

Synthesis & Characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) & Zn(II) Complexes of the Schiff Base N-(2-Benzoxazolyl)-N'-(2-oxo-3- indolinyldene)hydrazine

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The complexes of N-(2-benzoxazolyl)-N'-(2-oxo-3-indolinyldene)hydrazine (BIH) with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterised on the basis of their elemental analyses, conductivity, magnetic moment, TG, infrared and electronic spectral data. Metal to ligand ratio in all the chelates has been found to be 1:1. The schiff base behaves as a neutral tridentate in all the chelates, wherein the participation of lactam carbonyl in coordination has been observed. Cu(II), Ni(II), Fe(III) and Zn(II) complexes are suggested to have an octahedral geometry whereas Mn(II) complex has a dimeric octahedral structure with two chlorides as bridging centres. Co(II) complex is assigned a trigonal bipyramidal geometry. These chelates have been screened for fungicidal activity against two fungi, viz. *Curvularia pallescens* and *Fusarium equiseti* and found to be more active than the ligand and the respective metal salts.

Benzoxazole and its derivatives have been found to exhibit physiological activity and are also extensively used as spectrophotometric and gravimetric reagents¹⁻⁶. Literature survey reveals that metal complexes of neutral tridentate schiff bases derived from various O, N heterocyclic systems in general and 2-hydrazinobenzoxazoles, in particular, are very less studied. In this paper we are reporting the synthesis, characterisation and the fungicidal studies of the schiff base N-(2-benzoxazolyl)-N'-(2-oxo-3-indolinyldene)hydrazine (BIH) [derived from 2-hydroxy-3-pseudoindolone (isatin) and 2-hydrazinobenzoxazole] and its Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

All the solvents and reagents used were of AR grade. The conductivity measurements were made on a Digital conductivity meter model D₁ 909 using necessary calibrations. Infrared spectra of the ligand and the metal chelates were recorded on a Perkin-Elmer spectrophotometer model 577 in the range 4000-200 cm⁻¹ in the form of KBr pellets. The electronic spectra were recorded on a UV-visible spectrophotometer DMR-21 in the range 1000-300 nm in nujol mull at room temperature. Magnetic susceptibilities were obtained at room temperature using Faraday

technique. Thermogravimetric analyses were carried out in a manually operated thermobalance.

2-Hydrazinobenzoxazole and the schiff base were prepared by the literature methods⁷⁻⁹. All the complexes except Cu(II) complex were prepared by refluxing ethanolic solutions of metal chlorides (0.01 mol) and the ligand (0.02 mol) for 3-4 hr and subsequently adjusting the pH to about 7. The Cu(II) complex separated out on mixing the alcoholic solutions of copper(II) chloride and the ligand in 1:2 mole ratio.

All the complexes are stable in air and moisture and decompose at high temperatures (Table 1). The complexes are insoluble in water, sparingly soluble in acetone, and highly soluble in DMF, DMSO and dioxan. The low molar conductance values (~2-10 mho cm² mol⁻¹) of the complexes in DMF show that they are non-electrolytic in nature. The elemental analyses (Table 1) indicate metal to ligand ratio as 1:1 for all the metal chelates.

The infrared spectrum of the ligand shows a broad band around 3250-3150 cm⁻¹ assignable to νNH (free) and νNH (ring) involved in hydrogen bonding with lactam carbonyl. A sharp band at 1700 cm⁻¹ is attributed to νC=O (lactam). Further, two strong bands at 1665 and 1640 cm⁻¹ are assigned to free νC=N of azomethine group at position-3 of isatin ring and the ring azomethine of oxazole moiety. A sharp peak at 1030 cm⁻¹ is ascribed to νC-O-C of oxazole ring. The infrared spectra of Mn(II), Fe(III) and Co(II) complexes exhibit sharp peaks at 3375, 3225 and 3400 cm⁻¹ respectively assignable to free νNH. A band around 3175-3125 cm⁻¹ in these complexes is attributed to νNH (ring stretching). The spectra of Ni(II), Cu(II) and Zn(II) complexes exhibit a broad band in the region 3550-3300 cm⁻¹ which is attributed to the presence of coordinated water¹⁰. This is further evidenced by the thermogravimetric analysis which shows mass loss equivalent to one mol of water per mol of complex in the region 150-160°C for Ni(II), Cu(II) and Zn(II) complexes. The presence of sharp bands at 3310 and 3150 cm⁻¹ can be attributed to free νNH in the Cu(II) and Zn(II) complexes indicating its non-involvement in coordination. A downward shift of 20-40 cm⁻¹ in the νC=O (lactam) in all the complexes clearly indicate the participation of oxygen of lactam carbonyl in coordination. A red shift in both the νC=N (free & ring azomethine) suggests the coordination through both the nitrogens. The band observed at 1030 cm⁻¹ due to νC-O-C of oxazole ring was found to be unchanged in all the complexes,

Table 1—Analytical Data of Complexes

Compound	m.p., °C	Found (Calc.), %				
		M*	C	H	N	Cl
BIH (C ₁₅ H ₁₀ N ₄ O ₂)	229	—	65.00 (64.75)	3.62 (3.60)	20.00 (20.14)	—
[Cu C ₁₅ H ₁₂ N ₄ O ₃ Cl ₂]	290(d)	14.50 (14.75)	41.91 (41.81)	2.80 (2.79)	13.21 (13.01)	16.55 (16.49)
[Ni C ₁₅ H ₁₂ N ₄ O ₃ Cl ₂]	250(d)	13.91 (13.79)	42.35 (42.28)	2.91 (2.81)	13.21 (13.15)	16.75 (16.68)
[Co C ₁₅ H ₁₀ N ₄ O ₂ Cl ₂]	310(d)	14.21 (14.44)	44.21 (44.15)	2.51 (2.45)	13.80 (13.75)	17.25 (17.41)
[Mn C ₁₅ H ₁₀ N ₄ O ₂ Cl ₂] ₂	340(d)	13.75 (13.81)	44.55 (44.46)	2.41 (2.47)	13.75 (13.83)	17.60 (17.54)
[Fe C ₁₅ H ₁₀ N ₄ O ₂ Cl ₃]	320(d)	12.75 (12.68)	40.82 (40.88)	2.25 (2.27)	12.75 (12.72)	24.30 (24.19)
[Zn C ₁₅ H ₁₄ N ₄ O ₄ Cl ₂]	340(d)	14.25 (14.52)	40.21 (39.97)	3.00 (3.11)	12.60 (12.43)	15.80 (15.76)

*By atomic absorption spectroscopy.

ruling out the participation of ring oxygen in coordination. New peaks in the regions 630-550, 580-500 and 395-290 cm⁻¹ have been attributed to $\nu\text{M}-\text{O}$, $\nu\text{M}-\text{N}$ and $\nu\text{M}-\text{Cl}$ vibrations respectively¹⁰. In the case of Mn(II) complex, the band observed at 240 cm⁻¹ is assigned to bridging $\nu\text{M}-\text{Cl}$ vibration. Thus, the infrared spectra of the complexes reveal that the ligand is acting as a neutral tridentate with oxygen of lactam carbonyl and nitrogens of the azomethine groups as the coordinating centres.

The Mn(II) BIH complex showed magnetic moment of 4.7 B.M. at room temperature which is low for a high spin complex. This may be due to metal-metal interaction¹¹ associated with dimeric nature of the complex as observed in the Mn(II) complexes of several other tridentate ligands. Further, the dimeric structure is inconsistent with the IR data, wherein the $\nu\text{M}-\text{Cl}$ (bridging) is observed at 240 cm⁻¹. For Fe(III) complex, a magnetic moment of 5.9 B.M. is indicative of a high spin octahedral geometry. The weak bands observed in the electronic spectrum of Mn(II) complex at 14080 and 23500 cm⁻¹ are not of much help in deciding the transitions. Hence, dimeric structure with octahedral geometry for the Mn(II) complex with chloride bridging has been proposed. The electronic spectral bands for Fe(III) complex are observed at 23300 and 28600 cm⁻¹. The weak bands are not of much help in deciding the transitions. The observed magnetic moment value for Co(II) BIH complex is 5.3 B.M. The electronic spectrum of the complex displays three distinct intense bands at 13330, 16400 and 22730 cm⁻¹. The higher value of magnetic moment and relatively rich, electronic spectrum suggests high spin five-coordinate trigonal bipyramidal stereochemistry. The bands observed at 13330, 16400 and 22730 cm⁻¹ are attributed to ${}^4A_2(F) \rightarrow {}^4E'(F)$, ${}^4A_2(F) \rightarrow {}^4A_2'(P)$ and

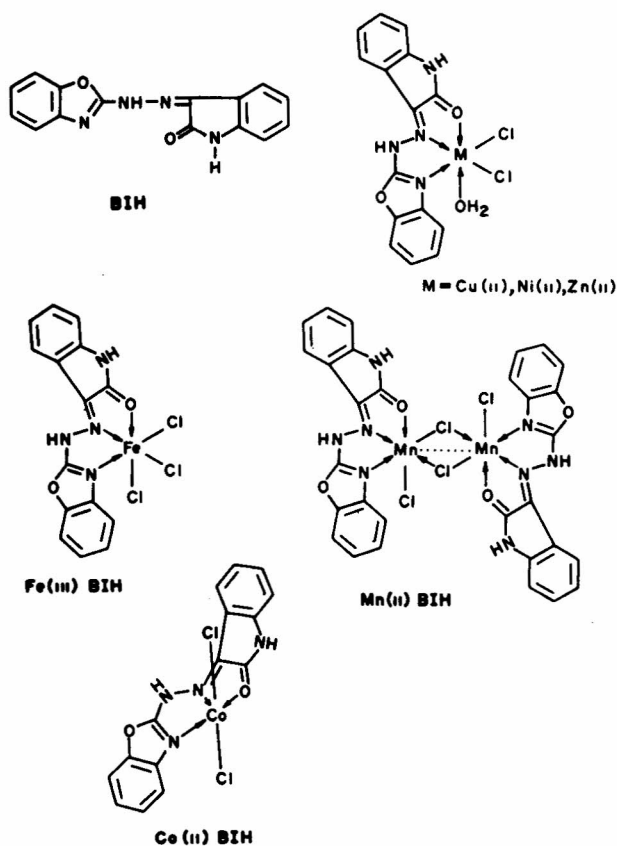
${}^4A_2(F) \rightarrow {}^4E''(P)$ transitions respectively. The electronic spectral band transitions and the magnetic moment values are indicative of a five-coordinated trigonal bipyramidal Co(II) BIH complex¹².

In the electronic spectrum of Ni(II) BIH complex, four bands are observed at 11000, 14700, 16000 and 21050 cm⁻¹. The bands at 21050 and 16000 cm⁻¹ are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions respectively¹³. The weak band at 11000 cm⁻¹ is assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. The band observed at 14700 cm⁻¹ is attributed to the spin-forbidden transition between the triplet and the singlet states i.e. ${}^3A_{2g} \rightarrow {}^1T_{1g}$ transition. These transitions are indicative of octahedral geometry¹⁴. The observed magnetic moment of 3.0 B.M. is in agreement with an octahedral geometry¹⁵.

The observed room temperature magnetic moment of Cu(II) BIH complex is 1.75 B.M. which corresponds to the presence of single unpaired electron. The electronic spectrum of Cu(II)-BIH complex shows a broad band in the region 12500-15400 cm⁻¹ which is attributed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition¹⁶. The position and width of the band indicates distorted octahedral geometry. The other bands at 25000 and 32250 cm⁻¹ are assigned to charge transfer transitions. The proposed structures of the metal chelates are shown in Fig. 1.

Fungicidal activity

These compounds were screened for fungicidal activity against two fungi, viz. *Curvularia pallescens* and *Fusarium equiseti* at 1000 ppm concentration using potato sucrose agar (PSA) medium and the poison food technique^{17,18}. The cultures were inoculated in the centre of test plates and incubated for 96 hr at 31-32°C. After the incubation period, the growth of the



1000 ppm concentration for *Curvularia pallescens* and *Fusarium equiseti*, respectively and the growth inhibiting capacities of the complexes against *C. pallescens* and *F. equiseti* follow the order: Co(II) > Ni(II) > Cu(II) > Fe(III) > BIH > Mn(II) > Zn(II); and Ni(II) > Fe(III) > Mn(II) > Cu(II) > Zn(II) = BIH > Co(II), respectively.

These results show that metallation has an overall effect of enhancing the growth inhibiting capacity against the fungi *Curvularia pallescens* and *Fusarium equiseti* and metal complexes of BIH appear promising in controlling the growth of harmful fungi.

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fungal colony was measured and the percentage inhibition was calculated by Eq. (1)

$$\% \text{ Inhibition} = \frac{100 (C - T)}{C} \quad \dots (1)$$

where C = diameter of the fungal colony in millimeter in the control plates; T = diameter of the fungal colony in the treated plates after 96 hr. The average percentage of growth inhibition is 43 and 21 for the ligand BIH at