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Synthesis, spectral and antimicrobial activity of Zn(II) complexes with Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3, 4-thiadiazole and benzaldehyde/2-hydroxyacetophenone/indoline-2,3-dione

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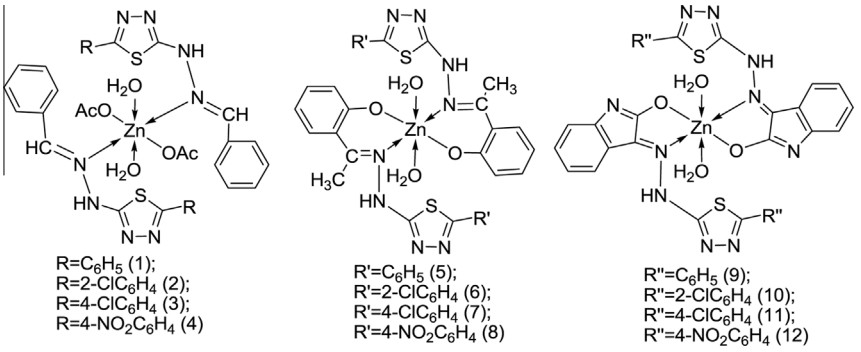
HIGHLIGHTS

- Zn(II) complexes with Schiff bases containing 1,3,4-thiadiazole ring have been synthesized and characterized.
- Schiff bases and their corresponding Zn(II) complexes are bactericidal in nature.
- Isatin derived compound 10 showed maximum activities against all microbes.
- MIC value of compound 10 was comparable to any commercial synthetic pesticide.

GRAPHICAL ABSTRACT



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ABSTRACT

Zn(II) complexes have been synthesized by reacting zinc acetate with Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thiadiazole and 2-hydroxyacetophenone/benzaldehyde/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 1:2 metal to ligands stoichiometry of the types $[ZnL_2(H_2O)_2]$(L = monoanionic Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thiadiazole and 2-hydroxyacetophenone/indoline-2,3-dione) $[ZnL'_2(OOCCH_3)_2(H_2O)_2]$ (L′ = neutral Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thiadiazole and benzaldehyde), and they were characterized by IR, ^{1}H NMR, and ^{13}C NMR. Particle sizes of synthesized compounds were measured with dynamic light scattering (DLS) analyser which indicates that particle diameter are of the range *ca.* 100–200 nm. All these Schiff bases and their complexes have also been screened for their antibacterial (*Bacillus subtilis* (*B. subtilis*), *Escherichia coli* (*E. coli*) and antifungal activities (*Colletotrichum falcatum* (*C. falcatum*), *Aspergillus niger* (*A. niger*), *Fusarium oxysporium* (*F. oxysporium*) *Curvularia pallescence* (*C.* pallescence). The antimicrobial activities have shown that upon complexation the activity increases.

Introduction

1,3,4-Thiadiazole derivatives are important class of biological active compounds showing anti-inflammatory, antimicrobial, antitumor properties [1–4], and other useful application are conducting polymer [5,6], solar cell [7], sensor [8,9], enzymatic application [10], energy storage [11], electrodes [12], anxiolytic activity [13], etc. Schiff base ligands are able to coordinate many elements

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Table 1
Physical properties and analytical data of Zn(II) complexes.

Complex	Mol. formula	% yield/color	Decomp. Temp. (°C)/λ_M^*	Molecular weight found(Cal.)	% Analysis found(Cal.)				
					C	H	N	S	Zn
1	$C_{34}H_{34}N_8O_6S_2Zn$	64/Light green	204/18	780(780.22)	52.22(52.34)	4.16(4.39)	14.12(14.36)	8.10(8.22)	8.11(8.38)
2	$C_{34}H_{32}N_8O_6Cl_2S_2Zn$	67/Yellow	270/19	849(849.11)	47.84(48.09)	3.45(3.80)	13.05(13.20)	7.34(7.55)	7.35(7.70)
3	$C_{34}H_{32}N_8O_6Cl_2S_2Zn$	71/Yellow	260/19	848(849.11)	47.80(48.09)	3.55(3.80)	13.07(13.20)	7.32(7.55)	7.45(7.70)
4	$C_{34}H_{32}N_{10}O_{10}S_2Zn$	74/Greenish-yellow	240/20	870(870.21)	46.84(46.93)	3.47(3.71)	16.02(16.10)	7.24(7.37)	7.37(7.52)
5	$C_{32}H_{30}N_8O_4S_2Zn$	70/White	280/12	719(720.17)	53.24(53.37)	4.12(4.20)	15.24(15.56)	8.45(8.90)	8.65(9.08)
6	$C_{32}H_{28}N_8O_4Cl_2S_2Zn$	72/Yellow	220/13	788(789.06)	48.44(48.71)	3.33(3.58)	14.04(14.20)	8.01(8.13)	8.11(8.29)
7	$C_{32}H_{28}N_8O_4Cl_2S_2Zn$	68/Yellow	280/13	788(789.06)	48.52(48.71)	3.48(3.58)	14.01(14.20)	8.07(8.13)	8.09(8.29)
8	$C_{32}H_{28}N_{10}O_8S_2Zn$	63/Brown	220/14	810(810.16)	47.21(47.44)	3.15 (3.48)	17.11(17.29)	7.64(7.92)	7.90(8.07)
9	$C_{32}H_{24}N_{10}O_4S_2Zn$	75/Orange	170/7	742(742.13)	51.48(51.79)	3.16(3.26)	18.55(18.87)	8.44(8.64)	8.63(8.81)
10	$C_{32}H_{22}N_{10}O_4Cl_2S_2Zn$	67/Brown	230/8	810(811.02)	47.19(47.39)	2.58(2.73)	17.04(17.27)	7.55(7.91)	7.71(8.07)
11	$C_{32}H_{22}N_{10}O_4Cl_2S_2Zn$	62/Chocolate	210/8	810(811.02)	47.14(47.39)	2.41(2.73)	17.14(17.27)	7.66(7.91)	7.71(8.07)
12	$C_{32}H_{22}N_{12}O_8S_2Zn$	72/Light orange	220/10	831(832.13)	46.03(46.19)	2.44(2.66)	20.02(20.20)	7.45(7.71)	7.41(7.86)

* $Ohm^{-1}\ cm^{-1}\ mol^{-1}$ (in DMSO).

and to stabilize them in various oxidation states. Furthermore, Schiff bases have been known to be used in the preparation of many potential drugs, and are known to possess a broad spectrum of biological activities such as antiviral [14], antifungal [15], antiparasitic [16], antibacterial [17], anti-inflammatory [18], antitumor [19], anti-HIV [20], and anticancer [21]. Schiff bases derived from 1,3,4-thiadiazole have been synthesized and extensively studied because they have some typical properties such as manifestations of original structures, thermal stability, significant biological properties, high synthesis flexibility and therapeutic utility [22]. Previously, many scientists reported that after complexation of transition metal complexes to Schiff bases microbial activity was generally increased [23].

Because of interesting observations on synthetic routes and applicability of zinc(II) complexes and Schiff bases, it was thought be of interesting to study the coordination behaviour of Schiff bases containing thiadiazole ring and to study their antimicrobial properties.

Experimental

Materials and reagents

The solvents and used chemicals were purchased from Merck and used without further purification. Zinc acetate dihydrate was purchased from Sigma–Aldrich.

Instruments

Melting points/decomposition temperature were determined on a Buchi 530 apparatus in open capillary tubes. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 kV, 10 mA) as the FAB gas. FT-IR spectra were recorded on a Shimadzu 8201 PC model FT-IR spectrophotometer as KBr disks. ^1H and ^{13}C NMR spectra were recorded on 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 Analyses were recorded by Elementar Vario EL III Carlo Erba 1108 models. Dynamic radiuses of synthesized complexes were measured with help of Nano BioChem DLS analyser. Powdered XRD were scanned by Philips Xpert X-ray diffractometer with CuKα (1.54056) radiation. 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. 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.

Synthesis of 5-[substituted phenyl] 2- mercapto-1,3,4-thiadiazole

5-[Substituted phenyl]-2-mercapto-1,3,4-thiadiazoles were prepared according to the method of Mishra et al. [24].

Preparation of 5-(substituted phenyl)-2-hydrazino-1,3,4-thiadiazole

A mixture of 5-[substituted phenyl]-2-mercapto-1,3,4-thiadiazole and hydrazine hydrate in 1:1 molar ratio in ethanol was refluxed for about 4–5 h on water bath. The reaction mixture was cooled to room temperature; within an hour the compound precipitated from the clear solution. It was filtered off, washed and recrystallized in ethanol.

Synthesis of Schiff bases (L_1–$L_{12}H$)

A mixture of 5-[substituted phenyl]-2-hydrazino-1,3,4-thiadiazole and benzaldehyde/2-hydroxyacetophenone/indoline-2, 3-dione in 1:1 molar ratio was refluxed in ethanol (25 cm^3) containing few drops of conc. HCl for 5–6 h. The product was separated out on evaporation of the ethanol which was recrystallized in ethanol/ether (1:1).

Synthesis of zinc(II) complexes

Zn(II) complexes with ligands L_1–L_4

An ethanolic solution (30 cm^3) of Zn(II) acetate dihydrate (0.01 mol) was added to a refluxing solution of appropriate Schiff base (L_1–L_4) (0.02 mol) in ethanol (30 cm^3). The reaction mixture was refluxed for about 8–11 h. The colored complex was obtained. The complex was filtered off, washed thoroughly with ethanol and dried under *vacuo* at room temperature. The complexes were obtained as powdered material.