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Structure of $La_4Mo_2O_{11}$ Containing Isolated Mo_2O_{10} Cluster Units

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Abstract. $La_4Mo_2O_{11}$, $M_r = 923.51$, tetragonal, $P4_2/n$, $a = 12.989$ (1), $c = 5.6523$ (7) Å, $V = 953.6$ (1) Å^3, $Z = 4$, $D_x = 6.432$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 201.5$ cm^{-1}, $F(000) = 1600$, $T = 295$ K, $R = 0.018$ for 1478 observed reflections. $La_4Mo_2O_{11}$ is isostructural with $Nd_4Re_2O_{11}$ and contains isolated Mo_2O_{10} units. The Mo—Mo distance is 2.5905 (5) Å and the Mo—O distances are in the range 1.847 (2)–2.207 (2) Å. The units are interconnected with LaO_8 pseudo cubes and bicapped trigonal prisms in which the ranges of the La—O distances are 2.3853 (2)–2.637 (2) Å and 2.368 (2)–2.903 (2) Å respectively.

Introduction. Over the past several years, numerous studies have been made on the reduced oxides of molybdenum in combination with the rare earths and yttrium. However, only a few compounds have been well characterized crystallographically, mainly because of the lack of single crystals. Recently, by using high-temperature solid-state synthesis (s.s.s.) in a sealed molybdenum crucible and fused salt electrolysis (f.s.e.), single crystals of various rare-earth molybdenum oxides were obtained. Most of these compounds are characterized by strong Mo—Mo bonds which lead to the formation of quasi-discrete Mo clusters or infinite Mo chains. Thus, Mo_2 pairs and Mo_8 clusters formed by capping two faces of an Mo_6 octahedron occur, respectively, in $La_2Mo_2O_7$

[f.s.e. (Moini, Subramanian, Clearfield, Di Salvo & McCarroll, 1987)] and MMo_8O_{14} [f.s.e., $M =$ La (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990); s.s.s., $M =$ La, Ce, Pr and Nd (Gougeon & McCarley, 1991)]. Infinite chains having either the Mo_2, Mo_6 or Mo_{10} cluster as repeat unit are observed in $M_5Mo_2O_{12}$ [f.s.e., $M =$ Y, Gd and Dy (Torardi, Fecketter, McCarroll & Di Salvo, 1985)], $M_4Mo_4O_{11}$ [s.s.s., $M =$ Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (Gougeon, Gall & McCarley, 1991a)] and MMo_5O_8 [s.s.s., $M =$ La, Ce, Pr, Nd, Sm, Eu and Gd (Gougeon, Gall & Sergent, 1991)], respectively. Moreover, the first two types of chains along with chains made up of fused Mo_4 rhomboids have been obtained in $M_4Mo_{18}O_{32}$ [s.s.s., $M =$ Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (Gougeon, Gall & McCarley, 1991b)]. Finally, one quaternary structure type containing Mo_3 triangles with infinite Mo_2 chains [$La_3Mo_4XO_{14}$, $X =$ Si, $Mo_{1/3}Al_{2/3}$; f.s.e. (Betteridge, Cheetham, Howard, Jakubicki & McCarroll, 1984; McCarroll, Podejko, Cheetham, Thomas & Di Salvo, 1986)] has been the subject of a single-crystal X-ray study. We present here the crystal structure of $La_4Mo_2O_{11}$ containing Mo_2 dimers included in Mo_2O_{10} units. This new Mo compound is isostructural with $Nd_4Re_2O_{11}$ (Wilhelmi, Lagervall & Muller, 1970).

Experimental. Single crystals were obtained by heating a stoichiometric mixture of La_2O_3, MoO_3 and Mo in a sealed molybdenum crucible at about

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
La(1)	0.18158 (2)	0.11740 (2)	0.49603 (4)	0.385 (3)
La(2)	0.69731 (2)	0.11248 (2)	0.07729 (4)	0.416 (3)
Mo	0.59073 (2)	0.02427 (2)	0.57699 (6)	0.319 (4)
O(1)	0.7028 (2)	0.1477 (2)	0.5023 (5)	0.59 (4)
O(2)	0.3063 (2)	0.0298 (2)	0.2018 (5)	0.45 (4)
O(3)	0.5466 (2)	0.1255 (2)	0.7829 (5)	0.67 (4)
O(4)	0.3401 (2)	0.0433 (2)	0.6771 (5)	0.49 (4)
O(5)	0.5005 (2)	0.0849 (2)	0.3120 (5)	0.58 (4)
O(6)	0.250	0.250	0.250	0.50 (6)
O(7)	0.250	0.250	0.750	0.54 (6)

Table 2. *Selected bond distances* (Å)

Mo—Mo	2.5905 (5)		
Mo—O(3)	1.847 (2)	Mo—O(2)	1.961 (2)
Mo—O(4)	1.908 (2)	Mo—O(5)	2.059 (2)
Mo—O(5)	1.951 (2)	Mo—O(1)	2.207 (2)
La(1)—O(6)	2.3853 (2)	La(2)—O(1)	2.368 (2)
La(1)—O(7)	2.4118 (2)	La(2)—O(2)	2.430 (2)
La(1)—O(2)	2.474 (2)	La(2)—O(1)	2.447 (2)
La(1)—O(4)	2.492 (2)	La(2)—O(4)	2.502 (2)
La(1)—O(3)	2.575 (2)	La(2)—O(1)	2.520 (2)
La(1)—O(2)	2.585 (2)	La(2)—O(3)	2.574 (2)
La(1)—O(4)	2.635 (2)	La(2)—O(3)	2.716 (2)
La(1)—O(5)	2.637 (2)	La(2)—O(5)	2.903 (2)

1980 K for 48 h, cooling the crucible at 100 K h⁻¹ to 1300 K, and finally furnace cooling to room temperature.

An irregular-shaped crystal with dimensions $0.040 \times 0.042 \times 0.320$ mm (density not measured) was selected for the intensity data collection carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $12 \le 2\theta \le 26°$. The systematic absences ($hk0$, $h + k = 2n + 1$ and $00l$, $l = 2n + 1$) allow the space group to be $P4_2/n$. 1954 reflections were recorded in the range $2 \le 2\theta \le 64°$ with h: $0 \to 19$, k: $0 \to 19$, l: $0 \to 8$; ω–2θ mode was used with scan width $\Delta\omega = (1.00 + 0.35\text{tg}\theta)°$ and counter aperture $\Delta l = (2 + 0.5\text{tg}\theta)$ mm. Three orientation- and three intensity-control reflections were checked every 250 reflections and every hour respectively, and showed no significant variation. Data were corrected for Lorentz–polarization effects. An empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The minimum and maximum correction factors were 0.912 and 1.087. After averaging ($R_{int} = 0.013$), 1623 unique data were used to solve the structure with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. The function minimized in the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$. The refinement of all atoms anisotropically and of an extinction coefficient (78 variables) converged to $R = 0.018$, $wR = 0.024$, $S = 1.498$ for 1478 reflections with $F_o^2 > 2\sigma(F_o^2)$. The largest shift/e.s.d. was < 0.01. Maximum and minimum electron densities in the final difference Fourier map were 1.28 and -1.64 e Å^{-3} respectively; the final value of g was 2.05×10^{-7} (Stout & Jensen, 1968). A refinement of the occupancy factors for the La sites confirmed that they are fully occupied. Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with the *SDP-Plus* (Frenz, 1985) programs on a Digital MicroVAX 3100. Final atomic coordinates and B_{eq} values are reported in Table 1 and selected interatomic distances in Table 2.*
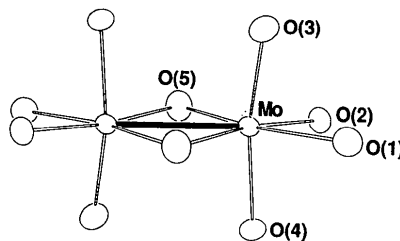
Fig. 1. O-atom numbering scheme in the Mo_2O_{10} dimeric unit.
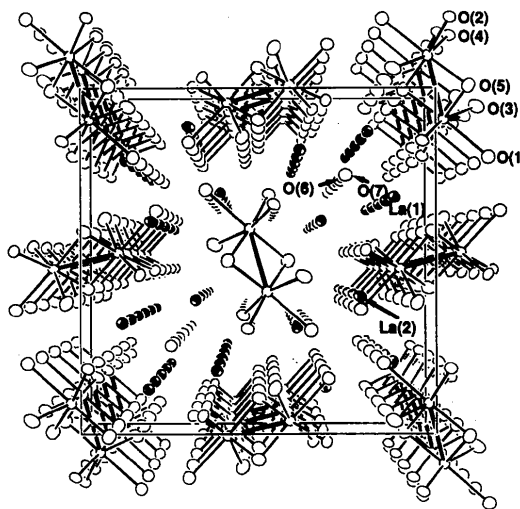
Fig. 2. Structure of $La_4Mo_2O_{11}$ viewed down the c axis. Mo—Mo bonds are shown by thick lines, Mo—O bonds by thin lines.

Discussion. The structure of $La_4Mo_2O_{11}$ is composed of isolated Mo_2O_{10} cluster units resulting from the edge sharing of two highly distorted MoO_6 octahedra related by an inversion centre (Fig. 1). These cluster units are held together by the La atoms to form the three-dimensional framework (Fig. 2). The distance between the two Mo atoms of the dimeric unit is 2.5905 (5) Å and corresponds approximately to a single bond. This is longer than the distance observed in the Mo_2 pairs occurring in $La_2Mo_2O_7$ [2.478 (4) Å], $Y_5Mo_2O_{12}$ [2.496 (1) Å] and MoO_2 [2.511 (1) Å] (Brant & Skapski, 1967) in which the formal Mo oxidation state is lower. In the last mentioned two compounds, the Mo_2 dimers form quasi-linear chains and are separated from each other by 3.221 (1) and 3.112 (1) Å respectively. In $La_2Mo_2O_7$, the Mo_2O_{10} units share corners in two dimensions to form layers which are separated from each other by the La atoms. The shortest distance between Mo_2 groups is 5.3684 (5) Å in $La_4Mo_2O_{11}$ and 3.888 Å in $La_2Mo_2O_7$. In $Nd_4Re_2O_{11}$, the Re atoms in the pairs are only 2.421 (1) Å apart, which reflects the presence of an Re=Re double bond. The Mo—O distances spread over a wide range, 1.847 (2)–2.207 (2) Å, with a mean value of 1.989 Å. The La(1) atoms and their O-atom environment are in a somewhat deformed fluorite arrangement. The La(1)—O distances are in the range 2.3853 (2)–2.637 (2) Å, with a mean value of 2.524 Å. The coordination around La(2) is also eightfold and can be described as a trigonal prism whose two rectangular faces are capped. The La(2)—O distances are in the range 2.368 (2)–2.903 (2) Å, with a mean value of

2.558 Å. The shortest distance between La atoms is 3.8258 (3) Å [La(2)–La(2)].

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Structure of Potassium Hexarhenium Nonabromide Pentasulfide: KRe6S5Br9

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Abstract. $K^+.[Re_6(S_5Br_3)Br_6]^-$, $M_r = 2035.80$, monoclinic, $C2/c$, $a = 16.914$ (11), $b = 9.526$ (4), $c = 17.671$ (11) Å, $\beta = 127.41$ (2)°, $V = 2261.5$ Å^3, $Z = 4$, $D_x = 5.979$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 488.14$ cm^{-1}, $F(000) = 3456$, $T = 293$ K, 101 parameters refined, $R = 0.034$ for 2077 reflections with $I \geq 3\sigma(I)$. The structure consists of a rock-salt-like ionic packing of K cations and complex anions; the latter are built from an octahedral Re_6 cluster surrounded by a pseudo-cube of eight disordered ligands (5 S + 3 Br) and then an octahedron of six terminal Br atoms. In contrast to the parent, but not isostructural compound $KRe_6Se_5Cl_9$, the environment of the K^+ ion is prismatic, instead of being octahedral, the signature of steric constraints.

Introduction. A number of members of the series $M^+.[Re_6Y_5X_9]^-$ have been previously synthesized

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