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The disordered cluster compound $CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$

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The title compound, calcium pentamolybdenum titanium decaoxide, is isomorphous with the $AMo_5(Ti_{0.7}Mo_{0.3})O_{10}$ (A = Sr and Eu) compounds. The smaller size of calcium induces a higher molybdenum content on the capping sites of the bioctahedral Mo_{10} clusters, leading to more Mo_{11} and Mo_{12} clusters in the crystal structure. The oxygen framework derives from the stacking of close-packed layers along the a direction in the $\ldots ABAC \ldots$ sequence. The Ca^{2+} ions occupy large cavities which result from the fusion of two cubo-octahedra and are surrounded by ten O atoms. The Ti^{4+} ion is octahedrally coordinated by the O atoms.

Comment

Among the molybdenum cluster compounds in solid-state chemistry, the $AMo_5(Ti_{0.7}Mo_{0.3})O_{10}$ (A = Sr and Eu) compounds (Tortelier *et al.*, 2001) constitute an interesting family. Indeed, contrary to other reduced molybdenum compounds in which the Mo clusters are well ordered, the $AMo_5(Ti_{0.7}Mo_{0.3})O_{10}$ compounds present a disordered mixture of bioctahedral Mo_{10}, Mo_{11} (monocapped Mo_{10} clusters) and Mo_{12} clusters (bicapped Mo_{10} clusters). Another intriguing feature of the latter compounds is the absence of solid solution between the Mo and Ti atoms and thus the quasi-invariance of the Mo:Ti ratio on the capping sites. We present here the crystal structure of the title isomorphous calcium compound, which has an Mo:Ti ratio slightly different to those observed for the Sr and Eu compounds.

As observed for the Sr and Eu compounds, the crystal structure of the title compound is based on a random mixture of Mo_{10}, Mo_{11} (monocapped Mo_{10} clusters) and Mo_{12} (bicapped Mo_{10} clusters) clusters due to the partial occupation of the capping Mo6 position (Fig. 1). The Mo_{10} cluster results from the edge-sharing of two octahedral Mo_6 clusters and is similar to those previously observed in the $R_{16}Mo_{21}O_{56}$ (R = La to Nd) compounds (Gall & Gougeon, 1993; Gall *et al.*, 1999). Consequently, atoms Mo1, Mo2, Mo3 and Mo4 are surrounded by five O atoms in a square-pyramidal environment and atom Mo5 of the shared edge by four O atoms, forming a flattened tetrahedron. The capping atom Mo6 is in a distorted octahedral environment of O atoms, as previously observed for the bicapped Mo_6 cluster in $NdMo_8O_{14}$ (Gougeon *et al.*, 1991). The Mo$\cdots$Mo distances within the clusters range from 2.5927 (4) to 2.8744 (5) Å. The main differences between the present Ca and the Sr/Eu compounds concern the distances between the Mo5 atoms of the shared edge [2.8744 (5) and 2.85 Å in the Ca and Sr/Eu compounds, respectively] and those between apical atoms Mo4 and Mo5 [2.5927 (4) and 2.6178 Å in the Ca and Sr/Eu compounds, respectively]. These variations are in agreement with previous findings in the infinite chains of edge-shared Mo_6 octahedra, which show that the bond distance between the Mo atoms of the shared edge is shorter when the apical–apical interaction is weaker and longer when the interaction between the apex Mo atoms is stronger (Gall *et al.*, 2002).

From Fig. 2(*a*), it is also interesting to note that the Mo clusters are arranged in layers perpendicular to the a axis (see below). As the shortest distance between Mo clusters is 3.1475 (4) Å within one layer and greater than 3.65 Å between adjacent layers, the structure can be considered to be two-dimensional with respect to the Mo network, although it is three-dimensional overall. The Mo—O distances range from 1.898 (4) to 2.149 (3) Å, as usually observed in reduced molybdenum oxides. The oxygen framework derives from the stacking of close-packed layers along the a direction in the $\ldots ABAC \ldots$ sequence. The B ($y \simeq \frac{1}{4}$) and C ($y \simeq \frac{3}{4}$) layers are entirely occupied by O atoms and thus have the composition $[O_{24}]$. In the A layers ($y \simeq 0.0$ and $\frac{1}{2}$), one third of the O atoms are missing or substituted by the Ca ions in an ordered way. Consequently, the latter layers can be formulated as $[O_{16}Ca_4\square_4]$, where $\square$ stands for the oxygen vacancies. In this close packing, all the tetrahedral interstices are empty, while

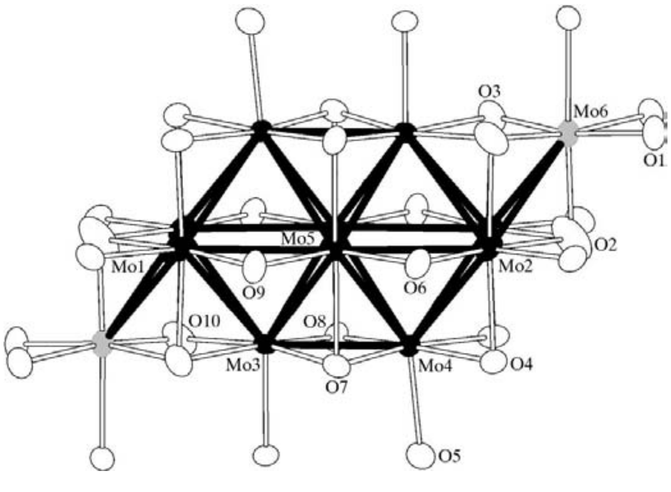

Figure 1
The Mo–O cluster unit in $CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$. The Mo atoms in black which fully occupy their site form the bioctahedral Mo_{10} cluster. The Mo atoms in light grey which cap the Mo_{10} cluster have an occupancy factor of 0.382 (3). Displacement ellipsoids are drawn at the 90% probability level.

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half of the octahedral interstices are filled by the Mo1, Mo2, Mo3, Mo4 and Mo5 atoms, which then form bioctahedral Mo_{10} clusters. In addition, one tenth of the octahedral sites are occupied statistically by atoms Mo6, which cap the faces of the bioctahedral Mo_{10}, and by atoms Ti1 (Fig. 2).

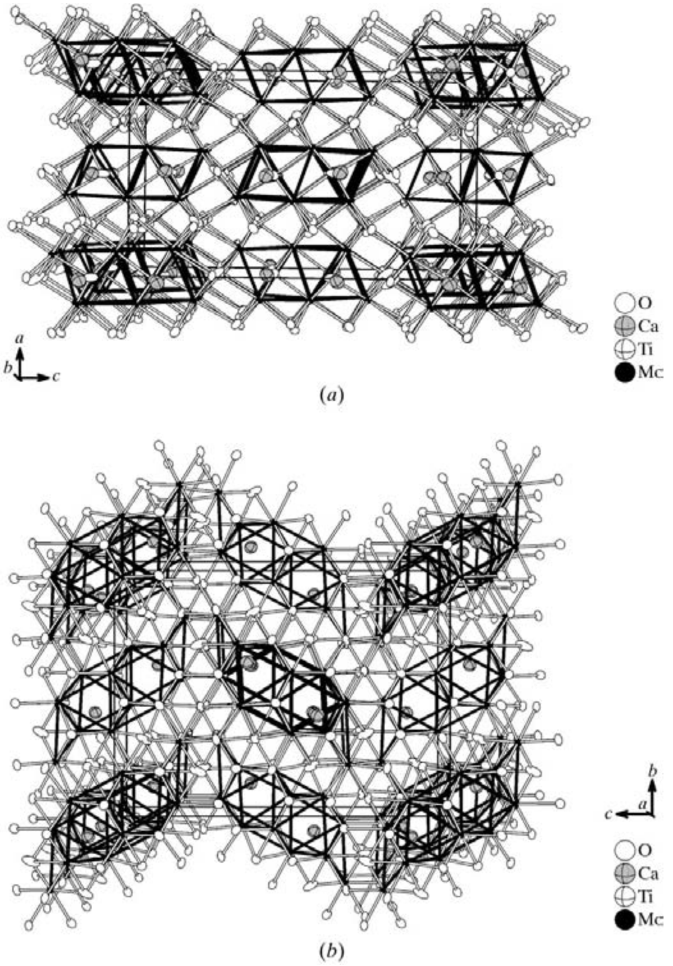

Figure 2
(*a*) A view of $CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$ along the *b* axis. Displacement ellipsoids are drawn at the 90% probability level. (*b*) A view of $CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$ along the *a* axis. Displacement ellipsoids are drawn at the 90% probability level.

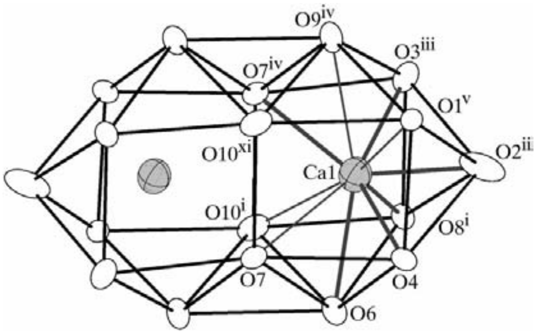

Figure 3
The environment of the Ca atoms (see *Comment*). The symmetry codes are as in Table 1.

The Ca^{2+} ions occupy large cavities which result from the fusion of two cubooctahedra. They are surrounded by ten O atoms with six nearest neighbours at distances ranging from 2.354 (2) to 2.657 (3) Å (thick grey lines in Fig. 3) and four second nearest neighbours at distances between 2.850 (3) and 3.053 (3) Å (thin grey lines in Fig. 3). In the Sr and Eu compounds, the cation-to-oxygen distances range from 2.50 to 3.23 Å with no clear gap.

The Ti atom, which occupies at 62% a position 0.362 (2) Å from that of the capping Mo6 atom, obviously has the same O-atom environment as the latter atom. It is thus surrounded by six O atoms, forming a highly distorted octahedron. The Ti—O distances vary between 1.848 (4) and 2.178 (4) Å, with a mean value of 2.00 Å. The latter value is in good agreement with the distance of 2.005 Å expected from the sum of the ionic radii of O^{2-} and Ti^{4+} in octahedral coordination, according to Shannon & Prewitt (1969). The oxidation state of +4 for the Ti atoms was also confirmed from the Ti—O bond lengths using the relationship of Brown & Wu (1976) [$s = (d_{Ti-O}/1.806)^{-5.2}$] which leads to a value of +3.8.

The shortest Mo···Ti distance is 2.904 (3) Å and this is identical to the distances observed in the Eu [2.903 (2) Å] and Sr [2.905 (2) Å] compounds. Such values preclude the existence of metallic Ti—Mo bonds and thus the formation of heteronuclear clusters.

Bond-valence calculations (Brown & Wu, 1976) performed on the Mo atoms led to values of 3.16, 3.23, 2.89, 2.73, 2.35 and 4.39 v.u. for atoms Mo1, Mo2, Mo3, Mo4, Mo5 and Mo6, respectively. This yields an average molybdenum oxidation state of +2.98 leading to about 34 electrons which are delocalized over the cluster. As expected, the oxidation state of the capping Mo6 atom is higher than those of the other Mo atoms. This is principally because atom Mo6 has the lowest coordination by other Mo atoms and therefore the fewest electrons available for metal-to-metal bonding.

Experimental

Single crystals of $CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$ were obtained by the reaction of TiO_2, MoO_3, $CaMoO_4$ and Mo with the nominal composition $CaMo_6Ti_2O_{15}$. $CaMoO_4$ was prepared by heating a stoichiometric mixture of $CaCO_3$ and MoO_3 in an open porcelain crucible at 1073 K for 24 h. Mo powder was heated under a flow of H_2 at 1273 K for 6 h prior to use. The initial mixture (*ca* 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under low argon pressure using an arc welding system. The charge was heated at a rate of 300 K h^{-1} to 1673 K and this temperature was held for 48 h. The vessel was then cooled at a rate of 100 K h^{-1} to 1373 K and finally furnace cooled. Subsequently, single-phase powders were obtained for compositons $CaMo_5(Mo_{1-x}Ti_x)O_{10}$, with x ranging from 0.55 to 0.65.

Crystal data

$CaMo_5(Mo_{0.38}Ti_{0.62})O_{10}$
$M_r = 746.06$
Orthorhombic, *Pbca*
$a = 8.97790$ (10) Å
$b = 11.4442$ (2) Å
$c = 15.0673$ (3) Å
$V = 1548.09$ (4) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 9.77$ mm^{-1}
$T = 293$ (2) K
0.06 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.642$, $T_{\max} = 0.698$

43304 measured reflections
4205 independent reflections
2960 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.057$
$S = 1.09$
4205 reflections

166 parameters
1 restraint
$\Delta\rho_{\max} = 1.75$ e Å^{-3}
$\Delta\rho_{\min} = -1.90$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca1—O8^{i}	2.354 (2)	Mo3—O10	2.068 (2)
Ca1—O2^{ii}	2.425 (3)	Mo3—O7	2.074 (2)
Ca1—O3^{iii}	2.432 (3)	Mo3—O6^{v}	2.086 (2)
Ca1—O4	2.557 (3)	Mo3—Mo4	2.5927 (4)
Ca1—O7^{iv}	2.645 (2)	Mo3—Mo5	2.6944 (4)
Ca1—O6	2.657 (3)	Mo3—Mo5^{vii}	2.7252 (4)
Ca1—O9^{iv}	2.850 (3)	Mo3—Mo6^{vii}	2.921 (2)
Ca1—O7	2.948 (3)	Mo4—O8	2.063 (2)
Ca1—O10^{i}	3.048 (3)	Mo4—O5	2.070 (2)
Ca1—O1^{v}	3.053 (3)	Mo4—O4	2.074 (2)
Mo1—O1^{vi}	1.989 (2)	Mo4—O7	2.095 (2)
Mo1—O2^{vii}	2.002 (3)	Mo4—O1^{ix}	2.106 (2)
Mo1—O9	2.013 (2)	Mo4—Mo5	2.7406 (4)
Mo1—O3^{vii}	2.034 (2)	Mo4—Mo5^{vii}	2.7886 (4)
Mo1—O4^{viii}	2.147 (2)	Mo5—O8^{vii}	2.028 (2)
Mo1—Mo2^{vii}	2.6829 (4)	Mo5—O6	2.049 (2)
Mo1—Mo6^{vii}	2.7564 (19)	Mo5—O9	2.071 (2)
Mo1—Mo5	2.7660 (4)	Mo5—O7	2.078 (2)
Mo1—Mo4^{vii}	2.7752 (4)	Mo5—Mo5^{vii}	2.8744 (5)
Mo1—Mo3	2.7869 (4)	Mo6—O2	1.898 (4)
Mo2—O6	2.004 (2)	Mo6—O10^{vii}	1.905 (3)
Mo2—O10^{vii}	2.004 (3)	Mo6—O3	1.950 (3)
Mo2—O2	2.005 (3)	Mo6—O1	2.026 (3)
Mo2—O4	2.038 (2)	Mo6—O5^{x}	2.042 (3)
Mo2—O5^{i}	2.079 (2)	Mo6—O9^{xi}	2.149 (3)
Mo2—Mo6	2.6891 (18)	Ti1—O5	1.848 (4)
Mo2—Mo4	2.7534 (4)	Ti1—O1^{ix}	1.870 (4)
Mo2—Mo5	2.7657 (4)	Ti1—O9^{xii}	1.891 (4)
Mo2—Mo3^{vii}	2.7852 (4)	Ti1—O3^{ix}	2.095 (4)
Mo3—O8	2.034 (2)	Ti1—O10^{xiii}	2.104 (4)
Mo3—O3^{vii}	2.053 (2)	Ti1—O2^{ix}	2.178 (4)

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

The final refinement cycles included the atomic coordinates, the anisotropic displacement parameters for all atoms and site-occupancy factors for the Mo6 and Ti1 sites, the sum of which was constrained to unity. Refinement of the occupancy factors of the O atoms did not reveal defects in oxygen. Because of the disordering of the Mo6 and Ti1 atoms, a reciprocal-space reconstruction of different planes was carried out, as well as long-exposure rotations along the three axes on a single crystal on the Nonius KappaCCD diffractometer. In both cases, no superlattice reflections or diffuse lines were observed.

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, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3044). Services for accessing these data are described at the back of the journal.

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