in the *cyclo*-hexaphosphate $Ca_2(NH_4)_2P_6O_{18}.6H_2O$ (Averbuch-Pouchot, 1990) whose structure is described with reticular parameters and a space group similar to that of $Ce_2P_6O_{18}.10H_2O$. The distribution of the anionic rings in the unit cell is also equivalent, but the geometry of the cationic polyhedra and their arrangement are of course quite different owing to the various valency states of the cations.

The Ce atom is coordinated to the 6 $O(E)$ atoms of the phosphate tetrahedra and to the three water molecules $O(W1)$, $O(W2)$ and $O(W3)$ with the average distances $Ce—O(E) = 2·50$ and $Ce—O(W) = 2·63$ Å (Table 2). The CeO_9 polyhedron formed from this environment is a distorted three-capped trigonal prism. Its axis is parallel to a diagonal direction [110] or [$\overline{1}$10]. The three cap atoms are $O(W1)$, $O(W2)$ and $O(E12)$. Such a coordination is commonly observed among the rare-earth compounds, for example it occurs in the neodymium *cyclo*-hexaphosphate (Trunov *et al.*, 1988).

As shown by Fig. 2, the P_6O_{18} rings form layers perpendicular to the c axis. The CeO_9 polyhedra interconnect the P_6O_{18} anions between layers along the c direction and inside a layer along the diagonal directions [110] and [$\overline{1}$10] to form a three-dimensional network.

Another characteristic feature of this structure is the presence of two free water molecules. $O(W4)$ and $O(W5)$, in channels parallel to the binary axis delimited by the P_6O_{18}–CeO_9 rows. The $O(W5)$—$O(W5)$ bond of $2·887$ Å corresponds to the smallest diameter of a channel. So, among the ten water molecules of the formula unit $Ce_2P_6O_{18}.10H_2O$, four of them do not take part in the coordination of the cation, but probably assure the cohesion between the anionic layers as is the case in the dodecahydrate $Nd_2P_6O_{18}.12H_2O$. The existence of short distances between the water molecules in the channel and
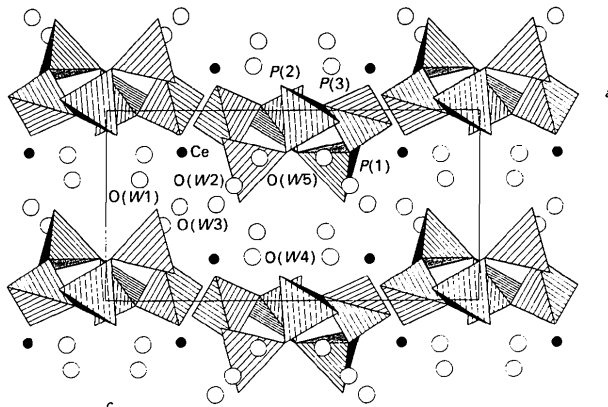
Fig. 2. Projection along the a axis of the atomic arrangement of $Ce_2P_6O_{18}.10H_2O$.

water molecules in the Ce coordination supports this hypothesis: in particular, $2·732$ for $O(W4)$—$O(W2)$ and $2·786$ Å for $O(W5)$—$O(W1)$.

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Structure of the Metastable Binary β-Mo₁₅Se₁₉

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Abstract. $Mo_{15}Se_{19}$, $M_r = 2939·34$, trigonal, $R\overline{3}c$, $a(rh) = 20·360 (1)$ Å, $\alpha(rh) = 26·981 (1)°$, $V(rh) = 1532·2 (1)$ Å³, $Z = 2$, $D_x = 6·371$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 281·28$ cm⁻¹, $F(000) = 2552$, $T = 295$ K, $R = 0·029$ for 781 observed reflections. The title compound constitutes the host structure of the
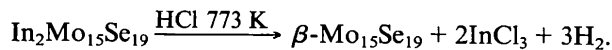
ternary compounds M_2Mo$_{15}$Se$_{19}$ (M = K, Rb, In, Tl, Ba). Its crystal structure is built up from an equal mixture of Mo$_6$Se$_8$ and Mo$_9$Se$_{11}$ cluster units linked together through Mo—Se interunit bonds. The absence of cationic charge transfer towards the Mo clusters results in an expansion of both types of clusters along the threefold axis and in a decrease of the intercluster distances.

Introduction. The structures of the ternary molybdenum chalcogenides are characterized by pseudomolecular units such as Mo$_6$$X_8$, Mo$_9$$X_{11}$ and Mo$_{12}$$X_{14}$ linked together through Mo—Mo and Mo—X interunit bonds to form a molybdenum-chalcogenide framework with large interconnected channels containing the ternary metal atoms (Chevrel & Sergent, 1982). We have recently shown that it is possible to extract the ternary element by means of low-temperature chemical reaction without disturbing the host structure. Thus, we have synthesized as powder sample the new metastable binary molybdenum chalcogenides Mo$_6$$X_8$, Mo$_9$$X_{11}$, α-and β-Mo$_{15}Se_{19}$, all isostructural with the starting ternary compounds M_xMo$_6$$X_8$, Tl$_2Mo_9$$X_{11}$, In$_3Mo_{15}Se_{19}$ and In$_2$Mo$_{15}$Se$_{19}$, respectively (Potel, Gougeon, Chevrel & Sergent, 1984).

More recently we performed these reactions on a single crystal in the cases of In$_3$Mo$_{15}$Se$_{19}$ and In$_2$Mo$_{15}$Se$_{19}$. We present here the crystal structure of the binary β-Mo$_{15}$Se$_{19}$.

Experimental. Single crystals of β-Mo$_{15}$Se$_{19}$ were obtained by action of HCl gas at 773 K on single crystals of In$_2$Mo$_{15}$Se$_{19}$ according to the following reaction:

$$\text{In}_2\text{Mo}_{15}\text{Se}_{19} \xrightarrow{\text{HCl 773 K}} \beta\text{-Mo}_{15}\text{Se}_{19} + 2\text{InCl}_3 + 3\text{H}_2.$$

The complete removal of indium was confirmed by qualitative micro analyses using a JEOL JSM-35 CF scanning electron microscope equipped with a Tracor energy-dispersive-type X-ray spectrometer. Crystals of In$_2$Mo$_{15}$Se$_{19}$ were grown by prolonged annealing of a mixture of In, Mo and Se at 1523 K in a silica tube (Potel, Chevrel & Sergent, 1981).

A crystal of dimensions 0·07 × 0·07 × 0·09 mm was selected for the intensity data collection carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $14 \le 2\theta \le 37°$. 2053 reflections were recorded in the range $2 \le 2\theta \le 60°$ with h $-28 \rightarrow 28$, k $-28 \rightarrow 28$, l $0 \rightarrow 28$, $k > h$ and $|l| > |h|$ (rhombohedral setting); ω–2θ mode was used with scan width $\Delta\omega = (1·0 + 0·35\tan\theta)°$ and counter aperture $\Delta l = (2 + 0·5\tan\theta)$ mm. Three orientation and three intensity control reflections were checked every 250

reflections and every hour, respectively and showed no significant variation. Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The minimum and maximum correction factors were 0·886 and 1·157. After averaging of the symmetry-related reflections ($R_{\text{int}} = 0·045$), 1274 unique reflections, of which 781 had $I \ge 2\sigma(I)$, were used to solve the structure.

The atomic coordinates of In$_2$Mo$_{15}$Se$_{19}$ (Potel *et al.*, 1981) were used as initial values in the first stage of structure refinement. Subsequently, isotropic and anisotropic thermal parameters for all atoms as well as the extinction coefficient were introduced in the full-matrix least-squares refinement on F. The final values of R and wR were 0·029 and 0·033, respectively, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0·04F_o^2)^2]$ and $S = 0·962$ using 781 reflections with $I \ge 2\sigma(I)$ and 54 variables. The largest shift/e.s.d. was $< 0·01$ and final value of $g = 2·73 \times 10^{-8}$ (Stout & Jensen, 1968). The largest residual on the final difference map was 3·05 e Å^{-3} [near Se(1)]. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray*

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

$$B_{\text{eq}} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	0·49818 (4)	0·69255 (4)	0·36968 (4)	0·53 (2)
Mo(2)	0·22468 (4)	0·04038 (4)	0·36761 (4)	0·53 (2)
Mo(3)	0·4130 (1)	$\frac{1}{2} - x$	0·250	0·54 (2)
Se(1)	0·18482 (4)	0·80685 (4)	0·55594 (4)	0·64 (2)
Se(2)	0·54368 (5)	0·91827 (5)	0·18296 (5)	0·68 (2)
Se(3)	0·0641 (2)	$\frac{1}{2} - x$	0·750	0·76 (2)
Se(4)	0·44577 (3)	x	x	0·864 (8)
Se(5)	0·17689 (3)	x	x	0·703 (7)

Table 2. *Selected interatomic distances* (Å)

|Mo(1)—Mo(1)|$_\Delta$	2 × 2·674 (2)	|Mo(2)—Mo(2)|$_\Delta$	2 × 2·699 (2)
Mo(1)$_\Delta$—Mo(1)$_\Delta$	2 × 2·828 (2)	|Mo(3)—Mo(3)|$_\Delta$	2 × 2·682 (1)
		Mo(2)$_\Delta$—Mo(3)$_\Delta$	2·722 (3)
			2·831 (3)
Mo(1)—Mo(2) (intercluster)	3·281 (1)		
Δ(1)–Δ(1)	2·370	Δ(2)–Δ(3)	2·300
Mo(1)—Se(4)	2·531 (1)	Mo(2)—Se(5)	2·535 (1)
Mo(1)—Se(1)	2·555 (1)	Mo(2)—Se(2)	2·570 (1)
	2·578 (2)		2·619 (1)
	2·597 (2)	Mo(2)—Se(3)	2·711 (3)
Mo(1)—Se(2) (interunit)	2·569 (2)	Mo(2)—Se(1) (interunit)	2·609 (2)
		Mo(3)—Se(2)	2 × 2·518 (3)
		Mo(3)—Se(3)	2 × 2·584 (1)

\|Mo—Mo\|$_\Delta$ is the distance between Mo atoms related through the threefold axis and thus forming an Mo$_3$ triangle perpendicular to these, called the intratriangle distance in the text.
Mo$_\Delta$—Mo$_\Delta$ is the distance between Mo atoms of different Mo triangles, called intertriangle distance.

Crystallography (1974, Vol. IV). All the calculations were performed on a PDP11/60 with the *SDP* programs (B. A. Frenz & Associates, Inc., 1982). Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are given in Table 1 and selected interatomic distances in Table 2.*

Discussion. The three-dimensional packing of the Mo_6Se_8 and Mo_9Se_{11} cluster units in β-$Mo_{15}Se_{19}$ (Fig. 1) is obviously identical with that observed in the parent compound $In_2Mo_{15}Se_{19}$ (Potel *et al.*, 1981). Thus, the Mo_6Se_8 unit which consists of an Mo_6 octahedron inscribed in a pseudocube Se_8 is centered on the 2(*b*) position and has C_{3i} symmetry. The Mo_9Se_{11} unit resulting from the condensation of two Mo_6Se_8 units has D_3 symmetry [on a 2(*a*) position] (Fig. 2). However the Mo—Mo bond lengths in both types of clusters differ mainly from those

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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 54071 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
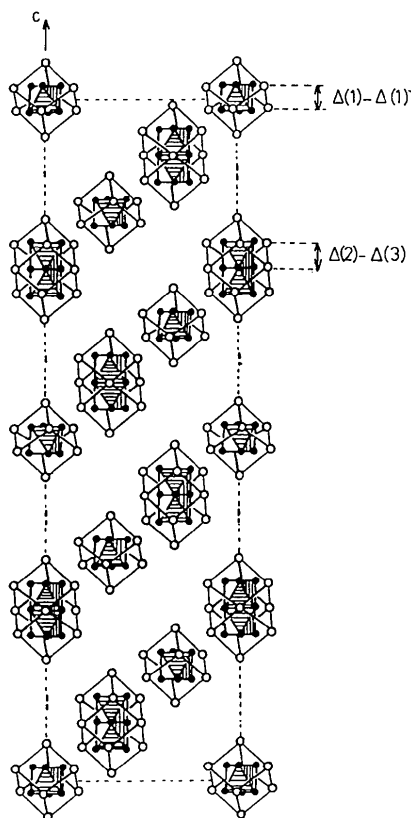
observed in the indium phase. Indeed, it is well known that in the Mo-cluster chalcogenides, the ternary metal atom enters the structure as donating electrons to the clusters and consequently affects the Mo—Mo bond lengths in a significant way. Thus, the absence of charge transfer towards the Mo_6 cluster in β-$Mo_{15}Se_{19}$ leads to a lengthening of the intra- and intertriangle Mo(1)—Mo(1) distances [2·686 (2) and 2·772 (10) Å, respectively in $In_2Mo_{15}Se_{19}$] which are now of the same magnitude as those observed in Mo_6Se_8 which constitutes the host structure of the ternary compounds $M^{n+}Mo_6Se_8$. For the latter, an expansion of the Mo_6 cluster was also found when the cationic charge decreased (Yvon, 1979). This expansion is also reflected by the interplane distance $\Delta(1)$–$\Delta(1)$ which increases from 2·30 Å in $In_2Mo_{15}Se_{19}$ to 2·37 Å in β-$Mo_{15}Se_{19}$ (2·38 Å in Mo_6Se_8). Similarly, the $|Mo(2)—Mo(2)|_\Delta$ and $|Mo(3)—Mo(3)|_\Delta$ intratriangle as well as the two $Mo(2)_\Delta$—$Mo(3)_\Delta$ intertriangle distances within the Mo_9 cluster are longer in the In-free material

Fig. 1. Projection of the structure of β-$Mo_{15}Se_{19}$ onto the hexagonal (110) plane. Filled circles: Mo atoms; empty circles: Se atoms

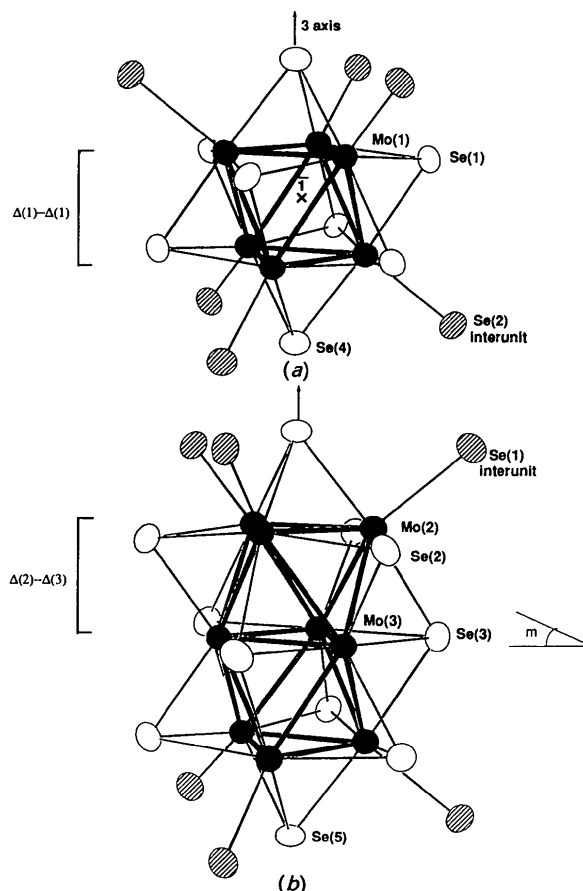Fig. 2. Mo_6Se_8 and Mo_9Se_{11} cluster units with their numbering scheme. Hatched Se atoms belong to neighbouring cluster units.

[2·673 (2), 2·680 (4), 2·712 (5) and 2·808 (6) Å, respectively in In$_2$Mo$_{15}$Se$_{19}$]. Thus, the overall result is again an expansion of the Mo$_9$ cluster along the threefold axis [Δ(2)–Δ(3) 2·28 Å in In$_2$Mo$_{15}$Se$_{19}$]. Notable differences between the two parent structures also occur with respect to the separation of the Mo$_6$Se$_8$ and Mo$_9$Se$_{11}$ units. Indeed, as expected the removal of indium leads to a shortening of the Mo(1)—Mo(2) interunit bond which decreases from 3·389 (3) to 3·281 (1) Å. To a lesser extent, the Mo(1)—Se(2) and Mo(2)—Se(1) interunit bonds also shorten from 2·589 (6) to 2·569 (2) and from 2·641 (5) to 2·609 (2) Å, respectively.

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Structure of High-Pressure MnGeO$_3$ Ilmenite

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Abstract. A single-crystal X-ray study confirms that one of the high-pressure polymorphs of manganese germanate, MnGeO$_3$, has an ilmenite structure with MnO$_6$ and GeO$_6$ octahedra sharing edges to form fully ordered Mn and Ge layers of six-membered rings on (0001). The distortion and height of the GeO$_6$ octahedra in MnGeO$_3$ ilmenite are comparable with those observed in other germanate ilmenites. The crystal data for MnGeO$_3$ ilmenite are: $M_r = 175·55$, trigonal, $R\bar{3}$ [symmetry operators $(0,0,0), (\frac{1}{3},\frac{2}{3},\frac{2}{3}),(\frac{2}{3},\frac{1}{3},\frac{1}{3}) + (x,y,z; -y,x-y,z; y-x,-x,z; -x,-y,z; y,y-x,-z; x-y,x,-z)]$, $a = 5·0148$ (5) Å, $c = 14·324$ (1) Å, $V = 311·97$ (7) Å^3, $Z = 6$, $D_x = 5·54$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7093$ Å, $\mu = 197·8$ cm^{-1}, $F(000) = 486$, $T = 298$ K, $R = 0·018$ ($wR = 0·017$), 187 unique reflections used for refinements, crystal synthesized at 1273 K and 4·87 GPa.

Introduction. Manganese germanate, MnGeO$_3$, crystallizes with the orthopyroxene structure under ambient conditions (Fang & Townes, 1969; Herpin, Whuler, Boucher & Sougi, 1971). With increasing pressure and temperature, the orthopyroxene form (MnGeO$_3$ I) transforms to a clinopyroxene form (MnGeO$_3$ II) and then to an ilmenite form (MnGeO$_3$ III) at 3·0 GPa and 987 K (Ringwood & Seabrook, 1963). The magnetic structure of MnGeO$_3$ III has been investigated in a powder neutron diffraction study with the TOF method (Tsuzuki, Ishikawa, Watanabe & Akimoto, 1974). Although that paper and another by Susaki, Konno & Akimoto (1985) include some structural data for MnGeO$_3$ ilmenite, to the best of the authors' knowledge, no structure refinement of this phase has ever been published. The purpose of this paper is to present details and results from a structure refinement of MnGeO$_3$ III using the method of single-crystal X-ray diffraction and to compare this compound with other germanate ilmenites.

Experimental. The crystals of MnGeO$_3$ ilmenite were grown from a powder sample of MnGeO$_3$ pyroxene that was packed in a Pt capsule and held at 4·87 GPa and 1273 K for three hours in a girdle-type apparatus (Ingrin & Liebermann, 1989). After careful examination of several crystals obtained from the

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