



A Convenient Synthesis of Antimony Nanorods using 1,2,4,5-Benzenetetracarboxylic Acid

NTAOTE DAVID SHOOTO

Applied Chemistry and Nano-Science Laboratory, Department of Chemistry, Vaal University of Technology P.O. Box X021, Vanderbijlpark 1900, South Africa

Corresponding author: E-mail: ntaotes@vut.ac.za

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1,2,4,5-Benzenetetracarboxylic acid (H₄Btec) is an ideal candidate for the synthesis of new coordination polymers compounds because of its four carboxyl groups bridging moieties with antimony ions having distorted coordination configuration. This work reports a new compound of coordination polymer, namely, [Sb₂(C₄H₄O₆)₂(Btec)(H₂O)]_n, [(C₄H₄O₆)₂ = tartrate and Btec⁴⁻ = 1,2,4,5-benzenetetracarboxylic anion] has been synthesized under reflux. The physical and chemical properties of coordination polymers; Sb₂(C₄H₄O₆)₂(Btec)(H₂O) was affirmed by scanning electron microscope, Fourier transform infrared spectroscopy, X-ray powder diffraction, thermogravimetric analyses and photoluminescence spectroscopy.

Keywords: 1,2,4,5-Benzenetetracarboxylic acid, Coordination polymers, Photoluminescence, Antimony.

INTRODUCTION

The structural design of coordination polymers continues to draw attention of researchers worldwide because of their unique attributes such as versatility [1-3], fascinating architecture [4] and network topology [5]. More importantly coordination polymers have been applied in numerous applications, including waste water treatment [6], gas storage and separation [7,8], heterogeneous catalysis [9], non-linear optics [10] and drug delivery [11]. Polycarboxylate such as -benzenetetracarboxylic acid (H₄Btec) is centro-symmetric; it is an important multidentate ligand that has multiple coordination modes [12,13]. Because of its four carboxyl groups, it can display a variety of coordination modes to afford numerous coordination polymers of 1D chains, 2D layers and 3D networks [14-16].

Antimony(III) has (5s²) valence electrons that are structural directing agents and may lead to the distortion of coordinate configuration of antimony along with potential redox sites, giving rise to unique properties in antimony(III) based materials. Such materials have attracted significant attention because of their applications in many areas. This work reports [Sb₂(C₄H₄O₆)₂(Btec)(H₂O)]_n coordination polymer synthesized under reflux. This new compound is based on tetragonal and monoclinic nanorods building unit. The surface morphology

of antimony(III) nanorods was characterized by SEM, the functional groups were confirmed by FTIR, the crystalline phase was affirmed by XRD, thermal stability was measure by TGA. In addition, the luminescent property of this compound was investigated in solvent at room temperature.

EXPERIMENTAL

A new compound of coordination polymer based on antimony(III) viz., [Sb₂(C₄H₄O₆)₂(Btec)(H₂O)]_n was synthesized by reflux method as shown in Fig. 1. A solution was prepared by dissolving potassium antimony tartrate (3 g) and 1,2,4,5-benzenetetracarboxylic acid (3 g) in *N,N*-dimethylformamide (100 mL). The solution was refluxed, stirred and maintained the temperature at 100 °C for 24 h. The obtained powder was isolated, washed and dried in oven at 30 °C.

RESULTS AND DISCUSSION

Scheme-I shows the proposed structure of [Sb₂(C₄H₄O₆)₂(Btec)(H₂O)]_n. All four carboxyl groups of each H₄Btec are deprotonated. All oxygen atoms from deprotonated carboxyl groups are used as connecting atoms. Each oxygen atom from deprotonated carboxyl groups coordinate to one Sb atom adopting 1,2,4,5-polydentate chelating mode. The remaining four oxygen atoms of H₄Btec ligand remain unused.

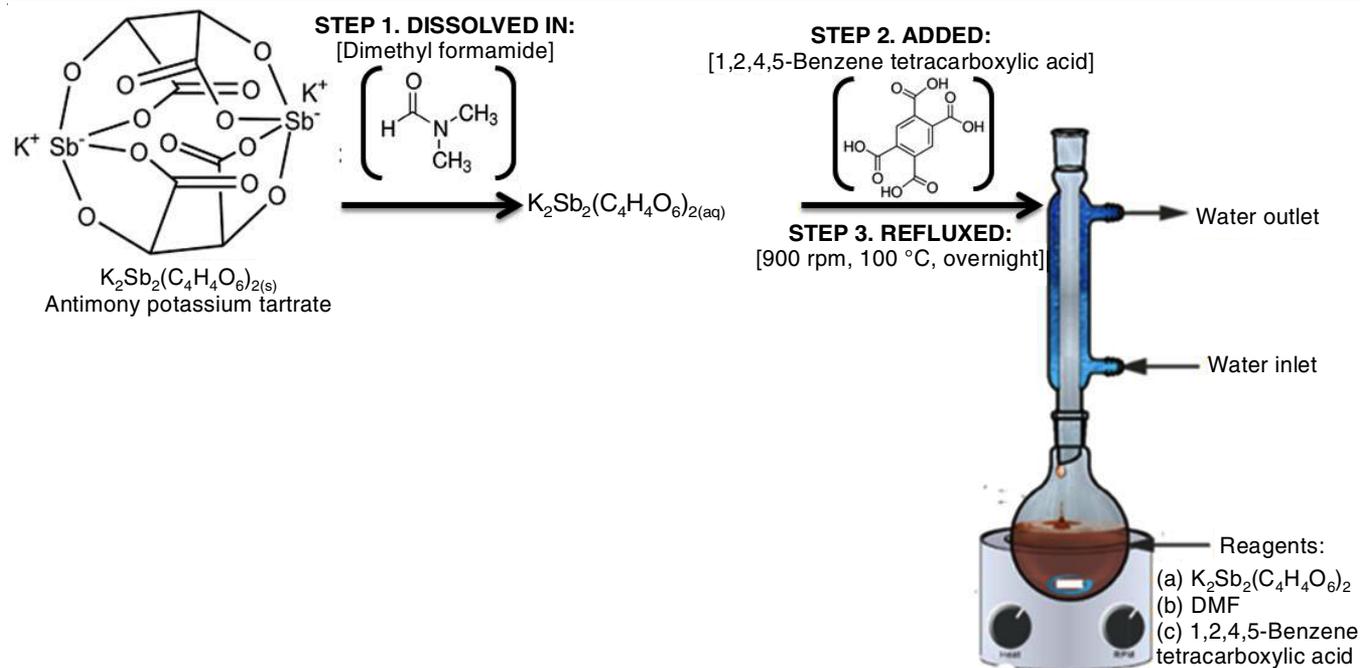
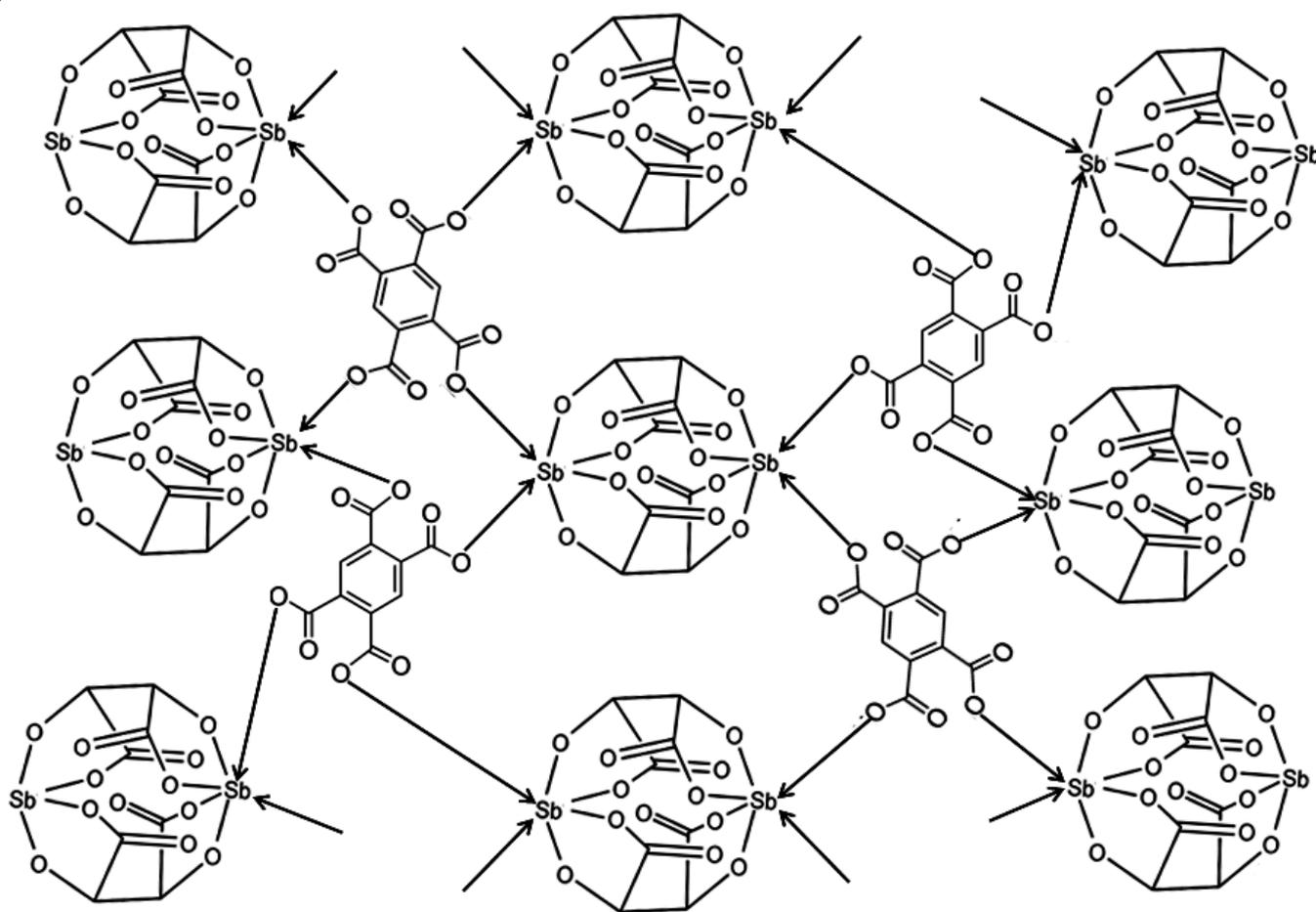


Fig. 1. $[Sb_2(C_4H_4O_6)_2(Btec)(H_2O)_n]$ coordination polymers preparation and proposed structure



Scheme-I: Proposed structure of $[Sb_2(C_4H_4O_6)_2(Btec)(H_2O)_n]$, showing the local coordination environment of antimony

The surface morphology of $[Sb_2(C_4H_4O_6)_2(Btec)(H_2O)_n]$ is shown in Fig. 2a-b. Overview image in low magnification is shown in Fig. 2a. Enlarged images in high magnification are

shown in Fig. 2b. Fig. 2a image shows uniformly distributed particles. The particles in Fig 2b revealed nanorods exhibiting mixed shapes and some were irregular.

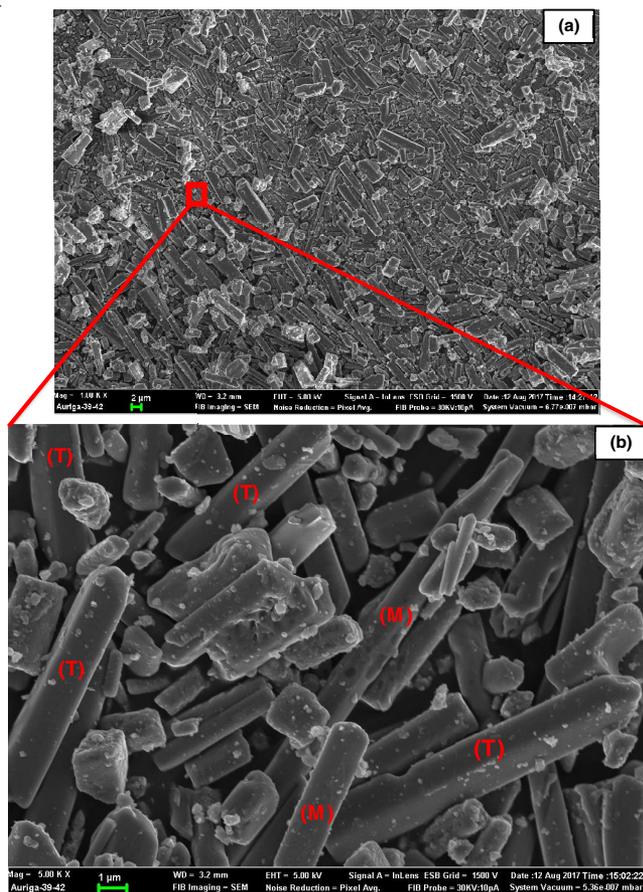


Fig. 2. (a-b). SEM images of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymers

X-ray diffraction was measured to affirm the crystalline phase of the sample. The XRD data of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ was collected in the range of $10\text{-}90^\circ$. The pattern of the compound is shown in Fig. 3. The XRD results relieved two dominating phase (tetragonal and monoclinic) this is consistent with SEM image in Fig. 2b. The (T) marked nanorods on Fig. 2b are tetragonal and (M) are monoclinic phase of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$.

The FTIR spectra of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymers is shown in Fig. 4. The absorption band in the region around 3571 cm^{-1} was assigned to (O-H) stretching,

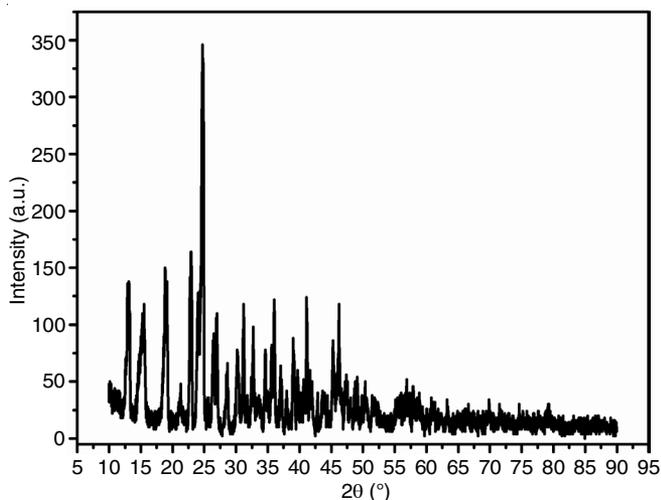


Fig. 3. XRD spectra of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymers

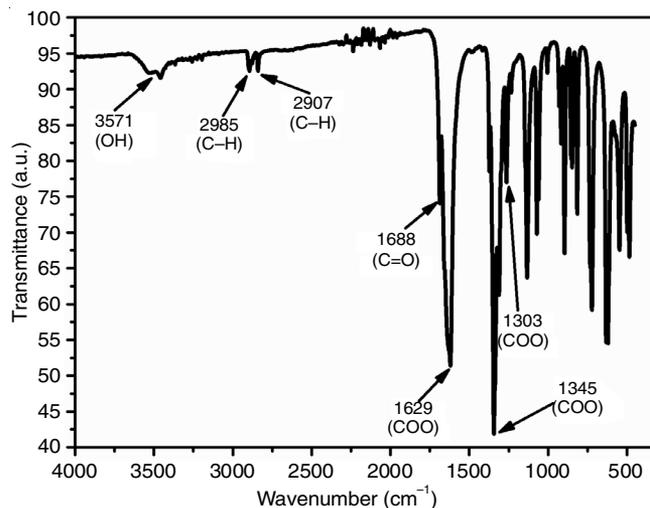


Fig. 4. FTIR spectra of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymers

of H_2O molecules. Two narrow bands observed at 2985 and 2927 cm^{-1} were attributed to (C-H) vibrations. Free carboxyl (C=O) group is usually observed around $1750\text{-}1700\text{ cm}^{-1}$, however band at 1688 suggests that (C=O) are coordinated. The (COO) band of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ was observed at 1629 cm^{-1} , while asymmetric and symmetric stretching vibrations of (COO) were observed at 1345 and 1303 cm^{-1} , respectively. The asymmetric and symmetric stretching vibration difference of 284 and 326 cm^{-1} respectively between the carboxylate groups suggest polydentate coordination.

Thermogravimetric analysis of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ was carried out from $30\text{ to }900^\circ\text{C}$ as shown in Fig. 5. The TGA plot shows weight loss in the temperature range of $40\text{-}100^\circ\text{C}$, which indicates the removal of coordinated water molecules occurred with a loss of 4%. Decomposition of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ began at 180°C ; in the temperature range of $180\text{-}252^\circ\text{C}$ the removal of multidentate coordinated Btec ligands occurred with a loss of 17%. Another weight loss of 24% between 209 and 335°C corresponds to the removal of tartrate ions and the remaining residual weight was 25.6% corresponding to Sb_2O_3 .

Photoluminescence (PL) performance is displayed in Fig. 6a-b. The luminescent properties of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$

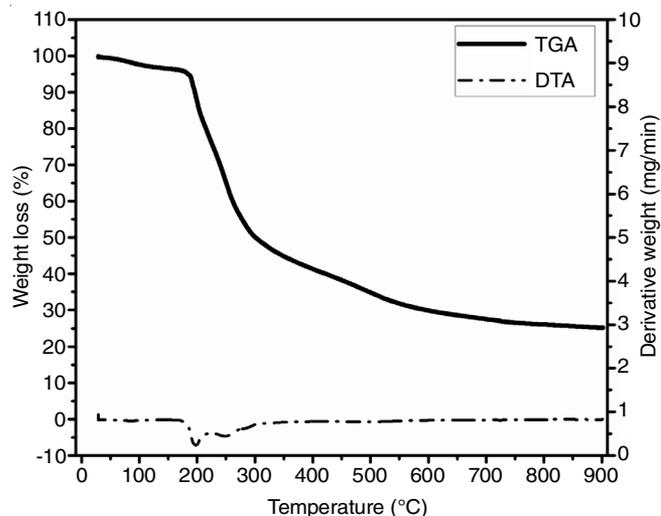


Fig. 5. TGA and DTA plots of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymers

coordination polymers was measured in solvent. Fig. 6a shows the excitation peak at 330 nm and Fig. 6b shows three emission peaks at 370 nm attributed to the solvent and at 445 and 480 nm attributed to $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$. Ji *et al.* [17] reported that free 1,2,4,5-benzenetetracarboxylic acid ligand showed the emission peak at 397 nm [17]. This in comparison to two emission peaks of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ at 445 and 480 nm, show red shift due to ligand-to-metal charge transfer (LMCT).

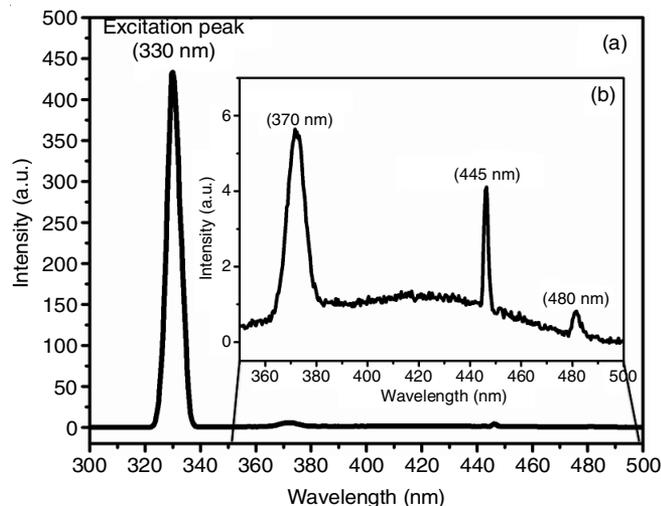


Fig. 6. (a) Full spectra of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination polymer from 300 to 500 nm, (b) spectra from 350 to 500 nm

In conclusion, a new antimony coordination compound based on Btec^{4-} anions has been synthesized by reflux. Characterization of $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ nanorods revealed two phase of the compound; tetragonal and monoclinic can be obtained by adopting reflux preparation method. Thus reflux of $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2$ and H_4Btec in DMF yielded $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Btec})(\text{H}_2\text{O})]_n$ coordination compounds. Furthermore, the luminescent property of the compound was investigated in solvent at room temperature.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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