

Synthesis, spectroscopic investigation and *in vitro* fungicidal action of novel Schiff's base ligand and its metal chelates

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ABSTRACT: Novel Schiff's base ligand and its metal chelates of Mn(II) and Co(II) metal have been synthesized and structural investigation done by using spectroscopic methods. Mn(II) and Co(II) metal chelates of synthesized ligand have been prepared by using their chloride and acetate salts. All metal complexes are characterized by elemental analyses, molar conductance, magnetic moment measurements and spectral (UV-Vis, IR and ESR) studies. Ligand acts in tetradentate manner and coordinate to metal ions through nitrogen and oxygen donor atoms. The low value of molar conductance in DMSO indicate that metal chelates are non-electrolyte *i.e.* showing non-electrolytic behaviour. Values of magnetic moment and electronic spectral data suggested octahedral geometry for the Mn(II) and Co(II) complexes. Ligand and metal chelates are screened *in-vitro* for fungicidal activity against fungi *i.e.* *Aspergillus flavus*, *Aspergillus niger* and *Fusarium oxysporum*.

Keywords: Mn(II), Co(II), chelates, spectroscopic, Schiff's base ligand, octahedral, fungicidal

INTRODUCTION

The coordination chemistry has been significantly enriched due to the synthesis of metal chelates, in which the metal is coordinated through sulphur, nitrogen and oxygen donor atoms¹⁻⁵. Metal chelation is involved in many essential biological processes where the coordination can occur between metal ions and donor atoms present in ligand. In coordination chemistry, Schiff's base chelates are attracted attention by both inorganic and bioinorganic researchers⁶⁻⁷. Aza-oxo group containing ligands come into view, that these types of compounds and their metal chelates are very potential and used as antibacterial, antifungal, anticancer agents as well as due to their other biological properties⁸⁻¹³. This research article focuses on synthesis of N₂O₂ donor Schiff's base ligand and its metal chelates of manganese(II) and cobalt(II) ions derived from benzil and nicotinic hydrazide. The formation of the chelates has been confirmed by using spectral studies. The *in vitro* antifungal activity against three fungi stains (*A. flavus*, *A. niger* and *F. oxysporum*) has been examined.

MATERIALS AND METHODS

All used, commercial chemicals have been used as received. Benzil, and nicotinic hydrazide are

(AR grade) procured from Sigma Aldrich, Bangalore, India. All used solvents were of spectroscopic grade and used as received.

Scheme of Synthesis of Schiff's base ligand benzil-bis(nicotinichydrazone)

In a hot stirred ethanolic solution of benzil (0.005 mol, 1.0511 g) nicotinic hydrazide (0.01 mol, 1.3714 g) has been added drop wise. The reaction was refluxed for 15 hrs. at temperature 75°C and then cooled for 5 hrs. at room temperature. Reaction solution has been kept in an ice bath. After one hour, the precipitation procedure took place and obtained precipitate filtered off, washed with distilled water and recrystallized by using appropriate solvent and dried in vacuum Figure 1.

Synthesis of Schiff's base metal chelates

All chelates have been produced by using condensation process, *i.e.*, by condensation of ligand [benzil-bis(nicotinichydrazone)] and divalent metal salts in molar ratio 2:1. Hot solution of divalent metal salt of Mn(II) and Co(II) has been added in hot ethanolic solution of ligand. The resulting solution is refluxed continue for 15-22 hrs. On overnight cooling, coloured precipitates

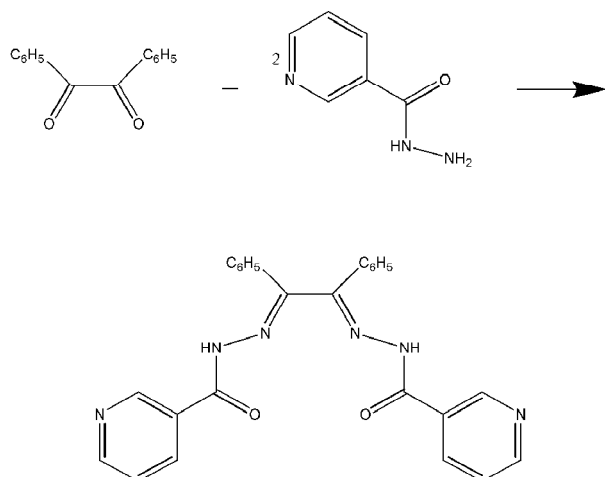


Figure 1: Synthesis of Schiff's base ligand

are formed which filtered off, washed with ethanol and dried in vacuum. The obtained yields are found approximately 55-65%.

Physical measurements

Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on FT-IR spectrum BX-II spectrophotometer in KBr pellet. Magnetic susceptibility was measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. Electronic impact mass spectrum was recorded on JEOL, JMS-DX-303 Mass Spectrometer. The electronic spectra were recorded in DMSO on Shimadzu UV-visible mini-1240 spectrophotometer. EPR spectra of all complexes were recorded at room temperature (RT) on E_4 -EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay.

Fungicidal screening

The introductory fungicidal screening of synthesized compounds at concentration 1000 ppm was performed *in vitro* by poison food technique¹⁴⁻¹⁵. Fungicidal investigation of synthesized metal complexes has been done against fungi *A. flavus*, *A. niger* and *F. oxysporum* DMSO and Captan employed as a control and standard fungicide, respectively. This technique is mostly used to evaluate the antifungal activity. The antifungal agent (synthesized compounds) is incorporated into the molten agar at a desired final concentration (1000 ppm) and mixed well with media. Then, the media is poured into petri dishes.

After overnight pre-incubation, the inoculation has been done by a mycelia disc ranging from 2 to 5 mm, which is deposited in the centre of the plate. After further incubation under suitable conditions for the fungal strain tested, the diameters of fungal growth in control and sample plates have been measured and the antifungal effect is estimated by the following formula:

The inhibition of growth of fungi was expressed in percentage and determined by using following relation which is given below:

$$I (\%) = (CT)/C \times 100$$

Where I = % Inhibition,

C = Radial diameters of the colony in control,

T = Radial diameter of the colony in test compound.

RESULTS AND DISCUSSION

The transition metal complexes were synthesized by reacting synthesized Schiff's base ligand in the presence of divalent metal salts in 2:1 ratio, respectively, in ethanolic medium. On the basis of elemental analysis, the complexes have been found to have the composition, which are given in Table 1. The molar conductance values of the complexes in DMSO lies in the range of $17-35 \text{ cm}^2 \text{ mol}^{-1}$. These values suggested their non-electrolytic behaviour¹⁶⁻¹⁸. Thus the complexes may be formulated as $[\text{M}(\text{L})\text{X}_2]$ [where M = Mn(II) and Co(II)X = Cl, CH_3COO].

¹H-NMR spectrum of Schiff's base ligand

The ¹H-NMR spectrum of the Schiff's base ligand (L) in DMSO- d_6 give signals which are attributed to aromatic proton Ar-H (6H) at δ 7.89 ppm (m), NH (4H) at δ 12 ppm. This data support to the presence of different protons in ligand.

Mass spectrum of Schiff's base ligand

The electron impact mass spectrum of ligand confirms the proposed formula by showing a peak at 446 amu (atomic mass 448). It also shows a series of peaks 384 amu, 353 amu, 263 amu, 228 amu, 162 amu, 151 amu, 133 amu etc., corresponding to various fragments. Their intensity gives an idea of the stability of fragments.

IR Spectra

In IR spectra of metal complexes bands in the region $2850-2880 \text{ cm}^{-1}$ and $1590-1630 \text{ cm}^{-1}$ corresponding to the presence of the aromatic

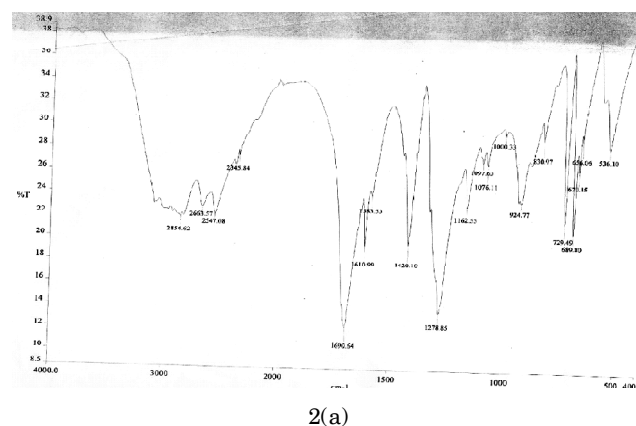
Table 1
Physical properties and analytical data of Mn(II) and Co(II) complexes

Compound	Colour	M.P. (°C)	M. Wt.	Molar conductance	Yield (%)	Elemental Analysis found (calculated)			
						C	H	N	M
Schiff's base ligand	Light Yellow	85	448.73	-	68	69.47 (69.52)	4.41 (4.45)	18.65 (18.71)	-
[Mn(L)Cl ₂]	Pink	>200	574.66	24	58	54.12 (54.29)	3.33 (3.48)	14.47 (14.61)	10.02 (10.25)
[Mn(L)(SO ₄)]	Light Pink	>250	599.66	231	54	51.98 (52.02)	3.18 (3.33)	14.00 (14.00)	9.11 (9.16)
[Co(L)Cl ₂]	Brown	>360	583.27	25	61	53.41 (53.49)	3.40 (3.42)	14.28 (14.40)	10.68 (10.89)
[Co(L)(CH ₃ COO) ₂]	Light Brown	>340	630.27	27	55	57.10 (57.11)	4.08 (4.12)	13.13 (13.32)	10.01 (10.08)

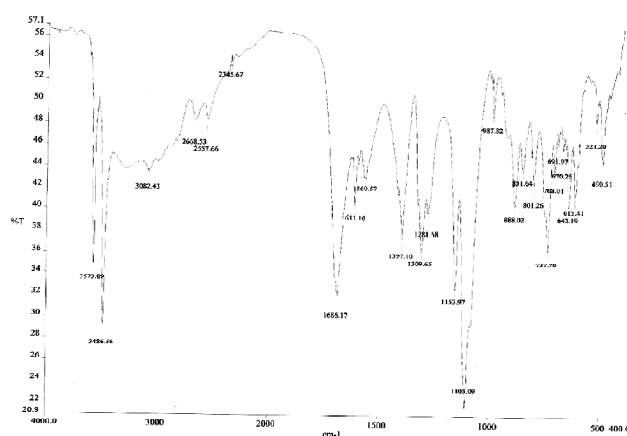
stretching, azomethine group (C=N) Figure 2(a)¹⁹. This binding of donor atoms to metal ion is also supported by the appearance of new IR bands at 438-480 and 590-610 cm⁻¹ due to <(M-N) and <(M-O) vibrations²⁰. This discussion reveals that the nitrogen atoms of azomethine group and oxygen atom coordinate to metal ions as tetradentate chelate to form complexes.

Bands due to anions

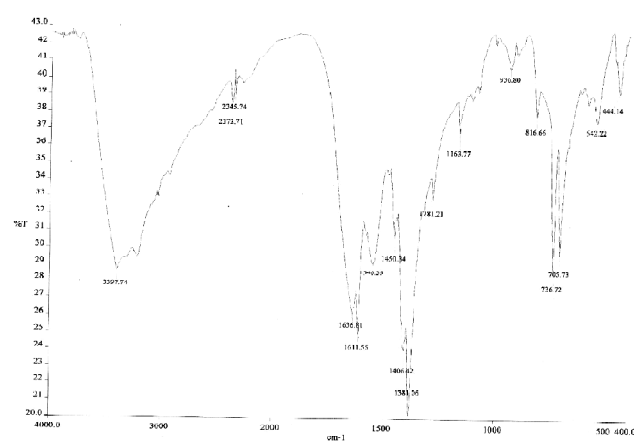
In IR spectra of chloride complexes, bands corresponding to (M-Cl) were observed at 345-330 cm⁻¹²¹. Spectrum of sulphate complex of Mn(II) shows that band ν_3 splitted at 1153 cm⁻¹ and 1105 cm⁻¹ and a peak at 987 cm⁻¹ correspond to unidentate behaviour of sulphate ion²² Figure 2(b). The acetate Mn(II) and Co(II) complexes show IR bands in the range 1406-1321 cm⁻¹ and 1281-1321 cm⁻¹ due to ν_{as} (OAc) and ν_s (OAc) stretching vibrations²³. Differences between ν_{as} (OAc)- ν_s (OAc) were found in between the range of 80-169 cm⁻¹ which indicate that acetato group coordinated to metal ion in monodentate manner²⁴ Figure 2(c).



2(a)



2(b)



2(c)

Figure 2: IR spectra of (a) Schiff's base ligand (b) [Mn(L)(SO₄)] (c) [Co(L)(CH₃COO)₂]

Magnetic moment

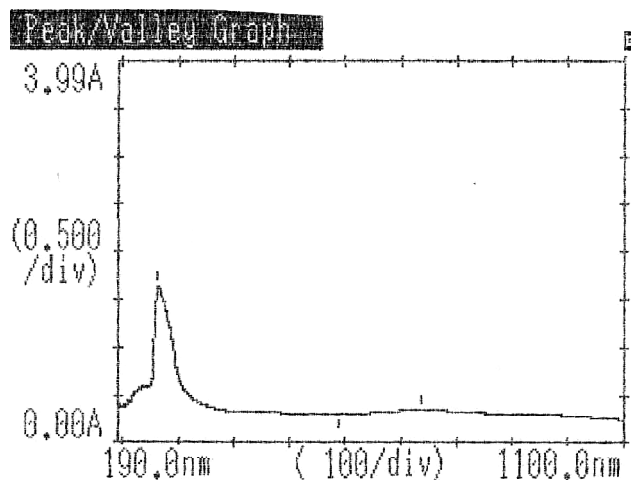
The magnetic moment observed for Mn(II) and Co(II) complexes lies in the range 5.92-5.95 B.M. and 4.79-4.92 B.M. corresponding to presence of five and three unpaired electrons, respectively²⁵⁻²⁶. The observed magnetic moments of Mn(II) and Co(II) complexes are given in Table 2.

Electronic spectra

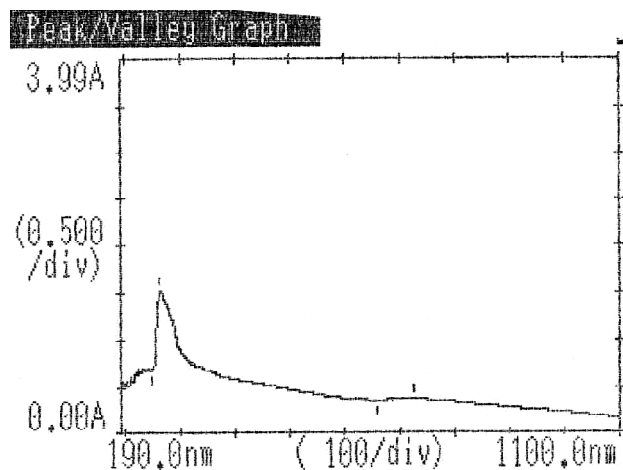
The electronic spectra of Mn(II) complexes displayed the absorption bands in the range of 17,850-18,518 cm^{-1} , 23,034-24,096 cm^{-1} , 26,809-28,188 cm^{-1} and 34,482-37,735 cm^{-1} . These transitions may be assigned to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_g$ (4D) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (P)²⁷. These transitions revealed the octahedral geometry for the Mn(II) complexes Figure 3. The electronic spectra of Co(II) complexes under study displayed the absorption bands in the range of 9310-9940 cm^{-1} , 16,290-19,143 cm^{-1} and 20,510-22,339 cm^{-1} . These transitions may be assigned to the ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$, and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$. The transitions were corresponding to the octahedral geometry of the Co(II) complexes²⁸ Table 2.

Ligand field parameters

The ligand field parameters like B, C (Racah parameters), 10 Dq, covalency factor and LFSE were calculated for complexes. Slater Condon-shortly repulsion parameters F_2 and F_4 are related to Racah parameters B and C as: $B = F_2 - 5F_4$ and $C = 35F_4$. The electron-electron repulsion in the complexes was more than in the free ion, resulting in an increased distance between electrons, and thus, affects the size of the orbital. On increasing delocalization, the value of β decreases up to less than one in the complexes. The value of β can be calculated from the Nephelauxetic parameter for (hx) for the metal ion (km) as $(1-\beta) = hxXkm$. The value of the parameter hx for Mn(II) complexes was calculated by using the covalency contribution of Mn(II), while for the calculation of β , we used the numerical value of B for Mn(II) and Co(II) free ion is 786 cm^{-1} , and 1120 cm^{-1} respectively. The observed values for parameter β and hx suggested that the complexes, reported here, had appreciable ionic character²⁹⁻³⁰. The calculated values of the ligand field parameters are given in Table 3.



(a)



(b)

Figure 3: Electronic Spectra of 3(a) [Mn(L)Cl₂]₃(b) [Co(L)Cl₂]₃

Electron spin resonance (ESR)

An ESR spectra is readily detected even for large zero-fields splitting, because d^5 is an odd electron system whose ground state is a Kramer's doublet and whose degeneracy is only completely removed by a magnetic field. The broad signal in the polycrystalline ESR spectra of Mn(II) complexes is attributed to forbidden transitions, where $M = \pm 1$ ($M =$ electron spin quantum number). The broadening of spectra is due to immobilization of Mn(II) ion in the ligand results because the rotational motion of Mn(II) is highly restricted. Another origin of line broadening is due to spin relaxation, which is temperature dependent. All the Mn(II) complexes, under study, shows isotropic ESR spectra, Figure 4, when recorded

Table 2
Electronic spectral data and magnetic moment of the complexes

Compound	$\lambda_{max}(cm^{-1})$	Magnetic Moment (B.M.)
[Mn(L)Cl ₂]	17,850, 23,034, 26,809	5.92
[Mn(L)(SO ₄)]	18518, 24096, 28188	5.95
[Co(L)Cl ₂]	9310, 16290, 20510	4.79
[Co(L)(CH ₃ COO) ₂]	9940, 19143, 22339	4.92

Table 3
Ligand field parameters for the complexes

Compound	$\lambda_{max}(cm^{-1})$	Dq	B'	C	F_2	F_4	LFSE (KJ mol ⁻¹)	h_x	β
[Mn(L)Cl ₂]	17,850, 23,034, 26,809	1785	692	3222	1152	92	256.22	1.71	0.88
[Mn(L)(SO ₄)]	18518, 24096, 28188	1851	711	3397	1196	97	365.69	1.42	0.90
[Co(L)Cl ₂]	9310, 16290, 20510	931	591	-	-	-	133.63	-	0.52
[Co(L)(CH ₃ COO) ₂]	9940, 19143, 22339	994	777	-	-	-	142.67	-	0.69

as polycrystalline sample. The X-band ESR spectra of the Co(II) complexes were recorded at liquid nitrogen temperature in polycrystalline form. The ESR spectra of Co(II) complexes with $g_{iso} = 2.012.04$ correspond to the tetragonal symmetry around the Co(II) ion, (Table 4)³¹. As a consequence of the fast spin-relaxation time of high-spin Co(II) ion, the signals are observed only at low temperature.

Fungicidal screening

The fungicidal screening data showed that ligand and its metal complexes exhibited antifungal activity and it is important to note that the metal chelates exhibited more inhibitory effects than the parent ligand. The increased activity of complexes can be explained based on chelation theory³². On chelation, the polarity of the metal ion will be reduced due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups. Further, it increases the delocalization of the π electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and thus blocks the metal binding sites on enzymes of microorganisms. These metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism. The variation in the activity of different

Table 4
ESR spectral data of The Mn(II) And Co(II) complexes

Complex	$g_{ }$	g_{\perp}	g_{iso}
[Mn(L)Cl ₂]	-	-	2.01
[Mn(L)(SO ₄)]	-	-	2.04
[Co(L)Cl ₂]	2.0225	1.9409	2.3511
[Co(L)(CH ₃ COO) ₂]	2.3817	2.1530	2.2292

complexes against different organisms depend either on the permeability of the cells of the microbes or difference in ribosomes of microbial cells. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration of tested compounds was increased the activity also increased. The activity data of tested compounds is given in Table 5.

Table 5
Fungicidal screening result of ligand and its complexes at concentration 1000 ppm

Complex	<i>A. flavus</i>	<i>A. niger</i>	<i>F. oxysporum</i>
Schiff's base ligand	30	NA	45
[Mn(L)Cl ₂]	70	68	90
[Mn(L)(SO ₄)]	97	70	85
[Co(L)Cl ₂]	75	70	55
[Co(L)(CH ₃ COO) ₂]	95	98	90

CONCLUSION

Continuing the synthetic strategies, ligand (N_2O_2 type) benzil-bis(nicotinichydrazone) and its Mn(II), Co(II) complexes have been synthesized. The ligand interacted to Mn(II) and Co(II) metal ion in bidentate manner and formed stable complexes. Based on IR spectral study, it was concluded that ligand coordinated to metal ion in tetradentate manner *i.e.* through nitrogen and oxygen donor atoms. IR, UV and EPR spectroscopic characterization study revealed that Mn(II) and Co(II) complexes possessed an octahedral geometry Figure 4. The antifungal screening of all investigated compound provided information about biological activity of ligand and its complexes which is important in model compounds study.

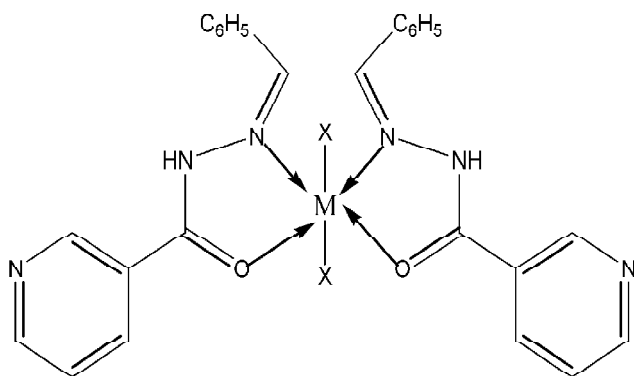


Figure 4: Proposed chemical structure of Schiff's base metal complexes

M = Mn(II), Co(II) and X = Cl⁻, CH₃COO⁻

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