The application of thermal analysis in the study of single-crystal-to-single-crystal transformation

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Coordination polymers (CPs), which retain their crystallinity in the exchange reactions with the anion or cation guests or in substitution reactions at the metal centre by the single-crystal-to-single-crystal (SC-SC) transformation, represent a new class of materials and can be considered as molecular containers. Such transformation are important for heterogeneous catalysis and can be used to obtain improved gas adsorption systems. Among the thermally induced SC-SC transformations reported to date, most are based on guest molecule exchange in porous CPs networks or in metal-organic frameworks.

The reaction of $Co(CH_3COO)_2 \cdot 4H_2O$ with H_2bdc and S-nia in a solvent mixture of CH_3OH, dmf, and H_2O resulted in pink block-shaped crystals with the composition $\{[Co_2(\mu_2\text{-}OH_2)(bdc)_2(S\text{-}nia)_2(H_2O)(dmf)] \cdot 2dmf \cdot H_2O\}_n$ (**1**). By heating in vacuum at 105 °C for 4 hours compound **1** was transformed into the desolvated compound $[Co_2(bdc)_2(S\text{-}nia)_2]_n$ (**2**) (where H_2bdc=1,4-benzenedicarboxylic acid and S-nia=thionicotinamide). The SC-SC transformation is accompanied by a pink to dark blue colour change. This transformation involves a change in the coordination environment of Co(II) and the replacement of solvent molecules with less volatile ligand molecules.

Thermal analysis of compound **1** has allowed the study of the sequencing of solvent removal processes with the formation of compound **2** and the determination of the temperature range in which it retains its structure (fig). Thus, the compound **1** initially loses a lattice water molecule (35-77 °C) followed by the removal of one coordinated water molecule and three dmf molecules (77-170 °C), the latest water molecule is lost in the range of 170-180 °C. Immediately after it, the thermal degradation of the S-nia ligand begins, thus representing the maximum thermal stability step of compound **2**.

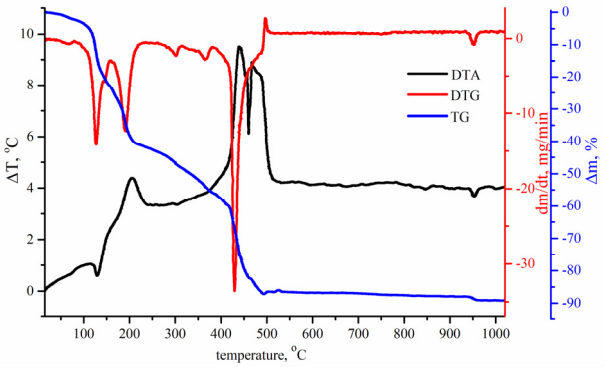

Figure. TG/DTG/DTA patterns of **1**

This study indicates that vacuuming allows the displacing of desorption temperature of the studied coordination compounds with 70 °C and keeping of the crystalline structure of the intermediate compound. The thermal analysis has indicated that at higher temperatures degradation of the newly formed compound begins immediately after the solvent molecules are eliminated, making it impossible to obtain the intermediate compound at the normal pressure.

Acknowledgement. D.C. & L.C. thank Grant for Young Scientists (16.80012.02.05F) for financial support.