

Zinc(II) Complexes of Schiff Bases Derived from *Bis*-(2-hydrazino-1,3,4-thiadiazole-5-yl)Arene/ Alkanes: Synthesis, Spectral Characterization and Biological Properties

ARTI VISHWKARMA[®], A.K. SRIVASTAVA[®], O.P. PANDEY[®] and S.K. SENGUPTA^{*,®}

Department of Chemistry, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur-273009, India

*Corresponding author: E-mail: sengupta@hotmail.co.uk

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A novel series of zinc(II) complexes of type [ZnL(H_2O)₂], has been synthesized by the reaction of zinc(II) acetate dihydrate with Schiff bases (H_2L) derived from *bis*-(2-hydrazino-1,3,4-thiadiazole-5-yl)arene/alkanes and 2-hydroxynaphthaldehyde/3,5-dichlorosalicyldehyde in presence of a base. The structures of all the zinc complexes were proposed by elemental analysis and spectroscopic data (IR, ¹H, ¹³C NMR). TGA investigations were carried out to confirm the presence of coordinated water molecules in the zinc complexes. The powder crystal structure of one particular zinc complex has been analyzed by XRD diffraction method and SEM studies have been carried out to investigate the surface morphology. The biological studies reveal that the synthesized zinc complexes possess good antimicrobial properties against different species of pathogenic fungi and bacteria.

Keywords: Zn(II), Schiff bases, bis-(2-Hydrazino-1,3,4-thiadiazole-5-yl)arene/alkanes, Antimicrobial activity.

INTRODUCTION

Several substituted 1,3,4-thiadiazoles and related compounds have diverse application in pharmacological and technological areas. Derivatives of 1,3,4-thiadiazoles are well known to have wide application in the field of agriculture, medicine and industry (liquid crystals, photographic materials, manufacturing of dyes, *etc.*) [1-12]. The reason of such excellent properties of 1,3,4-thiadiazoles moiety are basically due to presence of azomethine linkage. 1,3,4-Thiadiazoles have been used as potential additives [13].

A series of 1,3,4-thiadiazole derivatives have been synthesized as anti-virulence agents against *Xoo* infection in rice [14]. Some heteroaromatic 1,3,4-thiadiazole derivatives are known to exhibit antithyroid activity [15] and anti-leishmanial properties [16]. Diosgenin derivatives bearing 1,3,4-thiadiazole moieties have been reported as antitumor agents [17]. Dual fluorescence effects have been demonstrated by some 1,3,4thiadiazole derivatives [18]. Some charge transfer molecular complexes (CX) of 1,3,4-thiadiazole [19] have been synthesized and microwave spectra of 1,3,4-thiadiazole derivatives have also been reported [20]. A number of zinc(II) complexes (Zn^{II}CX) with 1,3,4-thiadiazoles ligands have been studied for their physical and pharmacological and medicinal properties [21-23]. Antidiabetic potential [24] of the zinc(II) complexes with 1,3,4-thiadiazoles have also been tested; whereas some zinc(II) complexes with 1,3,4-thiadiazoles are known to exhibit photoluminescence and fluorescence properties [25].

In this work, studies on a series of zinc(II) complexes with Schiff bases derived from *bis*-(2-hydrazino-1,3,4-thiadiazole-5-yl)arene/alkanes (BHTDZA/A) and 2-hydroxynaphthaldehyde (HNAPD)/3,5-dichlorosalicyldehyde (DCSAD) are reported. These compounds have been characterized with the help of different physico-chemical techniques and their biological activities have also been studied against five microbes.

EXPERIMENTAL

The solvents were purchased from Merck and zinc(II) acetate dihydrate was procured from Aldrich, USA. Buchi 530 apparatus was used to determine the melting points. Elemental analysis was performed with a Vario EL III Carlo Erba 1105 CHN analyser and elemental (C, H, N) analysis indicated that calculated and observed values were within acceptable limits. IR spectra were recorded in KBr using Shimadzu 8201 PC model spectrophotometer while NMR spectra were recorded

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in DMSO- d_6 solvent by a Bruker DRX-300 spectrometer using tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) data of six-coordinated Zn(II) metal complexes were studied using a Perkin-Elmer-STA 6000 thermal analyser instrument. Powder X-ray diffraction (XRD) dimensions were recorded using an X-ray powder diffractometer (Bruker AXS DB Advance) with CuK α radiation ($\lambda = 1.5406$ Å). The SEM micrographs of Zn(II) metal complexes were obtained on a JOEL model JSM-6390LV scanning microscope.

Synthesis of BHTDZA/A: Reported method of Maffii *et al.* [26] was used to synthesize the (BHTDZA/A). Carbon disulphide (0.25 mol) was added slowly to an alcoholic solution of appropriate dihydrazide (0.11 mol) and KOH (0.25 mol) with continuous stirring and the solid mass thus obtained was treated with conc. H_2SO_4 in installments. The reaction mixture was poured in chilled water and the precipitate, thus obtained, was filtered, dried up and recrystallized from absolute alcohol. The resultant precipitate was further refluxed with hydrazine hydrate (0.25 mol) in ethanol for 4-5 h. The mixture was cooled and the precipitate thus obtained was filtered off, dried and recrystallized from ethanol. Yield: 71-85%

Synthesis of Schiff bases: Appropriate (BHTDZA/A) (0.02 mol) and 2-hydroxynaphthaldehyde (HNAPD)/3,5-dichlorosalicyldehyde (DCSAD) (0.04 mol) were dissolved in ethanol (25 mL) in 1:2 ratio followed by addition of few drops of conc. HCl and the whole mixture was refluxed for 7-8 h. The reaction mixture was reduced to 10 mL, cooled and ether was added to separate the precipitate, which was filtered off, dried and recrystallized from alcohol [27,28].

Synthesis of Zn^{II}CX (1-6): The synthesis of Zn^{II}CXs, involves the addition of zinc(II) acetate dihydrate (0.02 mol) to the ethanolic solution (25 mL) of appropriate Schiff base (0.02 mol) and NaOH (0.02 mol). The reaction mixture was refluxed for 11-14 h. Yellow or brown precipitates thus obtained was filtered off, washed with ethanol and dried under *vacuo*. Analytical data of the Zn^{II}CXs are given in Table-1 and reaction pathways are shown in Fig. 1.

[ZnL¹(H₂O)₂]: FT-IR (KBr, v_{max} , cm⁻¹): 3431 (-OH), 3237 (-NH), 1620 (-C=N), 1105 (C-S-C), 515 (Zn-O), 469 (Zn-N). ¹H NMR (DMSO-*d*₆) δ ppm: 10.54 (s, -NH), 5.45 (s, 2H, -OH), 8.64 (s, 2H, -CH), 7.28-8.01 (m, 12H, naphth.-H), 2.54 (t, 4H, -CH₂). ¹³C NMR (DMSO-*d*₆) δ ppm: 167.3, 163.1 (2C, -C=N, thiadiazole), 159.5 (2C, -C=N), 120.8-148.4 (20C, naphth.-C), 27.2 (2C, -(CH₂)₂-).

[ZnL²(H₂O)₂]: FT-IR (KBr, v_{max} , cm⁻¹): 3423 (-OH), 3234 (-NH), 1625 (-C=N), 1103 (C-S-C), 512 (Zn-O), 465 (Zn-N). ¹H NMR (DMSO- d_6) δ ppm: 10.49 (s, -NH), 5.46 (s, 2H, -OH),



Fig. 1. Reaction route for the synthesis of zinc(II) complexes of N_2O_2 type Schiff bases

8.59 (s, 2H, -CH), 7.27-7.92 (m, 12H naphth.-H), 1.86 (m, 4H, -CH₂), 2.61 (t, 4H, -CH₂). ¹³C NMR (DMSO- d_6) δ ppm: 167.3, 163.1 (2C, -C=N, thiadiazole), 159.5 (2C, -C=N), 120.7-150.7 (20C, naphth.-C), 26.8, 28.7 (4C, -(CH₂)₄-).

[ZnL³(H₂O)₂]: FT-IR (KBr, v_{max} , cm⁻¹): 3437 (-OH), 3239 (-NH), 1626 (-C=N), 1106 (C-S-C), 521 (Zn-O), 471 (Zn-N). ¹H NMR (DMSO-*d*₆) δ ppm: 10.57 (s, -NH), 5.53 (s, 2H, -OH), 8.71 (s, 2H, -CH), 7.30-8.10 (m, 16H naphth.-H and Ar-H). ¹³C NMR (DMSO-*d*₆) δ ppm: 163.5, 167.5 (2C, -C=N, thiadiazole), 159.7 (2C, -C=N), 121.2-152.6 (26C, aromatic-C).

[ZnL⁴(H₂O)₂]: FT-IR (KBr, v_{max} , cm⁻¹): 3445 (-OH), 3248 (-NH), 1628 (-C=N), 1107 (C-S-C), 528 (ZnO), 475 (ZnN). ¹H NMR (DMSO-*d*₆) δ ppm: 10.68 (s, -NH), 5.54 (s, 2H, -OH), 8.84 (s, 2H, -CH), 7.79 (s, 2H, Ar-H), 7.54 (s, 2H, Ar-H), 2.56 (t, 4H, -CH₂). ¹³C NMR (DMSO-*d*₆) δ ppm: 163.3, 167.5 (2C, -C=N, thiadiazole), 160.5 (2C, -C=N), 122.1-155.3 (12C, aromatic-C), 27.4 (2C, -(CH₂)₂-).

[ZnL⁵(H₂O)₂]: FT-IR (KBr, v_{max}, cm⁻¹): 3442 (-OH), 3244 (-NH), 1627 (-C=N), 1105 (C-S-C), 524 (Zn-O), 472 (Zn-N).

	TABLE-1
A	ANALYTICAL DATA OF THE SYNTHESIZED ZINC(II) COMPLEXES OF N ₂ O ₂ TYPE SCHIFF BASES

Compounds	m f		Elementa	ıl analysis (%): Four	nd (calcd.)		
Compounds	111.1.	С	Н	Ν	Ν	Zn	
[ZnL1(H2O)2]	$C_{28}H_{24}N_8O_4ZnS_2$	50.12 (50.49)	4.11 (3.63)	9.51 (9.63)	16.65 (16.82)	9.71 (9.82)	
$[ZnL^2(H_2O)_2]$	$C_{30}H_{32}N_8O_4ZnS_2$	51.51 (51.91)	4.53 (4.07)	9.14 (9.24)	15.98 (16.14)	9.30 (9.42)	
$[ZnL^{3}(H_{2}O)_{2}]$	$C_{32}H_{24}N_8O_4ZnS_2$	53.78 (53.82)	3.33 (3.39)	8.95 (8.98)	15.65 (15.69)	9.02 (9.16)	
$[ZnL^4(H_2O)_2]$	$C_{20}H_{16}N_8O_4ZnS_2Cl_4$	34.00 (34.14)	2.23 (2.29)	9.06 (9.11)	15.81 (15.92)	9.22 (9.29)	
[ZnL5(H2O)2]	$C_{22}H_{20}N_8O_4ZnS_2Cl_4$	36.05 (36.11)	2.70 (2.75)	8.73 (8.76)	15.26 (15.31)	8.89 (8.93)	
$[ZnL^6(H_2O)_2]$	$C_{24}H_{16}N_8O_4ZnS_2Cl_4$	38.21 (38.35)	2.06 (2.15)	8.47 (8.53)	14.85 (14.91)	8.62 (8.70)	

¹H NMR (DMSO- d_6) δ ppm: 10.63 (s, -NH), 5.52 (s, 2H, -OH), 8.81 (s, 2H, -CH), 7.76 (s, 2H, Ar-H), 7.52 (s, 2H, Ar-H), 2.63 (m, 4H, -CH₂), 1.91 (t, 4H, -CH₂). ¹³C NMR (DMSO- d_6) δ ppm: 163.8, 167.7 (2C, -C=N, thiadiazole), 160.3 (2C, -C=N), 122.0-155.1 (12C, aromatic-C), 27.2, 29.3 (4C, -(CH₂)₄-).

[ZnL⁶(H₂O)₂]: FT-IR (KBr, v_{max} , cm⁻¹): 3451 (-OH), 3248 (-NH), 1629 (-C=N), 1109 (C-S-C), 540 (Zn-O), 479 (Zn-N). ¹H NMR (DMSO-*d*₆) δ ppm: 10.72 (s, -NH), 5.58 (s, 2H, -OH), 8.89 (s, 2H, -CH), 7.82 (s, 2H, Ar-H), 7.58 (s, 2H, Ar-H), 7.56 (m, 4H, Ar-H). ¹³C NMR (DMSO-*d*₆) δ ppm: 164.2, 167.9 (2C, -C=N, thiadiazole), 160.7 (2C, -C=N), 122.4-155.7 (18C, aromatic-C).

Tested organisms: Pathogenic fungal strains such as *A. niger, A. alternate* and *H. oryzae* and bacterial strains such as *E. coli* and *B. subtilis* were selected based on their experimental and pharmacological importance. The fungal and bacterial strains were cultured on agar medium and incubated for 21-25 h at 29-37 °C.

Antifungal activity: The antifungal activity of all synthesized Schiff base and their corresponding zinc(II) complexes were studied against three pathogenic fungal strains (*A. niger*, *A. alternate* and *H. oryzae*) by agar plate technique. The antifungal activity results were recorded as percentage of inhibition and compared with fluconazole which was used as standard drug. For each zinc complexes, 1% standard solution was prepared in DMSO and 1mL of solution was mixed with 9 mL of solvent. Three concentrations *viz.* 10, 100, 1000 ppm stock solution were prepared for each zinc complex and 1 mL of each concentration solution was mixed with 9 mL of agar medium in sterlized petri plates. After the medium was ready, fungus strain was inoculated in the center of each plate and the assay plates were incubated at 29 ± 2 °C for nearly 7 days.

Antibacterial activity: The antibacterial activity of all the synthesized Schiff base and their respective zinc(II) complexes were screened against the two bacteria (*E. coli* and *B. subtilis*) by agar well diffusion method. Tetracycline was taken as standard and the antibacterial activity of each complex was evaluated in DMSO and the effects were recorded by measuring the inhibition zone (mm) around each disk after 24 h.

RESULTS AND DISCUSSION

A series of zinc(II) complexes were synthesized by the reactions of Zn(OAc)₂·2H₂O with synthesized Schiff bases in ethanol. All zinc(II) complexes are air stable and soluble in DMSO and DMF. The electrical conductance measurements in DMF indicate that zinc(II) complexes are non-electrolytic nature. The presence of two water molecules in the zinc(II) complexes has been confirmed by TG, which shows weight loss at 140-180 °C, corresponding to coordinated water molecules (Fig. 2).

Infrared spectra: The IR spectra give valuable information concerning the functional groups and coordination behaviour of Schiff bases to the metal ion [29]. Both Schiff bases and their zinc(II) complexes show bands 3182-3045 cm⁻¹ due to v(Ar-H). Schiff bases (H₂L¹, H₂L², H₂L³) shows a medium band at 3235 cm⁻¹ while (H₂L⁴, H₂L⁵, H₂L⁶) exhibit a band at 3247 cm⁻¹ indicates the presence of v(N-H), which remains



Fig. 2. TG curve of ZnL3(H2O)2 complex

unaltered in the zinc(II) complexes confirming the non-intervention of (N-H) group in bond formation. Schiff bases (H₂L¹, H₂L², H₂L³) exhibit one strong band at 1635 cm⁻¹ while (H₂L⁴, H₂L⁵, H₂L⁶) display this band at 1640 cm⁻¹ attributed to v(C=N), which shifts to lower frequency (nearly by 15-10 cm⁻¹) in the zinc(II) complexes indicating the coordination of azomethine nitrogen to the zinc(II) ion. A new band appears in zinc(II) complexes 470 cm⁻¹ assignable to v(Zn-N).

The appearance of a broad band at 2965 cm⁻¹ in Schiff bases (H_2L^1, H_2L^2, H_2L^3) and at 2885 cm⁻¹ in Schiff bases (H_2L^4, H_2L^5, H_2L^5) H_2L^6) is due to the intramolecular H-bonding of -OH group. This band vanishes in the corresponding zinc(II) complexes suggesting the coordination of phenolic oxygen to Zn^{2+} ion through deprotonation. It was confirmed by the appearance of a band at 540-512 cm⁻¹ in Zn(II) complexes assignable to v(Zn-O). A strong band at 1109 cm⁻¹ confirms the presence of v(C-S-C) vibration in the free Schiff bases, which remains almost unaffected in the zinc(II) complexes, indicating noncoordination of thiadiazole ring to metal atom. The presence of coordinated water molecules in the zinc(II) complexes was confirmed by a broad band at 3431-3420 cm⁻¹ and two weaker bands also appear in the regions 810-745 and 745-720 cm⁻¹ attributable to (-OH) rocking and wagging modes of vibrations, respectively.

¹H NMR spectral studies: The ¹H NMR spectra of Zn(II) complexes have been recorded in DMSO- d_6 and the following conclusions were obtained by comparing the spectra of Schiff bases and their Zn(II) complexes. The Schiff bases (H_2L^1, H_2L^2 , H_2L^3) exhibit signal at δ 11.50 ppm while (H_2L^4 , H_2L^5 , H_2L^6) shows signal at δ 12.11 ppm due to phenolic protons, which vanishes in the corresponding Zn(II) complexes, hence it proves that hydroxyl group reacted with Zn(II) ions via deprotonation. Schiff bases and its Zn(II) complexes showed multiplet at δ 7.27-8.09 ppm attributed to aromatic protons. Schiff bases exhibit signals at δ 10.49 and 8.31 ppm because of hydrazino NH and azomethine protons, respectively. In Zn(II) complexes, the first signal remains unaltered while second signal shows downfield shift indicating the drainage of the azomethine nitrogen to the central metal ion. Schiff bases (H_2L^1, H_2L^4) and its Zn(II) complexes exhibit a signal at δ 2.54 ppm while ligands (H_2L^2, H_2L^5) and its Zn(II) complexes display

signals at δ 2.61 and 1.85 ppm assignable to methylene protons. A new signal at δ 5.5 ppm in all Zn(II) complexes is due to water protons.

¹³C NMR spectral studies: ¹³C NMR spectral data of the synthesized Zn(II) complexes were recorded in solvent DMSO*d*₆. All Schiff bases show signal at δ 157 ppm attributable to azomethine carbons which shifts downfield in their corresponding Zn(II) complexes due to the coordinate bonding of azomethine nitrogen to the metal ion. Schiff bases and their corresponding Zn(II) complexes display signals at about δ 163, 167 ppm attributable to the thiadiazole ring carbons. Schiff bases, H₂L¹, H₂L⁴ and its Zn(II) complexes shows a signal at δ 26.8 ppm and 28.7 ppm whereas H₂L², H₂L⁵ and its Zn(II) complexes show a signal at δ 27.1 ppm assignable to methylene carbons. A number of signals were observed at δ 120.5-148.7 ppm in the ¹³C NMR spectra is assignable to the aromatic carbons.

XRD studies: The XRD pattern of $[ZnL^2(H_2O)_2]$ is displayed in Fig. 3. The particles size of the Zn(II) complexes were calculated by Debye-Scherer formula [30] given as:

$$D = \frac{0.94\lambda}{\beta\cos\theta}$$

where, D = size of the particle, λ = wavelength of X-ray used, β = full width at half maximum (FWHM) and θ = Bragg's angle of diffraction. The particles size was found to be in the range 15 to 44 nm, which falls in the nano range.



The $[ZnL^2(H_2O)_2]$ were evaluated for *hkl* indexing by comparing the powder XRD data from the database of diffraction pattern (ICDD-JCPDS). The *hkl* index (Table-2) revealed that the representative $[ZnL^2(H_2O)_2]$ has monoclinic crystal system having space group $P2_1/m$.

SEM studies: The SEM studies were carried out in order to examine the surface morphology of selected $[ZnL^2(H_2O)_2]$ complex and the micrograph obtained is shown in Fig. 4. The surface morphology of the $[ZnL^2(H_2O)_2]$ was found to be globular and the particles were irregularly arranged in the micrograph.



Fig. 4. SEM image of ZnL²(H₂O)₂ complex

Biological studies: The results obtained proved that the synthesized zinc(II) complexes have the capacity to inhibit the growth of pathogenic fungal and bacterial strains under observation. All the zinc(II) complexes were found to be more toxic than the corresponding Schiff bases. The reason behind the increased toxicity of the zinc(II) complexes can be explained by chelation theory, according to which chelation reduces the polarity of the central metal ion, as the positive charge is partially shared by the Schiff bases. It facilitates the permeation of the zinc(II) complexes through lipid layer of cell membranes [31].

In vitro antifungal activity of all the synthesized Zn(II) complexes was studied against *A. niger*, *A. alternate* and *H. oryzae* using fluconazole as standard and the results were recorded in percentage of inhibition at 10, 100 and 1000 ppm concentration. The activity of Schiff bases enhances upon complexation and the activity increases with increase in concentration of the Zn(II) complexes. The antifungal activity results show that Zn(II) complexes (**4**, **5** and **6**) were more effective against fungal strains and all the Zn(II) complexes were more active against *A. niger* (Table-3).

The antibacterial activity of the synthesized zinc(II) complexes were carried out against the bacterial strains *E. coli* and *B. subtilis*, using tetracycline as standard and the results

TABLE-2
UNIT CELL PARAMETERS AND OBSERVED AND CALCULATED X-RAY DIFFRACTION DATA OF ZnL ² (H ₂ O) ₂

a = 9.02002 Å, b = 11.33452 Å, c = 14.67260 Å, β = 93.08044, V = 1497.9236 Å ³							
d (obs.)	d (calcd.)	$\Delta(d)$	$I/Im \times 100$	20 (obs)	2θ (calcd.)	Δ (2 θ)	h k l
9.08187	9.00699	0.07488	100	9.731	9.812	-0.081	100
7.44404	7.49544	-0.005140	11.02	11.879	11.797	0.082	101
6.13878	6.15252	-0.013740	14.39	14.417	14.385	0.032	012
5.83533	5.83893	0.003590	9.95	15.171	15.162	0.009	-102
5.00827	4.97685	-0.031420	10.51	17.695	17.808	-0.113	112
4.51600	4.52055	0.004550	8.67	19.642	19.622	0.020	121

TABLE-3 ANTIFUNGAL DATA OF THE SYNTHESIZED ZINC(II) COMPLEXES OF N_2O_2 TYPE SCHIFF BASES									
	% Fungicidal inhibition (ppm)								
Compounds	A. niger			A. alternate			H. oryzae		
	10	100	1000	10	100	1000	10	100	1000
$[ZnL^1(H_2O)_2]$	37	53	66	-	28	43	-	18	32
$[ZnL^2(H_2O)_2]$	34	47	63	-	-	39	-	14	30
$[ZnL^{3}(H_{2}O)_{2}]$	48	56	68	37	45	57	15	28	58
$[ZnL^4(H_2O)_2]$	54	64	75	47	54	64	21	38	61
[ZnL5(H2O)2]	52	61	73	43	51	61	18	35	53
$[ZnL^{6}(H_{2}O)_{2}]$	59	67	79	49	58	66	27	41	62
Standard	100	100	100	100	100	100	100	100	100

were obtained by measuring the diameter of zone showing complete inhibition (mm). The antibacterial activity results indicate that the zinc(II) complexes were more effective against *B. subtilis*, while Zn(II) complex (**6**) shows good antibacterial properties. The effective antifungal and antibacterial activities of Zn(II) complex (**6**) is due to chloro group at phenyl ring, while poor activity of Zn(II) complexes (**1** and **2**) may be due to the methylene chain (Table-4).

TABLE-4					
ANTIBACTERIAL DATA OF THE SYNTHESIZED					
ZINC(II) COMPI	LEXES OF N ₂ O ₂ TYPE	E SCHIFF BASES			
Compounds	Compounds Zone of inhibition (mm)				
Compounds -	E. coli	B. substilis			
$[ZnL^{1}(H_{2}O)_{2}]$	-	-			
$[ZnL^{2}(H_{2}O)_{2}]$	-	-			
[ZnL3(H2O)2]	14	16			
$[ZnL^4(H_2O)_2]$	12	21			
[ZnL5(H2O)2]	10	20			
$[ZnL^6(H_2O)_2]$	15	23			
Tetracycline	28	25			

Conclusion

The N₂O₂ type Schiff bases were synthesized from *bis*-(2-hydrazino-1,3,4-thiadiazole-5-yl)arene/alkanes (BHTDZA/ A) and 2-hydroxynaphthaldehyde/3,5-dichlorosalicyldehyde (HNAPD/DCSAD), which were used to form stable complexes with Zn²⁺ ion. An octahedral geometry of zinc(II) complexes has been proposed by the spectral data. The TG analysis confirmed the presence of water molecules in the synthesized Zn(II) complexes. The XRD studies confirmed that the Zn(II) complexes are in nano-range and have monoclinic crystal system. The synthesized zinc(II) complexes show moderate antifungal and antibacterial activities due to the chelation effect and Zn(II) complexes of Schiff bases containing chloro group are found to be more toxic.

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CONFLICT OF INTEREST

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

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