Ag$_{1.91}$Cs$_{1.16}$Mo$_9$S$_{11}$: a novel quaternary reduced molybdenum sulfide containing Mo$_9$ clusters

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Ag$_{1.911 (6)}$Cs$_{1.16 (3)}$Mo$_9$S$_{11}$, silver caesium nonamolybdenum undecasulfide, is isostructural with the archetype h-Mo$_9$Se$_{11}$. Its crystal structure consists of Mo$_9$S$_{11}$S$_6$ cluster units centered on the Wyckhoff site 2d and interconnected through inter-unit Mo—S bonds. The Mo–S framework delimits channels in which the Cs$^+$ cations are disordered. The Ag atoms are located on mirror planes around the threefold axes between two consecutive Mo$_9$S$_{11}$S$_6$ units.

Comment

In a previous paper, we reported the synthesis, crystal structures and physical properties of three isostructural selenide compounds, viz. Ag$_{2.6}$CsMo$_9$Se$_{11}$, Ag$_{4.1}$ClMo$_9$Se$_{11}$ and h-Mo$_9$Se$_{11}$, all of which crystallize in a new structure type containing Mo$_9$ clusters (Gougeon et $al.$, 2004). We present here the crystal structure of the sulfide Ag$_{1.91}$Cs$_{1.16}$Mo$_9$S$_{11}$, which is isostructural with the three previously reported compounds.

The crystal structure of Ag$_{1.91}$Cs$_{1.16}$Mo$_9$S$_{11}$ (Fig. 1) contains Mo$_9$S$_{11}^i$S$_6^a$ cluster units. The i-type ligands cap Mo triangular faces and the a-type ligands are in apical positions for the
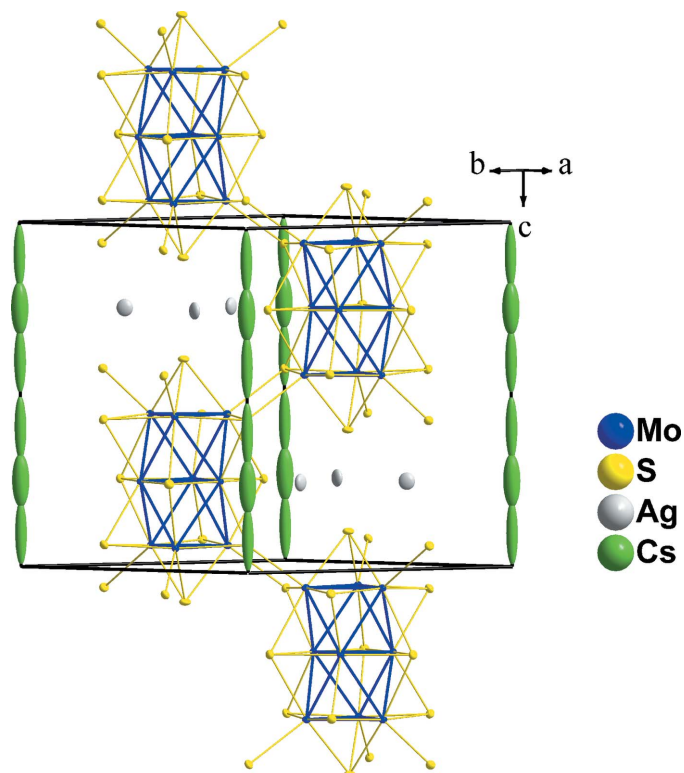

Figure 1
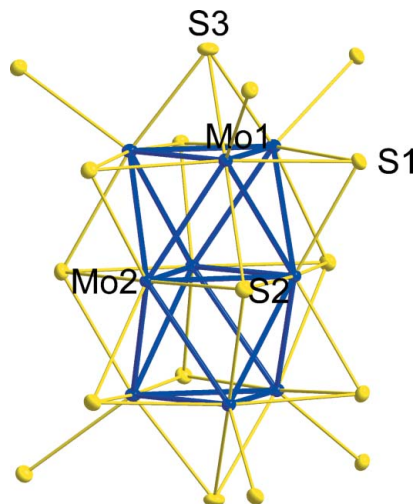View of the crystal structure of Ag$_{1.91}$Cs$_{1.16}$Mo$_9$S$_{11}$, with displacement ellipsoids drawn at the 50% probability level.

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

external Mo1 atoms (Fig. 2); for details of the *i*- and *a*-type ligand notation, see Schäfer & von Schnering (1964). The Mo_9S_{11} cluster unit is centered at a *2d* position with $\bar{6}$ symmetry. The Mo—Mo distances within the Mo_9 cluster are 2.6376 (3) and 2.7232 (4) Å for Mo_3 triangles that are formed by Mo atoms related through the threefold axes, and 2.6867 (2) and 2.7255 (2) Å for the other Mo_3 triangles. The S atoms bridge either one (S1 and S3) or two (S2) Mo triangular faces of the cluster. Moreover, the S1 atoms are linked to a Mo atom of a neighboring cluster. The Mo—S bond distances range from 2.4172 (7) to 2.5788 (4) Å. Each Mo_9S_{11} cluster is interconnected to six adjacent clusters *via* Mo1—S1 bonds to form the three-dimensional Mo–S framework, the connectivity formula of which is $Mo_9S_5^iS_{6/2}^{i-a}S_{6/2}^{a-i}$. A result of this arrangement is the shortest intercluster Mo1···Mo1 distance of 3.4025 (3) Å, indicating only a weak metal–metal interaction. The latter value is shorter than the value of 3.6614 (4) Å observed for the selenide $Ag_{2.6}CsMo_9Se_{11}$ (Gougeon *et al.*, 2004), as expected from the smaller size of the S atoms.

The alkali metal cations occupy distorted tricapped trigonal prismatic cavities formed by S atoms. The Cs—S distances spread over the wide range 3.243 (3)–3.960 (10) Å. The Ag atoms are located on mirror planes around the threefold axes between two consecutive Mo_9S_{11} units. They are surrounded by five S atoms forming a distorted square-based pyramid, with Ag—S distances in the range 2.5018 (8)–2.7754 (6) Å.

Experimental

Single crystals of $Ag_{1.91}Cs_{1.16}Mo_9S_{11}$ were prepared from a mixture of Cs_2MoS_4, MoS_2, Ag and Mo with the nominal composition $Ag_2CsMo_9S_{11}$. 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, the temperature held for 48 h, then cooled at a rate of 100 K h^{-1} to 1373 K and finally allowed to cool in the furnace to room temperature.

Table 1
Selected bond lengths (Å).

Mo1—S3	2.4172 (7)	Mo2—Mo2^i	2.7232 (4)
Mo1—S1	2.4688 (5)	Ag—S2^v	2.5018 (8)
Mo1—S1^i	2.4877 (5)	Ag—S3^{vi}	2.7088 (7)
Mo1—S1^{ii}	2.5458 (5)	Ag—S3^{vii}	2.7088 (7)
Mo1—S2	2.5788 (4)	Ag—S1^{iv}	2.7754 (6)
Mo1—Mo1^{iii}	2.6376 (3)	Ag—S1^i	2.7754 (6)
Mo1—Mo2	2.6867 (2)	Cs1—S2^{viii}	3.5396 (7)
Mo1—Mo2^{iii}	2.7255 (2)	Cs1—S1^{ix}	3.8555 (5)
Mo2—S2	2.4549 (8)	Cs2—S1^{ix}	3.243 (2)
Mo2—S2^i	2.4654 (8)	Cs2—S1^x	3.752 (11)
Mo2—S1^{iv}	2.4736 (5)	Cs2—S2^{viii}	3.960 (10)
Mo2—S1^i	2.4736 (5)		

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

In the first stage of the refinement, the atomic positions of the Mo and S atoms were taken as those of Mo and Se in $Ag_{2.6}CsMo_9Se_{11}$ (Gougeon *et al.*, 2004). A subsequent difference Fourier synthesis revealed the Ag atoms and a quasi-continuous electron density along the *c* axis due to the Cs atoms. The position of the Cs atoms was modelled with two partly occupied Cs sites using second-order tensors for the anisotropic displacement parameters. The shortest contacts between two Cs atoms are 1.78 (2) (Cs1—Cs2) and 2.26 (4) Å (Cs1—Cs2). Anharmonic treatment of the Cs1 and Cs2 positions using the program *JANA2000* (Petříček & Dušek, 2000) was unsuccessful. The final occupation factors for the Cs and Ag atoms were refined freely. The highest peak and the deepest hole in the final Fourier map are located 0.41 Å from Cs1 and 0.42 Å from Ag, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); method used to solve structure: coordinates from Gougeon *et al.* (2004); 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 Nonius KappaCCD X-ray diffractometer system of the 'Centre de diffractométrie de l'Université de Rennes I' (www.cdifx.univ-rennes1.fr).

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