

Synthetic and Structural Investigations of Co (II) Complexes of Tridentate Ligands

Abstract

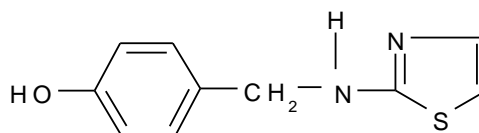
Using tridentate ligands, Co (II) complexes of the composition CoL_1X_2 and CoL_2X_2 (where $\text{L}_1 = p\text{-hydroxybenzylidene-2-aminothiazole}$, $\text{L}_2 = p\text{-hydroxybenzylidene-2-amino-6-methylpyridine}$ and $\text{X} = \text{So}_4^{4-}$, CH_3COO^- and NO_3^-) have been prepared. Ligands were characterized with the help of elemental analyses, IR, NMR and mass spectral studies while complexes were characterized on the basis of elemental analyses, magnetic susceptibility measurements, IR and electronic spectral studies. The studies showed that the complexes are of high spin type having magnetic moment corresponding to three unpaired electrons and indicating distorted octahedral environment around the central metal ion.

Keywords: Mannich bases, Co (II) complexes, magnetic moment, IR, NMR and Konig's treatment.

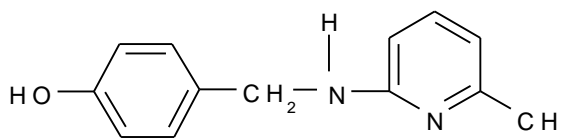
Introduction

Mannich bases (ligands) and their transition metal complexes are well known class of organic and inorganic compounds and have been studied extensively in the recent years due to the selectivity and sensitivity of the ligands towards various metal ions¹⁻³. Now a days, the metal chelates of these Mannich bases are widely studied subjects because of their applications in pharmaceutical and polymer chemistry⁴. Mannich bases prepared from heterocycles bearing nitrogen, sulphur and thiazole moieties constitute the core structure of a number of biologically interesting compounds. The chemistry of thiazole and related compounds are of considerable interest⁵⁻⁶ due to their presence in the histidyl residue of proteins. As a ligand it also provides a potential binding site for metal ions. Hence, it is thought of interest to synthesize some new heterocyclic Mannich bases and their cobalt (II) complexes and characterize them on the basis of spectral and magnetic studies.

Proposed structures of MB₁ and MB₂:



(MB₁)



(MB₂)

Experimental

All the chemicals used were of A.R. grade. The purity of these compounds was checked by thin layer chromatography (TLC). The spots were developed exposing the slides in iodine vapor chamber.



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Synthesis of Ligands**Preparation of Schiff Bases****Preparation of p-hydroxybenzylidene-2-iminothiazole (SB₁)**

1.22gm 4-Hydroxybenzaldehyde and 1.0gm 2-aminothiazole were dissolved in 20ml ethanol and refluxed for 14 hours over water bath using water condenser. The obtained solution was allowed to cool at room temperature. The concentrated solution was cooled in refrigerator and obtained product was filtered, washed with ether and dried under reduced pressure over anhydrous calcium chloride.

Preparation of p-hydroxybenzylidene-2-imino-6-methylpyridine (SB₂)

1.22gm 4-Hydroxybenzaldehyde in ethanol was mixed with an ethanolic solution of 1ml of 2-amino-6-methylpyridine (dissolved in 20ml ethanol). Mixture was refluxed for 12 hours over a water bath using water condenser. The obtained solution was allowed to cool at room temperature and the concentrated solution was cooled in refrigerator for 24 hours. The obtained product was filtered, washed with acetone several times and followed by ether. It was recrystallized with absolute alcohol and dried under reduced pressure over anhydrous calcium chloride.

Preparation of Mannich Bases**Preparation of p-hydroxybenzylidene-2-aminothiazole (MB₁) derived from p-hydroxybenzylidene-2-iminothiazole (SB₁)**

The titled Mannich Base was prepared by stirring p-hydroxybenzylidene-2-iminothiazole (2.04 gm) with 20ml of methanol. The product is then cooled to 0°C and sodiumborohydride (0.2gm) was added over a period of 1 hour in three or four installments. Slowly the temperature was raised to room temperature. A dark brown solution resulted and then solvent was slowly evaporated. A solid colored powder was obtained. It was then washed with ethanol and dried in air, a deep brown colored crystal were obtained.

The mass spectra of the ligand exhibit m/z values: 205, 189, 107, 122, 113 and 99 assignable to C₁₀H₁₀N₂OS, C₁₀H₁₀N₂S, C₇H₇O, C₇H₈NO, C₄H₅N₂S and C₃H₃N₂S molecular ion.

Preparation of p-hydroxybenzylidene-2-amino-6-methylpyridine (MB₂) derived from p-hydroxybenzylidene-2-imino-6-methylpyridine (SB₂)

The titled Mannich Base was prepared by stirring p-hydroxybenzylidene-2-amino-6-methylpyridine (2.12gm) with 20ml of methanol. The product was then cooled to 0°C and then sodiumborohydride (0.2gm) was added with it in three or four installments with continuous stirring over a period of 1 hour. Slowly the temperature was raised to room temperature. A light brown colored solution resulted and then solvent was slowly evaporated. A solid chocolate colored powder is obtained. It was then washed with alcohol and dried in air.

The mass spectra of the ligand exhibit m/z values: 214, 198, 176, 121, 107 and 93 assignable to C₁₃H₁₄N₂O, C₁₃H₁₄N₂, C₁₂H₁₂N₂O, C₇H₉N₂, C₆H₇N₂, and C₆H₇N molecular ion.

Preparation of Metal Complexes

A general method was used for the preparation of trivalent cobalt (II) complexes. The cobalt acetate/ sulphate/ nitrate were used in 1:2:metal: ligand ratio with MB₁ and MB₂. Ethanol and water were used as solvent. The resulting mixture was stirred for 15-20 minutes and refluxed for 3-4 hours on a water bath. The precipitated complex was filtered and washed with ethanol, ether and dried in air.

Physical Measurements

All Mannich bases were analyzed for C, H, S and N on Thomas CH analyzer-35-Carlo Erba-1106 and some on Coleman-N-analyzer at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. The percentage of cobalt (II) in complexes was determined by AAS methods from Geological survey of India, Lucknow. Infra-red spectra of the ligands and their cobalt (II) complexes were recorded in KBr pellets on Perkin Elmer spectrophotometer at R.S.I.C., C.D.R.I., Lucknow. Mass spectra of ligands were determined on Jeol, JMS-D-300 double focusing spectrometer at R.S.I.C., C.D.R.I., Lucknow. The electronic spectrum of the complexes in (DMF/Ethanol) solution were recorded on UV5704SS (Double Beam UV-VIS spectrophotometer) in the range of 380-1100nm at Department of Chemistry, I.B.S., Khandari, Agra. Magnetic susceptibility measurements of the synthesized cobalt (II) complexes were carried out at the room temperature on Vibrating Sample Magnetometer EG & G Model: 155 at R.S.I.C., I.I.T., Chennai. Melting points of the compounds were checked by open capillary tube and are uncorrected. The NMR spectra of all the ligands were recorded in DMSO at R.S.I.C., C.D.R.I., Lucknow.

Results and Discussion

Cobalt (II) complexes were soluble in ethanol, methanol, DMF and DMSO. The analytical estimations and melting points of the complexes are presented in the Table: - 1. The results of the elemental analyses showed that all the complexes have 1:2 (metal: ligand) stoichiometry.

NMR Spectral Studies

The NMR spectra of the Mannich bases (MB₁ and MB₂) were recorded in DMSO, assigned as a solvent peak in the spectrum at δ 3.41 ppm. A doublet may be due to heterocyclic proton (2H) present in thiazole ring was observed in the spectrum at δ 7.0 ppm⁷ in MB₁ while a triplet at δ 7.2 ppm equivalent was observed may be due to 3H proton present in pyridine ring in MB₂. A singlet was observed at δ 5.3-5.7 ppm equivalent to 1H, may be assigned as -OH proton on para position while a doublet at δ 6.4-6.68 ppm equivalent to 4H was present in the aromatic benzene ring⁸ in both the Mannich bases. A singlet was observed at δ 2.56 ppm equivalent to 2H of -CH₂ group attached with the benzene ring⁹. A singlet at δ 5.56-5.58 ppm equivalent to the 1H proton of secondary -NH group was present in these Mannich bases. These data are in good agreement with other spectrometric results (Table: -2)

Infra-Red Spectral Studies

Infra-red spectral data and their tentative assignments are shown in Table: - 3. The infra-red spectra of SB₁ and SB₂ show the bands at ~1605-1610 cm⁻¹ due to azomethine¹⁰ ($\nu_{>C=N}$) which were disappeared in the spectrum of MB₁ and MB₂ and new bands were observed in the region ~3358-3365 cm⁻¹ due to the secondary amino group¹¹ $\nu_{(CH_2-NH)}$. In cobalt (II) complexes, these bands were shifted to higher frequency region by ~9-30 cm⁻¹ indicating the involvement of nitrogen of secondary amino group in complexation with metal ions¹². This is confirmed by the appearing of band at ~461-490 cm⁻¹ due to $\nu_{(M-N)}$ vibrations¹³.

In the infra-red spectra of all the complexes, a broad band at ~3452-3520 cm⁻¹ due to $\nu_{(OH)}$ disappeared thus indicating the deprotonation of phenolic OH. The bands observed at ~1230-1480 cm⁻¹ in the ligands is due to $\nu_{(C-O)}$ phenolic mode. These bands are shifted to higher frequency region (~1242-1251) cm⁻¹ for the complexes of MB₁ while shifted to lower frequency region 10-30 cm⁻¹ in case of cobalt (II) complexes of MB₂. This indicates that the ligands are bonded to the metal ion through the phenolate oxygen¹⁴. The involvement of phenolate oxygen is further supported by the band appearing at 514-550 cm⁻¹ due to $\nu_{(M-O)}$ vibrations¹⁵.

The characteristic infra-red bands in the spectrum of the MB₁ are observed at ~ 1513 $\nu_{(C=N \text{ cyclic})}$, ~ 1352 $\nu_{(C-N \text{ cyclic})}$ and ~ 830 $\nu_{(C-S-C)}$ cm⁻¹ of the thiazole moiety¹⁶. The position of the former two bands remains unaltered in all the complexes ruling out the possibility of coordination of thiazole ring nitrogen. The position of latter band shifted to higher frequency by 5-15 cm⁻¹ in all the complexes indicating the coordination of ring S-atom to the metal ions. This may be due to the electron drainage from the substituents by resonance. The vibration modes due to $\nu_{(M-S)}$ coordination¹⁷ were observed at 300-365 cm⁻¹ in all the complexes confirming the participation of thiazole ring S-atom in complexation.

The strong absorption band due to pyridine ring occurring at ~1498 cm⁻¹ ($\nu_{(C-N-C)}$ pyridine) has shifted to higher frequency region by ~10-25 cm⁻¹ in the complexes showing the participation of nitrogen atom of pyridine in the complexation¹⁸. This is also supported by the appearance of band in the far infra-red region ~500-520 cm⁻¹ due to $\nu_{(M-N)}$ vibrations¹⁹.

The above discussion indicates that both the ligands (MB₁ and MB₂) are tridentate in nature with ONS and ONN donor system having distorted octahedral environment around metal ion.

Electronic Spectral Studies

The absorption spectra of the newly synthesized cobalt (II) complexes give three spin allowed transitions at around 8130– 8368 cm⁻¹, 17391–17699 cm⁻¹ and 20202 – 20529 cm⁻¹ which are assignable to ${}^4T_{1g} \leftarrow {}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)(\nu_2)$, and ${}^4T_{1g} \leftarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively. This favors the distorted octahedral geometry for these Cobalt (II) complexes. The magnetic moment values of the complexes were found to be in the range of 4.1-4.8 B.M. corresponding

to three unpaired electrons, indicating the distorted octahedral environment around the metal ion⁽²⁰⁻²¹⁾.

By applying the Konig's theory treatment to cobalt (II) complexes of MB₁ and MB₂, various ligand field parameters viz. ν_2 / ν_1 , Dq/B, B and β_{35} have been found to be 2.14 – 1.34, 1.64 – 2.68, 881.9 – 896.6 and 0.90 – 0.92 respectively. These values are in good agreement with the reported values for distorted octahedral cobalt (II) complexes²². The values of electronic spectral data are given in Table: - 4. The significance of these parameters and methods of calculations are reported elsewhere²³.

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Aim of the Study

As Mannich bases and their metal complexes have wide range of applications in various field i.e. antimalarial, anti-cancerous, anti HIV etc, it is thought of interest to synthesize some new heterocyclic Mannich bases and their transition metal complexes and screen them for their antimicrobial studies.

Endnotes

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Table –1
Physical Properties, Analytical Data and Magnetic Moment Values of Co (II) Complexes of MB₁ and MB₂

S. No.	Ligand/Complexes (mol. Formulae)	Dec. (°C)	For. Wt.	Color	Percentage of Elements (Found/Calculated)					μ_{eff} (B.M.)
					C	H	N	S	M	
1	C ₁₀ H ₁₀ N ₂ OS (MB ₁)	150	206.0	Dark brown	57.9/ 58.2	4.8/ 4.8	13.2/ 13.5	15.5/ 15.5	-	-
1.1	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ · (CH ₃ COO) ₂	285	588.9	Coffee Brown	48.30/ 48.90	4.51/ 4.41	9.02/ 9.50	10.30/ 10.86	9.85/ 10.01	4.34
1.2	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ · (NO ₃) ₂	170	594.9	Dark Brown	40.10/ 40.34	3.10/ 3.36	14.05/ 14.12	10.70/ 10.75	9.10/ 9.90	4.80
1.3	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ · SO ₄	270	566.9	Light Brown	42.30/ 42.33	3.40/ 3.52	9.80/ 9.87	16.80/ 16.93	10.30/ 10.38	4.56
2	C ₁₃ H ₁₄ N ₂ O (MB ₂)	190	214.0	Light brown	72.8/ 72.9	6.5/ 6.5	13.5/ 13.0	-	-	-
2.1	Co(C ₁₃ H ₁₄ N ₂ O) ₂ · (CH ₃ COO) ₂	220	604.9	Coffee Brown	59.10/ 59.51	5.30/ 5.62	9.02/ 9.25	9.70/ 9.73	-	4.12
2.2	Co(C ₁₃ H ₁₄ N ₂ O) ₂ · (NO ₃) ₂	280	610.9	Dark Brown	50.89/ 51.07	4.32/ 4.58	13.10/ 13.75	9.50/ 9.64	-	4.32
2.3	Co(C ₁₃ H ₁₄ N ₂ O) ₂ · SO ₄	210	582.9	Light Brown	53.60/ 53.52	4.62/ 4.80	9.10/ 9.60	9.87/ 10.10	-	4.76

Table-3
Important Infra-Red Frequencies (cm⁻¹) of MB₁ and Co (II) Complexes

S. No.	Ligand/Complexes	Ligand Modes						Coordination Modes		
		U(OH)	U(CH ₂ =NH)	U(C-O) Phenolic	U(C=N) cyclic	U(C-N) cyclic	U(C-S-C) thiazole	U(M-O)	U(M-N)	U(M-S)
1	C ₁₀ H ₁₀ N ₂ OS	3452	3358	1230	1513	1350	830	-	-	-
1.1	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ (OAc) ₂	-	3382	1242	1518	1350	848	518	462	341
1.2	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ (NO ₃) ₂	-	3370	1258	1513	1356	837	520	461	347
1.3	Co(C ₁₀ H ₁₀ N ₂ OS) ₂ SO ₄	-	3386	1242	1516	1348	848	516	454	363

Table-3
Important Infra-Red Frequencies (cm⁻¹) of MB₂ And Co (II) Complexes

S.No.	Ligand/Complexes	Ligand Modes				Coordination Modes		
		U(OH)	U(CH ₂ =NH)	U(C-O) Phenolic	U(C-N-C) pyridine	U(M-O)	U(M-N)	U(M-N) pyridine
1	C ₁₃ H ₁₄ N ₂ O	3520	3365	1480	1498	-	-	-
1.1	Co(C ₁₃ H ₁₄ N ₂ O) ₂ (OAc) ₂	-	3386	1465	1510	532	481	513
1.2	Co(C ₁₃ H ₁₄ N ₂ O) ₂ (NO ₃) ₂	-	3382	1465	1511	525	485	510
1.3	Co(C ₁₃ H ₁₄ N ₂ O) ₂ SO ₄	-	3384	1466	1514	530	482	516
1.4		-	3384	1465	1512	542	484	518

Table-2
NMR Spectral Data of MB₁ and MB₂

S.No	Compounds	Chemical shifts	Peak Position	No. of Protons	Group Assigned
1	C ₁₀ H ₁₀ N ₂ OS	5.3	Singlet	1H	-OH (proton on para position)
		7.0	Doublet	2H	Thiazole ring
		6.4	Doublet	4H	Aromatic Benzene ring
		2.56	Singlet	2H	-CH ₂
		5.58	Singlet	1H	-NH
2	C ₁₃ H ₁₄ N ₂ O	5.7	Singlet	1H	-OH (proton on para position)
		7.2	Triplet	3H	Pyridine ring
		2.56	Singlet	2H	-CH ₂
		5.56	Singlet	1H	-NH
		6.68	Doublet	4H	Aromatic ring
		2.55	Triplet	3H	-CH ₃ (Pyridine ring)

Observed and Calculated Transition Energies (cm⁻¹) for Co (II) Complexes of MB₁ and MB₂

S. No.	Spectral Data and Parameters		Complexes		
			Co (C ₁₀ H ₁₀ N ₂ OS) ₂ .(OAc) ₂ /Co (C ₁₃ H ₁₄ N ₂ O) ₂ .(OAc) ₂	Co (C ₁₀ H ₁₀ N ₂ OS) ₂ . (NO ₃) ₂ /Co (C ₁₃ H ₁₄ N ₂ O) ₂ . (NO ₃) ₂	Co (C ₁₀ H ₁₀ N ₂ OS) ₂ . SO ₄ /Co (C ₁₃ H ₁₄ N ₂ O) ₂ . SO ₄
1.	Experimental spin allowed bands (cm ⁻¹)	v ₁ v ₂ v ₃	8196/8271 17482/17637 20450/20325	8368/8250 17699/17606 20534/20449	8130/8264 17391/17513 20202/20408
2.	Racah parameters Numerical Fitting (cm ⁻¹)	B C	896.6/882.9 4153.9/4090.4	884.3/892.6 4096.9/4135.4	881.9/892.6 4085.3/4135.4
3.	Crystal field splitting Energy	10 Dq	9321/9397	9376/9384	9369/9336
4.	Nephelauxetic ratio and (%) covalence character	β ₃₅ β %	0.92/0.90 7.66/9.07	0.91/0.91 8.92/8.07	0.90/0.91 9.17/8.07
5.	Ratio between v ₁ , v ₂ and v ₃	v ₂ /v ₁ v ₃ /v ₁	2.14/2.14 2.50/2.46	2.15/2.14 2.49/2.48	2.14/2.14 2.48/2.49
6.	Spin orbit coupling constant	λ	232/223	225/229	226/230
7.	Slator-Condon Parameters	F ² F ⁴	1490.01/1467.24 118.68/116.86	1469.57/1483.37 117.05/118.15	1465.58/1483.37 116.73/118.15
8.	Crystal field and nephelauxetic parameters for the ligands used in the complexes (cm ⁻¹)	f h	1.03/1.04 0.33/0.41	1.04/1.04 0.37/0.37	1.02/1.03 0.41/0.37
9.	Mean and Exact pairing energy	π Π Π/B	5022.73/4954.44 1945.78/1916.04 2.17/2.17	4962.59/5004.45 1919.08/1937.11 2.17/2.17	4944.46/4999.39 1913.88/1937.11 2.17/2.17