



Reversible desorption and absorption of water in a zinc-based coordination polymer nanostructure



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ABSTRACT

A zinc-based coordination polymer $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**), (3-HClb = 3-chloro benzoic acid), has been synthesized and structurally characterized by single crystal X-ray crystallography. It composed from one-dimensional zigzag chains but secondary hydrogen bonding interaction, extended its structure and two-dimensional supramolecular network was formed. Compound **1** nanostructure was synthesized by sonochemical procedure. Reversible desorption and adsorption of water in this zinc coordination polymer were studied by IR spectroscopy, thermo gravimetric and differential thermal analyses (TG-DTA), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

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1. Introduction

The design of crystal structures and control of molecular arrangements of coordination polymers has attracted much attention in recent years [1,2]. The compounds with backbones constructed by metal ions as “nodes” and ligands as “linkers” form a family of polymers, which are called “coordination polymers [3,4]. The architecture of coordination polymers can be reasonably well predicted rests upon the simple premise that the coordination geometry of metal ions can be propagated with rigid bridging ligands [4–7]. The arrangement of the components in coordination polymers mostly only exist in the solid-state [8]. The building blocks interact through coordination interactions and weaker forces such as hydrogen bonds, stacking or van der Waals interactions in solution giving some small molecular units, and then, thanks to self-assembly processes coordination polymers grow based on the same interactions [9,10]. Synthesizing of these types of compound is frequently used in several applications such as electronics, catalysis, luminescence, drug delivery and separation [11–13]. Structures of coordination polymers can so far only be determined by X-ray crystallographic methods and characterizations in solution usually prove only the existence of oligomeric fragments [9,12]. Recent advances in nanostructured materials

have been led by the development of new synthetic methods that provide control over size, morphology, and nano/microstructure [14]. Nanostructured materials have been prepared by a variety of synthetic methods. Among a variety of these methods, the utilization of ultrasound for nanomaterials synthesis has been extensively examined over many years, and in recent years, most researchers use it as one of the most powerful tools in nanostructured materials synthesis [15]. Both chemical and physical phenomena associated with high-intensity ultrasound are responsible for the production or modification of nanomaterials. Most notable are the consequences of acoustic cavitation: the formation, growth, and implosive collapse of bubbles [16–20]. Solid-state structural transformations involving coordination polymers induced by light, heat, guest removal, uptake or exchange, expansion of coordination numbers, oxidation of metal centers, condensation, or reactions between the ligands are very fascinating [21–24]. The vacant coordination sites at the metal centers created by the removal of ligands are often found to be re-established by the free donor sites of the neighbouring ligands or guest molecules in the solid [25–27]. Herein, we wish to report a zinc-based coordination polymer, $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**), which was characterized by IR spectroscopy, thermogravimetric analysis, single-crystal X-ray diffraction. Moreover, we would like to study solid-state thermal conversion of compound **1** nanostructures, synthesized by sonochemical process, to $[\text{Zn}(3\text{-Clb})_2]_n$ (**2**). Also the reversibility of this solid-state conversion was studied.

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2. Experimental

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. The molecular structure plots were prepared using Mercury. PARSONIC 15S ultrasonic bath (with the frequency 28 kHz) was used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in ATR form, in the range of 400–4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's numbers. Intensity data for $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**) was collected with an Oxford Diffraction SuperNova CCD diffractometer using Mo $K\alpha$ radiation, the temperature during all data collections was maintained at 130.0(1) K using an Oxford Cryosystems cooling device. The structures were solved by direct methods and difference Fourier synthesis [28]. Thermal ellipsoid plots were generated using the program ORTEP-3 [29] within the WINGX suite of programs [30]. The thermal behavior was measured with a PL-STA 1500 apparatus between 20 and 550 °C, with a heating rate of 5 °C min^{-1} , under a nitrogen atmosphere. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) with step-size of 0.01671 (°). The X-ray source was operated under voltage and current of 40 kV and 30 mA, respectively. Bragg–Brentano was used as a source – detector geometry with scintillation detector. Additional attachments or peripheral equipment such as anti-scatter slit (1°), divergence slit (1°), monochromator and soller slit (0.04 rad) were also used in this diffractometer. The samples were prepared as fine powders on silicon based material. Simulated XRD powder patterns based on single crystal data were prepared using the Mercury software. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

2.2. Synthesis of $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**)

1.5 mmol (0.258g) 3-chloro per benzoic acid was dissolved in 20 mL H_2O and was mixed and stirred with solution of 1.5 mmol (0.084 g) KOH in 5 mL H_2O at 100 °C for an hour. Then solution of 0.75 mmol (0.222 g) $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 5 mL H_2O was added to the mixture in a drop wise manner and heated at 100 °C for an hour. After filtering, it was allowed to evaporate for several days and then suitable white crystals were obtained. d.p. = 256 °C, yield: 0.117 g, 39.5% based on final product. The crystals of **1** were prepared and structurally analyzed previously from the reaction between $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ and sodium 3-chlorobenzoate, too [31].

2.3. Sonochemical synthesis of $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**) nano structures and studies the reversible desorption and adsorption of water in it

In order to synthesize the nanostructures of compound **1**, a reaction was done with 3 mmol of KOH (0.168 g), 3-chloro per benzoic acid (0.516 g) and 1.5 mmol (0.445 g) of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in ultrasonic bath. First of all, 3 mmol of 3-chloro per benzoic acid and KOH were mixed in 20 mL water and stirred for 1 h at 100 °C. After that, the obtained mixture was placed in ultrasonic synthesizer and then a solution of 1.5 mmol $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 5 mL H_2O was added to mixture in a drop wise manner under the ultrasonic irradiation. The white precipitates were formed. The obtained precipitate was filtered, subsequently washed with water and then dried. d.p. = above 300 °C, yield: 0.503 g, 85.0% based on final product. In order to preparation of compound $[\text{Zn}(\mu_2\text{-3-Clb})_2]_n$

(**2**), powders of compound **1**, was heated at 135 °C in a furnace and static atmosphere of air for 3 h. The color of this compound did not change during this process (d.p. = 105 °C). In order to study reversibility of this conversion, compound **2** precipitate was immersed in water for three days (d.p. = above 300 °C).

3. Result and discussion

The reaction between 3-chloro perbenzoic acid (3-HClpb) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ resulted in formation of crystalline materials (Tables 1 and 2) with general formula of $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**). Fig. 1a shows the primary structural building unit of **1**. 3-Clb[−] is bridging between two Zn ions and can be considered as a bidentate ligand (Fig. 1). One type of Zn(II) ion is present in **1** and four oxygen atoms from four 3-Clb[−] ligand and one oxygen atom of a water molecule coordinate to each Zn(II) ion. Finally, we could consider Zn(II) ion with ZnO_5 coordination sphere (Figs. 1 and S1 in the SI). Coordination environment around Zn(II) ion is approximately trigonal bipyramidal and the coordinated water molecule exists in equatorial situation (Fig. S1 in the SI). Compound **1** is a one-dimensional coordination polymer (Fig. 1b) but secondary hydrogen bonding interactions (Table 3) between two adjacent subunits or chains (Fig. 2a) results in formation of two-dimensional supramolecular network (Fig. 2b). TG-DTA data (Fig. 3a) indicated that compound **1** single crystals are stable up to 105 °C and endothermic releases of its coordinated water molecule occurs between 105 and 152 °C with the mass loss of 6.5% (Calc. 4.6%). It seems that the guest-free phase of **1** is thermally stable up to 180 °C (Fig. 3a). Between 180 and 510 °C, thermal decomposition of 3-Clb[−] occurred with an endothermic and two exothermic peaks at 330, 440 and 490 °C, respectively. Finally ZnCl_2 with observed and calculated mass residue of 40.1% and 34.5% probably was formed at 510 °C (Fig. 3a).

The reaction between 3-HClpb and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in water by sonochemical process results in formation of white powder which

Table 1
Crystal data and structure refinement for compound $[\text{Zn}(\mu_2\text{-3-Clb})_2\cdot\text{H}_2\text{O}]_n$ (**1**).

Identification code	1
Empirical formula	$\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{O}_5\text{Zn}$
Formula weight	394.49
<i>T</i> (K)	100.0(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	31.828(6)
<i>b</i> (Å)	6.1480(12)
<i>c</i> (Å)	7.4510(15)
α (°)	90.00
β (°)	97.10(3)
γ (°)	90.00
<i>V</i> (Å ³)	1446.8(5)
<i>Z</i>	4
<i>D</i> _{Calc} (g cm ^{−3})	1.811
Absorption coefficient (mm ^{−1})	2.084
<i>F</i> (000)	792
Crystal size (mm)	0.06 × 0.05 × 0.05
θ (°)	3.838–31.728
Index ranges	−45 ≤ <i>h</i> ≤ 45 −8 ≤ <i>k</i> ≤ 8 −9 ≤ <i>l</i> ≤ 9
Independent reflections	2049
Data/restraints/parameters	12478/0/105
Goodness-of-fit on <i>F</i> ²	1.103
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0262 <i>wR</i> ₂ = 0.0683
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.0269 <i>wR</i> ₂ = 0.0687

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