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Synthesis of novel Schiff bases and its transition metal complexes

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ABSTRACT

Novel transition metal [Cu(II), Ni(II), Zn(II), La(II)] complexes of bidentate Schiff base ligand obtained from 2-hydroxy-3-formylquinoline and substituted p-iodoaniline have been prepared and characterized by physical, spectral and analytical data. The synthesized Schiff base act as bidentate ligand for the complexation reaction with Cu(II), Ni(II), Zn(II) and La(II) ions. The new compounds, possessing the general formula $[M(L)_2]$ where $[M= Cu(II), Ni(II), Zn(II) \text{ and } La(II)]$ show square planar geometry.

Key words: Schiff bases, quinoline, transition metal complexes of Cu(II), Zn(II), Ni(II) and La(III).

INTRODUCTION

Schiff bases derived from condensation of aromatic aldehydes and aromatic amines form an important group of compounds in synthetic chemistry due to their useful physical and chemical properties and large number of reactions they undergo. Schiff bases are also used widely in pharmaceutical industry and have interesting pharmacological activities [1-5].

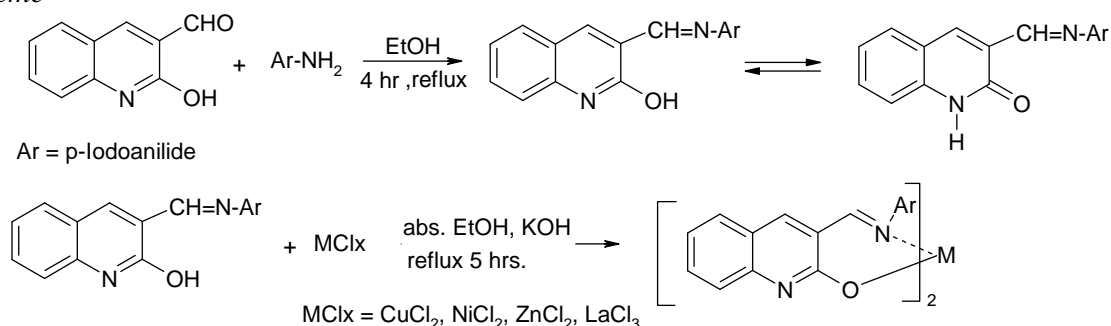
Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. Many biologically important Schiff bases have been reported in the literature possessing, antibacterial, antifungal, antimicrobial, anticonvulsant, antiHIV, anti-inflammatory, antitumor and catalytic activities.[6-11]

Metal complexes of the heavy metals such as Gold, Tb(III), Eu(III), Ln(III), Y(III), Gd(III), Pt(II) and Ir(III)(can be used as efficient phosphorescent emitters)[13,14-19,20-22]are used as organic phosphors. The OLEDs prepared with heavy metal complexes such as Ir(III) or Pt(II) complexes are the most efficient OLEDs reported to the date, with theoretical internal quantum efficiencies of 100 % [28] due to harvest of both singlet and triplet excitations[23-27].

Searching for highly efficient fluorescence complex of light metal [Cu(II), Zn(II), Ni(II), La(II)] complex is a topic of current interest. The heterocyclic based ligand having electron donating or withdrawing groups has increased or decreased effect on the intensity of absorption or shifted absorption wavelength on either side^[28].

EXPERIMENTAL SECTION

Scheme



Synthesis of Schiff bases (3-*(E)*-[(4-iodophenyl)imino]methyl}quinolin-2-ol) using 2-hydroxy-3-formylquinoline and p-iodo aniline.[29-30]

Dissolve 0.1 mol of 2-hydroxy-3-formylquinoline derivative in 300 ml of absolute alcohol in 500 ml round bottom flask fitted with spiral reflux condenser and calcium chloride guard tube. Add equivalent amount of p-iodoaniline (0.1 mol) and catalytic amount of acetic acid. Reflux the reaction mixture in water bath for about 4 hours. Cool the reaction mixture and filter the resulting solid by using Whatmann filter paper number 41 on suction pump and recrystallized by using ethyl acetate. Dry it in hot air oven and record m.p.(230⁰C).

¹H NMR CDCl₃(90MHz)δ in ppm:- 8.9 (s), 8.7 (d), 8.4 (d), 7.7 (t), 7.5 (m), 7.3 (m), 7.2 (m), 7.0 (m), 6.4 (t).

Mass spectra- m/z = 375,358, 248, 230.1, 219.4, 171.3, 145.4, 126, 128, 117.

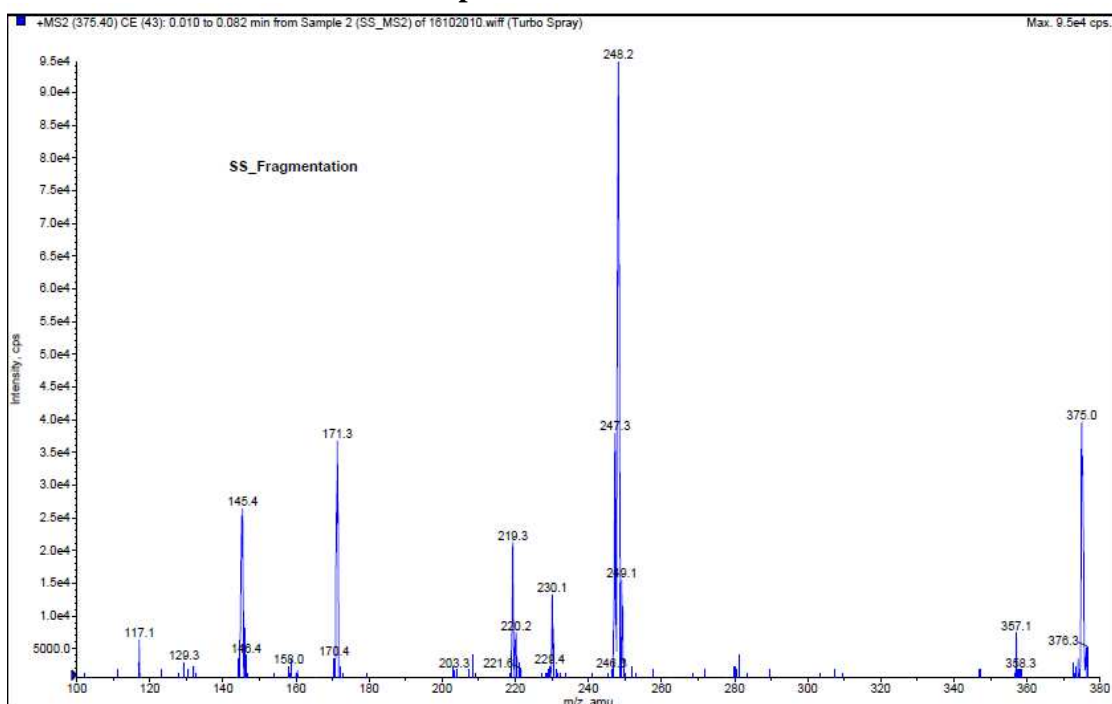
Synthesis of Cu (II), Zn(II), Ni(II) and La(III) complexes of Schiff bases (3-*(E)*-[(4-iodophenyl)imino]methyl}quinolin-2-ol).

Dissolve 1.50 mmol of Schiff base in 50 ml of absolute alcohol in 100 ml round bottom flask fitted with reflux condenser and calcium chloride guard tube. Add 0.75 mmol of corresponding metal salt (CuCl₂, NiCl₂, ZnCl₂, LaCl₃) and stir the reaction mixture, add 1.50 mmol potassium hydroxide in it. Reflux the reaction mixture for about 5 hours in water bath so that color of reaction mixture changes. Cool the content and poured it into 100 g crushed ice. Filter the solid separated and dry in oven at 70-80⁰C.

RESULTS AND DISCUSSION

Schiff base was synthesized by condensing 2-hydroxy-3-formylquinoline and p-iodo aniline as per the procedure reported in literature.[29-30] It was characterized by ^1H NMR spectroscopy. The hydroxyl proton was observed at about 11 ppm. It was exchanged with D_2O , confirming phenolic $-\text{OH}$ group and labile nature and $[-\text{HC}=\text{N}-]$ azomethine proton was observed at 8.9 ppm. Aromatic protons were observed from 8.7 to 6.4 ppm and coupling constants were confirmed. Typical AB pattern (two adjacent doublets) due to 4-iodo aniline part was also observed in ^1H NMR spectrum.

Mass spectrum of schiff base



The mass spectrum of Schiff's base showed $[M+1]$ molecular ions fragment at 375, thus confirming the condensation of two molecules of aldehyde and aniline. Further fragmentation peaks due to loss of hydroxyl group was observed at m/z 358 and due to loss of iodine was observed at m/z 248.

CONCLUSION

A Novel Schiff base (3- $\{(E)\text{-}[(4\text{-iodophenyl})\text{imino}]\text{methyl}\}$ quinolin-2-ol) was synthesized and confirmed by ^1H NMR and Mass spectroscopy. Its transition metal complexes with Cu (II), Zn(II), Ni(II) and La(III) were synthesized. Further work is in progress to characterize the transition metal complexes and its fluorescence properties are being studied in details.

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