

The Effect of Synthetic Procedures on Formation of Two Silver Coordination Polymers and their Antibacterial Activities

Mahnoosh Zamani Isfahani^a, Kamran Akhbari^{a,*} and Anukorn Phuruangrat^b

^aSchool of Chemistry, College of Science, University of Tehran, Tehran, Iran

^bDepartment of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, Thailand

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The effect of synthesis procedure on formation of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) and $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) coordination polymers (py-4-c = pyridine-4-carboxylate) were studied. Pyridine-4-carboxylic acid (Hpy-4-c) was deprotonated by KOH and the anionic ligand was become available for interaction with the metal ion. AgNO_3 was added to the ligand solution with two different rates in two conditions of bulk and ultrasonic bath which yielded to $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) on stirrer and a different coordination polymer in ultrasonic bath, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2). Formation of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) and $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) were investigated with different analyses such as Powder X-ray Diffraction (PXRD), Fourier-Transform Infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Thermogravimetric analysis (TGA). Moreover, antibacterial activity of the samples was investigated against both gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria's.

Keywords: Antibacterial, Coordination polymer, Nanostructure, Silver, Sonochemical

INTRODUCTION

Coordination polymer (CP) refers to the compounds made from metal ion and organic ligand units with infinite structures and thermal and chemical stability [1], which have attracted lots of attentions in the past years. CPs are normally linked by coordinative bonds or some other weak chemical interactions and automatic self-assemble is the synthesis process of these compounds [2,3]. Nano coordination polymers (NCPs) are one of the coordination polymers group which are consisting of nanoscale dimensions [3]. These compounds are well known for their various applications in micro porosity [4], ion exchange [5,6], catalysis, gas storage [7-9], gas separation and drug delivery [10]. Human safety against bacteria's and microorganisms had been an important challenge during all decades. Thus, there is always a serious competition between scientists to achieve the most effective antibacterial compounds and products. While antibacterial activity of

some metals such as silver, copper and zinc has been clarified, coordination polymers of these metals are successful in destroying the bacteria's [11-13]. Moreover, simplicity of recycling the CPs, and less environmental pollutants, are considerable points in utilizing these compounds [14]. Besides, optimizing the size, shape and surface area for the CPs, could play an important role in their synthesis [15,16]. Different selection of the organic ligand is directly effective in resulting structure [17]. In this work we used AgNO_3 as a metal ion source, and isonicotinic acid (pyridine-4-carboxylic acid) as an organic ligand for synthesis of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ coordination polymer. $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) is a three-dimensional coordination polymer with μ_2 -bridging ligand of py-4-c [18]. The metal ion solution was added to the ligand solution with two different ways. The reaction was also carried out under ultrasound irradiation too. Data analyses confirmed formation of another coordination polymer in ultrasonic bath, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) [19,20]. Different analyses and especially antibacterial test against both gram-negative (*E. coli*) and gram-positive

*Corresponding author. E-mail: akhbari.k@khayam.ut.ac.ir

(*S. aureus*) bacteria's were utilized to evaluate the formation and bactericidal activity of the resulting coordination polymer samples.

EXPERIMENTAL

Materials

All reagents such as pyridine-4-carboxylic acid, KOH and AgNO₃ were supplied by Merck chemical company.

Physical Techniques

PARSONIC 15S ultrasonic bath (with the frequency of 28 kHz) was utilized for ultrasonic irradiation. IR spectra were achieved by Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany), in the range of 400-4000 cm⁻¹ with 16 scan's numbers and ATR form. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) with step-size of 0.01671 (degree). Simulated XRD powder patterns and molecular structure plots based on single crystal data were prepared using the Mercury software. Philips XL 30 was utilized as scanning electron microscope to characterize the morphology of the samples. Elemental analyses (for C/H/N) were determined using Heraeus CHN-O- rapid analyzer. Thermal behavior of the samples was evaluated by PL-STA 1500 apparatus (20-800 °C, heating rate in nitrogen atmosphere: 10 K min⁻¹). All diagrams were plotted by excel and origin software's.

Antimicrobial Test

The antibacterial properties of the samples were evaluated against *Escherichia coli* (ATCC 25923, Gram-negative bacterium) and *Staphylococcus aureus* (ATCC 25922, Gram-positive bacterium) using agar well diffusion method. *E. coli* and *S. aureus* were cultured in separate plates for 24 h. Plates containing Mueller Hinton Agar were utilized. Both bacteria's with the concentration of 0.5 McFarland (1×10^8 CFU/mL) were cultured on Mueller Hinton Agar plates by sterile swabs. Wells with the diameter of 4 mm were created in plates and solutions of the samples with the concentration of 10000 $\mu\text{g mL}^{-1}$ by 3% of DMSO were prepared. 80 μL of each sample was inoculated into created wells. Plates were incubated for 24 h at 37 °C.

The inhibition zones for each sample were measured and reported in millimeters.

Synthesis of [Ag₂(μ_2 -py-4-c)₂]_n (1) and {[Ag(py-4-c)(Hpy-4-c)]_{1/2}·[Ag(py-4-c)]_n} (2) Coordination Polymers

4.5 mmol of pyridine-4-carboxylic acid was added to 15 mL of H₂O. By the means of deprotonating the carboxylic acid group in ligand, 4.5 mmol of KOH was added to the solution and the reaction took place under reflux condition for 3 h at 120 °C. After losing H⁺ of the ligand, the anionic ligand became available for interaction with Ag⁺ ion and formation of silver coordination polymers. Four solutions in four beakers were prepared by this method. Moreover, four solutions of dissolved AgNO₃ (4.5 mmol) in 15 mL of H₂O were prepared separately. Two of the ligand solutions were placed on stirrer with no heat for 1 h. The AgNO₃ solution was added quickly (B1) to one of them and slowly (drop by drop) to another one (B2). In another experiment, two of the ligand solutions were placed in ultrasonic bath under ultrasound irradiation for 1 h and AgNO₃ solution was added quickly (S1) to one of them and slowly (S2) to another one. The resulting powders were separated from solution, washed with water (three times) and dried in oven for 4 h at 60 °C. Anal. Calcd. (%) for C₁₂H₈Ag₂N₂O₄ (1): C, 35.47; H, 1.97; N, 6.90; found (%): C, 34.92; H, 1.91; N, 6.82 (for B1) and C, 35.22; H, 2.00; N, 6.97 (for B2). Anal. Calcd. for C₁₂H_{8.5}N₂O₄Ag_{1.5} (2): C, 35.45; H, 2.11; N, 6.89; found: C, 35.50; H, 2.04; N, 6.90% (for S1) and C, 35.39; H, 2.02; N, 6.84 (for S2).

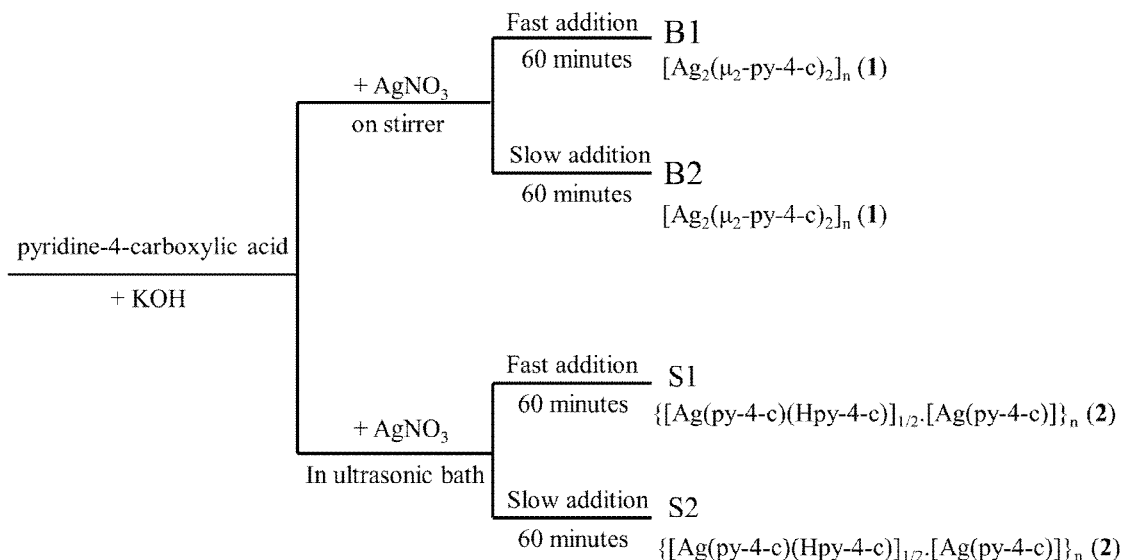
Experimental Procedure

Four experiments were carried out and four samples were achieved (Scheme 1). In slow procedures, AgNO₃ solution was added drop by drop in 30 minutes. In all experiments after adding AgNO₃ solution, the amount of produced precipitation made trouble for the magnet spinning.

RESULTS AND DISCUSSION

Fourier Transforms Infrared (FT-IR) Spectroscopy

Investigation of FT-IR spectra for all samples clarified the successful formation of silver coordination polymers. In



Scheme 1. Diagram of the reactions between AgNO_3 and pyridine-4-carboxylic acid

pyridine-4-carboxylic acid (L) spectrum, the C-O and C=O bonds appeared at 1320 and 1700 cm^{-1} , respectively but in silver coordination polymers, symmetric and asymmetric mode of COO^- , are appeared in 1375 and 1550 cm^{-1} , respectively. A broad band in the range of $2250\text{--}2750\text{ cm}^{-1}$ which is related to hydrogen bond in carboxylic acid of the ligand spectra (L) is omitted in four prepared samples because of deprotonation and replacing by silver ion. Moreover, stretch bands of aromatic C=C were appeared between 1400 and 1600 cm^{-1} (Fig. 1).

Powder X-ray Diffraction Analysis (PXRD)

Comparison between the powder X-ray diffraction (PXRD) patterns of the samples and simulated PXRD patterns of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) and $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}.\text{[Ag}(\text{py-4-c})]\}_n$ (2) coordination polymers, confirmed the formation of compound 1 in B1 and B2 samples and compound 2 in S1 and S2 samples (Fig. 2). The average grain size of B1, B2, S1 and S2 were calculated using Scherrer's equation and the values of 372 nm , 407 nm , 501 nm and 600 nm were obtained, respectively.

Brief Structural Description of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) and $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}.\text{[Ag}(\text{py-4-c})]\}_n$ (2)

The reaction between pyridine-4-carboxylic (Hpy-4-c)

acid, KOH and AgNO_3 with molar ratio of 1:1:1 produced two types of three-dimensional coordination polymers with monoclinic crystal system and $P2_1/c$ space group. $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) coordination polymer, which was observed in B1 and B2 samples, contains two types of silver ions with $a = 8.259(2)\text{ \AA}$, $b = 19.371(5)\text{ \AA}$, $c = 7.308(2)\text{ \AA}$, $\beta = 91.704(4)^\circ$, $V = 1168.7(5)\text{ \AA}^3$ and $Z = 4$ [18]. In 1, Ag1 which is coordinated to one nitrogen and two oxygen atoms with disordered T-shape AgO_2N coordination sphere and Ag2 is coordinated to two nitrogen atoms with linear AgN_2 coordination sphere (Fig. 3a). $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}.\text{[Ag}(\text{py-4-c})]\}_n$ (2) coordination polymer, which was observed in S1 and S2 samples, consists of two building blocks with $a = 8.1668(16)\text{ \AA}$, $b = 19.611(4)\text{ \AA}$, $c = 7.4083(15)\text{ \AA}$, $\beta = 92.90(3)^\circ$, $V = 1185.0(4)\text{ \AA}^3$ and $Z = 4$ [19]. In one of the blocks, Ag1 ion with linear coordination is coordinated to two nitrogen atoms of Hpy-4-c and py-4-c. Hydrogen bonds assembled this part to two different carboxylate groups. In the other block, Ag2 is coordinated to one oxygen atom of monodentate carboxylate and one nitrogen atom of pyridine ring with distorted linear coordination sphere (Fig. 3b). R. Atencio *et al.*, were synthesized compound 2 from the reaction between pyridine-4-carboxylic acid and AgBF_4 with 1:1 molar ratio in mixture of ethanol and water [20] and J.-Q. Xu

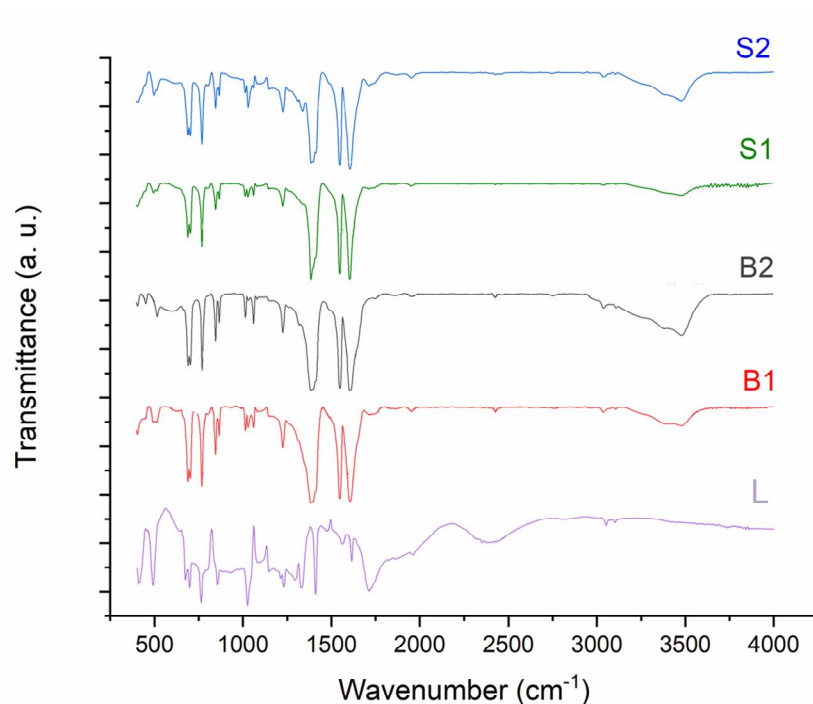


Fig. 1. FT-IR spectra of pyridine-4-carboxylic acid (L), bulk fast reaction (B1), bulk slow reaction (B2), sonochemical fast reaction (S1) and sonochemical slow reaction (S2).

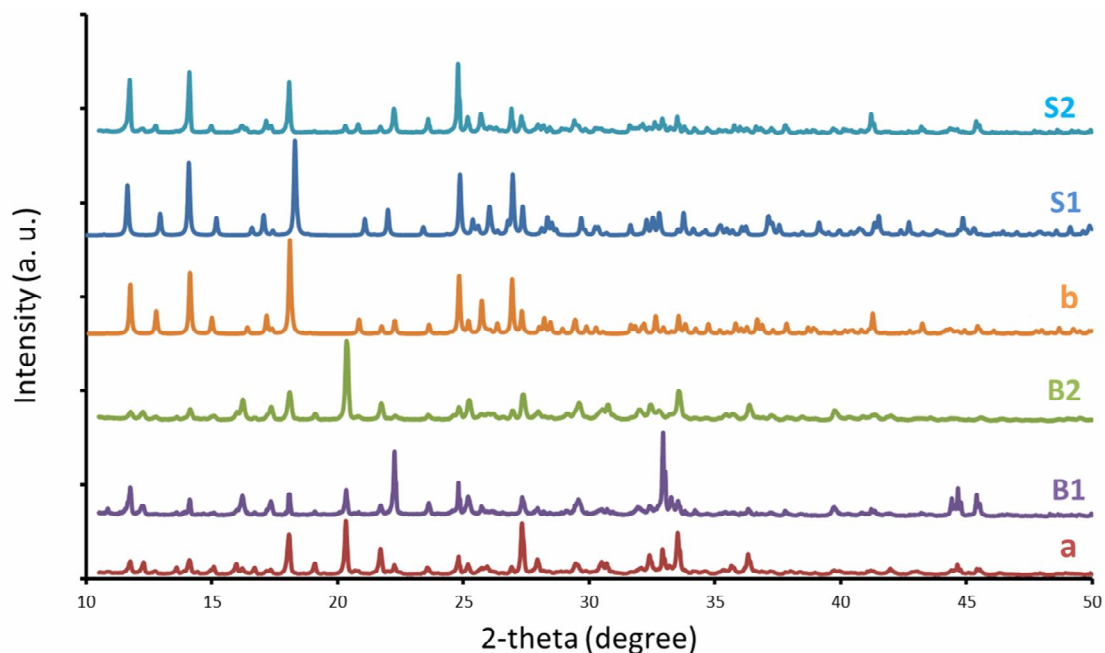
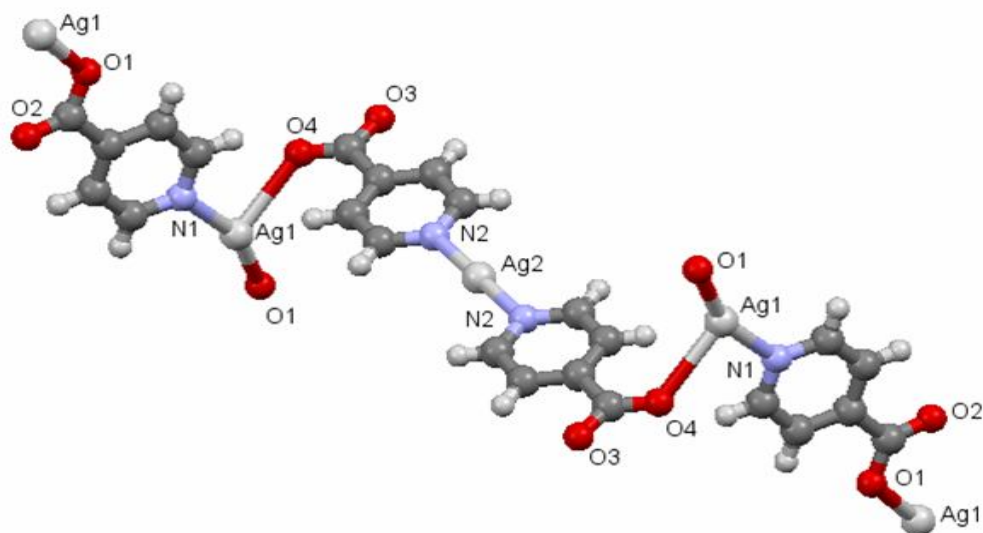


Fig. 2. PXRD patterns of obtained samples; simulated pattern of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (a), bulk fast reaction (B1), bulk slow reaction (B2), simulated pattern of $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2} \cdot [\text{Ag}(\text{py-4-c})]\}_n$ (b), sonochemical fast reaction (S1) and sonochemical slow reaction (S2).

a



b

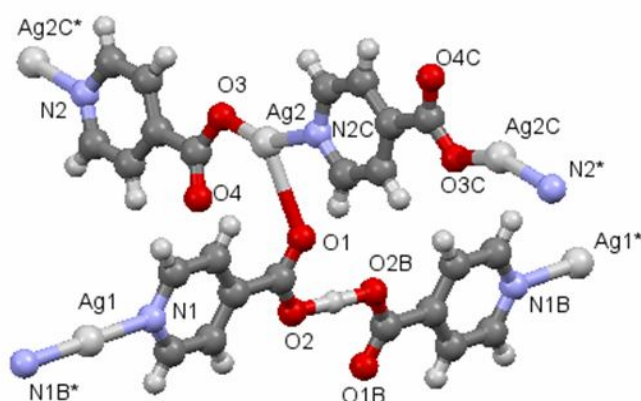


Fig. 3. Two different 3-D structures obtained a) in bulk situation, $[Ag_2(\mu_2\text{-py-4-c})_2]_n$ (1) and b) in ultrasonic bath $\{[Ag(\text{py-4-c})(\text{Hpy-4-c})]_{1/2} \cdot [Ag(\text{py-4-c})]\}_n$ (2).

et al., were reported the synthesis of 2 with hydrothermal reaction between $AgNO_3$, pyridine-4-carboxylic acid and imidazole under autogenously pressure with molar ratio of 1:1:1 at 170 °C for 4 days [19]. Thus in this work, $\{[Ag(\text{py-4-c})(\text{Hpy-4-c})]_{1/2} \cdot [Ag(\text{py-4-c})]\}_n$ (2) coordination polymer was synthesized with green sonochemical reaction at room temperature and within one hour.

SEM Images

Morphology of the obtained samples is directly

dependent to the rate of adding $AgNO_3$ solution to the ligand solution. In both bulk and sonochemical experiments, when the $AgNO_3$ solution was added slowly to the ligand solution, the morphology of the obtained samples (B2 and S2, respectively) is mainly micro size which is more fine in comparison with adding the precursors to each other quickly (Fig. 4). It is obvious that in B2 and S2 samples there was enough time for nucleation and growth. Fast addition of $AgNO_3$ solution to ligand solution in bulk sample (B1) results in formation of nanoleaves (Fig. 4a) and in similar

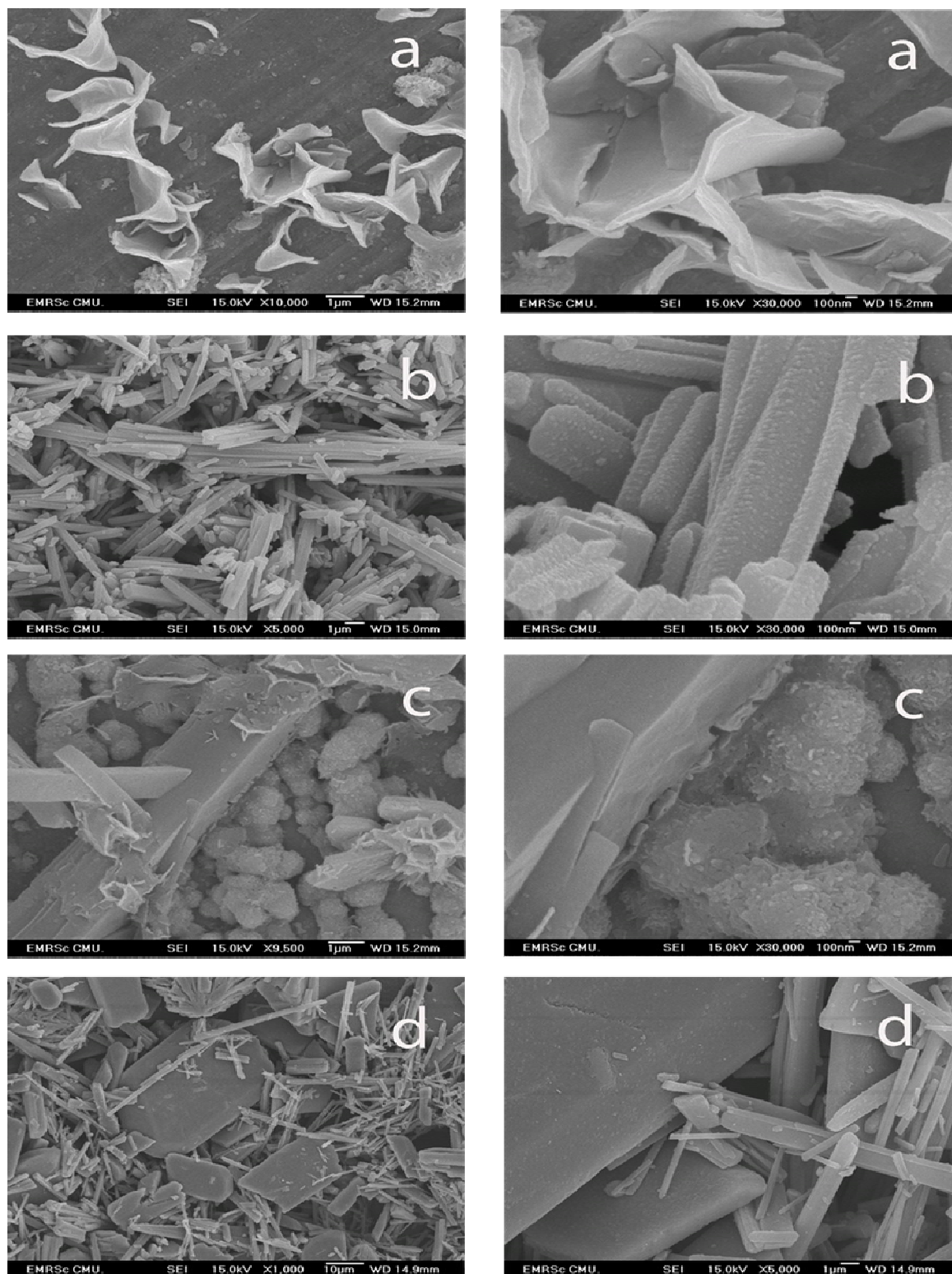


Fig. 4. SEM images for a) bulk fast reaction (B1), b) bulk slow reaction (B2), c) sonochemical fast reaction (S1) and d) sonochemical slow reaction (S2).

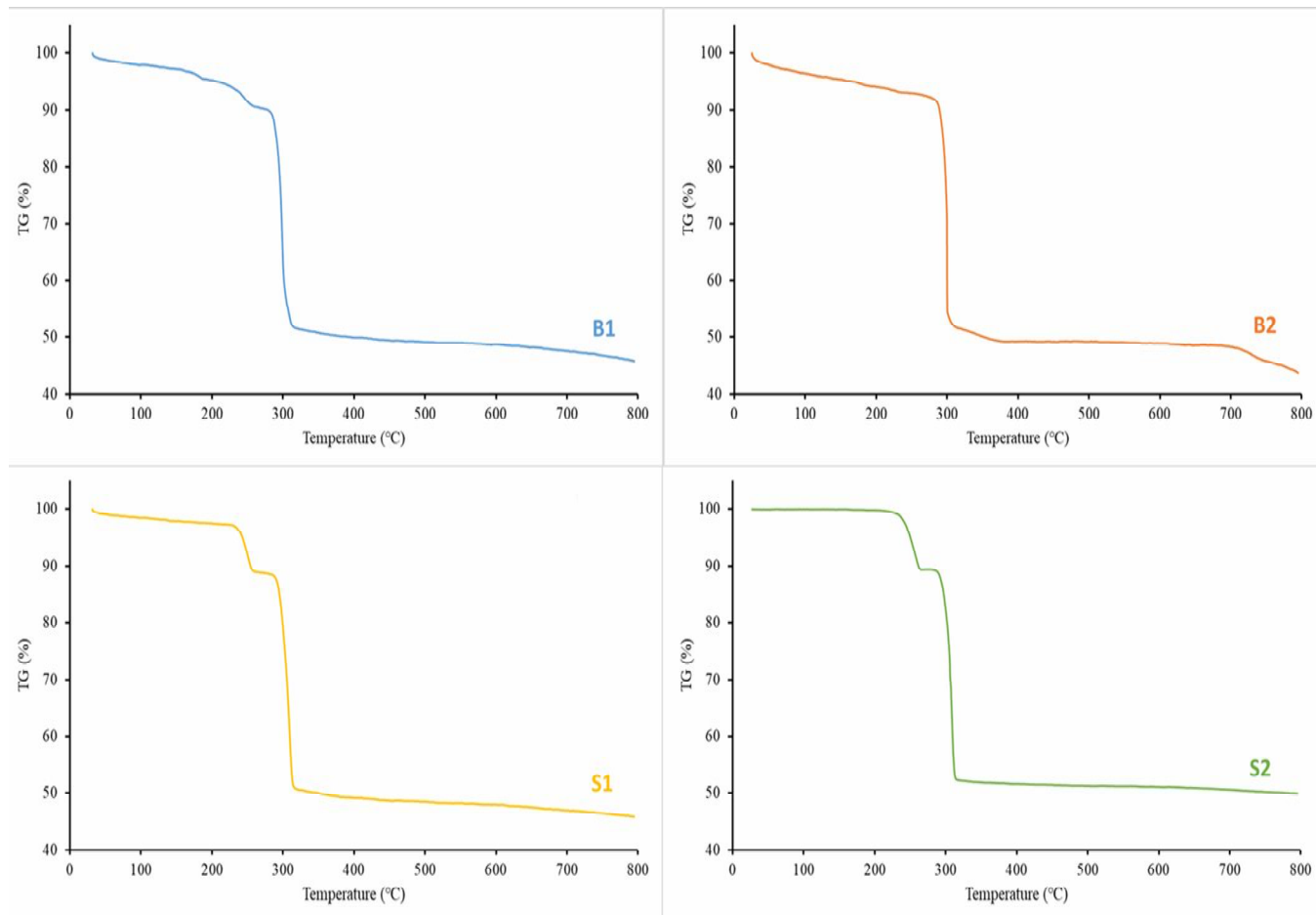


Fig. 5. Thermal behavior of: bulk fast reaction (B1), bulk slow reaction (B2), sonochemical fast reaction (S1) and sonochemical slow reaction (S2).

condition with sonochemical process (S1), microstructures with various morphology were obtained (Fig. 4c).

Thermogravimetric Analysis

Thermogravimetric (TG) of the obtained samples showed the thermal stability of B1, B2, S1 and S2 samples (Fig. 5). B1 and B2 samples showed gradual weight loss up to 230 °C with the mass loss of about 9% which could attributed to the removal of 1.0 mol (10.8% calc.) CO₂. The observed weight loss up to 370 °C could be attributed to the last step of decomposition of the organic ligand accompanied by formation of metallic silver, while in S1 and S2 samples which are synthesized with sonochemical

process, one step with the mass loss of 10% (in S1) and 12% (in S2) is observed between 230-260 °C, which could attributed to the decomposition of the ligands in {[Ag(py-4-c)(Hpy-4-c)]_{1/2}[Ag(py-4-c)]_n} (2) and removal of 1.0 mol (10.8% calc.) CO₂. Similar thermal behaviour was observed for compound 2 in its previous report [20]. The second weight loss between 280-320 °C could be attributed to the last steps of decomposition of the organic moiety, accompanied by formation of metallic silver.

Bactericidal Tests

The antibacterial properties of the achieved samples were tested against *Escherichia coli* (ATCC 25923, Gram-

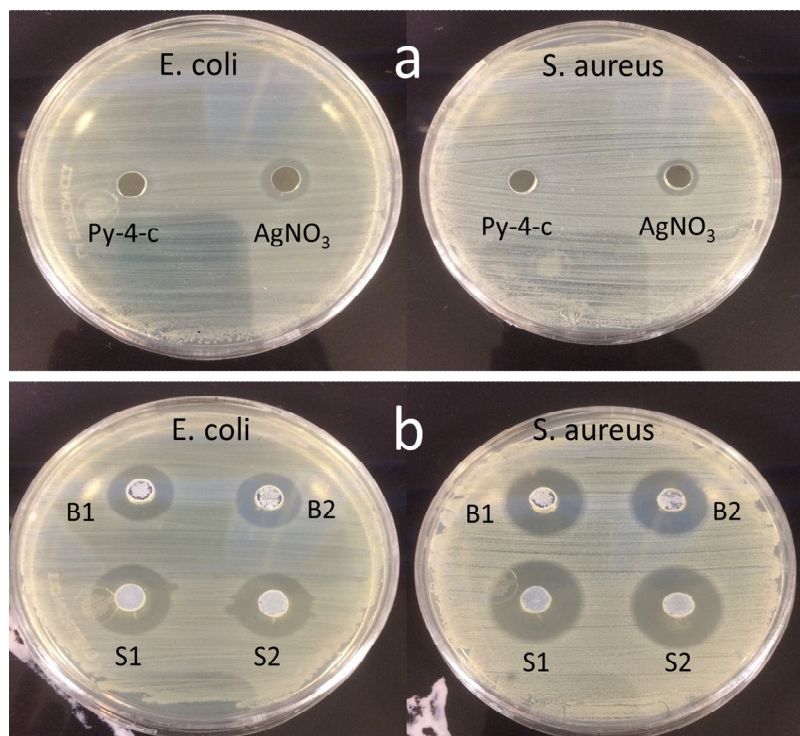


Fig. 6. Antibacterial activity of a) pyridine-4-carboxylic acid and AgNO_3 and b) achieved samples; B1) bulk fast reaction, B2) bulk slow reaction, S1) sonochemical fast reaction and S2) sonochemical slow reaction.

negative bacterium) and *Staphylococcus aureus* (ATCC 25922, Gram-positive bacterium) using agar well diffusion method in 24 h. The amount of the existing Ag^+ ion and py-4-c ligand in compound 1 (which has the higher Ag^+ content than compound 2) was calculated and the proportion was applied in the concentration of AgNO_3 and ligand used for the antibacterial test. Since the ligand, pyridine-4-carboxylic acid, has no bactericidal activity and antibacterial activity for the existing amount of Ag^+ ion in the two silver coordination polymers is insignificant (Fig. 6a), observed inhibition zones for the samples are mainly attributed to the $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) and $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) coordination polymers (Fig. 6b). Comparison between outcomes of the various experiments displays an obvious difference between bulk and sonochemical prepared samples especially in *S. aureus* which is more sensitive than *E. coli*. Resulting samples which were synthesized with sonochemical process (S1 and S2), showed bigger inhibition zones against bulk samples

(B1 and B2), (Fig. 6b). It seems that $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) has better antibacterial activity than $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1). In addition B1 (with the average grain size of 372 nm) and S1 (with the average grain size of 501 nm), which has nano size dimension (Fig. 4), showed better antibacterial activity than B2 (with the average grain size of 407 nm) and S2 (with the average grain size of 600 nm), respectively. Figure 7 indicated that between these two coordination polymers and four samples of them, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) which was synthesized with sonochemical fast reaction (S1) could be used as a very good antibacterial agent. Interestingly its antibacterial property is very better than its comprised component.

CONCLUSIONS

The reaction between AgNO_3 , pyridine-4-carboxylic acid and KOH with molar ratio of 1:1:1 was

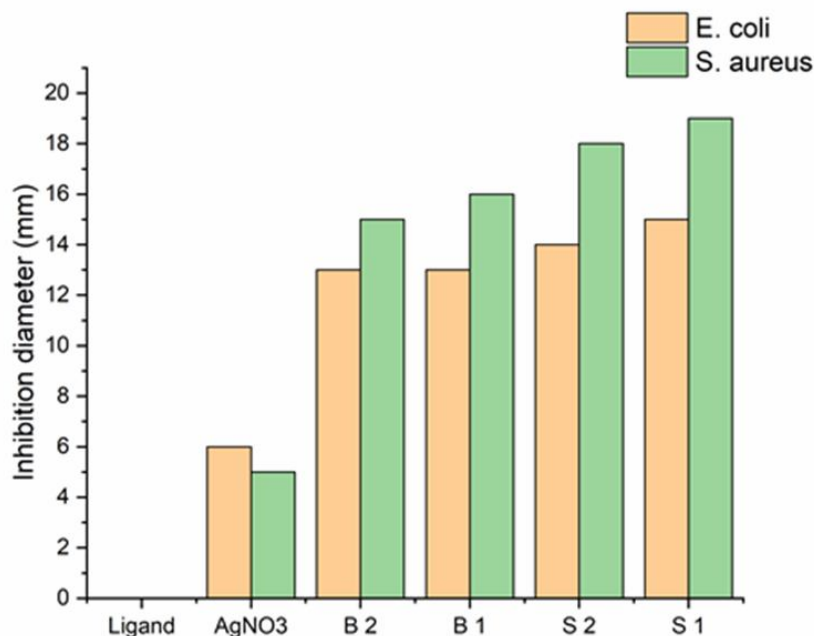


Fig. 7. Schematic diagram for comparison the antibacterial activity of the obtained samples (B1: bulk fast reaction, B2: bulk slow reaction, S1: sonochemical fast reaction and S2: sonochemical slow reaction).

carried out with four different ways. The reaction was done quickly (1) and slowly (2) in two conditions of bulk (B) and ultrasonic bath (S) which was resulted in formation two types of three-dimensional coordination polymers with monoclinic crystal system and $P2_1/c$ space group. Formation of $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1) was observed on stirrer and a different coordination polymer was obtained in ultrasonic bath, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2). These two coordination polymers have very similar crystal lattice parameters and crystal structure. Synthesis of compound 2 was reported by two research groups previously, but in this work, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) coordination polymer was synthesized with green sonochemical reaction at room temperature within one hour. Investigating the antibacterial activity of the samples against gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria's, displayed an obvious difference between bulk and sonochemical prepared samples especially in *S. aureus* which is more sensitive than *E. coli*. Resulting samples which were synthesized with sonochemical process (S1 and S2), showed bigger inhibition zones against bulk samples (B1 and B2). It seems that $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-}$

$\text{c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) has better antibacterial activity than $[\text{Ag}_2(\mu_2\text{-py-4-c})_2]_n$ (1). In addition B1 (with the average grain size of 372 nm) and S1 (with the average grain size of 501 nm), which have nano size dimensions, showed better antibacterial activity than B2 (with the average grain size of 407 nm) and S2 (with the average grain size of 600 nm), respectively. It seems that between these two coordination polymers and four samples of them, $\{[\text{Ag}(\text{py-4-c})(\text{Hpy-4-c})]_{1/2}[\text{Ag}(\text{py-4-c})]\}_n$ (2) which was synthesized with sonochemical fast reaction (S1) could be used as a very good antibacterial agent. Interestingly its antibacterial property is very better than its comprised component.

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