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Synthesis and spectral characterization of Zn(II) microsphere series for antimicrobial application

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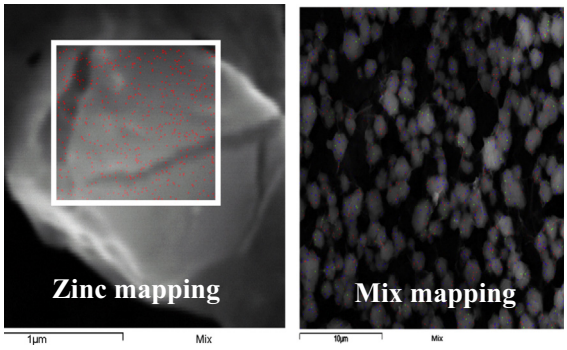
HIGHLIGHTS

- Nano-sized zinc(II) complexes were synthesized and well characterized.
- Schiff base and Zn(II) complexes showed significant antimicrobial activities.
- Zn(II) complexes look like a microsphere and their sizes are 1–2 μm.

GRAPHICAL ABSTRACT



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ABSTRACT

Microsphere series have been synthesized by reacting zinc(II) acetate dihydrate with Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thiadiazole/oxadiazole/triazole with salicylaldehyde. Elemental analysis suggests that the complexes have 1:2 and 1:1 stoichiometry of the type $[Zn(L)_2(H_2O)_2]$ and $[Zn(L')(H_2O)_2]$; LH = Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thia/oxadiazole with salicylaldehyde; $L'H_2$ = Schiff bases derived from 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazole and salicylaldehyde and were characterized by elemental analyses, IR, ^1H NMR and ^{13}C NMR spectral data. Scanning electron microscopy (SEM) showed that synthesized materials have microsphere like structure and there EDX analysis comparably matches with elemental analysis. For the antimicrobial application Schiff bases and their zinc(II) complexes were screened for four bacteria e.g. *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Streptococcus pyogenes* and four fungi e.g. *Cyrtomium falcatum*, *Aspergillus niger*, *Fusarium oxysporium* and *Curvularia pallescence* by the reported method. Schiff base and Zn(II) compounds showed significant antimicrobial activities. However, activities increase upon chelation. Thermal analysis (TGA) data of compound (10) showed its stability up to 300 °C.

Introduction

Zinc has been known to be an essential trace element in eukaryotes for more than a century [1]. There is 2–3 g of zinc in adult humans, making it one of the most prevalent "trace" elements. In particular, zinc salicylate has been approved by the US Food and Drug Administration for use as an anti-oxidant, carbonless copying paper and stabiliser for polymers [2]. Metal zinc complexes became attractive for their interesting properties such as antimicrobial [3], enzymatic activity [4], personal care [5], anti-HIV drug [6], and photoluminescence as well as electroluminescence, etc. [7]. In other hand 1,3,4-thiadiazoles and their Schiff bases have received significant importance because of their diverse

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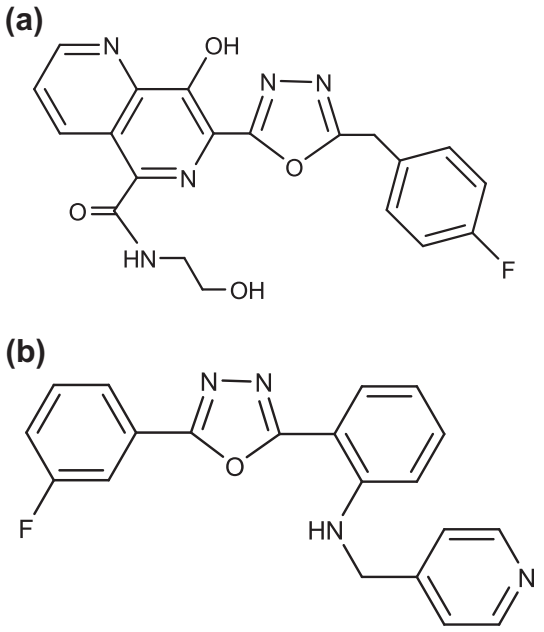

Fig. 1. Oxadiazole derived compound patented for; (a) anti-HIV drugs; (b) anti-cancer drugs.

biochemical, antifungal and antibacterial application [8,9]. Oxadiazole derivatives have been found to possess tuberculostatic [10], antiviral [11], antibacterial [12,13], antimalarial [14], fungicidal [15], anticonvulsant [16], anti-inflammatory [17], analgesic [18,19] and insecticidal [20] activities. 7-(-5-{4-fluorobenzyl}-1,3,4-oxadiazole-2-yl)-8-hydroxy-N-(2-hydroxym ethyl)-1,6-naphthyri-dine-5-caboxamide (Fig. 1a) have been patented for the HIV integrase inhibition [21] and 2-{5-(3-florophenyl)-1,3,4-oxadiazole-2-yl}-N-(pyridin-4-ylmethyl) aniline (Fig. 1) patented as anticancer agent [22]. Triazoles and their derivatives are found to be associated with various biological activities, such as anticonvulsant, antifungal, anticancer, anti-inflammatory and antibacterial properties [23–27]. Several compounds containing 1,2,4-triazole ring are well known for drugs and there amino derived Schiff bases well known for antimicrobial properties [28–30]. Salicylaldehyde isonicotinoyl hydrazone was patented for protection against retinal disease [31].

In this paper, we report the synthesis, spectroscopic, microscopic, thermal study and antimicrobial activities of zinc(II) complexes with Schiff bases derived from substituted heterocycles (thiadiazole, oxadiazole and triazole) with salicylaldehyde.

Experimental

Reagents

All reagents were purchased from Aldrich, solvents used were purified by proper methods and Milli-Q water was used for all experiments.

Instruments

Melting points were determined on a Buchi 530 apparatus in open capillary tubes. IR spectra were recorded on a Shimadzu 8201 PC model FT IR spectrophotometer as KBr disks. ^{1}H 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. The thermal degradation processes and stabilities of the zinc complexes was investigated using a thermo-gravimetric analyzer (Mettler Toledo TGA/SDTA851 with *Star* software) under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 500 °C. For scanning electron microscopy (SEM), gold sputter coating were carried out on desired zinc(II) complexes samples at pressure ranging in between 1 and 0.1 Pa. Sample was loaded in the machine, which was operated at 10^{-2} to 10^{-3} Pa with EHT 15.00 kV with 300 V collector bias using Leo microscope SEMs were recorded. Transmission electron microscope (TEM) analysis for zinc complexes was performed by a JEOL 1200EX. The JEOL 1200EX TEM with tungsten, operated at an accelerating voltage of up to 120 kV. The optical densities of microbial solutions were evaluated by using a VARIAN 50 bio UV–Vis spectrophotometer instruments. Zinc was estimated gravimetrically as its dioxide ZnO_2 [32]. 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. 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.

General procedure for the synthesis of zinc(II) complexes

The route for the preparation of zinc(II) complexes is shown in Fig. 2.

Synthesis of Schiff base hydrazone derived from 5-(substituted aryl)-2-hydrazino-1,3,4-(thiadiazole, oxadiazole) and salicylaldehyde (L_1H–L_8H)

A mixture of 5-[substituted aryl]-2-hydrazino-1,3,4-(thia/oxadiazole) and salicylaldehyde in 1:1 M ratio respectively was refluxed in ethanol (30 cm^3) containing few drops of concentrated sulphuric acid for 5–6 h [33]. The product separated on evaporation of the ethanol was recrystallized from ethanol–ether mixture (1:1).

Synthesis of Schiff base hydrazone derived from 5-(substituted aryl)-3-hydrazino-1,2,4-(triazole) and salicylaldehyde (L'_9H_2–$L'_{12}H_2$)

A mixture of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazole and salicylaldehyde in 1:2 M ratio in an ethanol (30 cm^3) containing a few drops of concentrated sulphuric acid was refluxed for ca. 4–7 h [34]. On concentrating the solution up to ~10 cm^3, crystals appeared which were filtered and recrystallized from ethanol–ether mixture (1:1).

Synthesis of zinc(II) complexes (1–8)

An ethanolic solution (30 cm^3) of zinc(II) acetate dihydrate (0.01 mol) was added to a refluxing solution of appropriate Schiff base (L_1H–L_8H) (0.02 mol) in ethanol (30 cm^3) containing alcoholic solution of sodium acetate (0.02 mol). The reaction mixture was refluxed for about 8–13 h. The coloured complex was obtained. The complex was filtered off, washed thoroughly with ethanol and dried under *vacuo*.

Complex (1). Yield 70%; colour: cream; decomp. temp. 210–212 °C; IR (KBr) cm^{-1}: 3490 (—OH), 3165 (—NH), 2950 (Ar—H), 1620 (C=N azomethine), 1580 (C=N thiadiazole), 1545 (C=C), 1348 (C—O), 1155 (N—N), 1050 (C—S—C), 805, 745 (—OH wagging and rocking), 485 (Zn—O), 435 (Zn—N); ^{1}H NMR (DMSO-d_6): δ 12.45 (s, 2H,