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Synthesis, spectral characterization and biological activity of zinc(II) complexes with 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases

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ABSTRACT

New Zn(II) complexes have been synthesized by the reactions of zinc(II) acetate with Schiff bases derived from 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole and benzaldehyde, 2-hydroxyacetophenone or indoline-2,3-dione. All these complexes are soluble in DMF and DMSO; low molar conductance values indicate that they are non-electrolytes. Elemental analyses suggest that the complexes have 1:1 stoichiometry of the type $[ZnL(H_2O)_2]$, $[ZnL'(OAc)_2(H_2O)_2]$ (L = dianionic Schiff bases derived from 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxyacetophenone or indoline-2,3-dione; L′ = neutral Schiff bases derived from 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole and benzaldehyde) and they were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and FAB mass. All these Schiff bases and their complexes have also been screened for their antibacterial activities against *Bacillus subtilis*, *Escherichia coli* and antifungal activities against *Colletotrichum falcatum*, *Aspergillus niger*, *Fusarium oxysporium* and *Carvularia pallescence* by petriplates methods.

1. Introduction

Metal complexes of Schiff bases are playing an important role in the development of coordination chemistry, which is evident in number of publications, including physicochemical studies [1] and biological aspects [2–6]. Triazoles and their derivatives are found to be associated with various biological activities, such as anticonvulsant, antifungal, anticancer, anti-inflammatory and antibacterial properties [7–15]. Several compounds containing 1, 2, 4-triazole ring are well known for drug synthesis [7]. 1, 2, 4-Triazole containing amino group is also important for obtaining various Schiff bases with well known antimicrobial properties [16–23]. The Zn(II) complexes of Schiff bases are also biologically active and they exhibit enhanced activities as compared to their parental ligands [22,24–26]. Several complexes of various transition metals with Schiff bases derived from 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole have been reported from our laboratory [27]. The ligands have donor sites with ONNO sequence and varied coordination ability. In this article we report the synthesis, characterization, antifungal and antibacterial activity of Zn(II) complexes derived from Schiff bases of 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole.

2. Experimental

2.1. Materials and reagents

The solvents were purchased from Merck and used without further purification. Zinc acetate dihydrate was purchased from Aldrich. The ligands were prepared as reported in literature [28].

2.2. Instruments

Melting points were determined by Buchi 530 apparatus in open capillary tubes. IR spectra were recorded by Shimadzu 8201 PC model FT IR spectrophotometer as KBr disks. ^{1}H and ^{13}C NMR spectra were recorded by a Bruker DRX-300 spectrometer using DMSO-d_6 as solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to an internal standard of Me_4Si. Elemental analysis was recorded by Elementar Vario EL III Carlo Erba 1108 models. Zinc was estimated gravimetrically as its dioxide ZnO_2. A known weight of the compound was decomposed by concentrated nitric acid and the mass was extracted with distilled water. Sodium carbonate solution was added. The precipitate obtained was filtered by Whatmann filter paper No. 41, and finally ignited in silica crucible to zinc oxide. Elemental analysis (C, H, N, Zn) indicates that the found and calculated values were within acceptable limits (±0.5). Molar conductance of 10^{-3} M solutions of the complexes in DMSO was recorded on a Hanna EC 215 conductivity meter by using 0.01 M KCl water solution as calibrant. Magnetic measurements were

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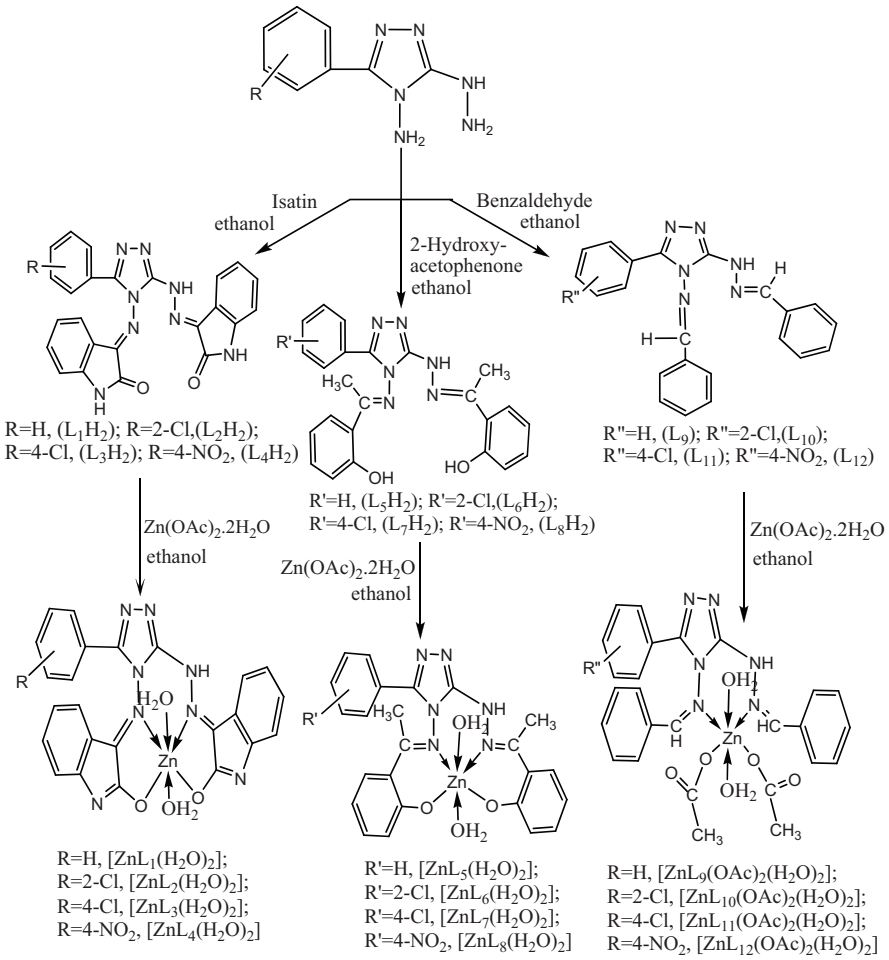

Fig. 1. Reaction scheme for the preparation of Schiff bases and their zinc(II) complexes.

carried out on a Sherwood Scientific magnetic balance according to the Gouy method. The purity of compounds was checked by thin layer chromatography on silica gel plate using ether and ethyl acetate as a solvent system. Iodine chamber was used as a developing chamber.

2.3. Synthesis of 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole

A mixture of 3-(substituted phenyl)-4-amino-5-mercapto-1, 2, 4-triazole and $N_2H_4{\cdot}H_2O$ in molar proportions in ethanol was boiled under reflux for 4–5 h on a water bath. The reaction mixture was cooled at room temperature, within an hour the compound separated from the clear solution. It was filtered, washed and recrystallized in ethanol.

2.4. Synthesis of Schiff bases

A mixture of 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxyacetophenone/indoline-2,3-dione/benzaldehyde in 1:2 molar ratio in an alcoholic medium containing a few drops of conc. HCl was refluxed for 5–6 h. The product separated on evaporation of the alcohol was recrystallized in ethanol.

2.5. Synthesis of zinc(II) complexes

A general procedure was followed to synthesize these complexes. The procedure involves the addition of the appropriate ligand (0.04 mol) to an aqueous ethanolic solution of zinc acetate dihydrate (0.04 mol) and sodium acetate (0.08 mol). The mixture was refluxed for 10–11 h on a water bath. Light yellow or brown precipitate obtained was filtered, washed with ethanol and hot water and dried *in vacuo* at room temperature. The complexes were obtained as powdered material.

The details of the reactions along with the analytical data of the product are given in Table 1. The general reaction scheme is given in Fig. 1.

2.6. Biological activity study

2.6.1. Bio safety during the antibacterial and antifungal activity

Bacteria/fungi are potentially hazardous and care should be taken while working with them. Standard bio safety lab techniques were followed while handling bacteria/fungi and various media. Gloves were used during all experimentation, and any accidental spills were immediately sterilized using 70% isopropanol/water followed by bleach. The work area was also sterilized with 70% isopropanol/water after completion of work. Unused media and bacterial suspensions were first deactivated with commercial bleach for 1 h before being disposed in bio safety bags. All material that had come in contact with bacteria (e.g., pipette tips, tubes, agar plates, etc.) was also thrown in bio safety bags in tightly closed bins. Bio safety bags were autoclaved for 2 h before final disposal.

2.6.2. Antimicrobial activity

Synthesized Schiff bases and Zn(II) complexes were screened for their antimicrobial activity against two bacterium (*E. coli* and

Table 1
Physical properties and analytical data of Zn(II) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases.

Complex	Colour	Molecular weight found (cal.)	% Analysis found (cal.)			
			C	H	N	Zn
$[ZnL_1(H_2O)_2]$	Brown	546(547.86)	52.55(52.61)	3.20(3.31)	20.34(20.45)	11.85(11.94)
$[ZnL_2(H_2O)_2]$	Brown	581(582.10)	49.41(49.50)	2.86(2.94)	19.12(19.24)	11.11(11.23)
$[ZnL_3(H_2O)_2]$	Yellow	581(582.12)	49.43(49.50)	2.85(2.94)	19.16(19.24)	11.10(11.23)
$[ZnL_4(H_2O)_2]$	Orange	590(592.85)	48.50(48.62)	2.80(2.89)	21.16(21.26)	10.95(11.03)
$[ZnL_5(H_2O)_2]$	Cream	524(525.89)	54.71(54.81)	4.55(4.60)	15.87(15.98)	12.30(12.44)
$[ZnL_6(H_2O)_2]$	Cream	559(560.34)	51.32(51.44)	4.10(4.14)	14.95(15.00)	11.60(11.67)
$[ZnL_7(H_2O)_2]$	Yellow	558(560.34)	51.35(51.44)	4.11(4.14)	14.93(15.00)	11.62(11.67)
$[ZnL_8(H_2O)_2]$	Brown	569(570.89)	50.33(50.49)	4.00(4.06)	17.10(17.17)	11.40(11.46)
$[ZnL_9(OAc)_2(H_2O)_2]$	White	584(585.94)	53.20(53.29)	4.75(4.82)	14.29(14.34)	11.10(11.16)
$[ZnL_{10}(OAc)_2(H_2O)_2]$	Muddy	618(620.39)	50.25(50.34)	4.30(4.39)	13.45(13.55)	10.45(10.54)
$[ZnL_{11}(OAc)_2(H_2O)_2]$	Yellow	620(620.39)	50.20(50.34)	4.31(4.39)	13.46(13.55)	10.47(10.54)
$[ZnL_{12}(OAc)_2(H_2O)_2]$	White	630(630.94)	49.33(49.49)	4.25(4.31)	15.45(15.54)	10.20(10.37)

B. subtilis) and four fungal (*C. falcatum*, *A. niger*, *F. oxysporium* and *C. pallescence*) organisms by different two ways.

2.6.2.1. Growth of inhibition. All Schiff bases and Zn(II) complexes were screened for their activity against four fungal organisms *C. falcatum*, *A. niger*, *F. oxysporium* and *C. pallescence* and two bacteria namely *B. subtilis*, *and E. coli* by petridishes method [29]. Fungicidal and bactericidal activity of each compound was evaluated at three different concentrations, *i.e.*, 10, 100 and 1000 ppm. For each compound 1% standard solution was prepared and 1 ml of the solution was diluted with 9 ml of the solvent (DMSO). Petridishes of equal diameter were sterilized at 180 °C. Stock solutions of each compound were prepared for three concentration *viz.* 10, 100 and 1000 ppm. Solution of 1 ml of each concentration was poured in presterilized petridishes and 9 ml of agar medium was added immediately. Each dish was rotated on the table top in order to achieve thorough mixing of medium with the compound. After this, fungus and bacterial strain was inoculated in the dishes (diameter 5 mm). These set were then inoculated at 30 ± 2 °C. The colony diameter of the test organism was measured with mm scale after 6 days. The percentage inhibition of the growth of the test organism was calculated by following formula

$$\text{inhibition}\,(\%) = \frac{\text{Cd} - \text{Td}}{\text{Cd}} \times 100$$

where Cd = colony diameter of control; Td = colony diameter of treated set.

2.6.2.2. Minimum inhibitory concentration MIC (ppm). The minimum inhibitory concentration to 99% kill of the bacterial population (MIC) of against the bacterial strain was determined by reported methods [30]. Bacteria were grown overnight in 10 ml of LB, 37 °C for *E. coli* and 30 °C for *B. subtilis* at 220 rpm. A total of 100 μl of the overnight culture was subcultured in 10 ml of LB, 220 rpm and grown to exponential phase (OD_{600} = 2.3299), and 1 ml was then inoculated into LB broth containing various concentrations of Schiff base and there Zn(II) complexes (OD_{600} = 1.000) maintained by adding DMSO. Cultures were then grown for 24 h, 220 rpm and bacterial growth was determined by measuring the optical density at 600 nm. Fungal MIC was measured by reported methods [31].

3. Results and discussion

Zn(II) complexes are sparingly soluble in common solvents; however, these complexes are soluble in DMF and DMSO. The molar conductivity values for all Zn(II) complexes in (10^{-3} M) were in range of 6–15 Ω^{-1} cm^2 mol^{-1} suggesting them to be non-electrolytes. Magnetic susceptibility measurement shows that the weight of complexes is unaffected in magnetic field which indicates that they are diamagnetic.

3.1. Infrared spectra

The characteristic FT-IR spectral bands of Zn(II) derivatives are given in Table 2. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. Schiff bases (L_1H_2–L_4H_2) appear to exist in both keto and enol tautomeric forms (Fig. 2) suggested by a broad band (solution spectra) at 2600 cm^{-1}, due to intramolecular H-bonded OH group. The spectra of Schiff bases show a medium band at 3175 cm^{-1} due to ν(N–H) which remains almost at the same position in complex indicating the non involvement of N–H group in bond formation. The ligands show one medium intensity band at 1630 cm^{-1} assignable [27] to ν(C=N) which shifts to 1605 cm^{-1} in the complexes. This shift indicates the coordination of azomethine nitrogen to metal ion [32–35]. The bands at 435–400 cm^{-1} are assigned [35] to ν(Zn–N). L_5H_2–L_8H_2 Schiff bases show broad band at 2640 cm^{-1} due to intramolecular H-bonded OH group. This band disappears in their corresponding Zn(II) complexes indicating the coordination of phenolic oxygen to zinc metal ion through deprotonation. This is further supported by shift in phenolic ν(C–O) band from 1285 cm^{-1} (in the free ligand) to 1380–1310 cm^{-1} in the complexes. The coordination through phenolic oxygen further confirmed by the appearance of band at 480–445 cm^{-1} assignable [36] to ν(Zn–O). The presence of coordinated water in the complexes [37] is indicated by a broad band in the region 3400 cm^{-1} and two weaker bands in the region 810–750 and 730–700 cm^{-1} due to ν(–OH) rocking and wagging mode of vibrations, respectively [38]. The complexes with ligands L_9–L_{12} show strong bands in the region 1750–1720 cm^{-1} which are assigned to ν($OOCCH_3$). In complexes Zn–O band appears at 402–380 cm^{-1} [39], which indicates that metal zinc is bonded to acetate molecule. Further, the absorption at 1616 and 1410 cm^{-1}, confirm the monodentate nature of the acetate ion in complexes with ligand L_9–L_{12} [39].

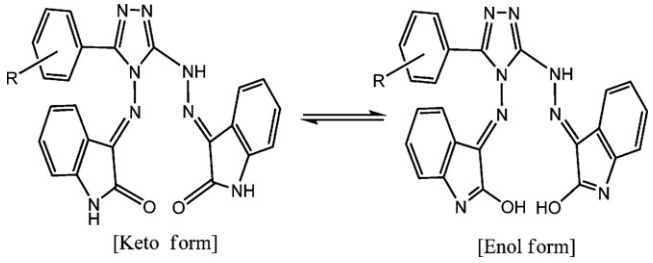

Fig. 2. Synthesized Schiff bases in tautomeric forms.

Table 2
The importance infra red frequencies in (cm^{-1}) of Zn(II) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases.

Complex	IR frequency (cm^{-1})							
	ν(O–H)	ν(N–H)	ν(CH_3COO)	ν(C=N)	ν(C=C)	Phenolic ν(C–O)	ν(Zn–O)	ν(Zn–N)
$[ZnL_1(H_2O)_2]$	3430	3175	–	1595	1575	1375	450	425
$[ZnL_2(H_2O)_2]$	3434	3170	–	1580	1580	1350	452	435
$[ZnL_3(H_2O)_2]$	3340	3172	–	1600	1615	1343	455	419
$[ZnL_4(H_2O)_2]$	3445	3170	–	1588	1570	1380	445	430
$[ZnL_5(H_2O)_2]$	3435	3170	–	1580	1575	1355	460	415
$[ZnL_6(H_2O)_2]$	3436	3175	–	1615	1578	1350	465	410
$[ZnL_7(H_2O)_2]$	3438	3180	–	1605	1595	1310	462	400
$[ZnL_8(H_2O)_2]$	3446	3185	–	1610	1598	1340	470	405
$[ZnL_9(OAc)_2(H_2O)_2]$	3425	3155	1735	1595	1576	–	480	420
$[ZnL_{10}(OAc)_2(H_2O)_2]$	3432	3165	1740	1580	1585	–	475	422
$[ZnL_{11}(OAc)_2(H_2O)_2]$	3431	3170	1750	1590	1592	–	472	425
$[ZnL_{12}(OAc)_2(H_2O)_2]$	3442	3175	1745	1610	1580	–	470	430

3.2. ^1H NMR spectra

The proton magnetic resonance spectra of these complexes have been recorded in DMSO-d_6. Chemical shifts for protons in different environments have been given in Table 3. Schiff bases derived from indoline-2, 3-dione of type (L_1H_2–L_4H_2) exhibit signals at 12.40 and 5.5 ppm due to hydrazino NH proton and indoline-2, 3-dione NH proton, respectively. In zinc(II) complexes indoline-2, 3-dione NH peak disappears. Multiplet is observed at 7.00–7.75 ppm due to aromatic protons in the Schiff bases and their corresponding Zn(II) complexes. Zinc (II) complexes show new signal at 5.6 ppm which are assigned for water protons.

Schiff bases derived from 2-hydroxyacetophenone (L_5H_2–L_8H_2) exhibit signals at 12.66 and 10.50 ppm due to hydrazino NH and phenolic –OH proton respectively and phenolic protons disappear in their corresponding Zn(II) complexes; this confirms that the hydroxyl group reacted with metal ion *via* deprotonation. Multiplet is observed at 7.00–7.70 ppm due to aromatic protons in the Schiff bases and their corresponding Zn(II) complexes. Schiff bases (L_5H_2–L_8H_2) and their corresponding Zn(II) complexes also exhibit a signal at 1.15–1.30 ppm due to methyl protons and zinc(II) complexes ($[ZnL_5{\cdot}H_2O)_2]$–$[ZnL_8{\cdot}(H_2O)_2]$) show new signal at 5.4 ppm due to the water protons.

The ^1H NMR spectra of Schiff bases of type (L_9–L_{12}) exhibit signals at 12.4 and 8.10 ppm due to NH and azomethine protons, respectively. In zinc(II) complexes, the first signal remains almost at the same position but the second signal shifts downfield. The downfield shift indicates the deshielding effect due to the coordination of azomethine nitrogen to central metal ion. Complexes of type ($[ZnL_9(OAc)_2{\cdot}(H_2O)_2]$–$[ZnL_{12}(OAc)_2{\cdot}(H_2O)_2]$) show signal at 2.48–2.50 ppm due to methyl protons of coordinated acetate molecules [34]. Schiff bases and their corresponding Zn(II) complexes show multiplet at 6.98–7.80 ppm due to aromatic protons. Zinc(II) complexes also show new signal at 5.5 ppm due to the water protons.

3.3. ^{13}C NMR spectra

The ^{13}C NMR spectra of these complexes were recorded (Table 3) in DMSO-d_6. Schiff bases derived from Indoline-2, 3-dione (L_1H_2–L_4H_2) show signals at δ 156 and δ 147 for their azomethine carbons and they shift downfield in their corresponding zinc(II) complexes due to the coordination through azomethine nitrogens.

Schiff bases derived from 2-hydroxyacetophenone (L_5H_2–L_8H_2) show signals at δ 164 and δ 154 for their azomethine carbons and they shift downfield in zinc metal complexes due to coordination through the azomethine nitrogen. For $–CH_3$ carbon, a signal appears at δ 13.5 in ligands and their corresponding complexes.

Schiff bases derived from benzaldehyde (L_9–L_{12}) show signals at δ 174 and δ 166 for their azomethine carbons and they shift downfield in their corresponding zinc(II) complexes due to coordination through the azomethine nitrogen. The complexes of type ($[ZnL_9(OAc)_2{\cdot}(H_2O)_2]$–$[ZnL_{12}(OAc)_2{\cdot}(H_2O)_2]$) show signals at δ 23.5 (CH_3) and δ 181.5 (–COO) due to the presence of coordinated acetate molecules.

Schiff bases of type (L_1H_2–L_8H_2, and L_9–L_{12}) and their corresponding zinc(II) complexes show signals at about δ 158 and δ 152 assignable for triazole ring carbons. For aromatic ring, a number of signals appear.

3.4. FAB mass spectra

The molecular weight of the complexes, as determined from their FAB-mass spectra, is given in Table 1. Elemental analysis values are in close agreement with the values calculated from

Table 3
^1H NMR and ^{13}C NMR spectral band (ppm) of Zn(II) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases.

Compound	NMR data				^{13}C NMR			
	–NH(s)	$–CH_3$(s)	Aromatic ring (M)	–HC=N(S)	–COO	$–CH_3$	–C=N	Aromatic ring
$[ZnL_1(H_2O)_2]$	12.40	–	7.02–7.51	–	–	–	166.3,156.7	150.2,131.2,130.6,130.2,129.4,127.5,126.6,122
$[ZnL_2(H_2O)_2]$	12.42	–	7.02–7.55	–	–	–	166.1,156.1	150.3,138.7,132.5,130.3,130.0,129.4,128.9,127.3,126.7
$[ZnL_3(H_2O)_2]$	12.41	–	7.00–7.65	–	–	–	166.2,156.2	151.2,135.2,130.2,129.5,128.9128.7,126.7,122
$[ZnL_4(H_2O)_2]$	12.40	–	7.05–7.70	–	–	–	166.3,156.4	149.5,147.9,130.2,127.7,126.6,124.8,122.3
$[ZnL_5(H_2O)_2]$	12.44	1.15	6.95–7.45	–	–	13.3	165.3,157.2	131.3,130.7,129.5,127.5,121.4,116,115.9
$[ZnL_6(H_2O)_2]$	12.45	1.18	6.92–7.40	–	–	13.4	165.4,157.3	135.2,130.2,129.9,128.7,121.4,116.3,115.9
$[ZnL_7(H_2O)_2]$	12.41	1.24	6.90–7.35	–	–	13.5	165.7,157.5	148.3,137.5,130.2,127.3,124.5,121.3,116.2,116.2,115.9
$[ZnL_8(H_2O)_2]$	12.40	1.30	6.91–7.37	–	–	14.2	165.8,157.7	150.3,131.4,130.9,130.6,129.7,128.9,127.8
$[ZnL_9(OAc)_2(H_2O)_2]$	12.30	2.48	6.98–7.70	8.26	181.3	23.6	166.6,158.5	150.3,138.6,132.8,131.4,130.7,129.6,129.1,129.8,127.6
$[ZnL_{10}(OAc)_2(H_2O)_2]$	12.45	2.54	7.05–7.80	8.31	181.5	23.4	167.3,158.5	150.9,136.6,131.5,130.5,129.6,128.6
$[ZnL_{11}(OAc)_2(H_2O)_2]$	12.43	2.52	7.04–7.75	8.34	181.8	23.8	167.1,158.6	150.8,131.2,132.2,131.0,129.7,128.6,126.9
$[ZnL_{12}(OAc)_2(H_2O)_2]$	12.40	2.57	7.00–7.80	8.28	182.6	23.5	167.4,158.9	151.0,132.1,132.8,131.5,129.9,128.7,127.4

Table 4
Fungicidal screening data of Zn(II) complexes of 3-[substituted phenyl]-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases.

Compound	% Fungicidal inhibition ppm											
	C. falcatum			*A. niger*			*F. oxysporium*			*C. pallescence*		
	1000	100	10	1000	100	10	1000	100	10	1000	100	10
$[ZnL_1(H_2O)_2]$	75	55	40	70	50	35	73	54	38	70	52	42
$[ZnL_2(H_2O)_2]$	95	81	56	91	80	50	93	79	52	90	70	51
$[ZnL_3(H_2O)_2]$	91	80	56	89	76	47	90	75	50	87	67	49
$[ZnL_4(H_2O)_2]$	83	70	50	81	69	50	85	72	60	82	64	53
$[ZnL_5(H_2O)_2]$	70	60	40	75	61	45	69	58	43	67	58	43
$[ZnL_6(H_2O)_2]$	90	77	58	85	67	51	87	74	54	84	64	50
$[ZnL_7(H_2O)_2]$	85	73	60	80	64	49	83	70	51	80	64	49
$[ZnL_8(H_2O)_2]$	80	69	59	77	63	50	79	64	51	78	65	55
$[ZnL_9(OAc)_2(H_2O)_2]$	69	58	41	85	60	33	81	65	51	65	55	45
$[ZnL_{10}(OAc)_2(H_2O)_2]$	85	65	45	87	69	48	92	66	54	85	58	48
$[ZnL_{11}(OAc)_2(H_2O)_2]$	80	63	51	81	63	44	91	74	57	81	57	47
$[ZnL_{12}(OAc)_2(H_2O)_2]$	75	68	48	82	61	45	91	61	46	79	52	46
Standard	100	100	100	100	100	100	100	100	100	100	100	100

Table 5
Bactericidal Screening data of Zn(II) complexes of 3-[substituted phenyl]-4-amino-5-hydrazino-1, 2, 4-triazole Schiff bases.

Compound	% Bactericidal inhibition concentration in ppm					
	B. subtilis			*E. coli*		
	1000	100	10	1000	100	10
$[ZnL_1(H_2O)_2]$	63	52	36	64	56	38
$[ZnL_2(H_2O)_2]$	69	59	43	71	61	44
$[ZnL_3(H_2O)_2]$	65	54	40	67	58	42
$[ZnL_4(H_2O)_2]$	68	58	37	68	60	40
$[ZnL_5(H_2O)_2]$	62	53	31	63	56	34
$[ZnL_6(H_2O)_2]$	67	57	37	70	62	39
$[ZnL_7(H_2O)_2]$	63	53	35	65	57	36
$[ZnL_8(H_2O)_2]$	66	55	33	67	60	34
$[ZnL_9(OAc)_2(H_2O)_2]$	59	47	30	62	49	32
$[ZnL_{10}(OAc)_2(H_2O)_2]$	66	54	35	68	57	39
$[ZnL_{11}(OAc)_2(H_2O)_2]$	62	49	34	66	51	38
$[ZnL_{12}(OAc)_2(H_2O)_2]$	65	51	31	67	55	35
Standard	100	100	100	100	100	100

molecular formulas assigned to these complexes, which is further supported by the FAB-mass studies.

3.5. Microbial activity

Microbial studies suggested that all the Schiff bases are antimicrobial active and their Zn(II) complexes shows importantly raised antibacterial and antifungal activities. The antibacterial, antifungal results are systematized in Tables 4 and 5 and MIC of the 2-chloro substituted Zn(II) complexes are shown in Table 6. The comparative data for active compounds and standard drug used for present study is shown in Fig. 3. This experimental observation indicates that increases chelation, bacterial and fungal growth inhibition also increases. Previously reported [40,41] observation shows that heterocyclic ring has cell wall damaged capacity, in newly synthesized Schiff bases have oxadiazole ring which contact with the microbes cell wall and damaged this causes microbes dead. The actual mechanism of increased activity of complexes is not certain but factors like solubility, dipole moment and cell permeability mechanism and their enzymatic action may be the possible reason.

In antifungal strain we observed that the all ligands and Zn(II) complexes are more active against *C. falcatum*. Substitution of the ligands increases the activity against bacteria and fungi. 2-Chloro

Table 6
Minimum inhibitory concentration results in ppm.

Microbes	MIC in ppm		
	$[ZnL_2(H_2O)_2]$	$[ZnL_6(H_2O)_2]$	$[ZnL_{10}(OAc)_2(H_2O)_2]$
B. subtilis	>2000	>2200	>2250
E. coli	>1700	>1750	>1900
C. falcatum	>1300	>1400	>1450
A. niger	>1450	>1600	>1700
F. oxysporium	>1400	>1500	>1550
C. pallescence	>1500	>1700	>1800

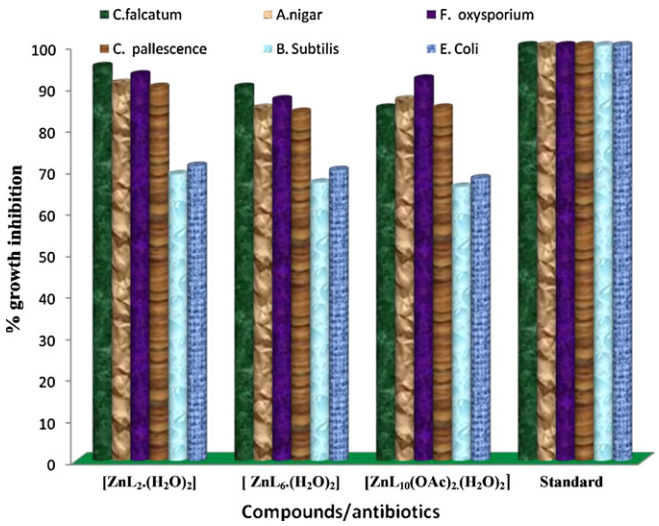

Fig. 3. *In vitro* antibacterial and antibacterial spectrum of compounds $[ZnL_2(H_2O)_2]$, $[ZnL_6(H_2O)_2]$, $[ZnL_{10}(OAc)_2(H_2O)_2]$ Standard (gentamycine for antibacterial and fluconazole for antifungal) at 1000 ppm concentration.

substituted ligands/compounds are more active than the other substituted ligands/compounds due to the chelating properties of 2-chloro group. The compound $[ZnL_2(H_2O)_2]$ is more active against all bacteria and fungi because they have additional heterocyclic ring (indoline-2,3-dione). All Schiff bases and Zn(II) complexes are more active against *E. coli.*

4. Conclusions

The new zinc(II) complexes with Schiff bases derived from 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole have been synthesized and characterized on the basis of analyses, electrical conductance, magnetic moment and spectral data. The Schiff bases derived from 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole and isatin/2-hydroxyacetophenone act as dibasic tetradentate ligands coordinating through the two azomethine nitrogens and two oxygen atoms to the metal ion. The ligands derived from 3-substituted phenyl-4-amino-5-hydrazino-1, 2, 4-triazole and benzaldehyde act as neutral, bidentate ligands. The six-coordinated structures of complexes have been proposed. Antifungal and antibacterial activity of the ligands and the complexes have also been evaluated which show that activity increases on chelation.

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