

Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉, a monoclinic variant of the hexagonal In₃Mo₁₅Se₁₉ type**P. Gougeon,* D. Salloum and M. Potel**Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS No. 6226, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cedex, France
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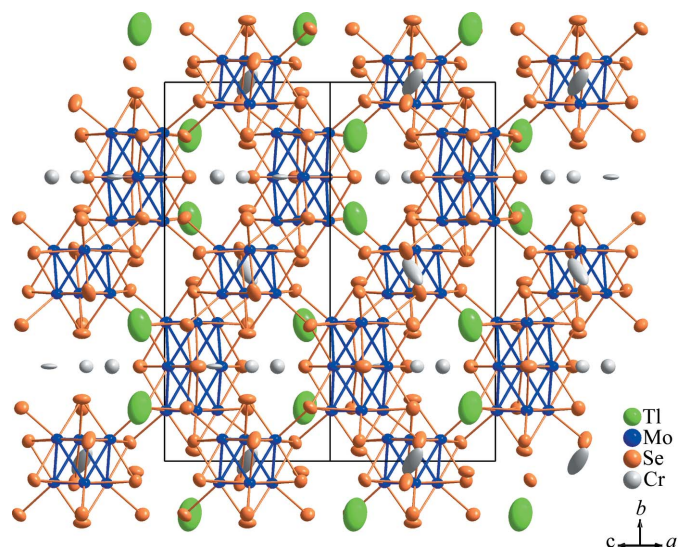
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The monoclinic compound Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉ (chromium thallium pentadecamolybdenum nonadecaselenide) represents a variant of the hexagonal In₃Mo₁₅Se₁₉ structure type. Its crystal structure consists of an equal mixture of Mo₆Se₈Se₆ and Mo₉Se₁₁Se₆ cluster units. The Mo and Se atoms of the median plane of the Mo₉Se₁₁Se₆ unit, as well as three Cr ions, lie on sites with *m* symmetry (Wyckoff site 2*e*). The fourth Cr ion is in a 2*b* Wyckoff position with $\bar{1}$ site symmetry.

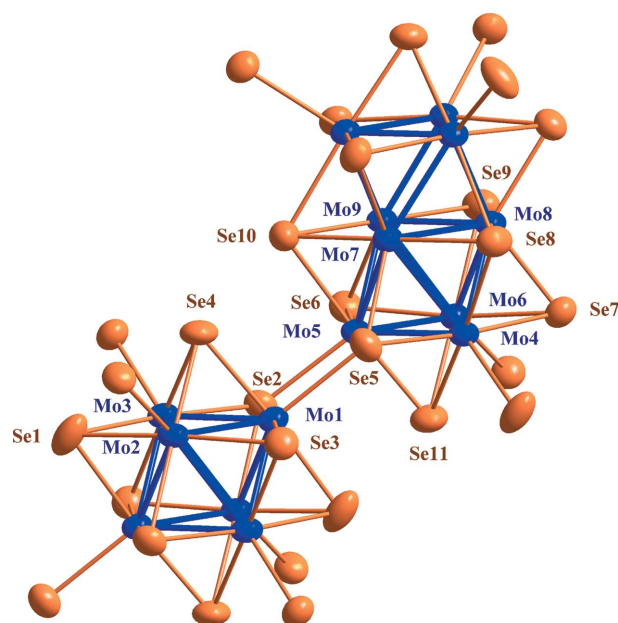
Comment

Thirty years ago, Grüttner *et al.* (1979) reported the crystal structures of the hexagonal compounds In_{2.9}Mo₁₅Se₁₉ and In_{3.3}Mo₁₅Se₁₉, which were the first compounds containing a transition metal cluster with a nuclearity higher than six, namely the bioctahedral Mo₉ cluster. This cluster, which results from the face-sharing of two Mo₆ octahedra, co-exists with the octahedral Mo₆ cluster in equal proportions. Both clusters are surrounded by Se atoms to form Mo₆Se₈Se₆ and Mo₉Se₁₁Se₆ units that share some of their Se atoms to create the three-dimensional Mo–Se framework. The In atoms occupy two crystallographically different positions, depending on their formal oxidation state of +1 or +3. While the In⁺ site is fully occupied, the In³⁺ site presents a nonstoichiometry that leads to compositions ranging from In_{0.9}In₂Mo₁₅Se₁₉ to In_{1.3}In₂Mo₁₅Se₁₉. Interest in these Mo cluster compounds lies not only in their structural aspects but also in their physical properties, because they show superconductivity with high critical magnetic fields at about 4 K. We present here the synthesis and the crystal structure of Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉, which constitutes a monoclinic variant of the In₃Mo₁₅Se₁₉ structure type.

A view of the crystal structure of Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉ is shown in Fig. 1. The Mo–Se framework is similar to that of the In₃Mo₁₅Se₁₉ compounds and consists of an equal mixture of Mo₆Se₈Se₆ and Mo₉Se₁₁Se₆ cluster units interconnected through Mo–Se bonds (Fig. 2). The first unit can be described

**Figure 1**

A view of Cr_{1.45(2)}Tl_{1.87(4)}Mo₁₅Se₁₉, along [101]. Displacement ellipsoids are drawn at the 97% probability level.

**Figure 2**

Plot showing the atom-numbering scheme and the inter-unit linkage of the Mo₉Se₁₁Se₆ and Mo₆Se₈Se₆ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

as an Mo₆ octahedron surrounded by eight face-capping inner Seⁱ and six apical Se^a ligands; for details of the i- and a-type ligand notation, see Schäfer & Schnering (1964). The Mo₉ core of the second unit results from the one-dimensional *trans* face-sharing of two octahedral Mo₆ clusters. The Mo₉ cluster is surrounded by 11 Seⁱ atoms capping the faces of the dioctahedron and six apical Se^a ligands above the terminal Mo atoms. The Mo₆Se₈Se₆ and Mo₉Se₁₁Se₆ units are centred at 2*a* and 2*e* Wyckoff positions and thus have point group symmetries $\bar{1}$ and *m*, respectively, instead of $\bar{3}$.. and $\bar{6}$.. in the hexagonal In₃Mo₁₅Se₁₉ compounds. The Mo–Mo distances within the Mo₆ clusters are between 2.6769 (8) and 2.7252 (7) Å, and

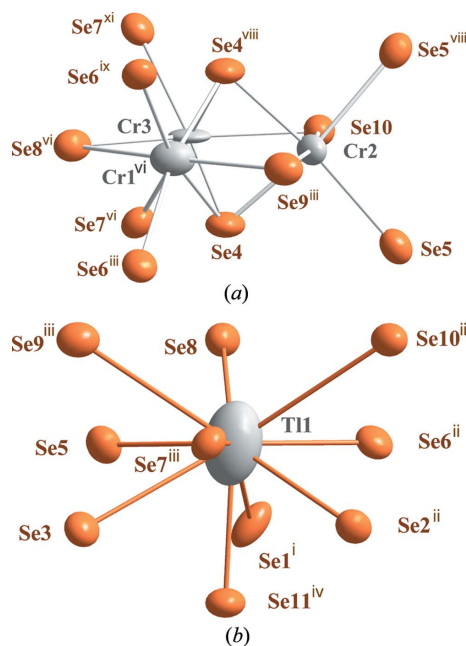


Figure 3

(a) The distribution of Cr1, Cr2 and Cr3. (b) The environment of Tl1. [Symmetry codes are given in Table 1. Additionally: (viii) $x, -y + \frac{1}{2}, z$; (ix) $x + 1, -y + \frac{1}{2}, z$; (xi) $x + 1, -y + \frac{1}{2}, z + 1$.]

those within the Mo₉ clusters are between 2.6278 (9) and 2.7491 (7) Å. These values are comparable with those observed in the In₃Mo₁₅Se₁₉ compounds.

The Se atoms bridge either one (Se1 to Se7) or two (Se8, Se9 and Se10) Mo triangular faces of the clusters. Moreover, atoms Se1, Se2, Se3, Se5, Se6 and Se7 are linked to an Mo atom of a neighbouring cluster. The Mo–Se bond distances range from 2.5436 (9) to 2.6610 (6) Å within the Mo₆Se₈Se₆ unit and from 2.5421 (7) to 2.7001 (8) Å within the Mo₉Se₁₁Se₆ unit. Each Mo₉Se₁₁Se₆ unit is connected to six Mo₆Se₈Se₆ units (and *vice versa*) via Mo–Se^{a-i} bonds to form the three-dimensional Mo–Se framework, the connective formula of which is Mo₉Se₅Se_{6/2}Se_{6/2}^{a-i}, Mo₆Se₂Se_{6/2}Se_{6/2}^{a-i}. As a result of this arrangement, the shortest intercluster Mo···Mo distance between the Mo₆ and Mo₉ clusters is 3.4409 (8) Å, indicating only a weak metal–metal interaction. This distance is a little shorter than the value of 3.512 (8) Å observed for In_{3,3}Mo₁₅Se₁₉.

The main difference between Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉ and the indium compounds lies in the distribution of the trivalent cations. Indeed, in addition to the triangular group of distorted octahedral sites located between two consecutive Mo₆Se₈Se₆ units, the Cr atoms partially occupy a supplementary site located at the mid-point of the *a* axis (2*b* position). In the monoclinic compound Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉, atoms Cr1, Cr2 and Cr3 occupy the distorted octahedral sites located between two consecutive Mo₆Se₈Se₆ units that are occupied by trivalent indium in the In₃Mo₁₅Se₁₉ compounds (Fig. 3*a*). The loss of the threefold axis leads to three crystallographically independent sites with site-occupancy factors of 0.619 (6),

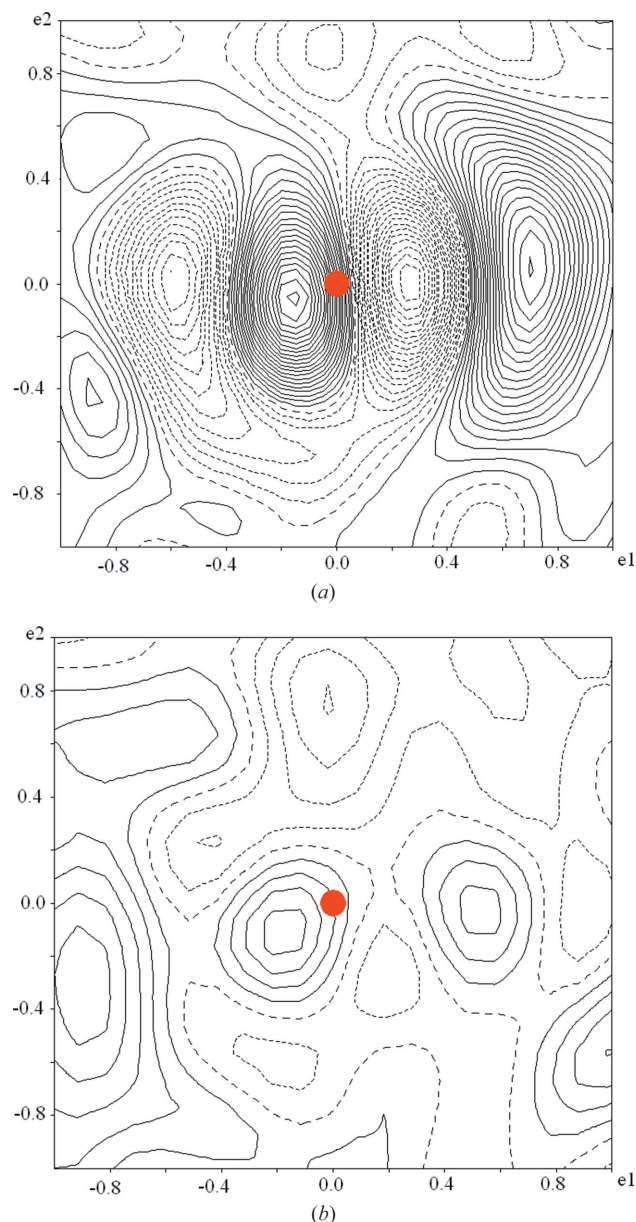


Figure 4

Difference Fourier maps around the Tl1 mean position (large central circles), showing (a) harmonic refinement (minimum and maximum densities: -9.84 and $11.02 \text{ e } \text{\AA}^{-3}$, respectively; step: $0.5 \text{ e } \text{\AA}^{-3}$), and (b) anharmonic refinement (minimum and maximum densities: -2.08 and $2.92 \text{ e } \text{\AA}^{-3}$, respectively; step: $0.5 \text{ e } \text{\AA}^{-3}$).

0.313 (6) and 0.125 (6), compared with the trivalent indium with site occupancies of 0.29 (5) for In_{2,9}Mo₁₅Se₁₉ and 0.44 (2) for In_{3,3}Mo₁₅Se₁₉. The Cr–Se distances are in the ranges 2.515 (2)–2.850 (3), 2.524 (3)–2.798 (2) and 2.501 (8)–2.9635 (6) Å for the Cr1, Cr2 and Cr3 sites, respectively. Atoms Cr4 in the 2*b* Wyckoff position also occupy a distorted octahedral site of Se atoms with Cr–Se distances ranging from 2.3096 (6) to 2.9635 (6) Å.

The Tl⁺ cation of Cr_{1.45}Tl_{1.87}Mo₁₅Se₁₉ replaces the monovalent In⁺ in the large ten-coordinated sites of the Se atoms (Fig. 3*b*). While the In⁺ site centred on the threefold axis has 3₂ symmetry, the Tl⁺ site has no imposed symmetry. The Tl–

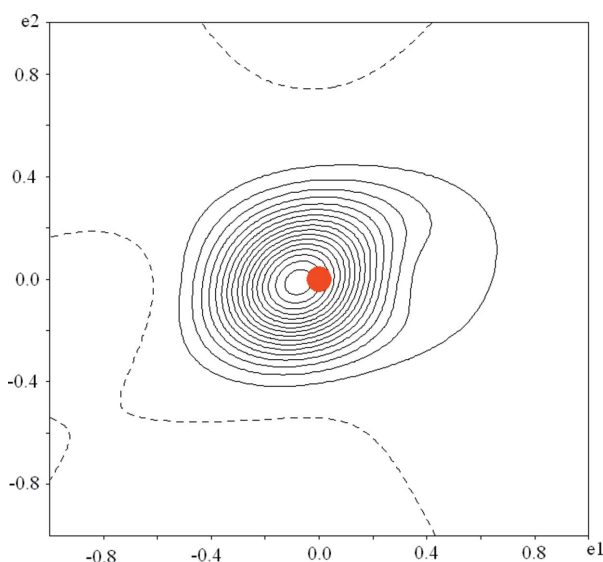


Figure 5

Anharmonic probability density function map of Tl1 in the bc plane (minimum and maximum densities: -0.086 and 8.7905 \AA^{-3} , respectively; step: 0.5 \AA^{-3}).

Se distances range from 3.1152 (11) to 4.2214 (9) \AA . The large U_{iso} value for Tl, which is about five times higher than those for the Mo atoms and three to four times higher than those for the Se and Cr atoms, is due to the large voids that it occupies and does not result from an artefact due to the correlations (0.506 in our case) between the atomic displacement parameters (ADPs) and the site-occupation factor of the Tl atom. This is corroborated by the fact that similar ratios are observed in other reduced molybdenum chalcogenides such as $\text{Tl}_2\text{Mo}_6\text{Se}_6$ (Potel *et al.*, 1980*a*) or $\text{Tl}_2\text{Mo}_9\text{S}_{11}$ (Potel *et al.*, 1980*b*), in which the Tl sites are fully occupied. While in the $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$ structure type, the monovalent In^+ site is fully occupied, in the title compound the Tl^+ site is only 0.935 (2) occupied. This probably results from the higher temperature used during the crystal growth process, which leads to a loss of TlSe because of its high volatility at 1773 K . It is interesting to note that a similar site-occupation factor of 0.94 (1) is found when refining using *SHELXL* (Sheldrick, 2008) a model with two Tl positions and harmonic ADPs and with only one twinning matrix.

Experimental

Single crystals of $\text{Cr}_{1.453}\text{Tl}_{1.87}\text{Mo}_{15}\text{Se}_{19}$ were prepared from a mixture of Cr_2Se_3 , MoSe_2 , TlSe and Mo with the nominal composition $\text{Cr}_{1.5}\text{Tl}_2\text{Mo}_{15}\text{Se}_{19}$. Before use, Mo powder was reduced under flowing H_2 gas at 1273 K for 10 h in order to eliminate any trace of oxygen. The binaries Cr_2Se_3 , MoSe_2 and TlSe were obtained by heating stoichiometric mixtures of the elements in sealed evacuated silica tubes for about 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 then 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 , held at that temperature for 48 h , cooled at 100 K h^{-1} to 1373 K and finally furnace cooled.

Crystal data

$\text{Cr}_{1.453}\text{Tl}_{1.87}\text{Mo}_{15}\text{Se}_{19}$
 $M_r = 3396.7$
 Monoclinic, $P2_1/m$
 $a = 9.7347$ (1) \AA
 $b = 19.2639$ (3) \AA
 $c = 9.7987$ (1) \AA
 $\beta = 118.9305$ (8) $^\circ$

$V = 1608.22$ (4) \AA^3
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 36.91 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.10 \times 0.05 \times 0.04 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{\text{min}} = 0.097$, $T_{\text{max}} = 0.331$

36020 measured reflections
 10161 independent reflections
 6942 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.087$
 $S = 1.49$
 10161 reflections

231 parameters
 $\Delta\rho_{\text{max}} = 4.01 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.97 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (\AA).

Tl1—Se1 ⁱ	3.6290 (11)	Mo5—Mo9	2.7300 (7)
Tl1—Se2 ⁱⁱ	3.4600 (11)	Mo5—Se2	2.6890 (6)
Tl1—Se3	3.7414 (8)	Mo5—Se5	2.6337 (10)
Tl1—Se5	3.2114 (11)	Mo5—Se6	2.6285 (11)
Tl1—Se6 ⁱⁱⁱ	3.1803 (7)	Mo5—Se10	2.6808 (5)
Tl1—Se7 ⁱⁱⁱⁱ	3.1152 (11)	Mo5—Se11	2.5421 (7)
Tl1—Se8	4.1426 (13)	Mo6—Mo7	3.8222 (9)
Tl1—Se10 ⁱⁱ	4.1250 (12)	Mo6—Mo8	2.7491 (7)
Tl1—Se11 ^{iv}	3.2515 (11)	Mo6—Mo9	2.7032 (5)
Mo1—Mo1 ^v	3.8353 (6)	Mo6—Se3 ^{vii}	2.6742 (9)
Mo1—Mo2	2.6769 (8)	Mo6—Se6	2.6536 (7)
Mo1—Mo2 ^v	2.7252 (7)	Mo6—Se7	2.5952 (6)
Mo1—Mo3	2.6992 (6)	Mo6—Se9	2.7001 (8)
Mo1—Mo3 ^v	2.7098 (8)	Mo6—Se11	2.5511 (8)
Mo1—Mo5	3.4409 (8)	Mo7—Mo8	2.7127 (10)
Mo1—Se1 ^v	2.5771 (8)	Mo7—Mo9	2.6851 (13)
Mo1—Se2	2.6214 (10)	Mo7—Se5	2.5885 (8)
Mo1—Se3	2.5704 (10)	Mo7—Se5 ^{viii}	2.5885 (8)
Mo1—Se4	2.5575 (7)	Mo7—Se8	2.6093 (9)
Mo1—Se5	2.6610 (6)	Mo7—Se10	2.5939 (10)
Mo2—Mo2 ^v	3.8047 (9)	Mo8—Mo9	2.6863 (9)
Mo2—Mo3	2.6967 (9)	Mo8—Se7	2.5594 (6)
Mo2—Mo3 ^v	2.6906 (8)	Mo8—Se7 ^{viii}	2.5594 (6)
Mo2—Mo6 ⁱⁱⁱ	3.4797 (8)	Mo8—Se8	2.5981 (15)
Mo2—Se1	2.5574 (7)	Mo8—Se9	2.6152 (15)
Mo2—Se2 ^v	2.5654 (9)	Mo9—Se6	2.5775 (8)
Mo2—Se3	2.6055 (6)	Mo9—Se6 ^{viii}	2.5775 (8)
Mo2—Se4	2.5760 (9)	Mo9—Se9	2.6073 (11)
Mo2—Se6 ⁱⁱⁱ	2.6456 (9)	Mo9—Se10	2.6096 (11)
Mo3—Mo3 ^v	3.8142 (8)	Cr1—Se4 ⁱ	2.515 (2)
Mo3—Mo4 ^{vi}	3.5231 (6)	Cr1—Se6 ⁱⁱ	2.750 (2)
Mo3—Se1	2.6149 (8)	Cr1—Se8	2.850 (3)
Mo3—Se2	2.5821 (8)	Cr1—Se9 ⁱⁱ	2.821 (3)
Mo3—Se3 ^v	2.5555 (8)	Cr2—Se4	2.524 (3)
Mo3—Se4	2.5436 (9)	Cr2—Se5	2.798 (2)
Mo3—Se7 ^{vi}	2.6346 (9)	Cr2—Se9 ⁱⁱⁱ	2.788 (6)
Mo4—Mo5	2.6441 (6)	Cr2—Se10	2.738 (6)
Mo4—Mo6	2.6278 (9)	Cr3—Se4	2.501 (8)
Mo4—Mo7	2.7347 (5)	Cr3—Se7 ^{vi}	2.782 (7)
Mo4—Mo8	2.6931 (7)	Cr3—Se8 ^{vi}	2.859 (8)
Mo4—Se1 ⁱ	2.6523 (9)	Cr3—Se10	2.886 (8)
Mo4—Se5	2.6306 (8)	Cr4—Se1	2.3096 (6)
Mo4—Se7	2.6382 (8)	Cr4—Se5 ^{vi}	2.9635 (6)
Mo4—Se8	2.6873 (7)	Cr4—Se11 ^{vi}	2.7815 (8)
Mo4—Se11	2.5507 (8)	Cr1—Cr2 ⁱ	3.231 (5)
Mo5—Mo6	2.6431 (8)	Cr1—Cr3 ⁱ	3.216 (12)
Mo5—Mo7	2.7095 (6)	Cr2—Cr3	3.295 (10)
Mo5—Mo8	3.8244 (6)		

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

Numerous crystals were tested on a Nonius KappaCCD diffractometer. Most of them presented a substantial mosaic spread, leading to unreliable lattice parameters having values close to those of a hexagonal system. For these crystals, the mosaicity as calculated by *DENZO* (Otwinowski & Minor, 1997) was of about 2° , indicating that they are strongly twinned. For the studied crystal, the mosaicity was only $0.496(1)^\circ$, as usually observed for good single crystals. On the other hand, all the Bragg spots found using the φ/χ procedure (Duisenberg *et al.*, 2000) could be indexed, indicating that if the crystal were twinned the twinning was very minor. Consequently, the integration of the Bragg spots from the collected frames was made with the orientation matrix deduced from the φ/χ procedure and, in order to take into account the possible existence of non-overlapping spots at high diffraction angles, large integration boxes were used. The structure was solved using *SIR97* (Altomare *et al.*, 1999) and subsequent difference Fourier syntheses, and was refined in an anisotropic approximation down to $R = 0.077$. Because the lattice parameters are close to those of a hexagonal system, the existence of twin domains was envisaged in the studied crystal. As the space group $P2_1/m$ is a subgroup of index 3 of the space group $P6_3/m$, six twin domains can exist, according to the procedure implemented in *JANA2006* (Petříček *et al.*, 2006), which decomposes a point group into co-sets with respect to a subgroup. Consequently, six twin matrices corresponding to the identity (**T1**) and the clockwise (**T2**) and anticlockwise (**T3**) threefold rotations about b , and the three inverse matrices of these (**T4**, **T5**, and **T6**), were introduced into the refinement. This lowered the R factor to 0.055. At this stage, analysis of the difference Fourier map revealed positive and negative residual peaks of 11.02 and $-9.84 \text{ e } \text{\AA}^{-3}$, respectively, around the Tl1 atom (Fig. 4a). Fourth-order tensors in the Gram–Charlier expansion (Johnson & Levy, 1974) of the thallium displacement factor were used to better describe the electronic density around the cationic site. The residual R value dropped to 0.0489 and the residual difference electron-density extrema in the vicinity of Tl1 dropped to 2.92 and $-2.08 \text{ e } \text{\AA}^{-3}$ (Fig. 4b). Fig. 5 shows the anharmonic probability density function map for Tl1 in the bc plane. The absence of a significant negative region indicates that the refined model can be considered valid (Bachmann & Schulz, 1984). At the end of the refinement, the fractional volumes of the twin domains were

$0.947(2)$, $0.008(1)$, $0.011(1)$, $0.0262(4)$, 0 and $0.0079(4)$ for matrices **T1**–**T6**, respectively. Refinement of the occupancy factors of Tl and Cr led to the final stoichiometry $\text{Cr}_{1.45(2)}\text{Tl}_{1.870(4)}\text{Mo}_{15}\text{Se}_{19}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *JANA2006*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3024). Services for accessing these data are described at the back of the journal.

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