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# SYNTHESIS, CRYSTAL STRUCTURE, AND THERMAL DECOMPOSITION STUDY OF THE NEW [TETRAAQUA-*BIS*-(MONOHYDROGEN SQUARATE)]ZINC(II) COMPLEX

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In this paper, we report the synthesis and the crystal structure of a new $Zn^{II}$-monosquarato complex: $[Zn(HC_4O_4)_2(OH_2)_4]$, where we have a combination of the oxygen donor and hydrogen bond acceptor capabilities of monosquarate anion, as well as its thermal behavior. From crystallographic point of view, the complex $[Zn(HC_4O_4)_2(OH_2)_4]$ is isomorphous to the already described complexes $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe, Cd) crystallized in the triclinic space group *P*-1. In $[Zn(HC_4O_4)_2(OH_2)_4]$, the metal center is coordinated in an octahedral geometry by six O atoms: four water molecules and two monosquarate ($HC_4O_4^-$) ligands arranged in a *trans* configuration to each other. Packing in this solid is dominated by intermolecular O—H···O hydrogen bonding. The monosquarate anions are associated *via* the shortest hydrogen bonds which exist in this crystal structure ($d_1$(O···O) = 2.433(3) Å, $d_2$(O···O) = 2.450(3) Å) to form "*head-to-tail*" infinite one-dimensional chains. Adjacent chains are interconnected by $[Zn(OH_2)_4]^{2+}$ units. The thermal stability of the compound was investigated by the TG and DSC techniques, and the results suggest that the nanopowder of ZnO (average crystallite size of ZnO particles = 22 nm) is obtained as a final product, through a dehydration / decomposition process.

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*Keywords*: monosquarate complexes, zinc, crystal structure, thermal study

## 1. Introduction

Squaric acid ($H_2C_4O_4$) is a diprotic acid having two enol groups with pKa values of 1.2-1.7 and 3.2-3.5, as well as two highly polarized carbonyl groups [1-3]. Deprotonation of the squaric acid gives the monoanion ($HC_4O_4^-$) and the square-planar dianion ($C_4O_4^{2-}$) with an increased charge density on the oxygen atoms [4].

The unique structure of squaric acid and anionic derivatives – cyclic compounds with aromaticity, four carbon-oxygen partial double bonds – provides not only versatile proton acceptor sites [5] at the carbonyl function for hydrogen bonding but also binding sites to metal ions [6, 7]. As ligand in metallic complexes, squaric acid acts in deprotonated forms: ($HC_4O_4^-$) and ($C_4O_4^{2-}$), and exhibits various coordination modes: monodentate, chelating, 1,2-μ-, 1,3-μ-bridging [8]. In 2001, Hall and Williams reviewed the coordination chemistry of squaric acid derivatives [9] with the emphasis on structure and properties.

For 3*d*-transition metals, three types of metal squarate complexes are known: $[M(C_4O_4)(OH_2)_4]$ (M = Mn, Fe, Co, Ni, Cu, Zn) [10, 11], $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe, Cd) [12-14], and $[M(C_4O_4)(OH_2)_2]$, (M = Mn, Fe, Co, Ni, Cu, Zn) [15-17]. While for tetraaqua metal squarate complexes, $[M(C_4O_4)(OH_2)_4]$, (M= Fe, Co, Ni, Zn), the structures are well-known: polymeric chain structures with $C_4O_4^{2-}$ as a bridge ($\mu$-2) ligand between two metal ions in the *trans*

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position, for corresponding complexes with monosquarate anion as ligand, $[M(HC_4O_4)_2(OH_2)_4]$, the information are scarce. A CSD survey [18] on these $[M(HC_4O_4)_2(OH_2)_4]$ complexes revealed that there are only three known crystal structures and they are all isostructural with space group *P*-1, with layer-type structures [12-14].

The monohydrogen squarate anions ($HC_4O_4^-$) can be associated *via* strong hydrogen bonds to form *head-to-tail chains*, *head-to head cyclic dimers* or *tetramers* [19].

In this paper, we report the synthesis and the crystal structure of a new $Zn^{II}$-monosquarato complex: $[Zn(HC_4O_4)_2(OH_2)_4]$, where we have a combination of the oxygen donor and hydrogen bond acceptor capabilities of monosquarate anion, as well as its thermal behavior.

From crystallographic point of view, the complex $[Zn(HC_4O_4)_2(OH_2)_4]$ is isomorphous to the already described complexes $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe, Cd) [12-14] crystallized in the triclinic space group *P*-1.

With regard to the thermal behavior of the title complex, the results indicated dehydration in the first two steps (T < 210ºC) and decomposition in two subsequent steps (up to 310ºC and 400ºC respectively); the total weight loss of 78.53% corresponds to the formation of ZnO. The solid products resulted from each thermal decomposition step were isolated and structurally characterized by means of elemental analysis, and X-ray powder diffraction.

## 2. Experimental

### 2.1. Chemicals and methods

**Chemicals:** Squaric acid, $Zn(NO_3)_2 \cdot 6H_2O$ were purchased and used without further purification.

**Physical Measurements:** Elemental analyses for carbon and hydrogen were carried out with a Heraeus CHNO-Rapid apparatus.

Thermal analysis TG-DSC was followed with a Netzsch 449C STA Jupiter. Samples were placed in closed Al crucible and heated with $1 K \cdot min^{-1}$ from room temperature to 550°C, under the flow of $20 mL \cdot min^{-1}$ dried air. An empty Al crucible was used as reference.

Powder diffraction patterns were recorded with a Stoe Imageplate-detector IP-PSD.

### 2.2. Synthesis of $[Zn(HC_4O_4)_2(OH_2)_4]$, 1

Stoichiometric amounts of $Zn(NO_3)_2 \cdot 6H_2O$ (0.298g, 1 mmol) and (squaric acid) (0.114 g, 1 mmol) were dissolved in water (40 ml) and stirred at 50°C for 30 min. Colourless single crystals of **1** suitable for X-ray diffraction studies have been obtained by slow evaporation in air of the resulted aqueous solution. $[Zn(HC_4O_4)_2(OH_2)_4]$, **1**: calc (%): C 26.43, H 2.77; found: C 26.31, H 2.59.

### 2.3. Crystallographic Studies

For intensity data collection a single crystal of **1** was mounted on a glass fiber and placed directly in a cold stream of dinitrogen. Crystal data, parameters in data collection and convergence results are listed in Table 1.

*Table 1. Crystal data, data collection parameters, and convergence results for compound* **1**

| | **1** |
|---|---|
| Empirical formula | $C_8H_{10}O_{12}Zn$ |
| Moiety formula | $C_8H_{10}O_{12}Zn$ |
| Formula mass | 363.53 |
| Crystal habit, color | block, colorless |
| Crystal dim. (mm) | 0.42 x 0.4 x 0.4 |
| Crystal system | Triclinic |
| Space Group | *P*-1 |
| $a$ [Å] | 5.0919(5) |
| $b$ [Å] | 7.3113(7) |
| $c$ [Å] | 8.7536(7) |
| $\alpha$ [°] | 66.440(6) |
| $\beta$ [°] | 77.254(7) |
| $\gamma$ [°] | 75.480(7) |
| V [$Å^3$] | 286.50(5) |
| Z | 1 |
| D [$g.cm^{-1}$] | 2.107 |
| F000 | 184 |
| $\mu$(Mo-$K_\alpha$) [$mm^{-1}$] | 2.216 |
| Diffractometer | STOE IPDS 2θ |
| T [K] | 100 (2) |
| θ range | 4.68– 29.66 |
| Refl. collected | 3003 |
| Unique refl. | 1308 |
| $R_{int}$ | 0.0734 |
| Reflections I>2σ(I) | 1291 |
| Parameters refined | 115 |
| $R_1$[2σ(I)] | 0.0513 |
| $R_1$ (all data) | 0.0534 |
| $wR_2$ | 0.1325 |
| GooF | 1.092 |
| Diff. peak/ hole [e/$Å^3$] | 1.464/ -1.792 |

Data collection was performed on a STOE IPDS 2θ (Mo-$K_\alpha$ radiation, $\lambda$= 0.71073 Å, graphite monochromator) image plate diffractometer. The unit cell parameters were obtained by least-squares refinement of 8896 reflections. The structure was solved by direct methods (SHELXS-97) [20] and refined by full matrix least-squares procedures based on $F^2$ with all measured reflections (SHELXL-97) [20]. The MULABS [21] program was used for absorption correction. Non-hydrogen atoms were assigned anisotropic displacement parameters. The positions of the hydrogen atoms were obtained as local maxima of electron density in a Fourier difference synthesis and were freely refined; H(3) attached to O(3) was treated as riding on the oxygen atom with $U_{iso}(H) = 1.2U_{eq}(O)$. The O-H bond distances in the water molecules were idealized to 0.84 Å. These positions are in agreement with classical hydrogen bonds between the water oxygen atom and two close acceptors.

Searches in the Cambridge Structural Database (CSD) [18] refer to Version 5.34. All searches were restricted to error-free data without disorder and to entries for which 3D coordinates were available.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 929462. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

## 3. Results and discussion

### 3.1. Crystal structure

We will first describe the experimentally observed crystal structure and then we discuss the thermal behavior of **1**.

The compound crystallizes in the very popular centrosymmetric space group *P*-1 and it is isomorphous to $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe, Cd) described previously in the literature. [12-14].

The central Zn atom has octahedral coordination geometry composed of six oxygen atoms: two from the monohydrogen squarate ligands and four from water molecules (Figure 1). Selected distances and angles are presented in Table 2.

*Table 2. Selected distances and angles for* ***1***

| Distances, Å | | | |
|---|---|---|---|
| Zn(1)-O(1) | 2.115(2) | Zn(1)-O(6) | 2.100(2) |
| Zn(1)-O(5) | 2.035(2) | | |
| **Angles, °** | | | |
| O(5)-Zn(1)-O(6) | 92.10(8) | O(6)-Zn(1)-O(1) | 90.24(8) |
| O(5)-Zn(1)-O(1) | 88.96(8) | | |

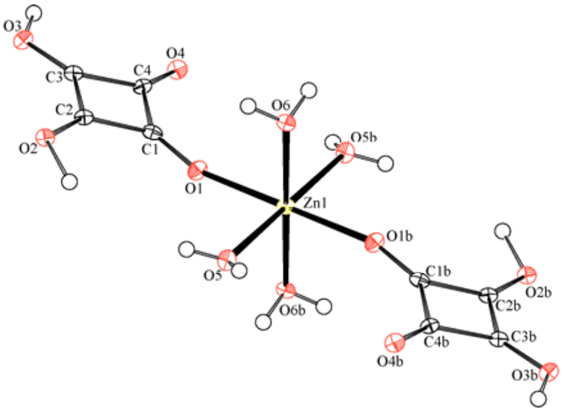

*Fig. 1. The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level [22] and H atoms are represented by spheres of arbitrary radius.*

In the squarate monoanions there are two short C – O bonds and two long C – O bonds; this elongation of the bond lengths C(2) - O(2) [1.287(4) Å] and C(3) - O(3) [1.265(4) Å] as compared with nonprotonated C(4) - O(4) [1.236(4) Å] is in agreement with the presence of H(2) and H(3) bonded to O(2) and O(3) respectively. The H atoms in the anions lie on inversion centers connecting adjacent units.

Intermolecular interactions stabilize the crystal structure of this compound.

The monosquarate anions interact *via* the shortest hydrogen bonds which exist in this crystal structure ($d_1(O\cdots O)$ = 2.433(3) Å, $d_2(O\cdots O)$ = 2.450(3) Å) to form "*head-to-tail*" infinite one-dimensional chains propagated in the *ab* plane. The chains are running parallel along the *c*-axis.

These hydrogen bonds are shorter than those observed in the anionic monosquarate dimers described in our previous work [23] or those observed in the isomorphous compounds $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe; with $d_{1Mn/Fe}(O\cdots O)$ = 2.463(3)/2.458(3) Å, $d_{2Mn/Fe}$ $(O\cdots O)$ = 2.483(3)/2.470(3) Å ) [13].

Adjacent chains are interconnected by $[Zn(OH_2)_4]^{2+}$ cations giving rise to a sheet structure (Fig.2).

The shortest Zn-Zn separation amounts to 5.0919Å, which corresponds to the lattice parameter *a*.

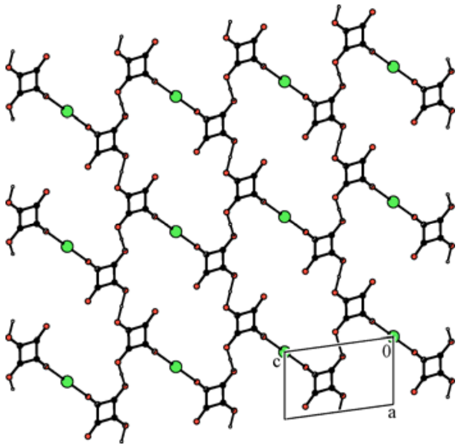

*Fig. 2. Representation of $[HC_4O_4]_n$ chains in the molecular structure of $[Zn(HC_4O_4)_2(OH_2)_4]$. Water molecules omitted for clarity.*

The water molecules also participate in hydrogen-bonds network: the equatorial water molecules strengthen the assembly of the chains into sheets; the aqua oxygen O(5) acts as a hydrogen-bond donor towards O(2) from squarate anion of an adjacent chain (d(O···O) = 2.725(3) Å).

In the *b* direction, the two other *trans*-aqua ligands (labeled O(6) and O(6b) in Fig.1), link two adjacent sheets *via* two sets of three intermolecular O—H···O hydrogen bonds [O(5)—H···O(6) and two O(6)—H···O(4)] giving rise to a layer-type structure (Fig.3).

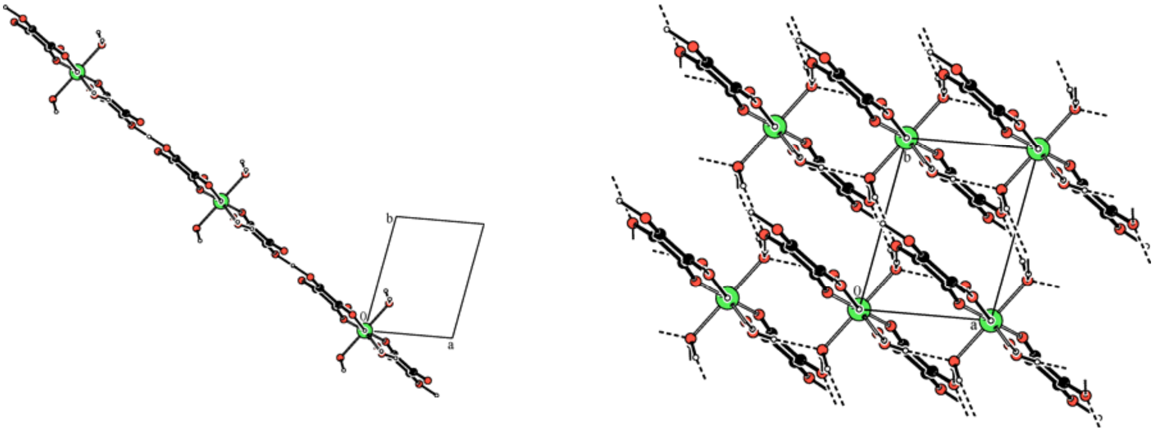

*Fig. 3. Crystal structure of $[Zn(HC_4O_4)_2(OH_2)_4]$.*

The hydrogen bond parameters are presented in Table 3.

*Table 3. Hydrogen-bond geometry (Å ,°)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O(2)--H(2)···O(2)$^{i}$ | 1.22 | 1.22 | 2.433(3) | 180 |
| O(3)--H(3)···O(3)$^{ii}$ | 1.22 | 1.22 | 2.450(3) | 180 |
| O(5)--H(50)···O(2)$^{i}$ | 0.83(4) | 1.90(4) | 2.725(3) | 174(5) |
| O(5)--H(51)···O(6)$^{iii}$ | 0.83(3) | 1.91(4) | 2.742(3) | 174(5) |
| O(6)--H(60)···O(4)$^{iv}$ | 0.83(5) | 1.86(5) | 2.686(3) | 176(5) |
| O(6)--H(61)···O(4)$^{v}$ | 0.85(4) | 2.00(4) | 2.758(3) | 149(3) |

$^{i}$ = -x,1-y,1-z; $^{ii}$ = -2-x,1-y,1-z; $^{iii}$ = 1-x,-y,-z, $^{iv}$ = 1+x,y,z, $^{v}$ = -1-x,1-y,-z.

### 3.2. Thermal study (TG-DSC)

Thermal reactivity of metal carboxylates is a topic of general importance in materials science; thermal decompositions reactions of metal carboxylates are convenient routes for obtaining simple and mixed oxides with various structures. Among metal carboxylates, the simplest metal formates, acetates and oxalates have been more intensely investigated but other unsaturated and aromatic carboxylates such as squarate have gained increased importance in the last decades.

Solid-state thermal studies of several metal squarate and mixed ligand of the metal squarate complexes have been reported [24-28], indicating a high thermal stability of the squarate moiety.

TG/DSC measurements were performed in dry air atmosphere under dynamic conditions. The thermal decomposition pathway of $[Zn(HC_4O_4)_2(OH_2)_4]$ consists of four stages (Fig. 4). The solid products resulted from each thermal decomposition step were isolated and structurally characterized by means of elemental analysis.

The proposed pathway for thermal decomposition of $[Zn(HC_4O_4)_2(OH_2)_4]$ together with TG-DSC curves over the whole temperature range (25-530ºC) are given in Fig.4:

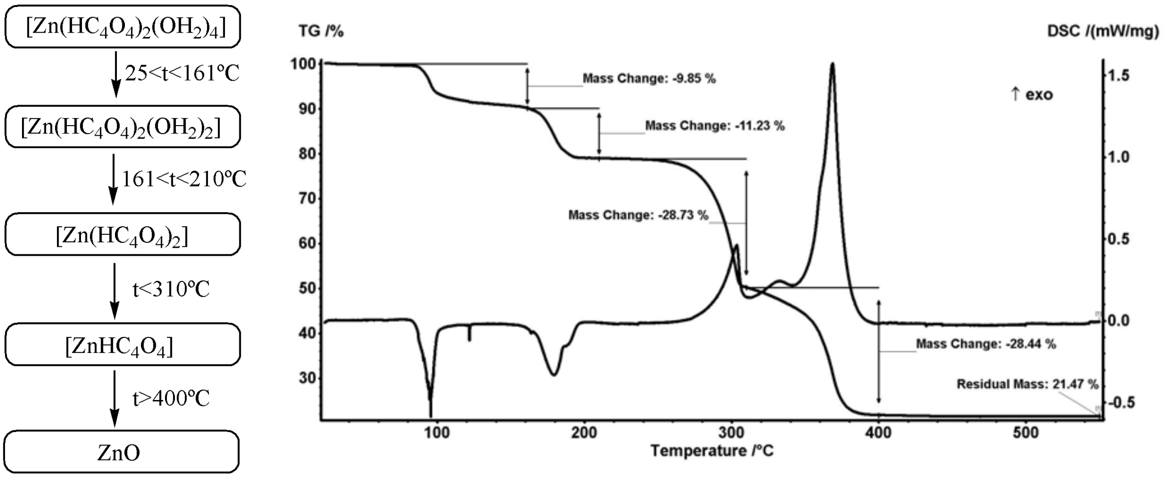

*Fig. 4. TG-DSC curves for $[Zn(HC_4O_4)_2(OH_2)_4]$ over the whole temperature range (25-530ºC).*

- The first stage was attributed to the partial dehydration of the complex compound (25-161ºC; mass loss%: exp. 9.85; calcd. 9.91); the two more labile water molecules from the apical positions have been released at this point. This step is accompanied by an endothermic effect with a maximum at 95.7°C. The proposed formula for the resulting complex is $[Zn(HC_4O_4)_2(OH_2)_2]$: calcd. (%): C 29.33, H 1.85; found: C 29.09, H 1.96.

The DSC endothermic peak at 122.1°C, with no evident mass loss, can be attributed to the rearrangement in the hydrogen bond network.

- The second stage (161-210ºC; mass loss%: exp. 11.23; calcd. 9.91), corresponds to the loss of the remaining coordinated water molecules. The mass loss is accompanied by an endothermic effect with maximum at 179.3ºC. The intermediate compound obtained at 210ºC, has the proposed formula $[Zn(HC_4O_4)_2]$: calcd. (%): C 32.96, H 0.69; found: C 32.06, H 1.11.

In the third (up to 310ºC) and fourth stages (up to 400ºC), monosquarate ligand is decomposed in successive exothermic processes, with mass losses of 28.73% and 28.44% respectively, corresponding to the release of four moles of CO/squarate molecule. This behavior of squarate molecule has been reported earlier [29]. Both steps are accompanied by exothermic effects, with maxima at 303.7°C, 332.9°C and 368.8°C (strongest). At 310ºC, the resulting compound has a molecular formula – $C_4HO_4Zn$ – corresponding to the ($[Zn(HC_4O_4)]$) fragment: calcd. (%): C 26.92, H 0.56; found: C 27.59, H 0.63.

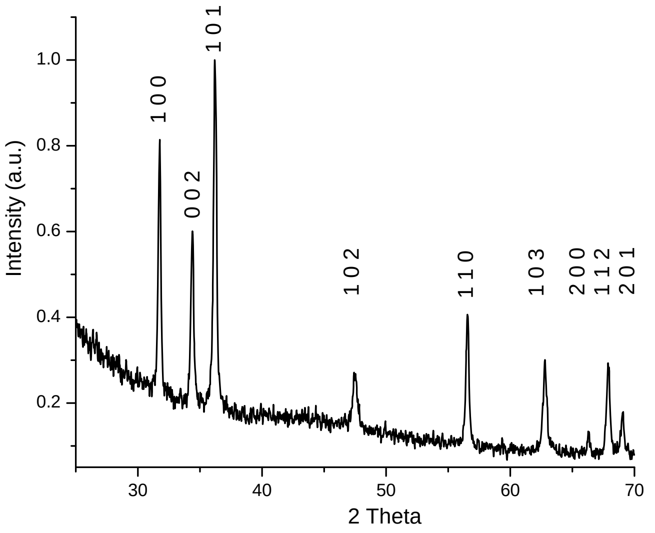

*Fig. 5. The XRD pattern for ZnO, the final product of decomposition process of* ***1***

The total experimental mass loss of 78.53% is in good agreement with the theoretical mass loss, 77.68%, deduced from the overall thermal decomposition process, leading to ZnO. The residue identification was done by powder X-Ray diffraction. The XRD data presented in Fig. 5 sustain the formation of ZnO as final product. All patterns can be indexed to a hexagonal wurtzite structure (ASTM 80-0075). The crystallite size of the sample can be estimated from the Scherrer equation. The strongest peak (101) at $2\theta = 36.17^{o}$ was used to calculate the average crystallite size of ZnO particles. The average crystallite size of the sample is 22 nm.

## 4. Conclusions

The synthesis, the crystal structure and the thermal behavior of a new $Zn^{II}$-monosquarato complex: $[Zn(HC_4O_4)_2(OH_2)_4]$, have been described in this paper.

The complex $[Zn(HC_4O_4)_2(OH_2)_4]$ is isomorphous to the $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe, Cd) complexes, but the hydrogen bonds ($d_1(O\cdots O) = 2.433(3)$ Å, $d_2(O\cdots O) = 2.450(3)$ Å), which stabilize the crystal structure of this compound, are shorter than those observed in the isomorphous compounds $[M(HC_4O_4)_2(OH_2)_4]$, (M = Mn, Fe; with $d_{1Mn/Fe}(O\cdots O) = 2.463(3)/2.458(3)$ Å, $d_{2Mn/Fe}$ $(O\cdots O) = 2.483(3)/2.470(3)$ Å ).

The thermal stability of the compound was investigated by the TG and DSC techniques, and the results suggest that the nanopowder of ZnO with average crystallite size of 22 nm is obtained as a final product, through a dehydration / decomposition process.

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