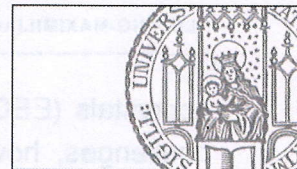


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Review Report

for the PhD thesis

Achieving Balanced Cocrystals of Energetic Materials via Coagglomeration and their Applications

submitted by Mr. **Veerabhadragouda B. Patil, M. Sc.**

Although being discussed controversially in the society, energetic materials are essential for civil use as well as for military applications. The search for new energetic materials, combining high performance with safe handling, cheap synthesis and high environmental compatibility represents a hot topic in the internationally highly competitive field of energetic materials science. The present PhD thesis submitted by Mr. Veerabhadragouda B. Patil is located in this intriguing and challenging area of chemistry. In his thesis Mr. Patil impressively shows how new combined energetic materials with interesting and useful properties can be prepared simply by applying coagglomeration synthetic methods starting from well known and currently used energetic molecules.

The concept, on which the thesis of Mr. Patil is based, is to my opinion strong and opens a new way of approaching energetic materials with tailored properties. The literature describes a nearly endless number of energetic molecules with excellent energetic performance; most of them are too sensitive, however, to allow for a practical application. Instead of looking for new, less sensitive compounds and possibly facing difficult and expensive syntheses, the combination of known energetic molecules with other less sensitive in one crystalline material would lead, much easier, to less sensitive but still well performing substances. A further development of this concept is the idea to combine two energetic molecules, preferably two molecules, which are currently in use, to one crystalline material, which is more stable and easier to handle as its components, which however does not lose the energetic properties of its components and even can perform better than the single components. Such materials, called energetic-energetic

cocrystals (EECC), would fulfill all requirements discussed before; they introduce new challenges, however, touching the problems of interaction between the components leading to crystallization and further of crystal engineering allowing for tunable and reproducible cocrystal size, shape and density. Topic of the thesis of Mr. Patil and scope of his investigations was to optimize and modify existing methods as well as to develop and probe new methods for the production of EECCs, which would possibly overcome issues of sensitivity, scalability and reproducibility. Mr. Patil has accepted this really great challenge and presents in his thesis important results, which open the doors for further systematic studies.

The thesis of Mr. Patil starts with a nice introduction into the research background, the advantages and the problems connected with the synthesis of cocrystals. This introduction is followed by a detailed description of the materials and methods used, including the preparation methods and the analyses of the energetic materials. Both these parts are well written and describe very clearly the topic.

In the main part of the thesis Mr. Patil describes his results on the synthesis of new energetic materials by combination of known energetic molecules. To avoid the problems, connected with the formation of real cocrystals, in which there is an ordered distribution of the components in the solid, Mr. Patil applies the straight forward technique of coagglomeration. According to this technique agglomerates of crystals of the single components are formed with the macroscopic material displaying the properties of a *de-facto* cocrystal. Coagglomeration is much easier to perform and upscaling techniques are available.

In a first part of the PhD studies Mr. Patil investigated coagglomerated crystals of TATB and DATB with selected cyclic nitramines (BCHMX and RDX). The basic idea was an attractive interaction between the components by hydrogen bonding to facilitate the formation of cocrystals. In fact, Mr. Patil was able to prove the formation of coagglomerated crystals (CACs) between TATB and RDX, HMX, BCHMX and ϵ -CL-20 by PXRD, FTIR and Raman spectroscopy. In the materials obtained, HMX was present in the δ -form and CL-20 in the β -form. In the case of DATB the densities of the obtained materials were about 99% of the theoretical density of the mixed crystal. For TATB the densities were higher than those of the pure nitramines. The detonation parameters of the DATB and TATB cocrystals resulted to be lower than those of the starting nitramines, as expected. The detonation energies of the mixed crystals proved to be higher than the energies, expected from the respective percentage of the components.

Very interesting are from my point of view the results described by Mr. Patil on the formation of coagglomerated crystals between CL-20 and BCHMX. While cocrystallization of the two components is really difficult, coprecipitation of the two nitramines followed by an agglomeration in *n*-butanol results finally in the formation of a coagglomerated microcrystalline material. For the successful formation of this material the agglomeration medium and the molar ratio of the compounds proved to be of essential importance. The cocrystals with CL-20 displayed a significantly lower impact sensitivity as compared to that of pure CL-20. PXRD experiments showed, CL-20 to be

present as its β -modification. Combined IR/Raman and XPS investigations indicated the presence of strong hydrogen bonding in the crystalline materials.

In the hands of Mr. Patil, the coagglomeration strategy proved to be the right one. He was also able to prepare and investigate coagglomerated crystals of HNS and HNAB with selected nitramines (RDX, HMX, BCHMX and CL-20). The synthesis involves the coprecipitation of HNS or HNAB with the corresponding nitramine applying solvent/antisolvent techniques, followed by coagglomeration in *n*-butanol or CHCl_3 . The coagglomerates with HNS turned out to be finer-grained than those with HNAB. The CACs HNS/RDX, HNAB/RDX and HNAB/BCHMX showed a higher impact resistance than that of the pure components. For CL-20 the combination with HNS and HNAB resulted destabilizing, however. The detonation parameters of the CACs containing HNS and HNAB were lower than those of the pure nitramines, while the detonation energies of the cocrystals were higher than the expected energies based on the percentage of the components. Interestingly this difference resulted higher than the corresponding difference for the analogous CACs with DATB and TATB. A relationship between the detonation velocities of the CACs and their crystal densities confirmed the presence of CL-20 as its β -form.

Mr. Patil investigated also the formation of composite microparticles of electrically conductive polyaniline with selected nitramines (RDX, HMX, BCHMX and CL-20). The synthesis proceeded by coprecipitation from a mixed solution of the components, followed by coagglomeration of the resulting coprecipitates. The formation of the composite particles is based essentially on the building of charge-transfer complexes, which explains the lower thermal stability of the composites as compared to that of the starting nitramines. PXRD experiments showed clearly, that the preparation of the composite particles was accompanied by a change of the polymorph modifications of the components: for CL-20 from ϵ to β form and for HMX from β to α form. Interestingly FESEM images showed the presence of superficially coated nitramine crystals with rounded crystal edges, which changed the impact sensitivity of HMX, present in its α -form, to 6.4 J. As a comparison, pure α -HMX is highly impact sensitive (1.9 J). On the whole, the polyaniline composites prepared by Mr. Patil display interesting sensitivity characteristics and together with the easy preparation might be considered as possible initiator components for various charges.

Mr. Patil was also able to prepare coagglomerated crystals of selected cyclic nitramines (RDX, HMX, BCHMX) with the nitrogen rich compound BTATZ. The synthesis involves the coprecipitation of the respective nitramine and BTATZ by solvent/antisolvent technique and subsequent coagglomeration in CHCl_3 using different stirrers: a linear stirrer and a cross-stirrer. Remarkably, the approach with the cross-stirrer yielded better crystal morphology, better surface quality and higher density of the coagglomerates. The CACs obtained displayed a slightly reduced thermal stability as compared to that of the pure nitramines. An exception were the RDX based CACs, which decomposed. Based on PXRD, FTIR and Raman investigations, Mr. Patil established the order for matching between the structure of BTATZ and the structure of the nitramines to be $\text{RDX} < \text{HMX} < \text{BCHMX} < \text{CL-20}$. The spatial compatibility between the components has an essential

influence on the intermolecular interactions (π,π -stacking and H-bonding), which influences the impact sensitivity and the crystal density.


An important part of the thesis of Mr. Patil is represented by studies oriented towards a possible application of the new energetic materials. Thus, HMX/BCHMX cocrystals might be of interest for composite rocket propellants, CL-20/BCHMX cocrystals might be used in detonators and RDX/BCHMX cocrystals might be candidates for components in gun powder. Of course, the way from a laboratory synthesis and characterization to a practical application (implying industrial production) is long and uncertain; the availability of the materials and their energetic properties, presented in the thesis of Mr. Patil, represents a first step and stimulates further activity in this direction.

Reading the thesis of Mr. Patil, one gets the impression, that he has worked on his thesis with great interest and enthusiasm. He has performed the syntheses of the energetic materials demonstrating very good experimental skills. For the characterization of the energetic crystalline coagglomerates he has elegantly used modern analytical techniques.

The thesis of Mr. Patil is logically structured, the results are described in detail, the relevant literature is adequately cited. A part of his excellent results has been published in eight papers in high level international peer reviewed journals. Five more manuscripts are in preparation or have been submitted and are in process of reviewing. Mr. Patil has also shown his expertise in five posters and three oral presentations at important international conferences.

Summarizing, the PhD thesis submitted by Mr. Veerabhadragouda B. Patil meets all formal, linguistic and scientific standards required for a high-level PhD thesis. I strongly recommend to accept the dissertation submitted by Mr. Patil for defense.

Munich, May 26th, 2024



Professor Dr. Konstantin Karaghiosoff

