

Cs₂Mo₁₅S₁₉: a novel ternary reduced molybdenum sulfide containing Mo₆ and Mo₉ clusters

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The crystal structure of dicaesium pentadecamolybdenum nonadecasulfide, Cs₂Mo₁₅S₁₉, consists of a mixture of Mo₆S₈S₆ and Mo₉S₁₁S₆ cluster units in a 1:1 ratio. Both units are interconnected *via* inter-unit Mo—S bonds. The Cs⁺ cations occupy large voids between the different cluster units. The Cs and two inner S atoms lie on sites with 3 symmetry (Wyckoff site 12c) and the Mo and S atoms of the median plane of the Mo₉S₁₁S₆ cluster unit on sites with 2 symmetry (Wyckoff site 18e).

Comment

In a previous paper, we presented the syntheses, crystal structures and physical properties of the series of compounds Rb_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2} ($n = 1, 2, 3$ and 4; Picard *et al.*, 2000). The crystal structures consist of an equal mixture of Mo₉S₁₁ and Mo_{6n}S_{6n+2} ($n = 1-4$) cluster units interconnected *via* Mo—S bonds. The Rb⁺ cations occupy large voids between the different cluster units. The interest of these Mo cluster compounds lies not only in their fascinating structural aspect, but also in their interesting physical properties. Indeed, the Rb_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2} ($n = 1, 2, 3$, and 4) compounds are superconducting, with critical temperatures ranging from 4.2 to 11 K.

In the Cs—Mo—S system, we reported a decade ago the crystal structure of Cs₄Mo₂₁S₂₅ (Gougeon & Potel, 1993), which constitutes the second member of the series Cs_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2}, and recently that of the third member, Cs₆Mo₂₇S₃₁ (Picard *et al.*, 2003). We present here the crystal structure of Cs₂Mo₁₅S₁₉.

The title compound (Fig. 1) is isomorphous with In₂Mo₁₅Se₁₉ (Potel *et al.*, 1981) and constitutes the first member of the Cs_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2} series. Its crystal structure contains Mo₆S₈ⁱS₆^a and Mo₉S₁₁ⁱS₆^a cluster units in equal proportion. The *i*-type ligands cap Mo triangular faces and the *a*-type ones are in apical positions for the external Mo atoms (Fig. 2).

The Mo₉S₁₁ and Mo₆S₈ cluster units are centred at $6a$ (D_3 or 32 symmetry) and $6b$ positions (S_6 or $\bar{3}$ symmetry), respectively. The Mo—Mo distances within the Mo₆ clusters are

2.6854 (4) Å for the intra-triangle distances (distances within the Mo₃ triangles formed by the Mo atoms related through the threefold axis) and 2.7629 (3) Å for the inter-triangle distances. The Mo—Mo distances within the Mo₉ clusters are 2.6823 (3) and 2.6893 (5) Å for the intra-triangle distances between the Mo1 and Mo2 atoms, respectively, and 2.7271 (2) and 2.7826 (2) Å for those between the Mo₃ triangles.

The S atoms bridge either one (atoms S1, S3, S4 and S5) or two (atom S2) 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 2.4170 (8) to 2.4725 (6) Å within the Mo₆S₈ unit and from 2.3977 (6) to 2.6240 (5) Å within the Mo₉S₁₁ unit. Compared with

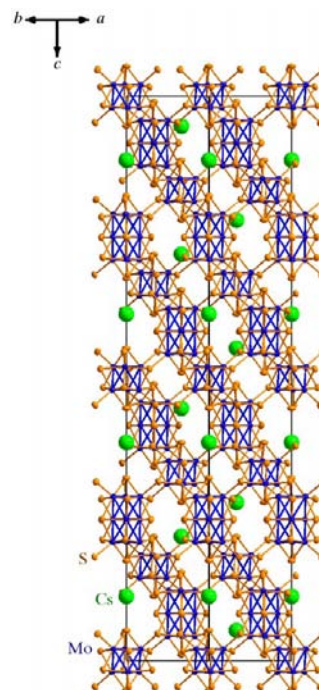


Figure 1
A view of Cs₂Mo₁₅S₁₉ along [110].

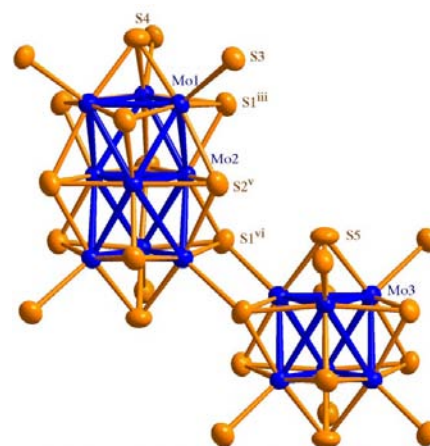


Figure 2
A plot showing the atom-numbering scheme and the inter-unit linkage of the Mo₉S₁₁S₆ and Mo₆S₈S₆ cluster units in Cs₂Mo₁₅S₁₉. Displacement ellipsoids are drawn at the 97% probability level. Symmetry codes are as in Table 1.

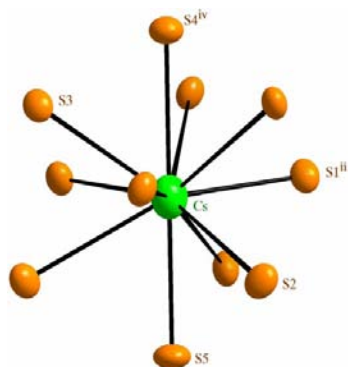


Figure 3
The environment of the Cs⁺ ion. [Symmetry codes: (ii) $x - y - 1, -2 - y, \frac{1}{2} - z$; (iv) $-\frac{1}{3} - x, -\frac{2}{3} - y, \frac{1}{3} - z$.]

Rb₂Mo₁₅S₁₉, the Mo—Mo and Mo—S distances in both units are quite similar to those observed in the Rb analogue, since the greatest differences are 0.006 and 0.01 Å for the Mo—Mo and Mo—S bonds, respectively. This clearly shows that the number of electrons per Mo₆ and Mo₉ cluster should be almost the same in both compounds.

Each Mo₉S₁₁ unit is interconnected to six Mo₆S₈ units (and *vice versa*) via Mo1—S3 bonds (or Mo3—S1 bonds) to form the three-dimensional Mo—S framework, the connective formula of which is Mo₉S₅S_{6/2}^{i-ac-a-i}, Mo₆S₂S_{6/2}^{i-ac-a-i}. The result of this arrangement is that the shortest intercluster Mo1—Mo3 distance between the Mo₆ and Mo₉ clusters is 3.2934 (3) Å, indicating only a weak metal–metal interaction. This value is slightly larger than the value of 3.246 (2) Å observed for Rb₂Mo₁₅S₁₉, as expected from the larger size of the Cs⁺ cations.

The alkali-metal cations are in a pentacapped trigonal prismatic environment of S atoms (Fig. 3). The Cs—S distances span a wide range, *viz.* 3.2825 (6)–3.7497 (6) Å.

Cs₂Mo₁₅S₁₉ was found to be superconducting at 2.7 K (4.2 K for Rb₂Mo₁₅S₁₉) from ac (alternating current) susceptibility measurements on a batch of single crystals.

Experimental

Single crystals of Cs₂Mo₁₅S₁₉ were prepared from a stoichiometric mixture of Cs₂MoS₄, MoS₂ and Mo. All handling of materials was

Table 1
Selected interatomic distances (Å).

Cs—S ¹	3.2825 (6)	Mo1—Mo2 ^{ix}	2.7826 (2)
Cs—S ⁵	3.4080 (11)	Mo2—S ^{1vii}	2.3977 (6)
Cs—S ^{4iv}	3.5640 (11)	Mo2—S ^{2v}	2.4721 (7)
Cs—S ²	3.7465 (5)	Mo2—Mo2 ^{viii}	2.6893 (5)
Cs—S ³	3.7497 (6)	Mo3—S ⁵	2.4170 (8)
Mo1—S ⁴	2.4189 (8)	Mo3—S ¹	2.4429 (6)
Mo1—S ¹ⁱⁱⁱ	2.4328 (6)	Mo3—S ^{3xii}	2.4481 (6)
Mo1—S ^{1vii}	2.4554 (7)	Mo3—S ^{3xiii}	2.4703 (6)
Mo1—S ³	2.5130 (6)	Mo3—S ^{3xiv}	2.4725 (6)
Mo1—S ^{2v}	2.6240 (5)	Mo3—Mo3 ^v	2.6854 (4)
Mo1—Mo ^{1viii}	2.6823 (3)	Mo3—Mo3 ^{xv}	2.7629 (3)
Mo1—Mo2	2.7271 (2)		

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

performed 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 at that temperature for 48 h, cooled at 100 K h⁻¹ to 1373 K and finally furnace cooled.

Crystal data

Cs₂Mo₁₅S₁₉
M_r = 2314.06
Trigonal, R $\bar{3}$ _c
a = 9.50120 (10) Å
c = 56.4199 (6) Å
V = 4410.82 (8) Å³
Z = 6
D_x = 5.227 Mg m⁻³

Mo K α radiation
Cell parameters from 22 219 reflections
 θ = 2.9–40.3°
 μ = 9.94 mm⁻¹
T = 293 (2) K
Irregular block, black
0.34 × 0.25 × 0.21 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.098, T_{max} = 0.203
33 032 measured reflections

3042 independent reflections
2575 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
 θ_{max} = 39.9°
h = -16 → 17
k = -15 → 17
l = -101 → 101

Refinement

Refinement on F²
R[F² > 2 σ (F²)] = 0.030
wR(F²) = 0.062
S = 1.16
3042 reflections
57 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 51.7289P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 2.99 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -1.98 \text{ e } \text{Å}^{-3}$
Extinction correction: SHELXL97
Extinction coefficient: 0.000784 (16)

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: EvalCCD (Duisenberg, 1998); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999) program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Bergerhoff, 1996); software used to prepare material for publication: WinGX (Farrugia, 1999).

Intensity data were collected on the Nonius KappaCCD X-ray diffractometer system of the Centre de diffractométrie de l'Université de Rennes I (<http://www.cdifx.univ-rennes1.fr>).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1041). Services for accessing these data are described at the back of the journal.

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