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Synthesis, Characterization, Biological and Thermal Studies of Cu(II) Complexes of Salen and Tetrahedrosalen Ligands

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A series of mononuclear salen type copper(II) complexes, $[CuL^n]$ (n = 1-4), and their corresponding tetrahydrosalen complexes, $[CuH_2L^n]$ (n = 1,2) were prepared by the reaction of the N_2O_2 ligands with Cu(II) ion in ethanol, where H_2L^1 = N,N-bis(3,5-di-tert-butylsalicylidene)-2,2-dimethyle-1,3-diaminopropan, H_2L^2 = N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-diamino-propane, H_2L^3 = N,N-bis(4-methoxysalicylidene)-2,2-dimethyle-1,3-diaminopropan; H_2L^4 = N,N-bis(4-methoxysalicylidene)-1,2-diaminopropane, $H_2[H_2L^1]$ = N,N-bis(2-hydroxyl-3,5-di-tert-butylphenyl)-2,2-dimethyle-1,3-diaminopropan and $H_2[H_2L^2]$ = N,N-bis(2-hydroxyl-3,5-di-tert-butylphenyl)-1,2-diaminopropane. The prepared ligands and complexes were characterized by the combination of IR, UV-Vis, NMR (as far as possible), elemental and thermal analyses. All prepared compounds were also evaluated for their antibacterial (Escherichia coli and Staphylococcus aureus) and antifungal (Candida albicans) activities by the disc diffusion method. The compounds were found have no remarkable antimicrobial activities.

Keywords: Cu(II) complex, Salen, Schiff base, Thermal analysis, Biological activity

INTRODUCTION

Schiff base ligands and their metal complexes have attracted great and growing interest in chemistry and biology for many years due to their facile synthesis and wide applications [1-3]. Considerable attention has focused on the syntheses of new copper(II) complexes of salen-type ligands containing bulky groups because of their role in the development of coordination chemistry, and in inorganic biochemistry [4,5], catalysis [6,7], optical materials [8,9] and so on.

Prior to this work, other groups reported the synthesis and characterization of salen-type ligands with bulky groups and their metal complexes [10-13]. However, a literature survey reveals that little work has been done on biological activity and thermal properties of tetradentate Schiff base ligands with bulky groups and their Cu(II) complexes [4,14,15]. The present paper describes the synthesis, spectral and thermal studies of new Cu(II) complexes derived from N,N-bis(3, 5-di-tert-butylsalicylidene)-2,2-dimethyle-1,3-diaminopropan (H_2L^1), N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-diamino propane (H_2L^2), N,N-bis(4-methoxysalicylidene)-2,2-dimethyle-1,3-diaminopropan (H_2L^3), N,N-bis(4-methoxy-salicylidene)-1,2-diamino propane (H_2L^4), N,N-bis(2-hydroxyl-3,5-di-tert-butylbenzyl)-2,2-dimethyle-1,3-diamino-propan ($H_2[H_2L^1]$), and N,N-bis(2-hydroxyl-3,5-di-tert-butylbenzyl)-1,2-diamino propane ($H_2[H_2L^2]$) (Fig. 1). TG studies of the prepared Cu(II) complexes show that the decomposition takes place in one step for $[CuL^1]$ and in two or

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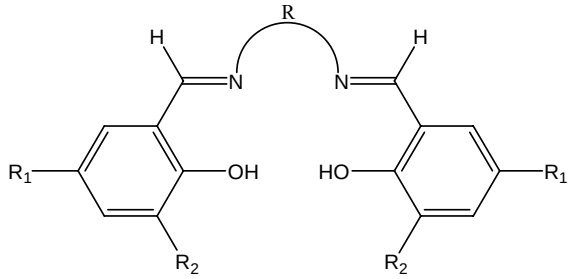
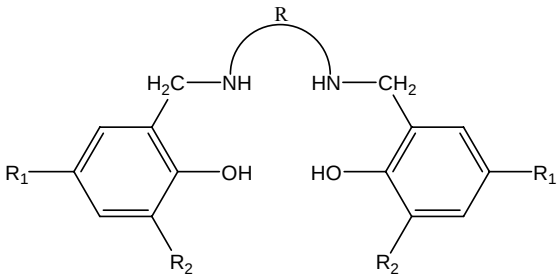


H_2L^n (n =1-4)



$H_2[H_2L^n]$ (n =1,2)

Ligand	R	R_1	R_2
H_2L^1	$-CH_2C(CH_3)_2CH_2-$	t-Bu	t-Bu
H_2L^2	$-CH_2(CH_3)HC-$	t-Bu	t-Bu
H_2L^3	$-CH_2C(CH_3)_2CH_2-$	MeO	H
H_2L^4	$-CH_2(CH_3)HC-$	MeO	H
$H_2[H_2L^1]$	$-CH_2C(CH_3)_2CH_2-$	t-Bu	t-Bu
$H_2[H_2L^2]$	$-CH_2(CH_3)HC-$	t-Bu	t-Bu

Fig. 1. Chemical structures of the prepared ligands.

three steps for other complexes.

All prepared compounds were screened for the antibacterial and antifungal activities against *Escherichia coli* (E. Coli), *Staphylococcus aureus* (S. Aureus), and *candidia albicans* (C.A.). The investigation of antibacterial screening data revealed that the prepared salen and tetrahedrosalen ligands (H_2L^n (n = 1-4) and $H_2[H_2L^n]$ (n = 1,2), as well as their Cu(II) complexes have no remarkable inhibition against microorganisms studied here.

EXPERIMENTAL

Materials and Methods

All chemicals and solvents were of reagent grade and purchased commercially. 3,5-Di-tert–butyl-2-hydroxy-benzaldehyde was prepared according to the method reported in the literature [16]. ^1H and ^{13}C $\{^1H\}$ NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer. Electronic spectral measurements were carried out using Perkin-Elmer Lamda spectrophotometer in the range 200-900 nm. Elemental analyses (C, H and N) were performed on an Elementar Vario EL III elemental analyzer. TGA were carried out on a PerkinElmer TG/DTA 6200 at a heating rate of 10 ºC min^{-1} under a nitrogen atmosphere. Infrared spectra were recorded as pressed KBr discs, using a Unicom Galaxy Series FTIR 5000 spectrophotometer (4000-400 cm^{-1}).

Procedure for Biological Activity Study

All prepared compounds were screened for their activity against *Escherichia Coli*, *Staphylococcus aureus*, and *candidia albicans* strains by disc diffusion method as gram negative, gram positive and fungal organisms, respectively. The muller hinton agar and subro dextrose agar were used to culture bacteria and fungal, respectively. The culture media was poured into sterile plates and microorganisms were introduced onto the surface of agar plates individually. The blank sterile discs measuring 6.4 mm in diameter were soaked in a known concentration of the test compounds. Then the soaked discs were implanted on the surface of the plates. A blank disc was soaked in the DMSO and implanted as negative control on each plate along with the standard drugs. The plates were incubated at 37 ºC (24 h) and 27 ºC (48 h) for bacterial and fungal strain, respectively. The inhibition zones were measured and compared with the controls.

General Procedure for the Synthesis of H_2L^n (n = 1-4) Ligands

A solution of diamine (1 mmol) in absolute EtOH (10 ml) was added to a stirring solution of appropriate aldehyde (2 mmol) in absolute EtOH at 50 ºC over a period of 15 min. The solution was heated in water bath over a period of 2 h at 70 ºC, then cooled and let to stand at 0 ºC. The obtained yellow solid was filtered off, washed with cooled n-hexane/methanol (4/1) and dried in air. The characterization data of synthesized compounds are given in Table 1 and Table 2. The results of elemental analyses are as follows:

H_2L^1. Anal. Calcd. for $C_{35}H_{54}N_2O_2$: C, 78.60; H, 10.18; N, 5.24%. Found: C, 78.5; H, 10.3; N, 5.4%.

H_2L^2. Anal. Calcd. for $C_{33}H_{50}N_2O_2$: C, 78.21; H, 9.94; N, 5.53%. Found: C, 78.2; H, 10.1; N, 5.7%.

H_2L^3. Anal. Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56%. Found: C, 68.2; H, 7.2; N, 7.6%.

H_2L^4. Anal. Calcd. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18%. Found: C, 66.5; H, 6.5; N, 8.3%.

General Procedure for the Synthesis of Hydrogenated Ligands, $H_2[H_2L^n]$ (n = 1,2)

To a solution of H_2L^n (n = 1,2) (1 mmol) in EtOH (10 ml) at room temperature was added $Na_2B_4O_7$ (0.2 g) and then $NaBH_4$ (4.5 mmol) in small portions over 30 min. When the addition was complete, the reaction mixture was stirred at room temperature for additional 2 h. The solvent was removed under reduced pressure. To the residue was added NH_4Cl (2.5 g) in water (25 ml), and the mixture was extracted with CH_3Cl (3 × 10 ml). The organic fractions were combined, washed with water, and dried over anhydrous $MgSO_4$. The solution was filtered, and chloroform was removed on a rotary evaporator to afford the product. The characterization data of synthesized compounds are given in Table 1 and Table 2. The results of elemental analyses are as follows:

$H_2[H_2L^1]$. Anal. Calcd. for $C_{35}H_{58}N_2O_2$: C, 78.01; H, 10.85; N, 5.25%. Found: C, 78.1; H, 10.6; N, 5.4%.

$H_2[H_2L^2]$. Anal. Calcd. for $C_{33}H_{54}N_2O_2$: C, 77.6; H, 10.66; N, 5.48%. Found: C, 77.5; H, 10.8; N, 5.6%.

General Procedure for the Synthesis of Copper(II) Complexes

To a stirring solution of H_2L^n (n = 1-4) (0.5 mmol) in methanol (10 ml) was added a solution of $Cu(CH_3COO)_2{\cdot}6H_2O$ (0.75 mmol) in mthanol (10 ml). To the stirring mixture was added triethylamine (1 mmol), and the resulting green solution was warmed at 50-60 ºC for 30 min. The product was collected by filtration, washed with cold methanol and crystallized from $CHCl_3$/MeOH (2:1). The characterization data of synthesized complexes are listed in Table 1 and Table 2. The results of elemental analyses are as follows:

CuL^1 (1). Anal. Calcd. for $C_{35}H_{52}N_2O_2Cu$: C, 70.49; H, 8.87; N, 4.70; Cu, 10.66%. Found: C, 70.2; H, 8.5; N, 4.5; Cu, 10.7%.

CuL^2 (2). Anal. Calcd. for $C_{33}H_{48}N_2O_2Cu$: C, 69.74; H, 8.51; N, 4.93; Cu, 11.18%. Found: C, 69.6; H, 8.67; N, 4.8; Cu, 10.8%.

$CuL^3.H_2O$ (3). Anal. Calcd. for $C_{21}H_{24}N_2O_4Cu.\ H_2O$: C, 54.13; H, 5.63; N, 6.01; Cu, 13.64%. Found: C, 54.32; H, 5.9; N, 5.8; Cu, 14.1%.

CuL^4 (4). Anal. Calcd. for $C_{19}H_{20}N_2O_4Cu$: C, 56.50; H, 4.99; N, 6.94; Cu, 15.73.64%. Found: C, 56.3; H, 4.9; N, 6.7; Cu, 15.6%.

$Cu[H_2L^1].1/2$ EtOH (5). Anal. Calcd. for $C_{35}H_{56}N_2O_2Cu.\ 0.5CH_3CH_2OH$: C, 69.36; H, 9.54; N, 4.49; Cu, 10.19%. Found: C, 69.5; H, 9.4; N, 4.3; Cu, 10.4%.

$Cu[H_2L^2]$ (6). Anal. Calcd. for $C_{33}H_{52}N_2O_2Cu$: C, 69.25; H, 9.16; N, 4.89; Cu, 11.10%. Found: C, 69.4; H, 9.2; N, 4.7; Cu, 11.5%.

RESULTS AND DISCUSSION

The condensation reaction of 2,2-dimethyl-1,3-diaminopropane and 1,2-diaminopropane with substituted aromatic aldehydes in ethanol, gave good yield of the salen-type products H_2L^n (n = 1-4) (Fig. 1). Ligands were precipitated either directly after filtration or after the volume of the filtrate cold solution had been reduced. The prepared ligands are air stable, soluble in absolute ethanol, $CHCl_3$ and acetonitrile. The characterization data are given in experimental section, Tables 1-3.

IR Spectra

The most characteristic IR bands of the prepared ligands and their Cu(II) complexes are listed in Table 2. A comparison

Table 1. The Characterization Data of the Prepared Compounds

Compound	Color	Mol. Formula	m.p. (ºC)	Yield (%)
H_2L^1	Yellow	$C_{35}H_{54}N_2O_2$	190-92	90
H_2L^2	Yellow	$C_{33}H_{50}N_2O_2$	150-53	77
H_2L^3	Yellow	$C_{21}H_{26}N_2O_4$	79-82	48
H_2L^4	Yellow	$C_{19}H_{22}N_2O_4$	90-94	38
$H_2[H_2L^1]$	White	$C_{35}H_{58}N_2O_2$	-	50
$H_2[H_2L^2]$	Colorless oil	$C_{33}H_{54}N_2O_2$	-	80
1	Green	$C_{35}H_{52}N_2O_2Cu$	>250	65
2	Green	$C_{33}H_{48}N_2O_2Cu$	>250	55
3	Green	$[C_{21}H_{24}N_2O_4Cu].H_2O$	>250	43
4	Green	$C_{19}H_{20}N_2O_4Cu$	>250	46
5	Green	$[C_{35}H_{56}N_2O_2Cu].0.5CH_3CH_2OH$	>250	51
6	Green	$C_{33}H_{52}N_2O_2Cu$	>250	38

of the spectra of free ligands and complexes show a remarkable similarity in the range 1650-1200 cm^{-1}. A strong band observed in the spectra of salen H_2L^n (n = 1-4) ligands in the region of 1620-1631 cm^{-1} attributable to the azomethine group. This band is shifted to lower wave numbers (1618-1624 cm^{-1}) in the spectra of [CuL^n], indicating coordination of the azomethine nitrogen to the copper(II) ion (Table 2). The IR spectra of all prepared ligands show strong bands at 1230-1280 cm^{-1} assigned to C-O stretching mode. The ν(C-O) is significantly affected by the coordination to the metal ions. Thus, an up-frequency shift between 27-64 cm^{-1} was detected [17].

The IR spectra of the $H_2[H_2L^1]$ and $H_2[H_2L^2]$ exhibit narrow intense bands in the region 3259-3329 cm^{-1} due to *ν*(NH), while they have no bands over the range 1620-1631 cm^{-1}, indicating the absence of the azomethine group. As can be seen from Table 2, in the IR spectra of hydrogenated $Cu[H_2L^n]$ complexes prepared in air, the *ν*(NH) modes are shifted to lower frequencies (3215-3230 cm^{-1}) and any bands in the region 1620-1631 cm^{-1} attributable to *ν*(C=N) modes have not been observed, indicating that the expected oxidative dehydrogenation (-CH_2-NH- → -CH=N-) of hydrogenated ligands in their complexation did not takes place as reported for similar Cu(II) complexes [14,18].

The metal-oxygen and metal-nitrogen-stretching frequencies are sometimes very difficult to assign. Using a dataset of tetradentate Cu(II) salen-type complexes [19,20], the coordination of the azomethine nitrogen is confirmed with the presence of new bands between 534-546 cm^{-1} for all complexes. The Cu-O stretching frequencies for the prepared complexes would be at 304-476 cm^{-1}.

NMR Spectra

The ^1H NMR and $^{13}C\{^1H\}$ NMR spectral results, obtained for all ligands at ambient temperature in $CDCl_3$, together with the hydrogen assignments are presented in Table 3. All H_2L^n (n = 1-4) ligands show a broad singlet in the region δ_H 13.65-14.05 ppm assigned to OH proton, as was confirmed by deuterium exchange, when D_2O was added to $CDCl_3$ solution. The -CH=N- imine protons of H_2L^1 and H_2L^3 exhibit a singlet resonance in the region δ_H 8.44 ppm and δ_H 8.16 ppm, respectively. The presence of two signals at ≈8.40 and ≈8.15 ppm for the azomethine protons in the spectra of H_2L^2 and H_2L^4, respectively, indicate the nonequivalent nature of the azomethine protons. The ^{13}C NMR spectrum of H_2L^2 exhibits 19 signals for 25 different carbons (the discrepancy between the numbers of expected and observed carbon signals may be explained by the overlapping of resonance frequencies of some carbons).

Table 2. Tentative Assignments of Some Selected IR[a] Frequencies (cm^{-1}) and UV-Vis Data of the Prepared Compounds

Compound	ν (C=N)	ν (C-O)	Ph-ring C=C	ν (NH)	Cu-O	Cu-N	λ_{max} (nm) (ε ($M^{-1}cm^{-1}$)) in $CHCl_3$
H_2L^1	1631	1275	1464 1600	-	-	-	270 (12650), 326 (11970), 431 (430)
H_2L^2	1629	1273	1475 1595	-	-	-	271 (11400), 336 (8600), 430 (120)
H_2L^3	1624	1286	1514 1581	-	-	-	276 (11800), 310 (8950), 399 (630)
H_2L^4	1620	1286	1530 1575	-	-	-	278 (11250), 319 (8830), 402 (745)
$H_2[H_2L^1]$	-	1236	1450 1480	3329	-	-	282 (12800), 320 (210)
$H_2[H_2L^2]$	-	1252	1442 1481	3259, 3275	-	-	300 (12300), 327 (350)
1	1624	1321	1456 1531	-	397, 483	525, 559	281 (11520), 390 (6350), 430 (740), 625 (150)
2	1624	1325	1438 1530	-	349, 478	528	295 (12100), 390 (5750), 438 (440), 576 (120)
3	1624	1311	1442 1532	-	372, 403, 456	580, 459	292 (12400), 357 (7750), 428 (450), 613(150)
4	1628	1312	1444 1532	-	442, 459	580	297 (12230), 357 (7400), 430 (510), 577 (240)
5	-	1300	1439 1470	3230	411, 488	498, 546	309 (11300), 444 (526), 612 (422)
6	-	1311	1441 1475	3215, 3202	446, 461	523, 542	301 (12100), 438 (436), 570 (182)

[a]In KBr discs.

Electronic Spectra

The electronic spectra of the prepared ligands and their Cu(II) complexes, recorded in $CHCl_3$ solution, were very similar and displaed main features at 270-280, 310-325 and 400-430 nm (Table 2). The intense absorption band at short wavelengths 270-290 nm may be assigned for π-π* aromatic rings transitions [21]. The weak broad absorption band at 310-325 nm may be assigned to the n-π* and π-π* electronic transition associated with the -HC=N- linkages, also the absorption maxima at 400-430 nm attributable to an n-π* transition of dipolar zwitterionic keto-amine tautomeric structures of ligands [21,22]. The weaker band in the 570-625 nm spectral region of complexes is assigned to the d-d transitions. The observed trend in the d-d band maximum shifts to a longer wavelength with increasing of the bridging, **R**, chain length (Fig. 1) is similar to the trend with stereochemistry observed for their analogs [14,23]. The ligand-field absorption of the bulky group containing complexes, **1**, **3** and **5**, is also red shifted about 36-50 nm compared to those of their methoxy containing analogs in $CHCl_3$ [23]. Thus, the observed red shifts in the d-d band is affected both by the steric effect of bulky *t*-Bu groups in the salicylaldehyde moieties and increasing of methylene backbone length in Cu(II) complexes. It is interesting that the solution spectra of **5** and **6** are very similar to each other and low energy band at about 570-630 nm is blue shifted

Table 3. The ^{1}H and $^{13}C\{^{1}H\}$ NMR Data of the Prepared Ligands

Compound	δ_{OH}	$\delta_{HC=N}$	$\delta_{Sal.H}$	$\delta_{Me.and\ t\text{-}Bu.H}$	Others	δ_{C}
H_2L^1	13.98 (br,s)	8.44 (s,2H)	7.44 (d,2H) 7.19 (br,2H)	1.50 (s,18H) 1.34 (s,18H) 1.14 (s,6H)	3.50 (s,4H)	166.9, 158.2, 140.1, 136.8, 127.1, 126.0, 117.9, 68.2, 36.4, 35.1, 34.2, 31.6, 29.5, 24.6
H_2L^2	13.65 (br,s)	8.44 (s,1H) 8.40 (s,1H)	7.41 (br,2H) 7.12 (br,2H)	1.46 (m,21H) 1.31 (s,18H)	3.7-3.9 (m,3H)	167.5, 165.7, 158.2, 158.1, 140.2, 136.8, 136.7, 127.2, 127.1, 126.14, 126.09, 117.9, 65.7, 64.9, 35.1, 34.2, 31.5, 29.5, 20.5
H_2L^3	14.05 (br,s)	8.16 (s,2H)	7.12 (d,2H) 6.37-6.44 (m,4H)	1.06 (s,6H)	3.81 (s,6H) 3.41 (s,4H)	165.8, 164.7, 163.8, 132.8, 112.2, 106.4, 101.2, 66.4, 55.4, 36.2, 24.2
H_2L^4	13.70 (br,s)	8.20 (s,1H) 8.14 (s,1H)	7.09 (br,1H) 7.07 (br,1H)	1.37 (d,3H)	3.78 (br,s,6H) 3.62 (m,3H)	165.3, 164.6, 163.6, 163.5, 163.45, 132.5, 112.3, 106.4, 106.36, 101.15, 101.12, 64.6, 64.1, 55.3, 20.3
$H_2[H_2L^1]$	-	-	7.30 (d,2H) 6.95 (d,2H)	1.49 (s,18H) 1.36 (s,18H) 1.05 (s,6H)	4.01 (s,4H) 2.59 (s,4H)	154.7, 140.7, 135.9, 123.6, 123.1, 122.1, 57.5, 54.3, 35.2, 34.8, 34.3, 32.0, 29.9, 24.7
$H_2[H_2L^2]$	-	-	7.2-7.3 (m,2H) 6.96 (d,1H) 6.90 (d,1H)	1.44 (m,18H) 1.31 (m,18H) 1.01 (d,3H)	3.9-4.1 (m,4H) 3.05 (m,1H) 2.82 (m,2H)	154.1, 153.7, 141.6, 141.0, 136.4, 136.8, 125.3, 124.0, 123.7, 123.4, 121.9, 121.5, 53.1, 52.7, 51.9, 49.8, 35.2, 34.9, 34.23, 34.19, 31.7, 29.8, 29.7, 18.3, 17.7

compared to that observed for **1** and **2**.

Antibacterial and Antifungal Activities

The investigation of antibacterial screening data revealed that all tested compounds except **1** did not show any remarkable antibacterial activity against E. Coli, as gram negative bacteria, and antifungal activity against C. A. (Table 4).

The weak antibacterial activity of **1**, **3** and **5** compared to **2**, **4** and **6** against S. aureus, as gram positive bacteria, may be

Table 4. Zone Inhibition of the Prepared Compounds

Compounds	Staphylococcus aureus (mm)	Escherichia coli (mm)	Candida albicans (mm)
H_2L^1	11	-	-
H_2L^2	-	-	-
H_2L^3	-	-	-
H_2L^4	-	-	-
$H_2[H_2L^1]$	-	-	-
$H_2[H_2L^2]$	-	-	-
1	14	20	-
2	-	-	-
3	13	-	
4			
5	7		
6			13
DMSO	-	-	-
Standard drugs	Penicillin 33 mm	Gentamicin 18 mm	Nistatin 25 mm

-Indicates bacteria are resistant to the compounds. Zone of inhibition are reported in mm of diameter. Disks were inoculated with 5 mg of the compounds dissolved in DMSO.

explained by differences in their charge density distribution [24].

Thermal Analysis

The thermal properties of the prepared complexes were examined by thermal gravimetric analysis (TG-DTA). Compounds were heated up to 600 ºC in a nitrogen atmosphere. The TG-DTA results are listed in Table 5 and show good agreement with the formula suggested from the analytical data (experimental section). TG data suggest that the framework of **1** is stable up to 320 ºC. Above 350 ºC, the TG of **1** showed a major weight loss attributed to decomposition of the compound and formation of metal oxide (found: 86.35, calcd.: 86.66%).

The TG curve for **2** (Fig. 2) refers to three stages of mass losses within the temperature range 150-540 ºC. The first stage at 150-280 ºC with a mass loss of 9.62% (calcd.: 9.91%) corresponds to the loss of C_3H_6N. The second stage at 320-385 ºC with a mass loss of 39.91% (calcd.: 38.25%) corresponds to the loss of $C_{15}H_{21}O$ and the third stage of decomposition at the temperature range 390-545 ºC is roughly assigned to the loss of $C_{15}H_{21}N$ with a mass loss of 37.30% (calcd.: 37.90%).

Figure 3 illustrates the thermal behavior of the **3** showing a

Table 5. Thermal Analysis Data for Metal Complexes

Compound, M.F. (M. Wt.)	Dissociation stages	Temperature range in TG (ºC)	Weight loss, found (Calculated) (%)	Decomposition assignment
1, $C_{35}H_{52}N_2O_2Cu$ (595.85)	Stage I	320-450	86.35 (86.66)%	The loss of organic moiety
2, $C_{33}H_{48}N_2O_2Cu$ (567.83)	Stage I	150-280	9.62 (9.91)	The loss of C_3H_6N
	Stage II	320-385	39.91 (38.25)	The loss of $C_{15}H_{21}O$
	Stage III	390-545	37.30 (37.90)	The loss of $C_{15}H_{21}N$
3, $C_{21}H_{26}N_2O_5Cu$ (449.97)	Stage I	50-158	2.96 (4.0)	1 mol lattice H_2O
	Stage II	270-360	33.14 (33.1)	The loss of C_8H_7ON
4, $C_{19}H_{20}N_2O_4Cu$ (403.92)	Stage I	120-300	19.84 (20.57)	The loss of $C_4H_7N_2$
	Stage II	330-380	25.33 (26.27)	The loss of C_7H_6O
5, $C_{36}H_{59}N_2O_{2.5}Cu$ (623.4)	Stage I	100-150	4.20 (3.70)	The loss of 0.5 C_2H_5OH
	Stage II	160-250	16.36 (16.05)	The loss of $C_5H_{12}N_2$
	Stage III	295-360	24.42 (30.16)	The loss of $C_{14}H_{20}$
6, $C_{33}H_{52}N_2O_2Cu$ (572.32)	Stage I	230-300	66.81 (66.1)	The loss of organic moiety $C_{28}H_{42}$
	Stage II	320-370	13.17 (12.60)	The loss of $C_3H_8N_2$

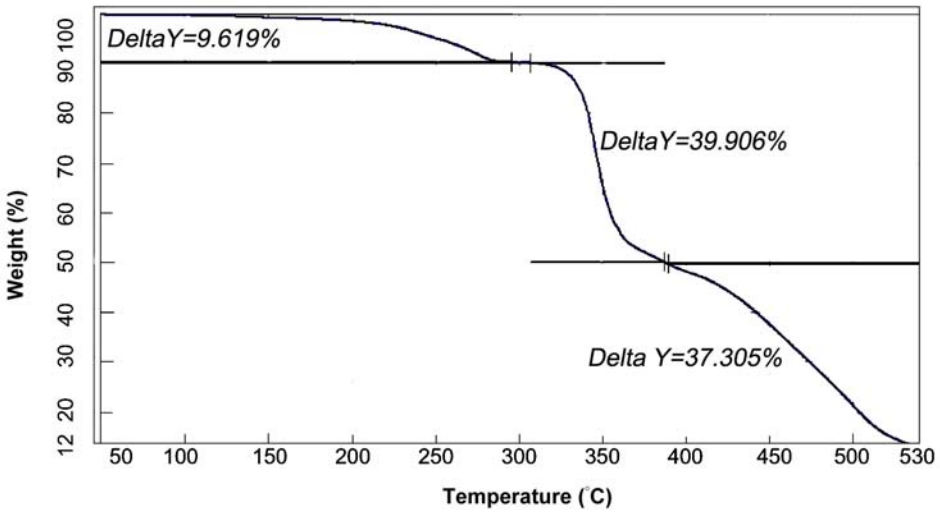


Fig. 2. TGA curve of **2**.

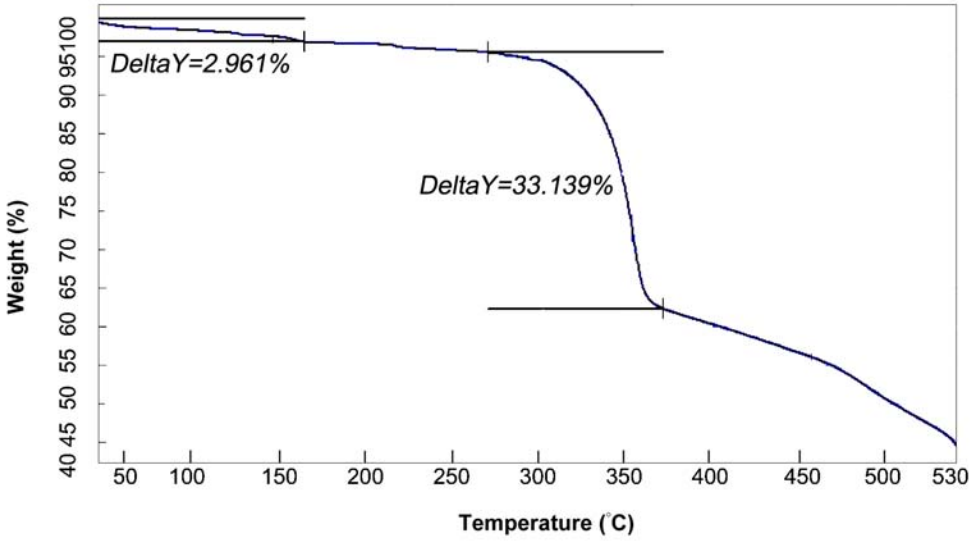


Fig. 3. TGA curve of **3**.

three stage mass loss on TG curves. As seen, the complex loses about 2.96% and 33.14% of its weight at 50-158 and 320-370 ºC, respectively. In the first stage, 1 mol of water was released (calcd.: 4.0%). This indicates that only one lattice water molecule is present in the complex. The second stage is the loss of part of the organic ligand, C_8H_7NO.

Compound **6** revealed major decomposition in the temperature range of 230-300 ºC with weight loss of 66.81% (calcd.: 66.1%). The second stages in the temperature range 320-370 ºC with weight loss of 13.17 (calcd.: 12.60%) represented the loss of the rest of the organic moiety (Fig. 4).

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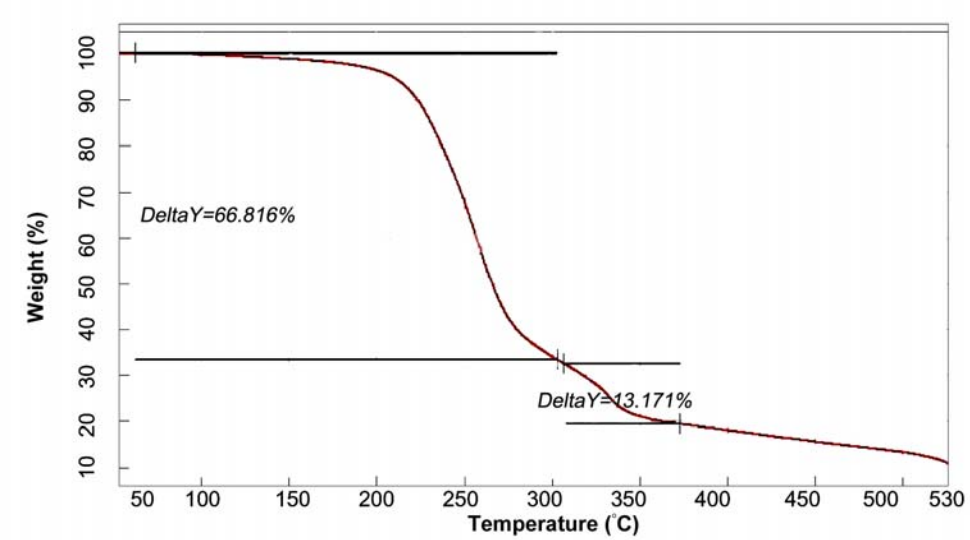

Fig. 4. TGA curve of **6**.

ELECTRONIC SUPPLEMENTARY MATERIAL

The TG/DTA data of the prepared compounds (**1-6**) can be obtained free of charge *via* http://www.araku.ac.ir/~h_khanmohammadi

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