

At the Edge: the Novel Zintl Compound Cs(Cs,K)₆[K(Si₄)₂]

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The complex issue of chemical bonding in intermetallic chemistry plays a pivotal role whose understanding is crucial to gain deeper insights into relationships of structure, physical properties and reactivity. The silicides of the alkali metals represent polar intermetallic compounds which can be explained by the Zintl-Klemm concept.^[1] Within the binary compounds $M_4\text{Si}_4$ ($M = \text{Na, K, Rb, Cs}$) two structure types are found:^[2] the NaSi type for $M = \text{Na}$, and the KGe type for $M = \text{K to Cs}$. Therein, isolated tetrahedral cluster anions, $[\text{Si}_4]^{4-}$ represent the main structural motif, according to the formal charge distribution $[M^+]_4[(3b)\text{Si}^{1-}]_4$. Although the lattice parameters of the binary silicides vary significantly, the substructure of the anions remains almost unchanged. Namely, structural alterations depend on the influence of the variation of cations. With cations of similar size (K, Rb, Cs) the solid solutions $\text{Rb}_{4x}\text{M}_{4-4x}\text{Si}_4$ ($M = \text{K, Cs}$ and $0 \leq x \leq 1$) with complete miscibility are observed,^[3] following Vegard's rule. For cations that differ much more in size a more distinct implication is expected and perceived in the ordered structures of $M_7\text{LiSi}_8$ ($M = \text{K, Rb, Cs}$) and Rb_7NaSi_8 of the Rb_7NaGe_8 type.^[4] Here we present a new Zintl compound which is located at the edge of these two boundary effects. $\text{Cs}(\text{Cs,K})_6[\text{K}(\text{Si}_4)_2]$ crystallizes in the Rb_7NaGe_8 type forming red transparent prisms. However, the structure exhibits only partial ordering of the alkali cations. The crystal structure contains one type of $[\text{Si}_4]^{4-}$ with local symmetry $3m$, built by two non-equivalent Si atoms. Each K1 atom connects two of these anions to $[\text{K}(\text{Si}_4)_2]^{7-}$ units *via* two μ^3 contacts, revealing an exceptionally short K-Si distance of 2.945(1) Å. Additionally, two cationic positions with different environments are found. Cs1 is coordinated octahedrally by Si with distances of 4.119(2) Å. The coordination sphere around the anionic unit is completed by the cationic site 24 *d* at distances of 3.5 Å to 3.8 Å. Thereby, this general position is mixedly occupied by K2 and Cs2 with a ratio of 12 : 13. According to the trend within the ionic radii of alkali metals, the partial ordering of the cations in the presented structure is not surprising and more than reasonable.

References:

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