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$CaMo_5O_8$

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$CaMo_5O_8$ (calcium pentamolybdenum octaoxide) crystallizes in the space group $P2_1/c$ and belongs to the $LaMo_5O_8$ structure type. Its crystal structure consists of $Mo_{10}O_{18}$ cluster units, interconnected through Mo—Mo bonds of 2.7669 Å to form infinite molybdenum oxide chains. These are interconnected through Mo—O—Mo bonds to create four-sided channels, in which the Ca^{2+} cations are located.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mo–O) = 0.003 Å
R factor = 0.031
wR factor = 0.073
Data-to-parameter ratio = 31.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Among the reduced molybdenum oxides, the AMo_5O_8 (A = Ca, Sr, Pb, Sn, Eu, La, Ce, Pr, Nd, Sm and Gd) compounds constitute an interesting family, because they can tolerate a change in the number of electrons available for Mo—Mo bonding (often called metal-centred electrons or MCE), induced by the valence of the *A* cation, without a significant change in the basic structure. Consequently, various electrical behaviours are observed as a function of the MCE. If we exclude the Ca compound, all other compounds were obtained as single crystals that allowed studies of the variation of the Mo—Mo and Mo—O distances with respect to the size of the cation and the MCE. $CaMo_5O_8$ was first mentioned by Torardi & McCarley (1981) and the structure was refined using powder data by Steiner & Reichelt (1997). Comparison of various interatomic distances found in $CaMo_5O_8$ by Steiner & Reichelt (1997) with those of the compounds AMo_5O_8 with divalent *A* elements, the structures of which were determined

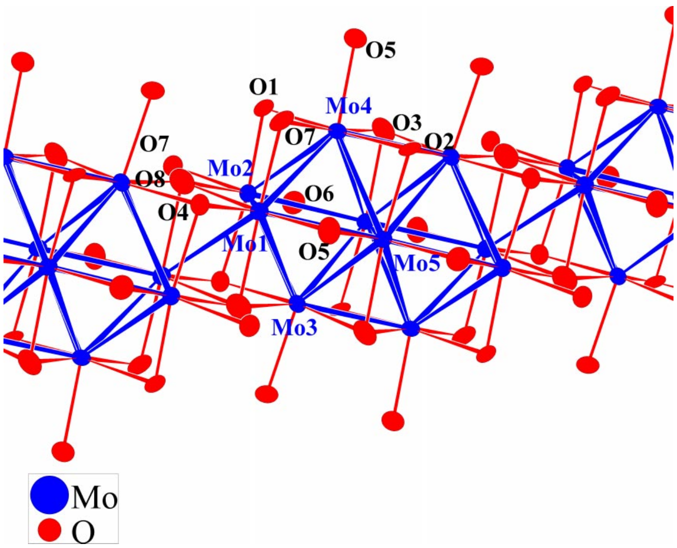

Figure 1
Fragment of a bioctahedral cluster chain of $CaMo_5O_8$. Displacement ellipsoids are drawn at the 97% probability level. Mo—Mo bonds longer than 2.9 Å are not shown.

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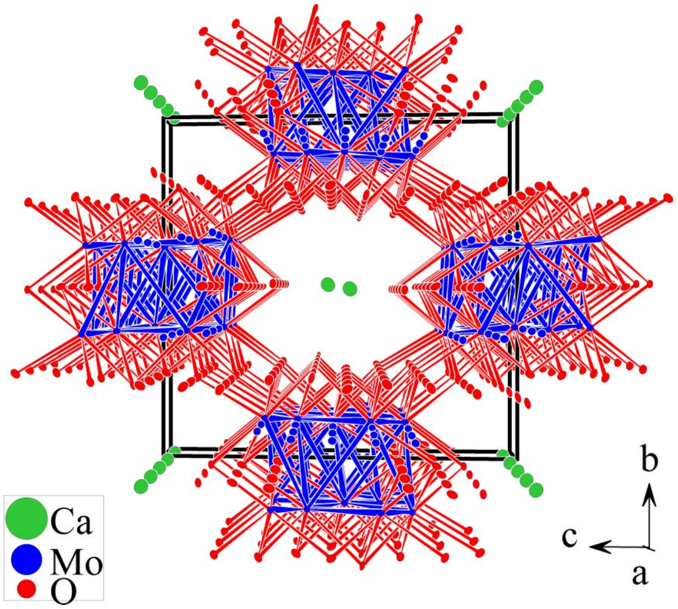

Figure 2
View of $CaMo_5O_8$ along [100].

from single-crystal data, showed large differences. In particular, unexpected Mo—O distances up to 2.4 Å are observed, leading to a mean value of 2.087 Å, inconsistent with the values of 2.062, 2.064 and 2.061 Å found in $SrMo_5O_8$, $SnMo_5O_8$ and $PbMo_5O_8$, respectively. On the other hand, an overall displacement parameter was used in their refinement. Consequently, we found it necessary to refine the structure of $CaMo_5O_8$ from single-crystal data. Our model presents s.u. values about ten times lower for the bonds and all atoms were refined anisotropically. Contrary to the results of Steiner & Reichelt (1997), our results agree perfectly well with the previous refinements made on single crystals of $SrMo_5O_8$ (Gall & Gougeon, 1994), $SnMo_5O_8$ (Gougeon *et al.*, 1990) and $PbMo_5O_8$ (Dronskowski & Simon, 1989; Dronskowski *et al.*, 1991). Thus, the various Mo—O distances are now similar to those of $SrMo_5O_8$, $SnMo_5O_8$ and $PbMo_5O_8$, with an average value of 2.061 Å. The Mo—Mo distances are also close to those reported for $SrMo_5O_8$. This corroborates previous studies that show that the size of the cation has little effect on the Mo—Mo bonds for a given MCE (Gall, 1993). The intercluster Mo1—Mo1 distance which reflects the MCE is now 2.7669 (13) Å and thus close to the value of 2.7651 (9) Å observed in $SrMo_5O_8$ (Gall & Gougeon, 1994), instead of 2.81 (1) Å for the model of Steiner & Reichelt (1997).

Experimental

Single crystals were obtained by heating a stoichiometric mixture of starting materials $CaMoO_4$, MoO_3 and Mo in a sealed molybdenum crucible at *ca* 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

$CaMo_5O_8$
$M_r = 647.78$
Monoclinic, $P2_1/c$
$a = 7.550$ (5) Å
$b = 9.068$ (5) Å
$c = 9.983$ (5) Å
$\beta = 110.07$ (4)°
$V = 642.0$ (6) Å^3
$Z = 4$
$D_x = 6.702$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.3$–16.1°
$\mu = 10.31$ mm^{-1}
$T = 293$ (2) K
Irregular, black
0.12 × 0.11 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.755$, $T_{\max} = 1.00$
4174 measured reflections
3965 independent reflections
2812 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 39.9°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -18 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.073$
$S = 1.05$
3965 reflections
128 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.82P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.99$ e Å^{-3}
$\Delta\rho_{\min} = -2.44$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00189 (13)

Table 1
Selected interatomic distances (Å).

Ca—O1^{i}	2.394 (3)	Mo3—O3	2.042 (3)
Ca—O1^{ii}	2.421 (3)	Mo3—O2^{viii}	2.057 (3)
Ca—O4^{iii}	2.481 (3)	Mo3—O4^{vii}	2.068 (3)
Ca—O7^{ii}	2.592 (3)	Mo3—O6	2.087 (3)
Ca—O5^{iv}	2.647 (3)	Mo3—O8	2.145 (3)
Ca—O3^{v}	2.662 (3)	Mo3—Mo4^{xi}	2.5943 (19)
Ca—O2^{i}	2.689 (3)	Mo3—Mo5^{xii}	2.6957 (12)
Ca—O8^{iii}	2.874 (3)	Mo3—Mo5	2.7541 (13)
Ca—O2^{vi}	3.018 (3)	Mo3—Mo1^{ix}	2.7625 (13)
Ca—O6^{iii}	3.035 (3)	Mo3—Mo2	2.8250 (17)
Mo1—O5^{vii}	2.028 (3)	Mo4—O3^{x}	2.052 (3)
Mo1—O7^{viii}	2.041 (3)	Mo4—O7^{viii}	2.063 (3)
Mo1—O8^{ix}	2.106 (3)	Mo4—O5	2.064 (3)
Mo1—O4^{vii}	2.111 (3)	Mo4—O1^{ix}	2.074 (3)
Mo1—O8	2.122 (3)	Mo4—O2^{xiii}	2.091 (3)
Mo1—Mo2^{ix}	2.6830 (11)	Mo4—Mo3^{x}	2.5943 (19)
Mo1—Mo4	2.7587 (14)	Mo4—Mo5^{x}	2.7229 (16)
Mo1—Mo3^{ix}	2.7625 (13)	Mo4—Mo2^{ix}	2.7373 (12)
Mo1—Mo5^{x}	2.765 (2)	Mo4—Mo1	2.7587 (14)
Mo1—Mo1^{ix}	2.7669 (13)	Mo4—Mo5^{ix}	2.7653 (13)
Mo1—Mo2	3.0343 (15)	Mo5—O5^{xiv}	2.021 (3)
Mo1—Mo3	3.078 (2)	Mo5—O6^{vii}	2.022 (3)
Mo2—O1	1.915 (3)	Mo5—O3^{xii}	2.063 (3)
Mo2—O6^{vii}	1.948 (3)	Mo5—O2^{viii}	2.071 (3)
Mo2—O4^{vii}	2.047 (3)	Mo5—Mo3^{xii}	2.6957 (12)
Mo2—O8^{ix}	2.100 (3)	Mo5—Mo2	2.715 (2)
Mo2—O7	2.117 (3)	Mo5—Mo4^{xi}	2.7229 (16)
Mo2—Mo1^{ix}	2.6830 (11)	Mo5—Mo3	2.7541 (13)
Mo2—Mo5	2.715 (2)	Mo5—Mo4^{ix}	2.7653 (13)
Mo2—Mo4^{ix}	2.7373 (12)	Mo5—Mo1^{xi}	2.765 (2)
Mo2—Mo3	2.8250 (17)	Mo5—Mo5^{xii}	2.8288 (12)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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