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REVIEW

of Mgr inż. Judyta Rećko's dissertation titled

**“Otryzmowanie i badanie koordynacyjnych związków wybuchowych
zawierających 4,4',5,5'-tetranitro-1H,1H'-2,2'-biiimidazol”**

done at Faculty of Advanced Technologies and Chemistry,
Military University of Technology, Warsaw

Submitted dissertation is focused on preparation and study of the new explosives based on coordination compounds of cations of the selected metals and anion of 4,4',5,5'-tetranitro-1H,1H'-2,2'-biiimidazole (TNBI) and subsequent verification of two from them in multicomponent rocket propellants. Dissertation is sectioned into Introduction and eight Chapters.

In the List of abbreviations, which precedes the Introduction, the author gives chemical names of the substances used, but in the case of RDX, HMX and PETN she gives only technical names instead of the IUPAC terminology; correctly thus should be there 1,3,5-trinitro-1,3,5-triazinane, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane and 2,2-bis [(nitrooxy) methyl] propane-1,3-diol dinitrate.

Introduction – here the author briefly characterizes the reasons for the search and development of new energetic materials, especially with a high nitrogen content. In this connection author makes a note on the energetic polymers and energetic complexes with metal cations as the central atom

The first Chapter presents basic information about the coordination compounds, their division and types. Both theories about the nature of interactions between ligands and the central ions are mentioned, i.e. Crystalline field theory and Ligands field theory.

The second Chapter is very extensive (43 pages) and very well written. It presents a literature search of the energetic coordination materials based on ammonia, hydrazine, carbohydrazide, aliphatic amines, urea, guanidine, but mainly on azaaromatic substances. In the case of cobalt complexes of the tetrazole derivatives, I would like to mention two of my practical experiences here. One is from the production of detonators for the high temperature and pressure environments at the Schlumberger Co. in Rosharon, Texas, where (5-cyano-1H-tetrazolo)pentaaminocobalt (III) diperchlorate was originally used, but due to its toxicity, it was replaced by an analogue, based on 5-chloro-1H-tetrazole. And the second one concerns BNCP, which exploded to us while mixing on its suspension in pure water on an electromagnetic stirrer (*the reason was not found*). The conclusion reached by the author from this

chapter has a much broader significance for further research in this area than is the assignment of this submitted dissertation.

The third Chapter – here the methods are given and briefly described which were used to characterize of the prepared samples. The author effectively used all the testing possibilities that her workplace could provide. Here I would like to make one comment on the method used: in the case of determining the sensitivity to an electric spark, the device is not specified, but according to the description of the embodiment it resembles the LANL methodology (*Larson TE et al : Electrostatic sensitivity testing of explosives in Los Alamos, in: Inst. Phys. Conf. Ser. No. 118: Section 2 {Electrostatic '91} IOP Publishing Ltd., 1991, 107-117*). This method corresponds to a measurement using a spark gap, where the discharge passes through an air gap, and a considerable part of the electrical energy is consumed to heat the surroundings and it is thus, therefore, more or less a thermal decomposition of the sample. We compared this method with the one, in which the discharge passes in the sample (electrodes touch the sample) and we obtained results which were different in several orders of magnitude (*in the second case they were in mJ – a comparison of both these approaches is published in CEJEM 2006, 3 (3), 27-44.*). The second approach is a part of the Czech Defense Standard No. ČOS137601 (a part of STANAG).

The fourth Chapter shortly treats about purpose and scope of work. The main goal of this dissertation was to design and obtain new coordinating compounds containing metal cations and anion of the 4,4',5,5'-tetranitro-1H,1H'-2,2'-biiimidazole (TNBI) and subsequently specification of their physicochemical and explosive properties, including testing of them as components of the rocket propellants.

The fifth Chapter deals with preparation of the TNBI complexes of copper, zinc, nickel, cadmium and cobalt. For characterization of these complexes, the author used elemental analysis, IR and NMR spectroscopies, DTA and TG and photographic documentation of crystals. In the case of the copper complex, the author presents the results of the Koenan's test and in Table 23 also its explosive characteristics. Based on the results of the prepared complexes characterization, the author has selected for further explosive testing the copper and zinc complexes of TNBI. I consider the results obtained here to be an important contribution to the knowledge about the metallic complexes with the energetic ligands in general.

Q1: TNBI was prepared by nitration of biimidazole in phosphoric acid in the presence of phosphorus pentoxide. Have you considered how to process of the waste nitration mixture? Nitration in sulfuric acid in the presence of oleum is probably unacceptable due to the aggressiveness of the nitration mixture, isn't it? You did not try to use this approach, did you?

The sixth Chapter deals with the extended investigation of explosion properties of the copper and zinc complexes of TNBI (CuTNO and ZnTNO). With the exception of determining the detonation rate, other tests are focused on the TNBI copper complex, better on its stampings with 8% Viton A. This is

a determination of brisance (*comparison with results for TNT, PETN and RDX*) and a cylinder test, monitored by X-rays (*comparison with TNT*): while both the brisance and the detonation rate of the CuTNO/Viton A mixture is close to those values of TNT, the Guerny energy values differ much from each other (*the author rightly justifies the lower value for CuTNO/Viton by the presence of solid copper compounds in its detonation products*).

The seventh Chapter represents examination of the possibility using of the copper and zinc complexes of TNBI as substituents of RDX in the heterogenous rocket propellants of the HTPB/AP/Al type. In this chapter, the author verified the compatibility of CuTNO and ZnTNO with ammonium perchlorate using differential thermal analysis, and prepared 12 samples of the rocket fuel, two of which were the reference ones. For these samples she measured characteristics of their burning. The author explains the influence of CuTNO and ZnTNO on the burning of the propellant, as well as very goodly explains also the mutual difference between the effects of CuTNO and ZnTNO on this burning. Here I would afford to object the location of the burning rate equation in the text on page 91 (*above Table 33*); this equation should be placed outside the coherent text (*for a better clarity*) and with numbering, as it is common in the literature.

The eighth Chapter is a summary of the results obtained together with conclusions. The results show that the initiation reactivity of the prepared complexes is higher than that of TNBI alone and the copper salt exceeds the ZnTNO reactivity. All these facts were very well explained by the author both in the corresponding Chapters and in the conclusion of the whole work.

Q2: *All prepared complexes contain complexly bound water in the molecule. However, no water leaks ("drying") are recorded on the thermograms of both the CuTNO and ZnTNO while from the TG records of the Cd, Ni and Co complexes these leaks are possible to deduce. What does the author think about it?*

Overall impression: the work is written clearly, with a logical division, it reads itself well. From the whole text it is possible to feel the vocational approach of author to the given problem is feels.

Publication activity: in the SciFinder database it was possible to find a total of 12 papers to July 18th, on which Mgr inž. Judyta Rečko is a co-author, 6 of which were presented at the international seminars NTREM in the Czech Republic, 2 are published in reviewed journals and 4 in impacted journals. The Scopus database presents 5 works on which she is a co-author, they are cited 9 times (*without self-citations, her h-index = 2*). Topics of all her publications, with one exception, are compatible with topic of her dissertation.

Taking into consideration quality of the Mgr inž. Judyta Rečko dissertation and the results and level of her publication activity I recommend her dissertation for defence.

Pardubice, July 18th, 2020

