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Na_{2.9}KMo₁₂S₁₄: a novel quaternary reduced molybdenum sulfide containing Mo₁₂ clusters with a channel structure

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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{Mo–S}) = 0.001$ Å; disorder in main residue; R factor = 0.027; wR factor = 0.073; data-to-parameter ratio = 48.8.

The crystal structure of trisodium potassium dodecamolybdenum tetradecasulfide, Na_{2.9(2)}KMo₁₂S₁₄, consists of Mo₁₂S₁₄S₆ cluster units interconnected through interunit Mo–S bonds and delimiting channels in which the Na⁺ cations are disordered. The cluster units are centered at Wyckoff positions $2d$ and have point-group symmetry 3.2 . The K atom lies on sites with 3.2 symmetry (Wyckoff site $2c$) between two consecutive Mo₁₂S₁₄S₆ units. One of the three independent S atoms and one Na atom lie on sites with $3.$ symmetry (Wyckoff sites $4e$ and $4f$). The other Na atom occupies a $2b$ position with $\bar{3}.$ symmetry. The crystal studied was a merohedral twin with refined components of 0.4951 (13) and 0.5049 (13).

Related literature

For a previous report on the compounds K_{1+x}Mo₁₂S₁₄ ($x = 0, 1.1, 1.3, \text{ and } 1.6$), see: Picard *et al.* (2006). For details of the i - and a -type ligand notation, see: Schäfer & von Schnering (1964). For the program *JANA2000*, see: Petříček & Dušek (2000). The twinning was identified using the TwinRotMat routine in *PLATON* (Spek, 2009).

Experimental

Crystal data

Na_{2.90}KMo₁₂S₁₄
 $M_r = 1705.89$
Trigonal, $P\bar{3}_1c$
 $a = 9.3664$ (1) Å

$c = 16.2981$ (2) Å
 $V = 1238.26$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 7.24$ mm⁻¹
 $T = 100$ K

0.08 × 0.07 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical
(de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.550, T_{\max} = 0.572$

37291 measured reflections
2536 independent reflections
2376 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.13$
2536 reflections

52 parameters
 $\Delta\rho_{\max} = 2.74$ e Å⁻³
 $\Delta\rho_{\min} = -1.84$ e Å⁻³

Table 1
Selected bond lengths (Å).

Mo1–S3	2.3855 (10)	Mo2–Mo2 ^v	2.6440 (5)
Mo1–S1 ⁱ	2.4620 (8)	Mo2–Mo2 ^{iv}	2.6745 (5)
Mo1–S1	2.4822 (8)	Mo2–Mo2 ^l	2.6765 (4)
Mo1–S1 ⁱⁱ	2.4944 (8)	K1–S3	2.9460 (13)
Mo1–S2	2.5907 (7)	K1–S2 ^{vi}	3.4188 (7)
Mo1–Mo1 ⁱⁱⁱ	2.6296 (5)	K1–S2 ^{vii}	3.4188 (7)
Mo1–Mo2	2.7155 (4)	K1–S2 ^{viii}	3.4188 (7)
Mo1–Mo2 ^l	2.7803 (4)	Na1–S2 ^{ix}	3.3131 (17)
Mo2–S1	2.4589 (7)	Na1–S1 ^x	3.856 (12)
Mo2–S2	2.4655 (7)	Na1–S2 ^{xii}	3.898 (11)
Mo2–S2 ⁱⁱⁱ	2.4904 (8)	Na2–S1 ^{xiii}	3.210 (12)
Mo2–S2 ^{iv}	2.5866 (7)	Na2–S2 ^{xiii}	3.56 (2)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); 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 (www.cdifx.univ-rennes1.fr).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2051).

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supplementary materials

Acta Cryst. (2013). E69, i38 [doi:10.1107/S1600536813013603]

Na_{2.9}KMo₁₂S₁₄: a novel quaternary reduced molybdenum sulfide containing Mo₁₂ clusters with a channel structure

Patrick Gougeon, Philippe Gall and Diala Salloum

Comment

In a previous paper, we reported the synthesis, the crystal structures and, the physical properties of the compounds K_{1+x}Mo₁₂S₁₄ ($x=0, 1.1, 1.3, \text{ and } 1.6$) which crystallize in a new structural type only based on the Mo₁₂ cluster (Picard *et al.*, 2006). We present here the crystal structure of the sulfide Na_{2.9}KMo₁₂S₁₄ which is isomorphous with the latter compounds (Picard *et al.*, 2006). Its crystal structure (Fig. 1) contains Mo₁₂S₁₄ⁱS₆^a cluster units (for details of the i- and a-type ligand notation, see Schäfer & von Schnering (1964)). The i-type ligands cap Mo triangular faces and the a-type ones are in apical position for the external Mo1 atoms (Fig. 2). The Mo₁₂S₁₄ cluster unit is centred at a 2 d (D₃ or 32 symmetry) position. The Mo—Mo distances within the Mo₁₂ clusters are 2.6296 (5) Å for the distances in the triangles formed by the Mo1 related through the threefold axis and 2.6764 (4) Å in the triangles formed by the Mo2 atoms. The distances between the triangles formed by the Mo1 and Mo2 atoms are 2.7155 (4) and 2.7803 (4) Å and those between the two Mo₂ triangles, 2.6440 (5) and 2.6745 (5) Å. The sulfur atoms bridge either one [S1 and S3] or two [S2] Mo triangular faces of the clusters. Moreover the S1 atoms are linked to a Mo atom of a neighboring cluster. The Mo—S bond distances range from 2.3855 (10) to 2.5907 (7) Å. Each Mo₁₂S₁₄ unit is interconnected to 6 adjacent ones *via* Mo1—S1 bonds to form the three-dimensional Mo—S framework, the connective formula of which is Mo₁₂S₈ⁱS_{6/2}^aS_{6/2}^{a-i}. It results from this arrangement that the shortest intercluster Mo1—Mo1 distance between the Mo₁₂ clusters is 3.4025 (3) Å, indicating only weak metal-metal interaction. The Na cations reside in large channels extending along the *c* axis (Fig. 3). The Na1 cations occupied distorted tri-capped trigonal prismatic cavities of sulfur atoms and the Na2 are in an octahedron compressed along the threefold axis. The Na—S distances spread over a wide range 3.210 (12) - 3.898 (11) Å. The K cation is eight-coordinated with six S2 atoms at 3.4188 (7), forming an octahedron compressed along the threefold axis, and the remaining two S3 atoms capping two opposite faces of the octahedron at 2.9460 (13).

Experimental

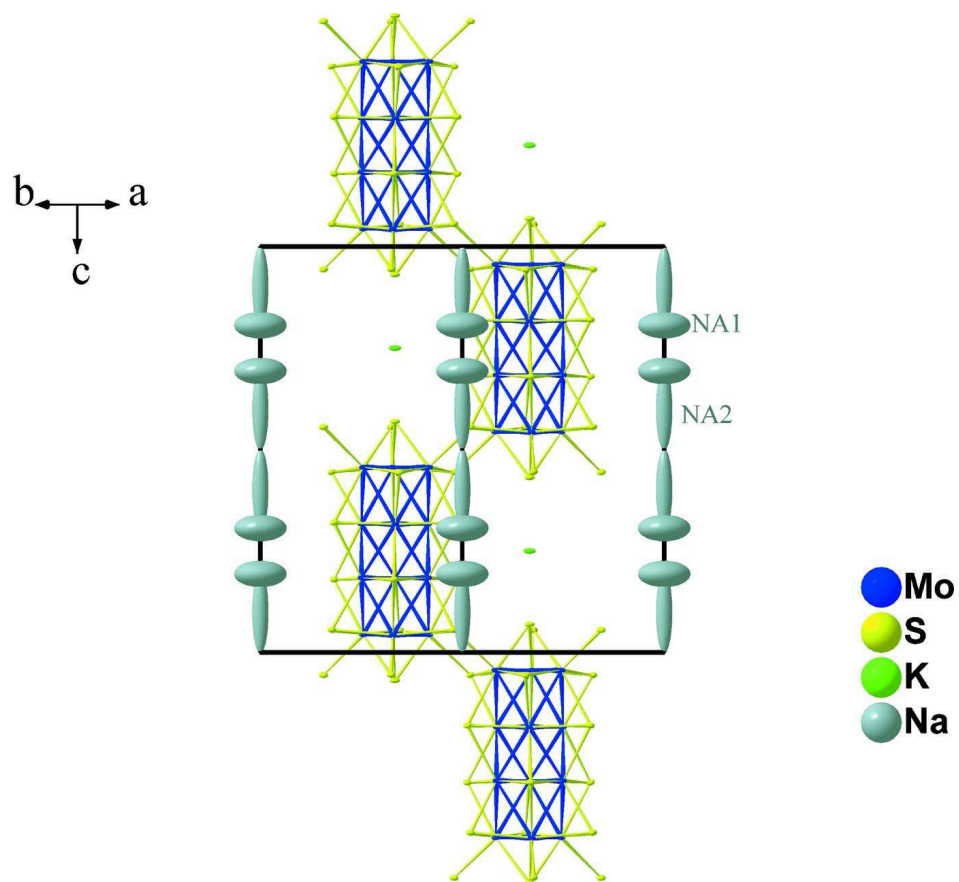
Single crystals of Na_{2.9}KMo₁₂S₁₄ were obtained by treating crystals of KMo₁₂S₁₄ in a basic reducing solution of Na₂S₂O₃/NaOH at 333 K for 3 days. The KMo₁₂S₁₄ compound was prepared by oxidation of single crystals of K_{2.3}Mo₁₂S₁₄ in an aqueous solution of iodine at 363 K for 48 h. Single crystals of K_{2.3}Mo₁₂S₁₄ were prepared from a mixture of K₂MoS₄, MoS₂, and Mo with the nominal composition K₂Mo₃S₄. 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 1773 K, temperature which was held for 6 h, then cooled at 100 K/h down to 1373 K and finally furnace cooled. All handlings of materials were done in an argon-filled glove box.

Refinement

In the first stage of the refinement, the atomic positions of the Mo and S atoms were deduced from those in $\text{KMo}_{12}\text{S}_{14}$ (Picard *et al.*, 2006). A subsequent difference-Fourier synthesis reveals the potassium atom and a quasi-continuous electron density along the *c* axis due to the sodium atoms. The latter was modelled with two partly occupied sodium sites (4 e and 2 b positions) using second-order tensors for the anisotropic displacement parameters. Anharmonic treatment of the Na1 and Na2 atoms using the program JANA2000 (Petříček & Dušek, 2000) was unsuccessful. The final occupation factors for the Na atoms were refined freely. The highest peak and the deepest hole in the final Fourier map are located 1.07 Å from Na2 and 0.58 Å from Mo2, respectively. Analysis of the intensity data using the TwinRotMat routine of PLATON (Spek, 2009) revealed the studied crystal was twinned by merohedry with $[\bar{1}00, 0\bar{1}0, 001]$ as the twin matrix. The ratio of the twin components was refined to 0.4951 (13):0.5049 (13). The Na content found seems reliable since the cationic electron transfer towards the Mo_{12} cluster deduced from our refinement is +3.9 and is in agreement with the maximal limit of +4 that the Mo_{12} cluster can accept to be well bonded and with the semi-conductor behavior observed on a single-crystal. Indeed, a lower stoichiometry in Na would lead to a metallic behavior. This is also confirmed by semi-quantitative analyses by energy dispersive spectroscopy (eds) which indicated roughly stoichiometries comprised between 2.6 and 3.2 for the Na content.

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT* (Nonius, 1998); data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Figure 1**

View of $\text{Na}_{2.9}\text{KMo}_{12}\text{S}_{14}$. Displacement ellipsoids are drawn at the 50% probability level.

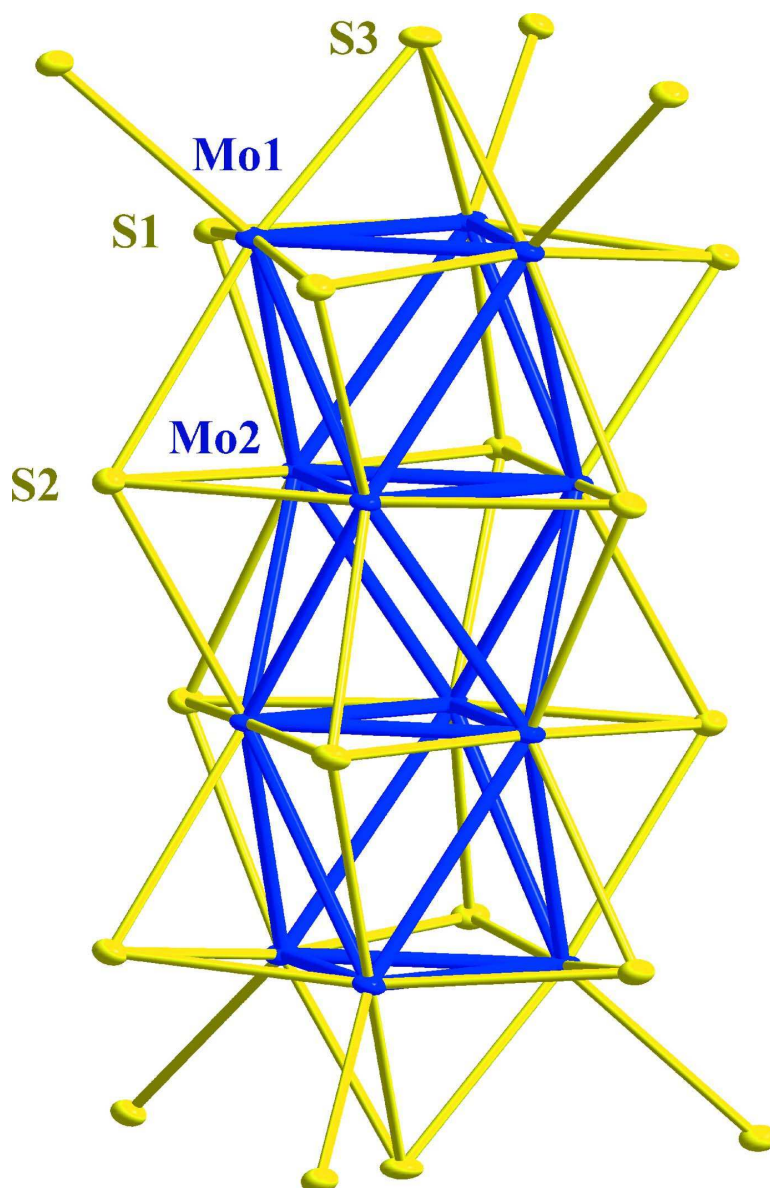
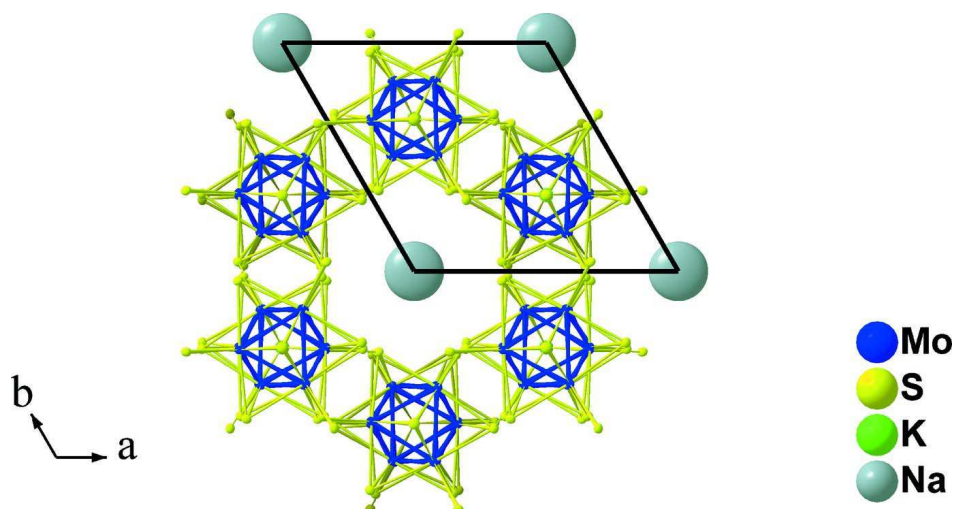


Figure 2

Plot showing the atom-numbering scheme of the $\text{Mo}_{12}\text{S}_{14}\text{S}_6$ cluster units. Displacement ellipsoids are drawn at the 50% probability level.


Figure 3

View of $\text{Na}_{2.9}\text{KMo}_{12}\text{S}_{14}$ along the c axis showing the channels. Displacement ellipsoids are drawn at the 50% probability level.

Trisodium potassium dodecamolybdenum tetradecasulfide

Crystal data

$\text{Na}_{2.90}\text{KMo}_{12}\text{S}_{14}$
 $M_r = 1705.89$
 Trigonal, $P\bar{3}1c$
 $a = 9.3664(1) \text{ \AA}$
 $c = 16.2981(2) \text{ \AA}$
 $V = 1238.26(2) \text{ \AA}^3$
 $Z = 2$
 $F(000) = 1558$

$D_x = 4.575 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 5780 reflections
 $\theta = 3.5\text{--}39.8^\circ$
 $\mu = 7.24 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Multi-faceted crystal, black
 $0.08 \times 0.07 \times 0.07 \text{ mm}$

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ scans ($\kappa = 0$) + additional ω scans
 Absorption correction: analytical
 (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.550$, $T_{\max} = 0.572$

37291 measured reflections
 2536 independent reflections
 2376 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\max} = 39.8^\circ$, $\theta_{\min} = 3.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 16$
 $l = -29 \rightarrow 27$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.13$
 2536 reflections
 52 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 4.9317P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.84 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00032 (9)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mo1	0.50983 (3)	0.16646 (3)	0.043656 (15)	0.00973 (6)	
Mo2	0.66853 (3)	0.16929 (3)	0.183610 (15)	0.00826 (5)	
S1	0.68780 (10)	0.04088 (9)	0.05564 (4)	0.01069 (11)	
S2	0.36482 (9)	0.02520 (9)	0.17966 (4)	0.01064 (11)	
S3	0.6667	0.3333	−0.06924 (8)	0.0129 (2)	
K1	0.6667	0.3333	−0.2500	0.0195 (3)	
Na1	0.0000	0.0000	0.1936 (13)	0.36 (4)	0.71 (5)
Na2	0.0000	0.0000	0.099 (3)	0.40 (4)	0.74 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01224 (10)	0.01354 (11)	0.00434 (9)	0.00714 (8)	−0.00045 (7)	0.00041 (7)
Mo2	0.01081 (9)	0.01033 (10)	0.00371 (9)	0.00535 (8)	−0.00034 (6)	−0.00060 (7)
S1	0.0143 (3)	0.0125 (3)	0.0063 (2)	0.0074 (2)	−0.0003 (2)	−0.00134 (19)
S2	0.0121 (2)	0.0118 (2)	0.0064 (2)	0.0047 (2)	−0.0014 (2)	−0.0007 (2)
S3	0.0172 (3)	0.0172 (3)	0.0044 (4)	0.00859 (16)	0.000	0.000
K1	0.0264 (5)	0.0264 (5)	0.0058 (6)	0.0132 (3)	0.000	0.000
Na1	0.47 (6)	0.47 (6)	0.12 (2)	0.24 (3)	0.000	0.000
Na2	0.045 (4)	0.045 (4)	1.12 (12)	0.023 (2)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Mo1—S3	2.3855 (10)	S3—Mo1 ⁱⁱⁱ	2.3855 (10)
Mo1—S1 ⁱ	2.4620 (8)	S3—Mo1 ⁱ	2.3855 (10)
Mo1—S1	2.4822 (8)	K1—S3	2.9460 (13)
Mo1—S1 ⁱⁱ	2.4944 (8)	K1—S3 ^{vii}	2.9460 (13)
Mo1—S2	2.5907 (7)	K1—S2 ^{viii}	3.4188 (7)
Mo1—Mo1 ⁱⁱⁱ	2.6296 (5)	K1—S2 ^{ix}	3.4188 (7)
Mo1—Mo1 ⁱ	2.6296 (5)	K1—S2 ^x	3.4188 (7)
Mo1—Mo2	2.7155 (4)	K1—S2 ⁱⁱ	3.4188 (7)
Mo1—Mo2 ⁱ	2.7803 (4)	K1—S2 ^{xi}	3.4188 (7)
Mo2—S1	2.4589 (7)	K1—S2 ^{xii}	3.4188 (7)
Mo2—S2	2.4655 (7)	Na1—Na2	1.55 (5)
Mo2—S2 ⁱⁱⁱ	2.4904 (8)	Na1—Na1 ^{xiii}	1.84 (4)
Mo2—S2 ^{iv}	2.5866 (7)	Na1—S2 ^{xiv}	3.3131 (17)
Mo2—Mo2 ^v	2.6440 (5)	Na1—S2 ^{xv}	3.3131 (17)

Mo2—Mo2 ^{iv}	2.6745 (5)	Na1—S1 ^{xvi}	3.856 (12)
Mo2—Mo2 ⁱⁱⁱ	2.6765 (4)	Na1—S1 ^{xvii}	3.856 (12)
Mo2—Mo2 ⁱ	2.6765 (4)	Na1—S1 ⁱ	3.856 (12)
Mo2—Mo1 ⁱⁱⁱ	2.7803 (4)	Na1—S2 ^{xviii}	3.898 (11)
S1—Mo1 ⁱⁱⁱ	2.4620 (8)	Na1—S2 ^{xiii}	3.898 (11)
S1—Mo1 ⁱⁱ	2.4944 (8)	Na1—S2 ^{xix}	3.898 (11)
S1—Na2 ^{vi}	3.210 (12)	Na2—S1 ⁱ	3.210 (12)
S2—Mo2 ⁱ	2.4904 (8)	Na2—S1 ^{xvi}	3.210 (12)
S2—Mo2 ^{iv}	2.5866 (7)	Na2—S1 ^{xvii}	3.210 (12)
S2—Na1	3.3131 (17)	Na2—S2 ^{xiv}	3.56 (2)
S2—K1 ⁱⁱ	3.4188 (7)	Na2—S2 ^{xv}	3.56 (2)
S3—Mo1—S1 ⁱ	92.320 (19)	Mo1 ⁱⁱⁱ —S1—Mo1 ⁱⁱ	127.81 (3)
S3—Mo1—S1	91.819 (19)	Mo1—S1—Mo1 ⁱⁱ	84.55 (3)
S1 ⁱ —Mo1—S1	169.89 (3)	Mo2—S1—Na2 ^{vi}	99.6 (9)
S3—Mo1—S1 ⁱⁱ	89.07 (3)	Mo1 ⁱⁱⁱ —S1—Na2 ^{vi}	98.08 (6)
S1 ⁱ —Mo1—S1 ⁱⁱ	93.84 (4)	Mo1—S1—Na2 ^{vi}	160.3 (4)
S1—Mo1—S1 ⁱⁱ	95.45 (3)	Mo1 ⁱⁱ —S1—Na2 ^{vi}	114.5 (6)
S3—Mo1—S2	171.28 (3)	Mo2—S2—Mo2 ⁱ	65.37 (2)
S1 ⁱ —Mo1—S2	84.81 (3)	Mo2—S2—Mo2 ^{iv}	63.873 (19)
S1—Mo1—S2	89.74 (2)	Mo2 ⁱ —S2—Mo2 ^{iv}	62.735 (18)
S1 ⁱⁱ —Mo1—S2	99.32 (2)	Mo2—S2—Mo1	64.912 (19)
S3—Mo1—Mo1 ⁱⁱⁱ	56.554 (16)	Mo2 ⁱ —S2—Mo1	66.315 (19)
S1 ⁱ —Mo1—Mo1 ⁱⁱⁱ	118.03 (2)	Mo2 ^{iv} —S2—Mo1	118.36 (3)
S1—Mo1—Mo1 ⁱⁱⁱ	57.50 (2)	Mo2—S2—Na1	154.66 (8)
S1 ⁱⁱ —Mo1—Mo1 ⁱⁱⁱ	131.58 (2)	Mo2 ⁱ —S2—Na1	89.74 (2)
S2—Mo1—Mo1 ⁱⁱⁱ	117.822 (17)	Mo2 ^{iv} —S2—Na1	101.5 (3)
S3—Mo1—Mo1 ⁱ	56.554 (16)	Mo1—S2—Na1	110.7 (3)
S1 ⁱ —Mo1—Mo1 ⁱ	58.24 (2)	Mo2—S2—K1 ⁱⁱ	92.19 (2)
S1—Mo1—Mo1 ⁱ	117.29 (2)	Mo2 ⁱ —S2—K1 ⁱⁱ	150.01 (3)
S1 ⁱⁱ —Mo1—Mo1 ⁱ	130.870 (19)	Mo2 ^{iv} —S2—K1 ⁱⁱ	90.10 (2)
S2—Mo1—Mo1 ⁱ	115.293 (18)	Mo1—S2—K1 ⁱⁱ	123.66 (3)
Mo1 ⁱⁱⁱ —Mo1—Mo1 ⁱ	60.0	Na1—S2—K1 ⁱⁱ	109.13 (14)
S3—Mo1—Mo2	119.13 (2)	Mo1 ⁱⁱⁱ —S3—Mo1	66.89 (3)
S1 ⁱ —Mo1—Mo2	113.78 (2)	Mo1 ⁱⁱⁱ —S3—Mo1 ⁱ	66.89 (3)
S1—Mo1—Mo2	56.254 (17)	Mo1—S3—Mo1 ⁱ	66.89 (3)
S1 ⁱⁱ —Mo1—Mo2	137.91 (2)	Mo1 ⁱⁱⁱ —S3—K1	140.47 (2)
S2—Mo1—Mo2	55.315 (17)	Mo1—S3—K1	140.47 (2)
Mo1 ⁱⁱⁱ —Mo1—Mo2	62.662 (9)	Mo1 ⁱ —S3—K1	140.47 (2)
Mo1 ⁱ —Mo1—Mo2	91.183 (8)	S3—K1—S3 ^{vii}	180.0
S3—Mo1—Mo2 ⁱ	116.65 (2)	S3—K1—S2 ^{viii}	70.407 (11)
S1 ⁱ —Mo1—Mo2 ⁱ	55.546 (18)	S3 ^{vii} —K1—S2 ^{viii}	109.593 (11)
S1—Mo1—Mo2 ⁱ	114.41 (2)	S3—K1—S2 ^{ix}	109.593 (11)
S1 ⁱⁱ —Mo1—Mo2 ⁱ	138.42 (2)	S3 ^{vii} —K1—S2 ^{ix}	70.407 (11)
S2—Mo1—Mo2 ⁱ	55.112 (17)	S2 ^{viii} —K1—S2 ^{ix}	171.43 (2)
Mo1 ⁱⁱⁱ —Mo1—Mo2 ⁱ	89.759 (7)	S3—K1—S2 ^x	109.593 (11)
Mo1 ⁱ —Mo1—Mo2 ⁱ	60.181 (8)	S3 ^{vii} —K1—S2 ^x	70.407 (11)
Mo2—Mo1—Mo2 ⁱ	58.275 (11)	S2 ^{viii} —K1—S2 ^x	63.43 (2)
S1—Mo2—S2	93.26 (3)	S2 ^{ix} —K1—S2 ^x	109.349 (11)

S1—Mo2—S2 ⁱⁱⁱ	87.06 (3)	S3—K1—S2 ⁱⁱ	70.407 (11)
S2—Mo2—S2 ⁱⁱⁱ	173.83 (2)	S3 ^{vii} —K1—S2 ⁱⁱ	109.593 (11)
S1—Mo2—S2 ^{iv}	117.76 (2)	S2 ^{viii} —K1—S2 ⁱⁱ	109.349 (11)
S2—Mo2—S2 ^{iv}	90.68 (3)	S2 ^{ix} —K1—S2 ⁱⁱ	63.43 (2)
S2 ⁱⁱⁱ —Mo2—S2 ^{iv}	94.62 (3)	S2 ^x —K1—S2 ⁱⁱ	78.22 (2)
S1—Mo2—Mo2 ^v	144.46 (2)	S3—K1—S2 ^{xi}	109.593 (11)
S2—Mo2—Mo2 ^v	120.668 (19)	S3 ^{vii} —K1—S2 ^{xi}	70.407 (11)
S2 ⁱⁱⁱ —Mo2—Mo2 ^v	60.414 (17)	S2 ^{viii} —K1—S2 ^{xi}	78.22 (2)
S2 ^{iv} —Mo2—Mo2 ^v	56.852 (18)	S2 ^{ix} —K1—S2 ^{xi}	109.349 (11)
S1—Mo2—Mo2 ^{iv}	150.83 (2)	S2 ^x —K1—S2 ^{xi}	109.349 (12)
S2—Mo2—Mo2 ^{iv}	60.265 (17)	S2 ⁱⁱ —K1—S2 ^{xi}	171.43 (2)
S2 ⁱⁱⁱ —Mo2—Mo2 ^{iv}	120.634 (19)	S3—K1—S2 ^{xii}	70.407 (11)
S2 ^{iv} —Mo2—Mo2 ^{iv}	55.862 (18)	S3 ^{vii} —K1—S2 ^{xii}	109.593 (11)
Mo2 ^v —Mo2—Mo2 ^{iv}	60.428 (12)	S2 ^{viii} —K1—S2 ^{xii}	109.349 (11)
S1—Mo2—Mo2 ⁱⁱⁱ	115.260 (19)	S2 ^{ix} —K1—S2 ^{xii}	78.22 (2)
S2—Mo2—Mo2 ⁱⁱⁱ	117.738 (19)	S2 ^x —K1—S2 ^{xii}	171.43 (2)
S2 ⁱⁱⁱ —Mo2—Mo2 ⁱⁱⁱ	56.865 (19)	S2 ⁱⁱ —K1—S2 ^{xii}	109.349 (11)
S2 ^{iv} —Mo2—Mo2 ⁱⁱⁱ	117.009 (17)	S2 ^{xi} —K1—S2 ^{xii}	63.43 (2)
Mo2 ^v —Mo2—Mo2 ⁱⁱⁱ	60.350 (10)	Na2—Na1—Na1 ^{xiii}	180.000 (2)
Mo2 ^{iv} —Mo2—Mo2 ⁱⁱⁱ	89.670 (5)	Na2—Na1—S2 ^{xiv}	86.1 (4)
S1—Mo2—Mo2 ⁱ	119.02 (2)	Na1 ^{xiii} —Na1—S2 ^{xiv}	93.9 (4)
S2—Mo2—Mo2 ⁱ	57.760 (19)	Na2—Na1—S2	86.1 (4)
S2 ⁱⁱⁱ —Mo2—Mo2 ⁱ	116.843 (19)	Na1 ^{xiii} —Na1—S2	93.9 (4)
S2 ^{iv} —Mo2—Mo2 ⁱ	115.061 (17)	S2 ^{xiv} —Na1—S2	119.54 (9)
Mo2 ^v —Mo2—Mo2 ⁱ	90.323 (5)	Na2—Na1—S2 ^{xv}	86.1 (4)
Mo2 ^{iv} —Mo2—Mo2 ⁱ	59.222 (10)	Na1 ^{xiii} —Na1—S2 ^{xv}	93.9 (4)
Mo2 ⁱⁱⁱ —Mo2—Mo2 ⁱ	60.0	S2 ^{xiv} —Na1—S2 ^{xv}	119.54 (9)
S1—Mo2—Mo1	57.07 (2)	S2—Na1—S2 ^{xv}	119.54 (9)
S2—Mo2—Mo1	59.773 (17)	Na2—Na1—Na2 ^{xiii}	180.000 (2)
S2 ⁱⁱⁱ —Mo2—Mo1	115.73 (2)	Na1 ^{xiii} —Na1—Na2 ^{xiii}	0.000 (2)
S2 ^{iv} —Mo2—Mo1	147.71 (2)	S2 ^{xiv} —Na1—Na2 ^{xiii}	93.9 (4)
Mo2 ^v —Mo2—Mo1	147.951 (10)	S2—Na1—Na2 ^{xiii}	93.9 (4)
Mo2 ^{iv} —Mo2—Mo1	111.157 (13)	S2 ^{xv} —Na1—Na2 ^{xiii}	93.9 (4)
Mo2 ⁱⁱⁱ —Mo2—Mo1	90.180 (8)	Na1—Na2—S1 ⁱ	102.6 (9)
Mo2 ⁱ —Mo2—Mo1	62.075 (8)	Na1—Na2—S1 ^{xvii}	102.6 (9)
S1—Mo2—Mo1 ⁱⁱⁱ	55.650 (19)	S1 ⁱ —Na2—S1 ^{xvii}	115.4 (7)
S2—Mo2—Mo1 ⁱⁱⁱ	116.776 (19)	Na1—Na2—S1 ^{xvi}	102.6 (9)
S2 ⁱⁱⁱ —Mo2—Mo1 ⁱⁱⁱ	58.573 (17)	S1 ⁱ —Na2—S1 ^{xvi}	115.4 (7)
S2 ^{iv} —Mo2—Mo1 ⁱⁱⁱ	151.11 (2)	S1 ^{xvii} —Na2—S1 ^{xvi}	115.4 (7)
Mo2 ^v —Mo2—Mo1 ⁱⁱⁱ	110.082 (13)	Na1—Na2—Na2 ^{xx}	180.000 (2)
Mo2 ^{iv} —Mo2—Mo1 ⁱⁱⁱ	144.903 (10)	S1 ⁱ —Na2—Na2 ^{xx}	77.4 (9)
Mo2 ⁱⁱⁱ —Mo2—Mo1 ⁱⁱⁱ	59.650 (8)	S1 ^{xvii} —Na2—Na2 ^{xx}	77.4 (9)
Mo2 ⁱ —Mo2—Mo1 ⁱⁱⁱ	88.804 (7)	S1 ^{xvi} —Na2—Na2 ^{xx}	77.4 (9)
Mo1—Mo2—Mo1 ⁱⁱⁱ	57.157 (12)	Na1—Na2—Na1 ^{xiii}	0.000 (1)
Mo2—S1—Mo1 ⁱⁱⁱ	68.80 (2)	S1 ⁱ —Na2—Na1 ^{xiii}	102.6 (9)
Mo2—S1—Mo1	66.67 (2)	S1 ^{xvii} —Na2—Na1 ^{xiii}	102.6 (9)

Mo1 ⁱⁱⁱ —S1—Mo1	64.26 (2)	S1 ^{xvi} —Na2—Na1 ^{xiii}	102.6 (9)
Mo2—S1—Mo1 ⁱⁱ	136.36 (4)	Na2 ^{xx} —Na2—Na1 ^{xiii}	180.000 (1)

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