SYNTHESIS AND STRUCTURAL CHARACTERISATION OF SOME TRANSITION METAL COMPLEXES OF PIPERIDINOBENZYL SEMICARBAZIDE AND THEIR ANTIBACTERIAL STUDY

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ABSTRACT

Four coordinated Cu (II), Co (II), Ni (II) and Zn (II) complexes of piperidinobenzyl semicarbazide, a Mannich base derived from semicarbazide, piperidine and benzaldehyde, have been synthesised and screened for their antibacterial activity. The geometry of the complexes has been proposed. The ligand system coordinates with the metal ion in a bidentate manner through the oxygen atom of the carbonyl group and nitrogen atom of semicarbazide group.

Key words : Piperidinobenzyl Semicarbazide, Antibacterial

INTRODUCTION

Studies of metal complexes of the benzaldehyde based Mannich bases have been reported in literature[1–4]. Because of the ready accessibility, diverse chemical activity[5] and pharmacological properties[6,7] such as analgesic, antipyretic, anticancerous, bacteriocidal and fungicidal have made the study of semicarbazide a viable source of signify and magnify the observations and results for the betterment of human life. Keeping the above facts in mind and in continuation of our research work[8,9] on transition metal complexes with Mannich base, the present communication reports the synthesis of piperidinobenzyl semicarbazide (PBSC) by reacting semicarbazide, piperidine and benzaldehyde in 1 : 1 : 1 mole ratio and its complexation characteristics with Cu (II), Co (II), Ni (II) and Zn (II) salts.

EXPERIMENTAL

General procedure for preparation of PBSC

In a typical procedure, semicarbazide, piperidine and benzaldehyde were taken in 1 : 1 : 1 mole ratio in ice–cold condition. Semicarbazide was mixed with piperidine and stirred to get a clear solution. Benzaldehyde was then added dropwise and the mixture was stirred in ice–bath. Then the resulting reaction mixture was kept at room temperature for three days. The solid product formed was filtered, washed with water to remove unreacted semicarbazide and

pipeidine followed by CCl_4 to remove any unreacted benzaldehyde. The product, PBSC was then dried and recrystallised from methanol (58%), m.p. 168–170°C.

Synthesis of metal complexes using PBSC

Ni (II), Cu (II), Co (II) and Zn (II) complexes have been synthesised using PBSC as a ligand. Since the ligand being insoluble in water, all the complexes were prepared in non–aqueous media. In a typical procedure, PBSC was dissolved in chloroform and mixed with an ethanolic solution of the metal salt in 2 : 1 mole ratio. The reaction mixture was gently warmed on a water–bath for 30 min. The resulting solid complex formed was separated, washed with distilled water and recrystallised from ethanol and dried.

RESULTS AND DISCUSSION

The analytical data alongwith some physical properties of the complexes are summarised in Table 1. On the basis of analytical data, all the complexes were found to possess 1 : 2 (M : L) stoichiometry. The DMSO solution of the complexes has low molar conductance values indicating their non–electrolytic nature[10] (Table–1). The magnetic susceptibility values are consistent with that of square–planar geometry for Cu (II), Ni (II) and tetrahedral for Co (II) and Zn (II) complexes.

Table 1. Analytical data of the complexes

Complex (Colour)	% Analysis, Found (calc.)				Yield %	μ_{eff} (B.M.)	λ_m (mho cm^{-2} mol^{-1})
	M	C	H	N			
[Cu PBSC)2] Pale green)	11.1 (11.4)	54.9 (56.3)	5.7 (6.8)	19.4 (20.1)	56	1.7	2.4
[Co PBSC)2] (pink)	10.2 (10.6)	55.4 (56.2)	5.9 (6.8)	20.9 (20.2)	59	4.1	1.9
[Ni (PBSC)2] (green)	10.3 (10.7)	56.1 (56.4)	6.3 (6.8)	19.4 (20.3)	53	–	1.7
[Zn [PBSC)2] (yellow)	10.8 (11.7)	55.4 (55.6)	6.1 (6.7)	19.3 (19.9)	58	–	1.3

In order to study the binding mode of Mannich base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. The IR spectrum of the ligand shows band in the region around 3440 cm^{-1}, which is due to hydrazinic nitrogens. The band at 2960 cm^{-1} is due to N–NH of symmetric stretching. The band appearing in the region around 1680 cm^{-1} is due to C=O group of the ligand. The band at 1180 cm^{-1} is due to N–N stretching frequency. The band at 1680 cm^{-1} is absent in the complex, which is due to

enolization of the ligand, *i.e* the carbonyl group is converted into the enolic C–O form. Hence the band at 1590–1575 cm^{-1} is assigned as C=N bands. The asymmetric and symmetric C–N stretching frequencies are assigned to 1440 and 1020 cm^{-1} for semicarbazide[11]. The ligand shows a band at 1140 cm^{-1} assigned to N–N bond of the ligand, which is shifted to higher frequency side in the complexes around 1150 to 1115 cm^{-1}, which indicates the monodentate linkage of N–N residue. The band at 3180 cm^{-1} observed in the ligand is absent in the complexes, suggesting deprotonation of –NH of the ligand prior to its coordination to the metal. Some new bands were found around 530–540, 440–450 cm^{-1} of M–O, M–N bonds, respectively[12, 13], which further confirms that the ligands are bidentate in nature.

The ^{1}H–NMR spectra of the ligand and its zinc complex were recorded in DMSO–d_6 solution. The ligand shows a multiplet between 7.2 and 7.9 δ, which is due to aromatic protons. It shows the signal at 6.8 δ, which is assigned to the –CH group. A broad absorption around 6.3 δ is due to the –NH proton and piperidine –N–CH$_2$ at 2.6 δ. The singlet corresponding to one proton at 10.7 δ is assigned to –N=C–OH group. In the complex, the multiplets observed at 7.1 and 7.9 δ is due to aromatic protons. Shifting of –CH and –NH protons downfield confirms the involvements of (N) NH nitrogen in coordination to the metal ion. The signal observed at 10.7 δ in the ligand was absent in the complex suggesting that the ligand is in enol form, followed by coordination of carbonyl oxygen to the metal via deprotonation. The ^{13}C–NMR spectrum is also in support of the expected signals.

The electronic absorption spectra of the ligand and its Cu (II), Co (II), Ni (II) and Zn (II) complexes were recorded in DMSO solution. The Cu (II) complex shows a broad band at 10828 cm^{-1} and a well–defined shoulder around 21840 cm^{-1}, attributed to $^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and $^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions, which favour the square planar geometry around the central metal ion[14-16]. This is further supported by the magnetic susceptibility value (1.7 B.M.). The Co (II) complex exhibited a band at 16720 cm^{-1}, which is assigned to $^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ for tetrahedral geometry[17]. This is further confirmed by its magnetic susceptibility value (4.1 B.M.) The Ni (II) complex is diamagnetic suggesting the square planar geometry. The electronic absorption spectrum of the nickel complex shows a d–d band at 22080 cm^{-1} assigned to $^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition[18]. Absence of any band below 10,000 cm^{-1} rules out the possibility of tetrahedral structure for the nickel chelate. Zn (II) is found to be diamagnetic as expected for d^{10} configuration and may have tetrahedral geometry.

The ESR spectrum of copper complex provides informations, which are important in studying the metal ion environment. The X–band ESR spectra of the Cu (II) complex was recorded in DMSO at liquid nitrogen temperature and also at room temperature. The spectrum of the copper complex shows one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. However, this complex at liquid nitrogen temperature shows four well resolved peaks with low intensities in the low field region and one intense peak in the high field region. The copper complex exhibited the $g_{\parallel}$

value of 2.256 and g_1 value of 2.072. These indicates that the ground state of Cu is predominantly $d_{x^2-y^2}$. The $g_{||}$ value is less than 2.3 for the complex indicating its covalent nature[19,20]. The spin–orbit coupling constant λ value (-496 cm^{-1}) calculated using the relations, $g_{av} = 1/3 [g_{||} + 2g_1]$ and $g_{av} = 2(1-2\lambda/10Dq)$, are less than the free Cu^{II} ion (-832 cm^{-1}), which also supports covalent character of M–L bond in the complex. The G value of 3.60 indicates negligible exchange interaction of Cu–Cu in the complex. The in–plane σ–bond strength represented by molecular orbital coefficient, α^2 (covalent in–plane σ–bonding) and β^2 (covalent in–plane π–bonding) were calculated using the following equations:

$$\alpha^2 = -(A_{||} / 0.036) + (g_{||} - 2.0023) + 3/7 (g_\perp - 2.0023) + 0.04$$

$$\beta^2 = (g_{||} - 2.0023) E/-8\lambda\alpha^2$$

If the value of $\alpha^2 = 0.5$, it indicates complete covalent bonding, while the value of $\alpha^2 = 1.0$ suggests complete ionic bonding. The observed value of α^2 (0.81) of the complex[21] is less than unity, it indicates that the complex has some covalent character in the ligand environment.

The cyclic voltammogram of Cu (II) complex (0.01 M) in MeCN was recorded in 0.7 to -1.1 V potential range at scan rate mV/s. It shows cathodic reduction peaks, one at -0.154 (Ip$_c$, 16.19 μA) and another at -0.710 V during the forward scan. The first cathodic peak is due to Cu (II) to Cu (I) reduction, as judged from the magnitude of the current function and the second one is due to Cu (I) to Cu (0) reduction. During the reverse scan, only one anodic peak at -0.046 V (Ip$_a$, 79.6 μA) is observed. This anodic peak corresponds to Cu (I) to Cu (II) oxidation. The ratio between the anodic and cathodic currents suggested that the process is simple one electron transfer, quasi–reversible process[22, 23].

The ligand PBSC and complexes were tested for antibacterial acivity. Mueller–Hinton agar was used for testing the susceptibility of microorganism by well diffusion method[24] using DMSO as solvent, at a concentration of 100μg/10μL against Gram positive (*Staphylococcus aureus*, *B. subtilis*) and Gram negative (*Escherichia coli*, *P. auroginosa*) bacteria. The zone of inhibition against the growth of microorganisms were determined at the end of an incubation period of 24 h at 37°C and the results are presented in Table 2. It was found that the metal complexes are more active than the free ligand. The increase in antibacterial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity effect of the metal and ligand[25].

Table 2. Antibacterial activity of metal complexes of PBSC

No.	Compound	Inhibition zone (mm) at concentration (100 µg/µL)			
		S. aureus	*E. coli*	*B. subtilis*	*P. auroginosa*
1.	PBSC	10	13	7	12
2.	[Cu(PBSC)₂]	20	23	18	24
3.	[Co(PBSC)₂]	18	17	16	18
4.	[Ni(PBSC)₂]	17	21	15	23
5.	[Zn(PBSC)₂]	15	16	12	16

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