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"Synthesis, Characterisation and Biological Studies of N-(1-Morpholinobenzyl) Benzamide and Its Transition Metal Complexes"

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The Mannich base -N-[1-morpholino 4-methyl benzyl] benzamide was synthesised by reported method and characterised by elemental analyses, I.R. and NMR spectral data. The complexes of the Mannich base with a number of transition metals were prepared and characterised by elemental analyses, molar conductance, magnetic susceptibility, electronic, IR and NMR spectral studies. TGA was also performed in a number of complexes. The biological screening of the Mannich base and few of metal complexes was also carried out.

Keyword: Mannich base, NMR & biological screening.

1. Introduction

Mannich bases have played a vital role in the development of synthetic organic Chemistry. It is well known from the literature that the compounds containing amide moiety as a functional group have been found to possess donor properties and exhibit a wide range of biological activities^[1-6].

Metal Complexes of Mannich bases form an interesting class of compounds, which find extensive applications in various fields^[7-8]. Among the very few number of and variety of transition metal complexes of Mannich bases are of particular interest, because of their synthetic flexibility structure diversities, bonding interaction, biological significance and other multiple applications^[9-11]. Keeping these facts in view this work has been carried out.

2. Experimental

All the reagents and chemicals used were of A.R. grade or equivalent purity 4-methyl. Benzaldehyde, benzamide, morpholine and all the metal salts were procured from the reputed firms, while Titanium (III) Chloride was prepared in the lab by the reported method. Ethanol was purified by double distillation before use, while all other solvents were used as procured.

3. Preparation of the Ligand

The Mannich base was prepared by mixing ethanolic solution of benzamide with morpholine and treated with benzaldehyde in the molar ratio of 1:1:1. The reaction mixture was stirred under ice bath condition. A yellow solid was separated by filtration & washed with distilled water.

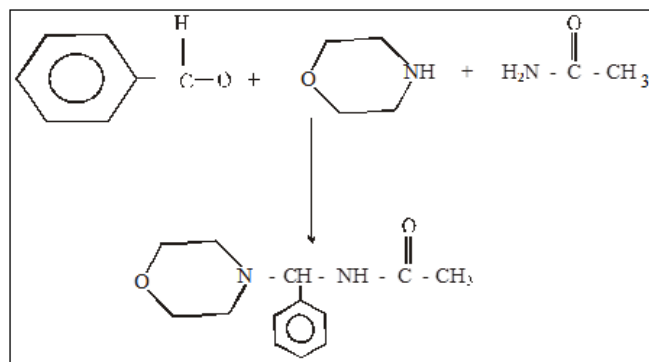


Figure 1

The Mannich base was characterised by the determination of melting point, elemental analyses, IR and NMR spectra.

4. Preparation of the Complexes

The solution of the Mannich base was added to the solution of the respective metal salt. A solid complex

was obtained in each case. It was filtered washed and dried in vacuum dessicator over fused CaCl_2 .

5. Result and Discussion

The complexes are coloured solids except those of MoO_2 (VI), Ru (II) and UO_2 (VI). The elemental analyses of the complexes revealed 1:2 metal ligand ratio. The molar conductance values at 25° and 10^{-3} M dilution, suggested 1:1 electrolytic nature for Ti (III), Mn (III), V (III), Fe (III), Co (III), Ru (III) and MoO (V) complexes while the complexes of Ru (II), MoO_2 (VI) and UO_2 (VI) were non electrolytes.

The measurement of magnetic moment by Gouy's balance suggested paramagnetic nature for Ti (III), V (III), Fe (III), Ru (III) and MoO (V) complexes while the complexes of Ru (II), Co (III), MoO(VI) and UO_2 (VI) were diamagnetic in nature.

6. Electronic spectra & Magnetic Moment

The Ti (III) complex shows magnetic moment of 1.70 B.M. This value is closed to the calculated value for d^1 system (1.73 B.M.) like Ti (III) and show paramagnetic character for the complex. The electronic spectrum of the complex shows a single band at 19600 cm^{-1} , which may be assigned to ${}^2T_{2g} \longrightarrow {}^2E_g$ transition⁹. This is characteristic of Ti (III) octahedral complex.

The magnetic moment of the vanadium (III) complex is 2.94 B.M. which is nearly equal to the calculated value for d^2 system like V (III). The electronic spectrum of V (III) complex exhibited band at 16200 cm^{-1} and shoulder at 20800 cm^{-1} . The low energy band may be assigned to the ${}^3T_{1g}(f) \longrightarrow {}^3T_{2g}(f)$ transition in octahedral symmetry and high energy band to ${}^3T_{1g}(f) \longrightarrow {}^3T_{1g}(p)$ transition¹².

The magnetic moment of Ru (III) complex is 1.94 B.M. The electronic spectrum shows bands at 10330 , 16129 , 24390 and 35087 cm^{-1} may be assigned to the transition ${}^2T_{2g} \longrightarrow {}^4T_{1g}$, ${}^2T_{2g} \longrightarrow {}^4T_{2g}$, ${}^2T_{2g} \longrightarrow {}^2A_{2g}$, ${}^2T_{1g}$ and $\pi \longrightarrow T_{2g}(\pi^*)$ levels respectively¹¹. These are characteristic of an octahedral geometry.

The Ru (II) complex is diamagnetic in nature. The electronic spectrum of the complex in CH_2Cl_2 shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligand in accordance

with the assignments made for other similar octahedral ruthenium (II) complex¹³⁻¹⁴.

The magnetic moment of Mn (III) complex is 4.90 B.M. which is in expected range for d^4 system like Mn (III) and suggested paramagnetic nature for the complex and revealed high spin nature of the complex. It supported octahedral symmetry. Unusually Mn (III) has 5D electronic ground state and in an octahedral symmetry, a single absorption band is expected due to spin allowed transition ${}^5E_g \longrightarrow {}^5T_{2g}$ however even for symmetrical ligand field, they are subject to Jahn-Teller distortion for high spin d^4 configuration¹⁵.

The complex shows two bands assignable to ${}^5B_{1g} \longrightarrow {}^5T_{2g}$ at 18500 cm^{-1} transition and other band at 25000 cm^{-1} may be assigned to Mn $\longrightarrow (d\pi)-\pi^*$ (azomethine¹⁶).

The magnetic moment of Fe (III) complex is 5.97 B.M. corresponding to five unpaired electron and high spin state of Fe(III) ion. Three bands have been observed in the electronic spectrum of the complex at 11235 , 21740 and 27780 cm^{-1} assignable to ${}^6A_{1g} \longrightarrow {}^4T_{1g}$, ${}^6A_{1g} \longrightarrow {}^4T_{2g}$ and ${}^6A_{1g} \longrightarrow {}^4E_g$ transitions respectively suggesting an octahedral geometry¹⁷.

The magnetic study of Co (III) complex indicated diamagnetic nature for the complex, as expected for low spin d^6 ion.

The electronic spectrum shows bands at 15140 , 21110 and 23330 cm^{-1} . These bands have been assigned to ${}^1A_{1g} \longrightarrow {}^3T_{2g}$, ${}^1A_{1g} \longrightarrow {}^1T_{1g}$ and ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ transitions respectively¹⁸.

The magnetic moment of MoO(V) complex is 1.70 B.M. which is very near to calculated value for one unpaired electron. The electronic spectrum shows bands at 14200 , 19610 and 25000 cm^{-1} which have been assigned to ${}^2B_2 \longrightarrow {}^2E$ ($d_{xy} \longrightarrow d_{xz} - d_{yz}$), ${}^2B_2 \longrightarrow {}^2B_1$ ($d_{xy} \longrightarrow d_{x^2} - d_{z^2}$) and ${}^2B_2 \longrightarrow {}^2A_1$ ($d_{xy} - d_{z^2}$) transitions respectively. The complex can be best considered as octahedral with strong tetragonal distortion (C_{4r} symmetry) resulting from Mo=O bond¹⁹.

The electronic spectrum of MoO_2 (VI) & UO_2 (VI) complexes show only charge transfer band.

Table 1: Physical Data of Ligand and its Complexes

Sl No	Molecular Formula of Ligand/Complex	M.P. ^o C	Colour	Elemental analyses				Magnetic Moments in (B.M.)	Molar Conductance	Electrolyte Type
				% of C	% of H	% of N	% of M			
1	C ₁₉ H ₂₂ O ₂ N ₂	138	Yellow	72.82 (72.97)	6.70 (6.75)	9.39 (9.45)	-	-	-	-
2	[Ti(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	181	Deep Yellow	60.79 (60.93)	5.89 (5.92)	7.82 (7.89)	6.70 (6.77)	1.71	65	1:1
3	[V(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	183	Dark Yellow	60.60 (60.67)	5.83 (5.89)	7.83 (7.86)	7.02 (7.16)	2.94	70	1:1
4	[Mn(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	186	Brown	60.28 (60.33)	5.80 (5.86)	7.79 (7.828)	7.60 (7.66)	4.96	70	1:1
5	[Co(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	188	Pink	59.92 (60.00)	5.79 (5.83)	7.71 (7.77)	8.08 (8.19)	Dia magnetic	65	1:1
6	[Fe(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	185	Dark brown	60.19 (60.25)	5.81 (5.85)	7.79 (7.81)	7.80 (7.81)	5.97	65	1:1
7	[Ru(C ₁₉ H ₂₂ O ₂ N ₂) ₂ .2H ₂ O] Cl	205	Green	56.62 (56.69)	5.50 (5.51)	7.30 (7.34)	13.00 (13.25)	1.96	70	1:1
8	[Ru(C ₁₉ H ₁₃ O ₂ N ₂) ₂ .2H ₂ O]	201	Dull White	59.39 (59.42)	5.70 (5.77)	7.70 (7.72)	13.81 (13.89)	Dia magnetic	Non electrolyte	-
9	[MoO(C ₁₉ H ₂₂ O ₂ N ₂) ₂].2H ₂ O] Cl	199	Yellow	57.19 (57.21)	5.51 (5.56)	7.39 (7.41)	12.69 (12.71)	1.78	65	1:1
10	[MoO ₂ (C ₁₉ H ₂₂ O ₂ N ₂) ₂]	200	White	60.00 (60.16)	5.81 (5.84)	7.70 (7.79)	13.30 (13.37)	Dia magnetic	Non-Electrolyte	-
11.	[UO ₂ (C ₁₉ H ₂₂ O ₂ N ₂) ₂]	251	White	50.19 (50.23)	4.84 (4.88)	6.49 (6.51)	27.60 (27.67)	Dia magnetic	Non-Electrolyte	-

Cacl. values are given in brackets.

7. Infra-Red Spectra

The IR spectra of the ligand and its metal complexes were recorded in KBr phase and compared in order to find out the possible coordination sites. The IR spectrum of the ligand showed bands at 3380, 1600 and 1100 cm⁻¹ assignable to ν (N-H), amide ν (C=O) and ν (C-N-C) of morpholine respectively. In the IR spectra of the complexes, the band due of ν (N-H) appeared almost unchanged, excluding the possibility the coordination through this group. The amide ν (C=O) and ν (C-N-C) bands showed substantial negative shifts, indicating coordination through oxygen atom of amide moiety and nitrogen of morpholine entity present in the ligand (8). These coordination sites were further supported by the appearance of non-ligand bands in the for IR region of the complex at 510 and 465 cm⁻¹ assignable to ν M-O and ν M-N vibrations respectively^[20].

The IR spectra of the complexes showed some other non-ligand bands in the region of 3490-3510 cm⁻¹ attributable to ν O-H of water molecule. The coordinated nature of these water molecules is suggested by two other non-ligand bands in the regions of 835-850 cm⁻¹ and 740-750 cm⁻¹ due to wagging and rocking modes. The coordinated nature of water molecules in further supported by

TGA. The loss of water molecules accused in the temperature range of 170-190 °C. In UO₂(VI), bands at 910 and 930 cm⁻¹ indicated linear character of UO₂group. In the case of MoO(V) complex, the bands at 950 cm⁻¹ may be assigned to Mo = O moiety. The bands at 960 and 910 cm⁻¹ in MoO₂ (VI) complex suggested is nature of O=Mo=O moiety.

The NMR spectra of the ligand exhibited an absorption peak at 6.2 δ and 10.1 δ assignable to N-H proton and to N=C-OH proton respectively. The disappearance of these peaks in the complex indicated the coordination via the dissociation of -OH proton of the ligand. The signal due to morpholine ν -CH₂ proton at 2.6 δ also shifted down field, suggesting coordination of morpholine nitrogen.

8. Conclusion

On the basis of studies performed an octahedral geometry has been proposed for all the synthesised complexes, with possible distortion due to Mo=O moiety in the case of MoO(V) complex.

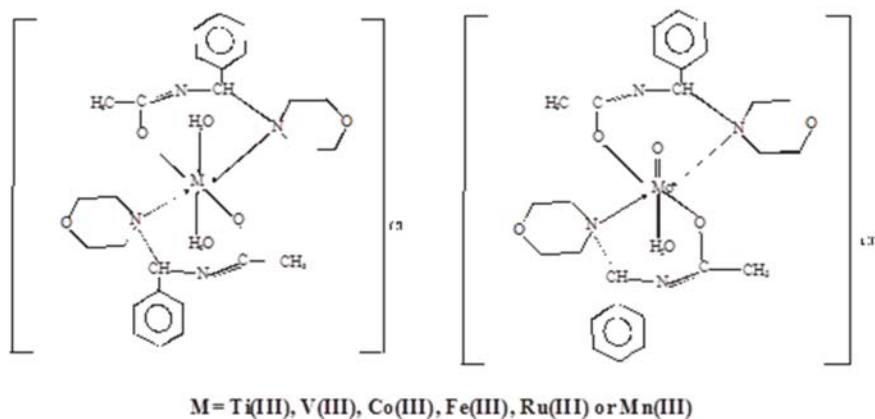


Figure 2

Figure 3

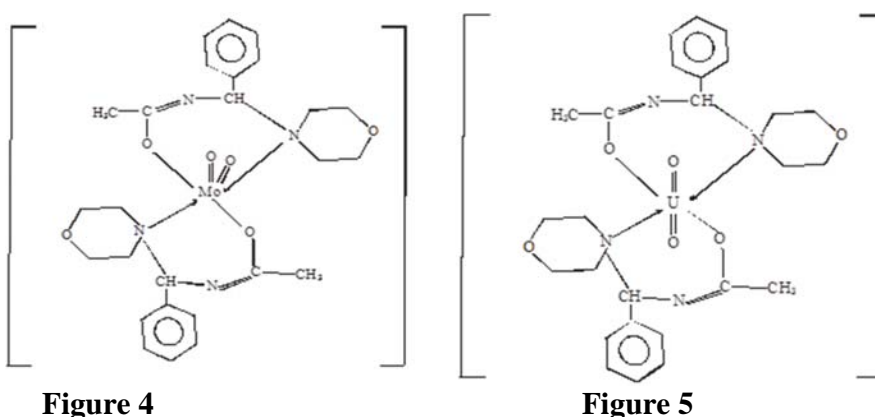


Figure 4

Figure 5

9. Antibacterial Activity

The ligand and few of its metal complexes were tested for antibacterial activity. Muller Hinton agar was used for testing the susceptibility by well diffusion method^[21] using DMSO as solvent,

at a concentration of 0.01 M Gram positive and Gram negative bacteria. The zone of inhibition was determined at the end of incubation period of 24h at 37°C. The metal complexes appeared to be more potent than the ligand (Table-2). Ampicillin was used as standard.

Table 2: Antibacterial Activity of Mannich Base and its complexes

Compound	Inhibition Zone (mm)			
	s.aureus	E. coli	P. aeruginosa	B. subtilis
Mannich Base	15	17	18	16
[Ti L ₂] Cl	18	20	22	21
[V L ₂] Cl	17	19	21	20
[Mn L ₂] Cl	18	21	22	20
[Fe L ₂] Cl	18	20	22	21
[Co L ₂] Cl	18	21	22	20
[Ru L ₂] Cl	19	22	23	21
[Ru L ₂] Cl	18	20	21	20
[MoO(V) L ₂] Cl	18	20	22	20

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