Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 96 (2012) 493–500

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic studies and biological evaluation of some transition metal complexes of azo Schiff-base ligand derived from (1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one) and 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde

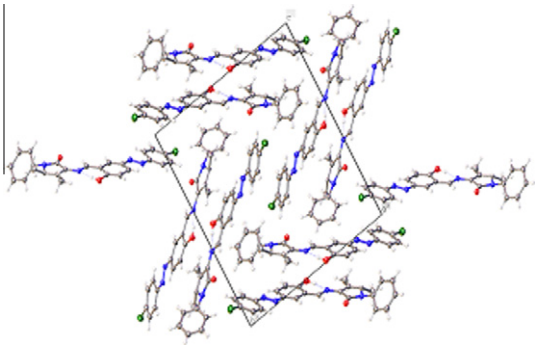
C. Anitha [a], C.D. Sheela [b], P. Tharmaraj [a,*], S. Sumathi [a]

[a] Department of Chemistry, Thiagarajar College, Madurai 625 009, India
[b] Department of Chemistry, The American College, Madurai 625 002, India

HIGHLIGHTS

- Azo Schiff base is coordinated to the metal ion in a tridentate fashion.
- Co(II) and Cu(II) complexes cleave DNA.
- The investigated metal(II) complexes exhibit higher antimicrobial activity than the ligand.
- All the complexes display fluorescence and can potentially serve as photoactive materials.
- The azo Schiff base exhibits second harmonic generation (SHG) efficiency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2012
Received in revised form 30 March 2012
Accepted 21 May 2012
Available online 2 June 2012

Keywords:
Salicylaldehyde
Azo Schiff base
Metal complexes
Antimicrobial activity
DNA study
SEM
Spectroscopy

ABSTRACT

A series of metal(II) complexes of VO(II), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized from the azo Schiff base ligand 4-((*E*)-4-((*E*)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (CDHBAP) and characterized by elemental analysis, spectral (IR, UV–Vis, ^{1}H NMR, ESR and EI-mass), magnetic moment measurements, molar conductance, DNA, SEM, X-ray crystallography and fluorescence studies. The electronic absorption spectra and magnetic susceptibility measurements of the complexes indicate square pyramidal geometry for VO(II) and octahedral geometry for all the other complexes. The important infrared (IR) spectral bands corresponding to the active groups in the ligand and the solid complexes under investigation were studied and implies that CDHBAP is coordinated to the metal ions in a neutral tridentate manner. The redox behavior of copper(II) and vanadyl(II) complexes have been studied by cyclic voltammetry. The nuclease activity of the above metal(II) complexes shows that the complexes cleave DNA. All the synthesized complexes can serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The antibacterial and antifungal activities of the synthesized ligand and its metal complexes were screened against bacterial species (*Staphylococcus aureus, Salmonella typhi, Escherichia coli, Bacillus subtilis, Shigella sonnie*) and fungi (*Candida albicans, Aspergillus niger, Rhizoctonia bataicola*). Amikacin and Ketoconozole were used as references for antibacterial and antifungal studies. The activity data show that the metal complexes have a promising biological activity comparable with the parent Schiff base ligand against bacterial and fungal species. The second harmonic generation (SHG) efficiency of the ligand was measured and the NLO (non-linear optical) properties of the ligand are expected to result in the realization of advanced optical devices in optical fiber communication (OFC) and optical computing. The SEM image of the copper(II) complex implies that the size of the particles is 1 μm.

* Corresponding author. Tel.: +91 9442555836; fax: +91 452 2311875.
E-mail address: rajtc1962@gmail.com (P. Tharmaraj).

1386-1425/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.05.053

1. Introduction

Azo Schiff base complexes are considered to be the most important stereochemical models in transition metal coordination chemistry due to their preparative accessibility and structural variety [1]. The Schiff bases of 4-aminoantipyrine are considered to be pyrazolone derivatives and the metal chelates of pyrazolone derivatives have evoked great interest due to their applicability as potential ligands for a large number of metal ions and are reported to demonstrate biological [2], clinical [3], pharmacological [4] and analytical [5] applications. Several researchers have focused on synthesis and characterization of Schiff bases derived from 4-aminoantipyrine [6–15]. A search through literature reveals that, no work has been done on the transition metal(II) complexes of azo Schiff base derived from (1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one) and 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde.

The aim of this work is to synthesize and characterize transition metal(II) complexes of azo Schiff base 4-((*E*)-4-((*E*)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (CDHBAP) along with their biological activity against some bacteria and fungi. Further more, the role of vanadium in the biosphere is very important due to the fact that mammals require vanadium at the nano to pico molar level and several lower organisms have vanadium requirement at a much higher level and also important in the fuel industry [16–18]. Due to the importance of vanadium metal, we also aimed to prepare and characterize the vanadyl complex of antipyrine derivative.

2. Experimental

The chemicals and solvents were purchased from Aldrich Chemical & Co. and the solvents were purified by standard methods. Elemental analyses were carried out using a Perkin–Elmer 2400 II elemental analyzer. The metal content was estimated by oxalate-oxide method [19]. Molar conductance of the complexes was measured in DMSO at room temperature using a Systronic Conductivity Bridge 304. Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark1 Gouy balance. Infrared spectral studies were carried out on a Shimadzu FT IR 8000 spectrophotometer using KBr discs. UV–Vis spectra were obtained using a THERMO SPECTRONIC 6 HEXIOS α and fluorescence spectra were determined with an ELICO SL174 Spectrofluorometer. NMR spectra were recorded on Bruker DRX-300, 300 MHz NMR Spectrometer using TMS as reference. ESR spectra of the Cu(II) and VO(II) complexes were recorded in Varian E-112 machine at 300 and 77 K using TCNE (tetracyanoethylene) as the g-marker. Cyclic voltammetric measurements for Cu(II) and VO(II) complexes in DMSO were carried out on a Electrochemical analyzer CH Instruments (USA) using a three electrode cell containing an Ag/AgCl reference electrode, Pt wire auxiliary electrode and glassy carbon working electrode with tetrabutylammonium perchlorate as supporting electrolyte. Electron-ionization (EI) mass spectra were recorded by JEOL-GC Mass Spectrometer MATE-2.

2.1. Synthesis of 4-((E)-4-((E)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (CDHBAP)

The diazonium salt, 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde [20] (2.60 g, 0.01 mol) in ethanol was condensed by refluxing with an ethanolic solution of (1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one) (2.03 g, 0.01 mol) for 3 h. The solution was allowed to stand at room temperature and the solid obtained was washed with ethanol and recrystallized (Fig. 1).

2.2. Synthesis of metal(II) complexes

A solution of metal(II) chloride/sulfate ($VOSO_4{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$) in ethanol (1 mmol) was stirred with an ethanolic solution of (CDHBAP) (0.5 g, 1 mmol) in the presence of 1 mmol of NaOH on a magnetic stirrer. On concentration, the solid complex precipitated was filtered, washed

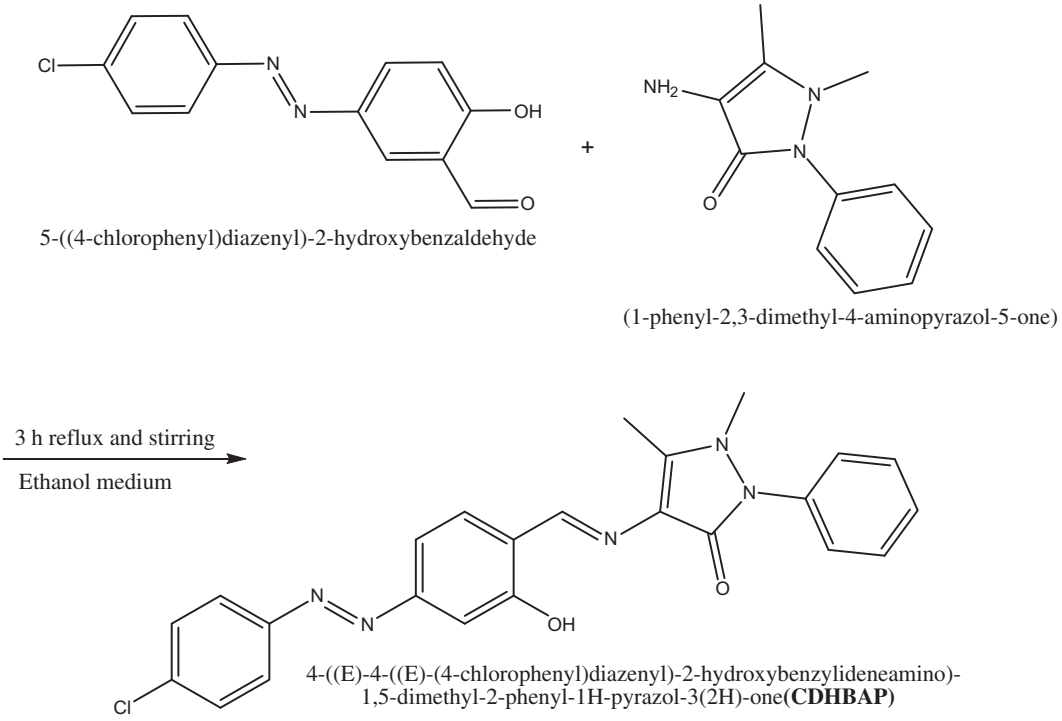


Fig. 1. Synthesis of Schiff base ligand (CDHBAP).