Prof. Gozin

It was a pleasure to read and evaluate the Ph.D. thesis entitled "**Achieving Balanced Cocrystals of Energetic Materials via Co-agglomeration and Their Applications**", written by Mr. Veerabhadragouda B. Patil. I should state that the scope, amount, and quality of the research work described in this thesis are very high, reflected by the number and level of publications emanating from this thesis. As a frequent reviewer of many manuscripts in this field, as well as many Ph.D. theses from my and other universities, this thesis is impressive, much all required criteria of innovation, understanding of the state-of-the-art in the field, and research depth, and as such, should be accepted by the University of Pardubice.

The central theme of this thesis is to achieve improved stability and energetic properties of nitramines, which are a recurring functional group in many explosives, including RDX, HMX, and CL-20. Despite their widespread use, most nitramine-based explosives are sensitive to friction and mechanical impact *stimuli*. Thus, the safe handling of these materials remains a significant challenge. High-energy materials with other functional groups and consequent reduced sensitivity have been explored to address these issues. However, in most cases, the energetic properties like heat of formation, detonation velocity, and detonation pressure are not as attractive as nitramine-based explosives.

The preparation, solid-state structure, and properties evaluation of co-crystals of two different molecules is a highly active and productive area of research in energetic materials, pharmaceuticals, agro-chemicals, and several other fields. Typically, the combination of two different energetic materials often gives rise to improved energetic properties compared to their parent materials. This change could be attributed to the changes in packing arrangements of these molecules in their crystal lattice, which has a significant effect on detonation properties and on materials' stability. Although energetic co-crystal formation with nitramines has been explored before, till now, there is a lack of general guidelines and scalable and reliable protocols for preparing these co-crystals. In this thesis, a clever approach to preparing co-crystals resulted in materials that showed improved stability versus their parent of nitramines. For this purpose, various insensitive energetic materials like DATB, TATB, HNS, and BTATz were combined with energetic nitramines like RDX, CL-20, HMX, and BCHMX.

In Chapter 1, Mr. Patil provides a general introduction to the topic of energetic co-crystals, describing the different techniques for co-crystal formation and the most recent achievements in this competitive field. Chapter 2 provides a detailed description of these materials and the methods used for their preparation. It is important to mention that the energetic co-agglomerated crystals (CACs), described in this thesis, were extensively characterized using various techniques like powder XRD, IR, and Raman spectroscopies. Mr. Patil also explained in detail the changes observed in the spectra of the obtained co-crystals compared to their parent materials, providing a sound and impressive theoretical explanation for these changes. Finally, Mr. Patil also gives an account of all the experimental and theoretical techniques used to evaluate the energetic properties of these materials.

Chapter 3 has five different sections, each dealing with an additive that was used to form the co-crystals with the energetic nitramine derivatives. These include DATB and TATB in Chapter 3.1, BCHMX in Chapter 3.2, HNS and in Chapter 3.3, polyaniline derivative (PANi) in Chapter 3.4, and BTATz in Chapter 3.5. A general trend observed in all cases was a significant reduction in the sensitivity of all co-agglomerated crystals compared to the parental energetic materials. Mr. Patil explained these observations nicely by discussing the spatial arrangement in the crystal lattice. Additionally, all the polymorphisms observed in the case of materials like CL-20 and HMX were adequately characterized by using techniques such as DSC-TGA, as well as IR and Raman spectroscopies. However, there was a certain drawback regarding the formation of all explored co-crystals, as there was a slight reduction in the decomposition temperature, as compared to the parent materials. More specifically, the exothermic peaks observed in DSC were shifted to slightly lower temperatures.

In Chapter 4, the potential applications of the prepared CACs were discussed in detail. For this purpose, the CACs derived from HMX/BCHMX and CL-20/BCHMX combination were tested as potential solid oxidizers for propellant systems, and the results were impressive. The futuristic applications of other CACs as components in ammunition and detonation charges were also discussed in this chapter.

After evaluating this thesis, I found some minor issues that should be corrected.

1) In general, I think the writing of the thesis can be improved. Sometimes, the writing was not sufficiently clear to convey the message that the writer intended to deliver, not allowing a reader to easily follow the scientific rationale.

2) On page 42, the weight of the samples utilized for DTA analysis is written as 0.05 g (50 mg). This seems very high, especially for energetic compounds. This information should be checked and verified.

3) On page 50, it is reported that for the preparation of nitrocellulose GRADE C Type I gunpowder, it was phlegmatized with 30% alcohol. Which alcohol was used for this purpose?

4) For forming the CACs, is there any specific reason for choosing a 1:4 weight ratio between co-formers and nitramines?

5) The compound numbers should be included in parentheses throughout the thesis. For example, (32) HMX-TATB and so on.

6) On page 67, Mr. Patil writes that the use of TATB, as an additive to form CACs with cyclic nitramines, is much more advantageous in comparison to DATB. However, in the Conclusion section of the same chapter, it is mentioned that DATB gives "much finer" properties than TATB. In my opinion, these two statements are contradictory and confusing. From the physiochemical data, it is obvious that TATB should be the favored additive.

7) On Page 79, the typo, ;thus this this work…' should be corrected.

8) On Page 79, Section 3.2.2 , Mr. Patil observed that the nature of the solvent has a marked effect on the nature of the co-agglomeration of crystals. This was evident when switching the solvent from ethyl acetate to ethyl formate. Did Mr. Patil consider conducting similar experiments in which the n-heptane anti-solvent is replaced with another anti-solvent? For example, replacing n-heptane with hexane or pentane?

9) While epsilon is the best-performing polymorph of CL-20 in its pure form, it is observed that during co-crystal formation, beta-CL-20 is the preferred polymorph in most cases. Are there any plausible explanations for these phenomena?

10) For clarity and convenience, I propose that the properties of all the synthesized CACs in this thesis could be presented in a tabular form. For instance, if CL-20 is taken as the base material, the effect of additives like DATB, TATB, BCHMX, PANi, and BTATz should be presented. If possible, the best-performing material should be highlighted. A similar comparison could be made with other materials, like RDX and HMX.

The results described in this Ph.D. thesis create a valuable and promising approach that has great potential to be used in future applications. The scientific content of this thesis is excellent. In addition to selecting important goals for investigation, Mr. Patil demonstrated a very high level of expertise and a deep understanding of science and technology in his research field. He showed an excellent knowledge of molecular design and a comprehensive understanding of related analytical techniques and their results. In light of the presented research's quality and scope, this work should be accepted as a Ph.D. thesis after correcting the above-mentioned comments.