THERMALLY GUIDED DEHYDRATION OF BINUCLEAR [Ni$_2$(en)$_2$(H$_2$O)$_6$(pyr)]·4H$_2$O COMPLEX: A FURTHER INSIGHT

Nemanja N. Stojanović[1*], Aleksandra A. Janićijević[2], Aco J. Janićijević[3]

[1] Joint Laboratory for Advanced Materials of SASA, Section for Amorphous Materials,
  Faculty of Technical Sciences Čačak, University of Kragujevac, Svetog Save 65, 32000 Čačak, Serbia,
[2] Belgrade Polytechnic, Katarine Ambrozić 3, 11000 Belgrade, Serbia,
[3] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

[*] Corresponding author: nemanja.edu@yahoo.com

Abstract: Thermally prompted dehydration of binuclear [Ni$_2$(en)$_2$(H$_2$O)$_6$(pyr)]·4H$_2$O complex occurs within a 326 K to 410 K temperature region, presenting an asymmetrical DSC peak. The process is endothermal and results in the loss of 10 molecules of water accounting for 26.8% of the total mass of the sample. Values of the apparent activation energy of 71 kJ/mol and 93 kJ/mol were determined by using Kissinger's and the isoconversional KAS approach, respectively. The probable reaction mechanism was determined by Dollimore's analysis. Deconvolution of the experimental DSC peak on different heating rates shows that the mechanism of dehydration changes with the change in the heating regime. Using the linear compensation effect, values of invariant activation energy of 61 kJ/mol as well as of Arrhenius pre-exponential factor of $6·10^7$ min^{-1} were determined.

Keywords: coordination polymer, Ni(II) complex, dehydration; thermal analysis; compensation effect; kinetic parameterization.

1. INTRODUCTION

The decade behind us witnessed a growing interest in transition metal complexes and their popularization in scientific research is ongoing. Properties such as biological and catalytic activity, coordination capacity, polymerization, the possibility of establishing highly porous surfaces and many others, make them very interesting candidates for the current and future research ventures [1–3]. Coordination polymers represent inorganic or organometallic polymer structures containing metal cation centers which are linked by ligands [4]. Being chemically a very flexible ligand [5], 1,2,4,5-benzene-tetracarboxylate acid (BTCA) enables the creation of various multilayered polymer structures. The abundance of hydrogen bonds in transition metal-BTCA complexes provides a potential for designing coordination polymers with numerous tailored properties.

This paper, which is intended to serve as a unique supplement to the already published investigation of thermally induced polymerization of a particular Ni(II) complex being [Ni$_2$(en)$_2$(H$_2$O)$_6$(pyr)]·4H$_2$O (where *en* stands for ethylenediamine and *pyr* stands for tetra-anion of pyromellitic acid, i.e. BTCA) [6,7], focuses solely on thermally activated dehydration, by combining thermogravimetry (TGA) and non-isothermal differential scanning calorimetry (DSC). Utilizing these naturally synergic experimental procedures, we look into the kinetics and dehydration mechanism of the complex in relation to the predefined heating regime, hoping to enrich previous findings and contribute to

fundamental understandings of the given process.

2. EXPERIMENTAL PROCEDURES

The [Ni$_2$(en)$_2$(H$_2$O)$_6$(pyr)]·4H$_2$O 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.

A 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 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 using Kissinger's well-known relation $\log(\beta / T_{peak}^2) = f(1 / T_{peak})$ [11] and the isoconversional Kissinger-Akahira-Sunose (KAS) method [12, 13]. The 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 pursuit of elementary steps, i.e., single-step reactions of the dehydration, change of the dehydration mechanism with the change of the heating regime were tracked by deconvoluting the DSC peak acquired on different heating rates. Deconvolution itself was performed using appropriate software solutions [15, 16] by employing the Gaussian-Lorentzian mixed function [17]. Before deconvolution, experimental noise was reduced using the Savitzky-Golay method [18]. Invariant activation energy and Arrhenius pre-exponential factor were determined using the linear compensation effect [19, 20].

3. RESULTS AND DISCUSSION

The investigated complex is thermally stable up to about 50 °C when gradual degradation begins. In the first stage of thermal degradation, the complex loses 10 water molecules, i.e., completely dehydrates. All of the DSC thermographs obtained on different heating rates show a distinctive peak corresponding to the dehydration (Figure 1). It is noticeable that the peak moves towards higher temperatures with the increasing heating rate. Therefore, the process is thermally activated. The shape of the peak changes as well, implying a change in the mechanism of the dehydration itself, that is, the nature of the slow step of the reaction.
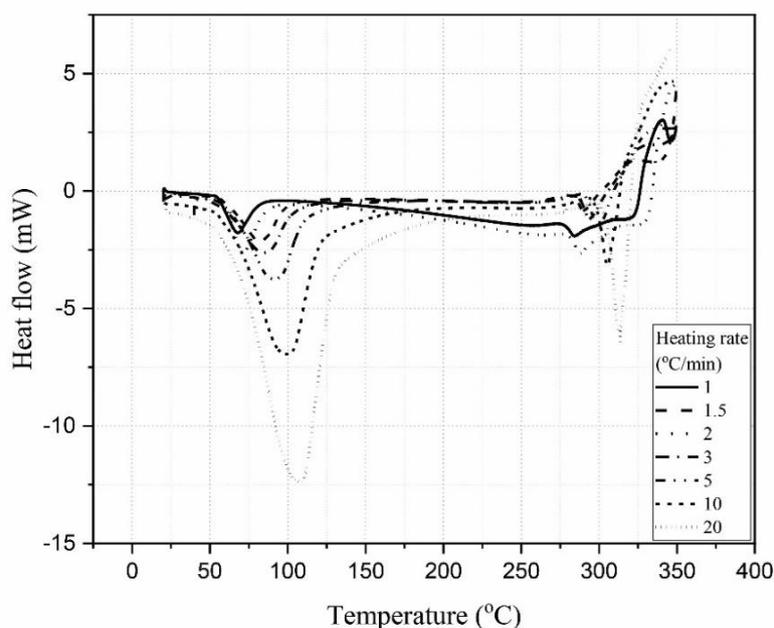
Figure 1. DSC thermographs with the distinctive first peak attributed to the dehydration of the complex.

The calculated loss of mass of the sample of 26.8% shows excellent agreement with the experimental results, $\Delta m = 26.9\%$. Without any further analysis, it should be said that the second step, manifested as the second DSC peak in the temperature region of about 275 °C to 325 °C (Figure 1), corresponds to CO and both *en* groups leaving the structure, causing a mass loss of 21.9% (theoretically 22.2%). During the third and final step, $C_8H_2O_4$ probably leaves the structure as well, relating to a mass loss of 22.5% (theoretically 24.9%).

Measured temperature values of the dehydration peak maxima for different heating rates allow us to estimate the apparent activation energy via Kissinger's method (Figure 2). From the slope of the fitted graph line, we obtained the value of (71 ± 5) kJ/mol. The last three points in the graph, corresponding to heating rates of 1 °C, 1.5 °C and 2 °C, seem to deviate from the direction of the first four ones. Their exclusion from the set gives a more accurate match and a value of (84 ± 3) kJ/mol.
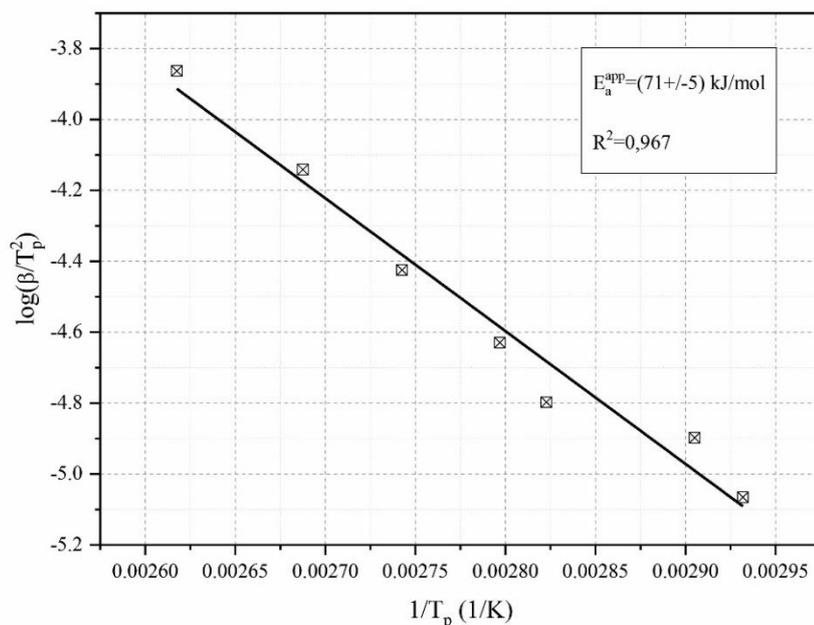
Figure 2. *Kissinger's graph of the dehydration process.*
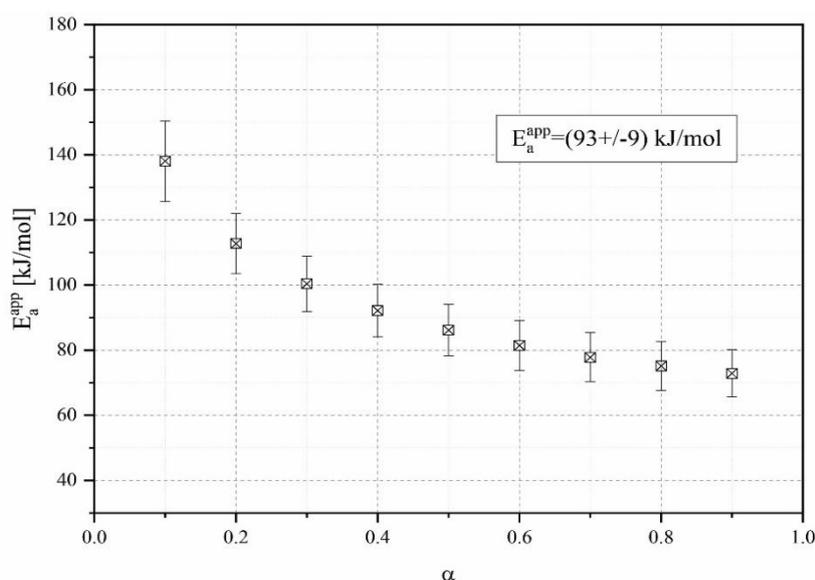
Figure 3. *Apparent activation energy according to the KAS method.*

KAS isoconversional method yielded an average value of (93±9) kJ/mol (Figure 3). In the domain of the absolute error, this is in agreement with the value obtained by Kissinger's method for the set of the last four heating rates, i.e., 3 °C/min, 5 °C/min, 10 °C/min and 20 °C/min.

The apparent energy of activation declines as dehydration occurs (Figure 3). Vyazovkin and Linert showed that the decreasing E^{app}-α dependence corresponds to the kinetics of an endothermic, reversible reaction accompanied by an irreversible one [21]. For such a reaction E^{app} is limited by the sum of the activation energy of the irreversible reaction and the enthalpy of the reversible reaction when the degree of the conversion (α) is low, i.e., at the beginning of the process. At high values of α, the apparent activation energy is limited only by the activation energy of the irreversible reaction. Reversible dehydration of crystalline hydrates, as well as other reversible processes, show a characteristic shape of the E^{app}-α curve [22].
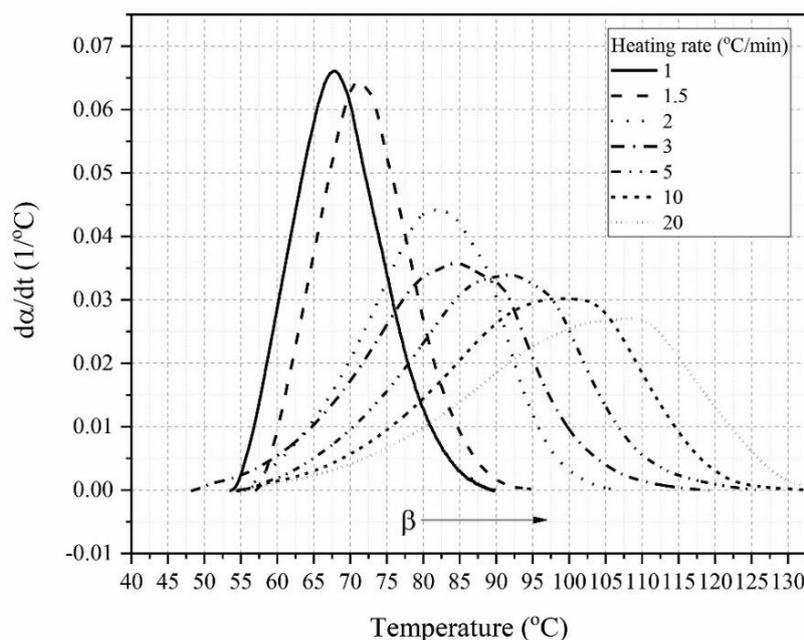
Figure 4. *Experimental DSC peak progressing with the increasing heating rate.*

The experimental peak is asymmetric at all heating rates while changing its asymmetry with the β increasing, indicating the complexity of the process (Figure 4). It is possible to assume that the kinetic models F2 and F3 – which describe reactions of the second and the third order, respectively – govern the process at lower heating rates, while at the higher ones, models D3 and R3 tend to dominate, i.e., three-dimensional diffusion and reaction at the phase boundary, respectively (Table 1). Thus, with the increase in the heating rate the diffusion of water molecules from the bulk of the sample becomes a limiting, slow step of the dehydration.

Table 1. *Dollimore's parameters of the dehydration process and probable reaction models*

β (°C/min)	α at t$_{peak}$	Width at half height	Asymmetry factor	Reaction models
1	0.48	14.56	0.99	F2, F3
1.5	0.45	14.85	0.88	F2, F3
2	0.50	21.20	0.96	B1
3	0.55	25.59	1.22	B1
5	0.57	27.33	1.37	B1
10	0.61	30.96	1.51	D3, R3
20	0.69	35.02	2.23	D3, R3

The experimental DSC peak was deconvoluted into three smaller ones, with a quite considerable overlapping of it with the cumulative one. At heating rates of 1 °C/min and 1.5 °C/min, the areas of the separated peaks stand in the ratio of 1:5:2 and 1:6:3, in the same order. At heating rates of 2 °C/min and 3 °C/min this ratio is 1:3:3, whilst at 5 °C/min, 10 °C/min and 20 °C/min, the ratio is 1:2:4. This may further support the claim that the reaction is thermally activated and that the mechanism of the dehydration, being a complex process, changes with respect to the changing heating rate (Figure 5).
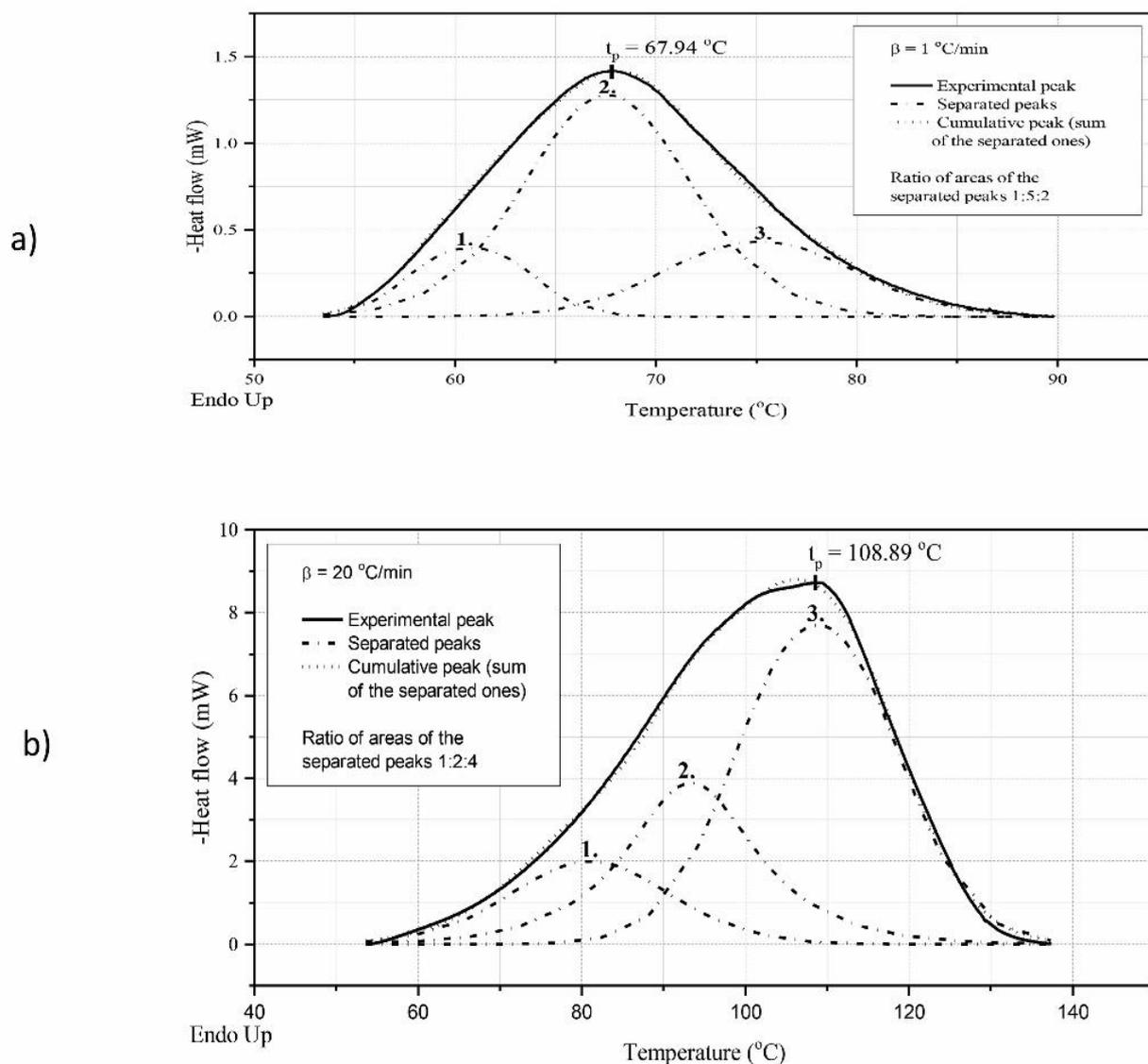
Figure 5. Increasing the heating rate affects the dehydration mechanism, progressing from F2, F3 reaction models on 1 °C/min to D3, F3 reaction models on 20 °C/min.

To determine the invariant kinetic parameters, we used the value of the apparent activation energy of (71±5) kJ/mol as found by the Kissinger method, as well as models of high $g(\alpha)$ linearity [23] in the full 1/T range. Concerning the decades-old debate regarding the true nature of the kinetic compensation effect [24], obtained values are (61±7) kJ/mol for the invariant activation energy and $(6\pm1) \cdot 10^7$ 1/min for the invariant Arrhenius pre-exponential factor (Figure 6). The invariant activation energy shows a good agreement with the apparent activation energy determined by the Kissinger method within the domain of the absolute error.
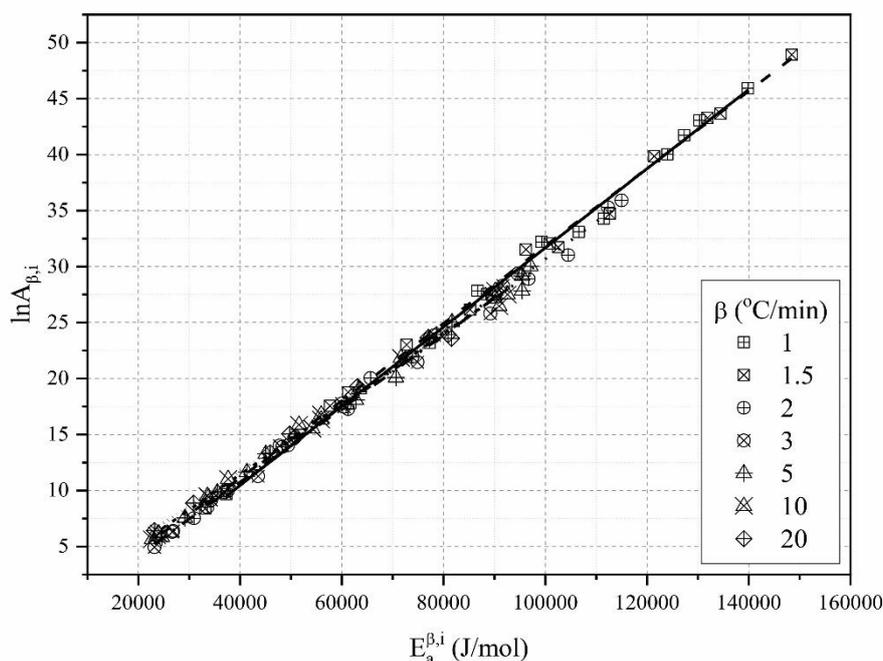
Figure 6. The dehydration process manifests a linear compensation effect

4. CONCLUSION

The coordination polymer [Ni$_2$(en)$_2$ (H$_2$O)$_6$(pyr)]·4H$_2$O 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 implying that the process is thermally activated. The peak changes its shape as well, which is attributed to a change in the mechanism of dehydration. The dehydration is endothermal and the sample further loses 21.9% of its mass in the temperature range of about 275 °C to 325 °C, corresponding to CO and both *en* groups leaving the structure. C$_8$H$_2$O$_4$ probably leaves the structure as well, during the third and final step.

Using the Kissinger 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 with the occurrence of dehydration, which is indicative of an endothermic, reversible reaction accompanied by an irreversible one. With the increase in the heating rate, the diffusion of water molecules from the bulk of the sample becomes a limiting, slow step of dehydration.

Deconvolution of the DSC peak further supported the fact that the reaction is thermally activated and that the mechanism of dehydration changes regarding the changing heating rate. Using the linear compensation effect, we obtained values of (61±7) kJ/mol for the invariant activation energy and (6±1) ·10^7 1/min for the invariant Arrhenius pre-exponential factor. The invariant activation energy shows a good agreement with apparent activation energy using the Kissinger method.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[1] D. Zhang, G. X. Jin, *Bimetallic nickel complexes of trimethyl phenyl linked salicylaldimine ligands: Synthesis, structure and their*

ethylene polymerization behaviors, Inorg. Chem. Commun., Vol. 9 (2006) 1322–1325.

[2] M. C. Rodriguez-Arguelles, M. B. Ferrari, F. Bisceglie, C. Pelizzi, G. Pelosi, S. Pinelli, M. Sassi, *Synthesis, characterization and biological activity of Ni, Cu and Zn complexes of isatin hydrazones*, J. Inorg. Biochem., Vol. 98 (2004) 313–321.

[3] K. Gedrich, I. Senkovska, N. Klein, U. Stoeck, A. Heerwig, M. Lohe, I. Baburin, U. Mueller, S. Kaskel, *A Highly Porous Metal-Organic Framework with Open Nickel Sites*, Angewandte Chemie (International ed. in English), Vol. 49 (2010) 8489–92.

[4] S. R. *Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Ohrstrom, M. O'Keeffe, M. P. Suh, J. Reedijk, Terminology of metal–organic frameworks and coordination polymers* (IUPAC Recommendations 2013)*, Pure and Applied Chemistry, 85–8 (2013) 1715.*

[5] Y. Luo, K. Bernot, G. Calvez, S. Freslon, C. Daiguebonne, O. Guillou, N. Kerbellec, T. Roisnel, *1,2,4,5-Benzene-tetra-carboxylic acid: a versatile ligand for high dimensional lanthanide-based coordination polymers*, Cryst. Eng. Comm., Vol. 15 (2013) 1882–1896.

[6] N. N. Begović, N. N. Stojanović, A. M. Radulović, S. B. Ostojić, V. A. Blagojević, B. Simonović, D. M. Minić, *Thermally induced polymerization of binuclear [Ni₂(en)₂(H₂O)₆(pyr)]· 4H₂O complex*, Thermochimica Acta, Vol. 607 (2015) 82–91.

[7] J. D. Zdravković, D. Poleti, J. Rogan, N. N. Begović, V. A. Blagojević, M. M. Vasić, D. M. Minić, *Thermal stability and degradation of binuclear hexaaqua-bis(ethylenediamine)-(μ₂-pyromellitato)dinickel(II) tetrahydrate*, J. Therm. Anal. Calorim., Vol. 123 (2016) 1715–1726.

[8] D. Poleti, D. R. Stojaković, B. V. Prelesnik, R. M. Herak, *Structure of binuclear hexaaqua-μ-[1,2,4,5-benzenetetracarboxylato(4-)]-bis(ethylenediamine)dinickel(II) tetrahydrate*, Acta Cryst., C44 (1988) 242–245.

[9] M. E. Brown, *Handbook of Thermal Analysis and Calorimetry*, Principles and practice, Elsevier 1998.

[10] TA Instruments, *Thermal Analysis*, T-2006A (2017) 42, 52–54.

[11] H. E. Kissinger, Reaction Kinetics in Differential Thermal Analysis, Anal. Chem., Vol. 29 (1957) 1702.

[12] H. E. Kissinger, *Variation of Peak Temperature With Heating Rate in Differential Thermal Analysis*, J. Res. Natl. Bur. Std., Vol. 57 (1956) 217.

[13] T. Akahira, T. Sunose, *Joint Convention of Four Electrical Institutes, Research Report*, Chiba Inst. Technol. (Sci. Technol.), Vol. 16 (1971) 22.

[14] D. Dollimore, *Thermal Analysis*, Analytical Chemistry, Vol. *68*–12 (1996) 63–72.

[15] Origin, Version 2018. OriginLab Corporation, Northampton, MA, USA.

[16] M. Wojdyr, *Fityk: a general-purpose peak fitting program*, J. Appl. Cryst. 43, (2010) 1126-1128.

[17] TA Instruments, *Deconvolution of Thermal Analysis Data using Commonly Cited Mathematical Models*, TA431 (2020).

[18] E. Ostertagova, O. Ostertag, *Methodology and Application of Savitzky-Golay Moving Average Polynomial Smoother*, Global Journal of Pure and Applied Mathematics, Vol. 12–4 (2016) 3201–3210.

[19] M. C. Gupta, S. G. Viswanath, *Kinetic compensation effect in the thermal degradation of polymers*, Journal of Thermal Analysis, Vol. 47 (1996) 1081–1091.

[20] N. Sbirrazzuoli, *Interpretation and Physical Meaning of Kinetic Parameters Obtained from Isoconversional Kinetic Analysis of Polymers*, Polymers, Vol. 12–6 (2020) 1280.

[21] S. Vyazovkin, W. Linert, Kinetic analysis of reversible thermal decomposition of solids, Int. J. Chem. Kinet, Vol. 27–1 (1995) 73–84.

[22] S. Vyazovkin, C. A. Wight, *Kinetics in solids*, Annu. Rev. Phys. Chem., Vol. 48 (1997) 125–49.

[23] A. Khawam, D. R. Flanagan, *Solid-State Kinetic Models: Basics and Mathematical Fundamentals*, J. Phys. Chem. B, Vol. 110 (2006) 17315–17328.

[24] J. Šestak, *Kinetic Compensation Effect: Facts and Fiction of Linear Plots Using Arrhenius Law*, In: H. G. Wiedemann (eds), Thermal Analysis, Birkhauser, Basel 1980.

ТЕРМИЧКИ ВОЂЕНА ДЕХИДРАЦИЈА БИНУКЛЕАРНОГ [Ni₂(en)₂(H₂O)₆(pyr)]·4H₂O КОМПЛЕКСА: ДАЉИ УВИД

Сажетак: Термички изазвана дехидрација бинуклеарног $[Ni_2(en)_2(H2O)_6(pyr)]\cdot4H_2O$ комплекса одвија се у температурском опсегу од 326 K до 410 K, дајући асиметрични DSC пик. Процес је ендотерман и резултује губитком 10 молекула воде, што чини 26,8% укупне масе узорка. Вредности привидне енергије активације од 71 kJ/mol и 93 kJ/mol одређене су употребом Kissinger-овог и изоконверзионог KAS приступа, тим редом. Вероватни механизам реакције добијен је Dollimore-овом анализом. Деконволуција експерименталног DSC пика на различитим брзинама загревања показује да се механизам дехидрације мења са променом режима загревања. Помоћу линеарног компензационог ефекта одређене су вредности инваријантне енергије активације од 61 kJ/mol, као и Arrhenius-овог предекспоненцијалног фактора од $6\cdot10^7$ min⁻¹.

Кључне речи: координациони полимер, Ni(II) комплекс, дехидрација, термичка анализа, компензациони ефекат, кинетичка параметризација.