# Azo Complexes of Cu(II), Co(II), Ni(II), Cd(II), Th(IV), and UO<sub>2</sub>(VI) Ions. Mixed-Ligand Complexes, Pyrolysis Products and Biological Activity

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## ABSTRACT

The reactions of azo ligand, 2-[2'-carboxyphenylazo]-5,5-dimethyl-1,3cyclohexane-dione, (H<sub>2</sub>L), with the metal ion Cd(II), Cu(II), Ni(II), Co(II), Th(IV), or UO<sub>2</sub>(VI) in the presence of LiOH as a deprotonating agent, yielded binary mononuclear complexes. The binary Cu(II) complex reacts with the ligands 1,10-phenanthroline or 2-aminopyridine to form mixed-ligand complexes. All the binary complexes of Cd(II), Cu(II), and Ni(II) have octahedral configurations, while the Co(II) complex is square-planar. The binary complexes of Th(IV) and

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UO<sub>2</sub>(VI) have distorted dodecahedral geometries. The mixed-ligand complexes have octahedral configurations. Thermal studies on these complexes showed the possibility of obtaining new complexes pyrolytically, where the complexes decompose through several isolable as well as non-isolable intermediates during heating. The structures of all complexes and the corresponding thermal products were elucidated by elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments, <sup>1</sup>H NMR and TG–DSC measurements as well as by mass spectroscopy. The ligand and some of the complexes were found to activate the enzyme pectinlyase.

Key Words: Azo complexes; Mixed-ligand; Pyrolysis; Biological activity.

#### INTRODUCTION

The widespread application of azo compounds and their metal chelates as dyes, acid–base redox indicators, metallochrome, and histological stains have attracted the interest of many investigators.<sup>[1–5]</sup> The sulfonated dye congo red (CR) is clinically useful as a histological stain for amyoid, as well as an HIV protease and reverse transcriptase inhibitor. CR has been shown to inhibit the conversion of the "good" form of scrapie prion protein to the "bad". The CR crystal structure as well as a model far its complex with HIV protease have been described.<sup>[6]</sup>

Azo dyes exhibit strong pharmacological activities and are also used for dyeing food stuff and preserving food grains.<sup>[7,8]</sup> Pectinlyase is one of the pectinases which is a group of enzymes used in fruit and textile industries.<sup>[9]</sup> These enzymes break down complex polysaccharides of plant tissues into simpler molecules like galacturonic acid. The role of acidic pectinases in bringing down the cloudiness and bitterness of fruit juices is well established.<sup>[10]</sup> Recently, there has been a good number of reports on the application of alkaline pectinases in the textile industry for the retting and degumming of fiber crops, production of good quality paper, fermentation of coffee and tea, oil extractions, and treatment of pectic waste water.<sup>[10]</sup>

In this paper, we report the synthesis and characterization of binary complexes of 2-[2'-carboxyphenylazo]-5,5-dimethyl-1,3-cyclohexanedione (H<sub>2</sub>L) Fig. 1, with the transition metal ions Cd(II), Cu(II), Co(II), and Ni(II) and the actinide metal ions Th(IV) and UO<sub>2</sub>(VI). Also described are mixed ligand complexes of Cu(II) ion with H<sub>2</sub>L and 2-aminopyridine (2-ampy) or 1,10-phenanthroline (1,10-phen). Thermal studies explored the possibility of obtaining new complexes which cannot be prepared from solutions.



*Figure 1.* Structures of 2-[2'-carboxyphenylazo]-5,5-dimethyl-1,3-cyclohexanedione (H<sub>2</sub>L), 2-aminopyridine (2-ampy), and 1,10-phenanthroline (1,10-phen).

#### EXPERIMENTAL

#### Materials

All chemicals used in the present investigation were from BDH, Analar or Merck and included  $Cd(NO_3)_2 \cdot 4H_2O$ ,  $Cu(NO_3)_2 \cdot H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Th(NO_3)_4 \cdot 5H_2O$ , and  $UO_2(NO_3)_2 \cdot 5H_2O$ , 2-aminopyridine, 1,10-phenanthroline, LiOH  $\cdot$  H<sub>2</sub>O, nitric acid, hydrochloric acid, ammonia, murexide, eriochrome black T and xylenol orange indicators, hexamethylenetriamine, and ethylenediaminetetraacetic acid disodium salt. The solvents used were methanol, ethanol, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). These solvents were reagent grade. The organic ligand (H<sub>2</sub>L) was prepared by literature methods<sup>[11,12]</sup> through coupling the diazonium salt 2-aminobenzoic acid with 5,5-dimethyl-1,3-cyclohexanedione. The coupling occurs in sodium acetate medium. The purity of the ligand was checked by elemental analyses, <sup>1</sup>H NMR, and TLC.

#### **Analyses and Physical Measurements**

Electronic spectra of solutions of the organic ligand  $(H_2L)$  and their complexes in DMF were recorded on a Jasco model V-550 UV-Vis spectrophotometer. IR spectra were recorded on a Perkin–Elmer 437 ER spectrometer using KBr discs; polyethylene was used as a calibrant. 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 using the relation  $\mu_{\rm eff} = 2.828(\chi_{\rm m} \cdot T)^{1/2}$  B.M., where  $\chi_{\rm m}$  is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. <sup>1</sup>H NMR spectra (DMSO- $d_6$ ) were recorded at room temperature on a Varian FT-290.90 MHz spectrometer, using TMS as an internal standard. TG-DSC measurements were carried out on a Shimadzu thermogravimetric analyzer using the TA-50 WSI program. Mass spectra were recorded at 70 eV and 300 °C on a MS 5988 Hewlett-Packard mass spectrometer. Melting or decomposition points were determined on a Gallenkamp, melting point apparatus, England. Conductivities were measured in solutions of the complexes in DMF  $(10^{-3} \text{ M})$  using a model LBR WTWD-812 Weilheim conductivity meter, fitted with a model LTA 100 cell. Analyses of the metals followed decomposition of their complexes with concentrated nitric acid. The resultant solutions were diluted with water and filtered to remove the precipitated ligand. The solutions were then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. Microanalyses of carbon, hydrogen, nitrogen, and sulfur were carried out at the Microanalytical Center, Cairo University, Giza, Egypt.

## **Preparation of the Metal Complexes**

The binary complexes as well as the mixed-ligand complexes were prepared in the presence of  $\text{LiOH} \cdot \text{H}_2\text{O}$  as a deprotonating agent.

#### Preparation of the Binary Complexes

Molar Ratio  $M: H_2L: LiOH = 1:1:1$ . A mixture of  $LiOH \cdot H_2O$  (0.17 g, 4 mmol) and  $H_2L$  (1.15 g, 4 mmol) in 50 mL of methanol was added to the metal salt (4 mmol) dissolved in the least amount of water, namely  $Cd(NO_3)_2 \cdot 4H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Th(NO_3)_4 \cdot 5H_2O$ , or  $UO_2(NO_3)_2 \cdot 5H_2O$ . The reaction mixture was refluxed for 3 hr with constant stirring and was left to cool at room temperature to ensure the complete formation of metal complexes. The precipitated solid complexes were filtered, washed several times with 50% (v/v) methanol–water to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether and dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

Preparation of the Mixed-Ligand Complexes

Molar Ratio Cu(II):  $H_2L$ : 2-ampy or 1,10-phen: LiOH = 1:1:1:1. A mixture of LiOH  $\cdot$  H<sub>2</sub>O (0.17 g, 4 mmol) and H<sub>2</sub>L (1.15 g, 4 mmol), and

2-aminopyridine (0.376 g, 4 mmol) or 1,10-phenanthroline (0.79 g, 4 mmol) in 60 mL of methanol was added to  $Cu(NO_3)_2 \cdot 3H_2O$  (0.97 g, 4 mmol) dissolved in the least amount of water. The reaction mixture was refluxed for 4 hr with constant stirring and was left to cool at room temperature to ensure the complete formation of the metal complexes. The precipitated solid complexes were filtered, washed several times with 50% (v/v) methanol-water to remove any traces of the unreacted starting materials. Finally, the mixed-ligand complexes were washed with diethyl ether and dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

Pyrolytic Preparation of Some Metal Complexes

New solid metal complexes (9)–(11), Table 1, were prepared pyrolytically by heating the corresponding mother complexes (4), (6), and (7), respectively, to the temperatures at which the exothermic or the endothermic peak is observed. The complex under investigation was placed in a porcelain crucible and heated slowly in an oven to the maximum temperature of 350 °C. The heating rate did not exceed 5 °C min<sup>-1</sup>. The heating was continue until it reached the temperature at which the exothermic or endothermic peak was observed in the DSC curve of the original complex. The complex was kept at this temperature for a further 1/2 hr, to ensure the removal of all of the liberated species and to avoid the occurrence of a backward reaction to the original complex. The new product was allowed to cool to room temperature and then was characterized.

Pyrolytic Preparation of  $[Cu(L)(2-ampy)_2]$  (9)

This compound was prepared by heating complex (4) to  $170 \,^{\circ}$ C till constant weight. The color of the complex is olive green, which differed from the color of the mother complex.

Pyrolytic Preparation of [Ni(HL)(NO<sub>3</sub>)(OH<sub>2</sub>)] (10)

This compound was prepared by heating complex (6) at  $160 \,^{\circ}\text{C}$  to a constant weight. The color of the complex is deep brown which differed from the color of the mother complex.

Pyrolytic Preparation of [Th(HL)(L)]NO<sub>3</sub> (11)

This compound was prepared by heating complex (7) at  $196 \,^{\circ}$ C to a constant weight; the color changed from yellow to brown.

Table 1.	Analytica	ll and physical	data of or	ganic liga	nd, H <sub>2</sub> L, and its	metal comple	xes.	
			;		Ele	emental analyse	s, found (Calc.)	%
Compounds	F. W.	Color	(C)	Y 1eld (%)	С	Н	Ν	Metal
$H_2L$	288.30	Yellow	241	86	62.70 (62.49)	5.90 (5.59)	9.59 (9.72)	I
$\begin{array}{c} C_{15}H_{16}N_2O_4 \\ \textbf{(1)} \left[Cd(HL)_2\right] \cdot H_2O \\ CHC_2M \cdot C_{2M}O \end{array}$	705.01	Yelow	>250	81	50.90 (51.11)	4.80 (4.57)	8.30 (7.95)	16.01 (15.94)
$\begin{array}{c} C_{30} C_{30} C_{30} C_{30} C_{30} C_{30} \\ (2) \left[ Cu(HL)_2 \right] \\ C & U & C_{10} \\ C & U & C_{10} \\ \end{array}$	638.13	Pale green	>250	76	56.50 (56.47)	4.80 (4.74)	8.50 (8.78)	9.70 (9.96)
C30H30CUN4C8 (3) [Cu(HL) <sub>2</sub> (1,10-phen)] $C$ H $C_{1N}$ O	818.34	Pale green	>250	71	61.30 (61.64)	4.90 (4.68)	10.30 (10.27)	7.60 (7.76)
C42H38CUN6O8 (4) [Cu(HL)(2-ampy) <sub>2</sub> NO3] · CH <sub>3</sub> OH C24H3, ChN5O8	633.12	Green	>250	59	49.30 (49.32)	5.00 (4.93)	15.20 (15.49)	9.93 (10.04)
(5) $[Co(HL)_2] \cdot H_2O$	651.53	Brown	>250	67	55.20 (55.30)	4.90 (4.95)	8.30 (8.59)	9.17 (9.04)
$\begin{array}{c} C_{30} C_{30} C_{31} C_{31} C_{40} \\ \textbf{(6)} \left[ Ni(HL) NO_3 (OH_2)_2 \right] \cdot 3H_2 O \\ C & H & Ni N & O \\ \end{array}$	498.06	Brown	>250	74	36.30 (36.17)	5.00 (5.06)	8.37 (8.44)	11.93 (11.78)
(7) [Th((HL) <sub>2</sub> NO <sub>3</sub> (OH <sub>2</sub> )]NO <sub>3</sub> C H N O Th	948.65	yellow	>250	99	38.20 (37.98)	3.40 (3.40)	8.30 (8.56)	24.62 (24.46)
(8) $[UO_2(HL)_2(OH_2)_2] \cdot 1_2^{\frac{1}{2}}H_2O$	907.67	Yellow	>250	70	39.80 (39.70)	4.40 (4.11)	6.00 (6.17)	I
(9) $[Cu(L)(2-ampy)_2]$ $C_{2-H_2,C_{1}N,CO}$	538.06	Olive green	>250	84	55.50 (55.81)	4.77 (4.87)	15.28 (15.62)	11.90 (11.81)
$(10) [Ni(HL)NO_3(OH_2)]$	426.00	Deep brown	>250	85	42.55 (42.29)	4.13 (4.02)	9.70 (9.86)	13.80 (13.78)
C151177411308 (11) [Th(HL)(L)]NO3 C30H29N5O11Th	867.62	Brown	>250	91	41.64 (41.53)	3.28 (3.37)	8.00 (8.07)	26.50 (26.74)

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Pectinlyase Enzyme Testing

The compounds were tested according to the method of Collmer *et al.* as follows:

- A 100 μl DMF solution of each compound was added to a reaction mixture consisting of 1.0 mL of pectinlyase enzyme (100 unit/mL), 1.0 mL of citrus pectin (0.5%), 0.5 mL of CaCl<sub>2</sub>, and 100 mL of *tris* buffer (pH 9.0).
- 2. The reaction mixture was incubated at  $25 \,^{\circ}$ C for 60 min.
- 3. The reaction was stopped by adding 3.5 mL of 0.5 HCl.
- 4. The UV-vis spectrum of the reaction mixture in each case was measured at 235 nm using a UV-visible spectrophotometer.
- 5. The results were recorded in Table 6 as percentage of the control, i.e. without any compound.
- 6. The action of enzyme without tested compounds (control) was considered to be 100%.
- 7. The action of the ligand and metal complexes on the enzyme were compared with the control. Percentages over 100% were considered as activation, while those less than 100% were considered as inactivation.

## **RESULTS AND DISCUSSION**

The reactions of the rigid-structure azo ligand,  $(H_2L)$ , with the metal ions Cd(II), Cu(II), Ni(II), Co(II), Th(IV), or UO<sub>2</sub>(VI) in the presence of LiOH as deprotonating agent, yielded the binary mononuclear complexes, Figs. 3 and 5–8, structures (1), (2), (5)–(8). The binary Cu(II) complex of H<sub>2</sub>L reacts with the ligand 1,10-phen or 2-ampy to form the mixed-ligand complexes, Fig. 4, structures (3) and (4). The isolated binary and mixed-ligand complexes were amorphous upon removal of the solvent. Tables 1, 3–6 show the results obtained.

The following representative equations illustrate the formation of some of the complexes obtained:

Metal nitrate :  $H_2L$  : LiOH = 1 : 1 : 1

$$2H_{2}L + Cd(NO_{3})_{2} \cdot 4H_{2}O + LiOH$$

$$\rightarrow [Cd(HL)_{2}] \cdot H_{2}O + LiNO_{3} + HNO_{3} + 4H_{2}O \qquad (1)$$
(1)

$$2H_{2}L + Cu(NO_{3})_{2} \cdot 3H_{2}O + LiOH$$
  

$$\rightarrow [Cu(HL)_{2}] + LiNO_{3} + HNO_{3} + 4H_{2}O$$
(2)
(2)

$$2H_{2}L + Co(NO_{3})_{2} \cdot 6H_{2}O + LiOH$$
  

$$\rightarrow [Co(HL)_{2}] \cdot H_{2}O + LiNO_{3} + HNO_{3} + 6H_{2}O$$
(3)
(5)

$$H_{2}L + Ni(NO_{3})_{2} \cdot 6H_{2}O + LiOH$$

$$\rightarrow [Ni(HL)NO_{3}(OH_{2})_{2}] \cdot 3H_{2}O + LiNO_{3} + 2H_{2}O$$
(4)
(6)

$$2H_{2}L + Th(NO_{3})_{4} \cdot 5H_{2}O + LiOH$$

$$\rightarrow [Th(HL)_{2}NO_{3}(OH_{2})]NO_{3} + LiNO_{3} + HNO_{3} + 5H_{2}O$$
(5)
(7)

$$2H_{2}L + UO_{2}(NO_{3})_{2} \cdot 5H_{2}O + LiOH \rightarrow [UO_{2}(HL)_{2}(OH_{2})_{2}] \cdot 1\frac{1}{2}H_{2}O + LiNO_{3} + HNO_{3} + 2\frac{1}{2}H_{2}O$$
(6)  
(8)

Copper nitrate :  $H_2L$  : 1,10-phen or 2-ampy : LiOH = 1 : 1 : 1 : 1

$$2H_{2}L + 1, 10\text{-phen} + Cu(NO_{3})_{2} \cdot 3H_{2}O + LiOH$$
  

$$\rightarrow [Cu(HL)_{2}(1, 10\text{-phen})] + LiNO_{3} + HNO_{3} + 4H_{2}O$$
(7)  
(3)

$$H_{2}L + 2(2-ampy) + Cu(NO_{3})_{2} \cdot 3H_{2}O + LiOH + CH_{3}OH$$
  

$$\rightarrow [Cu(HL)(2-ampy)_{2}NO_{3}] \cdot CH_{3}OH + LiNO_{3} + 4H_{2}O$$
(8)
(4)

#### **IR SPECTRA**

The IR spectra of the free ligand  $(H_2L)$  and its metal complexes are listed in Table 2. The organic ligand  $(H_2L)$  which has a rigid structure, forms the following tautomers:

The IR spectrum of the free ligand (H<sub>2</sub>L) provides evidence for the azo form in the solid state, where the band observed at 1479 cm<sup>-1</sup> is characteristic of v(N=N).<sup>[14–18]</sup> The bands due to v(NH) or v(OH) of the enolic hydroxyl group which would appear at ~3200 cm<sup>-1</sup> were not observed. This indicates that the tautomer (a) in Fig. 2 is the predominant structure for the azo ligand H<sub>2</sub>L. The broad band observed at 3364 cm<sup>-1</sup> in the spectrum of the free ligand (H<sub>2</sub>L) is assigned to v(OH) of the carboxylic group which is also hydrogen bonded. The carbonyl group of the COOH group was observed at 1703 cm<sup>-1</sup>. In all complexes the band due to v(OH) of the carboxylic group is absent, indicating its deprotonation on complexation. The participation of the carboxylate group in complex formation is also confirmed by the

		Table 2.	Characteris	stic IR Ba	nds (cm <sup>-</sup>	$^{1})^{a}$ of organic	ligand, H <sub>2</sub> L, a	and its me	tal comple	xes.
Compounds	μ(OH)	$\nu$ (CH) aromatic	$\nu$ (CH) aliphatic	ν(C=0)	$\nu(N=N)$	$\nu_{\rm es}({\rm COO}-)$	$\nu_{\rm s}({\rm COO}-)$	ν(M-O)	u(M-N)	Additional bands
H <sub>2</sub> L (Ligand)	3364 br	3064 m	2956 m 2876 m	1703 m 1676 s 1646 s	1479 m				I	
(1)		3062 s	2953 s 2869 s	1681 s 1625 m	1449 m	1491 m	1389 m	684 m 631 m	529 m	3414 br (lattice water)
(2)	I	3068 s	2958 s 2877 s	1677 m 1604 m	1409 m	1533 m	1345 m	660 m 630 m	562 m	I
(3)	I	3073 m	2953 s 2874 s	1677 s 1646 m	1406 m	1478 m	1320 m	629 m	560 m 457 m	1576 s (coordinated C=N of
(4)	I	3066 m	2959 s 2959 s 2876 s	1679 m 1611 m	1408 m	1497 m	1317 m	697 m 657 m	529 m 456 m	1,10 <sup>-</sup> pucu) 3429 s v(OH) of CH <sub>3</sub> OH, 3163 br (coordinated
										Note that the second s
(5)	I	3067 s	2955 s 2876 s	1676 m 1646 m	1407 m	1478 m	1319 m	661 m	560 m	3409 br (lattice water)

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(continued)

					Table	e 2. Continue	.bd			
Compounds	ν(OH)	$\nu$ (CH) aromatic	$\nu$ (CH) aliphatic	ν(C=0)	$\nu(N=N)$	$\nu_{es}(COO-)$	$\nu_{s}(COO-)$	μ(M-O)	$\nu(M-N)$	Additional bands
(9)		3069 m	2955 s 2874 s	1678 m 1609 m	1410 m	1518 m	1333 m	695 m 682 w 647 m	490 m	3511 br (coordinated water), 3398 br (lattice water), 1369 m and 1054 s m(NO.) (coordinated)
(L)		3068 m	2953 s 2876 m	1674 s 1610 m	1412 m	1507 m	1322 m	690 m 657 m 619 m	559 m	3484 $V_{0,2}$ (coordinated water) 3484 $\mu$ and 1033 s $\nu$ (NO <sub>3</sub> ) (coordinated), 1385 s ionic NO <sub>3</sub> rroum
8)	I	3064 m	2945 s 2874 m	1672 s 1643 m	1444 m	1495 m	1312 m	686 m 630 m	571 m	3522 br (coordinated water), 3405 br (lattice water), 928 s (antisymmetric $v_3$ (O=11=O)
(6)		3074 m	2961 s 2873 m	1641 m	1412 s	1534 s	1466 s	699 m 657 m 595 m	532 m 486 m	3187 br (coordinated NH <sub>2</sub> group), 980 s (pyridine ring breathing mode)
(10)		3070 m	2956 s 2870 m	1638 m 1592 s	1402 m	1528 s	1445 s	687 w 650 m 595 m	542 m 496 w	3473 br (coordinated water, 1328 s and 1051 s ν(NO <sub>3</sub> ) (coordinated)
(11)	I	3071 m	2956 s 2870 m	1681 m	1454 s	1494 s	1454 s	699 m 629 m 567 m	530 m	3424 br (coordinated enolic OH group), 1392 s (ionic NO <sub>3</sub> group)
Note: s, stroi	ng; br, bi	road; m, m	edium; and	w, weak.						



*Figure 2.* The possible tautomers for the ligand 2-[2'-carboxyphenylazo]-5,5-dimethyl-1,3-cyclohexanedione (H<sub>2</sub>L) in solution.

disappearance of the bands due to v(C=0) of the COOH group and appearance of two new bands at 1478-1533 and 1312-1389 cm<sup>-1</sup> assigned to  $v_{as}(COO^{-})$  and  $v_{s}(COO^{-})$ , respectively. This indicates that the carboxylate group behaves as a monoanionic, monodentate group.<sup>[19-22]</sup> The stretching vibrations of carbonyl groups of the  $\beta$ -diketone moiety of the ligand (H<sub>2</sub>L) were observed at 1676 and 1646 cm<sup>-1</sup>. The first band is slightly affected in all complexes of (H<sub>2</sub>L), while the second band was shifted to lower frequencies  $(20-35 \text{ cm}^{-1})$  except for the complexes (3), (5), and (8). The azo group in the free ligand (H<sub>2</sub>L) was observed at  $1479 \text{ cm}^{-1}$  and shifted to lower frequencies  $(30-73 \text{ cm}^{-1})$  in all of the metal complexes. From the above results it can be concluded that the free ligand (H<sub>2</sub>L) behaves either as a monoanionic, bidentate ligand, via one of the oxygens of the carboxylate group and the neighboring nitrogen atom of the azo group or as a monoanionic, tridentate ligand via one of the oxygen atoms of the carboxylate group, the neighbouring nitrogen atom of the azo group and the oxygen atom of one of the carbonyl groups of the  $\beta$ -diketone moiety. The IR spectrum of the uranyl complex showed a strong band at  $928 \text{ cm}^{-1}$  assigned to the antisymmetric  $v_3(O=U=O)$  vibration.

The mixed-ligand 1,10-phenanthroline complex (3), showed a new band at  $1576 \text{ cm}^{-1}$ , which would be due to the coordinated C=N group of 1,10-phenanthroline.<sup>[23-26]</sup> The mixed 2-aminopyridine complex (4), showed two

new bands at  $3163 \text{ cm}^{-1}$  and  $978 \text{ cm}^{-1}$ . The second band is assigned to the skeletal vibration of the pyridine ring,<sup>[27]</sup> breathing mode, while the first band is due to the coordinated NH<sub>2</sub> group.

The coordinated NO<sub>3</sub> group in complexes (6) and (7) showed two bands at 1033-1054 and 1304-1369 cm<sup>-1</sup> and may be assigned to the asymmetric and symmetric stretches  $v_1$  and  $v_2$  of the nitrate group. We can conclude that the NO<sub>3</sub> group is coordinated in a unidentate manner.<sup>[28]</sup> The nitrate anion<sup>[29]</sup> in complex (7) also showed a band at 1385 cm<sup>-1</sup>. The IR spectra of the complexes showed new bands at 576-699 and 456-571 cm<sup>-1</sup>, assigned to v(M-O) and v(M-N), respectively. The v(OH) frequencies of lattice water molecules or solvated CH<sub>3</sub>OH were observed at 3398-3414 and 3429 cm<sup>-1</sup>, respectively,<sup>[23]</sup> while the IR spectra of the complexes display the absorption peaks of coordinated water molecules at 3484-3522 cm<sup>-1</sup>.

## **Nuclear Magnetic Resonance Spectral Studies**

The assignments of the main signals in the <sup>1</sup>H NMR spectra of the free ligand (H<sub>2</sub>L) and its diamagnetic cadmium complex are listed in Table 3. The free ligand showed a signal at  $\delta$  15.73 ppm (s, 1H) due to the carboxylic group proton. This signal is absent in the complex [Cd(HL)<sub>2</sub>] · H<sub>2</sub>O (1). This indicates the deprotonation of the carboxylic group during the formation of the metal complexes. The free ligand also showed signal due to the aromatic protons at  $\delta$  7.27–8.05 ppm (m, 4H) which was slightly shifted downfield

Compound	(COOH) <sup>a</sup>	(CH) aromatic	(CH) aliphatic	Additional signals
H <sub>2</sub> L (Free ligand)	15.73 (s, 1H)	7.27–8.05 (m, 4H)	1.05 (s, 6H)	5.24 (s, 1H) proton of active methylene, $2.5-2.66$ (d, $J = 5.2$ Hz, 4H) protone of CH <sub>2</sub> group.
(1)	_	7.29–8.15 (m, 4H)	1.03 (s, 6H)	5.27 (s, 1H) proton of active methylene, $2.51-$ 2.58 (d, $J = 4.7$ Hz, 4H) proton of CH <sub>2</sub> groups, 3.04 (s, 2H) lattice water.

*Table 3.* <sup>1</sup>H NMR Data ( $\delta$ , ppm) for organic ligand, H<sub>2</sub>L, and its diamagnetic cadmium complex.

Note: s, singlet; d, doublet; and m, multiplet.

<sup>a</sup>Chemical shifts with reference to TMS.

in the complex. The signal due to the aliphatic protons was observed at  $\delta$  1.05 ppm (s, 6H) due to the CH<sub>3</sub> groups of the ligand (H<sub>2</sub>L) and was slightly shifted upfield in the complex (1). The lattice water molecule was observed at  $\delta$  3.04 ppm (s, 2H) for complex (1).

#### **Conductivity Measurements**

The conductance of solutions of the complexes in DMF  $(10^{-3} \text{ M})$  are shown in Table 4. Complex (7) is a 1 : 1 electrolyte while the other complexes are non-electrolytes.

#### **Magnetic Moments and Electronic Spectra**

The UV-Visible spectra of the free ligand H<sub>2</sub>L and its metal complexes were carried out as DMF ( $10^{-3}$  M) solutions. The values of band positions (cm<sup>-1</sup>) and molar absorptivities ( $\varepsilon_{max}$  L cm<sup>-1</sup> mol<sup>-1</sup>) together with the magnetic moment values are listed in Table 4. The UV-visible spectra of the ligand showed bands at 35,088, 28,409, and 23,981 cm<sup>-1</sup> assigned to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ , and charge transfer transitions within the molecule, respectively. The bands of the free ligand were slightly shifted to blue or red regions in all complexes, while new bands were observed in the visible region for the Cu(II), Co(II), and Ni(II) complexes due to d  $\rightarrow$  d transitions.

The magnetic moment of the binary complex of Cu(II), (2) is 1.95 BM. The visible bands of this complex exhibit two transition bands at 19,231 and 15,221 cm<sup>-1</sup> which unambigously may be assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  transitions, respectively, corresponding to a distorted octahedral geometry around the copper ion.<sup>[28]</sup> The proposed structure of the binary complex (2) is shown in Fig. 3. The actual geometry of the complex whether the *fac* or *mer* is not known.

The mixed-ligand complexes of Cu(II) with 1,10-phenanthroline, (3) and 2-aminopyridine, (4), showed magnetic moment values,  $\mu_{eff}$ , in the range 1.87–1.89 BM. These values correspond to one unpaired electron and offer evidence for the mononuclear structures of the complexes. The mixed-ligand complexes of Cu(II) exhibited two transitions bands in the regions 19,084–19,231 and 15,083–15,221 cm<sup>-1</sup>. The transitions including the mixed-ligand complexes are similar in energies to those of the binary complex (2). This indicates that the geometry of the copper ion in the mixed-ligand complexes is distorted octahedral. The proposed structures of the mixed-ligand-1,10-phenanthroline complex (3) and that of the mixed-ligand-2-aminopyridine complex (4) are shown in Fig. 4.

Table 4.	Molar conductance, magnetic mo	ment and electron	ic spectral data, $(cm^{-1})$ for the ligand, $H_2L$ ,	and metal complexes.
Compounds	Molar conductance <sup>a</sup> $(Ohm^{-1} cm^2 mol^{-1})$	$\mu_{ m eff}^{ m b}$ (BM)	$\pi \to \pi^*, n \to \pi^*$ and charge transfer transitions $(\varepsilon_{\max} \operatorname{Lcm}^{-1} \operatorname{mol}^{-1})$	$d \rightarrow d$ Transitions $(\varepsilon_{\max} L  cm^{-1}  mol^{-1})$
H,L	I		35,088, 28,409, 23,981	
(Free ligand)			(2,243), (4,300), (3,580)	
	10.50	Diam	35,088, 28,329, 23,866	
			(2,010), (4,440), (3,590)	
(5)	9.80	1.95	34,965, 28,409, 23,981	19,231, 15,221
			(2,243), (4,360), (3,510)	(340), (253)
(3)	14.60	1.87	34,943, 28,409, 23,981	19,084, 15,083
			(1,850), (3,450), (3,580)	(340), (217)
(4)	7.25	1.89	35,088, 28,090, 24,096	19,920, 15,480
			(2,243), (4,360), (3,580)	(420), (340)
(5)	6.14	2.71	34,246,28,571,24,213	22,321, 18,975
			(2,130), (4,360), (3,500)	(360), (470)
(9)	4.60	2.89	34,014, 28,409, 23,148	20,121, 14,663
			(2,400), (4,030), (3,450)	(410), (340)
( <u>1</u> )	87.40	Diam	33,784,28,248,23,866	
			(2,920), (4,040), (3,670)	
(8)	5.25	Diam	34,014,28,490,23,095	
			(2,243), (4,360), (3,580)	
(6)	6.35	1.94	34,783,28,449,22,779	19,493, 14,936
			(2,130), (4,206), (3,270)	(480), (366)
(10)	9.50	2.93	34,305,28,449,22,753	19,940, 15,540
			(2,220), (4,110), (3,380)	(436), (390)
(11)	48.90	Diam	33,784, 28,531, 22,396	
			(2,630), (3,860), (3,720)	
<sup>a</sup> DMF solutic <sup>b</sup> Measuremer	ons, $10^{-3}$ , at $28 ^{\circ}$ C. Its were taken at $27 ^{\circ}$ C.			

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Figure 3. Suggested structure of the binary Cu(II) complex, [Cu(HL)<sub>2</sub>] (2).

The binary Co(II) chelate, (5) has the room temperature magnetic moment of 2.71 BM, as expected for a square-planar Co(II) complex.<sup>[30,31]</sup> The visible spectra exhibit peaks at 22,321 and 18,975 cm<sup>-1</sup>, assignable to  ${}^{2}A_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}A_{1g} \rightarrow {}^{2}E_{2g}$  transitions, respectively, and are compatible



*Figure 4.* Suggested structures of the mixed-ligand 1,10-phenanthroline and 2-aminopyridine Cu(II) complexes,  $[Cu(HL)_2(1,10-phen)]$  (3) and  $[Cu(HL)(2-ampy)_2NO_3]$ . CH<sub>3</sub>OH (4).

with a square-planar geometry. The proposed structure of the binary cobalt(II) complex is shown in Fig. 5.

The magnetic moment of the binary Ni(II) complex (6) is 2.89 BM, suggesting its octahedral structure.<sup>[31]</sup>

The bands in the region 20,121 and 14,663 cm<sup>-1</sup> are assignable to the electronic transitions  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ , respectively. The proposed structure of the binary Ni(II) complex is shown in Fig. 6.

The binary complexes of Cd(II), Th(IV), and UO<sub>2</sub>(VI) are diamagnetic and the electronic spectra of the complexes are dominated only by the ligand bands. The elemental analyses and <sup>1</sup>H NMR spectrum showed that the Cd(II) complex (1) has an octahedral configuration, Fig. 7.

The complexes of Th(IV), (7), and the  $UO_2(VI)$  complexes (8) have the coordination number 8 and are in distorted dodecahedral geometry. The proposed structures of Th(IV) and the  $UO_2(VI)$  complexes are shown in Fig. 8.

#### **Thermal Analyses**

The results of TG-DSC analyses of the binary and mixed-ligand complexes are shown in Table 5. The results show good agreement with the



*Figure 5.* Suggested structure of the binary cobalt(II) complex,  $[Co(HL)_2] \cdot H_2O(5)$ .

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*Figure 6.* Suggested structure of the binary Ni(II) complex,  $[Ni(HL)NO_3(OH_2)_2] \cdot 3H_2O$  (6).

theoretical formulae as suggested from the analytical data. The complexes (1), (5), (6), and (8) become anhydrous at 76–110 °C. The loss of hydrated water molecules was accompanied by an endothermic peak with  $\Delta H$ , 33.67–71.50 J/g. The molecule of CH<sub>3</sub>OH in the outer sphere of the complex (4)



Figure 7. Suggested structure of the binary Cd(II) complex, [Cd(HL)<sub>2</sub>] · H<sub>2</sub>O (1).

			•		)		
		% Weight	DSC pea	(C) (k		-	
Compounds	Temperature range (°C)	loss found (Calc.)	Endo	Exo	$\Delta H~({ m J}/{ m g})$	Composition of the residue	Probable composition of the expelled groups
H <sub>2</sub> L (Free ligand)	50 - 312	35.70 (35.38)	259		63.59	$C_{11}H_{10}N_2O$	One molecule of CO <sub>2</sub> , one molecule of CO and one molecule of CH <sub>2</sub> -CH <sub>2</sub> .
(nungu	312-619	86.10 (86.02)	447		14.11	$C_3H_4N$	One molecule of CO, half molecule of
							$C_2N_2^a$ , half molecule of $N_2$ and three molecules of $CH \equiv CH^b$
(1)	40 - 76	2.72 (2.55)	76		41.32	[Cd(HL) <sub>2</sub> ]	One molecule of lattice water
	76-295	31.66 (31.49)	225		19.07	$[Cd(C_{22}H_{18}N_4O_2)]$	Two molecules of CO <sub>2</sub> , Two molecules of
							CO and two molecules of CH <sub>3</sub> -CH <sub>3</sub>
	295 - 530	58.02 (58.16)	442		297.55	$[Cd(C_{14}H_{14})]$	Two molecules of CO, one molecule of
							$C_2N_2^a$ , one molecule of $N_2$ and two
							molecules of HC≡CH <sup>D</sup>
(2)	50 - 289	31.50 (31.34)		252	-108.40	$[Cu(C_{22}H_{18}N_4O_2)]$	Two molecules of $CO_2$ , two molecules of
							CO and two molecules of CH <sub>3</sub> -CH <sub>3</sub>
	289 - 467	52.84 (52.65)	447		52.66	[Cu(C <sub>18</sub> H <sub>18</sub> )]	Two molecules of CO, one molecule of
							$C_2N_2^a$ and one molecule of $N_2$
(3)	50 - 280	31.60 (31.28)	I	249	-63.77	$[Cu(C_{20}H_{18}N_4)(1,10-$	Two molecules of CO <sub>2</sub> , four molecules of
						Phen)]	CO and two molecules of CH <sub>3</sub> -CH <sub>3</sub>
	280 - 530	55.53 (55.72)	442		100.76	$[Cu(C_{10}H_{10})(1,10-$	One molecule of $C_2 N_2^{a}$ , one molecule of $N_2$
						phen)]	and four molecules of $HC \equiv CH^{b}$
(4)	40 - 108	5.22 (5.06)	105		62.93	[Cu(HL)(2-	One molecule of CH <sub>3</sub> OH
						ampy) <sub>2</sub> NO <sub>3</sub> ]	
	108 - 179	15.00 (15.01)	170		126.22	$[Cu(L)(2-ampy)_2]$	One molecule of HNO <sub>3</sub>
	179 - 271	28.97 (28.91)		255	-39.71	$[Cu(C_{13}H_{14}N_2)(2-$	Two molecules of CO <sub>2</sub>
						mpy)2]	
	271 - 459	67.83 (67.49)	449	I	97.13	$Cu(C_{11}H_{14}N_2)$	Two molecules of CO and two molecules of
							2-ampy.

Table 5. Thermal analyses data for the organic ligand, H<sub>2</sub>L, its metal complexes.

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(5)	40 - 110	2.80 (2.76)	104		71.50	$[Co(HL)_2]$	One molecule of lattice water
	110-312	33.61 (33.46)	259		54.41	$[Co(C_{22}H_{18}N_4O_2)]$	Two molecules of CO <sub>2</sub> , two molecules of
							CO and two molecules of $CH_3 \equiv CH_3$
	312-553	70.56 (70.30)	466		65.80	$[Co(C_{10}H_{10})]$	Two molecules of CO, one molecule of
							$C_2N_2^{a}$ , one molecule of $N_2$ and four
							molecules of HC≡CH <sup>b</sup>
(9)	40 - 102	10.79 (10.85)	85		33.67	$[Ni(HL)NO_3(OH_2)_2]$	Three molecules of lattice water
	102 - 160	14.60(14.46)	160		26.51	$[Ni(HL)NO_3(OH_2)]$	One molecule of coordinated water
	160 - 348	39.68 (39.55)		318	-152.58	$[Ni(C_{14}H_{14}N_2O_2)]$	One molecule of coordinated water, one
							molecule of HNO <sub>3</sub> and one molecule
							of CO <sub>2</sub>
	348-431	62.30 (62.04)	411		44.22	$[Ni(C_9H_8N)]$	Two molecules of CO, one molecule of
							CH <sub>3</sub> —CH <sub>3</sub> and half molecule of C <sub>2</sub> N <sub>2</sub> <sup>a</sup>
(2)	50 - 196	8.63 (8.54)		196	-32.10	$[Th(HL)(L)NO_3]$	One molecule of coordinated water and one
							molecule of HNO <sub>3</sub> .
	196 - 408	30.42 (30,36)		291	-198.33	$[Th(C_{13}H_{14}N_2O)_2]$	One molecule of HNO <sub>3</sub> , two molecules of
							CO <sub>2</sub> and two molecules of CO
(8)	40 - 110	3.30 (2.97)	105		60.62	$[UO_2(HL)_2(OH_2)_2]$	One and half molecules of lattice water.
	110 - 196	7.12 (6.94)	188		130.21	$[UO_2(HL)_2]$	Two molecules of coordinated water.
	196–411	44.73 (44.40)	400		45.40	$[UO_2(C_7H_8)_2]$	Two molecules of CO <sub>2</sub> , four molecules of CO
							two molecules of CH <sub>3</sub> -CH <sub>3</sub> , one
							molecule of $C_2N_2^a$ and one molecule of $N_2$

<sup>&</sup>lt;sup>a</sup>Cyanogen molecule (NCCN). <sup>b</sup>Acetylene molecule.

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*Figure 8.* Suggested structures of the binary Th(IV) and UO<sub>2</sub>(VI) complexes,  $[Th(HL)_2NO_3(OH_2)]NO_3$  (7) and  $[UO_2(HL)_2(OH_2)_2] \cdot 1\frac{1}{2}H_2O$  (8).

was eliminated at 108 °C. The loss of the methanol molecule from the previous complex was accompanied by an endothermic peak at  $\Delta H$ , 62.93 J/g. The coordinated water or CH<sub>3</sub>OH molecules were eliminated from the complexes at relatively higher temperatures than the lattice water<sup>[32]</sup> or outer sphere

Compound	% of the activation or inactivation of the enzyme pectinlyase
H <sub>2</sub> L (Free ligand)	149.13
(1) $[Cd(HL)_2] \cdot H_2O$	111.67
(2) $[Cu(HL)_2]$	81.31
(4) $[Cu(HL)(2-ampy)_2NO_3] \cdot CH_3OH$	94.11
(5) $[Co(HL)_2] \cdot H_2O$	157.78
(6) [Ni(HL)NO <sub>3</sub> (OH <sub>2</sub> ) <sub>2</sub> ] · 3H <sub>2</sub> O	151.55
(7) [Th(HL) <sub>2</sub> NO <sub>3</sub> (OH <sub>2</sub> )]NO <sub>3</sub>	153.28
(8) $[UO_2(HL)_2(OH_2)_2] \cdot 1\frac{1}{2}H_2O$	142.56

Table 6. Percentage activation or inactivation of the tested compounds.

*Note*: The control (the reaction mixture including the enzyme without any additives) was considered to be 100%, values above 100% are considered as activation while values less than 100% are considered as inactivation.

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CH<sub>3</sub>OH molecules. There are three routes for the removal of coordinated water molecules from the complexes which are described below:

- 1. The coordinated water molecules are eliminated in a separate step, as in complex (8). The elimination of coordinated water molecules in this step (196 °C) is accompanied by an endothermic peak and leads to a non-isolable complex.
- 2. Partial elimination of coordinated water molecules from the complex. This is observed in complex (6) which loses one molecule of coordinated water at 160 °C ( $\Delta H = 26.51 \text{ J/g}$ ) which leads to an isolable complex [Ni(HL)(OH<sub>2</sub>)(NO<sub>3</sub>)].
- 3. Elimination of coordinated water molecule(s) accompanied by loss of HNO<sub>3</sub>, as in complex (7) at 196 °C ( $\Delta H = -32.10 \text{ J/g}$ ) and leads to an isolable complex, [Th(HL)(L)(NO<sub>3</sub>)].

The elimination of the HNO<sub>3</sub> molecule from complex (4) at 170 °C ( $\Delta H = 126.22 \text{ J/g}$ ) occurred in a separate step and leads to the isolable complex [CuL(2-ampy)<sub>2</sub>]. The removal of HNO<sub>3</sub> from the complex involves a NO<sub>3</sub><sup>-</sup> ion and a proton from the organic ligand.

The mixed-ligand complexes are thermally stable to >200 °C. The complexes start to decompose at a relatively higher temperatures, >260 °C, and the organic ligand loses gaseous compounds CO<sub>2</sub>, CO, (CN)<sub>2</sub>, HC=CH, CH<sub>3</sub>-CH<sub>3</sub>, etc.

#### **Pyrolysis Studies**

The structures of the obtained new products were elucidated on the basis of elemental analyses, IR and electronic absorption spectra, magnetic moments, and <sup>1</sup>H NMR measurements as well as by mass spectroscopy (Tables 1, 3, and 5). The UV-Visible spectra of the heated products (9)–(11) showed the ligand bands as in the original complexes, but slightly shifted to longer or shorter wave numbers (cm<sup>-1</sup>). The IR spectra of the pyrolytic products showed the disappearance of v(C=0) of the COOH group and the appearance of two new strong bands at 1494–1534 and 1445–1466 cm<sup>-1</sup> due to  $v_{as}(COO)$  and  $v_s(COO)$ , respectively. This indicates that the carboxylic group behaves as a monoanionic bidentate group.<sup>[20,23,33,34]</sup> All of the pyrolysis products showed the bands due to v(M-O) and v(M-N) at 567–699 and 486–542 cm<sup>-1</sup>, respectively.

## [Cu(L)(2-ampy)<sub>2</sub>] (9)

The IR spectrum showed the disappearance of bands corresponding to the coordinated carbonyl groups of COOH and the  $\beta$ -diketone moiety. The disappearance of the latter bands may be due to tautomerism (keto  $\leftrightarrow$  enol) in the  $\beta$ -diketone ring. The enolic OH group loses its proton, which combines with the NO<sub>3</sub> ion to form the eliminated HNO<sub>3</sub> molecule. This was confirmed by the disappearance of  $v(NO_3)$  from the IR spectrum of the heated product. The v(N=N)band was observed at  $1412 \text{ cm}^{-1}$ , indicating that this group is still coordinated to the copper ion. The remaining IR bands of the heated product are as in the original complex (4) except for the disappearance of the band at  $3529 \text{ cm}^{-1}$  due to v(OH) of CH<sub>3</sub>OH. Conductivity measurements of the thermal product in DMF solution revealed the non-electrolytic nature of the complex. The magnetic moment,  $\mu_{\rm eff}$ , of the heated product was 1.94 BM, which reveals the presence of one unpaired electron and shows no copper-copper interaction. The absorption bands observed in the visible region at 19,493 and 14,936 cm<sup>-1</sup> are due to  $d \rightarrow d$  transitions and are assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  transitions, respectively, corresponding to a distorted octahedral geometry of the copper ion.<sup>[28]</sup> From the above results and the elemental analyses in Table 1 the product obtained on heating may be represented as  $[Cu(L)(2-ampy)_2]$  as indicated in Eq. (9) and its proposed structure is shown in Fig. 9. The actual geometries of the aminopyridine rings whether cis or trans is not known.

$$[Cu(HL)(2-ampy)_2(NO)_3] \cdot CH_3OH$$

$$\xrightarrow{170 \,^{\circ}C} [Cu(L)(2-ampy)_2] + HNO_3 + CH_3OH \qquad (9)$$

$$(9)$$



*Figure 9.* Structure of  $[Cu(L)(2-ampy)_2]$  (9) obtained by heating complex (4) to 170 °C.

#### Ni(HL)(NO<sub>3</sub>)(OH<sub>2</sub>)] (10)

The IR spectrum of the heated product showed the disappearance of the band due to lattice water molecules  $(3398 \text{ cm}^{-1})$ , and the remaining IR bands are as those as seen in the mother complex. The low conductance of a DMF solution of this product proved that it is a non-electrolyte. The magnetic moment of the heated product was 2.93 BM, suggesting that it has an octahedral structure.<sup>[32]</sup> The transition bands at 19,940 and 15,540 cm<sup>-1</sup> are assignable to  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$  [10] transitions, respectively. From the above results and the elemental analyses in Table 1, the product obtained on heating may be represented as [Ni(HL)(NO<sub>3</sub>)(OH<sub>2</sub>)] as indicated in Eq. (10) and its proposed structure is shown in Fig. 10.

$$[\text{Ni(HL)(NO_3)(OH_2)_2]} \cdot 3\text{H}_2\text{O}$$

$$\xrightarrow{160 \,^\circ\text{C}} [\text{Ni(HL)(NO_3)(OH_2)]} + 4\text{H}_2\text{O}$$
(10)
(10)

#### $[Th(HL)(L)]NO_3(11)$

The IR spectrum showed the disappearance of the band due to the coordinated carbonyl group of the  $\beta$ -diketone moiety. This may be due to the formation of an enolic –OH group, which is confirmed by a band observed at 3424 cm<sup>-1</sup>. The deprotonation of one –OH group and its combination with a NO<sub>3</sub><sup>-</sup> ion, leads to the elimination of a HNO<sub>3</sub> molecule. This was



*Figure 10.* Structure of  $[Ni(HL)(NO_3)(OH_2)]$  (10), obtained by heating of complex (6) at 160 °C.

also supported by the disappearance of the bands at 1304 and  $1033 \text{ cm}^{-1}$ , due to the coordinated  $NO_3^-$  group. The band due to the ionic  $NO_3^-$  group was observed at  $1392 \text{ cm}^{-1}$ . The IR spectrum of the heated product showed the overlap between  $v_s(COO^-)$  and v(N=N) and both appear as a strong single band at 1454 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed a signal corresponding to the coordinated enolic OH group at  $\delta$  16.02 ppm (s, 1H), which confirms the presence of the tautomers (keto  $\leftrightarrow$  enol) in the  $\beta$ -diketone moiety. The disappearance of the signal at  $\sim \delta$  5.27 ppm, due to the proton of the active methylene group in the  $\beta$ -diketone moiety also supports the presence of the enol form. The <sup>1</sup>H NMR spectrum of the heated product showed signals assigned to the aromatic protons at  $\delta$  7.20–8.13 ppm (m, 6H) and the aliphatic protons at  $\delta$  3.45 ppm (s, 8H) and  $\delta$  1.06 ppm (s, 12H). The conductance of a DMF solution of the heated product indicates that it is a 1:1 electrolyte, confirming the presence of the  $NO_3^-$  anion in the outer sphere of the complex. The electronic spectrum of the diamagnetic thermal Th(IV) product is dominated by the ligand bands (see Table 5).

From the above results and its elemental analyses in Table 1, the product obtained on heating may be represented as  $[Th(HL)(L)]NO_3$  as indicated in Eq. (11) and which has a distorted dodecahedral geometry. Its proposed structure is shown in Fig. 11.

$$[\text{Th}(\text{HL})_2(\text{NO}_3)(\text{OH}_2)]\text{NO}_3 \xrightarrow{196 \,^\circ\text{C}} [\text{Th}(\text{HL})(\text{L})]\text{NO}_3 + \text{HNO}_3 + \text{H}_2\text{O}$$
(11) (11)

Mass Spectra

Mass spectral data are consistent with the formulations  $[Cu(L)(2-ampy)_2]$ (9) and  $[Th(HL)(L)]NO_3$  (11) which give the parent ions at m/z 539 (calculated value 538.06) and 868 (calculated value 867.62), respectively.

The mass spectrum of complex (9), shows the presence of a mass fragment corresponding to  $C_{20}H_{20}N_4O_4Cu^+$ , m/z 444.75 (2.18%), which loses a CO<sub>2</sub> molecule to give the fragment  $C_{19}H_{20}N_4O_2Cu^+$ , m/z 400.30 (8.80%), followed by the loss of a  $C_5H_6N_2$  molecule to give the fragment  $C_{14}H_{14}N_2O_2Cu^+$ , m/z 306.20 (2.32%) and finally the fragment due to CuO<sup>+</sup> is present at m/z 80.10 (3.81%).

Complex (11) shows the presence of a mass fragment corresponding to  $C_{30}H_{29}N_4O_8Th^+$ , m/z 807.45 (8.60%), which loses a  $CO_2$  molecule to give the fragment  $C_{29}H_{29}N_4O_6Th^+$ , m/z 764.0 (3.50%) then loses a  $C_6H_4N_2$  molecule to give the fragment  $C_{23}H_{25}N_2O_6Th^+$ , m/z 658 (8.0%), followed by the loss of a  $CH_3-CH_3$  molecule to give the fragment  $C_{21}H_{19}N_2O_6Th^+$ ,

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(11)

*Figure 11.* Structure of  $[Th(HL)(L)]NO_3$  (11) obtained by heating complex (7) to 196 °C.

m/z 628.50 (8.82%) and finally the fragment due to ThO<sup>+</sup> is present at m/z 248.15 (28.67%). The fragmentation pattern is shown in Fig. 12.

#### **Biological Activities of Metal Complexes**

The investigated compounds were tested as modulators of the enzyme pectinlyase produced by the thermophilic fungus *Thermomyces lanuginosus*. The activations of this enzyme given by our compounds may help in the improvement of their action in many industries. The metal complexes of the free ligand H<sub>2</sub>L gave the same activities and were comparable with those of the free ligand, except for the binary Cu(II) complex (2) and the mixed 2-ampy complex (4), which resulted in decrease of the enzyme activity. From the above results we can conclude that the free ligand H<sub>2</sub>L activates the enzyme pectinlyase. All the tested metal complexes also activate the enzyme pectinlyase except for the complexes (2) and (4). The activations of this enzyme by our compounds may help in the improvement of their action in many industries.



Figure 12. Fragmentation pattern of complex (11).

#### CONCLUSIONS

The reaction of the azo ligand  $H_2L$  with the metal ions Cd(II), Cu(II), Ni(II), Co(II), Th(IV), or UO<sub>2</sub>(VI) in the presence of LiOH as a deprotonating agent, yielded binary mononuclear complexes.

The binary Cu(II) complex of (H<sub>2</sub>L) reacts with the ligands 1,10phenanthroline or 2-aminopyridine to form mixed-ligand complexes. From the results of both the <sup>1</sup>H NMR and IR spectra, the free ligand H<sub>2</sub>L behaves either as a monoanionic, bidentate ligand through the oxygen atom of the carboxylate group and the nitrogen atom of the azo group, or as a monoanionic tridentate ligand through the oxygen atom of the carboxylate group, the nitrogen atom of the azo group and the oxygen atom of one carbonyl group of the  $\beta$ -diketone moiety. The mixed-ligand 1,10-phen behaves as a neutral bidentate ligand through the nitrogen atoms of the rings, while 2-ampy behaves as a neutral monodentate ligand via the amino group. The binary Cu(II), Ni(II), and Cd(II) complexes have octahedral configurations, while the binary complex of Co(II) has a square-planar geometry. The binary complexes of Th(IV) and UO<sub>2</sub>(VI) have distorted dodecahedral geometries. The mixed-ligand complexes have octahedral configurations.

The actual possible geometric isomers for the synthesized complexes are not determined and would be interesting to investigate them in a further study.

The thermal studies explored the possibility of obtaining new complexes which cannot be prepared from solutions. The  $v_{as}(COO)$  and  $v_s(COO)$  of the heated products indicate that the carboxylate group behaves as a monoanionic, bidentate group. The geometries of the heated product are similar to the original complexes. Although some of the original complexes lose two molecules of coordinated water, the resulted complexes compensate the decrease in coordination sites through the change in the mode of coordination of the carboxylate group.

The free ligand  $(H_2L)$  activates the enzyme pectinlyase. All the tested metal complexes activate the enzyme pectinlyase except for the complexes (2) and (4).

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