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$Na_{2.54}Cs_{1.14}Mo_9S_{11}$, a quaternary reduced molybdenum sulfide containing Mo_9 clusters

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(o–S) = 0.001 Å
Disorder in solvent or counterion
R factor = 0.029
wR factor = 0.067
Data-to-parameter ratio = 42.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Sodium caesium nonamolybdenum undecasulfide, $Na_{2.54}Cs_{1.14}Mo_9S_{11}$, is isostructural with $Ag_{1.91}Cs_{1.16}Mo_9S_{11}$. Its crystal structure consists of $Mo_9S_{11}S_6$ cluster units with crystallographic $\overline{6}$ (C_{3h}) symmetry and interconnected through interunit Mo—S bonds. The Mo–S framework delimits channels in which the Cs^+ cations are disordered. The Na^+ cations are located on the mirror planes around the threefold axis between two consecutive $Mo_9S_{11}S_6$ units.

Comment

In a recent paper, we reported the crystal structure of the sulfide compound $Ag_{1.91}Cs_{1.16}Mo_9S_{11}$ (Salloum *et al.*, 2005), which is isostructural with three selenide compounds $Ag_{2.6}CsMo_9Se_{11}$, $Ag_{4.1}ClMo_9Se_{11}$ and η-Mo_9Se_{11} (Gougeon *et al.*, 2004). All these structures crystallize in a new structure type containing bioctahedral Mo_9 clusters. By replacing silver cations with sodium cations, we were able to synthesize the isostructural new quaternary sulfide compound $Na_{2.54}Cs_{1.14}Mo_9S_{11}$, (I), that is presented here.

Compound (I) contains $Mo_9S^{i}_{11}S^{a}_{6}$ cluster units based on the bioctahedral Mo_9 cluster (Fig. 1). The i-type ligands cap

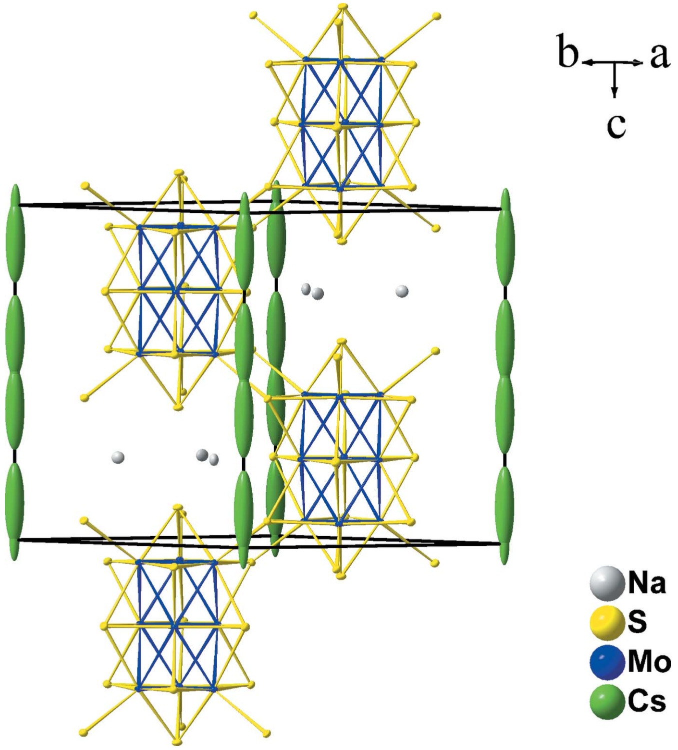

Figure 1
View of $Na_{2.54}Cs_{1.14}Mo_9S_{11}$, with displacement ellipsoids drawn at the 50% probability level.

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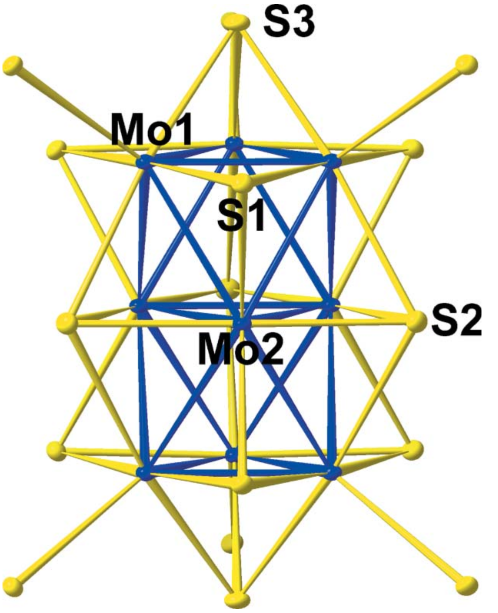

Figure 2
Plot showing the atom-numbering scheme of the $Mo_9S_{11}S_6$ cluster units.

Mo triangular faces and the *a*-type ligands are in apical positions for the external Mo1 atoms (Fig. 2); for details of the *i*- and *a*-type ligand notation, see Schäfer & von Schnering (1964). The centre of the Mo_9S_{11} cluster unit is located at the Wyckoff 2*d* position and thus exhibits C_{3h} or $\overline{6}$ symmetry. The intracluster Mo—Mo distances are 2.6186 (4) and 2.6925 (6) Å within the Mo_3 triangles formed by the Mo atoms related through the threefold axis, and 2.6712 (3) and 2.6951 (3) Å, respectively, for those between the latter Mo_3 triangles. All these Mo—Mo distances are shorter than in the silver analogue, as expected from the increase of the cationic charge from +3.07 in the silver compound to +3.68 in (I). The S 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 2.4153 (11) to 2.6286 (8) Å compared with 2.4172 (7) to 2.5788 (4) Å in the silver compound. The longest distance corresponds to the interunit Mo1—S1 bonds which ensure the interconnection between the Mo_9S_{11} unit, and thus the three-dimensionality of the Mo–S framework. The connectivity formula of the latter might be represented as $Mo_9S^{i}_{5}S^{i\text{-}a}_{6/2}S^{a\text{-}i}_{6/2}$. As a result of this arrangement, the shortest intercluster Mo1—Mo1 bond is 3.5781 (5) Å, which is greater than the value of 3.4025 (3) Å observed for $Ag_{1.91}Cs_{1.16}$-Mo_9S_{11}.

The Cs^+ cations in the 4*e* positions occupy distorted tricapped trigonal prismatic cavities built of S atoms, and those in the 2*b* positions are in a trigonal antiprismatic environment. The Cs—S distances spread over a wide range, from 3.406 (12) to 4.01 (3) Å. The Na^+ ions are located on mirror planes around the threefold axis between two consecutive Mo_9S_{11} units. They are surrounded by five S atoms, forming a distorted square-based pyramid with Na—S distances in the range 2.666 (3)–2.8450 (19) Å.

Experimental

Single crystals of (I) were prepared from a mixture of Cs_2MoS_4, MoS_2, Na_2S and Mo with the nominal composition $Na_2CsMo_9S_{11}$. All handling of materials was done in an argon-filled glove-box. 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 a rate of 300 K h^{-1} to 1773 K, held for 48 h, then cooled at a rate of 100 K h^{-1} to 1373 K and finally cooled to room temperature by switching off the furnace.

Crystal data

$Na_{2.54}Cs_{1.14}Mo_9S_{11}$
$M_r = 1425.92$
Hexagonal, $P6_3/m$
$a = 9.8888$ (2) Å
$c = 11.6398$ (3) Å
$V = 985.74$ (4) Å^3
$Z = 2$
$D_x = 4.804$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 17022 reflections
$\theta = 2.0$–39.1°
$\mu = 8.80$ mm^{-1}
$T = 293$ (2) K
Truncated octahedron, black
0.11 × 0.09 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.562$, $T_{max} = 0.678$
20415 measured reflections
2112 independent reflections
1618 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 40.0°$
$h = -14 \rightarrow 17$
$k = -16 \rightarrow 17$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.067$
$S = 1.16$
2112 reflections
50 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 6.9989P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.84$ e Å^{-3}
$\Delta\rho_{min} = -2.10$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00082 (11)

Table 1
Selected bond lengths (Å).

Mo1—S3	2.4153 (11)	Mo2—S1^{iii}	2.5136 (8)
Mo1—S1	2.4978 (8)	Mo2—S1	2.5136 (8)
Mo1—S1^{i}	2.5046 (8)	Mo2—Mo2^{iv}	2.6925 (6)
Mo1—S2^{i}	2.5696 (6)	Na—S2^{v}	2.666 (3)
Mo1—Mo1^{i}	2.6186 (4)	Na—S3^{vi}	2.724 (2)
Mo1—S1^{ii}	2.6286 (8)	Na—S1^{vii}	2.8450 (19)
Mo1—Mo2^{i}	2.6712 (3)	Cs1—S1^{ii}	3.4590 (8)
Mo1—Mo2	2.6951 (3)	Cs2—S1^{viii}	3.406 (12)
Mo2—S2^{i}	2.4551 (12)	Cs2—S1^{ii}	3.94 (4)
Mo2—S2	2.4652 (12)	Cs2—S2^{ix}	4.01 (3)

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

In the first stage of the refinement, the atomic positions of the Mo and S atoms were taken as identical to those in $Ag_{1.91}Cs_{1.16}Mo_9S_{11}$ (Salloum *et al.*, 2005). A subsequent difference Fourier synthesis revealed the Na atoms and a quasi-continuous electron density along the *c* axis due to the Cs atoms. As in $Ag_{1.91}Cs_{1.16}Mo_9S_{11}$, the latter was modelled with two partly occupied Cs sites (4*e* and 2*b* positions instead of 4*e* and 2*a* in the silver analogue) using second-order tensors for the anisotropic displacement parameters. Anharmonic treatment of atoms Cs1 and Cs2 using the program *JANA2000* (Petříček & Dušek, 2000) was unsuccessful. The final occupation factors for the Na and Cs atoms were refined freely to values of 0.845 (11), 0.57 (3) and 0.284 (18) for Na, Cs1 and Cs2, respectively.

The highest peak and the deepest hole in the final Fourier map are located 1.74Å from Cs2 and 0.47Å from Cs1, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: coordinates taken from an isostructural compound; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

Intensity data were collected on the diffactometer system of the Centre de Diffractométrie de l'Université de Rennes I (URL: http://www.cdifx.univ-rennes1.fr).

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