



## Synthesis, characterization, and antimicrobial studies on some bivalent metal complexes

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### ABSTRACT

The Metal complexes of iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) with Schiff base derived from 2,5-dihydroxyacetophenone and *s*-benzylthiocarbazate have been synthesized and characterized by elemental analysis, molar conductance, molecular weight, magnetic susceptibility measurements, electronic and infrared spectra. The molar conductivity data show them to be non-electrolytes. The Schiff base behaves as tridentate dibasic ONS donor towards metal ions. Antibacterial activities of the ligand and its complexes have also been screened against various organisms and it is observed that the coordination of metal ions has pronounced effect on the bacterial activity of ligand.

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### INTRODUCTION

The Metal complexes of Schiff bases have played a important role in the development of coordination chemistry and have many applications in various fields. metal complexes have a variety of applications in biology and industry due to their role in catalysis and organic synthesis[1-4].

The Transition metal complexes of Schiff bases have been studied coordination compounds in the past few years, since they are found to be an importance as biochemical, analytical and antimicrobial reagents [5, 6]. Metal complexes of ligands derived from *S*-alkyldithiocarbazic acid have raised considerable interest due to their applications in chemistry and biology as well as in the catalysis of chemical and petrochemical processes [7, 8]. Aside from showing interesting physico-chemical properties, carcinostatic activities have been found for metal complexes of dithiocarbazic acid and the Schiff base derived from its *s*-methyl ester [9]. Hence, it was thought worthwhile to prepare the metal complexes with Schiff base derived from 2,5-dihydroxyacetophenone and *s*-benzylthiocarbazate and characterized by various physico-chemical methods.

### EXPERIMENTAL SECTION

All the chemicals and solvents were of AR grade and used as received. *S*-benzylthiocarbazate and 2,5-dihydroxyacetophenone were prepared by literature methods [10, 11].

#### Synthesis of Schiff base ligand

A hot ethanolic solution (20 ml) of 2,5-dihydroxyacetophenone (50 mmol) was added to a hot solution of *s*-benzylthiocarbazate (50 mmol) in 25 ml ethanol and the reaction mixture was refluxed for 4–5 hr. on a water

bath. A coloured solid mass separated out on cooling was filtered, washed several times with ethanol, diethyl ether and, subsequently, dried over solid  $\text{CaCl}_2$  in a desiccator. The purity of the ligand was checked by TLC. The ligand was insoluble in non-polar solvents, viz. acetone, alcohol and benzene and soluble in polar solvents like DMF and DMSO. Yield: 70%. m.p. 180°C.

### Synthesis of Metal Complexes

A solution of the Schiff base ligand (5 mmol) in the minimum quantity of (~25 ml) of DMF was mixed with an ethanolic solution (~30 ml) of the metal salt (5 mmol) and the mixture was heated under reflux on a sand bath for 3–4 hr. In the case of Fe(II) complex methanol was used in place of ethanol. The coloured products obtained with different metals were filtered, washed with ethanol, methanol and diethyl ether and dried in vacuo over anhydrous  $\text{CaCl}_2$ . The yields of the complexes were in the range of 60–70%.

The carbon, hydrogen, nitrogen and sulphur analyses of ligand and complexes were performed by micro analytical section of RSIC, CDRI, Lucknow. The IR spectra of the complexes and ligand were recorded as KBr pellets using a Perkin–Elmer RX-I 783 spectrometer. Diffuse reflectance spectra of the complexes were recorded on Varian Carry 2390 spectrophotometer using a barium sulphate as standard. Magnetic susceptibility measurements of the complexes were made on a Gouy balance using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant. Molecular weight was determined by the Rast Camphor method. Metal contents were estimated after decomposition of the complexes with concentrated HCl and  $\text{HNO}_3$  as per literature procedure [12]. The antibacterial activities of the compounds were assessed against *S aureus*, *Bacillus*, *E. coli* and *Klebsiella* by cup plate methods [13].

**Table 1. Analytical and Physical data of complexes**

Compound	Colour	Mol. Wt.	Analysis, %					$\Lambda^{\text{M}}$ , $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
			C	H	N	S	M	
$\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}_2\text{O}_2$	Yellow	332	51.13 (52.78)	4.73 (4.81)	8.03 (8.43)	19.01 (19.27)	---	---
$[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}_2)(\text{H}_2\text{O})_3]$	Brownish Red	430.10 (439.84)	42.49 (43.73)	4.10 (4.55)	6.25 (6.37)	14.01 (14.57)	11.89 (12.71)	10.20
$[\text{Co}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}_2)(\text{H}_2\text{O})_2]_2$	Pale Brown	759.00 (849.86)	44.52 (45.22)	3.05 (3.76)	6.12 (6.59)	14.30 (15.07)	12.78 (13.88)	8.40
$[\text{Ni}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}_2)(\text{H}_2\text{O})_3]$	Grey	428.60 (442.71)	42.96 (43.43)	4.15 (4.52)	6.05 (6.33)	13.69 (14.47)	12.85 (13.28)	9.10
$[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}_2)]$	Greenish Yellow	765.40 (787.08)	47.78 (48.79)	3.10 (3.55)	7.00 (7.11)	15.51 (16.26)	15.69 (16.61)	9.45
$[\text{Zn}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O}_2)(\text{H}_2\text{O})]$	Creamy White	405.48 (413.37)	45.28 (46.48)	3.19 (3.87)	6.10 (6.77)	14.85 (15.49)	15.12 (15.82)	11.20

## RESULTS AND DISCUSSION

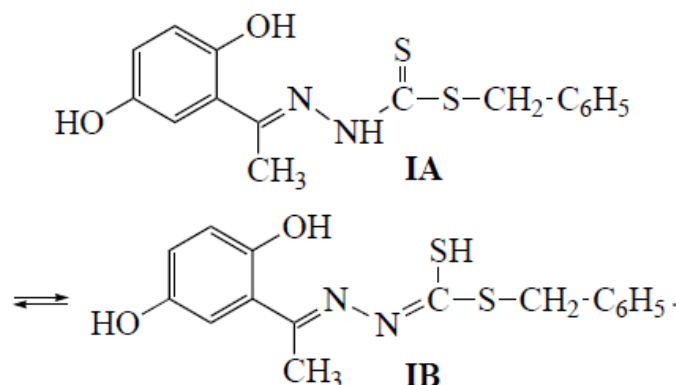
The analytical data (Table 1) indicate that the metal : ligand stoichiometry is 1 : 1 in all the complexes. All the complexes possess high melting point, air stable and soluble in DMF and DMSO. The observed molar conductance of these complexes measured in dimethylformamide solutions are 8.40–11.20  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  and there by indicate their non-electrolyte nature.

The reaction of 2,5-dihydroxyacetophenone with s-benzylthiocarbamate in 1 : 1 molar ratio in ethanolic medium yields the Schiff base (I). The formulation of this Schiff base is confirmed by its IR and  $^1\text{H}$  NMR data. The  $^1\text{H}$  NMR spectrum of the Schiff base in  $\text{DMSO-d}_6$  shows signals at 12.11 and 6.92–7.62 ppm due to OH and phenyl ring protons, respectively. The signals due to NH,  $\text{SCH}_2$  and methyl protons were observed at 11.66, 4.50 and 2.20 ppm, respectively. The presence of NH proton resonance and the absence of -SH proton resonance further support the thionic nature of the free ligand [14].

The schiff base exhibits a strong band at  $1030 \text{cm}^{-1}$  due to the  $\nu(\text{C}=\text{S})$  band which indicates the thione nature of the ligand. This is further supported by the presence of a band at  $3100 \text{cm}^{-1}$  due to  $\nu(\text{NH})$  band of hydriized residue.

The disappearance of both the  $\nu(\text{C}=\text{S})$  and  $\nu(\text{NH})$  bands, in the spectra of complexes suggest the thioenolization of the C=S group Scheme (IB) and coordination of the thiolic sulphur to metal [15]. This is further supported by the appearance of a new band at  $720 \text{cm}^{-1}$  due to the  $\nu(\text{C}=\text{S})$  stretch. A strong band associated with the (C=N)

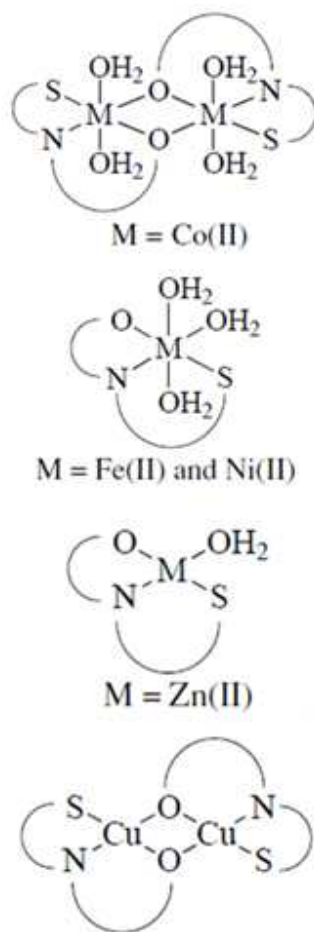
(azomethine) stretch appears at  $1615\text{ cm}^{-1}$  in the free ligand and this band undergoes a bathochromic shift by  $18\text{--}21\text{ cm}^{-1}$  in the complexes, thereby indicating the participation of the azomethine at  $3400\text{ cm}^{-1}$  in the ligand spectrum is assigned to phenolic OH and absence of this band in the spectra of complexes suggest the coordination of the phenolic oxygen atom [16]. This is further supported by the shift of the  $\nu(\text{C-O})$  (phenolic) band from  $1255$  of the ligand to  $1275\text{--}1295\text{ cm}^{-1}$  in the complexes. The ligand band at  $3515\text{ cm}^{-1}$  due to  $\nu(\text{C5-phenolic})$  is remain unchanged in complexes suggesting it's out of coordination. In the far IR region, additional medium bands in the regions  $510\text{--}540$ ,  $430\text{--}480$  and  $380\text{--}395\text{ cm}^{-1}$  are assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  and  $\nu(\text{M-S})$  modes respectively [17].



In the spectra of all complexes (except copper), in addition to the fundamental band observed at  $\sim 3500\text{ cm}^{-1}$ , characteristic bands are observed in the region  $1560\text{--}1590$  and  $754\text{--}781\text{ cm}^{-1}$  indicating the presence of coordinated water [18]. Thus IR spectral data suggest the tridentate dibasic ONS donor nature of ligand. The electronic spectrum of manganese complex exhibits weak absorption bands at  $17200$ ,  $20809$  and  $22025\text{ cm}^{-1}$  due to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ ,  ${}^4\text{A}_{1g}$  transitions, respectively in an octahedral field. The extremely weak intensities of these bands are indicative of their doubly forbidden nature [19]. The electronic spectrum of Fe(II) complex shows bands at  $10820$ ,  $14280$  and  $22220\text{ cm}^{-1}$ . The first two bands may be assigned to  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition, while the latter high-energy broad band may be due to ligand  $n \rightarrow \pi^*$  transition probably mixed with a charge transfer band. Various crystal field parameters  $Dq = 1082\text{ cm}^{-1}$ ,  $B = 584$ ,  $\beta = 0.550$ ,  $C = 2339\text{ cm}^{-1}$  and  $\beta^0 = 45\%$  have been calculated using known equations [16]. The Fe(II) complex exhibits magnetic moment of  $5.20\text{ B.M.}$ , which is consistent with a high spin octahedral geometry. The Co(II) complex shows two  $d-d$  bands at  $8100$  and  $19300\text{ cm}^{-1}$  due to the transitions,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{v } 1)$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) (\text{v } 3)$ , respectively, indicative of an octahedral structure [20]. The electronic spectral parameters have been calculated using the known equation [21] and values are found to be  $Dq = 949\text{ cm}^{-1}$ ,  $B = 634\text{ cm}^{-1}$ ,  $\beta = 0.652$ ,  $\beta^0 = 34.80$ . The reduction of the Racah parameter ( $B$ ) from the free ion value of  $971\text{ cm}^{-1}$  and the  $\beta^0$  indicate the presence of strong covalence in the compound [18]. The room temperature magnetic moment of Co(II) complex is  $4.80\text{ B.M.}$  suggesting a high spin octahedral configuration. The Ni(II) complex exhibits three bands at  $9480$ ,  $15385$  and  $25975\text{ cm}^{-1}$  assignable to transitions  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ , respectively, indicating octahedral geometry. The ligand field parameters for Ni(H) complex are:  $Dq = 948\text{ cm}^{-1}$ ,  $B = 861\text{ cm}^{-1}$ ,  $\beta = 0.82$ ,  $\beta^0 = 18\%$  and  $\lambda = -142$ . The  $\beta^0$  value and the reduction  $B$  from the free ion value of  $1056\text{ cm}^{-1}$  suggest the presence of strong metal-ligand covalent bonding [22]. The Ni(II) complex shows a magnetic moment  $3.00\text{ B.M.}$  that is expected for a six-coordinate Ni(II) complex. The Cu(II) complex shows a series of bands at  $17690$ ,  $18680$ ,  $23881\text{ cm}^{-1}$  due to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ,  ${}^3\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and CT, transitions, respectively expected for square planar Cu(II) complexes [23].

The magnetic moment value of Cu(II) complex is found to be  $1.80\text{ B.M.}$ , which is well within the expected range of square planar complexes. The Zn(II) and Cd(II) complexes were found to be diamagnetic as expected for  $d^{10}$  ions and do not show any  $d-d$  transitions. Although molecular weight measurements of Fe(II) complex was not possible due its insolubility in common organic solvents but such measurements on Mn(II) and Ni(II) complexes indicated their octahedral dimeric structure.

The ligand and its metal complexes were screened for their antimicrobial activity. It is observed that metal complexes have higher activity (zone of inhibition 12-15 mm) than the free ligand (zone of inhibition 9 mm). Such increased activity of the metal complexes can be explained on the basis of overtone concept and chelation theory [24]. The polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of  $\pi$ -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors which also increase the activity are solubility, conductivity and bond length between the metal and ligand [25-28]



**Fig-1**

Based on the above observations of IR, electronic spectral data, elemental analyses, molecular weight determination and magnetic susceptibility measurements we proposed phenoxo-bridged dimeric octahedral structure for the Co(II), monomeric octahedral to Fe(II) and Ni(II), square planar to Cu(II), while tetrahedral structure to Zn(II) complexes, respectively (fig. 1).

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