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## Phosphorus, Sulfur, and Silicon and the Related Elements

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

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## SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND ANTIFUNGAL ACTIVITY OF SOME MIXED LIGAND COMPLEXES OF Zn(II), Cd(II), AND Hg(II)

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*A series of new mixed ligand complexes of Zn(II), Cd(II), and Hg(II) with citronellal thiosemicarbazone [3,7-dimethyl-6-octene-1- $\alpha$ 1 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- $\alpha$ (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 radial growth method. The results of antifungal activity show that metal complexes show enhanced higher activity than the free ligands.*

*Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements to view the free supplemental file.*

**Keywords** Antifungal activity; radial growth method; thiosemicarbazone

## INTRODUCTION

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

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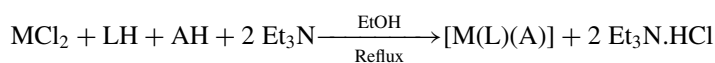
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role in biological systems and have been a subject of great interest for research.<sup>6–10</sup> It has been reported that zinc group metal compounds showed anti-HIV-I activities,<sup>11</sup> and this has provided an impetus for further studies in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

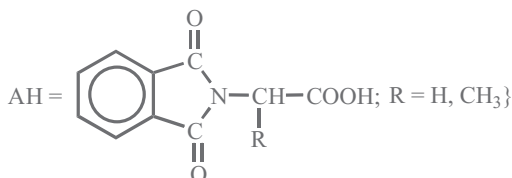
N-protected amino acids and thiosemicarbazones are potential organic ligands that have aroused much interest because of their interesting bonding patterns and potential biological applications of their metal complexes.<sup>12,13</sup> The biological activities of thiosemicarbazones ligands have been attributed to their trace metal complexing abilities, and their metal compounds have been generally found to possess enhanced therapeutic properties.<sup>14</sup> As an extension of the work described in our previous communication,<sup>15,16</sup> 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.

## RESULTS AND DISCUSSION

A systematic study of the reactions of metal(II) chlorides with ligands DOTSC (LH) and *N*-phthaloyl glycine (A<sub>1</sub>H) or *N*-phthaloyl alanine (A<sub>2</sub>H) in 1:1:1 molar ratio in anhydrous EtOH in the presence of Et<sub>3</sub>N have been carried out. The reactions can be represented by the following equation:



{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  $\sim 300^\circ\text{C}$ .

## 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  $\nu(\text{C}=\text{N})$  shift of the DOTSC from  $1595 \text{ cm}^{-1}$  to lower frequency in the spectra of the metal complexes indicates coordination of the azomethine nitrogen atom.<sup>17</sup> The appearance of a new band in the  $448\text{--}487 \text{ cm}^{-1}$  region is assigned to  $\nu(\text{M}-\text{N})$  and

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

Compound Empirical formula	Color and physical state	Yield (%)	Mp (°C)	% Analysis Found (Calcd.)				Molar Cond. <sup>a</sup> (Ω <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> )	Mol. Wt. found (Calcd.)	
				C	H	N	S			
[Zn (DOTSC) ( <i>N</i> -phthgly)] [Zn(C <sub>21</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S)]	Yellow sticky solid	78	293 <sup>d</sup>	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) ( <i>N</i> -phthala)] [Zn(C <sub>22</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> S)]	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) ( <i>N</i> -phthgly)] [Cd(C <sub>21</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S)]	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) ( <i>N</i> -phthala)] Cd(C <sub>22</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> S)]	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) ( <i>N</i> -phthgly)] [Hg(C <sub>21</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S)]	Yellow sticky solid	82	307 <sup>d</sup>	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) ( <i>N</i> -phthala)] [Hg(C <sub>22</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> S)]	Yellow solid	79	313 <sup>d</sup>	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.

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

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

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

### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the  $[\text{M}(\text{L})(\text{A})]$  type complexes have been recorded in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  (Table II). The <sup>1</sup>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  $\delta$  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 ( $\text{CH}=\text{N}$ ) shifts downfield from  $\delta$  7.45 ppm in the ligand DOTSC to  $\delta$  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.<sup>15</sup>
- (iii) The free *N*-phthaloyl glycine ( $\text{A}_1\text{H}$ ) exhibits a signal at  $\delta$  4.51 ppm due to  $\text{NH}^+$ , *N*-phthaloyl alanine ( $\text{A}_2\text{H}$ ) exhibits singlet at  $\delta$  9.26 ppm due to carboxylate proton ( $\text{COOH}$ ), and the absence of these signals in the spectra of complexes suggests the deprotonation of  $\text{COOH}$  group of *N*-phthaloyl amino acids and coordination of  $\text{COO}$  group to metal ion.

### <sup>13</sup>C NMR Spectra

The <sup>13</sup>C NMR spectra of ligands DOTSC (LH), *N*-phthaloyl amino acids (AH), and their  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$ , and  $\text{Hg}(\text{II})$  complexes were recorded in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  (Table III). The <sup>13</sup>C resonance signals have been assigned according to chemical shift theory. A considerable upfield shift ( $\sim 2\text{--}3\text{ ppm}$ ) takes place in the position of  $-\text{C}-\text{S}$  ( $177.7\text{ ppm}$ , DOTSC) and  $\text{C}=\text{N}$  ( $148.0\text{ ppm}$ , DOTSC), indicating coordination through the azomethine nitrogen and the thiol group.<sup>15,23</sup>

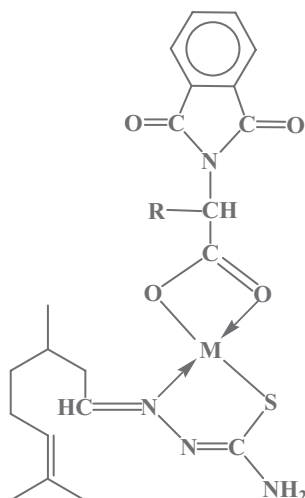
The <sup>13</sup>C NMR spectra of the complexes show a downfield shift of  $\sim 4\text{ ppm}$  in the position of carboxylic carbon signal as compared to its position in the parent *N*-phthaloyl amino acid, revealing bidentate nature of  $\text{COO}$  group of the ligand.<sup>15,24</sup>

**Table II**  $^1\text{H}$  NMR spectral data ( $\delta$  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)( <i>N</i> -phthgly)]	0.92 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.12–1.37 (m, 2H, $\text{CH}_2$ in C-4); 1.40–1.51 (m, 1H, $\text{CHCH}_3$ ); 1.61 & 1.67 (2s, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 1.80–1.97 (m, 2H, $\text{CH}_2$ in C-5); 2.02–2.31 (m, 2H, $\text{CH}_2$ in C-2); 5.08 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.21 & 7.26 (2s, 2H, $\text{NH}_2$ ); 7.52 (t, 1H, $\text{CH}=\text{N}$ )	4.39 (s, 2H, $\text{NCH}_2$ ); 7.72–7.93 (m, 4H, $\text{C}_6\text{H}_4$ )
[Zn (DOTSC)( <i>N</i> -phthala)]	0.95 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.17–1.34 (m, 2H, $\text{CH}_2$ in C-4); 1.36–1.41 (m, 1H, $\text{CHCH}_3$ ); 1.59 & 1.68 (2s, 6H, 3H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 1.70–2.28 (2m, 4H, $2\text{CH}_2$ in C-2 & C-5); 5.09 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.23 & 7.26 (2 br s, 2H, $\text{NH}_2$ ); 7.62 (t, 1H, $J = 5.8$ , $\text{CH}=\text{N}$ )	1.72 (d, 3H, $J = 7.2$ , $\text{CH}_3$ ); 5.05 (q, 1H, $\text{NCH}$ ); 7.80 (m, 4H, $\text{C}_6\text{H}_4$ )
[Cd(DOTSC)( <i>N</i> -phthgly)]	0.93 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.14 & 1.35 (2m, 2H, $\text{CH}_2$ in C-4); 1.38–1.51 (m, 1H, $\text{CHCH}_3$ ); 1.60 & 1.68 (2s, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 1.81–2.01 & 2.05–2.33 (2m, 4H, $\text{CH}_2$ in C-2 & C-5); 5.10 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.23 & 7.26 (2 br s, 2H, $\text{NH}_2$ ); 7.61 (t, 1H, $J = 5.8$ , $\text{CH}=\text{N}$ )	4.34 (s, 2H, $\text{NCH}_2$ ); 7.67–7.87 (m, 4H, $\text{C}_6\text{H}_5$ )
[Cd(DOTSC)( <i>N</i> -phthala)]	0.95 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.12 & 1.27 (2m, 2H, $\text{CH}_2$ in C-4); 1.32–1.45 (m, 1H, $\text{CHCH}_3$ ); 1.59 & 1.67 (2s, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 2.03 & 2.35 (2m, 4H, $\text{CH}_2$ in C-2 & C-5); 5.07 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.21 & 7.23 (2br s, 2H, $\text{NH}_2$ ); 7.79 (t, 1H, $J = 5.8$ , $\text{CH}=\text{N}$ )	1.78 (d, 3H, $J = 7.2$ , $\text{CH}_3$ ); 5.10 (q, 1H, $\text{NCH}$ ); 7.87 (m, 4H, $\text{C}_6\text{H}_4$ )
[Hg(DOTSC)( <i>N</i> -phthgly)]	0.94 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.17 & 1.36 (2m, 2H, $\text{CH}_2$ in C-4); 1.40–1.43 (m, $\text{CHCH}_3$ ); 1.60 & 1.68 (2s, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 2.12 & 2.28 (2m, 4H, $\text{CH}_2$ in C-2 & C-5); 5.08 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.20 & 7.26 (2 br s, 2H, $\text{NH}_2$ ); 7.72 (t, 1H, $J = 5.8$ , $\text{CH}=\text{N}$ )	4.40 (s, $\text{NCH}_2$ ); 7.76–8.01 (m, 4H, $\text{C}_6\text{H}_4$ )
[Hg(DOTSC)( <i>N</i> -phthala)]	0.92 (d, 3H, $J = 6.6$ , $\text{CHCH}_3$ ); 1.14 & 1.35 (2m, 2H, $\text{CH}_2$ in C-4); 1.38–1.45 (m, 1H, $\text{CHCH}_3$ ); 1.57 & 1.66 (2s, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 2.14 & 2.31 (2m, 4H, $\text{CH}_2$ in C-2 & C-5); 5.10 (t, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 7.21 & 7.28 (2 br s, 2H, $\text{NH}_2$ ); 7.81 (t, 1H, $J = 5.8$ , $\text{CH}=\text{N}$ )	1.71 (d, 3H, $J = 7.2$ , $\text{CH}_3$ ); 4.92 (q, $\text{NCH}$ ); 7.85 (m, 4H, $\text{C}_6\text{H}_4$ )

**Table III**  $^{13}\text{C}$  NMR spectral data ( $\delta$  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)( <i>N</i> -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 <sub>2</sub> ); 123.4, 131.8 & 133.9 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.2 (CO); 176.9 (COO)
[Zn (DOTSC)( <i>N</i> -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 <sub>3</sub> ); 47.3 (NCH); 123.2, 131.0 & 133.5 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.2 (CO); 176.9 (COO)
[Cd(DOTSC)( <i>N</i> -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 <sub>2</sub> ); 122.9, 131.8 & 134.1 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.3 (CO); 174.2 (COO)
[Cd(DOTSC)( <i>N</i> -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 <sub>3</sub> ); 47.4 (NCH); 122.9, 131.1 & 133.6 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.4 (CO); 176.9 (COO)
[Hg (DOTSC)( <i>N</i> -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 <sub>2</sub> ); 122.4, 132.0 & 133.9 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.0 (CO); 174.4 (COO)
[Hg (DOTSC)( <i>N</i> -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 <sub>3</sub> ); 47.2 (NCH); 123.0, 131.4 & 134.2 (C <sub>o</sub> , C <sub>i</sub> & C <sub>m</sub> of C <sub>6</sub> H <sub>4</sub> ); 167.2 (CO); 176.3 (COO)



(where  $M = \text{Zn(II)}, \text{Cd(II)}$  and  $\text{Hg(II)}$ ;  $R = \text{H}, \text{CH}_3$ )

**Figure 1** Proposed structure formula for the complexes  $[\text{M(L)(A)}]$ .

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  $4000\text{--}200\text{ cm}^{-1}$  range on a Shimadzu FT-IR 8400 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were collected in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  solution using TMS as internal standard on a JEOL FX 300 FT-NMR spectrometer at 300.40 and 75.45 MHz frequencies for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR,



respectively. Sulfur was estimated gravimetrically as  $\text{BaSO}_4$ , and metal contents were determined gravimetrically by a procedure in the literature<sup>25</sup> after digesting the organic matter with aquaregia and then with concentrated sulfuric acid and evaporating the residue to dryness. The ligands DOTSC<sup>16</sup> and *N*-phthaloyl amino acids<sup>26</sup> used were synthesized by reported methods. Molar conductances were measured in  $10^{-3}\text{M}$  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.

## 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  $\text{P}_2\text{O}_5$ . Yield: 90% (5.72 g); mp  $58^\circ\text{C}$ ; IR ( $\text{cm}^{-1}$ ): 3408s, 3265s, br ( $\text{NH}_2$ ); 3162s,  $\nu(\text{NH})$ ; 1595s,  $\nu(\text{C}=\text{N})$ ; 928w,  $\delta(\text{C}=\text{S})$ ; 820m,  $\nu(\text{CS})$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  in Hz): 0.98 (d, 3H,  $J = 6.6$ ,  $\text{CHCH}_3$ ); 1.19–1.26 & 1.32–1.34 (2m, 2H,  $\text{CH}_2$  in C-4,  $\text{H}_\alpha + \text{H}_\beta$ ); 1.37–1.39 (m, 1H,  $\text{CHCH}_3$ ); 1.60 & 1.68 (2s, 6H,  $(\text{CH}_3)_2\text{C}=\text{CH}$ ); 1.74–1.80 (m, 1H,  $\text{CH}_2$  in C-2,  $\text{H}_\beta$ ); 1.94–2.12 (m, 2H,  $\text{CH}_2$  in C-5); 2.18–2.28 (m, 1H,  $\text{CH}_2$  in C-2,  $\text{H}_\alpha$ ); 5.10 (t, 1H,  $\text{CH}=\text{C}(\text{CH}_3)_2$ ); 6.92 & 7.12 (2br s, 2H,  $\text{NH}_2$ ); 7.45 (t, 1H,  $J = 5.8$ ,  $\text{CH}=\text{N}$ ); 10.59 (s, 1H,  $\text{NHC}=\text{S}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  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  $\text{C}_{11}\text{H}_{21}\text{N}_3\text{S}$  (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  $140$ – $160^\circ\text{C}$ . 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 ( $\text{A}_1\text{H}$ ).** Yield: 85% (10.46 g); mp  $191$ – $192^\circ\text{C}$ ; IR ( $\text{cm}^{-1}$ ): 3163,  $\nu(\text{NH})$ ; 1750s,  $\nu(\text{CO})_{\text{asym}}$ ; 1700br,  $\nu(\text{CO})_{\text{sym}} + \nu(\text{COO})_{\text{asym}}$ ; 1400w,  $\nu(\text{COO})_{\text{sym}}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  in Hz): 4.49 (s, 2H,  $\text{NCH}_2$ ); 4.51 (s, 1H,  $\text{N}^+\text{H}$ ); 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 40.3 ( $\text{CH}_2$ ); 125.2, 134.2, 136.0 ( $\text{C}_o$ ,  $\text{C}_i$  &  $\text{C}_m$  of  $\text{C}_6\text{H}_4$ ); 167.2 (CO); 170.3 (COO); Anal. Found for  $\text{C}_{10}\text{H}_7\text{NO}_4$  (205.17): C, 58.61; H, 3.46; N, 6.80. Calcd. C, 58.55; H, 3.44; N, 6.83%.

***N*-Phthaloyl alanine ( $\text{A}_2\text{H}$ ).** Yield: 79% (10.38 g); mp  $161$ – $162^\circ\text{C}$ ; IR ( $\text{cm}^{-1}$ ): 3424br,  $\nu(\text{OH})$ ; 1744s,  $\nu(\text{CO})_{\text{asym}}$ ; 1715br,  $\nu(\text{CO})_{\text{sym}} + \nu(\text{COO})_{\text{asym}}$ ; 1395 w,  $\nu(\text{COO})_{\text{sym}}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  in Hz): 1.74 (d, 3H,  $J = 7.2$ ,  $\text{CH}_3$ ); 5.08 (q, 1H, NCH) 7.85 (m, 4H,  $\text{C}_6\text{H}_4$ ); 9.26 (s, 1H, COOH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 14.9 ( $\text{CH}_3$ ); 47.1 (CH); 123.5, 131.5, 133.1 ( $\text{C}_o$ ,  $\text{C}_i$  &  $\text{C}_m$  of  $\text{C}_6\text{H}_4$ ); 167.2 (CO); 174.7 (COO); Anal. Found for  $\text{C}_{11}\text{H}_9\text{NO}_4$  (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  $\text{CdCl}_2$  (1.19 g, 6.5 mmol) in anhydrous ethanol ( $\sim 40$  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  $\sim 8$  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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