

A₁₀Tl₆O₂ (A = K, Rb) cluster compounds combining structural features of thallium cluster anions and of alkali metal sub-oxides

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New alkali metal thallideoxides, A₁₀Tl₆O₂ (A = K, Rb), crystallize in a unique structure consisting of hypoelectronic [Tl₆]⁶⁻ clusters in the shape of compressed octahedra, together with oxygen-centred alkali metal octahedra that have been identified as constitutive of alkali metal sub-oxides.

When reacted with electropositive elements, thallium has been proved to form diverse types of homoatom cluster that can be rationalized only by employing different bonding systematics.¹ Classical examples² like (Tl⁻)_n in NaTl and [Tl₄]⁸⁻ in Na₂Tl can be described in terms of the Zintl–Klemm concept,³ assuming two-electron two-center bonds within the polyanionic framework. [Tl₅]⁷⁻ in Na₂K₂₁Tl₁₉ contains less electrons than would be necessary in order to reach an electron octet, and thus the Zintl–Klemm concept does not apply.⁴ Instead, this cluster can be well understood in terms of Wade's rules,⁵ in analogy to boranes. Finally, the strongly axially compressed [Tl₆]⁶⁻ octahedra, as formed in ATl (A = K, Cs), are electronically deficient even in respect to Wade's rules, and thus have been denoted as hypoelectronic.⁶

One of our long term goals has been to realize isolated Tl⁻ ions in a solid matrix, which we expect to give straight evidence for the degeneracy of the 6p orbitals being lifted through relativistic effects,⁷ while forming a closed shell and a diamagnetic (p_{1/2})² ground state.⁸ For this purpose, we have added oxygen as a third component to the alkali metal/thallium systems under investigation, aiming to synthesize Cs₃TlO, amongst others. During respective experimental trials, we recently discovered Cs₈Tl₈O.⁹ This first alkali metal thallideoxide consists of a novel [Tl₈]⁶⁻ cluster anion with a valence electron concentration in agreement with the extended Wade–Mingos condensation concept.¹⁰

In this paper we report on the synthesis and crystal structures of two new alkali metal thallideoxides A₁₀Tl₆O₂ (A = K, Rb).† According to X-ray single crystal structure analyses, the compounds crystallize in a novel structure type (Fig. 1). The crystal structure consists of isolated Tl₆ and [O1A₆] units, stacked to form bilayers in a distorted rock salt arrangement. These bilayers are separated by one-dimensional chains of edge-sharing [O2A_{4/2}A_{2/1}] octahedra. The resulting arrangement is rather unusual and strongly anisotropic, and thus deserves a special discussion.

First, to understand the crystal structure, interatomic separations have to be considered. The distances of the crystallographically-distinct oxygen atoms from the alkali metals differ significantly ($\bar{d}(\text{O1-Rb}) = 2.73 \text{ \AA}$ vs. $\bar{d}(\text{O2-Rb}) = 2.85 \text{ \AA}$;

$\bar{d}(\text{O1-K}) = 2.59 \text{ \AA}$ vs. $\bar{d}(\text{O2-K}) = 2.74 \text{ \AA}$). The bond lengths for the O2 atoms correspond well to the respective sums of tabulated ionic radii ($r(\text{O}^{2-}) + r(\text{K}^+) = 2.78 \text{ \AA}$; $r(\text{O}^{2-}) + r(\text{Rb}^+) = 2.89 \text{ \AA}$; all values for CN = 6).¹¹ The even shorter distances for O1 atoms are due to the increase in the surrounding electrostatic potential. A similar decrease for the O–A distances was observed in rubidium sub-oxides (cf. Rb₆O: $\bar{d}(\text{O-Rb}) = 2.75 \text{ \AA}$)¹² or ternary alkali metal aurideoxides (K₃AuO: $\bar{d}(\text{O-K}) = 2.62 \text{ \AA}$; Rb₃AuO: $\bar{d}(\text{O-Rb}) = 2.75 \text{ \AA}$).¹³ It is interesting to note that binary sub-oxides in the K/O system, in contrast to the (Rb,Cs)/O systems, have not been known so far. The isolated [O1K₆] group in K₁₀Tl₆O₂ can be therefore regarded as the first example of a potassium sub-oxide building unit.

Under closer inspection, both the coordination of O1 and O2 by the alkali metals turn out to be strongly distorted. In the case of O2, the irregularities of the A₆ polyhedra cannot be solely assigned to the well-known difference between shared and unshared edges. The unshared edges vary significantly in length (3.79 Å vs. 5.07 Å for K₁₀Tl₆O₂; 3.89 Å vs. 5.23 Å for Rb₁₀Tl₆O₂). Also related to this phenomenon, the oxygen ions are shifted off-center, thus forming a zig-zag type chain along [001]. As can be seen from Fig. 2, these special features are caused by the anisotropy of the overall crystal structure, in particular the anisotropy of the direct environment of the [O_A_{4/2}A_{2/1}] chains. The [Tl₆]⁶⁻ units are situated opposite to

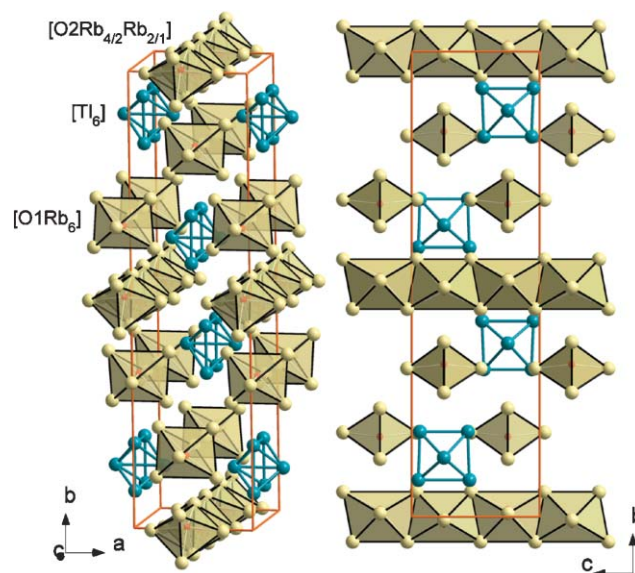


Fig. 1 Perspective representation (left) and [100] projection (right) of the crystal structure of Rb₁₀Tl₆O₂ (orange lines mark the unit cell, Tl₆ clusters are blue, [O1Rb₆] and $\frac{1}{2}$ [O2Rb_{4/2}Rb_{2/1}] groups are yellow).

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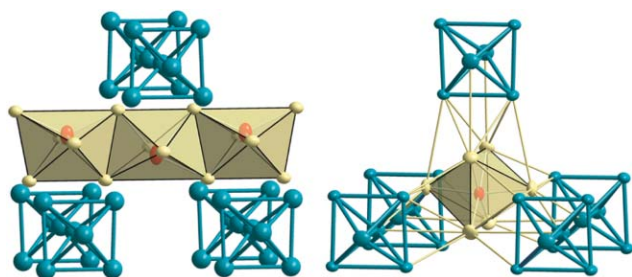


Fig. 2 The $1/2$ -[O₂Rb_{4/2}Rb_{2/1}] chains (left) and [O₁Rb₆] octahedron (right) with emphasized neighbored Tl₆ groups (thermal ellipsoids set at 75%). For colour code, see Fig. 1.

the substantially shorter edges of the octahedra. These seem to generate a significant negative potential that attracts the alkali metal cations and repels the oxygen anions.

The environment of the O₁A₆ octahedron is also anisotropic: it is surrounded by five Tl₆ groups in a shape of a square pyramid (Fig. 2). This causes compression of the octahedron axis in the pyramid base and a shift of the O₁ atom off the octahedron center, away from the top of the pyramid.

These clearly relevant interactions between the (A/O)ⁿ⁺ and Tlⁿ⁻ sub-lattices seem to be primarily Coulombic, since the alkali metal–thallium separations are far too long ($d(\text{K-Tl}) > 3.55 \text{ \AA}$; $d(\text{Rb-Tl}) > 3.69 \text{ \AA}$) to be regarded as covalent. The Tl₆ clusters are well isolated, separated from each other by $> 4.80 \text{ \AA}$ for K₁₀Tl₆O₂ or $> 5.14 \text{ \AA}$ for Rb₁₀Tl₆O₂. The corresponding alkali metal oxide groups can thus be regarded as [O₁A₆]⁴⁺ and $1/2$ -[O₂A₄]²⁺ cations, and the six electrons released are transferred to the Tl₆ units, forming [Tl₆]⁶⁻ polyanions. The Tl₆ groups in the considered compounds provide further examples of hypoelectronic clusters (valence electron concentration = 24e, which is less than $6 \times 4 + 2 = 26e$, the polyhedral electron number predicted by Wade's rules).

The [Tl₆]⁶⁻ clusters occur in the shape of a distorted octahedron (Fig. 3), which is strongly compressed along one of its originally 4-fold axes (K₁₀Tl₆O₂: $d(\text{Tl3-Tl3}) = 3.58 \text{ \AA}$; Rb₁₀Tl₆O₂: $d(\text{Tl3-Tl3}) = 3.57 \text{ \AA}$; for comparison, the lengths of the other space diagonals are 4.93 \AA for the potassium compound and 4.94 \AA

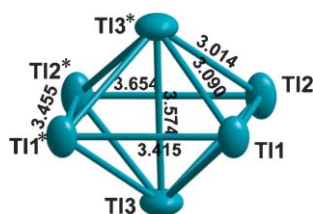


Fig. 3 The [Tl₆]⁶⁻ cluster of Rb₁₀Tl₆O₂ (unlabelled Tl atoms are those of the asymmetric unit, Tl atoms labelled with an asterisk are at equivalent positions $(-x, y, -z)$, thermal ellipsoids set at 50%). Interatomic distances (\AA) and selected angles ($^\circ$) in (a) Rb₁₀Tl₆O₂: Tl1–Tl3 3.090(1) \times 2, Tl1–Tl1 3.415(2), Tl1–Tl2 3.455(2), Tl2–Tl3 3.014(1) \times 2, Tl2–Tl1 3.455(2), Tl2–Tl2 3.654(2), Tl3–Tl2 3.014(1) \times 2, Tl3–Tl1 3.090(1) \times 2, Tl3–Tl3 3.574(2); Tl2–Tl1–Tl1 92.0(1), Tl1–Tl2–Tl2 88.0(1); and (b) K₁₀Tl₆O₂: Tl1–Tl3 3.094(1) \times 2, Tl1–Tl1 3.390(1), Tl1–Tl2 3.432(1), Tl2–Tl3 3.010(1) \times 2, Tl2–Tl1 3.432(1), Tl2–Tl2 3.704(2), Tl3–Tl2 3.010(1) \times 2, Tl3–Tl1 3.094(1) \times 2, Tl3–Tl3 3.578(1); Tl2–Tl1–Tl1 92.6(1), Tl1–Tl2–Tl2 87.4(1).

for the rubidium compound). This distortion is intrinsic for [Tl₆]⁶⁻ cluster anions and can be understood in terms of the Jahn–Teller theorem. The compression of the octahedron along one of its diagonals reduces its point group symmetry to D_{4h} , thus splitting the t_{1u} molecular orbital (MO) into e_u and a_{2u} MOs, the latter becoming antibonding. As a result, the 24 valence electrons now occupy exclusively bonding or non-bonding MOs, thus stabilizing the cluster. This structural feature was already observed for the [Tl₆]⁶⁻ clusters in ATl (A = K, Cs).⁶ However, the clusters in the latter cases are less compressed (the lengths of the shortest octahedra diagonals were found to be 3.81 \AA in KTI and 3.74 \AA in CsTI) resulting in smaller band gaps for the [Tl₆]⁶⁻ clusters (e.g. 0.35 eV in KTI)⁶ as compared to A₁₀Tl₆O₂ (0.96 eV in Rb₁₀Tl₆O₂). Both calculations were performed on the extended Hückel approximation level by applying the same basis set.¹⁴

Our approach to extending the already thoroughly investigated binary alloys of alkali metals and thallium using a third component, e.g. oxygen, seems to open up a new and rather fertile field. In particular, the sharpened bonding situation, particularly the formation of clearly distinguishable, prevalently ionic (alkali metal/oxygen) and covalent (homoatom clusters) partial structures, allows for a more reliable electron count, providing a sound basis for understanding and classifying the extended and rather intricate family of thallium cluster ions.

Notes and references

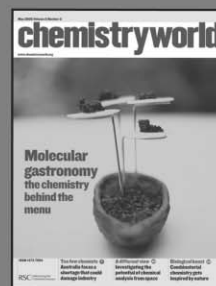
† All operations were performed under dried argon (Schlenk technique or glove box, M. Braun, H₂O/O₂ < 0.1 ppm). The materials utilized were alkali metals (K, 99%, Merck, purified by hot filtration and distillation; Rb prepared from RbCl, 99%, Aldrich, by reduction with Ca, twice distilled), alkali metal monoxides (K₂O and Rb₂O, both prepared from their corresponding metals by oxidation with appropriate quantities of oxygen) and elemental thallium (99.9+%, Sigma–Aldrich, dried before use at 150 $^\circ\text{C}$ in a dynamic vacuum of 10^{-3} mbar). Single crystals of A₁₀Tl₆O₂ (A = K, Rb) were obtained by reaction of A, A₂O and Tl in the molar ratio 9 : 6 : 4.5. The mixtures (1–2 g) were sealed under Ar in Ta ampoules, heated for 24 h at 500 $^\circ\text{C}$ and subsequently cooled down to room temperature at a rate of 2 $^\circ\text{C h}^{-1}$. The alkali metal excesses were distilled off at 180 $^\circ\text{C}$ (A = K) and 90 $^\circ\text{C}$ (A = Rb) in a dynamic vacuum of 10^{-3} mbar. The as-synthesized products were pure, according to X-ray powder diffraction and are extremely sensitive to air and moisture. According to high temperature X-ray diffraction (Stoe & Cie GmbH, Mo-K α , $\lambda = 0.7093 \text{ \AA}$, $4^\circ < 2\theta < 40^\circ$, temperature intervals 25 $^\circ\text{C}$) both compounds are stable up to ca. 300 $^\circ\text{C}$. At higher temperatures, Rb₁₀Tl₆O₂ decomposes to the thallium-rich Rb₈Tl₈O thallosexide, whereas K₁₀Tl₆O₂ decomposes to a yet to be identified phase. This thermal behaviour explains why a slightly sub-stoichiometric amount of thallium should be used in the initial mixtures. The reactions of stoichiometric mixtures lead to products contaminated with the decomposition phases to a larger extent.

Crystal data: Intensity data were collected on a Bruker AXS APEX Smart-CCD diffractometer system (monochromatized Mo-K α radiation, $T = 293 \text{ K}$). **K₁₀Tl₆O₂:** Orthorhombic, *Cmcm* (no. 63), $a = 8.3755(4)$, $b = 32.1025(13)$, $c = 8.8634(5) \text{ \AA}$ (powder data, Cu-K α , $\lambda = 1.5406 \text{ \AA}$), $V = 2383.1(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 4.597 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 42.2 \text{ mm}^{-1}$, $F(000) = 2768$, 12778 measured reflections, 1626 symmetry independent reflections ($2\theta_{\text{max}} = 56.00^\circ$, $R_{\text{int}} = 0.0463$), 58 refined parameters, $R_1 = 0.0355$, $wR_2 = 0.0918$ ($1473 F_0 > 4\sigma(F_0)$), $R_1 = 0.0395$, $wR_2 = 0.0950$ (all). CCDC 299380. **Rb₁₀Tl₆O₂:** Orthorhombic, *Cmcm* (no. 63), $a = 8.7176(1)$, $b = 33.2934(3)$, $c = 9.1242(1) \text{ \AA}$ (powder data, Cu-K α , $\lambda = 1.5406 \text{ \AA}$), $V = 2648.19(5) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 5.300 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 54.6 \text{ mm}^{-1}$, $F(000) = 3488$, 12077 measured reflections, 1486 symmetry independent reflections ($2\theta_{\text{max}} = 52.00^\circ$, $R_{\text{int}} = 0.1226$), 58 refined parameters, $R_1 = 0.0567$, $wR_2 = 0.1312$ ($1105 F_0 > 4\sigma(F_0)$), $R_1 = 0.0760$, $wR_2 = 0.1431$ (all). CCDC 299381. The authors are grateful to Dr. Jürgen Nuss for collecting the single crystal data. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601802e

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