Inorganica Chimica Acta 382 (2012) 171-176

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

Solid state irreversible anion-exchange on one-dimensional silver(I) coordination polymer nanostructures

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ARTICLE INFO

Article history: Received 15 November 2010 Received in revised form 14 December 2011 Accepted 17 December 2011 Available online 24 December 2011

Keywords: Anion exchange Solid state reaction Silver Nanoparticle

1. Introduction

Coordination polymer is a general term used to indicate an infinite array composed of metal ions and organic moiety as bridging and linker ligands. The central metallic atoms and organic ligands are two important operatives in design and construction of desirable frameworks [1–3]. The coordination polymers convert into supramolecular aggregates via self-assembly by non-covalent interactions [4-7]. These huge intriguing structures have gained chemists interest because of their unique potential applicability as functional materials in many areas such as storage, exchange, and catalysis [8-13]. Anion exchange is an important property of coordination polymers and it has attracted increasing attention in recent years. Any network with cationic metals as center ion would include free counter anions in the channels or pore and could be applied as the anion-exchange materials [14,15]. The trapped anions in the cavity can be exchanged with different anions [16–18]. Ion exchange has been observed in solution phase in most cases but ion exchange in solid-state would be observed, too [19-21]. During this decade; the simplicity, low cost, high output and low pollution are the reasons for developing the solid-state reaction [22-26]. The coordination polymer $[Ag(\mu-bpfb)(NO_3)]_n$ (1) has been synthesized as bulk and nano-size. Both obtained nanorods and bulk form were used as reagents for anion exchange reactions in solid state. The obtained products from anion replacement are $[Ag(\mu-bpfb)(ClO_4)]_n$ (2), [Ag $(\mu$ -bpfb)(SCN)]_n (**3**) and $[Ag(\mu$ -bpfb)(N₃)]_n (**4**) nanostructures. The compounds 1-4 were calcinated at 673 K and the silver nanoparticles were obtained after decomposition.

ABSTRACT

A new one-dimensional silver(I) coordination polymer $[Ag(\mu-bpfb)(NO_3)]_n$ (1), bpfb = N,N'-bis(4-pyridylformamide)-1,4-benzene, has been synthesized and characterized by IR, NMR spectroscopy and single crystal X-ray crystallography. Nanorods compound **1** were obtained by sonochemical process and characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The nitrate ions of compound **1** in nanostructure exchange with perchlorate, thiocyanate and azide anions by the solid state reaction. Three new compounds $[Ag(\mu-bpfb)(CIO_4)]_n$ (**2**), $[Ag(\mu-bpfb)(SCN)]_n$ (**3**) and $[Ag(\mu-bpfb)(N_3)]_n$ (**4**), were characterized by IR spectroscopy, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The silver nanoparticles were obtained from direct calcination of compounds **1–4** nanostructures in an electrical furnace at 673 K.

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2. Experimental

All reagents for the synthesis and analysis were commercially available and used as received. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo K α radiation. The structure was solved by direct methods and refined by full-matrix leastsquares techniques on F^2 . X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with monochromated Cu k α radiation. The samples were characterized with a scanning electron microscope with gold coating.

2.1. Synthesis of N,N'-bis(4-pyridyl formamide)-1,4-benzene (bpfb)

At room temperature, 1 g (9.2 mmol) of 1,4-phenylenediamine (bpfb) was dissolved in 50 ml of dry THF. To this solution was added 5 g of the commercially available hydrochloride salt of isonicotinoyl chloride. After stirring for 30 min, 10 ml of triethylamine was added and the mixture was stirred overnight. After evaporation to dryness, the yellow residue was poured into an aqueous solution (50 ml) of Na₂CO₃ (1.2 M) and then the product filtered. The precipitant was washed with distilled water and yellowish powder was obtained after drying at ambient temperature ca. 75% yield [27].

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 1646(s), 1542(w), 1443(br), 1407(w), 1314(w), 840(w), 661(w).



Note

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^{0020-1693/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.12.032

¹**H NMR** (DMSO, *δ*): 10.54 (s, 2H, NH); 8.77 (d, 4H, H-py); 7.87 (d, 4H, H-Py); 7.78 (s, 4H, H-Ar) ppm.

2.2. Synthesis of $[Ag(\mu-bpfb)(NO_3)]_n$ (1)

The N,N'-bis(4-pyridylformamide)-1,4-benzene (bpfb) (0.159 g, 0.50 mmol) was dissolved in DMF (5 mL) and this solution poured into a test tube. An equal amount (1:1) mixture of DMF and aceto-nitrile (5 mL) was layered on top of bpfb solution; then a solution of AgNO₃ (0.085 g, 0.5 mmol) in acetonitrile (5 mL) carefully added on top of the mesosphere layer without its disturbing. The gray single crystals were obtained after a month in mesosphere layer, d.p. >300 °C.

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 1656(s), 1555(w), 1513(br), 1415(w), 1340(w), 1310(s), 840(w), 661(w), 522(w). *Anal.* Calc. for $C_{18}H_{14}AgN_5O_5$: C, 22.1; H, 2.87; N, 14.35. Found: C, 21.8; H, 2.91; N, 14.13%.

¹**H NMR** (DMSO, *δ*): 10.51 (s, 2H, NH); 8.78 (d, 4H, H-py); 7.86 (d, 4H, H-Py); 7.77 (s, 4H, H-Ar) ppm.

¹³**C NMR** (DMSO, *δ*):163.6, 150.2, 141.9, 134.7, 121.5, 120.8 ppm.

2.3. Synthesis of $[Ag(\mu-bpfb)(NO_3)]_n$ (1) nanorods by sonochemical process

To prepare the nanorods of compound **1** by sonochemical process was used ultrasonic bath (138 W) for 1 h. A proper volume, 30 mL acetonitrilic solution of AgNO₃ (0.3 mmol, 0.05 g) was poured into 30 mL prepared solution of ligand (bpfb) in DMF (0.3 mmol, 0.095 g), under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with ethanol and then dried, d.p. >300 °C.

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 1656(s), 1555(w), 1513(br), 1415(w), 1340(w), 1310(s), 840(w), 661(w), 522(w).

¹**H NMR** (DMSO, *δ*): 10.51 (s, 2H, NH); 8.78 (d, 4H, H-py); 7.86 (d, 4H, H-Py); 7.77 (s, 4H, H-Ar) ppm.

¹³**C NMR** (DMSO, *δ*):163.6, 150.2, 141.9, 134.7, 121.5, 120.8 ppm.

2.4. Synthesis of nano-structure $[Ag(\mu-bpfb)(X)]_n(X^- = ClO_4^-, N_3^- and SCN^-)$ from nano-rods of $[Ag(\mu-bpfb)(NO_3)]_n(\mathbf{1})$ by solid-state reaction

(a) The obtained percipitate (0.2 g) nanorods of compound **1** and the excess amount of NaClO₄ were added to each other and grinded for one hour. The nano-structure of compound **2** was washed with ethanol, subsequently dried at air atmosphere.

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 1656(s), 1555(w), 1513(br), 1415(w), 1083(s), 840(w), 661(w), 522(w).



Scheme 1. Showing of preparation of nanostructure compounds **2–4** from nanostructure $[Ag(\mu-bpfb)(NO_3)]_n$ (**1**) and preparation of silver nanoparticles from calcination of compounds **1–4**.

(b) The 0.2 g nanorods of compound **1** and the excess quantities of KSCN as solids were added to each other and grinded for one hour. The nano-structure of compound **4** were washed with ethanol and subsequently dried at air atmosphere.

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 2143(s), 2100(s), 1656(s), 1555(w), 1513(br), 1415(w), 840(w), 661(w), 522(w).

(c) The 0.2 g nanorods of compound **1** and the excess amount of NaN_3 were grinded for one hour in solid-phase. The nano-structures of compound **3** were washed with ethanol and subsequently dried at air atmosphere.

IR (cm⁻¹) selected bands: 3340(s), 3025(s), 2029(s), 1656(s), 1555(w), 1513(br), 1415(w), 840(w), 661(w), 522(w).

2.5. Synthesis of silver nanoparticles by direct thermal decomposition of compounds 1–4

The 0.1 g precipitate of compound **1–4** was calcinated at 673.15 K in an electrical furnace at static air atmosphere for 2 h. By this process, the gray silver nanoparticles were obtained.



Fig. 1. The IR spectra of compound (**a**) $[Ag(\mu-bpfb)(NO_3)]_n$ (**1**); (**b**) $[Ag(\mu-bpfb)(CIO_4)]_n$ (**2**); (**c**) $[Ag(\mu-bpfb)(SCN)]_n$ (**3**); and (**d**) $[Ag(\mu-bpfb)(N_3)]_n$ (**4**).

3. Results and discussion

The single crystals of $[Ag(\mu-bpfb)(NO_3)]_n$ (1) have been prepared by diffusion method. This compound was obtained as bulk powder by direct adding the reagents solution to each other. Compound 1 has been synthesized as nanostructure by sonochemical method. Nanorods of compound 1 have been used as precursor for synthesis of compound $[Ag(\mu-bpfb)(ClO_4)]_n$ (2), $[Ag(\mu-bpfb)(SCN)]_n$ (3) and $[Ag(\mu-bpfb)(N_3)]_n$ (4) as nanostructure in solid state. After heating all the synthesized nanostructures, $[Ag(\mu-bpfb)(X)]_n$ (X⁻ = ClO₄⁻, SCN⁻, N₃⁻), at 673 K, silver nanoparticles were obtained (Scheme 1).

The IR spectra of compound **1** at nano-size and bulk form show the absorption bands at around 3025 cm^{-1} are corresponding to the C–H modes of the aromatic rings of ligand bpfb. The variable intensity absorption bands in the frequency range 1400– 1580 cm^{-1} are corresponding to ring vibrations of the "py" ring. The characteristic bands of the nitrate anion appear at 1335 cm⁻¹. The broad absorption band at 3340 cm^{-1} is assigned to the v (NH) modes (Fig. 1). The ¹HNMR spectrum shows a broad signal at 10.51 ppm assigned to the NH protons. In aromatic region, two doublet bands have been observed at 8.78 and 7.86 that assigned to protons of the pyridine rings and one singlet signal at 7.77 ppm assigned to four protons of middle aromatic ring. The ¹³C NMR spectrum shows six distinct signals, 163.6, 150.2, 141.9, 134.7, 121.5, 120.8 ppm, assigned to aromatic carbon atoms of bpfb ligand.

Also, the structure of compound **1** was determined by X-ray crystallography. The X-ray crystallography data shows Ag(I) atoms

are connected by covalent bonds to two nitrogen atoms (N1, N20) of pyridyl groups of bpfb ligand in one direction. Therefore, this polymer grows in one dimension along *c* crystallographic axis (Fig. 2a). The chains were connected by hydrogen bonds. So, these connections cause the structure grows in second dimension and the sheets form. Two distinct oxygen atoms (O1s, O2s) of nitrate groups connect to the hydrogen atoms of amidic groups (N–H…O) in the ligand structure (Fig. 2b). The sheets connect by π - π stacking interactions and the structure grows as three-dimensional supermolecule (Fig. 2c).

Decomposition behavior of compound (1) was investigated in static air atmosphere from ambient temperature to 700 °C (Fig. 8). Crystal form and nanostructure of the compound (1) have various thermal stabilities. The crystal form of the compound (1) is stable up to 320 °C and nanostructure to 180 °C at which temperatures the organic coordinated ligand exit (calc: 65.22%, obs: 60.81%). So, this point shows that compound 1 in nano form is less stable than in the bulk form. The experimental mass loss of 20.78% is consistent with the calculated value of 12.7% for the elimination of one molecule of NO₃. After nitrate molecule leaves the residue, gray powder would be silver metal (calc: 22.095%, observed: 22.12%). Two fragments exit during two exothermic processes (Fig. 8).

Fig. 3a, b show X-ray powder diffraction (XRD) patterns of the simulated X-ray crystallography data and bulk form of compound **1**. Good matches were observed between the patterns of simulated X-ray crystallography data and the X-ray powder diffraction in bulk form and nano-size of compound **1**.



Fig. 2. Showing (**a**) a fragment of the one-dimensional chain in compound **1** along crystallographic c axis [001]; (**b**) hydrogen bonds form the 2D coordination polymer; and (**c**) The π - π stacking interaction in supermolecule structure (Ag = violet, O = red, C = gray, N = blue). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. The XRD patterns of (**a**) simulated from single crystal X-ray data of compound **1**; (**b**) bulk form and nono-size as synthesized of compound **1**; (**c**) nano-structure of compound **2**; (**d**) nanostructure of compound **3**; and (**e**) nanostructure of compound **4**.

The nanorods of compound 1 were synthesized at ultrasound irradiation with the power of 138 W and characterized by IR spectroscopy, X-ray powder diffraction and Scanning Electron Microscopy. The IR spectroscopy data and XRD pattern of compound 1 nanorods are as the same as the IR spectroscopy data and XRD pattern of single crystal and bulk form (Figs. 1a and 3b). The nanostructure of compound 1 has been shown by Scanning Electron Microscopy (Fig. 4a). The nano-rods of compound 1 were used as precursor to prepare the nano-structures of compounds 2, 3 and **4**. After grinding the compound **1** with NaClO₄, KSCN and NaN₃ in solid phase, nano-structures of compounds 2, 3 and 4 were obtained. The IR spectra of compounds 2, 3 and 4 show the absorption bands of the C-H modes of the aromatic rings, the vibrations of the "py" ring and (NH) modes. These visible bands are as the same as the observed bands in the IR spectrum of compound **1**. But, the band at 1335 cm⁻¹ of the nitrate anion completely disappears in the spectrum of compounds 2, 3 and 4. The absorption band at 1083 cm⁻¹ is assigned to the perchlorate anion vibration mode in the IR spectrum of compound 2 (Fig. 1b) and the absorption band at 2100 cm^{-1} in the compound **3** is assigned to the thiocyanate anion vibration mode (Fig. 1c). Also, the absorption band at 2029 cm⁻¹ is assigned to the azide anion vibration mode in the compounds 4 (Fig. 1d). The nano-structures of compounds 1-4 have different XRD patterns (Fig. 3). Acceptable matches, with



Fig. 4. The SEM images of compound (**a**) $[Ag(\mu-bpfb)(NO_3)]_n$ (**1**); (**b**) $[Ag(\mu-bpfb)(ClO_4)]_n$ (**2**); (**c**) $[Ag(\mu-bpfb)(SCN)]_n$ (**3**); and (**d**) $[Ag(\mu-bpfb)(N_3)]_n$ (**4**) nanostructures.

slight different in 2θ , were observed between the simulated from single-crystal X-ray data patterns and those from the experimental



Fig. 5. XRD pattern of silver nanoparticles produced by calcinations of compounds 1–4.

powder X-ray diffraction patterns of single-crystal sample and nano-structured compound **1** (Fig. 3a and b). The XRD patterns of compounds **2–4** show these nano-structures have retained their crystalline forms after grinding but as the patterns show these four structures are completely different. The nano-structures were characterized by Scanning Electron Microscopy (Fig. 4).

Gray nanoparticles were obtained from direct calcination of compounds **1–4** nanostructures at 673.15 K in an electrical furnace. The X-ray powder diffractions show silver metal is the obtained product from calcination of compounds **1–4** (Fig. 5). The SEM images of these silver nanoparticles were observed in Fig. 6. The obtained silver nanoparticles have different sizes. The average sizes of the silver nanoparticles from direct calcination of compounds **1–4** have been shown in Fig. 7. The average sizes of obtained silver nanoparticles from calcination of compounds **1–4** have been shown in Fig. 7. The average sizes of obtained silver nanoparticles from calcination of compounds **1–4** are 57, 60, 37 and 45 nm, respectively. The least size of silver nanoparticles are observed from calcination of [Ag(μ -bpfb)(SCN)]_n (**3**) nanostructures and the maximum size of silver nanoparticles were obtained from calcination of [Ag(μ -bpfb)(ClO₄)]_n (**2**).

4. Conclusion

In summary a new 1D coordination polymer $[Ag(\mu-bpfb)(NO_3)]_n$ (1), as single crystal, bulk form and nano-size could convert to the new compounds by anion exchange in solid state. By grinding the compound 1 nanostructure and NaClO₄, KSCN and NaN₃ in solid phase, the products with formulas $[Ag(\mu-bpfb)(ClO_4)]_n$ (2), $[Ag(\mu-bpfb)(SCN)]_n$ (3) and $[Ag(\mu-bpfb)(N_3)]_n$ (4) were obtained. The silver nanoparticles are prepared from calcination of compounds 1–4 at 673 K. The silver nanoparticles produced by calcination of compound 1–4 have different sizes because of having different structure formulas. So, the role of the counter ion in the initial structure as precursor is very important and it has direct influence on the size and morphology of products.

Acknowledgment

Support of this investigation by Tarbiat Modares University is gratefully acknowledged.

Appendix A. Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. 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.2011.12.032.



Fig. 6. The SEM images of silver nanoparticles produced from calcinations of (**a**) $[Ag(\mu-bpfb)(NO_3)]_n$ (**1**); (**b**) $[Ag(\mu-bpfb)(ClO_4)]_n$ (**2**); (**c**) $[Ag(\mu-bpfb)(SCN)]_n$ (**3**); and (**d**) $[Ag(\mu-bpfb)(N_3)]_n$ (**4**).



Fig. 7. The histogram of silver nanoparticles prepared by direct calcination at 673 K from compound (**a**) $[Ag(\mu-bpfb)(NO_3)]_n$ (**1**); (**b**) $[Ag(\mu-bpfb)(ClO_4)]_n$ (**2**); (**c**) $[Ag(\mu-bpfb)(SCN)]_n$ (**3**); and (**d**) $[Ag(\mu-bpfb)(N_3)]_n$ (**4**).



Fig. 8. Thermal behavior of compound **1** (red diagrams belong to nano-size and black ones belong to bulk-size). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

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