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\textsubscript{1} and MB\textsubscript{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\textsuperscript{[1]}, and have been reported to consists pronounced pharmaceutical, analytical and industrial uses\textsuperscript{[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 therapeutic importance\textsuperscript{[4-5]}. Metal complexes of amide moiety have been studied extensively recent years due to the selectivity and sensitivity of the Mannich base ligands towards various ions\textsuperscript{[6-11]}, and exhibit a variety of biological activities such as antibacterial, antifungal, anti T.B. activity, anti HIV activity, antiviral, antiulcer and antihypertensive\textsuperscript{[12-18]}. The present studies have been completed by the reduction of Schiff base ligands through the reaction with heterocyclic compound like furfuraldehyde and sulphua 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\textsuperscript{[19]}, and estimation of halogen by volhard’s methods as ionized form as silver chloride\textsuperscript{[20]} gravimetrically. The metal percentage in CO (II) metal complexes were determined by standard method\textsuperscript{[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\textsubscript{1} and MB\textsubscript{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\textsubscript{1} and MB\textsubscript{2} was carried out on MASPEC System (MSW/9629) using 200 °C intel temperature at RSIC, IIT-Madras.
Synthesis of Mannich base C13H14N2O5S (MB1)/C11H12N2O5S (MB2) Ligand
The above ligands were synthesised by refluxing sulphanilamide/sulphadimidine (10mmol, 2.14gms in 25 ml EtOH / 1.72gms 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 °C and sodium borohydride (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 an air, deep yellow/reddish yellow crystals of MB1 and MB2 ligand was obtained. Above ligand hae been synthesise on behalf of known methods [26-28]

The analytical and mass spectral data obtained for the ligand MB1/MB2 are representing below.

Analysis calculated for C13H14N2O5S/C11H12N2O5S
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 MB1, 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 MB2 ligand.

Synthesis of Metal Complexes
The cobalt chloride/cobalt sulphate (5mmol in 25 ml ethanol), was added slowly to a alcoholic solution of ligand MB1/MB2 (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 reveals 1:2 metal: ligand stereochemistry for all these complexes. The analytical data is given in table-2

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

| Methods of Calculation | Observed and Calculated Transitions | B | 10Dq | β % | ββ% | δV | δV% | v2-v1 | v3/v1 | Dq/B |
|------------------------|-----------------------------------|---|------|-----|------|----|-----|------|-------|------|
| Exptl                  | v1 17200                         | 19800 | 808 | 19070 | 9150 | 8.93 | 700 | 3.82 | 11.06 |
| (a)                    | Fitted                           | Fitted | 951 | 860 | 10655 | 9167 | 0.89 | 2650 | 20.54 |
| (b)                    | 19850                             | Fitted | 857 | 9150 | 0.88 | 12.0 | -1372 | 10522 | 2.57 |
| (c)                    | 6678                             | Fitted | 19800 | 817200 | 954000 | 3.66 | 14.0 |
| (d)                    | 8050                             | 17200 | 19800 | 808 | 19070 | 9150 | 8.93 | 700 | 3.82 | 11.06 |
| Exptl                  | 17500                             | 19850 | 859 | 9320 | 8.87 | 12.0 | -155 | 13.23 | 0.036 |
| (a)                    | Fitted                           | Fitted | 948 | 954 | 10730 | 9320 | 0.87 | 2681 | 3.00 |
| (b)                    | 17068                             | Fitted | 958 | 986 | 10780 | 9363 | 0.87 | 2681 | 3.00 |
| (c)                    | 8182                             | Fitted | 854 | 9320 | 0.87 | 12.0 | -2 | 0.02 | 1.09 |
| (d)                    | 17500                             | 19850 | 854 | 9320 | 0.87 | 12.0 | -2 | 0.02 | 1.09 |
| Exptl                  | 17580                             | 20030 | 853 | 9360 | 0.87 | 13.0 | -155 | 13.23 | 0.036 |
| (a)                    | Fitted                           | 19875 | 958 | 986 | 10780 | 9363 | 0.87 | 2681 | 3.00 |
| (b)                    | 20261                             | Fitted | 864 | 9363 | 0.88 | 12.0 | -3 | 0.77 | 1.09 |
| (c)                    | 8217                             | Fitted | 864 | 9363 | 0.88 | 12.0 | -3 | 0.77 | 1.09 |
| (d)                    | 17580                             | 20030 | 864 | 9363 | 0.88 | 12.0 | -3 | 0.77 | 1.09 |
| Exptl                  | 17700                             | 19750 | 780 | 9400 | 0.80 | 20.0 | -1240 | 6.69 | 12.96 |
| (a)                    | Fitted                           | 18510 | 937 | 9400 | 0.96 | 14.0 | 1924 | 14.13 | 10335 | 2.40 |
| (b)                    | 20614                             | Fitted | 840 | 9417 | 0.96 | 14.0 | 1924 | 14.13 | 10335 | 2.40 |
| (c)                    | 7365                             | Fitted | 837 | 9400 | 0.96 | 14.0 | 1924 | 14.13 | 10335 | 2.40 |
| (d)                    | 17700                             | 19750 | 780 | 9400 | 0.96 | 14.0 | 1924 | 14.13 | 10335 | 2.40 |
| Table 2: Analytical estimations and magnetic moment value of the Mannich base complexes

| Metal Complexes | Colour         | EFF (B.M.) | Analytical (%) found/Caled |
|-----------------|----------------|------------|----------------------------|
| CO (MB1):Cl2    | Pinkish Brown | 4.5        | C% H% O% N% S% Cl% M%       |
|                 | 43.52          | 3.9        | 19.74                      |
|                 |                | 7.84       | 8.88                      |
|                 |                | 9.8        | 8.3                       |
| CO (MB1):SO4    | Reddish Black  | 4.8        | 42.01                      |
|                 |                | 3.8        | 25.78                      |
|                 |                | 7.5        | 12.9                      |
| CO (MB2):Cl2    | Yellowish Brown| 4.75       | 41.64                      |
|                 |                | 3.8        | 15.13                      |
|                 |                | 8.83       | 10.11                      |
| CO (MB2):SO4    | Reddish Brown  | 5.1        | 39.99                      |
|                 |                | 3.71       | 24.22                      |
|                 |                | 8.54       | 14.56                      |
|                 |                | 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 $^4T_{1g}$ 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$_2$/MB$_3$ in detail. 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 $^4T_{1g} \rightarrow ^2T_{2g}$ (F) ($v_1$), $^4T_{1g} \rightarrow ^2A_{1g}$ (v$_2$) and $^4T_{1g} \rightarrow (P)$ (v$_3$), in order to increasing energy. The increased intensity of these bands indicate some tetragonal distortion and the possession 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 interelecronic parameter (B) for the present CO (II) complexes were calculated by using the following equation [29]. The value of transitions v$_1$, v$_2$ and v$_3$ may be obtained by using Konig’s equation [30].

The spectral data and values of various ligand field parameters such as v$_1$, v$_2$, v$_3$, B,C,F,$^2$, $^4$, 10Dq, f, h, β, β%, v$_3$/v$_1$ and v$_3$/v$_2$ 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 octahedral geometry [35-40] by using following equation for d$^7$ ion.

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

Where, X = -4.5 B – 5 Dq ± $\frac{1}{2}$ (225 B2 + 100 Dq2 + 180 Dq2.B)/12

In fact, in d$^7$ configuration 4T$_{1g}$ ($^5$$_g$ e$^2$$_g$) 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 assignamm should be given in table- 4. The, Mannich base ligand MB$_3$ shows the IR spectrum band at 3380 cm$^{-1}$ characteristic of streaching vibration of vN-H of –CH$_2$-NH$_2$ 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 v (M-N) stretching [41-42] indicating the coordination through nitrogen with CO (II) ion. A stretching band observed at 1268 cm$^{-1}$ due to v(C-O-C) of heterocyclic furan ring in the above ligand and band appeared at 1230-1244 cm$^{-1}$ in both complexes, suggestive of the coordination of oxygen atom of v(C-O-C) with cobalt metal ion. The low frequency bands appeared at 682-681 cm$^{-1}$ due to v (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 vCO-NH-group, indicating the noninvolvement in coordination.

The new band appeared at 310 cm$^{-1}$ and 339 cm$^{-1}$ in complexation due to v(M-Cl) and v(M-S) stretching modes respectively. The appeared band at 1090 cm$^{-1}$ and 627 cm$^{-1}$ in sulphato complex [CO (MB$_2$)$_2$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$_2$-N$-$H- group to vN-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 vM-N stretching. The ligand observed a band at 1040 cm$^{-1}$ may be assigned to vC-O-C group of heterocyclic furan ring. On complexation, this band is undisturbed, indicating noninvolvement of oxygen in coordination. Absorption due to the sulphato group in CO (II) complex [CO (MB$_2$)$_2$SO$_4$] observed at 1097 cm$^{-1}$ and 620 cm$^{-1}$ indicating the coordination through sulphate ion. The other IR band in complexes [CO (MB$_2$)$_2$Cl$_2$] and [CO (MB$_2$)$_2$SO$_4$] observed at 320 cm$^{-1}$ and 370 cm$^{-1}$ suggests the vM-Cl and vM-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** | **CO (MB$_2$)$_2$Cl$_2$** | **CO (MB$_2$)$_2$SO$_4$** |
|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 1 | Observed Spin Allowed Transitions (cm$^{-1}$) | v$_1$ 8050 | 8180 |
| | | v$_2$ 17200 | 17500 |
| | | v$_3$ 19800 | 19850 |
| 2 | Racah Parameters from Numerical Fitting (cm$^{-1}$) | B 857 | 854 |
| | | C 1726 | 1732 |
| | | f$^2$ 1103.55 | 1110 |
| 3 | Slater Condon Parameters (cm$^{-1}$) | f$^4$ 49.31 | 51.2 |
| 4 | Crystal Field Parameters from Numerical Fitting (cm$^{-1}$) | 10D$_q$ 9150 | 9320 |
| 5 | Crystal Field and nephelauxetic Parameters for the ligands used | f 1016.66 | 1035.55 |
Table 4: Infrared Spectra Data (in cm⁻¹) of Mannich Bases and their CO (II) Metal Complexes

| S. N. | Ligand/Complex | ν-CH₂-NH | ν-CO-NH | ν-asymmetric SO₂ | ν-symmetric SO₂ | ν-CO-C | ν-N-M | ν-M-O | νCl | νM-S |
|-------|----------------|---------|--------|------------------|----------------|--------|------|-------|-----|------|
| 1     | MB₁            | 3380b   | 1705w  | 1334m           | -              | 1150m  | 1268s| -     | -   | -    |
|       | CO(MB₁)Cl₂    | 3392b   | 1706m  | 1324m           | -              | 1154s  | 1230m| 541s  | 682m| 310w |
|       | CO(MB₁)SO₄     | 3422m   | 1706s  | 1323s           | -              | 1153m  | 1244m| 540w  | 681s| -    | 339m|
| 2     | MB₂            | 3350b   | -      | 1339w           | 3269w          | 1152s  | 1047m| -     | -   | -    |
|       | CO(MB₂)Cl₂    | 3407b   | -      | 1338b           | -              | 1152m  | 1043m| 542s  | 320m| -    |
|       | CO(MB₂)SO₄     | 3384b   | -      | 1336b           | -              | 1153m  | 1040w| 540w  | -   | 370w |

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