A new Mannich base and its transition metal (II) complexes – Synthesis, structural characterization and electrochemical study

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Abstract. A new Mannich base, N-(1-morpholinobenzyl) semicarbazide (MBS), formed by the condensation of morpholine, semicarbazide and benzaldehyde, and its Cu(II), Ni(II), Co(II) and Zn(II) complexes have been synthesized. Their structures have been elucidated on the basis of analytical, magnetic, electrical conductivity and spectral study as well as elemental analyses. The complexes exhibit square-planar geometry. The monomeric and non-electrolytic nature of the complexes is evidenced by their magnetic susceptibility and low conductance data. The electrochemical property of the ligand and its complexes in acetonitrile solution was studied by cyclic voltammetry. The X-band ESR spectra of the Cu(II) complex in DMSO at 300 and 77 K were recorded and their salient features are reported.

Keywords. Mannich base; N-(1-morpholinobenzyl) semicarbazide; transition metal (II) complexes; spectral study; electrochemical behaviour.

1. Introduction

Metal complexes of Mannich bases have been studied[1–5] 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.[6] Much work has been done so far on isolation of solid complexes of different aromatic aldehydes or ketones, semicarbazones with transition metals.[7,8] A search through the literature reveals that no work has been done on the condensation of morpholine, benzaldehyde and semicarbazide. It is well known from the literature that semicarbazide compounds containing the amide moiety have a strong ability to form metal complexes. Therefore, it was thought worthwhile to synthesise some metal complexes of this type of Mannich base and investigate its bonding characteristics. We herein report a new Mannich base, N-(1-morpholinobenzyl) semicarbazide formed by the three-component condensation, containing active hydrogen on nitrogen (morpholine), benzaldehyde and semicarbazide. In this ligand system, dicoordination takes place via the N and O of semicarbazide. The proposed structure of the synthesised Mannich base is given in scheme 1.

2. Experimental

All the reagents used for the preparation of the ligand and the complexes were Merck products. Spectroscopic grade solvents were used for the spectral and cyclic voltammetric measurements. The carbon, hydrogen and nitrogen contents in each samples were done at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. ^{1}H-NMR and ^{13}C-NMR spectra of the samples were measured in DMSO-d_6 at Madurai Kamaraj University, Madurai. The IR spectra were recorded as KBr pellets using a Perkin–Elmer 783 spectrophotometer. UV-Vis spectra of the complexes
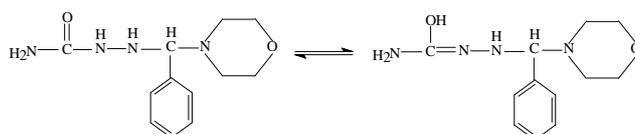
Scheme 1. Structure of the Mannich base ligand.

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were recorded on a Shimadzu UV-1601 spectrophotometer. The X-band ESR spectra of the copper was recorded in DMSO at 300 and 77 K on a Varian 112 ESR spectrophotometer using tetracyanoethylene (TCNE) as the internal standard at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Mumbai. Magnetic susceptibility measurements of the complexes were done using a Gouy balance. Copper sulphate was used as the calibrant. Cyclic voltammogram of the complexes was recorded in acetonitrile solution at 300 K using a three-electrode cell comprising reference Ag/AgCl, auxillary Pt and working glassy carbon electrodes. Molar conductivity was measured on a Systronic conductivity bridge with a dip-type cell, using 10^{-3} M solution of complexes in DMSO. FAB-mass spectrum of the complex was recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas. Accelerating voltage was 10 kV and spectra were recorded at room temperature.

2.1 *Synthesis of Mannich base*

Semicarbazide hydrochloride (1·11 g, 10 mmol) in 20 ml of ethanol was neutralized with ammonia. To this solution morpholine (0·9 ml, 10 mmol) was added dropwise with constant stirring under the same condition. After 5 min the colourless solid obtained was filtered and recrystallized from ethanol (yield: 80%; m.p. 217°C).

2.2 *Synthesis of metal complexes*

A solution of 5 mmol of MCl_2 [where M = Cu(II), Ni(II), Co(II) and Zn(II)] and the Mannich base (1·25 g, 5 mmol) in ethanol and chloroform (1 : 6) mixture (40 ml) was boiled under reflux for ≈ 3 h. The resulting solution was concentrated to a third of its volume and cooled to 0°C for 12 h. The precipitated complexes were filtered, washed with ethanol and dried *in vacuo*. The proposed structure of the complexes is given in scheme 2.

3. Results and discussion

The elemental analyses show 1 : 2 (metal : ligand) stoichiometry for all the complexes. The analytical data of ligand and the complexes are given in table 1. They correspond well with the general formula ML_2, where M = Cu(II), Ni(II), Co(II) and Zn(II);

$L = (C_{12}H_{18}N_4O_2)$. The absence of chloride is evident from Volhard's test. The low conductance of the chelates supports the non-electrolytic nature of the metal complexes.

3.1 *Electronic absorption spectra*

The UV-Vis spectrum of copper complex in DMSO solution displays a broad band at 10718 cm^{-1} and a well-defined shoulder around 22831 cm^{-1}, attributable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions which strongly favour square-planar geometry around the central metal ion.[9–11] The broadness of the band can be taken as an indication of distortion from perfect planar symmetry. This is further supported by the magnetic susceptibility value (1·83 BM). The nickel complex is diamagnetic suggesting square-planar geometry. The electronic absorption spectrum of the nickel complex shows a *d–d* band at 23077 cm^{-1} assigned as $^1A_{1g} \rightarrow {}^1B_{1g}$ transition,[10] which also indicates the square planar geometry. Absence of any band below 10,000 cm^{-1} rules out the possibility of tetrahedral structure for this nickel chelate. The cobalt complex shows a *d–d* band at 16216 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which confirms square-planar geometry. This is further confirmed by its magnetic susceptibility value (3·85 BM).

3.2 *IR spectra*

In order to study the binding mode of the Mannich base to the metal ion in the complexes, the IR spectrum of the free ligand (Mannich base) was compared with the spectra of the complexes. The IR spectrum of the ligand shows bands in the regions
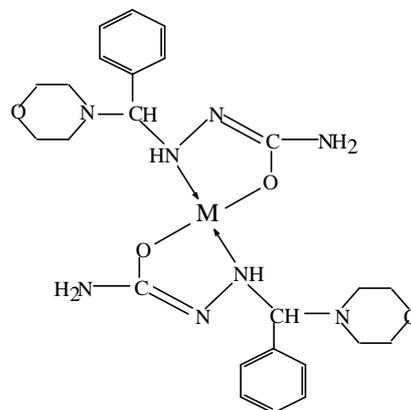
Scheme 2. The proposed structure of the complexes.

Table 1. Physical characterization, analytical, molar conductance and magnetic susceptibility data of the complexes.

Compound/ complex	Colour	Found (calculated) (%)				l m (mho cm^2 mol^{-1})	Mol. wt.	M.p./ decomp.* (°C)	$m_{eff.}$ (BM)
		M	C	H	N				
[C$_{12}$H$_{18}$N$_4$O$_2$]	Colourless	–	57·14 (57·58)	6·88 (7·25)	21·62 (22·38)	–	250·30	195	–
[C$_{24}$H$_{34}$N$_8$O$_4$Cu]	Green	11·62 (11·30)	51·59 (51·28)	6·73 (6·10)	19·62 (19·94)	2.1	562·13	217	1·83
[C$_{24}$H$_{34}$N$_8$O$_4$Co]	Pink	10·73 (10·57)	50·91 (51·70)	6·01 (6·15)	19·87 (20·10)	1.7	557·52	200	4·8
[C$_{24}$H$_{34}$N$_8$O$_4$Ni]	Pale green	10·93 (10·53)	50·12 (51·72)	6·01 (6·15)	19·58 (20·11)	1.5	557·30	225	–
[C$_{24}$H$_{34}$N$_8$O$_4$Zn]	Colourless	9·02 (11·59)	51·01 (51·11)	5·69 (6·08)	19·11 (19·87)	1.5	563·96	216	–

*decomp. = decomposition temperature

Table 2. ^{13}C-NMR spectrum of zinc complex.

Assignment	Values (ppm)
C$_1$,C$_{1'}$	38·8
C$_2$,C$_{2'}$	39·9
C$_3$,C$_{3'}$	43·9
C$_4$,C$_{4'}$	140·8
C$_5$,C$_{5'}$	129·3
C$_6$,C$_{6'}$	128·6
C$_7$,C$_{7'}$	134·5
C$_8$,C$_{8'}$	157·5

3240 and 1600 cm^{-1}, which are assigned to $n_{(N-H)}$ and $n_{(C=O)}$ of semicarbazone respectively. The bands due to $n_{(C-O)}$ and $n_{(C=N)}$ are located in the regions 1135 and 1664 cm^{-1} respectively.[12,13] In the spectra of semicarbazone complexes, the $n_{(C=O)}$ mode of the free ligand is not observed indicating the enolisation of C=O followed by deprotonation and complexation with metal ions. The $n_{(C=N)}$ mode of ligand is found to shift to lower wave numbers suggesting the coordination of the azomethine nitrogen to the central metal ion. The band at 3240 cm^{-1} observed in the ligand is absent in the complexes, suggesting deprotonation of –NH of the ligand prior to the coordination to the metal. This is further confirmed on the basis of ^{1}H-NMR studies. On the basis of this evidence, it is concluded that the ligand acts as a monobasic bidentate manner in all the complexes.

In the far-infrared region all the complexes exhibit bands around 530–470 and 460–416 cm^{-1} which

are assignable to $n_{(M-O)}$ and $n_{(M-N)}$ modes respectively. Due to the larger dipole moment change in the vibration of M–O band in comparison to that in the M–N band, the band due to $n_{(M-O)}$ usually occurs in the higher frequency[14] region and is usually sharp and stronger than $n_{(M-N)}$. These observations are in accordance with the structure of M(II) complexes with semicarbazone ligands in which the central metal ion acquires a coordination number of four.

3.3 *FAB mass spectra*

FAB mass spectrum of the ligand shows the molecular ion peak at m/z 250. The copper (C$_{24}$H$_{34}$N$_8$O$_4$Cu) complex shows the molecular ion peak at m/z 562. Both the complex and the ligand show the base peak at m/z 164, which is due to the fragment, C$_8$H$_{10}$N$_3$O. The data confirm the stoichiometry of the metal complexes as being of the [ML$_2$] type.

3.4 ^{1}*H-NMR spectra*

^{1}H-NMR spectra of the ligand and its zinc and nickel complexes were recorded in DMSO-d_6 solution. The ligand shows a multiplet between 7·06 and 7·88 *d*, which is due to aromatic protons. It shows the signal at 6·7 *d* assigned to the –CH group. A broad absorption around 6·2 *d* is due to the NH proton; morpholine –N–CH$_2$ at 2·2 *d* and morpholine O–CH$_2$ at 3·7 *d*. The singlet corresponding to one proton at 10·9 *d* is assigned to –N=C–OH group. In the complexes, the multiplet observed in 7·18–7·20 and 7·92–8·10 *d* is due to aromatic protons. Shifting of –CH and –NH protons to the downfield confirms the involvement of azomethine nitrogen in coordina-

Table 3. Antibacterial activities of metal (II) complexes.

Compound	*S. flexneri*	*S. typhi*	*P. aeruginosa*	*S. aureus*	*E. coli*	*K. pneumoniae*
Ampicillin	18	18	16	11	13	13
MBSc	10	–	–	–	8	–
Cu(II) complex	22	14	17	15	18	16
Co(II) complex	13	6	9	12	10	14
Ni(II) complex	17	8	10	9	12	12
Zn(II) complex	23	12	17	12	18	13
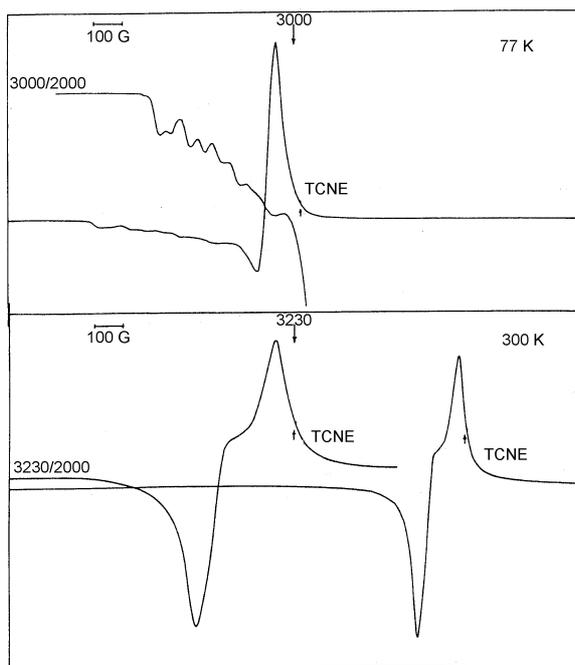
Figure 1. The X-band ESR spectrum of the copper complex, recorded in DMSO at 300 and 77 K.

tion to the metal ion. The peak observed at 10·9 *d* in the ligand was absent in the complexes suggesting that the ligand is in enol form followed by coordination of carbonyl oxygen to the metal ion via deprotonation. Similarly, the ^{13}C-NMR spectrum is in support of the expected signals (table 2).

3.5 *Cyclic voltammetry*

Cyclic voltammogram of the copper complex in MeCN solution using $LiClO_4$ as supporting electrolyte (1·1 to –1·2 V potential range) shows a well defined redox process corresponding to the formation of the copper(II)/copper(III) couple at $Ep_a = 0.209$ V and the associated cathodic peak at $Ep_c = 0.155$ V. This couple is found to be reversible with $\Delta Ep = 0.054$ V and the ratio of cathodic to anodic peak

currents ($Ip_c/Ip_a \sim 1$) corresponding to a simple one-electron process. The complex also shows a quasi-reversible peak in cathodic direction at $Ep_c = -0.67$ V which is due to the reduction of copper(II) → copper(I). In the anodic direction, the direct oxidation takes place at $Ep_a = -0.48$ V which is due to copper(I) → copper(II) oxidation. The reversibility of the copper(II)/copper(III) couple of the complex was unaffected by varying the scan rates ranging from 50 to 250 mVs^{-1} with peak potentials.

3.6 *ESR spectra*

The X-band ESR spectrum of the copper complex, recorded in DMSO at 300 and 77 K, is shown in the figure 1. The *g* tensor values of copper complex can be used to derive the ground state. In square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbitals giving $^2B_{1g}$ as the ground state with $g_{11} > g_\perp > 2$. From the observed values it is clear that $A_{11} = 137 > A_\perp = 47$; $g_{11} = 2.35 > g_\perp = 2.08 > 2$ and the ESR parameters of the complexes coincide well with related systems which suggest that the complex has square-planar geometry and the system is axially symmetric.[15–17] According to Hathaway[18] $G = g_{II}-2/g_\perp-2$; if the value of G is larger than four, exchange interaction is negligible because the local tetragonal axes are misaligned. For present copper complex, the *g* value is 4·4, which suggests that the local tetragonal axis is aligned parallel or slightly misaligned and consistent with $d_{x^2-y^2}$ ground state.

The in-plane *s*-bonding covalency parameter, a^2 is found to be 0·80, indicates that the complex has covalent character. The out-of-plane *p*-bonding (g^2) and in-plane *p*-bonding (b^2) parameters are also calculated. The observed b^2 (0·70) and g^2 (1·34) values indicate that there is substantial interaction in the in-plane bonding whereas the out-of-plane bonding is completely ionic. This is also confirmed by the values of orbital reduction factors[19] (K_{II} and $K_\perp$). In the case of pure *s*-bonding $K_{II} \sim K_\perp$ implies considerable

in-plane p-bonding while for out-of-plane p-bonding $K_{II} > K_{\perp}$. For copper complexes the observed order is K_{II} (0·56) $< K_{\perp}$ (1·072) implying the presence of significant in-plane p-bonding.

4. Conclusion

A new Mannich base, N-(1-morpholinobenzyl) semi-carbazide and its metal (II) complexes have been synthesized and characterized by elemental analyses and spectral study.

Acknowledgements

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