

Contents lists available at ScienceDirect

## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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

# Synthesis, spectroscopic characterization and thermal behavior of metal complexes formed with N'-(1-(4-hydroxyphenyl)) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH)

### Sara F. Ahmed, Ola A. El-Gammal, Gaber Abu El-Reash\*

Department of Chemistry, Faculty of Science, Mansoura University, P.O. Box 70, Mansoura, Egypt

#### ARTICLE INFO

Article history: Received 16 January 2011 Received in revised form 8 March 2011 Accepted 26 April 2011

Keywords: Hydrazone derivatives Coats-Redfern Heterocyclic schiff base Horowitz-Metzger pH-metry

#### ABSTRACT

Complexes of Co(II), Ni(II), Cu(II), Mn(II), Cd(II), Zn(II), Hg(II) and U(IV)O<sub>2</sub><sup>2+</sup> with N'-(1-(4-hydroxyphenyl) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH) are reported and have been characterized by various spectroscopic techniques like IR, UV–visible, <sup>1</sup>H NMR and ESR as well as magnetic and thermal (TG and DTA) measurements. It is found that the ligand behaves as a neutral bidentate, monoanionic tridentate or tetradentate and dianionic tetradentate. An octahedral geometry for [Mn(H<sub>3</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>], [Co<sub>2</sub>(H<sub>2</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes, a square planar geometry for [Cu<sub>2</sub>(H<sub>2</sub>OPAH)Cl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O complex, a tetrahedral structure for [Cd(H<sub>3</sub>OPAH)Cl<sub>2</sub>], [Zn(H<sub>3</sub>OPAH)(OAc)<sub>2</sub>] and [Hg(H<sub>3</sub>OPAH)Cl<sub>2</sub>]H<sub>2</sub>O complexes. The binuclear [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O complex contains a mixed geometry of both tetrahedral and square planar structures. The protonation constants of ligand and stepwise stability constants of its complexes at 298, 308 and 318 K as well as the thermodynamic parameters are being calculated. The bond lengths, bond angles, HOMO, LUMO and dipole moments have been calculated to confirm the geometry of the ligand and the investigated complexes. Also, thermal properties and decomposition kinetics of all compounds are investigated. The interpretation, mathematical analysis and evaluation of kinetic parameters (*E*<sub>a</sub>, *A*, *AH*, *AS* and *AG*) of all thermal decomposition stages have been evaluated using Coats–Redfern and Horowitz–Metzger methods.

© 2011 Published by Elsevier B.V.

#### 1. Introduction

Hydrazones are an important class of ligands which present in numerous physiological and biological applications as antimicrobial, antitumour agents, insecticides, anticoagulants, anticonvulsant, analgesic, antioxidants, anti-inflammatory, antiplatelet, antitubercular and plant growth regulators [1–4].

Metal complexes of hydrazones have found applications as catalysts [5], luminescent probes [6], nonlinear optics and molecular sensors [7]. Moreover, it has been recently shown that pyridoxal isonicotinyl hydrazone can be used in the treatment of iron overload [8].

We were thus motivated to undertake a systematic study of preparation and characterization of a new transition metal complex formed with N'-(1-(4-hydroxyphenyl) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH) and Cu(II), Co(II), Ni(II), Mn(II), Cd(II), Zn(II), Hg(II) and U(IV)O<sub>2</sub><sup>2+</sup> ions.

\* Corresponding author. Tel.: +20 100373155. E-mail address: gaelreash@mans.edu.eg (G.A. El-Reash).

#### 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 N) were performed with a Perkin-Elmer 2400 series II analyzer. IR spectra (4000-400 cm<sup>-1</sup>) 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. <sup>1</sup>H NMR measurements in d<sub>6</sub>-DMSO at room temperature were carried out on a Varian Gemini WM-200 MHz spectrometer at the Microanalytical Unit, Cairo University. Thermogravimetric measurements (TGA, DTA, 20–1000 °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 4 scans with 10-fold increase in the receiver again. A powder spectrum was obtained in a 2 mm guartz capillary at room temperature.

<sup>1386-1425/\$ –</sup> see front matter  $\ensuremath{\mathbb{C}}$  2011 Published by Elsevier B.V. doi:10.1016/j.saa.2011.04.055

#### 2.2. Procedure for the pH-metric titration

The pH-metric measurements were carried out with Hanna Instrument 8519 digital pH meter. The titrations were preformed at different temperatures (298, 308 and 318 K). The experimental procedure involves the pH-metric titration of the following solutions against standardized free carbonate sodium hydroxide solution (11.1 mM) in 50% (v/v) dioxane–water at constant ionic strength KCl (1 M) which is shown in Figs. 1S–3S (Supplementary Materials). The solution mixtures (i–iii) were prepared as follows:

- (i) 1.25 ml HCl (12.1 mM)+1.25 ml KCl (1 M)+12.5 ml dioxane+10 ml bidistilled H<sub>2</sub>O.
- (ii) 1.25 ml HCl (12.1 mM)+1.25 ml KCl (1 M)+2.5 ml (5 mM) H<sub>3</sub>OPAH+10 ml dioxane+10 ml bidistilled H<sub>2</sub>O.
- (iii) 1.25 ml HCl (12.1 mM)+1.25 ml KCl (1 M)+2.5 ml H<sub>3</sub>OPAH (5 mM)+10 ml dioxane+0.5 ml metal ion (M<sup>n+</sup>)(5 mM) [where M<sup>n+</sup> = Cu(II), Mn(II), Ni(II), Cd(II), Hg(II), Co(II), U(IV)O<sub>2</sub> and Zn(II)]+9.5 ml bidistilled H<sub>2</sub>O.

The total volume was adjusted to 25 ml by adding dioxane in each case.

# 2.3. Synthesis of N'-(1-(4-hydroxyphenyl) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH)

2-Hydrazino-2-oxo-N-phenyl-acetamide was synthesized according to the general literature method [9].  $H_3$ OPAH was synthesized according to the following scheme:



2-hydrazino-2-oxo-N-phenyl-acetamide



p-hydroxy acetophenone



insoluble in common organic solvents, partially soluble in DMSO and DMF and found to be non-electrolytes.

Type I (the ligand reacts in a neutral manner):

$$MCl_2 \cdot 2H_2O + H_3OPAH \xrightarrow{EtOH, NaOAc} [M(H_3OPAH)Cl_2] \cdot mH_2O$$

where m = 1 for M = Hg and m = 0 for M = Cd.

$$Zn(CH_3COO)_2 \cdot 2H_2O + H_3OPAH \xrightarrow{EtOH}_{reflux, 3 h} [Zn(H_3OPAH)(OAc)_2]$$

$$MnCl_2 \cdot 4H_2O + H_3OPAH \xrightarrow{EtOH, NaOAc} [Mn(H_3OPAH)_2Cl_2]$$

Type II (the ligand reacts in a monoanionic manner):

$$CoCl_2 \cdot 6H_2O + H_3OPAH \underset{reflux, 3 h}{\overset{KtOH, NaOAC}{\longrightarrow}} [Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$$

 $CuCl_2 \cdot 2H_2O + H_3OPAH \overset{EtOH, NaOAc}{\underset{reflux, 3 \ h}{\overset{}}} [Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$ 

**Type III** (the ligand reacts in a dianionic manner): UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O

+ 
$$H_3OPAH \xrightarrow{EtOH}_{reflux, 3h} [(UO_2)_2(HOPAH)(OAc)_2(H_2O)_2]$$

#### N'-(1-(4-hydroxyphenyl) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH)

The pale yellow precipitate ( $H_3$ OPAH) was filtered off, washed several times with ethanol and recrystallized from hot ethanol and finally dried in vacuum desiccators over anhydrous CaCl<sub>2</sub> (m.p. 270 °C).

#### 2.4. Synthesis of metal complexes

A hot ethanolic solution of the respective metal chlorides (Co(II), Ni(II), Cu(II), Mn(II), Cd(II), Hg(II)) or acetates (Zn(II) and U(VI)O<sub>2</sub>) (1.0 mmol) was added to hot ethanolic solution of  $H_3$ OPAH (0.297 g, 1.0 mmol). The resultant mixture was heated under reflux for 2–3 h. 0.5 g of sodium acetate in 30 ml bidistilled water was added as a buffering agent except in case of zinc and uranyl complexes. The formed precipitates were filtered off, washed with ethanol followed by diethyl ether and dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>. The physical and analytical data of the isolated complexes are listed in Table 1. The complexes have high melting points and

$$NiCl_2 \cdot 6H_2O + H_3OPAH \underset{reflux, 3 h}{EtOH, NaOAc} [Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O$$

#### 2.5. Molecular modeling

**EtOH** 

Refulx, 4h

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 by the use of MM+ force-field as implemented in hyperchem 8.0 [10]. The low lying obtained from MM+ 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.

#### 3. Results and discussion

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

#### **Table 1** Analytical and physical data of H<sub>3</sub>OPAH and its metal complexes.

Compound empirical formula (F. Wt.)	Colour	m.p. (°C)	% Found (Calcd.	Yield (%)			
			M	Cl	С	Н	
H <sub>3</sub> OPAH, C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> (297.31)	Pale yellow	290	-	_	64.10 (64.64)	5.19 (5.09)	92
[Cu <sub>2</sub> (H <sub>2</sub> OPAH)Cl <sub>3</sub> (H <sub>2</sub> O)]H <sub>2</sub> O, C <sub>17</sub> H <sub>22</sub> Cl <sub>3</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>5</sub> (581.82)	Deep green	>300	21.10 (21.84)	18.31 (18.28)	34.86 (35.09)	3.62 (3.81)	81
[Co <sub>2</sub> (H <sub>2</sub> OPAH) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ], C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>10</sub> (853.43)	Reddish brown	>300	13.85 (13.81)	8.29 (8.31)	45.09 (45.03)	4.28 (4.25)	72
[Ni <sub>2</sub> (HOPAH)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O, C <sub>16</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>3</sub> Ni <sub>2</sub> O <sub>6</sub> (537.63)	Pale green	>300	21.65 (21.83)	13.33 (13.19)	35.33 (35.74)	3.49 (3.56)	88
[Mn(H <sub>3</sub> OPAH) <sub>2</sub> Cl <sub>2</sub> ], C <sub>32</sub> H <sub>30</sub> Cl <sub>2</sub> MnN <sub>6</sub> O <sub>6</sub> (720.46)	Brown	>300	7.65 (7.63)	9.63 (9.84)	53.33 (53.35)	4.39 (4.20)	75
[Cd(H <sub>3</sub> OPAH)Cl <sub>2</sub> ], C <sub>16</sub> H <sub>15</sub> CdCl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> (480.63)	White	>300	23.28 (23.39)	14.88 (14.75)	39.80 (39.98)	3.25 (3.15)	80
[Zn(H <sub>3</sub> OPAH)(OAc) <sub>2</sub> ], C <sub>20</sub> H <sub>21</sub> N <sub>3</sub> O <sub>7</sub> Zn (480.79)	White	>300	13.55 (13.60)	-	50.01 (49.96)	4.41 (4.40)	89
[Hg(H <sub>3</sub> OPAH)Cl <sub>2</sub> ]H <sub>2</sub> O, C <sub>16</sub> H <sub>17</sub> Cl <sub>2</sub> HgN <sub>3</sub> O <sub>4</sub> (586.82)	Pale brown	>300	34.80 (34.18)	12.01 (12.08)	32.87 (32.75)	2.81 (2.92)	76
$[(UO_2)_2(HOPAH)(OAc)_2(H_2O)_2], C_{20}H_{23}N_3O_{13}U_2$ (989.47)	Orange	>300	48.01 (48.11)	-	24.23 (24.28)	2.86 (2.84)	80



Scheme 1. H<sub>3</sub>OPAH.

#### 3.1. IR and <sup>1</sup>H NMR spectra

The most important IR bands of H<sub>3</sub>OPAH (Structure 1) and its complexes with probable assignments are given in Table 2. The ligand has multi-coordination sites which gave variable coordination modes. A comparison of the spectrum of H<sub>3</sub>OPAH and its complexes revealed that the ligand coordinates in the ketone and enol forms. H<sub>3</sub>OPAH (in KBr) shows two bands at 1596 and 1606 cm<sup>-1</sup> assignable to  $\nu$ (C=N) (azomethine) and  $\nu$ (C=C) phenyl vibrations, respectively[11]. The sharp band located at 1655 cm<sup>-1</sup> is attributed to  $\nu$ [(C=O)<sup>2</sup> + (C=O)<sup>3</sup>] vibrations. The medium band observed at 3304 cm<sup>-1</sup> is attributable to  $\nu$ (N<sup>4</sup>H)[12] and  $\nu$ (N<sup>1</sup>H)[13] vibrations, respectively. The bands at 3386 and 1262 cm<sup>-1</sup> are due to  $\nu$ (OH) and  $\delta$ (OH) vibrations [14]. The medium intensity bands at 1066 and

11/4 cm <sup>-1</sup> are attributed to $V(N-N)[15]$ and $V(C-O)[16]$ vibrations,
respectively. No bands at $18001960cm^{-1}$ and $23002400cm^{-1}$
are observed so intramolecular hydrogen bonding (N-H $\cdots$ O)
[17] is ruled out suggesting the presence of the ligand in keto
form.

The <sup>1</sup>H NMR spectrum of H<sub>3</sub>OPAH in d<sub>6</sub>-DMSO shows three signals at  $\delta$  = 10.98, 10.81 and 9.92 ppm relative to TMS assignable to N<sup>4</sup>H, N<sup>1</sup>H [12] and OH [17] protons, respectively. The multiplets at 6.50–8.00 ppm are assigned to phenyl ring protons [17], while the signal at 3.41 is due to –CH<sub>3</sub> proton [17].

 $H_3$ OPAH behaves as a neutral OO bidentate ligand via the oxygen atoms of the two carbonyl groups. This behavior is found in [Cd(H<sub>3</sub>OPAH)Cl<sub>2</sub>](Structure 2), [Hg(H<sub>3</sub>OPAH)Cl<sub>2</sub>]H<sub>2</sub>O and [Mn(H<sub>3</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>] complexes and revealed by: (i) the shift of

Table 2
Principle infrared bands of H₃OPAH and its metal complexes.

Compound	v(C=N)	$v(C=0)^2$	$v(C=0)^{3}$	$\nu(N^1H)$	$v(N^4H)$	v(C-O)	v(O-H)	$\delta(O-H)$	$\nu(C=N)^*$	$v(C-0)^{*}$	$\nu(N-N)$	v(M-O)	v(M-N)
	.()	.(= =)	.(= =)	. (	. (	.(= =)	.()	-(	.()	.(= =)	. (	.( = )	. (
H₃OPAH	1596	1655	1655	3304	3304	1174	3386	1262	-	-	1060	-	-
$[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$	1579	1646	1633	Broad	Broad	1180	-	-	-	-	1074	501	434
$[Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O$	1583	-	-	-	-	1174	Broad	1267	16321622	1166	1074	503	447
$[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$	1582	-	1675	-	3310	1168	3383	1255	1615	1113	1073	509	446
$[Mn(H_3OPAH)_2Cl_2]$	1600	1657	1648	3361	3361	1174	Broad	1267	-	-	1074	501	-
$[Cd(H_3OPAH)Cl_2]$	1599	1707	1671	3280	3337	1167	3362	1260	-	-	1074	506	-
[Hg(H <sub>3</sub> OPAH)Cl <sub>2</sub> ]H <sub>2</sub> O	1596	1652	1652	3286	3260	1174	3384	1265	-	-	1074	516	-
[Zn(H <sub>3</sub> OPAH)(OAc) <sub>2</sub> ]	1587	1666	1656	3264	3217	1176	3378	1260	-	-	1074	501	446
$[(UO_2)_2(HOPAH)(OAc)_2(H_2O)_2]$	1580	-	-	-	-	1170	3380	1257	16351620	1127	1074	524	447



two  $\nu$ (C=O) to lower and higher wavenumber depending upon the metal salt used and (ii) the  $\nu$ (C=N) (azomethine) and  $\nu$ (N–N) bands remain practically unaltered indicating that the azomethine group is not participated in bonding. The <sup>1</sup>H NMR spectrum of [Cd(H<sub>3</sub>OPAH)Cl<sub>2</sub>] in d<sub>6</sub>-DMSO shows three signals at  $\delta$ =13.62, 11.29 and 10.986 ppm relative to TMS which may be assigned to OH, N<sup>4</sup>H and N<sup>1</sup>H protons, respectively, confirming the neutral behavior of the ligand.

The IR spectrum of  $[Zn(H_3OPAH)(OAc)_2]$  complex (Structure 3) shows that H<sub>3</sub>OPAH coordinates in neutral NO bidentate ligand through C=N (azomethine) and C=O<sup>2</sup> groups. This behavior is suggested by: (i) the shift of  $\nu$ (C=N) (azomethine) to lower wavenumber and  $\nu$ (C=O)<sup>2</sup> to higher wavenumber, (ii) the position of  $\nu$ (C=O)<sup>3</sup> band remains practically unaltered indicating that this group is not participated in bonding and (iii) the shift of  $\nu$ (N–N) to higher wavenumber.

In  $[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$  complex (Structure 4), H<sub>3</sub>OPAH behaves as a monoanionic ONO tridentate ligand through the deprotonated OH,  $(C=O)^2$  groups and the N of the azomethine group. This behavior is supported by: (i) the disappearance of  $\nu(OH)$  band, (ii) the shift of  $\nu(C=N)$  (azomethine) to lower wavenumber and  $\nu(N-N)$  to higher wavenumber (iii) the shift of  $\nu(C=O)^2$  band to lower frequency and  $\nu(C-O)$  band to higher frequency.

H<sub>3</sub>OPAH behaves as monoanionic tetradentate ligand coordinating through the oxygen atom  $(C=O)^3$  and new azomethine group from one side, and the deprotonated enolic oxygen atom  $(=C-O^{-})^2$  and C=N (azomethine) group from the other one. This mode of chelation is found in  $[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$  complex (Structure 5). This behavior is supported by: (i) the absence of  $(C=O)^3$  with simultaneous appearance of new broad bands at 1615 cm<sup>-1</sup> assignable to the conjugation (-C=N-N=C-) system [18] and band at 1113 cm<sup>-1</sup> assignable to  $\nu(C-O)$  [16] and (ii) the shift of  $\nu(N-N)$  to higher wavenumber.

Finally, H<sub>3</sub>OPAH behaves as dianionic tetradentate ligand coordinating through the deprotonated enolic oxygen atom  $(=C-O^{-})^2$ and C=N (azomethine) from one side, and the deprotonated enolic oxygen atom  $(=C-O^{-})^3$  and new azomethine group from the other one. This mode of chelation is found in [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O (Structure 6) and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes. This behavior is supported by: (i) the absence of both (C=O) with simultaneous appearance of new broad bands at 1620, 1635 cm<sup>-1</sup> for Ni(II) and 1622, 1632 cm<sup>-1</sup> for U(VI) assignable to the conjugation (-C=N-N=C-) system [18] and band at 1113, 1127 cm<sup>-1</sup> assignable to  $\nu$ (C-O) [16] and (ii) the shift of  $\nu$ (N–N) to higher wavenumber.

The absorption bands of the coordinated acetate groups were observed at 1454 and 1322 cm<sup>-1</sup> indicating a monodentate acetate anion character [19,20]. Moreover, the IR spectrum exhibits two bands at 931 and 860 cm<sup>-1</sup>, assigned to the asymmetric stretch-



Scheme 4.







Scheme 6.

ing frequency ( $\nu_3$ ) and the symmetric stretching frequency ( $\nu_1$ ), respectively, of the dioxouranium ion [17,21]. The force constant (*F*) for the bonding sites of  $\nu$ (U=O) is calculated by the method of McGlynn et al. [22];  $F_{U-O}$  value is found to be 7.15 mdynes Å<sup>-1</sup>. Also, the U–O bond distance is calculated by the method of Jones [23];  $R_{U-O}$  value is 1.73 Å. The U–O bond distance falls in usual range as reported earlier [24] and extremely in accordance with the bond length calculated by the use of MM+ force field (as implemented in hyperchem 8.0 [10]).

New bands observed in all complexes at 501–524 and 434–447 cm<sup>-1</sup> are tentatively assigned to the  $\nu$ (M–O) [25] and  $\nu$ (M–N) [26], respectively.

The broad bands at  $\approx$ 3399–3454, 868–850, and at  $\approx$ 567 cm<sup>-1</sup> in the IR spectra of the investigated complexes are referred to  $\nu$ (OH),  $\Delta$ (H<sub>2</sub>O),  $p_r$ (H<sub>2</sub>O) and  $P_w$ (H<sub>2</sub>O) vibrations for the coordinated water. The broad band centered at 3500 cm<sup>-1</sup> in the spectra of the studied complexes may be due to hydrated water. To verify between the coordinated and hydrated water, TGA measurement was carried out.

#### 3.2. Spectral and magnetic studies

Electronic spectra were measured in dimethylsulfoxide (DMSO) solution for  $H_3$ OPAH and its metal complexes. The tentative assignments of the significant spectral absorption bands, magnetic moments and ligand field parameters of metal complexes are given in Table 3.

The electronic spectrum of the ligand shows two bands at 33,112 and 28,735 cm<sup>-1</sup>. The strong band at 33,112 cm<sup>-1</sup> is due to  $\pi \rightarrow \pi^*$  transition of the benzene ring [27]. The  $n \rightarrow \pi^*$  transitions associated to the azomethine and carbonyl function overlap at 28,735 cm<sup>-1</sup> [28]. These bands undergo a shift to higher energy in the spectra of complexes [27], suggesting the coordination of imino nitrogen atom and oxygen atom of carbonyl group with the central metal ion [29]. The Cl  $\rightarrow M^{2*}$  ( $M^{2*} = Cu^{2*}$ , Ni<sup>2+</sup> and Mn<sup>2+</sup>) transition is generally found in the 28,735 cm<sup>-1</sup> region and would contribute to the higher energy  $n \rightarrow \pi^*$  band [30].

The electronic spectrum of  $[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$  complex shows two bands at 15,974 and 18,382 cm<sup>-1</sup> assignable to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$  transitions [30], respectively, in a octahedral configuration. The calculated values of ligand field parameters ( $D_q = 743$  cm<sup>-1</sup>, B = 774 cm<sup>-1</sup> and  $\beta = 0.79$ ) are in good agreement with those reported for octahedral Co(II) complexes. Also, the value of  $\mu_{eff}$  (5.06 B.M.) is an additional evidence for an octahedral structure.

The complex  $[Ni_2(HOPAH) Cl_2(H_2O)_2]H_2O$  has a magnetic moment value (3.14 B.M.) which is lower than the measured value per one nickel atom which is in

Table 3

Spectral absorption bands, magnetic moments and ligand field parameters of H<sub>3</sub>OPAH metal complexes.

Compound	Band position (cm <sup>-1</sup> )	Assignment	$\mu_{ m eff}$ (B.M.)
H <sub>3</sub> OPAH	33,446 28,735	$\begin{array}{c} \pi \rightarrow \pi^* \\ n \rightarrow \pi^* \end{array}$	-
$[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$	15,974 18,382	$\label{eq:constraint} \begin{array}{c} {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \\ {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p) \end{array}$	5.06
$[\mathrm{Ni}_2(\mathrm{HOPAH})\mathrm{Cl}_2(\mathrm{H}_2\mathrm{O})_2]\mathrm{H}_2\mathrm{O}$	17,667 21,929	${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P) \\ {}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$	3.14
[Cu <sub>2</sub> (H <sub>2</sub> OPAH)Cl <sub>3</sub> (H <sub>2</sub> O)]H <sub>2</sub> O	14,326 25,906	${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ LMCT	1.91
[Mn(H <sub>3</sub> OPAH) <sub>2</sub> Cl <sub>2</sub> ]	24,630 27,932	$\label{eq:A1g} \begin{array}{c} {}^6A_{1g} \rightarrow {}^4T_{1g}(G) \\ {}^6A_{1g} \rightarrow {}^4T_{2g}(G) \end{array}$	6.50
[(UO <sub>2</sub> ) <sub>2</sub> (HOPAH)(OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	23,696 27,932	${}^{1}\Sigma^{+}{}_{g} \rightarrow {}^{2}\pi_{4}$ $n \rightarrow \pi^{*}$	Diam.

Diam., diamagnetic.

LMCT, ligand to metal charge transfer.



Fig. 2. ESR spectra of [Cu<sub>2</sub>(H<sub>2</sub>OPAH)Cl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O.

#### Table 4

Kinetic parameters evaluated by Coats-Redfern equation for H<sub>3</sub>OPAH complexes.

Complex	Peak	Mid temp (K)	E <sub>a</sub> (kJ/mol)	A (s <sup>-1</sup> )	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (kJ/mol K)	$\Delta G^*$ (kJ/mol)
$[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$	1st	355	28.55	$2.84\times10^4$	25.60	-0.161	82.86
	2nd	651	109.51	$1.95  imes 10^5$	104.09	-0.150	201.97
	3rd	736	84.48	$4.13\times10^5$	78.36	-0.144	185.04
[Ni <sub>2</sub> (HOPAH)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O	1st	354	28.86	$2.26\times10^4$	25.91	-0.162	83.63
	2nd	576	128.89	$2.75  imes 10^5$	124.10	-0.146	208.38
	3rd	708	105.44	$4.62  imes 10^5$	99.55	-0.143	201.37
	4th	1029	528.45	$3.56\times10^{6}$	519.89	-0.129	653.47
[Cu <sub>2</sub> (H <sub>2</sub> OPAH)Cl <sub>3</sub> (H <sub>2</sub> O)]H <sub>2</sub> O	1st	335	48.86	$4.15\times10^4$	46.07	-0.157	98.82
	2nd	492	125.31	$1.51 \times 10^5$	121.22	-0.149	194.98
	3rd	576	126.21	$1.02  imes 10^5$	121.42	-0.154	210.41
	4th	665	176.82	$1.92  imes 10^6$	171.29	-0.131	258.58
	5th	846	72.57	$3.92 \times 10^5$	65.53	-0.146	189.47
	6th	1027	501.37	$3.31\times10^{6}$	492.84	-0.130	626.73
$[Mn(H_3OPAH)_2Cl_2]$	1st	656	94.33	$1.13\times10^{6}$	88.88	-0.135	177.80
	2nd	839	163.89	$1.08  imes 10^6$	156.92	-0.137	272.75
	3rd	983	285.65	$6.94\times10^{5}$	277.48	-0.143	418.05
$[Zn(H_3OPAH)(OAc)_2]$	1st	576	163.17	$7.90\times10^{5}$	158.38	-0.137	237.57
	2nd	717	108.87	$2.12\times10^5$	102.91	-0.150	210.62

#### Table 5

Kinetic parameters evaluated by Horowitz–Metzger equation for H<sub>3</sub>OPAH complexes.

Complex	Peak	Mid temp (K)	E <sub>a</sub> (kJ/mol)	A (s <sup>-1</sup> )	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (kJ/mol K)	$\Delta G^*$ (kJ/mol)
$[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$	1st	355	28.42	$2.75\times10^4$	25.46	-0.161	82.82
	2nd	651	109.88	$1.98 \times 10^5$	104.46	-0.150	202.25
	3rd	736	84.79	$4.06\times10^5$	78.67	-0.145	185.45
[Ni <sub>2</sub> (HOPAH)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O	1st	354	28.88	$2.36\times10^4$	25.93	-0.162	83.52
	2nd	576	128.37	$2.76 \times 10^{5}$	123.58	-0.146	207.84
	3rd	709	105.23	$4.81  imes 10^5$	99.33	-0.143	201.02
	4th	1030	528.32	$3.52  imes 10^6$	519.76	-0.129	653.54
[Cu <sub>2</sub> (H <sub>2</sub> OPAH)Cl <sub>3</sub> (H <sub>2</sub> O)]H <sub>2</sub> O	1st	335	48.65	$4.13\times10^4$	45.87	-0.157	98.63
	2nd	492	126.34	$1.52 \times 10^5$	122.25	-0.149	195.98
	3rd	576	126.36	$1.00 \times 10^5$	121.57	-0.154	210.64
	4th	665	176.95	$1.95  imes 10^6$	171.42	-0.131	258.63
	5th	846	72.59	$4.55 \times 10^5$	65.56	-0.145	188.45
	6th	1027	501.58	$3.25\times10^{6}$	493.04	-0.130	627.08
$[Mn(H_3OPAH)_2Cl_2]$	1st	656	94.34	$1.17\times10^{6}$	88.89	-0.135	177.62
	2nd	839	163.28	$1.25 \times 106$	156.30	-0.136	271.05
	3rd	983	285.19	$6.41\times10^{5}$	277.02	-0.143	418.23
[Zn(H <sub>3</sub> OPAH)(OAc) <sub>2</sub> ]	1st	576	162.63	$9.30\times10^5$	157.84	-0.136	236.25
	2nd	717	107.42	$2.09\times10^{5}$	101.46	-0.150	209.26



 $\label{eq:Fig.3.} Coats-Redfern plot of first degradation step for (A) [Co_2(H_2OPAH)_2Cl_2(H_2O)_4], (B) [Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O, (C) [Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O, (D) [Mn(H_3OPAH)_2Cl_2] and (E) [Zn(H_3OPAH)(OAc)_2] complex.$ 

turn less than that reported for d<sup>8</sup>-octahedral and/or tetrahedral complexes and higher than that for diamagnetic square-planar complexes. The values may suggest the existence of the complexes in a mixed stereochemistry [31]. Such assumption is also confirmed by one band at 17,667 cm<sup>-1</sup> assignable to  ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$  transition consistent with a tetrahedral configuration in addition to another band at 21,929 cm<sup>-1</sup>, respectively, referring to a square planar geometry [32].

The electronic spectrum of  $[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$  exhibits two bands: an asymmetric broad band at 14,326 cm<sup>-1</sup> and a more intense band at 25,906 cm<sup>-1</sup>. The latter band may be assigned to ligand metal charge transfer transition. The asymmetric band is assigned to  ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$  transition. The band position

and the magnetic moment value (1.91 B.M.) can be taken as an evidence for the square-planar configuration [17,25].

The [Mn(H<sub>3</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>] complex shows a band at 24,630 and at 27,932 cm<sup>-1</sup> which may be due to  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$  and  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$  transitions, respectively, in an octahedral configuration [33] around the metal ion. Also, the value of magnetic moment (6.5 B.M.) is in the range measured for high spin d<sup>5</sup> system.

Finally, the [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex shows two bands in its spectrum, the first at 27,932 cm<sup>-1</sup> is due to charge transfer, probably H<sub>3</sub>OPAH  $\rightarrow$  O=U=O, while the second band at 23,696 cm<sup>-1</sup> can be definitely assigned to the  ${}^{1}\Sigma^{+}{}_{g} \rightarrow {}^{2}\pi_{4}$  transition [34].



**Fig. 4.** Horowitz–Metzger plot of first degradation step for (A)  $[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$ , (B)  $[Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O$ , (C)  $[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$ , (D)  $[Mn(H_3OPAH)_2Cl_2]$  and (E)  $[Zn(H_3OPAH)(OAc)_2]$  complex.

#### 3.3. ESR spectra

The copper complex displays an axial ESR powder spectrum (Fig. 1) with  $g_{||} = 2.21$  and  $g_{\perp} = 2.08$  indicating that the  $d_{x^2-y^2}$  is the ground state. In axial symmetry, the *g*-values are related to the *G* factor by the expression,  $G = (g_{||} - 2)/(g_{\perp} - 2)$ . The value of *G* which is 2.86 and also the value of  $g_{||} > g_{\perp} > 2.0023$  are consistent with a square-planar geometry [35,36]. The ESR spectrum (Fig. 2) is similar to the ESR spectra of the binuclear Cu(II) complexes [37,38]. The line broadening is probably due to insufficient spin-exchange

narrowing toward the coalescence of four copper hyberfine lines to a single line.

#### 3.4. Thermogravimetric studies

Thermal data showed that the crystal water molecules are volatilized within the temperature range 75–125 °C, while the coordinated water molecules are removed in the temperature range 120–200 °C. The TGA of  $[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$  complex was discussed in detail as a representative example. In TG thermogram

7.26

35

86.3

90

140.

59.38

42.31

28.03

07

57.

14.85

16.77

57.14

22

15.

-15.36

57.22

16.58

-13.95

10.05 pK<sub>3</sub>

11.41

11.95 рК<sub>1</sub>

10.61

11.80  $pK_2$ 

12.14

10.71 pK<sub>3</sub>

11.88

12.26

H<sub>3</sub>OPAH

 $pK_2$ 

pK<sub>3</sub>

pK<sub>1</sub>

 $pK_2$ 

pK<sub>1</sub>

of this complex, the first stage at 32–91 °C with weight loss of 3.05 (Calcd. 3.18%) is corresponding to the loss of the one lattice water molecule. The second step with weight loss of 3.11 (Calcd. 3.18%) at 183–255 °C is attributed to the elimination of H<sub>2</sub>O. It is clear that, the TG thermograms for the investigated complexes displayed high residual part indicating high stability of the formed chelates.

#### 3.5. Kinetic data

The kinetic and thermodynamic parameters of thermal degradation process have been calculated using Coats-Redfern and Horowitz-Metzger models [39,40].

A number of pyrolysis processes can be represented as a first order reaction. Particularly, the degradation of a series of H<sub>3</sub>OPAH complexes was suggested to be first order [41], therefore we assume n = 1 for the remainder of the present text. The other thermodynamic parameters of activation can be calculated by Eyring equation [42]:

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

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

 $\Delta G = \Delta H - T \Delta S$ (5)

Thermodynamic parameters such as activation energy  $(E_a)$ , preexponential factor (A), entropy of activation ( $\Delta S$ ), enthalpy of activation ( $\Delta H$ ) and free energy of activation ( $\Delta G$ ) of decomposition steps were calculated using Coats-Redfern [39] and Horowitz-Metzger [40] methods (Tables 4 and 5). In both methods, the lift side of Eqs. (3) and (4) are plotted against 1/T and  $\theta$ , respectively (Figs. 3 and 4). From the results, the following remarks can be pointed out:

- The high values of the energy of activation,  $E_a$  of the complexes reveal the high stability of such chelates due to their covalent bond character [43].
- The positive sign of  $\Delta G$  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 nonspontaneous processes. Also, the values of the activation,  $\Delta G$ 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  $\Delta H$  [44–46].
- The negative values of  $\Delta S$  for the degradation process indicate that more ordered activated complex than the reactants or the reaction is slow [42].

#### 3.6. pH-metric studies

The proton-ligand formation constants and the stability constants of its metal complexes at 298, 308 and 318K were determined. The values of the average number of protons  $\bar{n}_A$ , the average number of ligand molecules attached per metal ion and the free ligand exponent (pL) were calculated at different pH values by applying Irving and Rossotti equation [47]. Plotting of  $\bar{n}_A$  versus pH (Fig. 4S, Supplementary Materials) gives a curve which is suitable to calculate the ligand constants ( $\log K_1$ ,  $\log K_2$  and  $\log K_3$ ) (Table 6). The first value is due to the OH proton while the second and the third are due to the amide (NHCO) protons. The stability constants of the complexes were calculated by half method. The titration curves of the complexes were drawn as in Figs. 5S-10S (Supplementary Materials) (Table 7). The data reveal that,  $\log K_1$  is higher than  $\log K_2$  or  $\log K_3$  for the same complex because the vacant sites of the metal ions are more freely available for binding the first ligand more than the second or the third.

Table 6

	Entropy change ( $\Delta S$ , J mol <sup>-1</sup> K <sup>-1</sup> )	
	Enthalpy change (∆H, kJ/mol)	
		318K
nodynamic parameters.	؛ (∆G, kJ/mol)	308 K
mperatures and its thern	Free energy change	298 K
ter and KCl at different te		318K
in 50% (v/v) dioxane-wat	t	308 K
on constants of H <sub>3</sub> OPAH	Dissociation constan	298 K
Dissociatic	Ligand	

Table 7

Stability	constants (	of metal	ions_H_	OPAH co	mnlovoc	in 50%	(w w)	diovane_w	water and	KCl at	different	tomporatur	<u> </u>
διαυππιγ	CONSTANTS	JI IIIetai	10115-03		Inplexes	III 30/6	( V / V )	uloxalle-v	valei anu	NUI dl	umerent	temperature	es.

Cation	Dissociation cor	Dissociation constant											
	298 K		308 K		318 K								
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	log K <sub>2</sub>							
Ni(II)	14.29	7.16	13.46	6.62	12.06	6.10							
Co(II)	17.05	9.05	15.43	8.24	13.04	8.03							
Cu(II)	26.09	11.28	22.34	9.11	17.22	7.17							
Mn(II)	9.97	6.51	7.45	4.98	5.94	1.97							
Cd(II)	9.84	6.80	6.37	5.21	5.37	2.05							
Hg(II)	7.63	5.29	6.44	4.48	5.45	4.13							
Zn(II)	16.69	7.47	14.76	5.67	11.45	4.20							
U(VI)	17.49	5.79	16.59	5.61	16.00	5.45							

Table 8

Thermodynamic parameters of metal ions-H<sub>3</sub>OPAH complexes in 50% (v/v) dioxane-water, 1 M KCl at different temperatures.

Ligand	Free energy	y change ( $\Delta$	G, kJ/mol)				Enthalpy ch	ange ( $\Delta H$ , kJ/mol)	Entropy change ( $\Delta S$ , kJ/mol K)	
	298 K		308 K		318 K					
Co(II)	-100.58	-51.33	-91.78	-49.93	-82.98	-48.53	-362.82	-93.05	-0.88	-0.14
Ni(II)	-82.42	-42.48	-78.42	-40.68	-74.42	-38.88	-201.62	-96.12	-0.40	-0.18
Cu(II)	-150.26	-65.85	-128.36	-55.55	-106.46	-45.25	-802.88	-372.79	-2.19	-1.03
Mn(II)	-56.46	-39.79	-46.06	-27.19	-35.66	-14.59	-366.38	-415.27	-1.04	-1.26
Cd(II)	-56.09	-41.73	-44.29	-28.73	-32.49	-15.73	-407.73	-429.13	-1.18	-1.30
Hg(II)	-42.92	-31.13	-37.72	-28.63	-32.52	-26.13	-197.88	-105.63	-0.52	-0.25
Zn(II)	-98.26	-44.19	-85.66	-34.79	-73.06	-25.39	-473.74	-324.31	-1.26	-0.94
UO <sub>2</sub> (VI)	-99.64	-32.94	-98.44	-33.01	-97.24	-33.08	-135.40	-30.85	-0.12	0.007

Furthermore, the thermodynamic parameters,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were obtained by linear least square fit of pK against 1/T with an intercept equals  $\Delta S^{\circ}/2.303R$  and a slope of  $\Delta H^{\circ}/2.303R$  (Figs. 11S–15S, Supplementary Figures). The free energy ( $\Delta G^{\circ}$ ) change can be estimated using the relationships:

 $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ 

The data of the thermodynamic functions are recorded in Table 8 and the data reveal the following remarks:

- (1) The stepwise stability constants decrease with increasing temperature indicating that the complexation processes are unfavorable with increasing temperature.
- (2) All ΔG° values are negative indication of spontaneous character of chelation.
- (3) The negative values of  $\Delta S^{\circ}$  indicate that the complexation processes are entropically unfavorable.
- (4) The negative values of  $\Delta H^{\circ}$  suggest that the chelation processes are accompanied by generation of heat (i.e. the processes are exothermic).

#### 3.7. Molecular modeling

The molecular structure along with atom numbering of  $H_3$  OPAH and its metal complexes are shown in Structures 1–9 where Structures 7–9 are in Supplementary Materials. From the analysis of the data in Tables 1S–18S (Supplementary Materials) calculated

for the bond lengths and angles for the bond, one can conclude the following remarks:

- (1) The N(10)–N(11) bond length becomes slightly longer in complexes as the coordination takes place via N atoms of -C=N-N=C- group that is formed on deprotonation of OH group in [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes [12].
- (2) The C(8)–O(12) bond distance in [Cu<sub>2</sub>(H<sub>2</sub>OPAH)Cl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O, [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O, [Mn(H<sub>3</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>], [Cd(H<sub>3</sub>OPAH)Cl<sub>2</sub>], [Hg(H<sub>3</sub>OPAH)Cl<sub>2</sub>]H<sub>2</sub>O and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes becomes longer due to the formation of the M–O bond which makes the C–O bond weaker except [Co<sub>2</sub>(H<sub>2</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] and [Zn(H<sub>3</sub>OPAH)(OAc)<sub>2</sub>] complexes in which this bond distance remains practically unaltered indicating that this group is not participated in bonding. The C(9)–O(13) bond distance in all complexes becomes longer due to the formation of the M–O bond [28].
- (3) In  $[Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O$  and  $[(UO_2)_2(HOPAH)(OAc)_2(H_2O)_2]$  complexes, C(8)-O(12) bond distance is more longer due to the deprotonation at N(7) which leads to a higher single bond character for C(8)-O(12). On the other hand, in  $[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$ ,  $[Ni_2(HOPAH)Cl_2(H_2O)_2]H_2O$  and  $[(UO_2)_2(HOPAH)(OAc)_2(H_2O)_2]$  complexes, C(9)-O(13) bond distance is more longer due to the deprotonation at N(10)

#### Table 9

Some energetic properties of H<sub>3</sub>OPAH and its complexes calculated by PM3 method.

Compound	Total energy (kcal/mol)	Binding energy (kcal/mol)	Electronic energy (kcal/mol)	Heat of formation (kcal/mol)	Dipole moment (D)	HOMO (eV)	LUMO (eV)
H <sub>3</sub> OPAH	$-8.05\times10^4$	-4067.57	$-5.33\times10^5$	-34.123	1.74	-8.90	-0.43
[Ni <sub>2</sub> (HOPAH)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O	$-1.57  imes 10^5$	-5046.37	$-1.11  imes 10^6$	-526.02	7.97	-8.60	-1.70
$[Co_2(H_2OPAH)_2Cl_2(H_2O)_4]$	$-2.41\times10^{5}$	-9774.73	$-2.59\times10^{6}$	-894.21	15.72	-7.64	-1.93
$[Cu_2(H_2OPAH)Cl_3(H_2O)]H_2O$	$-1.64 imes10^5$	-4625.05	$-1.11 imes10^{6}$	-231.57	4.83	-8.63	-1.80
$[Mn(H_3OPAH)_2Cl_2]$	$-1.84 imes10^5$	-8320.55	$-2.02 imes10^{6}$	-127.98	4.60	-4.34	-0.97
$[Zn(H_3OPAH)(OAc)_2]$	$-1.21\times10^{5}$	-5458.11	$-9.81\times10^{5}$	-159.09	5.28	-9.20	-1.29
[Hg(H <sub>3</sub> OPAH)Cl <sub>2</sub> ]H <sub>2</sub> O	$-9.58\times10^5$	-4193.73	$-6.65\times10^5$	-87.61	12.99	-9.31	-1.65

which leads to a higher single bond character for C(9)-O(13) [28].

- (4) In [Cu<sub>2</sub>(H<sub>2</sub>OPAH)Cl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O, [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes, C(9)–N(10) and N(7)–C(8) bond distances are shortened due to the formation of a double bond character.
- (5) The bond angles of the hydrazone moiety of H<sub>3</sub>OPAH are altered somewhat upon coordination but the angles around the metal undergo appreciable variations upon changing the metal center [48]. The largest change affects C(9)–N(10)–N(11), C(9)–C(8)–O(12), N(7)–C(8)–C(9), N(10)–C(9)–O(13), O(12)–C(8)–N(7) and N(10)–C(9)–C(8) angles which are reduced or increased on complex formation as a consequence of bonding [12].
- (6) The bond angles in complexes namely, [Cd(H<sub>3</sub>OPAH)Cl<sub>2</sub>], [Zn(H<sub>3</sub>OPAH)(OAc)<sub>2</sub>] and [Hg(H<sub>3</sub>OPAH)Cl<sub>2</sub>]H<sub>2</sub>O are quite near to a tetrahedral geometry predicting sp<sup>3</sup> hybridization. On the other hand, [Cu<sub>2</sub>(H<sub>2</sub>OPAH)Cl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O and [Ni<sub>2</sub>(HOPAH)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O complex afforded a square planar geometry with dsp<sup>2</sup> hybridization and quite near to a tetrahedral geometry predicting sp<sup>3</sup> hybridization. Also, [Mn(H<sub>3</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>], [Co<sub>2</sub>(H<sub>2</sub>OPAH)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] and [(UO<sub>2</sub>)<sub>2</sub>(HOPAH)(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complexes afforded octahedral geometry.
- (7) The lower HOMO energy values show that molecule donating electron ability is weaker. On contrary, the higher HOMO energy implies that the molecule is a good electron donor. LUMO energy represents the ability of a molecule receiving electron as in Table 9 [49].

#### 4. Conclusion

A new series of complexes, Structures 2–9, were prepared from the novel ligand N'-(1-(4-hydroxyphenyl) ethylidene)-2-oxo-2-(phenylamino) acetohydrazide (H<sub>3</sub>OPAH). Geometry optimization and conformational analysis have been performed and the perfect agreement with spectral studies allows for suggesting the exact structure of all studies complexes. The stability of complexes was explained and kinetic parameters ( $E_a$ , A,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) of all the thermal decomposition stages have been evaluated using Coats–Redfern and Horowitz–Metzger methods.

#### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.04.055.

#### References

- [1] S. Rollas, S.G. Küçükgüzel, Molecules 12 (2007) 1910-1939.
- [2] P. Vicini, M. Incerti, I.A. Doytchinova, P. La Colla, B. Busonera, R. Loddo, Eur. J. Med. Chem. 41 (2006) 624–632.

- [3] H.J.C. Bezerra-Netto, D.I. Lacerda, A.L.P. Miranda, H.M. Alves, E.J. Barreiro, C.A.M. Fraga, Bioorg. Med. Chem. 14 (2006) 7924–7935.
- [4] Y.P. Kitaev, B.I. Buzykin, T.V. Troepolskaya, Russ. Chem. 39 (1970) 441-456.
- [5] O. Pouralimardan, A.C. Chamayou, C. Janiak, H. Hosseini-Monfared, Inorg. Chim. Acta 360 (2007) 1599–1608.
- [6] C. Basu, S. Chowdhury, R. Banerjee, H.S. Evans, S. Mukherjee, Polyhedron 26 (2007) 3617–3624.
- [7] M. Bakir, O. Green, W.H. Mulder, J. Mol. Struct. 873 (2008) 17-28.
- [8] J.L. Buss, J. Neuzil, P. Ponka, Biochem. Soc. Trans. 30 (2002) 755-757.
- [9] L.A. Cescon, A.R. Day, J. Org. Chem. 27 (1962) 581-586.
- [10] HyperChem version 8.0, Hypercube, Inc.
- [11] N.L. Alpert, W.E. Keiser, H. Szmanski, A Theory and Practice of Infrared Spectroscopy, Plenum Press, New York, 1970.
- [12] O.A. El-Gammal, Spectrochim. Acta A 75 (2010) 533-542.
- P.B. Sreeja, M.R.P. Kurup, A. Kishore, C. Jasmin, Polyhedron 23 (2004) 575–581.
   K.A. Ketcham, I. Garcia, J.K. Swearingen, A.K. El-Sawaf, E. Bermejo, A. Castineiras, D.X. West, Polyhedron 21 (2002) 859–865.
- [15] U. El-Ayaan, I.M. Kenawy, Y.G. Abu El-Reash, J. Mol. Struct. 871 (2007) 14–23.
- [16] N.S. Biradar, B.R. Patil, V.H. Kulkarni, J. Inorg. Nucl. Chem. 37 (1975) 1901–1904.
- [17] U. El-Ayaan, G.A. EL-Reash, I.M. Kenawy, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 327-342.
- [18] D.K. Rastogi, S.K. Sahni, V.B. Rana, S.K. Dua, Transition Met. Chem. 3 (1978) 56–60.
- [19] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986, p. 231.
- [20] K. Chanda, P.K. Sharma, B.S. Gray, R.P. Singh, J. Inorg. Nucl. Chem. 42 (1980) 187–193.
- [21] F. Quilés, Vib. Spectrosc. 18 (1998) 61–75.
- [22] S.P. McGlynn, J.K. Smith, W.C. Neely, J. Chem. Phys. 35 (1961) 105-116.
- [23] L.H. Jones, Spectrochim. Acta 15 (1959) 409-411.
- [24] T.H. Rakha, N. Nawar, G.M. Abu Reash, Synth. React. Inorg. Met.-Org. Chem 26 (1996) 1705-1718.
- [25] J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.
- [26] J.R. Ferraro, W.R. Walkers, Inorg. Chem. 4 (1965) 1382–1386.
- [27] D.X. West, A.K. El-Sawaf, G.A. Bain, Transition Met. Chem. 23 (1998) 1-6.
- [28] A.A.R. Despaigne, J.G. da Silva, A.C.M. do Carmo, O.E. Piro, E.E. Castellano, H. Beraldo, J. Mol. Struct. 920 (2009) 97–102.
- [29] R.S. Joseyphus, C.J. Dhanaraj, M.S. Nair, Transition Met. Chem. 31 (2006) 699-702.
- [30] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
- [31] A.A. El-Asmy, T.Y. Al-Ansi, R.R. Amin, M. Mounir, Polyhedron 9 (1990) 2029–2034.
- [32] F.A. El-Saied, A.A. El-Asmy, W. Kaminstry, D.X. West, Transition Met. Chem. 28 (2003) 954–960.
- [33] M. Mohan, M. Kumar, Transition Met. Chem. 10 (1985) 255–258.
- [34] U. El-Ayaan, M.M. Youssef, S. Al-Shihry, J. Mol. Struct. 936 (2009) 213-219.
- [35] M.L. Miller, S.A. Ibrahim, M.L. Golden, M.Y. Daresboury, Inorg. Chem. 42 (2003) 2999–3007.
- [36] A. Diaz, A. Fragosa, R. Cao, V. Verez, J. Carbohydr. Chem. 17 (1998) 293–303.
- [37] O. Khan, T. Mallah, J. Gouteron, S. Jeanin, Y. Jeanin, J. Chem. Soc. Dalton trans. (1989) 1117–1126
- [38] B.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143–207.
- [39] A.W. Coats, I.P. Redfern, Nature 20 (1964) 68–69.
- [40] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464-1468.
- [41] A. Broido, J. Polym. Sci. Part A-2 7 (1969) 1761–1773.
- [42] A.A. Frost, R.G. Pearson, Kinetics and Mechanisms, Wiley, New York, 1961.
- [43] T. Taakeyama, F.X. Quinn, Thermal Analysis Fundamentals and Applications to Polymer Science, John Wiley and Sons, Chichester, 1994.
- [44] P.B. Maravalli, T.R. Goudar, Thermochim. Acta 325 (1999) 35-41.
- [45] K.K.M. Yusuff, R. Sreekala, Thermochim, Acta 159 (1990) 357-368.
- [46] S.S. Kandil, G.B. El-Hefnawy, E.A. Baker, Thermochim. Acta 414 (2004) 105–113.
- [47] H.M. Irving, H.S. Rossotti, J. Chem. Soc. (1954) 2904–2910.
- [48] A.A.R. Despaigne, J.G. da Silva, A.C.M. do Carmo, F. Sives, O.E. Piro, E.E. Castellano, H. Beraldo, Polyhedron 28 (2009) 3797-3803.
- [49] S. Sagdinc, B. Koksoy, F. Kandemirli, S.H. Bayari, J. Mol. Struct. 917 (2009) 63-70.