

Synthesis, Characterization and Antimicrobial Studies of Mn(II), Fe(III) and Co(II) Complexes of 2-*cis*-3,7-Dimethyl-2,6-Octadiene-1-Semicarbazone

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Complexes of Mn(II), Fe(III) and Co(II) with 2-*cis*-3,7-dimethyl-2,6-octadiene-1-semicarbazone formed by condensation of semicarbazone hydrochloride and 2-*cis*-3,7-dimethyl-2,6-octadiene-1-al have been synthesized and their physico-chemical properties have been investigated by elemental analysis, magnetic measurements, molar conductance, electronic spectroscopy and infrared spectroscopy. The ligand was found to be bidentate chelating agent for the metal ions. All these complexes have been tested *in vitro* for their antimicrobial activity against bacteria *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) and fungi *Candida albicans* and *Aspergillus niger*.

Key Words: Mn(II), Fe(II), Co(II), Complexes, 2-*cis*-3,7-dimethyl-2,6-octadiene-1-semicarbazone.

INTRODUCTION

Hydrazones semicarbazone and their metal complexes have been extensively used in many biological processes¹⁻⁶ such as anti-tubercular^{7,8}, antiinflammatory⁹, anticancerous¹⁰ and pharmacological agents¹¹⁻¹⁴ and many important vital enzymatic metals presents in the cell¹⁵. Many metal complexes of semicarbazone have been known for their pharmacological properties including activity against tuberculosis¹⁶, bacterial¹⁷ and viral function¹⁸. In continuation of our work^{19,20} for the formation of transition metal complexes of 2-*cis*-3,7-dimethyl-2,6-octadiene-1-al, we report here the preparation, characterization and antimicrobial studies of Mn(II), Fe(III) and Co(II) complexes of the 2-*cis*-3,7-dimethyl-2,6-octadiene-1-semicarbazone.

EXPERIMENTAL

Synthesis of Ligand: Ethanolic solution of 2-*cis*-3,7-dimethyl-2,6-octadiene-1-al was added to an aqueous solution of semicarbazide hydrochloride (1 g) and sodium acetate (100 mg). The reaction mixture was stirred and refluxed for about 6 h. The bright yellow crystals separated were washed with water, dried and recrystallized from alcohol and characterized on the basis of analytical and spectral data.

Preparation of metal-complexes: An aqueous solution of the corresponding metal salt, semicarbazide hydrochloride and sodium acetate was refluxed with hot ethanolic solution of 2-cis-3,7-dimethyl-2,6-octadiene-1-al in 1 : 2 molar ratio for about 4 h. The reaction mixture was cooled and ammonium hydroxide was added till ammonical and refluxed again for 1½ h and cooled. The precipitate was filtered, washed with water and alcohol and dried in vacuum over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The physical appearance and analytical data of the various metal-complexes are summarized in Table-1. The metal -omplexes are found to be bright coloured and hence give a broad absorption in the visible region. The molar conductance of the complexes in nitrobenzene is in the range 0.4 to 0.7 ohm⁻¹ mol⁻¹ cm². The very low values indicate that these metal-chelates are non-electrolytes in nitrobenzene and are neutral in nature.

TABLE-1
ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS
OF METAL-CHELATES

CompOUNDS	Colour	% Analysis: Found (Calcd.)				μ_{eff} (B.M.)	Mol. cond. (ohm ⁻¹ mol ⁻¹ cm ²)
		M	C	H	N		
Ligand (C ₁₁ H ₁₉ N ₃ O)	Bright yellow	—	62.20 (63.21)	8.90 (9.14)	19.45 (20.07)	—	—
[MnL ₂ (H ₂ O) ₂]	Brownish yellow	10.15 (10.78)	51.30 (51.85)	7.90 (8.30)	15.85 (16.49)	6.30	0.4
[FeL ₂ Cl] ₂	Reddish brown	10.30 (10.95)	50.10 (51.82)	6.80 (7.51)	16.10 (16.48)	4.50	0.6
[CoL ₂ H ₂ O] ₂	Greenish blue	10.65 (11.47)	50.85 (51.45)	7.90 (8.24)	7.80 (8.18)	4.76	0.7

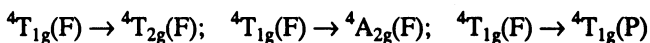
The observed magnetic moment of Fe(III) complex is 4.5 B.M. Low value of magnetic moment indicates a possible contribution from intramolecular anti-ferromagnetic exchange process and a dimeric structure has been suggested for the complex. The observed value of 6.3 B.M. in the case of Mn(II) complex suggests an octahedral geometry. Co(II) complex possesses a magnetic moment value of 4.76 B.M. The observed magnetic moments for the spin free octahedral Co²⁺ (T_{1g}) have excess of spin only value and it may be due to the orbital contribution of both the ground state (⁵T_{2g}²E_g) and the first excited state (⁴T_{2g}³E_g).

Electronic spectra of the ligand are characterized by two bands lying at 37600 and 24000 cm⁻¹ which can be assigned to n → σ* and n → π* transitions respectively. These transitions are observed with high intensity.

The electronic spectrum of Fe(III) complexes shows an intense band at 23146 cm⁻¹ which is due to charge transfer transition. A weak shoulder is located at 30300 cm⁻¹. Since the ground state for Fe(III) high spin complexes is ⁶A₁, all

transitions are expected to be weak and frequently observed by charge transfer bands.

The electronic spectrum of Co(III) complex is characterized by two bands at 95900 cm^{-1} and 22726 cm^{-1} due to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. The expected octahedraal transitions of cobalt are:



The middle band is due to a transition of two electrons, which is forbidden and gives a weak band, and again ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$ are very close in octahedral transition. Due to these factors detection of the middle band is very difficult.

The significant IR spectral bands of the ligand and the complexes along with their probable assignments are given in Table-2.

TABLE-2
SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF 2-*cis*-3,7-DIMETHYL-2,6-OCTADIENE-1-SEMICARBAZONE AND ITS METAL CHELATES

S.No.	Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
1.	Ligand	1635	1680	—	—
2.	Mn(II) chelate	1580	1136	526	419
3.	Fe(III) chelate	1575	1134	524	420
4.	Co(II) chelate	1580	1182	525	416

The ligand exhibits bands of high intensity at about 3480, 3300, 3210 and 3120 cm^{-1} . The group $-\text{NH}-\text{CONH}_2$ accounts for these bands. These may be assigned to the asymmetric $\nu(\text{NH})$ of terminal $-\text{NH}_2$ group and the symmetric $\nu(\text{NH})$ of the NH_2 and two NH groups²¹. It has been suggested that the vibrations of the terminal $-\text{NH}_2$ group are responsible for the two bands at higher frequency region, as they are all present in the spectra of complexes at about the same frequencies or a slight shift to the higher frequency region. Therefore in these semicarbazones the secondary $-\text{NH}$ group would be responsible for the lower frequency bands between 3210 and 3150 cm^{-1} . In the metal complexes, the intensity of these bands is considerably lowered. Moreover, the number of bands in this region decreases, and they become broad. These observations are attributed to the fact that the hydrazine nitrogen atom of $-\text{N}-\text{NH}-\text{CO}-$ participates in coordination. The bands at 1680 cm^{-1} may be assigned to $\nu(\text{C}=\text{O})$ group. This band is not observed in the spectrum of the chelates and a new band appears around 1134 cm^{-1} . This may be due to enolization and subsequent coordination of this carbonyl group in this complex²².

A strong band in the spectrum of the ligand at 1610–1580 cm^{-1} may be assigned to azomethine stretching modes²³. In the metal complexes, this band is shifted to lower frequency region indicating the participation of the azomethine nitrogen atom in coordination. The bands of medium intensity between 1210–1150 cm^{-1} may be due to the deformation and rocking modes of NH_2 . The combination bands due to $\nu(\text{C}-\text{N})$ and $\pi(\text{C}-\text{H})$ appear at approximately 880–830 cm^{-1} in the spectrum of the chelates. A broad feature at approximately

3500 cm^{-1} in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecule. In addition, a strong band at approximately 950–870 cm^{-1} suggests that water molecules are coordinated²⁴. The medium intensity bands at 525–500 and 430–400 cm^{-1} may be assigned to $\nu(\text{M—N})$ and $\nu(\text{M—O})$ respectively²⁵.

Based on the above observations, it has been inferred that the ligand behaves as a univalent bidentate, coordinating through the azemethine nitrogen and enolic oxygen atoms. All these studies suggest octahedral structures for Mn(II), Fe(III) and Co(II) complexes. Based on the available data, a chlorine bridged dimeric structure has been tentatively suggested for Fe(III) complex.

Antimicrobial activity has been carried out against gram +ve bacterium, e.g., *S. aureus* and gram -ve bacterium, e.g., *E. coli*. Antifungal activity is carried out against *A. niger* and *C. albicans*. These complexes exhibit enhanced activity when compared with the biological activity of ligand fragment. The compounds show more biological effect against both the bacterial strains and fungal strains. The MIC values of the complexes have been represented in Table-3.

TABLE-3
MINIMUM INHIBITORY CONCENTRATION (MIC) VALUES IN MOLAR CONCENTRATIONS ($\times 10^{-4}$) OF THE LIGAND AND ITS METAL-CHELATES

S.No.	Compounds	Bacteria		Fungi	
		<i>E. coli</i>	<i>S. aureus</i>	<i>A. Niger</i>	<i>C. albicans</i>
1.	Ligand	0.156	0.165	0.182	0.185
2.	[MnL ₂ (H ₂ O) ₂]	0.174	0.210	0.205	0.286
3.	[FeL ₂ Cl] ₂	0.341	0.338	0.242	0.335
4.	[CoL ₂ (H ₂ O) ₂]	0.320	0.315	0.251	0.321

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