

Research Letter

Antifungal and Spectral Studies of Cr(III) and Mn(II) Complexes Derived from 3, 3'-Thiodipropionic Acid Derivative

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The Cr(III) and Mn(II) complexes with a ligand derived from 3, 3'-thiodipropionic acid have been synthesized and characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR, UV, and EPR spectral studies. The complexes are found to have $[\text{Cr}(\text{L})\text{X}]_2$ and $[\text{Mn}(\text{L})\text{X}]_2$ compositions, where L = quinquedentate ligand and X = NO_3^- , Cl^- and OAc^- . The complexes possess the six coordinated octahedral geometry with monomeric compositions. The evaluated bonding parameters, A_{iso} and β , account for the covalent type metal-ligand bonding. The fungicidal activity of the compounds was evaluated in vitro by employing Food Poison Technique.

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1. Introduction

The synthesis of the coordination compounds of the Schiff's base ligands having N,S-donor binding sites has attracted a considerable attention because of their potential biological activities [1–3]. The main features of these compounds are their preparative accessibility, diversity, structural variability and versatile coordinating properties. These compounds have also been widely investigated to examine the effect of metallation on the antipathogenic activities of such ligand systems. The studies of antipathogenic behavior of these chemically modified species are of paramount importance for designing the metal-based drugs. These compounds have been found to be more effective when they are administered as metal complexes [4–6].

In view of these aspects and our preceding work, we report here the synthesis, spectral, and antifungal studies of Cr(III) and Mn(II) complexes derived from ligand, 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline).

2. Experimental

The ligand 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline) (Figure 1) was

synthesized according to the literature method [7]. The complexes were synthesized by refluxing 1 mmol of the metal salt (nitrate, chloride, and acetate) with 1 mmol of ligand in acetonitrile for 8–14 hours at 70–80°C. The resulting mixture was kept in refrigerator overnight at 0°C. The solid powder was filtered, washed with cold acetonitrile and dried under vacuum over P_4O_{10} .

The fungicidal activity of the compounds was screened in vitro by employing Food Poison Technique [7] against the plant pathogens viz. *Alternaria brassicae*, *Aspergillus niger*, and *Fusarium oxysporum*.

Microanalytical analyses were performed on a Carlo-Erba 1106 analyzer. IR spectra were recorded as KBr pellets in the region 4000–200 cm^{-1} on an FT-IR spectrum BX-II spectrophotometer. The electronic spectra were recorded on Shimadzu UV mini-1240 spectrophotometer using DMSO/DMF as a solvent. EPR spectra were recorded in solid and solution forms on an E4-EPR spectrometer at room temperature and liquid nitrogen temperature operating in X-band region. The molar conductance of complexes was measured in DMSO/DMF at room temperature on an ELICO (CM 82T) conductivity bridge. The magnetic susceptibility was measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as callibrant.

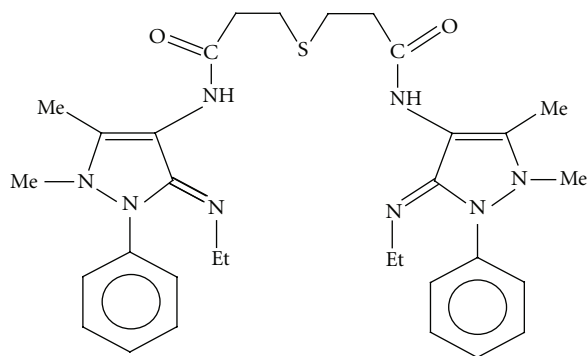
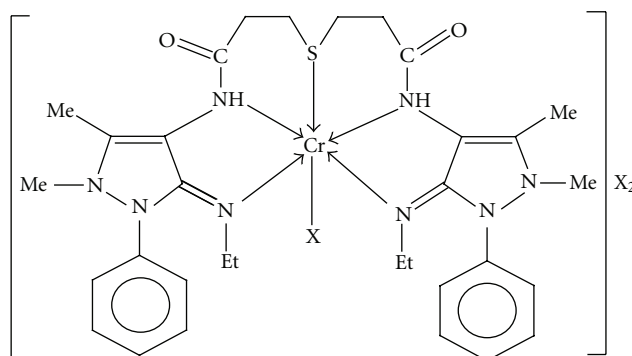


FIGURE 1: Structure of ligand.

FIGURE 2: Structure of $[\text{Cr}(\text{L})\text{X}]\text{X}_2$ complexes, where $\text{X} = \text{NO}_3^-$, Cl^- and OAc^- .

3. Results and Discussion

The microanalytical data, magnetic moments, and other physical properties of complexes are summarized in Table 1. As we reported earlier [7], the ligand coordinates to the metal atom in the NNSNN fashion via five binding sites and forms the stable complexes having $[\text{Cr}(\text{L})\text{X}]\text{X}_2$ and $[\text{Mn}(\text{L})\text{X}]\text{X}_2$ compositions. The molar conductance value accounts for the 1 : 2 and 1 : 1 electrolytic nature of Cr(III) and Mn(II) complexes, respectively, (Table 1) [8]. The magnetic moments of these complexes lie in the range 3.78–3.89 (Cr^{III}) and 5.89–5.98 B.M. (Mn^{II}).

The IR spectrum of the free ligand shows bands at 1647, 1621, 1532, 768 cm^{-1} due to $\nu(\text{C}=\text{O})$ amide I, $\nu(\text{C}=\text{N})$ azomethine, NH in-plane-bending (amide III) vibrations and $\nu(\text{C}-\text{S})$, respectively. On coordination, the position of $\nu(\text{C}=\text{N})$, amide III and $\nu(\text{C}-\text{S})$, bands is altered, which indicates that the nitrogen atoms of C=N and NH groups, and the sulphur atom of the C-S group are coordinated to the central metal atom. Further, the IR spectrum of the ligand also shows a band at 3225 cm^{-1} due to the $\nu(\text{NH})$ stretching vibration. On coordination, this band shows a negative shift, which is in further support of coordination of the NH group through nitrogen. However, the amide I band does not show any considerable change in its position on complexation, which suggests that the C=O group does not participate in coordination [7, 9, 10]. The IR spectra of complexes also give the new bands at 407–497 and 312–328 cm^{-1} due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ stretching vibrations [7, 11]. This discussion reveals that the ligand coordinates to metal atom in the NNSNN manner. The complexes also show the IR bands due to coordinated anions [12].

The electronic spectra of complexes were recorded in DMF/DMSO solution. The electronic spectra of Cr(III) complexes exhibit the absorption bands in the range 13280–19231, 25028–27027, and 36764–37735 cm^{-1} due to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})(\nu_2)$, and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$ spin allowed d-d transitions, respectively. These bands suggest an octahedral geometry for Cr(III) complexes (Figure 2) [13].

The electronic spectra of Mn(II) complexes show the absorption bands in the range 16970–19540, 22280–24390, and 26109–27624 cm^{-1} . These absorption bands may be

assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} ({}^4\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{2g} ({}^4\text{G})$, and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g} ({}^4\text{G})$ transitions, respectively. These bands suggest that the complexes possess an octahedral geometry [13]. The complexes also show the band in the region 34843–38022 cm^{-1} due to a charge transfer transition. Different ligand field parameters have been evaluated for the complexes and the value of covalency factor β (0.43–0.79) reflects the covalent nature of the L \rightarrow M bond. The covalency factor β was evaluated by using the expression $\beta = B_{\text{complex}}/B_{\text{free ion}}$, where B is the Racah interelectronic repulsion parameter. The value of B lies in the range 542–784 and 418–763 cm^{-1} for Cr(III) and Mn(II) complexes, respectively.

The X-band EPR spectra for Cr(III) complexes in solid form show a broad signal at $g_{\text{iso}} = 1.9829\text{--}2.2870$. The signal does not show hyperfine splitting due large line widths. The EPR results of Cr(III) complexes are consistent with the presence of hexacoordinated Cr(III) centers [14].

The EPR spectra for Mn(II) complexes in solid form give broad signal at $g_{\text{iso}} = 1.9763\text{--}2.1351$ both at room temperature and at liquid nitrogen temperature. However, the EPR spectra of complexes in solution (RT and LNT) show the hyperfine splitting and give six lines at $g_{\text{iso}} = 1.9835\text{--}2.5961$ (${}^{55}\text{Mn}$, $I = 5/2$). The hyperfine coupling constant A_{iso} was evaluated and its values (90.0–96.0) are consistent with the complexes having Mn(II) central metal atom in an octahedral field [15].

The results of the antipathogenic activity of compounds are summarized in Table 2. The fungal inhibition capacity of the compounds was compared with the standard fungicide Captan. The data indicate that the complexes possess greater fungicidal activity in comparison to ligand which is due to their higher lipophilicity. This modified fungicidal behaviour of the complexes is based on the Overtone's Concept and Chelation Theory [7].

4. Conclusions

The spectral analysis of the compounds reveals that the ligand acts as quinquedentate chelate and bound to the metal atoms through NNSNN-donor sites. The bonding parameters account for the covalent nature of L \rightarrow M bond. The

TABLE 1: Analytical data, magnetic moments, and physical properties of complexes.

S. No.	Complex	Color	m.p. (°C)	Molar conductance, ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	μ_{eff} (B.M.)	Elemental analyses data (%) calcd. (found)			
						M	C	H	N
1	[Cr(L)NO ₃](NO ₃) ₂ CrC ₃₂ H ₄₂ N ₁₁ SO ₁₁	Greyish green	286	207	3.78	6.19 (6.15)	45.71 (45.74)	5.00 (4.97)	18.33 (18.29)
2	[Cr(L)Cl]Cl ₂ CrC ₃₂ H ₄₂ N ₈ SO ₂ Cl ₃	Greyish green	270	200	3.80	6.84 (6.80)	50.49 (50.44)	5.52 (5.49)	14.73 (14.68)
3	[Cr(L)OAc](OAc) ₂ CrC ₃₈ H ₅₁ N ₈ SO ₈	Dark green	272	219	3.89	6.26 (6.22)	54.87 (54.82)	6.14 (6.11)	13.48 (13.52)
4	[Mn(L)NO ₃]NO ₃ MnC ₃₂ H ₄₂ N ₁₀ SO ₈	Cream	296	116	5.98	7.03 (6.96)	49.17 (49.11)	5.38 (5.31)	17.93 (17.87)
5	[Mn(L)Cl]Cl MnC ₃₂ H ₄₂ N ₈ SO ₂ Cl ₂	Dark Cream	288	120	5.89	7.54 (7.47)	52.75 (52.68)	5.77 (5.71)	15.39 (15.32)
6	[Mn(L)OAc]OAc MnC ₃₆ H ₄₈ N ₈ SO ₆	Cream	298	90	5.91	7.08 (7.02)	55.75 (55.81)	6.19 (6.13)	14.45 (14.39)

TABLE 2: Antifungal activity data of the compounds.

Compound	Fungal inhibition (%) (conc. in $\mu\text{g mL}^{-1}$)								
	<i>A. brassicae</i>			<i>A. niger</i>			<i>F. oxysporum</i>		
	100	200	300	100	200	300	100	200	300
Ligand	40	52	62	35	50	58	42	60	66
[Cr(L)NO ₃](NO ₃) ₂	45	58	67	45	56	64	48	68	72
[Cr(L)Cl]Cl ₂	46	58	66	44	55	63	48	66	74
[Cr(L)OAc](OAc) ₂	45	59	66	45	56	63	46	66	75
[Mn(L)NO ₃]NO ₃	42	56	65	40	54	62	45	62	68
[Mn(L)Cl]Cl	44	55	64	38	52	60	45	62	68
[Mn(L)OAc]OAc	42	55	65	40	54	60	44	63	70
Standard (Captan)	70	80	100	75	90	100	65	75	100

complexes are six coordinated with metal atom surrounded by an octahedral coordinating species. The screening of fungicidal activity of compounds led to the conclusion that complexes possess moderate antipathogenic behavior than the free ligand.

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