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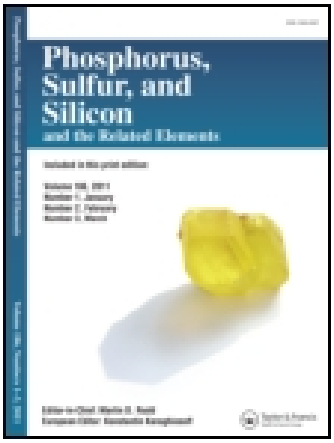

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Synthesis, Spectroscopic Characterization, and Antifungal Activity of Some Mixed Ligand Complexes of Zn(II), Cd(II), and Hg(II)

Renu Sharma [a] & Meena Nagar [a]
[a] Department of Chemistry , University of Rajasthan , Jaipur, India
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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND ANTIFUNGAL ACTIVITY OF SOME MIXED LIGAND COMPLEXES OF Zn(II), Cd(II), AND Hg(II)

Renu Sharma and Meena Nagar
Department of Chemistry, University of Rajasthan, Jaipur, India

A series of new mixed ligand complexes of Zn(II), Cd(II), and Hg(II) with citronellal thiosemicarbazone [3,7-dimethyl-6-octene-1-a1 thiosemicarbazone (LH)] and* N*-phthaloyl amino acids (AH) have been synthesized by the reaction of metal(II) chloride with ligands citronellal thiosemicarbazone (DOTSC) and N-phthaloyl glycine [1,3-dihydro-1,3-dioxo-2H-isoindole-2-acetic acid (A_1H)] or* N*-phthaloyl alanine [1,3-dihydro-1,3-dioxo-α(methyl)-2H-isoindole-2-acetic acid (A_2H)] in 1:1:1 molar ratio in dry refluxing ethanol. All the complexes have been characterized by elemental analyses, molar conductance measurement, molecular weight measurement, IR, and multinuclear NMR (^1H and $^{13}C\{^1H\}$) spectral studies. IR, ^1H, and $^{13}C\{^1H\}$ NMR spectral studies suggest the involvement of azomethine-N, thiol-S atoms of the thiosemicarbazone moiety and both carboxylate-O of* N*-phthaloyl amino acid moiety in coordination with central metal(II) ion, and four coordinated geometries have been assigned to these complexes. The free ligands and metal complexes have been screened for their antifungal activity against two fungal strains, Fusarium moniliformae and Macrophomina phaseolina, using the the radial growth method. The results of antifungal activity show that metal complexes show enhanced higher activity than the free ligands.

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Keywords Antifungal activity; radial growth method; thiosemicarbazone

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INTRODUCTION

The mixed ligand complexes of metal ions have been extensively studied following the recognition that they play an important role in biological processes.[1–3] Mixed ligand complexes with a metal ion bound to two different and biochemically important ligands have aroused interest as models for metalloenzymes-substrate complexes.[4,5] The physiologically interesting mixed ligand complexes of amino acids with heavy metal ions play an important

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Address correspondence to Meena Nagar, Department of Chemistry, University of Rajasthan, Jaipur- 302 004, India. E-mail: nagar_meena@yahoo.com

role in biological systems and have been a subject of great interest for research.[6–10] It has been reported that zinc group metal compounds showed anti–HIV-I activities,[11] and this has provided an impetus for further studies in this field.

N-protected amino acids and thiosemicarbazones are potential organic ligands that have aroused much interest because of their interesting bonding patterns and potential biological applications of their metal complexes.[12,13] The biological activities of thiosemicarbazones ligands have been attributed to their trace metal complexing abilities, and their metal compounds have been generally found to possess enhanced therapeutic properties.[14] As an extension of the work described in our previous communication,[15,16] it was considered relevant to prepare mixed ligand complexes of zinc group metal with these potential organic ligands. The present work has the objectives of seeking more information concerning the nature of bonding and comparative ligating capability of these ligands towards metal (II) ions.

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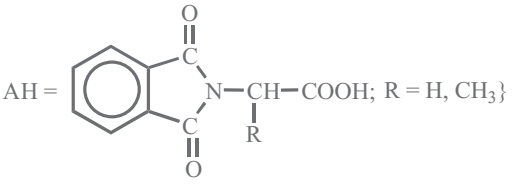
RESULTS AND DICUSSION

A systematic study of the reactions of metal(II) chlorides with ligands DOTSC (LH) and *N*-phthaloyl glycine (A_1H) or *N*-phthaloyl alanine (A_2H) in 1:1:1 molar ratio in anhydrous EtOH in the presence of Et_3N have been carried out. The reactions can be represented by the following equation:

$$MCl_2 + LH + AH + 2\ Et_3N \xrightarrow[\text{Reflux}]{\text{EtOH}} [M(L)(A)] + 2\ Et_3N.HCl$$

{Where M = Zn(II), Cd(II) and Hg(II); LH = Citronellal thiosemicarbazone;



The analytical data of the complexes together with their molar conductance are given in Table I. The data are consistent with the proposed formulae for the complexes. All the complexes are insoluble in water and slightly soluble in common organic solvents but readily soluble in DMSO and DMF. The molecular weight measurement data of these complexes are consistent with their monomeric nature. The molar conductance data suggest the non-electrolytic nature of complexes. All the complexes are stable at room temperature and decompose upon heating at ~300°C.

IR Spectra

A study and comparison of infrared spectra of thiosemicarbazone (DOTSC), *N*-phthaloyl amino acids, and their mixed ligand complexes (Table S2, available online in the Supplemental Materials) imply that both ligands behave as a monobasic bidentate ligand. The ν (C=N) shift of the DOTSC from 1595 cm^{-1} to lower frequency in the spectra of the metal complexes indicates coordination of the azomethine nitrogen atom.[17] The appearance of a new band in the 448–487 cm^{-1} region is assigned to ν (M—N) and

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Table I Analytical data for of mixed ligand complexes of Zn(II), Cd(II), and Hg(II) with citronellal thiosemicarbazone (LH) and *N*-phthaloyl amino acids (AH)

Compound Empirical formula	Color and physical state	Yield (%)	Mp (°C)	% Analysis Found (Calcd.)					Molar Cond.[a] (Ω^{-1} cm^2 mole^{-1})	Mol. Wt. found (Calcd.)
				C	H	N	S	M		
[Zn (DOTSC) (*N*-phthgly)] [$Zn(C_{21}H_{26}N_4O_4S)$]	Yellow sticky solid	78	293[d]	50.72 (50.86)	5.20 (5.28)	11.38 (11.29)	6.52 (6.46)	13.22 (13.19)	1.33	502 (496)
[Zn (DOTSC) (*N*-phthala)] [$Zn(C_{22}H_{28}N_4O_4S)$]	Yellow solid	83	285	51.71 (51.82)	5.45 (5.53)	11.05 (10.98)	6.32 (6.29)	12.79 (12.82)	1.25	504 (510)
[Cd(DOTSC) (*N*-phthgly)] [$Cd(C_{21}H_{26}N_4O_4S)$]	Yellow solid	87	286	46.37 (46.46)	4.89 (4.83)	10.41 (10.32)	5.98 (5.90)	20.62 (20.70)	1.53	535 (543)
[Cd(DOTSC) (*N*-phthala)] $Cd(C_{22}H_{28}N_4O_4S)$]	Yellow solid	83	278	47.32 (47.44)	5.12 (5.07)	10.15 (10.06)	5.68 (5.75)	20.11 (20.18)	1.35	548 (557)
[Hg (DOTSC) (*N*-phthgly)] [$Hg(C_{21}H_{26}N_4O_4S)$]	Yellow sticky solid	82	307[d]	39.85 (39.96)	4.21 (4.15)	8.78 (8.87)	5.14 (5.08)	31.62 (31.78)	1.42	622 (631)
[Hg (DOTSC) (*N*-phthala)] [$Hg(C_{22}H_{28}N_4O_4S)$]	Yellow solid	79	313[d]	40.82 (40.92)	4.23 (4.37)	8.74 (8.68)	5.03 (4.97)	31.02 (31.09)	1.62	657 (645)

d = Dec.

[a]Molar conductance determined at 298 K in 10^{-3} M DMF solution.

supports coordination of nitrogen of azomethine group.[18] The band having considerable ν(C=S) character, shift from 820 cm^{-1} in the uncomplexed DOTSC to 735–752 cm^{-1} from spectra of the complexes, indicates coordination of thione/thiolato sulfur atom.[19] The ν (M−S) band has been assigned in the 342–372 cm^{-1} range and supports coordination of the thione/thiolato sulfur atom.[20] Upon loss of the N(3) hydrogen from the thiosemicarbazone moiety in the complex, an additional carbon–nitrogen double bond, N(3) = C(2), is formed. This new ν (C=N) vibration band is observed in the 1532−1561cm^{-1} region.[18]

In the IR spectra of *N*-phthaloyl amino acids, the imido $\nu CO_{(sym)} + \nu COO_{(asym)}$ and $\nu COO_{(sym)}$ vibrations are observed at 1700–1715 cm^{-1} and 1395–1400 cm^{-1}, respectively. The broad band appearing around ∼1700 cm^{-1} due to $\nu CO_{(sym)} + \nu COO_{(asym)}$ in ligands is splits into two after complexation.[21] The sharp band at 1702–1708 cm^{-1} and a medium intensity band at 1578–1595 cm^{-1} may be due to $\nu CO_{(sym)}$ and $\nu COO_{(asym)}$ vibrations, respectively. The lower shift of the order of 140–168 cm^{-1} in the $\nu COO_{(asym)}$ frequency [$\Delta\nu = \nu COO_{(asym)}$—$\nu COO_{(sym)}$] upon complexation indicates chelating nature of the carboxylate group of *N*-phthaloyl amino acids.[22] The band appearing in the region 413–439 cm^{-1} may be due to M−O vibrations.

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^{1}H NMR Spectra

The ^{1}H NMR spectra of the [M(L)(A)] type complexes have been recorded in $CDCl_3$ and DMSO-d_6 (Table II). The ^{1}H NMR spectra display the expected signals of different type of protons presented in the complexes, but a comparison of the spectra of the ligand with those of the complexes can lead to the following conclusions:

(i) The free ligand DOTSC exhibits a signal at δ 10.59 ppm due to N(3) proton. The absence of this signal in the spectra of the complexes suggests that the proton has been lost via thioenolization and coordination of sulfur atom.

(ii) The aldehyde hydrogen (CH=N) shifts downfield from δ 7.45 ppm in the ligand DOTSC to δ 7.52–7.81 ppm in the spectra of complexes, consistent with the formation of a coordination band between the azomethine nitrogen and metal ion.[15]

(iii) The free *N*-phthaloyl glycine (A_1H) exhibits a signal at δ 4.51 ppm due to $\overset{+}{N}H$, *N*-phthaloyl alanine (A_2H) exhibits singlet at δ 9.26 ppm due to carboxylate proton (COOH), and the absence of these signals in the spectra of complexes suggests the deprotonation of COOH group of *N*-phthaloyl amino acids and coordination of COO group to metal ion.

^{13}C NMR Spectra

The ^{13}C NMR spectra of ligands DOTSC (LH), *N*-phthaloyl amino acids (AH), and their Zn(II), Cd(II), and Hg(II) complexes were recorded in $CDCl_3$ and DMSO-d_6 (Table III). The ^{13}C resonance signals have been assigned according to chemical shift theory. A considerable upfield shift (∼2–3 ppm) takes place in the position of −C−S (177.7 ppm, DOTSC) and C=N (148.0 ppm, DOTSC), indicating coordination through the azomethine nitrogen and the thiol group.[15,23]

The ^{13}C NMR spectra of the complexes show a downfield shift of ∼4 ppm in the position of carboxylic carbon signal as compared to its position in the parent *N*-phthaloyl amino acid, revealing bidentate nature of COO group of the ligand.[15,24]

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Table II ^{1}H NMR spectral data (δ ppm) of mixed ligand complexes of Zn(II), Cd(II), and Hg(II) with citronellal thiosemicarbazone (LH) and *N*-phthaloyl amino acids (AH)

Compound	LH moiety	AH moiety
[Zn (DOTSC)(*N*-phthgly)]	0.92 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.12–1.37 (m, 2H, CH_2 in C-4); 1.40–1.51 (m, 1H, **CH**CH_3); 1.61 & 1.67 (2s, 6H, (**CH$_3$**)$_2$C=CH); 1.80–1.97 (m, 2H, CH_2 in C-5); 2.02–2.31 (m, 2H, CH_2 in C-2); 5.08 (t, 1H, **CH**=C $(CH_3)_2$); 7.21 & 7.26 (2s, 2H, NH_2); 7.52 (t, 1H, CH=N)	4.39 (s, 2H, NCH_2); 7.72–7.93 (m, 4H, C_6H_4)
[Zn (DOTSC)(*N*-phthala)]	0.95 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.17–1.34 (m, 2H, CH_2 in C-4); 1.36–1.41 (m, 1H, **CH**CH_3); 1.59 & 1.68 (2s, 6H, 3H, (**CH$_3$**)$_2$C=CH); 1.70–2.28 (2m, 4H, 2CH_2 in C-2 & C-5); 5.09 (t, 1H, **CH**=C$(CH_3)_2$); 7.23 & 7.26 (2 br s, 2H, NH_2); 7.62 (t, 1H, $J = 5.8$, CH=N)	1.72 (d, 3H, $J = 7.2$, CH_3); 5.05 (q, 1H, NCH); 7.80 (m, 4H, C_6H_4)
[Cd(DOTSC)(*N*-phthgly)]	0.93 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.14 & 1.35 (2m, 2H, CH_2 in C-4); 1.38–1.51 (m, 1H, **CH**CH_3); 1.60 & 1.68 (2s, 6H, (**CH$_3$**)$_2$C=CH); 1.81–2.01 & 2.05–2.33 (2m, 4H, CH_2 in C-2 & C-5); 5.10 (t, 1H, **CH**=C$(CH_3)_2$; 7.23 & 7.26 (2 br s, 2H, NH_2); 7.61 (t, 1H, $J = 5.8$, CH=N)	4.34 (s, 2H, NCH_2); 7.67–7.87 (m, 4H, C_6H_5)
[Cd(DOTSC)(*N*-phthala)]	0.95 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.12 & 1.27 (2m, 2H, CH_2 in C-4); 1.32–1.45 (m, 1H, **CH**CH_3); 1.59 & 1.67 (2s, 6H, (**CH$_3$**)$_2$C=CH); 2.03 & 2.35 (2m, 4H, CH_2 in C-2 & C-5); 5.07 (t, 1H, **CH**=C$(CH_3)_2$); 7.21 & 7.23 (2br s, 2H, NH_2); 7.79 (t, 1H, $J = 5.8$, CH=N)	1.78 (d, 3H, $J = 7.2$, CH_3); 5.10 (q, 1H, NCH); 7.87 (m, 4H, C_6H_4)
[Hg(DOTSC)(*N*-phthgly)]	0.94 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.17 & 1.36 (2m, 2H, CH_2 in C-4); 1.40–1.43 (m, **CH**CH_3); 1.60 & 1.68 (2s, 6H, (**CH$_3$**)$_2$C=CH); 2.12 & 2.28 (2m, 4H, CH_2 in C-2 & C-5); 5.08 (t, 1H, **CH**=C$(CH_3)_2$); 7.20 & 7.26 (2 br s, 2H, NH_2); 7.72 (t, 1H, $J = 5.8$, CH=N)	4.40 (s, NCH_2); 7.76–8.01 (m, 4H, C_6H_4)
[Hg(DOTSC)(*N*-phthala)]	0.92 (d, 3H, $J = 6.6$, CH**CH$_3$**); 1.14 & 1.35 (2m, 2H, CH_2 in C-4); 1.38–1.45 (m, 1H, **CH**CH_3); 1.57 & 1.66 (2s, 6H, (**CH$_3$**)$_2$C=CH); 2.14 & 2.31 (2m, 4H, CH_2 in C-2 & C-5); 5.10 (t, 1H, **CH**=C$(CH_3)_2$); 7.21 & 7.28 (2 br s, 2H, NH_2); 7.81 (t, 1H, $J = 5.8$, CH=N)	1.71 (d, 3H, $J = 7.2$, CH_3); 4.92 (q, NCH); 7.85 (m, 4H, C_6H_4)

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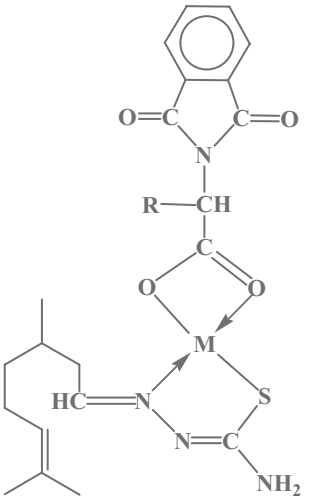
Table III ^{13}C NMR spectral data (δ ppm) of mixed ligand complexes of Zn(II), Cd(II), and Hg(II) with citronellal thiosemicarbazone (LH) and *N*-phthaloyl amino acids (AH)

Compound	LH moiety	AH moiety
[Zn (DOTSC)(*N*-phthgly)]	17.6 (C-9); 19.4 (C-10); 25.2 (C-5); 25.7 (C-8); 30.6 (C-3); 36.7 (C-4); 40.5 (C-2); 124.1 (C-6); 131.4 (C-7); 146.1 (C-1); 173.9 (CS)	40.1 (CH_2); 123.4, 131.8 & 133.9 (C_o, C_i & C_m of C_6H_4); 167.2 (CO); 176.9 (COO)
[Zn (DOTSC)(*N*-phthala)]	17.6 (C-9); 19.3 (C-10); 25.8 (C-5); 25.9 (C-8); 30.6 (C-3); 36.8 (C-4); 40.2 (C-2); 123.9 (C-6); 131.2 (C-7); 145.9 (C-1); 174.5 (CS)	14.7 (CH_3); 47.3 (NCH); 123.2, 131.0 & 133.5 (C_o, C_i & C_m of C_6H_4); 167.2 (CO); 176.9 (COO)
[Cd(DOTSC)(*N*-phthgly)]	17.4 (C-9); 19.3 (C-10); 25.4 (C-5); 25.7 (C-8); 30.8 (C-3); 36.8 (C-4); 40.2 (C-2); 124.2 (C-6); 131.6 (C-7); 145.9 (C-1); 174.2 (CS)	40.4 (CH_2); 122.9, 131.8 & 134.1 (C_o, C_i & C_m of C_6H_4); 167.3 (CO); 174.2 (COO)
[Cd(DOTSC)(*N*-phthala)]	17.6 (C-9); 19.4 (C-10); 25.3 (C-5); 26.1 (C-8); 30.7 (C-3); 36.6(C-4); 39.9 (C-2); 123.6 (C-6); 131.4 (C-7); 146.1 (C-1); 174.3 (CS)	14.6 (CH_3); 47.4 (NCH); 122.9, 131.1 & 133.6 (C_o, C_i & C_m of C_6H_4); 167.4 (CO); 176.9 (COO)
[Hg (DOTSC)(*N*-phthgly)]	17.6 (C-9); 19.4 (C-10); 25.6 (C-5); 25.8 (C-8); 31.1 (C-3); 36.4 (C-4); 40.5 (C-2); 123.9 (C-6); 131.8 (C-7); 146.2 (C-1); 173.9 (CS)	40.5 (CH_2); 122.4, 132.0 & 133.9 (C_o, C_i & C_m of C_6H_4); 167.0 (CO); 174.4 (COO)
[Hg (DOTSC)(*N*-phthala)]	17.3 (C-9); 19.6 (C-10); 25.4 (C-5); 26.1 (C-8); 31.2 (C-3); 36.1 (C-4); 40.2 (C-2); 124.1 (C-6); 131.4 (C-7); 145.9 (C-1); 174.1 (CS)	14.4 (CH_3); 47.2 (NCH); 123.0, 131.4 & 134.2 (C_o, C_i & C_m of C_6H_4); 167.2 (CO); 176.3 (COO)



(where M = Zn(II), Cd(II) and Hg(II); R=H, CH_3)

Figure 1 Proposed structure formula for the complexes [M(L)(A)].

On the basis of above spectral data, the four-coordinated geometry has been suggested for these complexes (Figure 1).

Antifungal Activity

The antifungal activity results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition versus control (Supplemental Materials, Table S1).

CONCLUSION

The mixed ligand metal(II) complexes isolated during the present study demonstrated that the interaction of metal(II) chloride with citronellal thiosemicarbazone and *N*-phthaloyl amino acids leads to complexes with 1:1:1 stoichiometry, and they are found to be mononuclear. The bidentate nature of both type of ligands have been suggested on the basis of spectral evidences. All the complexes showed enhanced antifungal activity over the parent ligands.

EXPERIMENTAL

All the reactants and solvents used were of analytical grade. Triethylamine was distilled over KOH pellets. Solvents were dried by conventional methods and distilled prior to use. Elemental analyses were carried out on Elemental Vario EL III Carlo Erba 1108 analyzer. The IR spectra were recorded with KBr pellets in the 4000–200 cm^{-1} range on a Shimadzu FT-IR 8400 spectrometer. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were collected in $CDCl_3$ and DMSO-d_6 solution using TMS as internal standard on a JEOL FX 300 FT-NMR spectrometer at 300.40 and 75.45 MHz frequencies for ^{1}H and $^{13}C\{^{1}H\}$ NMR,

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respectively. Sulfur was estimated gravimetrically as $BaSO_4$, and metal contents were determined gravimetrically by a procedure in the literature[25] after digesting the organic matter with aquaregia and then with concentrated sulfuric acid and evaporating the residue to dryness. The ligands DOTSC[16] and *N*-phthaloyl amino acids[26] used were synthesized by reported methods. Molar conductances were measured in 10^{-3}M DMF solution on a conductivity meter model 1601/E. Molecular weights of these complexes were determined by cryoscopic method by using Backmann's thermometer. Melting points of solids were determined in sealed capillaries, and the decomposition temperatures of sticky solids were determined on a melting point block.

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Synthesis of Ligands

Synthesis of citronellal thiosemicarbazone (LH). Thiosemicarbazide (2.55 g, 28 mmol) was dissolved in 5% aqueous glacial acetic acid (50 mL) on a boiling water bath. The solution was slowly added, with stirring, to a freshly prepared ethanolic solution (50 mL) of 3,7-dimethyl-6-octenal (5 mL, 28 mmol). The reaction mixture was refluxed on a water bath for 2 h and then kept in ice for overnight. The resulting white solid was filtered, recrystallized from water (25 mL)/ethanol (25L) mixture, and dried over P_2O_5. Yield: 90% (5.72 g); mp 58°C; IR (cm^{-1}): 3408s, 3265s, br (NH_2); 3162s, ν(NH); 1595s, ν(C=N); 928w, δ(C=S); 820m, ν(CS); ^{1}H NMR ($CDCl_3$, δ ppm, J in Hz): 0.98 (d, 3H, J = 6.6, CH**C**$\mathbf{H_3}$); 1.19–1.26 & 1.32–1.34 (2m, 2H, CH_2 in C-4, H_α + H_β); 1.37–1.39 (m, 1H, **C**HCH_3); 1.60 &1.68 (2s, 6H, ($\mathbf{CH_3}$)$_2$C=CH); 1.74–1.80 (m, 1H, CH_2 in C-2, H_β); 1.94–2.12 (m, 2H, CH_2 in C-5); 2.18–2.28 (m, 1H, CH_2 in C-2, H_α); 5.10 (t, 1H, **C**H=C$(CH_3)_2$); 6.92 & 7.12 (2br s, 2H, NH_2); 7.45 (t, 1H, J = 5.8, CH=N); 10.59 (s, 1H, NHC=S); ^{13}C NMR ($CDCl_3$, δ ppm): 17.6 (C-9); 19.5 (C-10); 25.2 (C-5); 25.6 (C-8); 30.6 (C-3); 36.6 (C-4); 40.3 (C-2); 124.2 (C-6); 131.2 (C-7); 148.0 (C-1); 177.7 (C=S); Anal. Found for $C_{11}H_{21}N_3S$ (227.37): C, 57.95; H, 9.25; N, 18.61; S, 14.21. Calcd. C, 58.11; H, 9.31; N, 18.48; S, 14.10%.

Synthesis of N-phthaloyl amino acids (AH). An intimate mixture of finely ground phthalic anhydride (60 mmol) and respective amino acids (60 mmol, viz., DL-glycine or L-alanine) was heated for 30 min with stirring in an oil bath at 140–160°C. After cooling, the solid material was dissolved in hot MeOH (40 mL), the filtered solution was diluted with water (40 mL), and the product was allowed to crystallize slowly, The reaction yields colorless needle shape crystals of *N*-phthaloyl amino acid.

N-Phthaloyl glycine ($\mathbf{A_1H}$). Yield: 85% (10.46 g); mp 191–192°C; IR (cm^{-1}): 3163, ν(NH); 1750s, $\nu(CO)_{asym}$; 1700br, $\nu(CO)_{sym}+\nu(COO)_{asym}$; 1400w, $\nu(COO)_{sym}$; ^{1}H NMR ($CDCl_3$, δ ppm, J in Hz): 4.49 (s, 2H, NCH_2); 4.51 (s, 1H, N^+H); 7.76–7.82(dd, 2H, J_1 = 5.4 Hz, J_2 = 3.0 Hz, Ar-H); 7.85–7.91(dd, 2H, J_1 = 5.4 Hz, J_2 = 3.0 Hz, Ar-H); ^{13}C NMR ($CDCl_3$, δ ppm): 40.3 (CH_2); 125.2, 134.2, 136.0 (C_o, C_i & C_m of C_6H_4); 167.2 (CO); 170.3 (COO); Anal. Found for $C_{10}H_7NO_4$ (205.17): C, 58.61; H, 3.46; N, 6.80. Calcd. C, 58.55; H, 3.44; N, 6.83%.

N-Phthaloyl alanine ($\mathbf{A_2H}$). Yield: 79% (10.38 g); mp 161–162°C; IR (cm^{-1}): 3424br, ν(OH); 1744s,$\nu(CO)_{asym}$; 1715br, $\nu(CO)_{sym}+\nu(COO)_{asym}$; 1395 w, $\nu(COO)_{sym}$; ^{1}H NMR ($CDCl_3$, δ ppm, J in Hz): 1.74 (d, 3H, J = 7.2, CH_3); 5.08 (q, 1H, NCH) 7.85 (m, 4H, C_6H_4); 9.26 (s, 1H, COO**H**); ^{13}C NMR ($CDCl_3$, δ ppm): 14.9 (CH_3); 47.1 (CH); 123.5, 131.5, 133.1 (C_o, C_i & C_m of C_6H_4); 167.2 (**C**O); 174.7 (**C**OO); Anal. Found for $C_{11}H_9NO_4$ (219.19): C, 60.30; H, 4.17; N, 6.34. Calcd. C, 60.28; H, 4.14; N, 6.39%.

Synthesis of Complexes

3,7-Dimethyl-6-octene-1-al thiosemicarbazone (DOTSC) (1.48 g, 6.5 mmol) was mixed with a solution of $CdCl_2$ (1.19 g, 6.5 mmol) in anhydrous ethanol (~40 mL), followed by addition of 1,3-dihydro-1,3-dioxo-2H-isoindole-2-acetic acid (*N*-phthgly) (1.33 g, 6.5 mmol). After shaking the reaction mixture, triethylamine (1.8 mL, 13 mmol) was added dropwise with constant stirring and refluxed for ~8 h. The precipitate was filtered and washed several times with hot ethanol and diethyl ether and dried under reduced pressure to give a yellow colored solid (yield 82%, 2.87 g).

All other complexes of this series have been synthesized using a similar method.

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