

Rb₄Mo₂₁Se₂₄ containing Mo₁₂ and Mo₁₅ clusters

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Rubidium molybdenum selenide, Rb₄Mo₂₁Se₂₄, crystallizes in the trigonal space group $R\bar{3}$. Its crystal structure consists of a mixture of Mo₁₂Se₁₄Se₆ and Mo₁₅Se₁₇Se₆ cluster units in a 1:2 ratio. Both units are interconnected through Mo–Se bonds. The Rb⁺ cations occupy large voids between the different cluster units.

Comment

The crystal structures of reduced molybdenum chalcogenides are characterized by metal–metal bonds which give rise to discrete clusters of diverse sizes and geometries. Compounds containing such clusters can be classified as two groups. The first group comprises the reduced molybdenum chalcogenides whose crystal structures contain only one type of cluster and is particularly well exemplified by the series of compounds $M_{n-2}Mo_{3n}X_{3n+2}$ ($M = Rb, Cs; X = S, Se$ or $Te; n = 3, 4, 5, 6, 7, 8, 10$ and 12) containing Mo₉, Mo₁₂, Mo₁₅, Mo₁₈, Mo₂₁, Mo₂₄, Mo₃₀ and Mo₃₆ clusters (Gougeon, 1984; Gougeon *et al.*, 1984, 1987, 1988, 1989*a,b*, 1990; Thomas *et al.*, 1997; Picard, Gougeon & Potel, 1999; Picard, Halet *et al.*, 1999). The second group is based on compounds containing clusters of odd and even nuclearity in equal proportion and is represented by the series of compounds Rb_{2n}Mo₉X₁₁Mo_{6n}X_{6n+2} ($n = 1, 2, 3, 4$ and 5 ; Picard, Gougeon & Potel, 1999). Interest in these Mo cluster compounds lies not only in their fascinating structural aspects, but also in their interesting physical properties. Indeed, the sulfides and selenides generally present superconducting or metal–insulator transitions at low temperature. We present here a new structural type, Rb₄Mo₂₁Se₂₄, also containing odd and even nuclearity clusters but in the ratio 1:2. Indeed, the crystal structure of Rb₄Mo₂₁Se₂₄ is made up of Mo₁₂Se₁₄Se₆ and Mo₁₅Se₁₇Se₆ cluster units in a 1:2 ratio. Both units share part of their Se atoms according to the connectivity formula Mo₁₂Se₈^{*i*}Se_{6/2}^{*i-a*}Se_{6/2}^{*i-a*}, 2Mo₁₅Se₁₁^{*i*}Se_{6/2}^{*i-a*}Se_{6/2}^{*i-a*} to form large voids in which the Rb⁺ ions reside. The Mo₁₂Se₁₄Se₆ and Mo₁₅Se₁₇Se₆ cluster units are similar to those reported previously in Rb₂Mo₁₂Se₁₄ (Gautier *et al.*, 1998) and Rb₃Mo₁₅Se₁₇ (Gougeon *et al.*, 1989*b*), respectively. The Mo cores of both units result from the mono-axial *trans*-face-sharing of three

and four octahedral Mo₆ clusters, respectively, and can be described alternatively as resulting from the stacking of four and five Mo₃ triangles, respectively. The Mo₁₂Se₁₄Se₆ unit possesses the same local symmetry ($\bar{3}$ or C_{3i}) and does not show any significant structural differences from that observed in Rb₂Mo₁₂Se₁₄. Indeed, the intracuster Mo–Mo and Mo–Se distances are similar within 0.008 Å in both compounds, indicating an identical cationic transfer towards the Mo₁₂Se₁₄Se₆ units. The symmetry of the Mo₁₅Se₁₇Se₆ unit is 3 or C_3 , while it is $\bar{6}$ or C_{3h} in Rb₃Mo₁₅Se₁₇. Despite the lowering of the local symmetry of the Mo₁₅Se₁₇Se₆ cluster unit due to the loss of the mirror plane, the different Mo–Mo and Mo–Se distances within the Mo₁₅Se₁₇Se₆ unit compare well with those found in Rb₃Mo₁₅Se₁₇. Indeed, the greatest deviations observed are 0.005 and 0.01 Å for the Mo–Mo and Mo–Se bonds, respectively. The shortest Mo–Mo distance between the Mo₁₂ and Mo₁₅ clusters is 3.267 (2) Å, and between the Mo₁₅ clusters is 3.280 (3) Å. The latter two distances are again similar to those found in Rb₂Mo₁₂Se₁₄ [3.279 (1) Å] and Rb₃Mo₁₅Se₁₇ [3.268 (2) Å]. The Rb1 atom is surrounded by 11 Se atoms forming a distorted trigonal prism capped on all faces. The other alkali-metal cations are arranged in finite chains along the threefold axis between two consecutive Mo₁₅Se₁₇Se₆ units in a distorted tri- or tetracapped trigonal prismatic environment of Se atoms. The cations at both ends of the finite chain are in a tetracapped trigonal prismatic arrangement, and the remaining cations are in a tricapped trigonal coordination. The latter environment is similar to that

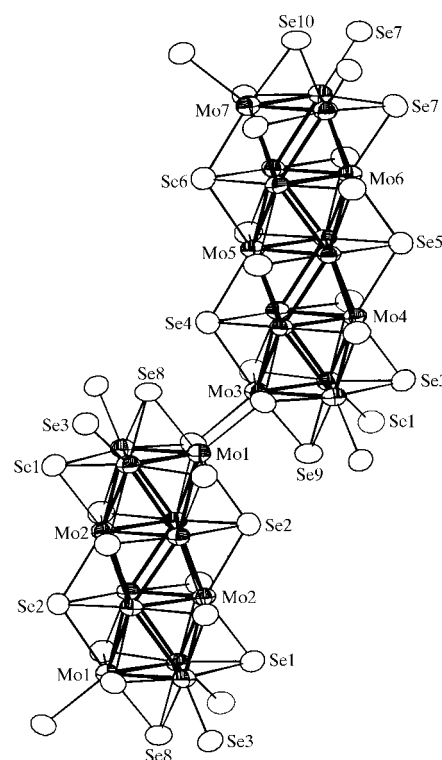


Figure 1

Plot showing the atom-numbering scheme and the inter-unit linkage of Mo₁₂Se₁₄Se₆ and Mo₁₅Se₁₇Se₆ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

encountered in the quasi-one-dimensional compounds $M_2Mo_6X_6$ (Potel, 1981). The Rb–Se distances spread over a wide range [3.508 (2)–3.973 (5) Å]. The shortest distance between adjacent Rb^+ cations is 4.695 (4) Å.

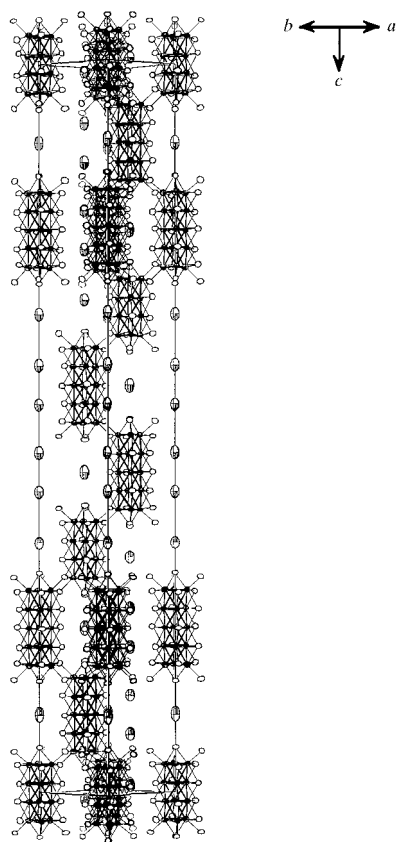


Figure 2
View of $Rb_4Mo_{21}Se_{24}$ along [110].

Experimental

Single crystals of $Rb_4Mo_{21}Se_{24}$ were obtained in an attempt to prepare $Rb_4Mo_{21}Se_{25}$. They were prepared from a mixture of $Rb_2Mo_6Se_6$, $MoSe_2$ and Mo in the proportions 2:6.5:2.5. The ternary compound $Rb_2Mo_6Se_6$ was synthesized from an ion-exchange reaction of $In_2Mo_6Se_6$ with RbCl at 1073 K, as described previously. All materials were handled 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 temperature was increased at a rate of 300 K h^{-1} to 1973 K and held for 6 h, then cooled at a rate of 100 K h^{-1} to 1373 K and finally furnace cooled.

Crystal data

$Rb_4Mo_{21}Se_{24}$
 $M_r = 4251.66$
Trigonal, $R\bar{3}$
 $a = 9.5078$ (2) Å
 $c = 87.797$ (2) Å
 $V = 6873.4$ (3) Å³
 $Z = 6$
 $D_x = 6.163\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 48 971 reflections
 $\theta = 1.0\text{--}40.3^\circ$
 $\mu = 28.81\text{ mm}^{-1}$
 $T = 293$ (2) K
Irregular, black
 $0.13 \times 0.04 \times 0.04\text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ ($\kappa = 0$) plus additional ω scans
Absorption correction: empirical (SORTAV; Blessing, 1995)
 $T_{\min} = 0.247$, $T_{\max} = 0.468$
33 750 measured reflections
9548 independent reflections

5050 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.094$
 $\theta_{\max} = 40.22^\circ$
 $h = -17 \rightarrow 12$
 $k = -15 \rightarrow 17$
 $l = -157 \rightarrow 158$
Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.117$
 $S = 0.959$
9548 reflections
149 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0399P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 2.96\text{ e \AA}^{-3}$
(near Mo5)
 $\Delta\rho_{\min} = -2.62\text{ e \AA}^{-3}$
(near Mo6)
Extinction correction: SHELXL97
Extinction coefficient: 0.000149 (5)

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Bergerhoff, 1996); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1436). Services for accessing these data are described at the back of the journal.

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