inorganic compounds

Redetermination of $Zn_2Mo_3O_8$

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The crystal structure of dizinc trimolybdenum(IV) octaoxide, $Zn_2Mo_3O_8$, has been redetermined from single-crystal X-ray data. The structure has been reported previously based on neutron powder diffraction data [Hibble *et al.* (1999). *Acta Cryst.* B**55**, 683-697] and single-crystal data [McCarroll *et al.* (1957). *J. Am. Chem. Soc.* **79**, 5410–5414; Ansell & Katz (1966) *Acta Cryst.* **21**, 482–485]. The results of the current redetermination show an improvement in the precision of the structural and geometric parameters with all atoms refined with anisotropic displacement parameters. The crystal structure consists of distorted hexagonal-close-packed oxygen layers with stacking sequence *abac* along [001] and is held together by alternating zinc and molybdenum layers. The Zn atoms occupy both tetrahedral and octahedral interstices with a ratio of 1:1. The Mo atoms occupy octahedral sites and form strongly bonded triangular clusters involving three MoO_6 octahedra that are each shared along two edges, forming a Mo_3O_{13} unit. All atoms lie on special positions. The Zn atoms are in 2*b* Wyckoff positions with 3*m*. site symmetry, the Mo atoms are in 6*c* Wyckoff positions with . *m*. site symmetry and the O atoms are in 2*a*, 2*b* and 6*c* Wyckoff positions with 3*m*. and . *m*. site symmetries, respectively.

Related literature

The synthesis of $Zn_2Mo_3O_8$ is described by McCarroll *et al.* (1957). For previous reports of the crystal structure, see: McCarroll *et al.* (1957); Ansell & Katz (1966); Hibble *et al.* (1999). $Zn_2Mo_3O_8$ is isotypic with the mineral kamiokite, $Fe_2Mo_3O_8$ (Kanazawa & Sasaki, 1986). For other compounds containing Mo_3O_{13} cluster units, see: Betteridge *et al.* (1984); Collins *et al.* (1989); Gall & Gougeon (2005); Gougeon & Gall (2007); McCarroll (1977); Torardi & McCarley (1985).

Experimental

Crystal data

$Zn_2Mo_3O_8$
M_r = 546.56

Hexagonal, $P6_3mc$
a = 5.7816 (2) Å
c = 9.9345 (3) Å
V = 287.59 (2) Å^3
Z = 2

Mo $K\alpha$ radiation
μ = 14.59 mm^{-1}
T = 293 K
$0.21 \times 0.13 \times 0.07$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical
  (de Meulenaer & Tompa, 1965)
  T_{min} = 0.048, T_{max} = 0.157

8536 measured reflections
790 independent reflections
778 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.013
$wR(F^2)$ = 0.029
S = 1.16
790 reflections
33 parameters
1 restraint

$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}
Absolute structure: Flack (1983),
  322 Friedel pairs
Flack parameter: 0.155 (15)

Table 1
Selected bond lengths (Å).

Mo1—O1	1.9549 (14)	Mo1—Mo1^i	2.5326 (2)
Mo1—O4	2.0286 (19)	Zn1—O3^{ii}	1.963 (3)
Mo1—O2	2.0804 (10)	Zn2—O1	2.0467 (18)
Mo1—O3	2.1415 (14)	Zn2—O2^{iii}	2.1431 (16)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $x, y+1, z$; (iii) $y, -x+y, z+\frac{1}{2}$.

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, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2235).

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supplementary materials

Redetermination of $Zn_2Mo_3O_8$

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Comment

The $M_2Mo_3O_8$ compounds, where M is a divalent metal such as Mg, Zn, Fe, Co, Ni, Zn and Cd, were first synthesized by McCarroll *et al.* (1957). They presented the results of structure determination on $Zn_2Mo_3O_8$ from photographic data (R = 0.118). Later, a refinement of the structure was accomplished by Ansell & Katz (1966) with a R factor of 0.069. Among the above compounds, it is interesting to note that $Fe_2Mo_3O_8$ is a mineral known as kamiokite (Kanazawa & Sasaki, 1986). The main structural feature of $Zn_2Mo_3O_8$ is the occurrence of Mo_3O_{13} cluster units sharing part of their oxygen atoms to form layers according to the connective formula $Mo_3O_4O_{6/2}O_{3/3}$. The oxygen atoms form an hexagonal-close-packing with a stacking sequence *abac* along [001] (Fig. 1). The Mo—Mo distance within the Mo_3 triangle (Fig. 2) is 2.5326 (2) Å which differs slightly from 2.524 (2) Å found previously and is equal to that found in the isotopic compound $Fe_2Mo_3O_8$ (2.5326 (5) Å). The Mo—O distances range from 1.9549 (14) to 2.1415 (14) Å compared to 1.928 (20) to 2.128 (30) Å in the previous determination based on single-crystal data (1.953 (4)–2.135 (4) in $Fe_2Mo_3O_8$). In our work, The ZnO_4 tetrahedra appear more regular with Zn—O distances of 1.963 (3) and 1.9687 (15) Å instead of 1.98 (1) and 1.99 (3) Å while the ZnO_6 octahedra are more distorted with Zn—O distances of 2.0467 (18) and 2.1431 (16) Å compared to 2.072 (20) and 2.123 (10) Å observed by Ansell & Katz (1966).

For other compounds containing Mo_3O_{13} cluster units, see: Betteridge *et al.* (1984); Collins *et al.* (1989); Gall & Gougeon (2005); Gougeon & Gall (2007); McCarroll (1977); Torardi & McCarley (1985).

Experimental

Single crystals of $Zn_2Mo_3O_8$ were obtained by the reaction of ZnO, 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 up to 1573 K, the temperature which was held for 48 h, then cooled at 100 K/h down to 1373 K and finally cooled down to room temperature by switching off the furnace.

Refinement

The highest peak and the deepest hole are located 0.68 Å and 0.74 Å from Mo1. The crystal under investigation was racemically twinned with a twin component ratio of 0.155 (15):0.845 (155).
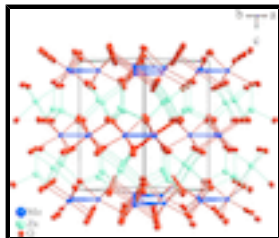
supplementary materials

Figures

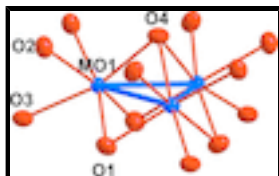Fig. 1. : View of $Zn_2Mo_3O_8$ along [110].

Fig. 2. : Plot showing the atom-numbering scheme of the Mo_3O_{13} cluster unit. Displacement ellipsoids are drawn at the 97% probability level.

dizinc trimolybdenum(IV) octaoxide

Crystal data

$Zn_2Mo_3O_8$	$Z = 2$
$M_r = 546.56$	$F_{000} = 500$
Hexagonal, $P6_3mc$	$D_x = 6.312$ Mg m^{-3}
Hall symbol: P 6c -2c	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 5.7816$ (2) Å	Cell parameters from 6245 reflections
$b = 5.7816$ (2) Å	$\theta = 0.9$–$44.0°$
$c = 9.9345$ (3) Å	$\mu = 14.59$ mm^{-1}
$\alpha = 90°$	$T = 293$ K
$\beta = 90°$	Irregular block, black
$\gamma = 120°$	$0.21 \times 0.13 \times 0.07$ mm
$V = 287.589$ (17) Å^3	

Data collection

Nonius KappaCCD diffractometer	790 independent reflections
Radiation source: fine-focus sealed tube	778 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 293$ K	$\theta_{max} = 44.0°$
φ scans ($\kappa = 0$) + additional ω scans	$\theta_{min} = 4.1°$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = -11 \rightarrow 7$
$T_{min} = 0.048$, $T_{max} = 0.157$	$k = -11 \rightarrow 11$
8536 measured reflections	$l = -16 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0117P)^2 + 0.2665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.029$	$\Delta\rho_{max} = 0.97$ e Å^{-3}
$S = 1.16$	$\Delta\rho_{min} = -1.06$ e Å^{-3}
790 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
33 parameters	Extinction coefficient: 0.0306 (13)
1 restraint	Absolute structure: Flack (1983), 322 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.155 (15)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Mo1	−0.29203 (3)	−0.146014 (13)	−0.925032 (13)	0.00373 (3)
Zn1	−0.6667	0.6667	−0.62348 (6)	0.00671 (7)
Zn2	−0.3333	0.3333	−0.68932 (6)	0.00606 (7)
O1	−0.16669 (16)	0.16669 (16)	−0.8086 (2)	0.00588 (19)
O2	−0.51182 (15)	−0.0236 (3)	−1.04041 (16)	0.0055 (2)
O3	−0.6667	−0.3333	−0.8210 (3)	0.0054 (4)
O4	0.0000	0.0000	−1.0666 (3)	0.0057 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.00333 (5)	0.00389 (4)	0.00377 (5)	0.00166 (2)	0.00017 (5)	0.00008 (2)
Zn1	0.00746 (10)	0.00746 (10)	0.00521 (15)	0.00373 (5)	0.000	0.000
Zn2	0.00647 (10)	0.00647 (10)	0.00525 (15)	0.00323 (5)	0.000	0.000
O1	0.0061 (4)	0.0061 (4)	0.0052 (5)	0.0028 (4)	0.0007 (2)	−0.0007 (2)
O2	0.0048 (3)	0.0056 (5)	0.0066 (6)	0.0028 (2)	0.0005 (2)	0.0011 (4)

O3	0.0063 (5)	0.0063 (5)	0.0038 (8)	0.0031 (2)	0.000	0.000
O4	0.0068 (5)	0.0068 (5)	0.0036 (8)	0.0034 (3)	0.000	0.000

Geometric parameters (Å, °)

Mo1—O1	1.9549 (14)	Zn1—O2^v	1.9687 (15)
Mo1—O1^i	1.9549 (14)	Zn1—O2^{vi}	1.9687 (15)
Mo1—O4	2.0286 (19)	Zn1—O2^{vii}	1.9687 (15)
Mo1—O2	2.0804 (10)	Zn2—O1	2.0467 (18)
Mo1—O2^{ii}	2.0804 (10)	Zn2—O1^{viii}	2.0467 (18)
Mo1—O3	2.1415 (14)	Zn2—O1^{ix}	2.0467 (18)
Mo1—Mo1^{iii}	2.5326 (2)	Zn2—O2^x	2.1431 (16)
Mo1—Mo1^i	2.5326 (2)	Zn2—O2^{xi}	2.1431 (16)
Zn1—O3^{iv}	1.963 (3)	Zn2—O2^{vii}	2.1431 (16)
O1—Mo1—O1^i	95.38 (11)	O1—Zn2—O1^{viii}	89.84 (8)
O1—Mo1—O4	100.30 (5)	O1—Zn2—O1^{ix}	89.84 (8)
O1^i—Mo1—O4	100.30 (5)	O1^{viii}—Zn2—O1^{ix}	89.84 (8)
O1—Mo1—O2	91.06 (7)	O1—Zn2—O2^x	96.01 (5)
O1^i—Mo1—O2	166.69 (5)	O1^{viii}—Zn2—O2^x	171.73 (8)
O4—Mo1—O2	89.96 (6)	O1^{ix}—Zn2—O2^x	96.01 (5)
O1—Mo1—O2^{ii}	166.69 (5)	O1—Zn2—O2^{xi}	96.01 (5)
O1^i—Mo1—O2^{ii}	91.06 (7)	O1^{viii}—Zn2—O2^{xi}	96.01 (5)
O4—Mo1—O2^{ii}	89.96 (6)	O1^{ix}—Zn2—O2^{xi}	171.73 (7)
O2—Mo1—O2^{ii}	80.41 (8)	O2^x—Zn2—O2^{xi}	77.60 (7)
O1—Mo1—O3	89.76 (6)	O1—Zn2—O2^{vii}	171.73 (7)
O1^i—Mo1—O3	89.76 (6)	O1^{viii}—Zn2—O2^{vii}	96.01 (5)
O4—Mo1—O3	164.96 (9)	O1^{ix}—Zn2—O2^{vii}	96.01 (5)
O2—Mo1—O3	78.60 (6)	O2^x—Zn2—O2^{vii}	77.60 (7)
O2^{ii}—Mo1—O3	78.60 (6)	O2^{xi}—Zn2—O2^{vii}	77.60 (7)
O1—Mo1—Mo1^{iii}	49.63 (4)	Mo1—O1—Mo1^{iii}	80.75 (7)
O1^i—Mo1—Mo1^{iii}	95.26 (4)	Mo1—O1—Zn2	137.21 (4)
O4—Mo1—Mo1^{iii}	51.38 (4)	Mo1^{iii}—O1—Zn2	137.21 (4)
O2—Mo1—Mo1^{iii}	97.78 (4)	Zn1^{xii}—O2—Mo1	119.89 (5)
O2^{ii}—Mo1—Mo1^{iii}	141.34 (3)	Zn1^{xii}—O2—Mo1^{xiii}	119.89 (5)
O3—Mo1—Mo1^{iii}	139.34 (4)	Mo1—O2—Mo1^{xiii}	102.68 (7)
O1—Mo1—Mo1^i	95.26 (4)	Zn1^{xii}—O2—Zn2^{xiv}	111.56 (8)
O1^i—Mo1—Mo1^i	49.63 (4)	Mo1—O2—Zn2^{xiv}	99.62 (5)
O4—Mo1—Mo1^i	51.38 (4)	Mo1^{xiii}—O2—Zn2^{xiv}	99.62 (5)
O2—Mo1—Mo1^i	141.34 (3)	Zn1^{xv}—O3—Mo1^{xiii}	118.84 (7)
O2^{ii}—Mo1—Mo1^i	97.78 (4)	Zn1^{xv}—O3—Mo1^{ii}	118.84 (7)
O3—Mo1—Mo1^i	139.34 (4)	Mo1^{xiii}—O3—Mo1^{ii}	98.68 (9)
Mo1^{iii}—Mo1—Mo1^i	60.0	Zn1^{xv}—O3—Mo1	118.84 (7)

O3^{iv}—Zn1—O2^{v}	114.79 (5)	Mo1^{xiii}—O3—Mo1	98.68 (9)
O3^{iv}—Zn1—O2^{vi}	114.79 (5)	Mo1^{ii}—O3—Mo1	98.68 (9)
O2^{v}—Zn1—O2^{vi}	103.67 (6)	Mo1^{iii}—O4—Mo1	77.25 (8)
O3^{iv}—Zn1—O2^{vii}	114.79 (5)	Mo1^{iii}—O4—Mo1^{i}	77.25 (8)
O2^{v}—Zn1—O2^{vii}	103.67 (6)	Mo1—O4—Mo1^{i}	77.25 (8)
O2^{vi}—Zn1—O2^{vii}	103.67 (6)		

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y-1, -x-1, z$; (iii) $-x+y, -x, z$; (iv) $x, y+1, z$; (v) $-x-1, -y+1, z+1/2$; (vi) $y-1, -x+y, z+1/2$; (vii) $x-y, x+1, z+1/2$; (viii) $-x+y-1, -x, z$; (ix) $-y, x-y+1, z$; (x) $y, -x+y, z+1/2$; (xi) $-x-1, -y, z+1/2$; (xii) $-x-1, -y+1, z-1/2$; (xiii) $-y-1, x-y, z$; (xiv) $-x-1, -y, z-1/2$; (xv) $x, y-1, z$.
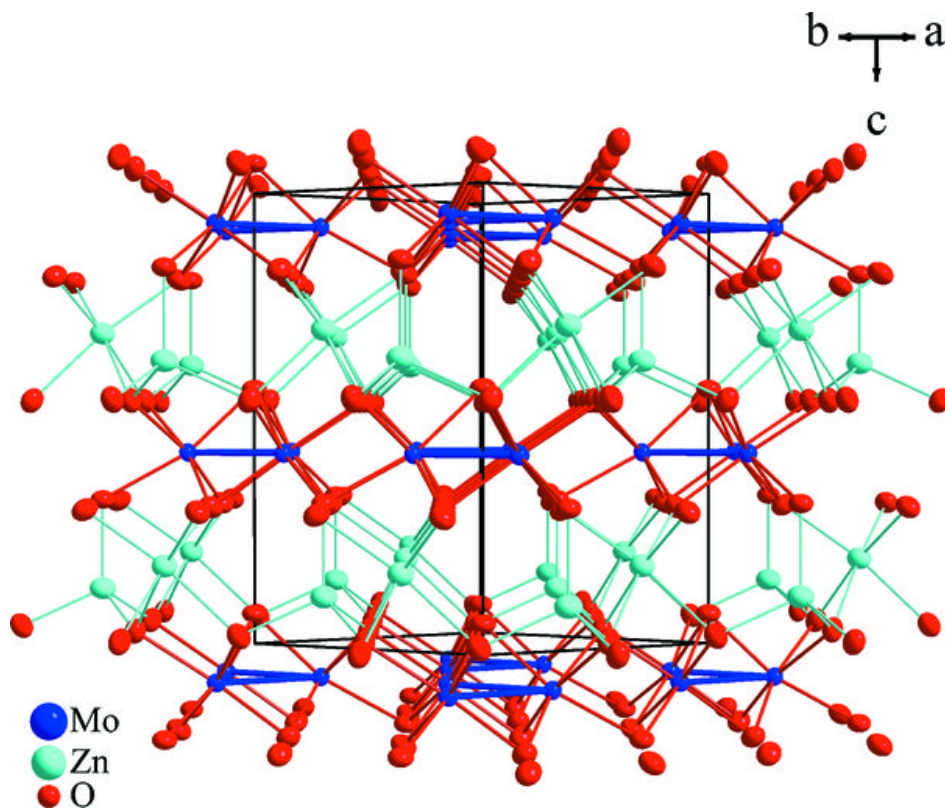
Fig. 1

Fig. 2