

Synthesis and structural studies of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of 2-methyl-benzoxazole-5-carboxylic acid (2-hydroxy-benzylidene)-hydrazide [MBCHBH]

Ch. RADHAKRISHNAMURTHY, M. RAVINDER and S. SRIHARI*

Department of Chemistry, Kakatiya University, Warangal - 506 009 (India).

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ABSTRACT

The complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 2-methyl-benzoxazole-5-carboxylic acid (2-hydroxy-benzylidene)-hydrazide [MBCHBH] have been synthesized and structurally characterized on the basis of analytical, conductance, thermal, magnetic and infrared, electronic and esr spectral data. The ligand MBCHBH behaves as a mononegative, tridentate one coordinating through phenolic oxygen, amid group oxygen and azomethine nitrogen.

Key words: Benzoxazole derivative complexes, synthesis, characterization.

INTRODUCTION

The chemistry of benzoxazole and its derivatives reported in the literature is interesting due to their biological importance possessing antimicrobial¹, antiviral², antihistamic³, antiinflammatory⁴ and antitumor⁵ properties. In view of the biological importance of this class of compounds, the authors have considered it worthwhile to make use of them as ligands for the preparation of metal complexes and their structural characterization for the characterization studies would throw light on the bonding nature of the ligands and its possible relationship with properties for which the ligands are known. Therefore, we present, herein, the synthesis and structural characterization of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of 2-methyl-benzoxazole-5-carboxylic acid (2-hydroxy-benzylidene)-hydrazide [MBCHBH] (fig.1).

EXPERIMENTAL

All the chemicals used were of AR or BDH grade. The ligand MBCHBH was prepared by refluxing an equimolar mixture of 2-methyl-benzoxazole-5-carboxylic acid hydrazide and 2-hydroxybenzaldehyde in alcohol (20ml) in presence of a few drops of acetic acid, for about one hour. The orange coloured product thus obtained was filtered, washed with water, dried and purified by recrystallization from methanol.

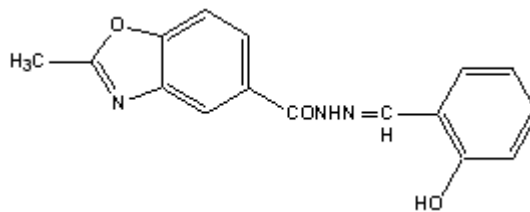


Fig. 1: MBCHBH

The Cr(III), Fe(III) and Hg(II) complexes with the ligand were prepared using respective metal chlorides and Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes using respective metal acetates. In the preparation of all the metal complexes, the metal and the ligand were combined in 1:2 mole ratio (the metal being in slight excess of what the ratio required) using required quantities of methanol or aqueous methanol for the metal salts and methanol for the ligands so as to effect their solubility. The contents were refluxed on a water bath for 2-3 hours and the solid that separated was filtered, washed with water, hot methanol and ether and dried in air.

The elemental analyses of the complexes were carried out by C.D.R.I., Lucknow. Conductance measurements were made in DMF at 10^{-3} M concentration on a Digisun digital conductivity meter, DI 909 model. Gouy balance calibrated with $\text{Hg}[\text{Co}(\text{NCS})_4]$ was used to measure the magnetic susceptibility of metal complexes at

room temperature. The IR spectra of the ligands and the metal complexes in KBr were recorded in the range $4000 - 400 \text{ cm}^{-1}$ using JASCO FT/IR 5300 spectrophotometer. The electronic spectra of the metal complexes were recorded on Shimadzu UV-Vis spectrophotometer UV-160 A and JASCO 7800 UV-Vis spectrophotometer. The Varian E-4 X-band spectrophotometer operating in the frequency range 8.8 – 9.6 GHz available with R.S.I.C., I.I.T. Chennai was employed in recording ESR spectrum of the Cu(II) complex in DMF at LNT.

RESULTS AND DISCUSSION

All the metal complexes (Table 1) are coloured, stable at room temperature and are non-hygroscopic. The metal complexes decompose, upon heating, without melting. The ligand and its metal complexes are insoluble in water, slightly soluble in methanol and acetone and fairly soluble in dimethylformamide.

Table 1: Analytical and physical data of metal complexes

Metal complex	Colour	Metal % Found (Cal)	Molar Cond. $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} B.M.
$[\text{Cr}(\text{MBCHBH} - \text{H})_2]\text{Cl}$	Red yellow	7.49(7.69)	75	3.82
$[\text{Mn}(\text{MBCHBH} - \text{H})_2]$	Dark brown	8.48(8.54)	16	5.73
$[\text{Fe}(\text{MBCHBH} - \text{H})_2]\text{Cl}$	Yellow green	8.01(8.21)	71	5.71
$[\text{Co}(\text{MBCHBH} - \text{H})_2]$	Purple	8.98(9.10)	14	4.82
$[\text{Ni}(\text{MBCHBH} - \text{H})_2]$	Red yellow	8.99(9.07)	15	3.23
$[\text{Cu}(\text{MBCHBH} - \text{H})_2]$	Green	9.68(9.74)	12	1.84
$[\text{Zn}(\text{MBCHBH} - \text{H})\text{OAc}]$	Yellow	15.58(15.62)	12	-
$[\text{Cd}(\text{MBCHBH} - \text{H})\text{OAc}]$	Light yellow	24.01(24.14)	12	-
$[\text{Hg}(\text{MBCHBH} - \text{H})\text{Cl}]$	Yellow	37.78(37.82)	12	-

Table 2: Electronic spectral data of the metal complexes of MBCHBH

Metal complex	Frequency (cm^{-1})	10DQ (cm^{-1})	B (cm^{-1})	β		
Cr- MBCHBH	16480	22850	31950	-	-	
Mn- MBCHBH	13010	19100	25700	-	-	
Fe- MBCHBH	12410	14180	20410	-	-	
Co- MBCHBH	9200(ν_1)	16050(ν_2)	23200(ν_3)	6852	777	0.800
Ni- MBCHBH	9380(ν_1)	14120(ν_2)	14500(ν_3)	9380	692	0.678
Cu- MBCHBH	15610	19960	-	-	-	-

The Cr(III) and Fe(III) Complexes record conductance values in the range $71-75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF indicating that they are 1:1 electrolytes. The Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes are, on the contrary, shown to be non-electrolytic with only residual conductance values.

The magnetic studies made on the complexes indicate that Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are paramagnetic corresponding to three, five, five, three, two and one electrons respectively and that Zn(II), Cd(II) and Hg(II) complexes are diamagnetic.

IR Spectra

The ligand shows, in its spectrum, a medium intensity band at 3230 cm^{-1} assigned to $\nu\text{O-H}$. This band disappears in the spectra of its complexes indicating that deprotonation of the group has taken place. A medium intensity band at 1230 cm^{-1} in the ligand assignable to $\nu\text{C-O}$ is seen to have undergone a positive shift by $30-50 \text{ cm}^{-1}$ in the complexes suggesting coordination through phenolic oxygen⁶. The positive shift observed may be attributed to the drift of electron density from oxygen to the metal ion resulting in greater ionic character of the C-O bond and a consequent increase in its vibration frequency⁷. The ligand records a somewhat broad, medium intensity band at 3430 cm^{-1} attributable to free $\nu\text{N-H}$ ⁸. This band remains unshifted in the spectra of complexes indicating nonparticipation of nitrogen of this group in coordination. The ligand displays a strong absorption band at 1590 cm^{-1} due to $\nu\text{C=O}$ of amide⁹. This band undergoes a lower shift by about 100 cm^{-1} indicating that the oxygen of this group is involved in bonding with the metal ion. A medium intensity band that shows up in the ligand at 1620 cm^{-1} due to $\nu\text{C=N}$ has been found lower shifted by about 20 cm^{-1} in the complexes. The downward shift of this frequency in the complexes suggests involvement of azomethine nitrogen in coordination¹⁰. This suggests that the ligand functions as mononegative, tridentate one coordinating through phenolic oxygen, amide group oxygen and azomethine nitrogen.

The coordination through phenolic oxygen and azomethine nitrogen is further substantiated

by the appearance, in all the complexes, of non-ligand bands in the far infrared region around 500 and 400 cm^{-1} assignable respectively to $\nu\text{M-O}$ and $\nu\text{M-N}$ vibrations^{11, 12}.

Electronic spectra

The electronic spectral frequencies observed for the complexes along with ligand field parameters for the Co(II) and Ni(II) complexes are given in Table 2. These frequencies may be assigned, in the increasing order, to the transitions as detailed below¹³.

Cr(III) complex: ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$

Mn(II) complex: ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$

Fe(III) complex: ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$

Co(II) complex: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$

Ni(II) complex: ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$

Cu(II) complex: ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$

Based on these transitions and the other data observed, octahedral geometry for the Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) complexes and tetragonal geometry for Cu(II) complex have been proposed^{14,15}. Further, the ligand field parameters 10DQ , B and β obtained for the Co(II) and Ni(II) complexes indicate that the metal-ligand bond in them is covalent in nature¹⁶.

ESR Spectra

The spectrum of Cu(II) complex is of anisotropic nature in that it has two peak envelopes, one of small intensity towards low field and other of large intensity towards high field. The small intensity envelope towards low field has been resolved into four peaks due to hyperfine interaction with copper nucleus ($I=3/2$) while the large intensity peak towards high field remains unresolved. The g_{\parallel} and g_{\perp} values of the complex are 2.23 and 2.01. In this complex, it is found that $g_{\parallel} > g_{\perp} > 2$ indicating that the unpaired electron lies in $d_x^2-d_y^2$ orbital with ${}^2\text{B}_{-1g}$ as the ground state¹⁶. The α^2 , β^2 and γ^2 values are 0.58, 0.92 and 0.80 suggesting appreciable/weak/moderate in-plane σ -bonding, in-plane π -bonding and out-of-plane π -bonding respectively¹⁷.

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