Synthesis and Thermogravimetric Behaviour of Ni(II), Cu(II) and Zn(II) Complexes of Triazine-Salicyldamine Schiff Bases

ABDULAZIZ ALI ALOMARI

Department of Chemistry, Faculty of Science and Arts in Mukwah, University of Al-Baha, Al-Mukwah 65931, Saudi Arabia

Corresponding author: Fax: +966 177247272; Tel: +966 177274111; E-mail: abomaz1389@yahoo.com

Synthesis, characterization and thermogravimetric behaviour of Ni(II), Cu(II) and Zn(II) complexes of Schiff bases derived from 4-phenyl-1,3,5-triazine-2,6-diamine and 5-chloro- salicylaldehyde (H_2L1), 5-bromo-salicylaldehyde (H_2L2) have been reported. The ligands were characterized by FT-IR, ^1H and ^{13}C NMR, UV-visible spectroscopy as well as elemental analysis. Spectral studies revealed that the ligands were acting as tetradentate chelating agents and coordinated to the metal center *via* deprotonated phenolate oxygen and azomethine nitrogen atoms in a 1:1 ligand to metal ratio. Thermal behaviour of the complexes has been evaluated using TGA. All complexes showed similar modes of three steps weight loss upon heating to 800 °C with gradual loss of organic and inorganic parts. The residues after heating corresponds to metal oxides, with copper complexes seemed to be the most stable and can be used in high-temperature catalytic cycles.

Keywords: Thermogravimetric analysis, Schiff bases, Triazine, Metal complexes, Catalysis.

INTRODUCTION

Schiff bases are important class of organic ligands. They play an essential role in the development of coordination chemistry as they readily form stable complexes with most of the transition elements exhibiting different coordination modes and functionalities[1-3]. They also have the privilege of being easy to prepare, stable at ambient conditions and do not require any especial considerations in preservation and handling[4]. Furthermore, their properties can be tuned by choosing appropriate substituents and can stabilize many different metals in various oxidation states[5-7].

Throughout the last decades, many researchers showed that Schiff base metal complexes have potential applications as antibacterial, anticancer, antioxidant and antiviral agents[8-11]. They also exhibited catalytic properties in homogeneous and heterogeneous catalysis[12-14].

Numerous compounds containing 1,2,4-triazine moiety are well known in natural materials and show interesting biological applications[15-17]. In addition, it is reported that salicyldehyde derivatives with one or more halogen atoms in the aromatic ring reveal a variety of biological activities comprising antibacterial and antioxidant[18].

In a previous work, synthesis, characterization and anti-oxidant activities of Schiff bases derived from 4-phenyl-1,3,5-triazine-2,6-diamine and salicylaldehyde with their nickel(II)

and zinc(II) complexes have been reported[19]. In this work, we expanded our research to include chloro- and bromo-substituted derivatives together with their Ni(II), Cu(II) and Zn(II) complexes. The new compounds were characterized by means of elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy, UV-visible and their thermal stability was examined by thermogravimetric analysis in order to test their stability in high-temperature catalytic cycles.

EXPERIMENTAL

4-Phenyl-1,3,5-triazine-2,6-diamine ($C_6H_9N_5$, FW 187.21), 5-chlorosalicylaldehyde (5-ClC_6H_3(OH)CHO; FW 156.57), 5-bromosalicylaldehyde (5-BrC_6H_3(OH)CHO; FW 201.03), triethylamine, copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate and zinc acetate dihydrate were purchased from Sigma-Aldrich and were used as received. All metal salts were of analytical grade. All other solvents were commercially available and used as received.

IR spectra were recorded with a Perkin-Elmer FT-IR spectrophotometer model Spectrum 2000 using KBr pellets as support in the range 4000-370 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded at room temperature on a JEOL ECA-400 spectrometer, operating with a frequency of 400 MHz, using DMSO-d_6 as solvent. Electronic spectra, in DMSO solution, were obtained using a Varian 50 Conc UV-visible spectrophoto-meter over the wavelength range 200-800 nm. Thermogravimetric

analysis was carried out on Perkin Elmer Precisely TGA 4000 thermogravimetric analyzer. The instrument was adjusted at a heating rate of 20 °C/min. The heating was performed from 50-900 °C.

Preparation of ligands

H$_2$L1: A solution of 5-chlorosalicylaldehyde (2 g, 12.77 mmol) in ethanol (40 cm^3) was mixed with a solution of 4-phenyl-1,3,5-triazine-2,6-diamine (1.19 g, 6.35 mmol) in ethanol (40 cm^3). The mixture was stirred under reflux for 2 h. The pale yellow powder formed was filtered and recrystallized from ethanol. It was dried in an oven (80 °C) for 0.5 h. The yield was 2.14 g (72 %). m.p. 120 °C, Anal. calcd. for [C$_{23}$H$_{15}$N$_5$O$_2$Cl$_2$; FW 464.35]: C, 59.43; H, 3.23; N, 15.07. Found: C, 59.62; H, 3.11; N, 15.51 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 3444 (-OH), 2374 (C-H), 1622 (C=N), 1275 (C-O).

H$_2$L2: The method was the same as for H$_2$L1, using 5-bromosalicylaldehyde (2 g, 9.94 mmol) and 4 phenyl-1,3,5-triazine-2,6-diamine (0.93 g, 4.96 mmol). The product was a pale yellow powder and the yield was 2.25 g (82 %). m.p. 118 °C, Anal. calcd. for [C$_{23}$H$_{15}$N$_5$O$_2$Br$_2$; FW 553.25]: C, 49.88; H, 2.71; N, 12.65. Found: C, 50.03; H, 2.22; N, 12.94 %. Selected FT-IR data (KBr, v_{max}, cm^{-1}): 3407 (-OH), 2371 (C-H), 1622 (C=N), 1278 (C-O).

Preparation of complexes

Preparation of NiL1: A solution of H$_2$L1 (0.60 g, 1.29 mmol) in ethanol (40 cm^3) was added to a solution of nickel(II) acetate tetrahydrate (0.32 g, 1.28 mmol) in ethanol (30 cm^3). A few drops of triethylamine were then added and the mixture was magnetically stirred and refluxed for 3 h. The light green powder formed was filtered and recrystallized from DMSO. The yield was 0.52 g (77 %). m.p. 169 °C, Anal. calcd. for [NiC$_{23}$H$_{17}$O$_4$N$_5$Cl$_2$; FW 557.04]: C, 49.50; H, 3.05; N, 12.57; Found: C, 50.20; H, 2.94; N, 12.98 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2873 (C-H), 1616 (C=N), 1319 (C-O), 542 (Ni-O).

Preparation of CuL1: The method was the same as for NiL1, using H$_2$L1 (0.50 g, 1.07 mmol) and Cu(II) acetate monohydrate (0.21 g, 1.05 mmol). The product was a dark green powder and the yield was 0.44 g (78 %). m.p. 310 °C, Anal. calcd. for [CuC$_{23}$H$_{17}$O$_3$N$_5$Cl$_2$; FW 543.89]: C, 50.75; H, 2.75; N, 12.87. Found: C, 50.05; H, 2.92; N, 13.10 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2851 (C-H), 1519 (C=N), 1317 (C-O), 565 (Cu-O).

Preparation of ZnL1: The method was the same as for NiL1, using H$_2$L1 (0.50 g, 1.07 mmol) and Zn(II) acetate dihydrate (0.23 g, 1.04 mmol). The product was a yellow and the yield was 0.42 g (75 %). m.p. 186 °C, Anal. calcd. for [ZnC$_{23}$H$_{17}$O$_4$N$_5$Cl$_2$; FW 563.74]: C, 48.95; H, 3.01; N, 12.41. Found: C, 49.54; H, 2.91; N, 12.30 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2857 (C-H), 1616 (C=N), 1314 (C-O), 542 (Zn-O).

Preparation of L2 complexes: The same procedure described above was used to prepare L2 complexes of Ni(II), Cu(II) and Zn(II) using L2 ligand in 1:1 metal to ligand ratio.

For Ni(II) complex, light green powder was obtained with a yield of 0.42g (76 %). m.p. 175 °C, Anal. calcd. for [NiC$_{23}$H$_{17}$O$_4$N$_5$Br$_2$; FW 645.94]: C, 42.72; H, 2.63; N, 10.83. Found: C, 43.56; H, 2.59; N, 11.14 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2374 (C-H), 1617 (C=N), 1321 (C-O), 537 (Ni-O).

Copper(II) complex was dark green and the yield was 0.39 g (70 %). m.p. 300 °C, Anal. calcd. for [CuC$_{23}$H$_{15}$O$_3$N$_5$Br$_2$; FW 632.79]: C, 43.61; H, 2.37; N, 11.06. Found: C, 43.07; H, 2.37; N, 11.06 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2346 (C-H), 1616 (C=N), 1320 (C-O), 563 (Cu-O).

Whereas zinc(II) complex was a yellow powder and the yield was 0.41 g (74 %). m.p. 220 °C, Anal. calcd. for [ZnC$_{23}$H$_{17}$O$_4$N$_5$Br$_2$; FW 652.64]: C, 42.28; H, 2.60; N, 10.72. Found: C, 42.06; H, 2.24; N, 11.12 %. Selected FTIR data (KBr, v_{max}, cm^{-1}): 2346 (C-H), 1617 (C=N), 1315 (C-O), 536 (Zn-O).

RESULTS AND DISCUSSION

The physical properties of the ligands and their complexes were listed in Table-1. Elemental analyses for the complexes confirmed 1:1 metal to ligand stoichiometry. The compounds were stable at room temperature in the solid state. The ligands were soluble in ethanol, methanol, acetone and high boiling point solvents like DMSO and DMF, whereas the complexes dissolved only in DMSO and DMF and not soluble in either ethanol or methanol.

IR spectra: The main stretching frequencies of the IR spectra of the ligands and their metal complexes were shown in Table-2.

The FT-IR spectra of L1 showed a characteristic broad band at 3444 cm^{-1} for intra-molecularly hydrogen bonded -OH group[20]. A strong peak due to C=N stretching at 1622 cm^{-1}, another strong peak at 1275 cm^{-1} assigned to C-O phenolic stretching and peaks in the region 1500-1000 cm^{-1} from benzene ring skeletal vibrations[21]. The peak at 825 cm^{-1} was due to aromatic C-H out-of-plane stretching mode. The result strongly supported the formation of the Schiff base.

TABLE-1
PHYSICAL PROPERTIES OF THE LIGANDS AND COMPLEXES

Compound	m.f.	Yield (%)	Colour	f.w.	Elemental analysis (%): Found (calcd.)		
					C	H	N
H$_2$L1	C$_{23}$H$_{15}$N$_5$O$_2$Cl$_2$	72	Yellow	464.35	59.62 (59.43)	3.11 (3.23)	15.51 (15.07)
H$_2$L2	C$_{23}$H$_{15}$N$_5$O$_2$Br$_2$	82	Yellow	553.25	50.03 (49.88)	2.22 (2.71)	12.94 (12.65)
NiL1.2H$_2$O	Ni[C$_{23}$H$_{13}$N$_5$O$_2$Cl$_2$]·2H$_2$O	77	Light green	557.04	50.20 (49.50)	2.94 (3.05)	12.98 (12.57)
CuL1.H$_2$O	Cu[C$_{23}$H$_{13}$N$_5$O$_2$Cl$_2$]·H$_2$O	78	Dark green	543.89	50.05 (50.75)	2.92 (2.75)	13.10 (12.87)
ZnL1.2H$_2$O	Zn[C$_{23}$H$_{13}$N$_5$O$_2$Cl$_2$]·2H$_2$O	75	Yellow	563.74	49.54 (48.95)	2.91 (3.01)	12.30 (12.41)
NiL2.2H$_2$O	Ni[C$_{23}$H$_{13}$N$_5$O$_2$Br$_2$]·2H$_2$O	76	Green	645.94	43.56 (42.72)	2.59 (2.63)	11.14 (10.83)
CuL2.H$_2$O	Cu[C$_{23}$H$_{13}$N$_5$O$_2$Br$_2$]·H$_2$O	70	Light green	632.79	43.07 (43.61)	2.37 (2.37)	11.06 (11.06)
ZnL2.2H$_2$O	Zn[C$_{23}$H$_{13}$N$_5$O$_2$Br$_2$]·2H$_2$O	74	Yellow	652.64	42.06 (42.28)	2.24 (2.60)	11.12 (10.72)

		TABLE-2				
		IR SPECTRAL DATA OF LIGANDS AND COMPLEXES, WAVE NUMBERS EXPRESSED (cm⁻¹)				
Compound	ν(O-H)	ν(C-H) Aliphatic	ν(C=N)	ν(C-O)	ν(M-O)	ν(M-N)
H_2L1	3444	2374	1622	1275	-	-
H_2L2	3407	2371	1622	1278	-	-
$NiL1.2H_2O$	3310 (H_2O)	2873	1616	1319	542	492
$CuL1.H_2O$		2851	1519	1317	565	
$ZnL1.2H_2O$		2857	1616	1314	542	508
$NiL2.2H_2O$	3301 (H_2O)	2374	1617	1321	537	
$CuL2.H_2O$		2346	1616	1320	563	-
$ZnL2.2H_2O$		2346	1617	1315	536	

The IR spectra of the nickel complexes differed from that of the ligands. It was noted that the -OH peak, observed for H_2L1 at 3444 cm⁻¹, was now observed at 3453 cm⁻¹ and was assigned to coordinated H_2O molecules in agreement with the results from the elemental analyses[22]. The peaks for C=N at 1622 cm⁻¹ and C-O at 1275 cm⁻¹ observed for the ligands were shifted to 1616 cm⁻¹ and 1319 cm⁻¹ respectively upon complexation[23]. The Ni-O peak is observed at 542 cm⁻¹. These suggested that the phenolic oxygens and imino nitrogens were coordinated to Ni(II).

For copper complex, the expected functional groups as previously discussed for the corresponding Ni(II) complex. The C=N and C-O peaks for $CuL1.H_2O$ were at 1616 cm⁻¹ and 1317 cm⁻¹ respectively. These were almost similar to those of the corresponding Ni(II) complex, suggesting similar bond strength. The Cu-O peak was observed at 565 cm⁻¹, which was higher than that of Ni-O peak (542 cm⁻¹), indicating a stronger M-O bond in the copper(II) complex[24,25]. Zinc complex IR spectra, as shown in Table-2, can be interpreted similarly as their Ni(II) and Cu(II) congeners.

¹H and ¹³C NMR spectra: The ¹H NMR spectra for H_2L1 was consistent with the expected structural formula of the ligand (Fig. 1).
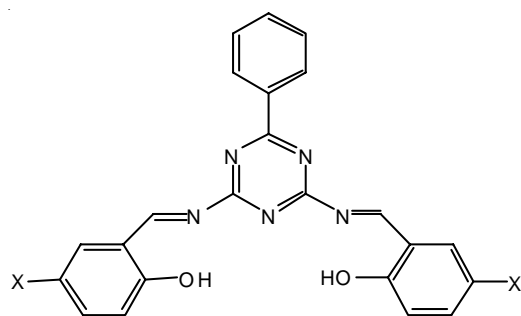
X = Cl for L 1 and Br for L2
Fig. 1. Proposed chemical structure of the ligands

A singlet at 10.19 ppm was due to phenolic hydrogen; a singlet at 8.21 ppm was due to imino hydrogen; and a multiplet in the range 6.72-7.70 ppm was due to the aromatic hydrogens. The integration ratio for these hydrogens was 1:1:5.7 respectively (expected ratio = 1:1:5.5) and supported the molecular symmetry for the Schiff base[26].

The ¹H NMR spectra of H_2L2 was closely similar and can be explained in the same way. The replacement of bromine atom in the 5ᵗʰ position of the salicyldehyde moiety didn't impose significant impact in the chemical shift values.

¹³C NMR spectra for both ligands show 12 peaks. Compared to H_2L1, Br atom in H_2L2 causes the chemical shift of the carbon atom directly attached to it to move towards lower energy (more shielded). At the same time, the two *ortho*-carbon atoms were deshielded and insignificant effects on the other carbon atoms were observed.

UV-visible spectra: The UV-visible spectral data of the ligands and their complexes in DMSO were listed in Table-3.

	TABLE-3		
	UV-VISIBLE OF THE LIGANDS AND COMPLEXES		
Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Tentative assignment
H_2L1	270	1.1×10^4	π-π*
	300	1.4×10^4	n-π*
H_2L2	279	1.5×10^4	π-π*
	345	1.6×10^4	n-π*
$NiL1.2H_2O$	1060	273	$^3A_{2g} \rightarrow {}^3T_{2g}$
	1010	318	$^3A_{2g} \rightarrow {}^3T_{1g}$(F)
	899	400	$^3A_{2g} \rightarrow {}^3T_{1g}$(P)
	407	1.5×10^4	CT
	271	1.9×10^4	π-π*
	400	-	n-π*
$CuL1.2H_2O$	700	200	d-d
	268	1.7×10^4	π-π*
	396	0.8×10^4	CT
$ZnL1.2H_2O$	272	2.0×10^4	π-π*
	390	1.4×10^4	CT

The UV-visible spectrum of a solution of H_2L1 in DMSO showed a high intensity broaden absorption band at about 270 nm (ε = 1.1×10^4 M^{-1} cm⁻¹) assigned to π-π* transition of the aromatic ring[27]. The n-π* transition of the azomethine chromophore was observed as a shoulder at the high intensity peak at about 300 nm (ε = 1.4×10^4 M^{-1} cm⁻¹). These values were in agreement with other Schiff bases reported in the literatures[28]. For example, the π-π* and n-π* transitions were observed 255 nm and 308 nm respectively[28].

For H_2L2, however, The UV-visible spectrum in DMSO showed a high intensity broaden absorption band at about 279 nm (ε = 1.5×10^4 M^{-1} cm⁻¹) assigned to π-π* transition of the aromatic ring. The n-π* transition of the azomethine chromophore was observed as a shoulder at the high intensity peak at about 345 nm (ε = 1.6×10^4 M^{-1} cm⁻¹)[29]. Thus, compared to H_2L1 (270 nm, 378 nm), there was no significant effect for the π-π* transition, while the n-π* transition was shifted to higher energy when Cl was replaced by Br.

For Ni(II) complex, the UV-visible spectra showed weak *d-d* bands 1060 (ε_max = 273 M^{-1} cm⁻¹), 1010 nm (ε_max = 318 M^{-1}

cm^{-1}) and 899 nm (ε_{max} = 400 M^{-1} cm^{-1}). These are consistent with an octahedral configuration at Ni(II)[30]. These bands were assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively and the value of Δ_o was 13,643 cm^{-1}. The peak at 407 nm (ε = 1.5 × 10^4 M^{-1} cm^{-1}) was assigned to metal-ligand charge transfer (MLCT)[31]. The spectrum was also compared with that of H$_2$L1. It was noted that the π-π* band observed for H$_2$L1 (270 nm) remained almost unshifted in the complex 271 nm (ε = 1.9 × 10^4 M^{-1} cm^{-1}). However, the n-π* band may be hidden under the strong MLCT band at 407 nm. Thus, this band was significantly red-shifted from about 300 nm to about 400 nm as a result of coordination to the Ni(II). UV-visible spectra of Cu(II) complex showed a broad *d-d* peak at 700 nm (ε_{max} = 200 M^{-1} cm^{-1}). Thus, [CuL1(H$_2$O)] was a mononuclear square pyramidal complex[32]. The π-π* and MLCT bands were at 268 nm (ε = 1.7 × 10^4 M^{-1} cm^{-1}) and 396 nm (ε = 0.8 × 10^4 M^{-1} cm^{-1}) respectively, which were almost the same as for the corresponding Ni(II) complex (271 nm, 407 nm) and may be similarly explained.

The UV-visible spectrum of Zn(II) complex showed that the MLCT and π-π* peaks 390 nm (ε = 1.4 × 10^4 M^{-1} cm^{-1}) and 272 nm (ε = 2 × 10^4 M^{-1} cm^{-1}) were at almost the same energy as the corresponding peaks for [CuL1].H$_2$O (396 nm, 268 nm). Thus, both metal ions have insignificant effect on the electronic transitions of the organic moiety. The MLCT peak was normally observed from 348 nm to 323 nm for Zn(II) complexes, involving electronic transitions from the full *d* orbitals of the metal ion (3d^{10}) to antibonding orbitals of the ligand[33].

Thermal analysis (TGA)

Thermogravimetric analysis for NiL1: The TGA thermogram (Fig. 2) measured from 50 °C up to 900 °C, showed that the NiL1 complex was stable up to 125 °C[34]. The first weight loss of 5.7 % at 125 °C corresponded to the loss of coordinated H$_2$O molecules (expected, 6.5 %). The next step represented a total weight loss of 83.6 % and was assigned to stepwise decomposition of the ligand (expected, 83.0 %). The amount of residue at 840 °C is 10.7 %. Assuming that the residue was NiO, the expected value was 13.4 %, which was within the acceptable experimental error.

TGA of CuL1: From the TGA curve of Cu(II) complex of L1, shown in Fig. 3, it was evident that the complex was
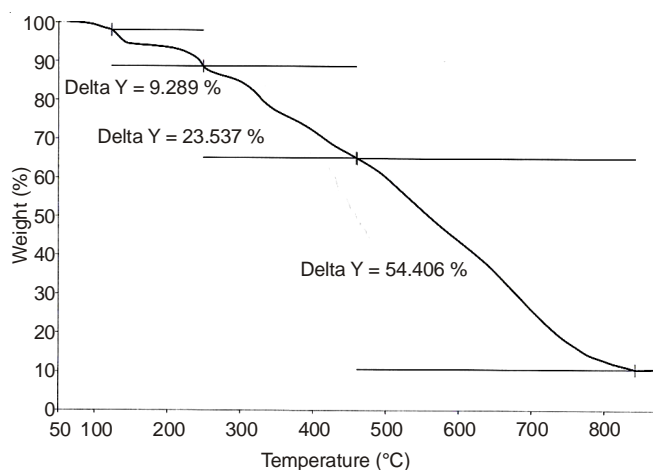

Fig. 2. TGA curve for NiL1.2H$_2$O

more stable than its Ni(II) counterpart. The first weight loss of 4.9 % at 75 °C corresponded to the loss of coordinated H$_2$O molecule (expected, 3.3 %). This result implied that there may be some water of hydration associated with the complex. The next step represented a total weight loss of 78.8 % and was assigned to stepwise decomposition of the ligand with the possibility of the formation of intermediates (expected, 85.4 %). The amount of residue at about 670 °C was 16.5 %.
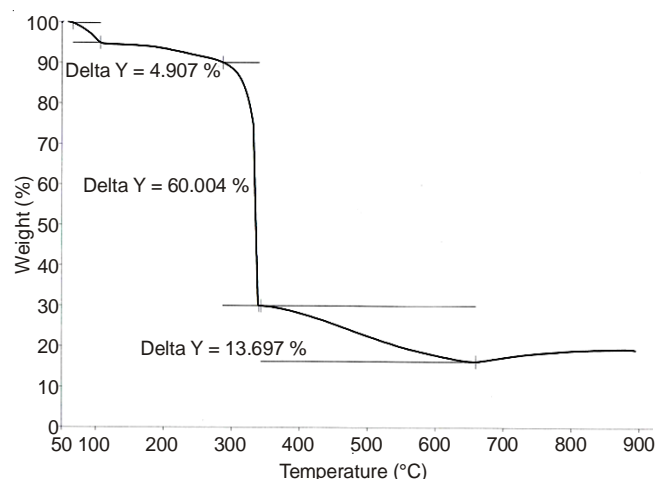

Fig. 3. TGA curve for CuL1.H$_2$O

TGA of ZnL1: On the other hand Zn(II)L1 complex revealed thermal stability up to 228 °C (Fig. 4). The first weight loss of 5.5 % at 130 °C corresponded to the loss of coordinated H$_2$O molecules (expected, 6.3 %). The next step represented a total weight loss of 81.3 % and was assigned to the decomposition of the ligand (expected, 82.4 %). The amount of residue at 780 °C was 13.2 %. Assuming that the residue was ZnO the expected value was 14.4 %, which was within the acceptable experimental error.
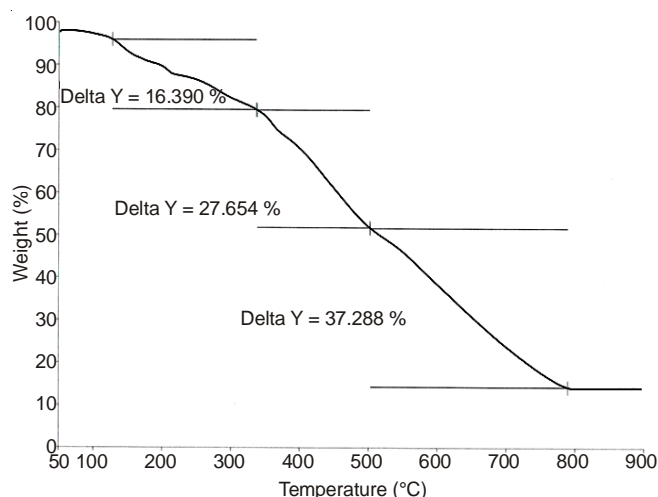

Fig. 4. TGA curve for ZnL1.2H$_2$O

Complexes of the bromo-substituted ligand L2, showed almost identical decomposition pattern, which comprised three decomposition steps, the first step ranged between 122-250 °C corresponded to the loss of coordinated and hydration water molecules, a second step ranged between 250-800 °C corres-

ponded to stepwise ligand dissociation and a residue of metal oxide usually above 800 °C. These results were summarized in Table-4.

TABLE-4
THERMAL ANALYSIS DATA FOR THE COMPLEXES

Compound	Step	Decomposition T_{max} (°C)	Eliminated species
NiL1·2H$_2$O	First	125	2H$_2$O
	Second	250-840	Ligand
	Third	> 840	Residue (NiO)
CuL1·H$_2$O	First	92	2H$_2$O
	Second	280-655	Ligand
	Third	670	Residue (CuO)
ZnL1·2H$_2$O	First	120	2H$_2$O
	Second	120-795	Ligand
	Third	800	Residue (ZnO)
NiL2·2H$_2$O	First	122	2H$_2$O
	Second	260-870	Ligand
	Third	> 870	Residue (NiO)
CuL2·H$_2$O	First	250	H$_2$O
	Second	270-870	Ligand
	Third	> 870	Residue (CuO)
ZnL2·2H$_2$O	First	220	2H$_2$O
	Second	280-860	Ligand
	Third	> 860	Residue (ZnO)

Conclusion

New Schiff bases of 4-phenyl-1,3,5-triazine-2,6-diamine were prepared *via* condensation reaction of the triazine with halo-substituted salicylaldehydes. Their nickel(II), copper(II) and zinc(II) complexes were also prepared. Spectroscopic and analytical data revealed that the complexes have the general formula ML with a 1:1 metal to ligand ratio.

Copper complexes appeared to be more thermally stable than their Ni(II) and Zn(II) analogues. In general, thermal stability of the chloro-ligand complexes followed the order:

Cu complex > Ni complex > Zn complex

The same trend was almost observed by the complexes of the bromo-ligand, with copper and nickel complexes being nearly the same, where zinc complex being the least stable.

All complexes showed three steps decomposition pattern ends up with the metal oxide.

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