Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (4): 1640-1649

(International Peer Reviewed Journal)

Synthesis, Spectroscopic Characterization and Biological Properties of Zinc(II) Complexes with Schiff bases Derived from Bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)arene/alkanes

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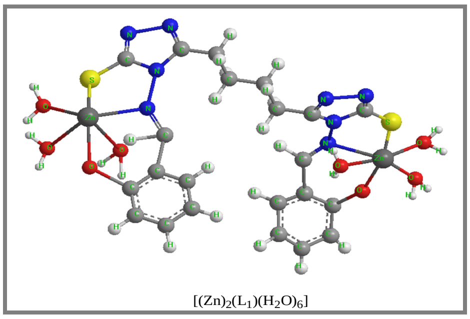
Accepted on 10th June, 2019

ABSTRACT

A novel series of binuclear zinc(II) complexes of type $[Zn_2(L)(H_2O)_6](H_4L=$*Schiff bases) has been synthesized by the reaction of zinc(II) acetate dihydrate with Schiff bases derived from bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)arene/alkanes and salicylaldehyde/2-hydroxyacetophenone in presence of base. The structures of these complexes were established on the basis of elemental analysis and spectral (IR and NMR) studies. The presence of coordinated water in metal complexes was confirmed by thermogravimetric analysis. Octahedral geometry for zinc(II) complexes have been proposed. The powder crystal structures of the complexes have been determined by XRD pattern. For surface morphology of the complexes SEM (scanning electron microscopy) has been carried out. The in vitro antibacterial and antifungal studies indicate that the synthesized complexes possess good antimicrobial properties against different species of pathogenic fungi and bacteria.*

Graphical Abstract



$[(Zn)_2(L_1)(H_2O)_6]$

Keywords: Schiff base, Zinc(II), IR, NMR, XRD, Antifungal, Antibacterial.

INTRODUCTION

Synthesis of coordination compounds is a subject of particular interest because of their various structural topologies and potential applications in different scientific field [1-6]. The nitrogen containing heterocycles are important part of most of the medicinal compounds. The chemistry of triazoles and their derivatives are in focus due to their synthetic and biological importance [7, 8]. The synthesis of Schiff bases is of quiet interest due to their wide applications in many chemical and biological aspects [9-11]. Schiff bases are versatile ligands having imine N and donor sites. The non bonding electron pair on the nitrogen atom in these compounds makes them prone to coordinate to metal ions in order to form Schiff base complexes. Transition metal ions enhance the biological activity of different ligands, and in some cases the activity has been observed only due to metal ions [12]. Being the second most abundant trace element in the human body, zinc has a significant role regulatory the metabolism of cells [13, 14] and is a part of more than two hundred metalloenzymes having catalytic, structural and regulatory role [15]. Zinc complexes have been widely recognized for their diverse biological activities such as antidiabetic [16], anticonvulsant [17], antimicrobial [18-24], anti-inflammatory [25], antioxidant [26], antitumor [27, 28] etc.

It devoted to the synthesis, spectral, thermal, SEM, XRD- structure analysis and biological activities of Zn(II) complexes with bis-(4-amino-5-mercapto-1,2,4-triazol-3yl)arene/alkanes derivatives.

MATERIALS AND METHODS

General Information: Melting points were obtained in open capillaries with the help of laboratory melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance III, 400 MHz spectrometer containing tetramethylsilane (TMS) as an internal reference and the chemical shifts expressed in ppm downfield from TMS. Samples were dissolved in dimethyl sulfoxide. IR spectra were recorded with a Thermo Nicolet, Avatar 370 spectrophotometer. Elemental analysis was performed with an Elemental Vario EL III C-H-N analyser. Elemental analysis indicated that calculated and observed values were within acceptable limits. The purity of compounds was checked by thin layer chromatography using silica gel plate with ether and ethyl acetate as solvent system. An iodine containing chamber was used as developing chamber. Zinc was estimated gravimetrically as zinc oxide (ZnO). Thermogravimetric analyses (TG/DTA) were carried out under nitrogen atmosphere with a heating rate of 20°C/min using a Perkin Elmer STA 6000 model instrument. The structural characterization of the complexes were carried out from the analysis of X-Ray powder diffraction (XRD) pattern obtained using an X-Ray powder diffractometer (Bruker AXS DB Advance) with Cu Kα radiation (λ=1.5406 Å). SEM micrograph of Zn(II) complexes were obtained on a JOEL model JSM- 6390LV scanning electron microscope.

Materials: All solvents and reagents used for the synthesis of the metal complexes were of analytical grade. Main solvents required for the synthesis work was ethanol and methanol which were used after distillation. Rest of the solvents and reagents were used as received with AR grade. Zinc(II) acetate dihydrate was purchased from Aldrich Chemical Company.

General Procedure for the synthesis of Bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)arene/ alkanes: Triazoles were synthesized by dropwise addition of carbon disulphide (0.02 mol) to the methanolic solution (30 cm^3) of appropriate acid dihydrazide (0.01 mol) and potassium hydroxide (0.02 mol) with continuous stirring. After 2-3 h a solid mass was obtained, which was refluxed with hydrazine hydrate (0.022 mol) for *ca.* 4 h. The reaction mixture was cooled at room temperature and then the mixture was poured in cold water followed by addition of dilute hydrochloric acid in order to precipitate out the desired product. The product was then filtered off, washed with ether and recrystallized from ethanol.

Synthesis and characterization of Schiff bases (L_1H_4 -L_6H_4): Bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)arene/alkanes (0.02 mol) was dissolved in ethanol (30 mL) followed by addition of salicylaldehyde/2-hydroxyacetophenone (0.04 mol) in 1:2 molar ratio respectively. Then added few drops of concentrated hydrochloric acid and refluxed for 7-8 h. The reaction mixture was concentrated to 10 mL and ether was added. The product was filtered off, washed with ether and dried under vacuo.

The reaction scheme for the synthesis of ligands and their corresponding Zinc(II) complexes are given in figure 1.

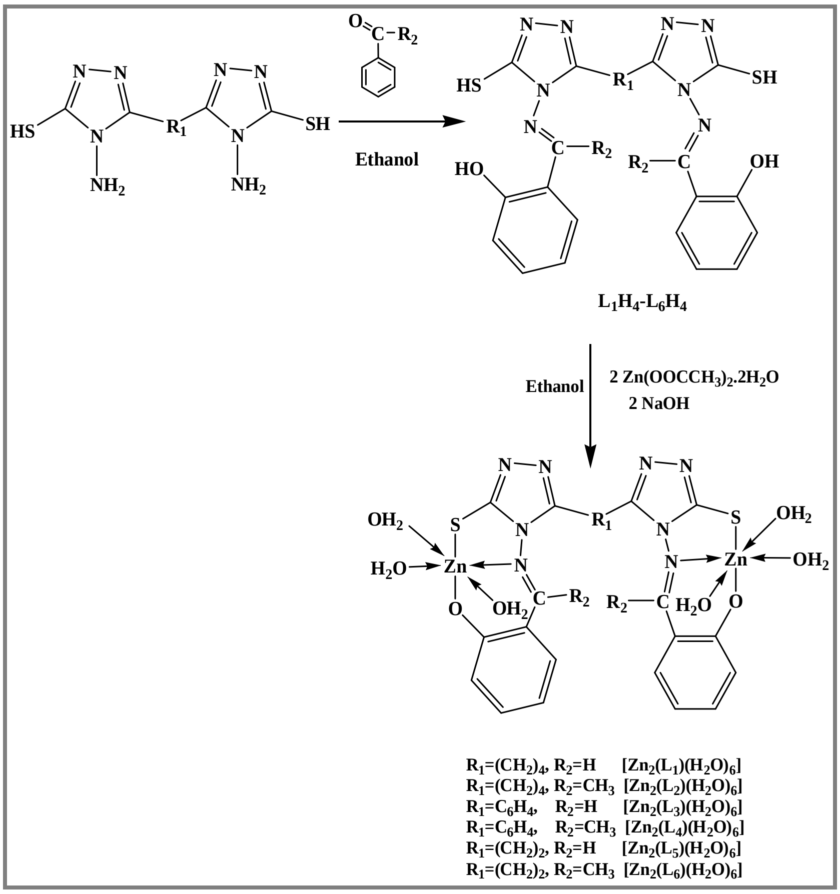


Figure 1. Reaction flowchart for the synthesis of Schiff bases and their zinc(II) complexes.

Synthesis and characterization of zinc(II) complexes(1-6): An ethanolic solution (25 cm^3) of zinc(II) acetate dihydrate (0.02 mol) was added to a refluxing solution of appropriate Schiff base (0.01 mol) in ethanol (25 cm^3) containing sodium hydroxide (0.02 mol). The reaction mixture was refluxed for about 10-12 h. The colored complex thus obtained was filtered off, washed thoroughly with ethanol and dried under *vacuo*.

Complex 1: $[(Zn)_2(L_1)(H_2O)_6]$, $C_{22}H_{30}O_8N_8S_2Zn_2$. Yield 64%, m.p. 202^{o}C. Anal. Calcd (%): C, 36.23; H, 4.12; N, 15.36; S, 8.78, Zn, 17.84. Found (%): C, 36.09; H, 4.01; N, 15.14; S, 8.56; Zn, 17.63. FT-IR (KBr) (ν; cm^{-1}): 3341 (-OH), 3115-3045 (Ar-H), 1618 (C=N), 1571 (-C=N, triazole ring), 482 (Zn-O), 432 (Zn-N), 415 (Zn-S). ^{1}H NMR (DMSO-d_6) [δ; ppm]: 8.64 (s, 2H, -CH), 7.12-7.53 (m, 8H, Ar-H), 5.45 (s, 6H, H_2O), 2.53 (m, 4H, $-CH_2$), 2.31 (m, 4H, $-CH_2$). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.7 (2C, -C=N, triazole), 155.3 (2C, -C=N), 153.4 (2C, -C=N, triazole), 127.7 (2C, Ar), 127.2 (2C, Ar), 126.5 (2C, Ar), 124.1 (2C, Ar), 123.4 (2C, Ar), 121.2 (2C, Ar), 27.2-27.8 (4C, $-(CH_2)_4-$).

Complex 2: $[(Zn)_2(L_2)(H_2O)_6]$, $C_{24}H_{34}O_8N_8S_2Zn_2$. Yield 62%, m.p. 240^{o}C. Anal. Calcd (%): C, 38.06; H, 4.49; N, 14.80; S, 8.46, Zn, 17.18. Found (%): C, 37.89; H, 4.23; N, 14.61; S, 8.28; Zn, 17.01. FT-IR (KBr) (ν; cm^{-1}): 3338 (-OH), 3110-3042 (Ar-H), 1615 (C=N), 1570 (C=N, triazole ring) 480 (Zn-O), 430 (Zn-N), 412 (Zn-S). ^{1}H NMR (DMSO-d_6) [δ; ppm]: 7.12-7.51 (m, 8H, Ar-H), 5.44 (s, 6H, H_2O), 2.55 (m, 4H, $-CH_2$), 2.33 (m, 4H, $-CH_2$), 1.27 (s, 6H, $-CH_3$). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.6 (2C, -C=N, triazole), 155.2 (2C, -C=N), 153.2 (2C, -C=N, triazole), 127.6 (2C, Ar), 127.1 (2C, Ar), 126.6 (2C, Ar), 124.2 (2C, Ar), 123.5 (2C, Ar), 121.4 (2C, Ar), 27.1-28.0 (4C, $-(CH_2)_4-$), 16.5 (2C, $-CH_3$).

Complex 3: $[(Zn)_2(L_3)(H_2O)_6]$, $C_{24}H_{26}O_8N_8S_2Zn_2$. Yield 58%, m.p. 249ºC. Anal. Calcd (%): C, 38.46; H, 3.47; N, 14.96; S, 8.54, Zn, 17.36. Found (%): C, 38.21; H, 3.23; N, 14.74; S, 8.37; Zn, 17.19. FT-IR (KBr) (ν; cm^{-1}): 3360 (-OH), 3124-3051 (Ar-H), 1620 (C=N), 1574 (-C=N, triazole ring), 485(Zn-O), 435 (Zn-N), 415 (Zn-S). ^1H NMR (DMSO-d_6) [δ; ppm]: 8.65 (s, 2H, -CH), 7.20-7.65 (m, 12H, Ar-H), 5.46 (s, 6H, H_2O). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.5 (2C, -C=N, triazole), 155.3 (2C, -C=N), 153.2 (2C, -C=N, triazole), 129.8 (1C, Ar), 129.7 (1C, Ar), 127.7 (2C, Ar), 127.4 (2C, Ar), 126.5 (2C, Ar), 126.4(1C, Ar), 126.2(1C, Ar), 125.4(1C, Ar), 125.1(1C, Ar), 124.1 (2C, Ar), 123.4 (2C, Ar), 121.2 (2C, Ar).

Complex 4: $[(Zn)_2(L_4)(H_2O)_6]$, $C_{26}H_{30}O_8N_8S_2Zn_2$. Yield 61%, m.p. 235ºC. Anal. Calcd (%): C, 40.17; H, 3.86; N, 14.42; S, 8.24, Zn, 16.74. Found (%): C, 39.97; H, 3.62; N, 14.26; S, 8.04; Zn, 16.56. FT-IR (KBr) (ν; cm^{-1}): 3355 (-OH), 3122-3047 (Ar-H), 1618 (C=N), 1572 (-C=N, triazole ring), 483 (Zn-O), 428 (Zn-N), 410 (Zn-S). ^1H NMR (DMSO-d_6) [δ; ppm]: 7.15-7.62 (m, 12H, Ar-H), 5.46 (s, 6H, H_2O), 1.28 (s, 6H, $-CH_3$). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.8 (2C, -C=N, triazole), 155.4 (2C, -C=N), 153.5 (2C, -C=N, triazole), 129.8 (1C, Ar), 129.6 (1C, Ar), 127.8 (2C, Ar), 127.3 (2C, Ar), 126.6 (2C, Ar), 126.3 (1C, Ar), 126.1(1C, Ar), 125.3 (1C, Ar), 124.9 (1C, Ar), 124.2 (2C, Ar), 123.5 (2C, Ar), 121.3 (2C, Ar), 17.5 (2C, $-CH_3$).

Complex 5: $[(Zn)_2(L_5)(H_2O)_6]$, $C_{20}H_{26}O_8N_8S_2Zn_2$. Yield 55%, m.p. 230°C. Anal. Calcd (%): C, 34.25; H, 3.71; N, 15.98; S, 9.13, Zn, 18.66. Found (%): C, 34.08; H, 3.57; N, 15.76; S, 8.92; Zn, 18.41. FT-IR (KBr) (ν; cm^{-1}): 3334 (-OH), 3122-3040 (Ar-H), 1618 (C=N), 1570 (-C=N, triazole ring), 478 (Zn-O), 431 (Zn-N), 410 (Zn-S). ^1H NMR (DMSO-d_6) [δ; ppm]: 8.62 (s, 2H, -CH), 7.12-7.55 (m, 8H, Ar-H), 5.49(s, 6H, H_2O), 2.51 (m, 4H, $-CH_{2-}$). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.3 (2C, -C=N, triazole), 155.3 (2C, -C=N), 153.2 (2C, -C=N, triazole), 128.3 (2C, Ar), 127.2 (2C, Ar), 126.8 (2C, Ar), 126.5 (2C, Ar), 123.2 (2C, Ar), 123.4 (2C, Ar), 27.2, (2C, $-(CH_2)_2-$).

Complex 6: $[(Zn)_2(L_6)(H_2 O)_6]$, $C_{22}H_{30}O_8N_8S_2Zn_2$. Yield 59%, m.p. 195°C. Anal. Calcd (%): C, 36.93; H, 4.19; N, 15.67; S, 8.95, Zn, 18.30. Found (%): C, 36.68; H, 4.02; N, 15.39; S, 8.74; Zn, 18.13. FT-IR (KBr) (ν; cm^{-1}): 3332 (-OH), 3115-3040 (Ar-H), 1616 (-C=N), 1568 (-C=N, triazole ring), 475 (Zn-O), 425 (Zn-N), 405 (Zn-S). ^1H NMR (DMSO-d_6) [δ; ppm]: 7.13-7.52 (m, 8H, Ar-H), 5.50 (s, 6H, H_2O), 2.51 (m, 4H, $-CH_2-$), 1.28 (s, 6H, $-CH_3$). ^{13}C NMR (DMSO-d_6) [δ; ppm]: 156.6 (2C, -C=N, triazole), 155.3 (2C, -C=N), 153.1 (2C, -C=N, triazole), 127.8 (2C, Ar), 127.3 (2C, Ar), 126.6 (2C, Ar), 124.1 (2C, Ar), 123.2 (2C, Ar), 121.5 (2C, Ar), 27.2, (2C, $-(CH_2)_2-$), 16.5 (2C, $-CH_3$).

Biological activities of zinc(II) complexes

Antifungal Activities: Antifungal activities of all Schiff bases and their corresponding complexes (1-6) were studied against three fungal strains (*A. niger, A. alternate, H. oryzae*) by agar plate technique at concentration of 1000, 100, 10 ppm with triplicate determination in each case. The results were recorded as percentage of inhibtion and compared with standard drug Fluconazole. For each compound 1% standard solution was prepared and 1mL of the solution was mixed with 9 mL of the solvent (DMSO). Three concentration viz. 10, 100, 1000 ppm stock solutions were prepared for each compound. In sterilized petriplates 1 mL of each concentration solution was mixed with 9 mL of agar medium. After the medium was prepared, fungus strain was inoculated in the center of each plate. The assay plates were incubated at 30ºC for 7days. The average percentage inhibition after 7 days was calculated using the formula:

$$\text{Percentage(\%) inhibition of mycelial growth} = 100(C-T)/C$$

Where, C= diameter of the fungus colony in control plate, T= diameter of the fungus colony in test plate.

Antibacterial Activities: Antibacterial activities of all Schiff bases and their respective complexes (1-6) were screened against Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli* by agar well diffusion method. The bacterial strains were grown in broth agar and incubated for 20 h at 37ºC for *E. coli* and 31ºC for *B. subtilis*. Tetracyclin was used as a standard for antimicrobial activity. Activity was studied by measuring the diameter of zones showing complete inhibition. The inhibition zone (mm) around each disk was measured after 24 h. Alternate studies on DMSO solution showed no activity against any bacterial strains.

Minimum inhibitory concentration (MIC): The minimum inhibitory concentration of zinc(II) complexes against bacterial strain was studied. The MIC was determined using the Broth dilution method. Cultures were grown for 24 h and bacterial growth was determined by measuring the optical density at 620 nm. Each tested compound were dissolved in 1 mL of DMSO separately to prepare stock solution and different concentration solution was prepared from the stock solution. The lowest concentration (µg mL^{-1}) of the test compound having no visible growth of bacteria were recorded.

RESULTS AND DISCUSSION

Zinc complexes were prepared by the reaction of the Schiff bases derived from bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)arene/alkanes and salicylaldehyde/2-hydroxyacetophenone with zinc(II) acetate dihydrate. All complexes are stable at room temperature and soluble in the solvents of DMSO, DMF.

Infrared spectra: In coordination complexes IR spectra provide valuable information regarding the nature of the functional group coordinated to the metal ion [29]. All Schiff bases and their zinc(II) complexes show bands 3128-3050 cm^{-1} due to ν(Ar-H). Schiff base exhibit strong band at 1618 cm^{-1} assigned to ν(C=N). In complexes this band shifts to lower frequency indicating contribution of azomethine nitrogen in bond formation with zinc ion. New band appear in complexes at 455-430 cm^{-1} due to ν(Zn-N). A broad band at 2680 cm^{-1} due to intramolecular H-bonded OH group in Schiff bases. This band disappear in corresponding zinc(II) complexes indicating the coordination of phenolic oxygen to zinc metal ion through deprotonation. It was confirmed by the appearance of the band at 475-445 cm^{-1} assignable to ν(Zn-O). A weak band at 2570-2490 cm^{-1} in the spectra of ligand was observed due to ν(S-H). This band was absent in the spectra of complex due to formation of ν(Zn-S), which was confirmed by appearance of a new band at 415-405 cm^{-1}. A broad band at 3380-3400 cm^{-1} arises due to ν(-OH) of coordination water molecules.

On the basis of IR spectral data, we inferred that the zinc metal ion is bonded with azomethine nitrogens, thiol sulphurs, phenolic oxygen and coordinated water oxygen's. These data confirmed that the synthesized ligands are tetrabasic, hexadentate chelating agents.

^{1}H NMR spectra: The proton magnetic resonance spectra of zinc(II) complexes have been analysed in deuterated dimethylsulphoxide. Schiff bases exhibit signal at 10.40 ppm phenolic protons, which disappears in the corresponding zinc(II) complexes; it proves that the hydroxyl group reacted with metal ion via deprotonation. Schiff bases and their corresponding zinc(II) complexes exhibit multiplet at 7.12-7.55 ppm due to aromatic protons. Schiff bases exhibit a signal at 3.2 ppm due to –SH proton, which disappears in the corresponding zinc(II) complex; that confirms the formation of Zn-S bond. Schiff bases (L_1H_4, L_3H_4, L_5H_4) and their corresponding zinc(II) complexes exhibit a signal at 8.10 ppm due to azomethine protons. Schiff bases (L_2H_4, L_4H_4, L_6H_4) and their corresponding zinc(II) complexes show a signal at 1.28 ppm assignable to methyl protons. Schiff bases (L_1H_4, L_2H_4) and their corresponding zinc(II) complexes show a signal at 2.32 and 2.54 ppm assignable to methylene protons. Schiff bases (L_5H_4, L_6H_4) and their corresponding zinc(II) complexes show a signal at 2.51 ppm assignable to methylene protons. All zinc(II) complexes show new signal at 5.4 ppm due to water protons.

^{13}C NMR spectra: ^{13}C NMR spectral data of zinc(II) complexes were recorded in DMSO-d$_6$. Ligands show signal at δ 155 for their azomethine carbons which shifts downfield in their respective zinc(II) complexes due to coordination with the azomethine nitrogen. Schiff bases and their corresponding zinc(II) complexes show signals at about δ 153-156 attributed to the triazol ring carbons. Schiff bases (L_2H_4, L_4H_4, L_6H_4) and their corresponding zinc(II) complexes possess a signal at δ 13.8 assignable to methyl carbons. Schiff bases (L_1H_4, L_2H_4) and their corresponding zinc(II) complexes show a signal at δ 27.1 and 28.0 assignable to methylene carbons. Schiff bases (L_5H_4, L_6H_4) and their corresponding zinc(II) complexes show a signal at δ 27.4 assignable to methylene carbons. A number of signals were observed in the spectra assignable to the aromatic ring.

Thermal analysis: In order to investigate the thermal stability of the complex $[(Zn)_2(L_1)(H_2O)_6]$, thermogravimetric analysis (TGA-DTG) was carried out upto 750°C. One of the reasons of thermogravimetric investigation is to confirm the existence or absence of water molecules in the structure of complexes. The TGA curve shows gradual weight loss at each step, indicating decomposition by fragmentation with rise in temperature. Weight loss of 14.80% (calc. 14.83%) in the range 105-152°C is assignable to the loss of coordinated water molecules. Gradual weight loss of 62.76% (calc. 62.85%) in the range 300-700°C is attributable to the complete decomposition of Schiff bases around the zinc ion and the complex was converted into 22.28% (calc. 22.32%) zinc oxide as final residue.

X-Ray diffraction study: The XRD pattern of the complex $[(Zn)_2(L_1)(H_2O)_6]$, clearly indicates the formation of nano-crystal. The particles size have been calculated by Debye-Scherer formula [30] given as $D=0.94\lambda/\beta\cos\theta$, where D is the size of the particle, λ is the wavelength of X-Ray used, β(expressed in radian) is the full width at half maximum (FWHM) and θ is the Bragg's angle of diffraction (Figure 2). The size of the particles was found to be in the range 15 nm to 29 nm which falls in the nano range.

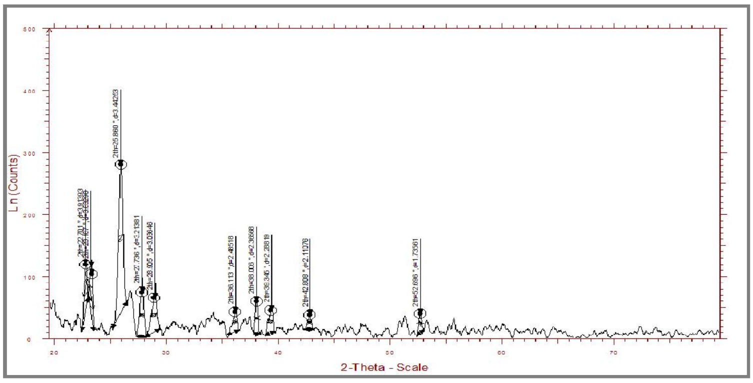


Figure 2. XRD Pattern for the complex $[(Zn)_2(L_1)(H_2O)_6]$.

The hkl indexing for the Zn(II) complexes were determined by comparing the powder XRD data from the database of diffraction pattern(ICDD-JCPDS). The Miller indices (hkl) relate the peak positions or d-spacing's to the lattice parameters by an equation specific to the crystal system. The initial unit cell (lattice) parameters were determined by trial and error method (Table 1). These unit cell parameters were refined from the regression analysis and the best crystal system and space group were assigned using CHECKCELL program. It was found that the zinc(II) complex have monoclinic crystal system with space group $P2_{1/c}$.

SEM analysis: Scanning Electron Microscope (SEM) analysis has been used to investigate the surface morphology of the complex $[(Zn)_2(L_1)(H_2O)_6]$. Fig. 3 shows scanning electron micrographs of the synthesized complex. The micrograph shows that there are irregular nanostructures of the synthesized complex (Figure 3).

Table 1. The unit cell parameters and observed and calculated X-Ray diffraction data of the Complex $[(Zn)_2(L_1)(H_2O)_6]$.

A=9.48911 Å,		b=9.22828 Å,		c=9.80723 Å,	β=90.92378º		V=858.6874 Å^3	
S.No.	**d(obs)**	**d(calc)**	**Δ(d)**	**I/Im×100**	**2 θ (obs)**	**2 θ (calc)**	**Δ(2 θ)**	**h k l**
1.	3.91390	3.91410	-0.00020	42.85	22.701	22.700	0.001	1 1 2
2.	3.83295	3.82972	0.00324	42.14	23.187	23.207	-0.020	-1 2 1
3.	3.44250	3.43711	0.00539	100	25.860	25.901	-0.041	-2 0 2
4.	3.21378	3.22013	-0.00635	27.54	27.736	27.680	0.056	-2 1 2
5.	3.08640	3.07882	0.00759	23.64	28.905	28.978	-0.073	0 1 3
6.	2.48519	2.48816	-0.00297	15.35	36.113	36.068	0.045	2 3 1
7.	2.36565	2.36793	-0.00229	21.39	38.006	37.968	0.038	0 1 4
8.	2.28817	2.28894	-0.00077	16.53	39.345	39.331	0.014	1 1 4
9.	2.11074	2.11056	0.00018	13.96	42.808	42.812	-0.004	-4 2 0
10.	1.73560	1.73482	0.00078	14.39	52.696	52.722	-0.026	3 4 2

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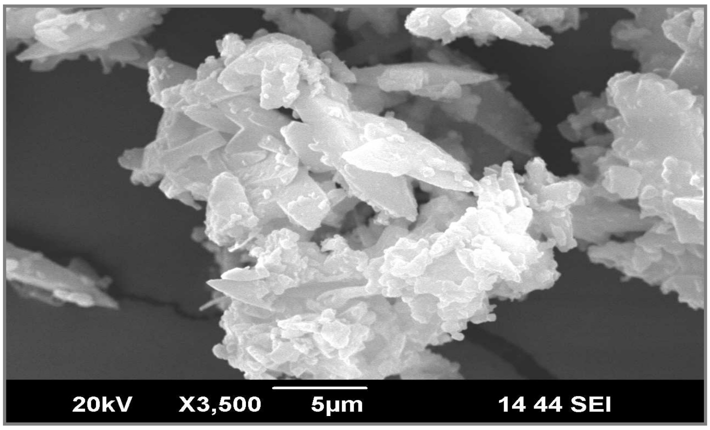

Figure 3. Scanning electron micrograph of complex $[(Zn)_2(L_1)(H_2O)_6]$.

APPLICATION

Antifungal and Antibacterial studies suggest that all the metal complexes possess higher activity than the corresponding Schiff bases. The results for antifungal, antibacterial activities are displayed in figure 4 and 5 and MIC results are shown in table 2. The comparative studies of compounds and standard drug are shown in figure 4 and 5. The higher antimicrobial activity of the metal complexes compared to Schiff bases is due to the change in structure, coordination and chelating tends to make

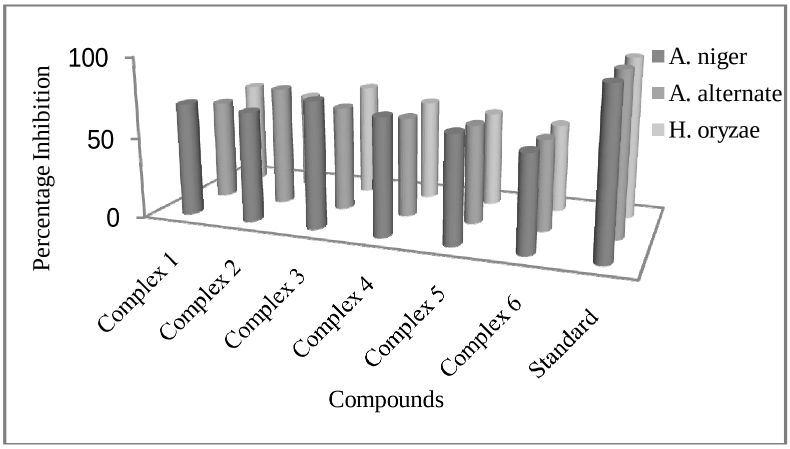

Figure 4. Comparison of antifungal activities of Complexes (1-6) and standard (Fluconazole) at 1000ppm concentration.

metal complexes to inhibit the growth of the microorganism. In antifungal activity we observed that all ligands and Zn(II) complexes are more active against *A. niger*. All Schiff bases and Zn(II) complexes were found to be more active against *E. coli.*

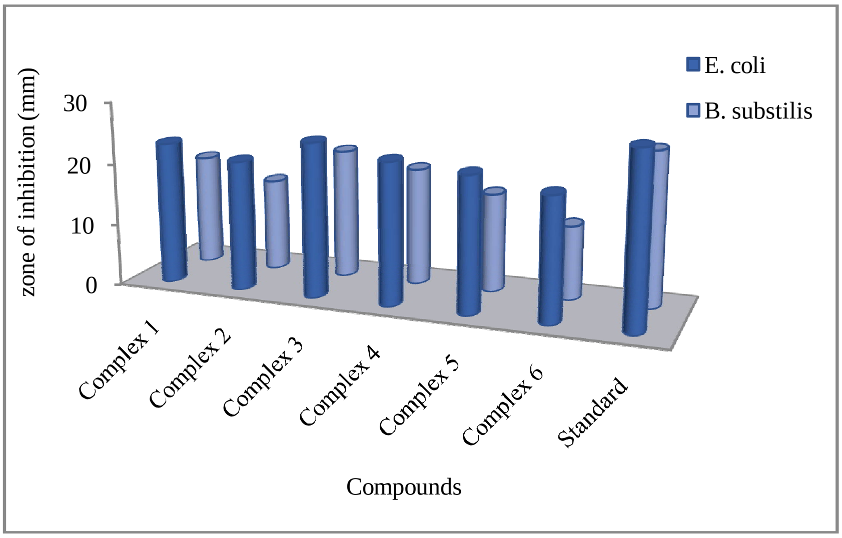

Figure 5. Comparison of antibacterial activity of Complexes (1-6) and standard (Tetracyclin).

Table 2. Minimum inhibitory concentration (MIC) results in (μg mL^{-1})

Compound	MIC	
	E. coli	*B.substilis*
$[(Zn)_2(L_1)(H_2O)_6]$	500	500
$[(Zn)_2(L_2)(H_2O)_6]$	71.42	500
$[(Zn)_2(L_3)(H_2O)_6]$	71.42	71.42
$[(Zn)_2(L_4)(H_2O)_6]$	71.42	500
$[(Zn)_2(L_5)(H_2O)_6]$	500	500
$[(Zn)_2(L_6)(H_2O)_6]$	500	500

(Results were recorded at concentrations 500, 71.42, 10.20, 1.45 and 0.2 μg mL^{-1})

CONCLUSION

The $N_2O_2S_2$ type Schiff bases were synthesized from Bis-(4-amino-5-mercapto-1,2,4 -triazol-3-yl)arene/alkanes and salicylaldehyde/2-hydroxyacetophenone, which were used to form stable complexes with Zn^{2+} ion. It acts as tetrabasic, hexadentate ligands and coordination takes place through azomethine nitrogen, mercapto sulfur, phenolic oxygen via deprotonation. An octahedral geometry of complexes has been confirmed by spectral data studies. The presence of water molecules in the complexes are supported by the result of thermogravimetric analysis. The data obtained from antifungal and antibacterial activities results show that all Zn(II) complexes are more biologically active against one or more bacterial or fungal strains than the parent ligands.

ACKNOWLEDGEMENTS

We are thankful to the UGC, New Delhi, for financial support. We are also thankful to the Head, SAIF, Cochin University for providing spectral data and Chemistry Department, DDU Gorakhpur University Gorakhpur for providing required facilities.

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