

## MS37- Mechanochemistry: structure and reaction

Chairs: Dr. Hamish Yeung, Dr. Tomislav Frisci

### MS37-P01

#### Photoinitiated solid-state [2+2] cycloaddition reaction in $[\text{Zn}_2(\text{H}_2\text{O})_2(2\text{-Amal})_2(\text{bpe})]$ (2-Amal = 2-Allylmalonate) crystal

Alexander Volodin<sup>1</sup>, Alexander Korlyukov<sup>1</sup>, Anna Vologzhanina<sup>1</sup>, Ekaterina Zorina-Tikhonova<sup>2</sup>, Aleksandr Chistyakov<sup>2</sup>, Aleksei Sidorov<sup>2</sup>, Igor Eremenko<sup>1,2</sup>

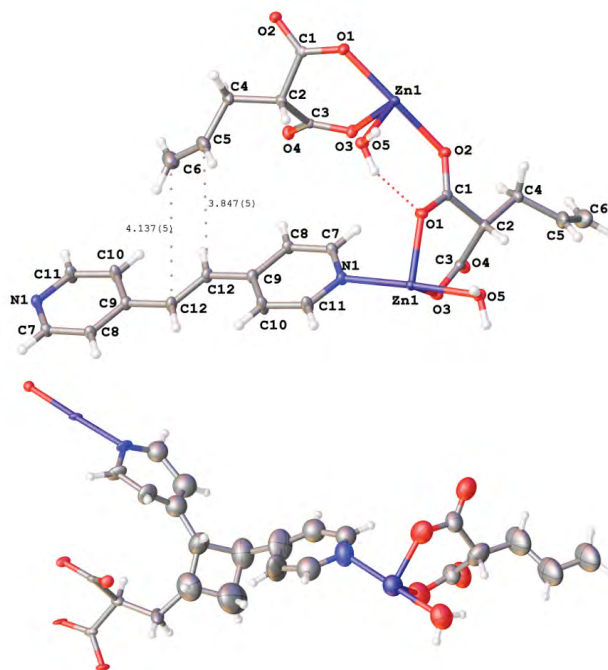
1. A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
2. Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia

email: [alex.d.volodin@gmail.com](mailto:alex.d.volodin@gmail.com)

Recently some of us demonstrated that a number of zinc(II) malonates containing 1,2-bis(pyridin-4-yl)ethylene undergo a photoinitiated [2+2] cycloaddition reaction in a single-crystal-to-single-crystal manner [1]. Here, we present the results of our study of a novel photo-sensitive zinc(II) coordination complex containing two unsaturated fragments, namely, 1,2-bis(pyridin-4-yl)ethylene (bpe) and 2-allylmalonate (2-Amal). This complex was obtained from aqueous solution of zinc(II) acetate, 2-allylmalonic acid ( $\text{H}_2\text{Amal}$ ) and 1,2-bis(pyridin-4-yl)ethylene (bpe). Ethylene fragments of 2-allylmalonate and bpe are in the reactive positions (Figure, top). At irradiation for 8 hours the complex underwent [2+2] cycloaddition in a single-crystal-to-single-crystal manner to form a 2-((2,3-di(pyridin-4-yl)cyclobutyl)methyl)malonate (Figure, bottom). As both compounds are 3D coordination polymers, the process is the 3D  $\rightarrow$  3D reaction. The conversion rate was 50% in respect to 2-Amal. Further irradiation was accompanied by destruction of the single crystal and formation of an insoluble reaction product.

Figure. Fragment of molecular packing of  $[\text{Zn}_2(\text{H}_2\text{O})_2(2\text{-Amal})_2(\text{bpe})]$  (top), and its photoreaction product (bottom).

This work was supported by the Russian Science Foundation (grant No. 17-13-01442) and the Russian Foundation for Basic Research (grant No. 16-33-60179).



#### References:

- [1] E.N.Zorina-Tikhonova, A.S.Chistyakov, M.A.Kiskin, A.S.Sidorov, P.V.Dorovatovskii, Ya.V.Zubavichus, E.D.Voronova, I.A.Godovikov, A.A.Korlyukov, I.L.Eremenko, A.V.Vologzhanina (2018). IUCrJ 5, in press. DOI: <https://doi.org/10.1107/S2052252518001641>.

**Keywords:** solid-state reaction, [2+2] cycloaddition, photoinitiated reaction