

RESEARCH PAPER

Sonochemical synthesis and characterization of nano-sized zinc(II) coordination complex as a precursor for the preparation of pure-phase zinc(II) oxide nanoparticles

Maryam Ranjbar^{1*}, Mostafa Yousefi^{1,2}, Nasrin Shahsavan³, Mohammad Yousefi³, Ehsan Jalilian⁴ and Lars Eriksson⁴

¹ Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

² National Iranian Oil Products Distribution Company (NIOPDC), Zahedan Region, Zahedan, Iran

³ Department of Chemistry, Faculty of Sciences, Islamic Azad University, Shahr-e-Rey Branch, Tehran, Iran

⁴ Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

ARTICLE INFO

Article History:

Received 26 December 2016

Accepted 27 February 2017

Published 14 April 2017

Keywords:

Crystal structure

Neocuproine

Sonochemical method

Thermal analyses

Zinc oxide nanoparticles

ABSTRACT

In current study, nanoparticles and single crystals of a Zn(II) coordination complex, [Zn(dmph)₂] (1), {dmph=2,9-dimethyl-1,10-phenanthroline(neocuproine)}, have been synthesized by the reaction of zinc(II) acetate, KI and neocuproine as ligand in methanol using sonochemical and heat gradient methods, respectively. The nanostructure of 1 was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), FT-IR spectroscopy and elemental analyses, and the structure of compound 1 was determined by single-crystal X-ray diffraction. The thermal stability of nano-sized 1 has been studied by thermogravimetric (TG) and differential thermal analyses (DTA). Structural determination of compound 1 reveals the Zn(II) ion is four-coordinated in a distorted tetrahedral configuration by two N atoms from a 2,9-dimethyl-1,10-Phenanthroline ligand and two terminal I atoms. The effect of supercritical condition on stability, size and morphology of nano-structured compound 1 has also been studied. The XRD pattern of the residue obtained from thermal decomposition of nano-sized compound 1 at 600 °C under air atmosphere provided pure phase of ZnO with the average particles size of about 31 nm.

How to cite this article

Ranjbar M, Yousefi M, Shahsavan N, Yousefi M, Jalilian E, Eriksson L. Sonochemical synthesis and characterization of nano-sized zinc(II) supramolecular compound as a precursor for the preparation of pure-phase zinc(II) oxide nanoparticles. *Nanochem Res*, 2017; 2(1):120-131. DOI: 10.22036/ncr.2017.01.011

INTRODUCTION

Particles of metal oxides that are in the nanometer size regime have attracted significant interests because of their atom-like size dependent properties. Recently, synthesis of metal oxide nanoparticles with new inorganic precursor has been interested, taking profit of the tools of organometallic chemistry [1-4]. A major interest at the moment is in the development of organometallic or inorganic compounds for

preparation of nanoparticles. Using of the novel compound can be useful and open a new way for preparing nanomaterials to control nanocrystal size, shape and distribution size [5]. A reduction in particle size to nanometer scale results in various interesting properties compared with the bulk properties.

ZnO is a polar inorganic crystalline material with many applications due to its unique combination of interesting properties such as non-toxicity,

* Corresponding Author Email: marandjbar@irost.ir

good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and low price [6,7]. ZnO is a well-known semiconductor with a wide direct band gap (3.37 eV) and a large exciton binding energy of 60 meV at room temperature [8,9]. In addition, it has a wide range of applications as solar cells, luminescent, electrical and acoustic devices, in gas and chemical sensors, as coatings, catalysts, micro-lasers, memory arrays and in biomedical applications [7,10]. Many methods have been developed to synthesize ZnO nanoparticles including thermal decomposition of a metal-organic frameworks (MOF) [11], thermolysis of Zn-oleate complex [12], sonochemical method by aqueous-alcoholic-ethylendiamin solutions of zinc nitrate and sodium hydroxide [13], electrophoretic deposition [14], sol-gel process [15], etc. Thermal decomposition method has some advantages such as simple process ability, and low cost to obtain high purity products; hence it is quite promising and facile route for industrial applications. So, thermal decomposition is a suitable route for preparing of ZnO.

The use of coordination supramolecular compounds as precursors for the preparation of inorganic nanomaterials such as zinc(II) oxide has not been investigated thoroughly. Coordination supramolecular compounds represent an important interface between synthetic chemistry and materials science. We have investigated the synthesis of single-phase hexagonal quasi-spherical ZnO nanoparticles with the average particles size of about 30 nm from thermal decomposition of the Zn(II) supramolecule, bis(2,6 diaminopyridinium) bis(pyridine-2,6-dicarboxylato)zincate(II), as the new precursor in the presence of dry methanol as solvent [16]. Morsali et al. [17] have reported the synthesis of hexagonal nano-rods ZnO from nanorods of a three-dimensional Zn(II) metal-organic framework, $[Zn_2(\text{btec})(\text{DMF})_2]_n$, as the new precursor. This group also worked on the synthesis of spherical ZnO nanoparticles from a new coordination polymer, $[Zn_3(\text{tza})_3(\text{H}_2\text{O})_3]_n$, by thermal decomposition at 500 °C for 4 h [18]. This article focuses on the simple synthetic preparation of nanostructures and single crystals of a Zinc(II) coordination complex, $[Zn(\text{dmph})I_2]$ (**1**), (dmph= 2,9-dimethyl-1,10-phenanthroline), using sonochemical and heat gradient methods, respectively. 1,10-Phenanthroline is the basic chemical moiety leading to an important class of chelating agent [19]. The choice of phenanthroline is mainly due to two factors. This hermetic moiety

can provide a further binding site for metal ions. Therefore, polyamine macrocyclics containing this moiety are expected to form more stable complexes than saturated polyamine ligands containing the same number of nitrogen donors. The insertion of phenanthroline in a macrocyclic framework may allow the resulting metal complexes to be solubilized in a polar solvent due to the hydrophobic characteristics displayed by this aromatic unit. It has therefore been increasingly used in both analytical and preparative coordination chemistry [20]. Metal complexes containing ligands such as 1,10-phenanthroline and bipyridine have gained importance because of their versatile roles as building blocks for the synthesis of metal dendrimers for supramolecular assemblies in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis polymerization, and biochemistry [21].

Ultrasonic irradiation is considered a green energy source because of shorter reaction times and higher yields in comparison with thermal energy sources. Due to these advantages, recently chemists have focused their attention on this type of energy source [22]. Sonochemistry is the research area in which molecules undergo a reaction as a result of employing powerful ultrasound radiation (20 kHz – 10 MHz) [23]. The results reveal that compared with traditional synthetic techniques, such as solvent diffusion technique, hydrothermal and solvothermal methods, ultrasonic synthesis is a simple, efficient, low cost, and environmentally friendly approach to nano-scale coordination supramolecular compound [24, 25]. These extreme conditions permit access to a range of chemical reaction space normally not accessible, for example many coordination supramolecular compounds have been synthesized via sonochemical method, such as: La(III)-LH₂ [25], Zr(IV)-Neocuproine [26], Cu(I)-Neocuproine [27], Pb(II)-LH₂ [28], Zr(IV)-Isophthalic acid [29], Cd(II)-Thioacetamide [30], Zr(IV)-LH₂ [31], and Zn(II)-LH₂ [16]. To proceed, we report the facile preparation of hexagonal wurtzite structure of ZnO nanoparticles by thermal decomposition of nano-sized compound **1** at 600 °C under air atmosphere and without any surfactant or capping molecules.

EXPERIMENTAL

Materials and physical techniques

All reagents and solvents used in this work were commercially available and employed without further purification. A multiwave ultrasonic

generator (Sonicator-4000; Misonix, 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 ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. Melting points were measured with a Thermo Scientific 9200 apparatus and are uncorrected. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus CHN-O- Rapid analyzer. FT-IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the range 400–3500 cm^{-1} using the KBr disk technique. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature in the 2θ range of 10–70°. The crystallite sizes of selected samples were estimated using the Scherrer formula. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [32]. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) of the title compound were performed on a computer-controlled PL-STA 1500 apparatus. 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 argon atmosphere. The samples were characterized by a scanning electron microscope (SEM) (Philips XL 30) equipped with an energy dispersive X-ray (EDAX) microanalysis with gold coating. Crystallographic measurements of compound **1** were carried out at 296(2) K using a Bruker APEX-II CCD area-detector diffractometer. The intensity data were collected using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied with the program SADABS [33]. The structure was solved by direct methods SHELXS-97 [34], and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [34] with refinement of F^2 against all reflections. 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 data collections and structure refinements of compound **1** are listed in Table 2.

Synthesis of $[\text{Zn}(\text{dmph})\text{I}_2]$ (**1**) as single crystal

To isolate single crystals of $[\text{Zn}(\text{dmph})\text{I}_2]$ (**1**), 2,9-dimethyl-1,10-phenanthroline (0.5 mmol,

0.104 g), zinc(II) acetate (0.5 mmol, 0.109 g) and potassium iodide (1 mmol, 0.116 g) were placed in the main arm of a branched tube to be heated. Methanol was carefully added to fill both arms, and then the arm heated was placed in oil bath at 60 °C. After 10 days, yellow crystals were deposited in the cooler arm which was filtered off, washed with water and air dried (0.241 g, yield: 73%), m.p. 300 °C. Anal. Calc. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{ZnI}_2$ (%): C, 31.86; H, 2.27; N, 5.31. Found (%): C, 32.11; H, 2.07; N, 5.35. FT-IR (cm^{-1}) selected bands observed were: 3427(b), 3052(w), 1621(w), 1589(w), 1503(s), 1425(w), 1371(w), 1150(w), 1028(w), 861(w), 780(w), 726(w), 548(w), and 433(w).

Synthesis of nano-structured $[\text{Zn}(\text{dmph})\text{I}_2]$ (**1**) by the sonochemical method

To prepare nano-sized $[\text{Zn}(\text{dmph})\text{I}_2]$ (**1**), a proper amount of the solution of zinc(II) acetate (10 ml, 0.1 M) and potassium iodide (20 ml, 0.1 M) in methanol was positioned in a high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 600 W. Then into this solution, a proper volume of neocuproine ligand solution (10 ml, 0.1 M) was added dropwise. After one hour, a white precipitate was formed. It was isolated by centrifugation (4000 rpm, 15 min), washed with water and acetone to remove residual impurities and finally dried in air (0.473 g, yield: 72%), m.p. 300 °C. Found (%): C, 32.74; H, 2.21; N, 5.05. FT-IR (cm^{-1}) selected bands observed were: 3421(b), 3051(w), 1622(w), 1589(w), 1503(s), 1427(s), 1371(w), 1150(w), 1027(w), 861(s), 780(w), 726(w), 548(w), and 439(w).

To study the effect of supercritical condition on stability, size and morphology of nano-structured compound **1**, 0.15 g of compound **1** obtained from sonochemical method along with 20 ml of water was transferred into a 50 ml Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 200 °C for 72 hour (Hydrothermal method). After cooling slowly to room temperature, white block shaped crystals of $[\text{Zn}(\text{dmph})\text{I}_2]$ (**1**) were collected and washed with water and acetone, and dried in air (yield: 0.114 g, 76%), m.p. 300 °C. Found (%): C, 32.28; H, 2.17; N, 5.31. FT-IR (cm^{-1}) selected bands observed were: 3424(b), 3053(w), 1619(w), 1589(w), 1501(s), 1426(s), 1369(w), 1150(w), 1028(w), 858(s), 780(w), 726(w), 547(w) and 440(w). Based on elemental analysis, FT-IR and melting point results, the nano-sized compound **1** were not decomposed, just the size

of particles decreased and also led to rod-like nanostructures morphology.

Synthesis of ZnO nanoparticles by thermal decomposition of compound 1

For preparation of zinc(II) oxide nanoparticles, degradation of the compound **1** obtained from sonochemical method was done at 600 °C with heating rate 5 °C/min under air atmosphere. After cooling, white precipitate was obtained. The powder XRD diffraction shows that degradation was completed and the entire organic compound was decomposed.

RESULTS AND DISCUSSION

The reaction of neocuproine as ligand with zinc(II) acetate and potassium iodide leads to formation of a Zn(II) coordination complex [Zn(dmph)₂] (**1**). Nanostructures of compound **1** were obtained in methanolic solution by ultrasonic irradiation at an ambient temperature and atmospheric pressure, while single crystals of

Table 1. FT-IR absorption peaks of neocuproine [35]

Peak (cm ⁻¹)	Assignments
3447 (w)	Free ν (N–H)
3064, 3036	Aromatic ν (C–H)
2990–2920	ν CH ₃
1671 (m), 1614 (m), 1591 (m), 1550 (w)	ν (C=C), ν (C=N)
1508 (m), 1494 (vm), 1423 (w)	
850, 732	out-of-plane CH in center ring

compound **1**, suitable for X-ray crystallography, were prepared by a heat gradient applied to a methanolic solution of the reagents (the “branched tube method”) (Scheme 1), and the structures were confirmed by FT-IR, elemental analysis and powder X-ray diffraction (XRD) patterns. Scheme 2 gives an overview of the methods used for the synthesis of compound **1** using the two different routes. This compound displayed distinct melting

Table 2. Crystal data and structure refinement for compound 1

Empirical formula	C ₁₄ H ₁₂ N ₂ I ₂ Zn
Formula weight	527.50
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	8.1114(7)
<i>b</i> (Å)	10.7727(8)
<i>c</i> (Å)	18.8627(15)
α (°)	90
β (°)	98.850(8)
γ (°)	90
Volume (Å ³)	1628.6(2)
<i>Z</i>	4
Density (calculated) (g/cm ³)	2.1512
Absorption coefficient (mm ⁻¹)	5.287
<i>F</i> (000)	984
Crystal size (mm ³)	0.04×0.11×0.54
Theta range for data collection (°)	3.6–34.25
Index ranges	-12 ≤ <i>h</i> ≤ 12; -17 ≤ <i>k</i> ≤ 16; -29 ≤ <i>l</i> ≤ 2
Reflections collected	6186
Independent reflections	1128
Absorption correction	Numerical
Refinement method	Full-matrix Least-squares on <i>F</i> ²
Parameters	173
Goodness-of-fit on <i>F</i> ²	1.39
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.036 <i>wR</i> ₂ = 0.0704
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.329 <i>wR</i> ₂ = 0.0954
$R_1 = \frac{\sum F_o - F_c }{\sum F_o }, wR_2 = \left[\frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2} \right]^{1/2}$	

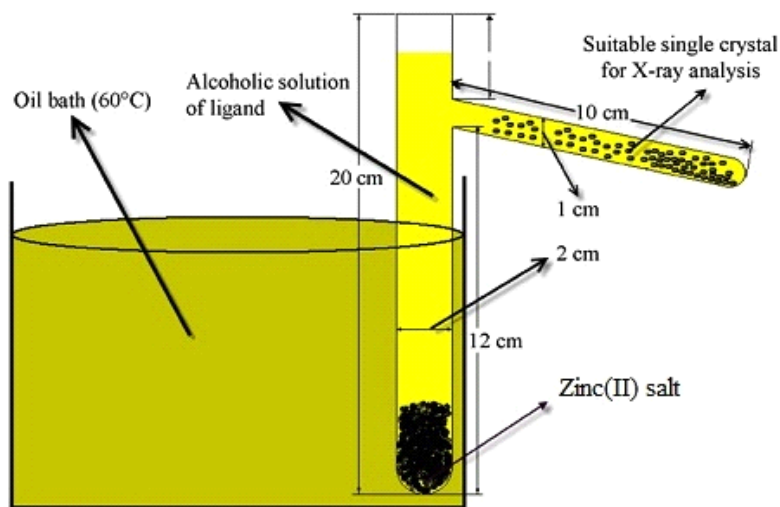
point and elemental analysis consistent with the formula $C_{14}H_{12}N_2ZnI_2$. The FT-IR spectra of the free neocuproine ligand, nanostructures produced by the sonochemical and hydrothermal methods, and of the bulk material produced by the branched tube method in the frequency range from 400-3500 cm^{-1} , are compared in Fig. 1. A comparison between FT-IR spectrum of free neocuproine ligand (Fig. 1a) and its Zn(II) nanostructures (Figs. 1b and 1c), obviously revealed that the ligand has been coordinated to Zn(II) ion, and new compound of **1** was formed. The elemental analysis and FT-IR spectra of nano-structured **1** prepared by the sonochemical and hydrothermal methods are similar to the data for the single crystalline material prepared by the branched tube method. The only difference among these characteristic peaks is either the peak intensity or a slight shift in the peak position. All distinct absorption peaks of ligand are exhibited in Table 1, and every absorption peak was assigned to corresponding vibration [35].

Fig. 2 shows the simulated XRD pattern from

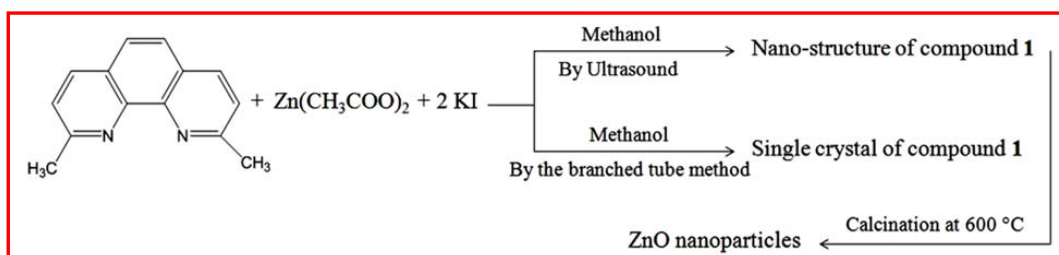
single crystal X-ray data (see below) of compound **1** (Fig. 2a) in comparison with the XRD pattern of the typical sample of compound **1** prepared by the sonochemical method (Fig. 2b) in the range $10^\circ < 2\theta < 50^\circ$. The XRD powder pattern of compound **1** could not be matched with the JCPDS cards due to the encapsulation of Zn(II) atoms with organic moiety. Acceptable matches, with slight differences in 2θ , were observed between the simulated and experimental powder X-ray diffraction patterns. This indicates that the compound obtained by the sonochemical method as nanoparticles is identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions. To estimate the particle size from the broadening of the XRD peaks the Scherrer formula is utilized.

$$d = \frac{(0.891 \lambda)}{\cos\theta_B \cdot [(B_{sample}^2 - B_{reference}^2)^{0.5}]} \quad (1)$$

In Eq. (1), λ , and θ_B are the wavelength of X-ray radiation, (1.5418 Å), the full-width



Scheme 1. Depiction of the branched tube for syntheses and isolation of single crystals of the zinc(II) coordination complex



Scheme 2. Materials produced and synthetic methods.

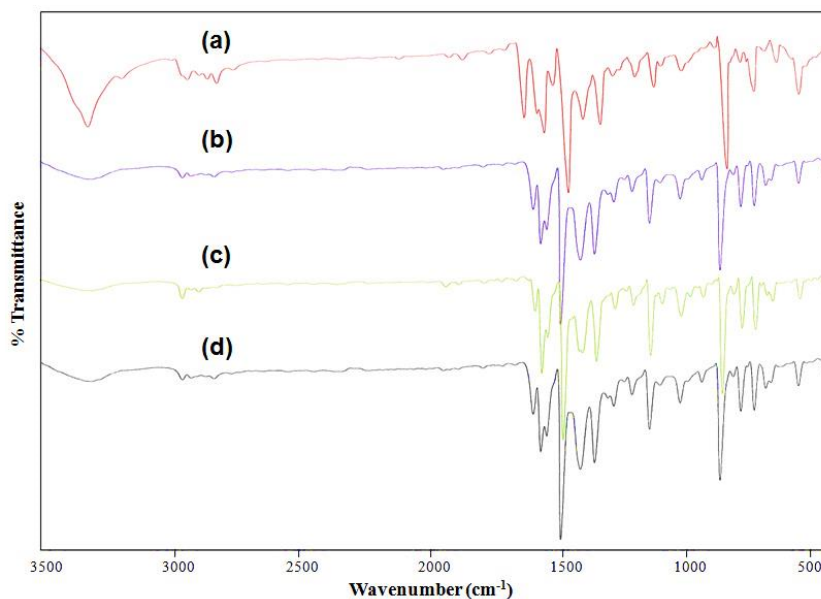


Fig. 1. FT-IR spectra of (a) neocuproine ligand, (b) nanoparticles of compound **1** prepared by sonochemical method, (c) hydrothermal method, and (d) bulk materials as synthesized of **1**.

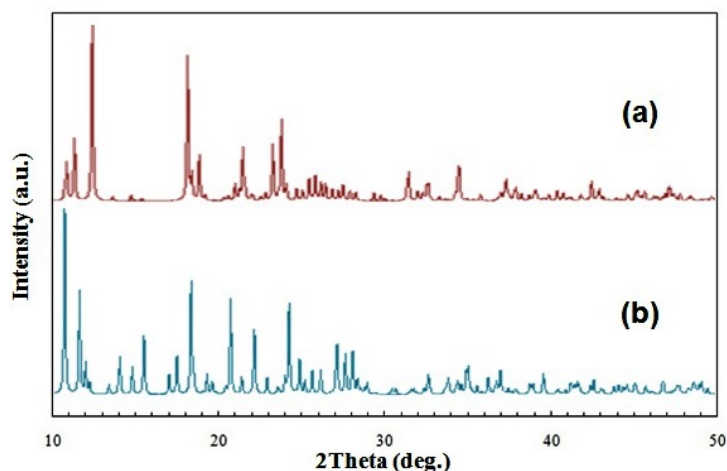


Fig. 2. XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, and (b) nanoparticles of compound **1** prepared by sonochemical method

at half-maximum, and the diffraction angle, respectively [36]. $B_{\text{reference}}$ (0.08) is the influence of the equipment to produce an incident X-ray which has to be subtracted to get the broadening effects due to the sample. The average particle size of the product was found to be around 85 nm, which was in agreement with the value obtained from the SEM image (Fig. 3a). The morphology of compound **1** prepared by the sonochemical and hydrothermal methods were characterized by scanning electron microscopy (SEM) and is shown in Fig. 3. The SEM image (Fig. 3a) shows that the

morphology of the compound **1** contains quasi-cubic shaped particles with a broad distribution. After hydrothermal treatment in an autoclave the compound **1** was not decomposed, just the size of particles decreased and also led to rod-like nanostructures morphology (Fig. 3b). In our previous work, we could obtain nanostructures of PbOHBr by thermal treatment method [32].

The structure of compound **1** was characterized by the single-crystal X-ray diffraction technique (Table 2). The molecular structure of the fundamental building unit for **1** is shown in

Fig. 4. In **1**, the Zn(II) ion is four-coordinated in a distorted tetrahedral configuration by two N atoms from a neocuproine ligand and two terminal I atoms. The structure of the bromine derivative **1** was reported previously [37]. The corresponding bond lengths (Å) and angles (°) around the Zn(II) center are listed in Table 3. The Zn—N bonds [average 2.109 Å] are somewhat shorter than the Zn—I distances [average 2.536 Å] and they are closed to such bond lengths found in other discrete 1,10-phenanthroline derivatives of zinc complexes [37-40]. In similar study on complex **1**, the Zn—N and Zn—I bond lengths are 2.058 and 2.55 Å, respectively [41]. The angle of two N atoms from phen ligand and Zn atom, N1—Zn1—N2, significantly is smaller than I1—Zn1—N2 and I2—Zn1—N1. The angles in title complex is also similar to that of found in other zinc complexes of 1,10-phenanthroline, regardless of geometry of the complex [35,41]. The packing of compound **1**, viewed approximately along b and c axes, is shown in Fig. 5. As shown in Fig. 5, the neocuproine acts as a bi-dentate ligand to join neighbouring zinc(II) centers to form a 3D neutral framework. This may be also an issue which needs to be investigated. The title complex crystallizes in the monoclinic system with $P2_1/c$ space group and four molecules per unit cell.

To examine the thermal stability of the nano-

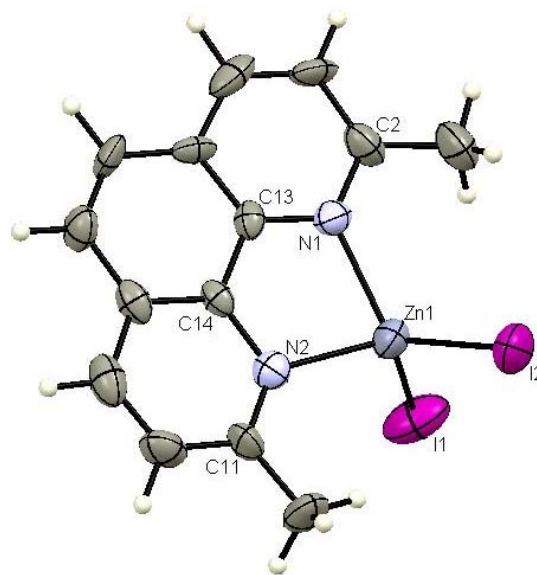


Fig. 4. Coordination environment of the $[Zn(dmph)I_2]$ (**1**) compound

sized compound **1** obtained from sonochemical method, thermogravimetric (TG) and differential thermal analyses (DTA) were carried out between room temperature and 600 °C under an argon flow (Fig. 6). During the heating process, TGA revealed that compound **1** is stable up to 140 °C at which temperature decomposition begins. The TG curve exhibits five distinct decomposition stages between

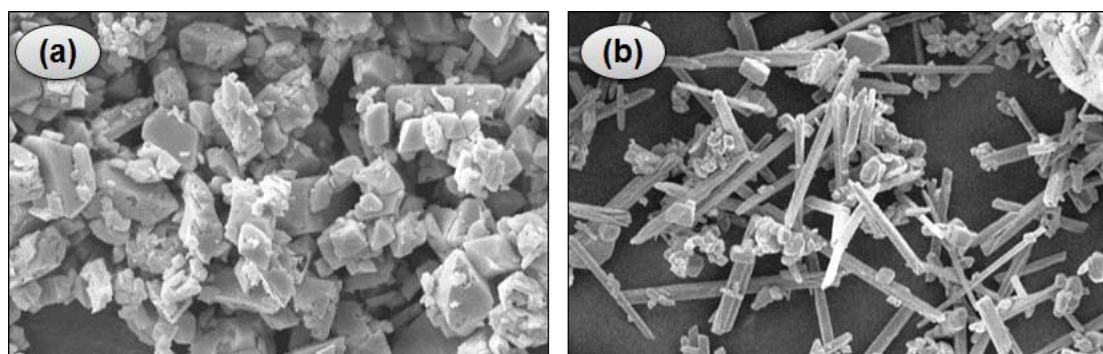


Fig. 3. SEM photographs of compound **1** nanoparticles prepared by (a) sonochemical method, and (b) hydrothermal method

Table 3. Selected bond lengths (Å) and angles (°) for compound **1**

Zn1—I1	2.538(1)	I1—Zn1—I2	113.82(4)	C2—N1—C13	119.7(6)
Zn1—I2	2.534(1)	I1—Zn1—N1	114.95(14)	Zn1—N2—C11	129.0(5)
Zn1—N1	2.121(6)	I1—Zn1—N2	110.66(15)	Zn1—N2—C14	108.8(4)
Zn1—N2	2.097(6)	I2—Zn1—N1	116.71(15)	C11—N2—C14	122.2(6)
N1—C2	1.360(1)	I2—Zn1—N2	114.65(16)		
N1—C13	1.368(9)	N1—Zn1—N2	82.2(2)		
N2—C11	1.287(10)	Zn1—N1—C2	129.5(5)		

140 °C to 290 °C may be ascribed to the removal of neocuproine ligand with a mass loss of 37.40 % (theoretically calculated as 39.4 %) and the mass loss between 290 °C to 550 °C is ascribed to removal of iodine atoms (observed: 49.40 %, calcd: 48.10

%). At higher temperatures, the decomposition of the compound occurs to ultimately give solid that appears to be ZnO (observed: 14.4 %, calcd: 15.5 %). Mass loss calculations of the end residue and the XRD pattern of the final decomposition

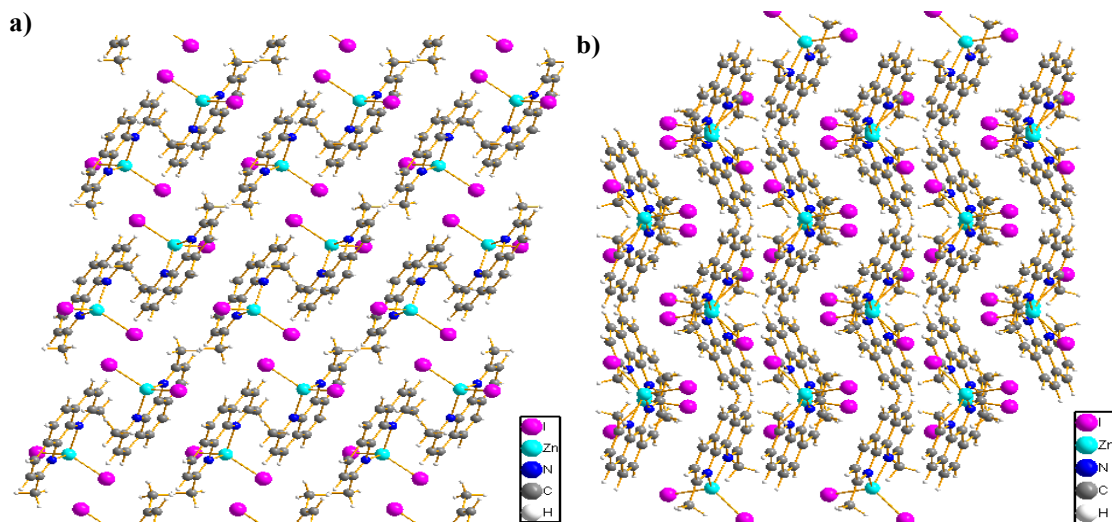


Fig. 5. A fragment of the 3D supramolecular compound 1, viewed along (a) the b direction, and (b) the c direction.

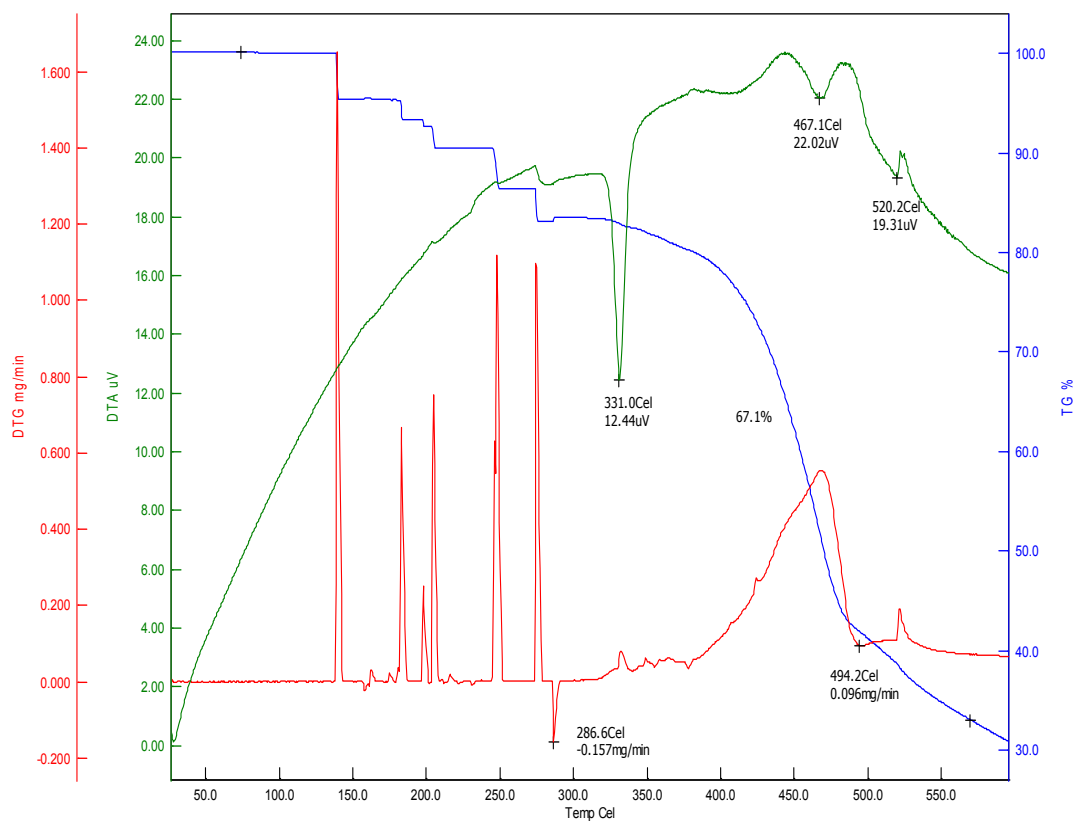


Fig. 6. Thermal behaviour of compound 1 nanoparticles prepared by sonochemical method

product (Fig. 7) show the formation of ZnO. The DTA curve of compound 1 indicates the decomposition of the compound takes place with three endothermic events at 331 °C, 467 °C, and 520 °C (Fig. 6).

To investigate the composition and phase information of the final calcination product, XRD was carried out. Fig. 7 provides the XRD pattern of zinc(II) oxide obtained from thermal decomposition of the compound 1 prepared from sonochemical method at 600 °C with heating rate 5 °C/min under air atmosphere. It can be seen that there are seven peaks corresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201), crystal planes, which matches to the hexagonal phase of ZnO named zincite (JCPDS card no. 36-1451, $a = 3.2498 \text{ \AA}$, $c = 5.2066 \text{ \AA}$, S.G. = $P6_3mc$ (186), and $Z = 2$) as observed from the corresponding XRD pattern. Compared with the standard diffraction

pattern, no peaks of impurities were detected, indicating high purity of the product. In addition, the intense and sharp diffraction peaks suggest the obtained product is crystalline. The broadening of the peaks indicated that the particles were at the nanometer scale, which is in agreement with that observed from SEM images (Figs. 8a and 8b). To estimate the particle size from the broadening of the XRD peaks the Scherrer formula is utilized, average particle size of the product was 31 nm. The evaluated particle sizes were reported in Table 4. These experiments indicate that the size of the coordination complex precursor correlates to the particle size of the formed ZnO nano-structures, and that the nano-sized precursor produces smaller particles of ZnO [43].

The morphology and size of the zinc(II) oxide nanoparticles were studied by SEM (Figs. 8a and 8b), which shows uniform nanometer scale quasi-spherical ZnO nanoparticles. They exhibited agglomerated particles with a homogeneous distribution. Agglomeration refers to adhesion of particles to each other because of *Van der Waals* forces of attraction, which is significantly higher in nanoparticles [42]. The size distribution histogram of ZnO nanoparticles (20-30 nm) is shown in Fig. 8c and indicates a relatively uniform distribution. For more characterization, EDAX was performed on the ZnO nanoparticles (Fig. 8d). The EDAX spectrum shows the presence of zinc as the only elementary component. This indicates that the product from direct calcination of compound 1 is pure ZnO nanoparticles.

Table 4. Evaluation of the size of ZnO nanoparticles by Scherrer equation

No.	nm
I	34.85
II	37.48
III	36.24
IV	28.93
V	25.69
VI	23.12
VII	38.92
VIII	26.70
X	26.20
Average	30.90

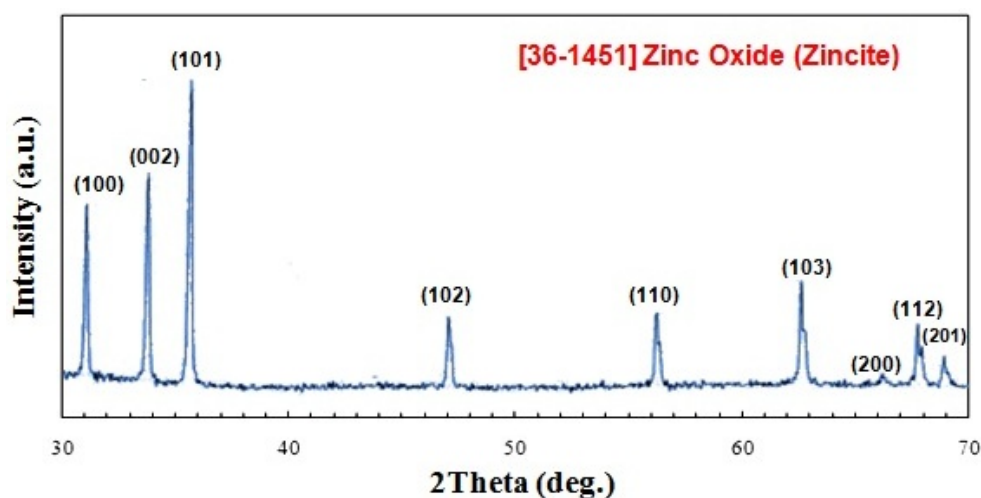


Fig. 7. XRD pattern of ZnO nanoparticles prepared by thermal decomposition of compound 1 at 600 °C

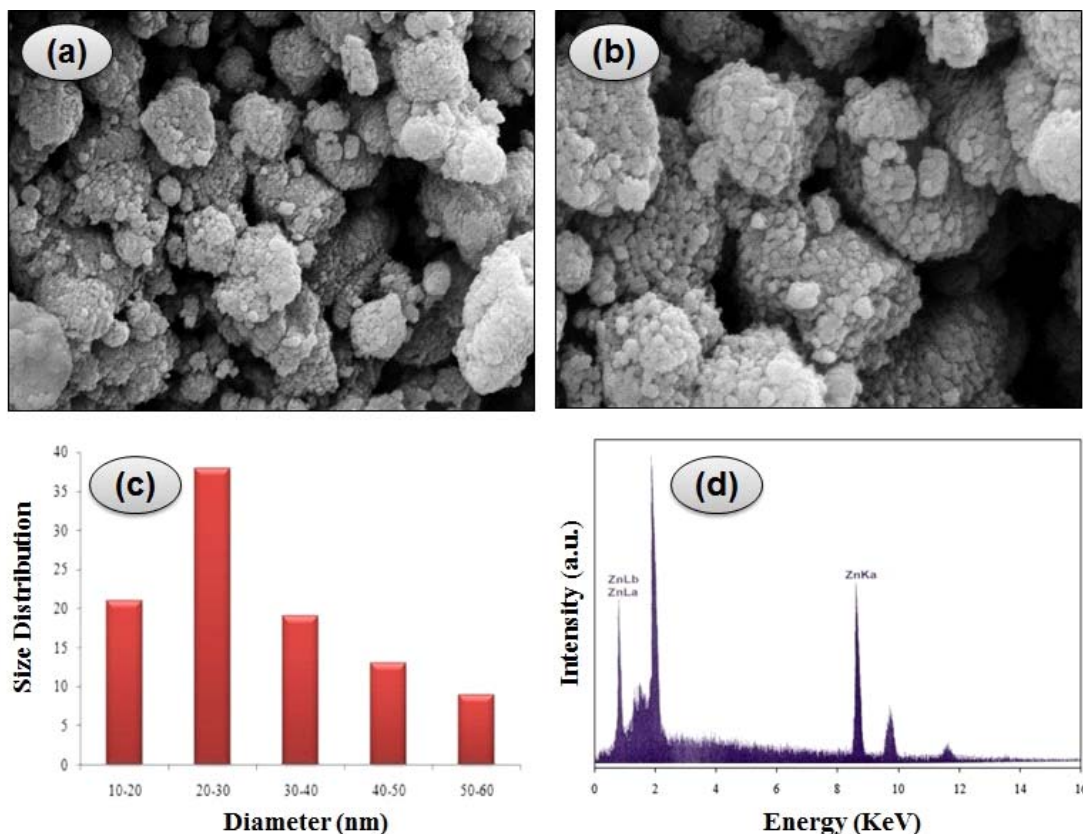


Fig. 8. (a,b) SEM photographs, (c) particle size distribution histogram, and (d) EDAX analysis of ZnO nanoparticles prepared by thermal decomposition of compound **1** at 600 °C.

CONCLUSION

In this study we have successfully demonstrated the synthesis of a nano-sized Zn(II) coordination complex, $[\text{Zn}(\text{C}_{14}\text{H}_{12}\text{N}_2)_2\text{I}_2]$ (**1**) using a thermal gradient approach and by sonochemical irradiation. Compound **1** has been found to be stable under hydrothermal treatment in an autoclave. Compound **1** was structurally characterized by single crystal X-ray diffraction. The crystal structure of compound **1** reveals that the Zn(II) ion is four-coordinated in a distorted tetrahedral configuration by two N atoms from a neocuproine ligand and two terminal I atoms. To proceed, compound **1** was decomposed at 600 °C under air atmosphere to produce ZnO nanoparticles and characterized by SEM, EDAX, and XRD techniques. The XRD pattern indicates that the well-crystallized zinc(II) oxide nanoparticles can be easily obtained under the current synthetic conditions. However, this method is fast and the product has a good separation with uniform nanometer scale particles. It does not need any additive, and yields smaller

particles. In overall, we can concluded that using nano-structured coordination complex can be appropriate precursors for production of nano-sized metal oxide materials with different and interesting morphologies. To the best of our knowledge, this is the first report on the synthesis of ZnO nanoparticles with this precursor.

Supplementary Material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-782684. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

ACKNOWLEDGMENTS

Authors are grateful to Iranian Research Organization for Science and Technology (IROST) and Islamic Azad University, Shahr-e Ray branch

and Nanotechnology Initiative Council for their unending effort to provide financial support to undertake this work.

CONFLICT OF INTERESTS

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

REFERENCES

- Hu M-L, Morsali A, Aboutorabi L. Lead(II) carboxylate supramolecular compounds: Coordination modes, structures and nano-structures aspects. *Coordination Chemistry Reviews*. 2011;255(23):2821-59.
- Safarifard V, Morsali A. Mechanochemical solid-state transformations from a 3D lead(ii) chloride triazole carboxylate coordination polymer to its bromide/thiocyanate analogs via anion-replacements: precursors for the preparation of lead(ii) chloride/bromide/sulfide nanoparticles. *CrystEngComm*. 2012;14(16):5130-2.
- Akhbari K, Morsali A. Thallium(I) supramolecular compounds: Structural and properties consideration. *Coordination Chemistry Reviews*. 2010;254(17):1977-2006.
- Robin AY, Fromm KM. Coordination polymer networks with O- and N-donors: What they are, why and how they are made. *Coordination Chemistry Reviews*. 2006;250(15):2127-57.
- Safarifard V, Morsali A. Sonochemical syntheses of nano lead(II) iodide triazole carboxylate coordination polymer: Precursor for facile fabrication of lead(II) oxide/iodide nano-structures. *Inorganica Chimica Acta*. 2013;398:151-7.
- Shinde VR, Gujar TP, Lokhande CD. LPG sensing properties of ZnO films prepared by spray pyrolysis method: Effect of molarity of precursor solution. *Sensors and Actuators B: Chemical*. 2007;120(2):551-9.
- Kunjara Na Ayudhya S, Tonto P, Mekasuwandumrong O, Pavarajarn V, Praserttham P. Solvothermal Synthesis of ZnO with Various Aspect Ratios Using Organic Solvents. *Crystal Growth & Design*. 2006;6(11):2446-50.
- Vafae M, Ghamsari MS. Preparation and characterization of ZnO nanoparticles by a novel sol-gel route. *Materials Letters*. 2007;61(14):3265-8.
- Kim Y-S, Tai W-P, Shu S-J. Effect of preheating temperature on structural and optical properties of ZnO thin films by sol-gel process. *Thin Solid Films*. 2005;491(1-2):153-60.
- Wu C, Qiao X, Chen J, Wang H, Tan F, Li S. A novel chemical route to prepare ZnO nanoparticles. *Materials Letters*. 2006;60(15):1828-32.
- Simeonidis K, Mourdikoudis S, Moulla M, Tsiaoussis I, Martinez-Boubeta C, Angelakeris M, et al. Controlled synthesis and phase characterization of Fe-based nanoparticles obtained by thermal decomposition. *Journal of Magnetism and Magnetic Materials*. 2007;316(2):e1-e4.
- Choi S-H, Kim E-G, Park J, An K, Lee N, Kim SC, et al. Large-Scale Synthesis of Hexagonal Pyramid-Shaped ZnO Nanocrystals from Thermolysis of Zn-Oleate Complex. *The Journal of Physical Chemistry B*. 2005;109(31):14792-4.
- Yadav RS, Mishra P, Pandey AC. Growth mechanism and optical property of ZnO nanoparticles synthesized by sonochemical method. *Ultrasonics Sonochemistry*. 2008;15(5):863-8.
- Liu CH, Zapien JA, Yao Y, Meng XM, Lee CS, Fan SS, et al. High-Density, Ordered Ultraviolet Light-Emitting ZnO Nanowire Arrays. *Advanced Materials*. 2003;15(10):838-41.
- Hui Z, Xiangyang M, Jin X, Junjie N, Deren Y. Arrays of ZnO nanowires fabricated by a simple chemical solution route. *Nanotechnology*. 2003;14(4):423.
- Ranjbar M, Mozaffari SA, Kouhestanian E, Salar Amoli H. Sonochemical synthesis and characterization of a Zn(II) supramolecule, bis(2,6 diaminopyridinium) bis(pyridine-2,6-dicarboxylato)zincate(II), as a novel precursor for the ZnO-based dye sensitizer solar cell. *Journal of Photochemistry and Photobiology A: Chemistry*. 2016;321:110-21.
- Karizi FZ, Safarifard V, Khani SK, Morsali A. Ultrasound-assisted synthesis of nano-structured 3D zinc(II) metal-organic polymer: Precursor for the fabrication of ZnO nano-structure. *Ultrasonics Sonochemistry*. 2015;23:238-45.
- Parast MSY, Morsali A. Synthesis and Characterization of New Zinc(II) Coordination Polymer with a Flexible Hetro-coordination Ligand via In Situ Reaction as a New Precursor for Zinc(II) Oxide Nano-sphere Particles. *Journal of Inorganic and Organometallic Polymers and Materials*. 2012;22(5):998-1002.
- Sammes PG, Yahioğlu G. 1,10-Phenanthroline: a versatile ligand. *Chemical Society Reviews*. 1994;23(5):327-34.
- Keypour H, Dehghani-Firouzabadi AA, Khavasi HR. Synthesis and characterization of three novel manganese(II) octaaza macrocyclic Schiff base complexes containing a phenanthroline and two pyridyl units as pendant arms. X-ray crystal structure determination of one manganese(II) complex. *Polyhedron*. 2009;28(8):1546-50.
- Amani V, Safari N, Khavasi HR, Mirzaei P. Iron(III) mixed-ligand complexes: Synthesis, characterization and crystal structure determination of iron(III) hetero-ligand complexes containing 1,10-phenanthroline, 2,2'-bipyridine, chloride and dimethyl sulfoxide, [Fe(phen)Cl₃(DMSO)] and [Fe(bipy)Cl₃(DMSO)]. *Polyhedron*. 2007;26(17):4908-14.
- Alizadeh A, Sedighian H, Ghanbaripour R. An Approach to the Synthesis of 7-Amino-6-imino-9-phenyl-6H-benzo[c]chromene-8-carbonitrile Derivatives via a Three-Component Reaction under Ultrasonic Irradiation. *Helvetica Chimica Acta*. 2014;97(3):447-52.
- Suslick KS, Choe S-B. Sonochemical synthesis of amorphous iron. *Nature*. 1991;353(6343):414.
- Safarifard V, Morsali A. Sonochemical syntheses of a new fibrous-like nano-scale manganese(II) coordination supramolecular compound; precursor for the fabrication of octahedral-like Mn₃O₄ nano-structure. *Ultrasonics Sonochemistry*. 2014;21(1):253-61.
- Ranjbar M, Yousefi M. Synthesis and Characterization of Lanthanum Oxide Nanoparticles from Thermolysis of Nano-sized Lanthanum(III) Supramolecule as a Novel Precursor. *Journal of Inorganic and Organometallic Polymers and Materials*. 2014;24(3):652-5.
- Ranjbar M, Lahooti M, Yousefi M, Malekzadeh A. Sonochemical synthesis and characterization of nano-sized zirconium(IV) complex: new precursor for the preparation of pure monoclinic and tetragonal zirconia nanoparticles. *Journal of the Iranian Chemical Society*. 2014;11(5):1257-64.
- Ranjbar M, Nabitabar M, Çelik Ö, Yousefi M. Sonochemical synthesis and characterization of nanostructured copper(II)

- supramolecular compound as a precursor for the fabrication of pure-phase copper oxide nanoparticles. *Journal of the Iranian Chemical Society*. 2015;12(3):551-9.
28. Ranjbar M, Yousefi M, Lahooti M, Malekzadeh A. Preparation and characterization of tetragonal zirconium oxide nanocrystals from isophthalic acid-zirconium (IV) nanocomposite as a new precursor. *International Journal of Nanoscience and Nanotechnology*. 2012;8(4):191-6.
 29. Ranjbar M, Yousefi M. Sonochemical Synthesis and Characterization of a Nano-Sized Lead (II) Coordination Polymer; A New Precursor for the Preparation of PbO Nanoparticles. *International Journal of Nanoscience and Nanotechnology*. 2016;12(2):109-18.
 30. Ranjbar M, Yousefi M, Nozari R, Sheshmani S. Synthesis and characterization of cadmium-thioacetamide nanocomposites using a facile sonochemical approach: A precursor for producing Cds nanoparticles via thermal decomposition. *International Journal of Nanoscience and Nanotechnology*. 2013;9(4):203-12.
 31. Ranjbar M, Yousefi M. Facile Preparation of Zirconia Nanostructures by New Method: Nano-Scale Zirconium(IV) Coordination Supramolecular Compound as Precursor. *Iranian Journal of Science and Technology, Transactions A: Science*. 2016:1-11.
 32. Copyright Cambridge Crystallographic Data Centre. p. 2001-5.
 33. Bruker AXS Inc. 2007 ed. USA2007.
 34. Sheldrick G. A short history of SHELX. *Acta Crystallographica Section A*. 2008;64(1):112-22.
 35. Viossat V, Lemoine P, Dayan E, Dung N-H, Viossat B. Synthesis, crystal structures and IR spectra of isotopic pseudopolymorphs complexes of Zn(II) by indole-2-carboxylic acid and 2,9-dimethyl-1,10-phenanthroline with different solvates (DMA, DMF or DMSO). *Journal of Molecular Structure*. 2005;741(1-3):45-52.
 36. Saadon R, Azeez OA. Chemical Route to Synthesis Hierarchical ZnO Thick Films for Sensor Application. *Energy Procedia*. 2014;50:445-53.
 37. Dehghani A, Amini MM, Najafi E, Tadjarodi A, Notash B. Dibromido(2,9-dimethyl-1,10-phenanthroline-[kappa]2N,N')zinc. *Acta Crystallographica Section E*. 2012;68(6):m811.
 38. Ahmadi R, Kalateh K, Ebadi A, Amani V, Khavasi HR. Dichlorido(6-methyl-2,2'-bipyridine-[kappa]2N,N') zinc(II). *Acta Crystallographica Section E*. 2008;64(10):m1266.
 39. Alizadeh R, Khoshtarkib Z, Chegeni K, Ebadi A, Amani V. Dibromido(6,6'-dimethyl-2,2'-bipyridine-[kappa]2N,N')zinc(II). *Acta Crystallographica Section E*. 2009;65(11):m1311.
 40. Alizadeh R, Kalateh K, Ebadi A, Ahmadi R, Amani V. Dichlorido(6,6'-dimethyl-2,2'-bipyridine-[kappa]2N,N')zinc(II). *Acta Crystallographica Section E*. 2009;65(10):m1250.
 41. Alizadeh R, Kalateh K, Khoshtarkib Z, Ahmadi R, Amani V. (6,6'-Dimethyl-2,2'-bipyridine-[kappa]2N,N') diiodidozinc(II). *Acta Crystallographica Section E*. 2009;65(11):m1439-m40.
 42. Edelstein AS, Cammaratra R. *Nanomaterials: synthesis, properties and applications*: CRC Press; 1998.