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Synthesis and Characterization of Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) Complexes of 2(α -mercaptoacylhydrazonyl) benzimidazole.

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ABSTRACT

The ligand 2(α -mercaptoacylhydrazonyl) benzimidazole (MAHB) have been synthesized and characterized. Co-ordination complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized by elemental analysis, conductance, thermal, magnetic data, Infrared and electronic spectral data. The ligand MAHB is behaving as a mono basic tridentate NNS donor. The ligand and its metal complexes were tested for anti microbial activity on the gram positive S. Aureus, E. Coli and Proteus.

Keywords: MAHB, Spectral, NNS donor, anti microbial

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INTRODUCTION

The chemistry of benzimidazole and its derivatives reported in the literature is interesting due to their valuable physiological properties such as antiviral, fungicidal, bactericidal. In addition to analytical applications[1,2]. 2-Hydrazino benzimidazole have been proved to be very active against the transition metal ions [3-5]. The mercaptan group has been found to be essential to the activity of number of enzymes in biological systems. As thio substituted Benzimidazoles contain biologically important groups such as Benzimidazole and mercaptan[6]. The aim of the present work is to synthesize and characterize 2(α - mercapto acyl hydrazonyl) benzimidazole and its Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

MATERIALS AND METHOD

All the chemicals used were either of AR or chemically pure grade. IR spectra were recorded using KBr discs in the $4000 \sim 400 \text{ cm}^{-1}$ region on Perkin – Elmer 1600 series. FTIR and in Nujol media in the $1000 \sim 200 \text{ cm}^{-1}$ region on a Perkin – Elmer IR spectrometer model No.17. Electronic spectra was recorded on a shimadzu UV – 160 spectrophotometer. The Elemental analysis was carried out using Heraus –CHN rapid analyzer. Metal contents were estimated using an AAS Perkin Elmer 2380, conductivity measurements were carried on Elico digital conductivity meter model No. CM-180. Magnetic susceptibilities of complexes were measured on a Faraday balance (CAHN-7600) using $\text{Hg}\{\text{Co}(\text{CNS})_4\}$ as calibrant. Diamagnetic corrections using Pascal's constants and temperature independent paramagnetic corrections were computed. EPR was recorded on Jeol SE-3X spectrometer at RT and liquid Nitrogen temperature. DTA data was established by using leeds and Northrup – USA instrument.

PREPARATION OF LIGAND (MAHB)

1.48 gms of 2-Hydrazino benzimidazole was dissolved in 50 ml of n-Butanol. 1.0 ml of thio glycolic acid ester was added to it and refluxed for 2 to 3 hours. The compound separates out on cooling. It was filtered and recrystallized from n-Butanol. Yield : 80% m.p. 205°C ; Anal. calcd for $\text{C}_9\text{H}_{10}\text{N}_4\text{OS}$: C 48.64; H 4.50; N 25.22; S 14.41; Found : C 48.59; H 4.51; N 25.19; S 14.39. $M^+ m/z$ 188. $^1\text{H NMR}$ (CDCl_3) δ 2 & δ 2.1 (- CH_2 -), 5.9 (- NH), IR bands (cm^{-1}), ν : 3203 (ν N-H Free), 3053 (ν N-H Ring), 1639 (ν C=O) 1576 (ν C=N Ring), 2800 (ν S-H), 683 (ν C-S); UV-VIS(cm^{-1}): 39687, 33557, 26737.

PREPARATION OF METAL COMPLEXES

To a methanolic solution (20 ml) of divalent/trivalent metal chloride (0.001 mol) Cr(III) (0.26 g); Mn(II) (0.197 g); Fe(III) (0.162 g); Co(II) (0.238 g); Ni(II) (0.237 g); Cu(II) (0.172 g) and Zn(II) (0.132 g), methanolic solution of MAHB (0.001 mol 0.22 g) was added. The pH of the reaction mixture was adjusted to 7 using 5% methanolic ammonia solution. The mixture was refluxed for 3 – 4 hrs. The complex which precipitated was filtered in hot condition, washed with methanol, petroleum ether and dried in vacuum. The purity of metal complexes was tested by TLC, using different solvent mixtures. Yields 60-70%.

RESULTS AND DISCUSSION

All the metal complexes except Zn(II) are colored and stable to air and moisture. They decompose at high temperatures. They are soluble in DMF and DMSO and insoluble in common organic solvents like methanol, acetone, chloroform etc. Elemental analysis shows that the metal to ligand ratio is 1:1 in Fe(III), Co(II), Ni(II) and Cu(II) complexes and a ratio of 1:2 in Cr(III), Mn(II) and Zn(II) complexes. The data suggests the presence of one chloride per divalent metal ion and two per trivalent metal ion Fe(III). In Cr(III) complex only one chloride is present.

The conductance studies were carried out in 1×10^{-3} M DMF solution. The low molar conductance values of Mn(II), Fe(III) and Zn(II) complexes is in the range $28 - 33 \text{ mho cm}^2 \text{ mol}^{-1}$ at room temperature indicate non-electrolytic nature of these metal complexes. The conductance data shows that Cr(III), Co(II), Ni(II) and Cu(II) complexes are electrolytes. In each metal complex one chloride is present in the outer sphere it is confirmed by analytical and conductance data. These data also indicate that one chloride ion per divalent and two chloride ions per trivalent metal ions are present, therefore indicating that the ligand behaving as a mono basic one. The differential thermal analysis of MAHB Fe(III), Co(II), Ni(II) and Cu(II) shows endotherms in

the range of 100 to 130° C which can be attributed to coordinated water. The thermogram of Cr(III) complex shows endotherm around 80° C which indicate the deaquation of crystal water[7,8].

IR SPECTRA OF MABH COMPLEXES

The number of bands observed in the IR spectra of metal complexes in comparison with those in free ligand suggest the preference of enolic tautomerism in metal binding. The spectra of all the complexes invariably show broad, strong bands in the range of 3200 to 3600 cm^{-1} which can be attributed to νOH of the enolised form and νNH which are not taking part in coordination. In the spectra of Cr(III), and Fe(III) complexes this band is relatively broader and stronger, thus suggesting the overlap of νOH (H_2O) and νOH (of enolic function). Further in place of the band at 1640 cm^{-1} in free ligand assigned to $\nu\text{C}=\text{O}$, the spectra of the complex show strong multiple bands which can be assigned to $\nu\text{C}=\text{N}$ of the enolised form and νNH . The position of these bands is in the range of 1600 to 1620 cm^{-1} . The band assigned to $\nu\text{C}=\text{N}$ (ring) in free ligand spectrum at 1576 cm^{-1} shows a clear downward shift and is present in the range of 1520 to 1550 cm^{-1} [9,10]. Involvement of one of the nitrogens of the substituted hydrazine side chain is further evidenced by the upward shift of $\nu\text{N}-\text{N}$ to the extent of 35 cm^{-1} in all the complexes. The $\nu\text{N}-\text{N}$ appearing at 1044 cm^{-1} in free ligand spectra is located at higher frequency (upto 1080 cm^{-1}) in the spectra of all the complexes[11]. Further the IR spectra of the complexes provide evidence in support of the involvement of SH group in coordination. This is indicated by the downward shift of $\nu(\text{C}-\text{S})$ to the extent of about 75 cm^{-1} [12]. The $\nu(\text{C}-\text{S})$ band observed at 683 cm^{-1} in free ligand has been observed to undergo -ve shift up to 608 cm^{-1} . The spectra do not provide any confirmatory evidence regarding the deprotonation of SH proton as there are broad strong bands due to νOH and νNH due to which the stretching of SH group cannot be pinpointed. However deprotonation of thiolic group is proposed based on the evidence provided by conductivity data. The presence of coordinated water is case of Cr(III) and Fe(III) complexes is concluded by the presence of non ligand bands at 1000 and 880 cm^{-1} which are assigned to rocking modes of water[13] and the bands at 660 to 608 cm^{-1} are assigned to wagging modes of water. This is further supported by DTA studies. In the Far IR spectra the non ligand bands in the range of 560 – 420 cm^{-1} in all the complexes are assigned to $\nu\text{M}-\text{O}$, $\nu\text{M}-\text{N}$ & $\nu\text{M}-\text{S}$ vibrations[14]. In case of Fe(III) non ligand bands at 300 cm^{-1} are assigned to coordinated chloride ions. Based on these observations it may be concluded that the ligand is behaving as a monobasic tridentate system employing the ring azomethine nitrogen and new azomethine nitrogen formed subsequent to enolisation and deprotonated thiolic group.

MAGNETIC DATA OF MABH COMPLEXES:

The magnetic moment of Cr(III) complex is 3.79 B.M., which is an expected value for d^3 system. The magnetic moment value of Mn(II) complex is 5.81 B.M., which is to be expected for d^5 system[15]. The Fe(III) complex has a magnetic moment value of 5.95 B.M., which corresponds to high spin d^5 configuration[16]. In Co(II) and Ni(II) complexes the magnetic moment values are 4.2 and 3.5 B.M., respectively. In Cu(II) complex the magnetic moment value is 2.15 B.M., fit into a distorted square planar geometry.

ELECTRONIC SPECTRA OF MABH COMPLEXES:

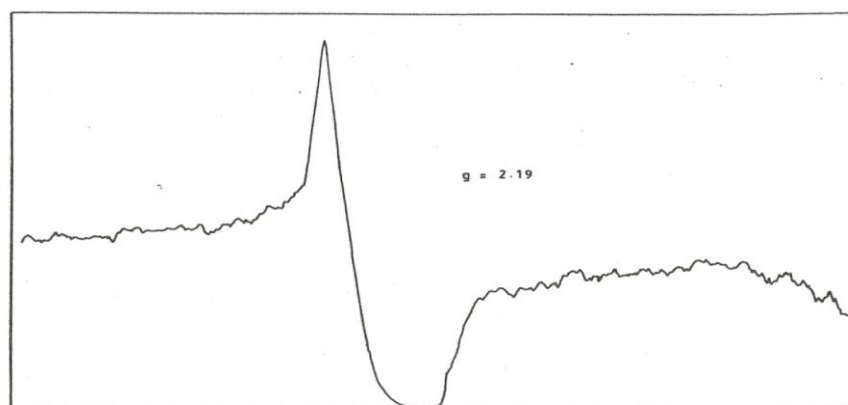
The electronic spectrum of Cr(III) complex exhibit medium intensity bands in the range of 18,018 to 36,231 cm^{-1} , which can be attributed to various d-d transitions that can be assigned for specific transitions corresponding to octahedral geometry. The band located at 18018 cm^{-1} can be assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition. Other two bands observed at 30,864 cm^{-1} and 36,231 cm^{-1} can be assigned ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$, ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ respectively which are characteristic of octahedral geometry[17]. The electronic spectrum of Mn(II) complex shows several weak bands in the range of 10,800 to 29,411 cm^{-1} , which are not of much help in assigning the transitions. Based on the other data octahedral geometry has been proposed. The electronic spectrum of Fe(III) complex exhibits weak absorptions at 21,739 cm^{-1} , 18,181 cm^{-1} and 15,384 cm^{-1} and cannot be assigned to specific transitions. Based on elemental analysis, IR and magnetic data octahedral geometry has been proposed for Fe(III) complex. The electronic spectrum of Co(II) complex shows two bands at 8348 cm^{-1} and 18348 cm^{-1} . These bands are assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transitions respectively. Tetrahedral geometry proposed [18]. The electronic spectrum of Ni(II) complex shows two bands at 11961 cm^{-1} and strong band on high intensity at 18018 cm^{-1} . These bands are assigned to ${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$ and ${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$ transitions respectively. Tetrahedral geometry is proposed. The electronic spectrum of Cu(II) complex shows a broad band in the region 18,181 cm^{-1} to 21,978 cm^{-1} . The position and shape of this band suggest the

merging of three electron transitions namely $2B_1 \rightarrow 2B_2$, $2B_1 \rightarrow 2A_2$ and $2B_1 \rightarrow 2E$ which are in accordance with the square planar geometry[19,20].

ESR SPECTRA OF Cu(II) COMPLEX:

The ESR spectrum of MAHB Cu(II) complex (Fig.1) was recorded at room temperature. DPPH with a g value of 2.0036 was used as the standard. The spectrum apparently consists of a single intense signal. The tendency of the g tensor is exhibiting isotropic behavior. The ESR spectrum which lack the hyperfine structure or anisotropic components, suggests the predominant effect due to exchange interactions among the Cu(II) ions. The g value ($g_{iso} = 2.19$) which is greater than the free electron value ($g_e = 2.0023$) indicates that the electron in the Cu(II) ion is largely delocalized. Hence conclusion drawn from the other experimental techniques is that the ligand environment around Cu(II) is square planar stands unaffected.

Figure 1: ESR spectrum of [Cu(MAHB)(H₂O)Cl]



CONCLUSION

MAHB is behaving as a mono basic tridentate system employing the ring azomethine nitrogen and new azomethine nitrogen formed subsequent to enolisation and deprotonated thiolic group thus providing an NNS sequence. The preference of enolised form in metal binding seems reasonable as the keto form cannot offer efficient chelating system in view of the seven membered ring, which will be formed when ring nitrogen and carbonyl oxygen are involved in bonding. It is justified to conclude that the five membered chelate formed by the enolised system will stabilize the complexes more than the seven membered chelate which can be formed by the keto system. All the complexes are homonuclear. Metal to ligand ratio in Fe(III), Co(II), Ni(II) and Cu(II) complexes is 1:1 and in case of Cr(III), Mn(II) and Zn(II) metal to ligand ratio is 1:2.

Based on analytical, thermal, conductivity, magnetic and spectral data Octahedral geometries have been proposed for Cr(III), Mn(II), Fe(III) and Zn(II) complexes, Tetrahedral geometry for Co(II) and Ni(II) complexes, square planar geometry for Cu(II) complex.

The proposed structures of Cr(III), Co(II), Ni(II) and Cu(II) are given in Fig.2, 3 & 4.

MOLECULAR MODELING

The possible geometries of metal complexes were evaluated using the molecular calculation with Arguslab²¹ software. The geometrical optimization of the structures obtained are present in Fig. 5, 6 & 7.

PHYSIOLOGICAL ACTIVITY

The culture was prepared by the addition of 1.5 g of Beef extract, 1.5 g of yeast extract, 5.0 g of peptone, 1.0 g dextrose, 3.5 g of NaCl, 3.68 g of dipotassium hydrogen phosphate, 1.32 g of mono potassium dihydrogen phosphate and 1.5 g of agar agar is one liter of water. The pH of the medium was adjusted to 7.0. The medium was sterilized at 120 ° C in an autoclave at 15 lbs pressure for 15-20 minutes. The medium was

cooled to 45-50 ° C. 20 ml of medium was poured in each of the Petri dishes. All the apparatus used were sterilized. *E. coli*, *S. aureus* and *Proteus* were introduced into the Petri plates and were grown. Bacteriological testing was done using paper disc method. Paper discs were soaked in the solutions of ligand and complexes in DMF. Solutions were prepared in 100µg/mL, in DMF. Paper discs were soaked in this solution and were dried. The dried paper discs were introduced into the fully grown culture plates of *E. coli*, *S. aureus* and *Proteus*.

The ligand MABH is fully active against *E. coli* and inactive against *Staph. Aureus* and *Proteus*. Except Co(II) complex remaining all complexes Cr(III), Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) are inactive against *E. coli*. Fe(III), Ni(II) and Cu(II) and are fully active against *Staph. aureus*. Cr(III), Mn(II), Co(II) and Zn(II) are inactive against *Staph. aureus*. Though the free ligand is inactive against *Proteus* all the metal complexes from Cr(III) to Zn(II) are active against *Proteus*.

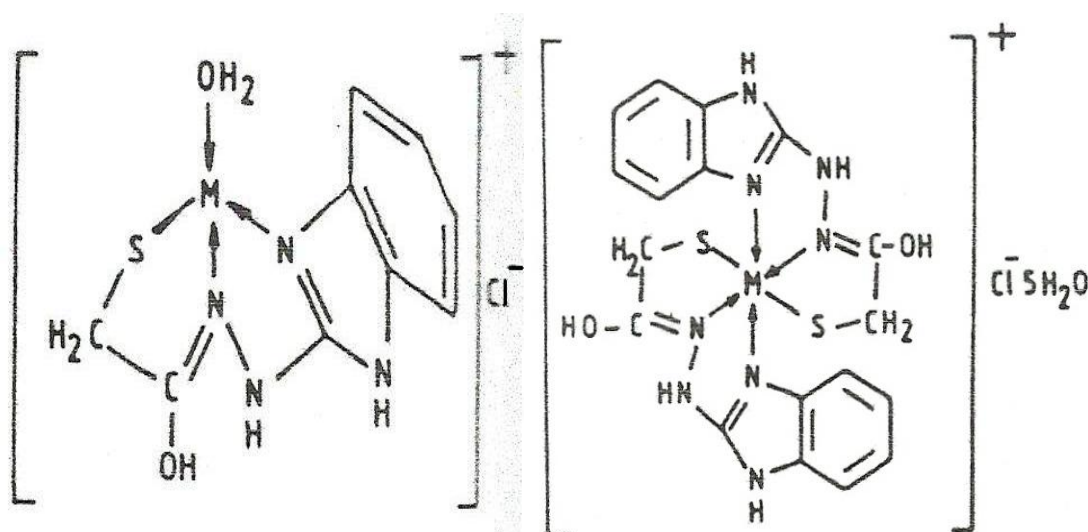


Figure 2: Proposed structure of $[M(MABH)H_2O.Cl]$

Figure 3: Proposed structure of $[M(MABH)_2]Cl.5H_2O$

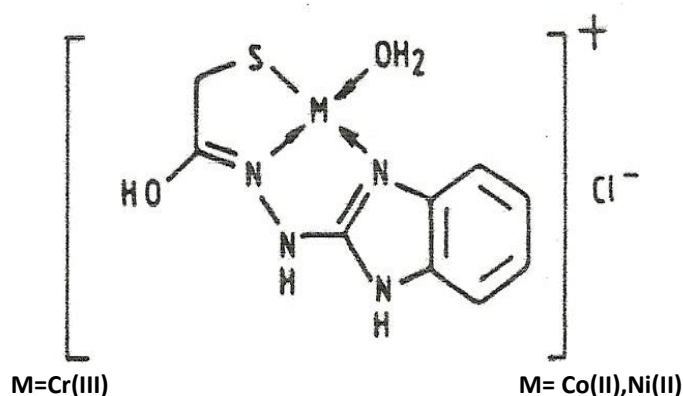


Figure 4: Proposed structure of $[Cu(MABH)H_2O]Cl$

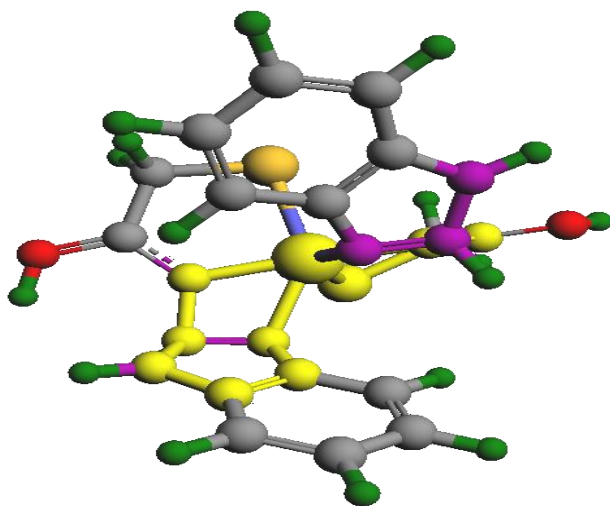


Figure 5: Molecular modeling structure of Mn(II) complex of MAHB (1:2) (81.03 kcal/mol)

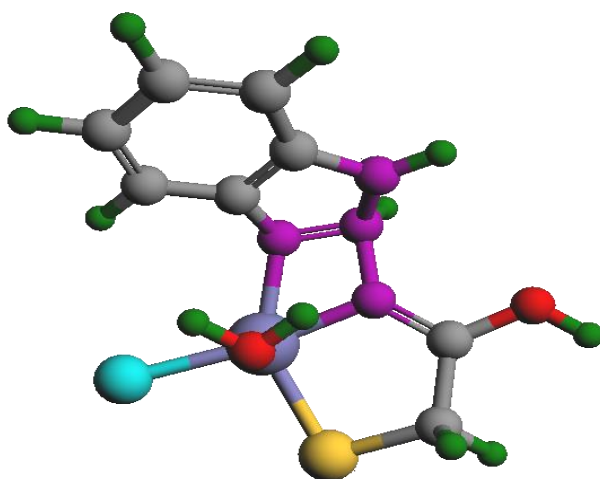


Figure 6: Molecular modeling structure of Fe(III) complex of MAHB (1:1) (52.82 kcal/mol)

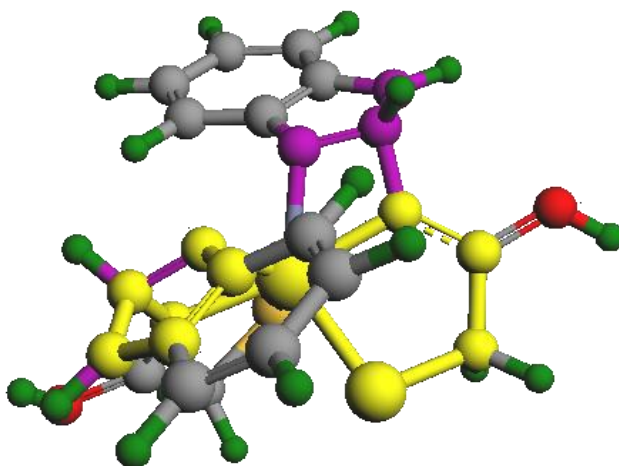


Figure 7: Molecular modeling structure of Zn(II) complex of MAHB (1:2) (72.94 kcal/mol)



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