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Synthesis and Physico-chemical Characterisation of New Mannich Bases and Their Paramagnetic Metal Complexes

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ABSTRACT

A new Mannich base,N-(morpholinobenzyl)benzamide (MBB),formed by the condensation of morpholine,benzamide and benzaldehyde and its Fe(II), Fe(III), Mn(III), Co(III), Ti(III), V(III), V(IV), MoO(V), Ru(II) and Ru(III) complexes haíe been Synthesized.Their probable structures haíe been determined on the basis of their microanalytical,IR,UV-vis ^{1}H NMR spectral data. All the complexes exhibit octahedral geometry. The molar conductance data suggested 1:1 electrolytic nature for all complexes except Ru(II) and Fe(II) which are non-electrolytes and V(IV) is 1:2 electrolyte. Based on these studies all the complexes haíe been assigned octahexzobity. The biological activities of the ligand and its metal chelates against the bacteria *E.coli,Staphylococcus aureus, Klebsiella pneumonia, Salmonella typhi, Pseudomonas aeruginosa* and *Shigella flexnri* are also reported. The complexes haíe higher activity than that of the free Mannich base and the control.

Key words: N-(morpholinobenzyl) benzamide, Morpholine, Benzamide and Mannich base.

INTRODUCTION

It is well known from the literature that the compounds containing amide moiety haíe a strong ability to form metal complexes and exhibit a wide range of biological actiíities[1-4]. The coordination chemistry of amide group has received much attention due to its diverse coordinating behaviour and the role it plays in biological process[5]. An amide group offers two potential sites, i.e., through oxygen and nitrogen for complexation with protons and metal ions. It is now generally accepted that for neutral amide groups, both protonation and metal ion binding will be at the amide oxygen[6]. Upon deprotonation the binding shifts to the amide nitrogen[7]. But, for certain reasons, like bit size and steric hindrance, the coordination may also take place at amide nitrogen.

Keeping these facts in view, an attempt has been made to synthesize and characterize the complexes of metals a new Mannich Base, N-(morpholinobenzyl) benzamide (MBB) which also contains amide moiety. The synthesis of N-(morpholinobenzyl)benzamide (MBB)and its complexation behaviour with Fe(II), Fe(III), Mn(III),Co(III),Ti(III), V(III),V(IV),MoO(V), Ru(II) and Ru(III) salts and the antibacterial activity of the complexes are described in this note.

EXPERIMENTAL

All the chemicals and reagents used were of AR grade or equivalent purity. Spectroscopic grade solvents were used for spectral analysis. The carbon, hydrogen, nitrogen and Chlorine content in each complex were performed at CDRI, Lucknow. The ligand as well as its corresponding metal complexes were analysed by standard methods. Conductivity measurements were carried out with Philips conductivity Bridge Model PR 9500 at room temperature and 10^{-3} M dilution. Magnetic susceptibility was determined by Gouy's balance. Copper sulphate was used as the calibrant.

The IR spectra were recorded in KBr pellets using a Perkin-Elmer 783 spectrophotometer. The UV-íis spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer. Ti(III) was prepared by the standard procedure while the other metals used as such.

Antimicrobial activity

The in vitro biological screening effects of the investigated compounds were tested against the bacteria, *S. aureus, S. typhi, K. pneumoniae, S. flexneri, P. aeruginosa, E. coli* by the well diffusion method using agar nutrient as the medium. The test solutions were prepared by dissolving the compounds in DMSO. In a typical procedure[8], a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using micropipette and the plate was incubated at 35°C for 25 h. During this period, the test solution was diffused and the growth of the inoculated micro organisms was affected. The inhibition zone developed on the plate was measured. Here ampicillin is used as the control.

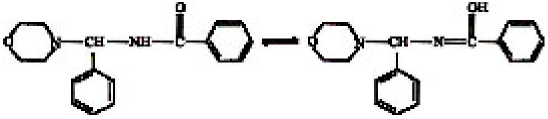
Synthesis of mannich base

Benzamide (1.21 g, 10 mmol) in 20 ml of ethanol was mixed with morpholine (0.9 ml, 10 mmol) with stirring to get a clear solution under ice cold condition. To the contents,benzaldehyde (1 ml, 10 mmol) was added dropwise using dropper with stirring for 15-20 min.The reaction mixture was then kept at room temperature for 5 days. The colourless solid obtained was filtered and recrystallized from ethanol (Yield: 70%; m.p. 85 °C).

The proposed structure of the ligand.

Synthesis of metal complexes

A solution of 5 mmol of metal salts and the Mannich base (10 mmol, 2.92 g) in 40 ml ethanol and chloroform mixture (1:6, v/v) was boiled under reflux at 58°C (b.p. of azeotropic mixture) for 3 h.



The resulting solution was concentrated and then cooled to 0°C for 12 h and the precipitated complexes were filtered, washed with ethanol and dried in vacuo.

RESULTS AND DISCUSSION

The analytical data of the synthesized and the complexes is given in table 1. The data suggested 1:2 (M:L) stiochiometry for all the complexes. The molar conductance values determined at 10^{-3} M dilution and 25°C in both DMF and DMSO suggested 1:1 electrolytic nature for Fe(III), Mn(III), Co(III), Ti(III), V(III), V(IV), MoO(V), and Ru(III)complexes where as Fe(II)and Ru(II) complex were non-electrolytic in nature. The V (IV) complex is 1:2 electrolyte.

IR spectrum of the ligand shows bands at 3380,1600 and 1100 cm^{-1} which have been assigned to ν(NH),amide ν(C=O) and ν(C-N-C) of morpholine group respeítiíely[9].In all the complexes, the υ(N-H) band appeared in the region 3330-3425 cm^{-1}.The amide ν(C=O)and ν(C-N-C) of morpholine bands displayed substantial negative shifts with fairly low intensity indicating coordination through the oxygen of amide moiety and nitrogen of morpholine entity present in the ligand.Some new bands were found around 420-400 cm^{-1} and 540-520 cm^{-1} assignable to the MoO(V) complex showed a band at 855 cm^{-1}assignable to Mo=O moiety. In all complexes the presence of water molecule is indicated by appearance of two non ligand bands in their IR spectra in the range of 3310–3400 cm^{-1} due to υ (OH) group of coordinated water molecule and 840–850 cm^{-1} due to wagging mode [10].

^{1}H NMR spectra of the ligand and its Ti (III) complex were recorded in DMSO-d_6 solution. The spectrum of the ligand shows the signals as follows: a broad absorption around 6.2 δ due to the

NH proton; morpholine N-CH_2 at 2.2 δ and morpholine O-CH_2 at 3.7 ä; the methyline proton appeared in 6.7 δ; the multiplet observed around 7.2 to 8.2 δ is assignable to the phenyl group. In the ligand spectrum, one absorption peak at 10.1 δ was observed which can be assigned to N=C-OH proton. The disappearance of the peaks at 10.1 δ and 6.2 δ in the spectrum of Ti (III) complex indicates that the coordination is taking place via the dissociation of the -OH proton also shifted downfield and appeared at 2.6 δ in the complex. This is an indication of the coordination of morpholine nitrogen.

Magnetic properties and electronic spectra

The magnetic moment of Fe (III) complex is 5.97 B.M., corresponding to five unpaired

Table 1: Analytical data of the complexes [Found %]

Compound/ Complex	Colour	M	C	H	N	Cl	Mol Wt.	$^{\lambda}$M mho cm^2 mol^{-1}	μ_{eff} (B.M.)
[$C_{18}H_{20}O_2N_2$]	Colourless	–	72.80	6.27	9.05	9.05	96.36	-	-
[$(C_{18}H_{20}O_2N_2)_2$Fe.2H_2O]Cl	Brown	7.78	60.04	6.39	7.78	4.93	179.50	1:1	5.97
[$(C_{18}H_{20}O_2N_2)_2$Mn.2H_2O]Cl	Light brown	7.27	60.38	6.43	7.83	4.96	715.50	1:1	4.90
[$(C_{18}H_{20}O_2N_2)_2$Co.2H_2O]Cl	White	8.17	59.79	6.37	7.75	4.91	722.50	1:1	Dima-gnetic
[$(C_{18}H_{20}O_2N_2)_2$Ti.2H_2O]Cl	Yellow	6.75	60.72	6.47	7.87	4.99	711.50	1:1	1.69
[$(C_{18}H_{20}O_2N_2)_2$V.2H_2O]Cl	Light yellow	7.14	60.46	6.44	7.84	4.97	714.50	1:1	2.92
[$(C_{18}H_{20}O_2N_2)_2$V.2H_2O]Cl_2	Yellow	6.80	57.60	6.13	7.47	9.47	750.00	1:2	1.74
[$(C_{18}H_{20}O_2N_2)_2$MoO.H_2O]Cl	Cream	14.75	57.03	6.07	7.39	4.69	757.50	1:1	1.76
[$(C_{18}H_{20}O_2N_2)_2$Ru.2H_2O]Cl	Green	14.65	56.51	6.02	7.33	4.64	764.50	1:1	1.88
[$(C_{18}H_{20}O_2N_2)_2$Ru.2H_2O]	Colourless	13.85	59.26	6.31	7.68	-	729.00	Non-elect-olyte	Dima-gnetic
[$(C_{18}H_{20}O_2N_2)_2$Fe.2H_2O]	Brown	8.19	63.16	6.73	8.19	-	684.00	Non-elect-rolyte	5.01

Table 2: IR spectral data of ligands and their complexes

Compound/Complexes	$\nu_{(NH)}$cm^{-1}	$\nu_{(C=O)}$cm^{-1}	$\nu_{(C-N-C)}$cm^{-1}	$\nu_{(M-O)}$cm^{-1}	$\nu_{(M-N)}$cm^{-1}
[$C_{18}H_{20}O_2N_2$]	3330	1600	1100	–	
[$(C_{18}H_{20}O_2N_2)_2$Fe.2H_2O]Cl	3403	1576	1082	541	422
[$(C_{18}H_{20}O_2N_2)_2$Mn.2H_2O]Cl	3351	1582	1097	522	421
[$(C_{18}H_{20}O_2N_2)_2$Co.2H_2O]Cl	3425	1597	1077	544	403
[$(C_{18}H_{20}O_2N_2)_2$Ti.2H_2O]Cl	3415	1575	1095	539	423
[$(C_{18}H_{20}O_2N_2)_2$V.2H_2O]Cl	3420	1585	1090	545	425
[$(C_{18}H_{20}O_2N_2)_2$V.2H_2O]Cl_2	3375	1599	1089	549	429
[$(C_{18}H_{20}O_2N_2)_2$MoO.H_2O]Cl	3380	1602	1091	550	432
[$(C_{18}H_{20}O_2N_2)_2$Ru.2H_2O]Cl	3350	1569	1099	555	439
[$(C_{18}H_{20}O_2N_2)_2$Ru.2H_2O]	3399	1564	1102	540	424
[$(C_{18}H_{20}O_2N_2)_2$Fe.2H_2O]	3378	1586	1093	542	419

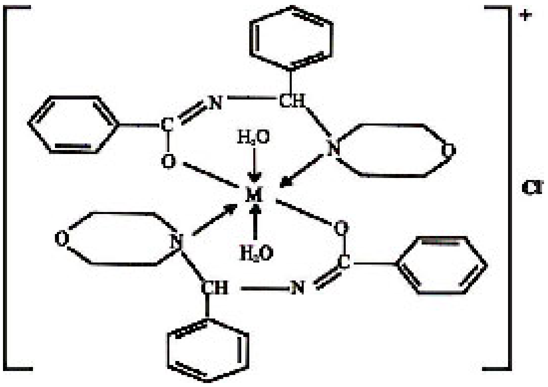
electrons and a high spin state of Fe (III) ion. Three bands at 11235, 21470 and 27780 cm^{-1} corresponding to $^{6}A_{1g}\rightarrow {}^{4}T_{1g}$, $^{6}A_{1g}\rightarrow {}^{4}T_{2g}$ and $^{6}A_{1g}\rightarrow {}^{4}E_{g}$ transition respectively, are observed in Fe (III) complex suggesting an octahedral geometry[11].

Magnetic moment for Mn(III) complex is 4.90 B.M. revealing the high spin nature of the complex, corresponding to four unpaired electrons. Electronic spectra show a strong band at 19680-20000 cm^{-1} which can be assigned due to ligand to metal charge transfer and a shoulder at 18000-180540 cm^{-1} may be assigned to the $^{5}E_{g}\rightarrow {}^{5}T_{2g}$ transition[12, 13].

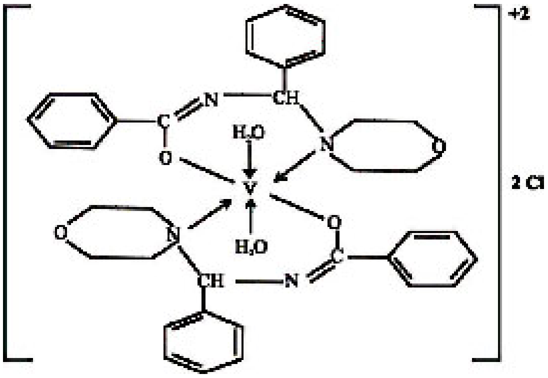
The Co (III) complex is diamagnetic (at 27^{0}C) as expected for a low spin d^{6} ion. The electronic spectra of Co(III) complex display band at 15110-15450,21095-21640 and 23370-23860 cm^{-1} . These are similar to those reported for other six coordinated Co(III) complex[12-15] and may be assigned to $^{1}A_{1g}\rightarrow {}^{3}T_{2g}$, $^{1}A_{1g}\rightarrow {}^{4}T_{1g}$ and $^{1}A_{1g}\rightarrow {}^{1}T_{2g}$ transition respectively.

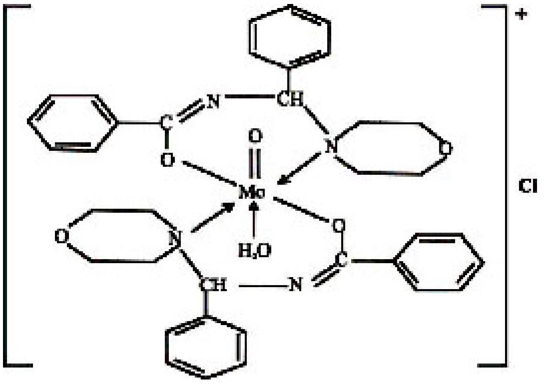
The Ti(III) complex shows magnetic moment of 1.69 B.M. for one unpaired electron. The higher value may be due to the orbital contribution. A single broad band has been observed at 19230 cm^{-1} for Ti(III) complex derived from the transition $^{2}A_{2g}\rightarrow {}^{2}E_{g}$ for an octahedral symmetry[16].

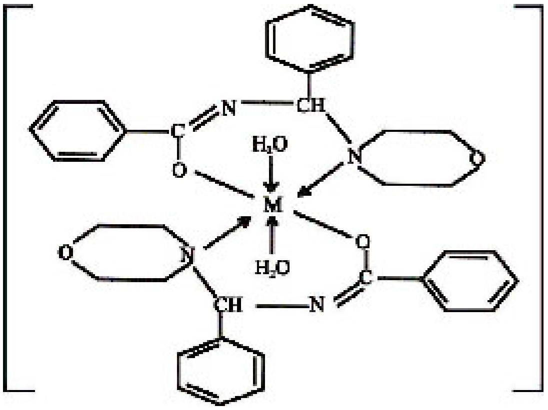
The electronic spectrum of V(III)complex exhibited a band at 16000 cm^{-1} with a shoulder at 20,500 cm^{-1}.The low energy band has been assigned to $T_{1g}\rightarrow {}^{3}T_{2g}$ and the high energy band to $^{2}T_{1g}\rightarrow {}^{3}T_{1g}$ (P) transition respectively. These bands are characterized of octahedral geometry[17].The electronic spectrum of V(IV) complex exhibited a single band at 12820 cm^{-1}.In the absence of finely resolved spectra, it was therefore, not appropriate



Where M= Ti(III), Mn (III)
Fe (III), Ru (III), V(III), CO(III)







Where M = Ru (II) of Fe (II)

to judge the geometry of the complex as regular octahedral[18].

The electronic spectrum of MoO(V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O band[19].The spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13000 cm^{-1} in the long wavelength region, is possibly due to first crystal field transition $^{2}B_{2}\rightarrow{}^{2}E$(dxy, dyz, dxz). The second crystal field transition at 19000 cm^{-1} is assignable to $^{2}B_{2}\rightarrow B_{1}(dxy\rightarrow dx^{2}-y^{2})$.The third peak was observed at 30,000 cm^{-1} assignable to $^{2}B_{2}\rightarrow{}^{2}A_{1}(dxy\text{-}dz^{2})$.

The μ_{eff} for this complex was found to be 1.88 B.M..as expected for an octahedral complex with t^{5}_{2g} configuration. Its electronic spectrum in chloroform displayed band at 17860,21500,27780 and 33900 cm^{-1},which may be assign to $^{2}A_{2g}\rightarrow{}^{4}T_{1g}$ $^{2}A_{2g}\rightarrow{}^{4}T_{2g}$, $^{2}A_{2g}\rightarrow{}^{2}A_{2g}$, $^{2}A_{1g}$ and charge transfer respectively. These are similar to those reported to octahedral Ru (III) complex[20].

The determination of magnetic susceptibility of Ru(II) complex by Gouy's method indicated diamagnetic nature of the complex .The electronic spectrum of the complex showed a single band assignable to CT transition.

The Fe(II) complex shows magnetic moment of 5.01 B.M. and bands at 13200 and 19340 cm^{-1} due to d-d and CT transition respectively.

On the basis of above mentioned evidences octahedral geometry may be suggested for all the complexes with possible distortion in case of MoO(V) complex due to Mo=O moiety.

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