Triel-rich mixed potassium indides/gallides: Ternary variants of binary trielides and the new 3:11 compound $K_{15}Ga_{43(2)}In_{10(2)}$

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Alkali gallides and indides exhibit a fascinating complex structural chemistry between electron-precise Zintl phases (e.g. NaIn), Wade cluster compounds (e.g. K$_3$Ga$_2$), boron-analogs (e.g. K$_4$In$_3$) and simple intermetallics (like e.g. KIn)$_2$. In a systematic experimental study, mixed In/Ga trielides have been synthesized from the elements to i. explore the 'coloring' of the polyanions with the two triels differing both in size and electronegativity and to ii. explore additional new polyanion topologies.

In the most In-rich indide KIn$_8$ [2,3] indium can be substituted by up to 1.12 atoms of Ga, which takes the more negatively charged tips of pyramids in the BaAl$_6$-type structure [1]. Starting from K$_3$Ga$_2$ [4] which is a Zintl phase in containing exo-bond close dodecahedra Ga$_8$ and one 4-bonded Ga per tripled formula unit, an only small amount of Ga can be substituted against In. This also holds for the related gallide K$_3$Ga$_{13}$. The new cluster compound of overall composition K$_3$(Ga/In)$_{13}$ with an In proportion of ≈20% and a very small In/Ga phase width crystallizes in a singular orthorhombic structure type (Cmmm, $a=1577.39$, $b=3354.71$, $c=654.97$ pm), which has been determined by means of single crystal X-ray data ($R_1=4.8\%$). It contains 6 K and 13 triel positions, of which one [In(1)] is a pure In site, four (denoted $M$) are mixed Ga-rich positions (82-92% Ga) and the remaining sites are occupied by Ga only. The In/Ga atoms form two crystallographically different icosahedra [$M^{1}_{12}$] [built up from $M(1)/Ga(2)/M(6)/Ga(8)$] and [$M^{2}_{12}$] [M(4)/M(9)/Ga(11)] (dark gray polyhedra) in a 2:1 ratio and the new [Ga$_{13}$] cluster [formed by Ga(5/7/10/13), light gray]. The latter consists of two pentagonal pyramids sharing one corner. The clusters are connected among each other and the 4-bonded $M(3)$ and Ga(12) atoms. According to $K_{3}M_{15}$,$M_{15}$,$M_{15}$, the compound obeys the Zintl concept ‘extended’ by the Jemmis electron counting rules, if the new double cluster is counted as ‘intermediately’ connected [5]. The experimental studies are accompanied by DFT band structure calculations.