



Nanopowders of 3D Ag^I coordination polymer: A new precursor for preparation of silver nanoparticles

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ABSTRACT

Nanopowders of novel three-dimensional Ag^I coordination polymer, [Ag₂(μ₈-SB)]_n (**1**) [H₂SB = 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenol] has been synthesized by the reaction of SB²⁻ and AgNO₃ by a sonochemical method. Reaction conditions, such as the concentration of the initial reagents and power of the ultrasonic device played important roles in the size, morphology and growth process of the final products. For the first time silver nanoparticles were synthesized from [Ag₂(μ₈-SB)]_n (**1**) coordination polymer by calcinations and hydrothermal methods. These nanopowders and nanoparticles were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM); transmission electron microscopy (TEM) and energy-dispersive X-ray spectra (EDS). Thermal stability and emission properties of nano and crystal samples of compound **1** were studied and compared with each other.

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1. Introduction

In recent years preparation and study of nano-materials are important area of research, especially because of their physical and chemical properties that depends on particle size. The self-assembly of molecular building blocks into targeted nanoscaled architectures at interfaces represents one of the major goals of supramolecular chemistry and material science, given the perspective of the potential applications of these systems in nanotechnology [1–4]. Metal–polymer materials of different types are the object of intense studies because of their interest for fundamental science and promise for different technical applications. In the past decade, several organic and inorganic materials [5] have been synthesized and investigated. Design of polymeric silver(I) complexes with fascinating structures has received much attention, shows a tendency to form coordination polymers with unique Ag–C bonds [6], but example [7] of nano silver(I) compounds are limited. On the other hand in recent years, the synthesis of silver nanoparticles has been a focal point of research and developmental activities in the area of nano-materials owing to the quest for their various technological applications. Silver nanoparticles exhibit remarkable size effects in biological and medicine-related properties. Recently, it has been found that the HIV-1 virus exclusively binds to silver

particles whose size is in the range of 1–10 nm [8], and that silver nanoparticles embedded in PVP show bactericide properties in complicated cases of infected burns and purulent wounds [9]. Silver nanoparticles have also been shown to exhibit excellent antibacterial activity against *Escherichia coli* [10]. In addition, films and powders of PVP containing silver nanoparticles have potential applications in the field of optical information [11,12]. In the field of catalysis, 15 nm silver nanoparticles supported onto alumina show catalytic activity as converters of simulated exhaust automobile gases [13]. Several methods can be applied to synthesize silver nanoparticles with well-defined shapes. The majority of the more straightforward approaches are based on the reduction of silver nitrate by sodium borohydride [14] or sodium citrate [15]. Some of the more diverse methods previously used include microwave plasma synthesis [16], electrolysis of Ag salts [17], rapid expansion of supercritical solvents [18,19], microemulsion [20], and photoreduction of Ag ions [21,22], but to the best of our knowledge no use of silver(I) coordination polymers to produce silver nanoparticles has been reported. In this paper we describe a simple synthetic sonochemical preparation of a new silver(I) coordination polymer with the 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenolate (SB²⁻) ligand based on O,C-donor atoms, then we report two simple synthetic preparation of silver nanoparticles from this coordination polymer, we also compare thermal resistance and emission properties of nanopowders of compound **1** with its crystalline form.

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2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. Double distilled water was used to prepare aqueous solutions. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with an PL–STA 1500 apparatus. The luminescent properties were investigated with a Shimadzu RF–5000 spectrofluorophotometer. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 . Structure solution and refinement was accomplished using SHELXL-97 program packages [23]. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using MERCURY software [24]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu $K\alpha$ radiation. The crystallite sizes of selected samples were estimated using the Paul Scherrer method. The samples were characterized with a scanning electron microscope with gold coating.

2.2. Synthesis of $[Ag_2(\mu_8-SB)]_n$ (1) and preparation of its single crystals

To isolate the single crystals of $[Ag_2(\mu_8-SB)]_n$, 1 mmol (0.250 g) of 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenol (H_2SB) was dissolved in 20 ml acetonitrile and was heated and stirred with solution of 2 mmol (0.114 g) KOH in 5 ml H_2O for an hour. After deprotonation of the ligand in this process, the solution was cooled to room temperature and then a solution of 2 mmol (0.340 g) $AgNO_3$ in 5 ml acetonitrile was added to the mixture and was stirred for an hour. After filtering it was allowed to stand in darkness at room temperature to evaporate for several days to obtain suitable crystals. The crystals were washed with acetone and air dried, d.p. $>370^\circ C$. Yield: 0.255 g (55%), (Anal. Calc. for $C_{12}H_8Ag_2O_4S$: C, 31.03; H, 1.72. Found: C, 30.01; H, 1.79%). IR (selected bands; in cm^{-1}): 552 s, 696 w, 723 w, 835 m, 1094 s, 1138 s, 1217 m, 1317 s, 1400 s, 1565 s, 2930 w, 3050 w.

2.3. Synthesis of $[Ag_2(\mu_8-SB)]_n$ (1) nanopowders by sonochemical method

To prepare the nanopowders of $[Ag_2(\mu_8-SB)]_n$ by sonochemical method, a high-density ultrasonic probe immersed directly into the solution of K_2SB (40 ml, 0.0125 M) in double distilled water, then into this solution, a proper volume of $AgNO_3$ aqueous solution (10 ml, 0.1 M) was added in drop wise manner. The solution was ultrasonically irradiated with the power of 18 W for an hour. The obtained precipitates were filtered, subsequently washed with double distilled water and then dried, d.p. = $272^\circ C$ (Anal. Calc. for $C_{12}H_8Ag_2O_4S$: C, 31.03; H, 1.72. Found: C, 30.25; H, 1.67%). IR (selected bands; in cm^{-1}): 549 s, 694 w, 723 w, 835 m, 1091 s, 1131 s, 1220 m, 1312 s, 1402 s, 1566 s, 2931 w, 3052 w. Certainly we should mention that different concentration of metal and ligand solution (0.02, 0.05 and 0.08 M) with different power of

ultrasonic irradiation (6, 12 and 18 W) were tested but appropriate nano-size of compound 1 obtained under the mentioned conditions. In order to obtain silver nanoparticles, precipitate of compound 1 was calcinated at $500^\circ C$ in a furnace and static atmosphere of air for 5 h.

2.4. Synthesis of silver nanoparticles by hydrothermal method

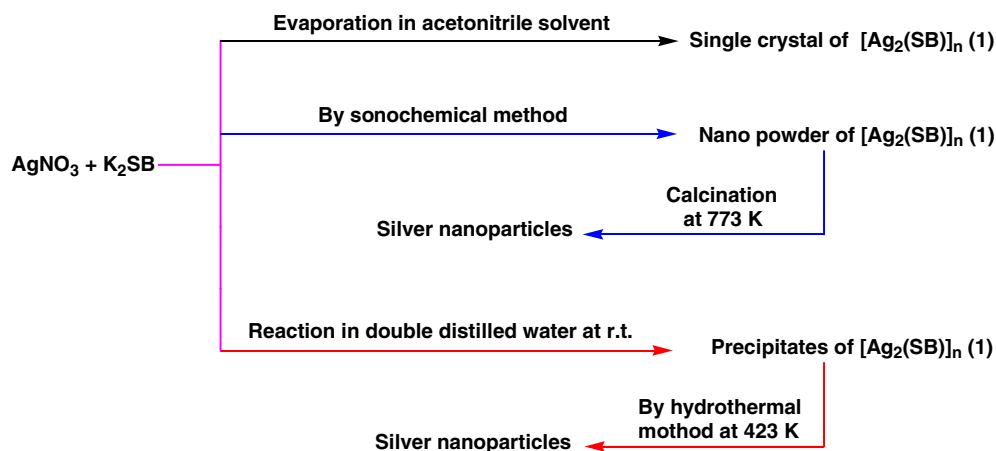
To prepare silver nanoparticles by hydrothermal method, precipitates of compound 1 (after reaction at room temperature with the same concentration as used in sonochemical method) in 20 ml double distilled water was posited in a hydrothermal bomb at $150^\circ C$. After 48 h the bomb was immediately cooled to $4^\circ C$ and the obtained precipitates were filtered, washed with double distilled water and then dried, neither d.p. and nor IR bands was observed.

3. Results and discussion

The Scheme 1 shows the reaction between silver(I) nitrate and K_2SB by three different methods.

Single crystal X-ray analysis reveals that compound $[Ag(\mu_8-SB)_2]_n$ (1) crystallizes in an orthorhombic setting with space group of $Fmm2$.¹ The phenolic oxygen atoms of the SB^{2-} ligand act as bi-donor bridging atoms where each oxygen atom of the Ph–O groups link to two different silver(I) ion (Fig. 1a). The structure of compound 1 may also be considered as a new type of coordination polymer of Ag(I) consisting of one-dimensional linear chains connected via phenolic bridging groups, running parallel to the b axis. The Ag atoms in this compound are involved in an η^2 interaction with two C_{ph} atoms of neighboring molecules (Fig. 1b). Thus, the Ag atoms in compound 1 are linked to two carbon atoms of phenyl moieties of SB^{2-} with distances $Ag-C2^i$ ($i: x, y + 1/2, z + 1/2$) = $Ag-C2^{iv}$ ($iv: -x + 1/2, -y, z + 1/2$) of 2.426(5) Å. Hence, the Ag^I coordination sphere is augmented to four and rather than exhibiting a AgO_2 coordination sphere, the compound can be considered to have a bihapto (O_2C_2Ag) center with coordination number of four (Fig. 1a). Ag–C bond lengths in other compounds with similar η^2 Ag–C interactions range from 2.40 to 2.70 Å [25–28], for example in the $[Ag(benzene)ClO_4]$ are 2.496 and 2.634 Å [29]. Some other Ag(I) polycyclic aromatic polymeric complexes containing of Ag–C(sp^2) bond report mean Ag–arene distances of 2.82–3.37 Å [30–35]. The dihedral angle formed by $Ag-C2-C3$ and $C3-C2-C1$ is $105.9(2)^\circ$ and also the dihedral angle of $C2^i(i: x, -y + 1, z)-C1-C2-C3$ is $5.3(8)^\circ$, indicating that the silver atoms interact with the π electrons of the aromatic rings. The individual polymeric chains are almost parallel to each other and further bridged via the Ag–C bonds, resulting in a three-dimensional framework as shown in Fig. 1b. The carbon atom that connected to the $-SO_2$ group is disordered over two positions in a 1:1 ratio, depending on the location of the C=C double bond, and so is the adjacent SO_2 group. The following restraints were applied for the disordered atoms: SIMU and DELU restraints for C1 to C4 and S1, O2 and O3. ISOR restraints for C3, C4 (standard deviation 0.01) and S1, O2 and O3 (standard deviation 0.002). The S=O distances were restraint to be the same within a standard deviation of 0.02. Each SB^{2-} anion in compound 1 acts as a eight donating bridging ligand via two O- and four C-atoms, connecting eight Ag^I ions in a μ_8 -6 mode (Fig. 1a). The phenolic groups of the SB^{2-} ligand act as bridging group

¹ The intensity data were collected within the range $2.26 \leq \theta \leq 28.25^\circ$ for a crystal of dimension $0.36 \times 0.36 \times 0.22$ mm³. Crystal data: formula, $C_{12}H_8Ag_2O_4S$; M_r , 463.98 g/mol; orthorhombic system, space group $Fmm2$; $a = 17.9958(18)$, $b = 7.0921(7)$, $c = 9.2580(9)$ Å, $V = 1181.6(2)$ Å³; $D_{calc} = 2.608$ Mg/m³ ($Z = 4$); $F(000) = 888$; $R(wR) = 0.0346$ (0.1005) for 821 reflections, with $I > 2\sigma(I)$; $R(wR) = 0.0349$ (0.1026) for all data.



Scheme 1. The produced materials from reaction of K_2SB ligand with silver(I)nitrate by three different methods.

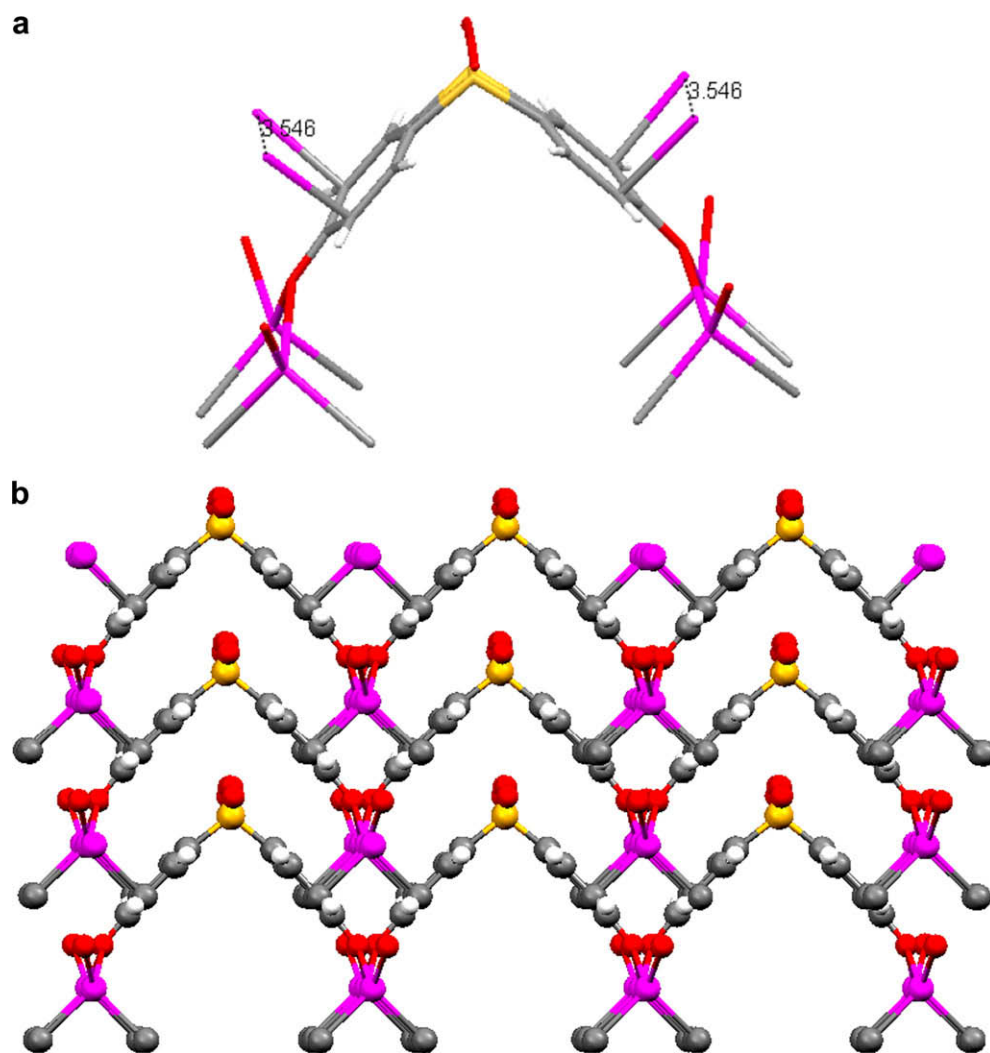


Fig. 1. (a) Molecular structure representations of compound **1**. (b) A fragment of the three-dimensional network in compound **1**, showing the Ag–C and Ag–O interactions (Ag = violet, O = red, C = gray, S = yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

via two O- and four C-atoms, a very novel and interesting coordination mode of this type compounds. Thus, strong bihapto aromatic coordination of Ag atoms in the compound **1** appears to be yet another factor which can make varying contributions to the

construction of a three-dimensional organic–inorganic Ag^{I} coordination polymer. The $\text{Ag}\cdots\text{Ag}$ distances in the compound **1** are 3.546 Å, and considerably longer than in the other polymeric structure [36].

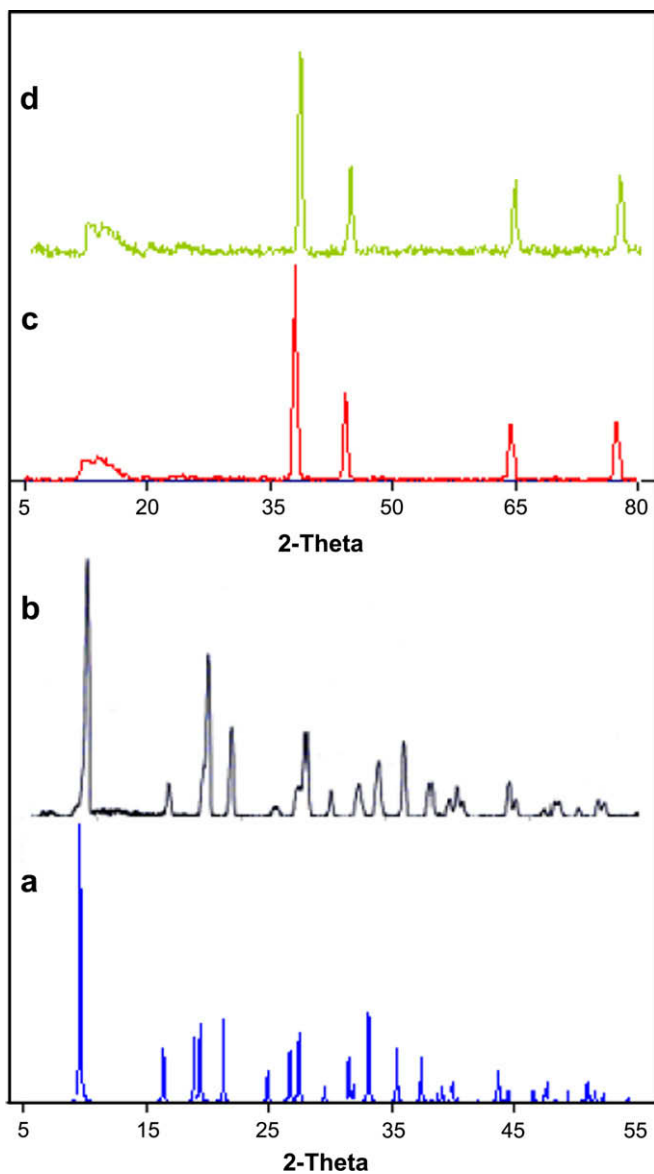


Fig. 2. XRD patterns; (a) simulated pattern based on single crystal data, (b) nanopowder of compound **1**, (c) silver nanoparticles prepared by hydrothermal method, (d) silver nanoparticles prepared by calcinations of compound **1** nanopowders.

Fig. 2a shows the simulated XRD pattern from single crystal X-ray data of the above compound and **Fig. 2b** shows the XRD pattern of a typical samples of $[\text{Ag}(\mu_8\text{-SB})_2]_n$ (**1**) prepared by the sonochemical process. Acceptable matches, with slight different in 2θ , were observed between the simulated from single-crystal X-ray data patterns (**Fig. 2a**) and those from the experimental powder X-ray diffraction patterns for nanopowders crystalline sample as obtained from the synthesis by sonochemical method (**Fig. 2b**). Results of XRD powder patterns indicate that the experimental data are in good agreement with the simulated XRD powder patterns based on single crystal data, hence this compound obtained as a mono-phase. The broadening of the peaks indicated that the particles were of nanometer scale. Estimated from the Paul Scherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [37], the average size of the particles is 15 nm, in agreement with that observed from SEM and TEM images.

The morphology, structure and size of the samples are investigated by scanning electron microscopy (SEM) and transmission

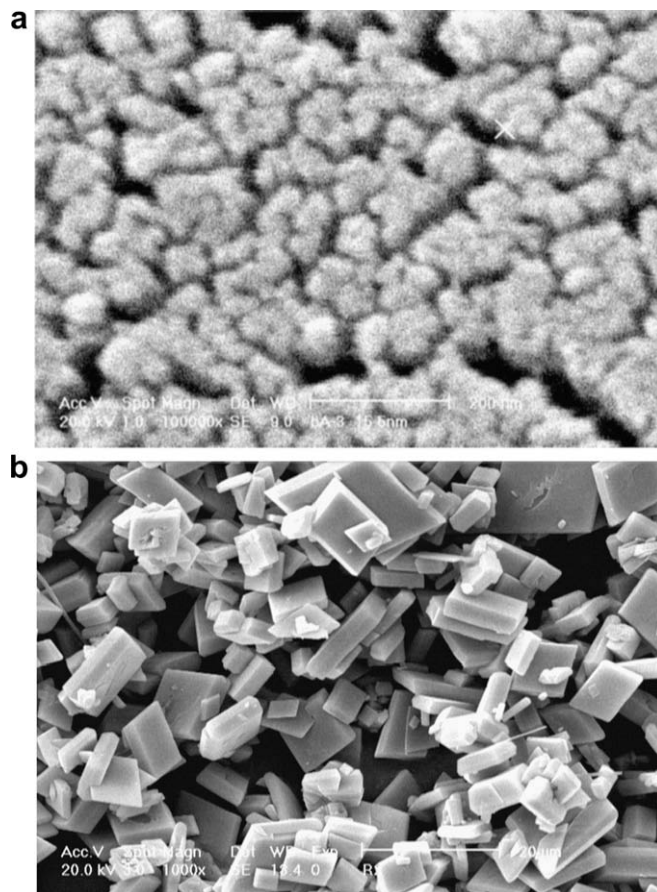


Fig. 3. SEM images of compound **1** nanopowders (a) and compound **1** microcrystals (b).

electron microscopy (TEM). **Fig. 3a** indicates that the original morphology of the nanopowders have the diameter varying between 15 and 20 nm. **Fig. 3b** shows the SEM image of microcrystals of compound **1** obtained from a 0.02 M solution of reagents by 6 W power of ultrasonic irradiation. It may be concluded that for this coordination polymer increase of the concentration and ultrasonic irradiation power change the morphology from microcrystals to nanopowders. TEM images of compound **1** nanopowders (**Fig. 4**) show powders with the diameter varying between 5 and 20 nm.

For further demonstration, the EDS analysis was performed for nanopowders of compound **1**. The EDAX spectrum given in **Fig. 5** shows the presence of Ag as the only elementary component. The success in preparing nanopowders of three-dimensional Ag^{I} coordination polymer was further confirmed by the elemental signatures of C, O and Ag in the energy-dispersive X-ray analysis spectrum as shown in **Fig. 5**.

Initially it was thought that silver(I) oxide is the finally stable product of calcinations and hydroxythermal method of compound **1**, but IR spectrum and XRD patterns (**Fig. 2c** and **d**) surprisingly indicated that in presence of oxygen atoms of the SO_2 and phenolic groups of SB^{2-} ligand and static atmosphere of air in calcinations process, Ag^{I} ions reduced to metallic silver. **Fig. 2c** and **d** shows the XRD patterns of silver nanoparticles prepared by hydrothermal method at 150 °C and calcinations of compound **1** nanopowders obtained by sonochemical method at 500 °C, respectively. Acceptable matches, with slight different in 2θ , were observed between the two patterns (**Fig. 2c** and **d**). The obtained patterns match with the standard patterns of cubic silver with the lattice parameters ($a = 4.0862 \text{ \AA}$ and $z = 4$) which are close to the reported values, (JCPDS card number 04-0783). The size of silver nanoparticles are

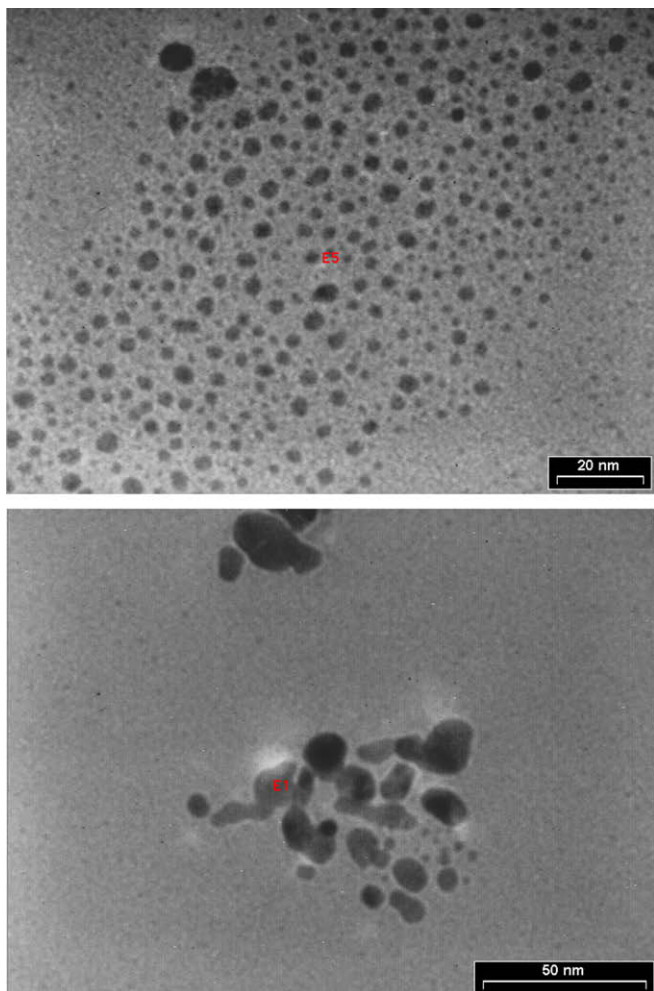


Fig. 4. TEM images of compound 1 nanopowders.

in good agreement with that estimated value obtained from the Paul Scherrer formula [37], the average size of the particles are 60 and 35 nm from the hydrothermal and sonochemical methods, respectively, in agreement with those observed from SEM images.

Fig. 6. shows the SEM images of silver nanoparticles obtained from the two methods, morphology and size of the particles are slightly different in the two samples obtained by two different

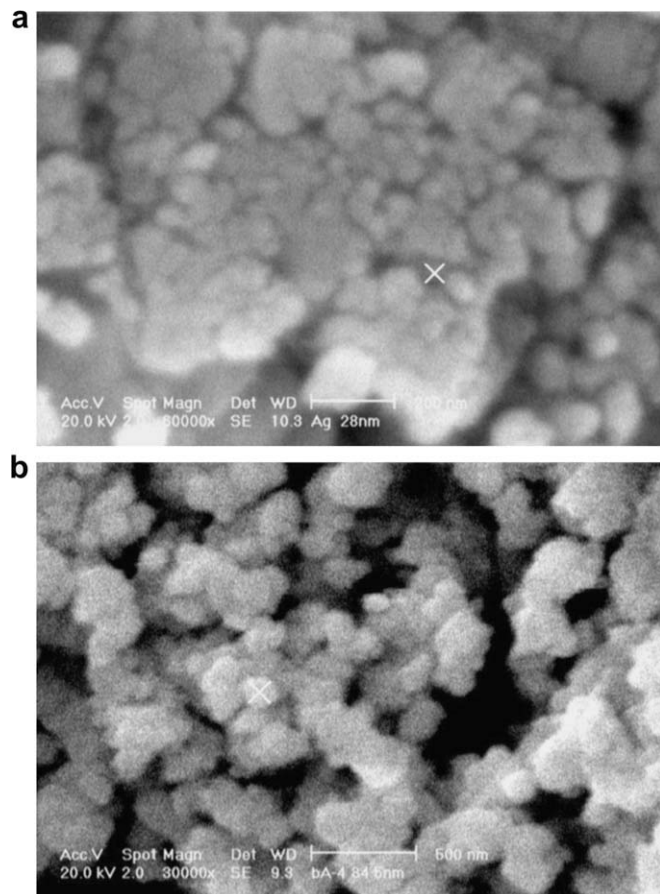


Fig. 6. SEM images of silver nanoparticles obtained by calcinations of compound 1 nanopowders (a) and by hydrothermal method (b).

methods. Calcinations of compound 1 nanopowder obtained by sonochemical method produce smaller particles (Fig. 6a) compared with the hydrothermal method (Fig. 6b). In the other word, probably it may be seen that with the same concentration of reagents, the sonochemical method is better than the hydrothermal method to produce silver nanoparticles from the coordination polymer.

To examine the thermal stability of nanopowders and single crystals of compound 1, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 40 and 610 °C in a static atmosphere of nitrogen (Fig. 7a and b, respectively).

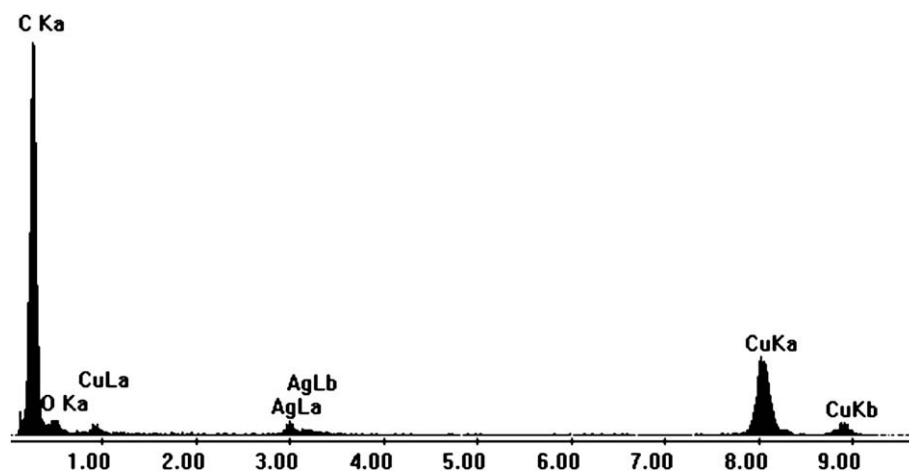


Fig. 5. Energy-dispersive X-ray analysis of compound 1 nanopowders.

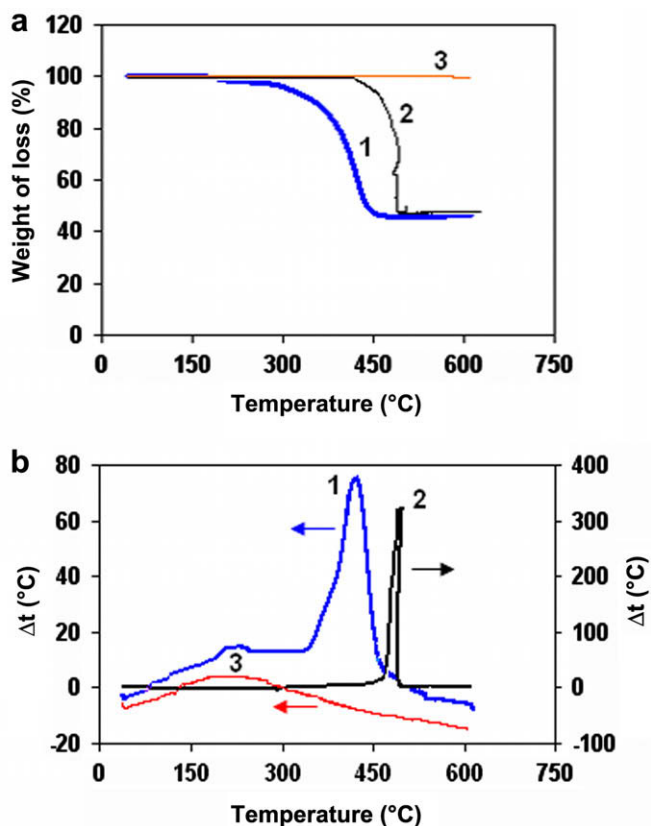


Fig. 7. TG (a) and DTA (b) of compound **1** nanoparticles (curve 1), compound **1** single crystals (curve 2) and silver nanoparticles (curve 3).

Single crystals of compound **1** is very stable and does not decompose up to 419 °C, at which temperature decomposition starts. In this stage, exothermic removal of SB^{2-} occurs between 419 and 502 °C with a mass loss of 53.0% (calcd 53.5%). Mass loss calculations show that the final decomposition product is metallic silver, (Fig. 7a,2). Nanopowders of compound **1** are much less stable at starts to decompose at 272 °C. The TG curve (Fig. 7a,1) exhibits a distinct decomposition stage between 272 and 480 °C with a mass loss of 54.2% (calcd 53.5%). Decomposition of compound **1** nanopowders starts at about 147° earlier than its single crystals, probably due to more heat that needed to annihilate the lattices of single crystal. This stabilization is annihilated approximately by produce nanopowders of this compound by sonochemical method.

The DTA curves displays a distinct endothermic effect at 492 °C for single crystals of compound **1** (Fig. 7b,2) and a broad effect with maximum intensity at 420 °C for nanopowders of this compound (Fig. 7b,1). About 72° difference between the two maximum intensity of DTA curves also show less stability of compound **1** nanopowders compared with its single crystals, that are in good agreement with TGA results.

In addition of IR spectrum and XRD pattern (Fig. 2c) for hydrothermal product, TG and DTA curves (Fig. 7a and b,3) confirm the production of metallic silver in a static atmosphere of nitrogen.

The solid state fluorescence spectra of H_2SB ligand, nanopowders and single crystals of compound **1** were studied (Fig. 8). The H_2SB ligand show a broad emission band with the maximum intensities at 426 and 433 nm upon excitation at 300 nm (Fig. 8b). No emission band observed for the nanopowders and single crystals of compound **1** (Fig. 8a and c, respectively) which can be attributed to the heavy atom effect [38–42] due to the coordination of the ligand to the $\text{Ag}(\text{I})$ centers. This effect extinguishes emissions of compound **1** and no difference was observed between the nano and crystal forms of this compound.

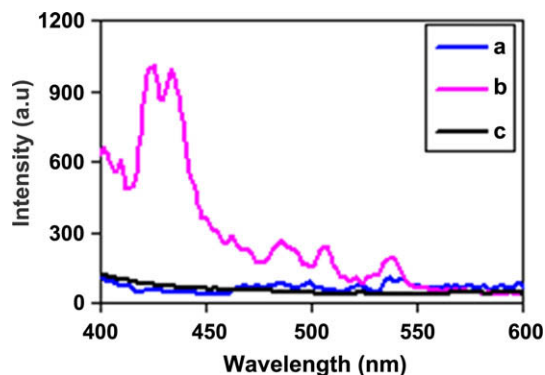


Fig. 8. The fluorescence spectra of compound **1** nanopowders (a), H_2SB ligand (b) and compound **1** single crystals (c), room temperature, $\lambda_{\text{exc}} = 300 \text{ nm}$.

4. Conclusions

Nanopowders of an organosilver(I) coordination polymer with a less-common η^4 -coordination mode of the phenyl rings, in addition to the normal phenolic coordination modes were synthesized by sonochemical method. Decreasing the size of this coordination polymer to nanometers results in less thermal stability of this compound compared with its single crystal sample, but this decrease has no effect on emission properties of this compound. The size of silver nanoparticles indicates that produce these nanoparticles from coordination polymers is a simple and effective method. The size of silver nanoparticles also shows that calcinations of Ag^{I} nanopowders of coordination polymers is better than hydrothermal method.

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Appendix A. Supplementary material

CCDC 645562 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.04.042.

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