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Na$_{4.25}$Mo$_{15}$S$_{19}$: a novel ternary reduced molybdenum sulfide containing Mo$_6$ and Mo$_9$ clusters

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Key indicators: single-crystal X-ray study; $T$ = 293 K; mean occupancy of Mo–S = 0.001 Å; disorder in solvent or counterion; $R$ factor = 0.030; $wR$ factor = 0.079; data-to-parameter ratio = 22.7.

The structure of Na$_4$Mo$_{15}$S$_{19}$, isotypic with Na$_{3.96}$Mo$_{15}$Se$_{19}$ [Salloum et al. (2013)]. Acta Cryst. E69, i67–i68. It is characterized by Mo$_6$S$_6$O$_6$ and Mo$_9$S$_{11}$O$_6$ (where $i$ represents inner and $a$ apical atoms) cluster units that are present in a 1:1 ratio. The cluster units are centered at Wyckoff positions 2$a$ and 2$c$, and have point-group symmetry 3 and 6, respectively. The clusters are interconnected through additional Mo–S bonds. The Na$^+$ cations occupy interunit voids formed by six or seven S atoms. One Mo, one S and one Na site (full occupancy) are situated on mirror planes, and two other S atoms. One Mo$_9$ cluster, one S and one Na site are situated on mirror planes, and two other S atoms and one Na site (full occupancy) are situated on threefold rotation axes.

Related literature

For previous reports on the crystal structure of the In$_{3-x}$Mo$_{15}$S$_{19}$ compounds, see: Grüttnner et al. (1979). For physical properties of this type of compounds, see: Seeber et al. (1979). The crystal structures of the substituted selenides H$_{0.76}$In$_{1.68}$Mo$_{15}$Se$_{19}$ and In$_{0.87}$K$_2$Mo$_{15}$Se$_{19}$ were reported by Salloum et al. (2006; 2007). For the isotypic sulfides In$_{3.7}$Mo$_{15}$S$_{19}$, In$_{1.6}Rb$_2$Mo$_{15}$S$_{19}$, In$_{2.2}$CsMo$_{15}$S$_{19}$, Sc$_3$Tl$_2$Mo$_{15}$S$_{19}$, Na$_3$Mo$_{15}$S$_{19}$ and Na$_{3.9}$Mo$_{15}$Se$_{19}$, see: Salloum et al. (2004a,b). For $V_{1.42}$In$_{1.83}$Mo$_{15}$Se$_{19}$, see: Gougeon et al. (2010). For details of the $i$- and $a$-type ligand notation, see: Schäfer & von Schnering (1964).

Experimental

Crystal data

Na$_{4.25}$Mo$_{15}$S$_{19}$

$M_r = 2145.95$

Hexagonal, $P6_3/m$

$a = 9.5340$ (1) Å

$c = 18.9803$ (3) Å

$V = 1494.11$ (3) Å$^3$

Absorption correction: analytical

$R_{	ext{int}} = 0.085$

$T = 293$ K

$\mu = 7.44$ mm$^{-1}$

$\omega$ scans

2850 measured reflections

1500 independent reflections

$R_{	ext{1}} = 0.030$

$R_{	ext{2}} = 0.079$

$S = 1.13$

Data collection

Nonius KappaCCD diffractometer

$R_{	ext{int}} = 0.085$

Absorption correction: analytical

$R_{	ext{1}} = 0.030$

$R_{	ext{2}} = 0.079$

$S = 1.13$

1500 reflections

Supporting information for this paper is available from the IUCr electronic archives (Reference: RU2060).

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Na$_{4.25}$Mo$_{15}$S$_{19}$: a novel ternary reduced molybdenum sulfide containing Mo$_6$ and Mo$_9$ clusters

D. Salloum, P. Gougeon and P. Gall

1. Comment

The reduced molybdenum compounds In$_{1+x}$Mo$_{15}X_{19}$ ($X$ = S, Se) (Grüttner et al., 1979; Salloum et al., 2004a) crystallize in an interesting structural type characterized by an equal mixture of Mo$_6$ and Mo$_9$ clusters and by In atoms that occupy two or three different crystallographically positions depending on their formal oxidation state of +1 or +3. Subsequently, isomorphous compounds such as Ho$_{0.76}$In$_{1.68}$Mo$_{15}$Se$_{19}$ (Salloum et al., 2006), In$_{0.71}$K$_2$Mo$_{15}$Se$_{19}$ (Salloum et al., 2007), V$_{1.42}$In$_{1.83}$Mo$_{15}$Se$_{19}$ (Gougeon et al., 2010), In$_{1.7}$Mo$_{15}$S$_{19}$ (Salloum et al., 2004a), In$_{1.8}$Rb$_2$Mo$_{15}$S$_{19}$, In$_{1.2}$CsMo$_{15}$S$_{19}$ and ScTl$_2$Mo$_{15}$S$_{19}$ (Salloum et al., 2004b) have been synthesized. In the latter compounds, the Ho, V and Sc atoms replace the trivalent indium and the K, Cs, and Tl atoms the monovalent one. Recently, we described the crystal structure of Na$_{3.9}$Mo$_{15}$Se$_{19}$ (Salloum et al., 2013) in which the sodium replaces the monovalent as well as the trivalent indium for the first time. We present here the sulfide analogue Na$_{4.25}$Mo$_{15}$S$_{19}$. The Mo—S framework of the title compound consists of the cluster units Mo$_6$S$_8$S$_6^a$ and Mo$_9$S$_{11}$S$_6^a$ in a 1:1 ratio (for details of the i- and a-type ligand notation, see Schäfer & von Schnering (1964)). Both components are interconnected through additional Mo—Se bonds (Figs. 1 and 2). The first unit can be described as an Mo$_6$ octahedron surrounded by eight face-capping inner S$^i$ and six apical S$^a$ ligands. The Mo$_6$ cluster is surrounded by 11 S$^i$ atoms capping one or two faces of the biocathedron and six S$^a$ ligands above the apical Mo atoms. The Mo$_6$S$_8$S$_6^a$ and Mo$_9$S$_{11}$S$_6^a$ units are centered at Wyckoff positions 2b and 2c and have point-group symmetry 32 and 6, respectively. The Mo—Mo distances within the Mo$_6$ cluster are 2.6900 (5) Å for the distances of the Mo triangles formed by the Mo1 atoms related through the threefold axis, and 2.7098 (6) Å for the distances between these triangles. The Mo—Mo distances within the Mo$_9$ clusters are 2.6349 (5) and 2.6756 (7) Å in the triangles formed by the atoms Mo2 and Mo3, respectively, and 2.7081 (4) and 2.7303 (4) Å for those between the Mo2$_3$ and Mo3$_3$ triangles. All the latter Mo—Mo distances are close to those observed in the selenide analogue indicating that the cationic charge transfer towards the Mo$_6$ and Mo$_9$ clusters are similar in both compounds. The S atoms bridge either one (S1, S2, S4 and S5) or two (S3) triangular faces of the Mo clusters. Moreover, atoms S1 and S2 are linked to an Mo atom of a neighboring cluster. The Mo—S bond distances range from 2.4184 (14) to 2.5624 (10) Å within the Mo$_6$S$_8$S$_6^a$ unit, and from 2.4033 (13) to 2.5947 (8) Å within the Mo$_9$S$_{11}$S$_6^a$ unit. In both cases, the shortest bonds involve the S4 and S5 terminal atoms and the longest ones correspond to the interunit Mo1—S2 and Mo2—S1 bonds. Each Mo$_6$S$_8$S$_6^a$ cluster is thus interconnected to six Mo$_9$S$_{11}$S$_6^a$ units (and vice versa) via Mo2—S1 bonds (and Mo1—S2 bonds, respectively), forming the three-dimensional Mo—S framework, the connective formula of which is Mo$_6$S$_8$S$_6^a$S$^i_{6}$S$^i_{6}$, Mo$_9$S$_{11}$S$_6^a$S$^i_{6}$S$^i_{6}$. It results from this arrangement that the shortest intercluster Mo1—Mo2 distance is 3.5202 (6) Å, indicating only weak metal-metal interactions between the Mo clusters. The Na$^{1+}$ cations are surrounded by seven S atoms forming a distorted tricapped tetrahedron. The S5 and S2 atoms forming the tetrahedron are at 2.699 (5) and 3.1669 (13) Å from the Na1 atom, and the capping S1 atoms are at 3.3609 (19) Å. The Na$^{2+}$ cations...
occupy partially at 75.1% a triangular group of distorted octahedral cavities around the threefold axis, which are formed by two Mo₆S₆S₆ and three Mo₉S₁₁S₆ units. The Na2—S distances are in the 2.538 (4) - 3.055 (4) Å range.

2. Experimental

Single crystals of Na₄.₂₅Mo₁₅S₁₉ were prepared from an ion exchange reaction on single crystals of InₓMo₁₅S₁₉ with an excess of NaI at 1073 K. The mixture was sealed under vacuum in a long silica tube. The end of tube containing the crystals of InₓMo₁₅S₁₉ and InI was placed in a furnace with about 5 cm of the other end out from the furnace, at about the room temperature. The furnace was heated at 1073 K for 48 h. After reaction, crystals of InI were observed at the cool end of the tube. The black crystals of the title compound were subsequently washed with water to remove the excess of InI. Qualitative microanalyses using a Jeol JSM 6400 scanning electron microscope equipped with a Oxford INCA energy- dispersive-type X-ray spectrometer did not reveal the presence of indium in the crystals and indicated roughly stoichiometries comprised between 3.8 and 4.4 for the Na content.

3. Refinement

No significant deviation from full occupancy was observed for Na1. The site occupation factor of Na2 was refined freely leading to the final stoichiometry Na₄.₂₅(4)Mo₁₅S₁₉.

Figure 1

View of Na₄.₂₅Mo₁₅S₁₉ along [110]. Displacement ellipsoids are drawn at the 97% probability level.
Figure 2
Plot showing the atom-numbering scheme and the interunit linkage of the Mo₉S₁₁S₆ and Mo₆S₈S₆ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

Tetrasodium pentadecamolybdenum nonadecasulfide

Crystal data

\[ \text{Na}_{4.25}\text{Mo}_{15}\text{S}_{19} \]
\[ M_r = 2145.95 \]
Hexagonal, \( P6_3/m \)
\[ a = 9.5340 (1) \, \text{Å} \]
\[ c = 18.9803 (3) \, \text{Å} \]
\[ V = 1494.11 (3) \, \text{Å}^3 \]
\[ Z = 2 \]
\[ F(000) = 1962 \]
\[ D_x = 4.770 \, \text{Mg m}^{-3} \]
Mo \( K\alpha \) radiation, \( \lambda = 0.71069 \, \text{Å} \)

Cell parameters from 16576 reflections
\[ \theta = 2.2–30.0^\circ \]
\[ \mu = 7.44 \, \text{mm}^{-1} \]
\[ T = 293 \, \text{K} \]
Multi-faceted crystal, black
\[ 0.18 \times 0.14 \times 0.08 \, \text{mm} \]

Data collection

Nonius KappaCCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
\( \phi \) scans \((\kappa = 0) + \) additional \( \omega \) scans

Absorption correction: analytical
(de Meulenaar & Tompa, 1965)
\[ T_{\text{min}} = 0.363, \ T_{\text{max}} = 0.591 \]
16576 measured reflections
1500 independent reflections
supplementary materials

1322 reflections with $I > 2\sigma(I)$

$R_{int} = 0.085$

$\theta_{max} = 30.0^\circ$, $\theta_{min} = 2.2^\circ$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.079$

$S = 1.13$

1500 reflections

66 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{1/4}$

Extinction coefficient: 0.00266 (19)

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 ($\AA^2$)

|      | $x$       | $y$       | $z$       | $U_{iso}/U_{eq}$ | Occ. (<1) |
|------|-----------|-----------|-----------|------------------|-----------|
| Mo1  | 0.84424 (3)| 0.01344 (3)| -0.058496 (18)| 0.01072 (12)    |           |
| Mo2  | 0.50077 (4)| -0.18303 (4)| 0.131678 (19)| 0.01177 (12)    |           |
| Mo3  | 0.34797 (5)| -0.16448 (5)| 0.2500     | 0.01301 (13)    |           |
| S1   | 0.71650 (10)| 0.02755 (11)| 0.05118 (5)  | 0.01268 (18)    |           |
| S2   | 0.36949 (11)| -0.01601 (11)| 0.13948 (5)  | 0.01344 (19)    |           |
| S3   | 0.05126 (16)| -0.30754 (17)| 0.2500     | 0.0171 (3)      |           |
| S4   | 0.0000   | -0.0000   | -0.15617 (9) | 0.0184 (3)      |           |
| S5   | 0.3333   | -0.3333   | 0.03365 (9)  | 0.0156 (3)      |           |
| Na2  | 0.7703 (5)| -0.0623 (4)| -0.2500     | 0.0283 (12)     | 0.751 (12) |
| Na1  | 0.3333   | -0.3333   | -0.1085 (3)  | 0.0789 (17)     |           |

Atomic displacement parameters ($\AA^2$)

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| Mo1  | 0.01252 (16) | 0.01051 (16) | 0.00816 (19) | 0.00050 (11) | 0.00061 (10) | -0.00031 (9) |
| Mo2  | 0.01434 (17) | 0.01410 (17) | 0.00778 (19) | 0.00078 (12) | -0.00017 (10) | -0.00005 (10) |
| Mo3  | 0.0153 (2)   | 0.0159 (2)   | 0.0075 (2)   | 0.00754 (17) | 0.000     | 0.000     |
| S1   | 0.0121 (4)   | 0.0138 (4)   | 0.0121 (4)   | 0.0064 (3)   | 0.0013 (3)  | 0.0005 (3) |
| S2   | 0.0154 (4)   | 0.0143 (4)   | 0.0112 (4)   | 0.0079 (3)   | 0.0001 (3)  | 0.0008 (3) |
| S3   | 0.0185 (6)   | 0.0198 (6)   | 0.0133 (7)   | 0.0098 (5)   | 0.000     | 0.000     |
| S4   | 0.0228 (5)   | 0.0228 (5)   | 0.0095 (8)   | 0.0114 (2)   | 0.000     | 0.000     |
| S5   | 0.0187 (4)   | 0.0187 (4)   | 0.0093 (7)   | 0.0094 (2)   | 0.000     | 0.000     |
| Na2  | 0.040 (2)    | 0.0256 (19)  | 0.026 (2)    | 0.0218 (16)  | 0.000     | 0.000     |
| Na1  | 0.0333      | -0.3333     | -0.1085 (3)  | 0.0789 (17)  |           |           |
### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°) | Distance (Å) |
|-----------------------|--------------|-----------|--------------|
| Mo1—S4                 | 2.4184 (14)  | S2—Mo1    | 2.5624 (10)  |
| Mo1—S1                 | 2.4492 (10)  | S2—Na2    | 2.781 (2)    |
| Mo1—S1\(\text{ii}\)   | 2.4565 (9)   | S2—Na1\(\text{iv}\) | 3.1669 (13) |
| Mo1—S1\(\text{iii}\)  | 2.4830 (9)   | S3—Mo3\(\text{iii}\) | 2.4419 (14) |
| Mo1—S2\(\text{iv}\)   | 2.5624 (10)  | S3—Na2\(\text{ii}\) | 2.538 (4)   |
| Mo1—Mo1\(\text{v}\)   | 2.6900 (5)   | S3—Mo2\(\text{v}\) | 2.5947 (8)  |
| Mo1—Mo1\(\text{vi}\)  | 2.6900 (5)   | S3—Mo2\(\text{iii}\) | 2.5947 (8)  |
| Mo1—Mo1\(\text{iii}\) | 2.7098 (6)   | S3—Na2\(\text{iv}\) | 3.055 (4)   |
| Mo1—Mo1\(\text{ii}\)  | 2.7098 (6)   | S4—Mo1\(\text{viii}\) | 2.4184 (14) |
| Mo1—Na2                | 3.7042 (8)   | S4—Mo1\(\text{ix}\) | 2.4184 (14) |
| Mo2—S5                 | 2.4033 (13)  | S4—Mo1\(\text{iii}\) | 2.4184 (14) |
| Mo2—S2                 | 2.4733 (9)   | S4—Na2\(\text{iv}\) | 2.649 (3)   |
| Mo2—S2\(\text{v}\)    | 2.5070 (9)   | S4—Na2\(\text{iii}\) | 2.649 (3)   |
| Mo2—S1                 | 2.5429 (10)  | S4—Na2\(\text{iv}\) | 2.649 (3)   |
| Mo2—S2\(\text{vii}\)  | 2.5947 (8)   | S5—Mo2\(\text{ix}\) | 2.4033 (13) |
| Mo2—Mo2\(\text{vii}\) | 2.6349 (5)   | S5—Mo2\(\text{v}\) | 2.4033 (13) |
| Mo2—Mo2\(\text{viii}\)| 2.6349 (5)   | S5—Na1    | 2.699 (5)   |
| Mo2—Mo3\(\text{v}\)   | 2.7081 (4)   | Na2—S3\(\text{iv}\) | 2.538 (4)   |
| Mo3—S3\(\text{vii}\)  | 2.4419 (14)  | Na2—S4\(\text{i}\) | 2.649 (3)   |
| Mo3—S3                 | 2.4504 (14)  | Na2—S4\(\text{v}\) | 2.649 (3)   |
| Mo3—S3\(\text{v}\)    | 2.4810 (10)  | Na2—S4\(\text{viii}\) | 2.781 (2)   |
| Mo3—S2\(\text{v}\)    | 2.4810 (10)  | Na2—S4\(\text{iv}\) | 2.781 (2)   |
| Mo3—Mo3\(\text{v}\)   | 2.6756 (7)   | Na2—S3\(\text{v}\) | 2.896 (3)   |
| Mo3—Mo3\(\text{vii}\) | 2.6756 (7)   | Na2—S3\(\text{v}\) | 3.055 (4)   |
| Mo3—Mo3\(\text{viii}\)| 2.7081 (4)   | Na2—S3\(\text{v}\) | 3.397 (6)   |
| Mo3—Mo2\(\text{v}\)   | 2.7081 (4)   | Na2—S3\(\text{v}\) | 3.397 (6)   |
| Mo3—Mo2\(\text{vii}\) | 2.7303 (4)   | Na2—S3\(\text{v}\) | 3.7042 (8)  |
| Mo3—Na2\(\text{v}\)   | 2.896 (3)    | Na1—S2\(\text{v}\) | 3.1669 (13) |
| S1—Mo1\(\text{v}\)    | 2.4565 (9)   | Na1—S2\(\text{v}\) | 3.1669 (13) |
| S1—Mo1\(\text{ii}\)   | 2.4830 (9)   | Na1—S2\(\text{v}\) | 3.1669 (13) |
| S1—Na1\(\text{v}\)    | 3.3609 (19)  | Na1—S1\(\text{v}\) | 3.3609 (19) |
| S2—Mo2\(\text{viii}\) | 2.5070 (9)   | Na1—S1\(\text{v}\) | 3.3609 (19) |

| Bond                  | Distance (Å) | Distance (Å) |
|-----------------------|--------------|--------------|
| S4—Mo1—S1             | 171.81 (4)   | Mo1—S1—Mo1\(\text{ii}\) | 66.65 (3)   |
| S4—Mo1—S1\(\text{ii}\)| 90.83 (2)    | Mo1—Mo1—S1\(\text{ii}\) | 134.06 (4)  |
| S1—Mo1—S1             | 89.17 (2)    | Mo1—Mo1—S1\(\text{ii}\) | 134.06 (4)  |
| S4—Mo1—S1\(\text{iii}\)| 90.20 (2)    | Mo1—Mo1—S1\(\text{iii}\) | 134.06 (4)  |
| S1—Mo1—S1\(\text{iii}\)| 88.56 (2)    | Mo1—S1—Mo1\(\text{iii}\) | 130.92 (4)  |
| S1—Mo1—S1\(\text{iv}\) | 171.12 (4)   | Mo1—S1—Mo1\(\text{iv}\) | 127.79 (8)  |
| S4—Mo1—S2\(\text{v}\) | 93.04 (8)    | Mo1—S1—Mo1\(\text{v}\) | 97.39 (3)   |
| S1—Mo1—S2\(\text{v}\) | 95.15 (3)    | Mo1—S1—Mo1\(\text{v}\) | 153.45 (7)  |
| S1—Mo1—S2\(\text{vii}\)| 91.20 (3)    | Mo2—S1—Na1\(\text{iv}\) | 94.64 (6)   |
| S1—Mo1—S2\(\text{v}\) | 97.55 (3)    | Mo2—S2—Mo3   | 66.88 (3)   |
| S4—Mo1—Mo1\(\text{v}\) | 56.21 (2)    | Mo2—S2—Mo2\(\text{v}\) | 63.88 (2)   |
| S1—Mo1—Mo1\(\text{v}\) | 116.82 (2)   | Mo3—S2—Mo2\(\text{v}\) | 65.76 (2)   |
| Bond  | Distance (Å) | Standard Deviation (Å) | Bond  | Distance (Å) | Standard Deviation (Å) |
|-------|--------------|-------------------------|-------|--------------|-------------------------|
| S1⁵—Mo1—Mo1⁴  | 117.37 (2)   | Mo2—S2—Mo1⁴            | 129.13 (4) |
| S1⁴—Mo1—Mo1⁴  | 56.53 (2)    | Mo3—S2—Mo1⁴            | 132.33 (4) |
| S2⁴—Mo1—Mo1⁴  | 135.73 (2)   | Mo2³⁻—S2—Mo1⁴          | 82.07 (3)  |
| S4—Mo1—Mo1⁴   | 56.21 (2)    | Mo2—S2—Na2⁴            | 133.09 (7) |
| S1—Mo1—Mo1⁴   | 117.46 (2)   | Mo3—S2—Na2⁴            | 66.52 (6)  |
| S1⁰—Mo1—Mo1⁴  | 57.48 (2)    | Mo2Ⅲ—S2—Na2⁴          | 100.94 (8) |
| S1Ⅲ—Mo1—Mo1⁴  | 116.43 (2)   | Mo1Ⅳ—S2—Na2⁴          | 87.68 (6)  |
| S2Ⅲ—Mo1—Mo1⁴  | 131.85 (2)   | Mo2—S2—Na1⁴            | 101.03 (3) |
| Mo1Ⅲ—Mo1—Mo1⁴ | 60.0         | Mo3—S2—Na1⁴            | 122.15 (9) |
| S4—Mo1—Mo1Ⅲ   | 116.37 (2)   | Mo2Ⅲ—S2—Na1⁴          | 160.14 (7) |
| S1—Mo1—Mo1Ⅲ   | 56.60 (2)    | Mo1Ⅳ—S2—Na1⁴          | 100.15 (7) |
| S1Ⅲ—Mo1—Mo1Ⅲ  | 115.84 (3)   | Na2Ⅳ—S2—Na1⁴          | 98.88 (10) |
| S1Ⅲ—Mo1—Mo1Ⅲ  | 56.08 (2)    | Mo3Ⅲ—S3—Mo3           | 66.31 (4)  |
| S2Ⅲ—Mo1—Mo1Ⅲ  | 138.14 (2)   | Mo3Ⅲ—S3—Na2Ⅳ          | 157.19 (11) |
| Mo1Ⅴ—Mo1—Mo1Ⅲ | 60.241 (8)   | Mo3Ⅲ—S3—Na2Ⅳ          | 136.50 (11) |
| S4—Mo1—Mo1Ⅱ   | 90.0         | Mo3Ⅲ—S3—Mo2Ⅳ          | 65.57 (3)  |
| S1—Mo1—Mo1Ⅱ   | 116.37 (2)   | Na2Ⅳ—S3—Mo2Ⅳ          | 119.39 (3) |
| S1Ⅲ—Mo1—Mo1Ⅱ  | 57.27 (2)    | Mo3Ⅲ—S3—Mo2Ⅳ          | 119.39 (3) |
| S1Ⅲ—Mo1—Mo1Ⅱ  | 56.34 (2)    | Mo3Ⅲ—S3—Mo2Ⅳ          | 119.39 (3) |
| S2Ⅲ—Mo1—Mo1Ⅱ  | 115.54 (3)   | Mo3Ⅲ—S3—Mo2Ⅳ          | 119.39 (3) |
| Mo1Ⅴ—Mo1—Mo1Ⅱ | 134.12 (2)   | Mo3Ⅲ—S3—Mo2Ⅳ          | 119.39 (3) |
| Mo1Ⅳ—Mo1—Mo1Ⅱ | 60.241 (8)   | Mo3Ⅲ—S3—Na2Ⅳ          | 128.66 (8) |
| Mo1Ⅳ—Mo1—Mo1Ⅱ | 59.518 (16)  | Mo3Ⅲ—S3—Na2Ⅳ          | 62.35 (7)  |
| S4—Mo1—Na2     | 45.53 (6)    | Na2Ⅳ—S3—Na2Ⅳ          | 74.15 (16) |
| S1—Mo1—Na2     | 142.51 (6)   | Mo2Ⅳ—S3—Na2Ⅳ          | 91.26 (5)  |
| S1Ⅲ—Mo1—Na2   | 83.36 (6)    | Mo2Ⅳ—S3—Na2Ⅳ          | 91.26 (5)  |
| S1Ⅲ—Mo1—Na2   | 103.55 (6)   | Mo1Ⅴ—S4—Mo1Ⅷ          | 67.58 (5)  |
| S2Ⅲ—Mo1—Na2   | 48.59 (6)    | Mo1Ⅴ—S4—Mo1Ⅷ          | 67.58 (5)  |
| Mo1Ⅴ—Mo1—Na2  | 99.04 (6)    | Mo1Ⅴ—S4—Na2Ⅲ          | 151.15 (7) |
| Mo1Ⅳ—Mo1—Na2  | 88.97 (5)    | Mo1Ⅴ—S4—Na2Ⅲ          | 93.82 (5)  |
| Mo1Ⅲ—Mo1—Na2  | 156.07 (6)   | Mo1Ⅴ—S4—Na2Ⅲ          | 93.82 (5)  |
| Mo1Ⅲ—Mo1—Na2  | 137.75 (5)   | Mo1Ⅴ—S4—Na2Ⅲ          | 93.82 (5)  |
| S5—Mo2—S2     | 91.79 (2)    | Mo1Ⅴ—S4—Na2Ⅲ          | 127.12 (7) |
| S5—Mo2—S2Ⅲ   | 90.96 (2)    | Mo1Ⅴ—S4—Na2Ⅲ          | 127.12 (7) |
| S2—Mo2—S2Ⅲ   | 172.09 (4)   | Mo1Ⅴ—S4—Na2Ⅲ          | 151.15 (7) |
| S5—Mo2—S1     | 92.26 (3)    | Na2Ⅳ—S4—Na2Ⅲ          | 79.75 (9)  |
| S2—Mo2—S1     | 89.86 (3)    | Mo1Ⅴ—S4—Na2Ⅲ          | 93.82 (5)  |
| S2Ⅲ—Mo2—S1   | 97.44 (3)    | Mo1Ⅴ—S4—Na2Ⅲ          | 127.12 (7) |
| S5—Mo2—S3Ⅷ   | 170.70 (4)   | Mo1Ⅴ—S4—Na2Ⅲ          | 151.15 (7) |
| S2—Mo2—S3Ⅷ   | 86.62 (4)    | Na2Ⅳ—S4—Na2Ⅲ          | 79.75 (9)  |
| S2Ⅲ—Mo2—S3Ⅷ  | 89.47 (4)    | Na2Ⅳ—S4—Na2Ⅲ          | 79.75 (9)  |
| S1—Mo2—S3Ⅷ   | 96.89 (3)    | Mo2Ⅴ—S5—Mo2Ⅹ          | 66.48 (4)  |
| S5—Mo2—Mo2Ⅶ  | 56.76 (2)    | Mo2Ⅴ—S5—Mo2Ⅹ          | 66.48 (4)  |
| S2—Mo2—Mo2Ⅶ  | 118.56 (2)   | Mo2Ⅴ—S5—Mo2Ⅹ          | 66.48 (4)  |
| S2Ⅲ—Mo2—Mo2Ⅶ | 57.44 (2)    | Mo2Ⅴ—S5—Na1           | 140.73 (3) |
| S1—Mo2—Mo2Ⅶ  | 136.00 (2)   | Mo2Ⅴ—S5—Na1           | 140.73 (3) |
| S3Ⅲ—Mo2—Mo2Ⅶ | 116.29 (3)   | Mo2Ⅴ—S5—Na1           | 140.73 (3) |
| S5—Mo2—Mo2Ⅷ   | 56.76 (2)    | S3Ⅹ—Na2—S4Ⅰ           | 89.92 (9)  |
| Bond | Structure | Bond Angle | Standard Deviation |
|------|-----------|------------|-------------------|
| S2—Mo2—Mo2viii | 58.68 (2) | S3iv—Na2—S4v | 89.92 (9) |
| S2viii—Mo2—Mo2viii | 117.32 (2) | S4—Na2—S4v | 84.49 (12) |
| S1—Mo2—Mo2viii | 131.42 (2) | S3iv—Na2—S2vii | 112.74 (10) |
| S3vii—Mo2—Mo2viii | 115.08 (3) | S4—Na2—S2vii | 154.21 (15) |
| Mo2vii—Mo2—Mo2viii | 60.0 | S4v—Na2—S2vii | 83.46 (4) |
| S5—Mo2—Mo3vii | 118.14 (2) | S3iv—Na2—S2iv | 112.74 (10) |
| S2—Mo2—Mo3vii | 115.63 (3) | S4—Na2—S2iv | 83.46 (4) |
| S2viii—Mo2—Mo3vii | 56.66 (2) | S4v—Na2—S2iv | 154.21 (15) |
| S1—Mo2—Mo3vii | 137.83 (3) | S2vi—Na2—S2iv | 97.94 (11) |
| S3vii—Mo2—Mo3vii | 54.99 (3) | S3iv—Na2—Mo3iv | 145.61 (16) |
| Mo2vii—Mo2—Mo3vii | 61.444 (11) | S4v—Na2—Mo3iv | 114.79 (9) |
| Mo2v—Mo2—Mo3vii | 90.670 (10) | S4v—Na2—Mo3iv | 114.79 (9) |
| S5—Mo2—Mo3 | 117.29 (2) | S2vi—Na2—Mo3iv | 51.78 (6) |
| S2—Mo3—Mo3 | 117.29 (2) | S4v—Na2—Mo3iv | 51.78 (6) |
| S2viii—Mo2—Mo3 | 58.940 (16) | S3iv—Na2—S3iv | 165.85 (15) |
| S1—Mo2—Mo3 | 133.65 (3) | S4—Na2—S3iv | 79.65 (9) |
| S3vii—Mo2—Mo3 | 54.52 (3) | S4v—Na2—S3iv | 79.65 (9) |
| Mo2vii—Mo2—Mo3 | 90.184 (10) | S2vi—Na2—S3iv | 75.81 (8) |
| Mo2v—Mo2—Mo3 | 60.600 (11) | S4v—Na2—S3iv | 75.81 (8) |
| Mo3vii—Mo2—Mo3 | 58.69 (2) | Mo3v—Na2—S3iv | 48.54 (6) |
| S3vii—Mo3—S3 | 173.69 (4) | S3iv—Na2—Na2v | 119.90 (13) |
| S3vii—Mo3—S2x | 89.88 (3) | S4—Na2—Na2v | 50.13 (5) |
| S3—Mo3—S2x | 93.48 (3) | S4v—Na2—Na2v | 50.13 (5) |
| S3vii—Mo3—S2 | 93.48 (3) | S2vi—Na2—Na2v | 105.50 (12) |
| S3—Mo3—S2 | 115.45 (4) | S2iv—Na2—Na2v | 105.50 (12) |
| S3vii—Mo3—Mo3viii | 117.00 (4) | Mo3v—Na2—Na2v | 94.49 (15) |
| S3—Mo3—Mo3viii | 56.69 (4) | S3iv—Na2—Na2v | 45.95 (11) |
| S2viii—Mo3—Mo3viii | 118.47 (2) | S4—Na2—Na2v | 59.90 (13) |
| S2—Mo3—Mo3viii | 118.47 (2) | S4v—Na2—Na2v | 50.13 (5) |
| S3vii—Mo3—Mo3viii | 57.00 (4) | S2vi—Na2—Na2v | 130.76 (6) |
| S3—Mo3—Mo3viii | 116.69 (4) | S2iv—Na2—Na2v | 130.76 (6) |
| S2viii—Mo3—Mo3viii | 115.45 (4) | Mo3v—Na2—Na2v | 154.49 (15) |
| S2—Mo3—Mo3viii | 116.54 (2) | S3iv—Na2—Na2v | 105.50 (11) |
| Mo3v—Mo3—S3 | 60.0 | Na2v—Na2—Na2v | 60.0 |
| Mo3v—Mo3—Mo3vii | 117.827 (15) | S3iv—Na2—Mo1 | 97.96 (5) |
| S3—Mo3—Mo2viii | 60.149 (14) | S4—Na2—Mo1 | 40.65 (3) |
| S2viii—Mo3—Mo2viii | 150.01 (3) | S4v—Na2—Mo1 | 124.10 (12) |
| S2—Mo3—Mo2viii | 57.58 (2) | S2vi—Na2—Mo1 | 139.27 (11) |
| Mo3v—Mo3—Mo2viii | 60.944 (12) | S2iv—Na2—Mo1 | 43.72 (2) |
| Mo3v—Mo3—Mo2x | 89.804 (10) | Mo3v—Na2—Mo1 | 87.79 (5) |
| S3vii—Mo3—Mo2x | 117.827 (15) | S3iv—Na2—Mo1 | 80.39 (5) |
| S3—Mo3—Mo2x | 60.149 (14) | Na2v—Na2—Mo1 | 79.33 (6) |
| S2viii—Mo3—Mo2x | 57.58 (2) | Na2vi—Na2—Mo1 | 87.34 (5) |
| S2—Mo3—Mo2x | 150.01 (3) | S3iv—Na2—Mo1xvii | 97.96 (5) |
| Mo3v—Mo3—Mo2x | 60.944 (12) | S4—Na2—Mo1xvii | 124.10 (12) |
| Mo3v—Mo3—Mo2x | 89.804 (10) | S4v—Na2—Mo1xvii | 40.65 (3) |
| S2viii—Mo3—Mo2x | 112.05 (2) | S2vi—Na2—Mo1xvii | 43.72 (2) |
| S2—Mo3—Mo2x | 59.911 (14) | S2iv—Na2—Mo1xvii | 139.27 (11) |
| Bond                  | Bond Angle (deg) | Symmetry Code |
|----------------------|------------------|---------------|
| S3—Mo3—Mo2\(^ix\)   | 117.957 (16)     |               |
| S2\(^v\)—Mo3—Mo2\(^ix\) | 56.42 (2)       |               |
| S2—Mo3—Mo2\(^ix\)   | 146.91 (3)       |               |
| Mo3\(^vii\)—Mo3—Mo2\(^ix\) | 89.333 (10)   |               |
| Mo3\(^vii\)—Mo3—Mo2\(^ix\) | 60.116 (12)    |               |
| Mo2\(^viii\)—Mo3—Mo2\(^ix\) | 146.475 (18)  |               |
| Mo2\(^vii\)—Mo3—Mo2\(^ix\) | 57.956 (12)    |               |
| S3\(^vii\)—Mo3—Mo2 | 59.911 (14)      |               |
| S3—Mo3—Mo2          | 117.957 (16)     |               |
| S2\(^v\)—Mo3—Mo2    | 146.91 (3)       |               |
| S2—Mo3—Mo2          | 56.42 (2)        |               |
| Mo3\(^viii\)—Mo3—Mo2 | 89.333 (10)     |               |
| Mo3\(^vii\)—Mo3—Mo2 | 60.116 (12)      |               |
| Mo2\(^viii\)—Mo3—Mo2 | 146.475 (18)    |               |
| Mo2\(^vii\)—Mo3—Mo2 | 57.956 (12)      |               |
| S3\(^vii\)—Mo3—Mo2 | 59.911 (14)      |               |
| S3—Mo3—Na2\(^iv\)   | 69.11 (8)        |               |
| S2\(^v\)—Mo3—Na2\(^iv\) | 61.70 (3)      |               |
| S2—Mo3—Na2\(^iv\)   | 61.70 (3)        |               |
| Mo3\(^viii\)—Mo3—Na2\(^iv\) | 125.80 (8)   |               |
| Mo3\(^vii\)—Mo3—Na2\(^iv\) | 174.20 (8)     |               |
| Mo2\(^viii\)—Mo3—Na2\(^iv\) | 93.43 (4)     |               |
| Mo2\(^vii\)—Mo3—Na2\(^iv\) | 93.43 (4)      |               |
| Mo2\(^v\)—Mo3—Na2\(^iv\) | 117.90 (3)     |               |
| Mo2—Mo3—Na2\(^iv\)  | 117.90 (3)       |               |
| Mo1—S1—Mo1\(^iii\)  | 67.06 (3)        |               |

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