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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

SPECTROCHIMICA ACTA

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

# Mono, bi- and trinuclear metal complexes derived from new benzene-1,4-bis(3-pyridin-2-ylurea) ligand. Spectral, magnetic, thermal and 3D molecular modeling studies

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# HIGHLIGHTS

- New bis (pyridylurea) ligand was prepared.
- The structure of the ligand was studied by different spectroscopic techniques.
- The solid complexes of the prepared ligand with some metal ions were isolated.
- The spectral, magnetic and thermal properties of these complexes were studied.
- 3D molecular modeling of the ligand and a representative complex were studied.

# ARTICLE INFO

Article history: Received 12 November 2012 Received in revised form 18 February 2013 Accepted 3 March 2013 Available online 13 March 2013

Keywords: Bis (pyridylurea) ligand Mono-, bi- and trinuclear metal complexes Magnetic Thermal studies Molecular modeling

# G R A P H I C A L A B S T R A C T

The optimized structure of the ligand, H<sub>2</sub>L.



# ABSTRACT

New bis (pyridylurea) ligand, H<sub>2</sub>L, was synthesized by the reaction of ethylpyridine-2-carbamate (EPC) and *p*-phenylenediamine. The ligand was characterized by elemental analysis, IR, <sup>1</sup>H NMR, electronic and mass spectra. Reaction of the prepared ligand with  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $VO^{2+}$  and  $UO_2^{2+}$  ions afforded mono, bi- and trinuclear metal complexes. Also, new mixed ligand complexes of the ligand H<sub>2</sub>L and 8-hydroxyquinoline (8-HQ) with  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Fe^{3+}$  ions were synthesized. The ligand behaves as bi- and tetradentate toward the transition metal ions, coordination via the pyridine -N, the carbonyl -O and/or the amidic -N atoms in a non, mono- and bis-deprotonated form. The complexes were characterized by elemental and thermal analyses, IR, electronic and mass spectra as well as conductance and magnetic susceptibility measurements. The results showed that the metal complexes exhibited different geometrical arrangements such as square planar, tetrahedral, octahedral and square pyramidal arrangements. The Coats–Redfern equation was used to calculate the kinetic and thermodynamic parameters for the different thermal decomposition steps of some complexes. 3D molecular modeling of the ligand, H<sub>2</sub>L and a representative complex were studied.

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# Introduction

Heterocyclic nitrogen ligands have been studied well because their interesting coordination chemistry and potential applications

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in electrochemical processes, antimicrobial and antitumour activities [1–6]. The coordination chemistry of pyridyl ureas is extremely rich. Such compounds act as multidentate ligands towards transition metals, coordination via the pyridine nitrogen atoms, the carbonyl oxygen atoms and the amide nitrogen atoms of the ligands in a non-, mono- and bis-deprotonated form are known [7]. Also, these ligands have been extensively used to construct various

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structures and functions through cooperative binding of transition metals and anions [8,9]. Pyridine amide compounds have been employed in catalysis [10,11]. Many derivatives of pyridine amide show anti-flammatory, antipyretic and analgesic activities and they are useful in the treatment of atherosclerosis [12]. Some Pt(II) complexes with amide compounds demonstrated notable antitumour and anticancer activity [13–17].

The work reported herein is focused on the synthesis and characterization of mono, bi- and tri-nuclear  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $VO^{2+}$ and  $UO_2^{2+}$  complexes of new benzene-1,4-bis(3-pyridin-2-ylurea) ligand, H<sub>2</sub>L, derived from the reaction between ethylpyridine-2carbamate (EPC) and *p*-phenylenediamine, Scheme 1. Also, new mixed ligand complexes of the ligand, H<sub>2</sub>L and 8-hydroxyquinoline (8-HQ) with  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Fe^{3+}$  ions are synthesized. The structure of the complexes are characterized by elemental and thermal analyses, IR, UV–Vis, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements. In addition, the kinetic and thermodynamic characteristics of the decomposition steps of some complexes have been studied employing Coats–Redfern equation.

# Experimental

#### Materials

Metal salts, ethylchloroformate, 2-aminopyridine, *p*-phenylenediamine, 8-hydroxyquinoline, EDTA, nitric acid were Aldrich, BDH or Merck products. Organic solvents were either spectroscopically pure or purified by the recommended methods [18–20] and tested for their spectral purity.

#### Physical measurements

FT-IR spectra were recorded on a Perkin–Elmer 293 spectrometer (4000–400 cm<sup>-1</sup>) in KBr pellets. Electronic spectra were recorded at room temperature on a Shimadzu model UV-1601 PC spectrophotometer (200–800 nm) as solutions in DMF. The <sup>1</sup>H NMR spectrum of the ligand as a solution in DMSO-d<sub>6</sub>, were recorded on a Varian (FT-290), 90 MHz spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded at 300 °C and 70 ev on a shimadzu QP spectrometer model MS-5988. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa products, Model MKI magnetic susceptibility balance. The effective magnetic moments were calculated from the expression  $\mu_{eff} = 2.828 (X_M T)^{1/2}$  B.M., where  $X_M$  is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds [21]. The conductivities of complexes were measured as a solution in DMF  $(10^{-3} \text{ M})$  using WTWD-812 Weilheium-conductivity meter model LBR, fitted with a cell model LTA100. Microanalyses of carbon, hydrogen and nitrogen were carried out at the microanalytical center, Cairo University, Giza, Egypt. Analyses of the metals followed the dissolution of the solid complex in concentrated HNO<sub>3</sub> and titrating the metal solutions complexometrically using 0.001 M EDTA solution [22]. ESR spectra of the complexes were recorded on a Bruker, E500, X-band spectrometer. TGA measurements were carried out on a shimadzu-50 thermal analyzer. Melting points of the compounds were determined using a Stuart melting points instrument.

# Synthesis of the organic ligand, H<sub>2</sub>L

The ligand, H<sub>2</sub>L, was prepared in two steps, Scheme 1.

#### Preparation of ethylpyridine-2-carbamate (EPC)

Ethylchloroformate (1.09 g, 10 mmol) was added dropwise to 2aminopyridine (0.94 g, 10 mmol) with one drop of piperidine, the reaction mixture was allowed to stand in ice-bath for few minutes due to the exothermic behavior of the reaction, after that the reaction mixture was fused on a hot plate under reflux for 6 h. The product was allowed to cool till room temperature, solidified by ethanol and diethylether, filtered off and recrystallized from ethanol then dried under vacuum to give buff crystals, yield 44%, m.p. 180 °C.

#### Preparation of benzene-1,4-bis(3-pyridin-2-ylurea), the ligand, H<sub>2</sub>L

A mixture of EPC (3.32 g, 20 mmol) and *p*-phenylenediamine (1.08 g, 10 mmol) in DMF (20 ml) was refluxed on a hot plate for 4 h. The reaction mixture was allowed to cool till room temperature, poured on crushed ice, filtered off and recrystallized from ethanol then dried under vacuum to give gray crystals, yield 58%, m.p. > 300 °C. The molecular formula of the ligand ( $C_{18}H_{16}N_6O_2$ , M.Wt = 348) is in good agreement with the stoichiometry concluded from analytical data and mass spectra.

#### Synthesis of the metal complexes

Ethanolic solutions of the ligand, H<sub>2</sub>L, and the metal salt, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, VOSO<sub>4</sub>·H<sub>2</sub>O or UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O were mixed in a 1:1, 1:2 and 1:3 (L:M) molar ratio. In the preparation of all complexes (except Fe<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> complexes), 0.1 g of sodium acetate was added as a buffering agent to raise the PH to 5. The resulting solutions were stirred for about 1 h then refluxed on a hot plate from 6 to 8 h. The solid complexes which separated out on hot were filtered off, washed with hot ethanol and diethylether and finally dried in vacuum desiccator over anhydrous CaCl<sub>2</sub>.



Scheme 1. Synthesis of the ligand, H<sub>2</sub>L.

Table 1							
Analytical a	and	physical	data	of the	metal	com	olexes.

	Complex	Molecular formula	Color	Yield (%)	m. p. (°C)	Elemental analysis, found (calcd.)			Formula weight		$\Omega_m$ ( $\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1}$ )	
						C (%)	H (%)	N (%)	M (%)	Found <sup>a</sup>	Calcd.	
1	$[Co_2(HL)_2](NO_3)_2$	$C_{36}H_{30}N_{14}O_{10}Co_2$	Brown	80.05	>300	45.6 (46.2)	2.8 (3.2)	20.1 (20.9)	13.6 (12.6)	935.5	935.8	108.3
2	$[Co_2(HL)_3]NO_3$	$C_{54}H_{45}N_{19}O_9Co_2$	Pale brown	81.36	>300	52.4 (53.1)	2.9 (3.7)	21.1 (21.8)	10.2 (9.6)	-	1220.8	69.4
3	$[Co_2(H_2L)(8-HQ)_2](NO_3)_2$	$C_{36}H_{28}N_{10}O_{10}Co_2$	Buff	86.34	>300	50.6 (49.2)	3.0 (3.2)	16.4 (16.0)	13.7 (13.4)	877.0	877.8	96.4
4	$[Ni_2(HL)_2](NO_3)_2 \cdot H_2O \cdot EtOH$	$C_{38}H_{38}N_{14}O_{12}Ni_2$	Green	88.34	>300	44.9 (45.6)	3.1 (3.8)	18.6 (19.6)	11.2 (11.7)	1000.2	999.4	126.8
5	[Ni <sub>3</sub> (L)(HL)(NO <sub>3</sub> ) <sub>3</sub> (EtOH)]	$C_{38}H_{35}N_{15}O_{14}Ni_3$	Dark green	90.60	>300	41.1 (41.4)	2.7 (3.2)	18.0 (19.0)	17.0 (16.0)	-	1101.1	25.7
6	$[Ni_2(H_2L)(8-HQ)_2](NO_3)_2$	$C_{36}H_{28}N_{10}O_{10}Ni_2$	Green	70.83	>300	48.4 (49.2)	2.9 (3.2)	17.5 (16.0)	13.7 (13.4)	878.0	877.4	91.7
7	$[Cu_2(HL)_2](NO_3)_2$	$C_{36}H_{30}N_{14}O_{10}Cu_2$	Brown	88.99	>300	46.4 (45.7)	2.5 (3.2)	19.8 (20.7)	13.8 (13.4)	946.3	945.0	115.6
8	$[Cu_3(L)_2(NO_3)_2]$	$C_{36}H_{28}N_{14}O_{10}Cu_3$	Pale brown	85.32	>300	42.8 (42.9)	2.4 (2.8)	19.4 (19.5)	18.7 (18.9)	-	1006.5	26.2
9	$[Cu_2(HL)_2(8-HQ)_2]$	$C_{54}H_{42}N_{14}O_6Cu_2$	Green	94.40	>300	58.9 (58.4)	2.8 (3.8)	17.0 (17.6)	12.3 (11.5)	-	1109.0	28.7
10	$[Fe(HL)_2(NO_3)(H_2O)]$	$C_{36}H_{32}N_{13}O_8Fe$	Brown	71.84	>300	52.6 (52.1)	3.1 (3.9)	21.7 (21.9)	6.5 (6.7)	830.0	830.0	29.9
11	$[Fe_2(HL)_2(L)(NO_3)_2(EtOH)_2]$	$C_{58}H_{56}N_{20}O_{14}Fe_2$	Brown	70.28	>300	50.6 (50.9)	3.2 (4.1)	19.6 (20.5)	8.4 (8.2)	-	1368.0	13.4
12	[Fe(H <sub>2</sub> L)(HL)(8-HQ)]NO <sub>3</sub>	$C_{45}H_{37}N_{14}O_8Fe$	Dark brown	75.12	>300	57.3 (56.4)	3.2 (3.9)	21.8 (20.5)	6.4 (5.8)	957.5	957	39.4
13	[VO(HL) <sub>2</sub> ]	$C_{36}H_{30}N_{12}O_5V$	Green	85.55	>300	59.1 (56.8)	3.5 (3.9)	22.4 (22.1)	_ (6.6)	760.3	760.9	6.4
14	[UO <sub>2</sub> (HL) <sub>2</sub> ]	$C_{36}H_{30}N_{12}O_{6}U$	Pale gray	78.80	>300	44.2 (44.8)	2.8 (3.1)	17.7 (17.4)	(24.6)	964.4	964	5.9

<sup>a</sup> Value obtained from mass spectra.

# Synthesis of mixed ligand complexes

An ethanolic solution of the metal salt,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$  or  $Fe(NO_3)_3 \cdot 9H_2O$  was added gradually to an ethanolic solution of the ligand,  $H_2L$ , in the molar ratio 1:2 (L:M). The resulting solutions were stirred for 0.5 h, then an ethanolic solution of 8-hydroxyl-quinoline (8-HQ) was added to the previous solution in the molar ratio 2:2 (8-HQ:M). The solutions were continuously stirred for 2 h then refluxed on a hot plate from 6 to 8 h. The solid complexes which separated out on hot were filtered off, washed with hot ethanol then diethylether and finally dried in vacuum desiccator over anhydrous CaCl<sub>2</sub>. All of the complexes prepared were stable at room temperature, non-hygroscopic, insoluble in common organic solvents except DMF. The analytical and physical data for the metal complexes are collected in Table 1.

#### 3D molecular modeling studies

The 3D molecular modeling of the ligand,  $H_2L$  and a representative complex was carried out on a Hyperchem 7.5 program [23]. It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It has ability to handle transition metal compounds.

#### **Results and discussion**

#### Characterization of the ligand

The structure of the ligand,  $H_2L$ , was investigated by elemental analyses, IR, <sup>1</sup>H NMR, UV–Vis and mass spectra. Anal. Calcd.%: C, 62.06; H, 4.59; N, 24.13. Found%: C, 61.50; H, 3.75; N, 23.50. The IR spectrum (cm<sup>-1</sup>) of the ligand, Table 2, showed characteristic bands at 3291 and 3053 corresponding to v(NH), strong band at

1692 corresponding to v(C=0) amide and bands due to the stretching frequencies of the pyridine ring appeared at 1578 and 1503 [24,25]. <sup>1</sup>H NMR spectral data ( $\delta$  ppm) of the ligand relative to TMS in DMSO-d<sub>6</sub> without and with D<sub>2</sub>O give further support of the suggested structure of the ligand. The aromatic proton signals of phenylene and pyridine rings appeared at 6.41-8.24, the proton signals of NH groups at 9.37 and 10.43 completely disappeared on adding D<sub>2</sub>O. The electronic spectrum of the ligand  $(10^{-3} \text{ M in DMF})$ , Table 3,  $\lambda_{\text{max}}$  (nm). Three bands at 238, 285 and 376 were characterized and can be assigned to  $\pi$ - $\pi$ <sup>\*</sup> transitions within the aromatic rings,  $\pi - \pi^*$  transitions within C=O and an intramolecular charge transfer (CT) transition within the whole molecule. The mass spectrum of the ligand, Fig. 1, showed the molecular ion peak at m/e = 348 amu, confirming its formula weight (F. W. = 348). The mass fragmentation pattern, shown in Scheme 2, supported the suggested structure of the ligand.

The optimized structure of the ligand was given in Fig. 2 and structural parameters were evaluated by means of a semi-empirical molecular orbital calculations at the PM3 level provided by Hyperchem 7.5 program. These data are found to be, surface area  $(Å^2) = 498.80$ , volume  $(Å^3) = 1001.22$ , HOMO energy (ev) = -8.45, LUMO energy (ev) = -0.45, heat of formation (Kcal/mol) = 28.66, electronic energy (ev) = -668960.38, dipole moment  $\mu$  (Debye) = 4.76 and bonds length C=O (C9–O10 and C21–O22) = 1.21 Å.

#### Characterization of the metal complexes

On the basis of elemental analysis, the metal complexes of the ligand,  $H_2L$ , were assigned to posses the compositions and molecular formulae listed in Table 1. The results reveal that the ligand,  $H_2L$ , acts as bi- and tetradentate towards the metal ions via the pyridine -N, the carbonyl -O and/or the amide -N atoms in a non, mono- and bis-deprotonated form.

#### Table 2

Important IR spectral data and their assignment for the ligand H<sub>2</sub>L and its metal complexes.

No.	Compound or complex	IR spectral bands (cm <sup>-1</sup> )						
		υ(OH) (H <sub>2</sub> O/ EtOH)	υ(NH)	υ(C=0)	Pyridine stretching vibrations	υ( <b>M</b> —0)	υ( <b>M</b> —N)	Other bands
	H <sub>2</sub> L	-	3291, 3053	1692	1578, 1503	-	-	-
1	$[Co_2(HL)_2](NO_3)_2$	-	3291, 3066	1681, 1624	1572, 1486	519	425	$vNO_3^-$ ionic 1405
2	$[Co_2(HL)_3]NO_3$	-	3294, 3069	1681, 1623	1573, 1482	521	422	vNO <sub>3</sub> <sup>-</sup> ionic 1405
3	$[Co_2(H_2L)(8-HQ)_2](NO_3)_2$	-	3289, 3073	1676, 1623	1570, 1482	516	427	vNO <sub>3</sub> <sup>-</sup> ionic 1387
4	$[Ni_2(HL)_2](NO_3)_2 \cdot H_2O \cdot EtOH$	3480 (br)	3289, 3057	1689, 1625	1579, 1495	519	423	$vNO_3^-$ ionic 1409
5	[Ni <sub>3</sub> (L)(HL)(NO <sub>3</sub> ) <sub>3</sub> (EtOH)]	3500 (br)	3289, 3076	1681, 1624	1569, 1482	522	437	vNO <sub>3</sub> <sup>-</sup> monodentate 1390, 1321, 1220
6	$[Ni_2(H_2L)(8-HQ)_2](NO_3)_2$	-	3290, 3072	1680, 1623	1572, 1477	513	424	vNO <sub>3</sub> <sup>-</sup> ionic 1383
7	$[Cu_2(HL)_2](NO_3)_2$	-	3291, 3056	1689,1617	1578, 1483	516	457	vNO <sub>3</sub> <sup>-</sup> ionic 1412
8	$[Cu_3(L)_2(NO_3)_2]$	-	3291, 3058	1673	1576, 1482	517	432	vNO <sub>3</sub> <sup>-</sup> bidentate 1410, 1322, 1221, 1053
9	$[Cu_2(HL)_2(8-HQ)_2]$	-	3291, 3052	1693, 1623	1579, 1474	518	411	-
10	$[Fe(HL)_2(NO_3)(H_2O)]$	3460 (br)	3289, 3054	1697	1579, 1511	-	435	$vNO_{3}^{-}$ monodentate 1409, 1316, 1222
11	$[Fe_2(HL)_2(L)(NO_3)_2(EtOH)_2]$	3440 (br)	3290, 3055	1696	1580, 1509	-	433	$vNO_{3}^{-}$ monodentate 1411, 1310, 1224
12	[Fe(H <sub>2</sub> L)(HL)(8-HQ)]NO <sub>3</sub>	-	3292, 3055	1694, 1632	1578, 1507	518	411	vNO <sub>3</sub> -ionic 1411
13	[VO(HL) <sub>2</sub> ]	-	3290, 3055	1693	1580, 1505	-	418	υ(V=0) 976
14	[UO <sub>2</sub> (HL) <sub>2</sub> ]	-	3294, 3056	1694	1580, 1508	-	416	υ(0=U=0) 943

#### Table 3

Electronic absorption spectral data (in DMF solution) and magnetic moment values.

No.	Compound or complex	Electronic	Electronic spectral bands $\lambda$ (nm)								
		π-π* (aromatic system)	$\epsilon_{max}$ (mol <sup>-1</sup> cm <sup>-1</sup> L)	π-π* (C==0)	$\epsilon_{max}$ (mol <sup>-1</sup> cm <sup>-1</sup> L)	СТ	$\epsilon_{max}$ (mol <sup>-1</sup> cm <sup>-1</sup> L)	d–d transition	$\epsilon_{max}$ (mol <sup>-1</sup> cm <sup>-1</sup> L)	(B.M.)	(B.M.)
	H <sub>2</sub> L	238	109	285	375	376	44	-	-	-	-
1	$[Co_2(HL)_2](NO_3)_2$	245	161	316	436	390	520	528	72	3.67	5.20
2	$[Co_2(HL)_3]NO_3$	249	1680	301	3940	399	211	534	39	4.32	6.11
3	[Co <sub>2</sub> (H <sub>2</sub> L)(8-HQ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	237	137	321	217	405	214	524	83	3.83	5.42
4	[Ni <sub>2</sub> (HL) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O·EtOH	253	261	303	424	416	82	537	56	2.74	3.88
5	[Ni <sub>3</sub> (L)(HL)(NO <sub>3</sub> ) <sub>3</sub> (EtOH)]	240	341	297	627	404	75	539	42	2.83	4.93
6	[Ni <sub>2</sub> (H <sub>2</sub> L)(8-HQ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	256	368	321	719	410	681	545	99	2.51	3.55
7	$[Cu_2(HL)_2](NO_3)_2$	225	537	307	1116	412	758	523	234	1.81	2.56
8	$[Cu_3(L)_2(NO_3)_2]$	212	4408	312	10857	410	6313	524	1703	1.64	2.83
9	[Cu <sub>2</sub> (HL) <sub>2</sub> (8-HQ) <sub>2</sub> ]	248	260	316	420	410	397	529, 746	147, 43	1.98	2.80
10	$[Fe(HL)_2(NO_3)(H_2O)]$	249	262	318	498	385	428	536	124	2.80	2.80
11	$[Fe_2(HL)_2(L)(NO_3)_2(EtOH)_2]$	219	570	298	3840	385	266	545	56	3.97	5.61
12	[Fe(H <sub>2</sub> L)(HL)(8-HQ)]NO <sub>3</sub>	220	278	307	544	428	94	539	106	2.43	2.43
13	[VO(HL) <sub>2</sub> ]	249	158	297	330	399	51	568	10	2.24	2.24
14	$[UO_2(HL)_2]$	244	150	298	351	509	24	-	-	-	-

<sup>a</sup>  $\mu_{\rm eff}$  (B.M.) of one cationic species in the complexes.

<sup>b</sup>  $\mu_{\rm eff}$  (B.M.) the total magnetic moments of all cations in the complex.

Molar conductivities of the complexes were measured in DMF ( $10^{-3}$  M solution), Table 1. The complexes **5**, **8**, **9**, **10**, **11**, **13** and **14** have  $\Omega_m$  values in the range 5.9–29.9  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> which fall within the range of non-electrolytes. The observed  $\Omega_m$  values of some complexes may be due to displacement of part of coordinated NO<sub>3</sub><sup>-1</sup> ions by DMF solvent molecules. It has been reported that DMF is a good donor solvent and can replace NO<sub>3</sub><sup>-1</sup> from the coordination sphere of the metal complexes [26]. The  $\Omega_m$  values of the complexes **2** and **12** are 69.4 and 39.4  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, respectively (1:1 electrolytes). The low value of  $\Omega_m$  of complex

**12** may be due to the low mobility of its bulk cations. The complexes **1**, **3**, **4**, **6** and **7** have  $\Omega_m$  values in the range 91.7–126.8  $\Omega^{-1}$  - cm<sup>2</sup> mol<sup>-1</sup> which fall in the range of 1:2 electrolytes [26].

#### IR spectra and mode of bonding

The IR spectral data of the metal complexes and their tentative assignments are listed in Table 2. Complexes **4**, **5**, **10** and **11** showed a broad band in the range  $3500-3440 \text{ cm}^{-1}$  assigned to v(OH) of the coordinated or uncoordinated H<sub>2</sub>O and/or EtOH molecules associated with the complexes, which are confirmed by ele-



Scheme 2. Mass fragmentation pattern of the ligand.



Fig. 2. The optimized structure of the ligand, H<sub>2</sub>L.

mental and thermal analyses. Two bands appearing at 1578 and 1503 cm<sup>-1</sup> are assigned to pyridine ring stretching vibrations in the free ligand, the 1578  $cm^{-1}$  band shows a slight shift to lower or higher wavenumber but the 1503 cm<sup>-1</sup> band shows a shift to lower frequency by  $8-29 \text{ cm}^{-1}$  indicating the coordination of the pyridine nitrogen atoms to the metal ions [27]. In case of complexes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **9** and **12**, the v(C=O) band of the coordinated ligand is doubled, one band being nearly coincident with the corresponding one of free ligand at 1692 cm<sup>-1</sup> and the other occurring at a lower frequency by  $60-75 \text{ cm}^{-1}$ . This result has been interpreted in terms of the presence of both coordinated and noncoordinated (C=O) group in the same ligand molecules [28]. One of the v(NH) bands of the coordinated ligand being nearly coincident with corresponding one of free ligand and the other shows slightly shift to a lower or a higher frequency and the intensity of this band has decreased suggesting coordination of the ligand with deprotonation of the amidic hydrogens. For complexes 8, 10, 11, 13 and 14, v(C=0) band of the coordinated ligand being nearly coincident with the corresponding one of the free ligand confirming that C=O group is not involved in complex formation and the intensity of one NH (amidic) bands of the coordinated ligand has decreased showing coordination of the ligand with deprotonation of the amidic hydrogens. The nitrate vibrations in complexes 5, 10 and 11 at 1411-1390, 1321-1310 and 1224-1220 cm<sup>-1</sup> are indicative of the presence of monodentate nitrato groups [29,30] since the separation of the two highest frequency bands (under  $C_{2V}$  symmetry) is small ( $<160 \text{ cm}^{-1}$ ). Complex **8** shows four bands at 1410, 1322, 1221 and 1053 cm<sup>-1</sup> assigned to the bidentate chelating nitrato groups [31]. The presence of ionic  $NO_3^-$  ions in complexes 1, 2, 3, 4, 6, 7 and 12 confirming by the appearance of the stretching vibration mode of ionic nitrate at 1412–1383  $\text{cm}^{-1}$  [32]. Complex **13** showed strong absorption band at 976 cm<sup>-1</sup>, which is assigned to the v(V=0) vibration [33]. Also, the characteristic band of the antisymmetric  $\upsilon_3(O=U=O)$  is observed in the IR spectrum of the uranyl complex (14) at 943  $\text{cm}^{-1}$  [34] indicating that the uranyl ion is linear. Appearance of the new bands at 522-513 and 457-411 cm<sup>-1</sup> which could be assigned to v(M-O) and v(M-N), respectively [35,36].

The IR spectrum of the free 8-hydroxyquinoline (8-HQ) shows a strong band at 1586 cm<sup>-1</sup> due to the stretching vibration of the C=N group [37]. This band is shifted to a higher wavenumber on coordination for complexes **3**, **6**, **9** and **12** suggesting that the lone pair on nitrogen is involved in the formation of a bond with the metal ion. Moreover, the broad stretching vibration at 3242 cm<sup>-1</sup> due to O–H group of the free 8-HQ ligand [38] was found to be absent in the latter complexes, suggesting the formation of an M–O bond with 8-hydroxyquinolinate. Thus, 8-hydroxyquinolinate in all mixed ligand complexes **3**, **6**, **9** and **12** is a bidentate chelating ligand.

#### Electronic spectra and magnetic moment measurements

The electronic absorption spectra measured in DMF solvent and the effective magnetic moments of the prepared metal complexes were determined. The data obtained are recorded in Table 3. The bands at 238, 285 and 376 nm of the free ligand show small shifts as a result of complex formation [39–41]. The band at 416–385 nm in the spectra of the complexes may be due to intramolecular LMCT [42]. Three different types of Cu(II) complexes were obtained, a binuclear complex [Cu<sub>2</sub>(HL)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (**7**), a trinuclear complex [Cu<sub>3</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**8**) and a mixed ligand complex [Cu<sub>2</sub>(HL)<sub>2</sub>(8-HQ)<sub>2</sub>] (**9**). The electronic spectra of Cu(II) complexes (**7** and **8**) showed one band at 523 and 524 nm, respectively, corresponding to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  transition in square-planar geometry [43]. In addition, the magnetic moments of the complexes (**7** and **8**) were 1.81 and 1.64 B.M., respectively, which are consistent with the proposed square-planar structure [44] of the complexes. However, the mixed ligand complex (**9**) showed two absorption bands at 746 and 529 nm, which can be assigned to  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  transitions within octahedral structure [45]. The observed magnetic moment value of complex (**9**) is 1.98 B.M. which indicates the presence of one unpaired electron per the Cu(II) ion, also confirming its octahedral geometry [46]. The values showed the presence of some spin–spin interaction between Cu(II) ions in the different complexes.

The effective magnetic moment values of Co(II) complexes, binuclear complexes  $[Co_2(HL)_2](NO_3)_2$  (1),  $[Co_2(HL)_3]NO_3$  (2) and  $[Co_2(H_2L)(8-HQ)_2](NO_3)_2$  (3) were found to be in the range 3.67– 4.32 B.M. These values are consistent with the presence of three unpaired electrons per the Co(II) ion in tetrahedral geometry [47]. The electronic spectra of the obtained Co(II) complexes in DMF solution exhibit one band at 528, 534 and 524 nm, respectively, the bands exhibit some shifts to lower wavelength than the expected value for tetrahedral complexes (600–700 nm) [47] which may be due to the formation of six coordinate species in DMF which is a coordinating solvent and the d–d transition bands shifted near 500 nm which the expected value for Co(II) ion in octahedral complexes [47].

For Ni(II) complexes, binuclear complexes  $[Ni_2(HL)_2](NO_3)_2 \cdot H_2$ . O·EtOH (**4**) and  $[Ni_2(H_2L)(8-HQ)_2](NO_3)_2$  (**6**) and a trinuclear complex  $[Ni_3(L)(HL)(NO_3)_3$  EtOH] (**5**) were obtained. The effective magnetic moment values of Ni(II) complexes were in the range 2.51–2.83 B.M. These values indicate the presence of two unpaired electrons per Ni(II) ion and confirming tetrahedral geometry around Ni(II) ion [48–50]. The results indicate some spin–spin coupling due to antiferromagnetic interaction [48]. The electronic spectra of all Ni(II) complexes (**4**, **5** and **6**) in DMF solution showed one band at 537, 539 and 545 nm, respectively, the shift of bands to lower wavelength may be explained by the coordination of DMF solvent with Ni(II) ions in the complexes and formation of octahedral structures.



Fig. 3. X-band ESR spectra of Cu<sup>2+</sup> complexes (7, 8, 9) and VO<sup>2+</sup> complex (13).



Fig. 4. Mass spectra of the [Fe(HL)<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)] (10), [Co<sub>2</sub>(HL)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (1) and [Co<sub>2</sub>(H<sub>2</sub>L)(8-HQ)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (3) complexes.

Three Fe(III) complexes were obtained which have different formulae, mononuclear complexes  $[Fe(HL)_2(NO_3)(H_2O)]$  (10), [Fe $(H_2L)(HL)(8-HQ)$  NO<sub>3</sub> (12) and a binuclear complex [Fe<sub>2</sub>(HL)<sub>2</sub>(-L)(NO<sub>3</sub>)<sub>2</sub>(EtOH)<sub>2</sub>] (11). The electronic spectra of the Fe(III) complexes showed one absorption band at 536-545 nm corresponding to  ${}^{6}A_{1} \rightarrow {}^{4}T_{2}$  electronic transition [51], suggesting an octahedral geometry around Fe(III) ion. The values of the magnetic moments of the mononuclear Fe(III) complexes (10 and 12) were 2.80 and 2.43 B.M., respectively, these values are too near from its being in a low spin  $(t_2g^5 eg^0)$  where the magnetic moment lies in the range 2.1–2.5 B.M. [52], which may be due to the effect of the strong fields of the ligand, H<sub>2</sub>L and the additional ligand, 8-HQ. This would lead to spin-pairing of the electrons and/or antiferromagnetic interactions between Fe(III) ions in neighboring molecules. The magnetic moment of the binuclear complex (11) is 3.97 B.M., lower than expected value (which is around 5.92 B.M.), perhaps due to antiferromagnetic interactions between Fe(III) ions in the complex.

The electronic spectrum of the mononuclear VO<sup>2+</sup> complex, [VO(HL)<sub>2</sub>] showed a d-d transition band at 568 nm which can be assigned to the <sup>2</sup>B<sub>2</sub>  $\rightarrow$  <sup>2</sup>E ( $\upsilon_1$ ) or <sup>2</sup>B<sub>2</sub>  $\rightarrow$  <sup>2</sup>B<sub>1</sub> ( $\upsilon_2$ ) transition and indicates that the geometry around VO<sup>2+</sup> ion is square-pyramidal [53]. The band at 976 cm<sup>-1</sup> in the IR spectrum of the vanadyl complex is characteristic for the proposed structure [54]. The magnetic moment value of the  $VO^{2+}$  complex is 2.24 B.M. which is higher than the expected for d<sup>1</sup>-system, suggesting an orbital contribution [55].

The electronic spectrum of the mononuclear  $UO_2^{+2}$  complex  $[UO_2(HL)_2]$  showed one absorption band at 509 nm, which is attributed to an electronic transition from the apical oxygens to f-orbitals of the uranium (VI) ion or due to charge transfer transition from the ligand to uranium (VI) ion [56].

# ESR spectra of $Cu^{2+}$ and $VO^{2+}$ complexes

ESR spectra of the Cu(II) complexes (**7**, **8** and **9**) and the V(IV) O complex (**13**) were recorded in the solid state at room temperature as shown in Fig. 3. The X-band ESR spectra of the Cu(II) complexes (**7** and **8**) exhibit a single broad line with g = 2.077 and 2.078, respectively. The *g*-values together with the shape of the ESR signals indicate the square-planar geometry around Cu(II) ions in these complexes [57,58]. The spectrum of the Cu(II) complex (**9**) exhibits two signals at  $g_{\perp} = 2.068$  and  $g_{\parallel} = 2.155$ , gav = 1/3 ( $g_{\parallel} + 2g_{\perp}$ ) = 2.097. The shape of the ESR signals is consistent with the octahedral geometry around the Cu(II) ions in this complex [57,58]. From the observed *g*-values, it is clear that  $g_{\parallel} > g_{\perp}$  which indicates that the unpaired electron is predominantly in the dx<sup>2</sup>-y<sup>2</sup> orbital [59–61] giving <sup>2</sup>B<sub>1g</sub> as the ground state. The *g* value is

#### Table 4

Results of thermogravimetric analysis (TGA) of some complexes.

Complex	Molecular formula of the complex (M. Wt.)	Temperature range (°C)	Wt loss% found (calcd.)	Decomposed product lost
(2)	$[Co_2(HL)_3]NO_3$	101-291	41.64(41.20)	$NO_2 + C_{27}H_{19}N_7O$
	(1220.8)	292-351	24.12(23.75)	$C_{17}H_{12}N_3O_2$
		352-424	22.98(22.77)	$C_{10}H_{14}N_8O_2$
			11.12(12.27)	Residue, 2CoO
(4)	[Ni <sub>2</sub> (HL) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O·EtOH	29–157	5.41(4.60)	Lattice EtOH
	(999.4)	158-467	80.86(80.45)	Lattice $H_2O + 2NO_2 + C_{36}H_{30}N_{12}O_4$
			13.98(14.95)	Residue, 2NiO
(5)	$[Ni_3(L)(HL)(NO_3)_3(EtOH)]$	38-174	4.48(4.18)	Coordinated EtOH
		175–347	46.44(46.77)	$3NO_2 + C_{22}H_{13}N_6O$
	(1101.1)	348-453	25.02(24.70)	$C_{13}H_{16}N_6O$
			23.98(24.35)	Residue, 2NiO·NiCO <sub>3</sub>
(7)	$[Cu_2(HL)_2](NO_3)_2$	173–298	43.33(42.54)	$2NO_2 + C_{20}H_{14}N_4$
	(945.0)	299–549	41.68(42.33)	$C_{16}H_{16}N_8O_5$
			15.00(15.13)	Residue, Cu <sub>2</sub> O
(8)	$[Cu_3(L)_2(NO_3)_2]$	39–293	35.91(35.47)	$2NO_2 + O_2 + C_{15}H_{11}N_3$
	(1006.5)	294-435	40.77(40.83)	$C_{21}H_{17}N_9O$
			23.32(23.70)	Residue, 3CuO
(13)	$[VO(HL)_2]$	186–312	53.62(53.75)	$C_{22}H_{15}N_7O_2$
	(760.9)	313-505	35.29(35.35)	$C_{14}H_{15}N_5O$
			11.10(10.90)	Residue, VO <sub>2</sub>

an important function for indicating covalent character of M—L bonds [62], for ionic character,  $g_{||} < 2.0023$  and for covalent character  $g_{||} > 2.0023$ . In the present complex (**9**), the *g* is more than 2.0023 indicating appreciable covalent character for the Cu—L bond [63]. In addition, exchange coupling interaction between the two copper centers is explained by the Hathaway expression  $[G = (g_{||} - 2.0023/(g_{\perp} - 2.0023)]$ , if *G* is greater than 4, the exchange interaction in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction is observed in the solid complex. The calculated *G*-value of Cu(II) complex (**9**) is 2.324, suggests some interaction between the Cu(II) centers.

The ESR spectrum of the  $[VO(HL)_2]$  complex (**13**) showed a sharp band with resolved hyperfine structure. The vanadium hyperfine coupling with the nearby <sup>51</sup>V (I = 7/2) nucleus showed 8-lines indicating that the VO<sup>2+</sup>-complex is mononuclear. The *g*-values of VO<sup>2+</sup>-complex were g = 2.061 and g = 2.112. These values agree with the *g*-tensor parameters reported for vanadium complexes with square-pyramidal geometry [64,65].

#### Mass spectra of the metal complexes

The mass spectra for most of the complexes were performed to confirm the molecular formulae. The molecular ion peaks are coincident with the formula weights of the complexes (see Table 1). This supports the identity of the structure. The mass spectra of the complexes  $[Co_2(HL)_2](NO_3)_2$ ,  $[Co_2(H_2L)(8-HQ)_2](NO_3)_2$  and  $[Fe(HL)_2(NO_3)(H_2O)]$ , Fig. 4, are taken as representative examples. The molecular ion peaks were observed at m/e 935.5, 877 and 830, respectively, which confirming the formula weights of these complexes.

#### Thermal studies

Thermogravimetric analysis (TGA) was used as a probe to proof the associated water or solvent molecules to be in the coordination sphere of the complexes or in the crystalline form, supports the elemental analysis. The results of TGA of some complexes (2, 4, 5, 7, 8 and 13) were recorded in Table 4. The following detailed description of the TG thermograms of the complexes (5, 8 and 13) is given as examples and the other TG thermograms were obtained similarly.

*TGA* of  $[Ni_3(L)(HL)(NO_3)_3(EtOH)]$  complex (**5**). The TG thermogram of  $[Ni_3(L)(HL)(NO_3)_3(EtOH)]$  complex (**5**) involves three decomposition steps in the ranges 38–174, 175–347 and 348–453 °C, Scheme 3. Elimination of coordinated C<sub>2</sub>H<sub>5</sub>OH molecule (calcd. 4.18%, found



Scheme 3. Proposed thermal decomposition pattern of [Ni<sub>3</sub>(L)(HL)(NO<sub>3</sub>)<sub>3</sub>(EtOH)].

4.48%) is the first step. The second step shows removal of the coordinated nitrate groups in a form of NO<sub>2</sub> and a fragment part ( $C_{22}H_{13}N_6O$ ) of the ligand (calcd. 46.77%, found 46.44%). In the last step, the complex undergoes decomposition of another part of the ligand ( $C_{13}H_{16}N_6O$ ) within the temperature range up to 453 °C, after which a constant weight was observed and 2NiO. NiCO<sub>3</sub> (calcd. 24.35%, found 23.98%) was the final residue.

TGA of  $[Cu_3(L)_2(NO_3)_2]$  complex (**8**). The TG thermogram of the  $[Cu_3(L)_2(NO_3)_2]$  complex (**8**) involves two decomposition steps in the ranges 39–293 and 294–435 °C, Scheme 4. The first step shows removal of the coordinated nitrate groups in a form of NO<sub>2</sub> and O<sub>2</sub> in addition of a fragment part ( $C_{15}H_{11}N_3$ ) of the ligand (calcd. 35.47%, found 35.91%). In the second step, the complex undergoes decomposition of another part of the ligand ( $C_{21}H_{17}N_9O$ ) within the temperature range up to 435 °C leading to the formation of 3CuO (calcd. 23.70%, found 23.23%) as the final residue.

TGA of  $[VO(HL)_2]$  complex (13). The thermal decomposition process of  $[VO(HL)_2]$  complex (13) started at 186 °C and finished at 505 °C



Scheme 4. Proposed thermal decomposition pattern of [Cu<sub>3</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>].

$$\begin{bmatrix} VO(C_{36}H_{30}N_{12}O_4) \\ complex (13) \\ M. Wt. = 760.9 \\ \end{bmatrix}$$

$$\begin{bmatrix} -C_{22}H_{15}N_7O_2 \\ 53.62 \%(53.75 \%) \\ found \%(calcd \%) \\ \end{bmatrix}$$

$$\begin{bmatrix} VO(C_{14}H_{15}N_5O_2) \end{bmatrix}$$

$$\begin{bmatrix} VO(C_{14}H_{15}N_5O_2) \end{bmatrix}$$

$$\begin{bmatrix} -C_{14}H_{15}N_5O \\ 35.29 \%(35.35 \%) \\ \end{bmatrix}$$

$$\begin{bmatrix} VO_2 \\ 11.10 \%(10.90 \%) \end{bmatrix}$$

Scheme 5. Proposed thermal decomposition pattern of [VO(HL)<sub>2</sub>].

and involves the removal of a fragment part ( $C_{22}H_{15}N_7O_2$ ) of the ligand (calcd. 53.75%, found 53.62%) in the 186–312 °C temperature range. In the second stage, the complex undergoes decomposition of another part of the ligand ( $C_{14}H_{15}N_5O$ ) within the temperature range up to 505 °C, leading to the formation of VO<sub>2</sub> (calcd. 10.90%, found 11.10%) as the final residue, Scheme 5.

The thermodynamic and kinetic parameters for the different thermal decomposition steps in the complexes (2, 4, 5, 7, 8 and 13) were evaluated graphically by employing the Coats-Redfern equation [66]. The results of the order (*n*), the activation energy ( $E^*$ ), the activation enthalpy ( $\Delta H^* = E^* - RT$ ), the activation entropy  $(\Delta S^* = R [\ln(Ah/KT) - 1])$  and the free energy of activation  $(\Delta G^* = \Delta H^*$ - $T\Delta S^*$ ) of the decomposition steps for the chosen complexes are listed in Table 5, where A is a pre-exponential factor, K is Boltzmann's constant and h is Plank's constant, respectively. The  $\Delta S^*$ values were found to be negative which indicated that the activated complex is more ordered than the reactant and/or the thermal decomposition reaction is slower than normal [67]. The positive sign of  $\Delta G^*$  revealed that the decomposition steps are non-spontaneous processes.  $\Delta G^*$  values increase with increasing the order of the decomposition stages which indicates that at high temperatures the ligand decomposes and requires more energy for its rearrangement in the activated state [68] this may be attributed to the structural rigidity of the remaining complex after the expulsion of one and more ligands, as compared with the precedent complex, which required more energy for its rearrangement before undergoing any compositional change. The positive values of  $\Delta H^*$ means that the decomposition processes are endothermic.

#### 3D Molecular modeling study

The molecular modeling of a representative complex,  $[Co_2(H_2-L)(8-HQ)_2]$  (NO<sub>3</sub>)<sub>2</sub> (**3**) is shown in Fig. 5. The C=O bonds (C9–O10 and C21–O22) are longer by 0.05 Å which indicate that the coordination take place through carbonyl groups with two O, N-donor of the ligand, H<sub>2</sub>L and two O, N-donor of the mixed ligand, 8-HQ at the equatorial positions in trans-arrangement to each other, is based on its square planar structure.

Based on the above results gained from elemental and thermal analyses, IR, electronic, mass and ESR spectra as well as conductance and magnetic moments studies, the geometrical structures of the complexes can be formulated as follows:



The proposed structures of the mononuclear complexes (10), (13) and (14).

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The order (*n*), temperature of decomposition and activation parameters ( $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta G^*$ ) for decomposition steps of some of the complexes.

No.	Complex	Step	Order (n)	T (°k)	$E^*$ (KJ mol <sup>-1</sup> )	$\Delta H^*$ (KJ mol <sup>-1</sup> )	$\Delta S^*$ (JK mol <sup>-1</sup> )	$\Delta G^*$ (KJ mol <sup>-1</sup> )
(2)	$[Co_2(HL)_3]NO_3$	1st	0.66	389	13.57	10.34	-173.4	77.79
		2nd	0.66	537	15.93	11.47	-181.6	108.99
		3rd	0.66	636	14.49	9.20	-181.1	124.38
(4)	[Ni <sub>2</sub> (HL) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O·EtOH	1st	0.66	413	6.47	3.04	-166.3	71.72
		2nd	0.66	603	18.9	13.89	-182.5	123.94
(5)	[Ni <sub>3</sub> (L)(HL)(NO <sub>3</sub> ) <sub>3</sub> (EtOH)]	1st	0	326	6.78	4.07	-167.8	58.77
		2nd	0.66	412	15.7	12.27	-176.3	84.91
		3rd	0.66	605	13.80	8.77	-180.4	117.9
(7)	$[Cu_2(HL)_2](NO_3)_2$	1st	0.66	531	16.94	12.53	-183.4	109.92
		2nd	0.66	677	14.64	9.011	-181.7	132.02
(8)	$[Cu_3(L)_2(NO_3)_2]$	1st	0.66	531	19.10	14.69	-180.8	110.69
		2nd	0.66	588	14.60	9.71	-180.2	115.67
(13)	[VO(HL) <sub>2</sub> ]	1st	0.66	551	14.17	9.59	-187.1	112.68
		2nd	0.66	660	14.53	9.04	-182.6	129.56



The proposed structures of the binuclear complexes (1), (4) and (7).



The proposed structure of the binuclear Co(II) complex (2).



The proposed structure of the binuclear Fe(III) complex (11).



The proposed structure of the trinuclear Ni(II) complex (5).



The proposed structure of the trinuclear Cu(II) complex (8).



The proposed structures of the mixed ligand complexes  $(\mathbf{3})$  and  $(\mathbf{6})$ .



The proposed structure of the mixed ligand complex (9)



The proposed structure of the mixed ligand complex (12).



Fig. 5. 3D molecular modeling structure of complex (3).

#### Conclusion

New bis (pyridylurea) ligand and its  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $VO^{2+}$ and  $UO_2^{2+}$  complexes were prepared and characterized by different spectroscopic techniques. There are variety in the geometrical structures of the prepared metal complexes: square planar, tetrahedral, octahedral and square pyramidal arrangements. The thermal decomposition as well as the thermodynamic and kinetic parameters were studied. 3D molecular modeling of the ligand and a representative Co(II) complex indicate that the coordination take place through carbonyl groups with two O, N-donor of the ligand, H<sub>2</sub>L and two O, N-donor of the mixed ligand, 8-HQ at the equatorial positions in trans-arrangement to each other, is based on its square planar structure.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.03.016.

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