

Synthesis of new hybrid hydrides by combination of anionic borohydride and imidazolate ligands: the first member, Li(BH₄)Im

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The family of borohydrides, also named tetrahydroborates has been studied extensively during the past few years. Being seen as a pseudo-chloride anion in the beginning, the tetrahedral BH₄ group is now regarded as a directional bridging ligand, coordinating metals preferably via its edges. This behavior was put into light by the recent discovery of porous gamma phase of Mg(BH₄)₂ [1].

The goal of this project is to extend the family of these porous hydrides by combining borohydrides with another directional bridging ligand: imidazolate ([C₃N₂H₃]⁻). Imidazolates have also been an important subject of interest in the recent years, because of the formation of porous zeolite-like networks with transition metals. However, simple alkali and alkali earth imidazolates have never been reported to this date. This is due to the incomplete coordination sphere of metals in these compounds. In fact the charge balance imposes a ratio of 1 to 2 and 1 to 4 between metals and coordination sites (nitrogen lone pairs of the imidazolate anion) for alkali and alkali-earth respectively, too low to have complete coordination sphere. Alkali and alkali-earth imidazolates are therefore thought to be reactive compounds and good precursors for mixed imidazolate-hydride materials.

Lithium, sodium and potassium imidazolates have been prepared for the first time in our laboratory and characterized by single crystal and powder diffraction. The coordination of imidazolate is highly unusual and the compounds, especially in LiIm. They are highly hygroscopic, that can be considered as a proof of their eagerness to complete the coordination sphere of the metal atoms.

Ball milling LiIm and LiBH₄ leads to the formation of a new compound of which the structure was partially solved from synchrotron radiation powder diffraction data. The compound has an orthorhombic unit cell and space group Imma. The cell parameters are: a = 6.051476, b = 15.099486 and c = 6.537907 Å. All atom positions were refined by the Rietveld method except the hydrogen atoms belonging to the borohydride group. The orientation of the BH₄ group and, therefore, its coordination mode still has to be determined. This information is crucial for further understanding of the coordination behavior of BH₄ group and for the synthesis of other mixed BH₄/Im compounds.

A new sample of the same compound will be prepared using Li¹¹B¹⁰D₄ to measure neutron diffraction. This method will allow precise localization of hydrogen atoms and determination

of coordination mode of the BH₄ group. We therefore apply for access to the PUS instrument at the JEEP II installation. Deuterated lithium imidazolate is unfortunately not available at a reasonable price. The sample will therefore contain 3 hydrogen atoms per formula unit (Li₂[C₃N₂H₃][11BD₄]; 20 mole % of H-atoms). The high background resulting from this will require long acquisition in order to suppress the noise.

[1] Filinchuk Y., Richter B., Jensen T.R., Dmitriev V., Chenryshov D., Hagemann H. Porous and dense Mg(BH₄)₂ frameworks: synthesis, stability and reversible absorption of guest species *Angew. Chem. Int. Ed.* 2011. V. 50. No 47. P. 11162-11166.