Structural Chemistry of Halide including Thallides
$A_8Tl_{11}X_{1-n}$ ($A = K, Rb, Cs; X = Cl, Br; n = 0.1–0.9$)

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Abstract: $A_8Tl_{11}$ ($A =$ alkali metal) compounds have been known since the investigations of Corbett et al. in 1995 and are still a matter of current discussions as the compound includes one extra electron referred to the charge of the $Tl_{11}^{7-}$ cluster. Attempts to substitute this additional electron by incorporation of a halide atom succeeded in the preparation of single crystals for the lightest triel homologue of the group, $Cs_8Ga_{11}Cl$, and powder diffraction experiments for the heavier homologues also suggested the formation of analogous compounds. However, X-Ray single crystal studies on $A_8Tl_{11}X$ to prove this substitution and to provide a deeper insight into the influence on the thallide substructure have not yet been performed, probably due to severe absorption combined with air and moisture sensitivity for this class of compounds. Here, we present single crystal X-Ray structure analyses of the new compounds $Cs_8Tl_{11}Cl_{0.8}$, $Cs_8Tl_{11}Br_{0.9}$, $Cs_5Rb_3Tl_{11}Cl_{0.5}$, $Cs_5.7K_2.3Tl_{11}Cl_{0.6}$ and $K_4Rb_4Tl_{11}Cl_{0.1}$. It is shown that a (partial) incorporation of halide can also be indirectly determined by examination of the Tl-Tl distances, thereby the newly introduced cdd/cd$_{av}$ ratio allows to evaluate the degree of distortion of $Tl_{11}^{7-}$ clusters.

Keywords: thallide; intermetallics; single crystal; X-ray structure analysis

1. Introduction

Naked cluster anions of the main group elements are well-known for group 14 and 15 elements in solid-state [1–4]. Most of these compounds can be described in terms of the Zintl-Klemm concept [5–7] by formally transferring the valence electrons of the electropositive element to the electronegative under formation of salt-like structures, so called polyanionic salts. Homotomic group 14 or 15 element polyanions are known since Zintl himself in 1930 stated the existence of $Pb_9^{4-}$ during potentiometric titrations in liquid ammonia solutions [5]. In contrast, the existence of naked group 13 element clusters is not self-evident due to lower values for the electron affinity of group 13 elements which results in a predominantly metallic character of the analogous compounds [3,8]. The first naked thallium cluster was described in 1967 by Hansen and Smith in the binary solid-state compound $Na_2Tl$ [9], which contains $Tl_4$ tetrahedra with a calculated formal charge of $-8$ by assuming complete electron transfer. These tetrahedral assemblies are related to the structures of $ATt$ ($A$: alkali metal, Tt: group 14 element) [10–12] and white phosphorus due to their formal iso-(valence)-electronic character. The largest (empty) thallide cluster is represented by the $Tl_{11}^{7-}$ cluster which is present in binary materials $A_8Tl_{11}$ [13,14] and $A_{15}Tl_{27}$ [15] ($A = K, Rb, Cs$). The $A_8Tl_{11}$ ($Tr =$ group 13 element) structure type was first described in 1991 for the lighter homologue indium in $K_8In_{11}$ [16], of which the crystal structure proved the presence of a naked, pentacapped trigonal prismatic shaped $In_{11}$ cluster, which was
assigned a charge of $-7$. Additionally, one extra-electron per formula unit is present, being responsible for the metallic character. The additional electron, referred to the charge of $-7$ of the cluster anion, is not necessary for the stability of the clusters [17] and can be replaced by halide atoms, which are located on a $-3$ void (Wyckoff position 6b) at the origin of the unit cell resulting in a diamagnetic character of the compounds. Halide incorporation was proven for the lighter homologue of the group, Cs$_8$Ga$_{11}$Cl by X-ray single crystal structure analysis [18]. Powder diffraction experiments suggested the formation of the heavier homologues Rb$_8$Ga$_{11}$Cl, Cs$_8$Ga$_{11}$X (X = Br, I), Rb$_8$In$_{11}$Cl, Cs$_8$In$_{11}$Cl, Cs$_8$Tl$_{11}$X (X = Cl, Br, I). Recently, continuative studies on halides A$_8$Tr$_{11}$ (Tr = Ga, In) have been reported [19]. However, the formation of Rb$_8$Tl$_{11}$Cl was termed as doubtful due to the lack of a significant change in the lattice constants compared to the binary phase Rb$_8$Tl$_{11}$, which also is a common problem for the remaining halide including thallides of this structure family. Therefore, well-resolved single crystal X-ray diffraction studies should provide a deeper insight into the involvement and the role of halide in A$_8$Tl$_{11}$X compounds. Thereby, we concentrated on the heavier alkali metals K, Rb and Cs as for sodium no experimental evidence of Tl$_{11}$X compounds is reported.

The questions we wanted to answer were: (1) How does the geometry of the thallide cluster change on halide incorporation; (2) Is there a Rb$_8$Tl$_{11}$Cl? (3) How do mixed cation sites affect the amount of halide incorporation?

In Section 3 (Results), we report on the first single crystal X-Ray structure determination of halide including thallides, Cs$_8$Tl$_{11}$Cl$_{0.8}$, Cs$_8$Tl$_{11}$Br$_{0.9}$, Cs$_8$Rb$_3$Tl$_{11}$Cl$_{0.5}$, Cs$_8$K$_2$Tl$_{11}$Cl$_{0.6}$ and K$_{3.98}$Rb$_{4.02}$Tl$_{11}$Cl$_{0.1}$. Subsequently, (Section 4, Discussions), the crystal structures are investigated according to the questions listed above.

2. Materials and Methods

All compounds have been synthesized via a stoichiometric approach using high temperature solid state techniques. Cesium and rubidium were produced by the reduction of the corresponding alkali metal halide with elemental calcium [20] and distilled twice, potassium was segregated for purification. Thallium lumps have been stored under inert atmosphere and were used without further purification. The starting materials were enclosed in tantalum crucibles (for stoichiometric approaches see Appendix A) which were subsequently placed in quartz glass ampoules and sealed under argon atmosphere. The same temperature program was used for all compounds: Heating to 700 °C with a heating rate of 50 °C/h, holding for 24 h, cooling to room temperature with a cooling rate of 3 °C/h to allow for crystallization.

All compounds are very sensitive towards moisture and oxygen and degeneration of the crystals was observed (gassing) in dried mineral oil within few hours. Suitable single crystals for X-ray structure analysis were isolated in dried mineral oil and mounted on a Rigaku SuperNova (Rigaku Polska Sp. Z o. o. Ul, Wroclaw, Poland) (Mo-source, Eos detector) using MiTeGen loops. Thereby, the transfer needed to be very quick as the crystals started to decompose as soon as the mineral oil film became too thin. Once being placed on the diffractometer in the nitrogen stream at 123 K the crystals remained stable and data collection was possible.

Powder diffraction samples were measured in sealed capillaries (0.3–0.5 mm) on a Powder on a STOE Stadi P diffractometer (STOE, Darmstadt, Germany) (monochromatic Mo-K$_{\alpha1}$ radiation $\lambda = 0.70926$ Å) equipped with a Dectris Mythen 1 K detector.

3. Results

All compounds crystallize in the K$_8$In$_{11}$ structure type (rhombohedral, spacegroup $R\overline{3}c$) and especially for the mixed alkali metal compounds many of the crystals happened to form typical “multicrystals”. Due to the presence of reverse/obverse twinning a R(obv) filter was applied during data reduction [21]. The materials naturally possess very high absorption coefficients ($\mu > 60$ mm$^{-1}$), therefore small single crystals have been chosen for the X-ray analyses. However, the data sets
still suffer from severe absorption effects which could be redused by carefully applying numerical absorption correction [21]. Thereby, the adjustment of the correct shape played a dominant role.

Table 1 lists the data for the structure determination. For the chloride including compounds two additional, unresolved but several times reproduced residual electron density peaks (∼1.5 Å beside the chlorine atom, ∼2.2 Å beside cesium; along the c-axis) are present, which we attribute to unresolved absorption effects as this direction is along the thinnest direction of the plate-like crystals. For the bromine including compounds this effect is not as dominant as for the chlorine including ones but still is observed.

Table 1. Crystal data and structure refinement details.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CSD number *</th>
<th>Mr [g mol⁻¹]</th>
<th>Crystal system</th>
<th>Space group</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
<th>V [Å³]</th>
<th>Z</th>
<th>F(000)</th>
<th>μ [mm⁻¹]</th>
<th>28-range for data collection [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs₈TlCl₈ &amp; Cs₈TlBr₈</td>
<td>434541</td>
<td>3339.71</td>
<td>Trigonal</td>
<td>R-3c</td>
<td>10.4691 (4)</td>
<td>10.5608 (3)</td>
<td>53.680 (19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>5058.8 (5)</td>
<td>6</td>
<td>8068.0</td>
<td>6.578</td>
<td>7.59 to 58.982</td>
</tr>
<tr>
<td>Cs₈Tl₃Br₉ &amp; Cs₈Tl₃Cl₉</td>
<td>434540</td>
<td>3385.20</td>
<td>Trigonal</td>
<td>R-3c</td>
<td>10.4691 (4)</td>
<td>10.5608 (3)</td>
<td>53.680 (19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>5157.9 (4)</td>
<td>6</td>
<td>8180.0</td>
<td>6.539</td>
<td>7.558 to 69.266</td>
</tr>
<tr>
<td>Cs₈TlCl₉ &amp; Cs₈TlBr₉</td>
<td>434539</td>
<td>3192.52</td>
<td>Trigonal</td>
<td>R-3c</td>
<td>10.3791 (5)</td>
<td>10.3791 (5)</td>
<td>51.909 (5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>4892.0 (5)</td>
<td>6</td>
<td>3192.5</td>
<td>6.492</td>
<td>7.694 to 54.202</td>
</tr>
<tr>
<td>Cs₈Tl₃Br₁₁ &amp; Cs₈Tl₃Cl₁₁</td>
<td>434538</td>
<td>3114.02</td>
<td>Trigonal</td>
<td>R-3c</td>
<td>10.3291 (9)</td>
<td>10.3291 (9)</td>
<td>51.909 (5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>4796.3 (9)</td>
<td>6</td>
<td>7726.0</td>
<td>6.339</td>
<td>7.758 to 54.198</td>
</tr>
<tr>
<td>Cs₈TlCl₁₁ &amp; Cs₈TlBr₁₁</td>
<td>434537</td>
<td>314.02</td>
<td>Trigonal</td>
<td>R-3c</td>
<td>10.0948 (4)</td>
<td>10.0948 (4)</td>
<td>51.909 (5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>4503.3 (4)</td>
<td>6</td>
<td>7944.0</td>
<td>6.052</td>
<td>7.91 to 69.18</td>
</tr>
</tbody>
</table>

* Further details of the crystal structure investigation(s) may be obtained from The Cambridge Crystallographic data centre CCDC on quoting the deposition number CSD-xxxxx or the the deposition number CCDC-xxxxxx at https://www.ccdc.cam.ac.uk/structures/ ?

With only cesium being present in Cs₈Tl₁₁Cl₈ & Cs₈Tl₁₁Br₀.₉ we obtained phase pure materials according to the powder diffraction pattern of the bulk material (Figure 1; refined cell constants at room temperature: Cs₈Tl₁₁Cl₈: a = 10.566 (5) Å, c = 53.67 (3) Å, R–3c; Cs₈Tl₁₁Br₀.₉: a = 10.613 (3) Å, c = 53.680 (19) Å).

The well-crystallized Cs₈Tl₁₁X crystals and the resulting good quality single crystal diffraction data allowed the splitting of one alkali metal position according to the site occupancy factor (s.o.f.) of the halide atom (see Section 4.3).

For the mixed alkali metal compounds, we always additionally observed less reduced A₁₅Tl₂₇ phases as a side product. This observation became reasonable when we determined the Nₐ value (number of electrons per thallium atom) which sums up to a value of 8/11 = 0.72 for A₈Tl₁₁, 15/27 = 0.55 for A₁₅Tl₂₇ and 7/11 = 0.63 for A₈Tl₁₁X. The formation of less reduced A₁₅Tl₂₇ were completely comprehensible if the higher reduced A₈Tl₁₁X (x < 1) phases would have formed when the halide content was significantly less than 1, because the overall degree of reduction was given by the stoichiometric approach for A₈Tl₁₁X. If less halide was incorporated, this is according to a higher degree of reduction and consequently, a less reduced phase was formed in addition. The remaining halide re-crystallized as (mixed) AX, of which we also could observe single crystals. The crystals for the mixed alkali metal compounds A₈Tl₁₁X were happened to form multicrystals together with A₁₅Tl₂₇.
and for the reported single crystals (except \(K_4\)\(Rb_4\)\(Tl_{11}\)\(Cl_{0.1}\)) the data quality was worse compared to Cs\(8\)\(Tl_{11}\)\(X\) phases. Therefore, the splitting of the alkali metal position could only be observed for \(K_4\)\(Rb_4\)\(Tl_{11}\)\(Cl_{0.1}\), for the remaining mixed alkali compounds splitting positions could not be reasonably introduced. In these cases, we only refined the s.o.f. of the halide (see Section 4.3).

![Figure 1](image1.png)

**Figure 1.** Measured (a) and calculated (c) powder diffraction patterns of Cs\(8\)\(Tl_{11}\)\(Cl_{0.8}\); Measured (b) and calculated (d) powder diffraction patterns of Cs\(8\)\(Tl_{11}\)\(Br_{0.9}\) (diffractograms generated by the program STOE WinXPOW [22]).

### 4. Discussions

#### 4.1. How Does the Geometry of the Thallide Cluster Change on Halide Incorporation?

All \(A_8\)\(Tl_{11}\) and \(A_8\)\(Tl_{11}X_x\) compounds include \(Tl_{11}^{7-}\) clusters, which are best described as a very compressed, fivefold-capped trigonal prism (Figure 2). Three symmetry independent thallium atoms are located on three different Wyckoff positions of space group \(R-3c\): \(Tl_1\)(12\(c\); 3-fold rotational axis), \(Tl_2\)(36\(f\); general position) and \(Tl_3\)(18\(e\); 2-fold rotational axis) build a cluster consisting of 11 Tl atoms with point group \(D_3\). The deviations from point group \(D_3\) are very small and are represented by a distortion of the height of the trigonal prism built by \(Tl_3\)-atoms. This distortion is also reflected in the distances of \(Tl_2\)–\(Tl_3\) (\(d(Tl_2\)–\(Tl_3) = cd\)) as there are two crystallographic independent distances present (\(d(Tl_2\)–\(Tl_3) = d(Tl_2\)–\(Tl_3\)\#5); \(d(Tl_3\#3\)–\(Tl_2) = d(Tl_3\#2\)–\(Tl_2)\)). The degree of distortion decreases with increasing similarity of the capping distances (cd).
we introduced a cdd/cd ratio (Equation (1)) which allowed for a quick estimation of the degree of distortion. The dependence of the prism (Tl3–Tl3) as well as the distance of the capping atom Tl2 to the mean plane built by Tl3 atoms on the amount of halide incorporation is clearly evident. In contrast, the height of the trigonal prism does not significantly change. Based on these observations we introduced a cdd/cdav ratio (cdd: capping distance difference; cdav: average capping distance; (Equation (1)) which allowed for a quick estimation of the degree of distortion. The dependence of the cdd/cdav ratio on the amount of halide is conspicuous and therefore allows for the evaluation of the involvement of halide atoms by solely analyzing the distances between heavy atom positions.

In Tables 2 and 3 the distances as well as the distortion angles are listed and the dependence on the amount of halide incorporation is clearly evident. In contrast, the height of the trigonal prism (Tl3–Tl3) as well as the distance of the capping atom Tl2 to the mean plane built by Tl3 atoms [d(Tl2-plane) = 0.5 Å in all compounds] do not significantly change. Based on these observations we introduced a cdd/cdav ratio (cdd: capping distance difference; cdav: average capping distance; (Equation (1)) which allowed for a quick estimation of the degree of distortion. The dependence of the cdd/cdav ratio on the amount of halide is conspicuous and therefore allows for the evaluation of the involvement of halide atoms by solely analyzing the distances between heavy atom positions.

Table 2. Selected distances in [Å] (numbering scheme according to [1,15]), tilt angle and cdd/cdav value for K8Tl11 and Rb8Tl11.

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>K8Tl11</th>
<th>Rb8Tl11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl2</td>
<td>Tl3</td>
<td>3.0476 (4)</td>
<td>3.060</td>
</tr>
<tr>
<td>Tl2</td>
<td>Tl3</td>
<td>3.1396 (4)</td>
<td>3.157</td>
</tr>
<tr>
<td>Tl1</td>
<td>Tl3</td>
<td>3.1304 (4)</td>
<td>3.147</td>
</tr>
<tr>
<td>Tl3</td>
<td>Tl3</td>
<td>3.2054 (7)</td>
<td>3.219</td>
</tr>
</tbody>
</table>

Tilt [°] 4.69 (2) 4.90

cdd/cdav [%] 2.97 3.12

Table 3. Selected distances in [Å] (numbering scheme according to [1,15]), tilt angle and cdd/cdav value for Cs8Tl11Cl0.8, Cs8Tl11Br0.9, Cs5Rb3Tl11Cl0.5 and Cs5.7K2.3Tl11Cl0.6 and K4Rb4Tl11Cl0.1.

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>Cs8Tl11Cl0.8</th>
<th>Cs8Tl11Br0.9</th>
<th>Cs5Rb3Tl11Cl0.5</th>
<th>Cs5.7K2.3Tl11Cl0.6</th>
<th>K4Rb4Tl11Cl0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl2</td>
<td>Tl3</td>
<td>3.0656 (4)</td>
<td>3.0743 (2)</td>
<td>3.0605 (6)</td>
<td>3.0554 (7)</td>
<td>3.0564 (2)</td>
</tr>
<tr>
<td>Tl2</td>
<td>Tl3</td>
<td>3.0632 (4)</td>
<td>3.0766 (2)</td>
<td>3.0896 (6)</td>
<td>3.0656 (4)</td>
<td>3.1298 (3)</td>
</tr>
<tr>
<td>Tl1</td>
<td>Tl3</td>
<td>3.0894 (4)</td>
<td>3.1006 (2)</td>
<td>3.1049 (7)</td>
<td>3.0884 (8)</td>
<td>3.1274 (3)</td>
</tr>
<tr>
<td>Tl3</td>
<td>Tl3</td>
<td>3.2019 (11)</td>
<td>3.2102 (4)</td>
<td>3.2025 (11)</td>
<td>3.1873 (11)</td>
<td>3.2104 (4)</td>
</tr>
</tbody>
</table>

Tilt [°] 0.12 (2) 0.069 (7) 0.94 (2) 0.34 (5) 2.352 (7)

cdd/cdav [%] 0.08 0.07 0.95 0.32 2.38

\[
\frac{\text{cdd}}{\text{cdav}} = \frac{|\text{cd}_2 - \text{cd}_1|}{(\frac{\text{cd}_2 + \text{cd}_1}{2})}; \quad \text{cd}_1 \leq \text{cd}_2 (1)
\]
4.2. Is There a Rb₈Tl₁₁Cl?

Despite numerous efforts we did not succeed in producing crystals of Rb₈Tl₁₁Cl of sufficient quality for a reliable determination of halide incorporation directly from the electron density maps. The incorporation of halide cannot be completely ruled out at this point as there is some residual electron density at Wyckoff position 6b according to the position of the halide atom in the previously discussed compounds. The s.o.f. for a chlorine atom at this position refined to a value of 0.08. However, the cdd/cdₐv ratio of 2.4% compared to 3.0% (K₈Tl₁₁) and 3.1% (Rb₈Tl₁₁) and a tilt angle of 2.4° (K₈Tl₁₁: 4.7°, Rb₈Tl₁₁: 4.9°) are very similar to the values found in K₄Rb₄Tl₁₁Cl₀.₁ and suggest a minimal involvement of chloride. Therefore, we assume that Rb₈Tl₁₁Cl does exist, but the amount of incorporated chlorine is less than 10%, which also is in line with the stated observations of Corbett et al. from powder diffraction experiments.

4.3. How Do Mixed Cation Sites Affect the Amount of Halide Incorporation?

It needs to be emphasized that for the preparation of all compounds the same stoichiometric approach was employed and the dependence of the amount of halide incorporation on the cesium content is conspicuous. Therefore, the cation positions needed to be examined more in detail. There are two different cation positions in the asymmetric unit corresponding to Wyckoff position 36f for A1 and Wyckoff position 12c for A2. For Cs₈Tl₁₁X the A2 position showed the previously mentioned splitting. By taking this splitting as well as free s.o.f. values for the halide (later fixed at the s.o.f. value for Cs2A) into account, a significantly improved model could be refined (Figure 3).

![Figure 3](image_url). Introduction of split positions and free s.o.f. values for the halide in Cs₈Tl₁₁Br₀.₉ results in an improved model (residual electron density maps, generated by Olex2 [23]).

For Cs₅Rb₃Tl₁₁Cl₀.₅ and Cs₅.₇K₂.₃Tl₁₁Cl₀.₆ the position of A1 is mixed occupied by both alkali metals and the s.o.f. values for cesium on the mixed position are very similar to the s.o.f. values of the halide position. The position of A2 is only occupied by the heavier alkali metal cesium, which is in accordance with the observations of Corbett et al. for the binary A₈Tl₁₁ phases [14]. In summary, this would mean a favored halide incorporation when cesium is present on both crystallographically independent alkali metal positions. To prove this assumption, we investigated the system K-Rb-Tl in a stoichiometric approach to produce K₄Rb₄Tl₁₁Cl which resulted in crystals of K₄Rb₄Tl₁₁Cl₀.₁ (besides the side products (K,Rb)₁₅Tl₂₇ and (K,Rb)Cl). Careful investigation of the data of K₄Rb₄Tl₁₁Cl₀.₁ showed the splitting of the A2 position, whereby convergence of the refinement was achieved when A1 and one splitting position are mixed occupied by Rb and K. The second splitting position Rb2A is exclusively occupied by Rb. The overall s.o.f. for A2 was fixed at unity using a SUMP restraint. At the max. peak of the residual electron density a chlorine atom was placed of which the s.o.f. refined at 0.103 (13) and was fixed according to the s.o.f. of Rb2A (Figure 4).
Distances within the distorted cubic arrangements as well as s.o.f. values for the halide/split position in Cs8Tl11X (X = Cl or Br) and K4Rb4Tl11Cl0.1 are listed in Tables 4 and 5 lists values for the halide/Cs2A (split position) in Cs8Tl11Cl0.8 Position 1–Position 2 K4Rb4Tl11Cl0.1

Table 4. Distances in [Å] within the distorted cubic arrangement around the halide/void and s.o.f. values for the halide/Cs2A (split position) in Cs8Tl11X (X = Cl or Br) and K4Rb4Tl11Cl0.1.

<table>
<thead>
<tr>
<th>Position 1–Position 2</th>
<th>Cs8Tl11Br0.9</th>
<th>Cs8Tl11Cl0.8</th>
<th>Position 1–Position 2</th>
<th>K4Rb4Tl11Cl0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs2A-X1</td>
<td>3.990 (2)</td>
<td>3.991 (9)</td>
<td>Rb2A-X1</td>
<td>3.80 (2)</td>
</tr>
<tr>
<td>Cs2B-void</td>
<td>4.388</td>
<td>4.354</td>
<td>K2B/Rb2B-void</td>
<td>4.096 (3)</td>
</tr>
<tr>
<td>Cs1-X1/void</td>
<td>3.6705 (4)</td>
<td>3.5876 (7)</td>
<td>K1/Rb1-X1/void</td>
<td>3.5994 (9)</td>
</tr>
<tr>
<td>s.o.f. (X1/Cs2A)</td>
<td>0.924 (6)</td>
<td>0.76 (2)</td>
<td>s.o.f. (X1/Rb2A)</td>
<td>0.103 (13)</td>
</tr>
</tbody>
</table>

Figure 4. Introduction of split positions and free s.o.f. values for the halide in K4Rb4Tl11Cl0.1 results in an improved model (residual electron density maps, generated by Olex2 [23]).

The resulting coordination sphere of the halide is best described as distorted cubic, where the longer distances are along the room diagonal of the cubic arrangement from the halide to the position of A2. This distance shortens significantly for X-A2 by introducing split positions (same s.o.f. as halide), resulting in a less distorted cubic arrangement (Figure 5). This cubic arrangement greatly resembles the coordination of the halide in the CsCl structure type (d(Cs-Cl) = 3.573 Å; d(Cs-Br) = 3.718 Å). The distances within the the distorted cubic arrangements as well as the s.o.f. values for the halide/Cs2A (split position) in Cs8Tl11Cl0.8 Position 1–Position 2 K4Rb4Tl11Cl0.1

Table 5. Distances in [Å] within the distorted cubic arrangement around the halide/void and s.o.f. values for the halide/Cs2A (split position) in Cs8Tl11X (X = Cl or Br) and K4Rb4Tl11Cl0.1.

<table>
<thead>
<tr>
<th>Position 1–Position 2</th>
<th>Cs8Tl11Br0.9</th>
<th>Cs8Tl11Cl0.8</th>
<th>Position 1–Position 2</th>
<th>K4Rb4Tl11Cl0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs2A-X1</td>
<td>3.990 (2)</td>
<td>3.991 (9)</td>
<td>Rb2A-X1</td>
<td>3.80 (2)</td>
</tr>
<tr>
<td>Cs2B-void</td>
<td>4.388</td>
<td>4.354</td>
<td>K2B/Rb2B-void</td>
<td>4.096 (3)</td>
</tr>
<tr>
<td>Cs1-X1/void</td>
<td>3.6705 (4)</td>
<td>3.5876 (7)</td>
<td>K1/Rb1-X1/void</td>
<td>3.5994 (9)</td>
</tr>
<tr>
<td>s.o.f. (X1/Cs2A)</td>
<td>0.924 (6)</td>
<td>0.76 (2)</td>
<td>s.o.f. (X1/Rb2A)</td>
<td>0.103 (13)</td>
</tr>
</tbody>
</table>

Figure 5. Distorted cubic arrangement around the halide (a); respectively void (b). Cs1: x, y, z; Cs1#1: 1 − y, x − y, z; Cs1#2: 1 − x + y, 1 − x, z; Cs1#3: 4/3 − x, 2/3 − y, 2/3 − z; Cs1#4: 1/3 + y, 2/3 − x + y, 2/3 − z; Cs1#5: 1/3 + x − y, −1/3 + x, 2/3 − z; Cs2A/B: x, y, z; Cs2A/B#1: 4/3 − x, 2/3 − y, 2/3 − z.

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Conflicts of interest: The authors declare no conflict of interest.

Table 5. Distances in [Å] within the cubic arrangement around the halide/void in Cs₅Rb₃Tl₁₁Cl₀.5 and Cs₅.7K₂₃Tl₁₁Cl₀.6. The s.o.f. values for Cs at the mixed occupied A₁ site resemble the s.o.f. values for the halide (numbering scheme according to Figure 5).

<table>
<thead>
<tr>
<th>Position 1–Position 2</th>
<th>Cs₅Rb₃Tl₁₁Cl₀.5</th>
<th>Cs₅.7K₂₃Tl₁₁Cl₀.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₂-X₁/void</td>
<td>4.099 (2)</td>
<td>4.002</td>
</tr>
<tr>
<td>A₁-X₁/void</td>
<td>3.6160 (13)</td>
<td>3.5492 (2)</td>
</tr>
<tr>
<td>s.o.f. (A₁ = Cs)</td>
<td>0.521 (12)</td>
<td>0.612 (9)</td>
</tr>
<tr>
<td>s.o.f. (X₁)</td>
<td>0.50 (4)</td>
<td>0.60 (4)</td>
</tr>
</tbody>
</table>

The same stoichiometric approach to produce the hitherto presented compounds also was employed by using solely potassium. Here, we only observed well crystallized halide-free K₈Tl₁₁ and K₁₅T₁₂₇ phases. The previously stated stability of the halide including A₈T₁₁X phases might not exclusively be caused by the effect of charge balance due to halide incorporation but by the stabilization of a preferably heavier halide atom in a distorted cubic arrangement including cesium preferentially (Figure 6). If less (or no) cesium is involved, then less (or even no) halide will be incorporated. If rubidium is involved as the heaviest alkali metal, then the amount of incorporated halide seems to be limited to approximately 10%. In return, the Tl₁₁ clusters themselves seem to tolerate any charge between 7⁻ and 8⁻.

Figure 6. The unit cell of Cs₈Tl₁₁Br₀.₉ shows the two characteristic components: Tl₁₁ clusters and the distorted cubic arrangement around the halide atom.


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Conflicts of Interest: The authors declare no conflict of interest.
Appendix

Stoichiometric approaches

\( \text{Cs}_8\text{TI}_{11}\text{Cl}_{0.8}: \) 0.445 g Cs (3.3 mmol), 1.076 g TI (5.3 mmol TI) and 0.081 g CsCl (0.51 mmol)

\( \text{Cs}_8\text{TI}_{11}\text{Br}_{0.9}: \) 0.413 g Cs (3.1 mmol), 0.998 g TI (4.9 mmol TI) and 0.091 g CsBr (0.44 mmol)

\( \text{Cs}_5\text{RbTI}_{11}\text{Cl}_{0.5}: \) 0.246 g Cs (1.9 mmol), 0.128 g Rb (1.5 mmol), 1.124 g TI (5.5 mmol) and 0.061 g RbCl (0.5 mmol)

\( \text{Cs}_5\cdot3\text{Kr}_2\cdot3\text{TI}_{11}\text{Cl}_{0.6}: \) 0.264 g Cs (2 mmol), 0.058 g K (1.5 mmol), 1.117 g TI (5.5 mmol) and 0.037 g KCl (0.5 mmol)

\( \text{K}_5\cdot9\text{KBr}_{4.02}\text{TI}_{11}\text{Cl}_{0.1}: \) 0.154 g Rb (1.8 mmol), 0.052 g K (1.3 mmol), 1.0134 g TI (5 mmol) and 0.034 g KCl (0.45 mmol)

References


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