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$Cs_6Mo_{27}S_{31}$: a novel ternary reduced molybdenum sulfide containing Mo_9 and Mo_{18} clusters

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The crystal structure of hexacaesium heptacosamolybdenum hentriacontasulfide, $Cs_6Mo_{27}S_{31}$, consists of a mixture of $Mo_9S_{11}S_6$ and $Mo_{18}S_{20}S_6$ cluster units in a 1:1 ratio. The units are connected through Mo—S bonds. Cs^+ cations occupy large voids between the different cluster units.

Comment

The crystal structures of the reduced molybdenum chalcogenides are characterized by metal–metal bonding that manifests itself as discrete clusters of diverse sizes and geometries. Up to now, 11 different Mo clusters with nuclearities in the range 3–36 have been synthesized in solid-state compounds. Clusters with a nuclearity higher than six, *i.e.* Mo_{3n} ($n = 3$, 4, 5, 6, 7, 8, 10 and 12) result from the one-dimensional *trans* face-sharing of $n-1$ Mo_6 octahedra. The Mo_{3n} clusters are surrounded by $3n+8$ chalcogenide atoms, thus forming $Mo_{3n}X^i_{3n+2}X^a_6$ units, which share the six external X^a atoms, hence creating the Mo–X framework. Large voids or channels, in which the cations reside, are formed between the $Mo_{3n}X_{3n+2}$ units. Compounds containing such clusters can be classified into two groups. The first group comprises the reduced molybdenum chalcogenides, the crystal structures of which contain only one type of cluster. This group is particularly well represented by the series of compounds $M_{n-2}Mo_{3n}X_{3n+2}$ (M = Rb and Cs; X = S, Se and Te; $n = 3$, 4, 5, 6, 7, 8, 10 and 12), which contain Mo_9, Mo_{12}, Mo_{15}, Mo_{18}, Mo_{21}, Mo_{24}, Mo_{30} and Mo_{36} clusters (Gougeon, 1984; Gougeon *et al.*, 1984, 1987, 1988, 1989*a*,*b*, 1990; Thomas *et al.*, 1997; Gautier *et al.*, 1998; Picard, Gougeon & Potel, 1999; Picard, Haletet *et al.*, 1999). The second group is based on compounds containing clusters of different nuclearities in equal proportion and is represented by the $Rb_{2n}Mo_9S_{11}Mo_{6n}S_{6n+2}$ ($n = 1$, 2, 3, 4 and 5) series of compounds (Picard *et al.*, 2000). Interest in these Mo cluster compounds lies not only in their fascinating structural aspect but also in their physical properties. For example, the $Rb_{2n}Mo_9S_{11}Mo_{6n}S_{6n+2}$ ($n = 1$, 2, 3 and 4) compounds are superconducting, with critical temperatures ranging from 4.2 to 11 K.

We present here the crystal structure of $Cs_6Mo_{27}S_{31}$, which contains $Mo_9S^i_{11}S^a_6$ and $Mo_{18}S^i_{20}S^a_6$ cluster units in equal proportion. This compound is isostructural with $Rb_6Mo_{27}S_{31}$ and is the third member of the $Cs_{2n}Mo_9S_{11}Mo_{6n}S_{6n+2}$ series. The Mo_9S_{11} and $Mo_{18}S_{20}$ cluster units are centred at 6*a* (*D*3 or 32 symmetry) and 6*b* positions (S_6 or $\overline{3}$ symmetry), respectively (Fig. 1). The Mo—Mo distances within the Mo_9 clusters are 2.6771 (3) and 2.6925 (4) Å for the intratriangle distances (distances within the Mo_3 triangles formed by Mo atoms related through the threefold axis), and 2.7313 (2) and 2.7820 (2) Å for the intertriangle distances. The Mo—Mo distances within the Mo_{18} clusters are 2.6341 (3)–2.6804 (3) Å for the intratriangle distances and 2.7139 (2)–2.7479 (2) Å for the distances between the Mo_3 triangles (Table 1). S atoms bridge either one (S1, S3, S5 and S6) or two (S2, S4 and S5) Mo triangular faces of the clusters. Moreover, atoms S1 and S3 are linked to an Mo atom of a neighbouring cluster. The Mo—S bond distances range from 2.4115 (5) to 2.6267 (4) Å within the Mo_9S_{11} unit and from 2.3982 (7) to 2.5857 (6) Å within the $Mo_{18}S_{20}$ unit. The Mo—Mo and Mo—S distances in both units are similar to those observed in $Rb_6Mo_{27}S_{31}$ (Picard *et al.*, 2000), since the greatest difference is 0.01 Å for the Mo—Mo and Mo—S bonds. This fact clearly shows that the number of electrons in each Mo_9 and Mo_{18} cluster should be almost the same in both compounds. Each Mo_9S_{11} unit is connected to six $Mo_{18}S_{20}$ units (and *vice versa*) *via* Mo1—S3 bonds (Mo3—S1), thus forming a three-dimensional Mo—S framework with a connectivity of $Mo_9S^i_5S^{i-a}_{6/2}S^{a-i}_{6/2}$, $Mo_{18}S^i_{14}S^{i-a}_{6/2}S^{a-i}_{6/2}$ (Fig. 2). As a result of this arrangement, the shortest Mo1—Mo3 distance

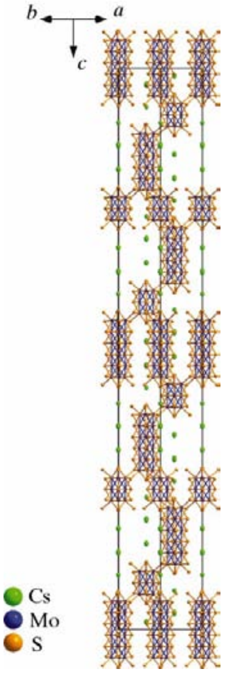

Figure 1
A view of the structure of $Cs_6Mo_{27}S_{31}$ along [110].

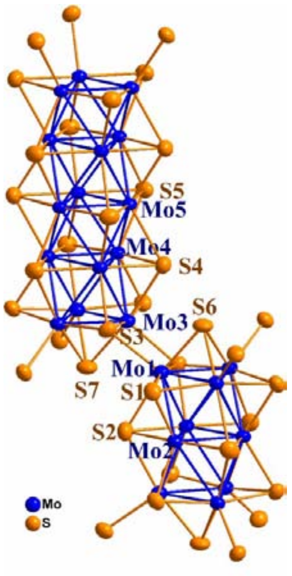

Figure 2
A structure diagram showing the atom-numbering scheme and the linkage of the $Mo_9S_{11}S_6$ and $Mo_{18}S_{20}S_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

between the Mo_9 and Mo_{18} clusters is 3.2864 (2) Å, indicating only weak metal–metal interactions. The Mo1—Mo3 distance is slightly longer than the distance of 3.223 (1) Å observed in $Rb_6Mo_{27}S_{31}$, as expected from the larger size of the Cs^+ cations.

The alkali metal cations are arranged in finite chains along the threefold axis between two adjacent Mo_9S_{11} and $Mo_{18}S_{20}$ units. The $Cs1^+$ and $Cs3^+$ cations at both ends of the finite chains are in a tetracapped trigonal-prismatic coordination around the S atoms, and the $Cs2^+$ cations are in a tricapped trigonal coordination (Fig. 3). The latter environment is similar to that encountered in the quasi-one-dimensional $M_2Mo_6X_6$ compounds (Potel, 1981). The Cs—S distances cover the range 3.2828 (5)–3.9872 (6) Å.

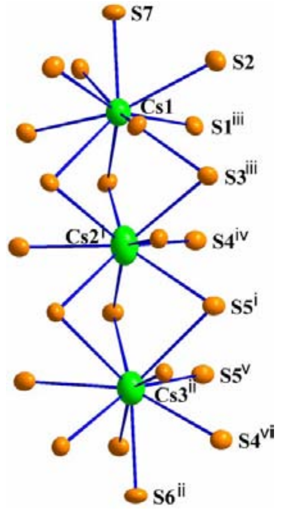

Figure 3
The coordination environments of the Cs^+ ions. [Symmetry codes: (i) $\frac{1}{3} + x - y, -\frac{1}{3} - y, \frac{1}{6} - z$; (ii) $\frac{7}{3} - x + y, \frac{2}{3} + y, \frac{1}{6} + z$; (iii) $\frac{4}{3} + y, -\frac{4}{3} + x, \frac{1}{6} - z$; (iv) $\frac{4}{3} - x, \frac{2}{3} - x + y, \frac{1}{6} + z$; (v) $\frac{4}{3} - x + y, -\frac{1}{3} + y, \frac{1}{6} + z$; (vi) $\frac{1}{3} + x, -\frac{4}{3} + x - y, \frac{1}{6} + z$.]

$Cs_6Mo_{27}S_{31}$ was found to be superconducting at 3.3 K (7 K for $Rb_6Mo_{27}S_{31}$) from alternating current susceptibility measurements on a batch of single crystals.

Experimental

Single crystals of $Cs_6Mo_{27}S_{31}$ were prepared from a mixture of Cs_2MoS_4, MoS_2 and Mo with an overall composition of $Cs_9Mo_{42}S_{48}$. All handling of the materials was carried out in an argon-filled glove-box. The initial mixture (~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 at that temperature for 48 h, cooled at 100 K h^{-1} to 1373 K, and finally furnace cooled. The product of the reaction appeared to be homogeneous and contained black and well faceted single crystals that were extracted by hand.

Crystal data

$Cs_6Mo_{27}S_{31}$
$M_r = 4381.70$
Hexagonal, $R\bar{3}c$
$a = 9.44240$ (5) Å
$c = 110.0790$ (7) Å
$V = 8499.62$ (8) Å^3
$Z = 6$
$D_x = 5.136$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 94 508 reflections
$\theta = 2.6$–40.3°
$\mu = 10.69$ mm^{-1}
$T = 293$ (2) K
Irregular block, black
0.20 × 0.17 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
φ scans ($\kappa = 0$) and additional ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.275$, $T_{max} = 0.454$
85 183 measured reflections
5858 independent reflections
4683 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 40.0°$
$h = -17 \rightarrow 17$
$k = -17 \rightarrow 14$
$l = -198 \rightarrow 198$

Table 1
Selected interatomic distances (Å).

Cs1—S1^{i}	3.2828 (5)	Mo2—S2	2.4708 (6)
Cs1—S7	3.3076 (9)	Mo2—Mo2^{v}	2.6925 (4)
Cs1—S2	3.6495 (4)	Mo3—S7	2.3982 (7)
Cs1—S3^{i}	3.7813 (6)	Mo3—S1^{vii}	2.4632 (5)
Cs2—S4^{ii}	3.5439 (6)	Mo3—S3	2.4905 (6)
Cs2—S5^{ii}	3.7232 (6)	Mo3—S3^{iii}	2.5025 (6)
Cs2—S3^{iii}	3.7255 (6)	Mo3—S4	2.5857 (6)
Cs3—S6	3.5535 (9)	Mo3—Mo3^{ix}	2.6341 (3)
Cs3—S5^{iv}	3.5857 (6)	Mo3—Mo4^{ix}	2.7139 (2)
Cs3—S4^{v}	3.6020 (6)	Mo3—Mo4	2.7479 (2)
Cs3—S5^{vi}	3.9872 (6)	Mo4—S4^{iii}	2.4711 (6)
Mo1—S6	2.4143 (7)	Mo4—S3^{iii}	2.4723 (5)
Mo1—S1	2.4322 (6)	Mo4—S4	2.4802 (6)
Mo1—S1^{vii}	2.4529 (6)	Mo4—S5	2.5787 (6)
Mo1—S3	2.5303 (6)	Mo4—Mo5^{iii}	2.6634 (2)
Mo1—S2	2.6267 (4)	Mo4—Mo5	2.6779 (2)
Mo1—Mo1^{v}	2.6771 (3)	Mo4—Mo4^{iii}	2.6804 (3)
Mo1—Mo2^{vii}	2.73130 (18)	Mo5—S5	2.4863 (6)
Mo1—Mo2	2.78199 (19)	Mo5—S5^{ix}	2.5047 (6)
Mo1—Mo3	3.2864 (2)	Mo5—S5^{x}	2.5800 (6)
Mo2—S1^{viii}	2.4115 (5)	Mo5—S4	2.5831 (6)
Mo2—S1	2.4117 (5)	Mo5—Mo5^{ix}	2.6679 (3)
Mo2—S2^{v}	2.4708 (6)	Mo5—Mo5^{x}	2.7139 (3)

Symmetry codes: (i) $\frac{4}{3} + y, x - \frac{4}{3}, \frac{1}{6} - z$; (ii) $-y, x - y - 1, z$; (iii) $2 - x + y, 1 - x, z$; (iv) $x, y - 1, z$; (v) $2 - x + y, -x, z$; (vi) $1 - x, -1 - y, -z$; (vii) $-y, x - y - 2, z$; (viii) $x - y - \frac{2}{3}, -\frac{4}{3} - y, -1 - z + \frac{7}{6}$; (ix) $1 - y, x - y - 1, z$; (x) $x - y, x - 1, -z$.

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Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\max} = 2.46$ e Å^{-3}
$wR(F^2) = 0.048$	$\Delta\rho_{\min} = -2.81$ e Å^{-3}
$S = 1.12$	Extinction correction: *SHELXL*97
5858 reflections	Extinction coefficient: 0.000148 (2)
99 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0133P)^2 + 67.7286P]$ where $P = (F_o^2 + 2F_c^2)/3$	

The highest residual peak was located 0.92 Å from Cs1 and the deepest hole was 0.58 Å from Cs3.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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 for this paper are available from the IUCr electronic archives (Reference: BC1009). Services for accessing these data are described at the back of the journal.

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