

# NEW SOLVATOMORPH OF TETRAKIS( $\mu_2$ -ACETATO-O,O')-BIS(ISONICOTINAMIDE-N)-DI-COPPER(II): SYNTHESIS, IR, TGA AND X-RAY STUDY

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**Abstract.** Dinuclear tetracarboxylato-bridged copper(II) complex,  $[\text{Cu}_2(\text{OAc})_4(\text{ina})_2] \cdot 2\text{dmsO}$  (**1**), where  $\text{OAc}^- = \text{CH}_3\text{COO}^-$ ,  $\text{ina}$ =isonicotinamide and  $\text{dmsO}$ =dimethylsulfoxide, has been prepared and crystal structure has been determined by single X-ray diffraction. The compound consists of dinuclear units, in which two Cu(II) ions are bridged by four *syn,syn*- $\eta^1:\eta^1:\mu$ -acetato bridges, showing a paddle-wheel cage-type with a square-pyramidal geometry. In the crystal structure, intermolecular N-H...O hydrogen bonds link the molecules into a 1D linear chain.

**Keywords:** copper, isonicotinamide, X-ray, paddle-wheel structure.

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## Introduction

The design and preparation of metal-organic frameworks have attracted intense interest in the field of supramolecular chemistry and crystal engineering owing to their potential applications as well as their structural variations that are currently of interest in the field of materials [1-7]. A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve diverse dimensionalities. Copper(II) metal-organic frameworks are of considerable interest because of their structural and photoluminescent biological function, catalytic and magnetic properties [8-11]. Isonicotinamide and its related compounds are reported to represent a group of small molecules as a drug candidate to prevent and/or reverse diabetes by protecting  $\beta$ -cells from damage and death [12].

The retrieval of Cambridge Structural Database (CSD) revealed that the combination of Cu(II) with isonicotinamide resulted in structural diversity, including mono- [13-15], binuclear [14, 16-18], 1D [7, 16, 19-21] and 2D polymeric arrays [7, 22, 23]. In all studies isonicotinamide coordinates to the copper(II) ion in a monodentate form through the pyridine N atom or in a bidentate one [16] thus providing possibilities for polymeric coordination networks. Pyridine-2,5-dicarboxylic acid combines the advantages of both organic multicarboxylic acids and heteroaromatic compounds and displays versatile coordination modes through its one N atom and four carboxylate O atoms, which in alliance with Cu(II) leads to the formation of coordination homometallic [23-27] and/or heterometallic [26, 28-30] polymers. With that in mind, in this contribution, we intended to extend the dimensionality of a new coordination compound obtained by the combination of isonicotinamide with pyridine-2,5-dicarboxylate ligands. However, in the synthetic conditions we were unable to obtain any new coordination compounds with simultaneous presence of pyridine-2,5-dicarboxylic acid and isonicotinamide ligand in one molecule, and a new solvatomorph of tetrakis( $\mu_2$ -acetato-O,O')-bis(isonicotinamide-N)-di-copper(II) was obtained instead. So, we report herein the synthesis and X-ray characterization of a binuclear mixed-ligand Cu(II) complex,  $[\text{Cu}_2(\text{OAc})_4(\text{ina})_2] \cdot 2\text{dmsO}$  (**1**), where  $\text{OAc}^- = \text{CH}_3\text{COO}^-$ ,  $\text{ina}$  = isonicotinamide and  $\text{dmsO}$  = dimethylsulfoxide.

## Experimental section

### Materials and methods

All reagents and solvents were obtained from commercial sources and were used without further purification. Elemental analysis was performed on an Elementar Analysen systeme GmbH Vario El III elemental analyzer. The IR spectra were obtained in vaseline oil on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range of 400 - 4000  $\text{cm}^{-1}$ . The thermogravimetric analysis (TGA) was carried out with a Derivatograph Q-1500 thermal analyzer in an air flow at a heating rate of 10  $^\circ\text{C}/\text{min}$  in the temperature range of 25 - 1000  $^\circ\text{C}$ .

### Synthesis of $[\text{Cu}_2(\text{OAc})_4(\text{ina})_2] \cdot 2\text{dmsO}$ (**1**).

$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (20 mg, 0.1 mmol), isonicotinamide (12.2 mg, 0.1 mmol) and pyridine-2,5-dicarboxylic acid (8.3 mg, 0.05 mmol) were dissolved in 8 mL mixture of methanol and dimethylsulfoxide (5:3). The reaction mixture was stirred in the ultrasonic bath at 60  $^\circ\text{C}$  for ~ 30 min, filtered off and then slowly cooled to 5  $^\circ\text{C}$  temperature giving green crystals. Yield: ~ 48 %. Anal. calc. for  $\text{C}_{24}\text{H}_{36}\text{N}_4\text{O}_{12}\text{S}_2\text{Cu}_2$  (%): C=37.71; H=4.71; N=7.33. Found: C=37.65; H=4.62; N=7.47. IR ( $\text{cm}^{-1}$ ): 3300(m), 3163(w), 2953(v.w), 2924(m), 2921(w), 2854(m), 2794(v.w), 1678(m), 1616(m), 1614(s), 1557(m), 1408(s), 1347(m), 1230(m), 1069(m), 1050(v.w), 1025(w), 722(m), 682(w).

**X-ray structure determination**

Diffraction measurement for **1** was carried out at room temperature on a Xcalibur "Oxford Diffraction" diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK $\alpha$  radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structure and to refine the proposed model were carried out with the programs SHELXS97 and SHELXL97 [31]. The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  by using the SHELXL97 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined by using a riding model. The X-ray data and the details of the refinement for **1** are summarized in Table 1. Selected geometric parameters for **1** are given in Tables 2 and 3. The figures were produced using the Mercury program [32]. CCDC-1408326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1

**Crystal and structure refinement data for compound 1.**

| Parameters  | Value   |
|---|---|
| Empirical formula   | C <sub>24</sub> H <sub>36</sub> N <sub>4</sub> O <sub>12</sub> S <sub>2</sub> Cu <sub>2</sub> |
| Formula weight  | 763.77  |
| Crystal system  | Triclinic   |
| Space group   | <i>P</i> -1   |
| <i>Z</i>  | 1   |
| <i>a</i> (Å)  | 7.3195(12)  |
| <i>b</i> (Å)  | 8.0763(12)  |
| <i>c</i> (Å)  | 13.833(2)   |
| $\alpha$ (°)  | 93.024(13)  |
| $\beta$ (°)   | 97.026(13)  |
| $\gamma$ (°)  | 96.063(13)  |
| <i>V</i> (Å <sup>3</sup> )  | 805.3(2)  |
| <i>D<sub>c</sub></i> (g/cm <sup>-3</sup> )  | 1.575   |
| $\mu$ (mm <sup>-1</sup> )   | 1.514   |
| <i>F</i> (000)  | 394   |
| Crystal size (mm)   | 0.12 x 0.12 x 0.05  |
| Reflections collected/unique  | 4284 / 2837 [R(int) = 0.0418]   |
| Reflections with [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]                             | 1977  |
| Data/ restraints/ parameters  | 2837 / 0 / 211  |
| GOF on $F^2$  | 0.987   |
| <i>R<sub>1</sub></i> , <i>wR<sub>2</sub></i> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] | 0.0592, 0.0943  |
| <i>R<sub>1</sub></i> , <i>wR<sub>2</sub></i> (all data)                           | 0.0943, 0.1101  |

Table 2

**Selected bond lengths (Å) and angles (°) in coordination metal environment in 1.**

| Bond   | <i>d</i> , Å   | Bond                                 | <i>d</i> , Å   |
|--|----------------|--------------------------------------|----------------|
| Cu(1)-O(1)   | 1.971(3)       | Cu(1)-O(4) <sup><i>i</i></sup>       | 1.977(3)       |
| Cu(1)-O(3)   | 1.980(3)       | Cu(1)-N(1)                           | 2.175(4)       |
| Cu(1)-O(2) <sup><i>i</i></sup>                           | 1.970(3)       |                                      |                |
| Angle  | $\omega$ , deg | Angle                                | $\omega$ , deg |
| O(2) <sup><i>i</i></sup> -Cu(1)-O(1)                     | 168.66(14)     | O(4) <sup><i>i</i></sup> -Cu(1)-O(3) | 168.50(14)     |
| O(2) <sup><i>i</i></sup> -Cu(1)-O(4) <sup><i>i</i></sup> | 88.76(14)      | O(2) <sup><i>i</i></sup> -Cu(1)-N(1) | 97.10(14)      |
| O(1)-Cu(1)-O(4) <sup><i>i</i></sup>                      | 88.96(15)      | O(1)-Cu(1)-N(1)                      | 94.21(14)      |
| O(2) <sup><i>i</i></sup> -Cu(1)-O(3)                     | 89.77(15)      | O(4) <sup><i>i</i></sup> -Cu(1)-N(1) | 98.12(15)      |
| O(1)-Cu(1)-O(3)  | 90.25(15)      | O(3)-Cu(1)-N(1)                      | 93.39(15)      |

Symmetry transformations used to generate equivalent atoms: <sup>*i*</sup> -*x*+2, -*y*+1, -*z*+1

Table 3

**Hydrogen bond distances (Å) and angles (°) for 1.**

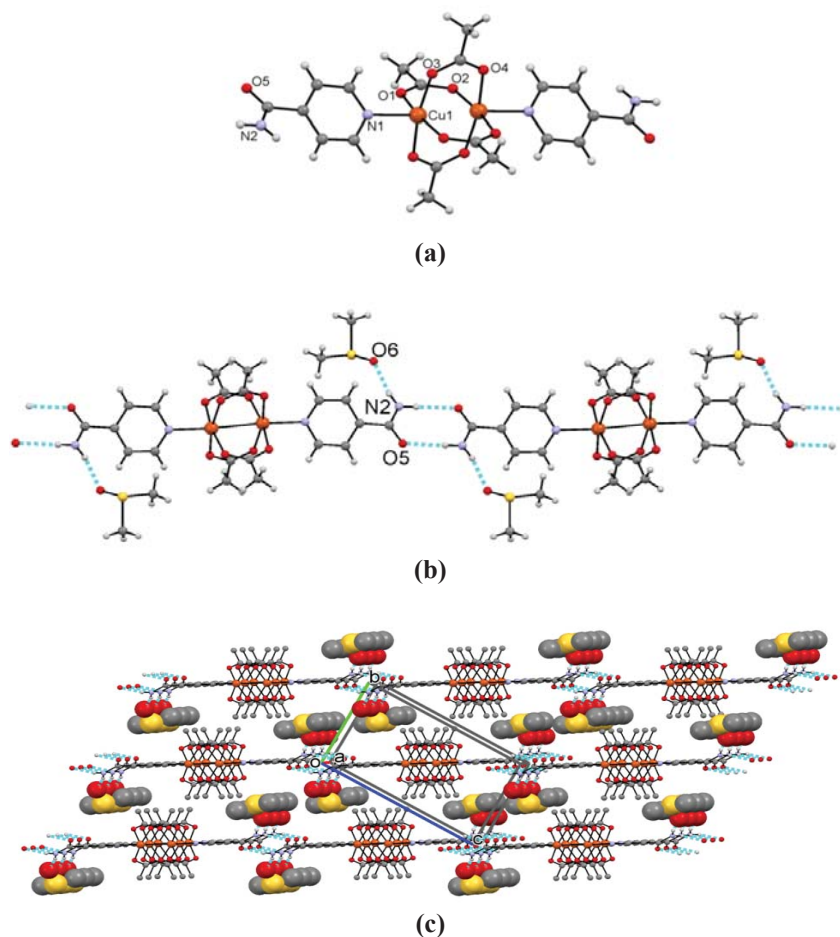
| <i>D-H</i> ⋯ <i>A</i> | <i>d</i> ( <i>D-H</i> ) | <i>d</i> ( <i>H</i> ⋯ <i>A</i> ) | <i>d</i> ( <i>D</i> ⋯ <i>A</i> ) | <(DHA) | Symmetry transformation for acceptor |
|-----------------------|-------------------------|----------------------------------|----------------------------------|--------|--------------------------------------|
| N(2)-H(1N1)⋯O(6)      | 0.88(4)                 | 2.05(5)                          | 2.913(6)                         | 169(4) | <i>x</i> , <i>y</i> -1, <i>z</i>     |
| N(2)-H(2N1)⋯O(5)      | 0.87(5)                 | 2.08(5)                          | 2.937(6)                         | 171(5) | - <i>x</i> , - <i>y</i> , - <i>z</i> |

## Results and discussion

### Crystal structure analysis

The interaction in the system  $\text{Cu}(\text{OAc})_2$  – isonicotinamide (*ina*) – pyridine-2,5-dicarboxylic acid (2,5-*pdc*) resulted in the acid-free dinuclear compound of the composition  $[\text{Cu}_2(\text{OAc})_4(\text{ina})_2] \cdot 2\text{dmsso}$  (**1**). Complex **1** represents chromophore being intensively green colored. Upon exposure to air, the adduct is stable in solid state and is soluble in water and common organic solvents such as methanol and *N,N*-dimethylformamide.

The complex structure **1** reproduces features for two reported binuclear Cu(II) complexes, solvent-free [17] and acetonitrile solvate [14] tetrakis( $\mu_2$ -acetato-*O,O'*)-bis(isonicotinamide-*N*)-di-copper(II). As it is evidenced from comparison of the unit cell dimensions and crystal systems, compounds **1** and the last one (*P*-1;  $a=7.200(1)$ ,  $b=8.103(1)$ ,  $c=13.449(1)$  Å;  $\alpha=90.41(0)$ ,  $\beta=96.33(0)$ ,  $\gamma=96.12(0)$  °;  $V=775.172$  Å<sup>3</sup>) [14] are isomorphous with consequential increase of the unit cell volume in **1** (Table 1). Compound **1** (Figure 1a) consists of centrosymmetric paddle-wheel dinuclear units with the two copper(II) atoms held together through four *syn,syn*- $\eta^1:\eta^1:\mu$ -acetate bridges (Cu–O distances vary from 1.970(3) to 1.980(3) Å) acting as equatorial ligands for each Cu(II) center. Each copper atom has a square-pyramidal geometry where the ‘peripheral’ coordination site on the metal ion is occupied by an isonicotinamide ligand coordinated through the pyridine nitrogen atom at a distance of 2.175(4) Å. The copper atoms are displaced by 0.196 Å from the basal planes toward the apical positions. The two amide functionalities of coordinated *ina* molecules are oriented in a linear fashion but pointing in opposite directions. Each amide moiety forms two symmetry related N–H  $\cdots$  O hydrogen bonds, with an adjacent metal complex, resulting in infinite linear chains (Figure 1b). The remaining N–H proton on each amide functionality forms a N–H  $\cdots$  O hydrogen bond ( $d(\text{N} \cdots \text{O})$  2.91 Å) to the included dimethylsulfoxide (Figure 1b,c). The Cu  $\cdots$  Cu separation within the paddle-wheel dinuclear core is 2.626 Å, and the Cu  $\cdots$  Cu distance between adjacent metal-complexes within each hydrogen-bonded chain is 17.0 Å. The shortest through-space inter-chain distance between Cu(II) ions is 6.325 Å.



**Figure 1.** View of the: dinuclear Cu(II) molecule (a); infinite chain of dinuclear Cu(II)-complexes held together by self-complementary amide  $\cdots$  amide hydrogen-bond interactions (b) and crystal packing in **1** with *dmsso* molecules shown in the space-filling mode, C-bound H-atoms are omitted for clarity (c).

The structural parameters of compound **1** compare well with some paddle-wheel copper(II) binuclear and polymeric related complexes, as shown in Table 4. The above findings together with the reported complexes reveal that monodentate 4-phenylpyridine affords longer Cu...Cu separations, while hexadentate 2,4,6-tri(4-pyridyl)-1,3,5-triazine ligand provides shorter Cu...Cu separations with lower deviation of Cu(II) from  $O_4$  - plane (Table 4).

Table 4

Structural data for some relevant paddle-wheel copper(II) complexes.

| Compound <sup>a</sup>   | Space group                        | Cu...Cu, Å | Deviation of Cu(II) from $O_4$ -plane, Å | Reference    |
|---|------------------------------------|------------|--|--------------|
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (ina) <sub>2</sub> ]·2dmsol ( <b>1</b> )                | <i>P</i> -1                        | 2.626      | 0.196                                    | Present work |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (ina) <sub>2</sub> ]                                    | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 2.648      | 0.212                                    | [17]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (ina) <sub>2</sub> ]·CH <sub>3</sub> CN                 | <i>P</i> -1                        | 2.611      | 0.191                                    | [14]         |
| [Cu <sub>2</sub> (OMba) <sub>4</sub> (ina) <sub>2</sub> ]                                   | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 2.637      | 0.203                                    | [18]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (4-ppy) <sub>2</sub> ]                                  | <i>I</i> 4 <sub>1</sub> / <i>a</i> | 2.654      | 0.211                                    | [33]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (ppca) <sub>2</sub> ]                                   | <i>C</i> 2/ <i>c</i>               | 2.644      | 0.209                                    | [34]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (4-acpy) <sub>2</sub> ]                                 | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 2.631      | 0.203                                    | [35]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (dpya) <sub>2</sub> ]                                   | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 2.648      | 0.210                                    | [36]         |
| [Cu <sub>2</sub> (OAc) <sub>4</sub> (CF <sub>3</sub> -py) <sub>2</sub> ]                    | <i>C</i> ccm                       | 2.623      | 0.202                                    | [37]         |
| {[Cu <sub>2</sub> (OAc) <sub>4</sub> (tpt) <sub>2</sub> ]·2CH <sub>3</sub> OH} <sub>n</sub> | <i>P</i> 2 <sub>1</sub> / <i>n</i> | 2.605      | 0.186                                    | [38]         |

<sup>a</sup>Abbreviation: *HMba*=4-Methylbenzoic acid;

4-*ppy*=4-phenylpyridine;

*ppca*=*N*-phenyl-4-pyridinecarboxamide;

4-*acpy*=4-acetylpyridine;

*dpya*=*N,N*-dimethyl-4-(pyridin-4-yl)diazanyl aniline;

*CF<sub>3</sub>-py*=4-trifluoromethylpyridine;

*tpt*= 2,4,6-tri(4-pyridyl)-1,3,5-triazine.

Notably, our survey of the Cambridge Structural Database (ConQuest Version 1.17) reveals 6 discrete compounds built up from Cu(II) atom, isonicotinamide molecule and acetate anion, 2 of them being mononuclear compounds, namely L-(diacetato)-diaqua-bis(4-carbamoyl-pyridine)-copper [38] and (acetato-O,O')-(acetato-O)-(acetic acid-O)-bis(isonicotinamide-N)-copper(II) acetic acid solvate [12], and 4 being binuclear compounds, tetrakis(μ<sub>2</sub>-acetato-O,O')-bis(isonicotinamide-N)-di-copper(II) acetonitrile solvate [12], bis-(μ<sub>2</sub>-acetato-O,O')-bis(acetato-O)-bis(isonicotinamide-N)-copper(II) methanol solvate [12], bis(μ<sub>2</sub>-acetato-O,O')-bis(acetato-O,O')-tetrakis(isonicotinamide-N)-di-copper(II) [39] and tetrakis(μ<sub>2</sub>-acetato-O,O')-bis(isonicotinamide-N)-di-copper(II) [17]. In all these compounds *ina* coordinates in monodentate mode through the pyridine N atom, while acetate ligands show diverse coordination modes: monodentate deprotonated [38], bidentate bridging modes [12,17] and combination of monodentate deprotonated-bidentate bridging modes [12], bidentate chelating-bridging modes [39] and monodentate protonated-monodentate deprotonated-bidentate chelating modes [12] within one compound.

### Infrared spectroscopy study

The IR spectrum confirms the presence of the organic ligands used in the synthesis (through the typical vibrations of pyridine rings, amide, and carboxylic groups) [40]. The spectrum exhibits very strong and broad bands due to stretching vibrations of coordinated carboxylate groups at 1408 cm<sup>-1</sup> ν<sub>s</sub>(COO) and 1614 cm<sup>-1</sup> ν<sub>as</sub>(COO) of acetate anions. The absorption bands at 3300, 3163 and 1619 cm<sup>-1</sup> can be attributed to ν(NH) and δ(NH<sub>2</sub>), respectively and the oscillations at 1557 and 1025 cm<sup>-1</sup> show the presence of aromatic rings. The vibrations at 2953, 2924 and 2854 cm<sup>-1</sup> are attributed to ν(CH), at 1347 cm<sup>-1</sup> to δ(CH) and the vibrations at 1678 and 1230 cm<sup>-1</sup> correspond to ν(C=O) and ν(C-N), respectively. The presence of dimethylsulfoxide in the complex is documented by the oscillations at 2794 cm<sup>-1</sup> ν<sub>as</sub>(CH<sub>3</sub>), 2921 cm<sup>-1</sup> ν<sub>s</sub>(CH<sub>3</sub>), 1069 and 1050 cm<sup>-1</sup> ν(-S=O), 722 cm<sup>-1</sup> ν(-C-S-C-) and 682 cm<sup>-1</sup> ν(-C-S-).

### Thermogravimetric analysis

The decomposition of **1** was investigated by combined TG-DTA. It was found that **1** has three separate weight loss steps (Figure 2). The first weight loss step is observed in the range of 165-188 °C corresponding to the loss of the two solvated *dmsol* molecules (found, 20.9%; calcd., 20.5 %). In the range of 195-239 °C takes place the second weight loss that can be attributed to two *ina* molecules (found, 31.5%; calcd., 31.7%). Both processes are endothermic. Beginning with 340 °C, a strong exothermic process was observed, with maximum at 430 °C, caused by oxidative degradation of the remaining compound. The final residue corresponds to CuO with no changes to 1000 °C.

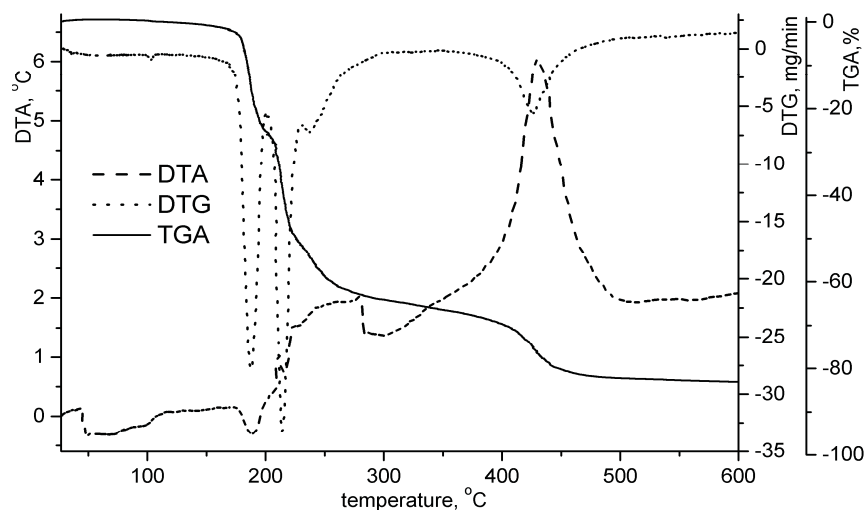


Figure 2. TG-DTA pattern of compound 1.

## Conclusions

A new dinuclear tetracarboxylato-bridged copper(II) solvatomorph  $[\text{Cu}_2(\text{OAc})_4(\text{ina})_2] \cdot 2\text{dmsO}$  (**1**) ( $\text{OAc} = \text{CH}_3\text{COO}^-$ ,  $\text{ina} = \text{isonicotinamide}$  and  $\text{dmsO} = \text{dimethylsulfoxide}$ ) was prepared and studied by IR spectroscopy, TGA analysis and single crystal X-ray method. Four carboxylate ligands bridge two copper ions in a *syn, syn*- $\eta^1:\eta^1:\mu$  mode showing a paddle-wheel unit. Isonicotinamide ligands coordinate to copper(II) in a monodentate form through the nitrogen atom of pyridine. The Cu(II) cation is pentacoordinated in a  $\text{NO}_4$ -environment in the shape of distorted square-pyramid. The amide moiety of isonicotinamide ligands forms  $\text{N-H} \cdots \text{O}$  hydrogen bonds resulting in infinite linear chains.

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