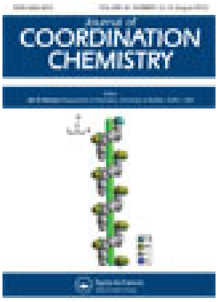


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Nanoparticles of a new zinc(II) coordination polymer: synthesis, characterization, thermal, and structural studies

Akram Hosseinian [a] , Sahand Jabbari [a] , Ali Reza Mahjoub [b] & Maryam Movahedi [c]

[a] Department of Engineering Science , College of Engineering, University of Tehran , P.O. Box 11365-4563, Tehran , Islamic Republic of Iran

[b] Department of Chemistry , Tarbiat Modares University , P.O. Box 14115-175, Tehran , Islamic Republic of Iran

[c] Department of Chemistry , Payame Noor Universtiy , PO Box 19395-3697, Tehran , Iran

Accepted author version posted online: 07 Jun 2012.Published online: 18 Jun 2012.

To cite this article: Akram Hosseinian , Sahand Jabbari , Ali Reza Mahjoub & Maryam Movahedi (2012) Nanoparticles of a new zinc(II) coordination polymer: synthesis, characterization, thermal, and structural studies, Journal of Coordination Chemistry, 65:15, 2623-2633, DOI: 10.1080/00958972.2012.700707

To link to this article: http://dx.doi.org/10.1080/00958972.2012.700707

Journal of Coordination Chemistry
Vol. 65, No. 15, 10 August 2012, 2623–2633

Nanoparticles of a new zinc(II) coordination polymer: synthesis, characterization, thermal, and structural studies

AKRAM HOSSEINIAN*†, SAHAND JABBARI†, ALI REZA MAHJOUB‡ and MARYAM MOVAHEDI§

†Department of Engineering Science, College of Engineering, University of Tehran, P.O. Box 11365-4563 Tehran, Islamic Republic of Iran
‡Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175 Tehran, Islamic Republic of Iran
§Department of Chemistry, Payame Noor Universtiy, PO Box 19395-3697 Tehran, Iran

(*Received 10 January 2012; in final form 3 April 2012*)

Nanoparticles of a Zn(II) coordination polymer {[Zn(DADMBTZ)($CH_3COO)_2]_n$, DADMBTZ = 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole} were synthesized by reaction of $Zn(NO_3)_2 \cdot 4H_2O$, CH_3COONH_4 and DADMBTZ by a sonochemical method. The nanoparticles were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. [Zn(DADMBTZ)($CH_3COO)_2]_n$ was structurally characterized by single-crystal X-ray diffraction. In this four-coordinate compound with nearly C_2 symmetry, DADMBTZ is bidentate. The metal lies in a pseudo-tetrahedral environment and is ligated by the two bithiazole ring nitrogen atoms and an oxygen from each of the two monodentate acetates; 2-D networks are formed *via* N–H···O hydrogen bonds. Thermal stability of [Zn(DADMBTZ)($CH_3COO)_2]_n$ was studied by thermal gravimetric and differential thermal analyses. A ZnO nanostructure was obtained by direct thermolyses at 500°C under air. The ZnO nanostructure was characterized by SEM, XRD, and FT-IR spectroscopy.

Keywords: Bithiazole; Nanoparticle; Coordination polymer; Zinc(II) oxide; Sonochemical; Thermal studies

1. Introduction

Design and preparation of coordination polymers has been widely studied as an important interface between synthetic chemistry and materials science. The syntheses of coordination polymers with different metal ions and ligands have led to a range of potential applications (e.g. molecular wires, electrical conductors, molecular magnets, in host–guest chemistry, and in catalysis) [1–10]. The d^{10} Zn^{2+} is associated with a flexible coordination environment so that geometries of these complexes can vary from tetrahedral to octahedral and severe distortions in the ideal polyhedra occur [11–20]. In contrast to inorganic nanomaterials, syntheses of nano-structured metal coordination polymers are sparse, and to date most investigations on coordination

---

*Corresponding author. Email: hoseinian@ut.ac.ir

ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.700707

polymers are only in the solid state and studies of their properties are limited to the macroscopic scale. As nanometer-scaled materials often exhibit size-dependent physical and chemical properties that cannot be observed in their bulk analogs, nano-sized coordination polymers are interesting candidates for applications in many fields, including catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing. Some recent studies about nano-scale coordination polymers were reported [21–28], but they are quite rare.

The development of metal oxide nanostructures has been pursued because of applications in catalysis, energy storage, magnetic data storage, sensors, and ferro fluids. ZnO has a band gap of 3.3 eV at room temperature with a free excision binding energy of 60 meV which is important among semiconductor materials for its unique properties, such as optical transparency, electric conductivity, piezoelectricity, and near-UV emission. ZnO nanostructures have wide-ranging applications in catalysis, photocatalysis, field effect transistors, resonators, short-wave optics, gas sensors, antibacterial agents, solar cell optoelectronic devices, and functional materials [29, 30].

Aromatic heterocyclic polymers containing bithiazole rings are good ligands because two nitrogen atoms in the bithiazole rings chelate metal ions to form stable five-membered rings [31, 32]. The use of bithiazole for preparing inorganic nano-structured coordination polymers has not been investigated thoroughly. This manuscript focuses on the simple preparation of a new nano-structured Zn(II) coordination polymer, $[Zn(DADMBTZ)(CH_3COO)_2]_n$, and its conversion into zinc(II) oxide nanostructure by calcination.

2. Experimental

With the exception of DADMBTZ, which was prepared by the procedure described previously [33], all reagents and solvents were commercially available and used as received. An ultrasonic bath (Tecna 6; 50–60 Hz and 138 W) was used for ultrasonic irradiation. ^{1}H NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer with ^{1}H chemical shifts determined relative to internal TMS. Infrared spectra were recorded on a Shimadzu IR-60 spectrometer from KBr pellets (4000–370 cm^{-1}). Electronic absorption spectra were recorded on a Shimadzu UV-Vis 2100 recording spectrophotometer. Microanalyses were carried out using a Heraeus CHN–O– rapid analyzer. An ultrasonic bath (Elmasonic; 50–60 Hz and 550 W) was used for ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The measurements were performed using a PL-STA 1500 Thermal/ Sciences in static air, with α-Al_2O_3 as the reference compound, at a heating rate of 5 K min^{-1}. In a ceramic crucible, 200 mg samples were contained. Melting point was measured on an Electrothermal 9100 apparatus. The samples were characterized with a scanning electron microscope with gold coating.

Crystallographic data of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ are given in table 1. X-ray diffraction measurements were performed at low temperature (120 K) using a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the φ–ω scan technique. Empirical absorption corrections were applied using SADABS. The structure was solved by direct methods and subsequent Fourier differences and refined with anisotropic displacement parameters.

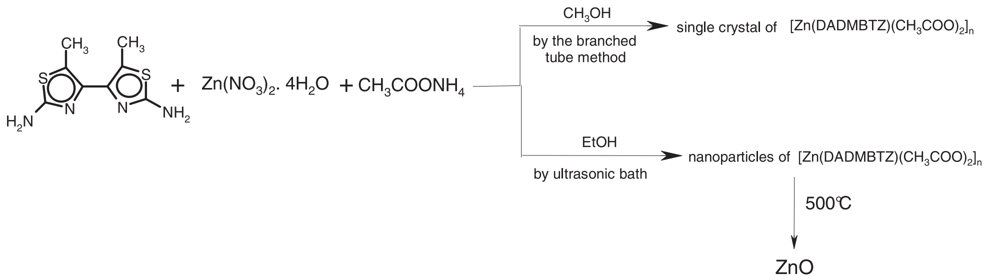
Table 1. Crystal data and structure refinement for $[Zn(DADMBTZ)(CH_3COO)_2]_n$.

Empirical formula	$C_{12}H_{16}N_4O_4S_2Zn$
Formula weight	409.78
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Fdd2*
Unit cell dimensions (Å, °)	
a	13.708(4)
b	26.301(7)
c	9.584(3)
α	90
β	90
γ	90
Volume (Å^3), Z	3455.7(16), 8
Calculated density ($Mg\,m^{-3}$)	1.575
Absorption coefficient (mm^{-1})	1.685
$F(000)$	1680
Crystal size (mm^3)	$0.45 \times 0.255 \times 0.20$
θ range for data collection (°)	3.10–28.04
Limiting indices	$-13 \le h \le 18$; $-29 \le k \le 34$; $-8 \le l \le 12$
Reflections collected	1098
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0275$, $wR_2 = 0.0711$
Completeness to θ (%)	98.9
Absorption correction	Psi-scan
Max. and min. transmission	0.7292 and 0.5176
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1098/1/105
Goodness-of-fit on F^2	1.020
R indices (all data)	$R_1 = 0.0307$, $wR_2 = 0.0716$
Largest difference peak and hole (e Å^{-3})	0.749 and −0.722

Hydrogen atoms attached to carbon and nitrogen were positioned geometrically, with U_{iso} values derived U_{eq} values of the corresponding carbon and nitrogen. The structure was refined with SHELXL-97 [34–36]. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company with monochromated Cu-Kα radiation. The crystallite sizes of selected samples were estimated using the Sherrer method. The molecular structure plots were prepared using ORTEP [37a] and simulated XRD powder pattern based on single crystal data was prepared with Mercury software [37b].

To prepare nanoparticles of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ a proper amount of solution of zinc(II) nitrate and ammonium acetate (0.1 M) in EtOH was placed in an ultrasonic bath, and into this solution, a proper volume of DADMBTZ solution (0.1 M) was added in drops. The resulting precipitate was filtered, subsequently washed with EtOH, and then dried. Found: C, 35.10; H, 3.85; N, 13.59. Calcd for $C_{12}H_{16}N_4O_4S_2Zn$ (409.78)(%): C, 35.14; H, 3.9; N, 13.67. IR data (KBr, cm^{-1}): 3285–3145 (s), 2950 (w), 1607 (s), 1514 (s), 1428 (w), 1380 (s), 1324 (vs), 1117 (w), 750 (w), 668 (w), 403 (w).

To isolate single crystals of $[Zn(DADMBTZ)(CH_3COO)_2]_n$, DADMBTZ (0.226 g, 1 mmol), zinc(II) nitrate (0.131 g, 0.5 mmol) and ammonium acetate (0.077 g, 1 mmol) were placed in main arm of the branched tube (Supplementary material). Methanol was carefully added to fill the arms, the tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 3 days, yellow crystals (d.p. 190°C), which had deposited in the cooler arm, were



Scheme 1. Materials produced and synthetic methods.

isolated, filtered off, washed with acetone and ether and air dried (yield 40%). Found: C, 35.20, H, 3.85, N, 13.59. Calcd for $C_{12}H_{16}N_4O_4S_2Zn$ (409.78)(%): C, 35.14, H, 3.9, N, 13.67.

IR data (KBr, cm^{-1}): 3285s–3145s ν(N–H), 2950w $\nu(C\text{–}H)_{al}$, 1607s ν(C=C)+ $\nu_{as}(COO^-)$, 1514s ν(C=N), 1428w and 1380s ν(skeletal vibration), 1324vs $\nu_s(COO^-)$, 1117w ν(C–S), 750w ν(C–S–C), 668w ν(C=S), 403w ν(Zn–N). ^{1}H-NMR ([D6]DMSO, 25°C, TMS) δ (ppm): 7.5 (4H, $2NH_2$), 2.2 (6H, $2CH_3$), and 1.7 (3H, CH_3). ^{13}C-NMR ([D6]DMSO, 25°C, TMS) δ (ppm): 177.3, 167.5, 138.7, 116.9, 23.0, and 12.5. UV-Vis in DMSO (λ_{max}, nm): 275.

The nano-scale compound was calcinated at 500°C under air for 1 h in an electric furnace alumina boat. The organic components were combusted and ZnO nanostructure was produced.

3. Results and discussion

Scheme 1 shows the reaction between zinc(II) nitrate, ammonium acetate, and DADMBTZ to form $[Zn(DADMBTZ)(CH_3COO)_2]_n$ in two different conditions. Figure 1(a) shows the simulated XRD pattern from single-crystal X-ray data of the above compound and figure 1(b) shows the XRD pattern of a typical sample of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ prepared by the sonochemical process. Acceptable matches, with slight difference in 2θ, were observed between the simulated from single-crystal X-ray data patterns (figure 1a) and those from the experimental powder X-ray diffraction patterns for nanoparticles as obtained from the sonochemical method (figure 1b), hence this compound is obtained as a mono-phase. Broadening of the peaks indicates that the particles are nanometer scale. Estimated from the Sherrer 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 [38].

The average size of the particles was 61 nm, in agreement with that observed from scanning electron microscopy (SEM) images. "Supplementary material" shows the SEM images of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ particles. The particle size ranged from 30 to 70 nm.

Differential thermal analyses (DTA) and thermogravimetric analysis (TGA) curves (Supplementary material) of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ recorded in static air from

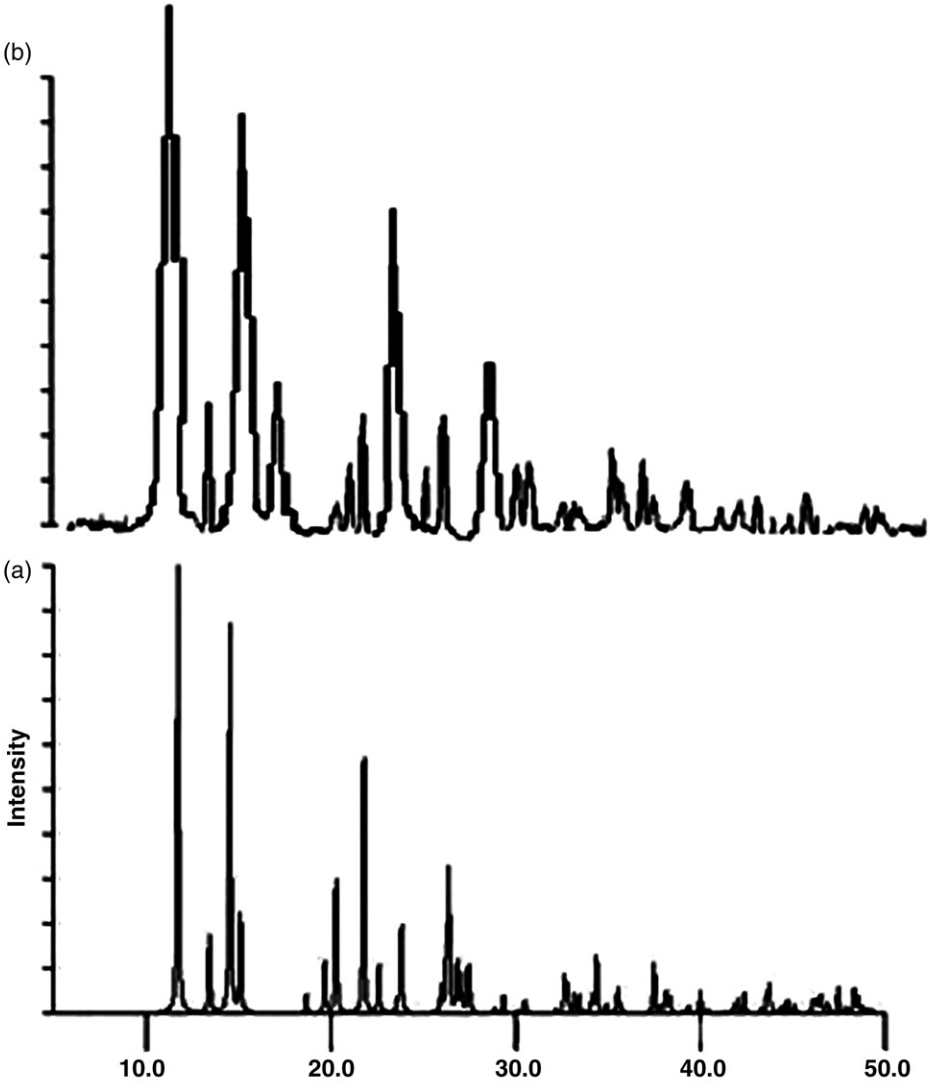


Figure 1. (a) Simulated XRD pattern from single-crystal X-ray data of $[Zn(DADMBTZ)(CH_3COO)_2]_n$; (b) The XRD pattern of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ nanoparticles.

ambient temperature to 700°C shows both crystalline and nanoparticles of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ are the same, the compound does not melt and is stable up to 168°C. Decomposition of acetate takes place at 309°C with an exothermic effect (observed 27%, Calcd 28.79%). The weight loss of 53% is equivalent to loss of two coordinated DADMBTZ (Calcd: 55.15%) with one exothermic effect at 584°C. The solid residue formed at 657°C is suggested to be ZnO (observed 20%, Calcd 19.86%).

Single X-ray crystal analysis reveals that $[Zn(DADMBTZ)(CH_3COO)_2]_n$ crystallizes in the orthorhombic space group Fdd2. The structure of [Zn(DADMBTZ)

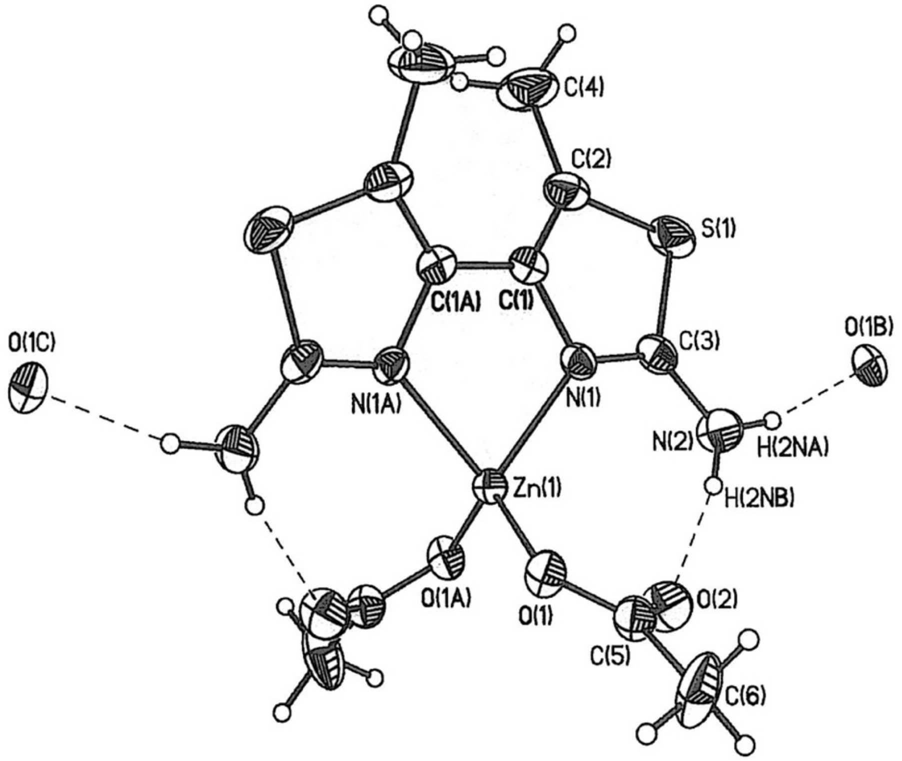


Figure 2. ORTEP drawing of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

$(CH_3COO)_2]_n$ is shown in figure 2 and important bond lengths and angles are given in table 2. In $[Zn(DADMBTZ)(CH_3COO)_2]_n$, zinc is four-coordinate in a distorted tetrahedral arrangement, bonded to two nitrogen atoms of DADMBTZ (N(1) and N(1A)) and to the two acetates *via* single oxygen atoms. The nitrogen atoms of NH_2 of the ligands are not coordinated. The metal coordination shows some deviations from ideal T_d symmetry. The angles around Zn are 81.84(2)° (for the internal angle N(1)–Zn(1)–N(1A)) and 118.58(2)° (for the O(1)–Zn(1)–O(1A) angles). Two Zn–N bond distances (Zn(1)–N(1) and Zn(1)–N(1A) = 2.05 Å) are equal and two Zn–O bond distances (Zn(1)–O(1) and Zn(1)–O(1A) = 1.954(2) Å), too. DADMBTZ is bidentate with five-membered chelate rings having internal angle 81.84(2)° and two monodentate acetates occupy the other positions.

The structure is stabilized by a network of intra and intermolecular hydrogen bonds involving oxygen of carboxylate and the terminal amino. Intramolecular interaction exists between hydrogen of NH_2 (H(2NB)) and uncoordinated oxygen of acetate. Intermolecular hydrogen bonding is observed between the other hydrogen of NH_2 H(2 NA) and oxygen of COO^- of the neighboring molecule (table 3; figures 2 and 3). Unit cell packing of the compound is given in figure 4.

Comparison of the free ligand with that in complex shows the effect of coordination, for example the range of C–N in complex is 1.308(4)–1.399(4) Å, is different from free

Table 2. Selected bond lengths (Å) and angles (°) for [Zn(DADMBTZ)($CH_3COO)_2]_n$.

Zn(1)–N(1A)	2.050(3)	N(1)–C(1)	1.399(4)
Zn(1)–N(1)	2.050(3)	N(1)–C(3)	1.308(4)
Zn(1)–O(1)	1.954(2)	N(2)–C(3)	1.331(5)
Zn(1)–O(1A)	1.954(2)	N(2)–H(2NA)	0.895
C(1)–C(2)	1.358(5)	N(2)–H(2NB)	0.874
C(1)–C(1A)	1.468(6)	C(2)–C(4)	1.500(6)
N(1A)–1–Zn(1)–N(1)	81.84(2)	C(2)–C(1)–N(1)	115.1(3)
O(1)–Zn(1)–O(1A)	118.58(2)	C(2)–C(1)–C(1A)	130.3(2)
O(1)–Zn(1)–N(1A)	112.62(2)	N(1)–C(3)–N(2)	124.4(3)
O(1A)–Zn(1)–N(1A)	112.78(2)	N(1)–C(3)–S(1)	113.5(3)
O(1)–Zn(1)–N(1)	112.78(2)	O(2)–C(5)–O(1)	122.3(3)
O(1A)–Zn(1)–N(1)	112.62(2)	O(2)–C(5)–C(6)	121.2(4)

Table 3. Hydrogen bonds in [Zn(DADMBTZ)($CH_3COO)_2]_n$.

D–H	*d*(D–H)	D(H···A)	∠DHA	*d*(D···A)	A
N2–H2NA	0.895	1.982	165.67	2.858(4)	O1 [$-x+1/4$, $y-1/4$, $z-1/4$]
N2–H2NB	0.874	1.964	167.50	2.823(4)	O2

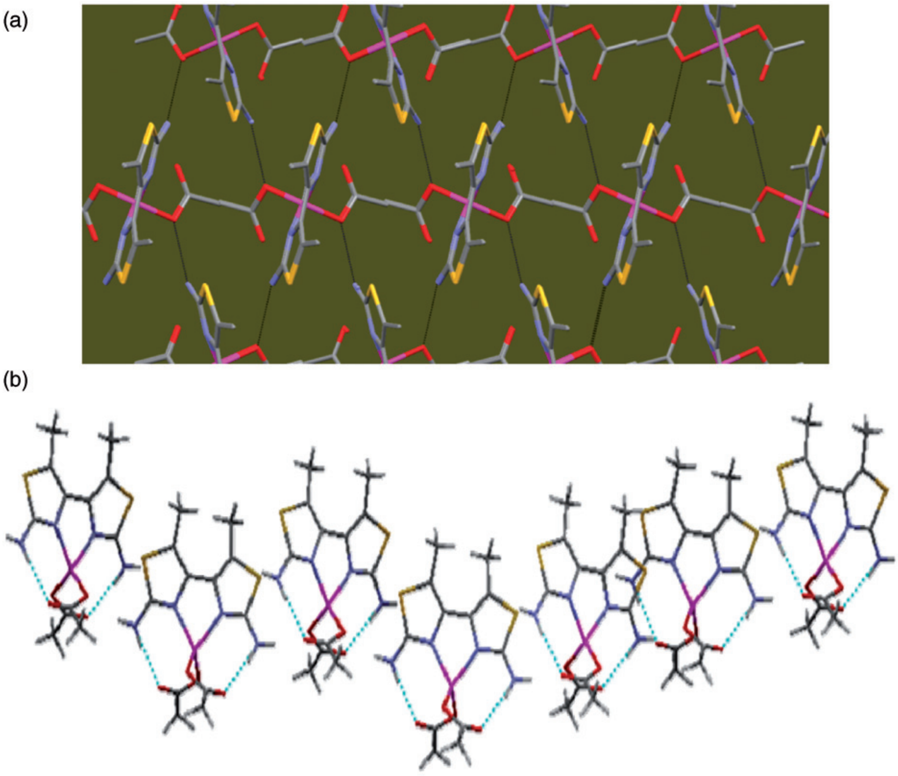


Figure 3. (a) Intramolecular hydrogen bonding in the compound. (b) Intermolecular hydrogen bonding of [Zn(DADMBTZ)($CH_3COO)_2]_n$.

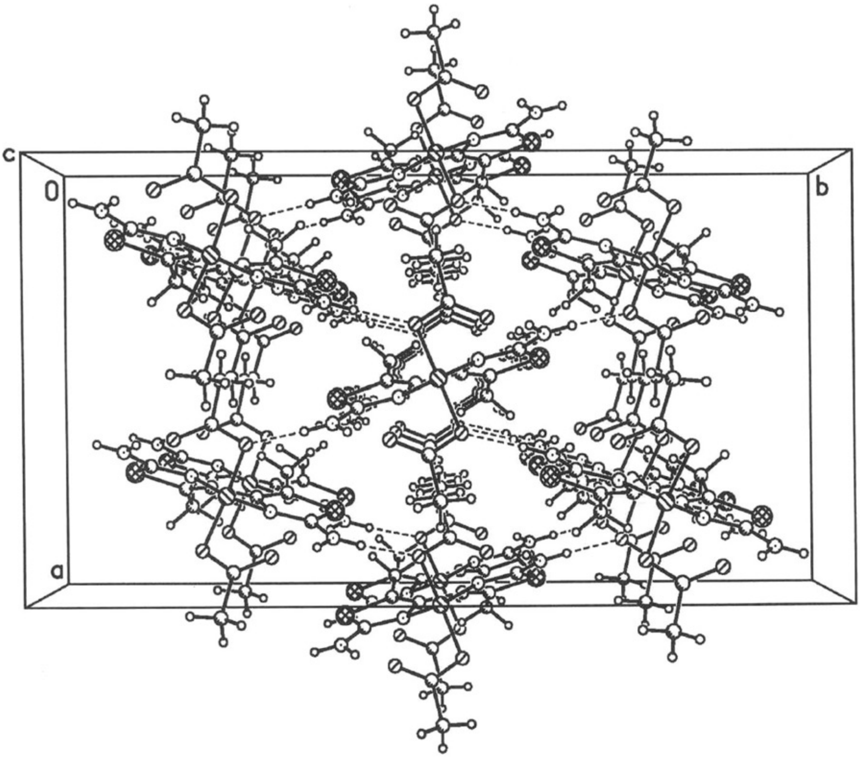


Figure 4. Unit cell of $[Zn(DADMBTZ)(CH_3COO)_2]_n$.

ligand (1.393(4)–1.399(4) Å), and also C(1)–C(1A) = 1.468(6) Å, in complex is shorter than that of free ligand (1.481(4)–1.485(4) Å). The distance between the two bithiazole nitrogen atoms in free ligands is almost 3.079 Å (two nitrogen atoms *trans*) whereas in complex, these distances are about 2.685 Å in DADMBTZ ligands (two nitrogen atoms *cis*).

The torsion angle of DADMBTZ in free ligand, ∠N(3)–C(4)–C(4′)–N(3′), is 59.6(4)°, and in complex ∠N(1)–C(1)–C(1A)–N(1A) = −24.54(5), showing a deviation from planarity of the thiazole ring of bithiazole. The C–N bond lengths in the bithiazole rings in free ligand are 1.393(4)–1.399(4) Å and in the compound 1.308(3)–1.399(3) Å, shorter than single bond length of 1.48 Å and longer than typical C=N distances of 1.28 Å, indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle. The bond length range of C–N of amido groups is 1.331(5) Å in complex, shorter than that of normal C–N single bonds, confirming nitrogen of amido is involved in delocalization.

UV-Vis spectra of compound in DMSO display intense absorptions at 275 nm, indicating that electronic transitions are mostly π–π^*, assigned to interligand charge transfer. The IR spectrum provides evidence of organic ligands coordinating through bithiazole nitrogen atoms. The IR spectrum of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ shows bonds at 1428 and 1380 cm^{-1} for skeletal vibration of bithiazole ring, suggesting coordination has occurred through the bithiazole nitrogen atoms [39].

The carboxylate has many binding modes, monodentate, and bidentate either by chelating, or by forming a bridge. Many complexes containing carboxylate groups play a key role in biochemical systems containing mono- or polymetallic sites [40]. The $\Delta\nu$ value (ν_{as}–ν_{sym}) in [Zn(DADMBTZ)($CH_3COO)_2$] of 283 cm^{-1} indicates that carboxylate coordinates Zn monodentate [41–45]. This is confirmed by the crystal structure.

Comparison of ^{1}H NMR spectra in free ligand with the ones of the complexes show a shift for the amine group from 6.5 for ligand to 7.5 for complex. ^{13}C NMR spectra of complex and the free ligand show carbons in the thiazole rings, with donor nitrogen, sulfur and amine, shift downfield from 164.1 ppm in free ligand to 177.3 ppm in complex. The ^{13}C-NMR spectrum shows two singlets at 22 and 177 ppm for methyl and carbonyl in compound.

The nanostructure of zinc(II) oxide was obtained by direct calcinations in air of $[Zn(DADMBTZ)(CH_3COO)_2]_n$, at 500°C. The XRD pattern of the obtained residue from calcinations of compound nanoparticles at 500°C is provided in "Supplementary material." The diffraction peaks which correspond to (100), (002), and (101) matches with the standard pattern of ZnO and indicate ZnO is hexagonal wurtzite structure (Zincite, JCPDS 36-1451) [46, 47]. No characteristic peaks of impurities are detected in the XRD pattern, indicating all organic precursors were completely decomposed.

The Fourier transform infrared (FT-IR) spectrum of calcinated sample (Supplementary material) has a strong band at 420 cm^{-1} attributed to Zn–O stretch, in accord with previous reports [48]. Bands at 3400 cm^{-1} correspond to O–H vibration, indicating water adsorbed on the ZnO nanostructure surface [49]. The SEM image of ZnO nanostructure from decomposition of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ nanoparticles at 500°C by direct calcinations under air is provided in "Supplementary material."

4. Conclusion

Nanoparticles of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ were produced by sonochemical method using zinc(II) nitrate, ammonium acetate, and DADMBTZ. The new nanoparticles were characterized by SEM, XRD, TGA, DTA, and FT-IR spectroscopy. $[Zn(DADMBTZ)(CH_3COO)_2]_n$ was structurally characterized by single-crystal X-ray diffraction. The sonochemical method is rarely used for syntheses of coordination polymer nanoparticles, but can be easily controlled and is expected to be applicable to fabrication of other nano-sized coordination polymers. ZnO nanostructure was obtained by direct thermolyses of $[Zn(DADMBTZ)(CH_3COO)_2]_n$ at 500°C under air. The ZnO nanostructure was characterized by SEM, XRD and FT-IR spectroscopy.

Supplementary material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited with the Cambridge Crystallography Data Centre, CCDC No. 289424 for $[Zn(DADMBTZ)(CH_3COO)_2]_n$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@cdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

The authors would like to acknowledge the financial support of University of Tehran for this research under grant number 24604/1/03. We thank the Tarbiat Modares University and also the Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure by X-ray crystallography.

References

[1] R. Matsuda, R. Kitaura, Y. Kubota, T.C. Kobayashi, M. Takata, S. Kitagawa. *Microporous Mesoporous Mater*., **129**, 296 (2010).
[2] R.-H. Zhang, X.-W. Zhou, Z.-H. Zhou. *J. Coord. Chem*., **63**, 3589 (2010).
[3] D.S. Chowdhuri, A. Rana, M. Bera, E. Zangrando, S. Dalai. *Polyhedron*, **28**, 2131 (2009).
[4] R.L. Davidovich, V. Stavila, D.V. Marinin, E.I. Voit, K.H. Whitmire. *Coord. Chem. Rev*., **253**, 1316 (2009).
[5] U. Englert. *Coord. Chem. Rev*., **254**, 537 (2010).
[6] F. Guang, Y. Zu-Pei, Z. Yin-Liz, S. Jia-Juanz, Z. Min-Yan, Y. Zhan-Jiang. *J. Coord. Chem*., **64**, 3475 (2011).
[7] R.L. LaDuca. *Coord. Chem. Rev*., **253**, 1759 (2009).
[8] P. Sepp, E. Colacio, A.J. Mota, R. Sillanp. *Inorg. Chim. Acta*, **363**, 755 (2010).
[9] J.J. Vittal. *Coord. Chem. Rev*., **251**, 1781 (2007).
[10] M.J.S. Fard-Jahromi, A. Morsali. *Ultrason. Sonochem*., **17**, 435 (2010).
[11] A. Lan, M. Padmanabhan, K. Li, H. Wu, T.J. Emge, M. Hong, J. Li. *Inorg. Chim. Acta*, **366**, 68 (2011).
[12] M.L. Han, J.G. Wang, J.J. Yao. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem*., **41**, 1268 (2011).
[13] D.S. Chowdhuri, A. Rana, M. Bera, E. Zangrando, S. Dalai. *Polyhedron*, **28**, 2131 (2009).
[14] H. Kwak, S.H. Lee, S.H. Kim, Y.M. Lee, B.K. Park, Y.J. Lee, J.Y. Jun, C. Kim, S.-J. Kim, Y. Kim. *Polyhedron*, **28**, 553 (2009).
[15] L. Hou, D. Li. *Inorg. Chem. Commun*., **8**, 190 (2005).
[16] X. Liu, X.-J. Yang, P. Yang, Y. Liu, B. Wu. *Inorg. Chem. Commun*., **12**, 481 (2009).
[17] Q.-G. Wang, Y.-S. Xie, F.-H. Zeng, S.-W. Ng, W.-H. Zhu. *Inorg. Chem. Commun*., **13**, 929 (2010).
[18] A. Erxleben. *Coord. Chem. Rev*., **246**, 203 (2003).
[19] M. Bochmann. *Coord. Chem. Rev*., **253**, 2000 (2009).
[20] W. Huang, H.-B. Zhu, S.-H. Gou. *Coord. Chem. Rev*., **250**, 414 (2006).
[21] J.K.-H. Hui, M.J. MacLachlan. *Coord. Chem. Rev*., **254**, 2363 (2010).
[22] E.H. Ryu, J.H. Lee, Y.S. Lee, J.M. Gu, S. Huh, S.J. Lee. *Inorg. Chem. Commun*., **14**, 1648 (2011).
[23] A.M. Spokoyny, D. Kim, A. Sumrein, C.A. Mirkin. *Chem. Soc. Rev*., **38**, 1218 (2009).
[24] L. Chen, Y. Shen, B.J. Yongming, C. Wang. *J. Solid State Chem*., **182**, 2298 (2009).
[25] A. Pramanik, G. Das. *Cryst. Eng. Comm*., **12**, 401 (2010).
[26] C.J. Hoeller, K.M.- Buschbaum. *Eur. J. Inorg. Chem*., 45 (2010).
[27] B.L. Wu, R.Y. Wang, H.Y. Zhang, H.W. Hou. *Inorg. Chim. Acta*, **375**, 2 (2011).
[28] S. Wu, W. Liu, X. Shen, C. Shi, H. Xu. *Physica E*, **41**, 101 (2008).
[29] M. Salavati, F. Davar, A. Khansari. *J. Alloys Compd*., **509**, 61 (2011).
[30] P.X. Gao, Y. Ding, W.L. Wang. *Nano Lett*., **3**, 1315 (2003).
[31] A. Hosseinian, A.R. Mahjoub. *J. Mol. Struct*., **985**, 270 (2011).
[32] A. Hosseinian, A.R. Mahjoub, M. Movahedi. *Int. J. Nano Dim*., **1**, 65 (2010).
[33] A. Hosseinian, A.R. Mahjoub. *Acta Cryst*., **E65**, m 1456 (2009).
[34] G.M. Sheldrick. *SHELXTL v. 5.10, Structure Determination Software Suite*, Bruker AXS Inc., Madison, WI, USA (1998).
[35] G.M. Sheldrick. *SHEXTL-97, A Program for Refining Crystal Structures (Version 5.10)*, Bruker AXS Inc., Madison, WI, USA (1997).

[36] G.M. Sheldrick. *SADABS*, Bruker AXS Inc., Madison, WI, USA (1997).

[37] (a) L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997); (b) *Mercury 1.4.1*, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).

[38] J. Yang, C. Lin, Z. Wang. *J. Lin. Inorg. Chem.*, **45**, 8973 (2006).

[39] F. Bei, F. Jian, X. Yang, X.L. Lu, X. Wang, S. Shanmuga Sudara Raj, H.-K. Fun. *Acta Crystallogr.*, **56**, 718 (2000).

[40] K. Nakamoto. *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York (1963).

[41] A.V.R. Warrier, R.S. Krishnan. *Spectrochim. Acta*, **24A**, 1243 (1971).

[42] A. Hosseinian, A.R. Mahjoub. *J. Coord. Chem.*, **63**, 4245 (2010).

[43] G.B. Deacon, R.J. Philips. *Coord. Chem. Rev.*, **33**, 227 (1980).

[44] (a) G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **30**, 227 (1980); (b) I. Dreveni, O. Berkesi, I. Janovics, J.A. Andor. *Vibr. Spectrosc.*, **2**, 205 (1991).

[45] M.A.S. Goher, M.A.M. Abu-Youssef, F.A. Mautner. *Polyhedron*, **15**, 453 (1996).

[46] K. Akhbari, A. Morsali. *J. Coord. Chem.*, **64**, 3521 (2011).

[47] B. Luo, W.L. Gladfelter. *J. Coord. Chem.*, **64**, 82 (2011).

[48] L.L. Wu, Y.S. Wu, Y.C. Shi, H.Y. Wei. *Rare Met.*, **25**, 68 (2006).

[49] R. Wahab, I.H. Hwang, Y.S. Kim, H.S. Shin. *Chem. Eng. J.*, **168**, 359 (2011).