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Comparative sensor studies for metal ion detection by Schiff base

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Schiff base ligand of 4-amino antipyrine and 5-nitro 3-methoxy salicylaldehyde was prepared and characterized by analytical and spectralmethods. UV-Vis and fluorescence spectral methods are used to investigate Schiff base ligand sensor ability towards metal ions. Change in colour of the Schiff base was observed with metal ions Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} visually. Schiff base exhibited emission band at 600 nm upon excitation at 560 nm in fluorescence studies. Quenching of fluorescence intensity was observed by addition of metal ions to ligand. Therefore, for metal ions detection the Schiff base ligand can be used.

Keywords: Metal ion detection, Schiff base, 4-aminoantipyrine, sensor studies.

Introduction

There are many analytical methods for detection of metal ions such as flame photometry, chromatography, atomic absorption spectroscopy, gravimetric and chemical analysis methods. These methods are useful to detect few selective metal ions and requires expensive apparatus involving multisteps. Therefore detection of metal ions by UV-Visible and fluorescence methods have received much importance. Among these, transition metal ion detection has gained importance due to their, essential role in environmental and biological processes.

4-Aminoantipyrine based heterocyclic compounds have a great importance as they are abundant in nature and have wide pharmacological activities[1–4]. 4-Aminoantipyrine is a temperature reducing pyrazole derivative[5]. Several derivatives of antipyrine were also evaluated as analgesic[6], anti-inflammatory[7], anti-microbial[8] and anti-cancer activity[9–11]. Antioxidant and Leishmanicidal activities[12]. More recently, Kose *et al.* reported that, 4-amino antipyrine Schiff base can be used to detect Al^{3+} ions in the presence of other metal ions[13]. A large number of Schiff base ligands are used as colorometric and fluorescence sensors. Schiff base ligands can form complexes with metal ions by phenolic OH and imine groups. Therefore Schiff bases can be used as chemosensors to detect metal ions, due to the binding sites. Schiff base of antipyrine derivatives have important applications in signal processing, optical interconnection[14, 15], non-linear optical[16] and photovoltaic properties[17,18].

In this work, Schiff base ligand was prepared from 3-methoxy 5-nitro salicylaldehyde and 4-aminoantipyrine and was characterized by UV-Vis, infrared, proton and ^{13}C NMR, and Mass spectral methods. Detection of metal ions Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, with Schiff base was carried out by visual colour change, electronicand fluorescence spectral methods.

Results and discussion

Characterization of the ligand: [2,3-dimethyl-1-phenyl-4-(3-methoxy, 5-nitro-2-hydroxy benzylideneamino)-pyrazole-5-one]:

The Schiff base was prepared from one equivalent of 3-methoxy-5-nitrosalicyaldehyde and 4-aminoantipyrine by condensation. The yellow product is stable at room temperature and soluble in organic solvents such as methanol, ethanol, acetonitrile, choloroform, dichloromethane, DMF and DMSO.

The analytical data of the ligand like m.p., elemental analysis and mol. wt. are summarized in Table 1.

Table 1. Analytical data of the Schiff base

Compound	M. formula	M. Wt.	m.p. (0°C)	C (%)	H (%)	N (%)
Schiff base	$C_{19}H_{18}N_4O_5$	382	210°C	59.68	4.71	14.65

Spectroscopic characterization of the Schiff base:

The electronic absorption spectrum (Fig. 1) of the Schiff base (in ethanol) exhibits two peaks at 250 nm and 340 nm. The peak at 250 nm is due to π-π^* transition and at 340 nm is assigned to transistion of n-π^* of Schiff base.

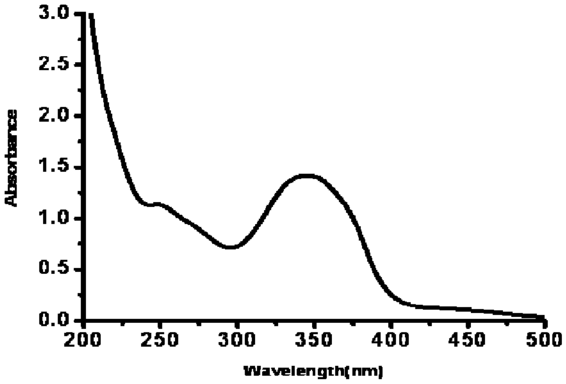


Fig. 1. UV spectrum of Schiff base ligand.

The IR spectrum of the ligands exhibits two bands at 3182–3059 and 3079–2932 cm^{-1} which are due to aromatic C-H asymmetric and symmetric stretching vibrations. It displays an intense band at 1656 cm^{-1} due to pyrazol carbonyl $\nu_{(C=O)}$ of the antipyrine ring. The $\nu_{(C=N)}$ band is observed at 1595 cm^{-1} of azomethine group. The ligand also exhibited a band at 2876–3724 cm^{-1} of due to intramolecular hydrogen bonded OH group. The phenolic $\nu_{(C-O)}$ bands are observed at 1330 cm^{-1}. The phenyl ring vibrations of ligand show bands in 1070–1100 cm^{-1} and 700–750 cm^{-1} regions.

The ^{1}H NMR spectrum of Schiff base is recorded in $CDCl_3$. Aromatic protons exhibits multiplet signals at δ 6.9–7.8, in ^{1}H NMR spectrum. The signals due to, =C-CH_3 at δ 2.4, -N-CH_3 at δ 3.2 and imine proton -CH=N- at δ 9.83, at δ 4.0 OCH_3 protons, OH proton at δ 13.4 as singlets.

The ^{13}C NMR Spectrum of the ligand is recorded in $CDCl_3$. The imine carbon (C_7) shows a signal at δ 163.7–164.7, =C -CH_3 (C_{10}) at δ 10.14–10.25 -N-CH_3 (C_{11}) at δ 35.21–35.61, C=O (C_{12}) at δ 161.7–160.6, C=C of antipyrine (C_8) gives δ 110–116 and (C_9) gives δ 134–158, remaining all the carbons appeared in aromatic region (C_1-C_6 and C_{13}-C_{18}) δ 110–160. -OCH_3 (C_{19}) exhibits a peak at δ 56.06.

Schiff base showed *m/z* parent peakat 383 (M^++1) corresponding to their formula weights in their mass spectra as given in Table 2.

Table 2. Mass spectral data of Schiff base

Compound	Molecular mass	Molecular ion peak *m/z*
Schiff base	382	383 [M+1]

Metal ion detection:

By visual color change:

The various metal ions Al^{3+} Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were detected (in 1:1 *M* ratio in ethanol) (Fig. 2) by ligand with visual color change.

Fig. 2. Colour changes of the Schiff base in the presence of various metal ion.

UV-Visible spectral studies:

The chemosensor behavior (Fig. 3) of the Schiff base ligand (0.1 mM) was observed by monitoringthe UV-Visible absorbtion spectral behavior by the addition of metal ions in methanol. A new peak was observed at 400–500 nm region, by the addition of metal ions to ligand. This indicating complex formation between metal and ligand through azomethine and oxygen atom of phenolic OH group.

Fluorescence emission studies:

Detection of metal ions by spectrofluorometrically with

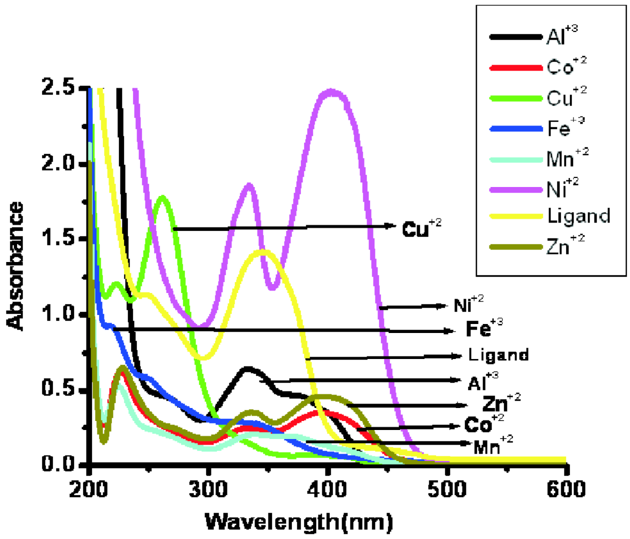


Fig. 3. UV-Vis spectral changes of the ligand in MeOH upon addition of metal ions in MeOH.

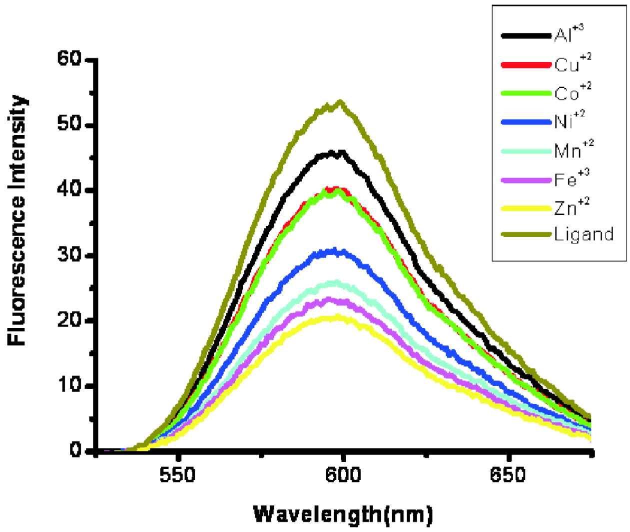


Fig. 4. Fluorescence emission spectra of the ligand with different metal ions in methanol (λ_{max}: 600 nm).

Schiff base ligand in methanol were performed. The resulting fluorescence intensity of metal ions are shown in Fig. 4. Schiff base exhibited emission band at 600 nm and excitation at 560 nm in its fluorescence spectra. Fluorescence quenching was caused by addition of metal ions. This is due to transfer of energy or electron between the metal ion and ligand, through quenching mechanism[19,20]. Thus Schiff base receptor is useful as fluorescene sensor for detection of metal ions.

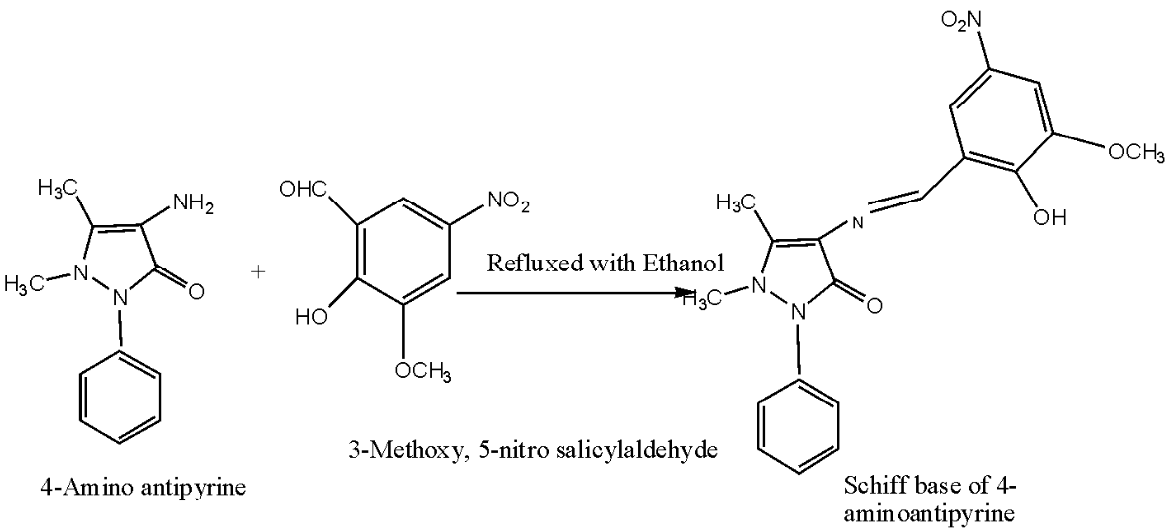
Experimental

Materials used:

4-Aminoantipyrine, 3-methoxy 5-nitro salicylaldehyde, methanol, ethanol chloroform, benzene, metal salts.

Synthesis of schiff base:

Schiff base were synthesized[21] by the condensation of 3-methoxy 5-nitro salicylaldehyde with 4-aminoantipyrine dissolved in ethanol (Scheme 1). The resulting reaction mixture was stirred on magnetic stirrer for 2 h. The coloured solid



Scheme 1. Synthesis of Schiff base.

precipitate was obtained was filtered and dried in the room temperature and finally stored in a $CaCl_2$ dessicator. The purity of the synthesized compound was checked by the TLC.

Physical measurements:

Electronic spectra was recorded on Schimadzu UV-Vis (model 1800) spectrophotometer. FT-IR spectra were recorded on Brucker IR spectrophotometer. Brucker 400 MHz spectrometer was used to record NMR spectra in $CDCl_3$. By ESI technique, mass spectra were recorded. Schimadzu spectrofluorimeter (RF 5301 PC) was used to record fluorescence spectra.

Conclusions

Schiff base ligand was prepared from 3-methoxy 5-nitro salicylaldehyde and 4-aminoantipyrine and characterized by analytical and spectroscopic studies. Sensor ability of the Schiff base ligand visualized through naked eye as well as by change in UV-Vis and fluorescent spectral properties in presence of various metal ion Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.

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