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Synthesis, Characterization and X-Ray Diffraction Studies of Some Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Schiff Base Derived from *p*-Dimethylamino benzaldehyde and Anthranilic Acid

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The solid complexes of Co(II), Ni(II), Cu(II) and Zn(II) with tridentate Schiff base (PDBAA) derived from *p*-dimethylamino benzaldehyde and anthranilic acid have been synthesized and characterized by elemental analysis, molar conductivity, IR, ^{1}H NMR, electronic spectra, magnetic susceptibility and X-ray diffraction spectra. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1 : 1 (metal : ligand). The metal chelates have a general formula [M(PDBAA)·H_2O] where M = Co(II), Ni(II), Cu(II) and Zn(II). IR spectral data suggest that the ligand PDBAA behaves as a monobasic tridentate ligand with N : N : O donor sequence towards metal ions. Magnetic susceptibility measurement indicates paramagnetic behaviour of all complexes except zinc complex. X-ray diffraction studies suggest monoclinic crystal system for these complexes.

Key Words: Co(II), Ni(II), Cu(II), Zn(II), *p*-Dimethylaminobenzaldehyde, Anthranilic acid, X-Ray diffraction.

INTRODUCTION

In Schiff base, azomethine nitrogen and other donor atoms like sulphur and oxygen play a vital role in coordination chemistry. Literature survey reveals that Schiff bases and their metal complexes exhibit important synthetic[1, 2] and catalytic[3] activities. A group of biochemists found their utility and importance in biological systems[1, 2, 4, 5]. Different Schiff bases and their metal complexes find applications as antituberculosis[6], anticonvulsant[7] and potential anthelmintic[8] agents. The chelation of ligands with transition metals is expected to form complexes with different structural geometry. Also it may enhance their biological activity after chelation. A Schiff base derived from *p*-dimethylaminobenzaldehyde and anthranilic acid was reported[9] to possess such biological activity. It is therefore planned to synthesize a Schiff base using *p*-dimethylaminobenzaldehyde and anthranilic acid and its metal complexes with Co(II), Ni(II), Cu(II) and Zn(II). The newly prepared complexes have been characterized by various spectral techniques. These metal complexes may have enhanced biological activity which may find their importance in the applied medicinal chemistry.

EXPERIMENTAL

Metal salts used for synthetic and analytical work were of AR/LR grade. All reagents and solvents used were purified by standard methods and dried before use.

Synthesis of Schiff base (PDBAA)[9]: *p*-Dimethylaminobenzaldehyde (1.4919 g, 0.01 mol) and anthranilic acid (1.3714 g, 0.01 mol) were taken in a round-bottom flask. 50 mL of absolute ethanol was added and the mixture was refluxed for 6 h on a water bath. The reaction mixture was poured in crushed ice, whereby orange precipitate was obtained. It was suction filtered, washed with water and cold ethanol and finally dried in an oven at 60°C. The pure Schiff base was recrystallized from distilled water (m.p. 186°C, yield 71%).

Synthesis of metal complexes [M(PDBAA)·H_2O]: 1% (w/v) Schiff base solution in hot distilled water was prepared. To this 1 mg/mL metal salt solution prepared in distilled water was added slowly with continuous stirring. The mixture was heated for 5 min on a burner whereby the metal complex was precipitated. After cooling, the precipitate was filtered, washed with distilled water and absolute ethanol. Each metal complex was dried under vacuum at room temperature and recrystalliszd from acetic acid.

Elemental analysis of the metal complexes was done by the reported method[10]. Solubilities of the metal complexes were investigated in various polar and non-polar solvents. Molar conductivity was measured in DMSO (10^{-3} M) solution using Toshniwal TSM-15 conductometer. Magnetic susceptibility measurements were made at room temperature on Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. Electronic absorption spectra were recorded on Shimadzu UV-2100 spectrophotometer, while IR spectra (KBr pellets) were recorded on a Shimadzu FTIR-4200 spectrometer in the range 4000–400 cm^{-1}. ^1H NMR spectra were recorded at 25°C using Brucker spectrospin at 200 MHz. X-Ray diffraction spectra were recorded on X-ray diffractometer supplied by M/s. Philips, Holland.

RESULTS AND DISCUSSION

The analytical data of the complexes and their magnetic moment values are given in Table-1. All the complexes are coloured solids, found to be stable at room temperature but decompose at high temperature. The metal complexes are soluble in hot glacial acetic acid and DMSO, while they are insoluble in other common organic solvents. The molar conductivity values of 10^{-3} M solutions of the complexes (0.81–1.13 S cm^2 mol^{-1}) in DMSO at room temperature show the non-electrolytic nature of the complexes. Sharma *et al.*[11] and Geary[12] have reported non-electrolytic compounds of Schiff base.

The IR spectra of all the metal complexes show broad band of medium intensity at 3450 cm^{-1} which have been assigned to the ν(OH) mode of coordinated water molecule. The new peak at *ca.* 840 cm^{-1} confirms the presence of coordinated water as reported in literature[16]. The infrared spectrum of the

TABLE-1
ELEMENTAL ANALYSIS, PHYSICAL AND SPECTROSCOPIC DATA OF THE SCHIFF BASE AND ITS METAL COMPLEXES

Compound [Colour]	m.f. (m.w.)	Yield % (m.p. °C)	Molar conductivity[a] ($S\ cm^2\ mol^{-1}$)	μ_{eff} (B.M.)	Found (calcd), %				IR[b] (cm^{-1})			Electronic absorbance [cm^{-1}] ($\varepsilon \times 10^4$) ($dm^3\ mol^{-1}\ cm^{-1}$)	^1H NMR[c] (ppm)
					C	H	N	M	ν(O—H)	ν(C=O)	ν(C=N)		
Ligand PDBAA [Orange]	$C_{16}H_{16}N_2O_2$ (268)	71 (186)	—	—	70.19 (71.64)	5.18 (5.97)	9.72 (10.45)	—	3100–2500	1680	1615	29499 (2.1) 40650 (1.4) 46083 (3.1)	6.45–7.70 (ring, m, 8H) 9.64 (OH, s, 1H) 9.03 (CH = N, s, 1H) 3.02 (NR_2 s, 6H)
Co(PDBAA)·H_2O [Creamish yellow]	$C_{16}H_{17}N_2O_3Co$ (343.93)	58 (>300)	0.81	4.61	55.76 (55.82)	4.89 (4.94)	8.10 (8.14)	17.08 (17.13)	—	1590	1540	22026 (0.1) 28902 (1.3) 39526 (1.0)	3.12 (NR_2, s, 6H)
Ni(PDBAA)·H_2O [Light green]	$C_{16}H_{17}N_2O_3Ni$ (343.69)	66 (>300)	0.93	3.33	55.81 (55.86)	4.87 (4.96)	8.08 (8.14)	17.01 (17.07)	—	1590	1540	29499 (0.6) 39370 (0.5)	3.18 (NR_2, s, 6H)
Cu(PDBAA)·H_2O [Green]	$C_{16}H_{17}N_2O_3Cu$ (348.55)	64 (>300)	0.95	1.79	54.98 (55.08)	4.81 (4.87)	8.01 (8.03)	18.19 (18.23)	—	1600	1550	14556 (0.02) 29240 (0.7) 39370 (0.6)	3.32 (NR_2, s, 6H)
Zn(PDBAA)·H_2O [Buff yellow]	$C_{16}H_{17}N_2O_3Zn$ (350.38)	62 (>300)	1.13	D	54.71 (54.79)	4.79 (4.85)	7.92 (7.99)	18.61 (18.65)	—	1590	1540	29240 (0.8) 39370 (0.8)	3.34 (NR_2, s, 6H)

[a]Solvent: DMSO [b]KBr pellets [c]Solvent: d_6-DMSO D = Diamagnetic.

ligand shows a broad band in the region 3100–2500 cm^{-1} which is a characteristic of ν(OH) stretching of carboxylic group[13]. In the spectra of metal complexes the broad band disappears indicating deprotonation of the ligand and involvement of carboxylic oxygen atom in bonding with metal ion. The ligand shows band at 1680 cm^{-1} which can be assigned to ν(C=O) mode of carboxylic group. This band is shifted to 1600 cm^{-1} in the corresponding spectra of metal complexes. Another band appearing at 1615 cm^{-1} in the spectrum of ligand is considerably lowered to 1540 cm^{-1} in the corresponding spectrum of metal complex indicating the involvement of the azomethine nitrogen atom during chelation. The weak band appearing in the region 640–550 and 540–400 cm^{-1} can be assigned to ν(M—N) and ν(M—O) stretching vibrations respectively. Similar assignments to ν(M—N) and ν(M—O) are reported in literature[14, 15, 17, 19].

Electronic spectrum of ligand, showed three high intensity bands lying at 29499, 40650 and 46083 cm^{-1} assigned to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions respectively in ligand[20]. The electronic absorption spectrum of Co(II) complex showing a band in the visible region at 22026 cm^{-1} is assignable to the transition $^4A_2 \rightarrow {}^4T_1(P)$ which is characteristic of tetrahedral geometry. The spectrum also shows an intense sharp band at 28902 cm^{-1} which is attributed to the ligand-to-metal charge transfer transition as observed in most of the Co(II) tetrahedral complexes[21]. This is further supported by the magnetic moment value found to be 4.61 B.M.[22–24].

The electronic absorption spectrum of Ni(II) complex exhibits bands at 29499 and 39370 cm^{-1} which are assigned to $^3T_1 \rightarrow {}^1T_2$ and ligand-to-metal charge transfer transition respectively, on the basis of tetrahedral geometry[25]. Ni(II) complexes with tetrahedral[26, 27] geometry are expected to show magnetic moment in the range of 2.80–3.00 B.M. The observed magnetic moment value for Ni(II) complexes is 3.33 B.M. which is the expected range of tetrahedral complex. Slightly abnormal value than the spin only value may be due to spin-orbit coupling[28].

The electronic absorption spectrum of Cu(II) complex showed bands at 14556, 29240 and 39370 cm^{-1} which are assigned to transition $^2B_{1g} \rightarrow {}^2A_{1g}$ and remaining two transitions are attributed to charge transfer transitions as observed in square-planar geometry[29]. This geometry is further supported by the observed magnetic moment value of Cu(II) complex which is 1.79 B.M. This value is in agreement with the spin only[30] value of single unpaired electron.

Zn(II) complex is diamagnetic in nature and its electronic absorption spectrum does not have *d-d* transition bands. The Zn(II) complex may be assigned square-planar geometry.

The ^1H NMR of these complexes were recorded using TMS as a standard and DMSO as a solvent. Data related to various protons is summarized in Table-1. The ^1H NMR spectrum of ligand (PDBAA) shows multiple signals in the range of 6.45–7.70 ppm, which are characteristic signals for aromatic ring protons. Similarly, signals at $\delta = 9.02$, 9.64 and 3.02 ppm were assigned to (CH=N, s, 1H), (OH, s, 1H) and (—NR_2, s, 6H) respectively.

The X-ray diffraction pattern for all the metal complexes has been determined between 2θ range from 5–80° and data has been summerized in Tables 2–5.

TABLE-2
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Co(PDBAA)·H_2O]

a (Å) = 10.0146 ± 0.0579
b (Å) = 17.4804 ± 0.1825
c (Å) = 13.3498 ± 0.0475
Standard deviation: 0.9%
α = 90°
β = 86.13°
γ = 90°

Volume $(Å)^3$ = 2331.68
D_{cal} = 0.9282 g/cm^3
D_{obs} = 1.1323 g/cm^3
Z = 4
Crystal system = monoclinic
Space group = $P_{2/m}$
% Porosity = 18.03

I/I_0	D_{obs}	D_{cal}	h	k	l
100	13.3393	13.3195	0	0	1
47	4.5510	4.5773	2	0	–1
15	4.4448	4.4280	2	1	–1
35	4.3517	4.3373	2	2	0
31	4.3002	4.3032	0	1	3
17	3.4702	3.4732	1	4	2
38	3.3658	3.3707	2	3	2

TABLE-3
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Ni(PDBAA)·H_2O]

a (Å) = 10.0136 ± 0.0768
b (Å) = 17.4069 ± 0.2401
c (Å) = 13.3959 ± 0.0595
Standard deviation: 1.2%
α = 90°
β = 86.60°
γ = 90°

Volume $(Å)^3$ = 2330.88
D_{cal} = 0.9277 g/cm^3
D_{obs} = 1.1886 g/cm^3
Z = 4
Crystal system = monoclinic
Space group = $P_{2/m}$
% Porosity = 21.95

I/I_0	D_{obs}	D_{cal}	h	k	l
100	13.3942	13.3724	0	0	1
28	4.5583	4.5934	2	0	–1
34	4.4720	4.4413	2	1	–1
31	4.4523	4.4575	0	0	3
30	4.3401	4.3342	2	2	0
12	3.4586	3.4625	1	4	2
35	3.3594	3.3603	2	3	2

TABLE-4
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Cu(PDBAA)·H_2O]

a (Å) = 10.0262 ± 0.0124
b (Å) = 17.3930 ± 0.0378
c (Å) = 13.3659 ± 0.0313
Standard deviation: 0.7%
α = 90°
β = 87.46°
γ = 90°

Volume $(Å)^3$ = 2328.54
D_{cal} = 0.9425 g/cm^3
D_{obs} = 1.0365 g/cm^3
Z = 4
Crystal system = monoclinic
Space group = $P_{2/m}$
% Porosity = 9.07

I/I_0	D_{obs}	D_{cal}	h	k	l
100	4.3709	4.3775	0	3	2
27	4.3153	4.3120	0	1	3
11	4.0885	4.0817	2	2	–1
13	3.8030	3.7899	2	3	0
35	3.7058	3.7042	2	2	2
21	3.5073	3.4786	0	5	0
23	3.4197	3.4510	1	4	2
52	3.3497	3.3388	3	0	0
10	3.2741	3.2789	3	1	0
24	3.1929	3.2017	1	5	1
11	3.1344	3.1257	1	0	–4
11	3.1052	3.1170	3	2	0
16	2.7791	2.7806	3	2	2
19	2.6072	2.6042	3	2	3
11	2.5349	2.5380	1	4	–4
22	2.4397	2.4417	4	0	–1
19	2.4285	2.4325	3	4	–2
15	2.2811	2.2810	4	3	1
14	2.2491	2.2503	4	3	–1
10	2.2288	2.2249	4	0	3
15	2.1445	2.1469	4	3	–2
15	1.8480	1.8473	5	1	3

The major refluxes have been indexed by using computer software. The data indicate the monoclinic crystal systems for all the complexes. Jejurkar *et al.*[31] have reported monoclinic system for such metal complexes.

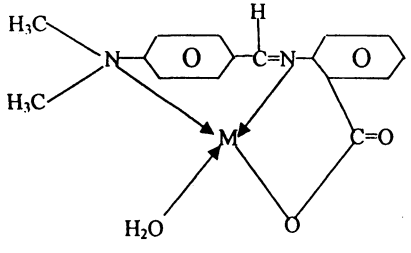
TABLE-5
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Zn(PDBAA)·H_2O]

a (Å) = 9.9278 ± 0.0623	Volume $(Å)^3$ = 2341.70
b (Å) = 17.7346 ± 0.0885	D_{cal} = 0.9424 g/cm^3
c (Å) = 13.3269 ± 0.0594	D_{obs} = 1.1228 g/cm^3
Standard deviation: 1.09%	Z = 4
α = 90°	Crystal system = monoclinic
β = 86.37°	Space group = $P_{2/m}$
γ = 90°	% Porosity = 16.07

I/I_0	D_{obs}	D_{cal}	h	k	l
100	13.3642	13.3001	0	0	1
3	6.6522	6.6075	1	2	0
8	4.5701	4.5912	1	2	–2
15	4.4312	4.4337	0	4	0
4	4.3162	4.3248	2	2	0
7	3.3775	3.3943	1	3	3
2	2.3059	2.3063	3	5	2
3	2.2964	2.2956	2	4	–4

Conclusion

The transition metal complexes obtained are coloured, insoluble in most of the solvents and highly stable (m.p. > 300°C). The stoichiometry of the metal complexes obtained has been found to be 1 : 1 (metal : ligand). All the metal complexes are having four coordinate geometry. Both Co(II) and Ni(II) complexes are having tetrahedral geometry, while Cu(II) and Zn(II) complexes are having square planar geometry. All the metal complexes are paramagnetic in nature except zinc complex. Electronic absorption spectrum of each metal complex exhibits intense peak at higher wavenumber; this can be attributed to a charge transfer transition. X-ray diffraction studies suggest monoclinic crystal system and space group $P_{2/m}$ for all the metal complexes.



where M = Co(II), Ni(II) [Tetrahedral], Cu(II), Zn(II) [Square Planar].

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