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Synthesis, characterisation and Electrochemical studies of transition metal CO(II) complexes of Mannich bases from newly synthesised Schiff bases ligand

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Abstract
The present study carried out by the preparation of Mannich base MB_1 and MB_2 ligand by the reduction of newly synthesized Schiff bases from furfuraldehyde with sulphacetamide/sulphanilamide, and their CO(II) metal complexes with preferred metal chloride/metal sulphate salt in ethanol with 2:1 molar ratio. All the complexes are found to be as colored solids. Which are characterized with the help of magnetic moment and electrochemical studies.

Keywords: Mannich bases, Schiff bases, transition metal complexes, electrochemical studies

Introduction

Many structure of hetrocycles having importance in drug design and synthesis is an important role in bioinorganic and medicinal chemistry. Compound containing hetrocyclic structures found to be high degree of binding affinity to biological system [1], and have been reported to consists pronounced pharmacological, analytical and industrial uses [2-3]. In past some decades, researchers have interest towards transition metal complexes of hetrocyclic aromatic Schiff bases bearing nitrogen, oxygen and sulphur donar atoms due to their therapatic importance [4-5]. Metal complexes of amide moiety have been studied extensively recent years due to the selectivity and sensivity of the Mannich base ligands towards various ions[6-11], and exhibit a variety of biological activities such as antibacterial, antifungal, anti T.B. activity, anti HIV activity, antiviral, antiulcer and antihypertensive [12-18]. The present studies have been completed by the reduction of Sciff base ligands through the reaction with heterocyclic compound like furfuraldehyde and sulpha drugs such as sulphacetamide /sulphanilamide in alcoholic solution.

Experimental

All of the used chemicals were analytical grade (Merch, BDH, S.D. Fine's and Sisco chemicals). The other chemical and solvent were used after purification by distillation, and metal salts used, were as such. The elemental analysis of carbon hydrogen and nitrogen was done on at R.S.I.C. Chandigarh. Estimation of sulphur in ligand and complexes were determined by standard method [19], and estimation of halogen by volhard's methods as ionized form as silver chloride [20] gravimetrically. The metal percentage in CO (II) metal complexes were determined by standard method [21-25], magnetic measurements of the prepared complexes were taken at room temperature on EG & G model 155 VSM at RSIC, IIT-madras, infrared spectra of ligand MB_1 and MB_2 and their chloro/sulphato complexes were studied on Perkin Elmer Spectrometer in the FT-IR region using KBr pellets at RSIC, Chandigarh and Alembic Ltd. Vadodara. Electronic spectra were recorded on ELISCO SL 171 Spectrophotometer by dissolving in (EtOH/DMF) at room temperature in, chemistry department, RBS College, Agra. Mass spectra of ligand MB_1 and MB_2 was carried out on MASPEC System (MSW/9629) using 200 ^{0}C intel temperature at RSIC, IIT-Madras.

Synthesis of Mannich base $C_{13}H_{14}N_2O_4S$ (MB_1)/ $C_{11}H_{12}N_2O_3S$ (MB_2) Ligand

The above ligands were synthesise by refluxing sulphacetamide/sulphanilamide (10mmol, 2.14gm in 25 ml EtOH / 1.72gm in methanol) with furfural (10mmol,0.96 ml in 25 ml EtOH/Methanol respectively) on water bath for 3-4 hours with stirring. The obtained product, cooled at 0 ^{0}C and sodium borohydried (10mmol, 0.39 gm) added over a period of 1-2 hours and stirred over a period of two hours, slowly the temperature was raised to room temperature and put it for 14-15 hour for evaporating of the solvent and then recrystallised with ethanol /acetone and dried in air, deep yellow/reddish yellow crystals of MB_1 and MB_2 ligand was obtained. Above ligand hace been synthesise on behaf of known methods [26-28].

The analytical and mass spectral data obtained for the ligand MB_1/MB_2 are representing below.

Analysis calculated for $C_{13}H_{14}N_2O_4S$/$C_{11}H_{12}O_3N_2S$

C 53.04/52.36, H 4.79/4.79, N 9.51/19.02, S10.89/12.70% Found; C 52.86/52.26, H 4.86/4.68, N9.48/19.13, S 10.96/12.74:Mass (m/z) 304/254, fragmented at m/e 57, 81, 100, 139, 165, 227, 250, 265, 295 and 304 with a higher peak at 193 for MB_1, and the fragmented intensities at m/e 53, 65, 76, 96, 108, 130, 140, 156, 172, 174, 211, 224, 236, 252 and 254 with highest peak at 81 for MB_2 ligand.

Synthesis of Metal Complexes

The cobalt chloride/cobalt sulphate (5mmol in 25 ml ethanol), was added slowly to a alcoholic solution of ligand MB_1/MB_2 (10mmol).The resulting mixture was stirred for half an hour and then refluxed for 2-3 hour on a water bath and then cooled the product and standing for evaporation slowly, washed and dried. The different colored crystals of different complexes with different metal salts and ligands in 1:2 metal ligand molar ratio, have been isolated and subjected to electrochemical studies.

Result and Discussion

All the complexes are soluble in ethanol, DMF and DMSO having low melting points. The analytical data reveales 1:2 metal: ligand stereochemistry for all these complexes. The analytical data is given in table-2

Table 1: Electronic Septracal studies of Cobalt (II) Complexes

Methods of Calculation	Observed and Calculated Transitions			B	10Dq	β	β %	δν	δν%	ν_2-ν_1	ν_2/ν_1	Dq/B
	ν_1	ν_2	ν_3	CO $(MB_1)_2Cl_2$								
Exptl	8050	17200	19800									
(a)	Fitted	Fitted	19070	808	9150	0.83	17.0	730	3.82			1.1
(b)	Fitted	19850	Fitted	951	10565	0.97	3.00	2650	13.35			1.1
(c)	6678	Fitted	Fitted	860	9167	0.88	12.0	-1372	20.54		2.57	1.06
(d)	8050	17200	19800	857	9150	0.88	12.0			10522		1.06
CO $(MB_1)_2$ SO_4												
Exptl.	8180	17500	19850									
(a)	Fitted	Fitted	19924	859	9320	0.88	12.0	74	0.37			1.08
(b)	Fitted	17068	Fitted	948	10730	0.97	3.00	432	2.53	9318	2.13	1.1
(c)	8182	Fitted	Fitted	854	9320	0.88	12.0	-2	0.02			1.09
(d)	8180	17500	19850	854	9320	0.87	13.0					1.09
CO $(MB_2)_2$ Cl_2												
Exptl	8220	17580	20030									
(a)	Fitted	Fitted	19875	853	9360	0.87	13.0	-155	0.77			1.09
(b)	Fitted	20261	Fitted	958	10780	0.98	2.0	2681	13.23	9363	2.13	1.11
(c)	8217	Fitted	Fitted	864	9363	0.88	12.0	-3	0.036			1.08
(d)	8217	17580	20030	864	9363	0.89	12.0					1.08
CO $(MB_1)_2$ SO_4												
Exptl.	8300	17700	19750									
(a)	Fitted	Fitted	18510	780	9400	0.80	20.0	-1240	6.69			1.2
(b)	Fitted	20614	Fitted	937	10905	0.96	4.0	2914	14.13			1.1
(c)	7365	Fitted	Fitted	840	9417	0.86	14.0	-935	12.69	10335	2.40	1.1
(d)	8300	17700	19750	837	9400	0.86	14.0					1.1

Table 2: Analytical estimations and magnetic moment value of the Mannich base complexes

Metal Complexes	Colour	EFF (B.M)	Analytical (%) found/Calcd						
			C%	H%	O%	N%	S%	CI%	M%
CO $(MB_1)_2Cl_2$	Pinkish Brown	4.5	43.52	3.9	19.74	7.84	8.88	9.8	8.3
			43.46	3.92	17.81	7.79	8.92	9.86	8.2
CO $(MB_1)_2SO_4$	Reddish Black	4.8	42.01	3.8	25.78	7.5	12.9	-	7.9
			41.99	3.79	25.81	7.53	12.93	-	7.92
CO $(MB_2)_2Cl_2$	Yellowish Brown	4.75	41.6	3.83	15.1	8.85	10.12	11.18	9.28
			41.64	3.8	15.13	8.83	10.1	11,0	9.28
CO $(MB_2)_2SO_4$	Reddish Brown	5.1	39.99	3.71	24.22	8.54	14.56	-	8.95
			40.06	3.66	24.25	8.49	14.58	-	8.8

1. Magnetic Measurement

The present four CO (II) metal complexes show magnetic moment values in the range 4.5 to 5.1 B.M., Which is higher than the spin only value of 3.89 B.M. due to the orbital contribution. These complexes are expected to have octahedral geometry, can be explained on the basis of octahedral symmetry involving a high degree of orbital contribution due to the three fold degeneracy of the [4] T_1g ground state.

2. Electronic Spectral Studies

CO (II) forms a great variety of structural environment, due to this, the electronic structure, thus the spectral and magnetic properties of the ion, are extremely varied. The beautiful pink to red brown color of octahedral coordinated oxygen ligated CO (II), as distinguished from the blue color of tetrahedrally ligated CO (II) is well known to every chemist. In present study, we will going to discuss the electronic spectra of CO (II) complexes of Mannich base ligand MB_1/MB_2 in detailed. The electronic spectra of isolated CO (II) complexes showed the presence of these bands given in table-1, Which may be assigned to the transition $^4T_1g \rightarrow {}^4T_2g$ (F) (ν_1), $^4T_1g \rightarrow {}^4A_2g$ (ν_2) and $^4T_1g \rightarrow$ (P) (ν_3), in order to increasing energy. The increased intensity of these bands indicate some tetragonal distortion and the possision of the bands closely resemble with the spectra of the other distorted octahedral CO (II) complexes [44]. The crystal field splitting energy (10Dq) and Racah interelectronic parameter (B) for the present CO (II) complexes were calculated by using the following equation [29]. The value of transitions ν_1, ν_2 and ν_3 may be obtained by using Konig's equation [30].

The spectral data and values of various ligand field parameters such as ν_1, ν_2, ν_3, B,C,F^2, F^4, 10Dq, f, h, β, β%, ν_3/ν_1 and ν_3/ν_2 are given in table-3, and significance of these parameters is given in literature [31-34]. The value of above mentioned parameters are in close agreement with the reported value for CO (II) complexes, having distorted octahedral geometry. In present study, we will report the results of the mean and exact spin-pairing energy of the newly prepared four CO (II) complexes with octrahedral geometry [35-40] by using following equation for d^4 ion.

$$\Pi = 4B + 4C - 60\,B^2 / 10\,Dq + X$$

Where, X = -4.5 B – 5 Dq ± ½ (225 B2 + 100 Dq2 + 180 Dq.B) 1/2

In fact, in d^7 configuration 4T1g ($t^5{}_2g\ e^2g$) mixes with three different 2Eg terms according to this exact spin pairing energies (Π) can be calculated with the help of following equation.

$$\Pi = 4B + 4C$$

$$\Pi / B = 0.3594\,\gamma + 0.5051$$

The value of Π and Π /B for the newly prepared CO (II) complexes are given in table-3

3-Infrared Spectral Studies:

Important IR frequencies and their tentative assignment are given in table- 4. The, Mannich base ligand MB_1 shows the IR spectrum band at 3380 cm^{-1} characteristic of streaching vibration of νN-H of $-CH_2$-NH< group. These bands have shifted in the spectra of both chloro / sulphato complexes, showing the involvement of nitrogen of this group in complexation. The new bands at 540-541 cm^{-1} are assigned to ν (M-N) stretching [41-42] indicating the coordination through nitrogen with CO (II) ion. A stretching band observed at 1268 cm^{-1} due to ν(C-O-C) of hetrocyclic furan ring in the above ligand and band appeared at 1230-1244cm^{-1} in both complexes, suggestive of the coordination of oxygen atom of ν(C-O-C) with cobalt metal ion. The low frequency bands appeared at 682-681 cm^{-1} due to ν (M-O) also suggest 43 the coordination through furyl oxygen. Another band appeared at 1708-1703 cm^{-1} in ligand and also in the complexes at the same position due to –CO-NH- group, indicating the noninvolvement in coordination.

The new band appeared at 310 cm^{-1} and 339 cm^{-1} in complexation due to ν(M-Cl) and ν(M-S) stretching modes respectively. The appeared band at 1090 cm^{-1} and 627 cm^{-1} in sulphato complex [CO $(MB_1)SO_4$], may be assigned sulphate moeity in complexation. The IR spectra of CO (II) complexes indicate nature through furfuryl oxygen and methylamine nitrogen sites. The IR spectra of ligand MB_2 shows the band at 3350 $cm^{-1,}$ assigned to the νN-H frequency. This band get shifted to higher frequencies in the IR spectra of complexes thereby, indicating the involvement of nitrogen of $-CH_2$-NH- group in bonding with metal.

The strong band appeared at 3269 cm^{-1}, may be due to $-SO_2$-NH- group to νN-H. In the present complexes, this band is disappeared, indicating the participation of nitrogen in coordination. The coordination of nitrogen is also confirmed by the presence of a low frequency band at (542-540 cm^{-1}) 41-42] assigned to νM-N stretching. The ligand observed a band at 1040 $cm^{-1;}$ may be assigned to νC-O-C group of hetrocyclic furan ring. On complexation, this band is undisturbed, indicating noninvolment of oxygen in coordination. Absorption due to the sulphato group in CO (II) complex [CO (MB_2) SO_4] observed at 1097cm^{-1} and 620 cm^{-1} indicating the coordination through sulphate ion. The other IR band in complexes [CO (MB_2) Cl_2] and [CO (MB_2) SO_4] observed at 320 cm^{-1} and 370 cm^{-1} suggests the νM-Cl and νM-S modes respectively. The above information indicate that the ligand behaves as bidentate with NN sites respectively.

Table 3: Electronic Spectral Data and Computed Values of Spectral Parameters for CO (II) Complexes

S. No.	Spectral Data and Parameters		Complexes			
			CO $(MB_1)_2Cl_2$	**CO $(MB1)_2SO_4$**	**CO $(MB_2)_2Cl_2$**	**CO $(MB_2)_2SO_4$**
1	Observed Spin Allowed Transitions (cm-1)	ν_1	8050	8180	8220	8300
		ν_2	17200	17500	17850	17700
		ν_3	19800	19850	20030	19750
2	Racah Parameters from Numerical Fitting (cm-1)	B	857	854	865	837
		C	1726	1792	1786	1866
3	Slator Condon Parameters (cm-1)	f^2	1103.55	1110	1120.1	1103.6
		f^4	49.31	51.2	51.02	53.31
4	Crystal Field Parameters from Numerical Fitting (cm-1)	10Dq	9150	9320	9360	9400
5	Crystal Fiield and nephelauxetic Parameters for the ligands used	f	1016.66	1035.55	1040	1044.44

	in the complexes (cm-1)	h	0.5	0.541	0.458	0.583
6	Nephelauxatic ratio and (%) covalence character	β	0.88	0.87	0.89	0.86
		β %	12	13	11	14
7	Ratio between n1,n2n3	ν^3/ν^1	2.45	2.42	2.43	2.37
		ν^3/ν^2	1.15	1.13	1.13	1.11
8	Mean Pairing Energy	π	21715.95	24319.39	24401.36	24650.38
9	Exact Spin Pairing Energy	P/B	1.22	1.25	1.24	1.3

Table 4: Infrared Spectra Data (in cm^{-1}) of Mannich Bases and their CO (II) Metal Complexes

S. N.	Ligand/Complex	n-CH_2-NH-	ν-CO-NH-	nasy-SO_2	n-SO_2-NH	nsym-SO_2	nC-O-C	nM-N	nM-O	nCl	nM-S
1	MB_1	3380 b	1705w	1334m	-	1150m	1268s	-	-	-	-
	$CO(MB_1)Cl_2$	3392b	1706m	1324m	-	1154s	1230m	541s	682m	310w	-
	$CO(MB_1)SO_4$	3422m	1706s	1323s	-	1153m	1244m	540w	681s	-	339m
2	MB_2	3350 b	-	1339w	3269w	1152s	1047m	-	-	-	-
	$CO(MB_2)Cl_2$	3407b	-	1338b	-	1152m	1043m	542s	-	320m	-
	$CO(MB_2)SO_4$	3384b	-	1336b	-	1153m	1040w	540s	-	-	370w

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