

The chemistry of bivalent samarium in ionic liquids

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Ionic liquids (ILs) are substances that arrested attention in the scientific world during the last 30 years due to many applications in the industry and research, like in biocatalysis, electrochemistry, analytical chemistry or nanotechnology^[6].

The aim of this work was the synthesis and characterization of a new crystal on the basis of bivalent Samarium in ILs. For that, the Samariumdihalogenides reacted with the alkaline earth metal halogenides (CaX_2 , SrX_2 , BaX_2 ; $\text{X} = \text{Br}, \text{Cl}, \text{I}$) The reaction medium was the IL 1-Buthyl-3-methylimidazole (bmimX).

The first step of the experimental part of this project was the synthesis of the bivalent Samariumhalogenids (SmBr_2 , SmCl_2 and SmI_2).

In the following exchange reactions of the alkaline earth metals by Samarium, in only one preparation a crystal was isolated and analyzed: In the ampule that contained SmI_2 and CaI_2 in bmimI, a green crystal was obtained. The new compound had the molecular formula $\text{C}_{48}\text{H}_{90}\text{Ca}_3\text{I}_{12}\text{N}_{12}\text{Sm}_{0,33}$. The compounds crystallized in a trigonal system.

According to their definition, ILs have a melting point below $100\text{ }^\circ\text{C}$ ^[1]. From special interest are ILs which are liquid at room temperature, so called room temperature ionic liquids (RTILs), because of their applications in chemistry as a solvent in synthesis. ILs consist of organic cations and organic or inorganic anions. Chemically regarded, ILs can be considered as salts. The low melting point originates due to the low charge in association with the delocalization of the charge and a low symmetry^[2]. Important cations and anions are depicted in figure 1. Since ILs consist of a combination of anions and cations there are many possibilities to combine both, which implies a change in chemical and physical properties. Properties that can be easily changed are for example the melting point, the solubility, the density or the viscosity. These changes contain a huge possibility for optimizing reaction conditions^[3], which introduced the name "designer solvents"^[4].

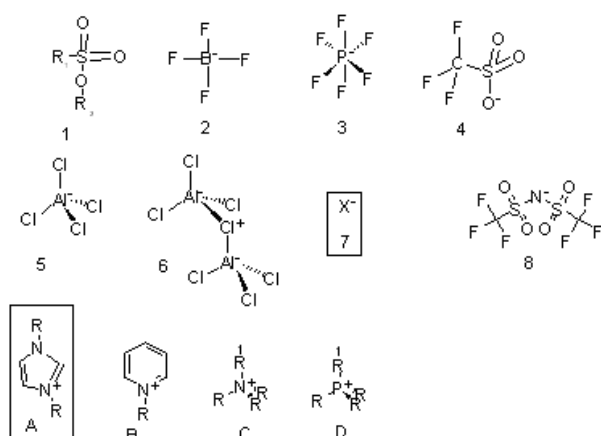


Figure 1. Important anions: 1 (alkyl sulfate), 2 (Tetrafluoroborate), 3 (Hexafluorophosphate), 4 (Trifluoromethylsulfonate), 5 (Tetrachloroaluminate), 6 (Heptachlorodialuminate), 7 (Halide), 8 (Bis(trifluoromethanesulfonyl)imide); important cations: A (Dialkylimidazolium ion), B (Alkylpyridinium ion), C (Tetraalkylammonium ion), D (Tetraalkylphosphate ion).

In this work, the IL Buthylmethylimidazoliumhalide (bmimX) acted as solvent as well as reagent. The used anions and cations are edged in figure 1.

The first target of this project was the synthesis of bivalent Samarium halides (Cl, Br, I). The second aim of the thesis was the substitution of earth alkaline metal halides in the corresponding IL by the corresponding Samarium halide. The earth alkaline metal halides (EAX_2) reacted with the IL to form crystals of the form: $\text{bmim}_6\text{EA}_3\text{X}_{12}$ ($\text{EA} = \text{Ca}, \text{Sr}$ and Ba). These two compounds were chosen, since they have similar properties like Sm^{2+} . These EA^{2+} and Sm^{2+} ions have the same charge and a comparable ionic radius. The $\text{bmim}_6\text{EA}_3\text{X}_{12}$ crystal crystallizes in the space group $\text{R}\bar{3}$. Previous works investigated, that Europium, which crystallizes isotype to Samarium in many compounds, also crystallizes in the space group $\text{R}\bar{3}$ with bmim-halides^[5].

The SmCl_2 and SmBr_2 salts were formed by a comproportionation reaction of elementary Samarium and Sm^{III} ($2\text{SmX}_3 + \text{Sm} \rightarrow 3\text{SmX}_2$)^[6]. The iodine component was synthesized by a reaction of elementary Samarium with HgI_2 in a Duranglas ampule in a stoichiometry of 1:1. The ampule was heated for seven days to $450\text{ }^\circ\text{C}$. The reaction was finished when there was no light orange dye visible and when a precipitation of elementary mercury could be observed. After the mercury was removed, the ampule was heated to $550\text{ }^\circ\text{C}$ for two days, to obtain a homogeneous product^[7]. All bivalent Samarium halides were purified via sublimation and characterized via XRD measurement.

Difficulties appeared since lanthanides prefer the oxidation state of +III and Samarium compounds easily react with smallest amounts of oxygen to Samarium oxides (e.g. SmO , Sm_2O_3). According to this high reactivity, all synthesis concerning Samarium had to be performed under inert conditions. Under argon atmosphere, the Samarium(II)halides and the corresponding earth alkaline halides were given to the corresponding IL in the following stoichiometry:



This mixture was heated to $160\text{ }^\circ\text{C}$ for 48 h and then cooled to room temperature over 72 h.

In only one approach, containing $\text{bmim}_6\text{Ca}_{3-y}\text{Sm}_y\text{I}_{12}$, a green, measureable crystal was obtained.

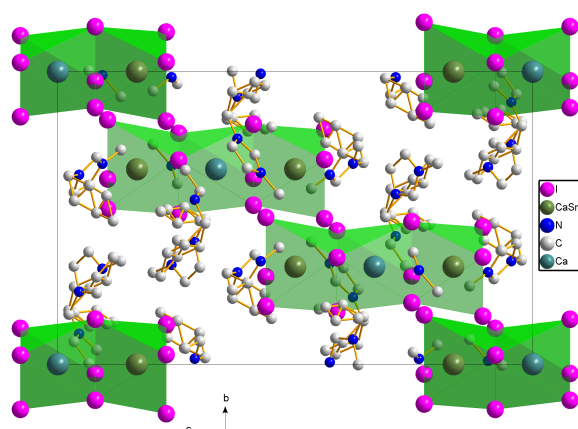


Figure 2. Crystal structure of $\text{bmim}_6\text{Ca}_{3-y}\text{Sm}_y\text{I}_{12}$ with the view direction along the a-axis.

The crystal crystallizes, as expected, in the space group $\text{R}\bar{3}$ with three formula units in the unit cell in a trigonal crystal

system. Figure 2 shows the crystal structure of $\text{bmim}_6\text{Ca}_{3-y}\text{Sm}_y\text{I}_{12}$ with the view direction along the a-axis. The lattice parameters are $a = 17.2950(11) \text{ \AA}$ and $b = 24.6964(16) \text{ \AA}$. The crystal consists of Calcium- and Samarium centers, which are surrounded by six iodine atoms each. Distorted octahedrons are built, which are bridged by two iodine atoms each (see figure 3.).

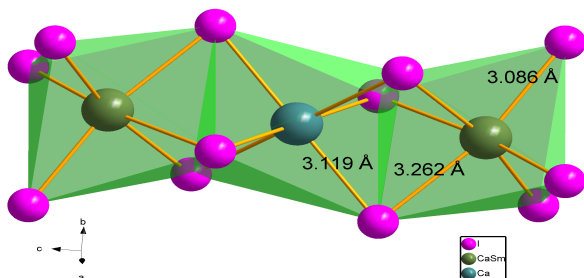


Figure 3. Octahedron structure with bond length between iodine and central atom.

Additionally six 1-Butyl-4-methyl-imidazolium cations coordinate around the metal centers.

The XRD study revealed an exchange rate of 0.5 % of Calcium atoms for Samarium atoms. The analyzed crystal has a molar mass of 2528.48 g/mol and a density of 1.96879 g/cm³.

Conclusively it was reached to obtain one crystal with the above described properties. In this crystal 0.5 % of Calcium atoms were changed against Samarium which is not a significantly high exchange rate. In all other approaches, no measureable crystal could be obtained. For having better results concerning exchange rate and for obtaining more crystals, the ratio of the stoichiometry in the ampoules and the reaction conditions (e.g. longer time of cooling to room temperature) can be changed.

Further research is necessary to prove these influences to the crystal growth and exchange reactions to obtain a convincing view with comparable data.

[1] A. Große Böwing, A. Jess, P. Wasserscheid, *Chemie Ingenieur Technik* **2005**, 77, No. 9.

[2] J. D. Holbrey, K.R. Seddon, *Ionic Liquids*, Clean Production Process. **1999**, 1, 223.

[3] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, 116, 5096-5100.

[4] *Chem. Eng. News*, **1998**, 76(13), pp 32-37.

[5] Grasmik, Viktoria, *Chemie der zweiwertigen Lanthanoide und Erdalkalometalle in ionischen Flüssigkeiten*, **2012**.

[6] M.D. Taylor, C. P. Carter, *J. inorg. nucl. Chem.* **1962**, 24, 387.

[7] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Zweiter Band, 1078-1084.

[8] P. Wasserscheid, T. Welton: Wiley-VCH, Weinheim, **2003**.