

TANDEM SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE AND METAL COMPLEXES

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ABSTRACT

In the present study of one pot tandem reductive Schiff base formation from nitroarenes carried out in the presence of iron powder and dilutes acid. In the present study new Schiff base compound derived from 2 nitro 5 methyl phenol with quinoxaline-2 carboxaldehyde and metal complexes. Schiff base and metal complexes are characterized.

INTRODUCTION

In an economically expanding world new sustainable concepts have to be developed in order to overcome growing problems of resource availability. The objective of organic synthesis is the construction of complex molecules from simpler ones; the importance of synthetic efficiency becomes immediately apparent and has been well-recognized. [1]

Multistep synthesis of specialty chemicals normally requires stoichiometrically excess reagents, leading to high effluent loads. Hence, search is now on for clean, non-hazardous and 'green' chemical transformations, which will have negligible bi-products and high selectivity.

Chemists are constantly working to discover new and improved reactions. One of the primary motivating goals of this research is the development of cleaner, more efficient transformations to shorten syntheses and save money on chemicals. The strategy of using reactions in tandem (multistep one-pot reactions) is also aimed at shortening synthesis.

Since the intermediates are not isolated it becomes easier to work with sensitive or unstable intermediates [2,3].

Tandem reactions have several advantages over a series of individual reactions. First, they allow construction of complex structures in as few steps as possible. In theory, they also eliminate the need for a purification step (or steps). Since the intermediates are not isolated it becomes easier to work with sensitive or unstable intermediates.

Green Context

In view of human health and environmental concerns, much attention is being paid to 'Green Chemistry', which is a chemical methodology to decrease or eliminate the use or generation of hazardous substances in the design, preparation and application of chemical production.

A Schiff base is the nitrogen analogue of aldehyde in which the C=O group is replaced by a C=N group and is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [4].

The reported Schiff bases exhibits antibacterial [5], antifungal [6] and antitumor activity [7]. This has led

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to concentrate deep research on this class of compounds.[8]. Similarly, the presence of hetero-atoms in the Schiff bases enhances activity [9].

Multidentate ligands are extensively used for the preparation of metal complexes with interesting properties. Among these ligands, Schiff bases containing nitrogen and phenolic oxygen donor atoms are of considerable interest due to their potential application in catalysis, medicine and material science [10].

Aminophenols are important to the pharmaceutical industry, since they have antibacterial and antitubercular action. Schiff bases obtained by the condensation of 2-aminophenol with some aldehydes/ketones find application as antituberculosis compounds. They also find application in the biophysical and clinical studies as metal ligand luminescence probes [11].

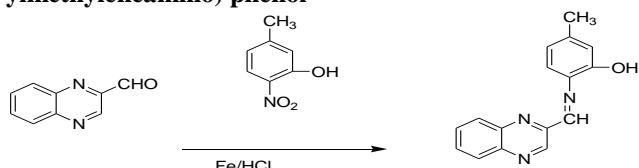
There are a number of reports regarding Schiff base formation between aminophenol and salicylaldehyde derivatives [12].

In this research, we report a one-pot, high-yield, facile, and inexpensive synthesis of Schiff base and new transition metal complexes of tridentate ONN donor Schiff base formed by the condensation of quinoxaline-2-carboxaldehyde and 2-nitro-5-methylphenol.

Experimental section:

The electronic spectra of the complexes were recorded in the region 200-1100 nm on a Thermo electron Nicolet evolution 300 UV-Vis spectrophotometer. Infrared spectra of the ligands and complexes were recorded using Jasco-8000 Fourier Transform Infrared Spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a Bruker AVAVCE III 400 MHz ¹H-NMR spectrometer using TMS as the internal standard. The EPR spectra of the complexes in DMF were recorded on Varian E-112 X/Q band spectrophotometer at liquid nitrogen temperature and the standard used was tetracyanoethylene with a *g* value of 2.0027. The magnetic susceptibility measurements were done at room temperature on a simple Gouy-type balance. TG analyses were carried out on a Perkin Elmer, Diamond thermo gravimetric analyzer at a heating rate of 10 °C per minute in an atmosphere of nitrogen.

Synthesis of Schiff base 5-methyl-2-(quinoxalin-2-ylmethyleneamino) phenol



Hydrochloric Acid (6.25 mmol) was added to a mixture of quinoxaline-2 carboxaldehyde (1.0 mmol), 2-nitro-5-methylphenol (1.0 mmol), and iron powder (10.20 mmol) in 40 ml of EtOH-H₂O (2:1 v/v) solution. The

reaction was heated to 65°C for 5 h before being filtered and recrystallization from methanol to yield yellow crystals; yield 90%; mp 225-226°C.

Preparation of Complexes

The complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by the following procedure:

The Schiff base 5-methyl-2-(quinoxalin-2-ylmethyleneamino)phenol (0.01 mol, 2.633 g) in 1:1 chloroform-methanol (50 mL) solution was added to a solution of manganese(II) acetate tetrahydrate (0.01 mol, 2.4510 g), ferric chloride (0.01 mol, 1.622 g), cobalt(II) acetate hexahydrate (0.005 mol, 1.245 g), nickel(II) acetate hexahydrate (0.005 mol, 1.244 g), copper(II) chloride dihydrate (0.01 mol, 1.705 g) or zinc(II)acetate dihydrate (0.005 mol, 1.097 g) in methanol (15 mL). The solution was then refluxed for three hours and left to cool at room temperature overnight. The crystalline complex separated out was filtered, washed with ether and dried in vacuum over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The complexes are found to be stable in air and non-hygroscopic. They are soluble in common solvents like ethanol, methanol, acetonitrile and DMF. The Co (II), Ni(II) and Zn(II) complexes are formed with metal to ligand ratio of 1:2. Other complexes are formed in 1:1 ratio. The very low conductance values of the complexes in DMF indicate the non-electrolytic nature of the complexes [13-15].

Infrared spectra

The IR spectrum of the ligand is compared with that of the complexes to know the changes during complex formation. On complexation the $\nu(\text{C}=\text{N})$ band at 1635 of the Schiff base shifts to lower or higher frequencies in the spectra of all the complexes indicating coordination of the azomethine nitrogen [16].

For the Schiff base, the $\nu(\text{C}=\text{N})$ stretching of quinoxaline ring is observed as a strong band at 1580. This band undergoes a small shift on complexation; such small shifts have been reported when ring nitrogens are involved in coordination to the metal [17,18].

The $\nu(\text{C}-\text{O})$ band for all the complexes appears at lower frequencies compared to that for the free ligand, suggesting the deprotonation and coordination of phenolic oxygen [19]. The manganese(II), cobalt(II), nickel(II) and the zinc(II) complexes exhibit a broad band in the region 3300-3400 due to the presence of water molecule. Appearance of new bands in the spectra of all the complexes in the regions 490-450 and 450-400 has been attributed to $\nu(\text{M}-\text{O})$ and $(\text{M}-\text{N})$, respectively. The IR spectrum of the acetato complex, $[\text{MnL}(\text{OAc})]\cdot\text{H}_2\text{O}$, displays sym (COO^-) at 1585 suggesting monodentate acetato coordination [20-21].



1H NMR spectra of the SCB and [Zn (SCB)].2H₂O

The signal at 9.70 ppm corresponds to phenolic –OH proton. The azomethine proton appears as a singlet at 8.98 ppm and all the eight aromatic protons appear as a multiplet in the range 7.80- 8.20 ppm. Protons of the methyl group attached to the phenolic ring resonate at 2.37 ppm as a singlet. The phenolic OH signal at 9.70 ppm observed in the spectrum of the ligand is not seen in the spectrum of the Zn(II) complex figure 2 indicating the participation of the phenolic OH group in chelation with proton displacement. The signal due to azomethine proton gets shifted upon complexation, which might probably be due to the donation of the lone pair of electrons by the nitrogen to the central metal atom, resulting in the formation of a coordinate linkage (M - N).

The aromatic and quinoxaline protons resonate as a number of complex multiplets in the region 7.46–8.20 ppm. The signal due to methyl group attached to the phenolic ring is observed almost at the same chemical shift for that in spectrum of the ligand. A broad singlet appeared in the region 3.91– 4.26 indicates the presence of water molecules in the complex.

Electronic spectra

Electronic spectra of the Schiff base and its complexes were taken in methanol (~5×10⁻⁴ molar) in the range 50000-10000 cm⁻¹.

The UV-Vis spectrum of the Schiff base shows two strong bands at 42500 and 26000 cm⁻¹ due to π - π^* transitions [22-24]. These π - π^* bands are not altered to a greater extent on complexation. The spectrum of the Mn(II) complex shows two shoulders at 10810 and 9300 cm⁻¹ assignable to 6A₁--4T₁ and 6A₁--4T₂ (G) transitions respectively [25]. The solution state electronic spectrum of the iron(III) complex did not show any d-d bands. Two charge transfer bands are seen at 24000 and 18200 cm⁻¹ respectively. The d-d bands are seen in the solid state spectra due to the high concentration of the complex in the solid state. Two bands are seen in the visible region at 11110 and 10200 cm⁻¹, and a weak broad band is observed in the near IR region at 6890 cm⁻¹ indicating a square pyramidal structure. Similar observations have been made by Martin and White for the five coordinated iron(III) dithiocarbamate complex [26].

For the cobalt(II) complex, a band with maxima at 18550 cm⁻¹s due to the 4T₁g(F)-4T₂g(P) transition[27]. The intensities of the d-d band is considerably increased possibly due to the influence of nearby intense charge-transfer transitions ($\log \epsilon = 3.36$). The other d-d transitions are masked by the strong charge transfer band, as has been observed in the case of similar Schiff base complexes [28]. For the nickel(II) complex, the band at 17450 is due to the 3A₂g-3T₁g transition of nickel(II) in octahedral environment. The intensity of this d-d band is also considerably increased possibly due to the influence of nearby intense charge transfer transitions.

The spectrum of [Cu(qamp)Cl] shows bands at 22220 and 16000 assignable to 2B₁g-2A₁g and 2B₁g-2E_g transitions, respectively [21] as expected for the square planar copper(II) complexes. The zinc(II) complex exhibits a charge transfer transitions at 18310 cm⁻¹.

Thermal analysis

The Schiff base exhibits a one stage decomposition which begins at 160 °C. The weight loss observed for the Mn(II), Co(II), Ni(II) and Zn(II) complexes in the range 40-140 °C is due to the removal of lattice water.

The TG data indicate the presence of one hydrated water molecule in the manganese(II), cobalt(II) and nickel(II) complexes, and two water molecules in the zinc(II) complex. All the compounds are found to be thermally stable and exhibit multi stage decomposition pattern. TG results show good agreement with the molecular formula arrived from the analytical data.

EPR spectra

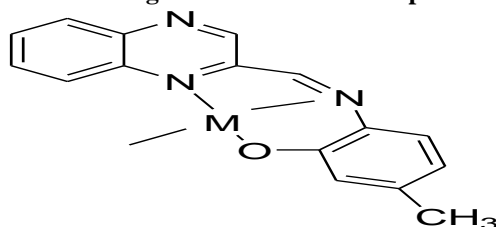
The X band EPR spectra of the manganese (II) complex is taken in polycrystalline state at 298 K and in DMSO at 77K where H is the magnetic field vector, g is the spectroscopic splitting factor, β is the Bohr magneton, D is the axial zero field splitting term, E is rhombic zero field splitting parameter and S is the electron spin vector [29]. The solid state EPR spectrum of the Mn(II) complex is characterized by the broad isotropic spectrum with a g value of 1.98. The solution spectrum gives six hyperfine lines with the spin forbidden transitions in between the lines. The spectrum gives a g value of 1.98 with an A value of 0.011 cm⁻¹.

The copper (II) ion, with a d⁹ configuration, has an effective spin of S= 3/2 and is associated with a spin angular momentum ms=1/2, leading to a doubly degenerate spin state in the absence of a magnetic field. For 3d⁹ copper (II) ion the appropriate spin Hamiltonian assuming a B₁g ground state is given by [30-34]

The EPR spectrum of the copper (II) complex in polycrystalline state gives an isotropic spectrum with a g value of 1.98. This spectrum exhibits a broad signal which arises from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra gives no information on the electronic ground state of the Cu(II) ion present in the complexes. [35-38]. Crystal structures of [Co(SCB)₂].H₂O and [Ni(SCB)₂].H₂O confirm the octahedral geometry of the complexes. Thus the Schiff base coordinates through azomethine nitrogen, phenolic oxygen and quinoxaline oxygen and acts as a monobasic tridentate ligand. Based on the analytical and physicochemical data we have proposed the following structures for the metal complexes.



Figure 1. Schiff base compound



M—Manganese acetate, M—Ferric chloride, M—Cuprous chloride, M—Zn acetate, M—Cobalt hydrate

Table 1. Analytical data of Schiff base compound

Compound	Color	Yield	Analytical data. Found (calculated)%				
			carbon	Hydrogen	Nitrogen	Metal	Cl
[SCB]	Yellow	85	72.50/72.86	4.20/4.85	15.74/15.94	----	----
SCB Mn	red	72	54.60/54.45	4.00/4.15	10.70/10.57	14.40/14.42	---
SCBFe	black	74	50.00/49.79	3.15/3.00	10.70/10.56	14.40/14.36	18.43
SCB Co	violet	80	63.75/62.98	4.25/4.16	14.00/14.12	9.80/9.66	---
SCB Ni	blue	75	63.70/63.90	4.00/3.86	13.05/12.78	9.80/9.76	----
SCB Cu	violet	75	53.68/53.22	3.40/3.44	11.70/11.24	17.95/17.60	9.95
SCB Zn	Violet	80	62.00/61.96	4.15/4.55	14.00/13.95	10.55/10.78	---

Table 2. List of IR spectral bands along with their tentative assignments

Compound	$\nu(\text{OH}) \text{ cm}^{-1}$	$\nu(\text{C=N})\# \text{ cm}^{-1}$	$\nu(\text{C=N}) * \text{ cm}^{-1}$	$\nu(\text{C-O})\$ \text{ cm}^{-1}$	$\nu(\text{M-O}) \text{ cm}^{-1}$	$\nu(\text{M-N}) \text{ cm}^{-1}$
[SCB]	3325	1635	1580	1265	--	---
SCB Mn	3300 b	1610	1585	1235	465	415
SCBFe	----	1585	1550	1255	490	425
SCB Co	3395b	1665	1580	1254	560	465
SCB Ni	3200 b	1675	1585	1255	450	435
SCB Cu	---	1612	1580	1255	425	410
SCB Zn	3381b	1675	1585	1255	445	425

b-broad, # azomethine, * quinoxaline, \$ phenolic

Table 3. List of absorption maxima

Compound	Absorption maxima (cm-1)	$\log \epsilon$ (ϵ in $\text{L mol}^{-1}\text{cm}^{-1}$)	Assignments
Schiff Base	42500	3.96	$\pi \rightarrow \pi^*$
	26000	3.81	$\pi \rightarrow \pi^*$
SCB Mn	41320	3.56	$\pi \rightarrow \pi^*$
	29850	3.25	$\pi \rightarrow \pi^*$
	26400	3.30	CT
	18280	3.27	CT
	10800	1.67	${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$
	9300	1.68	${}^6\text{A}_1 \rightarrow {}^4\text{T}_2(\text{G})$
SCBFe	42920	4.12	$\pi \rightarrow \pi^*$
	24000	3.96	CT
	18200	3.70	CT
SCB Co	41850	4.13	$\pi \rightarrow \pi^*$
	29400	3.88	$\pi \rightarrow \pi^*$
	26450	3.83	$n \rightarrow \pi^*$
	18550	3.83	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$
SCB Ni	41150	4.13	$\pi \rightarrow \pi^*$
	27850	3.88	$\pi \rightarrow \pi^*$
	17450	3.83	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$



SCB Cu	40320	3.74	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ CT ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2E_g$
	33900	2.44	
	28490	3.65	
	22220	2.08	
	16000	1.97	
SCB Zn	42200	3.72	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ CT
	30400	3.30	
	25840	3.31	
	18310	3.36	

Table 4. The TG of schiff base complexes

Compound	Temperature range	% loss	Fragment lost	Nature of water lost
SCB Mn	46-101	4.5	1 molecule	Lattice water
SCB Co	50-120	3.0	1 molecule	Lattice water
SCB Ni	50-130	3.0	1 molecule	Lattice water
SCB Zn	70-140	3.0	1 molecule	Lattice water

Figure 2. The NMR spectrum of Schiff Base

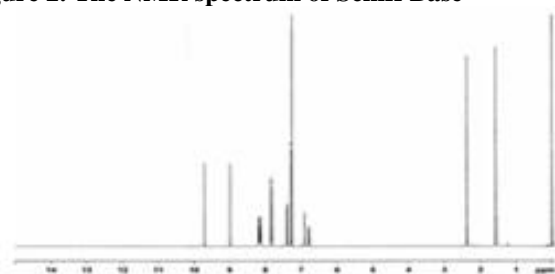


Figure 1 NMR of SCB

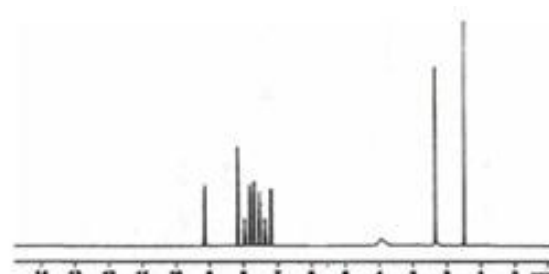


Figure 2 NMR of SCB Zn

Figure 3. The NMR spectrum of Zink complex

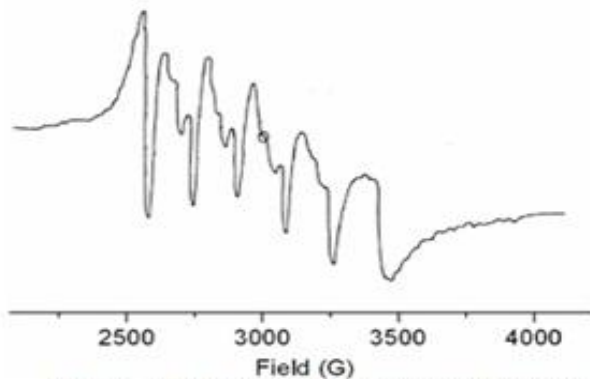


Figure 3 EPR spectra of the manganese (II) complex

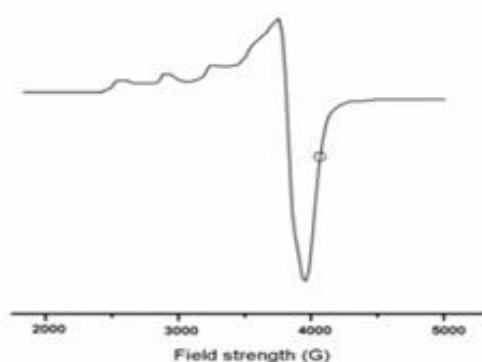


Figure 4 The EPR spectrum of the copper(II) complex

CONCLUSION

Green chemistry for chemical synthesis addresses our future challenges in working with chemical processes and products by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes that can simplify operations in chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign.

Schiff base have been prepared by a simple one pot tandem and environmentally friendly reductive imination procedure. This methodology uses only Fe (0) in acidic EtOH/H₂O as a reductant for nitroarenes, which upon reduction spontaneously condense with an aldehyde. Since the intermediate (amine) is not isolated it becomes easier to work with sensitive or unstable intermediates.



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