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Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Schiff Base Complexes Derived from Acetylacetone with 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one

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Neutral complexes of Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized from the Schiff base derived from acetylacetone and 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one. These complexes have been characterized by elemental and thermal analyses, molar conductivity and magnetic measurements, electronic, IR and ^{1}H, ^{13}C NMR spectral studies. All of the complexes exhibit octahedral geometry and show non-electrolytic behaviour.

Key Words: Schiff Base, Co(II), Ni(II), Cu(II) and Zn(II), Complex.

INTRODUCTION

Nucleotides, purines and pyrimidines have been studied as ligands largely on account of their presence in nucleic acids[1]. Pyrimidines have been studied extensively due to their important biological activities that are often augmented on complex formation with metal ions[2, 3]. β-Carbonyl compounds such as dibenzoylmethane, acetylacetone and acetoacetate are commonly used in organic chemistry and are well known as ligands[4, 5]. We recently reported the synthesis and characterization of some heterocyclic Schiff base complexes obtained from N-aminopyrimidine-2-one[6, 7] and N-aminopyrimidine-2-thione[8].

In this paper we report the synthesis and characterization of the 3*d* bivalent metal complexes of the Schiff base derived from acetylacetone and 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one. Spectral and magnetic studies have been used to characterize the structure of the complexes.

EXPERIMENTAL

MeOH, EtOH, $CHCl_3$, DMF, *n*-BuOH, toluene, Et_2O, *n*-heptane, acetylacetone and *p*-toluene sulfonic acid were obtained from E. Merck and Aldrich. The metal salts $Cu(AcO)_2 \cdot H_2O$, $Co(AcO)_2 \cdot 4H_2O$, $Zn(AcO)_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ were obtained from E. Merck. All solvents were dried and purified before use. Elemental analyses (C, H, N) were performed by using a Carlo-Erba 1106 elemental analyzer. The IR spectra were obtained using KBr discs (4000–400) cm^{-1} on a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the 900–200 nm range were obtained in DMF on a Unicam UV2-100 UV-Vis spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of the Schiff base ligands and

their transition metal complexes were determined in DMF at room temperature by using a Jenway model 4070 conductivitymeter. The ^{1}H- and ^{13}C- NMR spectra of the Schiff base were recorded with a Varian XL-200 NMR instrument. TG measurements were carried out by a Shimadzu-50 thermal analyzer.

Preparation of the Schiff base (LH): The Schiff base ligand was prepared by known method[9], by the condensation of the 0.2 g 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one and 1.5 mL acetylacetone (molar ratio 1 : 2.1) and *p*-toluenesulfonic acid catalyst were homogeneously mixed. The mixture was heated at 115°C and kept at this temperature for 30 min without any solvent in a $CaCl_2$ guard tube fitted round bottom flask of 50 mL. After cooling to room temperature the residue was treated with dry Et_2O and the crude product recrystallized from *n*-BuOH and dried in a vacuum desiccator. Yield was 0.302 g (58%), m.p. 239–241°C.

Preparation of the complexes: 0.75 g (2.00 mmol) of the ligand was dissolved in 30 mL of chloroform and a solution of 1.00 mmol of the metal salt [$Cu(AcO)_2 \cdot H_2O$ (0.20 g), $Co(AcO)_2 \cdot 4H_2O$ (0.25 g), $Zn(AcO)_2 \cdot 2H_2O$ (0.22 g) and $NiCl_2 \cdot 6H_2O$ (0.24 g)] in 15 mL methanol was added dropwise with continuous stirring. The mixture was stirred further for 1.5–2.5 h at 80°C. The precipitated solid was then filtered off, washed with Et_2O, followed by cold methanol/chloroform (1 : 1 ratio) and dried *in vacuo*.

RESULTS AND DISCUSSION

Reactions of LH with metal(II) salts yielded complexes possessing a 1 : 1 metal-ligand ratio. Schiff base ligand reacted with $Cu(AcO)_2 \cdot H_2O$, $Co(AcO)_2 \cdot 4H_2O$, $Zn(AcO)_2.2H_2O$ and $NiCl_2 \cdot 6H_2O$, and formed the complexes having only a 1 : 2 metal-ligand stoichiometry. The newly synthesized Schiff base complexes are very stable at room temperature in the solid state. All these metal complexes are generally soluble in DMF and DMSO. The elemental analytical data of the metal-complexes reveal that the compounds have a metal : ligand anion stoichiometry of 1 : 2 corresponding to the general formulae of $[M(L)_2] \cdot mH_2O$ where L is the anion of LH. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The colours, yields, melting points, IR. and electronic absorption spectral data of all the compounds are presented in Tables 1 and 2. The complexes are non-electrolytic in nature (0.1–4.6 Ω^{-1} cm^2 mol^{-1})[10].

Condensation of acetylacetone with 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one readily gives rise to the corresponding imines, which were easily identified by their IR, ^{1}H NMR and ^{13}C NMR spectra. Tridentate complexes were obtained from 1/2 molar ratio reactions with metal ions and LH ligand. The ligand LH, on reaction with metal salts, yields complexes corresponding to the general formula $[Co(L)_2]$, $[Cu(L)_2] \cdot H_2O$, $[Zn(L)_2] \cdot H_2O$ and $[Ni(L)_2] \cdot 4H_2O$.

The metal-to-ligand ratio of all the complexes was found to be 1 : 2. But the Cu(II), Ni(II) and Zn(II) complexes have one, four and one additional molecules of water of crystallization.

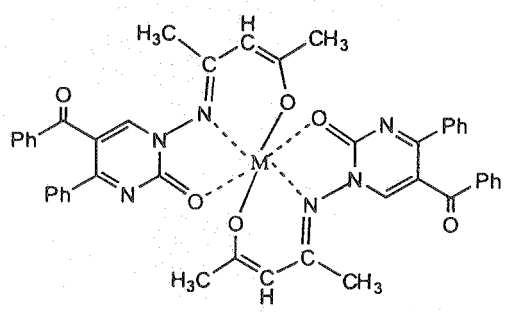
TABLE-1
ANALYTICAL AND PHYSICAL DATA OF ALL THE COMPOUNDS

Compounds	Yield (%)	μ_{eff} (B.M.)	Colour	m.p. (°C) (decomp.)	Elemental analysis (%) Calculated (Found)			Λ_M ($S\ cm^2\ mol^{-1}$)
					C	H	N	
$[Cu(L)_2]\cdot H_2OC_{44}H_{38}N_6O_7Cu$ (823.54 g/mol)	78	2.16	Green	317	63.95 (63.70)	4.60 (4.70)	10.17 (9.83)	1.6
$[Co(L)_2]C_{44}H_{36}N_6O_6Co$ (802.93 g/mol)	70	4.61	Light green	270	65.75 (66.10)	4.48 (4.52)	10.46 (10.40)	1.6
$[Ni(L)_2]\cdot 4H_2OC_{44}H_{44}N_6O_{10}Ni$ (874.71 g/mol)	66	3.36	Yelow	350	60.36 (60.50)	5.03 (4.90)	9.60 (9.65)	4.6
$[Zn(L)_2]\cdot H_2OC_{44}H_{38}N_6O_7Zn$ (827.37 g/mol)	74	diamag.	Cream	230	63.81 (63.70)	4.59 (4.45)	10.15 (9.80)	0.1

TABLE-2
CHARACTERISTIC IR AND ELECTRONIC SPECTRAL DATA OF THE METAL COMPLEXES

Compounds	OH/H_2O	ν(C=O)	ν(C=N)	ν(C–O)	ν(M–N)	ν(M–O)	λ_{max}, (ε_{max}, $M^{-1}cm^{-1}$)
$[Cu(L)_2]\cdot H_2O$	3410	1718 1669	1587	1160	470	530	763 (21), 593 (68), 330 (5400), 297 (6800)
$[Co(L)_2]$	–	1726 1667	1615	1150	422	535	677 (28), 560 (70), 412 (1865), 345 (4200)
$[Ni(L)_2]\cdot 4H_2O$	3325 3415	1719 1665	1605	1150	430	520	760 (14), 605 (38), 338 (5770)
$[Zn(L)_2]\cdot H_2O$	3405	1726 1675	1615	1165	455	535	340 (4610), 288 (6700)

Table-2 presents the important IR spectral bands of the ligand LH and its metal complexes. IR spectra of Schiff base ligand (LH) showed a broad band in the 3500–3400 cm^{-1} region which may be due to ν(OH) or ν(NH)[9, 11]. The intense band at 1190 cm^{-1} present in the IR spectrum of the Schiff base may be assigned to enolic (C—O) stretching mode. The pyrimidine ring shows characteristic stretching absorption bands at 3058 cm^{-1}. The phenyl group shows C—H stretching at 3030 cm^{-1} and C=C stretching at 1550 cm^{-1}. The bands at 1583 cm^{-1} can be assigned to ν(C=N) (pyrimidine)[6–9]. A strong band at 1720–1690 cm^{1}, 1190 cm^{-1} and 1633 cm^{-1} in the IR spectra of the free ligand assigned to ν(C=O), ν(C—O) and ν(C=N)[6–9, 11] respectively is changed by ± 10–25 cm^{-1} in the spectra of complexes, indicating coordination through azomethine nitrogen, enolic oxygen and carbonyl oxygen of Schiff base (Fig. 1). In the spectra of the Cu(II), Ni(II), Co(II) and Zn(II) complexes, the bands observed in the 470–422 and 535–520 cm^{-1} region may be due to ν(M—N) and ν(C—O), respectively[6–9, 11]. The IR. spectra of the complexes are characterized by the appearance of a broad band in the region 3400–3250 cm^{-1} due to the ν(O—H) frequency of water of crystallization. This water content was also identified by elemental analysis. Broad bands of the Cu(II),



M = Co(II), Ni(II), Cu(II) and Zn(II)

Fig. 1. Suggested structure of the complexes

Ni(II) and Zn(II) complexes in the 3410–3325 cm^{-1} region are assigned to the ν(OH) vibration of the water molecules[5-9, 11].

DMSO was used as a deuterated solvent to measure the ^1H NMR spectra of the ligand[9] and its zinc(II) complex except those of copper(II), cobalt(II) and nickel(II) because of their paramagnetic behaviour. The sharp singlet was observed at about δ 9.88 ppm due to enolic proton of the ligand. The singlet at δ 5.31 ppm and 2.38–1.88 ppm is due to (N—H) proton, (CH_3) proton in the spectrum of the ligand, respectively. In the spectra of the Schiff base the aromatic proton multiplet was observed between at δ 7.03–7.37 ppm. The ^1H NMR spectrum of zinc(II) complex shows approximately the same peaks as those of the free ligand with the exception that the peak due to the enolic group resonance is absent. This is considered as an additional evidence for the deprotonation of OH enolic.

DMSO was used as a deuterated solvent to measure the ^{13}C NMR spectra of the ligand[9]. The ^{13}C NMR spectrum of the ligand LH is characterized by the presence of a cluster of peaks at 196.2, 205.5, 68.3 and 63.6 ppm, due to aliphatic carbonyl group (C=O), aromatic carbonyl group (C=O) and olefinic carbon, respectively. The spectrum of the ligand shows a peak at 158.8 ppm which may be attributed to the CH=N group. The spectrum of the ligand shows a peak at 148.68 ppm which may be attributed to the pyrimidine ring (C=N) group. The spectrum of the ligand shows peaks in the region 117.3–158.0 ppm, due to aromatic carbons.

The electronic spectral data for the compounds are shown in Table-1. The spectra were recorded in DMF as solvent. In the spectrum of the Schiff base, the band of 390 nm is attributed to the azomethine chromophore π→π* transition. The bands at 300–235 nm are associated with the pyrimidine rings π→π* transition. These bands were observed at lower energies in the spectra of the complexes indicating involvement of the carbonyl oxygen, enolic oxygen and azomethine nitrogen in bonding. The electronic spectra of the Zn(II) complex which is diamagnetic, have bands in the 340–288 nm range and these bands may be due to the *n*→π* and π→π* transitions of the pyrimidine rings and azomethine group. The six-coordinated $[Cu(L)_2]$ complex is expected to be tetragonally distorted octahedral and is confirmed by the characteristic absorption at 763 nm assignable $^2E_g \rightarrow {}^2T_{2g}$ corresponding to the *d-d* transition band. The obtained value of the effective magnetic moment (2.16 BM) is typical for distorted octahedral Cu(II) chelates. The $[Ni(L)_2]\cdot 2H_2O$ complex shows two absorption bands at 605 and 760 nm which are attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transitions, respec-

tively, on the basis of an octahedral geometry. The observed magnetic moment for the Ni(II) complex of the Schiff base ligand at room temperature is found to be 3.36 BM which is in good agreement with octahedral Ni(II) complexes. The spectra of the cobalt(II) complex show two absorption bands at 677 and 560 nm which are assigned to $^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively, assuming an octahedral geometry for the complex. The octahedral geometry of the Co(II) complex is further confirmed by the value of the magnetic moment (4.61 BM)[12, 13].

Based on magnetic and conductivity measurements, their monomeric and non-electrolytic nature has been confirmed. The IR. spectra of metal complexes indicate bonding through carbonyl oxygen, azomethine nitrogen and enolic oxygen, while *d-d* transitions suggest a octahedral geometry[5–8, 13, 14].

The thermal stability of the complexes was investigated using TG technique at a heating rate of 10°C/min in N_2 atmosphere over the temperature range of 20–850.0°C. In the decomposition process of the M(II) complexes, the mass losses corresponded to H_2O, Ph-CH and the other organic moieties leaving in the first, second, third, fourth and fifth stages of the decomposition, respectively. The three or five stages of decomposition of the M(II) complex were irreversible. In the TG curve of the Cu(II), Zn(II) and Ni(II) complexes suffered loss of H_2O in the first stage of 38–130°C and the ligands gradually decomposed up to 230–580°C. This shows that the complexes contain 1, 1 and 4 moles of water of crystallization per complex molecule, respectively. Finally, the complexes decomposed to CuO, CoO, NiO and ZnO at higher temperatures[6, 8, 14]. It has been found that the complex possessing the Co(II) complex is more thermally stable than other complexes.

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