

Redetermination of $\text{Mn}_{1.44}\text{Mo}_8\text{O}_{11}$: evidence of pairwise distortion of octahedral molybdenum chains

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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{Mn}-\text{O}) = 0.003\text{ \AA}$
Disorder in main residue
 R factor = 0.033
 wR factor = 0.076
Data-to-parameter ratio = 32.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Redetermination of the structure of manganese octamolybdenum undeca-oxide, $\text{Mn}_{1.44}\text{Mo}_8\text{O}_{11}$, revealed a doubling of the unit cell. The structure consists of infinite chains of *trans*-edge-sharing Mo_6 octahedra cross-linked through O atoms to delimit tunnels in which the disordered Mn^{2+} cations reside. In comparison with the previous refinement [Carlson *et al.* (1989). *J. Less Common Met.* **156**, 325–339], the metallic chains exhibit a pairwise distortion, as expected from theoretical calculations.

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Comment

Since the first report of infinite chains of *trans*-edge-sharing Mo_6 octahedra in NaMo_4O_6 by Torardi & McCarley (1979), four other structure types containing similar molybdenum chains have been discovered: $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$ (McCarley, 1982), $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ (Carlson *et al.*, 1989), $\text{MMo}_8\text{O}_{10}$ ($M = \text{Li}, \text{Zn}$) (Lii *et al.*, 1986) and $\text{RE}_4\text{Mo}_4\text{O}_{11}$ ($\text{RE} = \text{Nd-Lu}$) (Gall *et al.*, 2002). An important difference between the Mo_6 octahedral chains present in the above compounds is the number of electrons available for Mo–Mo bonding [*i.e.* metal cluster electrons (MCE)], which governs the geometry of the chains. While they are regular in NaMo_4O_6 with 13 electrons per Mo_4 formula unit, they distort for MCEs greater than 13, as observed in $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$ and $\text{Ho}_4\text{Mo}_4\text{O}_{11}$. Extended Hückel theory calculations on NaMo_4O_6 , performed by Hughbanks & Hoffmann (1983), show that systems with MCEs greater than 13 per Mo_4 formula unit should distort because of the occupation of antibonding bands. Among the above compounds, $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$, although having 14.5 elec-

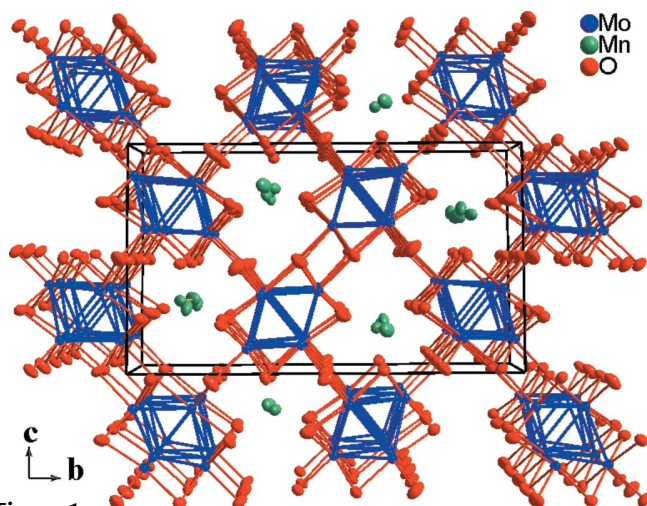


Figure 1

The crystal structure of $\text{Mn}_{1.44}\text{Mo}_8\text{O}_{11}$, viewed down the a axis, parallel to the direction of the chain direction. Displacement ellipsoids are drawn at the 97% probability level.

trons per Mo₄ formula unit, was reported to contain regular Mo₆ octahedral chains. As a consequence, we decided to redetermine the crystal structure of Mn_{1.5}Mo₈O₁₁ (Carlson *et al.*, 1989).

Our investigation shows that Mn_{1.5}Mo₈O₁₁ crystallizes in a larger unit cell with the lattice parameter of the axis parallel to the infinite chains doubled. It is interesting to note that Carlson *et al.* (1989) mentioned superstructure reflections that induce, at least, a quadrupling of this axis. In our case, we only observed a doubling and a quadrupling (see *Experimental refinement section*). A view of the crystal structure down the chain axis is shown in Fig. 1. It consists of infinite chains of Mo₆ clusters coupled together through O atoms (Carlson *et al.*, 1989). The most obvious point that underlined our study is the distortion of the infinite molybdenum octahedral chains (Fig. 2). The distortion results here from a symmetrical pairing of the apical Mo atoms with respect to the basal plane, accompanied by a long–short pattern of the Mo–Mo distances of the shared edges, analogous to the structures observed in the RE₄Mo₄O₁₁ series. In the title compound, the short Mo3–Mo7 and Mo4–Mo8 bond distances between apical Mo atoms are 2.6116 (3) and 2.6073 (3) Å, respectively, while the long ones, which are essentially non-bonding, are 3.0857 (3) and 3.0907 (4) Å. The bond distance between the Mo atoms of the shared edge is shorter [Mo1–Mo2 = 2.6544 (4) Å] when the apical–apical interaction is weaker, and longer [Mo5–Mo6 = 2.8607 (4) Å] when the interaction between apical Mo atoms is stronger. The Mo–O chains delimit tunnels parallel to the *a* axis in which the Mn²⁺ cations reside. The Mn1 and Mn3 cations are in distorted square-pyramidal environments of O atoms, and the Mn2 cation is surrounded by four O atoms forming a distorted tetrahedron. The shortest distances between the Mn sites are 1.0587 (15), 2.4041 (14) and 2.3751 (15) Å, which excludes adjacent sites from being occupied simultaneously.

Experimental

Single crystals of Mn_{1.44}Mo₈O₁₁ were prepared from a mixture of MnO₂ (Merck, 99%), MoO₃ (Cerac, 99.95%) and Mo (Plansee, 99.9999%) with the nominal composition Mn_{1.5}Mo₈O₁₁. Before use, Mo powder was reduced under H₂ flowing gas at 1273 K over a period of 10 h in order to eliminate any trace of oxygen. The initial mixture (*ca* 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low Ar pressure using an arc welding system. The charge was heated at a rate of 300 K h⁻¹ to 1773 K, held at that temperature for 72 h and then cooled at a rate of 100 K h⁻¹ to 1373 K. Finally, the reaction mixture was allowed to cool down in the switched-off furnace. The final product appeared homogeneous, with thin black needles in a black powder.

Crystal data

Mn _{1.44} Mo ₈ O ₁₁	<i>Z</i> = 4
<i>M_r</i> = 1022.63	<i>D_x</i> = 7.163 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 5.6971 (3) Å	<i>μ</i> = 12.11 mm ⁻¹
<i>b</i> = 16.9333 (12) Å	<i>T</i> = 293 (2) K
<i>c</i> = 9.8658 (8) Å	Needle, black
<i>β</i> = 94.900 (6)°	0.34 × 0.03 × 0.02 mm
<i>V</i> = 948.28 (11) Å ³	

Data collection

Nonius KappaCCD diffractometer	30855 measured reflections
<i>φ</i> and <i>ω</i> scans	6614 independent reflections
Absorption correction: multi-scan	4745 reflections with <i>I</i> > 2σ(<i>I</i>)
(<i>SADABS</i> ; Sheldrick, 2004)	<i>R</i> _{int} = 0.044
<i>T</i> _{min} = 0.181, <i>T</i> _{max} = 0.748	<i>θ</i> _{max} = 42.0°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0332 <i>P</i>) ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.033	+ 2.0205 <i>P</i>]
<i>wR</i> (<i>F</i> ²) = 0.076	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.06	(Δ/ <i>σ</i>) _{max} = 0.001
6614 reflections	Δ <i>ρ</i> _{max} = 2.53 e Å ⁻³
206 parameters	Δ <i>ρ</i> _{min} = -3.02 e Å ⁻³
	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.00024 (7)

Table 1

Selected bond lengths (Å).

Mo1–O6	2.010 (2)	Mo5–O5 ⁱ	2.004 (2)
Mo1–O3 ⁱ	2.061 (2)	Mo5–O10 ^{ix}	2.068 (2)
Mo1–O5 ⁱⁱ	2.074 (2)	Mo5–O6 ⁱ	2.075 (2)
Mo1–O1	2.075 (2)	Mo5–O8 ⁱ	2.104 (2)
Mo1–Mo2 ⁱⁱⁱ	2.6544 (4)	Mo5–Mo8	2.7732 (4)
Mo1–Mo8 ⁱⁱⁱ	2.8020 (4)	Mo5–Mo7	2.8009 (4)
Mo1–Mo7 ⁱⁱⁱ	2.8225 (4)	Mo5–Mo6 ⁱⁱ	2.8607 (4)
Mo1–Mo4 ⁱⁱⁱ	2.8244 (4)	Mo6–O12	2.0207 (3)
Mo1–Mo5 ⁱⁱⁱ	2.8393 (3)	Mo6–O9 ^{vi}	2.047 (2)
Mo1–Mo5 ^{iv}	2.8610 (3)	Mo6–O11 ^{vii}	2.089 (3)
Mo1–Mo3 ^{iv}	2.8755 (4)	Mo6–O7	2.1990 (3)
Mo2–O2	2.028 (2)	Mo6–Mo8 ^{vi}	2.7130 (4)
Mo2–O4 ^v	2.087 (2)	Mo6–Mo7 ^{vi}	2.7611 (4)
Mo2–O7	2.1025 (3)	Mo7–O9	2.080 (2)
Mo2–O12 ⁱⁱ	2.2845 (3)	Mo7–O2	2.091 (2)
Mo2–Mo8	2.7414 (4)	Mo7–O8 ⁱ	2.094 (2)
Mo2–Mo7	2.7758 (4)	Mo7–O1 ^x	2.097 (2)
Mo2–Mo4	2.8011 (4)	Mo7–O6	2.106 (3)
Mo2–Mo3 ^{vi}	2.8412 (4)	Mo8–O11 ^v	2.064 (2)
Mo2–Mo6	2.8426 (3)	Mo8–O10 ^{ix}	2.072 (2)
Mo2–Mo6 ⁱⁱ	2.8589 (3)	Mo8–O4 ^v	2.086 (2)
Mo3–O9	2.066 (2)	Mo8–O3 ^{ix}	2.113 (2)
Mo3–O8 ⁱ	2.079 (2)	Mo8–O10 ^v	2.171 (2)
Mo3–O5 ⁱⁱ	2.079 (2)	Mo8–Mo8 ^{xi}	3.0739 (6)
Mo3–O2 ⁱⁱ	2.093 (2)	Mn1–O8	2.039 (3)
Mo3–O1 ⁱ	2.100 (2)	Mn1–O2	2.091 (3)
Mo3–Mo7	2.6116 (3)	Mn1–O11	2.136 (3)
Mo3–Mo6 ⁱⁱ	2.7138 (4)	Mn1–O4 ^{vi}	2.203 (3)
Mo3–Mo5	2.7409 (4)	Mn1–O9 ^{vi}	2.346 (2)
Mo3–Mo7 ⁱⁱ	3.0857 (3)	Mn2–O4 ^{vi}	2.018 (3)
Mo4–O11 ^{vii}	2.055 (2)	Mn2–O9 ^{vi}	2.030 (3)
Mo4–O10 ^{viii}	2.074 (2)	Mn2–O1 ^{vi}	2.058 (3)
Mo4–O3 ^{ix}	2.093 (2)	Mn2–O8	2.129 (2)
Mo4–O4 ^v	2.099 (2)	Mn3–O11	2.216 (3)
Mo4–O3 ^{vii}	2.165 (2)	Mn3–O1	2.151 (3)
Mo4–Mo8 ^{vi}	2.6073 (3)	Mn3–O2	2.186 (3)
Mo4–Mo6	2.6935 (4)	Mn3–O9	2.281 (2)
Mo4–Mo5 ^{vi}	2.7132 (4)	Mn3–O8	2.328 (2)
Mo4–Mo8	3.0907 (4)		

Symmetry codes: (i) *x* – ½, –*y* + ½, *z* + ½; (ii) *x* – 1, *y*, *z*; (iii) *x* – ½, –*y* + ½, *z* – ½; (iv) *x* + ½, –*y* + ½, *z* – ½; (v) –*x* – 1, –*y*, –*z* + 1; (vi) *x* + 1, *y*, *z*; (vii) –*x*, –*y*, –*z* + 1; (viii) *x* + 1, *y*, *z* + 1; (ix) *x*, *y*, *z* + 1; (x) *x* + ½, –*y* + ½, *z* + ½; (xi) –*x* – 1, –*y*, –*z* + 2.

Several crystals were tested. Although most of them were of poor quality, two kinds of crystals were found. The first type had unit-cell parameters similar to those of the title compound, while the second type had a larger unit cell with *a*' = 2*a*, *b*' = *b* and *c*' = 2*c* (*a*, *b*, *c* being the unit-cell parameters of the title compound). However, the structure of the latter type of crystals could not be determined. The occupation factors for the Mn atoms in the title compound were refined freely, leading to the final stoichiometry Mn_{1.440(8)}Mo₈O₁₁.

The highest peak and the deepest hole in the final difference Fourier map are located 1.50 Å and 0.60 Å, respectively, from Mo2.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Intensity data were collected on the Nonius KappaCCD X-ray diffractometer system of the 'Centre de diffractométrie de l'Université de Rennes I' (URL: www.cdifx.univ-rennes1.fr).

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Brandenburg, K. (2001). *DIAMOND*. Version. 2.1e. Crystal Impact GbR, Bonn, Germany.
- Carlson, C. D., Brough, L. F., Edwards, P. A. & McCarley, R. E. (1989). *J. Less Common Met.* **156**, 325–339.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Gall, P., Barrier, N., Gautier, R. & Gougeon, P. (2002). *Inorg. Chem.* **41**, 2879–2885.
- Hughbanks, T. & Hoffmann, R. (1983). *J. Am. Chem. Soc.* **105**, 3528–3537.
- Lii, K. H., McCarley, R. E., Kim, S. & Jacobson, R. A. (1986). *J. Solid State Chem.* **64**, 347–358.

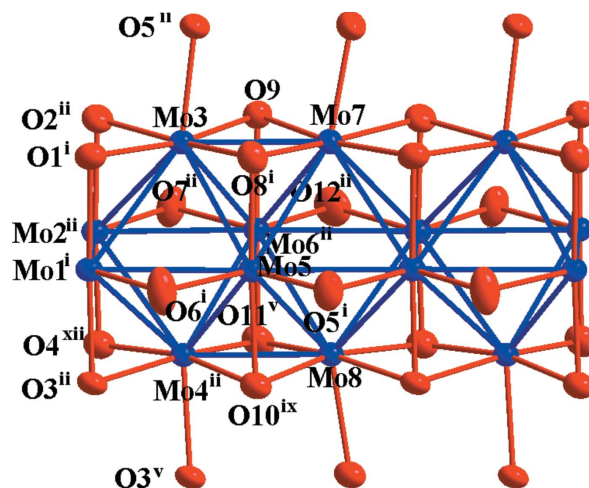


Figure 2

A section of one molybdenum oxide cluster chain. The repeat unit comprises two Mo₆ octahedra. The probability level of the ellipsoids is the same as in Fig. 1 and the symmetry codes are as in Table 1, except for symmetry operator (xii) $-2 - x, -y, 1 - z$.

- McCarley, R. E. (1982). *Philos. Trans. R. Soc. London Ser. A*, **308**, 141–157.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Torardi, C. C. & McCarley, R. E. (1979). *J. Am. Chem. Soc.* **101**, 3963–, 3964.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2004). *SADABS*. Bruker–Nonius AXS Inc., Madison, Wisconsin, USA.