Synthesis and Crystallization of Main Group Element Anions in Liquid Ammonia.

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Liquid ammonia can be used as a solvent for both inorganic and organic compounds due to its lower dielectric constant compared to water. In addition, the formation of kinetically stable blue solutions of alkali and alkaline earth metals offers a highly reactive medium for the reductive transformation of main group elements or precursor substrates into anionic compounds. The temperature and moisture sensitive crystals are prepared for X-ray diffraction under inert conditions according to the method described by Kottke and Stalke.

[Cs([18]crown-6)]4[Sn4Bi4]−12 NH3 can be crystallized from solution after dissolving the Zintl phase CsSnBi in liquid ammonia. It is the first eight atomic tin bismuth species. It can be described as a nortricyclane-like [Sn3Bi4]6− cage formally capped by a Sn2+ cation. Mass spectrometry shows evidence for a crystallographically not yet characterized [Sn3Bi4]6− anion in which all bonds can be described by 2e−2c-bonds. This is not the case for the capped anion. Electron localization function calculations show the existence of three-centre-bonding within the [Sn4Bi4]6− anion.

[Rb([2.2.2]crypt)]Rb6Sn9(OH)3(NH3)5 was obtained by dissolving an equimolar mixture of RbSn2 and Rb2Bi3 in liquid ammonia. The Sn9− anion shows a capped quadratic antiprismatic structure with a diagonal ratio of d close to one. The open quadrangular face, half of the adjacent triangular faces and one corner are capped by Rb+ cations. The latter form distorted octahedral and trigonal bipyramidal coordination spheres around the hydroxid ions with the hydrogen atom being one corner of the coordination polyhedron. Considering additional contacts to ammonia molecules, layers of [Rb6Sn9(OH)3(NH3)5]− result which are separated n by layers of [Rb([2.2.2]crypt)]+ complexes.

The reductive transformation of carbohydrates and their derivatives can lead to small anionic species as by-products. The treatment of both D-Glucurono-3,6lactone and glucuronic acid with a solution of rubidium in liquid ammonia leads to Rb2O2·RbNO2·3 NH3. Rb2O2·2 NH3 can be additionally obtained from glucuronic acid under identical reaction conditions. These two structures are the first amoniaties that contain alkali metal peroxides. They exhibit a peroxide bond length of 1.5431(19) Å in Rb2O2·RbNO2·3 NH3 and 1.530(11) Å in Rb2O2·2 NH3. This is in accordance with the bond length found by Jansen and Bremm in K2O2 [5] and slightly longer than the bond length reported by Föppl in the alkali peroxides.[6] To the best of our knowledge Na2O2·8 H2O is the only example of a crystal structure of a peroxide solvate.[7]

C60 fullerences can be reduced in liquid ammonia by direct reduction with rubidium. That leads to [Rb2(NH3)9][Rb2([18]crown-6)(NH3)4]C60·2 NH3. For each C4− there are two contacts (3.534(2) Å) 60 to [Rb2(NH3)9]2+ and two contacts (3.499(2) Å) to [Rb2([18]crown-6)(NH3)4]2+ complexes, which lead to the formation of a 3-dimensional network. These ion-ion contacts prohibit disorder in the anionic substructure that can often be observed in fulleride structures.[8]


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