Rb$_5$Mo$_{27}$Se$_{31}$, a novel ternary reduced molybdenum selenide containing Mo$_{12}$ and Mo$_{15}$ clusters

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The crystal structure of Rb$_5$Mo$_{27}$Se$_{31}$, pentarubidium heptacosamolybdenum hentriacontaselenium, consists of a mixture of Mo$_{12}$Se$_{14}$Se$_6$ and Mo$_{15}$Se$_{17}$Se$_6$ cluster units in a 1:1 ratio. Both types of cluster are interconnected through inter-unit Mo—Se bonds. Rb$^+$ cations occupy large voids between the different cluster units.

Comment

The crystal structures of reduced molybdenum chalcogenides are characterized by metal–metal bonding that manifests itself in discrete clusters of diverse sizes and geometries. To date, 11 different Mo clusters with nuclearities from three to 36 have been synthesized in solid-state chemistry. Clusters with nuclearities higher than six, *i.e.* Mo$_{3n}$ (n = 3, 4, 5, 6, 7, 8, 10 or 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 to form Mo$_{3n}X^i_{3n+2}X^a_6$ units. Whereas the inner ligands, denoted X^i in the notation of Schäfer & von Schnering (1964), are only linked to one cluster, the six external X^a ligands are shared between adjacent clusters to create the Mo—X framework. Large voids between the Mo$_{3n}X_{3n+2}$ units are thus formed, in which the cations reside.

The crystal structures of these compounds can be based on only one or two different types of Mo clusters. The first case is represented by the series of compounds M_{n-2}Mo$_{3n}X_{3n+2}$ (M = Rb or Cs and X = S, Se or Te; n = 3, 4, 5, 6, 7, 8, 10 or 12) containing 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, 1989a,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 exemplified by the series of compounds Rb$_{2n}$Mo$_9X_{11}$Mo$_{6n}X_{6n+2}$ (n = 1, 2, 3, 4 or 5; Picard *et al.*, 2000). Current interest in these Mo cluster compounds is associated not only with their fascinating structural aspect, but also with 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, Rb$_5$Mo$_{27}$Se$_{31}$, containing Mo$_{12}$Se$^i_{14}$Se$^a_6$ and Mo$_{15}$Se$^i_{17}$Se$^a_6$ cluster units in equal proportion. Both units share their Se^a atoms according to the connective formulae Mo$_{12}$Se$^i_8$Se$^{i-a}_{6/2}$Se$^{a-i}_{6/2}$ and Mo$_{15}$Se$^i_{11}$Se$^{i-a}_{6/2}$-Se$^{a-i}_{6/2}$ to form large cavities in which the Rb$^+$ ions are located. The Mo$_{12}$Se$_{14}$Se$_6$ and Mo$_{15}$Se$_{17}$Se$_6$ cluster units are similar to those reported previously in the compounds Rb$_2$Mo$_{12}$Se$_{14}$ (Gautier *et al.*, 1998) and Rb$_3$Mo$_{15}$Se$_{17}$ (Gougeon *et al.*, 1989a), in which they occur separately. The Mo cores of both units result from the *trans*-face-sharing of three or four octahedral Mo$_6$ clusters, respectively, and they can also be described as resulting from the stacking of four and five Mo$_3$ triangles, respectively.
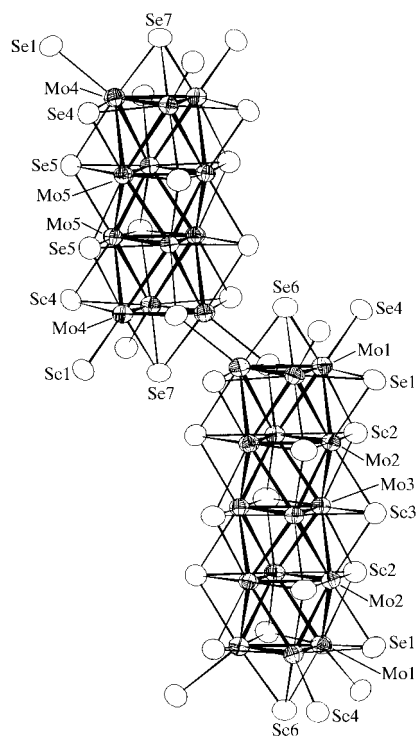

Figure 1
The structures of the two cluster types in Rb$_5$Mo$_{27}$Se$_{31}$, showing the atom-numbering scheme and the inter-unit linkage of the Mo$_{12}$Se$_{14}$Se$_6$ and Mo$_{15}$Se$_{17}$Se$_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

The Mo$_{12}$Se$_{14}$Se$_6$ unit possesses the same local symmetry ($\bar{3}$ or C_{3i}) as, and does not show any significant structural differences from, that observed in Rb$_2$Mo$_{12}$Se$_{14}$. Indeed, the intracluster Mo—Mo and Mo—Se distances are similar to within 0.009 and 0.006 Å, respectively, in both compounds, indicating an identical cationic charge transfer toward the Mo$_{12}$Se$_{14}$Se$_6$ units.

The symmetry of the Mo$_{15}$Se$_{17}$Se$_6$ unit is $\bar{6}$ or C_{3h}, as in Rb$_3$Mo$_{15}$Se$_{17}$. The different Mo—Mo and Mo—Se distances within the Mo$_{15}$Se$_{17}$Se$_6$ unit also compare well with those found in Rb$_3$Mo$_{15}$Se$_{17}$; the greatest deviations are 0.007 Å for Mo—Mo and 0.005 Å for Mo—Se.

The shortest Mo—Mo distance between the Mo_{12} and Mo_{15} clusters is 3.2780 (7) Å, similar to the values found in $Rb_2Mo_{12}Se_{14}$ [3.279 (1) Å] and $Rb_3Mo_{15}Se_{17}$ [3.268 (2) Å]. The $Rb1^+$ cation 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 $Mo_{15}Se_{17}Se_6$ units. The $Rb2^+$ cations at both ends of the finite chains are in a tetracapped trigonal prismatic environment of Se atoms, and the $Rb3^+$ cations are in a tricapped trigonal coordination. The latter environment is similar to that encountered in the quasi-one-dimensional compounds $M_2Mo_6X_6$ (Potel, 1981). The Rb—Se distances vary over a wide range [3.5156 (6)–3.954 (1) Å]. The shortest spacing between adjacent Rb^+ cations is 4.715 (3) Å.
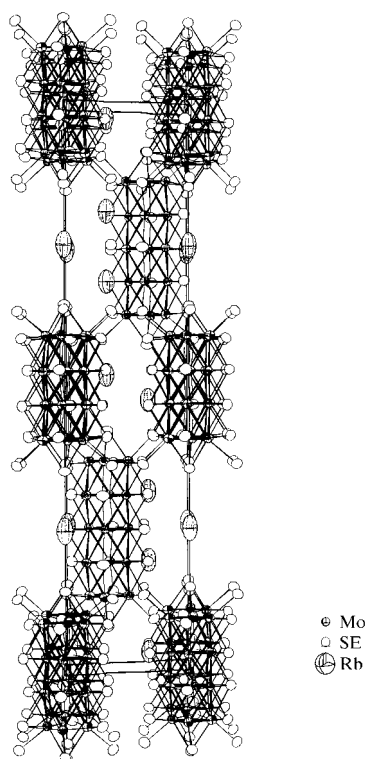

Figure 2
View of $Rb_5Mo_{27}Se_{31}$ along [010].

Experimental

Single crystals of $Rb_5Mo_{27}Se_{31}$ grew during an attempt to obtain $Rb_4Mo_{21}Se_{25}$ using 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 by Potel (1981). 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 charge was heated at the rate of 300 K h⁻¹ to 1973 K, at which temperature it was held for 6 h, then it was cooled at 100 K h⁻¹ to 1373 K and finally furnace cooled.

Crystal data

$Rb_5Mo_{27}Se_{31}$	Mo $K\alpha$ radiation
$M_r = 5465.49$	Cell parameters from 104 176
Hexagonal, $P6_3/m$	reflections
$a = 9.52080 (10)$ Å	$\theta = 1.0–40.3°$
$c = 37.5113 (5)$ Å	$\mu = 28.79$ mm⁻¹
$V = 2944.69 (6)$ Å³	$T = 293 (2)$ K
$Z = 2$	Irregular, black
$D_x = 6.164$ Mg m⁻³	$0.07 \times 0.05 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	6242 independent reflections
φ scans ($\kappa = 0$) plus additional ω scans	3113 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.086$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{max} = 40.2°$
$T_{min} = 0.090$, $T_{max} = 0.162$	$h = -17 \rightarrow 15$
58 800 measured reflections	$k = -17 \rightarrow 17$
	$l = -64 \rightarrow 68$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 3.5266P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.120$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 3.12$ e Å⁻³
6242 reflections	$\Delta\rho_{min} = -2.54$ e Å⁻³
100 parameters	

The largest difference peak lies 0.64 Å from the Mo4 atom.

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Bergerhoff, 1996); software used to prepare material for publication: SHELXL97.

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