

Sonochemical syntheses of a new fibrous-like nano-scale strontium(II) 3D coordination polymer; precursor for the fabrication of a strontium carbonate nanostructure



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ABSTRACT

Nanostructures of a new three-dimensional Sr(II) coordination polymer, $\{[\text{Sr}(\text{H}_2\text{IDC})_2(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\}_n$ (**1**) (H_2IDC = 4,5-imidazolecarboxylic acid), have been synthesized by a sonochemical process and characterized by field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRPD), FT-IR spectroscopy and elemental analyses. The effect of the concentration of the starting reagents on the size and morphology of nanostructured compound **1** has also been investigated. Structural determination of compound **1** reveals the Sr(II) ion is eight coordinated, bonded to one nitrogen atom and six oxygen atoms from the H_2IDC^- ligand and a water molecule. The thermal stability of compound **1** has been studied by thermal gravimetric (TG) and differential thermal analyses (DTA). Compound **1** polymerizes on heating the solid at 210 °C under a reversible crystal-to-crystal transformation, to form a new compound that is suggested to be the water-free compound, $[\text{Sr}(\text{H}_2\text{IDC})_2]_n$ (**2**), that was characterized by powder X-ray diffraction techniques. SrCO_3 nanostructures were simply synthesized by the solid-state transformation of compound **1** at 500 °C under an air atmosphere.

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1. Introduction

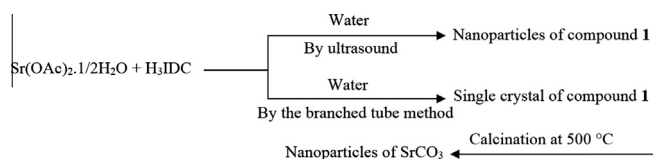
Crystal engineering of coordination polymers, which involves the self-assembly of polydentate organic ligands with appropriate functional groups and metal ions with specific directionality and functionality, is one of the facile routes to produce materials of technological importance [1]. Metal-ligand coordination bonds have been widely exploited in organizing molecular building blocks into diverse supramolecular architectures, making use of the strength of the coordination bonds and directionality associated with the metal ions. In the last ten years coordination polymers, especially 3-periodic coordination polymers, have become one of the main objects for crystal design [2–9]. The coordination chemistry of groups 1 and 2 metal compounds with organic ligands in the widest sense has been, until relatively recently, largely unknown compared to transition metal coordination networks. The reluctance to use alkaline-earth cations as building blocks for open framework materials can be attributed to their unpredictable coordination numbers and geometries as no ligand field stabilization effects govern their bonding. Although the closed shell s-block metal cations lack useful properties like magnetism or variable oxidation states, alkali and alkaline-earth metals are preferred to

transition or lanthanide metal ions because many of the s-block cations are non-toxic, cheap and soluble in aqueous media. Growing interest in the coordination chemistry of s-block elements is shown by several recent reports [10–12]. The size and shape of solid materials influence the chemical and physical properties. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which are commonly called nanomaterials. Recently, coordination polymer nanocrystals, nanosized coordination polymers with finite repeating units, have aroused a growing interest due to their special properties, distinctive from conventional bulk coordination polymers [13–16]. Making coordination polymers in any form in the nano-size is certainly a major step forward toward the technological applications of these new materials. Nanometer-sized structures of coordination polymers are fascinating to explore because they are interesting candidates for applications in gas storage, molecular recognition and separations, conductivity, catalysis, chirality, photonics and magnetic materials [17,18].

In recent years, the preparation and application of inorganic nano materials have been of major interest since they exhibit special properties in industry [19,20]. Strontium carbonate (SrCO_3) is a very important reagent and has many applications in industry: as a constituent of ferrite magnets for small direct current motors, as an additive in the production of glass for color television tubes [21] and in the production of iridescent and specialty glasses, pigments,

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Scheme 1. Materials produced and synthetic methods.

driers, paints, pyrotechnics, strontium metal and other strontium compounds [22]. The design and controlled synthesis of nanostructures with different sizes and morphologies is very important from the viewpoint of both basic science and technology [23]. However, compared with the great progress in the investigation of the properties of SrCO₃, studies on its synthesis, especially nanostructures, have been lagging far behind, and there are only a few reports on either the direct conversion process or the black ash process [24].

In this paper we would like to describe a simple synthetic sonochemical preparation of a nanostructured strontium(II) 3D coordination polymer, {[Sr(H₂IDC)₂(H₂O)]·(H₂O)}_n (**1**) (H₃IDC = 4,5-imidazoledicarboxylic acid). Nanostructured compounds have been prepared by a variety of synthetic methods, including liquid phase methods, gas phase techniques and mixed phase approaches. Among the variety of approaches, the utilization of ultrasound has been extensively examined over many years [25]. The powerful ultrasound radiation used in this method (20 kHz–10 MHz) induces chemical or physical changes during cavitation (formation, growth and implosive collapse of bubbles in a liquid) which can generate local hot spots having pressures of about 1000 bar, temperatures of roughly 5000 K, and a lifetime of a few microseconds; These extreme conditions permit access to a range of chemical reaction spaces normally not accessible, which allows for the synthesis of nano-sized materials [16,26,27]. The strontium(II) 3D coordination polymer, {[Sr(H₂IDC)₂(H₂O)]·(H₂O)}_n (**1**) can be spontaneously generated via coordination of Zn²⁺ to the six oxygen and one nitrogen atoms of the organic molecule, and one coordinated water molecule in H₂O solution by a branched tube method [28] (Scheme 1). Heating compound **1** at 210 °C removes the both coordinated and lattice water molecules under a reversible crystal-to-crystal transformation, to form a new compound that is suggested to be the water-free compound, [Sr(H₂IDC)₂]_n (**2**), that was characterized by powder X-ray diffraction techniques. Studies on crystal-to-crystal transformations involving coordination polymers and networks are more recent [29–32]. There are several types of structural transformations that are primarily influenced by the expansion of coordination number, thermal association, condensation, rearrangement of bonds or the removal/exchange of solvents [33]. To proceed, we report the simple synthesis of SrCO₃ nanoparticles by the solid-state transformation of compound **1**, calcined at 500 °C in air and without any surfactant or capping molecules.

2. Experimental

2.1. Materials and physical techniques

Starting reagents for the synthesis were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Merck and others). Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus CHN–O–Rapid analyzer. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500–4000 cm^{−1} using the KBr disk technique. Thermogravimetric

analysis (TGA) and differential thermal analyses (DTA) of the title compound were performed on a computer-controlled PL–STA 1500 apparatus. A single-phased powder sample of **1** was loaded into alumina pans and heated with a ramp rate of 10 °C/min from room temperature to 600 °C under an argon atmosphere. Crystallographic measurements of compound **1** were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software. Absorption corrections were applied with the program SADABS. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located and included in their calculated positions. The final full-matrix, least-squares refinement on F^2 was applied for all observed reflections [$I > 2\sigma(I)$]. Crystallographic data and details of the data collection and structure refinements of compound **1** are listed in Table 1. X-ray powder diffraction (XRPD) measurements were performed using a Philips X'pert diffractometer with monochromated Co K α radiation ($\lambda = 1.78897$ Å). The simulated XRD powder pattern, based on single crystal data, was prepared using MERCURY software [34]. Ultrasonic generation was carried out with a SONICA-2200 EP, input: 40 kHz/305 W. The samples were characterized using a field emission scanning electron microscope (FESEM) (Hitachi S-4160 Japan) with a gold coating.

2.2. Synthesis of {[Sr(H₂IDC)₂(H₂O)]·(H₂O)}_n (**1**) as single crystals

To isolate single crystals of {[Sr(H₂IDC)₂(H₂O)]·(H₂O)}_n (**1**), 4,5-imidazoledicarboxylic acid (0.156 g, 1 mmol) and strontium(II) acetate hemihydrate (0.644 g, 3 mmol) were placed in the main arm of the branched tube to be heated [28]. Water was carefully

Table 1
Crystal data and refinement details of {[Sr(H₂IDC)₂(H₂O)]·(H₂O)}_n (**1**).

Identification code	Compound 1
Empirical formula	C ₁₀ H ₁₀ N ₄ O ₁₀ Sr
Formula weight	433.84
<i>T</i> (K)	298(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	Cc
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.7601(11)
<i>b</i> (Å)	29.100(3)
<i>c</i> (Å)	6.8916(8)
α (°)	90
β (°)	134.707(2)
γ (°)	90
<i>V</i> (Å ³)	1391.1(3)
<i>Z</i>	4
<i>D</i> _{calc} (Mg/m ³)	2.071
Absorption coefficient (mm ^{−1})	3.946
<i>F</i> (000)	864
Crystal size (mm)	0.27 × 0.25 × 0.18
Theta range for data collection (°)	1.4–25.98
Index ranges	−7 ≤ <i>h</i> ≤ 12 −34 ≤ <i>k</i> ≤ 35 −8 ≤ <i>l</i> ≤ 5
Reflections collected	3929
Independent reflections	1861 [<i>R</i> _{int} = 0.0307]
Absorption correction	semi-empirical from equivalents
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1861/8/239
Goodness-of-fit (GOF) on <i>F</i> ²	1.104
Final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0215, <i>wR</i> ₂ = 0.0492
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0229, <i>wR</i> ₂ = 0.0643
Largest difference in peak and hole (e Å ^{−3})	0.302 and −0.304

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