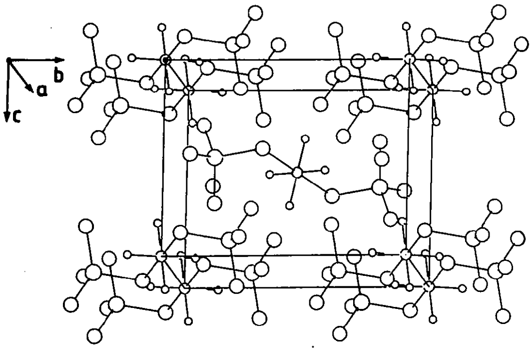

Fig. 2. $[Cu(TlI_4)_2(NH_3)_4]$. Kristallstruktur.

ordnet sich in die Reihe der Vergleichsstrukturen mit Tetraammindiiodokupfer(II)-Einheiten ein (Freckmann & Tebbe, 1980). Das tetraedrische Ion ist in dem Sinne verzerrt, daß der Bindungsabstand zum gleichzeitig an das komplexe Kation koordinierten Liganden I(4) deutlich länger als die übrigen ist. Als Folge variieren die Winkel am Zentralatom Tl, wobei die längere Bindung Tl—I(4) an den kleineren Winkeln beteiligt ist. In den übrigen bisher strukturell charakterisierten, nicht zusätzlich koordinierten Tetraiodothallat(III)-Gruppen sind die Abweichungen von der idealen Tetraeder-Geometrie naturgemaß geringer (Drew, Lewis & Walton, 1970; Glaser, Goggin, Sandström & Lutsko, 1982). Die an eine innenzentrierte Anordnung erinnernde Packung der Komplexe $[Cu(TlI_4)_2(NH_3)_4]$ (Fig. 2) wird durch kurze intermolekulare Kontakte $d(I\cdots I) = 3{,}948$, $3{,}973$ (2) Å bestimmt, an denen das gleichzeitig halbkoordinativ an Cu^{2+} gebundene Iodid-Ion I(4) beteiligt ist. Da allerdings keine bevorzugt gerichteten Wechselwirkungen zu erkennen sind, scheinen übliche van der Waals-Kontakte vorzuliegen.

Die Substanz wurde von Frau H. Borgmann dargestellt und analytisch charakterisiert. Die Kristalle wurden von Herrn N. Etzenbach gezüchtet. Diese Arbeit wurde durch Sachmittelspenden des Fonds der Chemischen Industrie und des Vereins der Freunde und Förderer der Universität zu Köln gefördert. Ich danke den Genannten für die Unterstützung.

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Structure of $Rb_3Mo_{15}Se_{17}$ Containing the New Mo_{15} Clusters

By P. Gougeon, M. Potel and M. Sergent

Laboratoire de Chimie Minérale B, Unité Associée au CNRS n° 254, *Université de Rennes-Beaulieu,*
Avenue du Général Leclerc, 35042 *Rennes CEDEX, France*

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Abstract. $Rb_3Mo_{15}Se_{17}$, $M_r = 3037{\cdot}83$, hexagonal, $P6_3/m$, $a = 9{\cdot}4842$ (8), $c = 21{\cdot}006$ (7) Å, $V = 1636{\cdot}3$ (5) Å^3, $Z = 2$, $D_x = 6{\cdot}165$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 284{\cdot}5$ cm^{-1}, $F(000) = 2638$, $T = 295$ K, $R = 0{\cdot}022$ for 824 observed reflections. The title compound contains for the first time the new condensed cluster unit $Mo_{15}Se_{17}$. The cluster units are linked together through Mo—Se interunit bonds and delimit large tunnels. The Rb ions are located either in these tunnels or in cavities situated between two consecutive units along the threefold axis.

Introduction. In the chemistry of the ternary molybdenum chalcogenides, it is now well known that the octahedral Mo_6 cluster condenses *via* face sharing to form larger clusters as the molybdenum oxidation state is lowered (Potel, 1981; Chevrel & Sergent, 1982). This condensation process is very well illustrated by the series of compounds of general formula $M_{2n-2}Mo_{6n}X_{6n+2}$ (M = Rb, Cs; X = S, Se; n = 1, 2, 3, 4 and 5) containing respectively Mo_6, Mo_{12}, Mo_{18}, Mo_{24} and Mo_{30} clusters (Gougeon, 1984). The latter four clusters consist of three, five, seven and nine face-linked Mo_6 octahedra. The only condensed cluster built up from an even number of Mo_6 clusters was up until now the Mo_9 cluster found to crystallize along with Mo_6 clusters in $In_2Mo_{15}Se_{19}$ or $In_3Mo_{15}Se_{19}$ (Potel, Chevrel & Sergent, 1981; Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber, 1979), or alone in $Ag_{3.6}Mo_9Se_{11}$ (Gougeon, Padiou, Le Marouille, Potel & Sergent, 1984).

Here, we report the crystal structure determination of $Rb_3Mo_{15}Se_{17}$ comprising the new Mo_{15} cluster. This cluster is the second example of a condensation of an even number of Mo_6 clusters.

Experimental. Single crystals were obtained by heating a mixture of $RbMo_3Se_3$ (Potel, Gougeon, Chevrel & Sergent, 1984) and Mo_3Se_4 in the ratio 3:2 at 2073 K for one day in a sealed molybdenum crucible and then cooling it at 100 K h^{-1} down to 1273 K.

The intensity data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. The approximate dimensions of the crystal fragment were 0·11 × 0·14 × 0·16 mm. The lattice parameters were refined from the angle values of 25 reflections with $13 < 2\theta < 30°$. 3529 reflections with $2 \leq 2\theta \leq 60°$ were collected with the following conditions: $-13 \leq h \leq 0$; $0 \leq k \leq 13$; $0 \leq l \leq 29$; ω–2θ mode with scan width $\Delta\omega = (0{\cdot}9 + 0{\cdot}35\mathrm{tg}\theta)°$ and counter aperture $\Delta l = (2 + 0{\cdot}5\mathrm{tg}\theta)$ mm. Three check reflections were measured every hour and showed no significant fluctuation in intensity. Data were corrected for Lorentz–polarization and an empirical absorption correction using *DIFABS* (Walker & Stuart, 1983) was applied. The minimum and maximum corrections were 0·813 and 1·229 respectively. The symmetry related reflections were then averaged to give 1652 unique data ($R_{\mathrm{int}} = 0{\cdot}038$) which were used to solve the structure with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier synthesis. The function minimized in the least-squares program was $\sum w \times (|F_o| - |F_c|)^2$ with $w = 4F_o^2/|\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2|$. The refinement of all atoms anisotropically and an extinction coefficient (60 variables) converged to $R = 0{\cdot}022$, $wR = 0{\cdot}021$, $S = 1{\cdot}065$ for 824 reflections with $F_o^2 > 2\sigma(F_o^2)$. The largest shift/e.s.d. was < 0·01. Maximum and minimum electron density in final difference Fourier map was +0·98 and −1·38 e Å^{-3} respectively; final value of g was $1{\cdot}03 \times 10^{-7}$ (Stout & Jensen, 1968). A refinement of the occupancy factors for the Rb sites confirmed the sites to be fully occupied.

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	0·51704 (7)	0·16167 (7)	0·53502 (2)	0·34 (1)
Mo(2)	0·68423 (6)	0·18028 (6)	0·64380 (2)	0·311 (9)
Mo(3)	0·5148 (1)	0·1623 (1)	$\frac{3}{4}$	0·30 (1)
Se(1)	0·33190 (8)	0·29061 (8)	0·95632 (3)	0·47 (1)
Se(2)	0·62958 (8)	−0·00102 (7)	0·14243 (3)	0·57 (1)
Se(3)	0·7058 (1)	0·0354 (1)	$\frac{3}{4}$	0·63 (2)
Se(4)	$\frac{1}{3}$	$\frac{2}{3}$	0·56052 (5)	0·54 (1)
Rb(1)	0	0	0·36093 (8)	2·23 (2)
Rb(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	2·77 (4)

Table 2. *Selected interatomic distances* (Å)

Mo(1)–Mo(1)	2 × 2·657 (1)	Mo(1)–Se(1)	2·598 (1)
Mo(2)	2·736 (1)	Se(1)	2·600 (1)
Mo(2)	2·773 (1)	Se(1)	2·630 (1)
Mo(2)–Mo(2)	2 × 2·670 (1)	Se(2)	2·688 (1)
Mo(3)	2·704 (1)	Se(4)	2·526 (1)
Mo(3)	2·718 (1)	Mo(2)–Se(1)	2·556 (1)
Mo(3)–Mo(3)	2 × 2·661 (1)	Se(2)	2·586 (1)
Mo(1)–Mo(1)$_{\mathrm{intercluster}}$	3·268 (2)	Se(2)	2·603 (1)
		Se(3)	2·681 (1)
		Mo(3)–Se(2)	2 × 2·688 (1)
		Se(3)	2·617 (1)
		Se(3)	2·629 (1)
Rb(1)–Se(1)	3 × 3·584 (1)	Rb(1)–Rb(1)	4·660 (3)
Se(2)	3 × 3·509 (1)	Rb(1)	5·842 (3)
Se(3)	3 × 3·777 (1)	Rb(1)–Rb(2)	5·951 (1)
Rb(2)–Se(2)	6 × 3·765 (1)		
Se(3)	3 × 3·515 (1)		
Se(4)	2 × 3·980 (1)		

Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the *SDP* (B. A. Frenz & Associates Inc., 1985) programs on a PDP 11/60. Final atomic coordinates and B_{eq} are reported in Table 1 and selected interatomic distances in Table 2.*

Discussion. The basic structural building block of $Rb_3Mo_{15}Se_{17}$ is the new condensed cluster unit $Mo_{15}Se_{17}$ shown in Fig. 1. The condensation process is obviously the same as for the Mo_9Se_{11} and $Mo_{6n}Se_{6n+2}$ (n = 2, 3, 4 and 5) units and arises here from the fusion of four elementary Mo_6Se_8 units *via* sharing of Mo_3Se_3 faces and loss of capping chalcogen atoms. Consequently, the Mo(1) atoms of the upper and lower triangles have the same environment as those of the Mo_6Se_8 unit in the rhombohedral $M$$Mo_6Se_8$ (M = Na, K, Pb, Sn, rare-earth, ...) compounds (Chevrel & Sergent, 1982): four Mo [two Mo(1) and two Mo(2)] and four Se atoms approximately coplanar with the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51421 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square. Chester CH1 2HU, England.

central Mo(1) atoms. This leaves the part of the Mo(1) coordination sphere which is outward from the cluster empty. This empty position is subsequently filled by an Se(1) atom of an adjacent unit which constitutes in turn the apex of the Mo(1) square pyramidal environment. The Mo(2) and Mo(3) atoms are surrounded by four Se atoms in butterfly shape and six Mo atoms, all belonging to the same unit. As observed in previous Mo-condensed cluster chalcogenides (Gougeon, 1984), the Mo—Mo distances fall into two classes: the first one corresponds to the Mo—Mo distances within the Mo_3 triangles perpendicular to the threefold axis which vary over a small range (2·657 to 2·670 Å) and the second one, to the Mo—Mo distances between Mo_3 triangles which range from 2·704 to 2·773 Å. The Mo—Se comprised between 2·526 and 2·688 Å, are of the same magnitude as those reported for other Mo-cluster selenides.

The stacking of the $Mo_{15}Se_{17}$ units is illustrated in Fig. 2. The $Mo_{15}Se_{17}$ is centered on a 2(*c*) special position and therefore has C_{3h} symmetry. Each $Mo_{15}Se_{17}$ unit is connected to six other units by short Mo(1)—Se(1) interunit bonds which are formed, as we have seen, between the Mo(1) atoms of the terminal Mo_3Se_3 triangles of one unit and the Se(1) atoms of the neighboring units. This intercluster connectivity is similar to that in the MMo_6X_8 compounds (Chevrel & Sergent, 1982) and thereby generates around each $Mo_{15}Se_{17}$ unit six long intercluster Mo(1)—Mo(1) distances of 3·268 Å which are indicative of a weak electronic coupling and responsible for the metallic behavior of $Rb_3Mo_{15}Se_{17}$.

The Rb(1) atoms, located on 4(*e*) positions, are coordinated to nine Se atoms at the corners of a tricapped trigonal prism with Rb(1)—Se distances in the range 3·509 to 3·777 Å. This Se prism must share one triangular face with another to constitute a larger complex Se_{15} bipolyhedron delimited by three $Mo_{15}Se_{17}$ related through the threefold axis in (0,0,*z*). The stacking of these Se_{15} bipolyhedra along the *c* axis leads to a one-dimensional channel in which the Rb(1) atoms are spaced with alternating distances of 4·660 and 5·842 Å.

The Rb(2) atoms, lying in 3(*d*) positions, are surrounded by eleven Se atoms: six are arranged as a trigonal prism with the remaining five capping all the

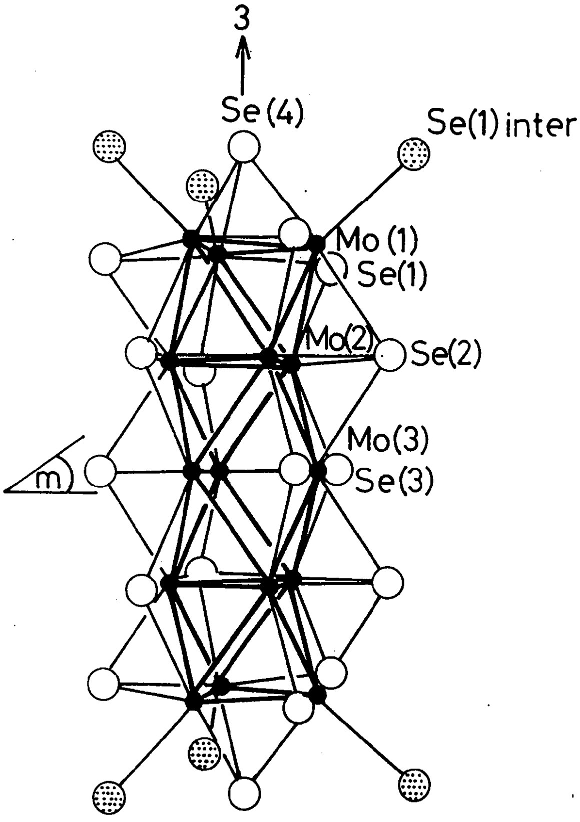

Fig. 1. $Mo_{15}Se_{17}$ units with the numbering scheme. Stippled atoms belong to neighboring units.

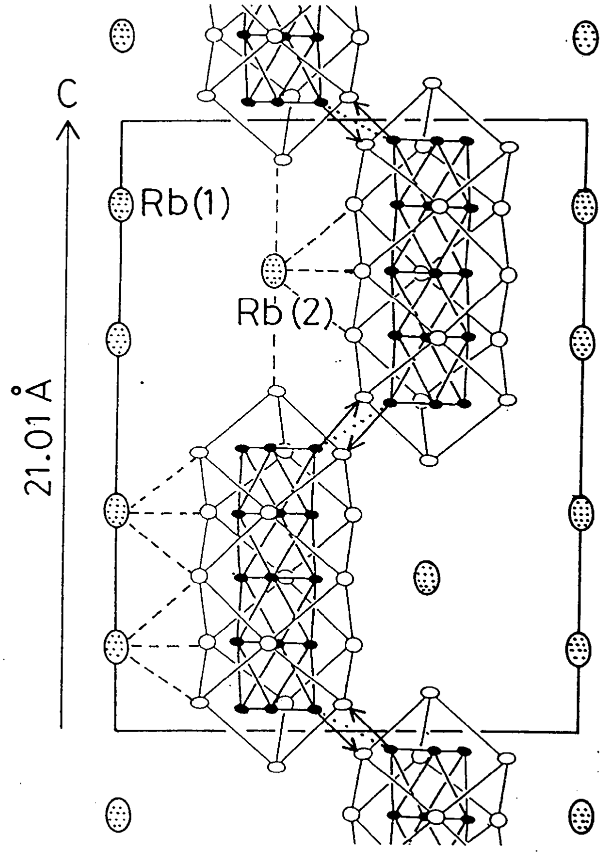

Fig. 2. Projection of the structure of $Rb_3Mo_{15}Se_{17}$ on the hexagonal (11$\bar{2}$0) plane. Filled circles: Mo atoms; empty circles: Se atoms. The thin lines define the Se polyhedra surrounding the Mo_{15} cluster. Arrows show the Mo—Se interunit bonds, the dotted lines the intercluster bonds and the dashed lines the Rb—Se bonds.

faces. For this site, the Rb(2)—Se distances vary from 3·515 to 3·980 Å.

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Structure de $Na_3M_3(CO_3)_5$ (M = Terre Rare, Ca, Na, Sr), rattaché à la Burbankite

Par Daria Ginderow

Laboratoire de Minéralogie–Cristallographie associé au CNRS, Université P. et M. Curie, T16, 4 place Jussieu, 75252 Paris CEDEX 05, France

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Abstract. $M_r = 616$, monoclinic, $P2_1$, $a = 10{\cdot}412\,(4)$, $b = 10{\cdot}414\,(4)$, $c = 6{\cdot}291\,(3)$ Å, $\gamma = 119{\cdot}80\,(5)^\circ$, $V = 591{\cdot}9$ Å^3, $Z = 2$, $D_x = 3{\cdot}46$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 6{\cdot}5$ mm^{-1}, $F(000) = 580$, $T = 295$ K, $R(F) = 0{\cdot}074$ for 2391 reflexions. The general formula of this rare-earth compound is $Na_3M_3(CO_3)_5$ with M = rare earth, Ca, Na, Sr. The three M sites are differently occupied, $M(1)$ has a coefficient of occupation of 1·114 (3), $M(2)$ 0·947 (3) and $M(3)$ 0·962 (3). These values show that the three sites are occupied by different atoms and they must be considered as a correction factor of the temperature factor computed with the formula of the compound. The structure is monoclinic and pseudo-hexagonal $P6_3mc$.

Introduction. $Na_3(TR_{1,22}Ca_{1,15}Na_{0,40}Sr_{0,24})(CO_3)_5$ avec $TR_{1,22}$ détaillé en $Ce_{0,56}$, $La_{0,44}$, $Nd_{0,12}$, $Pr_{0,06}$, $Sm_{0,02}$, $Gd_{0,01}$, $Y_{0,01}$, provient du gisement de cancrinite de Nlende, Kribi, Cameroun. Sa formule générale $Na_3M_3(CO_3)_5$ correspond à celle des carbonates de terre rare (TR) de type burbankite. La burbankite $(Na_{2,75}Ca_{0,25})(TR_{0,75}Ca_{0,95}Ba_{0,65}Sr_{0,65})(CO_3)_5$ (Voronkov & Shumyatskaya, 1968) présente une symétrie hexagonale alors que l'espèce étudiée, dénommée récemment remondite-(Ce), est monoclinique et pseudo-hexagonale (Cesbron, Gilles, Pelisson & Saugues, 1988).

Partie expérimentale. Cristal orange sphérique de diamètre 0,55 mm, paramètres cristallins obtenus sur diffractomètre Philips PW 1100 (anticathode au Mo) avec 25 réflexions $9 < \theta < 14^\circ$. Mesure des intensités par 'flying stepscan', angle de balayage de 1,50°, vitesse de scanning de 0,025 s par pas de 3/100° θ, domaine d'exploration de $2\theta \leq 90^\circ$ ($-20 \leq h \leq 18$, $0 \leq k \leq 20$, $0 \leq l \leq 10$). Réflexions de référence $0\bar{2}\bar{3}$, $0\bar{2}3$, 023 mesurées toutes les heures avec des variations respectives d'intensité 1,2, 0,7, 1,3%. Corrections de Lorentz–polarisation. Les effets de l'absorption ont été négligés. Sur 4971 réflexions indépendantes, 2391 réflexions ont été retenues avec $F_o \geq 14{,}3$ (échelle absolue) et $\sin\theta/\lambda \geq 0{,}149$ Å^{-1}. La fonction de Patterson tridimensionelle a confirmé que cette structure est isomorphe avec la burbankite (Voronkov & Shumyatskaya, 1968). Affinement des F_o et des coefficients de température par moindres carrés et en matrice complète à l'aide d'une version modifiée de *ORFLS* (Busing, Martin & Levy, 1962). Les facteurs de diffusion atomique sont ceux des *International Tables for X-ray Crystallography* (1974) pour les cations en tenant compte de la contribution de la dispersion anomale. Pour l'anion O^{2-}, les valeurs des facteurs de diffusion atomique sont ceux de Tokonami (1965). En fin d'affinement avec des facteurs d'agitation thermique anisotrope, $R = 0{,}074$ [$wR = 0{,}091$ avec $w = 1/\sigma^2(F_o)$] pour 2391 réflexions retenues, $S = 7{,}6$ avec 156 paramètres, $(\Delta/\sigma)_{\text{moyen}} = 0{,}079$, $\Delta\rho = 1{,}72$–$1{,}55$ e Å^{-3}. La valeur relativement élevée du R final semble liée à la complexité de la formule chimique. Programme utilisé pour les dessins: *ORTEP*II (Johnson, 1976). Ordinateur: Matra 570/CX.

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