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Pesticidal studies of an azo based heterocyclic Schiff base and its transition metal complexes

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ABSTRACT

The condensation of dialdehyde (**III**), obtained from *p*-nitro benzoic acid, with 2-amino-5-chloropyridine yielded an heterocyclic ligand bis(2-(5-chloropyridin-2-ylimino)phenyl)-4,4'-(diazene-1,2-diyl)dibenzoate (**BCDD**, **L**). The ligand was further converted to metal chelates with some divalent transition metal ions viz., **Co(II)**, **Ni(II)**, **Cu(II)** and **Zn(II)**. The synthesized complexes were characterized through elemental analyses, IR, NMR and electronic spectral data. The ligand **BCDD** acts as a hexadentate ligand and forms six-coordinated complexes with all these metal ions through two imine nitrogen's, two carbonyl oxygen's and two pyridine nitrogen's as 1:1 (metal : ligand) stoichiometry. Distorted octahedral geometry was suggested for all the metal complexes. The ligand and its complexes have been screened for their antipestal activities towards *Tribolium castaneum*, a red flour beetle as a storage food grain pest commonly found in India. The results showed that the metal complexes have higher antipestal activities as compared to ligand **BCDD**. The order of antipestal activities was **Cu(II)L** > **Zn(II)L** > **Ni(II)L** > **Co(II)L** > **L**.

Key words: Heterocyclic Schiff base, ligand, transition metal complexes, antipestal activities.

INTRODUCTION

The scientific storage of food grains to reduce the post-harvest loss is an important component of the food utilization system [1,2]. Many insects are responsible for enormous spoilage in storage. They attack food grains during pre and post-harvest stages. Pre-harvest attack mainly leads to quantitative loss but attacks during post-harvest stages lead to both quantitative and qualitative damages [3]. Several hundred insect species have been reported to be associated with stored grains and processed foods and out of them fifty species are considered dangerous [4,5].

Schiff bases are attracting biochemists as they are known to be medicinally important and are used to design medicinal compounds [6]. The azomethine (C=N) linkage in Schiff bases imports in elucidating the mechanism of transamination and resamination reactions in biological system [7,8]. It has been reported that the biological active compounds show greater activity when administered as metal complexes than as free organic compound [9]. The biomedical properties of free organic molecule upon chelation with suitable metal ion led to the implementation of metal complexes for several biomedical applications as therapeutically active possessing analgesic [10], antipyretic [11], anti-inflammatory [12], cytotoxic [13], antiviral [14], antitumorous [15] and antitubercular activity [16] etc. besides their applications as antimicrobial [17,18].

As Schiff bases are widely investigated for their potential to act as antipestal [19-21] we report here the synthesis of heterocyclic Schiff base ligand (BCDD) and its metal complexes and their pesticidal activities.

MATERIALS AND METHODS

All chemicals were obtained from Sigma-Aldrich and were used without further purification. Elemental analyses (C, H, N) were performed by the Carlo Erber Micro Analysis (Model-1106). Infrared spectra of the ligand and its metal complexes were recorded on FTIR Perkin Elmer 1710 spectrophotometer using KBr pellets. The electronic spectra of the metal complexes were recorded at 5×10^{-3} M in DMSO on an Agilent-8453 diode array spectrometer. ^1H NMR spectrum of the ligand was recorded on a Bruker AMX-300 spectrometer in DMSO- d_6 . Molar conductance of the complexes was determined in DMSO (10^{-3} M) at room temperature using a Toshniwal digital conductivity meter. Magnetic susceptibility measurements of the metal complexes in powder form were carried out on a Guoy balance. The metal contents of the complexes were determined by an Anti Unicam 929 Model AA spectrometer in solutions prepared by decomposing the compounds in aqua regia followed by in concentrated HCl.

2.2. Synthesis of ligand BCDD

Synthesis of ligand BCDD was initiated from the starting material *p*-nitrobenzoic acid (**I**) as shown in Scheme 1. The synthesis of 4,4'-bis(chlorocarbonyl)azobenzene (**II**) was carried out as per literature [22] method. Then, the dialdehyde (**III**) (1 mmol) and 2-amino-5-chloropyridine (2 mmol) in methanolic medium (50 ml) was refluxed for 10 hours. A reddish orange color precipitates were obtained, which were filtered and washed with methanol followed by ether and then, dried over anhydrous CaCl_2 under reduced pressure. The crude product was recrystallized from hot methanol, which gave pure ligand with a yield of 50 %, calculated from the starting compound *p*-nitrobenzoic acid. m.p., 155-157 °C; IR (KBr pellet, cm^{-1}): 3045, 2885, 1725, 1645, 1545, 1230, 625, 420; ^1H NMR (DMSO- d_6 ; δ ppm): 7.57 (8H, m, C_6H_4), 8.34 (8H, m, C_6H_4), 8.52 (6H, m, Pyridine ring), 8.73 (2H, s, HC=N); Elemental analysis (%): Anal. Calc. for $\text{C}_{38}\text{H}_{24}\text{N}_6\text{O}_4\text{Cl}_2$: C, 65.23; H, 3.43; N, 12.01; and found: C, 65.20; H, 3.39; N, 11.97.

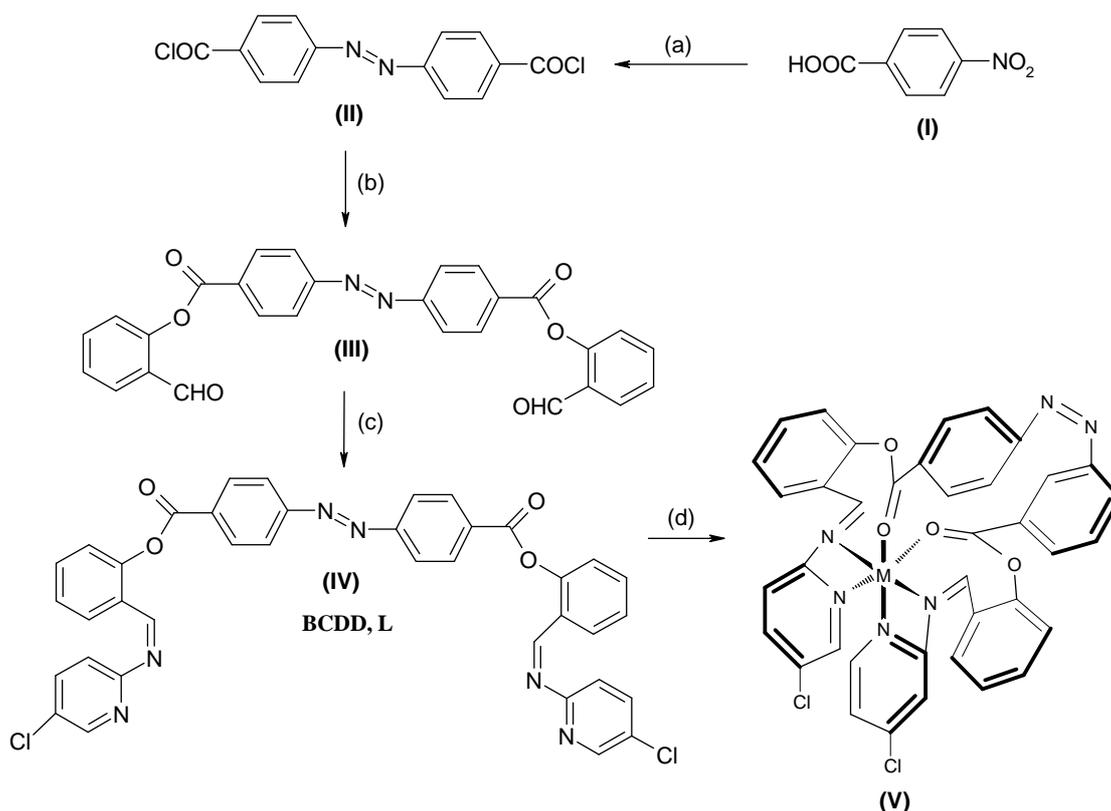
2.3. Synthesis of metal complexes

The metal(II) complexes of the ligand BCDD were prepared by similar procedure. A solution of BCDD (1 mmol) in methanol (20 ml) was added drop wise to a stirred solution of metal ion (1 mmol) in 5 ml of methanol at room temperature and then, the mixture was refluxed for four

hours. The precipitates were filtered and washed with water followed by methanol, ether and then dried in vacuum (yield in %, CoL = 35, NiL = 36, CuL = 39 and ZnL = 40).

RESULTS AND DISCUSSION

The synthetic procedure of ligand BCDD and its metal complexes is presented in Scheme 1. The reactions of divalent transition metal ions *viz.*, Co(II), Ni(II), Cu(II) and Zn(II) with the ligand BCDD in 1:1 molar ratio in methanol, yielded the corresponding metal chelates. The physical and analytical data of ligand BCDD and its metal complexes are given in Table 1 and Table 2. All the synthesized compounds are colored and stable to air and moisture. The yields of the complexes (35-40%) are lower than the yield of ligand (50%). The major reason may be due to the steric hindrance. The ligand and its metal complexes are insoluble in common organic solvents but are soluble in DMF and DMSO. All the compounds have elemental analysis consistent with their formulations. The molar conductance values (Table 1) of 281.34-293.33 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO medium indicate that the metal complexes are 1:2 electrolytes [23].



Scheme 1. Synthesis of BCDD and $[M(BCDD)]^{2+}$, $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II)
 (a) $\text{HCO}_2\text{HNEt}_3/\text{Pb}$, MeOH, r.t, $\text{PCl}_5/\text{CH}_2\text{ClCH}_2\text{Cl}$; (b) Salicylaldehyde, triethylamine, toluene, N_2 atm.; (c) 2-amino-5-chloropyridine, MeOH; (d) Acetate salts, MeOH

Table 1. Physical and analytical data of the ligand BCDD (L) and its metal(II) complexes

Compounds	Color	Elemental analyses Expt. (Calc.)				M.P. (°C)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
		C	H	N	M		
BCDD (L)	Reddish orange	65.20 (65.23)	3.39 (3.43)	11.97 (12.01)	-	155-157	-
[Cu(L)](AcO) ₂	Light green	59.66 (59.80)	3.10 (3.14)	10.96 (11.01)	8.28 (8.33)	228 (decomp.)	281.34
[Ni(L)] (AcO) ₂	Canary yellow	60.12 (60.18)	3.11 (3.16)	10.97 (11.08)	7.70 (7.74)	206 (decomp.)	292.15
[Co(L)] (AcO) ₂	Mustard brown	60.09 (60.16)	3.12 (3.16)	11.03 (11.08)	7.71 (7.77)	274 (decomp.)	290.74
[Zn(L)] (AcO) ₂	Dark yellow	59.62 (59.65)	3.07 (3.13)	10.93 (10.98)	8.50 (8.55)	225 (decomp.)	293.33

Table 2. Infrared spectra of the ligand BCDD (L) and its metal(II) complexes.

L	[Cu(L)] ⁺²	[Ni(L)] ⁺²	[Co(L)] ⁺²	[Zn(L)] ⁺²	Assignments
3045	3030	3025	3025	3030	ν_{C-H} of aromatic ring
2885	2875	2870	2875	2875	ν_{C-H} of azomethine
1725	1610	1615	1615	1610	$\nu_{C=O}$ of ester
1645	1525	1520	1525	1520	$\nu_{C=N}$ of azomethine
1545	1535	1540	1540	1535	$\nu_{C=C}$ of aromatic ring
1230	1225	1225	1200	1205	ν_{C-O} of ester
625	670	670	675	670	In-plane deformation of pyridine ring
420	460	465	460	465	Out of plane deformation of pyridine ring
-	555	560	555	560	ν_{M-O}
-	430	435	430	435	ν_{M-N}
-	330	335	330	335	ν_{M-N}

The condensation of 2-amino-5-chloropyridine with dialdehyde (**III**) to get BCDD was characterized through the ¹H NMR and IR spectra of the compound. In the IR spectrum of BCDD (Table 2), the stretching vibrational band due to $\nu_{C=O}$ at 1692 cm⁻¹ of dialdehyde was disappeared and appearance of characteristic imine $\nu_{C=N}$ band at 1645 cm⁻¹ was observed. A band at 2885 cm⁻¹ was attributed to ν_{C-H} of the azomethine groups. These observations confirm the condensation of dialdehyde with the primary amine, 2-amino-5-chloropyridine. A sharp band due to $\nu_{C=O}$ of the ester groups was observed at 1725 cm⁻¹. Two bands for in-plane and out of plane pyridine ring deformation were observed at 625 and 420 cm⁻¹ respectively. In ¹H NMR spectrum of BCDD, the presence of the azomethine group is characterized as a singlet at $\delta = 8.73$ ppm for two protons. The peak due to pyridyl ring protons was obtained in the form of multiplet at $\delta = 8.52$ ppm. Multiplet due to the aromatic protons linked to the azomethine group was observed at $\delta = 7.57$ ppm, whereas multiplet at $\delta = 8.34$ ppm was attributed for azobenzene protons. The relevant infrared absorption bands due to the co-ordinated chelates of the complexes with their possible assignment are given in Table 2.

All the metal chelates showed a sharp band in the region of 1525-1520 cm^{-1} which is attributed to the $\nu_{\text{C=N}}$ of azomethine groups, which was shifted towards lower frequency compared to the free ligand band indicating the coordination of azomethine nitrogen's in the complexes. A negative shift in the frequency of $\nu_{\text{C=O}}$ of the ester groups 1615-1610 cm^{-1} in the spectra of corresponding metal complexes indicate the coordination of carbonyl oxygen's of the ligand to the central metal ion. The shift in the bands due to in plane and out of plane deformation of pyridine of the ligand from 625,420 cm^{-1} to 675-670 and 465-460 cm^{-1} (Table 2) respectively in case of metal complexes indicates the coordination of pyridine nitrogen's. Also, in the low frequency region, the appearance of new bands in metal chelates at ~560, ~435 and ~330 cm^{-1} may be attributed to the $\nu_{\text{M-O}}$, $\nu_{\text{M-N}}$ and $\nu_{\text{M-N(pyridine)}}$, respectively. The ring skeletal vibrational bands of ligand were not affected by metal chelation.

The electronic spectra of the metal complexes gave characteristics *d-d* transitions to ascertain their structure. The Co(II)L complex gave three bands at 8500, 17400 and 20600 cm^{-1} , which may be assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$ transitions, respectively typical of an distorted octahedral geometry [24]. This has been further corroborated by the observed magnetic moment 4.92 BM [25]. The observed magnetic moment corresponds to a high spin octahedral Co(II) complex. The Ni(II)L complex also gave three bands at 8100, 14000 and 25200 cm^{-1} due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transitions, respectively. The Cu(II)L complex gave only one band due to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition at 17300 cm^{-1} . The electronic spectral data along with the observed magnetic moment of Ni(II)L (3.15 BM) and Cu(II)L (1.83 BM) complexes suggested for a distorted octahedral geometry.

4. Antipestal studies

The antipestal activities of the ligand BCDD and its transition metal complexes were investigated by adopting Bio-assay technique [26]. A red flour beetle (*Tribolium castaneum*), a storage food grain pest is taken as the test organism. The pest mortality was considered as the measure of effectiveness of the pesticide. For calculating percentage of mortality of pests a correction is applied by using Abbott's formula [27] which is given as:

$$\text{Corrected \% of mortality} = \frac{\text{X}-\text{Y}}{\text{X}} \times 100$$

X = remaining alive in the unreacted check lot.

Y = remaining alive in the treated check lot.

The results in Fig.1.reveal that the ligand and its metal complexes showed antipestal activities. It was observed that there was an appreciable increase in the antipestal activities in case of metal complexes compared to the uncomplexed ligand, BCDD. Cu(II) chelate was found to be the most effective as evidenced from the comparative study of their percentage mortality data of corresponding chelates. The order of antipestal activities was Cu(II)L> Zn(II)L>Ni(II)L>Co(II)L>L.

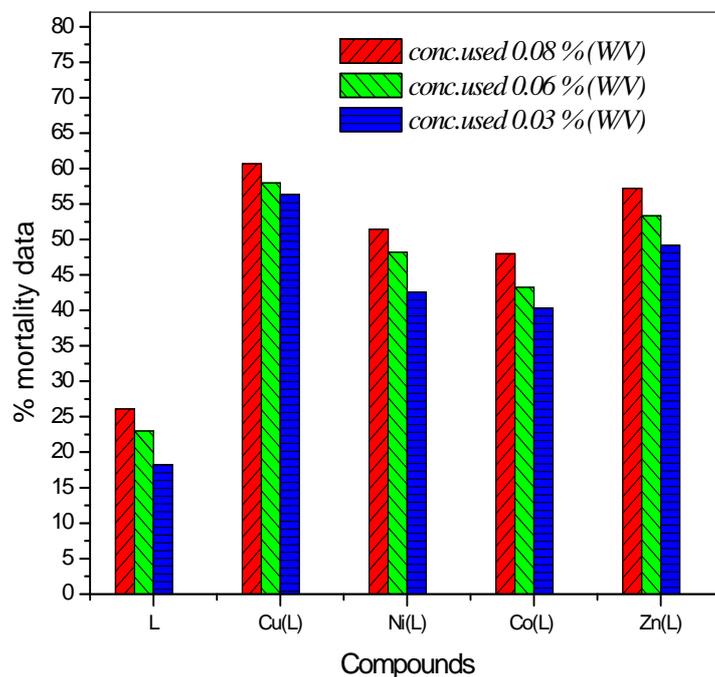


Fig.1. Percentage mortality data of the active compounds at different concentrations (Standard used for the antipestal activity is Bleomycin and Gallic acid, respectively)

CONCLUSION

The ligand BCDD acts as a hexadentate ligand and formed stable complex with Co(II), Ni(II), Cu(II) and Zn(II). The ligand showed antipestal activity but in comparison, the metal complexes of this compound showed a higher activity. The Cu(II) chelate showed higher activity in comparison to other chelates and the uncomplexed ligand.

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