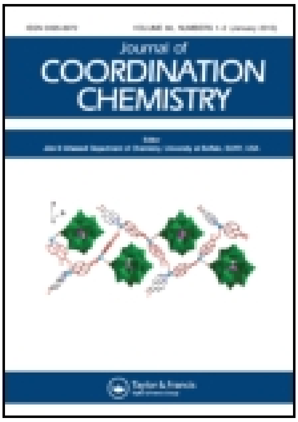
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:52
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and structural characterization of zinc(II) coordination compounds with pyterpy; new precursors for preparation of zinc(II) oxide nano-particles with different morphologies

Azadeh Mehrani [a] , Ali Morsali [a] & Parisa Ebrahimpour [b]
[a] Faculty of Sciences, Department of Chemistry , Tarbiat Modares University , Tehran , Iran
[b] School of Chemistry, University of Bristol , Bristol , UK

Accepted author version posted online: 16 Jan 2013.Published online: 15 Mar 2013.

To cite this article: Azadeh Mehrani , Ali Morsali & Parisa Ebrahimpour (2013) Synthesis and structural characterization of zinc(II) coordination compounds with pyterpy; new precursors for preparation of zinc(II) oxide nano-particles with different morphologies, Journal of Coordination Chemistry, 66:5, 856-867, DOI: 10.1080/00958972.2013.766334

To link to this article: http://dx.doi.org/10.1080/00958972.2013.766334

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

Journal of Coordination Chemistry
Vol. 66, No. 5, 10 March 2013, 856–867

Taylor & Francis
Taylor & Francis Group

Synthesis and structural characterization of zinc(II) coordination compounds with pyterpy; new precursors for preparation of zinc(II) oxide nano-particles with different morphologies

AZADEH MEHRANI†, ALI MORSALI*† and PARISA EBRAHIMPOUR‡

†Faculty of Sciences, Department of Chemistry, Tarbiat Modares University, Tehran, Iran
‡School of Chemistry, University of Bristol, Bristol, UK

(*Received 23 July 2012; in final form 5 November 2012*)

4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) was used as a ligand for preparing three zinc(II) coordination polymers, [Zn(pyterpy)(OAc)]ClO_4 (**1**), [Zn(pyterpy)I_2] (**2**), and [Zn$(pyterpy)_2$] $(ClO_4)_2\cdot(H_2O)_{2.9}$ (**3**). The two first coordination polymers were synthesized by slow evaporation while the last was prepared through hydrothermal method; all were characterized by IR spectroscopy and elemental analysis. The structures of **1–3** were determined by single-crystal X-ray diffraction. Pure phase ZnO nanoparticles with different sizes and morphologies were obtained by direct calcination of **1–3** and characterized by X-ray powder diffraction pattern and scanning electron microscopy.

Keywords: Coordination polymers; Nanoparticle; 4′-(4-pyridyl)-2; 2′ : 6′; 2″-terpyridine; Zinc(II); Crystal structure; ZnO

1. Introduction

Coordination polymers consist of metal ions and organic ligands as elementary units which lead to formation of infinite structures via coordination bonds and weak chemical bonds [1–3]. These compounds have attracted attention as they represent specific properties and reactivities not found in mononuclear compounds [4, 5]. Design and preparation of coordination polymers has become an exciting interface between synthetic chemistry and materials science [6].

Preparation of nano-materials is important because physical and chemical properties depend on particle size [7–9]. Self-assembly of molecular building blocks into targeted nanoscale architectures at interfaces represents a goal of supramolecular chemistry and materials science, with potential applications of these systems in nanotechnology [6, 10].

ZnO is a semiconductor with a wide direct band gap (3.37 eV) and a large exciton binding energy of 60 meV at room temperature [11]. Common usage of this compound is as

---

*Corresponding author. Email: morsali_a@modares.ac.ir

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2013.766334

gas and chemical sensor, catalyst, micro-lasers, in solar cells, luminescent and electrical devices, and memory arrays [12, 13].

Although there are many methods for preparation of nanoparticles including electrophoretic deposition, sol–gel process, vapor phase growth, homogeneous precipitation, and coordination polymers, the synthesis of different morphologies of ZnO nanoparticles is still demanding [14–19]. Herein, we report the synthesis of three new coordination polymers based on 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) and characterization of their structures by single crystal X-ray diffraction. These compounds are used as precursors for preparation of ZnO nanoparticles; calcinations of these compounds produce ZnO nanoparticles with different sizes and morphologies.

2. Experimental

2.1. *Materials and physical techniques*

All reagents were commercially available and used as received. Microanalyses were carried out using a Heraeus CHN–O–Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with monochromated CuK_α radiation ($\lambda = 1.54178$ Å). Crystallographic measurements were made using a BRUKER SMART 1000 CCD area-detector diffractometer equipped with graphite monochromated $Mo–K_\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 against all reflections. The molecular structure plots were prepared using ORTEPIII [20] and Mercury software [21]. The samples were characterized with a scanning electron microscope (SEM) with gold coating. Particles size distribution histogram has been drawn using the manual microstructure distance measurement program.

2.2. *Synthesis of zinc(II) complexes and preparation of their single crystals*

2.2.1. Synthesis of [Zn(pyterpy)(OAc)]ClO_4 (1) single crystals via slow evaporation. To synthesize **1**, 0.5 mmol (0.109 g) of zinc(II) acetate dihydrate and 1 mmol of $NaClO_4$ (0.122 g) were dissolved in 20 mL of dried methanol and this solution was added dropwise to 20 mL CH_2Cl_2 solution containing 0.5 mmol (0.156 g) of 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (figure 1). Yellow crystals were obtained by slow evaporation of this solution after 14 days. The crystals were washed with acetone and air dried. m.p.> 300 °C. Yield: 0.157 g (59%). IR (selected bands; in cm^{-1}): 411 (w), 511 (b), 622 (s), 655 (s), 670 (m), 735 (w), 800 (s), 837 (s), 1015 (s), 1100 (s), 1166 (s), 1335 (s), 1391 (s), 1415 (s), 1428 (s), 1479 (m), 1546 (m), 1614 (vs), 3085 (w). Anal. calc for $ZnC_{22}ClO_6H_{17}N_4$: C, 49.44; H, 3.21; N, 10.49%. Found: C, 48.72; H, 3.26; N, 10.31%.

2.2.2. Synthesis of Zn(pyterpy)I_2 (2) single crystals via slow evaporation. To synthesize **2**, 0.5 mmol (0.109 g) of zinc(II) acetate dihydrate and 1 mmol of potassium iodide (0.166 g) were dissolved in 20 mL of dried methanol and this solution was added to 20 mL CH_2Cl_2 solution containing 0.5 mmol (0.156 g) of pyterpy. Yellow crystals were obtained by slow evaporation after 10 days. The crystals were washed with methanol and air dried.

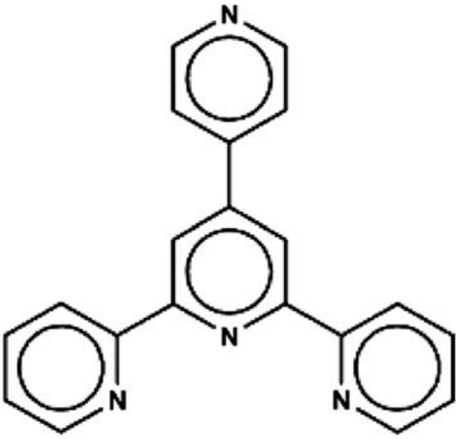


Figure 1. The structure of pyterpy.

Table 1. The crystal structural information for **1**, **2,** and **3**.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{22}H_{17}N_4O_2Zn{\cdot}ClO_4$	$C_{20}H_{14}I_2N_4Zn$	$C_{40}H_{28}N_8Zn$, 2(ClO_4), 2.9(H_2O)
Formula weight	534.24	629.54	937.19
Temperature (K)	100	100	100
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$
Unit cell dimensions	$a = 12.4679$ Å	$a = 11.9184$ Å	$a = 19.1778$ Å
	$b = 12.4866$ Å	$b = 14.5691$ Å	$b = 26.9773$ Å
	$c = 16.9743$ Å	$c = 11.9344$ Å	$c = 8.4954$ Å
	$\alpha = 90.00°$	$\alpha = 90.00°$	$\alpha = 90.00°$
	$\beta = 126.154°$	$\beta = 110.891°$	$\beta = 114.935°$
	$\gamma = 90.00°$	$\gamma = 90.00°$	$\gamma = 90.00°$
Volume	2133.72 $Å^3$	1936.06 $Å^3$	3985.53 $Å^3$
Z	4	4	4
Density (calculated)	1.663 $Mg\,m^{-3}$	1.562 $Mg\,m^{-3}$	1.552 $Mg\,m^{-3}$
Absorption coefficient	1.326 mm^{-1}	4.470 mm^{-1}	0.823 mm^{-1}
$F(0\,0\,0)$	1088	1192	1900.8
Theta range for data collection	2.02 to 27.68°	1.40 to 27.60°	1.39 to 27.51°
Index ranges	$-16<=h<=15$	$-15<=h<=15$	$-24<=h<=24$
	$-16<=k<=16$	$-18<=k<=19$	$-35<=k<=32$
	$-22<=l<=22$	$-15<=l<=15$	$-10<=l<=11$
Reflections collected	20,128	21,232	17,944
Independent reflections	3970 [R(int) = 0.0441]	3949 [R(int) = 0.0392]	4173 [R(int) = 0.0271]
Absorption correction	Multi-scan FS_ABSCOR (Rigaku, 2009)	Multi-scan FS_ABSCOR (Rigaku, 2009)	Multi-scan FS_ABSCOR (Rigaku, 2009)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4957/0/308	4504/0/245	4583/7/301
Goodness-of-fit on F^2	1.042	1.071	1.238
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0330$	$R1 = 0.0305$	$R1 = 0.0560$
	$wR2 = 0.0700$	$wR2 = 0.0754$	$wR2 = 0.1164$
R indices (all data)	$R1 = 0.0468$	$R1 = 0.0380$	$R1 = 0.0616$
	$wR2 = 0.0755$	$wR2 = 0.0796$	$wR2 = 0.1184$
Largest diff. peak and hole	0.510 and −0.431 e $Å^{-3}$	1.562 and −1.673 e $Å^{-3}$	0.625 and −0.802 e $Å^{-3}$

m.p.> 350 °C. Yield: 0.204 g (64%). Yield: 0.410 g (56%). IR (selected bands; in cm^{-1}): 505 (w), 628 (s), 796 (vs), 1007 (s), 1159 (m), 1247 (m), 1405 (vs), 1589 (vs), 3043 (m), 3429 (b). Anal. calc for $ZnC_{20}H_{14}N_4I_2$: C, 38.14; H, 2.24; N, 8.90%. Found: C, 37.82; H, 2.27; N, 8.75%.

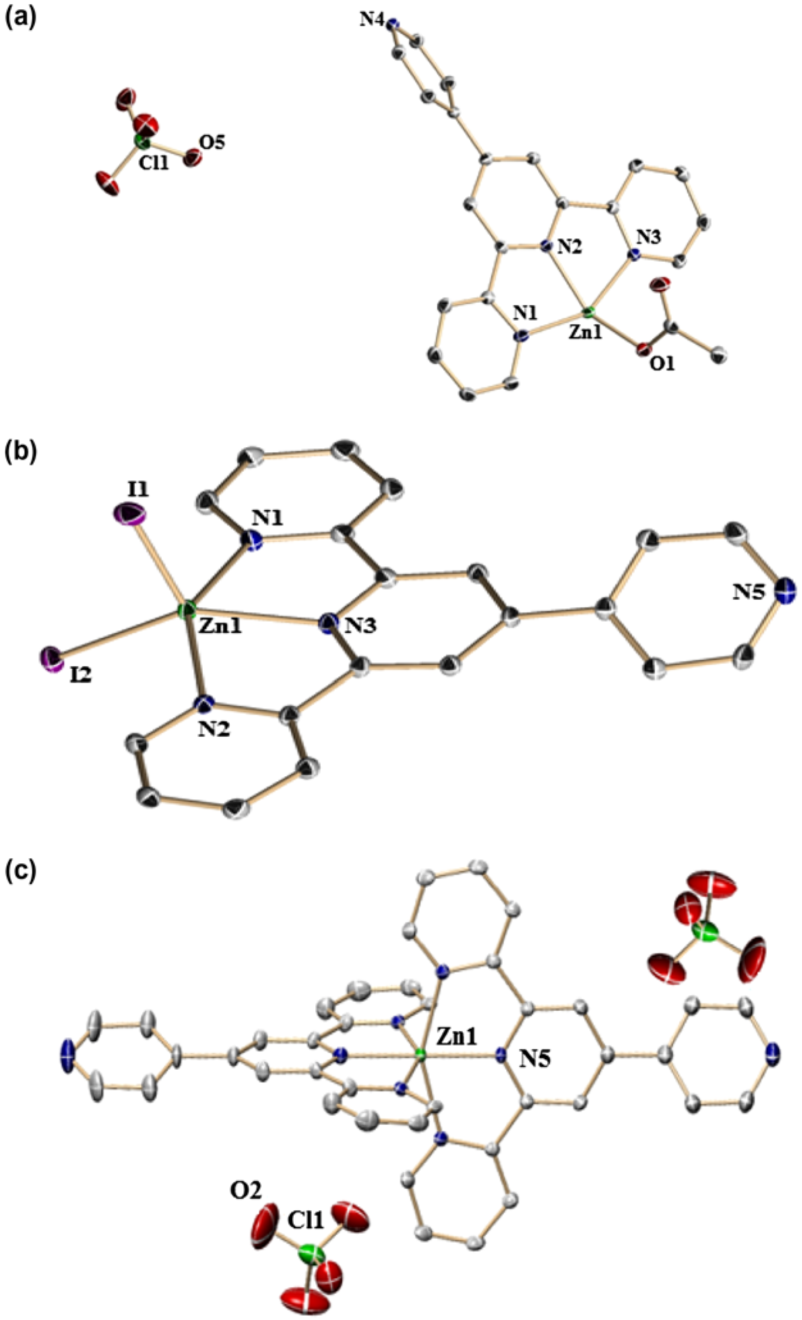


Figure 2. ORTEP representation of (a) **1**, (b) **2**, and (c) **3**.

2.2.3. Synthesis of Zn(pyterpy)$_2$](ClO$_4$)$_2$·(H$_2$O)$_{2.9}$ (3) single crystals via hydrothermal method. Single crystals of **3** were prepared by adding 0.5 mmol (0.149 g) of zinc nitrate hexahydrate, 1 mmol of sodium perchlorate (0.122 g) and 0.5 mmol (0.156 g) of pyterpy to 20 mL of distilled water. This mixture was transferred to a hydrothermal bomb and placed at 150 °C for 48 h. The yellow crystals were obtained by cooling the bomb to room temperature for 12 h. The crystals were washed with methanol and air dried. m.p. > 300 °C. Yield: 0.343 g (73%). IR (selected bands; in cm^{-1}): 623 (m), 791 (m), 1089 (vs), 1412 (m), 1472 (m), 1599 (m), 3449 (b). Anal. calc for $ZnC_{40}H_{34}N_8Cl_2O_{11}$: C, 51.14; H, 3.65; N, 11.94%. Found; C, 50.82; H, 3.68; N, 11.92%.

2.3. *Synthesis of ZnO nano-particles*

ZnO nano-particles were synthesized by thermolysis of **1–3** under air. Each complex (1.0 g) was heated to 400, 450, and 500 °C for 4 h. The resulting precipitates were dispersed in ethanol and nanoparticles were separated by centrifugation. As IR spectra show thermolyses of **1** and **2** have no impurities at 400 °C, the thermolysis temperature was selected as 400 °C. For **3** 450 °C was selected as the resulting ZnO has impurities at 400 °C. Formation of ZnO nanoparticles was confirmed by IR spectroscopy, high angle XRD, and SEM micrographs.

3. Results and discussion

3.1. *Crystal data and refinement details*

The crystal structure of **1** consists of monoclinic units of [Zn(pyterpy)(OAc)]ClO$_4$ with $P2_1/c$ space group (table 1). According to X-ray data, Zn(II) is five coordinate with disordered trigonal–bipyramidal ZnN$_4$O configuration [figure 2(a)]. Three nitrogens from

Table 2. Selected bond lengths and angles for **1**, **2**, and **3**.

Compound **1**		Compound **2**		Compound **3**	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
N4–Zn1^{i}	2.0787(18)	I1–Zn1	2.6060(6)	Zn1–N2	2.081(4)
Zn1–O1	1.9450(15)	I2–Zn1	2.6022(5)	Zn1–N5	2.086(3)
Zn1–N2	2.0601(17)	N1–Zn1	2.112(3)	Zn1–N4^{i}	2.157(3)
Zn1–N4^{ii}	2.0787(18)	N2–Zn1	2.196(3)	Zn1–N4	2.157(3)
Zn1–N1	2.1610(19)	N3–Zn1	2.212(3)	Zn1–N1^{i}	2.196(3)
O1–Zn1–N2	140.32(7)	N1–Zn1–N2	74.24(12)	N2–Zn1–N5	180
O1–Zn1–N4^{ii}	91.60(7)	N1–Zn1–N3	73.94(12)	N2–Zn1–N4^{i}	104.69(7)
N2–Zn1–N4^{ii}	128.08(7)	N2–Zn1–N3	146.29(13)	N5–Zn1–N4^{i}	75.31(7)
O1–Zn1–N1	103.24(7)	N1–Zn1–I2	141.08(10)	N2–Zn1–N4	104.69(7)
N2–Zn1–N1	76.26(7)	N2–Zn1–I2	99.86(9)	N5–Zn1–N4	75.31(7)
N4^{ii}–Zn1–N1	94.62(7)	N3–Zn1–I2	97.87(9)	N4^{i}–Zn1–N4	150.63(14)
O1–Zn1–N3	99.02(7)	N1–Zn1–I1	108.52(10)	N2–Zn1–N1^{i}	75.42(7)
N2–Zn1–N3	75.68(7)	N2–Zn1–I1	97.09(9)	N5–Zn1–N1^{i}	104.58(7)
N1–Zn1–N3	151.91(7)	N3–Zn1–I1	103.24(10)	N4^{i}–Zn1–N1^{i}	92.89(10)
N4^{ii}–Zn1–N3	101.70(7)	I2–Zn1–I1	110.383(18)	N4–Zn1–N1^{i}	94.42(9)

Notes: Symmetry transformations used to generate equivalent atoms for compound 1: i: −1+x, 0.5−y, −0.5+z; ii: 1+x, 0.5−y, −0.5+z.

Symmetry transformations used to generate equivalent atoms for compound 3: i: −x, y, 1.5−z.

terpy head of one pyterpy and the other from pyridine of another ligand are chelated to Zn. Ligands bridge two Zn ions. Oxygen coordinated from acetate and each cationic

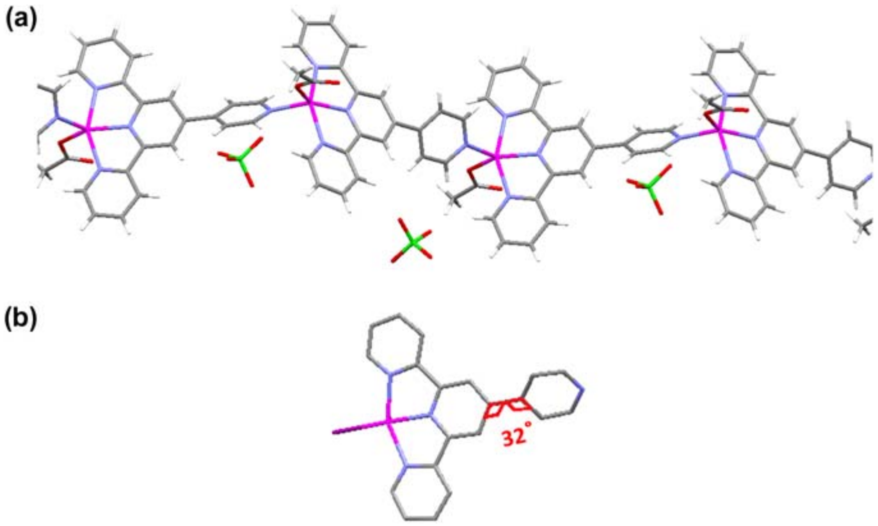


Figure 3. (a) Zigzag structure of **1**; (b) the angle difference between pyridine and terpyridine in **2**.

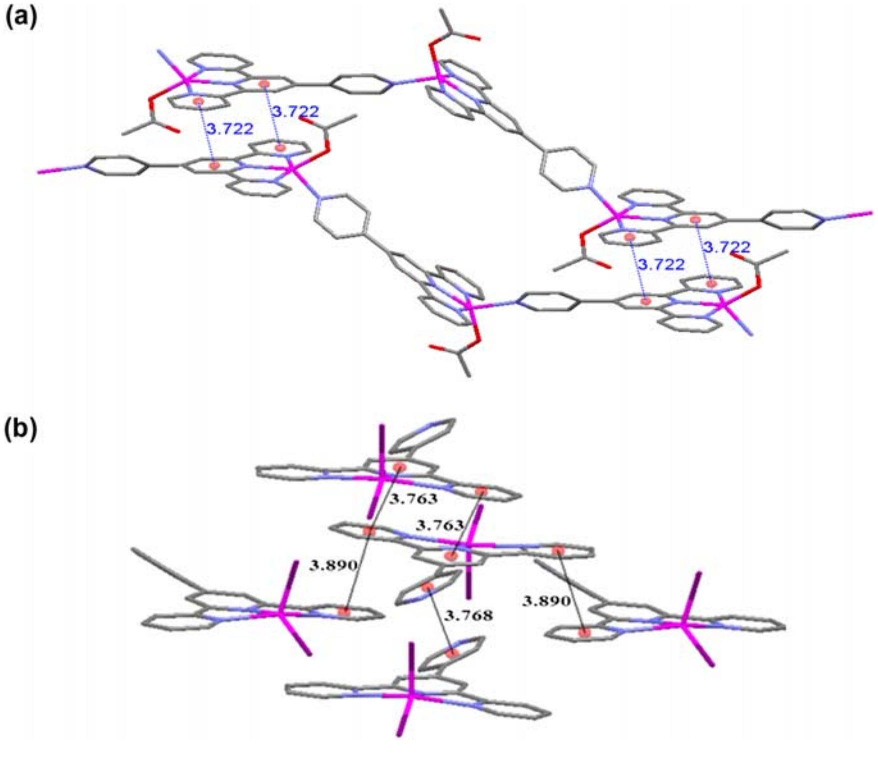


Figure 4. π–π interactions in (a) **1** and (b) **2**.

polymer contains CLO_4^- counter ions. Acetate is monodentate and pyterpy tetradentate. Zn–O and Zn–N bond lengths and angles are summarized in table 2.

Terpyrine and pyridine [figure 3(a)] have 42° angle difference and zigzag structure formed. This chain forms a 1-D coordination structure which turns to 2-D by π–π interactions with two pyridine rings of a terpyridine interacting between chains and recurs alternately [figure 4(a)]. The packing of **1** can be seen in figure 5(a).

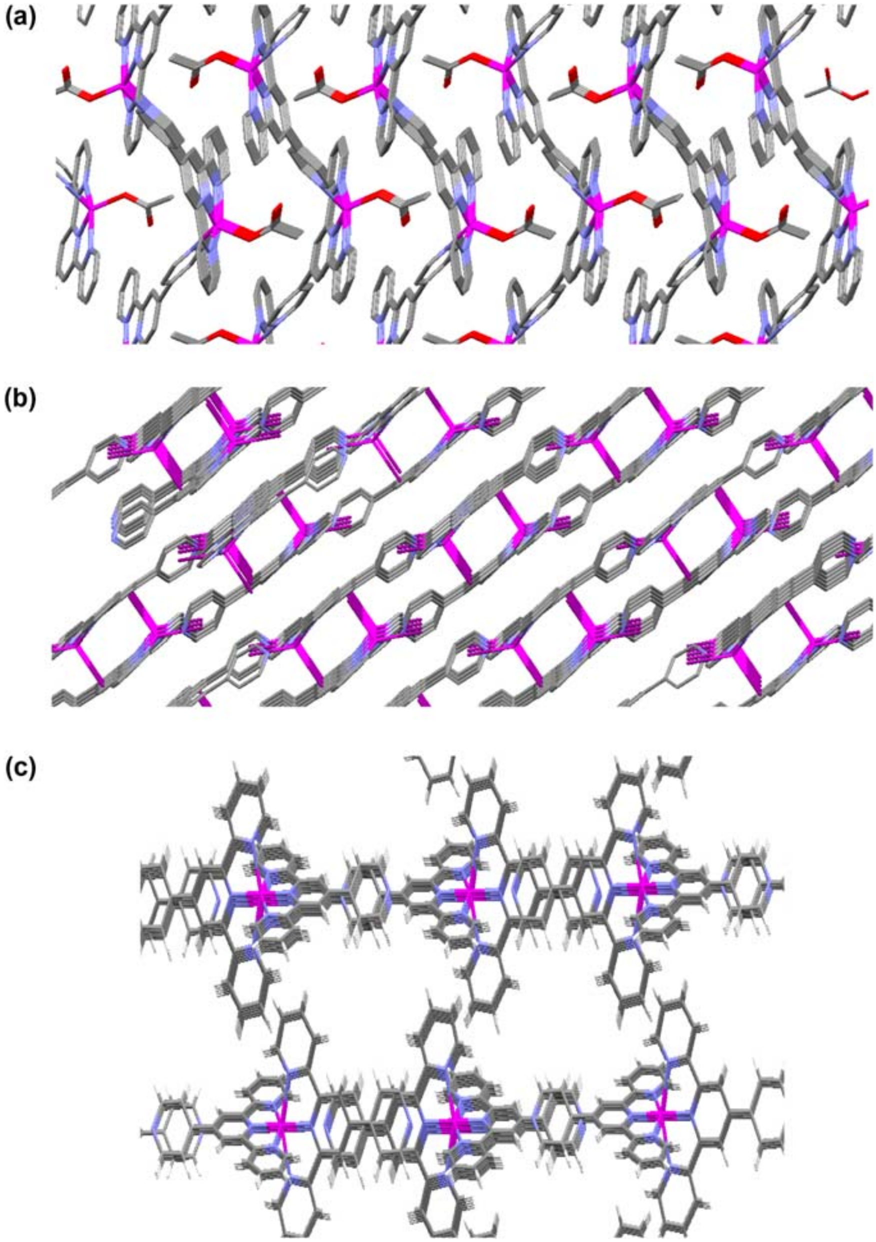


Figure 5. The packing of (a) **1**, (b) **2**, and (c) **3**.

Single crystal X-ray diffraction analysis of **2** showed that this compound consists of monoclinic units of [Zn(pyterpy)I_2] with $P2_1/n$ space group (table 1). Zn(II) has coordination number five with distorted square-pyramidal ZnN_3I_2 coordination [figure 2(b)]. Three nitrogens from terpy of pyterpy and two I^- coordinated Zn(II). Zn–I and Zn–N bond lengths and angles are summarized in table 2. Terpyridine and pyridine have approximately 30° angle difference [figure 3(b)]. As nitrogens of pyridine of pyterpy have no interactions

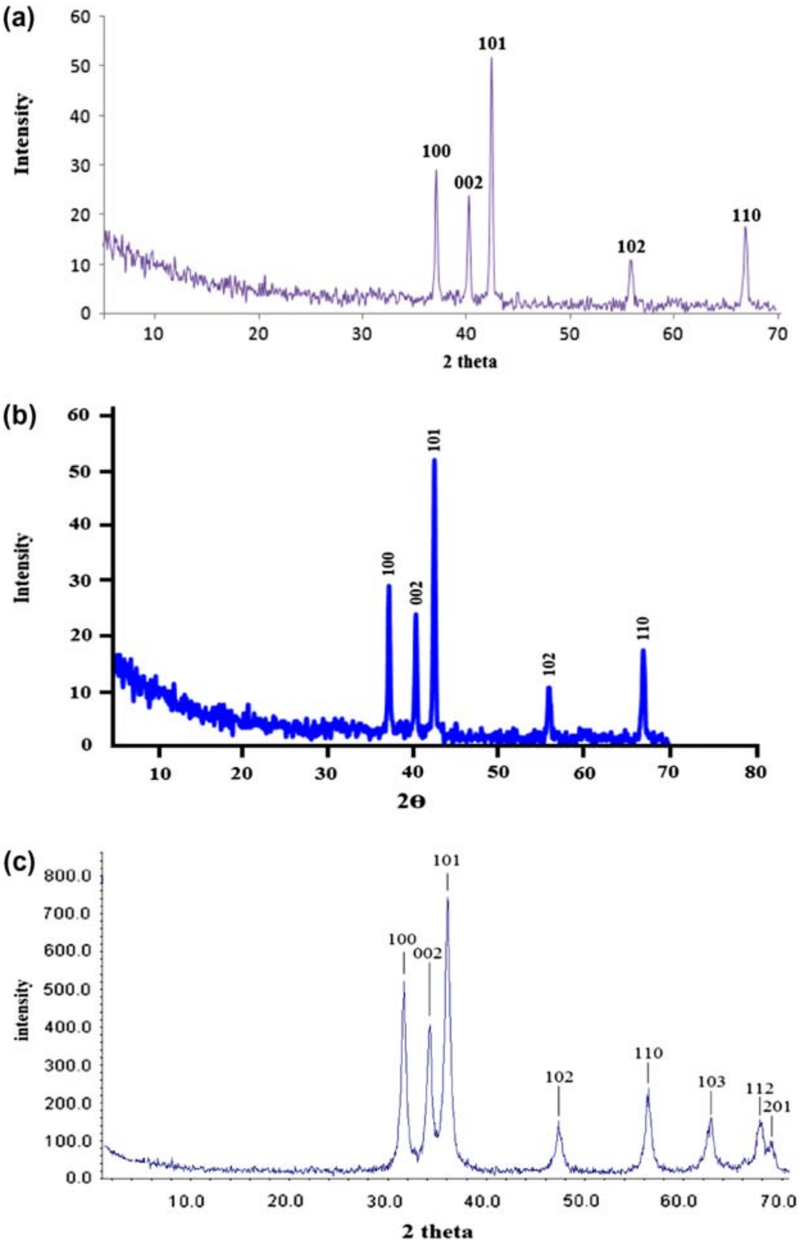


Figure 6. XRD pattern of ZNO nanoparticles obtained by thermolyses of (a) **1**, (b) **2**, and (c) **3**.

with zinc(II), the complex is not a coordination polymer. Secondary interactions of monomers just include π–π interactions (there is no H-bond interaction), leading to formation of supramolecular compound. These π–π interactions have two different lengths [figure 4(b)]. Figure 5(b) represents the packing of **2**.

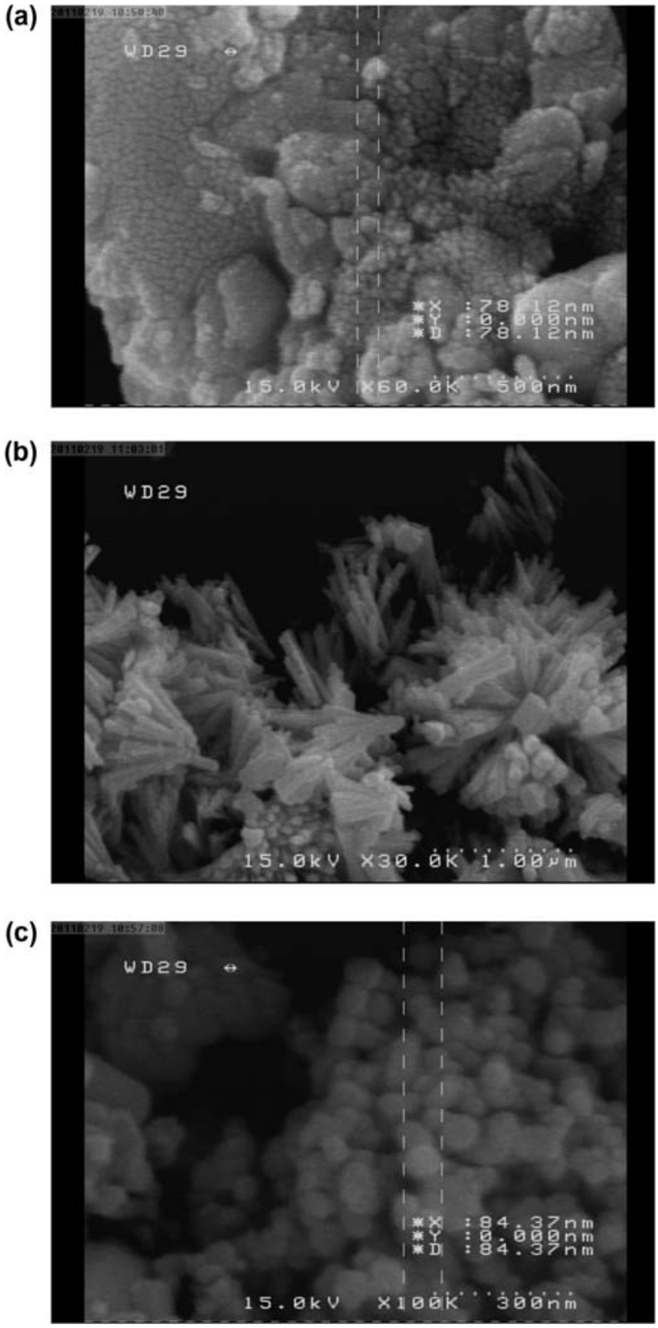


Figure 7. SEM micrograph of ZnO nanoparticles obtained by thermolyses of (a) **1**, (b) **2** and (c) **3**.

Single crystal X-ray diffraction analysis of **3** shows that this compound consists of monoclinic units of [Zn(pyterpy)$_2$(ClO$_4$)$_2$]·(H$_2$O)$_{2.9}$ which has *C*2/*c* space group (table 1). Determination of the structure of **3** by X-ray crystallography showed that Zn has coordination number six with distorted octahedral ZnN$_6$ coordination [figure 2(c)]. The structure is homoleptic and two ligands are coordinated to Zn(II). Three nitrogens from each terpy of pyterpy are coordinated to Zn(II). As py of pyridine of pyterpy has no interaction with any zinc(II), the complex is not a coordination polymer. Secondary interactions lead to formation of supramolecular compound [figure 5(c)]. Perchlorates are counter-ions and the

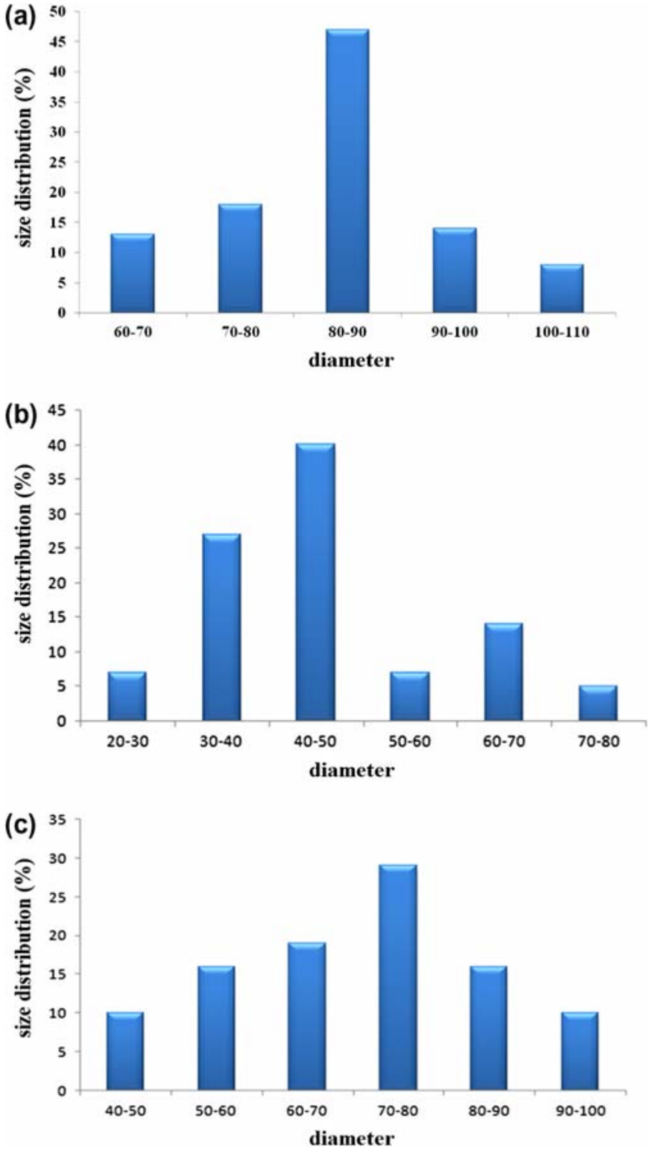


Figure 8. Particle size distribution of ZnO nanoparticles obtained by thermolyses of (a) **1**, (b) **2**, and (c) **3**.

H-bond between oxygen of perchlorate and hydrogen of water molecules trap water. The angle diversity between terpy and py is 21° to 35°.

3.2. *Characterization of ZnO nanoparticles*

ZnO nanoparticles, synthesized by thermolysis of these compounds, were characterized by IR spectroscopy, XRD pattern, and SEM micrograph. Figure 6 shows the XRD pattern of thermolysis products of these compounds. Acceptable matches with JCPDS file (36-1451), with slight differences in 2θ, show that the calcination products are single crystalline phase of ZnO hexagonal crystals with space group of $P6_3mc$ (186). In order to investigate the morphologies of these particles, the SEM micrographs of ZnO nanoparticles are recorded (figure 7). As the SEM micrographs show, calcination of **1** is agglomerated spherical nanoparticles with 80 nm diameter. Compound **2** calcination nanorods have a diameter of about 70–100 nm. Finally, calcination of **3** leads to formation of spherical nanoparticles of 50–60 nm diameter. For further investigation, size distribution histograms of ZnO nanoparticles have been prepared using the manual microstructure distance measurement program (figure 8). Compound **3** thermolysis has smaller nanoparticles.

4. Conclusion

Three Zn(II) coordination compounds have been synthesized and characterized by single crystal X-ray diffraction, IR spectroscopy, and elemental analysis. Thermolyses of these compounds lead to formation of ZnO nanoparticles with different sizes and morphologies. The ZnO nanoparticles were characterized by XRD and SEM. Size distributions of these nanoparticles have been obtained by the manual microstructure distance measurement program. This work confirms our previous work [22], with different coordination compounds producing different oxide sizes and morphologies. In our previous work, we used metal organic framework as a precursor for preparation of nanorod and nanospherical particles, while this work produced different shapes of nanorod and nanospherical particles using **1**, **2,** and **3**.

References

[1] R.C. Finn, J. Zubieta. *Inorg. Chem.*, **40**, 2466 (2001).
[2] A. Morsali, M.Y. Masoumi. *Coord. Chem. Rev.*, **253**, 1882 (2009).
[3] A.Y. Robin, K.M. Fromm. *Coord. Chem. Rev.*, **250**, 2127 (2006).
[4] J. Zhou, Y.Z. Yuan, X. Liu, D.Q. Li, Z. Zhou, Z.-F. Chen, K.-B. Yu. *J. Coord. Chem.*, **59**, 1477 (2006).
[5] K.L. Zhang, F. Zhou, H.Y. Gao, Z.C. Pan, J.G. Lin, R. Lin. *J. Coord. Chem.*, **61**, 1494 (2008).
[6] A. Askarinejad, A. Morsali. *Chem. Eng. J.*, **150**, 569 (2009).
[7] H. Sadeghzadeh, A. Morsali. *Polyhedron*, **29**, 925 (2010).
[8] M.J.S. Fard-Jahromi, A. Morsali. *Ultrason. Sonochem.*, **17**, 435 (2010).
[9] Z. Rashidi, A. Morsali. *J. Mol. Struct.*, **936**, 206 (2009).
[10] L. Hashemi, A. Morsali. *J. Inorg. Organomet. Polym. Mater.*, **20**, 856 (2010).
[11] M. Khanpour, A. Morsali, P. Retailleau. *Polyhedron*, **29**, 1520 (2010).
[12] F. Bigdeli, A. Morsali, P. Retailleau. *Polyhedron*, **29**, 801 (2010).
[13] F. Bigdeli, A. Morsali. *Mater. Lett.*, **64**, 4 (2010).
[14] F. Marandi, S. Chantrapromma, H.K. Fun. *J. Coord. Chem.*, **62**, 249 (2009).
[15] H.P. Xiao, J.G. Wang, A. Morsali, W.B. Zhang, X.H. Li. *J. Coord. Chem.*, **61**, 3703 (2008).
[16] F. Marandi, M. Ghorbanloo, A.A. Soudi. *J. Coord. Chem.*, **60**, 1557 (2007).

[17] H. Sadeghzadeh, A. Morsali. *J. Coord. Chem.*, **63**, 713 (2010).
[18] W. Cho, Y.H. Lee, H.J. Lee, M. Oh. *Angew. Chimi.*, **23**, 1720 (2011).
[19] S. Jung, W. Cho, H.J. Lee, M. Oh. *Angew. Chimi.*, **121**, 1487 (2009).
[20] L.J. Farrugia. *Ortep-3 for Windows. J. Appl. Cryst.*, **30**, 565 (1997).
[21] Mercury 1.4.1. *Copyright Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).
[22] K. Akhbari, A. Morsali. *J. Coord. Chem.*, **64**, 3521 (2011).