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Synthesis, spectral characterization and antibacterial and herbicidal activities of CMPP-glygly Schiff base and its Co(II), Ni(II),Ce(II), Mn(II) and Zn(II) Complexes

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ABSTRACT

A new serious of Co(II), Ni(II),Ce(II), Mn(II), and Zn(II) complexes derived from CMPP-Glygly have been synthesized and characterized by Elemental analysis, IR, UV and so on. The antibacterial test against E.coli and B. subtilis showed that the free ligand is more or less inactive against the two bacteria than the complexes. The herbicidal test against wheat and rape suggested that all the tested compounds own higher inhibition ability to monocotyledon than to dicotyledon.

Keywords: Metal complex, synthesis, Characterization, Antibacterial activity, Herbicidal activity.

1. INTRODUCTION

As versatile ligands, schiff bases are widely studied in recent years. Metal complexes of Schiff bases exhibit a broad range of biological activities such as antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral and antipyretic activities, and so on[1-5]. They have been extensively studied in great details for their various crystallographic, structural and magnetic features. They also play important roles in supramolecular assemblies, metallo-dendrimers and formation of stable complexes[6].

Gly-Gly dipeptide is the smallest dipeptide with remarkable biological and pharmic properties. Schiff bases derived from Gly-Gly dipeptide and their complexes do have significant interest because of their excellent chemical, electrochemical and photochemical properties as well as potential biological applications such as antitumor, herbicidal and antimicrobial activities[7-10]. The present study describes the synthesis, spectroscopic characterization and antibacterial, herbicidal activities of the Schiff base derived from Gly-Gly dipeptide and pyrazol-aldehyde, together with its metal complexes.

2. EXPERIMENTAL

All the regents were obtained from commercial sources were used of analytically pure grade. 5-cholor-3-methyl-1-phennyl-1H-pyrazol-4-carbaldehyde(CMPP) was synthesized according to the lecture[11]. A Carlo-Erba 1106 Elemental analyzer was utilized for elemental analysis. IR spectra were recorded (KBr disks) on a Perkin–Elmer FTIR spectrometer. Melting points were measured on a WRS-1B melting point apparatus and uncorrected. UV-Vis spectra were gotten on a UV-250IPC spectrometer. ^{1}H-NMR spectra were obtained on a Bruker AM400 MHz instrument with Me_4Si as internal reference.

2.1. Synthesis of CMPP-Gly-Gly Schiff base

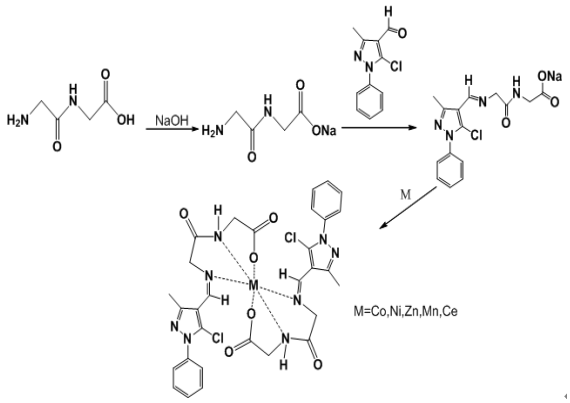

Figure - 1: Synthesis route of the CPMM-glygly and its complexes.

Figure 1 shows the synthesis route of CMPP-glygly schiff base. 10mmol NaOH was dissolved in 100 mL absolute ethanol, 10mmol gly-gyl dipeptide was added, the mixture was stirred for about 0.5h until the solution became clear. The solution was refluxed for about 2-3h and then cooled down to room temperature. The pale yellow precipitate was separated and recrystallized by absolute ethanol. m.p. 207-

210°C, Anal. Calc. For $C_{15}H_{16}ClN_4O_3Na$: C, 46.69; H, 4.15; N, 14.53%. Found: C, 46.89; H, 4.23; N, 14.38%. FT-IR (KBr, cm^{-1}) νmax: 3425(m, NH), 3030(w, phenyl-H), 1655 (m, C=N), 1599 (s, COO^-_{as}), 1400(s, COO^-_s), 1309(s), 1005(s), 760(s), 692(s). UV, 245(3.3), 270(3.7), 279(1.8). ^{1}HNMR (DMF-$_{D7}$, 400 Hz) δ: 8.3 (t, J＝2.7Hz, 1H), 7.8 (s, 1H), 7.1～7.6 (m, 5H), 4.61 (d, J＝3.8 Hz, 2H), 2.85 (d, J＝4.1 Hz, 2H), 1.65 (s, 3H)

2.2. Preparation of the metal complexes

The Co(II), Ni(II), Mn(II),Ce(II) and Zn(II) complexes were obtained by reacting the metal acetate and the CMPP-glygly schiff base in the molar ratio 1:2. The absolute ethanol solution of metal acetate was dropped into the absolute ethanol solution of CMPP-glygly schiff base, the mixture was refluxed for 4-5h. The solvent was evaporated and the precipitates were formed. The basic physical properties and the spectral data of each compound are as follows:

CMPP-glygly-Co, light purple, m.p. >320°C, Anal. Calc. For $Co(C_{15}H_{16}ClN_4O_3)_2$: C, 49.32; H, 4.38; N, 15.34%. Found: C, 49.48; H, 4.43; N, 15.23%. FT-IR (KBr, cm^{-1}) νmax: 3420(m, NH), 3018(w, phenyl-H), 1616 (m, C=N), 1574 (s, COO^-_{as}), 1386(s, COO^-_s), 1319(s), 1280(s), 694(s), 575(Co-N), 463(Co-O). UV: 257(3.4), 263(3.2), 277(0.7).

CMPP-glygly-Ni, light green, m.p. >320°C, Anal. Calc. For $Ni(C_{15}H_{16}ClN_4O_3)_2$: C, 49.33; H, 4.38; N, 15.34%. Found: C, 49.35; H, 4.26; N, 15.21%. FT-IR (KBr, cm^{-1}) νmax: 3397(m, NH), 3125(w, phenyl-H), 1616 (m, C=N), 1597 (s, COO^-_{as}), 1392(s, COO^-_s), 1304(s), 1279(s), 723(s), 556(Co-N), 446(Co-O). UV: 247(2.4), 256(2.5), 283(0.2).

CMPP-glygly-Ce, white, m.p. >320°C, Anal. Calc. For $Ce(C_{15}H_{16}ClN_4O_3)_2$: C, 49.34; H, 4.40; N, 15.36%. Found: C, 49.28; H, 4.56; N, 15.17%. FT-IR (KBr, cm^{-1}) νmax: 3335(m, NH), 3098(w, phenyl-H), 1649 (m, C=N), 1579 (s, COO^-_{as}), 1384(s, COO^-_s), 1317(s), 721(s), 548(Co-N), 419(Co-O). UV: 236(1.8), 257(2.6), 278(1.4).

CMPP-glygly-Mn, brown, m.p. >320°C, Anal. Calc. For $Mn(C_{15}H_{16}ClN_4O_3)_2$: C, 49.59; H, 4.41; N, 15.43%. Found: C, 49.68; H, 4.23; N, 15.56%. FT-IR (KBr, cm^{-1}) νmax: 3300(m, NH), 3092(w, phenyl-H), 1639 (m, C=N), 1585 (s, COO^-_{as}), 1389(s, COO^-_s), 1276(s), 706(s), 573(Co-N), 428(Co-O). UV: 247(2.4), 254(3.3), 278(0.5).

CMPP-glygly-Zn, white, m.p. >320°C, Anal. Calc. For $Zn(C_{15}H_{16}ClN_4O_3)_2$: C, 48.91; H, 4.35; N, 15.24%. Found: C, 49.98; H, 4.23; N, 15.13%. FT-IR (KBr, cm^{-1}) νmax: 3277(m, NH), 3098(w, phenyl-H), 1649 (m, C=N), 1593 (s, COO^-_{as}), 1395(s, COO^-_s), 1339(s), 1284(s), 671(s), 615(Co-N), 461(Co-O). UV: 231(1.1), 249(2.9), 283(0.3).

2.3. Antibacterial activity

The antibacterial activity of the test samples was determined by agar cup plate method using two organisms such as Bacillus subtilis and Escherichia coli. This method was based on diffusion of antibacterial component from paper disc to the surrounding inoculated nutrient agarmedium so that the growth of microorganisms was inhibited as circular zone around the paper disc. The concentration of test compounds was 1,0.5,0.25mg/mL in DMF. The test samples and standard drugs absorbed by a paper disc were placed in petri dishes which contained different organisms and incubated at 37 °C for 24 h. The zone of inhibition around the paper disc was measured after 24 h.

2.4. Herbicidal activity

The herbicidal evaluation was performed using wheat and rape as model plants, the growth inhibition effect on the dicotyledon rape and the monocotyledon wheat was examined with a standard Petri dish test. Briefly, the compounds to be tested were dissolved in DMF, and the solutions were diluted with water to the concentrations of 100 mg/L, 50 mg/L and 25 mg/L, respectively. The solution (4 mL) was added to a Petri dish and two pieces of filter paper were placed on the dish bottom. Ten seeds of each of rape and wheat were placed on the filter paper. The covered Petri dish was transferred into an artificial climate incubator, where the condition was controlled-temperature 25°C, room humidity 80%, light intensity 10 Klux, and photoperiod 12 h/day. The incubation was continued for 2 days. The lengths of all roots and stalks were measured and the percentage inhibition was calculated relative to controls using distilled water. The inhibition rate is calculated as follows:

$$\text{Inhibition rate} = \frac{\text{control treatment - drug treatment}}{\text{control treatment}} \times 100\%$$

3. RESULTS AND DISCUSSION

3.1. Elemental analysis, ^{1}HNMRand IR

In the ^{1}HNMR spectrum of the ligand, the signals at 7.1-7.6 are assigned to the protons of aromatic ring. The singlet at 8.3 and 7.8 ppm are attributed to the proton of the O=C-NH and N=C-H group, respectively. The signals at 4.61 and 2.85 ppm are assigned to the -CH_2 protons. The signals of the -CH_3 proton are observed at 1.65 ppm.

The IR spectra of the ligand as well as complexes have been measured in the region 4000-400 cm^{-1}(Table 1). The IR spectra of CMPP-glygly shows stretching band at 1655 cm^{-1} assigned to the ν(C=N). The ν(C=N) shift lower to 1649-1616 cm^{-1} after the CMPP-glygly and metal ions form

complexes. The ν(N-H) stretching band of CMPP-glygly is located at 3425 cm^{-1} and ν(N-H) bands appear at 3420-3277cm^{-1} in the complexes.

Table - 1: Selected IR spectral data (ν/cm^{-1}) of the CMPP-glygly and its complexes

Compounds	phC-H	N-H	C=N	s(COO^{-})	as(COO^{-})	M-O	M-N
CMPP-glygly	3030	3425	1655	1400	1599	-	-
CMPP-glygly-Co	3018	3420	1616	1386	1574	463	575
CMPP-glygly-Ni	3125	3397	1616	1392	1597	446	556
CMPP-glygly-Ce	3098	3335	1649	1384	1579	419	548
CMPP-glygly-Mn	3092	3300	1639	1389	1585	428	573
CMPP-glygly-Zn	3098	3277	1649	1395	1593	461	615

Table - 2: UV spectra data of of the free ligand and the complexes

Data	λ max(DMF, nm) and lgε		
Compounds	K	B	R
CMPP-glygly	**245(3.3)**	**270(3.7)**	**279(1.8)**
CMPP-glygly-Co	257(3.4)	263(3.2)	277(0.7)
CMPP-glygly-Ni	247(2.4)	256(2.5)	283(0.2)
CMPP-glygly-Ce	236(1.8)	257(2.6)	278(1.4)
CMPP-glygly-Mn	247(2.4)	254(3.3)	278(0.5)
CMPP-glygly-Zn	231(1.1)	249(2.9)	283(0.3)

Table - 3: The mean diameter data of the inhibition zone of the schiff base and the complexes

Compounds	Concentration (g/L)	Mean Diameter (cm)		Stand Error	
		E.coli	B. subtilis	E.coli	B. subtilis
CMPP-glygly	1	1.12	0.6	0.06	0
	0.5	1.07	0.6	0.06	0
	0.25	0.87	0.6	0.06	0
CMPP-glygly-Co	1	0.92	1.00	0.02	0.05
	0.5	0.80	0.87	0.05	0.06
	0.25	0.80	0.73	0	0.03
CMPP-glygly-Ni	1	1.07	1.00	0.06	0.1
	0.5	0.82	0.87	0.08	0.11
	0.25	0.80	0.6	0.1	0
CMPP-glygly-Ce	1	1.22	1.00	0.02	0.1
	0.5	0.93	0.92	0.08	0.08
	0.25	0.95	0.6	0.1	0
CMPP-glygly-Mn	1	1.03	0.95	0.2	0.3
	0.5	0.87	0.90	0.03	0.17
	0.25	0.73	0.70	0.06	0.17
CMPP-glygly-Zn	1	1.80	0.67	0	0.1
	0.5	1.03	0.88	0.06	0.3
	0.25	0.78	1.00	0.03	0.1

The ν(as, COO-) bond and ν(s, COO-) band appear at 1599-1574 cm^{-1} and 1400-1384cm^{-1} in the spectral of CMPP-glygly and its complexes, respectively. The difference between ν (as, COO-) and ν (s, COO-) band is about 200 cm^{-1}, which suggest that COO^- acts as a mono-dentate in the forming of the complexes [13]. The appearing of ν(M-O) and ν(M-N) proved that N atom and O atom are the possible ligand atoms. All these show that CMPP-glygly is a tridentate ligand, three ligand atoms are N atom of C=N, N atom of N-H, and O atom of COO^-.

3.2. UV

The UV spectral data of CMPP-glygly and the complexes are shown in table 2.

As can be seen from table 2, there are three absorption peaks in the spectra of the ligand which belong to the π-π * transition of benzene ring, the π-π * transition of conjugated system and the n-π * transition of conjugated system, respectively. This shows that there is a large conjugated system in the structure of the ligand. Compared with the ligand, the spectra of the complexes also show three absorption peaks, but the UV data of the metal complexes shift to a new wavelength. This shows that the electron might be rearrangement during the forming process of the complexes.

All the data of infrared, ultraviolet, ^{1}HNMR and element analysis suggest that the possible structure of the ligand and its complexes are as figure 2**:**

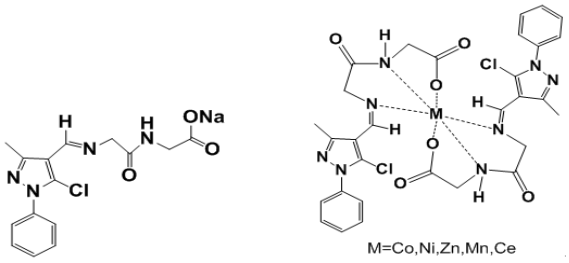

Figure - 2: The possible structure of the ligand and its complexes.

3.3. Antibacterial activities

The diameter data of the inhibition zone of the schiff base and the complexes are shown in table 4.

The mean diameter data of the inhibition zone show that the CMPP-glygly and the comlexes have certain antibacterial activity to Escherichia coli, while CMPP-glygly and low-concentration Ni(II), Ce(II) complex have no antibacterial activity to Bacillus subtilis. Though most diameter

Table 5 The inhibitory ratios（%） to root, shoot and stalk

Compounds	Concentration （μg/mL）	Rape stalk	wheat stalk	wheat Root
CMPP-glygly	100	94.72	58.02	72.83
	50	89.81	43.95	53.57
	25	71.58	53.55	47.24
CMPP-glygly-Co	100	81.04	29.01	66.30
	50	79.94	12.74	14.29
	25	60.11	30.60	26.99
CMPP-glygly-Ni	100	86.99	43.51	51.09
	50	82.10	1.27	15.18
	25	74.32	38.25	24.54
CMPP-glygly-Ce	100	97.40	53.44	75.00
	50	91.36	17.20	33.93
	25	76.50	37.16	5.52
CMPP-glygly-Mn	100	95.17	51.15	81.52
	50	74.07	9.55	1.79
	25	90.16	23.50	4.29
CMPP-glygly-Zn	100	96.80	40.46	54.35
	50	94.14	51.59	37.59
	25	90.44	56.28	27.91

of inhibition zones are smaller, antibacterial activity changes with the concentration changes. Among the complexes, CMPP-glygly-Zn owns the best bactericidal activity to E. coli with the mean diameter data of the inhibition zone about 1.8 cm.

3.4. Herbicidal activities

The inhibitory ratios of the schiff base and the complexes to wheat root, wheat shoot and rape stalk are shown in Table 5. As shown in Table 5, CMPP-glygly and its metal complexes have some herbicidal activity to the test plants. With the increasing of the concentration, the herbicidal activities of most compounds rise, others reach to the minimum at a certain concentration. The herbicidal activities of all the compounds to rape stalk are stronger than that to wheat shoot.

The herbicidal activity of CMPP-glygly to rape stalk is stronger than the cobalt complex and weaker than other complexes. The inhibitory ratios of same compound at same concentration to different crops are not same. The inhibition abilities of CMPP-glygly to wheat root and wheat shoot are stronger than most of the metal complexes.

4. CONCLUSION

A new Schiff base ligand derived from gly-gly and its five Co(II), Zn(II), Ce(II), Ni(II) and Mn(II) complexes were synthesized and characterized. Based on the elemental analysis, UV-Vis., IR, ^{1}H-NMR spectral data, the type of coordination of the ligand in its complexes were determined. The spectral data reveal that all the complexes were six coordinated and possess octahedral geometry around the metal ion. Antibacterial activity test showed that some compounds have stronger antibacterial activities with the concentration increasing. Antibacterial activities of some metal complexes are stronger than that of the ligand.

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