

[Tl₇]⁷⁻ Clusters in Mixed Alkali Metal Thallides Cs_{7.29}K_{5.71}Tl₁₃ and Cs_{3.45}K_{3.55}Tl₇

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ABSTRACT: Investigations in the ternary system Cs–K–Tl resulted in the unexpected formation of new ternary thallides Cs_{7.29}K_{5.71}Tl₁₃ and Cs_{3.45}K_{3.55}Tl₇. Single crystal X-ray structure analyses of both compounds reveal the presence of isolated Tl cluster units. Cs_{7.29}K_{5.71}Tl₁₃ crystallizes in the monoclinic space group *C2/c* (*a* = 30.7792(9) Å, *b* = 11.000(2) Å, *c* = 14.0291(4) Å, β = 112.676(4)°, *Z* = 4) and contains [Tl₆]⁶⁻ and [Tl₇]⁷⁻ clusters as thallium subunits. Cs_{3.45}K_{3.55}Tl₇ crystallizes in the tetragonal space group *I4₁/a* (*a* = 13.6177(2) Å, *c* = 25.5573(8) Å, *Z* = 8) and contains [Tl₇]⁷⁻ clusters exclusively. The formation of Cs_{7.29}K_{5.71}Tl₁₃ is obtained after slow cooling in addition to that of Cs_{3.45}K_{3.55}Tl₇ and can be suppressed by quenching the stoichiometric mixture. First dissolution experiments in liquid ammonia suggest thallium and amide as final oxidation products. Full relativistic band structure calculations of Cs₄K₃Tl₇ and Cs₈K₅Tl₁₃ showed a (pseudo) band gap around *E_F* for both compounds.

Alkali metal thallides can be described as materials at the frontier between ionic and intermetallic nature.^{1,2} While a low amount of alkali metal of less than 50% results in the formation of rather metallic compounds,^{3–7} increasing proportions lead to the formation of salt-like materials. The observed thallium subunits can then be well described by using the Zintl–Klemm formalism.^{8–11} The first structurally characterized Zintl phase goes back to E. Zintl himself, who reported on the synthesis and characterization of textbook-known NaTl in the early 1930s.¹² Interestingly, binaries in a 1:1 ratio (alkali metal:thallium) of the larger alkali metals were reported only in the late 1990s and 2000s by the group of J. D. Corbett. The dependence of the nature of the alkali metal involved on the formed thallium substructure is well evidenced in KTl¹³ and CsTl,¹⁴ which include isolated [Tl₆]⁶⁻ clusters instead of the three-dimensional Tl sublattice present in NaTl.^{12,15–17} A closer look at the crystal structures of KTl and CsTl shows that the solid-state structures differ significantly, as they crystallize in different space groups (KTl, *Cmcc*; CsTl, *Fddd*) and structure types. The major difference in the crystal structures of these binaries can be ascribed to one symmetry-independent alkali metal position.¹⁸ This suggests that potassium and cesium cannot be interchanged and emphasizes the importance of the different alkali metals in structure formation. This in general was proven for thallides in combinations of sodium and larger alkali metals in the past by Corbett et al., which showed a broad variety of new and surprising materials by applying mixed alkali metal approaches.¹⁸ In contrast, very little is known about the influence of mixing heavy alkali metals K and Cs. In the case of a single type of alkali metal, there are so far only five phases known that include discrete clusters. In Na₂Tl¹⁹ [Tl₄]⁴⁻ tetrahedra are present; A₈Tl₁₁ (*A* = K, Rb, Cs)^{20,21} includes the pentacapped trigonal prism [Tl₁₁]⁷⁻, which is also known as a double tetrahedral star.²² In metallic K₁₀Tl₇ the pentagonal bipyramid [Tl₇]⁷⁻ is present,²³ while in the above-mentioned KTl and

CsTl compressed [Tl₆]⁶⁻ octahedra are observed, which have been classified as “hypoelectronic” clusters due to the lack in electrons referred to Wade electron counting rules.^{13,14} In general, [Tl₆]⁶⁻ octahedra are obtained in different binary and ternary materials, e.g., A₁₀Tl₆O₂ (*A* = K, Rb),²⁴ Cs₁₀Tl₆TtO₄ (*Tt* = Si, Ge), or Cs₁₀Tl₆SnO₃.²⁵ Another very rare cluster unit is represented by the pentagonal bipyramidal [Tl₇]⁷⁻. While heteroatomic pentagonal bipyramidal entities are known to be accessible using solution chemistry,^{26,27} the homoatomic Tl₇ cluster represents a very rare structural moiety in the solid state. This subunit can be geometrically derived from an endohedral icosahedron by removing five vertices and is so far experimentally known only from the three compounds Na₉K₁₆Tl_{~25},²⁸ Na₁₂K₃₈Tl₄₈Au₂,²⁹ and K₁₀Tl₇.²³ Na₉K₁₆Tl_{~25} and Na₁₂K₃₈Tl₄₈Au₂ both show crystallographic peculiarities. In Na₉K₁₆Tl_{~25} the Tl₇ cluster is also part of the Tl₉ cluster, in which not all Tl positions are fully occupied.²⁸ Na₁₂K₃₈Tl₄₈Au₂ contains Tl₇ and Tl₉ clusters next to each other, and isolated Au⁻ atoms are present as further anionic species.²⁹ The alkali metal thallide including a Tl₇ cluster as the exclusive thallium substructure is K₁₀Tl₇, in which three extra electrons lead to the metallic nature of the material.²³ We report here on the synthesis, single crystal structure analysis, SEM/EDS measurements, dissolution experiment in liquid ammonia, and first band structure calculations of Cs_{7.29}K_{5.71}Tl₁₃ and Cs_{3.45}K_{3.55}Tl₇, which both include the rare [Tl₇]⁷⁻ cluster.

All materials were synthesized by classical high-temperature solid-state synthesis, starting from the elements. The title

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compound $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ was first observed together with KTl and $\text{K}_{3.826}\text{Cs}_{4.174}\text{Tl}_{11}$ during our systematic investigation of the mixed alkali metal system $\text{Cs}_{1-x}\text{K}_x\text{Tl}$ in the sample with the nominal composition CsK_2Tl_3 (see Supporting Information (SI) section 8). The approach according to the stoichiometric composition $\text{Cs}_4\text{K}_3\text{Tl}_7$ included both title compounds $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ and $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ next to each other and was characterized by single crystal X-ray structure analysis (Table 1, see SI sections 3 and 4 for the atomic coordinates and displacement parameters).

Table 1. Extract from the Crystallographic Data of $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ and $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$

Empirical formula	$\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$	$\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$
CSD number	2295683	2296130
Formula weight/g mol ⁻¹	3849.82	2026.95
Temperature/K	123	
Crystal system, space group	monoclinic, C2/c	tetragonal, I4 ₁ /a
a/Å	30.7792(9)	13.6177(2)
b/Å	11.0000(2)	=a
c/Å	14.0291(4)	25.5573(8)
β/deg	112.676(4)	90
Volume/Å ³ , Z	4382.7(2), 4	4739.39(18), 8
Radiation	Ag Kα (λ = 0.56087 Å)	
ρ _{calc} /(g cm ⁻³)	5.835	5.681
μ/mm ⁻¹	29.146	28.681
R _{int}	0.0577	0.0387
Final R indexes [I ≥ 2σ(I)]	R ₁ /wR ₂ = 0.0390/0.0650	R ₁ /wR ₂ = 0.0356/0.0530
Final R indexes [all data]	R ₁ /wR ₂ = 0.0514/0.0685	R ₁ /wR ₂ = 0.0554/0.0587

The powder diffraction analysis of the bulk material showed additionally $\text{K}_{3.79}\text{Cs}_{4.21}\text{Tl}_{11}$ being present (see SI Figure S15). The formation of the favored A_8Tl_{11} is commonly known to prevent phase purity of several thallide materials.^{20,21} Binary CsTl or KTl could not be indexed. Further $\text{Cs}_{1-x}\text{K}_x\text{Tl}$ approaches, also with a modified temperature program (quenching to room temperature), always resulted in the formation of a mixture of $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ and/or $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ (see Table 2 and SI section 8). Generally, $\text{Cs}_{8-x}\text{K}_x\text{Tl}_{11}$ is present as a side phase. Concerning the title compounds a

Table 2. Formation of $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ and $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ in $\text{Cs}_{1-x}\text{K}_x\text{Tl}$ Samples Depends on the Temperature Program Applied^a

Samples	Cooling rate		$\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$	$\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$
	5 K/h	Quenching		
Cs_2KTl_3	■		■	■
CsK_2Tl_3	■		■	■
CsKTl_2	■		■	■
CsKTl_2		■	■	
$\text{Cs}_4\text{K}_3\text{Tl}_7$	■		■	■
$\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$	■		■	■
$\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$		■	■	
$\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$		■	■	
$\text{Cs}_{7.56}\text{K}_{6.0}\text{Tl}_{13}$	■		■	■
$\text{Cs}_{7.56}\text{K}_{6.0}\text{Tl}_{13}$		■	■	

^a $\text{Cs}_{8-x}\text{K}_x\text{Tl}_{11}$ is always present. Related PXRD are given in SI section 8.

trend is discernible. While $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ is formed ubiquitously and independent from the temperature program applied, slow cooling additionally enables the formation of $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$. Vice versa, this can be suppressed, as upon quenching only a mixture of $\text{Cs}_{8-x}\text{K}_x\text{Tl}_{11}$ and $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ is formed. The exact ratio of potassium and cesium and even a small excess of alkali metal does not influence this observation, as the temperature program is crucial. SEM/EDS measurements of the metallic dark gray blocks support the composition of the single crystals (see SI section 12).

Since a 1:1 ratio of alkali metals:thallium was applied, the occurrence of $[\text{Tl}_6]^{6-}$ octahedra was expected as these clusters are observed in KTl and CsTl . This is indeed the case for $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$, but in addition to $[\text{Tl}_6]^{6-}$, $[\text{Tl}_7]^{7-}$ pentagonal bipyramids are also present in the crystal structure of the latter. In the unit cell of $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$, $[\text{Tl}_7]^{7-}$ clusters as the anionic moiety are exclusively present.

The compound $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ crystallizes in the monoclinic space group C2/c. The asymmetric unit consists of seven thallium and seven alkali metal atoms. The alkali metal sites are not randomly mixed occupied but can be subdivided into two cesium, three potassium, and two atomic sites mixed occupied by cesium and potassium. The $[\text{Tl}_6]^{6-}$ octahedron is built by the thallium atoms Tl1–Tl3 (Wyckoff position 8f), and the pentagonal bipyramid $[\text{Tl}_7]^{7-}$ is built by Tl4–Tl7 (Wyckoff position 8f/4e (Tl7)) (see Figure 1).

The second compound $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ crystallizes tetragonal in the space group I4₁/a and is formed by four crystallographically independent thallium atoms (Wyckoff sites 16f/8e (Tl7)), which form the pentagonal bipyramid (Figure 1b). Four alkali metal atoms complete the asymmetric unit and can be subdivided into one potassium (Wyckoff site 8c), two mixed occupied atomic sites, and one split position of cesium and potassium (Wyckoff sites 16f). For $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ the arrangements of the clusters can be described as hexagonal layers arranged in an AB stacking sequence of a distorted αU packing (see SI Figure S16). For comparison, according to Corbett et al. the clusters in K_{10}Tl_7 can be described as hcp packed.²³ A detailed structural description of both compounds can be found in section 6 of the SI.

In order to compare Tl_6 and Tl_7 clusters, respectively, a ratio $d_{\text{ap}}/d_{\text{eq}}$ of the averaged distances of the equatorial atoms (d_{eq} , pink distances in Figure 1c–e) and the distance of the apical atoms (d_{ap} , green distances in Figure 1c–e) can be calculated.²⁵ In an uncompressed octahedron, the value would calculate to $\sqrt{2} \approx 1.414$. Due to the axial compression, the $[\text{Tl}_6]^{6-}$ octahedra in general show smaller values between 0.98 and 1.16 (see SI Table S10). The values of $[\text{Tl}_7]^{7-}$ calculate also to a slightly smaller range of 1.02–1.08 (see SI Table S11). An uncompressed *closo*- Tl_7 cluster would afford a 9-fold negative charge in analogy to *closo*-2,4- $\text{C}_2\text{B}_5\text{H}_7$. Axial compression of these Tl_7 clusters in K_{10}Tl_7 was reported as a result of the “*hypoelectronic*” nature of $[\text{Tl}_7]^{7-}$.²³ For K_{10}Tl_7 , Corbett et al. suggested a 7-fold negative charge by analyzing extended Hückel molecular orbital (EHMO) calculations. Detailed theoretical investigations of the corresponding solid-state structure by Jansen et al. showed a pseudo band gap below E_{F} .³⁰ The integrated DOS between this gap and the Fermi level amounts to three electrons, which supports a $[\text{Tl}_7]^{7-}$ cluster. As the compounds reported here should be electronically balanced, we calculated the total DOS (for details see SI S6, 2.4). Mixed occupied sites are difficult to

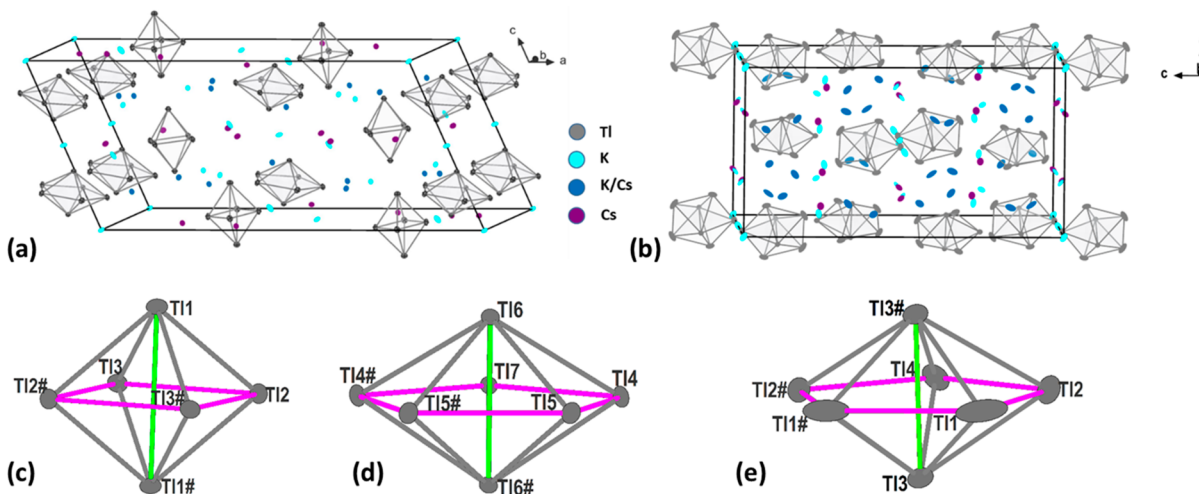


Figure 1. Unit cells of $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ (a) and $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$ (b) with the potassium atoms depicted in light blue, the mixed occupied atoms in dark blue, and the cesium atoms in purple. The $[\text{Tl}_6]^{6-}$ octahedron (c) (Tl atoms labeled with # are at equivalent positions $(1/2 - x, 1/2 - y, 1 - z)$) and pentagonal bipyramids $[\text{Tl}_7]^{7-}$ (d) (Tl atoms labeled with # are at equivalent positions $(1 - x, y, 1/2 - z)$) in $\text{Cs}_{7.29}\text{K}_{5.71}\text{Tl}_{13}$ and (e) (Tl atoms labeled with # are at equivalent positions $(1 - x, 1/2 - y, z)$) in $\text{Cs}_{3.45}\text{K}_{3.55}\text{Tl}_7$. The equatorial Tl–Tl distance is marked in pink, and the distances between the apical atoms (Tl1–Tl1 or Tl6–Tl6) are marked in green.

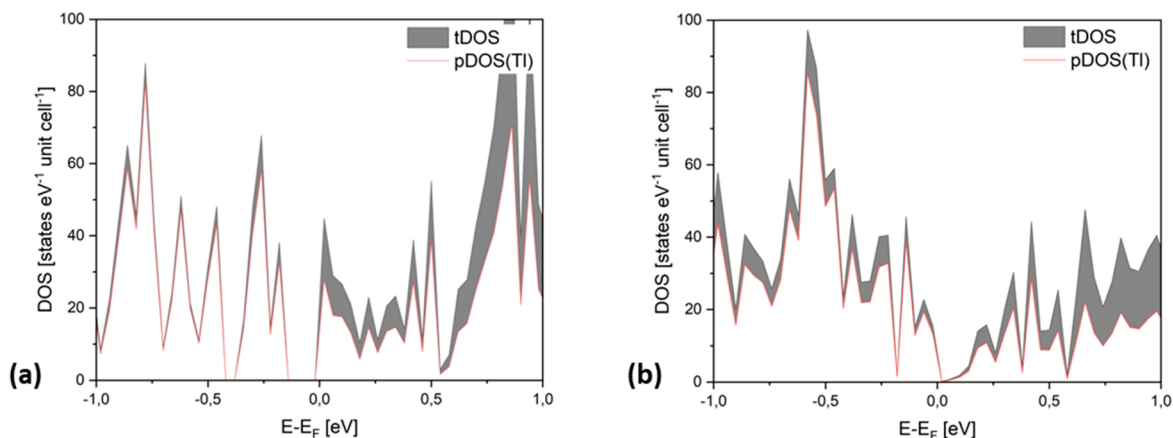


Figure 2. Total DOS (gray) and partial DOS of Tl (white) of the theoretical compounds $\text{Cs}_4\text{K}_3\text{Tl}_7$ (a) and $\text{Cs}_8\text{K}_5\text{Tl}_{13}$ (b).

address in band structure calculations as an enlargement of the unit cell results in intolerable expensive calculations for these heavy atom structures. Therefore, we assumed fully occupied sites for our first band structure calculations to get insight into the electronic nature of the new compounds. Both materials show a (pseudo) band gap around E_F (for $\text{Cs}_4\text{K}_3\text{Tl}_7$ it is left and for $\text{Cs}_8\text{K}_5\text{Tl}_{13}$ right of E_F ; slight deviations must be addressed in detailed calculations), which suggests the classification of a Zintl phase assuming complete electron transfer from the less electronegative alkali metals to thallium (Figure 2). The compounds reported here therefore yield a charge of -7 for the Tl_7 cluster and emphasize the packing effects on the obtained cluster compounds, as binary K_7Tl_7 cannot be obtained.

Salt-like Zintl phases including isolated clusters are of great interest in material science, as they provide p-block metal building blocks,³¹ which can be transferred and altered using solution chemistry methods.^{32–40} For homoatomic clusters, this is proven for groups 14–16. In contrast, no group 13 cluster has yet been obtained from dissolving trielide Zintl phases. Because of the relatively low charge of the group 13 clusters $[\text{Tl}_6]^{6-}$ and $[\text{Tl}_7]^{7-}$, these materials might be

appropriate representatives. Therefore, first dissolution experiments in liquid ammonia were carried out, which yielded thallium and alkali metal amide as final oxidation products (SI section 11). Similar observations have been made for $\text{Na}_{8-x}\text{A}_x\text{Tl}_4$ ($A = \text{K, Rb}; x = 0, 1$).^{41,42}

The occurrence of different clusters for isoelectronic thallide atoms in $[\text{Tl}_x]^{x-}$ ($x = 6, 7$), even within one crystal structure, emphasizes the filigree interplay of packing effects and stabilization of the thallide clusters. The simultaneous application of different heavier congeners of the alkali metals within one sample seems to provide new and unpredictable compounds for this class of materials. These mixed cation approaches allow the formation of electronically balanced clusters precast in salt-like Zintl phases. The homoatomic group 13 clusters might be appropriate representatives for investigating solution chemistry in the style of group 14 or 15 Zintl phases. Ongoing experiments will show whether it is possible to transfer homoatomic trielide clusters from solid state into solution or if this is limited to clusters right to the Zintl border.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c04034>.

Experimental and DFT calculation details, crystallographic data, additional structure description, powder diffraction patterns, and dissolution experiment in liquid ammonia (PDF)

■ Accession Codes

CCDC 2295683 and 2296130 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

Caution! The element thallium as well as compounds including it are highly toxic. The alkali metals are strongly reactive. The resulting products are very sensitive to air and moisture.

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