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Redetermination of the Structure of $LaMo_5O_8$ by Single-Crystal X-ray Diffraction

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Abstract

We have redetermined the structure of $LaMo_5O_8$ by single-crystal X-ray diffraction. Its structure has been determined previously by powder X-ray and neutron diffraction with rather high *R* factors resulting from impurities in the sample. The crystal structure of $LaMo_5O_8$ is based on $Mo_{10}O_{18}$ cluster units, the Mo cores of which are Mo_{10} bioctahedra resulting from the edge-sharing of two Mo_6 octahedra. These bioctahedral $Mo_{10}O_{18}$ cluster units share opposite O atoms to form infinite molybdenum oxide chains in which the Mo_{10} clusters are strongly linked through short Mo—Mo intercluster bonds of 2.6890 (7) Å and two weaker Mo—Mo bonds of 2.9108 (5) and 3.0911 (5) Å. These chains are then interconnected through Mo—O—Mo bonds to create four-sided channels in which the La^{3+} cations reside. The Mo—Mo distances within the Mo_{10} cluster range from 2.6102 (5) to 2.8279 (5) Å (average 2.749 Å). The Mo—O distances are in the range 1.990 (3)–2.146 (3) Å (average 2.076 Å). The La^{3+} cation is surrounded by ten O atoms at distances ranging from 2.443 (3) to 2.919 (3) Å with an eleventh O atom at 3.232 (3) Å.

Comment

The present work constitutes part of our program on the study of the structural and physical properties of the compounds MMo_5O_8 (M = Ca, Sr, Ba, Sn, Pb, La, Ce, Pr, Nd, Sm, Eu and Gd) containing chains of bioctahedral Mo_{10} clusters. The first member to have its structure established was $LaMo_5O_8$. The structure was determined *ab initio* from X-ray and neutron powder diffraction data by Hibble, Cheetham, Bogle, Wakerley & Cox (1988). However, in both cases the *R* values were rather high (0.11 and 0.114, respectively) as a result of impurities in the sample. Thus, the present work deals with the refinement of the crystal structure from new data collected from a single crystal in order to improve the accuracy of the structure and to enable a precise comparison between the structure of this compound and those of the others in the series.

The basic structural building block of $LaMo_5O_8$ is the bioctahedral cluster unit $Mo_{10}O_{18}$ which results from the metal-edge condensation of two Mo_6O_{12}-type cluster units (Fig. 1). The $Mo_{10}O_{18}$ cluster units are then linked on opposite edges *via* common O atoms to form infinite chains in which the Mo_{10} clusters are strongly linked through intercluster Mo—Mo bonds (Fig. 2*a*). These chains, which run parallel to the *a* axis, are then interlinked through O atoms to create one-dimensional four-sided channels where the cations reside (Fig. 2*b*).

Examination of Table 2 shows that the Mo—Mo distances are roughly the same as those established previously from powder samples while the Mo—O and La—O distances are very different. The Mo—Mo distances within the Mo_{10} double octahedron range between 2.6102 (5) and 2.8279 (5) Å with the shortest of these occurring between the apical atoms Mo(3) and Mo(4). The average value is 2.749 Å and does not differ significantly from those observed for the compounds with divalent [$SnMo_5O_8$ 2.746 Å and $PbMo_5O_8$ 2.745 Å (Gougeon, Potel & Sergent, 1990; Dronskowski & Simon, 1989; Dronskowski, Simon & Mertin, 1991)] or trivalent cations [$RE^{3+}Mo_5O_8$ 2.746–2.750 Å (Gougeon, Gall & Sergent, 1991; Gall, 1990, 1993)]. The intercluster distances are 2.6890 (7) (1 ×), 2.9108 (5) (2 ×) and 3.0911 (5) Å (2 ×) and are in the order of corresponding distances in the other compounds containing trivalent rare earth ions. In the $M^{2+}Mo_5O_8$ compounds (M = Ca, Sr, Sn, Pb and Eu) the two shortest intercluster distances Mo(1)—Mo(1) and Mo(1)—Mo(2) are much longer (*ca* 2.77 and 3.04 Å, respectively) while the third intercluster distance Mo(1)—Mo(3) remains about the same as that observed for the $RE^{3+}Mo_5O_8$ compounds. The range of the Mo—O distances in $LaMo_5O_8$ is 1.990 (3)–2.146 (3) Å with an average distance of 2.076 Å, which also corresponds with the data for the remaining $RE^{3+}Mo_5O_8$ compounds (2.074–2.078 Å).

The La^{3+} ions, which are in general positions, are surrounded by ten O atoms at distances ranging from 2.443 (3) to 2.919 (3) Å with an eleventh O atom at 3.232 (3) Å.

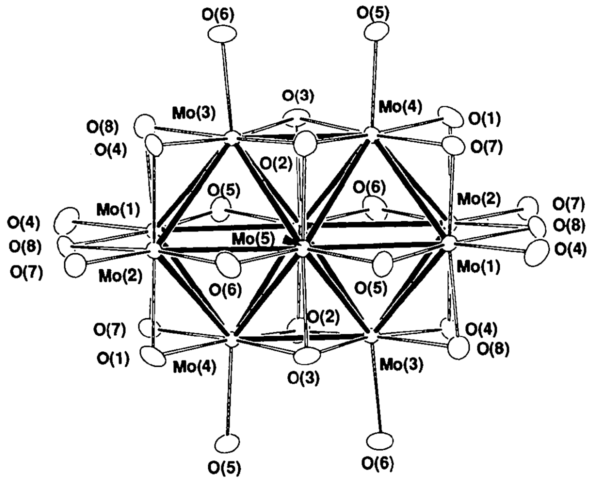

Fig. 1. The $Mo_{10}O_{18}$ cluster unit shown with its eight additional corner-linked O atoms. An inversion centre occurs at the mid-point of the Mo(5)—Mo(5) bond.

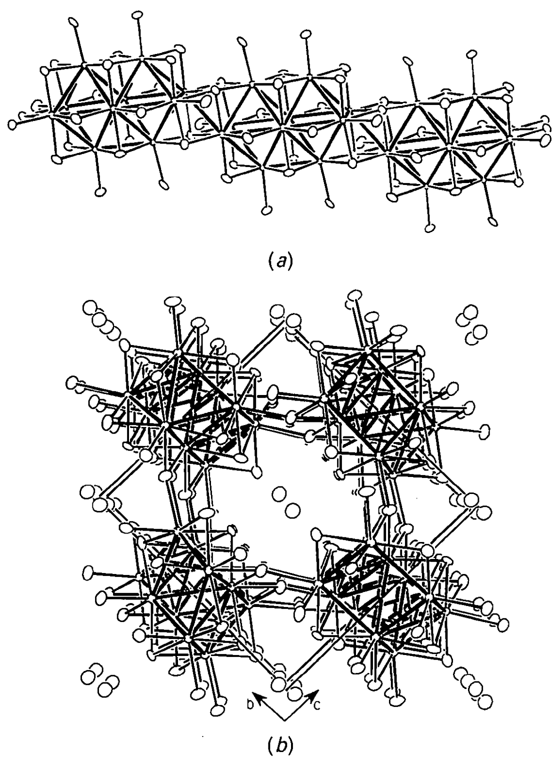

Fig. 2. (*a*) A section of a bioctahedral cluster chain of $LaMo_5O_8$. (*b*) View of the structure down the *a* axis. The unconnected open ellipsoids represent the La^{3+} cations.

Experimental

Single crystals were obtained by heating a stoichiometric mixture (starting materials: La_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

$LaMo_5O_8$
$M_r = 746.61$
Monoclinic
$P2_1/c$
$a = 7.571$ (1) Å
$b = 9.0862$ (7) Å
$c = 9.916$ (1) Å
$\beta = 109.064$ (5)°
$V = 644.8$ (1) Å^3
$Z = 4$
$D_x = 7.691$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.3$–$34.6°$
$\mu = 15.75$ mm^{-1}
$T = 295$ K
Irregular
$0.14 \times 0.12 \times 0.11$ mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.936$, $T_{\max} = 1.119$
3136 measured reflections
2712 independent reflections

2383 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.053$
$\theta_{\max} = 35°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 90 min
intensity variation: −0.1%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.033$
$S = 0.971$
2383 reflections
128 parameters
$w = 1/[\sigma^2(F_o) + 0.0004F_o^2 + 1]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 1.82$ e Å^{-3}
$\Delta\rho_{\min} = -0.81$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $1.024 (4) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$B_{\rm eq}$
La	0.26116 (3)	0.50420 (3)	0.54004 (2)	0.443 (3)
Mo(1)	0.60479 (5)	−0.11487 (4)	0.48630 (4)	0.288 (5)
Mo(2)	0.38294 (5)	−0.11760 (4)	0.67700 (4)	0.305 (5)
Mo(3)	0.17316 (5)	−0.12698 (4)	0.38316 (3)	0.244 (5)
Mo(4)	0.80851 (5)	−0.12966 (4)	0.29787 (3)	0.239 (5)
Mo(5)	−0.00274 (4)	−0.12239 (4)	0.58649 (3)	0.254 (5)
O(1)	0.3973 (4)	0.0060 (4)	0.8483 (3)	0.45 (5)
O(2)	−0.0013 (4)	−0.2223 (3)	0.9331 (3)	0.38 (4)
O(3)	−0.0125 (4)	0.0017 (4)	0.2310 (3)	0.41 (4)
O(4)	0.3922 (4)	−0.2492 (4)	0.0130 (3)	0.45 (5)
O(5)	0.7947 (4)	−0.2427 (4)	0.1152 (3)	0.48 (5)
O(6)	0.2001 (4)	−0.2412 (4)	0.2094 (3)	0.56 (5)
O(7)	0.6049 (4)	−0.2360 (4)	0.8286 (3)	0.44 (5)
O(8)	0.3844 (4)	−0.0069 (5)	0.3286 (3)	0.47 (5)

Table 2. *Selected bond distances* (Å)

The values in column (1) refer to the present study, columns (2) and (3) contain the values calculated with the positional parameters and unit cell obtained from the powder structure analysis using X-ray and neutron diffraction, respectively (Hibble *et al.*, 1988).

	(1)	(2)	(3)
Mo(1)—Mo(2)	2.6816 (5)	2.691	2.751
Mo(1)—Mo(4)	2.7876 (5)	2.786	2.818
Mo(1)—Mo(5)	2.8094 (5)	2.809	2.765

Mo(1)—Mo(3)	2.8124 (5)	2.802	2.771
Mo(1)—Mo(1)*	2.6890 (7)	2.711	2.737
Mo(1)—Mo(2)*	2.9108 (5)	2.905	2.916
Mo(1)—Mo(3)*	3.0911 (5)	3.072	3.066
Mo(2)—Mo(5)	2.7609 (5)	2.771	2.800
Mo(2)—Mo(4)	2.7288 (5)	2.741	2.761
Mo(2)—Mo(3)	2.8279 (5)	2.828	2.837
Mo(3)—Mo(4)	2.6102 (5)	2.642	2.678
Mo(3)—Mo(5)	2.6727 (5)	2.719	2.726
Mo(3)—Mo(5)	2.7558 (5)	2.760	2.785
Mo(4)—Mo(5)	2.7505 (5)	2.741	2.768
Mo(4)—Mo(5)	2.7605 (5)	2.776	2.775
Mo(5)—Mo(5)	2.8172 (7)	2.828	2.825
Mo(1)—O(5)	2.043 (3)	2.010	1.987
Mo(1)—O(7)	2.069 (3)	2.099	2.066
Mo(1)—O(4)	2.113 (3)	2.098	2.107
Mo(1)—O(8)	2.119 (3)	2.093	2.084
Mo(1)—O(8)	2.122 (3)	2.254	2.184
Mo(2)—O(6)	1.990 (3)	1.881	1.984
Mo(2)—O(1)	2.009 (3)	1.964	2.019
Mo(2)—O(4)	2.046 (3)	2.032	2.022
Mo(2)—O(8)	2.110 (3)	2.088	2.119
Mo(2)—O(7)	2.142 (3)	2.135	2.090
Mo(3)—O(3)	2.058 (3)	2.003	2.071
Mo(3)—O(2)	2.072 (3)	1.985	2.096
Mo(3)—O(4)	2.067 (3)	2.114	2.073
Mo(3)—O(6)	2.077 (3)	2.109	2.035
Mo(3)—O(8)	2.146 (3)	2.160	2.101
Mo(4)—O(3)	2.070 (3)	2.083	2.053
Mo(4)—O(7)	2.066 (3)	2.041	2.073
Mo(4)—O(1)	2.078 (3)	2.071	2.034
Mo(4)—O(5)	2.055 (3)	2.089	2.065
Mo(4)—O(2)	2.103 (3)	2.110	2.107
Mo(5)—O(5)	2.055 (3)	1.980	1.989
Mo(5)—O(6)	2.039 (3)	2.022	2.041
Mo(5)—O(2)	2.077 (3)	2.030	2.019
Mo(5)—O(3)	2.086 (3)	2.154	2.127
La—O(1)	2.443 (3)	2.459	2.473
La—O(1)	2.458 (3)	2.503	2.506
La—O(4)	2.487 (3)	2.497	2.556
La—O(7)	2.574 (3)	2.558	2.601
La—O(5)	2.676 (3)	2.775	2.688
La—O(8)	2.704 (3)	2.618	2.709
La—O(3)	2.732 (3)	2.781	2.726
La—O(2)	2.761 (3)	2.772	2.807
La—O(6)	2.860 (3)	2.957	2.919
La—O(2)	2.919 (3)	3.023	2.873
La—O(3)	3.232 (3)	3.163	3.166

Data were corrected for Lorentz–polarization effects and an empirical absorption correction 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 factor for the La site confirmed that it is fully occupied. All calculations were performed with the *MolEN* (Fair, 1990) programs on a Digital MicroVAX 3100.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Short Dynamically Symmetrical Hydrogen Bond in the Structure of $K[Mg(H_{0.5}SO_4)_2(H_2O)_2]$

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Abstract

The Mg atoms in the title compound, magnesium potassium hydrogendisufate(3−) dihydrate, are found at the centres of symmetry at the unit cell corners and are octahedrally coordinated by two water molecules and the O atoms from four SO_4 tetrahedra to form infinite kröhnkite-like $Mg(H_{0.5}SO_4)_2(H_2O)_2$ chains running down the *a* axis. The sulfate and hydrogensulfate ions are coupled to form an $(SO_4HSO_4)^{3-}$ group with O···O 2.478 (3) Å and with the H atom disordered around a symmetric double-minimum potential well. Crossed channels along the *a* and *b* axes are filled by tenfold-coordinated K atoms.