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$La_5Mo_6O_{21}$: a novel ternary reduced molybdenum oxide containing $\{Mo^{IV}\}_3$ clusters and isolated Mo^V centres

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The crystal structure of $La_5Mo_6O_{21}$ (pentalanthanum hexamolybdenum henicosaoxide) is made up of Mo_3O_{13} units containing triangular $\{Mo^{IV}\}_3$ clusters, three distorted Mo^VO_6 octahedral units and six interstitial La^{III} atoms. The Mo_3O_{13} unit consists of three edge-sharing $Mo^{IV}O_6$ units involving Mo—Mo bonding. The three Mo^VO_6 octahedra share their corners or edges with each other and with the Mo_3O_{13} units.

Comment

The $M_2Mo_3O_8$ compounds (M = Mg, Zn, Fe, Co, Ni, Zn and Cd) were the first identified reduced molybdenum compounds containing Mo_3O_{13} cluster units made up of three edge-sharing octahedral MoO_6 units (McCarroll *et al.*, 1957). In these compounds, the Mo atoms form strongly bonded triangular clusters containing six *d* electrons that fill three bonding orbitals. Six-electron Mo_3 clusters are also found in the quaternary compounds $LiRMo_3O_8$ (R = Sc, Y, In, Sm, Gd, Tb, Dy, Ho, Er and Yb; McCarroll, 1977). Subsequently, Mo_3 clusters containing seven *d* electrons were observed in $LiZn_2Mo_3O_8$ and $ScZnMo_3O_8$, and clusters containing eight electrons were observed in $Zn_3Mo_3O_8$ (Torardi & McCarley, 1985). In addition, the Mo_3O_{13} cluster unit has also been observed in co-existence with the tetrahedral MoO_4 unit in $Na_2In_2Mo_5O_{16}$ (Collins *et al.*, 1989) and with the octahedral MoO_6 unit in $La_3Mo_4SiO_{16}$ (Betteridge *et al.*, 1984). In $Na_2In_2Mo_5O_{16}$, the number of electrons per Mo_3 cluster has been evaluated as six, the Mo atom of the MoO_4 unit having a valence of +6. The present paper reports the synthesis and crystal structure of a new Mo_3O_{13} cluster compound, $La_5Mo_6O_{21}$. The structure of $La_5Mo_6O_{21}$ is made up of Mo_3O_{13} units containing triangular Mo_3 clusters (Fig. 1) and distorted MoO_6 octahedra that are corner- or edge-shared in a complex manner, as shown in Fig. 2. The Mo_3O_{13} units share atoms O14 and O17 to form infinite chains parallel to the *a* axis. The Mo—Mo distances within the Mo_3 triangle are 2.5548 (6), 2.5574 (6) and 2.5672 (4) Å, with an average value of 2.560 Å. This value differs from the values of 2.524 (2) and 2.6164 (5) Å found in $Zn_2Mo_3O_8$ and $Na_2In_2Mo_5O_{16}$, respectively, which also contain six *d* electrons per Mo_3O_{13} cluster. Furthermore, the shortest intercluster Mo—Mo distance is here 3.1489 (4) Å, compared with 3.1695 (5) and 3.235 (2) Å in $Na_2In_2Mo_5O_{16}$ and $Zn_2Mo_3O_8$, respectively. The Mo—O distances around atoms Mo1, Mo2 and Mo6 range from 1.785 (4) to 2.236 (4) Å, while those around the Mo atoms of the Mo_3 cluster are between 1.924 (4) and 2.110 (4) Å. From these Mo—O bonds, we could estimate the oxidation state of each independent Mo atom by using the empirical bond-length–bond-strength relationship developed by Brown & Wu (1976) for Mo—O bonds: $s(\text{Mo—O}) = [d(\text{Mo—O})/1.882]^{-6}$; in this formula, s(Mo—O) is the bond strength in valence units, d(Mo—O) is the observed Mo—O bond distance in Ångströms, 1.882 Å corresponds to an Mo—O single-bond distance and the exponential parameter −6 is characteristic of the Mo atom. These calculations for atoms Mo1, Mo2 and Mo6 resulted in values of +4.89 (5), +4.80 (5) and +5.03 (5), which are very close to the ideal value of +5. For atoms Mo3,

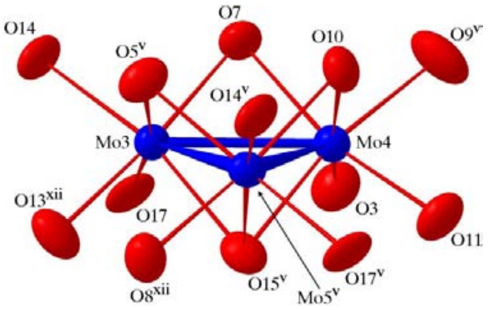

Figure 1
A view of the Mo_3O_{13} units. Displacement ellipsoids are drawn at the 97% probability level. [Symmetry codes: (v) $x + 1, y, z$; (xii) $-x + 3, y - \frac{1}{2}, -z + \frac{1}{2}$.]

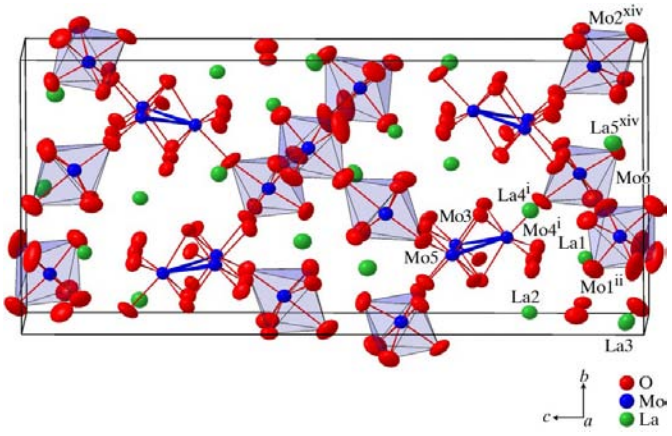

Figure 2
A view of the structure of $La_5Mo_6O_{21}$. [Symmetry codes: (i) $x - 1, y, z$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (xiv) $x, y + \frac{1}{2}, z$.]

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Mo4 and Mo5 forming the Mo_3 cluster, the calculated oxidation states are +3.86 (4), +4.08 (5) and +3.74 (5), respectively. Consequently, we could evaluate as six the number of electrons per Mo_3 cluster in $La_5Mo_6O_{21}$. The La atoms are surrounded by eight, nine or ten O atoms, forming complex polyhedra. The La—O distances range from 2.387 (4) to 3.007 (4) Å.

Experimental

Single crystals of $La_5Mo_6O_{21}$ were prepared from a stoichiometric mixture of La_2O_3, MoO_3 and Mo. 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 the rate of 300 K h^{-1} to 2223 K; the temperature was held for 5 min, then reduced at a rate of 100 K h^{-1} to 1373 K and finally allowed to cool in the furnace.

Table 1
Selected interatomic distances (Å).

La1—O3$^{\mathrm{i}}$	2.437 (5)	La5—O2$^{\mathrm{xi}}$	2.682 (5)
La1—O12$^{\mathrm{i}}$	2.481 (4)	La5—O13$^{\mathrm{x}}$	2.702 (5)
La1—O18	2.489 (5)	La5—O5$^{\mathrm{iv}}$	2.850 (3)
La1—O11$^{\mathrm{i}}$	2.513 (5)	Mo1—O4	1.797 (4)
La1—O1	2.546 (5)	Mo1—O20	1.915 (4)
La1—O4$^{\mathrm{ii}}$	2.597 (4)	Mo1—O19$^{\mathrm{ii}}$	1.947 (4)
La1—O21$^{\mathrm{ii}}$	2.716 (5)	Mo1—O21	2.002 (4)
La1—O19	2.729 (4)	Mo1—O18$^{\mathrm{ii}}$	2.033 (4)
La1—O20	2.910 (5)	Mo1—O18	2.090 (4)
La1—O9	2.929 (4)	Mo2—O1	1.877 (5)
La2—O11$^{\mathrm{i}}$	2.438 (4)	Mo2—O14$^{\mathrm{iv}}$	1.882 (3)
La2—O3	2.457 (5)	Mo2—O2	1.889 (5)
La2—O1	2.471 (5)	Mo2—O16$^{\mathrm{i}}$	1.980 (5)
La2—O12	2.494 (5)	Mo2—O12$^{\mathrm{i}}$	1.994 (4)
La2—O17	2.579 (3)	Mo2—O20	2.236 (4)
La2—O7$^{\mathrm{iii}}$	2.608 (5)	Mo3—O5$^{\mathrm{v}}$	1.963 (4)
La2—O10$^{\mathrm{iii}}$	2.653 (5)	Mo3—O13$^{\mathrm{xii}}$	1.987 (5)
La2—O5$^{\mathrm{iv}}$	2.840 (3)	Mo3—O17	2.013 (4)
La3—O12	2.443 (5)	Mo3—O7	2.025 (5)
La3—O16	2.462 (4)	Mo3—O15$^{\mathrm{v}}$	2.087 (4)
La3—O6$^{\mathrm{ii}}$	2.489 (4)	Mo3—O14	2.104 (4)
La3—O4$^{\mathrm{ii}}$	2.537 (5)	Mo3—Mo4	2.5574 (6)
La3—O1	2.627 (5)	Mo3—Mo5$^{\mathrm{v}}$	2.5672 (4)
La3—O20	2.643 (4)	Mo4—O11	1.924 (4)
La3—O2	2.658 (5)	Mo4—O3	1.958 (4)
La3—O21$^{\mathrm{v}}$	2.728 (5)	Mo4—O10	2.016 (5)
La3—O18$^{\mathrm{ii}}$	2.954 (6)	Mo4—O7	2.048 (4)
La4—O7$^{\mathrm{v}}$	2.536 (5)	Mo4—O15$^{\mathrm{v}}$	2.060 (3)
La4—O10	2.598 (4)	Mo4—O9$^{\mathrm{v}}$	2.069 (4)
La4—O15$^{\mathrm{vi}}$	2.617 (3)	Mo4—Mo5$^{\mathrm{v}}$	2.5548 (6)
La4—O13	2.622 (5)	Mo5—O17	1.985 (3)
La4—O11	2.636 (5)	Mo5—O5	1.986 (4)
La4—O3$^{\mathrm{v}}$	2.638 (5)	Mo5—O10$^{\mathrm{i}}$	2.019 (5)
La4—O19$^{\mathrm{vii}}$	2.648 (5)	Mo5—O8$^{\mathrm{iii}}$	2.055 (5)
La4—O8	2.749 (5)	Mo5—O15	2.086 (3)
La4—O9$^{\mathrm{v}}$	2.755 (4)	Mo5—O14	2.110 (4)
La4—O9$^{\mathrm{vii}}$	3.007 (4)	Mo6—O6	1.785 (4)
La5—O2	2.387 (4)	Mo6—O9	1.901 (4)
La5—O16	2.442 (5)	Mo6—O8$^{\mathrm{i}}$	1.961 (4)
La5—O6$^{\mathrm{viii}}$	2.556 (4)	Mo6—O13$^{\mathrm{xiii}}$	1.962 (4)
La5—O16$^{\mathrm{ix}}$	2.627 (5)	Mo6—O21$^{\mathrm{ii}}$	2.049 (4)
La5—O8$^{\mathrm{x}}$	2.638 (5)	Mo6—O19	2.073 (4)

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

Crystal data

$La_5Mo_6O_{21}$
$M_r = 1606.19$
Orthorhombic, $P2_12_12_1$
$a = 5.71550$ (5) Å
$b = 11.2429$ (1) Å
$c = 25.2146$ (2) Å
$V = 1620.26$ (2) Å^3
$Z = 4$
$D_x = 6.584$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 48 314 reflections
$\theta = 1$–40.3°
$\mu = 17.45$ mm^{-1}
$T = 293$ (2) K
Needle, black
0.45 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ scans ($\kappa = 0$) plus additional ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.116$, $T_{\max} = 0.690$
34 498 measured reflections

9991 independent reflections
9029 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.081$
$\theta_{\max} = 40.3°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = -44 \rightarrow 45$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.088$
$S = 1.07$
9991 reflections
291 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 6.5608P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 4.10$ e Å^{-3}
$\Delta\rho_{\min} = -4.15$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00036 (6)
Absolute structure: Flack (1983), 4349 Friedel pairs
Flack parameter: 0.393 (12)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

Intensity data were collected on the diffractometer system of the 'Centre de Diffractométrie de l'Université de Rennes I' (http://www.cdifx.univ-rennes1.fr).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1055). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bergerhoff, G. (1996). *DIAMOND*. University of Bonn, Germany.

Betteridge, P. W., Cheetham, A. K., Howard, J. A. K., Jakubicki, G. & McCarroll, W. H. (1984). *Inorg. Chem.* **23**, 737–740.

Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.

Collins, B. T., Fine, S. M., Potenza, J. A., Tsai, P. P. & Grennblatt, M. (1989). *Inorg. Chem.* **28**, 2444–2447.

Duisenberg, A. J. M. (1998). PhD thesis, University of Utrecht, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

McCarroll, W. H. (1977). *Inorg. Chem.* **16**, 3351–3353.

McCarroll, W. H., Katz, L. & Ward, R. (1957). *J. Am. Chem. Soc.* **79**, 5410–5414.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Torardi, C. C. & McCarley, R. E. (1985). *Inorg. Chem.* **24**, 476–481.