



Ultrasound-assisted fabrication of a new nano-rods 3D copper(II)-organic coordination supramolecular compound



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ABSTRACT

High-energy ultrasound irradiation has been used for the synthesis of a new copper(II) coordination supramolecular compound, $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**), (“phen” is 1,10-phenanthroline) with nano-rods morphology. The new nano-structure was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), FT-IR spectroscopy and elemental analyses. Compound **1** was structurally characterized by single crystal X-ray diffraction. The utilization of high intensity ultrasound has found as a facile, environmentally friendly, and versatile synthetic tool for the supramolecular coordination compounds.

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1. Introduction

Crystal engineering, the design and synthesis of supramolecular metal–organic coordination compounds is frontier field in research, not only for their variety of architectures and interesting molecular topologies but also because of their potential applications in zeolite-like catalysts, host–guest chemistry, gas storage, ion exchange, molecular recognition, photonic materials and magnetic [1–5]. High quality crystals of metal–organic coordination compounds, such as those suitable for single-crystal X-ray diffraction measurements, can usually be obtained by a variety of approaches using wet solution chemistry and/or solvothermal methods [6]. In many cases, long reaction times are needed, usually several days for solvothermal, and several weeks for diffusion methods. Furthermore, the reaction of framework building blocks under solvothermal conditions has to be carried out at high temperatures (usually 373–523 K) and pressures (1–10 MPa). Also, because of the huge potential for industrial applications of these compounds, it is important to develop novel and more efficient alternative synthesis techniques, which are techno-economically viable and could be scaled up in production of these compounds; so that to be considered applicable [7].

Compared to traditional energy sources (e.g., heat, light and electric potential), ultrasonic (US) irradiation provides rather unusual reaction conditions (a short duration of extremely high temperatures and pressures in liquids) that cannot be realized by other traditional methods [8–10]. On the other hand, recent advances in nanostructured coordination compounds have been led by development of new synthetic methods that provide control over size, morphology, and nano/microstructure. The utilization of high intensity US offers a facile, environmentally friendly, and versatile synthetic tool for the nanostructured materials [11]. Nano coordination compounds possess superior properties compared to their macroscopic counterparts in adsorption kinetics, magnetic resonance imaging, recognition, biosensing, optics, and storage. Moreover, small particles of these compounds are also effective in the preparation of membranes or films [12–14]. Sonochemistry is the research area in which chemical reactions are influenced by the application of powerful US radiation (20 kHz–10 MHz). US induces chemical or physical changes during cavitation. Acoustic cavitation is the formation, expansion, and subsequent implosive collapse of bubbles in a liquid medium [15]. When liquids are irradiated with US, the alternating expansive and compressive acoustic waves create bubbles (i.e., cavities) and make the bubbles oscillate. The oscillating bubbles can accumulate US energy while growing to a certain size (tens of mm). A bubble can overgrow and subsequently collapse within a very short lifetimes (with a heating and cooling rate of $>10^{10} \text{ K s}^{-1}$) and can be considered as

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adiabatic. A large energy concentration is achieved during the collapse, resulting in a local temperature of ~ 5000 K and a pressure of ~ 1000 bar. This energy is dispersed to the surroundings during the collapse and after-bounces, so that the gas temperature in the hot spot quickly returns to the ambient value [16]. As a result, various chemical reactions, even some reactions that were previously difficult to realize by other traditional methods, can also proceed at the room temperature using US irradiation [17].

Transition metal complexes, especially Cu(II) complexes, have been investigated widely [18–20]. For Cu(II) ion, there is one odd d-electron occupies in one of the d-orbitals which gives rise to structural flexibility. Copper is a bio-element and an active site in several metalloproteins and enzymes [21–23]. Further, Cu(II) is known to form complexes with variety of molecular geometries [24], such as tetrahedral, square planar, square pyramidal and octahedral. Ever since a variety of Cu-acetates coordination compounds were synthesized and characterized with an presence of aromatic amine (1,10-phenanthroline) [25–27]. Here, we report the experimental studies of a novel copper(II) coordination supramolecular polymer, $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**) and describe a simple sonochemical fabrication of nanostructures of this compound.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA) was used. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range $500\text{--}4000\text{ cm}^{-1}$ using the KBr disk technique. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Crystallographic measurements of compound **1** were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 100 K. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections [28]. Data reduction was performed with the SAINT software. Absorption corrections were applied with the program SADABS [28]. The structure was solved by direct methods with SHELXS-97 [29]. The refinement and all further calculations were carried out with SHELXL-97 [29]. The N- and C-bound H-atoms were included in calculated positions and treated as riding atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . Crystallographic data and details of data collections and structure refinements of compound **1** are listed in Table 1. X-ray powder diffraction (XRPD) measurements were performed using a Philips diffractometer manufactured by X'pert with monochromatized Cu $\text{K}\alpha$ radiation and simulated XRD powder patterns based on single crystal data were prepared using the Mercury [30]. The crystallite sizes of selected samples were estimated using the Scherrer method. The samples were characterized with a scanning electron microscope (Hitachi-4200) with gold coating. The molecular structure plots were prepared using Mercury [30] and ORTEPIII [31].

2.2. Synthesis of nano-rod of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**)

To prepare the nano-rod of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**), a 15 mL of a 0.01 M solution of copper(II) acetate in EtOH was positioned in a high-density ultrasonic probe, and

Table 1
Crystal data and refinement details of **1**.

Identification code	Compound 1
Empirical formula	$\text{C}_{30}\text{H}_{25}\text{BCu}_2\text{F}_4\text{N}_4\text{O}_6$
Formula weight	751.43
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 16.449(3)\text{ \AA}$ $b = 16.444(3)\text{ \AA}$ $c = 11.093(2)\text{ \AA}$
Volume	$3000.6(9)\text{ \AA}^3$
Z	4
Density (calculated)	1.663 Mg/m^3
Absorption coefficient	1.494 mm^{-1}
$F(000)$	1520.0
Crystal size	$0.2 \times 0.2 \times 0.2\text{ mm}^3$
Theta range for data collection	$2.21\text{--}28.28^\circ$
Index ranges	$-21 \leq h \leq 21$ $-14 \leq k \leq 21$ $-14 \leq l \leq 14$
Reflections collected	19,138
Independent reflections	7038 [$R(\text{int}) = 0.0800$]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7038/1/427
Goodness-of-fit on F^2	1.085
Final R. [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1264$

15 mL of a 0.01 M sodium tetrafluoroborate and 0.01 M 1,10-phenanthroline in EtOH was added dropwisely to that solution. After the end of the titration the solution remained in the bath for 1 h. The obtained precipitates were filtered off, washed with water and then dried in air.

Product: m.p. = $255\text{ }^\circ\text{C}$, yield: 69%. Found; C: 47.90, H: 3.32, N: 7.50%. Calculated for $\text{C}_{30}\text{H}_{25}\text{BCu}_2\text{F}_4\text{N}_4\text{O}_6$: C: 47.95, H: 3.35, N: 7.46%. IR (cm^{-1}) selected bonds: 713(m, C–H), 1026(m), 1100(vs C–F), 1155(s, Cl–O), 1455, 1576(s, aromatic ring), 1617(vs C–O), 3042(w, C–H_{aromatic}).

2.3. Synthesis of isolate single crystals of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**)

To isolate single crystals of $[\text{Cu}_2(\text{CH}_3\text{COO})_3(\text{phen})_2](\text{BF}_4)$ (**1**), sodium tetrafluoroborate (1 mmol), 1,10-phenanthroline (2 mmol) and copper(II) acetate (2 mmol) were placed in the main arm of a branched tube. Ethanol was carefully added to fill both arms. The tube was sealed and the main arm immersed in an oil bath at $60\text{ }^\circ\text{C}$ while the other arm was kept at ambient temperature. After 5 days, blue crystals that deposited in the cooler arm were isolated, filtered off, washed with acetone and ether and air dried.

Product: m.p. = $258\text{ }^\circ\text{C}$, yield: 48%. Found; C: 47.89, H: 3.36, N: 7.48%. Calculated for $\text{C}_{30}\text{H}_{25}\text{BCu}_2\text{F}_4\text{N}_4\text{O}_6$: C: 47.95, H: 3.35, N: 7.46%. IR (cm^{-1}) selected bonds: 710(m, C–H), 1027(m), 1100(vs C–F), 1156(s, Cl–O), 1453, 1576(s, aromatic ring), 1617(vs C–O), 3043(w, C–H_{aromatic}).

3. Results and discussion

The reaction between copper(II) acetate, 1,10-phenanthroline and sodium tetrafluoroborate leads to formation of a new crystalline material $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OOCCH}_3)(\text{phen})_2](\text{BF}_4)$ (**1**). Nano-structures of compound **1** were obtained in ethanol by US irradiation, while single crystals of compound **1**, suitable for X-ray crystallography, were prepared by a heat gradient applied to an ethanol solution of the reagents (the “branched tube method”) [32]. Fig. 1 gives an overview of the methods used for the synthesis

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