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Quaternary chalcogenides of the IVa metals with layered structures: preparation and crystal structures of $TlCuT^{IV}Q_3$ (T = Zr, Hf; Q = S, Se) and their relation to the Re_3B structure type

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Abstract

The new compounds $TlCuT^{IV}Q_3$ (T = Zr, Hf; Q = S, Se) were prepared by reacting intimate mixtures of Tl_2S or TlSe with stoichiometric amounts of the corresponding Group IV metal, Cu and the corresponding chalcogen at 870°C. The four compounds are isostructural and crystallize in *Cmcm*, $Z = 4$ with $a = 3.726(4)$ Å, $b = 13.987(9)$ Å, $c = 9.783(4)$ Å for $TlCuZrS_3$; $a = 3.847(1)$ Å, $b = 14.381(6)$ Å, $c = 10.150(1)$ Å for $TlCuZrSe_3$; $a = 3.694(1)$ Å, $b = 14.030(3)$ Å, $c = 9.750(3)$ Å for $TlCuHfS_3$; and $a = 3.831(1)$ Å, $b = 14.409(9)$ Å, $c = 10.124(2)$ Å for $TlCuHfSe_3$. Their crystal structures were determined from single crystal diffractometer data (Mo Kα radiation, ambient temperature) and refined to conventional R values of 0.016, 0.040, 0.019 and 0.031 respectively.

An outstanding feature of their crystal structures is the formation of infinite anionic layers, $^2_\infty$-$[CuT^{IV}Q_3]^-$ parallel to (010), which are separated by Tl^+ cations. These layers are built up by edge sharing TQ_6 octahedra and distorted CuQ_4 tetrahedra. Average T–Q distances are $\bar{d}$(Zr–S) = 2.586(1) Å, $\bar{d}$(Zr–Se) = 2.707(1) Å, $\bar{d}$(Hf–S) = 2.569(2) Å and $\bar{d}$(Hf–Se) = 2.694(1) Å. Cu–chalcogen distances are $\bar{d}$(Cu–S) = 2.318(2) Å and $\bar{d}$(Cu–Se) = 2.432(3) Å respectively. The thallium ions are in bicapped trigonal prismatic chalcogen coordinations. The atomic arrangement corresponds to that of $KCuZrS_3$; based on the thallium–chalcogen partial structure it can be regarded as a filled variant of an *anti*-Re_3B structure type.

Keywords: Crystal structure; Chalcogenides; Sulphides; Selenides; Zirconium; Hafnium; Thallium; Copper

1. Introduction

Complex chalcogenides of the heavier IVa metals with electropositive metals have only recently been the subject of investigations.

Thus a number of compounds with layered structures have been reported for the Ba–T^{IV}–S systems (T = Zr, Hf) [1–4]. They form a series of closely related compounds $Ba_{n+1}T_nS_{3n+1}$ which are intermediate between the layered K_2NiF_4 type ($n = 1$) and the perovskite type ($n = \infty$). These compounds are hence characterized by $T^{IV}S_6$ octahedra sharing common vertices.

Several different new complex chalcogenides of Zr and Hf have recently been described by Ibers and coworkers [5–7]. Their common structural feature is the octahedral chalcogen coordination of the IVa metals. However, different from $Ba_{n+1}T_nS_{3n+1}$, the octahedra are here connected through common edges. In Cu_2HfTe_3 [5] edge sharing leads to double octahedral chains, $^1_\infty$-HfTe3, which are connected by tetrahedrally coordinated copper atoms to form a three-dimensional framework. A similar structural motif is present in $NaCuZrSe_3$ [6], where double chains of edge sharing $ZrSe_6$ octahedra are connected by copper atoms to form infinite layers intercalated by the alkali cations. Interestingly the closely related structure of $KCuZrS_3$ [7] reveals a different layer geometry. Its layers are built up by *trans* chains of ZrS_6 octahedra, which in turn are connected through common corners.

We have recently determined the structure of Tl_2ZrSe_3 [8]. This unexpectedly pseudo-one-dimensional compound contains double octahedral chains, very similar to those found in $NaCuZrSe_3$. It was

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hence of interest to look whether this structural moiety would also be retained after (partial) substitution of Tl by Cu. This was the starting point for a structural investigation of the pseudo-binary sections $Tl_{2-x}Cu_{2x}T^{IV}Q_3$ (T = Zr, Hf; Q = S, Se, Te).

2. Experimental

Starting materials for the preparation of the title compounds were the elements of 99.9% purity obtained from Alfa Ventron. As a first step of the synthesis the congruently melting thallium chalcogenides Tl_2S and TlSe were prepared as master alloys. Intimate mixtures of the powdered components (1.5 to 2 g) were pelleted and sealed into silica tubes under a vacuum of 10^{-2} Pa. The samples were heated in steps up to 870°C, at which temperature they were annealed for 10 days. Thermal treatment was terminated by cooling to 400°C at a controlled rate of 2°C h^{-1}, followed by quenching into water. The reaction products thus obtained were of polycrystalline appearance. They showed metallic lustre even after prolonged exposure to air, indicating good stability against humidity. None of the investigated samples appeared to have been melted by the foregoing thermal treatment. Suitable crystals of plate-like shape were selected under the microscope. The rest of the crushed samples was re-annealed at 870°C for one week, yielding virtually single phase products, as was confirmed by the evaluation of the Guinier powder diagrams (Cu $K\alpha_1$ radiation) and their comparison with the theoretical powder diffraction diagrams obtained through the `finax` program [9] at a later stage of this study.

Preliminary crystallographic investigations were performed using Weissenberg techniques. They showed that the four compounds crystallized with orthorhombic symmetry. The comparable lattice dimensions and diffraction patterns indicated the presence of an isostructural series. The systematic extinctions hkl, $h + k \neq 2n$ and $h0l$, $l \neq 2n$ led to $Cmc2_1$ (No. 36), $C2cm$ (No. 40) or $Cmcm$ (No. 63) as possible space groups, out of which the centrosymmetric space group was successfully adopted in the course of the crystal structure refinements.

3. Structure determination

The crystals selected for the structure determination were mounted onto a four-circle diffractometer (Enraf–Nonius CAD4). The data collections were performed at a controlled temperature of 21(1)°C using graphite monochromated Mo $K\alpha$ radiation. Reflection data were collected over one octant of the reflection sphere in the angular range $2° \leqslant 2\theta \leqslant 56°$ for $TlCuZrSe_3$ and $2° \leqslant 2\theta \leqslant 54°$ for the other crystals. Reflection intensities were determined with conventional ω–2θ scans using an angular dependent scan width of $1.2° + 0.35° \tan\theta$ for $TlCuZrSe_3$ and $0.8° + 0.35° \tan\theta$ for the other compounds. The maximum scan time was 150 s. Crystal orientation and electronic stability were periodically checked on the basis of three control reflections, indicating only statistical fluctuations. The final cell dimensions were obtained by least squares refinements of the angular positions of 24 carefully centred reflections in the range $32° \leqslant 2\theta \leqslant 42°$.

The raw intensity data were subjected to the usual background, Lorentz and polarization corrections. The statistics of the normalized structure factor indicated the presence of a centre of inversion, indicating $Cmcm$ as the correct space group. The crystal structure of $TlCuZrSe_3$ was solved by direct methods [10]. The subsequent F-synthesis revealed the complete structure and confirmed the presumed isotypy with $KCuZrS_3$ [7]. Least squares refinements (F-refinement) with isotropic thermal parameters converged rapidly for all compounds. Anisotropic thermal displacements were refined in the final cycles. The subsequent difference syntheses showed no physically significant peaks. Crystallographic data and further details of the structure refinements are given in Table 1. All calculations were performed with programs of the MolEN crystallographic software package [11]. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography* [12,13]. In the final refinements an isotropic extinction correction was included. Absorption effects were accounted for by an empirical correction [14]. The final positional and thermal parameters are given in Table 2. Detailed lists of interatomic distances and bond angles are given in Table 3.

Tables of the anisotropic thermal parameters and lists of observed and calculated structure factors have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, under CSD No. 58999.

4. Discussion

The new compounds $TlCuZrS_3$, $TlCuZrSe_3$, $TlCuHfS_3$ and $TlCuHfSe_3$ crystallize with partially ionic structures. Their atomic arrangements correspond to that of $KCuZrS_3$ [7]. The characteristic feature of the crystal structures is the formation of infinite anionic layers $^{2}_{\infty}$-$[CuT^{IV}Q_3]$, which run parallel to (010) and are separated from each other by Tl^+ ions. (Fig. 1). In the anionic layers the IVa metals are

Table 1
Crystallographic data for $\mathrm{TlCuZrS_3}$, $\mathrm{TlCuZrSe_3}$, $\mathrm{TlCuHfS_3}$ and $\mathrm{TlCuHfSe_3}$

Compound	$\mathrm{TlCuZrS_3}$	$\mathrm{TlCuZrSe_3}$	$\mathrm{TlCuHfS_3}$	$\mathrm{TlCuHfSe_3}$
Space group	*Cmcm* (No. 63)			
Z	4	4	4	4
a (Å)	3.726(4)	3.847(1)	3.694(1)	3.831(1)
b (Å)	13.987(9)	14.381(6)	14.030(3)	14.409(9)
c (Å)	9.783(4)	10.150(1)	9.750(3)	10.124(2)
V (Å^3)	509.8	561.5	505.3	558.8
d_x (g cm^{-3})	5.94	7.05	7.14	8.13
M_r	455.32	596.0	542.591	683.28
μ (*Mo Kα*) (cm^{-1})	390.01	535.98	576.82	704.31
$F(000)$	792	1008	920	1136
Crystal dimensions (μm^3)	100 × 25 × 25	75 × 50 × 25	75 × 25 × 25	100 × 40 × 30
Structure refinement				
Unique reflections	369	409	369	366
Observed reflections $\geq 3\sigma(F_o^2)$	357	377	354	327
Variables	24	24	24	24
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma F_o\|$	0.016	0.040	0.019	0.031
$R_w = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w\|F_o\|^2]^{1/2}$	0.020	0.043	0.020	0.038
$w = [\sigma(F_o^2)^2 + 0.005(F_o^2)^2]^{-1/2}$				
Extinction coefficient	1.814×10^{-6}	1.458×10^{-6}	1.080×10^{-6}	6.293×10^{-7}
Residual electron density (e Å^{-3})	0.74	3.22	1.25	2.68

Table 2
Positional parameters and equivalent isotropic temperature factors for $\mathrm{TlCuZrS_3}$, $\mathrm{TlCuZrSe_3}$, $\mathrm{TlCuHfS_3}$ and $\mathrm{TlCuHfSe_3}$

Atom	x	y	z	B_{eq}
$\mathrm{TlCuZrS_3}$				
Tl	0.500	0.24188(2)	0.250	1.887(7)
Zr	0.500	0.500	0.000	0.65(1)
Cu	0.000	0.45831(7)	0.250	1.04(2)
S(1)	0.000	0.0603(1)	0.250	0.68(3)
S(2)	0.000	0.37620(9)	0.0473(1)	0.67(2)
$\mathrm{TlCuZrSe_3}$				
Tl	0.500	0.24727(8)	0.250	2.08(2)
Zr	0.500	0.500	0.000	1.06(4)
Cu	0.000	0.4607(2)	0.250	1.47(6)
Se(1)	0.000	0.0659(2)	0.250	0.90(4)
Se(2)	0.000	0.3720(1)	0.0479(2)	0.95(3)
$\mathrm{TlCuHfS_3}$				
Tl	0.500	0.24114(4)	0.250	1.93(1)
Hf	0.500	0.500	0.000	0.789(9)
Cu	0.000	0.4561(1)	0.250	1.19(3)
S(1)	0.000	0.0593(2)	0.250	0.83(6)
S(2)	0.000	0.3770(2)	0.0449(2)	0.76(4)
$\mathrm{TlCuHfSe_3}$				
Tl	0.500	0.24690(9)	0.250	1.62(2)
Hf	0.500	0.500	0.000	0.59(2)
Cu	0.000	0.4592(3)	0.250	1.03(6)
Se(1)	0.000	0.0649(2)	0.250	0.55(4)
Se(2)	0.000	0.3727(1)	0.0458(2)	0.46(3)

$B_{eq} = B_{11} + B_{22} + B_{33}/3$.

in fairly regular chalcogen coordinations. Along [100] $\mathrm{T^{IV}Q_6}$ octahedra share opposite edges, yielding *trans* octahedral chains connected with each other through common vertices. As can be seen from a projection along [100] (Fig. 2), the infinite layers thus formed adopt a corrugated conformation in order to provide tetrahedral sites for the copper atoms. Neighbouring layers are displaced relative to each other by $a/2$, resulting in a two-layer period along the stacking direction.

The thallium ions between the layers occupy almost the centres of trigonal prismatic voids of chalcogen atoms (Fig. 3). Their coordination is expanded by two further chalcogens through additional waist contacts along [001], which in the case of the selenides are found at significantly longer distances. The average Tl–Q bond lengths in the corresponding Zr and Hf compounds are in perfect agreement ($\bar{d}$(Tl–S) = 3.277(1) and 3.279(2) Å, $\bar{d}$(Tl–Se) = 3.347(1) and 3.351(2) Å respectively). These values correspond well with the sum of the ionic radii for $\mathrm{Tl^+}$ and $\mathrm{S^{2-}}$ or $\mathrm{Se^{2-}}$ (3.24 and 3.38 Å respectively) [15], indicating predominantly ionic interactions. From the symmetry of the chalcogen coordination of the $\mathrm{Tl^+}$ ions and from the isotypy with $\mathrm{KCuZrS_3}$, a marked sterical activity of the lone pair of electrons on $\mathrm{Tl^+}$ can reasonably be ruled out.

The bond distances in the individual $\mathrm{T^{IV}Q_6}$ octahedra lie close together. They compare well with those found in related compounds. The mean Zr–S distance in $\mathrm{TlCuZrS_3}$ calculates as 2.586(1) Å compared with 2.584(1) Å in $\mathrm{KCuZrS_3}$ [7] or 2.586(1) Å in $\mathrm{NaCuZrS_3}$ [6]. Average Zr–Se bond lengths in $\mathrm{KCuZrSe_3}$ [7] ($\bar{d}$ = 2.709(1) Å) and $\mathrm{NaCuZrSe_3}$ [6] ($\bar{d}$ = 2.692(1) Å) are close to that found in the present thallium compound (2.707(1) Å). The average octahedral Zr–Se bond length is rather insensitive to changes in the environment. Thus the average bond distances in $\mathrm{Cu_{2-x}Zr_{1+y}Se_3}$ [16], where octahedral double chains

Table 3
Interatomic distances (Å) and bond angles (deg) for the TlCuT^{IV}Q$_3$ phases

TlCuZrS$_3$			
Tl	S(1)	3.149(2) 2×	
Tl	S(2)	3.306(1) 4×	
Tl	S(2)	3.345(1) 2×	
Tl	Cu	3.554(1) 2×	
Tl	Tl	3.726(4) 2×	
Zr	S(1)	2.587(1) 2×	
Zr	S(2)	2.585(1) 4×	
Zr	Cu	3.129(0) 4×	
Zr	Zr	3.726(4) 2×	
S(1)	Zr	S(2)	87.2(0) 4×
S(2)	Zr	S(2)	87.8(0) 2×
S(2)	Zr	S(2)	92.2(0) 2×
S(1)	Zr	S(2)	92.8(0) 4×
S(1)	Zr	S(1)	180.0
S(2)	Zr	S(2)	180.0 2×
Cu	S(1)	2.347(1) 2×	
Cu	S(2)	2.291(1) 2×	
Cu	S(2)	3.717(1) 2×	
Cu	Cu	3.726(4) 2×	
S(1)	Cu	S(1)	105.1(1)
S(1)	Cu	S(2)	107.7(0) 4×
S(2)	Cu	S(2)	119.8(1)
S(1)	S(2)	3.567(1) 4×	
S(1)	S(2)	3.746(2) 4×	
S(1)	S(1)	3.726(4) 2×	
S(2)	S(2)	3.585(3)	
S(2)	S(2)	3.726(4) 2×	
TlCuZrSe$_3$			
Tl	Se(1)	3.240(2) 2×	
Tl	Se(2)	3.336(2) 4×	
Tl	Se(2)	3.476(2) 2×	
Tl	Cu	3.623(2) 2×	
Tl	Tl	3.847(1) 2×	
Zr	Se(1)	2.709(1) 2×	
Zr	Se(2)	2.706(1) 4×	
Zr	Cu	3.234(1) 4×	
Zr	Zr	3.847(1) 2×	
Se(1)	Zr	Se(2)	86.0(1) 4×
Se(2)	Zr	Se(2)	89.4(1) 2×
Se(2)	Zr	Se(2)	90.6(1) 2×
Se(1)	Zr	Se(2)	94.0(1) 4×
Se(1)	Zr	Se(1)	180.0
Se(2)	Zr	Se(2)	180.0 2×
Cu	Se(1)	2.447(3) 2×	
Cu	Se(2)	2.416(2) 2×	
Cu	Se(2)	3.846(3) 2×	
Cu	Cu	3.847(1) 2×	
Se(1)	Cu	Se(1)	103.6(2)
Se(1)	Cu	Se(2)	109.1(0) 4×
Se(2)	Cu	Se(2)	116.2(2)
Se(1)	Se(2)	3.693(2) 4×	
Se(1)	Se(2)	3.961(2) 4×	
Se(1)	Se(1)	3.847(1) 2×	
Se(2)	Se(2)	3.807(3)	
Se(2)	Se(2)	3.847(1) 2×	

Table 3 (*continued*)

TlCuHfS$_3$			
Tl	S(1)	3.149(3) 2×	
Tl	S(2)	3.319(2) 2×	
Tl	S(2)	3.324(2) 4×	
Tl	Cu	3.537	
Tl	Tl	3.694(1) 2×	
Hf	S(1)	2.576(1) 2×	
Hf	S(2)	2.565(2) 4×	
Hf	Cu	3.119(0) 4×	
Hf	Hf	3.694(1) 2×	
S(1)	Hf	S(2)	86.8(1) 4×
S(2)	Hf	S(2)	87.9(1) 2×
S(2)	Hf	S(2)	92.1(1) 2×
S(1)	Hf	S(2)	93.2(1) 4×
S(1)	Hf	S(1)	180.0(0)
S(2)	Hf	S(2)	180.0(0) 2×
Cu	S(1)	2.347(2) 2×	
Cu	S(2)	2.287(3) 2×	
Cu	S(2)	3.707(3) 2×	
Cu	Cu	3.694(1) 2×	
S(1)	Cu	S(1)	103.8(1)
S(1)	Cu	S(2)	107.42(4) 4×
S(2)	Cu	S(2)	122.0(1)
S(1)	S(2)	3.532(2) 4×	
S(1)	S(2)	3.735(3) 4×	
S(1)	S(1)	3.694(1)	
S(2)	S(2)	3.560(4)	
S(2)	S(2)	3.694(1) 2×	
TlCuHfSe$_3$			
Tl	Se(1)	3.248(2) 2×	
Tl	Se(2)	3.351(2) 4×	
Tl	Se(2)	3.455(2) 2×	
Tl	Cu	3.609(3) 2×	
Tl	Tl	3.831(1) 2×	
Hf	Se(1)	2.698(1) 2×	
Hf	Se(2)	2.692(1) 4×	
Hf	Cu	3.228(1) 4×	
Hf	Hf	3.831(1) 2×	
Se(1)	Hf	Se(2)	85.7(1) 4×
Se(2)	Hf	Se(2)	89.3(1) 2×
Se(2)	Hf	Se(2)	90.7(1) 2×
Se(1)	Hf	Se(2)	94.3(1) 4×
Se(1)	Hf	Se(1)	180.0(0)
Se(2)	Hf	Se(2)	180.0(0) 2×
Cu	Se(1)	2.447(3) 2×	
Cu	Se(2)	2.414(3) 2×	
Cu	Se(2)	3.851(3) 2×	
Cu	Cu	3.831(1) 2×	
Se(1)	Cu	Se(1)	103.0(2)
Se(1)	Cu	Se(2)	108.7(0) 4×
Se(2)	Cu	Se(2)	117.9(2)
Se(1)	Se(2)	3.667(2) 4×	
Se(1)	Se(2)	3.951(3) 4×	
Se(1)	Se(1)	3.831(1) 2×	
Se(2)	Se(2)	3.783(3)	
Se(2)	Se(2)	3.831(1) 2×	

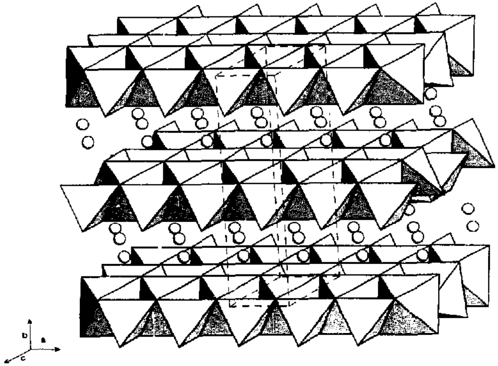

Fig. 1. Clinographic projection of the crystal structure of $TlCuZrS_3$ in polyhedral representation. Edge sharing ZrS_6 octahedra and CuS_4 tetrahedra are arranged in anionic layers parallel to (010), which are separated from each other by Tl^+ ions.

take part in the formation of a ${}^{3}_{\infty}$-framework, and in the partially ionic Tl_2ZrSe_3 [8], which is characterized by isolated octahedral double chains, are almost identical ($\bar{d}$(Zr–Se) = 2.716(2) and 2.708(2) Å respectively). The average bond lengths in the present hafnium compounds ($\bar{d}$(Hf–S) = 2.569(2) Å, $\bar{d}$(Hf–Se) = 2.694(1) Å) are slightly shorter than those of the Zr homologues. The latter is comparable with the average bond distances observed in $Tl_2Cu_2Hf_3Se_8$ (2.669(2) and 2.673(1) Å) [17]. Structural data on homologous hafnium sulphides are not known for comparison. It should, however, be noted that the mean Hf–S bond length in Ba_2HfS_4 [2] is significantly shorter ($\bar{d}$ = 2.455(10) Å).

The coordination of the copper atoms is less regular than that of the IVa metals, the symmetry of the CuQ_4 tetrahedra being C_{2v}. In all compounds the bond lengths Cu–Q(2) are shorter than Cu–Q(1), the corresponding bond angles Q(2)–Cu–Q(2) are, as a consequence, wider. The average bond lengths in the corresponding Zr and Hf compounds are identical within the estimated standard deviations. ($\bar{d}$(Cu–S) = 2.318(2) Å, $\bar{d}$(Cu–Se) = 2.432(3) Å). Comparable Cu–chalcogen distances are found in quaternary thios-

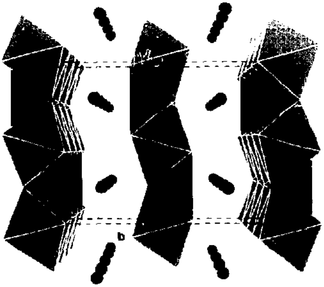

Fig. 2. Perspective projection of the crystal structure of $TlCuZrS_3$ along [100] showing the bicapped trigonal prismatic chalcogen coordination of the thallium atoms (full circles).

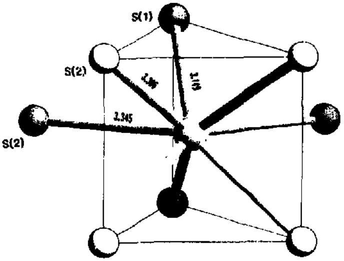

Fig. 3. Detailed view of the trigonal prismatic sulphur coordination of Tl^+ in $TlCuZrS_3$. The prism height corresponds to the a-translation. Distances are in angstroms.

pinels $CuCrZrS_4$ [18] and $CuCrZrSe_4$ [19], where the copper atoms attain a regular tetrahedral coordination.

Despite the fact that the complex layers in compounds with $KCuZrS_3$ type contain structural elements well known from close anion packing, the crystal structure itself cannot be rationalized by this concept. Focusing the view on the Tl–chalcogen partial structure reveals, however, an unexpected structural relationship with an atomic arrangement found in the Re_3B structure type (Re_3B, space group *Cmcm*, $a = 2.890$ Å, $b = 9.313$ Å, $c = 7.258$ Å, $Z = 4$) [20], which is characterized by a trigonal prismatic metal coordination on the boron atoms. As can be seen after normalization with `structure tidy` [21] (Table 4), there are only minute differences in the free positional parameters between the two arrangements. The close geometrical relationship is further demonstrated by a comparison of the axial ratios, which are found to lie within a close range (Table 5). The small variations in a/c ratios should be noted. These are the two lattice directions which are, for evident reasons, least affected by the occupation of the tetrahedral and octahedral interstices provided by an Re_3B type packing of trigonal prisms. Owing to this close relationship, the $KCuZrS_3$ structure type might well be regarded as a filled-up variant of an *anti*-Re_3B structure type.

Table 4

Comparison of the normalised structural parameters of Re_3B and Tl–chalcogen partial structure of $TlCuZrSe_3$

Atom	W.P.	*x*	*y*	*z*
Re1	8(f)	0	0.36550	0.06200
Re2	4(c)	0	0.07380	1/4
B	4(c)	0	0.75600	1/4
Se1	8(f)	0	0.37200	0.04790
Se2	4(c)	0	0.06590	1/4
Tl	4(c)	0	0.74730	1/4

Table 5

The axial ratios of compounds with the $KCuZrS_3$ structure type and Re_3B

Compound	Ref.	*a/b*	*a/c*	*b/c*
Re_3B	[20]	0.3103	0.3982	1.2831
$NACuZrS_3$	[6]	0.2872	0.3792	1.3200
$KCuZrS_3$	[7]	0.2681	0.3824	1.4266
$KCuZrSe_3$	[7]	0.2671	0.3813	1.4279
$KCuZrTe_3$	[7]	0.2672	0.3755	1.4054
$TlCuZrS_3$	this work	0.2663	0.3807	1.4297
$TlCuZrSe_3$	this work	0.2675	0.3790	1.4168
$TlCuHfS_3$	this work	0.2633	0.3789	1.4390
$TlCuHfSe_3$	this work	0.2659	0.3784	1.4233

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