
Mo(5)—O(17)	2.053 (5)	Mo(10)—O(9)	2.079 (5)
Mo(5)—O(16)	2.063 (5)	Mo(10)—O(23)	2.117 (5)
Mo(5)—O(15)	2.071 (5)	Mo(11)—O(20)	2.022 (5)
Mo(5)—O(4)	2.073 (5)	Mo(11)—O(6)	2.051 (5)
Mo(5)—O(13)	2.073 (5)	Mo(11)—O(24)	2.112 (5)
Mo(5)—O(14)	2.092 (5)	Mo(11)—O(23)	2.119 (5)
Mo(6)—O(15)	2.029 (5)	Mo(11)—O(21)	2.139 (5)
Mo(6)—O(3)	2.031 (5)		
(*b*) Mo_{10} subcluster			
Mo(12)—Mo(13)	2.6736 (9)	Mo(13)—O(1)	1.958 (5)
Mo(12)—Mo(15)	2.7531 (8)	Mo(13)—O(24)	2.048 (5)
Mo(12)—Mo(16)	2.7755 (9)	Mo(13)—O(21)	2.098 (5)
Mo(12)—Mo(14)	2.7908 (9)	Mo(13)—O(19)	2.160 (5)
Mo(13)—Mo(15)	2.7421 (9)	Mo(14)—O(26)	2.029 (5)
Mo(13)—Mo(16)	2.7474 (9)	Mo(14)—O(11)	2.053 (5)
Mo(13)—Mo(14)	2.8308 (8)	Mo(14)—O(27)	2.060 (5)
Mo(14)—Mo(15)	2.5879 (9)	Mo(14)—O(24)	2.075 (5)
Mo(14)—Mo(16)	2.6839 (9)	Mo(14)—O(23)	2.100 (5)
Mo(14)—Mo(16)	2.7152 (9)	Mo(15)—O(4)	2.011 (5)
Mo(15)—Mo(16)	2.7351 (9)	Mo(15)—O(26)	2.059 (5)
Mo(15)—Mo(16)	2.8013 (9)	Mo(15)—O(25)	2.069 (5)
Mo(16)—Mo(16)	2.838 (1)	Mo(15)—O(13)	2.097 (5)
Mo(12)—O(12)	2.034 (5)	Mo(15)—O(27)	2.124 (5)
Mo(12)—O(25)	2.047 (5)	Mo(16)—O(12)	2.036 (5)
Mo(12)—O(23)	2.106 (5)	Mo(16)—O(26)	2.045 (5)
Mo(12)—O(18)	2.129 (5)	Mo(16)—O(1)	2.058 (5)
Mo(12)—O(21)	2.142 (5)	Mo(16)—O(27)	2.071 (5)
Mo(13)—O(13)	1.919 (5)		
La environments			
La(1)—O(8) (×2)	2.572 (5)	La(2)—O(21)	2.879 (5)
La(1)—O(16) (×2)	2.689 (5)	La(2)—O(20)	2.888 (5)
La(1)—O(26) (×2)	2.699 (5)	La(2)—O(13)	3.206 (5)
La(1)—O(9) (×2)	2.721 (5)	La(3)—O(10)	2.405 (5)
La(1)—O(11) (×2)	2.741 (5)	La(3)—O(22)	2.441 (5)
La(1)—O(23) (×2)	2.748 (5)	La(3)—O(24)	2.536 (5)
La(2)—O(5)	2.477 (5)	La(3)—O(25)	2.593 (5)
La(2)—O(15)	2.487 (5)	La(3)—O(12)	2.653 (5)
La(2)—O(10)	2.582 (5)	La(3)—O(27)	2.726 (5)
La(2)—O(6)	2.596 (5)	La(3)—O(7)	2.738 (5)
La(2)—O(17)	2.666 (5)	La(3)—O(2)	2.847 (5)
La(2)—O(18)	2.708 (5)	La(3)—O(1)	2.905 (5)
La(2)—O(19)	2.835 (5)	La(3)—O(27)	2.947 (5)
La(2)—O(14)	2.837 (5)	La(3)—O(7)	3.142 (5)
La(2)—O(22)	2.873 (5)		

† Between the Mo_8 cluster and the Mo_{10} subcluster.
‡ Between the Mo_7 and Mo_{10} subclusters of different triclusters.
§ Between the Mo_7 and Mo_{10} subclusters of the same tricluster.

Single crystals were obtained by heating a mixture of overall composition '$La_6Mo_{31.5}O_{62.5}$' (starting materials: La_2O_3, MoO_3 and Mo) in a sealed molybdenum crucible at about 2273 K for 5 min. The crucible was then cooled at a rate of 100 K h^{-1} to 1300 K and finally furnace cooled to room temperature.

Data were corrected for Lorentz-polarization effects and an empirical absorption correction (*DIFABS*; Walker & Stuart, 1983) was applied to isotropically refined data. The structure was solved with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. A refinement of the occupancy factors for the La sites confirmed that they are fully occupied. All calculations were performed with the *MolEN* (Fair, 1989) programs on a Digital MicroVAX 3100.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71087 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1032]

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Structure of UOSe

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Abstract

The structure of UOSe, uranium oxyselenide, has been determined from a single crystal at 113 K. UOSe is isostructural with UOS and is of the PbFCl structure type. The structure contains a nine-coordinate U atom bonded to five Se atoms and four O atoms in a distorted tricapped trigonal prismatic arrangement. The U—Se distances are 3.012 (5) and 3.080 (5) Å; the U—O distance is 2.346 (4) Å.

Comment

A single crystal of UOSe was discovered in the reaction products of a combination of K_2Se, Cu, U and Se. In an attempt to explore further the synthesis of quaternary chalcogenides that are related to the recently reported series of compounds $KCuZrQ_3$ (Mansuetto, Keane & Ibers, 1992) and $NaCuMQ_3$ (Mansuetto, Keane & Ibers, 1993) K_2Se, Cu, U, and Se were combined in a molar ratio of 1:1:1:3. The mixture was loaded into a quartz tube under an argon atmosphere and evacuated to approximately 10^{-4} Torr (1 Torr = 133.322 Pa) and then sealed. The tube was heated in a furnace from room temperature to 1223 K over 7 h and held there for 1 week before being cooled back to room temperature at 4 K h^{-1}. A flat needle of UOSe was extracted from the melt by washing away the excess flux with water. The oxygen is presumed to have come from the quartz.

The structure of UOSe was first determined from powder data (Ferro, 1954) and found to be isostructural with UOS (Zachariasen, 1949). In the present work, this structure of UOSe has been confirmed and refined from data collected from a single crystal at 113 K. The structure is of the PbFCl type (Nieuwenkamp & Bijvoet, 1932) and comprises a nine-coordinate U atom in a distorted tricapped trigonal prism of five Se atoms and four O atoms. A view down the *b* axis is given in Fig. 1. The U—Se distances are comparable to those found in α-USe_2 [2.880–3.133 Å (Beck & Dausch, 1989)] and U_3Se_5 [2.80–3.18 Å (Moseley, Brown & Whittaker, 1972)], while the U—O distance agrees with that of 2.363 Å in UO_2 (Rundle, Baenziger, Wilson & McDonald, 1948).

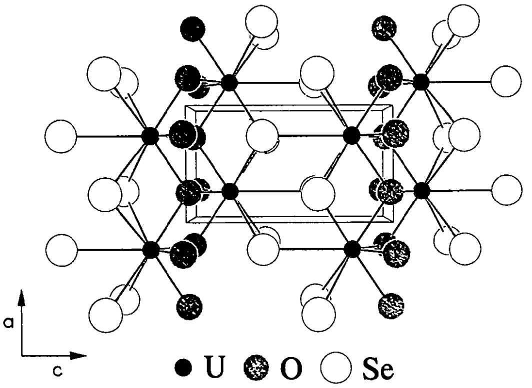

Fig. 1. View of UOSe down [010] with atoms labeled.

Experimental

Crystal data

UOSe
M_r = 332.99
Tetragonal
$P4/nmm$
a = 3.885 (4) Å
c = 6.947 (4) Å
V = 104.9 (2) Å^3
Z = 2
D_x = 10.547 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7093 Å
Cell parameters from 21 reflections
θ = 7.43–17.80°
μ = 94.31 mm^{-1}
T = 113 K
Flat needle
0.372 × 0.048 × 0.002 mm
Black

Data collection

Picker diffractometer
θ–2θ scans

R_{int} = 0.0644
θ_{max} = 30.07°

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