SYNTHESIS AND SPECTRAL STUDIES OF Ni (II) COMPLEX OF SCHIFF BASE DERIVED FROM p-DIMETHYLAMINO BENZALDEHYDE AND o-AMINOBENZOIC ACID

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ABSTRACT

The solid complex of Ni (II) with tetradentate schiff base (PDMBA) derived from p-dimethylaminobenzaldehyde and o-aminobenzoic acid have been synthesized and characterized by molar conductivity, elemental analysis, IR, ^{1}H NMR, magnetic susceptibility, electronic spectra and X-ray diffraction spectra. From the analytical and spectral data, the stoichiometry of the complex has been found to be 1 : 1 (metal : ligand). The metal chelates have a general formula [Ni (PDMBA) H_2O]. IR spectral data suggest that the lignad PDMBA behave as monobasic tetradentate lignad with N : N : O : O ⁻ donor sequence towards metal ions. Magnetic susceptibility measurement indicates paramagnetic behaviour of complex.

Key words: Non-electrolytic Ni (II), p-Dimethylaminobenzaldehyde, o-Aminobenzoic acid, X-Ray diffraction.

INTRODUCTION

In Schiff base (RCH = N-R), azomethine nitrogen and other donor atoms like sulphur, phosphorus and oxygen play a vital role in coordination chemistry. Literature survey supported that Schiff bases and their metal complexes exhibit important synthetic and catalytic activities[1,2]. A group of biochemists found their utility and importance in biological systems. The chelation of ligands with transition metals is expected to form complex with different structural geometry. It may enhance their biological activity after chelation also. A Schiff base derived from p-dimethylaminobenzaldehyde and o-aminobenzoic acid was reported to possess such biological activity[3,4]. It is therefore planned to synthesize a Schiff base using p-dimethylaminobenzaldehyde and o-aminobenzoic acid and its metal complex

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with Ni (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 and other area of industries.

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 (PDMBA)

p-Dimethylaminobenzaldehyde (1.4920 g, 0.01 mol) and o-aminobenzoic acid (1.3718 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 60ºC. The pure Schiff base was recrystallized from distilled water (m.p. 186ºC, yield 71%).

The ligand was prepared using methyl alcohol as a catalyst. The synthesis of ligand by nucleophilic addition reaction of p-dimethylaminobenzaldehybe and o-aminobenzoic acid.
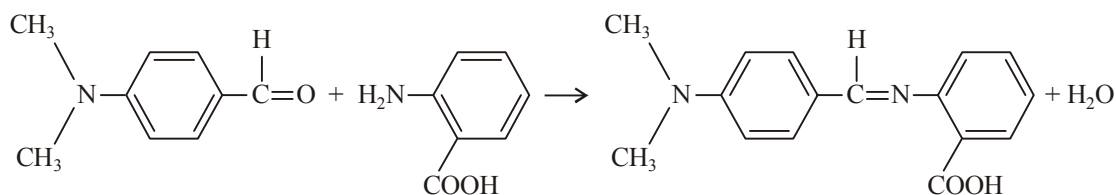
p-N,N- Dimethylaminobenzylidene aminobenzoic acid

Synthesis of metal complex [Ni (PDMBA) H$_2$O]

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 where in the metal complex was precipitated. After cooling, the precipitate was filtered, washed with distilled water and absolute ethanol. Metal complex was dried under vacuum at room temperature and recrystalliszd from acetic acid.

Elemental analysis of the metal complex was done by the reported method. Solubilities of the metal complex 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}. ^{1}H NMR spectra were recorded at 25ºC 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 ligand was prepared using ethyl alcohol as a catalyst. The synthesis of ligand was done by nucleophilic addition of p-dimethylaminobenzaldehyde and o-aminobenzoic acid. The analytical data and magnetic moment values of the complex are given in Table 1. The complex are coloured solids, and stable at room temperature but decompose at high temperature. The metal complex are soluble in hot glacial acetic acid and DMSO, but insoluble in other common organic solvents. The molar conductivity values of 10^{-3} M solutions of the complex (0.81-1.13 S cm^{2}mol^{-1}) in DMSO at room temperature show the non-electrolytic nature of the complex[5-8].
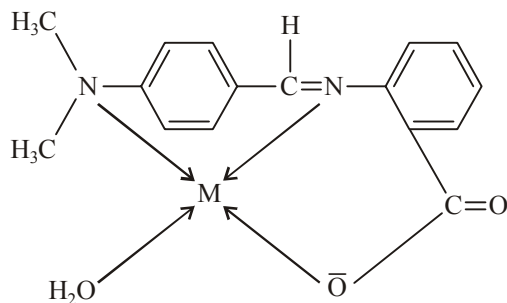
IR Spectra

The IR spectrum of the metal complex show broad band of medium intensity at 3450 cm^{-1} which has been assigned to the ν (OH) mode of coordinated water molecule. The new peak at 840 cm^{-1} confirms the presence of coordinated water as reported in literature[9,10]. The infrared spectrum of the ligand shows a broad band in the region 3100-2500 cm^{-1} which is characteristic of ν (OH) stretching of carboxylic group. In the spectrum of metal complex, the broad band disappears indicating deprotonation of the ligand and involvement of carboxylic oxygen ion 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 spectrum of metal complex. 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, 510-470 cm^{-1} can be assigned to ν(M-N), ν(M-O) and ν(M-O$^-$) stretching vibrations, respectively. Similar assignments to ν(M-N), ν(M-O) and ν(M-O$^-$) are reported.

Electronic spectra

Electronic spectrum of ligand showed three high intensity bands lying at 29500, 40652 and 46084 cm^{-1} assigned to n → π*, π → π* and σ → σ* transitions, respectively in ligand[11].

Table 1: Elemental analysis, physical and spectroscopic data of the Schiff base and its metal complex

Compd. (Colour)	m.f. (m.w.)	Yield % (m.p. °C)	Molar conduct-ivity[a] (S cm² mol⁻¹)	μ_{eff} (B.M.)	Found (calcd.) %				IR (cm⁻¹)			Electronic absorbance [cm⁻¹] (ε x 10⁴) (dm³ mol⁻¹ cm⁻¹)	¹H NMR (ppm)
					C	H	N	M	ν (O-H)	ν (C=O)	ν (C=N)		
Ligand PDMBA (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	29452 (2.1) 40651 (1.4) 4608 (3.1)	6.45-7.70 (ring. m. 5H) 9.64 (OH. s. 1H) 9.03 (CH = N, s, 1H) 3.02 (NR₂ s. 6H)
Ni (PDMBA) H₂O [light green]	$NiC_{16}H_{17}N_2O_3^-$ (34369)	66 (>300)	0.93	3.33	55.81 (55.86)	4.87 (4.96)	8.08 (8.14)	17.01 (17.07)	-	1590	1540	29494 (0.6) 39373 (0.5)	3.18 (NR₂ s. 6H)

The electronic absorption spectrum of Ni (II) complex exhibits bands at 29500 and 39372 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[12-14]. Ni (II) complex with tetrahedral[15,17] 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) complex is 3.33 B.M., which is the expected range of tetrahedral complex.

Where M = Ni (II) [Tetrahedral]

The ^1H NMR of this complex was recorded using TMS as a standard and DMSO as a solvent. Data related to various protons are summarized in Table 1. The ^1H NMR spectrum of ligand (PDMBA) shows multiple signals in the range of 6.45-7.70 ppm, which are characteristic signals for aromatic ring protons. Similarly, signals at δ 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 the metal complex has been determined between 2θ range from 5-80º and data have been summerized in Tables 2.

Table 2: Cell data and crystal lattice parameters for [Ni (PDMBA) H$_2$O]

a (Å) = 10.0136 ± 0.0768   Volume (Å)^3 = 2330.88
b (Å) = 17.4069 ± 0.2401   D$_{cal}$ = 0.9277 g/cm^3
c (Å) = 13.3959 ± 0.0595   D$_{obs}$ = 1.1886 g/cm^3
Standard deviation : 1.2%   Z = 4

I/I$_o$	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

I/I$_o$	D$_{obs}$	D$_{cal}$	h	k	l
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

CONCLUSION

The obtained transition metal complex are coloured, insoluble in most of the solvents and highly stable (m.p. > 300ºC). The stoichiometry of the metal complex obtained has been found to be 1 : 1 (metal : ligand). The metal complex is having four coordinate geometry (tetrahedral geometry). The metal complex is paramagnetic in nature. Electronic absorption spectrum of metal complex exhibits intense peak at higher wavenumber; this can be attributed to a charge transfer transition.

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