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K₂Mo₁₅S₁₉: a novel ternary reduced molybdenum sulfide containing Mo₆ and Mo₉ clusters

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mo–S) = 0.001 Å
R factor = 0.019
wR factor = 0.038
Data-to-parameter ratio = 36.2

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

$K_2Mo_{15}S_{19}$ (potassium molybdenum sulfide) crystallizes in the trigonal space group $R\bar{3}c$ and belongs to the $In_2Mo_{15}Se_{19}$ structure type. Its crystal structure consists of an equal mixture of Mo_6S_8 and Mo_9S_{11} cluster units interconnected through Mo—S bonds. The K⁺ cations occupy large voids between the different cluster units.

Comment

In a previous paper, we reported on the syntheses, structural and theoretical studies, along with physical properties, of an original new family with general formula $Rb_{2n}(Mo_9S_{11})$-$(Mo_{6n}S_{6n+2})$ (n = 1 to 4; Picard *et al.*, 2000). All members of the family crystallize in space group $R\bar{3}c$ with Z = 6 in the hexagonal setting. X-ray diffraction studies on single crystals showed that their crystal structures consist of an equal mixture of Mo_9S_{11} and $Mo_{6n}S_{6n+2}$ (n = 1 to 4) cluster units interconnected through Mo—S bonds with the Rb⁺ cations occupying large voids between the different cluster units. Electrical resistivity measurements carried out on single crystals showed that the four members are superconducting, with critical temperatures ranging from 4.2 K to 10.9 K. Investigation of the K—Mo—S system led only to the synthesis of the first member of the series, $K_2Mo_{15}S_{19}$, which becomes superconducting below 2 K.

The crystal structure of $K_2Mo_{15}S_{19}$ (Fig. 1) consists of an equal mixture of Mo_6S_8 and Mo_9S_{11} cluster units (Fig. 2) that are centred at positions $6a$ (D_3 or 32 symmetry) and $6b$ (S_6 or $\bar{3}$ symmetry), respectively. The Mo—Mo distances within the Mo_6 clusters are 2.6742 (4) Å for the intra-triangle distances (distances within the Mo_3 triangles formed by the Mo atoms related through the threefold axis) and 2.7730 (4) Å for the inter-triangle distances. The Mo—Mo distances within the Mo_9 clusters are 2.6779 (4) and 2.6870 (5) Å for the intra-triangle distances between the Mo1 and Mo2 atoms, respectively, and 2.7132 (4) and 2.7863 (4) Å for those between the Mo_3 triangles. The S atoms bridge either one (S1, S3, St1 and St2) or two (S2) Mo triangular faces of the clusters. Moreover the S1 and S3 atoms are linked to a Mo atom of a neighboring cluster.

Compared to $Rb_2Mo_{15}S_{19}$, 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 Mo_6 and Mo_9 clusters should be almost the same in both compounds. Each Mo_9S_{11} unit is interconnected to six Mo_6S_8 units (and *vice versa*) via Mo1—S3 bonds (Mo3—S1, respectively) to form the three-dimensional Mo—S framework, the connective formula of which is $Mo_9S^i_5S^{i-a}_{6/2}S^{a-i}_{6/2}$, $Mo_6S^i_8S^{i-a}_{6/2}S^{a-i}_{6/2}$.
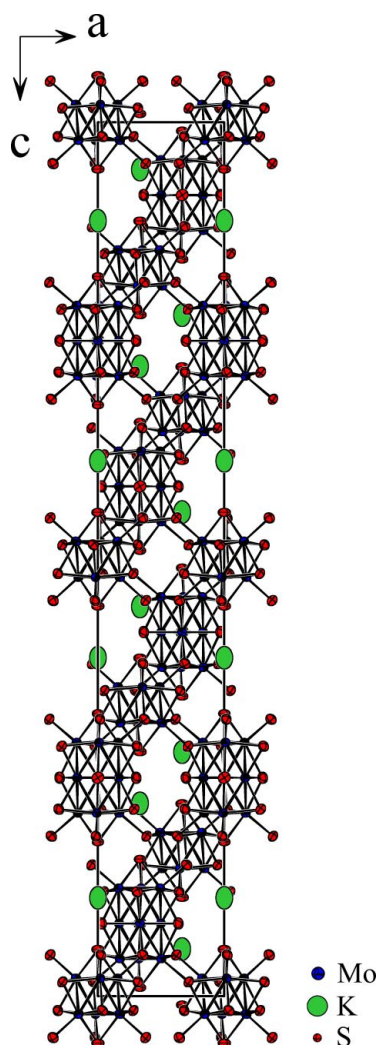
Figure 1
View of $K_2Mo_{15}S_{15}$ along [010].

Figure 2
Plot showing the atom-numbering scheme and the inter-unit linkage of the Mo_6S_8 and Mo_9S_{11} cluster units. Displacement ellipsoids are drawn at the 97% probability level.

As a result of this arrangement, the shortest intercluster Mo1—Mo3 distances between the Mo_6 and Mo_9 clusters is 3.2169 (4) Å, indicating only weak metal–metal interaction. The latter value is slightly shorter than the value of 3.246 (2) Å observed for $Rb_2Mo_{15}S_{19}$, as expected from the smaller size of the K^+ cations. The alkali metal cations occupy sites along the threefold axis between two consecutive Mo_6S_8 and Mo_9S_{11} units in a distorted pentacapped trigonal prismatic environment of S atoms.

Experimental

Single crystals of $K_2Mo_{15}S_{19}$ were obtained from a stoichiometric mixture of K_2MoS_4, MoS_2 and Mo. The potassium thiomolybdate was obtained by sulfuration of K_2MoO_4 at 723 K for two days under CS_2 gas carried by flowing argon. The molybdate K_2MoO_4 was synthesized by heating an equimolar ratio of K_2CO_3 and MoO_3 in an alumina vessel at 1073 K in air over two days. All handling of materials was 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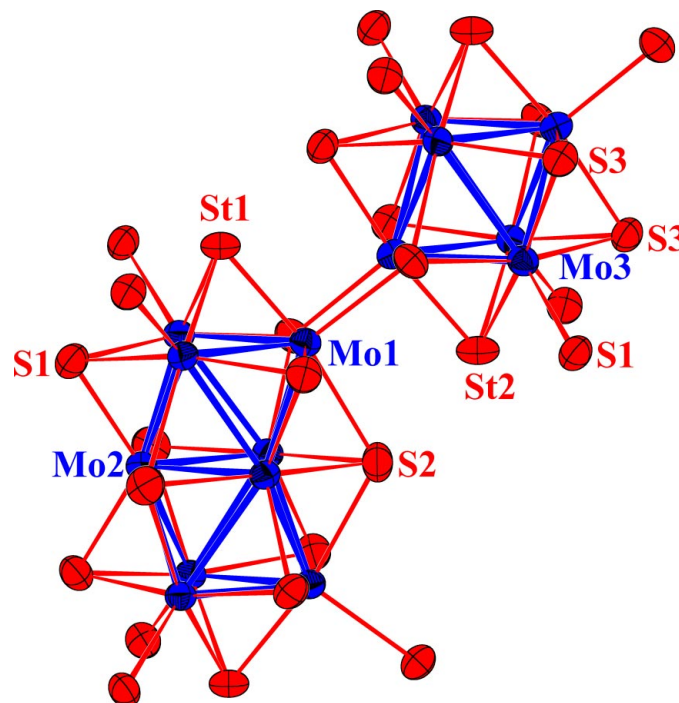 was heated at the rate of 300 K h^{-1} to 1873 K, a temperature which was held for 6 h, then cooled at 100 K h^{-1} to 1373 K and finally furnace cooled.

Crystal data

$K_2Mo_{15}S_{19}$	Mo $K\alpha$ radiation
$M_r = 2126.44$	Cell parameters from 25
Trigonal, $R\bar{3}c$	reflections
$a = 9.3857$ (9) Å	$\theta = 6.3–15.2°$
$c = 56.261$ (9) Å	$\mu = 8.00$ mm^{-1}
$V = 4292.1$ (9) Å^3	$T = 293$ (2) K
$Z = 6$	Pseudo-cube, black
$D_x = 4.936$ Mg m^{-3}	$0.10 \times 0.10 \times 0.08$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.016$
	$\theta_{max} = 34.9°$
$\theta–2\theta$ scans	$h = 0 \rightarrow 15$
Absorption correction: ψ-scan	$k = 0 \rightarrow 15$
(North *et al.*, 1968)	$l = -90 \rightarrow 90$
$T_{min} = 0.501$, $T_{max} = 0.527$	3 standard reflections
4181 measured reflections	frequency: 60 min
2102 independent reflections	intensity decay: <1%
1753 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0122P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$+ 8.4803P]$
$wR(F^2) = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2102 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
58 parameters	$\Delta\rho_{min} = -0.87$ e Å^{-3}
	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.000086 (4)

Table 1
Selected interatomic distances (Å).

Mo1—St1	2.4191 (7)	Mo3—St2	2.4217 (7)
Mo1—S1	2.4294 (6)	Mo3—S1^{v}	2.4330 (6)
Mo1—S1^{i}	2.4766 (6)	Mo3—S3^{vi}	2.4399 (6)
Mo1—S3^{ii}	2.4917 (6)	Mo3—S3	2.4588 (6)
Mo1—S2^{iii}	2.6206 (5)	Mo3—S3^{iii}	2.4659 (6)
Mo2—S1	2.3922 (6)	K—S1^{vii}	3.1776 (6)
Mo2—S1^{iv}	2.3922 (6)	K—St2	3.3203 (16)
Mo2—S2^{i}	2.4700 (6)	K—St1	3.5952 (16)
Mo2—S2^{iii}	2.4700 (6)	K—S3^{viii}	3.7234 (9)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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