Journal of Molecular Structure 1127 (2017) 314–321

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Bio-important antipyrine derived Schiff bases and their transition metal complexes: Synthesis, spectroscopic characterization, antimicrobial, anthelmintic and DNA cleavage investigation

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A R T I C L E I N F O

Article history:
Received 8 November 2015
Received in revised form
28 July 2016
Accepted 31 July 2016
Available online 2 August 2016

Keywords:
Azomethine
Anthelmintic
DNA
Schiff base
Transition metal complexes
Spectroscopy

A B S T R A C T

Spectroscopic (IR, NMR, UV–vis, ESR, ESI-mass), magnetic and TGA studies suggests octahedral geometry for all the Co^{II}, Ni^{II} and Cu^{II} complexes of the Schiff bases, derived from 4-aminoantipyrine and 8-formyl-7-Hydroxy-4-methylcoumarin/5-formyl-6-hydroxycoumarin, coordinated through ONO donor sites. Antibacterial (*Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa and Salmonella typhi*), antifungal (*Aspergillus niger, Aspergillus flavus and Cladosporium*) and DNA cleavage properties of the metal complexes are investigated. The results suggested that some of the synthesized compounds are potential antimicrobials. The synthesized compounds tested for their anthelmintic activities and it was found that Co^{II} and Ni^{II} complexes exhibited good anthelmintic properties.

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1. Introduction

Due to their wide spectrum of biological activities, heterocyclic compounds dominated medicinal chemistry. Antipyrine and its derivatives have wide applications in biological activities [1,2]. Along with biological activities, their interesting structural features have attracted many researchers to work on the metal complexes of antipyrine derivatives [3,4]. Antipyrine alone forms stable coordination bond with metal ions in monodentate fashion through carbonyl oxygen atom [5,6]. Subsequently it is reported that, 4-aminoantipyrine Schiff bases and their metal complexes possess numerous biological applications that include antifungal, antibacterial, analgesic, antipyretic and anti-inflammatory [7–9]. Transition metal complexes of pyrazole derivatives have received more attention as beneficial anticancer agents [10,11]. On the other side coumarin derivatives, well-known fluorescent molecules, also possess wide range of biological activities viz. antimicrobial, anti-allergic, anti-inflammatory, antitumor etc. [12–14] Coumarin derivatives have been found useful in the treatment of human immunodeficiency virus [15,16]. In vitro and in vivo studies have suggested the possible use of coumarins in the treatment of cancer as well [17].

Formation of coordination bond brings extensive changes in biological properties of ligand and also in metal ions [18] worth to mention chelation can cure many diseases. Very recently we have reported biological importance of different structural groups including coumarins and their metal complexes [19]. A review on Schiff bases and their antimicrobial activities elaborated the importance of this functional group in medicinal chemistry [20]. Spectroscopically active metal centers with stable, inert, and non-toxic nature are exceptionally valuable in biological systems [21].

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http://dx.doi.org/10.1016/j.molstruc.2016.07.123
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Here, in the present work, primary amino group of antipyrine is made to react with an aldehyde group of formyl coumarin thereby incorporating an azomethine group in the molecule which were further reacted with Co^{II}, Ni^{II} and Cu^{II} metal ions to form respective metal complexes. The newly synthesized Schiff bases and their metal complexes are characterized by various spectroscopic techniques. Selected newly synthesized compounds have been evaluated for their various biological properties.

2. Experimental

2.1. Analysis and physical measurements

Carbon, hydrogen and nitrogen were estimated by using Elemental Analyzer Carlo Erba EA1108 analyzer. Molar conductivity measurements were recorded on ELICO-CM-82 T Conductivity Bridge with a cell having cell constant 0.51 and magnetic moment was carried out by using faraday balance. The IR spectra of the Schiff bases and their Co^{II}, Ni^{II} and Cu^{II} complexes were recorded on a HITACHI-270 IR spectrophotometer. The ^1H NMR and ^{13}C NMR spectra of ligands were recorded in DMSO-d_6 on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. Mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system. The electronic spectra of the complexes were recorded in HPLC grade DMF and DMSO solvent on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200–1100 nm. The ESR spectrum was recorded on Varian-E-4X-band EPR spectrometer and the field set is 3000 G at modulation frequency of 100 kHz under room temperature using TCNE as g marker. Thermogravimetric analyses were done on PerkinElmer Diamond TG/DTA instrument and measured from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}.

2.2. Methods

All the chemicals used were of reagent grade. 7-hydroxy- 4-methylcoumarin [22], 6-hydroxy coumarin [22], 8-formyl- 7-hydroxy-4-methyl coumarin [23,24], and 5-formyl-6-hydroxy coumarin [24,25] have been synthesized according to the published procedure.

2.3. Synthesis of Schiff bases [SB-I, SB-II]

Fig. 1 represents the synthesis of Schiff bases. The Schiff base SBI has synthesized as given below. To the hot ethanolic solution (30 mL) of 4-aminoantipyrine (0.01 mol) was added hot ethanolic solution (30 mL) of 8-formyl-7-hydroxy-4- methylcoumarin. Then catalytic amount of hydrochloric acid (2–3 drops) was added. The reaction mixture was refluxed for 4–5 h. The progress was checked by TLC. The precipitate formed during reflux was filtered, washed with cold EtOH and recrystallized from hot EtOH.

In similar way Schiff base SB-II was synthesized with 5-formyl-6-hydroxycoumarin (0.01 mol).

2.4. Synthesis of Co^{II}, Ni^{II} and Cu^{II} complexes (**1–6**)

To an aq. alcoholic solution (15 mL) of 1 m mol of $CoCl_2 \cdot 6H_2O$/ $NiCl_2 \cdot 6H_2O$/$CuCl_2 \cdot 2H_2O$ was added an alcoholic solution (40 mL) of Schiff bases (2 m mol) and refluxed on water bath for 2 h. Then, to the reaction mixture was added 2 m mol of sodium acetate and reflux was continued for 3 h. The separated complex was filtered, washed thoroughly with water, ethanol, ether and finally dried in vacuum over fused $CaCl_2$.

2.5. Biological application studies

2.5.1. In vitro antibacterial and antifungal assay

The Schiff bases and their Co^{II}, Ni^{II} and Cu^{II} complexes have been studied for their antibacterial and antifungal activities by agar and potato dextrose agar diffusion method. The antibacterial and antifungal activities were done at 100, 50 & 25 mg mL^{-1} concentrations in DMF by using bacteria (*Escherichia coli, Staphylococcus aureus and Pseudomonas aeruginosa*) and fungi (*Aspergillus niger, Aspergillus flavus and Cladosporium*) by the MIC method [26]. These bacterial stains were incubated for 24 h at 37 °C and fungal stains were incubated for 48 h at 37 °C. Standard antibacterial (*Gentamycin*) and antifungal drug (*Fluconazole*) was used for comparison under similar conditions.

2.6. DNA cleavage experiment

DNA cleavage experiments were done according to the method

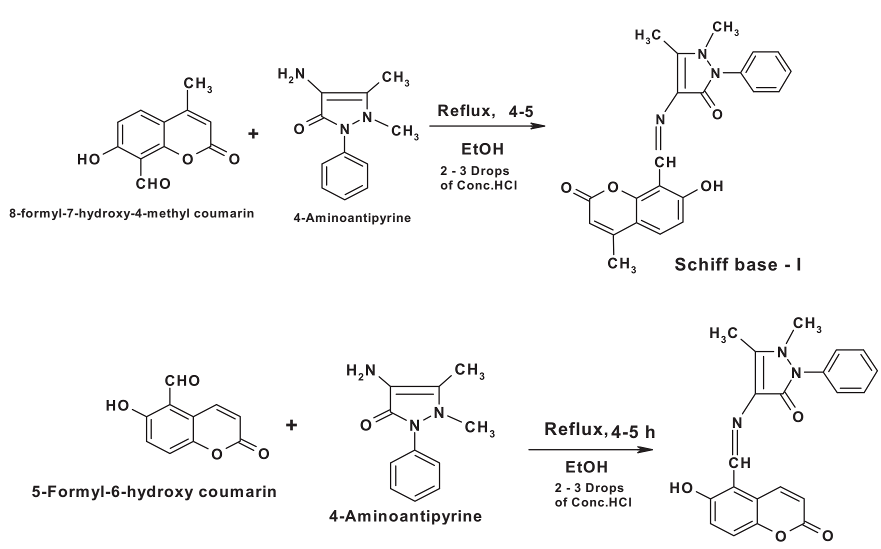

Fig. 1. Synthesis scheme and structure of Schiff Bases SB-I & SB-II

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