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Synthesis and thermogravimetric behavior of Ni (II), Cu (II) and Zn (II) complexes of Triazine-salicyldamine Schiff bases

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Abstract: Synthesis, characterization and thermogravimetric behavior 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) has been reported. The ligands were characterized by FT-IR, ^{1}H and ^{13}C NMR, UV-Vis spectroscopy as well as elemental analysis. Spectral studies reveal 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 behavior of the complexes has been evaluated using thermogravimetric analysis (TGA). All complexes show similar modes of three steps weight loss process upon heating to 800 ^{o}C with gradual loss of organic and inorganic parts. The residues after heating correspond to metal oxides, with copper complexes were found to be the most thermally stable.

Keywords: Thermogravimetric analysis; Schiff bases; Triazine; Metal complexes

1. 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 (Ceyhan *et al* (2013); Demirelli *et al* (2006); Golcu *et al* (2005); Dolaz *et al* (2004)). 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 (Yoon *et al* (2003)). Furthermore, their properties can be tuned by choosing appropriate substituents, and can stabilize many different metals in various oxidation states (Abdel-Latif *et al* (2007); Tang *et al* (2010); C. Maxim *et al* (2008)).

Throughout the last decades, many researchers show that Schiff base metal complexes have potential applications as antibacterial, anticancer, antioxidant and antiviral agents [Sunatsuki *et al* (2002); Ziessel (2001); Yamada (1999)). They also exhibit catalytic properties in homogeneous and heterogeneous catalysis (Kimura *et al* (1994); Lambert (1982)).

Numerous compounds containing 1,2,4 triazine moiety are well known in natural materials and show interesting biological applications (Singh *et al* (2007); Z.H. Chohan *et al* (2004); .Mashaly *et al* (1999)). 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 (Felton *et al* (1947)).

In a previous work, synthesis, characterization and antioxidant activities of Schiff bases derived from 4-phenyl 1, 3,5 triazine-2,6 diamine and hydroxyl salicylaldehyde with their nickel (II) and zinc (II) complexes has been reported (Ali *et al* (2012)). In this work, we expand our research to include chloro- and bromo- substituted derivatives together with their Ni(II), Cu(II) and Zn(II) complexes. This will give more inside to understand the effect of substituents in the activity of the complexes and their

applications. The new compounds were characterized by means of elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy, UV-Vis and their thermal stability was examined by thermogravimetric analysis (TGA).

2. Experimental:

2.1 Materials:

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 ($CuC_4H_6O_4.H_2O$; FW 199.65), nickel(II) acetate tetrahydrate ($NiC_4H_6O_4.4H_2O$; FW 248.86) and zinc acetate dihydrate ($C_4H_6O_4Zn.2H_2O$, FW 219.50) were purchased from sigma-Aldrich (Malaysia) and were used as received. All metal salts were of analytical grade. All other solvents are commercially available and used as received.

2.2 Physical measurements:

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}. ^{1}H 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 spectrophotometer 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.

2.3 Preparation of ligands:

2.3.1 H_2L1:

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 hours. The pale yellow powder formed was filtered and recrystallized from ethanol. It was dried in an oven (80^{o}C) for 30 min. The yield was 2.14 g (72%). Anal. Calc. for [$C_{23}H_{15}Cl_2N_5O_2$; 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, cm^{-1}): 3444 (m, -OH), 2374 (m, C-H), 1622 (s, C=N), 1275 (s, C-O).

2.3.2 H_2L2

The method is the same as for H_2L1, using 5-bromosalicylaldehyde (2g, 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%). Anal. Calc. for [$C_{23}H_{15}Br_2N_5O_2$; 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, cm^{-1}): 3407 (m, -OH), 2371 (m, C-H), 1622 (s, C=N), 1278 (s, C-O).

2.4 Preparation of complexes:

2.4.1 Preparation of NiL1:

A solution of H_2L1 (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 hours. The light green powder formed was filtered and recrystallized from DMSO. The yield was 0.52 g (77%). Anal. Calc. for [$NiC_{23}H_{17}O_4N_5Cl_2$; 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, cm^{-1}): 2873 (m, C-H), 1616 (s, C=N), 1319 (s, C-O), 542 (w, Ni-O)

2.4.2 Preparation of CuL1:

The method is the same as for NiL1, using H_2L1 (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%). Anal. Calc. for [$CuC_{23}H_{17}O_3N_5Cl_2$; 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, cm^{-1}): 2851 (m, C-H), 1519 (s, C=N), 1317(s, C-O), 565 (w, Cu-O).

2.4.3 Preparation of ZnL1:

The method is the same as for NiL1, using H_2L1 (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%). Anal. Calc. for [$ZnC_{23}H_{17}O_4N_5Cl_2$; 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, cm^{-1}): 2857 (m, C-H), 1616 (s, C=N), 1314 (s, C-O), 542 (w, Zn-O).

2.4.4 Preparation of L2 complexes:

The same procedure described above was used to prepare L2 Ni(II), Cu(II) and Zn(II) complexes 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%), Anal. Calc. for [$NiC_{23}H_{17}O_4N_5Br_2$; 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, cm^{-1}): 2374 (m, C-H), 1617 (s, C=N), 1321 (s, C-O), 537 (w, Ni-O).

Copper (II) complex is dark green, and the yield was 0.39 g (70%). Anal. Calc. for [$CuC_{23}H_{15}O_3N_5Br_2$; 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, cm^{-1}): 2346 (m, C-H), 1616 (s, C=N), 1320 (s, C-O), 563 (w, Cu-O).

Whereas zinc (II) complex is a yellow powder and the yield was 0.41 g (74%). Anal. Calc. for [$ZnC_{23}H_{17}O_4N_5Br_2$; 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, cm^{-1}): 2346 (m, C-H), 1617 (s, C=N), 1315(s, C-O), 536 (w, Zn-O).

3. Results and discussion:

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

Table 1 Physical properties of the ligands and complexes

Compound	Formula	Yield (%)	Colour	Formula wt	Found (Calcd.) %		
					C	H	N
H_2L1	$C_{23}H_{15}Cl_2N_5O_2$	72	Yellow	464.35	59.62(59.43)	3.11(3.23)	15.51(15.07)
H_2L2	$C_{23}H_{15}Br_2N_5O_2$	82	Yellow	553.25	50.03(49.88)	2.22(2.71)	12.94(12.65)
$NiL1.2H_2O$	$Ni[C_{23}H_{13}Cl_2N_5O_2].2H_2O$	77	Light green	557.04	50.20(49.50)	2.94(3.05)	12.98(12.57)
$CuL1.H_2O$	$Cu[C_{23}H_{13}Cl_2N_5O_2].H_2O$	78	Dark green	543.89	50.05(50.75)	2.92(2.75)	13.10(12.87)
$ZnL1.2H_2O$	$Zn[C_{23}H_{13}Cl_2N_5O_2].2H_2O$	75	Yellow	563.74	49.54(48.95)	2.91(3.01)	12.30(12.41)
$NiL2.2H_2O$	$Ni[C_{23}H_{13}Br_2N_5O_2.]2H_2O$	76	Green	645.94	43.56(42.72)	2.59(2.63)	11.14(10.83)
$CuL2.H_2O$	$Cu[C_{23}H_{13}Br_2N_5O_2].H_2O$	70	Light green	632.79	43.07(43.61)	2.37(2.37)	11.06(11.06)
$ZnL2.2H_2O$	$Zn[C_{23}H_{13}Br_2N_5O_2].2H_2O$	74	Yellow	652.64	42.06(42.28)	2.24(2.60)	11.12(10.72)

3.1 IR spectra:

The main stretching frequencies of the IR spectra of the ligands and complexes were shown in table 2

Table 2 IR spectral data of ligands and complexes, wave numbers expressed in cm^{-1}

Compound	υ O-H	υ C-H Aliphatic	υ C=N	υ C-O	υ M-O	υ 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 FT-IR spectra of L1 shows a characteristic broad band at 3444 cm^{-1} for intra-molecularly hydrogen bonded -OH group (S. Zolezzi et al (1999)). 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 1000 - 1500 cm^{-1} from benzene ring skeletal vibrations (L. Sacconi (1966)). The peak at 825 cm^{-1} is due to aromatic C-H out-of-plane stretching mode. The result strongly supports the formation of the Schiff base.

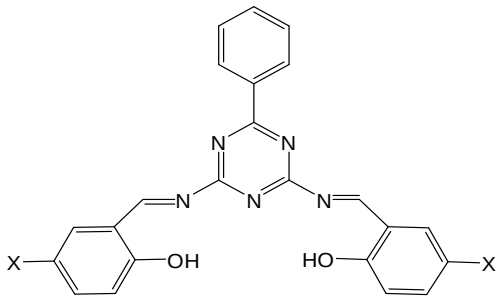
The IR spectra of the nickel complexes differ from that of the ligands. It is noted that the -OH peak, observed for H_2L1 at 3444 cm^{-1}, is now observed at 3453 cm^{-1}, and is assigned to coordinated H_2O molecules in agreement with the results from the elemental analyses (L. J. Bellamg (1975)). The peaks for C=N at 1622 cm^{-1} and C-O at 1275 cm^{-1}

observed for the ligands are shifted to 1616 cm^{-1} and 1319 cm^{-1} respectively upon complexation (M.G. Martin et al (1986)). The Ni-O peak is observed at 542 cm^{-1}. These suggest that the phenolic oxygens and imino nitrogens are 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 $CuL1.H_2O$ are at 1616 cm^{-1} and 1317 cm^{-1} respectively. These are almost similar to those of the corresponding Ni(II) complex, suggesting similar bond strength. The Cu-O peak is observed at 565 cm^{-1}, which is higher than that of Ni-O peak (542 cm^{-1}), indicating a stronger M-O bond in the copper(II) complex (G.C. Peroy (1975), D. M. Adams (1967)). Zinc complex IR spectra, as shown in table 2, can be interpreted similarly as their Ni (II) and Cu(II) congeners.

3.2 ^{1}H and ^{13}C NMR spectra:

The ^{1}H NMR spectra for H_2L1 is consistent with the expected structural formula of the ligand (Figure 1).



X = Cl for L1 and Br for L2

Figure 1 Proposed chemical structure of the ligands

A singlet at 10.19 ppm is due to phenolic hydrogen; a singlet at 8.21 ppm is due to imino hydrogen; and a multiplet in the range 6.72 - 7.70 ppm is due to the aromatic hydrogens. The integration ratio for these hydrogens is 1:1:5.7 respectively (expected ratio = 1:1:5.5), and supports the molecular symmetry for the Schiff base (Z.L. Yuan et al (2008)).

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

^{13}C 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.

3.3 UV-Vis spectra:

The UV-Vis spectral data of the ligands and their complexes in DMSO are listed in table

Table 3 UV-Vis 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	$^3A_{2g}$ → $^3T_{2g}$
	1010	318	$^3A_{2g}$ → $^3T_{1g}(F)$
	899	400	$^3A_{2g}$ → $^3T_{1g}(P)$
	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-Vis spectrum of a solution of H_2L1 in DMSO shows a high intensity broaden absorption band at about 270 nm ($\varepsilon = 1.1x10^4$ $M^{-1}cm^{-1}$) assigned to π-π^* transition of the

aromatic ring (P. Gili et al (1989)). The *n*-π^* transition of the azomethine chromophore is observed as a shoulder at the high intensity peak at about 300 nm ($\varepsilon = 1.4x10^4$ $M^{-1}cm^{-1}$). These values are in agreement with other Schiff bases reported in the literatures (A. Ray et al (2009)). For example, the π-π^* and *n*-π^* transitions were observed 255 nm and 308 nm respectively (A. Ray et al (2009)).

For H_2L2, however, The UV-Vis spectrum in DMSO shows a high intensity broaden absorption band at about 279 nm ($\varepsilon = 1.5x10^4$ $M^{-1}cm^{-1}$) assigned to π - π^* transition of the aromatic ring. The *n* - π^* transition of the azomethine chromophore is observed as a shoulder at the high intensity peak at about 345 nm($\varepsilon = 1.6x10^4$ $M^{-1}cm^{-1}$)(S. Zolezzi et al (1999)). Thus, compared to H_2L1 (270 nm, 378 nm), there is 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-Vis spectra shows weak *d-d* bands 1060 ($\varepsilon_{max} = 273$ $M^{-1}cm^{-1}$), 1010 nm ($\varepsilon_{max} = 318$ $M^{-1}cm^{-1}$), and 899 nm ($\varepsilon_{max} = 400$ $M^{-1}cm^{-1}$). These are consistent with an octahedral configuration at Ni(II) (David Nicholls (1975)). These bands are 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 is 13,643 cm^{-1}.

The peak at 407 nm ($\varepsilon = 1.5 \times 10^4$ $M^{-1}cm^{-1}$) is assigned to metal-ligand charge transfer (MLCT) (G. Ceyhan et al (2011)). The spectrum is also compared with that of H_2L1. It is noted that the π - π^* band observed for H_2L1 (270 nm) remains almost unshifted in the complex 271 nm($\varepsilon = 1.9 \times 10^4$ $M^{-1}cm^{-1}$). However, the *n* - π^* band may be hidden under the strong MLCT band at 407 nm. Thus, this band is significantly red-shifted from about 300 nm to about 400 nm as a result of coordination to the Ni(II).

UV-Vis spectra of Cu (II) complex shows a broad *d-d* peak at 700 nm ($\varepsilon_{max} = 200$ $M^{-1}cm^{-1}$). Thus, [CuL1(H_2O)] is a mononuclear square pyramidal complex (E. Suresh et al (1996)). The π - π^* and MLCT bands are at 268 nm($\varepsilon = 1.7x10^4$ $M^{-1}cm^{-1}$) and 396 nm(ε

= $0.8x10^4$ $M^{-1}cm^{-1}$) respectively, which are almost the same as for the corresponding Ni(II) complex (271 nm, 407 nm), and may be similarly explained.

The UV-Vis spectrum of Zn (II) complex shows that the MLCT and π - π^*peaks 390 nm($\varepsilon = 1.4x10^4$ $M^{-1}cm^{-1}$) and 272 nm($\varepsilon = 2x10^4$ $M^{-1}cm^{-1}$) are at almost the same energy as the corresponding peaks for [CuL1].H_2O (396 nm, 268 nm). Thus, both metal ions have insignificant effect on the electronic transitions of the organic moiety. The MLCT peak is 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 (Alaaddin *et al* (2002)).

3.4 Thermal analysis (TGA):

3.4.1 Thermogravimetric analysis for NiL1:

The TGA thermogram (Figure 2) measured from 50^{o}C up to 900 ^{o}C, shows that the NiL1 complex was stable up to 125^{o}C (M. Tumer et al (2007)). The first weight loss of 5.7% at 125^{o}C corresponds to the loss of coordinated H_2O molecules (expected, 6.5%). The next step represents a total weight loss of 83.6% and is assigned to stepwise decomposition of the ligand (expected, 83.0%). The amount of residue at 840^{o}C is 10.7%. Assuming that the residue is NiO, the expected value is 13.4%, which is within the acceptable experimental error.

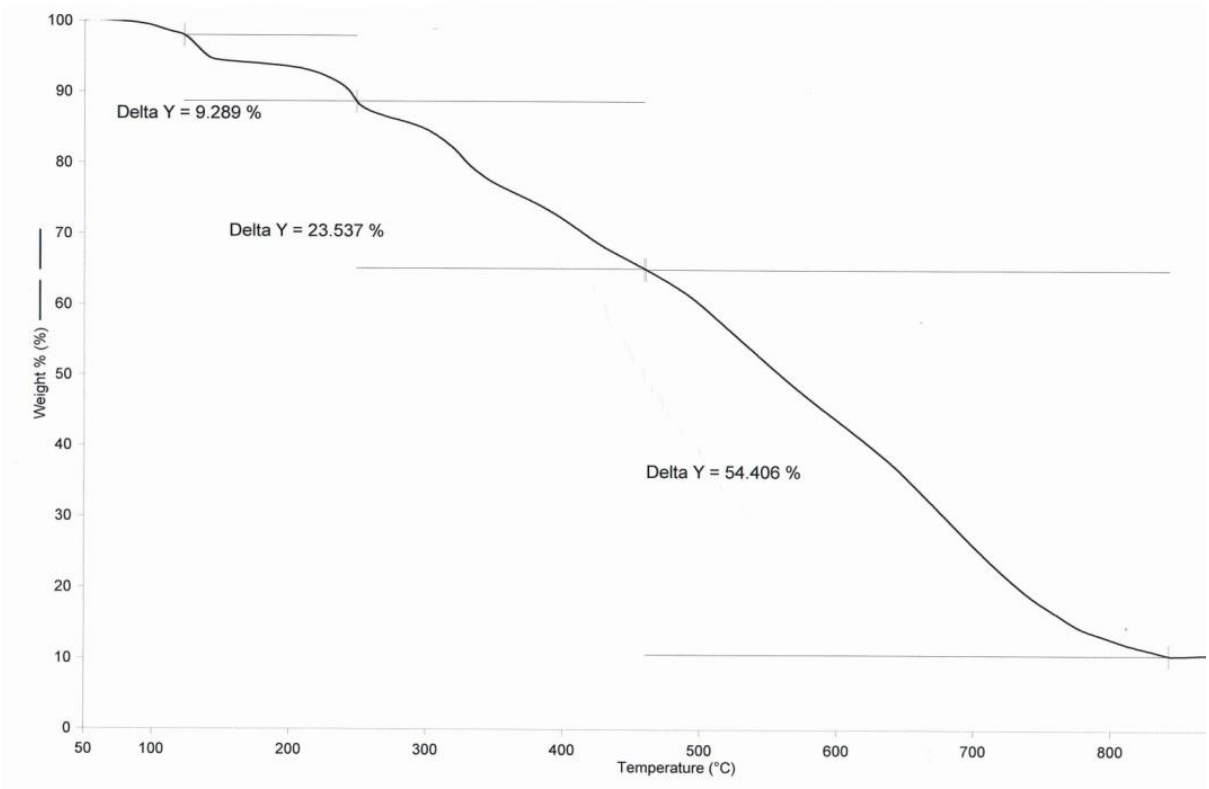


Figure 2: TGA curve for $NiL1.2H_2O$

3.4.2 TGA of CuL1:

From the TGA curve of Cu(II) complex of L1, shown in figure 3, it is evident that the complex is more stable than its Ni(II) counterpart.

The first weight loss of 4.9% at 75^oC corresponds to the loss of coordinated H_2O molecule (expected, 3.3%). This result implies that there may be some water of hydration associated with the complex. The next step represents a total weight loss of 78.8% and is 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^oC is 16.5%.

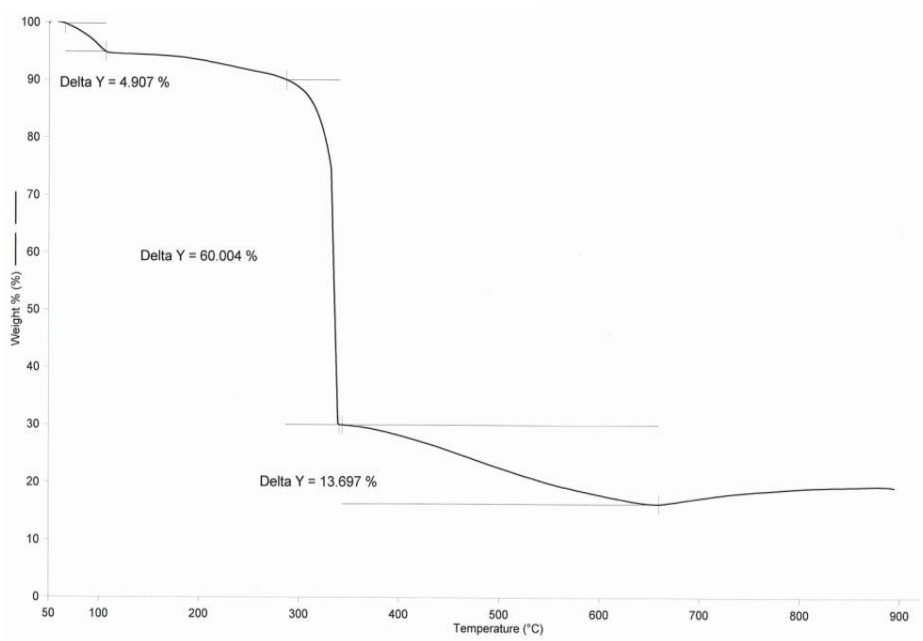


Figure 3: TGA curve for CuL1.H_2O

3.4.3 TGA of ZnL1:

On the other hand Zn(II)L1 complex reveals thermal stability up to 228^oC (Figure 4). The first weight loss of 5.5% at 130^oC corresponds to the loss of coordinated H_2O molecules (expected, 6.3%). The next step represents a total weight loss of 81.3% and is assigned to the decomposition of the ligand (expected, 82.4%). The amount of residue at 780^oC is 13.2%. Assuming that the residue is ZnO the expected value is 14.4%, which is within the acceptable experimental error.

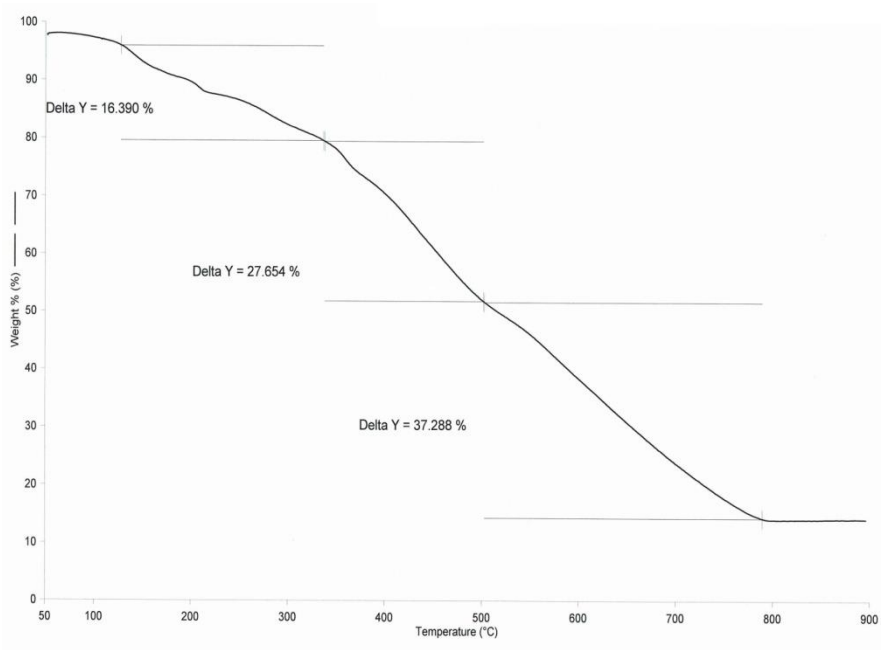


Figure 4: TGA curve for $ZnL1.2H_2O$

Complexes of the bromo-substituted ligand L2, show almost identical decomposition pattern, which comprises three decomposition steps, the first step ranges between 122 - 250 ^oC corresponds to the loss of coordinated and hydration water molecules, a second step ranges between 250 - 800 ^oC corresponds to stepwise ligand dissociation, and a residue of metal oxide usually above 800 ^oC. These results were summarized in table 4.

Table 4 Thermal analysis data for the complexes

Compound	Step	Decomposition T_{max} (°C)	Eliminated species
$NiL1.2H_2O$	First	125	$2H_2O$
	Second	250 - 840	Ligand
	Third	> 840	Residue (NiO)
$CuL1.H_2O$	First	92	$2H_2O$
	Second	280 - 655	Ligand
	Third	670	Residue (CuO)
$ZnL1.2H_2O$	First	120	$2H_2O$
	Second	120 - 795	Ligand
	Third	800	Residue (ZnO)
$NiL2.2H_2O$	First	122	$2H_2O$
	Second	260 - 870	Ligand

	Third	> 870	Residue (NiO)
$CuL2.H_2O$	First	250	H_2O
	Second	270 - 870	Ligand
	Third	> 870	Residue (CuO)
$ZnL2.2H_2O$	First	220	$2H_2O$
	Second	280 - 860	Ligand
	Third	> 860	Residue (ZnO)

All attempts to obtain suitable crystals for x-ray crystal structure determination were unsuccessful.

4. 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 reveal that the complexes have the general formula ML with a 1:1 metal to ligand ratio.

Copper complexes appear to be more thermally stable than their Ni(II) and Zn(II) analogues. In general, thermal stability of the chloro-ligand complexes follow 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 show three steps decomposition pattern ends up with the metal oxide.

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