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Synthesis, Characterization and Antimicrobial Studies of a New Mannich Base *N*-[Morpholino (phenyl)methyl]acetamide and Its Cobalt(II), Nickel(II) and Copper(II) Metal Complexes

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Abstract: A new Mannich base *N*-[morpholino(phenyl)methyl]acetamide (MBA), was synthesized and characterized by spectral studies. Chelates of MBA with cobalt(II), nickel(II) and copper(II) ions were prepared and characterized by elemental analyses, IR and UV spectral studies. MBA was found to act as a bidentate ligand, bonding through the carbonyl oxygen of acetamide group and CNC nitrogen of morpholine moiety in all the complexes. Based on the magnetic moment values and UV-Visible spectral data, tetracoordinate geometry for nitrato complexes and hexacoordinate geometry for sulphato complexes were assigned. The antimicrobial studies show that the Co(II) nitrato complex is more active than the other complexes.

Keywords: Chelates, Inhibition, Stoichiometry, Multiplet, Stereochemistry, Fungitoxicity.

Introduction

Metal chelates of Mannich bases form an interesting class of compounds, which find extensive applications in various fields^{1,2}. Among the very few number and variety of transition, inner transition and main group metal complexes of Mannich bases, those formed from bivalent transition metals are of particular interest, because of their synthetic flexibility, structural diversities, bonding interactions, biological significance, and other multiple applications³⁻⁵. We report here, the synthesis of the Mannich base MBA, which is a bidentate ligand. For, it contains two donor atoms: carbonyl oxygen and CNC nitrogen. With this ligand Co^{II}, Ni^{II}, and Cu^{II} (in the molar ratio 1:2) complexes have been prepared.

Experimental

High purity acetamide(Merk), benzaldehdye(Merk), morpholine(Merk) were used as supplied. All other solvents and metal salts used were of A.R. grade and used as received.

Synthesis of the Ligand

N-[Morpholino(phenyl)methyl]acetamide(MBA) was synthesized by employing the Mannich synthetic route⁷: Acetamide (5.90 g, 0.1 mol) was dissolved in minimum quantity of ethanol. To this solution, benzaldehdye (10 mL, 0.1 mol) followed by morpholine (9 mL, 0.1 mol) were added in small quantities with constant stirring in an ice bath. After 28 days, a yellow solid was obtained. It was washed with water and with acetone. The compound was dried in air and then at 60°C in an air oven and recrystallised from ethanol. The percentage yield of the compound was 73 and its melting temperature was 148-150°C.

Synthesis of the Complexes

The hot methanolic solution of the metal salt was added slowly with constant stirring to the hot ethanolic solution of the ligand in 2:1 mol ratio. The insoluble complexes⁸ formed, were filtered, washed with methanol and ethanol to remove the unreacted metal and ligand, dried in air and then in an air oven at 80°C.

Instruments

Micro elemental (C, H, and N) data were obtained with Carlo Erba 1108 elemental analyzer at RSIC, CDRI, Lucknow. Metal contents were estimated by usual procedure, after digesting the complexes with con. HNO₃. Sulphate was estimated gravimetrically as BaSO₄ and chlorides were estimated volumetrically by Volhard's method⁶. The conductance data were obtained in $\sim 10^{-3}$ M DMF solutions of the complexes at room temperature using a Systronics direct reading digital conductivity meter-304 with dip type conductivity cell. IR spectra were recorded using a spectrum-one Perkin Elmer FT-IR spectrometer employing KBr pellets. The UV-Visible regions were recorded in DMF solutions using double beam UV-Visible spectrometer, Perkin EZ-301 of working range 1100-190 nm. The ¹H and ¹³C NMR of the ligand were recorded on a Bruker instrument and on a JEOL-GSX 400 spectrometer employing TMS as internal reference and DMSO-d₆ as solvent. The FAB mass recorded for the ligand was carried out using a JEOL GC mate mass spectrometer. Electrochemical studies were performed on a Bio-Analytical System CV-50W electrochemical analyzer with three-electrode system of a glassy carbon electrode as the working electrode, a platinum wire as auxiliary electrode and Ag/AgCl as the reference electrode. The room temperature magnetic susceptibility measurements of the complexes were made by using a Gouy magnetic balance calibrated using mercury(II)tetrathiocyanatocobaltate(II).

Antimicrobial Studies

Antimicrobial activities⁹ of MBA and their metal complexes, such as Co^{II}, Ni^{II}, and Cu^{II} were tested *in vitro* against six bacterial species *E.coli*, *P.aeruginosa*, *S.typhi*, *B.subtilis*, *S. pyogenes*, and *S.aureus* and the fungal species *A. niger* and *A.flavus* by disc diffusion method using agar nutrient as medium and gentamycin as control. The paper disc containing the compound (10, 20, and 30 μ g/disc) was placed on the surface of the nutrient agar plate previously spread with 0.1 mL of sterilized culture of microorganism. After incubating this at 37°C for 24 h, the diameter of inhibition zone around the paper disc was measured.

Results and Discussion

Characterization of the Ligand

Infrared spectrum of MBA shows a sharp peak at 3297 cm⁻¹, which may be assigned to the v_{NH} of the secondary amide group¹⁰. The strong band at 1647 cm⁻¹ may be attributed to the $v_{C=O}$ stretching mode. The other strong bands appearing at 1493, 1449, and 1206 cm⁻¹ are indicative of bending vibrations of the methylene (δ_{CH2}) group and stretching vibration of the morpholine ring (v_{ring}). The medium absorption band at 1116 cm⁻¹ suggests the presence of new C-N-C bond pertaining to the formation of Mannich base by the insertion of morpholinobenzyl group on acetamide. The absorption band present at 1140 and 1072 cm⁻¹ may be assigned to the C-N-C frequency of morpholine. The strong bands at 1049 and 1034 cm⁻¹ may be attributed to v_{C-O-C} frequency of morpholine group. The band at 749 cm⁻¹ indicates the presence of monosubstitution of morpholine in MBA.

The UV-Visible spectrum¹¹ in DMF registers two intense split bands centered at 286 nm and 242 nm, which are presumably due to $n \rightarrow \pi^*$ transition of the carbonyl group and $\pi \rightarrow \pi^*$ transition of the carbonyl group and the benzene ring.

The ¹H NMR signal at δ =8.44 ppm may be assigned to the secondary amide NH proton. The methine proton shows a signal at δ =5.61 ppm. The multiplet in the range δ =7.44-7.28 ppm (7.44 ppm for C at the position 2&6 and the peaks at δ =7.36 and δ =7.28 ppm for C at 3&5 and 4, respectively) attributed to the protons of the benzene ring¹². The chemical shift of the protons of N(CH₂)₂ group of morpholine ring occurs at δ =2.51 ppm. The chemical shift of the protons of O(CH₂)₂ group of morpholine occurs at δ =3.58 ppm.

The ¹³C NMR spectrum¹³ shows the carbonyl carbon at δ =170.13 ppm. The signals observed between δ =139.71-127.76 ppm are due to aromatic carbons of benzamide. The resonance signals at δ =139.71, 128.64, 127.93 and 127.76 ppm are assigned to the carbons of the phenyl group at 1, 2&6, 3&5 and 4 positions respectively. The signals due to the C₁ carbon of benzene ring can be differentiated by its decreased peak height of δ =139.71 ppm. The signal at δ =66.70ppm is due to the O(CH₂)₂ group and that at δ =48.98 ppm is due to N(CH₂)₂ carbon of morpholine.

The mass spectrum¹⁴ of MBA was obtained on electron ionization mode, showing a very weak molecular ion peak at m/z = 234. This confirms the already assigned molecular mass to the Mannich base understudy. Thereupon, on fragmentation, intense signals at m/z = 143 & m/z = 114 are recorded. They are due to the removal of C₆H₅CH₂⁻ and CHO⁻ groups respectively. The next m/z signal at 86 is due to morpholine ion.

Characterization of the Complexes

To find out the stoichiometry¹⁵ of the complexes, the percentage of the metal ions, anions and CHN were determined. The molar conductance values reveal that all the complexes are non-electrolytes. The CHN analyses are also in good agreement with the calculated values (Table 1).

In the IR spectra¹⁶ of all the MBA complexes (Table 2), the stretching frequencies of C=O and C-N-C bonds are found lowered showing that both carbonyl oxygen and CNC nitrogen atoms are coordinated to the metal ions. So the ligand acts as ON donor. The IR spectrum of the sulphato complexes shows the presence of coordinated sulphato group. The bands at the ranges of 1150, 1000, and 900 cm⁻¹ are due to 'SO' stretching mode, v_3 of sulphato group. The triply degenerate 'OSO' bending mode, v_4 splits up into its components at about 650, 600, and 580 cm⁻¹ in the complexes. The frequencies at 750(v_1) and 500(v_2) are also observed. These are due to the bidentate chelation¹⁷ associated with the coordinated

sulphato group. The bands around 3300 - 3500, 1600 - 1650, 800 - 880, 600 - 690 and 460 - 530 cm⁻¹ found only in the spectra of Co^{II}, Ni^{II}, and Cu^{II}, sulphato complexes of MBA indicate the presence of coordinated water molecule¹⁸.

Complex	% C Obs.(Cal.)	% H Obs.(Cal.)	% N Obs.(Cal.)	%Metal Obs.(Cal.)	%Anion Obs.(Cal.)	$\begin{array}{c} \Lambda_{M} ohm^{\text{-1}} \\ cm^{2} mol^{\text{-1}} \end{array}$
Co(NO ₃) ₂ .MBA	30.48 (29.71)	3.05 (3.43)	5.81 (5.33)	10.77 (11.22)	24.12 (23.62)	21.39
CoSO ₄ .2MBA	42.00 (41.66)	4.61 (4.81)	7.85 (7.48)	8.13 (7.87)	12.54 (12.82)	31.44
Ni(NO ₃) ₂ .MBA	29.97 (29.71)	3.31 (3.43)	5.46 (5.33)	11.05 (11.18)	23.78 (23.62)	20.97
Cu(NO ₃) ₂ .MBA	33.12 (32.77)	3.98 (3.78)	6.09 (5.88)	13.25 (13.35)	25.84 (26.05)	15.06
CuSO ₄ .MBA.2H ₂ O	41.59 (41.62)	3.92 (3.85)	5.23 (5.39)	12.53 (12.24)	18.37 (18.50)	08.95

Table 1. Analytical and Conductance Data for Co^{II}, Ni^{II}, and Cu^{II} complexes of MBA.

Table 2. Important IR Absorption Bands (cm⁻¹) of MBA and of Co^{II}, Ni^{II}, and Cu^{II} complexes.

$\nu_{\rm NH}$	$v_{C=O}$	v_{CNC}	v ₃	ν_4	ν_1	v_2	v_5	ν_6
3297	1647	1116	-	-	-	-	-	-
3390	1598	1087	-	-	1313	1018	1429	824
3337	1630	1099	1144	751	854	461	-	-
			1099	631				
			984	574				
3295	1622	1095	-	-	1342	1028	1386	807
3548	1627	1101	-	-	1310	1052	1384	802
3485	1635	1109	1151	754	852	490	-	-
			1109	641				
			987	612				
	v _{NH} 3297 3390 3337 3295 3548 3485	$\begin{array}{c ccc} v_{\rm NH} & v_{\rm C=0} \\ 3297 & 1647 \\ 3390 & 1598 \\ 3337 & 1630 \\ \\ 3295 & 1630 \\ \\ 3295 & 1622 \\ 3548 & 1627 \\ 3485 & 1635 \\ \end{array}$	$\begin{array}{c cccc} v_{\rm NH} & v_{\rm C=O} & v_{\rm CNC} \\ \hline 3297 & 1647 & 1116 \\ \hline 3390 & 1598 & 1087 \\ \hline 3337 & 1630 & 1099 \\ \hline \\ 3295 & 1630 & 1095 \\ \hline 3548 & 1627 & 1101 \\ \hline 3485 & 1635 & 1109 \\ \hline \end{array}$	$\begin{array}{c ccccc} v_{\rm NH} & v_{\rm C=0} & v_{\rm CNC} & v_{3} \\ \hline 3297 & 1647 & 1116 & - \\ 3390 & 1598 & 1087 & - \\ 3337 & 1630 & 1099 & 1144 \\ & & & & & & \\ 3295 & 1622 & 1095 & - \\ 3548 & 1627 & 1101 & - \\ 3485 & 1635 & 1109 & 1151 \\ & & & & & & \\ 1109 & & & & & \\ 987 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

The Co^{II} nitrato complex exhibits electronic transition bands at 3841 cm⁻¹ due to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)(v_{1})$ transition, at 6719 cm⁻¹ due to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)(v_{2})$ transition, 15086 cm⁻¹ due to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)(v_{3})$ and the band at 28534 cm⁻¹ due to charge transfer¹⁹ transitions respectively. The calculated v_{2}/v_{1} ratio is below 1.75. Also the effective magnetic moment of nitrato complex is 4.58 B.M. These are the expected values for tetrahedral geometry. The Co^{II} sulphato complex exhibits electronic transition bands at 6951(v_{1}), 14982(v_{2}), and 18576(v_{3}) cm⁻¹ respectively due to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}$ (F)(v₁), ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(v_{2})$, and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(v_{3})$ transitions²⁰, respectively. The band at 24053 cm⁻¹ indicates the charge transfer transition. The calculated v_{3}/v_{1} ratio for Co^{II} sulphato complex is 2.67. The μ_{eff} value of this complex is 5.08 B.M. These are in agreement with the values expected for an octahedral Co^{II} complex. The number of bands, their energy positions and intensity confirm the octahedral stereochemistry for the sulphato complex. The Ni^{II} nitrato complex exhibits a band at 3945 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{2g}(F)$ transition, another at 8446 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}A_{2g}(F)$ transition and also at 15107 cm⁻¹ due to ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{2g}(P)$ transition²¹, respectively. The charge transfer transition bands occur at 24638 & 32471 cm⁻¹. The calculated v₂/v₁ ratio is 2.14. The μ_{eff} value of nitrato complex is 2.26 B.M. The number of bands, their energy positions and intensity suggest tetrahedral stereochemistry.

Nitrato and sulphato complexes of Cu^{II} exhibit electronic absorption bands at 9204&9425 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{2g}$ transitions respectively. The bands at 10388&12968 cm⁻¹ corresponds to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transition. The bands at 11915&15317 cm⁻¹ are due to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}(F)$ transitions and those appearing at 24062, 32008&35100 cm⁻¹ are characteristic of charge transfer transitions²² (ligand \rightarrow metal). The μ_{eff} value of nitrato complex is 2.26 B.M. and for sulphato complex is 1.83 B.M. The band positions and multi-component nature of the spectra suggest a geometry for the sulphato complex and a tetragonally distorted tetrahedral geometry for the nitrato complex respectively.

The electronic spectral parameters, Dq, B, β , β^{0} % and ligand field stabilization energy (LFSE)²³, were calculated for Co^{II} & Ni^{II} complexes. The order of Dq values among the Co^{II} complexes are found to be Co(NO₃)₂.MBA < CoSO₄.2MBA. The Dq value for the octahedral sulphato complex is greater than that of the tetrahedral Co^{II} nitrato complex. From the β^{0} % value, the covalent character of Co^{II} complexes is established. The percentage covalency²⁴ is more for the tetrahedral nitrato complex. The β^{0} % values are about 29 and 13 for the nitrato and sulphato complex of Co^{II} respectively, when the free ion value for the inter electronic repulsion parameter is incorporated.

The X band EPR spectra²⁵ of polycrystalline nitrato and sulphato complexes of Cu^{II} is recorded at LNT (77 K). The g values of the, nitrato and sulphato complexes of Cu^{II} are in the trend, $g_{\parallel} > g_{\perp} > g_{DPPh}$ suggesting that the unpaired electron lies predominantly in the d_{x2-y2} orbital. The nitrato and sulphato complexes of Cu^{II} showed EPR spectra of axial symmetry type indicating planar based distorted octahedral geometry around copper centre. The g_{\parallel} values of nitrato and sulphato complexes are less than 2.30 indicating the covalent nature.

The higher g_{\parallel} values may be due to the coordination of H_2O to the Cu^{II} ion in these complexes. The axial symmetry parameter²⁶ G value, which is a measure of interaction between the metal centers in the crystalline solids for the nitrato and sulphato complexes of Cu^{II} , is 7.21 and 7.50. This suggests the lack of change in interaction between two Cu^{II} centres in the unit cell of the complex.

The Cu(II) complex exhibited two quasireversible peaks. A cyclic voltammogram of Cu(II) displays two reduction peaks, first one at Epc= -0.65 V with an associated oxidation peak at Epa= -0.5 V and second reduction peak at Epc= -1.58 V with an associated oxidation peak at Epa= -1.8 V. This corresponds to the Cu(II) / Cu(I) and Cu(I) / Cu(0) respectively at a scan rate of 0.2 V/s. The value of Δ Ep are 1.5 and 2.02 for first and second redox couples respectively and increase with scan rate giving evidence for quasi-reversible nature associated with one electron reduction.

Antibacterial Activity

A comparison of diameters of the inhibition zones of the compounds investigated and listed in Tables 3 and 4 shows that Co^{II} nitrato complex exhibits highest antibacterial and antifungal activity against all the bacterial and fungal species studied. This is because, they have larger diameters of inhibition zones than even the control gentamycin at the same concentration and identical conditions. The complexes have more antibacterial and antifungal activities than the ligand against all the bacteria and fungi studied. This observation clearly indicates that the chelation increases the activity. The higher activity of the Co^{II} complex may be due to the fact that, Co(II) is an essential micronutrient during transcription and transformation of nucleic acids. Co^{II} complexes were shown to inhibit cellular protein and RNA synthesis. In Co^{II} nitrato complex, the unsaturated metal center present, achieves higher coordination number by binding with some of the functional groups of the protein. This leads to the increased uptake of the compound by the bacterium and thereby inhibiting its growth. Steric constraints are less for a tetrahedral complex than for an octahedral complex. So the tetrahedral complexes are biologically more active than the octahedral complexes²⁷.

Compound	I	Е. со	li	aer	P. ugin	osa	S	typl	ni	В.	subt	ilis	рy	S. ogei	nes	S.	aure	eus
Conc. (µg/disc)	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
Control MBA	12	15	20 08	10 04	13 08	18 09	14 04	17 06	22 06	11 _	14 06	18 09	10 04	12 04	16 06	12	17 07	20 10
Co(NO ₃) ₂ . MBA	18	21	24	17	22	27	20	28	30	23	26	32	18	24	29	25	28	35
CoSO ₄ .2 MBA	16	18	23	14	19	24	14	19	26	14	19	27	17	23	28	18	23	30
Ni(NO ₃) ₂ . MBA	09	12	17	06	09	15	10	12	16	08	14	18	14	19	22	10	10	18
Cu(NO ₃) ₂ .MBA	14	20	21	16	16	21	14	15	21	12	18	24	16	21	26	12	19	25
CuSO ₄ . MBA.2H ₂ O	15	19	22	15	18	22	11	16	22	10	19	21	15	18	25	16	18	24

Table 3. Antibacterial activity of ligand and its complexes.

Table 4. Antifung	al Activity	of Ligand	and its	Complexes
	,	- 0		

Compound		A. niger		A. flavus				
Conc. (µg/disc)	10	20	30	10	20	30		
MBA	04	04	05	04	05	05		
Co(NO ₃) ₂ .MBA	15	19	26	16	19	28		
CoSO ₄ .2MBA	14	18	24	13	17	25		
Ni(NO ₃) ₂ .MBA	11	17	20	10	14	19		
Cu(NO ₃) ₂ .MBA	12	15	21	11	15	23		
CuSO ₄ .MBA.2H ₂ O	10	16	23	12	16	24		



Figure 1. *N*-[Morpholino(phenyl)methyl] acetamide.



Figure 2. A.SO₄.MBA.2H₂O (A=Cu).





Figure 3. A. $(NO_3)_2$.MBA (A= Co, Ni and Cu).

Figure 4. CoSO₄.2MBA.

Antifungal Activity

The fungi toxicity of the free ligand is less severe than that of the metal chelates. A possible mechanism of toxicity may be speculated in the light of chelation theory²⁸. Chelation reduces considerably the polarity of the metal ion, mainly because of partial sharing of its positive charge with donor groups and a possible π -delocalization of electron over the chelate ring. This increases the liphophilic character of the neutral chelate, which favours its permeation through lipoid layers of fungus membranes. Furthermore, the mechanism of action of the compounds may involve the formation of hydrogen bond through the uncoordinated heteroatoms viz. O, S, and N with the active centers of the cell constituents, thus resulting in the interference with the normal cell process²⁹. These compounds have a greater chance of interaction with either the nucleotide bases or biologically essential metal ions present in the biosystem and also coordinatively unsaturated metal present in the metal complexes. The low activity of some of the complexes may be due to a mismatching of the geometry and charge distribution around the molecule with that around the pores of the fungal cell wall, preventing penetration and hence toxic reaction within the pores. As a corollary, the complex cannot reach the desired site of action on the cell wall to interfere with normal cell activity³⁰.

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