Ultrasonics Sonochemistry 31 (2016) 122–128

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Sonochemical synthesis of a new nano-sized cerium(III) supramolecular compound; Precursor for nanoceria

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ARTICLE INFO

Article history:
Received 7 November 2015
Received in revised form 17 December 2015
Accepted 18 December 2015
Available online 18 December 2015

Keywords:
Sonochemical method
Supramolecular compound
Nanoceria
Crystal structure
Cerium(III)

ABSTRACT

Using a sonochemical method, nanoparticles of a new Ce(III) supramolecular compound, $(NAMH^{+})_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ (**1**), (H_2pydc = 2,6-pyridinedicarboxylic acid, NAM = nicotinamide), have been synthesized. Compound **1** was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), FT-IR spectroscopy and elemental analyses, and its structure was determined by X-ray crystallography. It has been revealed that its structure consists of tetra-nuclear building units that extend to a 3D supramolecular network *via* non-covalent interactions mainly hydrogen bonding. The thermal stability of complex **1** both for its crystals and nanostructures has been studied by the thermal gravimetric (TG) method and compared with each other. The role of ultrasound irradiation power and the concentration of initial reactants on the size and morphology of the nano-structured complex **1**, has been investigated. Ceria nanoparticles were obtained upon the calcination of complex **1** at 800 °C under atmospheric air. Furthermore, the fluorescent properties of complex **1** at room temperature were studied.

1. Introduction

The design and synthesis of novel supramolecular coordination compounds is of great interest in coordination chemistry and solid-state chemistry due to their vast variety of applications. Several factors such as coordination bonding interactions, relatively strong hydrogen bonding and π–π stacking interactions, solvent molecules, counter ions and metal ions may be utilized into the design of new supramolecular compounds [1–4]. Considering the crucial role of the metal center in the construction of supramolecular compounds, the utilization of lanthanide elements in the construction of supramolecular compounds has been practiced vastly in the recent decade [5–8]. A wide spectrum of applications has been recognized for cerium-based supramolecular compounds which includes gas absorption, catalysis, magnetism, luminescence, molecular recognitions, optoelectronic devices, sensors, ion exchange and material science applications [9–12].

The combination of the abovementioned inherent characteristics of supramolecular compounds with the unique advantages associated with nanomaterials, furthermore expands the breadth of application of nano-supramolecular compounds to a plethora of medical applications [13]. Another novel and extremely attractive application of nano-supramolecular compounds is their role as precursor of nanomaterials such as nano-metal oxides [14–16].

Nano-size CeO_2, nanoceria, is a major compound in the useful rare earth family and its properties deviate significantly from those of the bulk material. Nanoceria has showed great performance in a variety of applications such as luminescent materials, catalysts (CO oxidation), chemical–mechanical polishing, UV blockers, fuel cells and water treatment [17–23]. Several techniques that include sol–gel, solvothermal, co-precipitation, micro emulsion and etc. have been developed for the production of nanoceria [24]. There are also a few reports on the synthesis of nanoceria from supramolecular compounds [25,26]. However, none have used the nano-supramolecular compounds of cerium(III) as the precursor.

Recently, we have focused our attentions on the construction, structures and properties of nano-sized supramolecular compounds *i.e.* nano-Ce(III) coordination polymer which could be a proper source for producing nanoceria [27]. We now report another new cerium-based nano-supramolecular compound $(NAMH^{+})_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ (**1**), (where H_2pydc is 2,6-pyridinedicarboxylic acid and NAM is nicotinamide) which has been synthesized using the ultrasonic method. Sonochemical synthesis is a simple, low cost, efficient and environmentally green approach to the preparation of nano-supramolecular compounds in comparison with traditional synthesis methods [28,29]. Acoustic

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http://dx.doi.org/10.1016/j.ultsonch.2015.12.014

cavitation is the underlying phenomenon responsible for sonochemistry and according to researches, it results in local hot spots with temperatures and pressures of about 5000 °C and 500 atm and heating and cooling rates greater than 10^9 K/s [30]. These unique conditions not only drive chemical reactions, but they can also help the formation of nano-sized supramolecular compounds through high-energy chemical reactions.

We also report on the crystal structure, thermal behaviors and fluorescent properties of the abovementioned nano-supramolecular compound (**1**).

2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available from Merck and Aldrich Company and used as received. Ultrasonic syntheses were carried out on a SONIC 3MX, (maximum 160 W at 37 kHz). Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses (C, H and N) were performed using ECS 4010 CHNSO analyzer. FT-IR spectra were recorded on Bruker Enquinox 55 spectrometer equipped with a single reflection Diamond ATR system over the range of 600–4000 cm^{-1}. Thermogravimetric analyses (TGA) were carried out under argon atmosphere on a TGA Q50 V6.3 Build 189 instrument at the heating rate of 20 °C min^{-1}. Scanning Electron Microscopy (SEM) was performed on a KYKY EM-3200. X-ray powder diffraction (XRPD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-K_α radiation (λ = 1.54056 Å). The simulated XRD powder pattern based on single crystal data was prepared using Mercury software [31]. Fluorescence analyses were performed on Perkin-Elmer LS50 model luminescence spectrometer.

X-ray crystallography: Single crystal X-ray data were collected at 150 K for compound **1** on Bruker CCD diffractometers using $Mo_{K\alpha}$ radiation. Data were corrected for absorption using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles [32]. Crystal structures were solved and refined against all F^2 values using the SHELXTL suite of programs [33]. Non-hydrogen atoms were refined anisotropically (except as noted), and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

The data were deposited in the Cambridge crystallographic data center with deposition number CCDC 969192.

2.2. Synthesis of $(NAMH^+)_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ *(1)*

A mixture of $Ce(NO_3)_3\cdot 6H_2O$ (0.074 g, 0.17 mmol), $pydcH_2$ (0.056 g, 0.34 mmol) and NAM (0.081 g, 0.66 mmol) in 8 ml of water was refluxed for 1 h. The resulting solution was left to stand at room temperature. Yellow crystals suitable for X-ray crystallography were obtained by slow evaporation after two weeks (yield 78%), m.p. >300 °C. Anal. Calcd for $C_{17}H_{19}CeN_3O_{13}$: C 33.3, H 3.1, N 6.8%. Found: C 32.9, H 3.2, N 6.3%. IR (cm^{-1}): 724 (s), 768 (m), 1077 (m), 1280 (m), 1365 (s), 1437 (m), 1565 (vs), 1614 (m), 1699 (m) and 3300 (br).

2.3. Synthesis of $(NAMH^+)_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ *(1)* nanoparticles

To synthesize the nanoparticles of **1**, a 24 ml solution of cerium (III) nitrate (0.035 M), 2,6-pyridinedicarboxylic acid (0.07 M) and nicotinamide (0.14 M) in water was positioned in an ultrasonic bath, operating at 37 kHz with a maximum power output of 160 W. The obtained precipitates were filtered off, washed with water and then dried in air (yield 64%), m.p. >300 °C. (Found C 32.9, H 3.2, N 6.8%). IR (cm^{-1}) selected bands: 723 (s), 767 (m), 1076 (m), 1279 (m), 1368 (s), 1440 (m), 1570 (vs), 1614 (m), 1699 (m) and 3310 (br).

To probe the effect of concentration of the initial compounds and the role of ultrasound irradiation power on size and morphology of the nano-structured coordination polymer **1**, the above experiment was repeated with a concentration of 0.07 M (into cerium(III) nitrate) and electrical powers of 40% and 100% from the ultrasonic generators.

2.4. Preparation of nanoceria

For the preparation of nano-sized cerium(IV) oxide, nanoparticles of compound **1** were placed at 800 °C in static atmosphere of air for 2.30 h.

3. Results and discussion

Reaction of 2,6-pyridinedicarboxylic acid and nicotinamide with cerium(III) nitrate hexahydrate leads to the formation of a new 3D supramolecular coordination compound of $(NAMH^+)_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ (**1**). The structure of supramolecular **1** was characterized by single-crystal X-ray diffraction method. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1. X-ray crystallography revealed that compound **1** crystallizes in the space group $P\bar{1}$ of the triclinic crystal system. The asymmetric unit of **1** consists of two independent Ce^{III} centres, three $pydc^{2-}$ and one $pydcH^-$ anionic ligands, four coordinated and two uncoordinated water molecules, and one protonated nicotinamide molecule (Fig. 1). The molecular structure of the fundamental building unit for supramolecular **1** is a tetra-nuclear structure (Fig. 2). There are two types of Ce^{III} ions in the tetra-nuclear structure and both are nine coordinated, however, their coordination environment is different. The Ce**1** cation is

Table 1
Crystal data and refinement details of $(NAMH^+)_2[Ce_4(pydc)_6(pydcH)_2(H_2O)_8]\cdot 8H_2O$ (**1**).

Empirical formula	$C_{34}H_{38}Ce_2N_6O_{26}$	
Formula weight	1226.94	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.0901(16) Å	α = 104.300(2)°
	b = 13.4074(18) Å	β = 94.890(2)°
	c = 13.9675(19) Å	γ = 100.390(2)°
Volume	2137.9(5) $Å^3$	
Z	2	
Density (calculated)	1.906 Mg/m^3	
Absorption coefficient	2.206 mm^{-1}	
$F(000)$	1216	
Crystal size	0.50 × 0.30 × 0.30 mm^3	
Theta range for data collection	3.31° to 26.73°	
Index ranges	$-15 \leqslant h \leqslant 15$	
	$-16 \leqslant h \leqslant 16$	
	$-17 \leqslant l \leqslant 17$	
Reflections collected	18973	
Independent reflections	8154 [R(int) = 0.0252]	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8154/0/613	
Goodness-of-fit on F^2	1.109	
Final R indices [I > 2 sigma(I)]	$R1$ = 0.0404, $wR2$ = 0.0986	
R indices (all data)	$R1$ = 0.0462, $wR2$ = 0.1013	
Largest diff. peak and hole	1.572 and −1.801 e $Å^{-3}$	