THERMALLY GUIDED DEHYDRATION OF BINUCLEAR $[Ni_2(en)_2(H_2O)_6(pyr)]\cdot 4H_2O$ COMPLEX: A FURTHER INSIGHT

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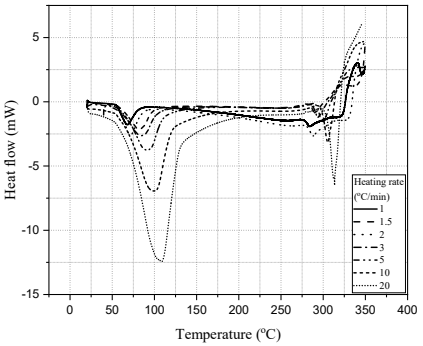
Experimental

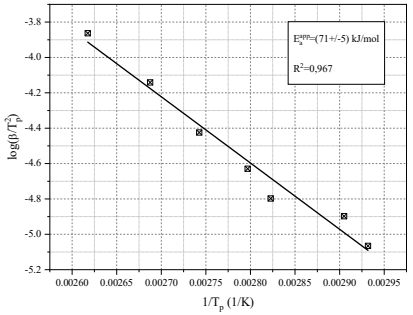
The $[Ni_2(en)_2(H_2O)_6(pyr)]\cdot 4H_2O$ complex was synthesized at the University of Belgrade Faculty of Technology and Metallurgy under the guidance of D. Poleti *et al*, who subsequently performed its structural characterization [8]. The complex was obtained via precipitation from a dilute aqueous solution of $[Ni(en)]^{2+}$ and pyr ions. Crystals of the complex were grown by recrystallization of the solution.

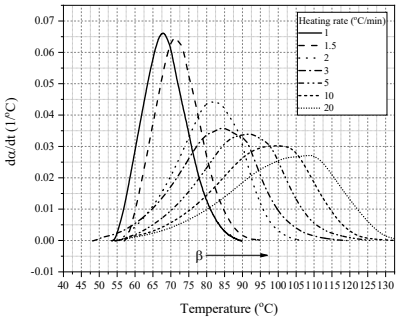
Thermal investigation was realized on TGA Q500 V6.3 Build 189 (TA Instruments) [9, 10] in the temperature region ranging from 25 °C to 350 °C, with preprogrammed heating rates (β) of 1 °C/min, 1.5 °C/min, 2 °C/min, 3 °C/min, 5 °C/min, 10 °C/min and 20 °C/min. Inside of the apparatus, a 10.3 mg sample was placed in a platinum dish and the measurements were conducted under a dynamic atmosphere of nitrogen with a fixed 50 ml/min flow.

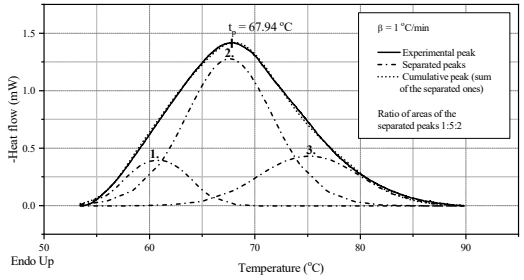
Values of the apparent activation energy (E^{app}) of the observed dehydration process were determined by using Kissinger's well-known relation $log(\beta/t^2)=f(1/t)$ [11] and the isoconversional Kissinger-Akahira-Sunose (KAS) method [12, 13]. Most probable kinetic model was suggested by Dollimore's analysis [14] of the experimental DSC peak, based on parameterization of its shape and asymmetry. In pursue of elementary steps, i.e. single step reactions of the dehydration, change of the dehydration mechanism with the change of the heating regime was tracked by deconvoluting the DSC peak acquired on different heating rates. Deconvolution itself was performed using appropriate software solutions [15, 16] by employing Gaussian-Lorentzian mixed function [17]. Before deconvolution, experimental noise was reduced using Savitzky-Golay method [18]. Invariant activation energy and Arrhenius pre-exponential factor were determined using the linear compensation effect [19, 20].

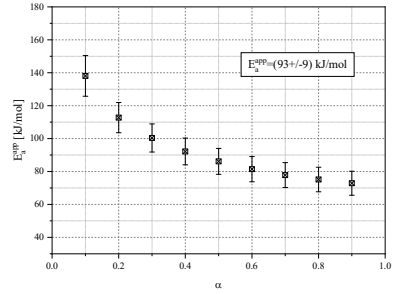
Results

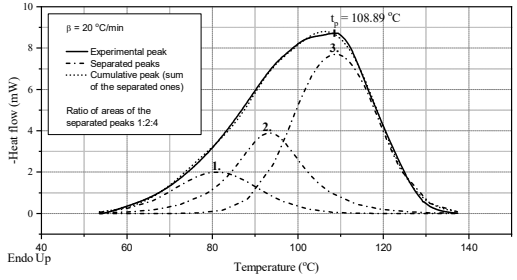


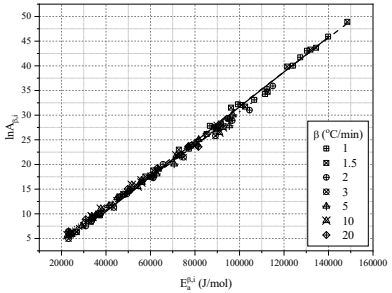












Conclusion

The coordination polymer $[Ni_2(en)_2(H_2O)_6(pyr)]\cdot 4H_2O$ is thermally stable up to about 50 °C, when gradual degradation begins. In the first stage of thermal degradation, the complex completely dehydrates losing its 10 water molecules (26.8% of its mass). The DSC peak moves towards higher temperatures with the increasing heating rate implaying that the process is thermally activated. The peak changes its shape as well, which is attributed to a change in the mechanism of the dehydration. The dehydration is endothermal and the sample further loses 21.9% of its mass in the temperature region of about 275 °C to 325 °C, corresponding to CO and both *en* groups leaving the structure. $C_8H_2O_4$ probably leaves the structure as well, during the third and final step.

Via Kissinger's method we obtained the value of the apparent activation energy of (71±5) kJ/mol and (84±3) kJ/mol excluding the data that correspond to heating rates of 1 °C, 1.5 °C and 2 °C. KAS isoconversional method gave an average value of (93±9) kJ/mol. Apparent activation energy declines as the dehydration occurs which is indicative of an endothermic, reversible reaction accopmanied by an irreversible one. With the increase of the heating rate the diffusion of water molecules from the bulk of the sample becomes a limiting, slow step of the dehydration.

Deconvolution of the DSC peak further supported that the reaction is thermally activated and that the mechanism of the dehydration changes with respect to the changing heating rate. Using the linear compensation effect, we obtained values of (61±7) kJ/mol for the invariant activation energy and $(6\pm1)\cdot10^7$ 1/min for the invariant Arrhenius pre-exponential factor. The invariant activation energy shows a good agreement with the Kissinger's apparent activation energy.