Annotation of the research publication series "Structure, thermal stability and decomposition mechanisms of main group element compounds»

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Research publication series (2015-2019) includes works in two scientific areas: the first one is devoted to experimental and theoretical studies of donor-acceptor stabilized compounds of elements of 13-15 groups and the send one concerns amidoboranes of main group metals.

Development of new technologies requires controlled synthesis of materials with desired properties and element composition. Binary and composite materials of main group elements find applications as light emitting diodes, UV photodetectors, transistors, solar batteries and ceramic materials with high chemical and thermal resistance. One of the ways to synthesize such materials for micro and optoelectronics is decomposition of single source precursors (SSP), which contain all the elements in desired chemical composition. Organoelement compounds are often used as SSP, but their use leads to undesired carbon contamination, which downgrades quality of semiconductor materials. In this context, use of hydrogen-containing SSP is very promising, since it allows eliminate carbon contamination. However, hydrogen derivatives of group 13-15 elements are unstable and easily polymerize.

Based on the results of quantum chemical computations, the concept of donor-acceptor stabilization of hydrogen derivatives of group 13-15 elements was proposed, which turned out to be very promising. In collaboration with research group of Honorary professor of SPbSU Manfred Scheer synthetic routes to these compounds have been developed, and structures, volatility and thermal stability of new mixed element hygrogen derivatives of 13-15 group elements were determined. It is shown that after the dissociation of donor molecule upon heating, processes of hydrogen elimination and polymerization take place, which is perspective for the production of inorganic polymers. It is established, that it is possible to turn the formed polymer back into monomeric complex using strong Lewis bases.

On the basis of theoretical studies it is predicted that hydrogen containing compounds of 13-15 group elements can be stabilized by strong Lewis acids. Design principles for the construction of very strong Lewis acids (Lewis superacids) of group 13 elements were developed. It is shown that the principal moment, which can significantly increase Lewis acidity, is the pyramidal surrounding of three-coordinated group 13 element. Our theoretical predictions about strong Lewis acidity of pyramidal group 13 Lewis acids have been recently

experimentally verified (Angew. Chem. Int. Ed. 2020, 59, 12402–12406). Such pyramidal Lewis acids are prospective components of Frustrated Lewis Pairs, which allow to activate small molecules without use of transition metals.

Other important aspect of our research is search for the solid compounds with high hydrogen content. Such compounds can serve as solid hydrogen carriers for hydrogen energetics. One of widely studied compounds – complex of boron hydride with ammonia – ammonia borane H_3NBH_3. However, its thermal decomposition proceeds in two steps and requires elevated temperatures (108-154 ºC) and is accompanied by release of undesired side products (ammonia, borazine). According to literature data, derivatives of ammonia boranes - amidobotanes MNH_2BH_3 (M=Li-K) undergo clear thermal decomposition in one stage at 84 ºC. However, before our works systematic studies of thermal stability of main group metal amidoboranes have been not carried out.

New synthetic approach was developed in or group, which allowed for the first time to synthesize rubidium and cesium amidoboranes. For the systematic experimental study of thermal stability of amidoboranes, an automatic tensimeter was developed and four tensimetry stands were constructed, which allowed carrying out prolonged (months) tensimetry measurements without an operator.

It is demonstrated for the first time that alkali and alkali earth metal amidoboranes $M(NH_2BH_3)_x$ (x=1, M=Li-Cs; x=2, M=Mg-Ba), and complex group 13 metal (Al,Ga,In) amidoboranes are thermally unstable already at room temperature. Thermal decomposition is accompanied by long (weeks) induction period, which is attributed to slow structural rearrangement. Upon temperature increase the induction period shortens. Quantum chemical computations showed that the key step in thermal decomposition of alkali and alkali earth metal amidoboranes is formation of M_3H unit. Therefore, upon modeling of hydrogen evolution it is important to consider at least three amidoborane molecules. Proposed decomposition mechanism agrees with experimental data.

Based on experimental and computational studies in 2015-2019, 45 papers were published in refereed scientific journals indexed in Web of Science (26 in Q1 journals according to SJR) with combined impact-factor 205.168. Two papers are highlighted on the front covers as the best publications in the issue. Results of work were presented at Russian and international conferences (one plenary, 3 invited and 6 oral presentations). Work was supported by RSF and joint SPbSU-DFG grants.