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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## Synthesis, Characterization, Antimicrobial, and Genotoxicity Activities of Acetoacetanilide-4-ethyl Thiosemicarbazone Complexes

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#### SYNTHESIS, CHARACTERIZATION, ANTIMICROBIAL, AND GENOTOXICITY ACTIVITIES OF ACETOACETANILIDE-4-ETHYL THIOSEMICARBAZONE COMPLEXES

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#### **GRAPHICAL ABSTRACT**



**Abstract**  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Pd^{2+}$ ,  $Cd^{2+}$ ,  $UO_2^{2+}$ , and  $VO^{2+}$  ions were found to form stable complexes with acetoacetanilide-4-ethyl thiosemicarbazone (H<sub>2</sub>L). The structures of the complexes were elucidated by analysis (elemental and thermal), spectroscopy (electronic, IR, ESR, and <sup>1</sup>H NMR spectra), and physical measurements (magnetic susceptibility and molar conductance). IR spectra suggest that H<sub>2</sub>L acts as a monodentate, bidentate, and/or tridentate ligand. The electronic spectra of the complexes and their magnetic moments provide information about the geometries. The room temperature solid state ESR spectra of the Cu(II) complexes show  $d_{x^2-y^2}$  as the ground state, suggesting tetragonally distorted octahedral geometry around the Cu(II) center. The kinetic and thermodynamic parameters for the different decomposition steps in [Ni(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O and [VO(L)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O complexes were calculated using the Coats–Redfern equation. Finally, the antimicrobial and genotoxic activities have been tested.

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Keywords Antimicrobial activity; genotoxic activity; ESR; thermal analysis; thiosemicarbazone complexes

#### INTRODUCTION

Thiosemicarbazones have been extensively studied because they have a wide range of actual or potential medical applications,<sup>1</sup> which include notably antiparasital,<sup>2</sup> antibacterial,<sup>3</sup> and antitumor activities.<sup>4,5</sup> Many thiosemicarbazones, such as marboran or triapine, are already used in medical practice. Their mechanism of action is still controversial in many respects, but it is known that heterocyclic thiosemicarbazones act by inhibiting ribonucleotide reductase, a key enzyme in the biosynthesis of DNA precursors.<sup>6–9</sup> In general, thiosemicarbazones are obtained by condensation of the corresponding thiosemicarbazide with aldehydes or ketones. Thiosemicarbazones possess a wide range of biological activity, depending on the parent aldehyde or ketone. Earlier reports on N(4)-substituted thiosemicarbazones have concluded that the presence of bulky groups at the N(4) position of the thiosemicarbazone moiety greatly enhances biological activity.<sup>10–12</sup>

The present work aims to synthesize and characterize complexes of acetoacetanilide-4-ethyl thiosemicarbazone (H<sub>2</sub>L), with Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, and VO<sup>2+</sup> ions. The possible modes of chelation, the geometry, and the nature of bonding of the complexes are discussed on the basis of various spectroscopic methods (<sup>1</sup>H NMR, IR, UV-Vis, ESR). In addition, the kinetic and thermodynamic characteristics of the decomposition steps for Ni<sup>2+</sup> and VO<sup>2+</sup> complexes have been studied employing Coats–Redfern equations. Their antimicrobial and genotoxic activities also have been tested.

#### **RESULTS AND DISSUCTION**

The isolated solid complexes are stable in air and easily soluble only in DMF and DMSO. Most of the complexes decompose when heated at >300°C. The molar conductance values in DMSO are 3–6  $\Omega^{-1}$  cm<sup>2</sup>mol<sup>-1</sup>, indicating that all complexes are non-electrolytes.<sup>13</sup> The color, melting points, and elemental analyses of the isolated complexes are listed in Table 1.

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

The IR spectrum of H<sub>2</sub>L (Figure 1) shows three bands at 3328, 3249, and 3188 cm<sup>-1</sup> assigned to  $\upsilon(N^4H)$ ,  $\upsilon(N^3H)$ , and  $\upsilon(N^1H)$  vibrations (Figure S1), respectively.<sup>14</sup> The strong band at 1669 cm<sup>-1</sup> and the medium one at 1605 cm<sup>-1</sup> are attributed to the  $\upsilon(C=O)$  and  $\upsilon(C=N)$  vibration.<sup>15</sup> The band at 798 cm<sup>-1</sup> is assigned to the  $\upsilon(C=S)$  vibration.<sup>15</sup> The



Figure 1 Acetoacetanilide-4-ethyl thiosemicarbazone.

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Table

					% Foun	ld (Calcd.)		
		Mp	Yield					
Compound	Color	(°C)	(%)	C	Н	М	x	$\Lambda_{m}^{\ast}$
H <sub>2</sub> L	White	110	06	56.21 (56.14)	6.47 (6.52)	1		
$[Cu(H_2L)(Oac)_2 (H_2O)] \cdot 2 H_2O$	Green	220	75	39.73 (39.70)	5.87 (5.80)	12.44 (12.40)	I	9
$[Cu(H_2L)Cl_2 (H_2O)_2] \cdot H_2O$	Brown	235	75	33.36 (33.45)	5.22 (5.18)	13.65 (13.60)	15.24 (15.21)	9
$[Pd(H_2L)Cl_2]$	Orange	>300	70	34.31 (34.27)	4.02(3.98)	23.38 (23.35)	15.64 (15.59)	5
$[Cu(H_2L)(SO_4) (H_2O)] \cdot H_2O$	Olive Green	290	80	33.11 (32.93)	4.69(4.68)	13.44 (13.41)	20.18 (20.26)	9
$[Ni(HL)(OAc)(H_2O)] \cdot 2 H_2O$	Yellow	>300	75	40.12(40.10)	5.97 (5.80)	12.98 (13.10)	Ι	5
$[Co(HL)(OAc)(H_2O)] \cdot 2 H_2O$	Brown	>300	80	40.11(40.10)	5.82 (5.80)	13.21 (13.10)	Ι	4
$[\mathrm{UO}_2(\mathrm{HL})_2] \cdot \mathrm{H}_2\mathrm{O}$	Yellow	>300	80	39.13 (39.29)	4.35 (4.56)	29.22 (29.95)	Ι	4
$[VO(L)(H_2O)] \cdot 2 H_2O$	Dark Green	>300	70	39.26 (39.29)	5.45 (5.58)	12.79 (12.82)	Ι	б
$[Cd(L)(H_2O)] \cdot H_2O$	Yellowish-white	240	75	36.74 (36.80)	4.75 (4.80)	26.49 (26.50)		4

 $X = Cl^{-}$  or  $SO_4^{2-}$ , \* in DMSO ( $\Omega^{-1}cm^2 mol^{-1}$ ).



Figure 2 Suggested structure of  $[Cu(H_2L)(OAc)_2(H_2O)] \cdot 2 H_2O$ .

absence of bands at v(OH) (~ 3400 cm<sup>-1</sup>) and v(SH) (2500–2600 cm<sup>-1</sup>) indicates that the ligand exists in the keto and thione forms.<sup>16</sup>

Upon comparison of the spectrum of the ligand with that of  $[Cu(H_2L)(OAc)_2(H_2O)] \cdot 2 H_2O$ , it is clear that there is a negative shift of v(C=S) vibration (788 cm<sup>-1</sup>). On the other hand v(C=O), v(C=N),  $v(N^1H)$ ,  $v(N^3H)$ , and  $v(N^4H)$  vibrations remain more or less at the same position (Table 2, Figure S1, available online in the Supplemental Materials). This indicates that the coordination to the metal ion occurred through the sulfur atom of the C=S group, and the other groups do not participate in coordination. Thus, the ligand acts as a neutral monodentate ligand via the thione sulfur atom (Figure 2).

In the case of the  $[Cu(H_2L)Cl_2(H_2O)_2] \cdot H_2O$  complex,  $H_2L$  acts as a neutral bidentate ligand coordinating via the carbonyl oxygen (C=O) and azomethine nitrogen (C=N) atom. This mode of chelation is supported by the shift of both v(C=N) and v(C=O) vibrations to lower wavenumber as shown in Table 1. The v(C=S),  $v(N^1H)$ ,  $v(N^3H)$ , and  $v(N^4H)$  vibrations are shifted to slightly higher wavenumbers, which indicates that they do not participate in coordination to the metal ion. Also, new bands were observed at 510 and 405 cm<sup>-1</sup> and assigned to v(Cu-O) and v(Cu-N),<sup>17</sup> respectively. The spectrum of the  $[Pd(H_2L)Cl_2]$  complex shows that the ligand behaves in the same manner as neutral bidentate ligand (Table 2, Figure 3).



Figure 3 Suggested structure of  $[Cu(H_2L)Cl_2(H_2O)_2] \cdot H_2O$  and  $[Pd(H_2L)Cl_2]$ .

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		Table 2	Infrared spec	stral data for	H <sub>2</sub> L and is	olated solid	complexes i.	n KBr				
Compound	v (C=0)	v (C=N)	v (C=N <sup>3</sup> )	v (N-N)	v (C=S)	v (C-S)	v (C-O)	v (N <sup>1</sup> H)	v (N <sup>3</sup> H)	v (N <sup>4</sup> H)	и (М-О)	v (M-N)
H <sub>2</sub> L	1669	1605		1030	798			3188	3249	3328		
$[Cu(H_2L)(Oac)_2(H_2O)] \cdot 2 H_2O$	1676	1608		1034	788			3191	3244	3322		
$[Cu(H_2L)Cl_2(H_2O)_2] \cdot H_2O$	1652	1593		1033	802			3190	3257	3329	510	405
$[Pd(H_2L)Cl_2]$	1658	1590		1042	801	I		3179	3248	3326	503	420
$[Cu(H_2L)(SO_4)(H_2O)] \cdot H_2O$	1652	1590		1040	785			3181	3253	3299	508	417
$[Ni(HL)(OAc)(H_2O)] \cdot 2 H_2O$		1595		1055	785	l	1110	3184	3254	3331	510	421
$[\mathrm{Co}(\mathrm{HL})(\mathrm{OAc})(\mathrm{H_2O})]\cdot 2\mathrm{H_2O}$		1593		1038	790		1110	3186	3250	3334	506	405
$[\mathrm{UO}_2(\mathrm{HL})_2]\cdot\mathrm{H}_2\mathrm{O}$		1594		1042	789	Ι	1119	3189	3248	3326	515	410
$[VO(L)(H_2O)] \cdot 2 H_2O$		1590	1615	1053	Ι	610	1135	3196		3325	515	408
$[Cd(L)(H_2O)] \cdot H_2O$		1595	1625	1045		620	1130	3190		3330	508	415



Figure 4 Suggested structure of  $[Cu(H_2L)(SO_4)(H_2O)]$ . H<sub>2</sub>O.

On the other hand, the IR spectrum of the  $[Cu(H_2L)(SO_4)(H_2O)] \cdot H_2O$  complex shows a shift of v(C=N), v(C=O), and v(C=S) vibrations to lower wavenumbers. This indicates that H<sub>2</sub>L acts as a neutral tridentate ligand coordinating via the carbonyl oxygen (C=O), the azomethine nitrogen (C=N), and the thione sulfur (C=S) atom. Also, the spectrum of this complex shows new bands at 508 and 417 cm<sup>-1</sup> assignable to v(Cu-O)and v(Cu-N),<sup>17</sup> respectively. The appearance of bands at 1058 and 920 cm<sup>-1</sup> assignable to the SO stretching vibrations suggests bidentate sulfate<sup>18</sup> (Figure 4).

Moreover, the IR spectra indicate that H<sub>2</sub>L acts as a mononegative tridentate ligand coordinating through the azomethine nitrogen (C=N), the thione sulfur (C=S), and the deprotonated enolized carbonyl oxygen (=C $-O^-$ ) atom. This behavior is observed in [Ni(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O, [Co(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O (Figure 5) and [UO<sub>2</sub>(HL)<sub>2</sub>] · H<sub>2</sub>O complexes. This mode of chelation is supported by: (i) the disappearance of  $\upsilon$ (C=O) with simultaneous appearance of new bands in the 1110–1119 cm<sup>-1</sup> region assignable to  $\upsilon$ (C-O)<sub>enolic</sub><sup>19</sup>; (ii) the shift of both  $\upsilon$ (C=N) and  $\upsilon$ (C=S) to lower wavenumber; (iii) the  $\upsilon$ (N<sup>1</sup>H),  $\upsilon$ (N<sup>3</sup>H), and  $\upsilon$ (N<sup>4</sup>H) vibrations are found more or less at same position, which indicates that they do not participate in coordination to the metal ions; and (iv) the appearance of new bands in the 506–515 and 405–421 cm<sup>-1</sup> regions assignable to  $\upsilon$ (M-O) and  $\upsilon$ (M-N). In addition, the spectrum of the [UO<sub>2</sub>(HL)<sub>2</sub>] · H<sub>2</sub>O complex displays two



Figure 5 Suggested structure of [Ni(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O and [Co(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O.

bands at 906 and 840 cm<sup>-1</sup> assigned to  $v_3$  and  $v_1$  vibrations of the dioxouranium ion, respectively. The value of  $v_3$  is used to calculate the force constant (F) of v(U=O) by the method of McGlynn and Smith:<sup>20</sup>

$$(v_3)^2 = (1307)^2 (F_{U-O})/14.103$$

The force constant obtained for uranyl complex was then substituted into the relation given by  $Jones^{21}$  to estimate the U–O bond length in Å.

$$R_{U-O} = 1.08 (F_{U-O})^{-1/3} + 1.17$$

The calculated  $F_{U-O}$  and  $R_{U-O}$  values are 6.776 mdayn Å<sup>-1</sup> and 1.740 Å, respectively, and fall in the usual range for uranyl complexes.

Finally, the IR spectral data of  $[VO(L)(H_2O)] \cdot 2 H_2O$  and  $[Cd(L)(H_2O)] \cdot H_2O$  (Figures 6 and S2) show that  $H_2L$  behaves as a binegative tridentate ligand coordinating to the metal ions through the azomethine nitrogen atom, the deprotonated thiol sulfur atom, and the deprotonated enolic carbonyl oxygen atom. This feature is supported by (i) the negative shift of v(C=N) vibration; (ii) the disappearance of the v(C=O) vibration with simultaneous appearance of new bands in the 1130–1135 cm<sup>-1</sup> range assignable to  $v(C=O)_{enolic}$ ; (iii) the disappearance of v(C=S) and  $v(N^3H)$  with simultaneous appearance of new bands in the 610–620 and 1615–1625 cm<sup>-1</sup> regions attributed to v(C=S) and  $v(C=N^3)$ ,<sup>22</sup> respectively; (iv) the appearance of new bands in the 508–515 and 408–415 cm<sup>-1</sup> regions assignable to v(V=O) and v(M-N), respectively; and (v) a band at 976 cm<sup>-1</sup> due to v(V=O) vibration in agreement with the square-pyramidal arrangement around the metal ion.<sup>23</sup>

In metal acetate complexes, the acetate group coordinates to the metal ions in a bidentate manner, where the difference between the two acetate bands is  $\Delta \nu \leq 180 \text{ cm}^{-1.24}$  Also, the bands of coordinated water observed at 815–857 and 533–592 cm<sup>-1</sup> are assigned to  $\rho_r(H_2O)$  and  $\rho_w(H_2O)$ , respectively.<sup>24</sup> Moreover, strong evidence for the presence or absence of water of crystallization and/or coordinated water is supported by the thermogram of all complexes.

The <sup>1</sup>H NMR spectroscopic data of H<sub>2</sub>L in d<sub>6</sub>-DMSO and of some complexes are listed in Table 3. In the free ligand, the aromatic protons appear at  $\delta$  7.0–7.6 ppm, and the signal at  $\delta$  2.0 ppm is assigned to the protons of the methylene group (–CH<sub>2</sub>–), while the signal of CH<sub>3</sub> protons appears at  $\delta$  1.9 ppm. Also the two signals at  $\delta$  3.6 and 1.2 ppm are ascribed to the protons of ethyl group. The N<sup>3</sup>H, N<sup>1</sup>H, and N<sup>4</sup>H protons appear at  $\delta$  10.6, 10.2, and 9.7 ppm, respectively.

The <sup>1</sup>H NMR of the [Pd(H<sub>2</sub>L)Cl<sub>2</sub>] complex shows three signals at  $\delta$  10.5, 10.3, and 9.8 ppm assignable to the protons of N<sup>3</sup>H, N<sup>1</sup>H, and N<sup>4</sup>H, respectively. The chemical shifts

							Aromatic	Ethyl g	roup
Compound	N <sup>3</sup> H	$N^1H$	N <sup>4</sup> H	$-CH_2-$	=СН-	$-CH_3$	protons	-СН2-	-CH <sub>3</sub>
H <sub>2</sub> L	10.6	10.2	9.7	2.0		1,9	7.0–7.6	3.6	1.2
$[Pd(H_2L)Cl_2]$	10.5	10.3	9.8	2.1		1.9	7.0-7.7	3.6	1.2
$[Cd(L)(H_2O)] \cdot H_2O$	—	10.3	9.7	—	4.6	2.0	7.2–7.6	3.7	1.3

Table 3 <sup>1</sup>H NMR data of H<sub>2</sub>L and its diamagnetic complexes

Compound	$\mu_{\rm eff}$ (BM)	Band position (nm)	$\begin{array}{c} D_q \ (cm^{-1}) \end{array}$	B (cm <sup>-1</sup> )	β	$\upsilon_2/\upsilon_1$
$[Ni(HL)(OAc)(H_2O)] \cdot 2 H_2O$	3.43	735; 440	903	813	0.78	1.67
$[Co(HL)(OAc)(H_2O)] \cdot 2 H_2O$	5.15	711; 580	763	803	0.83	2.15
$[Cu(H_2L)(OAc)_2(H_2O)] \cdot 2 H_2O$	2.05	678; 600	_		_	_
$[Cu(H_2L)Cl_2(H_2O)_2] \cdot H_2O$	1.98	682; 590	_		_	_
$[Cu(H_2L)(SO_4)(H_2O)] \cdot H_2O$	1.93	700; 600	_	_	_	_
$[VO(L)(H_2O)] \cdot 2 H_2O$	1.98	850	_		_	_
$[Pd(H_2L)Cl_2]$	Diam.	442	_	_	_	_
$[UO_2(HL)_2] \cdot H_2O$	Diam.	417; 359			—	

Table 4 Magnetic moments, electronic spectra, and ligand field parameters of metal complexes of H<sub>2</sub>L

are almost the same as those of the free ligand, confirming that these groups are not involved in coordination to the metal ion.

The <sup>1</sup>H NMR spectrum of the  $[Cd(L)(H_2O)] \cdot H_2O$  complex shows a new signal at  $\delta$  4.6, assigned to the proton of (-O-C=CH-) group, which is formed in the enolization of the C=O moiety. Also, the spectral data indicate the absence of a signal for the N<sup>3</sup>H proton due to the thioenolization.

#### Electronic, ESR Spectra, and Magnetic Moment Measurements

The electronic spectrum of the ligand in DMF shows two bands at 305 and 350 nm due to the  $\pi \to \pi^*$  and  $n \to \pi^*$  transitions, respectively.<sup>25</sup> Previous studies proved that the bands at 400–384 and 459–404 nm should be assigned to  $O \to M^{26}$  and  $S \to M^{27}$  transitions. The bands at 470–344 nm (DMF) in the spectra of the present complexes may therefore be due to  $O \to M$  and  $S \to M$  CT.

The electronic spectrum of  $[VO(L)(H_2O)] \cdot 2 H_2O$  shows a band at 580 nm (Table 4, Figure S3), assigned to  ${}^{2}B_2 \rightarrow {}^{2}E (\upsilon_2)$  in a square-pyramidal configuration.<sup>28</sup>

The electronic spectrum of  $[Ni(HL)(OAc)(H_2O)] \cdot 2 H_2O$  shows two bands at 735 and 440 nm attributed to  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$  transitions (Figure 8), respectively, in an octahedral geometry.<sup>29</sup> The calculated values of D<sub>q</sub>, B,  $\beta$ , and  $\nu_2/\nu_1$ lie in the range reported for an octahedral structure.<sup>29</sup> The position of  $\nu_1$  (8146 cm<sup>-1</sup>)



Figure 6 Suggested structure of  $[Cd(L)(H_2O)] \cdot H_2O$  and  $[VO(L)(H_2O)] \cdot 2 H_2O$  complexes.

is calculated theoretically. The magnetic moment ( $\mu_{eff.} = 3.43$  BM) provides additional evidence for an octahedral geometry.

The electronic spectrum of the [Co(HL)(OAc)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O complex exhibits two bands at 711 and 580 nm attributed to  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}(F)$  and  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$  transitions, respectively, in an octahedral configuration.<sup>29</sup> The calculated D<sub>q</sub>, B,  $\beta$ , and  $\nu_{2}/\nu_{1}$  values are in the range reported for an octahedral environment around Co(II) complexes.<sup>[29]</sup> The position of  $\nu_{1}$  (6541cm<sup>-1</sup>) is calculated theoretically.<sup>29</sup> Also, the value of the magnetic moment (5.15 BM) is additional evidence for an octahedral geometry around the Co(II) ion.

The Cu(II) complexes have magnetic moment values (1.93–2.05 BM), which correspond to those reported for d<sup>9</sup>-systems. The electronic spectra of [Cu(H<sub>2</sub>L)(OAc)<sub>2</sub>(H<sub>2</sub>O)] · 2 H<sub>2</sub>O, [Cu(H<sub>2</sub>L)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · H<sub>2</sub>O and [Cu(H<sub>2</sub>L)(SO<sub>4</sub>)(H<sub>2</sub>O)] · H<sub>2</sub>O complexes show broad bands in the 590–600 nm region with a shoulder in the 678–700 nm region, which may be assigned to  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}E_{g} \rightarrow {}^{2}A_{1g}$  transitions, respectively, in a tetragonally distorted octahedral configuration.<sup>30</sup>

The electronic spectrum of the  $[UO_2(HL)_2] \cdot H_2O$  complex shows two bands at 417 and 359 nm, which may be ascribed to  ${}^{1}\Sigma^{+}{}_{g} \rightarrow {}^{2}\pi_{u}$  transition for dioxouranium(VI) and charge transfer  $n \rightarrow \pi^*$  transition, respectively.<sup>31</sup>

The diamagnetic [Pd(H<sub>2</sub>L)Cl<sub>2</sub>] complex<sup>32</sup> shows a band at 442 nm, which is assigned to  ${}^{1}A_{1g} \rightarrow {}^{2}B_{1g}$  transition in a square-planar configuration.<sup>33</sup>

The room temperature solid state ESR spectra of copper complexes (Figure 7) exhibit axially symmetric g-tensor parameters with  $g_{//} > \gamma_{\perp} > 2.0023$ . The g values reflect that the Cu(II) center has a tetragonally distorted octahedral geometry with the unpaired electron residing in the  $d_{x2-y2}$  orbital.<sup>34</sup>

No band corresponding to the forbidden magnetic dipolar transition for the complexes was observed at half-field (ca. 1500 G, g = 4.0), ruling out any Cu–Cu interaction and

**Figure 7** Room temperature X-band ESR spectra of (a)  $[Cu(H_2L)(OAc)_2(H_2O)] \cdot 2 H_2O$ , (b)  $[Cu(H_2L)(Cl_2(H_2O)_2] \cdot H_2O$ , and (c)  $[Cu(H_2L)(SO_4)(H_2O)] \cdot H_2O$ .



			$A_{\prime\prime} \times 10^{-4}$			
Complex	g//	$g_{\perp}$	$(cm^{-1})$	G	$\alpha^2$	$\beta^2$
$[Cu(H_2L)(OAc)_2(H_2O)] \cdot 2 H_2O$	2.27	2.04	155	5.6	0.75	0.82
$[Cu(H_2L)Cl_2(H_2O)_2] \cdot H_2O$	2.26	2.06	160	4.3	0.76	0.75
$[Cu(H_2L)(SO_4)(H_2O)] \cdot H_2O$	2.23	2.05	160	4.6	0.75	0.65
$[VO(L)(H_2O)] \cdot 2 H_2O$	1.95	1.97	195	—	0.73	0.92

Table 5 ESR data of the copper(II) and oxovanadium(IV) complexes at room temperature

indicating that the complex is a mononuclear Cu(II) complex. In axial symmetry, the g-values are related by the expression,  $G = (g_{//} - 2)/(\gamma_{\perp} - 2) = 4$ , which measures the exchange interaction between copper centers in the solid.

According to Hathaway and Billing,<sup>35</sup> if the value of G is greater than 4, the exchange interaction between the copper(II) centers in the solid state is negligible, whereas when G is less than 4, a considerable exchange interaction is present in the solid complex. The calculated G values are given in Table 5. The G values are greater than four, suggesting no copper–copper exchange interaction, and these results are very consistent with the values of the effective magnetic moments.

In hexacoordinated Cu(II) complexes, tetragonal distortion from the octahedral symmetry due to the Jahn–Teller distortion is very common. Such complexes with different ligands are attractive mainly due to the variation in the coordination geometry and the spectral features.<sup>36,37</sup>

Hyperfine splittings for the complexes were not observed at higher fields, excluding any interaction of the nuclear spins of the nitrogen (I = 1) with the unpaired electron density on Cu(II). The absence of <sup>14</sup>N hyperfine coupling may be due to a relatively high tetrahedral distortion for this complex.<sup>38</sup>



Figure 8 Room temperature X-band ESR spectrum of [VO(L)(H<sub>2</sub>O)] · 2 H<sub>2</sub>O.

Molecular orbital coefficients,  $\alpha^2$  (a measure for the covalency of the in-plane  $\sigma$ bonding between a copper 3D orbital and the ligand orbitals) and  $\beta^2$  (covalent in-plane  $\pi$ -bonding), were calculated using the following equations,<sup>39–42</sup> where  $\alpha^2 = 1$  indicates complete ionic character. On the other hand  $\alpha^2 = 0.5$  denotes 100% covalent bonding with the assumption of negligibly small values of the overlap integral:

$$\alpha^{2} = \left(\frac{A_{//}}{0.036}\right) + (g_{//} - 2.0023) + \frac{3(g_{\perp} - 2.0023)}{7} + 0.04$$
$$\beta^{2} = \frac{(g_{//} - 2.0023)E}{-8\lambda\alpha^{2}}$$

where  $\lambda = -828 \text{ cm}^{-1}$  for the free copper ion and E is the electronic transition energy. In Table 5, the  $\alpha^2$  and  $\beta^2$  values indicate that there is a substantial interaction in the inplane  $\sigma$ -bonding, whereas the in-plane  $\pi$ -bonding is almost ionic. The higher value of  $\beta^2$ compared to that of  $\alpha^2$  indicates that the in-plane  $\pi$ -bonding is less covalent than the inplane  $\sigma$ -bonding. The  $\alpha^2$  value for the Cu(II) complex indicates a considerable covalency in the bonding between the copper(II) ion and the ligand.

The room temperature (300 K) ESR spectrum of  $[VO(L)(H_2O)] \cdot 2 H_2O$  gave a broad signal with poorly resolved eight hyperfine lines (Figure 8) similar to those reported for mononuclear vanadium molecule. In the powdered mono vanadium complex, the spectrum showed parallel and perpendicular features, which indicates axially symmetric anisotropy with well resolved 16-line hyperfine splitting characteristic for the interaction between the electron and the vanadium nuclear spin (I = 7/2). The spin Hamiltonian parameters are calculated and given in Table 5. The calculated ESR parameters indicate that the unpaired electron (d<sup>1</sup>) in the complex is present in the d<sub>xy</sub>-orbital, in accord with square pyramidal geometry.<sup>43</sup> The values obtained for the complexes agree well with the g-tensor parameters reported for distorted square pyramidal vanadium complexes.

The molecular orbital coefficients  $\alpha^2$  and  $\beta^2$  for the complexes were calculated using the following equations:<sup>44</sup>

$$\begin{aligned} A_{||} &= -P \bigg[ k + \frac{4}{7} \beta^2 + (g_e - g_{||}) + \frac{3}{7} (g_e - g_{\perp}) \bigg] \\ A_{\perp} &= -P \bigg[ k - \frac{2}{7} \beta^2 + \frac{11}{4} (g_e - g_{\perp}) \bigg] \\ g_e - g_{||} &= \frac{8 \alpha^2 \beta^2 \lambda}{E} \end{aligned}$$

Neglecting the second order effects and taking negative values for  $A_{//}$  and  $A_{\perp}$ , these equations are solved to obtain  $\alpha^2$  and  $\beta^2$ .

The spin-orbit coupling coefficient  $\lambda$  is assumed to be 170 cm<sup>-1</sup> for the M<sup>2+</sup> ion, *E* is the energy of  ${}^{2}B_{2} \rightarrow {}^{2}E$  electronic transition, and *k* is the Fermi contact term, which is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus. The lower values of  $\alpha^{2}$  as compared to  $\beta^{2}$  indicate that the in-plane  $\sigma$ -bonding is more covalent. These data are very consistent with other reported data.<sup>45</sup>

#### **Thermal Analysis**

The TG curve of  $[VO(L)(H_2O)] \cdot 2 H_2O$  complex displays 9.11% weight loss in the temperature range 60–130°C (Figure S4, Table 6), which correlates to two water molecules outside the coordination sphere. In the temperature range 130–220°C, the TG curve displays 4.55% weight loss, which could be correlated with the release of the coordinated water molecule.<sup>46</sup> Thermal degradation of the organic molecule starts above 220°C. Over the temperature range 220–462°C, the weight loss of 26.57% in the TG curve is most probably ascribed to the partial decomposition of the chelating agent with the elimination of the loosely bonded ( $C_2H_6N + C_3H_3N_2$ ) moiety. The final weight loss of 28.09% ending at 653°C is largely attributed to complete decomposition of the organic molecule alongside rupture of the chelate bond, leaving VO<sub>2</sub> + S and comprising 30.71% of the initial mass of the complex.

The TG curve of the [Ni(HL)(OAc)(H<sub>2</sub>O)]  $\cdot$  2 H<sub>2</sub>O complex displays 8.14% weight loss in the temperature range of 56–151°C (Figure S5), which correlates to the two water molecules outside of the coordination sphere. In the temperature range 151–245°C, the TG curve displays 17.34% weight loss, which could be correlated with the release of one coordinated water molecule as well as of the acetate group.<sup>46,47</sup> Thermal degradation of the organic molecule starts above 245°C. Over the temperature range of 245–439°C, the weight loss of 22.90% in the TG curve is most probably ascribed to the partial decomposition of the chelating agent with the elimination of the loosely bonded C<sub>3</sub>H<sub>7</sub>N<sub>2</sub>S moiety. The final weight loss of 35.13% ending at 650°C is largely attributed to complete decomposition of the organic molecule alongside rupture of the chelate bond, leaving NiO and comprising 16.60% of the initial mass of the complex.

For more information about the effects of the anions on the structural properties and bonding, the coefficients of the thermal behavior of the complexes and the heat of activation  $E^{\#}$  of the decomposition stages were determined from the TG thermograms for some steps of the decomposition of the VO<sup>2+</sup> and Ni<sup>2+</sup> complexes using the Coats–Redfern equations.<sup>48</sup> The other kinetic parameters,  $\Delta H^{\#}$ ,  $\Delta S^{\#}$ , and  $\Delta G^{\#}$ , were computed using the relationships:  $\Delta H^{\#} = E^{\#}$ –RT,  $\Delta S^{\#} = R[\ln(Ah/kT)-1]$ , and  $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ , where k is Boltzmann's constant and h is Planck's constant. The activation parameters are listed in Table 6. It has been found that some of the steps are unsuitable for kinetic analysis. The overlapping steps reflect slight differences between the calculated and found weight losses.

Some of the activation entropies  $\Delta S^{\#}$  are negative, indicating that the reactions are slow or the activated complex is more ordered than the reactants.<sup>49</sup> The positive values of  $\Delta H^{\#}$  mean that the decomposition processes are endothermic. All decomposition stages of the complexes show a best fit for (n = 1), indicating a first-order decomposition in all cases. Other n values (e.g., 0, 0.33, and 0.66) did not lead to better correlations. The values of  $\Delta G^{\#}$  increase significantly for the subsequent decomposition stages of a given complex due to increasing of T $\Delta S^{\#}$ .

#### **Antimicrobial Activity Bioassay**

The antimicrobial activity of the investigated ligand and complexes against *Bacillus Subtilis* and *Micrococcus sp.* is summarized in Table S1 (Supplemental Materials)

Complex	Wt. Ic	o%ss@	Temn range	Decomposition products		F.#	#S'V	$\Lambda H^{\#}$	# <u>5</u> V
(Mol. wt.)	Found	Calcd.	(°C)	(Formula wt.)	r	kJ mol <sup>-1</sup>	$f \mod^{-1} K^{-1}$	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>
[VO(L)(H <sub>2</sub> O)] ·	9.11	9.06	60-130	2 H <sub>2</sub> O (36.032)	0.995	149.7	57.9	146.8	126.3
2 H <sub>2</sub> O (397.329)	4.55	4.53	130–220	H <sub>2</sub> O (18.015)					
	26.57	27.97	220-462	$C_2H_6N + C_3H_3N_2$ (111.143)	0.985	26.7	-200.1	21.2	152.4
	28.09	29.48	462–653	$C_8H_7N$ (117.143)	0.989	346.7	49.4	340.0	299.7
	30.71	28.94	> 653	Residue, $VO_2 + S (114.998)$	I		Ι		
$[Ni(HL)(OAc)(H_2O)]$ .	8.14	8.02	56-151	2 H <sub>2</sub> O (36.032)					
2 H <sub>2</sub> O (449.150)	17.34	17.15	151-245	$H_2O + C_2H_3O_2$ (77.061)	0.995	149.7	52.6	144.1	108.9
	22.90	23.96	245-439	$C_3H_7N_2S$ (103.16)	0.937	73.5	-236.7	67.0	235.4
	35.13	35.22	439–650	$C_{10}H_{10}N_2 (158.194)$					
	16.60	16.63	>650	Residue, NiO (74.709)					

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#### CONCLUSION

The structures of the complexes of  $H_2L$  with  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Pd^{2+}$ ,  $Cd^{2+}$ ,  $UO_2^{2+}$ , and  $VO^{2+}$  ions were determined by elemental analyses, IR, <sup>1</sup>H NMR spectroscopy, molar conductance, magnetic, UV-Vis, ESR, and thermal analysis data. From the IR spectra, it is concluded that  $H_2L$  behaves as a monodentate, bidentate, and/or tridentate ligand. From the molar conductance data, it was found that all the complexes are non-electrolytes. The <sup>1</sup>H NMR spectrum of the free ligand shows that the OH and SH signals are absent. This indicates that the ligand exists in the keto and thione forms. On the basis of magnetic measurements, UV-Vis, and ESR, an octahedral geometry is suggested for all investigated complexes, except for the Pd(II) complex, which is square planar, and for the  $VO^{2+}$  complex, which is square-pyramidal. The ligand and the metal complexes prepared were also screened for their antibacterial activity against bacterial species *Bacillus subtilis* as Gram positive and *Micrococcus sp* as Gram negative bacteria. The activity data show that most of the metal complexes were more potent antibactrials than the parent ligand against these bacterial species. Moreover, the degradation powers of the tested compounds on the calf thymus DNA were high.

#### **EXPERIMENTAL**

#### **Apparatus and Reagents**

The IR absorption spectra were recorded with a Mattson 5000 FTIR spectrophotometer. The electronic spectra were measured with a Unicam UV/VIS spectrometer UV<sub>2</sub>. Thermogravimetric analysis was performed using an automatic recording thermobalance type 951 (DuPont instrument). Samples were subjected to heat at a rate of 10°C/min (25–800°C) in N<sub>2</sub>. <sup>1</sup>H NMR spectra for H<sub>2</sub>L and diamagnetic complexes in DMSO were recorded with an EM-390 (200 MHz) spectrometer. Carbon and hydrogen content for the ligand and its complexes was determined at the Microanalytical Unit, Mansoura University, Egypt. Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, VO<sup>2+</sup>, Cl, and SO<sub>4</sub><sup>2</sup> contents in the complexes were determined by well known standard methods.<sup>50</sup> ESR spectra were obtained with a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW, and modulation amplitude was set at 4 Gauss. The low field signal was obtained after 4 scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. All metal salts used were pure (Fluka, Aldrich, or Merck).

#### **Preparation of the Ligand**

Acetoacetanilide-4-ethyl thiosemicarbazone (Figure 1) was prepared by stirring a mixture of 4-ethyl-3-thiosemicarbazide (1.19 g, 0.1 mol) with acetoacetanilide (1.77 g, 0.1 mol) in EtOH (40 mL) and adding 2 mL of 5M HCl. The reaction mixture was stirred at room temperature for 4 h. The white precipitate was filtered off, washed with ethanol and  $Et_2O$ , and finally recrystallized from ethanol (mp 110°C; yield 90%). The purity of the compound was checked by TLC.

#### Preparation of the Complexes

The complexes were prepared by mixing equimolar amounts of  $H_2L$  with ethanolic and/or aqueous solution of the chloride salt of  $Cu^{2+}$ ,  $Cd^{2+}$ , and  $Pd^{2+}$  as potassium tetrachloropalladate; of the acetate salt of Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, and UO<sub>2</sub><sup>2+</sup>; and the sulfate salt of Cu<sup>2+</sup> and VO<sup>2+</sup>. In the case of VO<sup>2+</sup> and Cd<sup>2+</sup>, 0.1 g of sodium acetate was added as a buffering agent to raise the pH medium. The reaction mixture was heated under reflux on a water bath for 1–3 h. The precipitate was filtered off, washed with hot EtOH and/or H<sub>2</sub>O, and finally preserved in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

#### **Biological Activity (See Supplemental Materials)**

**Antimicrobial activity.** The ligand and its complexes have been tested as antibacterial agents at the Department of Microbiology, Faculty of Pharmacy, Mansoura University. Inhibition zone was measured<sup>51</sup> and compared with that of gentamicin solution (commercial antibiotic, Memphis Co., Egypt, 1000  $\mu$ g mL<sup>-1</sup>). The experimental control was DMF.

**Genotoxicity activity.** A solution of 2 mg of calf thymus DNA was dissolved in 1 mL of sterile distilled water (see Figure S6).

#### REFERENCES

- Duffy, K. J.; Shaw, A. N.; Delorme, E.; Dillon, S. B.; Erickson-Miller, C.; Giampa, L.; Huang, Y.; Keenan, R. M.; Lamb, P.; Liu, N.; Miller, S. G.; Price, A. T.; Rosen, J.; Smith, H.; Wiggall, K. J.; Zhang, L.; Luengo, J. I. J. Med. Chem. 2002, 45, 3573–3575.
- Du, X.; Guo, C.; Hansel, E.; Doyle, P. S.; Caffrey, C. R.; Holler, T. P.; McKerrow, J. H.; Cohen, F. E. J. Med. Chem. 2002, 45, 2695–2707.
- 3. Refat, M. S.; El-Deen, I. M.; Anwer, Z. M.; El-Ghol, S. J. Mol. Struct. 2009, 920, 149–162.
- 4. Scovill, J. P.; Klayman, D. L.; Franchino, D. G. J. Med. Chem. 1982, 25, 1261-1264.
- Papageorgiou, A.; Iakovidou, Z.; Mourelatos, D.; Mioglou, E.; Boutis, L.; Kotsis, A.; Kovala-Demertzi, D.; Domopoulou, A.; West, D. X.; Demertzis, M. A. Anticancer Res. 1997, 17, 247–251.
- 6. Raman, N.; Jeyamurugan, R. J. Coord. Chem. 2009, 62, 2375-2387.
- Szacilowski, K.; Macyk, W.; Drzewiecka-Matuszek, A.; Brindell, M.; Stochel, G. Chem. Rev. 2005, 105, 2647–2694.
- Demertzi, D. K.; Demertzis, M. A.; Miller, J. R.; Papadopoulou, C.; Dodorou, C.; Filousis, G. J. Inorg. Biochem. 2001, 86, 555–563.
- 9. Mozaar, A.; Elham, S.; Bijan, R.; Leila, H. New J. Chem. 2004, 28, 1227-1233.
- 10. Beraldo, H.; Gambino, D. Mini Rev. Med. Chem. 2004, 4, 31-39.
- 11. Singh, S.; Bharti, N.; Naqvi, F.; Azam, A. Eur. J. Med. Chem. 2004, 39, 459-465.
- Rebolledo, A. P.; Vieites, M.; Gambino, D.; Piro, O. E.; Castellano, E. E.; Zani, C. L.; Souza-Fagundes, E. M.; Teixeira, L. R.; Batista, A. A.; Beraldo, H. J. Inorg. Biochem. 2005, 99, 698–706.
- 13. Geary, W. J. J. Coord. Chem. 1971, 7, 81-122.
- Abu El-Reash, G. M.; Kenawy, I. M.; Ayaan, U. I.; Khatab, M. A. Synth. React. Inorg. Met.-Org. 1994, 24, 813.
- 15. Mostafa, S. I.; Bekheit, M. M. Chem. Pharm. Bull. Jpn. 2000, 48, 266-271.
- 16. Offiong, O. E.; Martelli, S. Transition Met. Chem. 1997, 22, 263-269.
- 17. Bekheit, M. M.; Elewady, Y. A.; Taha, F. I.; Mostafa, S. I. Bull. Soc. Chim. Fr. 1990, 128, 178–183.
- 18. Ibrahim, K. M.; Bekheit, M. M.; Abu El-Reach, G. M. Transition Met. Chem. 1991, 16, 189–192.

#### R. R. ZAKY

- Rakha, T. H.; Nawar, N.; Abu El-Reach, G. M. Synth. React. Inorg. Met.-Org. Chem. 1996, 26, 1705–1718.
- 20. McGlynn, S. P.; Smith, J. K. J. Chem. Phys. 1961, 35, 105-116.
- 21. Jones, H. Spectrochim. Acta 1958, 10, 395–399.
- Tamboura, F. B.; Haba, P. M.; Gaye, M.; Sall, A. S.; Barry, A. H.; Jouini, T. *Polyhedron* 2004, 23, 1191–1197.
- 23. Raman, N.; Kulandaisamy, A.; Thangarja, C. Trans. Met. Chem. 2003, 28, 29-36.
- Al-Hazmi, G. A. A.; El-Shahawi, M. S.; Gabr, I. M.; El-Asmy, A. A. J. Coord. Chem. 2005, 58, 713–733.
- 25. Chandra, S.; Saneetika, X. Spectrochim. Acta 2004, 60, 147–153.
- 26. West, D. X.; Salberg, M. M.; Bain, G. A.; Liberta, A. E. Trans. Met. Chem. 1997, 22, 180-184.
- Mostafa, S.; Bekheit, M. M.; El-Agez, M. M. Synth. React. Inorg. Met.-Org. Chem. 2000, 30, 2029–2049.
- 28. El-Metwally, N. M.; El-Shazly, R. M.; Gabr, I. M.; El-Asmy, A. A. Spectrochim. Acta 2004, 61, 1113–1119.
- 29. Lever, A. B. P. Inorganic Electronic Spectroscopy; Elsevier: Amsterdam, 1968.
- 30. Sacconi, L. Trans. Met. Chem. 1979, 4, 199.
- 31. Bhattacharya, R. G.; Bera, D. C. J. Ind. Chem. Soc. 1975, 52, 373.
- 32. Behave, N. S.; Kharat, R. B. J. Inorg. Nucl. Chem. 1980, 42, 977-983.
- 33. Babar, V. J.; Shinde, V. M. Ind. J. Chem. 1983, 22, 447.
- 34. Speier, G.; Csihony, J.; Whalen, A. M.; Pie-pont, C. G. Inorg. Chem. 1996, 35, 3519–3524.
- 35. Hathaway, B. J.; Billing, D. E. Coord. Chem. Rev. 1970, 5, 143-207.
- 36. Mesa, J. L.; Pizarro, J. L.; Arriortua, M. I. Cryst. Res. Technol. 1998, 33, 489-495.
- 37. Kasumo, V. T. Spectrochim. Acta A 2001, 57, 1649.
- 38. Wellman, J. A.; Hulsbergen, F. B. J. Inorg. Nucl. Chem. 1978, 40, 143-158.
- 39. Ray, R. K.; Kauffman, G. R. Inorg. Chim. Acta 1990, 173, 207–214.
- Jayasubramanian, K.; Samath, S. A.; Thambidurai, S.; Murugesan, R.; Ramalingam, S. K. *Trans. Met. Chem.* 1995, 20, 76–80.
- 41. Anthonisamy, V. S. X.; Murugesan, R. Chem. Phys. Lett. 1998, 287, 353-358.
- 42. Anthonisamy, V. S. X.; Anantharam, R.; Murugesan, R. Spectrochim. Acta A 1999, 55, 135–142.
- 43. Kiverlson, D.; Lee, S. K. J. Chem. Phys. 1964, 41, 1896–1903.
- 44. Karabulut, B.; Tufan, A. Spectrochim. Acta A 2006, 65, 742-748.
- 45. Warad, D. U.; Statish, C. D.; Kulkarni, V. H.; Bajgur, C. S. Ind. J. Chem. 2000, 39, 415–420.
- 46. Rakha, T. H.; Ibrahim, K. M.; Khalifa, M. E. Thermochim. Acta 1989, 144, 53-63.
- 47. Rakha, H.; Bekheit, M. M.; El-Agez, M. M. Synth. React. Inorg. 1999, 29, 449-472.
- 48. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68-69.
- 49. Kandil, S. S.; El-Hefnawy, G. B.; Baker, E. A. Thermochim. Acta 2004, 414, 105-113.
- 50. Vogel, A. I. Quantitative Inorganic Analysis; Longmans: London, 1989.
- Gerhardt, P. Manual of Methods for General Bacteriology; American Society for Microbiology: Washington, DC, 1981.