

MS32-P01 | IN SITU PXRD MONITORING THE MECHANOSYNTHESIS OF METAL-ORGANIC HALOGEN-BONDED COCRYSTALS

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In the last decade, in situ powder X-ray diffraction (PXRD) monitoring of mechanochemical reactions has become a prominent technique for studying the course and mechanisms of organic and metal-organic solid formation [1]. Following our previous study on mechanochemical syntheses of metal-organic halogen-bonded cocrystals [2], in this work we have investigated mechanochemical synthesis of cocrystals containing $\text{CoCl}_2\text{bzpy}_2$ (bzpy = 2-benzoylpyridine) and a halogen bond donor, 1,4-diiidotetrafluorobenzene (14tfib), by in situ PXRD. First, we performed experiments in solution, and have unexpectedly obtained three different products: two cocrystals with different metal-organic unit isomers, $\text{trans}-(\text{CoCl}_2\text{bzpy}_2)(14\text{tfib})_2$ and $\text{cis}-(\text{CoCl}_2\text{bzpy}_2)(14\text{tfib})_2$, and a cocrystal of 1:1 stoichiometry, $\text{cis}-(\text{CoCl}_2\text{bzpy}_2)(14\text{tfib})$. In order to determine whether single phases could be prepared, mechanochemical synthesis of obtained cocrystals was studied by in situ PXRD using synchrotron X-ray radiation. Three different liquid-assisted grinding experiments were monitored: grinding of $\text{CoCl}_2\text{bzpy}_2$ and 14tfib in the 1:2 molar ratio, one-pot grinding of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, bzpy and 14tfib in the 1:2:2 molar ratio and grinding of $\text{CoCl}_2\text{bzpy}_2$ and 14tfib in the 1:1 molar ratio. All three monitored reactions revealed presence of a cocrystal with cis isomer as an intermediate and fast conversions to a final, thermodynamically more stable product, $\text{trans}-(\text{CoCl}_2\text{bzpy}_2)(14\text{tfib})_2$, in less than 10 min. Single crystal X-ray diffraction experiments reveal that dominant supramolecular interactions in all obtained solids are $\text{I} \cdots \text{Cl}$ halogen bonds. In the trans- cocrystal halogen bonds form 2D networks while in cis- cocrystals 1D chains are formed.

[1] T. Friščić et al., *Nat. Chem.*, 2013, **5**, 66.

[2] K. Lisac and D. Cinčić, *CrystEngComm.*, 2018, **20**, 5955.