NEW METAL-ORGANIC FRAMEWORK/COORDINATION POLYMER SYNTHESIZED FROM ZINC AND *o*-HYDROXY DERIVATIVE OF TRUXILLIC ACID

Andreas Puškarić, Ivan Halasz, Jasminka Kontrec, Josip Bronić
Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia,
Corresponding author's e-mail: josip.bronic@irb.hr

ABSTRACT

New zinc containing metal-organic framework (Zn-truxillate) has been synthesized under mild hydrothermal conditions: temperature of 120 °C and reaction time of 72 h. The obtained product (small light-brown crystals) was characterized using several analytical methods, such as powder X-ray diffraction, infrared spectroscopy (FTIR), thermal methods (TG, DTG).

Keywords: metal-organic framework, zinc, carboxylate, XRD.

INTRODUCTION

Metal-organic frameworks (MOF) are crystalline materials with structures based on classic coordination bonds between metal cation and organic linkers (ligands) with specific complexing groups (carboxylates, phosphonates, nitrogen containing compounds, etc.). Due to the size and chemical properties of the ligand, obtained structure may have relatively large and stable pores that do not collapse upon removal of solvent (or other small molecules). MOFs have some interesting properties: high surface area (up to 7000 m^2 g^{-1})[1], large pore volume (up to 4,4 cm^3 g^{-1}) and low density (down to 0,2 cm^3 g^{-1})[2]. Also, the presence of both organic and inorganic components enables easier synthesis of the material of the desired properties (pore size, functionalized surface, particulate properties).

Due to their properties, MOFs potentially can be used in many different fields [3] such as gas storage [4], gas/vapor separation [5], catalysis, chemical sensing, drug delivery, etc. [6].

EXPERIMENTAL

The starting organic ligand l*α*,2*β*-di-*o*-hydroxyphenylcyclobutane-2*α*,4*β*-dicarboxylic acid dilactone (truxillic dilactone) was prepared by cycloaddition (dimerization) of *trans*-3-(2-hydroxyphenyl)acrylic acid (2-hydroxycinnamic acid) via photochemical reaction (UV light applied on solid state) for a few days [7]. 250W Hg-lamp was used as a source of UV light. Purification of the obtained material (dilactone) by recrystallization from DMF, yields thin plate-like crystals.

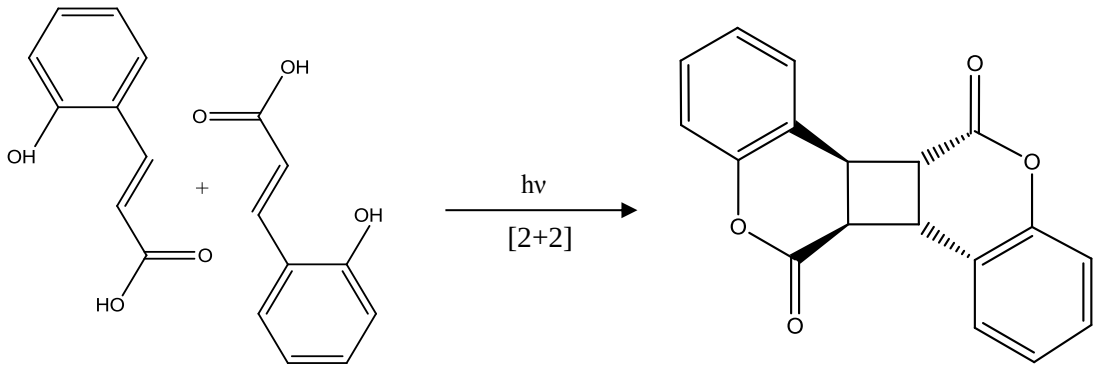

Figure 1. Photodimerization of *trans*-2-hydroxycinnamic acid into truxillic dilactone

The MOF syntheses were carried out hydrothermally. Truxillic dilactone (0.15 mmol) was suspended in 7 mL of water, then 0.6 mmol of KOH (aq, 5%) was added and system was stirred shortly. Subsequently, 0.6 mmol of $Zn(OAc)_2 \times 6\ H_2O$ (c = 0.1 mol dm^{-3}) solution was added. Teflon-lined autoclaves were sealed and heated for 72 h at 120 °C. Needle-like shaped crystalline product, was collected by centrifugation and dried overnight in the air at room temperature.

Infrared spectra were recorded on Perkin Elmer FTIR instrument (System 2000) using KBr pellets, in range 400 - 4000 cm^{-1}. Powder X-ray diffraction data were collected in 2θ range 5–50°, using Philips machine (model PW1820). For the crystal structure determination TOPAS software was used. Thermogravimetric measurements were made using Mettler TG-50 Thermal Gravimetric Analyzer, with heating rate of 5 °C min^{-1}, under air stream, from room temperature to 700 °C.

RESULTS AND DISCUSSION

Zn-truxillate has a $P2_1/c$ symmetry, with cell parameters: a = 9.041 Å, b = 24.125 Å, c = 12.409 Å, β = 94.948°.

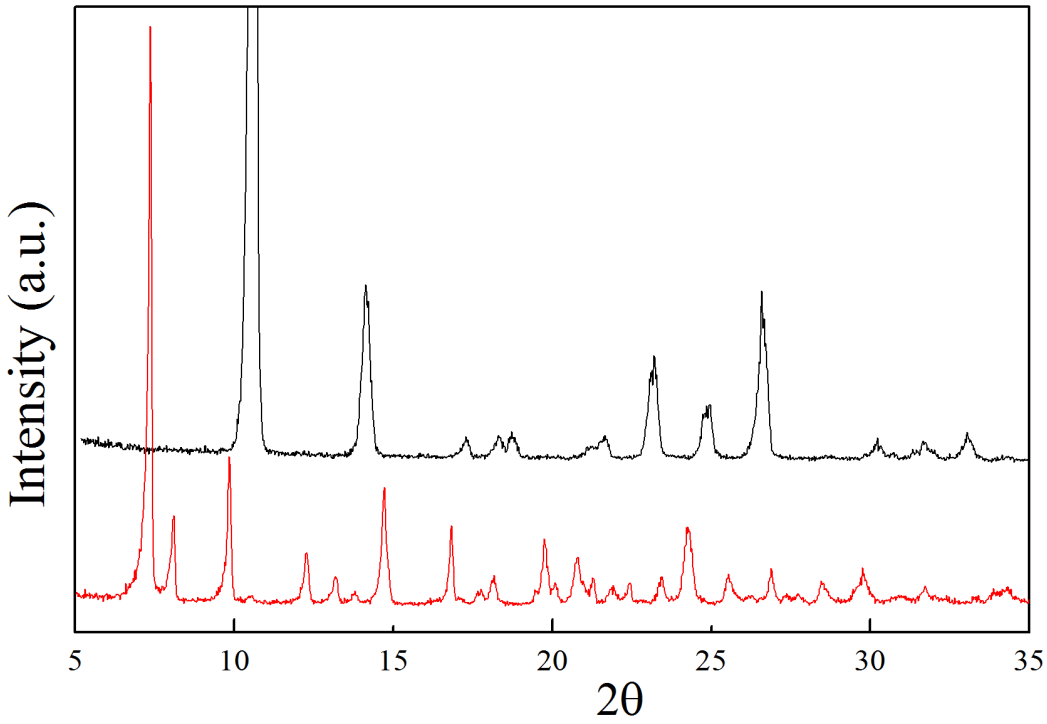

Figure 2. XRD patterns of dilactone (black) and Zn-truxillate (red)

Diffractograms (Fig. 2) of the starting ligand (dilactone) and product (Zn-truxillate) have completely different patterns, showing that final product does not contain unreacted material. Also, the unit cell of the new phase is larger than the one of dilactone, indicating that something (Zn) is incorporated to differently aligned and connected ligand molecules.

FTIR spectra of dilactone and Zn-truxillate (Fig. 3) also has quite different absorption maxima. Absorption peak at 1749 cm^{-1} in dilactone IR spectra corresponds to C=O stretching mode, but does not exist in Zn-truxillate (strongly shifted towards lower wavenumbers), indicating that lactone ring is opened (hydrolyzed part connected to Zn). In the IR spectra of Zn-truxillate, the band at 1581 cm^{-1} can be assigned to asymmetric carboxylate stretching,

while the band at 1410 cm^{-1} is assigned to the symmetric carboxylate stretching. Moreover, free/non-hydrogen bonded O–H stretching vibrations at 3587 and 3515 cm^{-1} are observed in Zn-truxillate IR spectra, also indicating opened lactone ring.

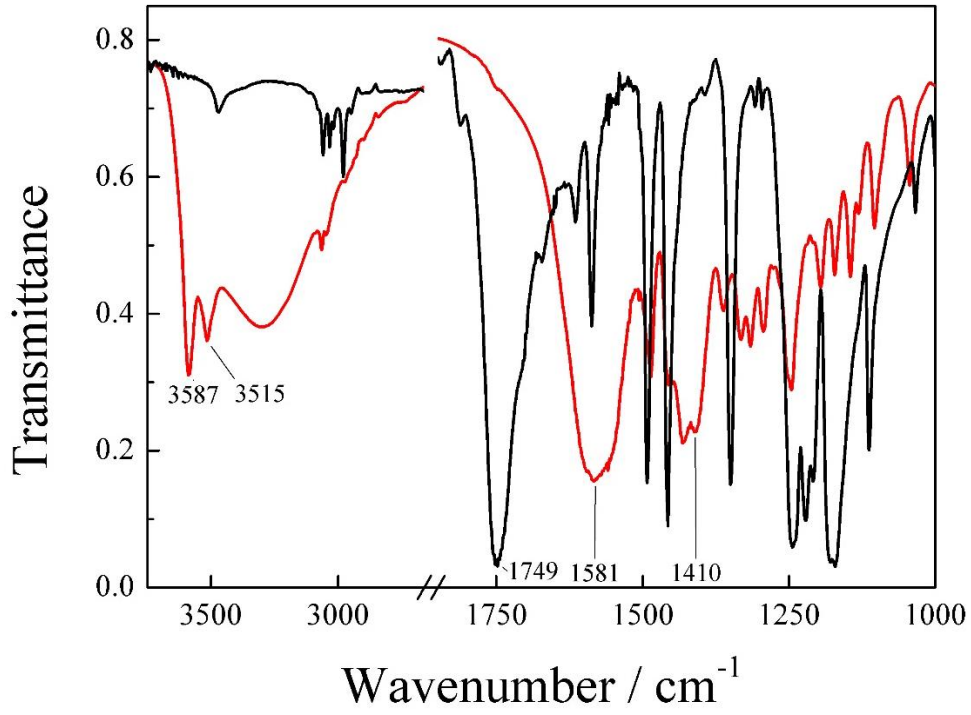

Figure 3. Infrared spectra of dilactone (black) and Zn-truxillate (red).

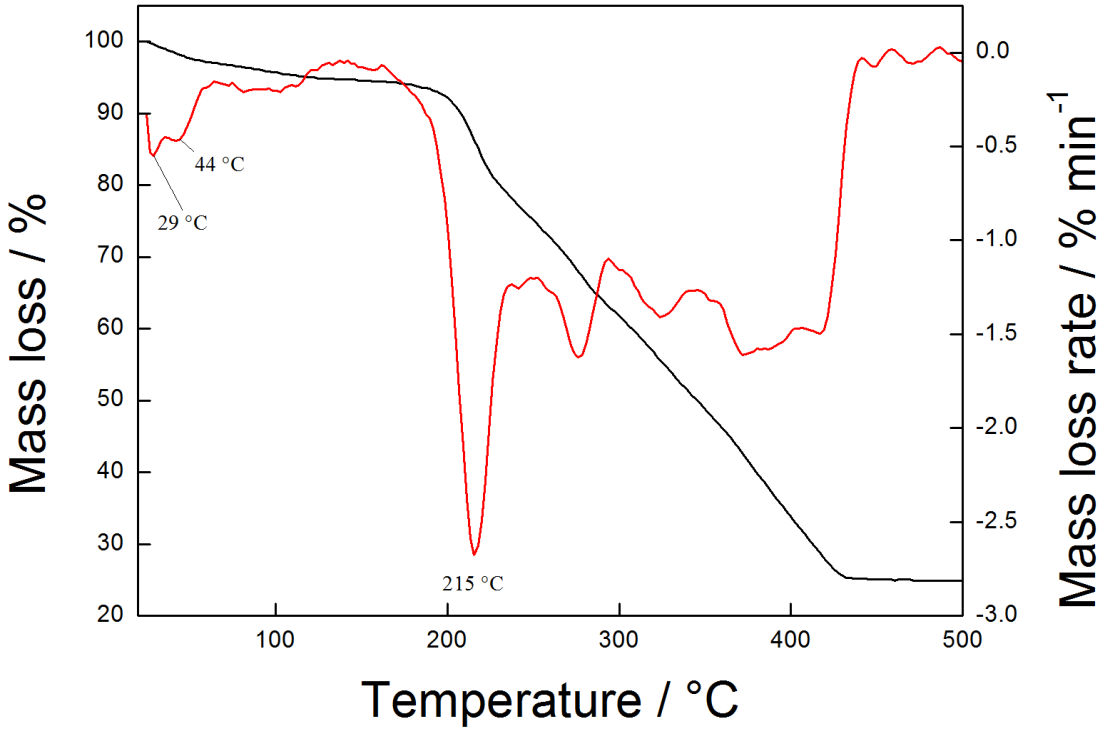

Figure 4. TG and DTG curves of the Zn-truxillate.

Wide maximum between 2500 and 3500 cm^{-1} also shows presence of water (moisture) within final product.

TG and DTG curves of the Zn-truxillate (Fig. 4) show two areas of mass losses. First one from room temperature to 130 °C, exhibits relatively small weight loss of 4.9%, which can be attributed to physisorbed water (moisture). Much wider and stronger mass loss is the second area between 155 and 450 °C, which corresponds to multistep decomposition of the organic ligand. At the same time, the mass loss is 69.5%.

Our several attempts to synthesize Zn-truxillate using monomeric *trans*-2-hydroxycinnamic acid have failed. In this way, we did not obtain Zn-truxillate crystals at all (not even as mixture of 2 phases), pointing out that dimer of *trans*-2-hydroxycinnamic acid (truxillic dilactone) is necessary for the synthesis.

CONCLUSION

New metal-organic framework material was prepared from zinc acetate and truxillic acid derivative. Unit cell parameters (determined by PXRD) reveal monoclinic system, while other characterization techniques (FTIR, TG, DTG) confirm that new phase (Zn-truxillate) have Zn bonded to ligand via oxygen.

ACKNOWLEDGEMENT

This work is realized in the frame of the projects 098-0982904-2953, financially supported by the Croatian Ministry of Science, Education and Sport.

REFERENCES

[1] O. Farha, I Eryazixi, N. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. Yazaydın, and J. T. Hupp., *J. Am. Chem. Soc.*, 2012, **134**, 15016–15021

[2] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, *Science*, 2002, 295**,** 469–472

[3] R. J. Kuppler, D. J. Timmons, Q-R. Fang, J-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, and H-C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042–3066.

[4] M. P. Suh, H. J. Park, T. K. Prasad, and D–W. Lim, *Chem. Rev.*, 2012, **112**, 782–835.

[5] J–R. Li, J. Sculley, H–C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.

[6] Q. Fang, J. Sculley, H–C. Zhou, G. Zhu, Chapter 5.01 *"Porous Metal–Organic frameworks"* in: *"Comprehensive Nanoscience and Technology, Volume 5: Self–Assembly and Nanochemistry"*, D.L. Andrews, G.D. Scholes and G.P. Wiederrecht (Eds.), Elsevier, 2011, 1-20.

[7] M. D. Cohen, G. M. J. Schmidt, F. I. Sonntag, *J. Chem. Soc.*, **1964**, 2000-2013.