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E: ISSN NO.: 2455-0817 *Remarking An Analisation*

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

Abstract

Using tridentate ligands, Cu (II) complexes of the composition CuL_1X_2 and CuL_2X_2 (where L_1 = p-hydroxybenzylidene-2-aminothiazole, L_2 = p-hydroxybenzylidene-2-amino-6-methylpyridine and X = Cl^-, So_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, Cu (II) complexes, magnetic moment, IR, NMR and ESR studies.

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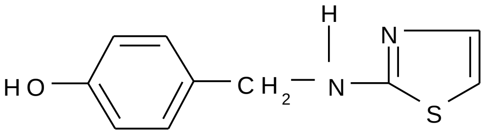
Introduction

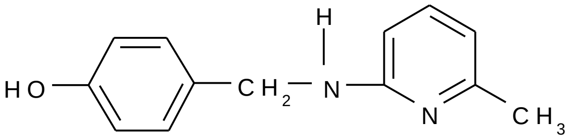
Mannich bases have played a predominant and valuable role in the development of coordination as well as medicinal chemistry. Mannich bases include various types of compounds and rapid development related mainly with these compounds aroused much interest and activity in the field of coordination chemistry, with the result that numerous interesting conclusions have been reached in recent years.

Metal complexes of Mannich bases have been studied[1-3] extensively in recent years due to the selectivity and sensitivity of the ligands towards various metal ions. To our knowledge, Mannich reaction is a three-component condensation reaction consisting of active hydrogen containing compound, formaldehyde and a secondary amine[4].Mannich bases form several complexes with transition metals due to the presence of lone pair of electrons on nitrogen atoms. Metal complexes of Mannich bases have played a central role in the development of coordination chemistry and have many applications in variours. Copper (II) complexes of N, O and S donor ligands have drawn much attention in the last decade because of their immense biological applications[5-6]. Therefore, it was thought to synthesize some copper (II) complexes of Mannich bases prepared from p-hydroxybenzaldehyde, 2-aminothiazole and 2-amino-6-methylpyridine. The antimicrobial studies of ligands and their copper (II) complexes are under study.

Proposed structures of MB_1 and MB_2:



(MB_1)



(MB_2)

Aim of the Study

As Mannich bases and their transition metal complexes have wide applications in various fields, it is thought of interest to synthesis some new copper (II) complexes and screen them for their antimicrobial studies.

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.

Synthesis of Ligands

Preparation of Schiff Bases

Preparation of p-hydroxybenzylidene-2-iminothiazole (SB$_1$)

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 (SB$_2$)

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 (MB$_1$) derived from p-hydroxybenzylidene-2-iminothiazole (SB$_1$):

The titled Mannich Base was prepared by stirring p-hydroxybenzylidine-2-iminothiazole (2.04 gm) with 20ml of methanol. The product is then cooled to 0^{o}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 crystals were obtained.

The mass spectra of the ligand exhibits m/z values: 205, 189, 107, 122, 113 and 99 assignable to $C_{10}H_{10}N_2OS$, $C_{10}H_{10}N_2S$, C_7H_7O, C_7H_8NO, $C_4H_5N_2S$ and $C_3H_3N_2S$ molecular ion.

Preparation of p-hydroxybenzylidene-2-amino-6-methylpyridine (MB$_2$) derived from p-hydroxybenzylidene-2-imino-6-methylpyridine (SB$_2$)

The titled Mannich Base was prepared by stirring p-hydroxybenzylidine-2-amino-6-methylpyridine (2.12gm) with 20ml of methanol. The product was then cooled to 0^{o}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 exhibits m/z values: 214, 198, 176, 121, 107 and 93 assignable to $C_{13}H_{14}N_2O$, $C_{13}H_{14}N_2$, $C_{12}H_{12}N_2O$, $C_7H_9N_2$, $C_6H_7N_2$, and C_6H_7N molecular ion.

Preparation of Metal Complexes

A general method was used for the preparation of trivalent copper (II) complexes. The copper chloride/ acetate/ sulphate/ nitrate were used in 1:2: metal: ligand ratio with MB$_1$ and MB$_2$. 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 copper (II) in complexes was determined by AAS methods from Geological survey of India, Lucknow. Infra-red spectra of the ligands and their copper (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 copper (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.

Review of Literature

Copper is known as an essential element involved in many biochemical processes supporting life. It is required for the biological function of at least 60 enzymes and takes part in many key biological functions including cellular respiration, DNA and RNA replication, maintenance of cell membrane integrity and sequestration of free radicals.

Copper exhibits oxidation states of +2 (the most common and stable) and +1 (only stable in aqueous solution if part of a stable complex ion). A few compounds containing copper (III) are also known e.g. K_3CuF_6 but this oxidation state of the metal is unimportant. A great majority of copper (II) complexes are blue or green in color. Some of these complexes may be red or brown and this is generally caused by a strong absorption in the ultraviolet region arising from the charge transfer transitions. These transitions tail off into the blue end of the visible spectrum, thereby causing the complexes to appear red or brown.

The measurement and interpretation of the d-d spectra of copper (II) complexes have provided a highly fruitful field for coordination chemists in the recent years. There are two reasons for this: first, copper (II) has a 'one hole' d^9 electronic configuration which should render the d-d spectra amenable to theoretical analysis. Secondly, the structural chemistry of copper (II) encompasses a remarkable variety of stereo-chemistries and coordination numbers. This can to some extent be rationalized in terms of the *Jahn-Teller effect* and a vast amount of crystallographic data has been accumulated. Indeed, it is probably true to say that more structural parameters have been measured for the coordination compounds of copper (II) than for those of any other transition metal ion. Such data are, of course, a prerequisite for extensive theoretical studies.

Copper (II) complexes of N, O and S donor ligands have drawn much attention in the last decade because of their immense biological applications[7-8].

Recently, *Mosoarca and coworkers*[9] synthesized copper (II) complexes with hexadentate Mannich base N, N'-tetra(antipyryl-4-methyl)-1,2-diaminoethane. The complexes were characterized by elemental analysis, electrical conductivities, electronic and IR spectroscopy. The electronic spectra of the complexes indicated the octahedral environment of the copper ion.

Costisor et al.[10] synthesized mixed-ligand complexes of copper (II) and cobalt (II) with N,N'-bis(4-antipyrylmethyl)piprazene and 2-aminobenzothiazole and characterized them with the help of elemental analysis, IR and Raman spectra. *Chandrasekhar and coworkers*[11] synthesized mixed-ligand complexes of copper (II) with sulphur donor ligands and characterized them by magnetic moment, electronic and IR spectral studies. On the basis of these spectral and magnetic spectral studies, an octahedral geometry has been assigned to these complexes.

Agarwal and Kumar[12] synthesized copper (II) mixed-ligand complexes of Mannich bases derived from 3-(dimethylamminomethyl)indole and veratraldoxime. The magnetic moment value of copper (II) complexes was 1.55 B.M. and the six coordinated copper (II) complexes possess two or more bands in the 5-16 kk. The complexes showed a broad band at 12300 cm^{-1} which may be assigned due to the transition $^2Eg \rightarrow {}^2T_{2g}$, characteristic of distorted copper (II) complexes. The broadening may be due to *Jahn-Teller distortion*.

We herein report the stereochemistry of newly synthesized copper (II) complexes of Mannich bases derived from 2-aminothiazole/2-amino-6-methylpyridine with p-hydroxybenzaldehyde.

Results and Discussion:

Copper (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. The magnetic moment values of all the copper (II) complexes derived from MB_1 and MB_2 were found in the range of 1.79-1.86 B.M., which were very close to the spin only value (1.73 B.M.). These magnetic moment values confirm the presence of one unpaired electron[13-14] in these copper (II) complexes and hence, offered the possibility of a distorted octahedral geometry[15-16] for the newly synthesized copper (II) complexes of MB_1 and MB_2.

NMR Spectral Studies

The NMR spectra of the Mannich bases (MB_1 and MB_2) 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 ppm[17] in MB_1 while a triplet at δ 7.2 ppm equivalent was observed may be due to 3H proton present in pyridine ring in MB_2. 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 ring[18] in both the Mannich bases. A singlet was observed at δ 2.56 ppm equivalent to 2H of $–CH_2$ group attached with the benzene ring[19].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 SB_1 and SB_2 show the bands at ~1605-1610 cm^{-1} due to azomethine[20] ($v_{>C=N}$) which were disappeared in the spectrum of MB_1 and MB_2 and new bands were observed in the region ~3358-3365 cm^{-1} due to the secondary amino group[21] $v_{(CH2-NH)}$. 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 ions[22]. This is confirmed by the appearing of band at ~461-490 cm^{-1} due to $v_{(-M-N)}$ vibrations[23].

In the infra-red spectra of all the complexes, a broad band at ~3452-3520 cm^{-1} due to $v_{(-OH)}$ disappeared thus indicating the deprotonation of phenolic OH. The bands observed at ~1230-1480 cm^{-1} in the ligands is due to $v_{(-C-O-)}$ phenolic mode. These bands are shifted to higher frequency region (~1242-1251) cm^{-1} for the complexes of MB_1 while shifted to lower frequency region 10-30 cm^{-1} in case of cobalt (II) complexes of MB_2. This indicates that the ligands are bonded to the metal ion through the phenolate oxygen[24]. The involvement of phenolate oxygen is further supported by the band appearing at 514-550 cm^{-1} due to $v_{(M-O)}$ vibrations[25].

The characteristic infra-red bands in the spectrum of the MB_1 are observed at ~ 1513 $v_{(C=N\ cyclic)}$, ~ 1352 $v_{(C-N\ cyclic)}$ and ~ 830 $v_{(C-S-C)}$ cm^{-1} of the thiazole moiety[26]. 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 $v_{(-M-S)}$ coordination[27] 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} ($v_{(C-N-C)}$ 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 complexation[28]. This is also supported by the appearance of band in the far infra-red region ~500-520 cm^{-1} due to $v_{(M-N)}$ vibrations[29].

The above discussion indicates that both the ligands (MB_1 and MB_2) are tridentate in nature with ONS and ONN donor system having distorted octahedral environment around metal ion.

Electronic Spectral Studies

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation[30]. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and number of d-d transitions. The electronic absorption spectra of the Mannich bases and their copper (II) complexes were recorded at room temperature using DMF as solvent. The electronic absorption spectra of these complexes are shown in Table: - 4

The spectrum of all the newly synthesized copper (II) complexes exhibited broad bands with two peaks in the range 9425-17668 cm^{-1} respectively in copper (II) complexes of MB_1 and 10020-17857 cm^{-1} respectively in copper (II) complexes of MB_2 (Table: - 4). These peaks were assigned due to the transition $^2E_g \rightarrow {}^2T_g$, which is in conformity with the distorted octahedral configuration around the copper ion[31]. The broadness of the band can be taken as an indication of distortion from perfect octahedral symmetry, which is further, supported by the magnetic susceptibility value (1.79-1.86 B.M.). The mean of the two peaks were taken as the 10 Dq values. Though three transitions $^2B_1 \rightarrow {}^2A_1$ (v_1), $^2B_1 \rightarrow {}^2B_2$ (v_2) and $^2B_1 \rightarrow {}^2E$ (v_3) are expected in copper (II) complexes of D_{2h} symmetry due to ***Jahn-Teller distortion***, they are often close in energy and give rise to a single broad band[32]. The spectrums of these copper (II) complexes also exhibit a band at 30120-28169 cm^{-1} which is assigned due to the charge transfer band[33-34]. The observed and related values of transitions from the electronic spectra of copper (II) complexes of MB_1 and MB_2 are given in Table: - 4.

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Table: -1

Physical Chatacterization & analytical Data of Copper (II) Complexes of MB_1 and MB_2

S.N.	Metal Complexes	M.P. (^OC)	Formula Weight	COLOR	FOUND(CALCULATED) %				
					C	H	N	S	M
1.	$C_{10}H_{10}N_2OS$	150	206.0	Dark Brown	57.92 (58.25)	4.80 (4.85)	13.45 (13.59)	15.50 (15.53)	-
1.1.	$Cu(C_{10}H_{10}N_2OS)_2Cl_2$	160	545.5	Brown	43.29 (43.99)	3.08 (3.66)	9.98 (10.26)	11.20 (11.73)	11.08 (11.64)
1.2.	$Cu(C_{10}H_{10}N_2OS)_2(0Ac)_2$	260	593.5	Chocolate Brown	40.10 (40.43)	2.95 (3.36)	8.95 (9.43)	10.35 (10.78)	10.32 (10.69)
1.3.	$Cu(C_{10}H_{10}N_2OS)_2(NO_3)_2$	230	619.5	Coffee Color	38.20 (38.74)	2.97 (3.22)	8.86 (9.03)	9.98 (10.33)	9.98 (10.25)
1.4.	$Cu(C_{10}H_{10}N_2OS)_2SO_4$	220	571.5	Chocolate Brown	41.20 (41.99)	3.10 (3.49)	9.35 (9.79)	10.86 (11.19)	10.96 (11.11)
2.	$C_{13}H_{14}N_2O$	190	214.0	Light Brown	72.80 (72.89)	6.50 (6.54)	13.00 (13.08)	-	-
2.1.	$Cu(C_{13}H_{14}N_2O)_2Cl_2$	195	561.5	Dark Brown	54.09 (55.56)	3.96 (4.98)	09.05 (9.97)	-	11.11 (11.30)
2.2.	$Cu(C_{13}H_{14}N_2O)_2(OAc)_2$	235	609.5	Grey	50.98 (51.18)	4.18 (4.59)	08.95 (9.18)	-	9.96 (10.41)
2.3.	$Cu(C_{13}H_{14}N_2O)_2(NO_3)_2$	240	643.5	Green	48.20 (48.48)	4.20 (4.35)	8.20 (8.70)	-	9.20 (9.86)

Table-2

NMR Spectral Data of MB_1 and MB_2

S.No	Compounds	Chemical shifts	Peak Position	No. of Protons	Group Assigned
1	$C_{10}H_{10}N_2OS$	5.3 7.0 6.4 2.56 5.58	Singlet Doublet Doublet Singlet Singlet	1H 2H 4H 2H 1H	-OH (proton on para position) Thiazole ring Aromatic Benzene ring $-CH_2$ -NH
2	$C_{13}H_{14}N_2O$	5.7 7.2 2.56 5.56 6.68 2.55	**Singlet** Triplet Singlet **Singlet** Doublet Triplet	1H 3H 2H 1H 4H 3H	-OH (proton on para position) Pyridine ring $-CH_2$ -NH Aromatic ring $-CH_3$ (Pyridine ring)

Table: - 3

Infra-Red Spectral Data of Ligands Mb_1 And Their Cu (II) Complexes (cm^{-1})

S. No.	Ligand/Complexes	Ligand Modes						Coordination Modes		
		$\upsilon_{(OH)}$	$\upsilon_{(CH2-NH)}$	$\upsilon_{(C-O)\ Phenolic}$	$\upsilon_{(C=N)\ cyclic}$	$\upsilon_{(C-N)\ cyclic}$	$\upsilon_{(C-S-C)\ thiazole}$	$\upsilon_{(M-O)}$	$\upsilon_{(M-N)}$	$\upsilon_{(M-S)}$
1	$C_{10}H_{10}N_2OS$	3452	3358	1230	1513	1350	830	-	-	-
1.1	$Cu(C_{10}H_{10}N_2OS)_2(Cl)_2$	-	3387	1243	1513	1356	838	519	490	348
1.2	$Cu(C_{10}H_{10}N_2OS)_2(OAc)_2$	-	3386	1245	1514	1352	845	525	480	347
1.3	$Cu(C_{10}H_{10}N_2OS)_2(NO_3)_2$	-	3385	1251	1511	1348	838	526	468	340
1.4	$Cu(C_{10}H_{10}N_2OS)_2SO_4$	-	3378	1240	1511	1354	859	520	484	364

Table- 3

Important Infra-Red Frequencies (cm^{-1}) of MB$_2$ and its metal complexes

S.No.	Ligand/Complexes	Ligand Modes				Coordination Modes		
		$U_{(OH)}$	$U_{(CH2=NH)}$	$U_{(C\text{-}O)\ Phenolic}$	$U_{(C\text{-}N\text{-}C)\ pyridine}$	$U_{(M\text{-}O)}$	$U_{(M\text{-}N)}$	$U_{(M\text{-}N)\ pyridine}$
1	$C_{13}H_{14}N_2O$	3520	3365	1480	1498	-	-	-
1.1	$Cu(C_{13}H_{14}N_2O)_2\ (Cl)_2$	-	3386	1458	1512	538	460	516
1.2	$Cu(C_{13}H_{14}N_2O)_2\ (OAc)_2$	-	3383	1457	1508	536	435	507
1.3	$Cu(C_{13}H_{14}N_2O)_2\ (NO_3)_2$	-	3385	1450	1511	528	451	520
1.4	$Cu(C_{13}H_{14}N_2O)_2\ SO_4$	-	3377	1457	1514	536	484	520

Table: - 4

The Observed and Related Values of Transitions and Cyrstal Field Parameter (10 Dq) Of Copper (II) Compexes of MB$_1$ AND MB$_2$

S.No.	Complexes	Absorption Band Positions	10 Dq
1	$Cu\ (C_{10}H_{10}N_2OS)_2.\ (OAc)_2$	9425 12870	11147
2	$Cu\ (C_{10}H_{10}N_2OS)_2.\ Cl_2$	10727 17668	14197
3	$Cu\ (C_{10}H_{10}N_2OS)_2.\ (NO_3)_2$	10869 15384	13126
4	$Cu\ (C_{10}H_{10}N_2OS)_2.\ SO_4$	9852 13123	11487
5	$Cu\ (C_{13}H_{14}N_2O)_2.\ (OAc)_2$	10438 14471	12454
6	$Cu\ (C_{13}H_{14}N_2O)_2.\ Cl_2$	10020 15723	12871
7	$Cu\ (C_{13}H_{14}N_2O)_2.\ (NO_3)_2$	10593 17857	14225
8	$Cu\ (C_{13}H_{14}N_2O)_2.\ SO_4$	10438 17301	13869