

# Synthesis, Characterization and Biocidal Studies of Some Binary and Ternary Metal Complexes of *Cis*-3, 7-dimethyl-2, 6-octadienethiosemicarbazone and L-alanine

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**Abstract** -The mixed ligand complexes of Cr<sup>III</sup>, Mn<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> with *cis*-3,7-dimethyl-2,6-octadienethiosemicarbazone (CDOTSC) and amino acid L-alanine were synthesized and characterized. The free ligand and its metal complexes have been tested in vitro against microorganism in order to assess their metal complexes properties. The analytical data, magnetic susceptibility, and spectral analysis agree well with the proposed composition of formed complexes. The IR spectral data suggest the involvement of sulphur and azomethine nitrogen in coordination to the central metal ion. It may be concluded that the CDOTSC act as neutral bidentate ligand and alanine acts as monoanionic bidentate ligand, coordinating through the carboxylate oxygen and amino nitrogen. The ligand act as a more powerful and potent bactericidal agent, thus killing more of the bacteria than the ligand.

**Keywords** - CDOTSC, amino acid, magnetic susceptibility.

## I. INTRODUCTION

Thiosemicarbazone of *cis*-3,7-dimethyl-2,6-octadienal and their metal complexes present a wide range of application that stretch from their use in analytical chemistry, through pharmacology to nuclear medicine. The presence of amide, imine and thion groups makes them potential polydentate ligand and it is not surprising that numerous thiosemicarbazone complexes have been prepared and characterized. In addition, in the last few years there has been a growing attention towards thiosemicarbazone related to their range of biological properties [1-4], specifically as antifungal, antiviral antibacterial and anticancer agent. The literature contain reviews on many aspect of the chemistry of these interesting compound, such as preparative method, bonding in metal complexes, spectral characteristic and

crystal structure [5-9]. The biological properties of semicarbazone and thiosemicarbazone are often related to metal ions is modified by coordination [10].

In the paper, synthesis and characterization of mixed ligand complex of transition metal with *cis*-3,7-dimethyl-2,6-octadienethio-semicarbazone and amino acid L-alanine are reported. The present paper is the extension of work [11-12].

## II. EXPERIMENTAL

### Physical measurements

The IR spectra were recorded with KBr pellets in the 4002-225 cm<sup>-1</sup> range on a Shimadzu FT-IR 8400/8900 spectrophotometer, <sup>1</sup>H NMR spectra were recorded on a Jeol 300 MHz FT-NMR system and electronic spectra were recorded on a Varian Carry 50 Bio -UV/visible spectrophotometer (Deptt. of Chemistry, University of Rajasthan). Magnetic moments were measured on a Goys balance. Molar conductance was measured in 10<sup>-3</sup>M DMF by conductivity meter model 1601/E. Elemental analysis was performed at the CDRI Lucknow. Molecular weights of these complexes were determined by Rast Camphor Method.

### Antibacterial screening

Antibacterial activity of these compound on selected bacteria *Staphylococcus aureus* gram (+) and *Escherichia coli* gram (-) was carried out using filter paper scarp diffusion method, culture media for growing bacteria consist of peptone, yeast, extract, beef extract, dextrose and agar. pH was maintained *Ca.* 6.5, small (8 mm diameter) circular scraps of filter paper were prepared for the purpose of bacterostatic slices. About 2 mg of

compound (the ligand and their ternary complex) was dissolved in 10 cm<sup>3</sup> DMSO (1%) to make a concentration of 0.2 mg/cm<sup>3</sup>. The solution (0.1 cm<sup>3</sup>) was poured into a small bottle containing 12 paper slices and it was ensured that all the solution was bottled. The bottle was covered with gauze sterilized by moist heat in an autoclave at 100° C using 15 lb in<sup>-2</sup> pressure for 15 minutes. Bacterial strain were inoculated onto the medium plates with absorbent cotton, and three previously prepared, bacteriostatic slices containing the compound were put on the medium plates. All plates were incubated at 35°C in 5% CO<sub>2</sub> for 24 hour and then examined. The average value of bacteriostatic diameter was calculated in mm from four experiments for each compound is given in Table I.

#### Material

All the metal salt was analar grade (BDH) and of merck they were used in the form of chlorides without further purification. Citral were purchased from merck and used without further purification, thiosemicarbazide was purchased from lancaster and recrystallized by hot H<sub>2</sub>O solvent and then were purified.

#### Synthesis of *cis*-3, 7-dimethyl-2, 6-octadienethiosemicarbazone (CDOTSC)

The ligand *cis*-3, 7-dimethyl-2,6-octadienethiosemicarbazone CDOTSC was prepared from the *cis*-3,7-dimethyl-2,6-octadienal and thiosemicarbazide in glacial ethanoic acid [12].

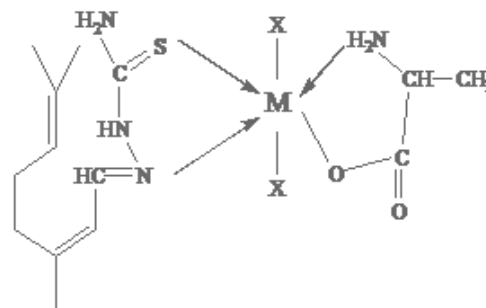
#### Preparation of complexes

All the complexes were prepared in EtOH. The metal complexes were prepared by mixing of a hot EtOH solution of ligand (CDOTSC) (0.02 mol) with an EtOH solution of respective metal chloride (0.02 mol) and L-alanine (0.02 mol). The reaction mixture was boiled under reflux on a water bath, for 6-8 hr, and then allowed to cool at room temperature. The resulting solid was filtered off and washed several times with anhydrous EtOH and dried under reduced pressure. All the complexes were synthesized by the same method.

### III. RESULT AND DISCUSSION

The reaction of metal chloride with CDOTSC and L-alanine in 1:1:1 molar ratio in ethanol results in the

formation of the complex as shown in fig. 1. Analytical and conductivity data of the complexes are presented in Table II.



(M = Mn, Co, Zn, Cd, Hg, X = Cl, H<sub>2</sub>O; M = Cr, Fe X = Cl)

Fig.1: Proposed Structure formula for the complexes

All the metal complexes are non-hygroscopic in nature, stable at room temperature and decompose on heating above 250°C. All the complexes are insoluble in water, slightly soluble in common organic solvent but readily soluble in DMSO and DMF. The molar conductivity data of these complexes are consistent with their non-electrolytic nature in DMF (10<sup>-3</sup>M) solution at RT. The molecular weight measurement data of these complexes reveals their monomeric nature. The IR spectra of various ligand complexes synthesized are compiled in Table III. The IR spectra of these complexes in comparison with free CDOTSC and L-alanine shows characteristic band position, shift, and intensities which can be correlated bidentate CDOTSC binding and bidentate L-alanine chelation beside metal binding through chlorine and water molecules is also evident from IR spectra [14-18]

#### IR spectra

IR spectral band of ligand and its metal complexes are presented in Table II. In principal, the ligand can exhibit thione-thiol tautomerism since it contain a thioamide – NH-C=S functional group. The ν (S-H) band at 2565 cm<sup>-1</sup> is absent in the IR spectrum of ligand but ν (N-H) band at 3237 cm<sup>-1</sup> is present, indicating that in solid state, the ligand remains as the thione tautomer. The position of band of the thiosemicarbazone appeared at 1610 cm<sup>-1</sup> is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen. This is also confirmed by the appearance of band in the range ν (C=N) of 420-480 cm<sup>-1</sup>, this has been assigned to

the  $\nu$  (M-N). The band appearing at  $1134\text{ cm}^{-1}$  ( $\nu$  (C=S)) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to metal ion. Thus it may be concluded that ligand behave bidentate chelating agent coordinating through azomethine nitrogen and thiolate sulphur.

As regarded chelation through L-alanine, the IR spectra shows characteristic band in the region  $3246\text{--}3150\text{ cm}^{-1}$  which are lower as compared to those of free  $\nu$   $\text{NH}_2$ , hence it can be concluded that the nitrogen of the L-alanine group is involved in coordination. The IR spectra show strong evidences in support of the involvement of carboxylate group in coordination. The  $\nu$   $\text{COO}^-$  (asym.) shows positive shift and  $\nu$   $\text{COO}^-$  (sym.) recorded negative shift which confirm the monodentatecity of the carboxylate group.

#### Electronic spectra

Electronic spectra of Cr(III) complexes recorded in DMF and shows band at  $17,980\text{ cm}^{-1}$  owing to the  ${}^4\text{A}_{2g} \rightarrow {}^4\text{E}_g$  and  ${}^4\text{B}_{2g}$  transition respectively the electronic spectra of Mn(II) complex display weak absorption band in region  $18,200\text{ cm}^{-1}$  -  $31,900\text{ cm}^{-1}$  characteristic of octahedral geometry<sup>17</sup>, these band may be assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$  ( ${}^4\text{G}$ )  $\nu_1$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$  ( ${}^4\text{G}$ )  $\nu_2$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$  ( ${}^4\text{D}$ )  $\nu_3$ , and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$  ( ${}^4\text{D}$ )  $\nu_4$  transition respectively. The electronic spectrum of Fe (III) is assigned in the region of  $18940\text{ cm}^{-1}$ ,  $22,520\text{ cm}^{-1}$ . The band at  $18,940\text{ cm}^{-1}$  observed to the and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$  transition for octahedral iron(III) spectra of Co(II) complexes shows bands  $13,870$ ,  $15,160$  and  $20,520\text{ cm}^{-1}$  which are assigned to  ${}^4\text{A}_2$  (F)  $\rightarrow {}^4\text{E}$  (F) and  ${}^4\text{A}_2$  (F)  $\rightarrow {}^4\text{E}$  transition respectively. Zn(II), Cd(II) and Hg(II) complexes being  $d^{10}$  ions are diamagnetic and do not shows d-d transition.

#### ${}^1\text{H NMR}$ spectra

The  ${}^1\text{H NMR}$  spectra of CDOTSC and its zinc, cadmium and mercury diamagnetic complexes are recorded in  $\text{D}_6$ -DMSO. In the spectrum of CDOTSC following signals were observed :  $\delta$  1.7 (s, 3H,  $-\text{CH}_3$ ) 1.9 (s, 6H,  $2\text{CH}_3$ ), 2.24 (m, 4H,  $2\text{CH}_2$ ), 4.8 (t, 1H,  $=\text{CH}$ ), 5.46 (d, 1H,  $=\text{CH}-\text{CH}=\text{N}$ ), 7.8 (d, 1H,  $\text{CH}=\text{N}$ ), 7.82 (s, 1H, NH), 7.21 (s, 2H,  $\text{NH}_2$ ). The  ${}^1\text{H NMR}$  spectra do not show significant differences between ligand and its metal complexes. On

the basis of above analysis the following structure (Fig. 1) may be suggested for the complex.

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Table I

Antibacterial activity data for CDOTSC, L-alanine and their ternary complexes

Compound	Concentration ( $\mu\text{g}/\text{disc}$ )	Average value of bacteriostatic diameter (mm)	
		Gram (+) <i>S. aureus</i>	Gram (-) <i>E. Coli</i>
L-alanine	2	10.0	9.5
CDOTSC	2	11.5	10.0
[Cr (CDOTSC) L-ala.Cl <sub>2</sub> ]	2	14.0	12.2
[Mn (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	2	16.5	15.5
[Fe (CDOTSC) L-ala.Cl <sub>2</sub> ]	2	18.5	17.5
[Co (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	2	18.0	16.5
[Zn (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	2	19.0	17.5
[Cd (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	2	18.5	17.0
[Hg (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	2	20.0	17.2

Table II

Elemental analysis and physical characteristics for CDOTSC and its metal complexes

Compound	Colour	Yield (%)	Found (Calcd.) (%)					Mol. Cond. <sup>a</sup> $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	$\mu$ (B.M.)	M. Wt. found (Calcd.)
			C	H	N	S	M			
CDOTSC	Yellow	89	58.77 (58.63)	8.36 (8.49)	18.60 (18.64)	14.19 (14.23)	-	-	-	219 (225)
[Cr (CDOTSC) L-ala.Cl <sub>2</sub> ]	Dark green	68	38.62 (38.54)	5.71 (5.77)	12.80 (12.84)	7.30 (7.35)	11.84 (11.92)	2.07	3.90	452 (436)
[Mn (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	Redish brown	75	39.82 (39.87)	6.38 (6.45)	13.20 (13.28)	7.55 (7.60)	12.98 (13.02)	1.87	5.87	430 (421)
[Fe (CDOTSC) L-ala.Cl <sub>2</sub> ]	Light brown	73	38.24 (38.20)	5.68 (5.72)	12.65 (12.73)	7.21 (7.28)	12.63 (12.69)	1.94	5.79	432 (440)
[Co (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	Brown	85	39.52 (39.49)	6.42 (6.39)	13.14 (13.16)	7.45 (7.53)	13.80 (13.84)	0.84	3.87	418 (425)
[Zn (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	Pale yellow	78	38.93 (38.90)	6.25 (6.29)	12.91 (12.96)	7.38 (7.42)	15.14 (15.13)	1.25	Diamag.	427 (432)
[Cd (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	Yellow	80	35.12 (35.08)	5.65 (5.68)	11.56 (11.69)	6.64 (6.69)	23.32 (23.45)	1.50	Diamag.	468 (479)
[Hg (CDOTSC) L-ala.Cl.OH <sub>2</sub> ]	Yellow	72	29.68 (29.63)	4.75 (4.79)	9.82 (9.87)	5.63 (5.65)	55.32 (55.35)	1.95	Diamag.	572 (567)

<sup>a</sup>Molar conductance determined at 298 K in 10<sup>-3</sup> M DMF solution.

Table III  
Main IR spectral vibrations for CDOTSC, L-alanine and their metal complexes

Compound	$\nu(\text{NH}_2)$ CDOTSC	$\nu(\text{NH}_2)$ L- alanine	$\nu$ (NH)	$\nu$ ( $\text{COO}^-$ )	$\nu$ (C=S)	$\nu$ (C=N)	$\nu$ (N- N)	$\nu$ (M- N)	$\nu$ (M- S)	$\nu$ (M- Cl)
L-alanine	-	3088 as 2950 s	-	1605 as 1415 s					-	-
CDOTSC	3470 as 3290 s	-	3310	-	1134	1610	955		-	-
[Cr (CDOTSC) L-ala.Cl <sub>2</sub> ]	3350 as 3280 s	3065 as 2956 s	3290	1597 as 1412 s	770 (w) 830 (m)	1603	949	435	345	337
[Mn (CDOTSC) L- ala.Cl.OH <sub>2</sub> ]	3350 as 3285 s	3150 as 2950 s	3305	1625 as 1410 s	765 (w) 735 (m)	1593	945	437	355	350
[Fe (CDOTSC) L-ala.Cl <sub>2</sub> ]	3410 as 3270 s	3175 as 2950 s	3280	1618 as 1403 s	820 (m) 780 (w)	1615	963	425	362	390
[Co (CDOTSC) L- ala.Cl.OH <sub>2</sub> ]	3420 as 3265 s	3232 as 2946 s	3275	1590 as 1410 s	755 (s)	1618	939	430	365	387
[Zn (CDOTSC) L- ala.Cl.OH <sub>2</sub> ]	3455 as 3260 s	3201 as 2952 s	3295	1565 as 1420 s	720 (w)	1587	950	432	362 (m)	393
[Cd (CDOTSC) L- ala.Cl.OH <sub>2</sub> ]	3420 as 3240 s	3193 as 2945 s	3290	1560 as 1409 s	724 (w)	1620	935	480	375 (w)	395
[Hg (CDOTSC) L- ala.Cl.OH <sub>2</sub> ]	3395 as 3262 s	3300 as 2950 s	3325	1600 as 1405 s	768 (s)	1598	940	470	340 (w) 335 (m)	320

as = antisymmetric : s symmetric