Dissolving Silicides: Syntheses and Crystal Structures of New Ammoniates Containing Si$_5^{2-}$ and Si$_9^{4-}$ Polyanions and the Role of Ammonia of Crystallisation

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The dissolution of the ternary material K$_6$Rb$_6$Si$_{17}$ in liquid ammonia yields the solvate compound Rb$_4$Si$_9\cdot$5NH$_3$, which contains fourfold negatively charged nine atom silicon clusters Si$_9^{4-}$. Using additionally the [2.2.2] cryptand during the dissolution results in the solvate [K(2.2.2-crypt)]$_2$Si$_5\cdot$4NH$_3$, in which the Si$_5^{2-}$ anion is present in the crystal structure. The Si$_5^{2-}$ anion has the shape of a nearly ideal trigonal bipyramid. The starting material K$_6$Rb$_6$Si$_{17}$ contains both Si$_4^{4-}$ and Si$_9^{4-}$ Zintl anions. In ammoniate crystal structures, Si$_9^{4-}$ anions are accessible independently of Si$_4^{4-}$ anions, and ammonia of crystallisation plays a major role in the observed crystal symmetry. For the cryptate structures of Si$_5^{2-}$ and Ge$_5^{2-}$ anions ammonia of crystallisation is obligatory despite the loss of crystal symmetry compared to the crystal structures of the heavier homologues Pb$_5^{2-}$ and Sn$_5^{2-}$.

Key words: Silicides, Zintl Anions, Liquid Ammonia, Crystal Structure Determination