

Poster Presentations

[MS45-P04] 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.[1]

[Cs([18]crown-6)]₄[Sn₄Bi₄]₁₂ NH₃ can be crystallized from solution after dissolving the Zintl phase CsSnBi in liquid ammonia.[2] 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 [3] 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]⁴⁻ 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 [4] *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]ⁿ⁻ 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 ammoniates 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 bondlength 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 fullerenes 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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