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Sc_{0.43(2)}Rb₂Mo₁₅S₁₉, a partially Sc-filled variant of Rb₂Mo₁₅S₁₉

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The structure of scandium dirubidium pentadecamolybdenum nonadecasulfide, Sc_{0.43(2)}Rb₂Mo₁₅S₁₉, constitutes a partially Sc-filled variant of Rb₂Mo₁₅S₁₉ [Picard, Saillard, Gougeon, Noel & Potel (2000), *J. Solid State Chem.* **155**, 417–426]. In the two compounds, which both crystallize in the $R\bar{3}c$ space group, the structural motif is characterized by a mixture of Mo₆S₈S₆ⁱ and Mo₉S₁₁S₆^a cluster units ('i' is inner and 'a' is apical) in a 1:1 ratio. The two components are interconnected through interunit Mo–S bonds. The cluster units are centred at Wyckoff positions *6b* and *6a* (point-group symmetries $\bar{3}$. and 32, respectively). The Rb⁺ cations occupy large voids between the different cluster units. The Rb and the 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 lie on sites with .2 symmetry (Wyckoff site 18e). A unique feature of the structure is a partially filled octahedral Sc site with $\bar{1}$ symmetry. Extended Hückel tight-binding calculations provide an understanding of the variation in the Mo–Mo distances within the Mo clusters induced by the increase in the cationic charge transfer due to the insertion of Sc.

Comment

In₂Mo₁₅Se₁₉ (Potel *et al.*, 1981) and In₃Mo₁₅Se₁₉ (Grüttner *et al.*, 1979), which crystallize in the $R\bar{3}c$ and $P6_3/m$ space groups, respectively, were the first compounds containing a molybdenum cluster with a nuclearity greater than 6. Indeed, their crystal structures contain an equal mixture of octahedral Mo₆ and bioctahedral Mo₉ clusters. Subsequently, compounds isotopic with In₂Mo₁₅Se₁₉, such as Al₂Mo₁₅S₁₉ (Alc = K, Rb or Cs; Picard *et al.*, 2002, 2000, 2004) or Ba₂Mo₁₅Se₁₉ (Gougeon *et al.*, 1989), as well as compounds isotopic with In₃Mo₁₅Se₁₉, such as In_{1.6}Rb₂Mo₁₅S₁₉ and ScTi₂Mo₁₅S₁₉ (Salloum *et al.*, 2004), have been obtained. Among the latter compounds, Rb₂Mo₁₅S₁₉ appears to be the first member of the series of compounds Rb_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2} ($n = 1, 2, 3$ and 4;

Picard *et al.*, 2000). In addition to their interesting crystal structures, the Rb_{2n}Mo₉S₁₁Mo_{6n}S_{6n+2} compounds become superconducting at low temperature. In an attempt to replace Tl with Rb in ScTi₂Mo₁₅S₁₉ (In₃Mo₁₅Se₁₉ type), we obtained the title new quaternary compound Sc_{0.43}Rb₂Mo₁₅S₁₉ belonging to the In₂Mo₁₅Se₁₉ structure type and constituting a partially Sc-filled variant of Rb₂Mo₁₅S₁₉.

The insertion of Sc into Rb₂Mo₁₅S₁₉ is evident from the variations in the unit-cell parameters: the *a* axis increases by *ca* 0.08 Å, while the *c* axis decreases by about 0.27 Å. A view of the crystal structure of Sc_{0.43}Rb₂Mo₁₅S₁₉ is shown in Fig. 1. The Mo–S framework is similar to that of Rb₂Mo₁₅S₁₉ and is based on an equal mixture of Mo₆S₈S₆ⁱ and Mo₉S₁₁S₆^a cluster units interconnected through Mo–S bonds (Fig. 2) [for details of the inner ('i') and apical ('a') ligand notation, see Schäfer & von Schnering (1964)]. The first unit can be described as an Mo₆ octahedron surrounded by eight face-capping inner Sⁱ (six S3 and two S5) and six apical S^a (S1) ligands. The Mo₉ core of the second unit results from the face-sharing of two octahedral Mo₆ clusters. The Mo₉ cluster is surrounded by 11 Sⁱ atoms (six S1, three S2 and two S4) capping the faces of the bioctahedron and six apical S^a ligands (S3) above the outer Mo atoms. The Mo₆S₈S₆ⁱ and Mo₉S₁₁S₆^a units are centred at the *6b* and *6a*

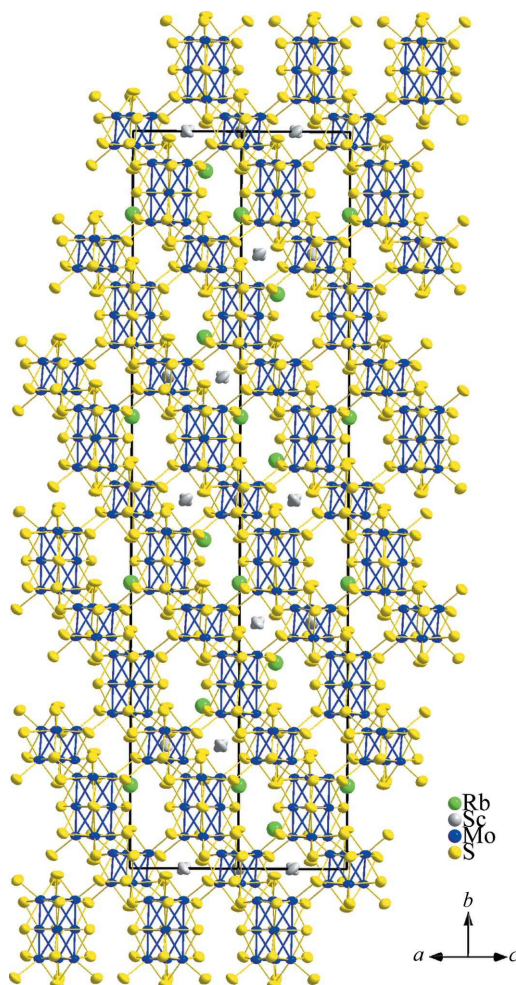


Figure 1
A view of Sc_{0.43}Rb₂Mo₁₅S₁₉ along [110].

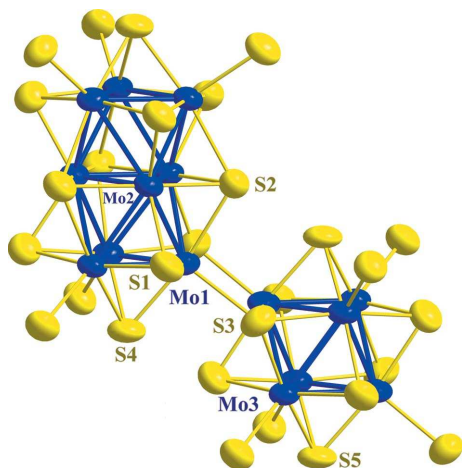


Figure 2

A plot showing the atom-numbering scheme and the inter-unit linkage of the $\text{Mo}_9\text{S}_{11}\text{S}_6$ and $\text{Mo}_6\text{S}_8\text{S}_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

positions and have point-group symmetries $\bar{3}$ and 32, respectively.

The Mo–Mo distances within the Mo_6 clusters are 2.6783 (6) Å for the intratriangle distances (distances within the Mo_3 triangles formed by atoms Mo3 related through the threefold axis) and 2.7393 (6) Å for the intertriangle distances. In $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, the latter two values are 2.676 (2) and 2.767 (2) Å, respectively. These variations reflect the different cationic charge transfer towards the Mo_6 clusters in the two parent compounds.

The Mo–Mo distances within the Mo_9 clusters are 2.6658 (5) and 2.6910 (8) Å for the distances in the triangles formed by atoms Mo1 and Mo2, respectively. In $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, the corresponding distances are 2.680 (2) and 2.688 (3) Å. The distances between the triangles formed by atoms Mo1 and Mo2 are 2.6958 (4) and 2.7663 (4) Å, respectively, in $\text{Sc}_{0.43}\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, compared with 2.719 (1) and 2.785 (2) Å, respectively, in $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$.

Although the structural response of the Mo_9 cluster with respect to the increase in charge transfer is more complex, we observe that the Mo1–Mo1 and two Mo1–Mo2 intertriangle distances are shorter in the Sc-filled compound. On the other hand, a slight increase in the Mo2–Mo2 bond distances occurs in the median Mo_3 triangle [2.688 (3) Å in $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$]. In order to explain these variations, we performed extended Hückel tight-binding (EHTB) calculations on $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$ using the program *YaEHMOP* (Landrum, 1997). The Mo and S extended Hückel parameters used by Picard *et al.* (2000) were considered. Total Mo_6 - and Mo_9 -projected DOS (density of states) and COOP (crystal orbital overlap population) curves for the different bonds discussed above and obtained from 36 k points of the irreducible wedge of the Brillouin zone are sketched in Figs. 3 and 4, respectively.

Assuming an ionic interaction between the inserted Sc atoms and the host material, the three electrons of the 3d transition metal should be transferred to the clusters.

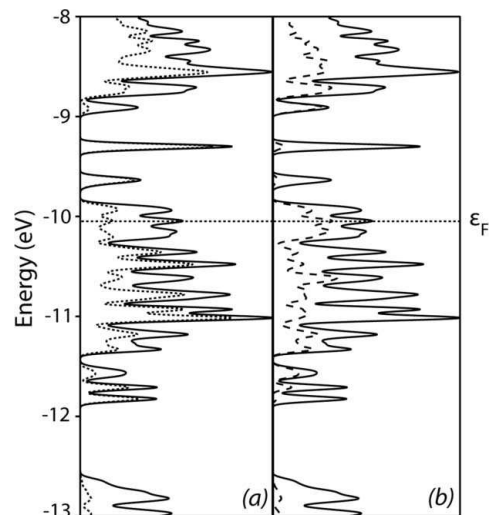


Figure 3

EHTB calculations for $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, showing (a) total (solid line) and Mo_6 -projected (dotted line) DOS, and (b) total (solid line) and Mo_9 -projected (dotted line) DOS.

Assuming a rigid-band model, the Fermi level corresponding to the electron count of the title compound is slightly higher in energy (*ca.* 0.02 eV) than that for $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$. The DOS at the Fermi level is mainly centred on Mo atoms belonging to both Mo_6 and Mo_9 clusters (Fig. 3). Therefore, both clusters should be affected by an increase in the anionic charge of the Mo–S network. As shown by the COOP curves of the Mo3–Mo3 intratriangle (solid line) and Mo3–Mo3 intertriangle (dotted line) bonds within the Mo_6 cluster, the increase in the metal electron count due to the insertion of Sc foresees a weak lengthening and a shortening of the Mo3–Mo3 bonds within the Mo_3 triangles and between the triangles, respectively. Such an evolution is in fact observed in $\text{Sc}_{0.4}\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, as mentioned above.

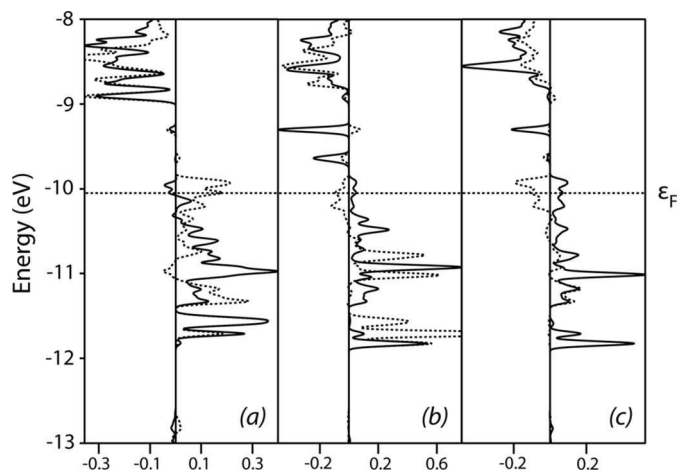


Figure 4

EHTB calculations for $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, showing (a) Mo3–Mo3 COOPs for intratriangle (solid line) and intertriangle (dotted line) distances of the Mo_6 cluster, (b) COOPs for the intratriangle Mo1–Mo1 (solid line) and Mo2–Mo2 (dotted line) bonds in the Mo_9 cluster and (c) COOPs for the intertriangle Mo1–Mo2 bonds of 2.719 (solid line) and 2.785 Å (dotted line).

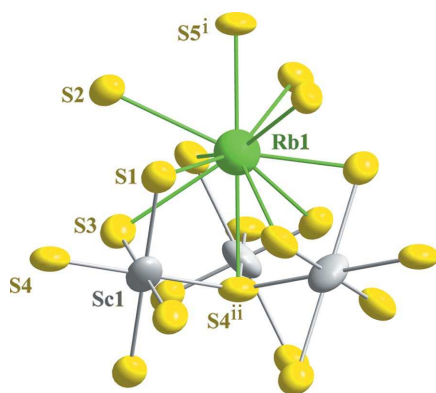


Figure 5

A view of the environment of the Rb^+ and Sc^{3+} cations. Displacement ellipsoids are drawn at the 97% probability level. Symmetry codes are as in Table 1.

Regarding the Mo_9 cluster (Fig. 4), the lengthening of the $\text{Mo2}-\text{Mo2}$ bonds and the shortening of the $\text{Mo1}-\text{Mo1}$ and $\text{Mo1}-\text{Mo2}$ bonds can be envisioned theoretically when extra electrons are added, and this is what is observed experimentally in $\text{Sc}_{0.43}\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$. The $\text{Mo}-\text{S}$ distances are almost unaffected by the cationic charge, and range between 2.4198 (13) and 2.4736 (10) Å within the $\text{Mo}_6\text{S}_8^{\text{i}}\text{S}_6^{\text{a}}$ unit and between 2.4125 (10) and 2.6065 (7) Å within the $\text{Mo}_9\text{S}_{11}^{\text{i}}\text{S}_6^{\text{a}}$ unit, as usual.

Finally, the three-dimensional packing arises from the interconnection of the $\text{Mo}_6\text{S}_8^{\text{i}}\text{S}_6^{\text{a}}$ and $\text{Mo}_9\text{S}_{11}^{\text{i}}\text{S}_6^{\text{a}}$ cluster units through $\text{Mo}-\text{S}$ bonds. Indeed, each $\text{Mo}_6\text{S}_8^{\text{i}}\text{S}_6^{\text{a}}$ unit is interconnected to six $\text{Mo}_9\text{S}_{11}^{\text{i}}\text{S}_6^{\text{a}}$ units (and *vice versa*) via $\text{Mo3}-\text{S1}$ and $\text{Mo1}-\text{S3}$ bonds, respectively, to form the three-dimensional $\text{Mo}-\text{Se}$ framework, the connective formula of which is $\text{Mo}_9\text{S}_5^{\text{i}}\text{S}_6^{\text{a-i}}\text{S}_6^{\text{a-i}}$, $\text{Mo}_6\text{S}_2^{\text{i}}\text{S}_6^{\text{a-i}}\text{S}_6^{\text{a-i}}$. The result of this arrangement is that the shortest intercluster $\text{Mo1}-\text{Mo3}$ distance between the Mo_6 and Mo_9 clusters is 3.2995 (4) Å, compared with 3.246 (2) Å in $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$, indicating only weak metal-metal interaction. This variation is consistent with the $\text{Mo}-\text{Mo}$ intercluster antibonding nature of the bands that lie in the vicinity of the Fermi level.

The Sc atoms occupy highly flattened octahedral sites [2.1718 (10) (×2), 2.7983 (3) (×2) and 2.9200 (10) Å (×2)] located near the Rb1 sites around the threefold axes. The alkali metal cation occupies a pentacapped trigonal prismatic site of S atoms, similar to that observed in $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$ (Fig. 5). The $\text{Rb}-\text{S}$ distances are spread over the wide range 3.2512 (10)–3.7554 (11) Å, while in $\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$ they are in the range 3.222 (3)–3.730 (3) Å. Thus, the insertion of Sc only leads to a slight decrease (*ca* 0.020 Å) of the $\text{Rb1}-\text{S4}$ and $\text{Rb1}-\text{S5}$ distances along the threefold axis, while the other distances are slightly increased (*ca* 0.027 Å).

Experimental

Single crystals of $\text{Sc}_{0.43}\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$ were prepared from a mixture of Sc_2S_3 , Rb_2MoS_4 , MoS_2 and Mo with the nominal composition $\text{ScRb}_2\text{Mo}_{15}\text{S}_{19}$. Rubidium thiomolybdate was obtained by sulfuration of Rb_2MoO_4 at 723 K for 2 d under CS_2 gas carried by flowing argon. The molybdate Rb_2MoO_4 was synthesized by heating an equimolar

ratio of Rb_2CO_3 and MoO_3 in an alumina vessel at 1073 K in air over a period of 2 d. Sc_2S_3 was prepared from the elements heated in a sealed evacuated silica tube at 1073 K for 2 d. All handling of materials was carried out 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 and the temperature held for 48 h. The charge was then cooled at a rate of 100 K h^{-1} to 1373 K before being finally furnace cooled.

Crystal data

$\text{Sc}_{0.43(2)}\text{Rb}_2\text{Mo}_{15}\text{S}_{19}$	$Z = 6$
$M_r = 2238.37$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}c$	$\mu = 10.92 \text{ mm}^{-1}$
$a = 9.5173 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 56.0061 (9) \text{ \AA}$	$0.13 \times 0.12 \times 0.09 \text{ mm}$
$V = 4393.33 (10) \text{ \AA}^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	13057 measured reflections
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	1431 independent reflections
$T_{\text{min}} = 0.298$, $T_{\text{max}} = 0.463$	1383 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	64 parameters
$wR(F^2) = 0.062$	$\Delta\rho_{\text{max}} = 1.09 \text{ e \AA}^{-3}$
$S = 1.25$	$\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$
1431 reflections	

The site-occupancy factor of the Sc1 atom was refined freely. Because the U_{eq} parameter of atom Rb1 was larger than that of the other atoms, the site-occupancy factor of Rb1 was also refined. It converged to 1.011 (5) and was consequently fixed to unity in the final refinement. It is interesting to note that Rb atoms often present large U_{eq} values (see, for example, Picard *et al.*, 2000; Solodovnikova & Solodovnikov, 2006; Liang *et al.*, 2009; Zhao *et al.*, 2011).

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: EVALCCD (Duisenberg *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1996); software used to prepare material for publication: SHELXL97.

Table 1

Selected bond lengths (Å).

Rb1–S1	3.2512 (10)	Mo1–Mo2 ⁱⁱⁱ	2.6958 (4)
Rb1–S5 ⁱ	3.3263 (19)	Mo1–Mo2	2.7663 (4)
Rb1–S4 ⁱⁱ	3.5475 (19)	Mo2–S1	2.4125 (10)
Rb1–S2	3.7306 (8)	Mo2–S1 ^v	2.4126 (10)
Rb1–S3	3.7554 (11)	Mo2–S2	2.4715 (11)
Sc1–S3	2.1718 (10)	Mo2–S2 ^{iv}	2.4715 (11)
Sc1–S4	2.7983 (3)	Mo2–Mo2 ⁱⁱⁱ	2.6910 (8)
Sc1–S1	2.9200 (11)	Mo3–S5	2.4198 (13)
Mo1–S4	2.4336 (14)	Mo3–S3	2.4513 (10)
Mo1–S1	2.4408 (10)	Mo3–S1 ⁱⁱ	2.4577 (10)
Mo1–S1 ⁱⁱⁱ	2.4786 (10)	Mo3–S3 ^{vi}	2.4641 (10)
Mo1–S3	2.5189 (10)	Mo3–S3 ^{vii}	2.4736 (10)
Mo1–S2	2.6065 (7)	Mo3–Mo3 ^{viii}	2.6783 (6)
Mo1–Mo1 ^{iv}	2.6658 (5)	Mo3–Mo3 ^{vii}	2.7393 (6)

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

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: FN3104). Services for accessing these data are described at the back of the journal.

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