Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, spectroscopic characterization and thermal behavior of metal complexes formed with (*Z*)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-N-phenylacetamide (H₂OI)

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ARTICLE INFO

Article history: Received 25 May 2011 Received in revised form 26 September 2011 Accepted 18 October 2011 Available online 26 October 2011

Keywords: Hydrazone derivatives Metal complexes Thermal analysis PM3

ABSTRACT

Complexes of Co(II), Ni(II), Cu(II), Cd(II), Zn(II) and U(IV)O₂ with (*Z*)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-*N*-phenylacetamide (H₂OI) are reported and have been characterized by various spectroscopic techniques like (IR, UV–Vis, ESR ¹H and ¹³C NMR) as well as magnetic and thermal (TG and DTA) measurements. It is found that the ligand behaves as a neutral tridentate, neutral tetradentate, monoanionic tridentate and dianionic tridentate. An octahedral geometry for all complexes except [Cu₂(H₂OI)(OAc)₄](H₂O)₂ and [Cu(HOI)Cl](H₂O)₂ which have a square planar geometry. Furthermore, kinetic parameters were determined for each thermal degradation stage of some studied complexes using Coats–Redfern and Horowitz–Metzger methods. The bond lengths, bond angles, HOMO, LUMO and dipole moments have been calculated to confirm the geometry of the ligand and the investigated complexes.

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1. Introduction

The hydrazones and their metal complexes have many important applications in analytical chemistry and pharmacology [1-3]. The biological activity of hydrazones becomes more carcinostatic and bacteriostatic upon chelation [2,4]. The hydrazones derived from simple aldehyde and ketones were reported [5-7].

Isatin is chemically 1H-indole-2,3-dione and is a versatile lead molecule for potential bioactive agents and its derivatives were reported to poss wide spectrum of activity like antibacterial [8], antifungal [9], anticonvulsant [10], antiHIV [11], antidepressant [12] and anti-inflammatory [13].

We were thus motivated to undertake a systematic study of preparation and characterization of transition metal complexes formed with (*Z*)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-*N*-phenylacetamide (H₂OI) and Co(II), Ni(II), Cu (II), Cd(II), Zn (II) and U(IV)O₂ ions.

2. Experimental

2.1. Physical measurements

All the chemicals were purchased from Aldrich and Fluka and used without further purification. Elemental analyses (C, H and

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N) were performed with a Perkin-Elmer 2400 series II analyzer. IR spectra (4000-400 cm⁻¹) for KBr discs were recorded on a Mattson 5000 FTIR spectrophotometer. Electronic spectra were recorded on a Unicam UV-Vis spectrophotometer UV2. Magnetic susceptibilities were measured with a Sherwood scientific magnetic susceptibility balance at 298 K. ¹H and ¹³C NMR measurements in DMSO at room temperature were carried out an EM-390 (200 MHz) spectrometer. Thermogravimetric measurements (TGA, DTA, 20-800 °C) were recorded on a DTG-50 Shimadzu thermogravimetric analyzer at a heating rate of 10 °C/min and nitrogen flow rate of 20 ml/min. ESR spectra were obtained on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power and modulation amplitudes were set at 1 mW and 4 Gauss, respectively. The low field signal was obtained after four scans with 10-fold increase in the receiver again. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

2.2. Synthesis of (Z)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-N-phenylacetamide (H₂OI)

(Z)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-*N*-phenyl-acetamide (H₂OI) was synthesized according to the following scheme:

The pale yellow precipitate (H_2OI) was filtered off, washed several times with ethanol and recrystallized from hot ethanol





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(Z)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-N-phenylacetamide

(H₂OI)

and finally dried in vacuum desiccators over an hydrous ${\rm CaCl}_2$ (m.p. 315 °C).

2.3. Synthesis of metal complexes

A hot ethanolic solution of the respective metal chlorides or acetates Co(II), Ni(II), Cu(II), Cn(II), Zn(II) and $U(VI)O_2$ (1.0 mmol) was added to a hot ethanolic solution of H_2OI (0.308 g, 1.0 mmol). The resultant mixture was heated under reflux for 2–3 h. The formed precipitates were filtered off, washed with ethanol followed by diethyl ether and dried in a vacuum desiccator over

anhydrous CaCl₂. The physical and analytical data of the isolated complexes are listed in Table 1. The complexes have high melting points and insoluble in common organic solvents; soluble in DMSO and DMF and found to be non-electrolytes.

2.4. Molecular modeling

An attempt to gain a better insight on the molecular structure of the ligand and its complexes, geometry optimization and conformational analysis has been performed using MM + force-field as implemented in hyperchem 8.03 [14]. The low lying obtained from

Table 1

Analytical and physical data of H2OI and its metal complexes.

Compound	Color	MP (°C)	Yield (%)	% Found (Calc.	% Found (Calc. d)			
Empirical formula (F.Wt.)				С	Н	Ν	М	Cl
H ₂ OIC ₁₆ H ₁₂ N ₄ O ₃ (308.29)	Yellow	315	92	63.42 (63.33)	4.1 (3.9)	18.2 (18.7)	_	_
[Co(OI)(H ₂ O) ₃]C ₁₆ H ₁₆ N ₄ CoO ₆ (419.25)	Red	>300	85	45.35 (45.8)	3.75 (3.8)	13.8 (13.4)	13.9 (14.1)	-
[Cu ₂ (H ₂ OI)(OAc) ₄](H ₂ O) ₂ C ₂₄ H ₂₈ Cu ₂ N ₄ O ₁₃ (707.59)	Brown	>300	85	41.72 (40.74)	3.95 (3.98)	7.75 (7.92)	17.5 (17.9)	-
[Cu(HOI)Cl](H ₂ O) ₂ C ₁₆ H ₁₅ ClCuN ₄ O ₅ (377.76)	Dark yellow	>300	85	51.2 (50.9)	3.87 (4.0)	14.67 (14.8)	13.4 (13.8)	9.64 (9.38)
[Ni(OI)(H ₂ O) ₃]C ₁₆ H ₁₆ N ₄ O ₆ Ni (419.02)	Dark orange	>300	86	45.6 (45.8)	3.7 (3.8)	13.6 (13.4)	13.72 (14.0)	-
[Ni(H ₂ OI)(OAc) ₂ (H ₂ O)]C ₂₀ H ₂₀ NiN ₄ O ₈ (503.08)	Brown	>300	86	47.6 (47.7)	4.19 (4.0)	11.3 (11.1)	11.5 (11.7)	-
$[Zn(HOI)(OAc)(H_2O)]C_{18}H_{16}ZnN_4O_6$ (448.72)	Dark yellow	>300	82	48.06 (48.2)	3.2 (3.4)	12.43 (12.5)	15.2 (14.6)	-
[Cd(H ₂ OI)(OAc) ₂ (H ₂ O)]C ₂₀ H ₂₀ CdN ₄ O ₈ (556.81)	Brown orange	>300	72	43.2 (43.1)	3.55 (3.6)	10.23 (10.1)	20.64 (20.2)	-
[UO ₂ (HOI)(OAc)(H ₂ O) ₂]C ₁₈ H ₁₈ UN ₄ O ₉ (672.39)	Orange	>300	88	31.98 (32.2)	2.55 (2.7)	8.45 (8.33)	35.3 (35.4)	-



Structure 1.

Table 2IR spectral bands of H_2OI and its metal complexes (cm⁻¹).

Compound	v(CN) ^a	v(C=0) ^{is}	v(C=0) ⁽⁵⁾	v(C=0) ⁽⁶⁾	v(NH) ^(1,2)	v(NH) ^{is}	v(C=N) ^b	v(N—N)	v(CO)	v(M0)	v(M—N)
H ₂ OI	1619	1740	1710	1684	3205	3290	-	950	-	-	-
$[Cd(H_2OI)(OAc)_2(H_2O)]$	1638	1690	1667	1682	3202	3291	-	965	-	520	460
$[Ni(H_2OI)(OAc)_2(H_2O)]$	1630	1691	1668	1685	3203	3291	-	930	-	518	463
$[Cu_2(H_2OI)(OAc)_4](H_2O)_2$	1602	1692	1687	1665	3208	3292	-	937	-	522	473
[Cu(HOI)Cl](H ₂ O) ₂	1610	-	1675	1683	3208	-	1635	932	1110	521	475
$[Zn(HOI)(OAc)(H_2O)_2]$	1609	-	1665	1681	3206	-	1643	940	1127	523	478
$[Co(OI)(H_2O)_3]$	1611	-	-	1682	-	-	1640	980	1095	526	465
$[Ni(OI)(H_2O)_3]$	1629	-	-	1682	-	-	1640	970	1198	520	467
[UO ₂ (HOI)(OAc)(H ₂ O) ₂]	1610	-	1708	1686	3204	-	1642	921	1090	517	470

^a Azomethine.

^b New. ^{is} Isatin.

¹³ Isatin.

MM+[15] was then optimized at PM3 using the Polak–Ribiere algorithm in RHF–SCF, set to terminate at an RMS gradient of 0.01 kcal mol⁻¹.

3. Results and discussion

The data of elemental analysis together with some physical properties of the complexes are summarized in Table 1.

3.1. IR and ¹H NMR Spectra

The most important infrared bands of H₂OI (Structure 1) and its metal complexes are listed in Table 2. The IR spectrum of H₂OI displays four bands at 1740, 1710, 1684, 1619, 3205 and 3290 cm⁻¹ assigned to $v(C=O)^{(is)}$, $v(C=O)^{(5)}$, $v(C=O)^{(6)}$, v(C=N) [16], $v(NH)^{(1,2)}$ and $v(NH)^{(4)}$ [17], respectively. Only one band is appeared related to both $v(C=O)^{(5)}$ and $v(C=O)^{(6)}$ groups.

In $[Cd(H_2OI)(OAc)_2(H_2O)]$ and $[Ni(H_2OI)(OAc)_2(H_2O)]$ (Structure 2) complexes, the ligand H₂OI acts as a neutral tridentate coordinating via carbonyl oxygen (C=O)^(is), carbonyl oxygen (C=O)⁽⁵⁾ and azomethine nitrogen (C=N) groups. This mode of complexation is supported by: (i) shift of v(C=O)^(is) and v(C=O)⁽⁵⁾ to lower wavenumbers. (ii) shift of v(C=N) and v(N–N) to higher wavenumber. Moreover, the infrared spectra of these complexes showed



Structure 2.

new bands at (520,518) and (460,463) cm⁻¹ assignable to v(M-O) and v(M-N), respectively [18]. In addition, the bands of coordinated water observed at (820,840) and (533,549) cm⁻¹,



are assigned to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively [19]. Moreover, strong evidence for the presence or absence of coordinated water supported by the thermogram of all complexes.

In the binuclear copper complex namely $[Cu_2(H_2OI)(OA-c)_4](H_2O)_2$ (Structure 3), the ligand H₂OI behaves as a neutral tetradentate coordinating via carbonyl oxygen of both $v(C=O)^{(5)}$, $v(C=O)^{(6)}$, carbonyl oxygen $v(C=O)^{(is)}$ and azomethine nitrogen (C=N) groups. This mode of complexation is supported by the shift of both $v(C=O)^{(5)}$, $v(C=O)^{(6)}$, $v(C=O)^{(is)}$, v(N-N) and v(C=N) to lower wavenumbers, Moreover, the infrared spectrum of the complex showed new bands at 522 and 473 cm⁻¹ assignable to v(M-O) and v(M-N) respectively [18]. Moreover two new bands at 1381 and 1580 cm⁻¹, attributable to vs(O-C-O) and vas(O-C-O) of acetate group, the difference (199 cm⁻¹) between those two bands indicates that the acetate group is monodentate [20].

In $[Cu(HOI)CI](H_2O)_2$ (Structure 4) and $[Zn(HOI)(OAc)(H_2O)_2]$ complexes the ligand H₂OI acts as a mononegative tridentate via enolic carbonyl oxygen $(C=O)^{(is)}$, carbonyl oxygen $(C=O)^{(1)}$ and azomethine nitrogen (C=N) groups. This mode of complexation is supported by the following observations: (i) The disappearance of $v(C=0)^{(is)}$ and $v(NH)^4$ with simultaneous appearance of new bands in the 1110–1127 cm^{-1} region and at 1635–1641 cm^{-1} which assignable to v(C=0) and $v(C=N^*)$ respectively. (ii) The v(C=N) is shifted to higher wavenumber. (iii) The $v(C=O)^{(5)}$ and v(N–N) are shifted to lower wavenumber. Moreover, the infrared spectra of these complexes showed new bands at (521,523) and (475,478) cm⁻¹ assignable to v(M-O) and v(M-N), respectively [18]. In addition, the bands of coordinated water observed at 830 and 541 cm⁻¹, are assigned to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively, in case of zinc complex [19]. Moreover, strong evidence for the presence or absence of coordinated water supported by the thermogram of all complexes.

In $[Co(OI)(H_2O)_3]$ (Structure 5) and $[Ni(OI)(H_2O)_3]$ complexes the ligand H_2OI acts as a binegative tridentate coordinating via enolic carbonyl oxygen (C=O)^(is), enolic carbonyl oxygen (C=O)⁽¹⁾



Structure 5.



and azomethine nitrogen (C=N) groups. This mode of complexation is suggested by the following observations: (i) The disappearance of both $v(C=O)^{(is)}$, $(C=O)^{(5)}$ and $v(NH)^4$ with simultaneous appearance of new bands in the $1095-1136 \text{ cm}^{-1}$ region and at 1629–1640 cm⁻¹ which may be assigned to v(C-O) and $v(C=N^*)$. respectively. (ii) The v(C=N) is shifted to lower wavenumber in case of $[Co(OI)(H_2O)_3]$ complex while shifted higher wavenumber in case of $[Ni(OI)(H_2O)_3]$ complex. (iii) shift of v(N-N) to higher wavenumber. Moreover, the infrared spectra of these complexes showed new bands at (526, 520) and (465, 467) cm⁻¹ assignable to v(M-O) and v(M-N), respectively [18]. In addition, the bands of coordinated water observed at (825,837) and (544,549) cm⁻¹,

are assigned to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively [19]. Furthermore, strong evidence for the presence or absence of coordinated water supported by the thermogram of all complexes.

In [UO₂(HOI)(OAc)(H₂O)](H₂O) complex (Structure 6) H₂OI acts as a mononegative bidentate ligand coordinating via enolic carbonyl oxygen $(C=O)^{(is)}$ and azomethine nitrogen (C=N) groups. This mode of complexation is supported by the following observations: (i) The disappearance of $v(C=O)^{(is)}$ and $v(NH)^4$ with simultaneous appearance of new bands in the 1090 cm^{-1} region and at 1642 cm⁻¹ which may be assigned to v(C-O) and $v(C=N^*)$, respectively. (ii) The v(C=N) and v(N-N) are shifted to lower wavenumber. Moreover, the infrared spectrum of the complexes showed new bands at 517 and 470 cm⁻¹ assignable to v(M-O) and v(M–N), respectively [18]. In addition, the bands of coordinated water observed at 844 and 542 cm⁻¹, are assigned to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively [19]. Furthermore, strong evidence for the presence or absence of coordinated water supported by the thermogram of all complexes.

The uranyl complex exhibits three bands at 921, 840 and 265 cm⁻¹, assigned to v_3 , v_1 and v_4 vibrations, respectively, of the dioxouranium ion [21]. The v_3 value is used to calculate the force constant (F) of v(U=O) by the method of McGlynn and Smith [22]:

$$(v_3)^2 = (1307)^2 (Fu-o)/14.103$$

The force constant obtained for uranyl complex was then substituted into the relation given by Jones [21]:

$$Ru-o = 1.08(Fu-o)^{-1/3} + 1.17$$

To give an estimate of the U–O bond length in Å. The calculated Fu-o and Ru-o values are 7.1 mdynes $Å^{-1}$ and 1.75 Å, respectively, fall in the usual range for the uranyl complexes [22]. The U-O bond distance falls in usual region as reported earlier [23] and extremely is consistent with the bond length calculated by the use of MM + force field (as implemented in hyperchem 8.03) [15].



Fig. 1. ¹H NMR spectrum of H₂OI.

3.2. Nuclear magnetic resonance spectral studies

The ¹H and ¹³C NMR spectra of H₂OI (Figs. 1 and 2) and its Cd(II) and U(VI)O₂ complexes were recorded in DMSO. The ¹H NMR spectrum of H₂OI in DMSO shows three signals at 11.35, 11.30 and 11.04 ppm assignable to the protons of $(NH)^1$, $(NH)^2$ and $(NH)^4$, respectively. The appearance of the signal of (NH)¹ and (NH)² at high value downfield from TMS suggests the presence of intramolecular hydrogen bonding. The multiplet signals observed in the 7.16–7.65 ppm region are assigned to the aromatic protons (Table 3). Also, the ¹H NMR spectrum of $[Cd(H_2OI)(OAc)_2(H_2O)]$ complex in DMSO shows three signals at 10.22, 10.01 and 9.87 ppm assignable to the protons of (NH)¹, (NH)² and (NH)⁴, respectively, indicating that these groups play no part in coordination. Finally, the ¹H NMR spectrum of [UO₂(HOI)(OAc)(H₂O)](H₂O) complex in DMSO shows two signals at δ = 11.05 and 8.15 ppm relative to TMS which may be assigned to (NH)^(1,2) amide protons. The NH proton shifted to higher field region than of the free ligand due to the absence of hydrogen bond. The NH proton is disappeared due to the enolization of (CO)^(is). From ¹³C NMR spectrum data (Table 4), for the cadmium complex, the signals for the $(C-O)^{is}$ carbon and $(C-O)^{(5)}$ carbon showed an downfield shift on complexation [24] while, C-N carbon showed an upfield shift on complexation compared with the free ligand. But in case of uranyl complex the signals for the (C-O)^{is} carbon showed an downfield shift on complexation while, C-N carbon showed an upfield shift on complexation compared with the free ligand. Furthermore, the appearance of new signals at δ = 179 ppm and δ = 53 ppm give strong evidence for the presence of the acetate group. The other ring carbon atoms did not show significant shifts.

3.3. Electronic spectra and magnetic moments

The magnetic moments, electronic spectral bands in DMSO and ligand field parameters of metal complexes are collected in Table 5.



Table 3

The ¹H NMR spectral data of H₂OI and its diamagnetic complexes.

Compound	$\rm NH^1$	NH ²	NH ⁴	Aromatic protons
H ₂ OI	11.04	11.3	11.35	7.16–7.65
[Cd(H ₂ OI)(OAc) ₂ (H ₂ O)]	8.87	9.01	9.22	7.13–7.87
[UO ₂ (HOI)(OAc)(H ₂ O) ₂]	11.05	8.15	-	6.94–7.92

Table 4

¹³C NMR chemical shifts in (ppm) assignments for H₂OI and its diamagnetic complexes.

Compound	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
H ₂ OI	115	145	165	134	156	158
[Cd(H ₂ OI)(OAc) ₂ (H ₂ O)]	114	143	176	124	168	160
[UO ₂ (HOI)(OAc)(H ₂ O) ₂]	112	142	174	125	160	162

Table 5

Magnetic moment, electronic bands and ligand field parameters of the complexes derived from H₂OI.

Compound	Band position (cm ⁻¹) (molar extinction coefficient, ϵ , L mol ⁻¹ cm ⁻¹)	D_{q}	В	β	µeff (B.M.)
[Co(OI)(H ₂ O) ₃]	16,949(1146), 17,730(1330), 18,868(1604), 21,186(615), 22,124(401), 24,272(98)	918.6	957	0.85	4.55
$[Ni(OI)(H_2O)_3]$	16,667(940), 17,730(1173), 18,727(1585), 20,408(861), 23,148(532), 24,937(311)	1029	1012	0.97	2.82
$[Ni(H_2OI)(OAc)_2(H_2O)]$	14,599(820), 17,212(1189), 18,215(1429), 20,833(765), 23,041(473), 25,510(284)	1054	1006	0.96	3.22
$[Cu(HOI)Cl](H_2O)_2$	14,085(1243), 18,083(1580), 19,268(2535), 20,325(1769)	-	-	-	2.1
$[Cu_2(H_2OI)(OAc)_4](H_2O)_2$	17,331(1117), 17,953(1379), 19,685(1730), 21,222(628)	-	-	-	1.41

Table 6

ESR data of the Copper (II) complexes at room temperature.

Complex	g_{\parallel}	g_{\perp}	A_{\parallel} (cm ⁻¹)	G	$g_{\parallel}/A_{\parallel}$	α^2	β^2
[Cu ₂ (H ₂ OI)(OAc) ₄](H ₂ O) ₂	2.20	2.05	-	3.7	-	-	-
[Cu(HOI)CI](H ₂ O) ₂	2.26	2.08	174	3.2	130	0.81	0.7

The electronic spectrum of $[Co(OI)(H_2O)_3]$ complex exhibits two bands at 16,949 and 18,868 cm⁻¹ attributed to ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions, respectively, in an octahedral configuration [25]. The calculated D_q , B and β values are in the range reported for an octahedral environment around Co(II) complexes. Also, the value of the magnetic moment (4.55 B.M.) is additional evidence for an octahedral geometry around the Co(II) ion.

The electronic spectra of $[Ni(OI)(H_2O)_3]$ and $[Ni(HOI)(OAc)_2]$ complexes are consistent with octahedral geometry showing two d-d transition bands in the 16,667–17,212 and 23,148–25,510 cm⁻¹ regions, assignable to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ (ν 2) and ${}^{3}A_{2g} \rightarrow {}^{4}T_{1g}(P)$ (ν 3) transitions, respectively [26,27]. The ligand field parameters, $\nu 2/\nu 1$ and the magnetic moment values lie in the range of octahedral structures.

The electronic spectrum of [Cu(HOI)Cl](H₂O)₂ complex exhibits two bands at 14,085 and at 20,325 cm⁻¹ regions. The first is centered at 14,085 cm⁻¹ and the other, which is more intense, is centered at 20,325 cm⁻¹. The band at 20,325 cm⁻¹ may be assigned to a symmetry-forbidden ligand \rightarrow metal charge transfer band [28–30] and band at 14,085 cm⁻¹ is assigned to the d-d transition corresponding to ${}^{2}T_{2g} \rightarrow {}^{2}Eg$; the band position is in agreement with those generally observed for planar copper(II) complexes.

The electronic spectrum of $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ complex show bands at 17,331, 17,953, 19,685, and 21,222 cm⁻¹ regions, suggesting square-planar geometry [31]. The lowering in µeff (1.41) of binuclear copper(II) complex may be attributed to the covalent nature of the copper-copper bond.

Finaly the U.V. spectrum of the $[UO_2(HOI)(OAc)(H_2O)_2]$ shows a band at 24,096 cm⁻¹ assinged to $1\Sigma g + \rightarrow 3\pi 4$. This band is similar to the OUO symmetric stretching frequency for the first excited state [32].

3.4. ESR spectra

The room temperature solid state ESR spectra of the copper complexes exhibit an axially symmetric *g*-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating that the copper site has a dx^2-y^2 ground-state characteristic of square planar or octahedral stereo-chemistry [33]. In axial symmetry, the *g*-values are related by the expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$. According to Hathaway [34], as value of G is greater than 4, the exchange interaction between copper (II) centers in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction is indicated in the solid complex. The calculated G values for the copper complexes except less than 4 suggesting copper–copper exchange interactions (Table 6). A forbidden magnetic dipolar transition for $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ is observed at half-field (ca. 1600 G, $g \approx 4.0$) but the intensity is very weak. The present ESR spectra

are similar to the ESR spectra of the reported binuclear Cu(II) complexes [35]. The appearance of the half-field signal confirms that the complex $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ has a binuclear unit that there exist a magnetic interaction between the two Cu(II) ions and in accordance with the subnormal effective magnetic moment.

The ESR spectra of $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ exhibit broad single line, nearly isotropic signal centered at g = 2.08 (Fig. 3) is attributable to dipolar broadening and enhanced spin lattice relaxation



Fig. 3. ESR spectra of (a) $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ and (b) $[Cu(HOI)CI](H_2O)_2$ at room temperature.

[36]. This line broadening is probably due to insufficient spin-exchange narrowing toward the coalescence of four copper hyperfine lines to a single line. Note that, the same kind of powder ESR line shapes; have also been observed for many tetrahedral or square planar binuclear Cu(II) complexes with a considerably strong intranuclear spin-exchange interaction [37].

An index of the increase of the tetrahedral distortion in the coordination sphere of copper is the decrease of A_{\parallel} with the increase of g_{\parallel} [38]. To quantify the degree of distortion of the Cu(II) complexes, the *f*-factor $g_{\parallel}/A_{\parallel}$ was calculated which is considered as an empirical index of tetrahedral distortion [39]. Its value ranges between 105 and 135 for square planar complexes, depending on the nature of the coordinated atoms. In the presence of a distorted tetrahedral structure, the values can be much larger [38]. In case of [Cu(HOI)CI](H₂O)₂ the value is 125 is evidence in support of the square planar geometry with no appreciable tetrahedral distortion. Molecular orbital coefficients, α^2 (a measure of the covalency of the

in-plane σ -bonding between a copper 3d orbital and the ligand orbitals) and β^2 (covalent in-plane π -bonding), were calculated by using the following equations [39–41]:

$$\begin{aligned} \alpha^2 &= (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04 \\ \beta^2 &= (g_{\parallel} - 2.0023)E/ - 8\lambda\alpha^2 \end{aligned}$$

where $\lambda = -828$ cm⁻¹ for the free copper ion and *E* is the electronic transition energy.

The covalency of the in-plane σ -bonding, $\alpha^2 = 1$ indicates complete ionic character, whereas $\alpha^2 = 0.5$ denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral. The β^2 parameter gives an indication of the covalency of the in-plane π -bonding. The smaller the β^2 the larger is the covalency of the bonding.

The values of α^2 and β^2 for the complexes indicate that the inplane σ -bonding and in-plane π -bonding are appreciably covalent,

Table 7	
The mole	(

The assignment of the theoretical parameters	The compound investigated	The theoretical data
Total energy Total energy Binding energy Isolated atomic energy Electronic energy Core-core interaction Heat of formation Dipole moment Homo Lumo	H ₂ OI	=-83217.3495906 (kcal/mol) =-132.615271563 (a.u.) =-4001.9382726 (kcal/mol) =-79215.4113180 (kcal/mol) =-560381.4220464 (kcal/mol) =477164.0724559 (kcal/mol) =-11.7972726 (kcal/mol) =1.893 (Debys) =-9.075751 =-1.121118
Total energy Total energy Binding energy Isolated atomic energy Electronic energy Core-core interaction Heat of formation Dipole moment Homo Lumo	[Co(OI)(H ₂ O) ₃]	=-123681.9579372 (kcal/mol) =-197.099721632 (a.u.) =-5009.4754122 (kcal/mol) =-118672.4825250 (kcal/mol) =-916678.9720145 (kcal/mol) =792997.0140773 (kcal/mol) =-477.7474122 (kcal/mol) =6.191 (Debys) =-0.07390385 =-8.95602
Total energy Total energy Binding energy Isolated atomic energy Electronic energy Core-core interaction Heat of formation Dipole moment Homo Lumo	[Ni(H ₂ OI)(OAc) ₂ (H ₂ O)]	=-155074.6517950 (kcal/mol) =-247.127157515 (a.u.) =-6026.9580220 (kcal/mol) =-149047.6937730 (kcal/mol) =11299189.8594042 (kcal/mol) =1144115.2076092 (kcal/mol) =-535.8460220 (kcal/mol) =6.837 (Debys) =-8.243506 =-1.122439
Total energy Total energy Binding energy Isolated atomic energy Electronic energy Core-core interaction Heat of formation Dipole moment Homo Lumo	[Cu(HOI)Cl](H ₂ O) ₂	=-117481.4214018 (kcal/mol) =-187.218538916 (a.u.) =-4090.8072558 (kcal/mol) =-113390.6141460 (kcal/mol) =-774194.8447954 (kcal/mol) =656713.4233936 (kcal/mol) =-43.0782558 (kcal/mol) =9.884 (Debys) =-5.455019 =-2.084122
Total energy Total energy Binding energy Isolated atomic energy Electronic energy Core-core interaction Heat of formation Dipole moment Homo Lumo	[Cu ₂ (H ₂ OI)(OAc) ₄](H ₂ O) ₂	=-218304.3220777 (kcal/mol) =-347.890038533 (a.u.) =-7154.5314157 (kcal/mol) =-211149.7906620 (kcal/mol) =-1865623.4495558 (kcal/mol) =1647319.1274780 (kcal/mol) =-534.1744157 (kcal/mol) =8.264 (Debys) =-9.32396 =-1.576875

and are consistent with very strong in-plane σ -bonding in these complexes. For the copper (II) complexes, the high values of β^2 compared to α^2 indicate that the in-plane π -bonding is less covalent than the in-plane σ -bonding. These data are well consistent with other reported values [40–43].

3.5. Molecular modeling

 H_2OI and its complexes are shown in (Structures 1–6). Analysis of the data in Tables (1S–12S) (Supplementary Materials) calculated for the bond lengths and angles for the bond, one can conclude the following remarks:

- 1. The lower HOMO energy values show that molecules donating electron ability is the weaker. On contrary, the higher HOMO energy implies that the molecule is a good electron donor. LUMO energy presents the ability of a molecule receiving electron [44] (Table 7).
- 2. The bond angles of the hydrazone moiety are altered somewhat upon coordination; the largest change affects C4—C2—O3 angle which are change from 127.5° on ligand to 119.6° on complexes as a consequence of bonding in case of [Cu(HOI)CI](H₂O)₂

Table	8
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TGA and DTA data for metal complexes.

complex while in case of $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ complex the largest change affects N12–N5–C4 from 117.4° to 127.9° finally in case of $[Co(OI)(H_2O)_3]$ complex the largest change affects O(22)–C(14)–N(15) from 128.7° to 119.5°.

- 3. All bond angles in Co, Ni complexes are quite near to an octahedral geometry predicting sp^3d^2 hybridization.
- 4. The bond angles in complexes namely $[Cu(HOI)CI](H_2O)_2$ and $[Cu_2(H_2OI)(OAc)_4](H_2O)_2$ are quite near to a square planar geometry predicting dsp² hybridization
- 5. All the active groups taking part in coordination have bonds longer than that already exist in the ligand (like N—H and C—O).
- There is a variation in C14—O22 bond lengths on complexation. It becomes slightly longer as the coordination takes place via O atoms of C—O group that is formed on deprotonation of C—OH.
- 7. There is a large variation in N5—N12 bond lengths on complexation. It becomes longer as the coordination takes place via N11 atom of azomethine group.

3.6. Thermal analysis

The TG–DTA results for solid complexes are depicted in Table 8. The results are in good agreement with the proposed formulae. Ta-

Compound	Temp. range (°C)	% Weight loss		Assignment
		Found	Calcd.	
[Co(OI)(H ₂ O) ₃]	130–190 190–800	12.81	12.89	Loss of 3 mol of coordinated water Start of deligation
$[Cu_2(H_2OI)(OAc)_4](H_2O)_2$	75–110	5.13	5.09	Loss of 2 mol of hydrated water
	110–315	8.73	8.79	Loss of 4 coordinated acetate group
	315–800	-	-	deligation
[Cu(HOI)Cl](H ₂ O) ₂	77–110	7.87	7.83	Loss of 2 mol of hydrated water
	110–255	8.31	8.35	Loss of 1 coordinated chloride ions
	255–800	-	-	deligation
[Ni(OI)(H ₂ O) ₃]	140–190 190–800	12.84	12.9	Loss of 3 mol of hydrated water Start of deligation
[Zn(HOI)(OAc)(H ₂ O)]	105–185	4.04	4.01	Loss of 1 mol of coordinated water
	185–295	13.78	13.70	Loss of 1 coordinated acetate group
	295–800	-	-	deligation
[Cd(H ₂ OI)(OAc) ₂ (H ₂ O)]	110–185	3.28	3.24	Loss of 1 mol of coordinated water
	185–305	21.85	21.91	Loss of 2 coordinated acetate group
	305–800	-	-	deligation
[UO ₂ (HOI)(OAc)(H ₂ O) ₂]	110-200	5.29	5.23	Loss of 2 mol of coordinated water
	200-315	9.11	9.05	Loss of 1 coordinated acetate group
	315-800	-	-	deligation
[Ni(H ₂ OI)(OAc) ₂ (H ₂ O)]	105–190	3.52	3.58	Loss of 1 mol of coordinated water
	190–315	24.02	24.35	Loss of 2 coordinated acetate group
	315–800	-	-	deligation

Table 9

Kinetic parameters of complexes evaluated by Coats-Redfern equation.

Compound	Peak	Mid temp. (K)	$E_{\rm a}$ (kJ/mol)	$A(S^{-1})$	ΔH^* (kJ/mol)	ΔS^* (kJ/mol K)	ΔG^* (kJ/mol)
[Co(OI)(H ₂ O) ₃]	1st	313	49.40	$\textbf{4.33}\times \textbf{10}^{4}$	46.79	-0.1565	95.85
	2nd	533	56.24	$1.70 imes 10^5$	52.06	-0.1491	127.05
	3rd	696	56.79	4.72×10^{5}	51.01	-0.1433	150.77
	4rd	937	99.44	7.82×10^{5}	91.64	-0.1416	224.45
[Ni(OI)(H ₂ O) ₃]	1st	337	35.51	$\textbf{4.27}\times\textbf{104}$	32.70	-0.1572	85.78
	2nd	547	31.91	$1.73 imes 10^5$	27.36	-0.1496	109.32
	3rd	762	137.35	$2.23 imes 10^6$	131.01	-0.1311	231.04
	4th	869	169.98	$\textbf{7.34}\times 10^5$	162.75	-0.1415	285.85
[Cu(HOI)Cl](H ₂ O) ₂	1st	547	167.08	$\textbf{5.06}\times \textbf{10}^{5}$	162.53	-140.75	239.56
	2nd	677	72.41	$4.06 imes 10^5$	66.78	-0.1443	164.52
	3rd	852	139.03	1.14×10^7	131.94	-0.1185	233.00

ble 6 concludes that there is a general decomposition pattern, whereby, the complexes decompose in three main stages. The first stage for all studied complexes is the loss of hydrated water molecules at 75-110 °C, followed in a second decomposition stage by the loss of the coordinated water, chloride or acetate ions at 110-315 °C, after that, the deligation process started at a temperature range of 190–800 °C, finally metal oxide formation takes place.

3.7. Kinetic data

The kinetic and thermodynamic parameters of thermal degradation process have been calculated using Coats-Redfern and

 Table 10
 Kinetic parameters of complexes evaluated by Horowitz-Metzger equation.

Horowitz–Metzger models [45,46]. Coats–Redfern relation is as follows:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$
(1)

where α represents the fraction of sample decomposed at time *t*, defined by: $\alpha = \frac{w_o - w_t}{w_o - w_c}$, w_o , w_t and w_∞ are the weight of the sample before the degradation, at temperature *t* and after total conversion, respectively. *T* is the derivative peak temperature. β is the heating rate = dT/dt, *E* and *A* are the activation energy and the Arrhenius pre-exponential factor, respectively. A plot of $\ln \left[-\frac{\ln(1-\alpha)}{T^2}\right]$ versus 1/T gives a straight line whose slope (E/R) and the pre-exponential factor (A) can be determined from the intercept.

Compound	Peak	Mid temp. (K)	$E_{\rm a}$ (kJ/mol)	$A(S^{-1})$	ΔH^* (kJ/mol)	ΔS^* (kJ/mol K)	ΔG^* (kJ/mol)
[Co(OI)(H ₂ O) ₃]	1st	313	49.40	$\textbf{4.33}\times 10^4$	46.79	-0.1565	95.85
	2nd	533	56.24	1.70×10^{5}	52.06	-0.1491	127.05
	3rd	696	56.79	4.72×10^{5}	51.01	-0.1433	150.77
	4rd	937	99.44	7.82×10^5	91.64	-0.1416	224.45
[Ni(OI)(H ₂ O) ₃]	1st	337	35.98	$\textbf{4.29}\times \textbf{10}^{4}$	33.17	-0.1572	86.24
	2nd	547	31.91	$1.73 imes 10^5$	27.36	-0.1496	109.32
	3rd	762	137.35	$2.23 imes 10^6$	131.01	-0.1311	231.04
	4th	869	169.98	$\textbf{7.34}\times 10^5$	162.75	-0.1415	285.85
[Cu(HOI)Cl](H ₂ O) ₂	1st	547	167.08	$\textbf{5.06}\times \textbf{10}^{5}$	162.53	-140.75	239.56
	2nd	677	72.41	4.06×10^{5}	66.78	-0.1443	164.52
	3rd	852	139.03	1.14×10^7	131.94	-0.1185	233.00



Fig. 4. Coats-Redfern plots of (a) first, (b) second, (c) third and (d) fourth degradation steps for [Co(OI)(H₂O)₃] complex.



Fig. 5. Horowitz-Metzger plots of (a) first, (b) second, (c) third and (d) fourth degradation steps for [Co(OI)(H₂O)₃] complex.

The Horowitz–Metzger relation [46] used to evaluate the degradation kinetics is:

$$\ln[-\ln(1-\alpha)] = \frac{E\theta}{RT_s^2}$$
(2)

where $\theta = T-T_s$, T_s is the DTG peak temperature, T is the temperature corresponding to weight loss W_t . A straight line should be observed between $\ln[-\ln(1-\alpha)]$ and θ with a slope of $\frac{E}{RT_s^2}$. A number of pyrolysis processes can be represented as a first order reaction. Particularly, the degradation of a series of H₂OI complexes was suggested to be first order [47], therefore we assume n = 1 for the remainder of the present text. The other thermodynamic parameters of activation can be calculated by Eyring equation [48]:

$$\Delta H^* = E_{\rm a} - RT \tag{3}$$

$$\Delta S^* = R \ln \frac{hA}{K_{\rm B}T} \tag{4}$$

$$\Delta G^* = \Delta H - T \Delta S \tag{5}$$

Thermodynamic parameters such as activation energy (E_a), preexponential factor (A), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy of activation (ΔG^*) of decomposition steps were calculated using Coats–Redfern [45] and Horowitz– Metzger [46] methods Tables 9 and 10. In both methods, the lift side of Eqs. (3) and (4) are plotted against 1/*T* and θ , respectively (Figs. 4 and 5). From the results, the following remarks can be pointed out:

The negative values of ΔS^* for the degradation process indicates more ordered activated complex than the reactants or the reaction is slow [48].

The high values of the energy of activation, Ea of the complexes reveals the high stability of such chelates due to their covalent bond character [49].

The positive sign of ΔG^* for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound, and all the decomposition steps are non-spontaneous processes. Also, the values of the activation, ΔG^* increases significantly for the subsequent decomposition stages of a given complex. This is due to increasing the values of $T\Delta S^*$ significantly from one step to another which overrides the values of ΔH^* [50–52].

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.10.036.

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