Asian Journal of Chemistry; *Vol. 23, No. 7 (2011), 3025-3028*

ASIAN JOURNAL OF CHEMISTRY

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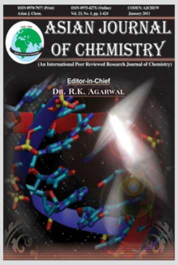

Synthesis and Antipestal Studies of a Novel Heterocyclic Multidentate Schiff Base and its Transition Metal Complexes

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(*Received*: 23 August 2010; *Accepted*: 9 March 2011) AJC-9721

A new heterocyclic multidentate Schiff base ligand *bis*[2-(6-methylpyridin-2-ylimino)phenyl]-4,4'-(diazene-1,2-diyl)dibenzoate (BMDD, L) and its metal chelates with some transition metal ions *viz.*, Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized through various spectral data and elemental analyses. The ligand BMDD acts as a hexadentate ligand and forms six-coordinated complexes with all these metal ions through two imine nitrogens, two carbonyl oxygens and two pyridine nitrogens. The ligand and its metal complexes have been screened for the antipestal activities towards *Tribolium castaneum* a red flour bettle as a storage food grain pest commonly found in India. The results showed that all the metal complexes have higher antipestal activities than the ligand. The order of antimicrobial activities was in order: Cu(II)L > Zn(II)L > Ni(II)L > Co(II)L > L.

Key Words: Multidentate Schiff base ligand, Transition metal complexes and antipestal activities.

INTRODUCTION

The food production and crop disease control for human welfare embraces many other elements to be taken into account in formulating policies for pesticidal research. The potential impact on non-target organisms by chemicals introduced into the environment is universally acknowledged and research must be aimed at minimizing risks to unintended recipients. Thus the scientific researchers in the field of crop protection, pest control and the use of pesticides have transcended national boundaries and have brought the whole world together in a 'global field' for eradication of hunger and poverty. In search of crop protection and pest control, Schiff bases are widely investigated for their potential to act as antipestal[1-5].

Schiff bases have attracted considerable attention in terms with their easy synthesis, structural diversity, chelating abilities and suitable donor sites. The azomethine (C=N) linkage in Schiff bases imports in elucidating the mechanism of transamination and resamination reactions in biological system[6,7]. It has also been suggested[8-10] that the ligands with nitrogen and oxygen donor systems might inhibit enzyme production, since the enzymes which require these groups for their activity appear to be especially more susceptible to deactivation by the metal ions upon chelation. Chelation reduces the polarity[8-10] of the metal ion mainly because of the partial sharing of its positive charge with the donor groups and possibly the π-electron delocalization within the whole chelate ring system thus formed during coordination. This process of chelation thus increases the lipophilic nature of the central metal atom, which in turn favours its permeation through the lipoid layer of the membrane. This in turn is responsible for increasing the hydrophobic character and liposolubility of the molecule in crossing cell membrane of the microorganism and hence enhances the biological utilization ratio and activity of the testing drug/compound.

Keeping the above facts in view, a new multidentate Schiff base heterocyclic ligand (BMDD, L) and its complexes with some divalent transition metal ions *viz.*, Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized. The ligand along with its metal(II) complexes were screened for their antipestal studies on *Tribolium castaneum*, a red flour beetle pest.

EXPERIMENTAL

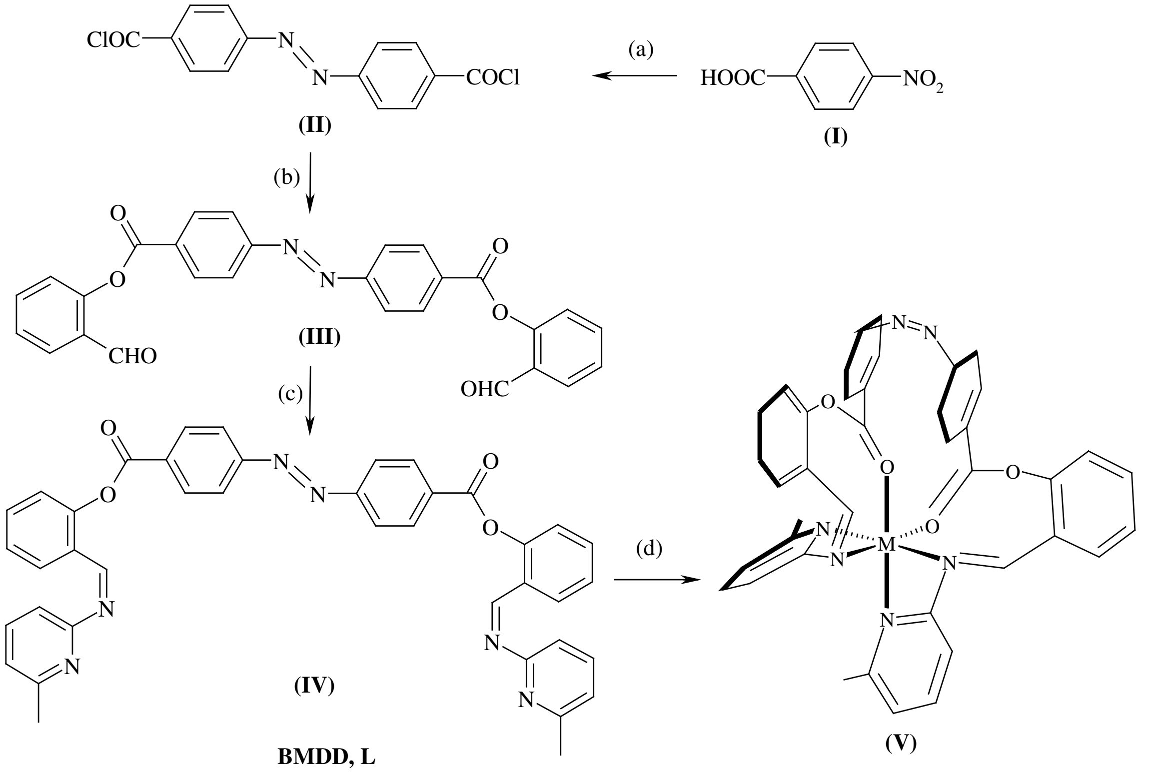
All chemicals used were of analytical grade. Hydrated acetate salts of transition metals *viz.*, $Cu(CH_3COO)_2{\cdot}H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$ and $Zn(CH_3COO)_2{\cdot}2H_2O$, PCl_5, *p*-nitrobenzoic acid, salicylaldehyde, triethylamine, 2-amino-6-methylpyridine were obtained from Sigma-Aldrich and were used directly. Absolute ethanol, methanol, diethyl ether solvents were obtained from Fluka and were distilled by standard methods prior to use.

The purity of all the compounds was checked by running their TLC for single spot on silica gel-4 G plate. Elemental analyses (C, H, N) were performed by the Carlo Erber Micro Analysis (Model-1106) from CDRI, Lucknow. 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. ^{1}H NMR spectrum of the ligand was recorded on a Brucker AMX-300 spectrometer in DMSO-d_6. The chemical shifts were reported relative to Me_4Si. 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.

Synthesis of *bis*[2-(6-methylpyridin-2-ylimino)phenyl]-4,4'-(diazene-1,2-diyl)dibenzoate (BMDD): Synthesis of ligand BMDD was initiated from the starting material *p*-nitrobenzoic acid (**I**) as shown in **Scheme-I**. The synthetic procedure of 4,4'-*bis*(chlorocarbonyl)azobenzene (**II**)[11] and dialdehyde (**III**)[12] was adapted from the reported method and the compounds were verified through elemental analyses. Then, the dialdehyde (1 mmol) was condensed with 2-amino-6-methylpyridine (2 mmol) in methanolic medium (50 mL). The mixture was refluxed for 10 h. A bright orange colour precipitate obtained, which was filtered off 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 42 %, calculated from the starting compound *p*-nitrobenzoic acid. m.p. 140 ºC; IR (KBr pellet, ν_{max}, cm^{-1}): 3035, 2895, 1730, 1635, 1600, 1540, 1225, 625, 420; ^{1}H NMR (DMSO-d_6; δ ppm): 2.30 (6H, s), 7.53 (8H, m), 8.34 (8H, m), 8.55 (6H, m), 8.70 (2H, s); elemental analysis (%): Anal. calcd. for $C_{40}H_{30}N_6O_4$: C, 72.94; H, 4.55; N, 12.76 and found: C, 72.90; H, 4.60; N, 12.72.

Synthesis of metal complexes: A solution of BMDD (1 mmol) in methanol (20 mL) was added drop wise to a stirred solution of the corresponding metal(II) acetate (1 mmol) in 5 mL of methanol at room temperature and the reaction mixture was refluxed for 4 h. The precipitate were filtered and washed with water followed by methanol, ether and then dried in vacuum [yield (%), Co(L)(OAc)$_2$ = 33, Ni(L)(OAc)$_2$ = 37, Cu(L)(OAc)$_2$ = 39 and Zn(L)(OAc)$_2$ = 36].

Antipestal studies: The antipestal activities of the ligand BMDD and its transition metal complexes were investigated by adopting bio-assay technique[13]. A red flour bettle (*Tribolium castaneum*), a storage food grain pest is taken as the test organism. The weighed quantity of the test compounds was dissolved in DMF and is diluted to different concentration, 3 mL of the solution of test compound is uniformly sprayed over the surface of 10 cm^2 round whatman's filter paper placed, over a pin cushion so that the entire filter paper is impregnated with the compound under trial. The treated filter paper is kept inside the petridish in which 25 adult pest were released. The pests were taken out from the laboratory control culture maintained for the testing purpose. For replication including one control were carried out for each concentration. The pests were



Scheme-I: Syntheses of BMDD and [M(BMDD)]$^{2+}$, M = Co(II), Ni(II), Cu(II) and Zn(II) its metal complexes: (a) NaOH, aq. glucose, CH_3COOH, PCl_5/CH_2ClCH_2Cl; (b) salicylaldehyde, triethylamine, toluene, N_2 atm.; (c) 2-amino-6-methylpyridine, MeOH; (d) metal acetate salts, MeOH kept in content for 24 h and then were taken out and kept on fresh petridishes after 24, 48 and 72 h[14]. The pests were examined one by one with naked eyes and categorized as done by earlier workers[15,16]. 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[17] which is given as:

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

X = Remaining alive in the unreacted check lot. Y= remaining alive in the treated check lot.

RESULTS AND DISCUSSION

The synthetic procedure of ligand BMDD and its metal complexes are presented in **Scheme-I**. Reactions of divalent transition metal ions *viz*., Co(II), Ni(II), Cu(II) and Zn(II) with the ligand BMDD in 1:1 molar ratio in methanol, yielded the corresponding metal chelates. The physical and analytical data of ligand BMDD and its metal complexes are given in Tables 1 and 2. All the synthesized compounds are coloured and stable to air and moisture. The yields of the complexes (33-39 %) are lower than the yield of ligand (42 %). The ligand and its metal complexes are insoluble in common organic solvents, but are soluble in DMF and DMSO. All the compounds have elemental analyses consistent with their formulations. The molar conductance values (Table-1) of 215.47-299.11 ohm^{-1} cm^2 mol^{-1} in DMSO medium indicate that the metal complexes are 1:2 electrolytes[18].

Characterizations of ligand and its metal complexes: The condensation of 2-amino-6-methylpyridine with dialdehyde to get BMDD was characterized from the ^{1}H NMR and IR spectra of the compound. In the infrared spectrum of BMDD (Table-2), the stretching vibrational band due to ν(C=O) at 1695 cm^{-1} of dialdehyde was disappeared and appearance of characteristics imine ν(C=N) band at 1635 cm^{-1} was observed. Another new band obtained at 2895 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-6-methylpyridine. A sharp band due to ν(C=O) of the ester groups was observed at 1730 cm^{-1}. Two bands for in-plane and out of plane pyridine ring deformation were observed at 625 and 420 cm^{-1}, respectively[19]. In ^{1}H NMR spectrum of BMDD, the presence of the azomethine group is also characterized as a singlet at δ = 8.70 ppm. A singlet at 2.3 ppm was characterized for the methyl protons. The peak due to pyridyl ring protons was obtained in the form of multiplet at δ = 8.55 ppm. Multiplet due to the aromatic protons linked to the azomethine group was observed at δ = 7.53 ppm, whereas at δ = 8.34 ppm was attributed for the azobenzene protons.

The relevant infrared absorption bands due to the coordinated 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 1535-1525 cm^{-1} was attributed to the ν(C=N) of azomethine groups, which was shifted by *ca.* 100 cm^{-1} towards lower frequency compared to the free ligand band indicating the coordination of azomethine nitrogens in the complexes. A negative shift in the frequency of ν(C=O) of the ester groups (1630-1620 cm^{-1}) in the spectra of corresponding metal complexes indicate the coordination of carbonyl oxygens 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

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE LIGAND BMDD (L) AND ITS METAL(II) COMPLEXES

Compounds	Colour	Elemental analyses (%) Expt. (calcd.)				m.p. (ºC)	Molar conductance (ohm^{-1} cm^2 mol^{-1})
		C	H	N	M		
BMDD (L)	Bright orange	72.90 (72.94)	4.60 (4.59)	12.72 (12.76)	–	140	–
[Cu(L)](AcO)$_2$	Apple green	62.93 (62.89)	4.36 (4.32)	9.96 (10.00)	7.54 (7.56)	235 (decomp.)	285.47
[Ni(L)] (AcO)$_2$	Yellowish green	63.32 (63.25)	4.40 (4.34)	9.98 (10.06)	6.98 (7.03)	300 (decomp.)	291.22
[Co(L)] (AcO)$_2$	Mustard brown	63.22 (63.24)	4.30 (4.34)	10.03 (10.06)	7.08 (7.05)	280 (decomp.)	295.68
[Zn(L)] (AcO)$_2$	Bright yellow	62.70 (62.75)	4.32 (4.31)	9.95 (9.98)	7.72 (7.76)	230 (decomp.)	299.11

TABLE-2
INFRARED SPECTRA OF THE LIGAND BMDD (L) AND ITS METAL(II) COMPLEXES

L	[Cu(L)]$^{2+}$	[Ni(L)]$^{2+}$	[Co(L)]$^{2+}$	[Zn(L)]$^{2+}$	Assignments
3035	3030	3025	3025	3030	ν(C-H) of aromatic ring
2895	2885	2890	2890	2885	ν(C-H) of azomethine
1730	1620	1625	1620	1625	ν(C=O) of ester
1635	1530	1525	1535	1530	ν(C=N) of azomethine
1540	1545	1545	1540	1545	ν(C=C) of aromatic ring
1225	1215	1220	1220	1205	ν(C-O) of ester
625	650	660	655	655	In-plane deformation of pyridine ring
420	440	445	450	455	Out of plane deformation of pyridine ring
–	550	555	554	550	ν(M-O)
–	450	455	450	455	ν(M-N)
–	335	330	335	330	ν(M-N)

ligand from 625 and 420 cm^{-1} to 660-625 and 455-420 cm^{-1} (Table-2), respectively in case of metal complexes indicate the coordination of pyridine nitrogens. Also, in the low frequency region, the appearance of new bands in metal chelates at *ca.* 550, 455 and 335 cm^{-1} may be attributed to the ν(M-O), ν(M-N) and ν(M-N$_{(pyridine)}$), respectively[20,21]. The ring skeletal vibrational bands of ligand were not much affected upon 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, 17300 and 20600 cm^{-1}, which may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively typical of an distorted octahedral geometry[22]. This has been further corroborated by the observed magnetic moment 4.95 BM[23]. The observed magnetic moment corresponds to a high spin octahedral Co(II) complex. The Ni(II)L complex also gave three bands at 8300, 14200 and 25200 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions, respectively. The Cu(II)L complex gave only one band due to $^2E_g \rightarrow {}^2T_{2g}$ transition at 17300 cm^{-1}. The electronic spectral data along with the observed magnetic moment of Ni(II)L (3.13 BM) and Cu(II)L (1.89 BM) complexes suggested for a distorted octahedral geometry[22,23].

Antipestal activity: Antipestal activities of the ligand and its metal complexes were evaluated against the red flour bettle (*Tribolium castaneum*), a storage food grain pest (Fig. 1). The results reveal that all the compounds showed antipestal activities. It was observed that there was an appreciable increase in the antipestal activities in case of metal complexes compared to the free ligand, BMDD. Cu(II) chelate was found to be the most effective as evidenced from the comparative study of their MIC values of corresponding chelates. The order of antipestal activities was Cu(II)L(OAc)$_2$ > Zn(II)L(OAc)$_2$ > Ni(II)L(OAc)$_2$ > Co(II)L(OAc)$_2$ > L.

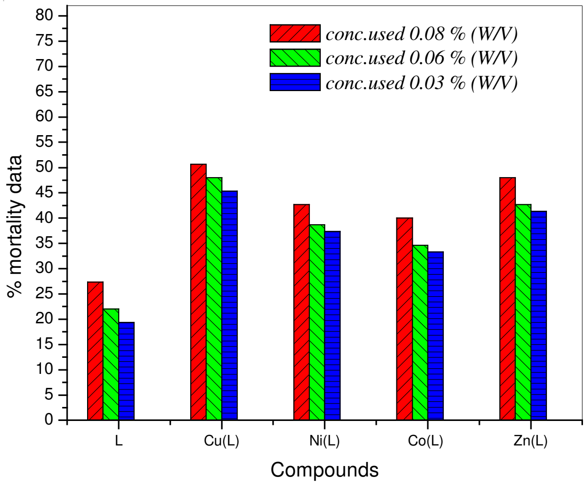


Fig. 1. Percentage mortality data of the active compounds at different concentrations. (Standard used for the antipestal activity is bleomycin and gallic acid, respectively)

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