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$Na_{15}K_6Tl_{18}H$: A Remarkable Hydrogen-Stabilized Zintl Phase with Isolated $(Tl_6H)^{7-}$ and $(Tl_{12}Na)^{13-}$ Polyanions

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Size tuning with mixed cations has been productive in the isolation of a variety of novel thallium clusters not present in binary alkali-metal−thallium systems.[2−5] Diverse sizes of cations provide more structural flexibility for the efficient packing of cations and polyanions within electronic requirements of the latter. Compounds with new types of isolated clusters may result, such as $Na_2K_{21}Tl_{19}$, (Tl_5^{7-}, Tl_9^{9-}),[2] $Na_4K_6Tl_{13}$ (icosahedral Tl_{13}^{10-}),[3] and the title compound. The occurrence of diverse thallium cluster anions appears related to approximate 1:1 charge:thallium ratios and a strong relativistic effect for the element where the Tl^- state ($6p_{1/2}$) is additionally favored,[3] and these afford an appropriate number of skeletal electrons for deltahedral clusters with significant Tl−Tl bond strength. Size and electronic tuning can also be effective within cluster anions through the inclusion of an appropriate heterometal.[5−7] The compound we report here is the first example with both octahedral and icosahedral clusters, as well as hydrogen. Comparisons of the new compound with the icosahedral $Na_4K_6Tl_{13}$[3] and the closely related $Na_{14}K_6Tl_{18}M$ (M = Mg, Zn)[5] together with synthetic and magnetic results will be used to rationalize the presence and necessity of hydrogen, evidently within the octahedron.

A pure phase of the title compound is obtained with the synthetic techniques we have used earlier,[2,3] fusion of the elements in stoichiometric proportions at 500 °C in a welded Ta container followed by quenching and then annealing at 250 °C for 7 days. The very small amount of hydrogen necessary (~0.02 wt %) probably comes from Na (99.9%, Alfa) or K (99.9%, Baker) or from moisture on or in the fused silica jacket in which the Ta tube is sealed and heated. The phase is very brittle, has a shiny black metallic luster, and is very easily oxidized by moisture. $Na_{15}K_6Tl_{18}H$ is a line compound since Guinier powder patterns yield the same lattice constant (within 0.006 Å, 6σ) for different starting compositions, as has always been the case for phases with isolated clusters.

Single-crystal studies[8] established a cubic structure ($Pm\bar{3}$) for "$Na_{15}K_6Tl_{18}$" that contains both a regular Tl_6 octahedron (O_h) and an almost regular, Na-centered Tl_{12} icosahedron (T_h) plus 20 free cations (see synopsis). The first implication of H came from the contrast between the electron deficiency predicted for a thallium cluster model and the compound's magnetic properties. The hydride model was further supported by subsequent synthetic results, charge balance, a probable 14-e^- closed-shell configuration for the octahedron, and its dimensions with respect to those in the closely related $Na_{14}K_6Tl_{18}M$ phases, M = Mg, Zn. Each of these is addressed below. The requirement of one hydrogen within the thallium octahedron makes the phase even more remarkable in the sense that it provides the first condensed-phase example of Tl−H interactions.

According to Wade's rules (and extended Hückel calculations), 14 skeletal electrons are expected for the closed-shell octahedral cluster (Tl_6^{8-}), and 26, for either the icosahedron (Tl_{12}^{14-}) or the centered $NaTl_{12}^{13-}$. Since there are only 21 alkali-metal atoms per cell, a one-electron deficiency in one of the cluster units was expected, although a Jahn−Teller distortion of a 13-e^- octahedron might be expected on the basis of results for KTl[9] and CsTl,[10] where there are 12 skeletal electrons in the $\sim D_{2h}$ or $\sim D_{4h}$ anions. However, susceptibility data for "$Na_{15}K_6Tl_{18}$" indicated only a Pauli-paramagnetic behavior (1.5-(2) × 10^{-3} emu/mol at 3 T) instead of the Curie−Weiss property seen earlier for the localized single-spin system in several phases containing Tl_{13}^{10-}.[3] ESR spectra were silent. The magnetic results strongly suggest that effectively all valence electrons are paired.

Since hydride could be a solution to the discrepancies, as it is elsewhere,[11] additional synthesis reactions were run at 800 °C for 5 h followed by slow cooling to room temperature under two conditions, both with and without a dynamic vacuum (dv, ~10^{-6} Torr). (Hydrogen is known to pass readily through Ta above about 500 °C.) The reactions in vacuum yielded *no* $Na_{15}K_6Tl_{18}$ but rather $Na_{12}K_{19}Tl_{24}$ as the major phase with $Na_{23}K_9Tl_{15.33}$[5] as a byproduct, while the usual reaction in a silica jacket gave only the title phase. Introduction of H_2 into the vacuum system outside the heated Ta container does likewise.

Definitive modifications of the new phase on the basis of size and electron count tuning were also found, namely, syntheses of isostructural phases with closed-shell anions that do not need hydrogen through substitution of divalent metals (M) for the centering Na to give $Tl_{12}M^{12-}$. Reactions targeted on $(Na_{14}M)K_6Tl_{18}$, M = Mg, Zn, Cd, and run with or without dv all produced pure $Na_{15}K_6Tl_{18}$-type phases with the expected shrinkage in lattice dimensions. On the other hand, a Ca reaction under vacuum again gave $Na_{12}K_{19}Tl_{24}$ as the major phase, while the usual method using a SiO_2 jacket again yielded "$Na_{15}K_6Tl_{18}$" with no line shifts. The presence of Mg and Zn centering the icosahedra in isostructural $Na_{14}K_6Tl_{18}M$ phases has been confirmed by subsequent single-crystal studies and EDAX analyses.[5] These synthetic results strongly support the hydride model for "$Na_{15}K_6Tl_{18}$", since closed-shell clusters Tl_6^{8-} and $Tl_{12}M^{12-}$ now match the 20 alkali-metal cations present. They also indicate that the hydride phase is thermodynamically less stable than any of the $Na_{14}K_6Tl_{18}M$ examples.

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[8] The structure was solved by direct methods (SHELX-86) from two octants of data collected up to $2\theta = 55°$ at room temperature on a CAD4 diffractometer (Mo Kα). Crystal data: cubic $Pm3$, $Z = 1$, a = 10.6405(4) Å (Guinier data, $\lambda = 1.540\ 562$ Å), $R(F)/R_w$ = 2.3%/2.6%, GOF = 1.13 for 395 independent reflections ($I > 3\sigma_I$, R_{int} = 5.5%) and 24 variables after absorption corrections ($\mu = 612\ cm^{-1}$).

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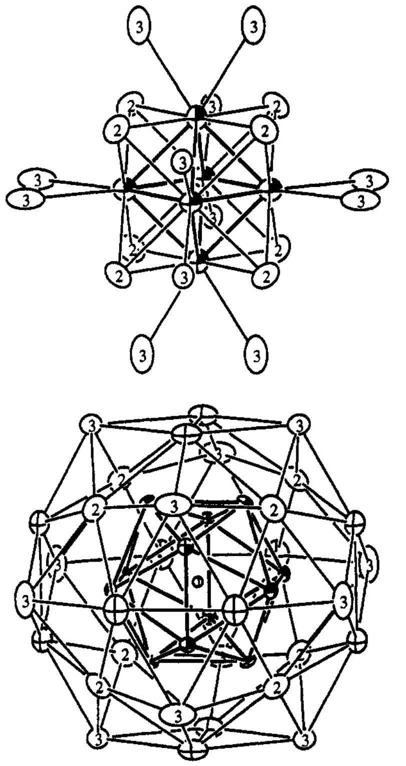

Figure 1. Alkali-metal environments around the polyanions in $Na_{15}K_6Tl_{18}H$ (90%): top, $(Tl_6H)^{7-}$; bottom, $(Tl_{12}Na)^{13-}$. Numbered ellipsoids are Na2 and Na3, while crossed ellipsoids are K. (Tl1−Tl1 = 3.276(1) Å; Tl1−H = 2.3161(9) Å; Tl2−Tl2 = 3.299(1), 3.3244(6) Å; Tl2−Na1 = 3.1569(5) Å.)

There is further supporting evidence for the hydride model from crystal structure and bonding studies. Comparisons of crystal symmetry, cluster packing, and cation distributions between $Na_{15}K_6Tl_{18}H$ ($Pm\bar{3}$, $Z = 1$, $a = 10.6405(4)$ Å) and $Na_4K_6Tl_{13}$ ($Im\bar{3}$, $Z = 2$, $a = 11.5075(7)$ Å) show that the structures are very closely related, viz., $[(Na_8^{8+})(K_{12}^{12+})][(Tl_{13}^{10-})(Tl_{13}^{10-})]$ vs $[(Na_8^{8+})(Na_6^{6+})(K_6^{6+})][(Tl_{12}Na^{13-})(Tl_6H^{7-})]$. The most substantial differences are (a) replacement of half of the icosahedral units related by *I*-centering with the smaller octahedra, (b) change of the Tl centering the icosahedron to Na, and (c) inclusion of H, apparently in the octahedron, in order to satisfy electronic requirements (below). Otherwise, the cation dispositions in the two phases show only slight coordinate shifts related to good cation−anion solvation and significant cluster bonding. Figure 1 shows the cation arrangements around the octahedron (top) and icosahedron (bottom) in $Na_{15}K_6Tl_{18}H$. All triangular faces in both are capped by a Na2 or a K atom, while Na3 is only exo-bound, two to each vertex of the former and one to the latter, respectively. The equivalent K positions in $Na_4K_6Tl_{13}$ are thus split equally into K and Na3 in $Na_{15}K_6Tl_{18}H$, as above. The very similar cation distributions in the two phases also mean that the octahedron and icosahedron are the only two interchangeable cluster units with suitable symmetry elements and a total charge near −20. The cation packings appear equally tight in the two phases; the largest voids in the new structure are four-coordinate (3 Na^+ + 1 K^+) with radii of 2.40 Å or less and chemically unacceptable for another cation. More importantly, the cavity is probably too small for hydride, judging from the interatomic distances in NaCl-type NaH (2.44 Å) and KH (2.85 Å).[12] Furthermore, the placement of H^- in such a cavity is quite unreasonable electronically because it would now leave the clusters *two* electrons short, e.g., $(A^+)_{20} \neq Tl_6^{8-}(Tl_{12}Na)^{13-}H^-$.[13] However, bonding an interstitial hydrogen in the octahedral hole in the Tl_6 ion to give Tl_6H^{7-} with d(Tl−H) = 2.316(1) Å would both seem plausible and solve the problem electronically. A centered H atom effectively oxidizes Tl_6^{8-} by one electron via the strong interaction of its 1s orbital with the extant a_{1g}^2 MO, the added a_{1g} level being high-lying and empty (compare $Nb_6I_{11}H$[14]). And although no normal Tl−H distances are available for reference, the 1.870 Å separation in TlH(g)[15] yields a very similar d(Tl−H) = 2.34 Å when corrected by Pauling's bond order equation to the corresponding $^1/_6$th bond order.

Small dimensional differences between the assigned Tl_6H^{7-} and the authentic Tl_6^{8-} exist as well. Interstitials usually increase the stabilities of clusters and decrease bond distances when no matrix effects are involved.[16] The Tl−Tl distance in the octahedron indeed decreases slightly, from 3.283(1) and 3.289(2) Å in $Na_{14}K_6Tl_{18}M$, M = Mg, Zn, respectively,[5] to 3.276(1) Å in Tl_6H^{7-}, even though the cells expand. While cation interactions with the icosahedral clusters remain basically the same from $Na_{15}K_6Tl_{18}H$ to $Na_{14}K_6Tl_{18}M$, as judged from cation−thallium distances, solvation of Tl_6^{8-} appears slightly stronger than that for Tl_6H^{7-} since the Na−Tl distances about Tl_6^{8-} are ~0.04 Å less, consistent with its higher charge.

The closed-shell configurations assigned to $Na_{15}K_6Tl_{18}H$ mean it is best classified as a metallic Zintl phase[3,17] since "Q" resistivity measurements run as before[3] show it to have a room-temperature resistivity of ~100 $\mu\Omega$·cm with a positive temperature coefficient of 0.34(1)% K^{-1}.

The present compound again demonstrates not only how delicately size factors and electronic requirements can combine to create unprecedented structures in which different polyanions are trapped but also how one small hydrogen atom can play such an amazing role in stabilizing a new compound. While NMR and PES (UPS) are practically ineffective in providing further evidence on the hydrogen because of its extremely low concentration in, and the metallic character of, $Na_{15}K_6Tl_{18}H$, neutron diffraction studies may provide further clarification. Tuning size and electron count via other heterometal anions such as Hg, Zr, Hf, Ni, Pd, Pt, Sm, or Yb seems promising, although many of these did not work in $Na_4A_6Tl_{13}$.[3]

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Supporting Information Available: Tables S1−4, giving crystallographic details, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances, Figures S1 and S2, showing magnetic susceptibility and resistivity results, and text presenting experimental details for the structure determination and property measurements (6 pages). Ordering information is given on any current masthead page.

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