



ISSN No: 0975-7384
CODEN(USA): JCPRCS

J. Chem. Pharm. Res., 2011, 3(6):905-911

Synthesis, Characterization and Fungicidal Activity of 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline ligand and its metal complexes

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ABSTRACT

*Novel Schiff base ligand 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline have been synthesized by the condensation of 1-phenylethanone with 3-chloro-4-methylaniline. Transition metal complexes of Mn(II), Fe(II), Co(II) and Ni(II) have also been synthesized. The ligand and its metal complexes were characterized based on mass spectral data, IR, ¹HNMR and ¹³CNMR spectroscopy. The spectral data of the metal complexes were interpreted on the basis of comparison with that of the free ligand. The analysis showed that the ligand coordinated to the metal ion through the azomethine nitrogen, the chloride and two aqua molecules. An octahedral geometry have been suggested for the metal complexes. The compounds were screened against *Aspergillus niger* *Macrophomina phaseolina*, *Fusarium oxysporum* and *Alternaria alternata*. Their potency have been discussed. It has been found that all the complexes are active and showed higher activity than the free ligand. Metal chelation affected the bioactive behavior of the organic ligand.*

Keywords: 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline, complexes, ligand, fungicidal, spectra.

INTRODUCTION

Coordination compounds and their complexes have significant importance in chemistry. Every year, number of reports is published on preparation of these compounds and their application in chemical reactions [1]. Coordination compounds have been reported to possess pharmacological activities such as anticancer [2], antitumour [3], amoebicidal [4], fungicidal [5], pharmacological [6] and antibacterial [7] activity among others. A large number of structurally novel ligands

derivatives have ultimately been reported to show substantial cytotoxic activity *in vitro* and *in vivo* [8]. Subsequent analysis of scientific literature revealed numerous reports on the antitumour activity of a variety of coordination compounds [9]. Coordination compounds have also been reported in clinical trials to demonstrate activity against prostate cancer [10] and malignant melanoma [11]. Metal complexes are a subject of increasing interest in bioinorganic and coordination chemistry.

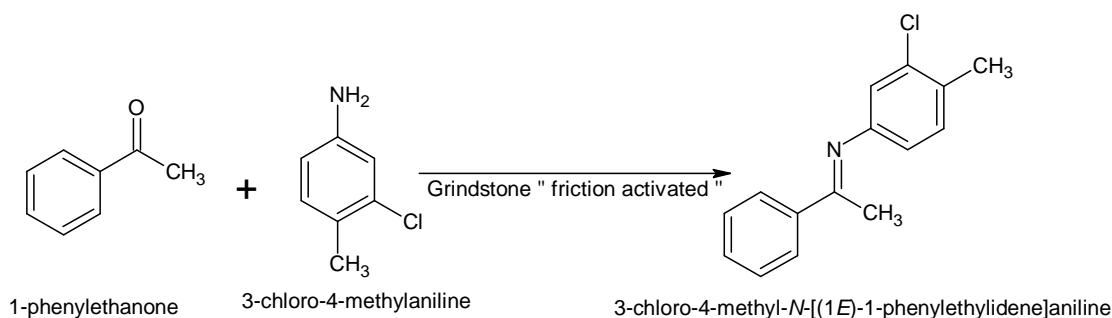
In this paper, we present synthesis, characterization and fungicidal activity of 3-chloro-4-methyl-*N*-[(1*E*)-1-phenylethylidene]aniline ligand and its metal complexes.

EXPERIMENTAL SECTION

The compounds used were Merck products, analytical grade. Melting points were determined in open capillary tubes using an electrothermal 9300 digital melting point apparatus. The IR spectra were recorded on Perkin Elmer RX-I Spectrophotometer. Mass spectra were recorded on JEOL SX102/DA-6000 mass spectrometer. ¹HNMR spectra were recorded at room temperature on Bruker WP 250 spectrometer in DMSO-d₆. Chemical shifts are given in ppm. ¹³CNMR spectra were recorded on Bruker 250 WM spectrometer in DMSO-d₆. Chemical shifts are given in ppm.

Synthesis of 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline ligand

A mixture of 3-chloro-4-methylaniline (1 mmol, 0.14g) and 1-phenylethanone (1mmol, 0.12g) was grinded in a mortar with a pestle made of porcelain for 5-10 minutes. The mixture turned pasty after few minutes of grinding. The reaction mixture was left overnight. The solid product obtained was recrystallized in absolute ethanol. The yield was recorded. The chemical reaction is shown in Equation 1.



Equation 1: Synthesis of 3-chloro-4-methyl-*N*-[(1*E*)-1-phenylethylidene]aniline

Synthesis of the metal complexes

Synthesis of 3-chloro-4-methyl-*N*-[(1*E*)-1-phenylethylidene]aniline ligand (2 mmol) was dissolved in 25 ml ethanol. 1 mmol of the respective metal chlorides {Mn(II), Fe(II), Co(II) or Ni(II)} was dissolved in ethanol. The two solutions were mixed together and refluxed for three hours. The product formed was recrystallized in ether. The yields were recorded.

Antifungal Screening

Bioefficacies of the synthesized compounds were checked *in vitro*. The *in vitro* antifungal activities of the ligand and its complexes have been evaluated against several fungi by the agar plate technique. The compounds were directly mixed with the medium in different concentrations. Controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the diameter of the fungal colony after four days. The amount of growth inhibition in each of the replicate was calculated by Equation 3.

$$\text{Equation 3: Percentage inhibition} = (C-T) \times 100/C$$

where C is the diameter of the colony on the control plate and T is the diameter of the fungal colony on the test plate.

RESULTS AND DISCUSSION

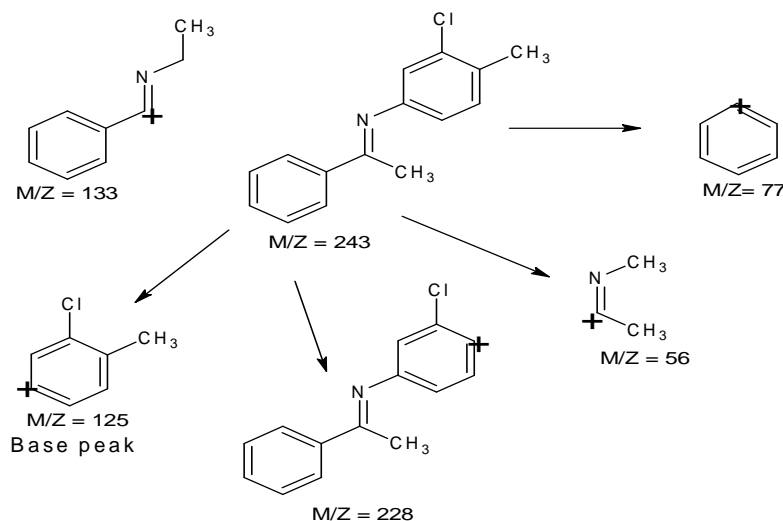
The physical data of the ligand and complexes are reported in Table-1. The formula weight of the complexes gave an indication that the complexes are dimeric in nature.

Table-1: Physical data of the ligand and metal complexes

Compound	Colour	Melting point °C	Yield %	Formula weight
CMPA	White	122	64	243
Mn(CMPA) ₂	Yellow	141	57	578
Fe(CMPA) ₂	Green	145	59	579
Co(CMPA) ₂	Cream	161	53	582
Ni(CMPA) ₂	White	163	58	582

*CMPA = 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene] aniline

The mass spectra of the ligand showed a molecular ion peak at M/Z 243 and a base peak at M/Z 125. Other fragmentation peaks are shown in Scheme-1.



Scheme 1: Mass spectra fragmentation pattern

The IR spectra of the ligand and metal complexes are presented in Table-2.

Table-2: IR spectra data of the ligand and complexes (cm⁻¹)

Compound	v(C-Cl)	v(C-H) Ar	v(C-H) Alk	v(C-C) Ar	v(C=N)	v(M-Cl)	v(M-N)	vOH(H ₂ O)
CMPA	1019	3048	2880	1531	1576	Absent	Absent	Absent
Mn(CMPA) ₂	1010	3084	2863	1525	1550	410	545	3313
Fe(CMPA) ₂	1011	3052	2889	1532	1551	418	523	3357
Co(CMPA) ₂	1011	3030	2876	1516	1556	421	521	3375
Ni(CMPA) ₂	1012	3061	2856	1533	1553	423	525	3384

*CMPA = 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene] aniline

The IR spectrum of the ligand was compared to the spectra of the complexes. The v(C-Cl) of the ligand appeared at 1019 cm⁻¹ but this band was shifted downfield (1010-1012cm⁻¹) in the spectra of the complexes [12]. This indicated that the chloride ion was involved in chelation. The v(C=N) absorption band appeared in 1576 cm⁻¹ in the ligand. This band was shifted to 1550 - 1556 cm⁻¹ in the complexes. This blue shift also suggested complexation [13]. The v(M-Cl) and v(M-N) bands were found at 410 – 423 cm⁻¹ and 521-545 cm⁻¹ in the complexes [14]. This absorption band were absent in the complexes. The vOH(H₂O) was absent in the ligand but were found at 3313 – 3323 cm⁻¹ in the complexes [15].

The ¹HNMR spectra of the ligand and metal complexes have been reported in Table-3.

Table-3: ¹HNMR spectra data of the ligand and complexes (δ, ppm)

Compound	Ar protons	HC=N proton	Alkyl protons	OH(H ₂ O)
CMPA	7.54-7.24	8.54	1.0	Absent
Mn(CMPA) ₂	7.52-7.27	7.34	0.9	4.3
Fe(CMPA) ₂	7.56-7.25	7.37	0.9	4.4
Co(CMPA) ₂	7.52-7.28	7.48	1.1	4.7
Ni(CMPA) ₂	7.58-7.28	7.39	1.1	4.9

*CMPA = 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene] aniline

The aromatic protons were found at δ 7.24-7.58 ppm in the ligand and complexes. The azomethine proton was found at δ 8.54 ppm. This band was shifted to δ 7.34-7.49 ppm in the complexes. This shift to lower frequency in the azomethine indicated complexation through the nitrogen atom of the azomethine. The alkyl protons were found at δ 0.9-1.1 ppm in the ligand and complexes. The OH(H₂O) was absent in the ligand but present in the complexes at δ 4.3 - 4.9 ppm [15].

The ¹³CNMR of the ligand/complexes are presented in Table-4.

Table-4: ^{13}C NMR spectra data of the ligand and complexes

Compound	Ar C	C-Cl	C=N	CH ₃
CMPA	114.0-149.0	70.9	155.0	14.8
Mn(CMPA) ₂	118.0-146.0	61.4	141.0	16.3
Fe(CMPA) ₂	117.0-144.0	61.6	142.0	14.2
Co(CMPA) ₂	116.0-142.0	60.3	143.0	15.7
Ni(CMPA) ₂	114.0-145.0	61.5	144.0	15.5

*CMPA = 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene] aniline

The aromatic carbons were found at δ 114-149 ppm in all the compounds. The alkyl protons were present at δ 14.2 – 16.3 ppm in the ligand and complexes. The C-Cl carbon appeared at δ 70.9 ppm in the ligand. This chemical shift value decreased in the complexes. They were found at δ 60.3 – 61.5 ppm. This decrease in chemical shift of the complexes suggested coordination through the chloride ion. The C=N signal appeared at δ 155 ppm in the ligand but was shifted downfield in the complexes (δ 141-144 ppm). This blue shift also suggested coordination through the nitrogen atom of the C=N [14].

The average percentage inhibition (mm) of the compounds against *Aspergillus niger*, *Macrophomina phaseolina*, *Fusarium oxysporum* and *Alternaria alternata* are shown in Table-5.

Table-5. Average Percentage Inhibition (mm) after 96 hours at 50 ppm concentration

Compound	<i>Aspergillus niger</i>	<i>Macrophomina phaseolina</i>	<i>Fusarium oxysporum</i>	<i>Alternaria alternata</i>
CMPA	47	43	49	53
Mn(CMPA) ₂	55	56	63	65
Fe(CMPA) ₂	53	61	54	68
Co(CMPA) ₂	66	65	76	60
Ni(CMPA) ₂	68	60	68	62

*CMPA = 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene] aniline

All the compounds were active against the fungi species. The complexes were more active than the free ligand against the fungi species. Co(CMPA)₂ showed the highest inhibitory activity. Metal chelation affected the bioactive behavior of the organic ligand.

On the basis of the spectra evidences, an octahedral geometry has been proposed for the complexes. Suggested geometry is presented in Figure-1.

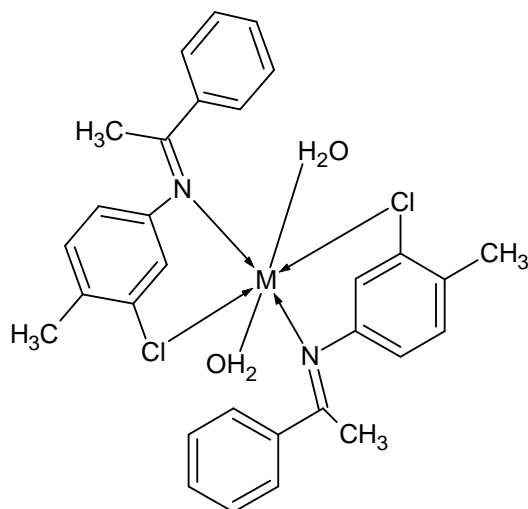


Figure 1: Suggested geometry of the metal complexes

M = Mn(II), Fe(II), Co(II), Ni(II)

CONCLUSION

Novel Schiff base ligand 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline has been synthesized by the condensation of 1-phenylethanone with 3-chloro-4-methylaniline. Transition metal complexes of Mn(II), Fe(II), Co(II) and Ni(II) were also synthesized. The ligand and its metal complexes were characterized based on mass spectral data, IR, ¹HNMR and ¹³CNMR spectroscopy. The spectral data of the metal complexes were interpreted on the basis of comparison with that of the free ligand. The analysis showed that the ligand coordinated to the metal ion through the azomethine nitrogen, the chloride and two aqua molecules. An octahedral geometry has been suggested for the metal complexes. The compounds were screened against *Aspergillus niger*, *Macrophomina phaseolina*, *Fusarium oxysporum* and *Alternaria alternata*. It has been found that all the complexes are active and show higher activity than the free ligand. Metal chelation affected the bioactive behavior of 3-chloro-4-methyl-N-[(1E)-1-phenylethylidene]aniline ligand.

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