

THERMAL STUDY OF NEW MULTINUCLEAR CYCLIC LIGAND – METAL COMPLEXES

Faliah Hassan Ali Al-Jeboori¹, Mohamad Jaber Al-Jeboori²
and Kafa Khalaf Hammud¹

¹Ministry of Science and Technology, Baghdad, Iraq.

²College of Education–Ibn–AL–Haitham, Baghdad University, Baghdad, Iraq.

ABSTRACT

The thermal properties of newly prepared 2,6-diformyl-p-cresol cyclic as multinuclear or polydentate ligand and a number of this Schiff base metal complexes in nitrogen atmosphere have been investigated by thermogravimetry (TG) and differential thermogravimetry (DTG). The thermo-analytical data of newly prepared N₄O₂S₄ donor cyclic polydentate ligand and its metal complexes were presented and discussed.

Keywords: TG/DTG, 2,6-diformyl-p-cresol, metals complexes, Cyclic polydentate.

INTRODUCTION

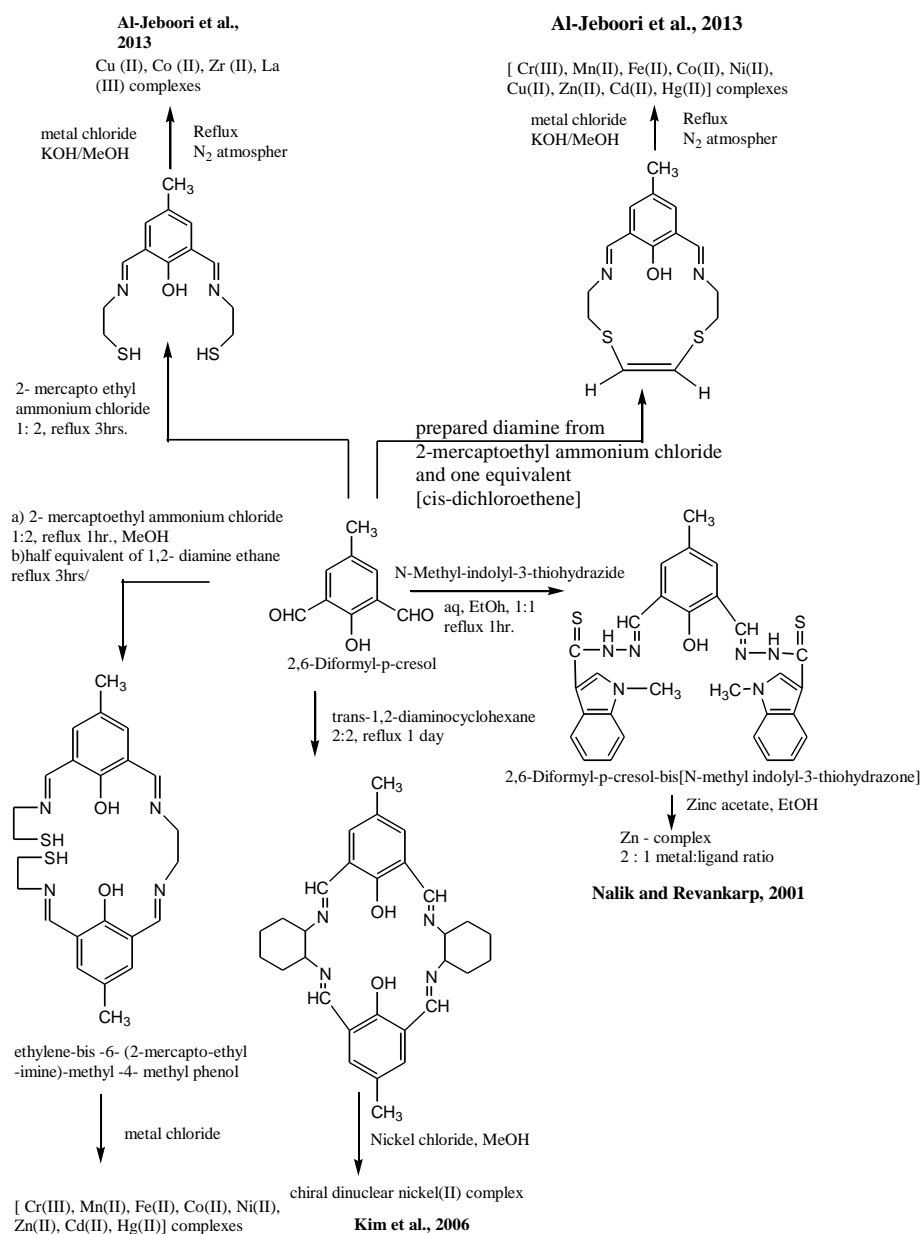
Schiff bases have a chelating structure and are moderate electron donors with easily electronic and steric effects¹. Polydentate ligands with a nitrogen, oxygen and sulfur donor atoms have received much attention due to the distinct trans- effect of these donors². Hetero-tridentate NSO ligands resulted from the combination of NOS displaying unique feature in manipulating the catalytic activity³. The synthetic macrocycles and their corresponding metal complexes had a great interest related to their mimic naturally-occurring macrocyclic molecules in structural features. The formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of macrocycle, on the nature of its donor atoms and on the complexing properties of the counterion. The syntheses of the macrocyclic ligands are generally carried out in the presence of a suitable salt⁴.

Different authors including our research group reported synthesis of these macrocyclic and/or macroacyclic derivatives containing 2, 6-diformyl-NOS polydentate and metal complexation (Scheme -1-) that may exhibit several important applications⁵⁻¹².

Thermogravimetric analysis (TGA) or thermogravimetry (TG) also applied at high-temperature kinetics and mechanisms in corrosive environments of gas, liquid, or solid. It is a powerful thermal technique with no direct chemical information showing a clear image of different high-temperature processes such as absorption, adsorption, sublimation, vaporization, decomposition, solid-solid reaction, solid-gas reaction, dehydration, or desolvation either by measuring weight losses or weight gains as a function of time. Samples can be subjected to thermal analysis by TGA/DTA instrumentation to study their thermal stability and to check water molecule presence¹³⁻¹⁵.

Several reported articles describe the thermal behavior of Schiff base and its metal complexes^{16,17}.

In spite of the relatively large number of thermal analysis reports on Schiff base metal complexes, less work was published on calculation of the kinetic and thermodynamic parameters of their decomposition^{6,7}.



Scheme 1: NOS 2,6-Diformyl -p- Cresol Macrocylic Derivatives and their metal complexes⁵⁻¹².

We previously reported the synthesis of macrocylic and macroacylic NOS polydentates derived from 2,6-diformyl -p- cresol and different amino compounds⁹⁻¹². Now, we have extended our work to encompass thermal TG/DTA study of newly prepared N₄O₂S₄ donor - cyclic polydentate ligand and its metal complexes.

EXPERIMENTAL PART

CHEMICALS

All common laboratory chemicals and reagents were from Aldrich and Fluka and have been used without further purifications.

MEASUREMENTS

An electrothermal apparatus Stuart melting point was used to measure the melting points. Infrared spectra were done with Shimadzu FTIR Shimadzu, Japan and Ultraviolet-Visible spectra with 1601PC, Shimadzu, Japan. Conductivity measurements were recorded at CDM 83 conductivity - meter (25°C) for (10⁻⁵-10⁻³) M solutions of the samples in DMSO or DMF.

Mass spectra for ligands and some complexes were obtained by (+) Laser adsorption technique using BRUKER DALTONICS. All isotopes distribution was compared to a computer generated distribution pattern. The spectra were recorded at Queen Mary, London University / United Kingdom.

^1H -, ^{13}C -, ^1H - ^1H , and ^1H - ^{13}C correlated NMR spectra for the ligands and some complexes were recorded in DMSO- d_6 , D_2O using a Bruker 400 MHz, Ex 400 MHz and a Jeol 270 MHz instruments with a tetramethylsilane (TMS) as an internal standard. The samples were recorded at Queen Mary/ University of London/United Kingdom. Elemental microanalyses were performed on a (C.H.N) analyzer, from Heraeus (Vario EI) at Free Berlin University/ Germany.

Synthesis of Ligand *Bis*{(4-methyl 2,6-diformylaminoN,N-di-1,2 ethylene 2,2-dithia)ethene [H₂L]}

To (2.5g, 1.6 mL, 15 mmole) of tetrachloroethene was added dropwise a solution of potassium hydroxide (3.3g, 60 mmole) dissolved in (15 mL) absolute methanol. The reaction mixture was stirred vigorously and refluxed for 0.5 hour. After cooling potassium chloride was removed by filtration, then a solution of 2-mercaptoethylammonium chloride (2.5g, 2.2 mmole) in (15 mL) methanol was added gradually; The reaction mixture was stirred under nitrogen atmosphere and refluxed for two hours.

The reaction mixture (yellow solution) cooled to room temperature, then 2,6-diformyl-4-methyl phenol (**d4**) (5.0g, 30 mmole) dissolved in (20 mL) of ethanol was added gradually; The reaction mixture was refluxed for three hours, and a yellow precipitate was observed after refluxing for one hour. The precipitate was filtered off, and washed several times with 1,2-dichloromethane (DCM). The crude product was recrystallized from absolute ethanol m.p.(280-284) $^{\circ}\text{C}$, 60 % yield, Analytical Calcd. For $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_2\text{S}_4$ (584.14): C, 57.50; H,5.51; N,9.58%, Found: C, 57.43; H,5.42; N,9.45%. ^1H NMR (DMSO- d_6), δ_{H} 8.87- 7.89(6H, C-H, 4H; O-H, 2H), δ_{H} 7.35-7.32, δ_{H} 7.15-7.11(aromatic protons, doublet of doublet), δ_{H} 4.10-3(N-CH₂), (δ_{H} 3.11, 2.91(8H, d, $J_{\text{H-H}} = 7.81$ Hz, SC-H₂), δ_{H} 2.21(6H, s, C-H₃). ^{13}C NMR (DMSO- d_6), δ_{C} 168.81(HC=N, azomethine), δ_{C} 118.53, 124.51,129.23, 140.34, 149.43 (aromatic carbons), δ_{C} 73.53 (alkene group), δ_{C} 65.51 (C-N), δ_{C} 35.61 (C-S), δ_{C} 21.50 (CH₃). Laser adsorption (+) mass spectrum (M/Z) 584.89[M⁺].UV-Vis (270 nm, 37037 cm^{-1} , ϵ_{max} 4000 $\text{molar}^{-1} \text{cm}^{-1}$, $\pi \rightarrow \pi^*$), (350 nm, 28571 cm^{-1} , ϵ_{max} 3524 $\text{molar}^{-1} \text{cm}^{-1}$, $n \rightarrow \pi^*$), (447 nm, 22371 cm^{-1} , ϵ_{max} 1390 $\text{molar}^{-1} \text{cm}^{-1}$, $n \rightarrow \pi^*$).I.R (KBr): ν (cm^{-1}): 3392 (O-H—N, broad, intramolecular hydrogen bonding); 1627(C=N, sharp); 1595, C=N, imine), 1350 (phenolic C—O); 1460 (C=C); 1124(S-CH₂); 1041 (C-S); 2918 (C-H, aliphatic, weak); 2854 (C-H, aromatic); 1350 (-CH₂); 1287 (C-O).

Synthesis of [H₂L] complexes with some metal ions

(1.36 mmole) of metal chloride in (10 mL) methanol was added dropwise under nitrogen blanket to a solution of [H₂L] (0.21g, 0.34 mmole) dissolved in (15 mL) methanol. The reaction mixture was stirred and pH was adjusted to Ca 9 by adding methanolic potassium hydroxide. The reaction mixture was filtered off and allowed to reflux for two hours. The precipitate was filtered off, washed several times with absolute ethanol and dried.

Chromium complex[Cr₄(L)(H₂O)₄Cl₈]Cl₂

Blue solid, m.p(224-229) $^{\circ}\text{C}$, 82% yield, Analytical Calcd. For [Cr₄C₂₈H₃₀N₄O₂S₄(H₂O)₄Cl₈]Cl₂ (1219.1): C, 27.56; H,3.11; N,4.61; Cr, 17.02; Cl,29.12%, Found: C, 27.71; H,3.22; N,4.55; Cr, 18.71; Cl,30.01%.I.R (KBr): ν (cm^{-1}): 3398 (-OH, broad); 842(OH, weak); 1598 (C=N imine, sharp); 1470 (C=C); 1151 (S-CH₂); 1112 (C-S, broad); 2929 (C-H, aliphatic, weak); 1379 (-CH₂); 1350 (C-O); 572, 538, 507, 491, 430 (M-N), (M-O), (M-S). UV-Vis (272 nm, 26764 cm^{-1} , ϵ_{max} 841 $\text{molar}^{-1} \text{cm}^{-1}$, ligand field), (420 nm, 23809 cm^{-1} , ϵ_{max} 60 $\text{molar}^{-1} \text{cm}^{-1}$, $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}^{\text{F}}$), proposed structure: Octahedral.

Manganese complex[Mn₄(L)(H₂O)₄Cl₈]Cl₂

Black brown solid, m,p>250 dec., 84% yield, Analytical Calcd. For [Mn₄C₂₈H₃₀N₄O₂S₄(H₂O)₄Cl₈]Cl₂ (1230.72): C, 27.30; H,3.08; N,4.55; Mn, 17.82; Cl,28.84%, Found: C, 27.56; H,3.12; N,4.61; Mn, 18.95; Cl,29.01%.I.R (KBr): ν (cm^{-1}): 3346 (-OH, broad); 819 (OH, weak); 1598 (C=N imine, sharp); 1429 (C=C); 1103 (S-CH₂, broad); 1103 (C-S, broad); 2862 (C-H, aromatic, weak); 1429(-CH₂, sharp); 1350 (C-O); 541, 478, 455, 418 (M-N), (M-O), (M-S).UV-Vis (272 nm, 36764 cm^{-1} , ϵ_{max} 1109 $\text{molar}^{-1} \text{cm}^{-1}$, ligand field), (450 nm, 22222 cm^{-1} , ϵ_{max} 200 $\text{molar}^{-1} \text{cm}^{-1}$, $^6\text{A}_{1g}^{\text{S}} \rightarrow ^4\text{T}_{2g}^{\text{G}}$), proposed structure: Octahedral.

Iron complex[Fe₄(L)Cl₄]Cl₂

Brown solid, m,p (201-204) $^{\circ}\text{C}$, 84% yield, Analytical Calcd. For [Fe₄C₂₈H₃₀N₄O₂S₄Cl₄]Cl₂ (1020.36): C, 32.93; H,2.94; N,5.48; Fe, 21.94; Cl,20.88%, Found: C, 33.10; H,3.01; N,5.85; Fe, 22.01; Cl,21.50%.%. I.R (KBr): ν (cm^{-1}): 3386 (-OH, broad); 1622 (C=N imine, sharp); 1431 (C=C); 1171 (S-

CH₂, broad); 1171 (C-S, broad); 2905 (C-H, aliphatic, weak); 2816 (C-H, aromatic); 1384(-CH₂, sharp); 1348 (C-O); 535, 505, 480, 430 (M-N), (M-O), (M-S).UV-Vis (273 nm, 36630 cm⁻¹, ε_{max}706 molar⁻¹ cm⁻¹, ligand field), (550 nm, 18181 cm⁻¹, ε_{max}50 molar⁻¹ cm⁻¹, B₂ → E), proposed structure: Tetrahedral.

Cobalt complex[Co₄(L)(H₂O)₈(Cl)₄]Cl₂

Deep brown solid, m.p (200-202) °C, 82% yield, Analytical Calcd. For [Co₄C₂₈H₃₀N₄O₂S₄(H₂O)₈(Cl)₄]Cl₂ (1176.72): C, 28.55; H,3.74; N,4.75; Co, 20.01; Cl,18.11%, Found: C, 28.91; H,3.81; N,4.91; Co, 20.53; Cl,18.41%.I.R (KBr): ν (cm⁻¹): 3429 (-OH, broad); 790 (OH); 1591 (C=N imine, sharp); 1460 (C=C); 1106 (S-CH₂, broad); 1105(C-S, broad); 2929 (C-H, aliphatic, weak); 2813 (C-H, aromatic); 1382 (-CH₂, weak); 1348 (C-O); 522, 430 (M-N), (M-O), (M-S).UV-Vis (273 nm, 36630 cm⁻¹, ε_{max}630 molar⁻¹ cm⁻¹, ligand field), (607 nm, 16474 cm⁻¹, ε_{max}98 molar⁻¹ cm⁻¹, ⁴T_{1g}^(F) → ⁴T_{1g}^(P)), (675 nm, 14814 cm⁻¹, ε_{max}113 molar⁻¹ cm⁻¹, ⁴T_{1g}^(F) → ⁴A_{2g}^(F)), proposed structure: Octahedral.

Nickel complex[Ni₄(L) (H₂O)₈Cl₄]Cl₂

Green solid, m,p>250 dec.°C, 80% yield, Analytical Calcd. For [Ni₄C₂₈H₃₀N₄O₂S₄(H₂O)₈Cl₄]Cl₂ (1175.84): C, 28.57; H,3.74; N,4.74.76; Ni, 19.98; Cl,18.11%, Found: C, 27.95; H,2.81; N,4.82; Ni, 20.31; Cl,19.01%.I.R (KBr): ν (cm⁻¹): 3450 (-OH, broad); 790 (OH); 1595 (C=N imine, sharp); 1421 (C=C); 1114 (S-CH₂); 1114 (C-S, broad); 2862 (C-H, aromatic, weak); 1421 (-CH₂, broad); 1350 (C-O); 510, 449 (M-N), (M-O), (M-S). UV-Vis (270 nm, 37037 cm⁻¹, ε_{max}591 molar⁻¹ cm⁻¹, ligand field), (360 nm, 27777 cm⁻¹, ε_{max}228 molar⁻¹ cm⁻¹, ³A_{2g}^(F) → ³T_{1g}^(P)), (390 nm, 14707 cm⁻¹, ε_{max}50 molar⁻¹ cm⁻¹, ³A_{2g}^(F) → ³T_{1g}^(F)), proposed structure: Square planar.Magnetic moment (μ_{eff}.=B.M.) of solid at 298K: X_g×10⁻⁶ Gram Susceptibility (2.11648), X_M×10⁻⁶ Molar Susceptibility (2499.72), X_A×10⁻⁶ Atom Susceptibility (3104.20), μ_{eff}. B.M. expt.(2.72)antiferromagnetism for polynuclear complex, μ_{eff}. B.M calc. (2.83), Suggested Structure: Octahedral.

Copper complex[Cu₄(L)Cl₄]Cl₂. H₂O

Green solid, m,p (250 -264) °C, 86% yield, Analytical Calcd. For [Cu₄C₂₈H₃₀N₄O₂S₄ Cl₄] Cl₂.H₂O (1069.16): C, 31.43; H,2.99; N,5.23; Cu, 23.77; Cl,19.92%, Found: C, 31.95; H,3.12; N,5.50; Cu, 24.85; Cl,20.01%.I.R (KBr): ν (cm⁻¹): 3438 (-OH, broad); 815 (OH, weak); 1593 (C=N imine, sharp); 1409 (C=C); 1118 (S-CH₂); 1116 (C-S); 2931 (C-H, aromatic, weak); 2812 (-CH₂); 1409 (C-O); 520, 472 (M-N), (M-O), (M-S).UV-Vis (373 nm, 36630 cm⁻¹, ε_{max}2593 molar⁻¹ cm⁻¹, ligand field), (395 nm, 28328 cm⁻¹, ε_{max}1500 molar⁻¹ cm⁻¹, charge transfer), (450 nm, 22222 cm⁻¹, ε_{max}100 molar⁻¹ cm⁻¹, ²B_g → ²E_g), proposed structure: Square planar.Conductivity in DMF Am (S.cm² mole⁻¹): 145 [(1:2) electrolyte nature].

Zinc complex[Zn₄(L)Cl₄]Cl₂. H₂O

Pale yellow solid, m,p>250 dec.°C, 82% yield, Analytical Calcd. For [Zn₄C₂₈H₃₀N₄O₂S₄ Cl₄]Cl₂.H₂O (1076.48): C, 31.79; H,2.84; N,5.29; Zn, 24.74; Cl,19.79%, Found: C, 32.01; H,2.79; N,5.33; Zn, 24.63; Cl,20.10%.I.R (KBr): ν (cm⁻¹): 3392 (-OH, broad); 798 (OH); 1602 (C=N imine, sharp); 1431 (C=C); 1108 (S-CH₂, broad); 1108 (C-S, broad); 2925 (C-H, aliphatic, weak); 2862 (C-H, aromatic); 1415 (-CH₂); 1344 (C-O); 550, 505, 417 (M-N), (M-O), (M-S).UV-Vis (273 nm, 36630 cm⁻¹, ε_{max}961 molar⁻¹ cm⁻¹, ligand field), (352 nm, 28409 cm⁻¹, ε_{max}289 molar⁻¹ cm⁻¹, charge transfer), proposed structure: Tetrahedral.Conductivity in DMF Am (S.cm² mole⁻¹): 152 [(1:2) electrolyte nature].

Cadmium complex[Cd₄(L)Cl₄]Cl₂. H₂O

Pale yellow solid, m,p>250 dec.°C, 85% yield, Analytical Calcd. For [Cd₄C₂₈H₃₀N₄O₂S₄ Cl₄]Cl₂.H₂O (1264.6): C, 26.99; H,2.41; N,4.49; Cd, 36.11; Cl,16.84%, Found: C, 27.03; H,2.44; N,4.53; Cd, 36.31; Cl,17.01%.I.R (KBr): ν (cm⁻¹): 3463 (-OH, broad); 873(OH); 1600 (C=N imine, sharp); 1406 (C=C); 1132 (S-CH₂, broad); 1097 (C-S, broad); 2885 (C-H, aromatic); 1413 (-CH₂, broad); 1348 (C-O); 530, 443, 416 (M-N), (M-O), (M-S).UV-Vis (271 nm, 26900 cm⁻¹, ε_{max}1116 molar⁻¹ cm⁻¹, ligand field), (364 nm, 27472 cm⁻¹, ε_{max}362molar⁻¹ cm⁻¹, charge transfer), proposed structure: Tetrahedral.Conductivity in DMF Am (S.cm² mole⁻¹): 152 [(1:2) electrolyte nature].

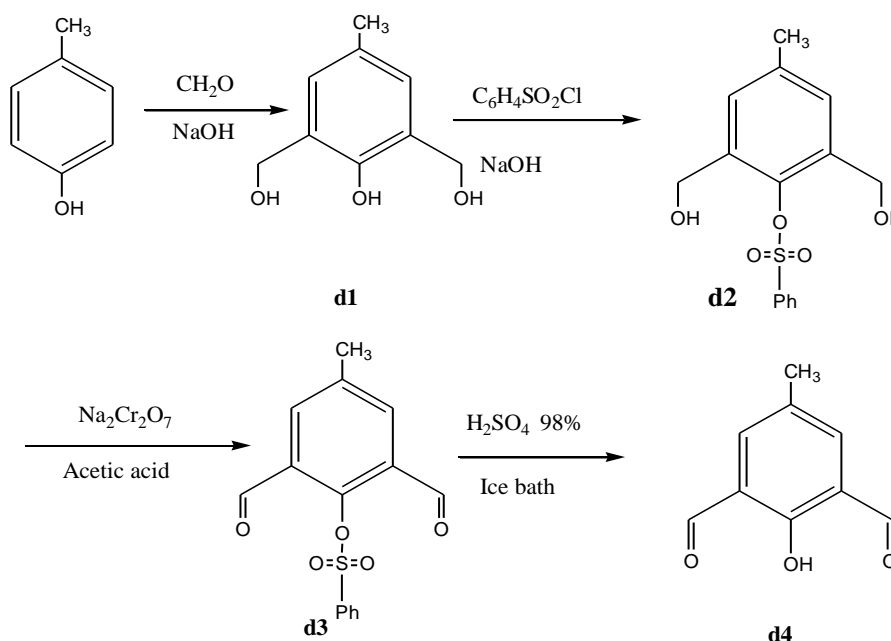
Mercury complex[Hg₄(L)Cl₄]Cl₂. H₂O

Deep gray solid, m,p>250 dec.°C, 85% yield, Analytical Calcd. For [Hg₄C₂₈H₃₀N₄O₂S₄Cl₄] Cl₂.H₂O (1617.41): C, 21.66; H,1.97; N,3.51; Hg, 50.15; Cl,13.17%, Found: C, 21.22; H,2.01; N,3.54; Hg, 50.25; Cl,14.01%.I.R (KBr): ν (cm⁻¹): 3467 (-OH, broad); 833 (OH); 1598 (C=N imine, sharp); 1425 (C=C); 1118 (S-CH₂, broad); 1118 (C-S, broad); 2974 (C-H, aliphatic, weak); 2866(C-H, aromatic);

1408 (-CH₂, broad); 1355 (C-O); 450, 420 (M-N), (M-O), (M-S).UV-Vis (271 nm, 36900 cm⁻¹, ε_{max} 1144 molar⁻¹ cm⁻¹, ligand field), (360 nm, 27777 cm⁻¹, ε_{max} 1857 molar⁻¹ cm⁻¹, charge transfer), proposed structure: Tetrahedral. Molar Conductivity in DMF Am (S.cm² mole⁻¹): 155 [(1:2) electrolyte nature].

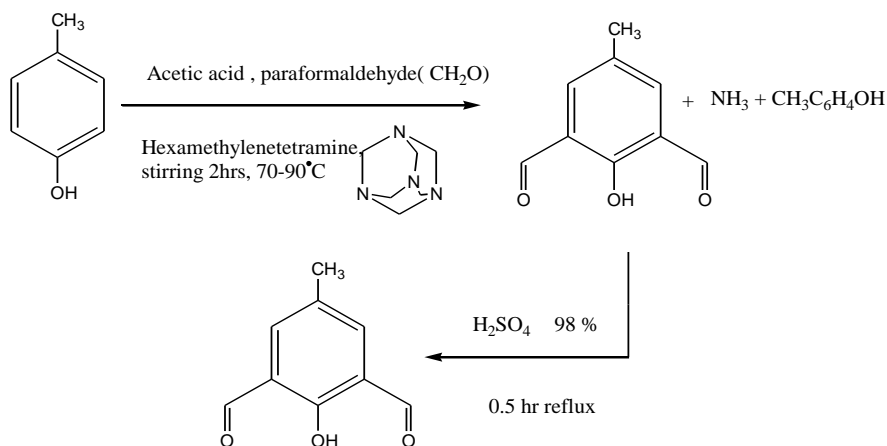
RESULTS AND DISCUSSION

According to published literature⁹, the parent compound was prepared in two different procedures. In the first procedure, the compound was prepared from the reaction of *p*-cresol with (37%) formaldehyde in presence of NaOH to form triol compound (**d1**), then benzoyl sulfonyl chloride was used as a protection group of the phenolic hydroxyl moiety and compound (**d2**) was formed. Other hydroxyl groups were oxidized by Na₂Cr₂O₇ in presence of acetic acid and compound (**d3**) is obtained. The removing of the protecting group was achieved by adding H₂SO₄ (98%) and compound (**d4**) is formed. This procedure is time and materials consuming.



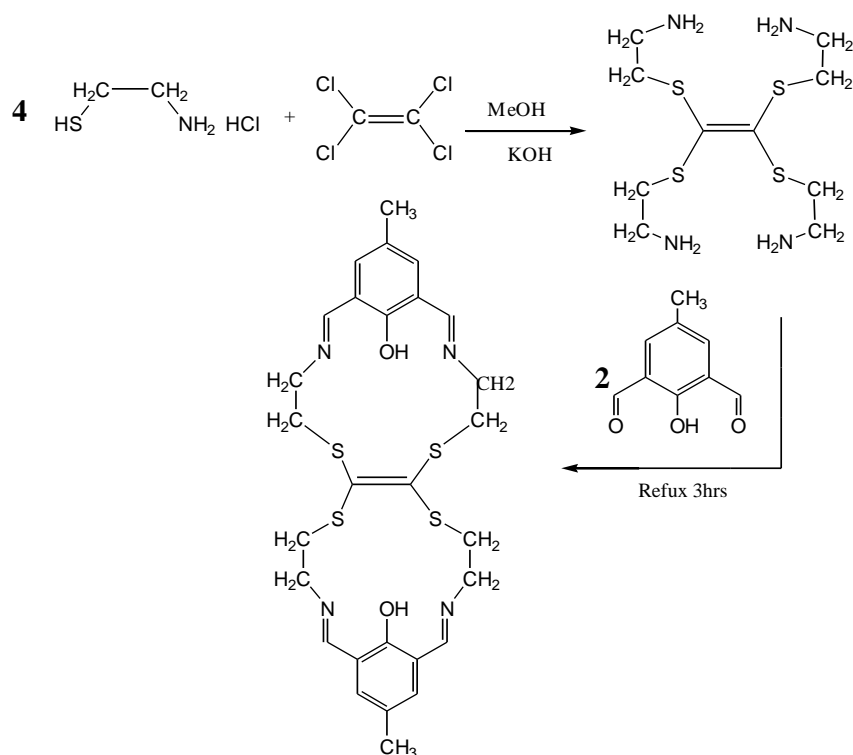
Scheme. 2: The Synthesis Rout of Compound [d4]

The second procedure used to prepare compound (**d4**) is one pot reaction. *p*-cresol, Paraformaldehyde, acetic acid and hexamethylenetetramine were mixed in MeOH at reflux to obtain compound (**d4**). Sulfuric acid (98%) was used to neutralized the ammonia and to dissolve the unreacted phenol. This procedure is straightforward formed and required short time to obtain compound (**d4**). The only disadvantage is the moderate yield obtained in comparison with the first procedure.



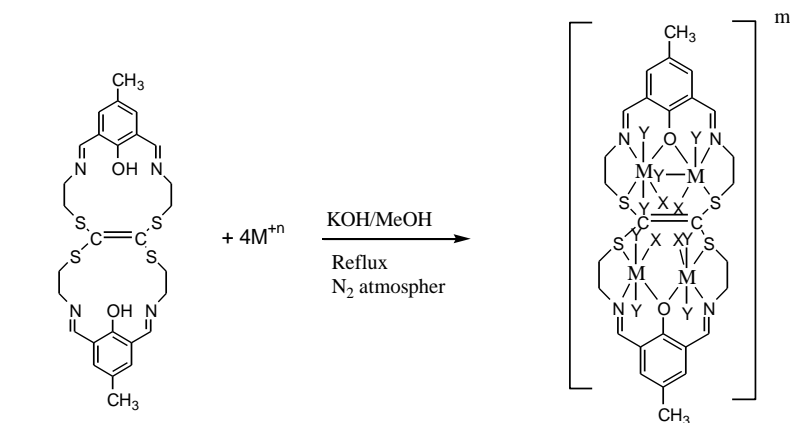
Scheme. 3: One Pot Synthesis Route of [d4]

The reaction of 2-mercaptoethylammonium chloride with tetrachloroethane in (4:1) mole ratio and in the presence of a methanolic solution of potassium hydroxide, resulted in the preparation of tetraaminecompound. The reaction of tetraaminecompound *in situ* with two equivalents of 2,6-diformyl-4-methyl phenol at reflux gave [H₂L] according to the following, Scheme (4).



Scheme. 4: Synthesis of [H₂L]

The complexes were prepared by a similar method, from the reaction of the ligands with metal chloride salt, according to general method shown in Scheme (5). The reaction was carried out in methanol, at reflux and under nitrogen atmosphere, in the presence of KOH as a base. Base choice was important and no pure complexes could be isolated using another base.



Where: $M = Cr^{+3}, Mn^{+2}$: $X = H_2O$: $Y = Cl$: $n = +3, +2$: $m = +2$
 $M = Co, Ni$: $X = Cl$: $Y = H_2O$: $n = +2$: $m = +2$
 $M = Fe, Cu, Zn, Cd, Hg$: $X = Cl$: $Y = 0$: $n = +2$: $m = +2$

Scheme. 5: The synthesis route of [H₂L] complexes

The complexes were prepared as in Scheme (5). All complexes were soluble in DMSO and DMF but not H₂O. Mn, Zn, and Cd complexes were soluble in CH₃OH while Co, Ni, and Cu complexes were soluble in C₂H₅OH. Also, Co, Cd, and Hg complexes were soluble in CH₂Cl₂.

Microanalysis of the complexes with metal and chloride analyses is in good agreement with the calculated values. Spectroscopic methods [IR, UV-Vis, Laser adsorption (+) mass spectroscopy, ^1H NMR], molar conductivity measurements and melting point were used to characterize the complexes. TG/DTG thermal curves of the newly prepared $\text{N}_4\text{O}_2\text{S}_4$ donor - cyclic polydentate ligand and its metal complexes were recorded in nitrogen atmosphere from 30 °C to 900 °C (Figs. 1-4) and their characteristic pyrolysis data are presented in Table 1). The TG curves were drawn as % mass loss vs. temperature TG curves. It had to be noted that all decomposition steps for the prepared ligand and its metal complexes can be confirmed with GC-MS, mass, XRD, and NMR instrumentations which is not available in this work.

Table 1: Thermo-analytical results for the investigated ligand and its metal complexes

Empirical Formula	Sample mass/ mg	m.p/ °C	Mass/%	Temperature/ °C
H_2L	4.865	280-284	99.3488	298.46
			57.2093	625.74
$[\text{Cr}_4(\text{L})(\text{H}_2\text{O})_4\text{Cl}_8]\text{Cl}_2$	14.553	224-229	99.9070	89.07
			93.4884	327.38
			87.06	474.29
$[\text{Mn}_4(\text{L})(\text{H}_2\text{O})_4\text{Cl}_8]\text{Cl}_2$	26.583	> 250dec.	98.7907	273.01
			90.9767	595.76
$[\text{Fe}_4(\text{L})\text{Cl}_4]\text{Cl}_2$	15.330	201-204	99.6279	260.28
$[\text{Co}_4(\text{L})(\text{H}_2\text{O})_8(\text{Cl})_4]\text{Cl}_2$	38.129	200-202	99.9070	51.43
			97.1163	207.51
			91.5349	305.95
			84.5581	465.63
$[\text{Ni}_4(\text{L})(\text{H}_2\text{O})_8\text{Cl}_4]\text{Cl}_2$	23.936	>250 dec.	99.6279	121.47
			91.8140	312.34
			81.2093	507.84
$[\text{Cu}_4(\text{L})\text{Cl}_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$	17.669	250-264	98.7907	194.34
			90.1395	273.01
			80.0930	580.72
$[\text{Zn}_4(\text{L})\text{Cl}_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$	29.804	>250 dec.	99.3488	210.54
			94.8837	455.78
			93.7674	673.26
			61.3953	342.09
			49.9535	495.92

Bis{(4-methyl 2,6-diformylaminoN,N-di-1,2-ethylene-2,2-dithia)ethane [H_2L] melted at (280-284) °C. From the TG/DTG curve (Fig.1), it appears that the sample decomposes in two stages. The first mass loss was observed at 298.46 °C with a mass loss of 0.6512 % and the second decomposition stage at 625.74 °C with a mass loss of 42.7907%. The thermal decomposition results suggested that the first stage corresponding to the endothermic melting point of the prepared ligand while the second mass loss is due to the decomposition of $\text{C}_8\text{H}_{12}\text{S}_4$ from the parent compound by breakage of C-C and C-N bonds as shown in Scheme (6).

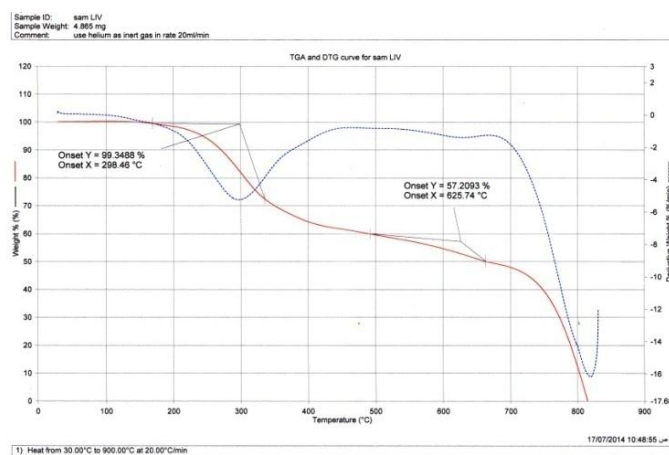
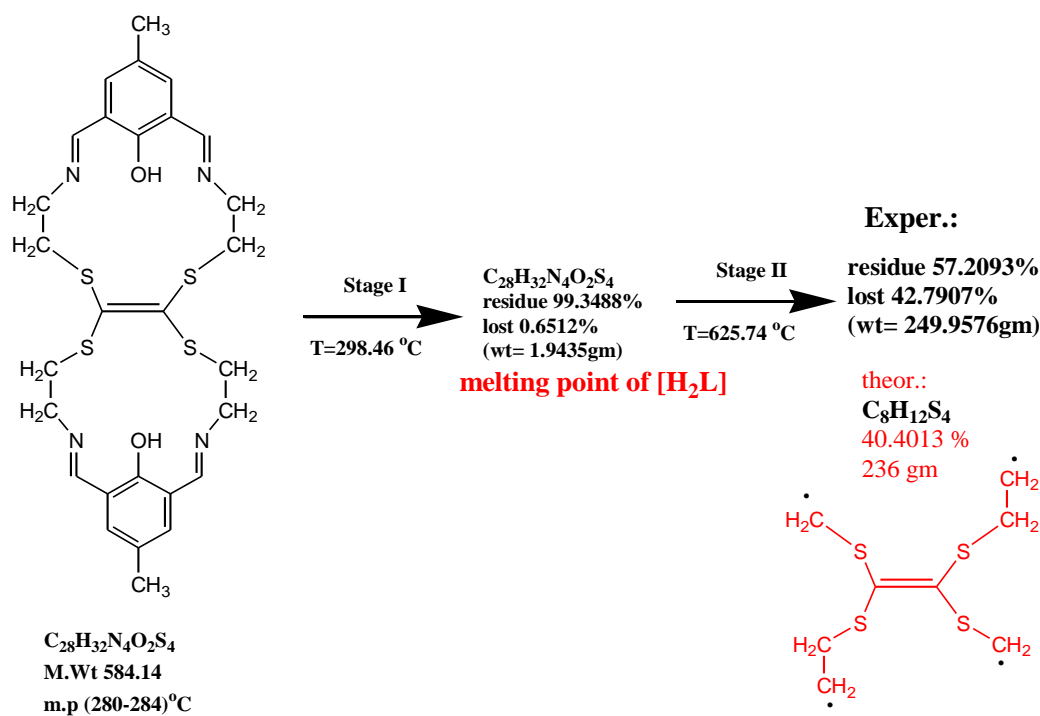


Fig. 1: TG/DTG curve of [H_2L]



Scheme. 6: Suggested TG/DTG thermal degradation of [H₂L]

The thermal decomposition of Cr – complex [Cr₄C₂₈H₃₀N₄O₂S₄(H₂O)₄Cl₈]Cl₂ takes place in temperature range of (89-500)°C (Table 1, Fig.2) with three stages. In the first stage, the complex does not appear to lose any species which was observed at 89.07 °C with a mass loss of 0.093 %. In the second stage, the stable complex decomposed at 327.38 °C and a mass loss of 6.5116% due to losing four water molecules or two chlorine radicals which is more acceptable. With chlorine losing consideration, the third stage reflects a high decomposition temperature (474.29 °C) and a mass loss of 12.9302% with evolution of C₂S₄ as radicals. All TG/DTG stages for this complex were disabling to confirm its melting point with absence of hydrated water molecules (Scheme (7)).

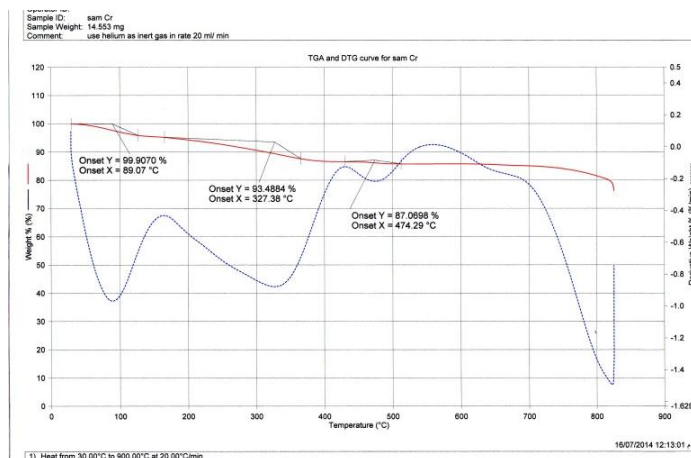
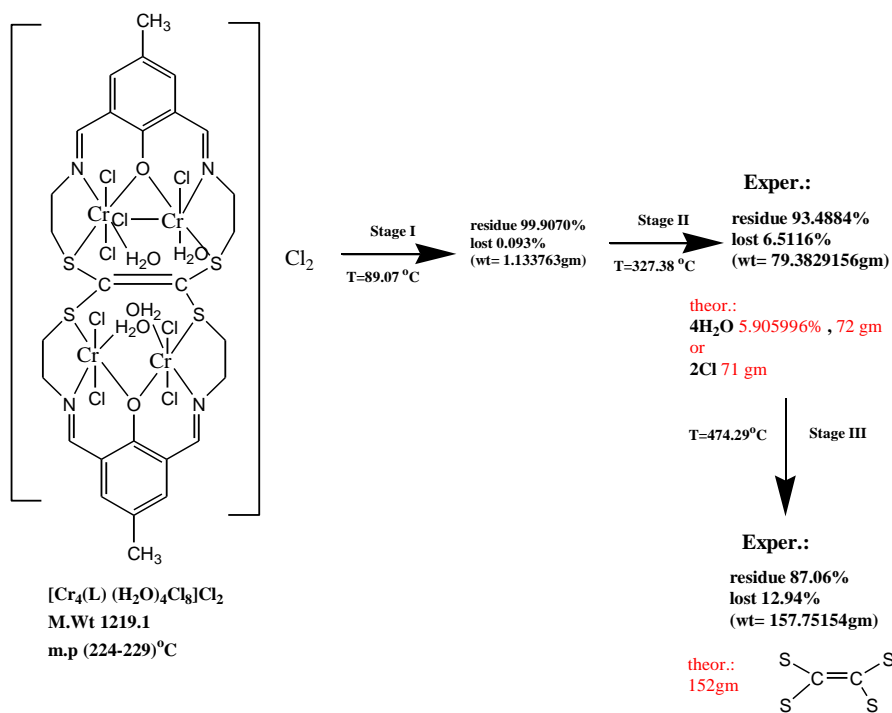


Fig. 2: TG/DTG curve of Cr- complex



Scheme. 7: Suggested TG/DTG thermal degradation of Cr-complex

TG /DTG data indicates two steps for Mn-complex $[\text{Mn}_4\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2\text{S}_4(\text{H}_2\text{O})_4\text{Cl}_8]\text{Cl}_2$ thermal decomposition with temperature maxima at (273.01 and 595.76) °C (Table 1, Fig. -). First mass loss of 1.2963% is corresponding to melting point. The next step indicates losing 2Cl as a radical species and 2H₂O (Scheme (8)).

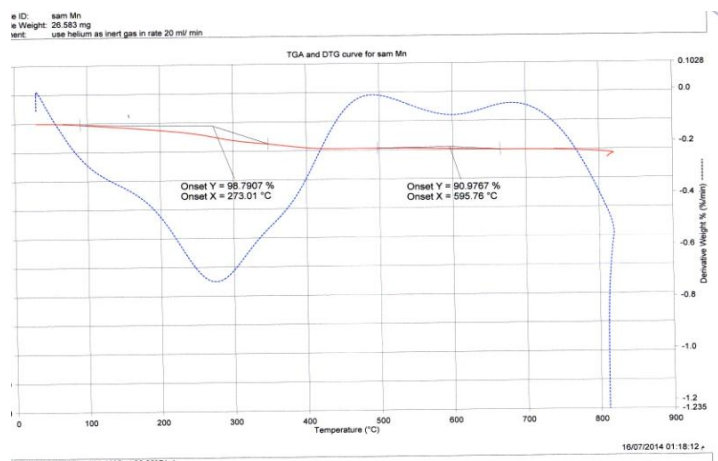
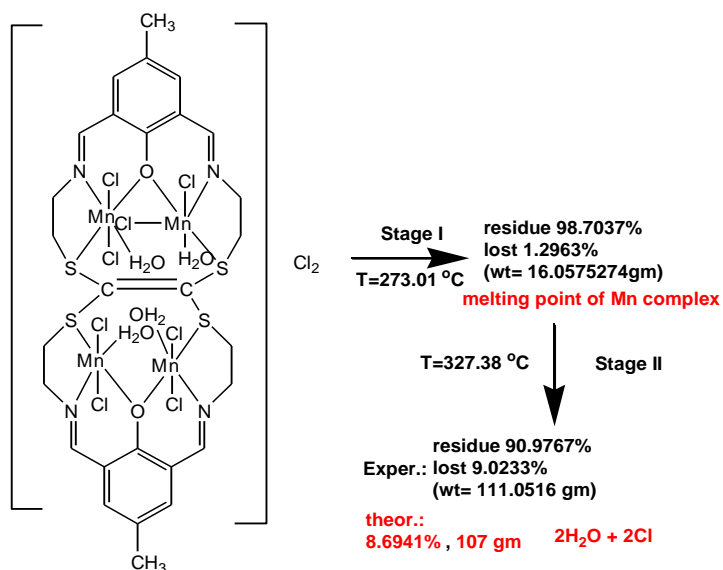


Fig. 3: TG/DTG curve of Mn- complex



$[\text{Mn}_4(\text{L})(\text{H}_2\text{O})_4\text{Cl}_8]\text{Cl}_2$

M.Wt 1230.72

m.p. >250 °C, dec.

Scheme 8: Suggested TG/DTG thermal degradation of Mn-complex

The TG/DTG curve for Fe-complex $[\text{Fe}_4\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2\text{S}_4\text{Cl}_4]\text{Cl}_2$ (Fig. 4) shows one mass loss in 260.28 °C with 0.3721 % (Table 1) due to losing four hydrogen as radical species and indicating its excellent thermal stability (Scheme (9)).

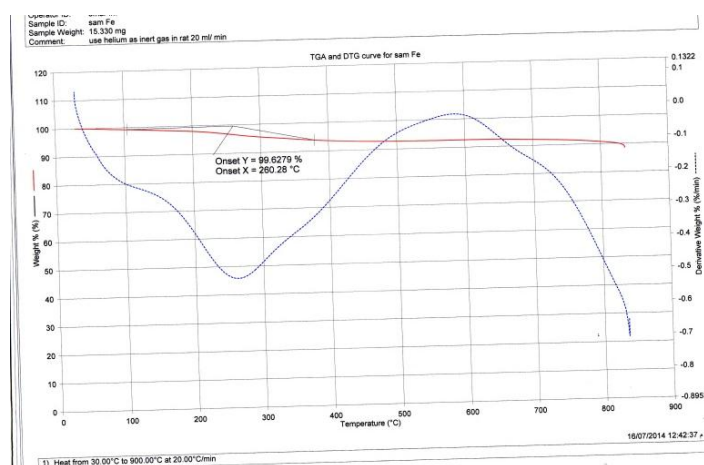
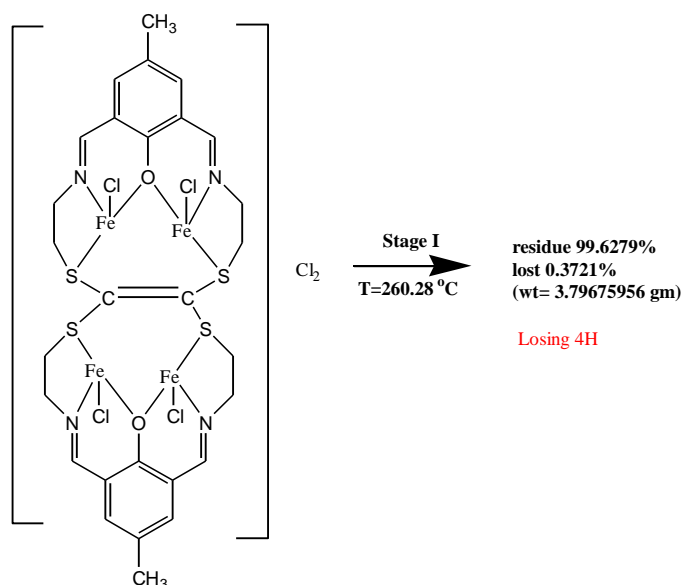


Fig. 4: TG/DTG curve of Fe- complex



[Fe₄(L)Cl₄]Cl₂
 M.Wt 1020.36
 m.p (201-204) °C

Cl₂ $\xrightarrow[\text{T}=260.28\text{ }^\circ\text{C}]{\text{Stage I}}$ residue 99.6279%
 lost 0.3721% (wt= 3.79675956 gm)
 Losing 4H

Scheme. 9: Suggested TG/DTG thermal degradation of Fe-complex

With Co-complex[Co₄C₂₈H₃₀N₄O₂S₄(H₂O)₈(Cl)₄] Cl₂, the TG/DTG curve (Table 1, Fig. 5) with four endothermic peaks indicates that mass change occurs at 51.43 °C with 0.093% without clear sign of pyrolysis. At 207.51°C, the second stage begins with mass loss of 2.8837% suggested complex melting point or losing of Cl radical species. The third endothermic stage observes at 305.95°C and 8.4651% as percentage weight loss may indicate the decomposition of (Cl + C₂H₄S) radicals while the last stage suggests the losing of C₁₁H₁₂N₂O of 15.4419 % at 465.63 °C (Scheme (10)).

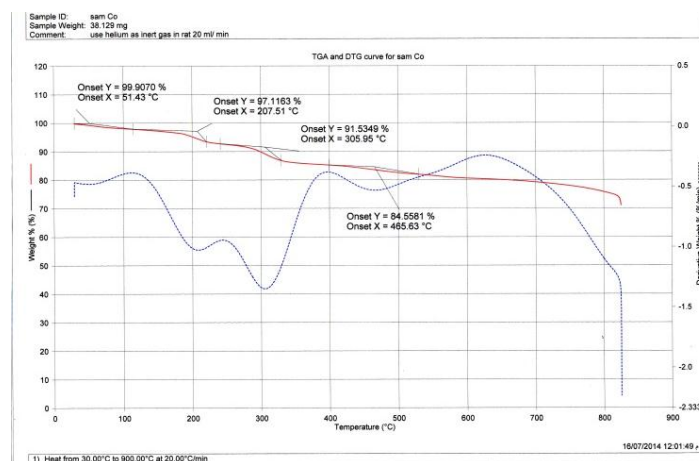
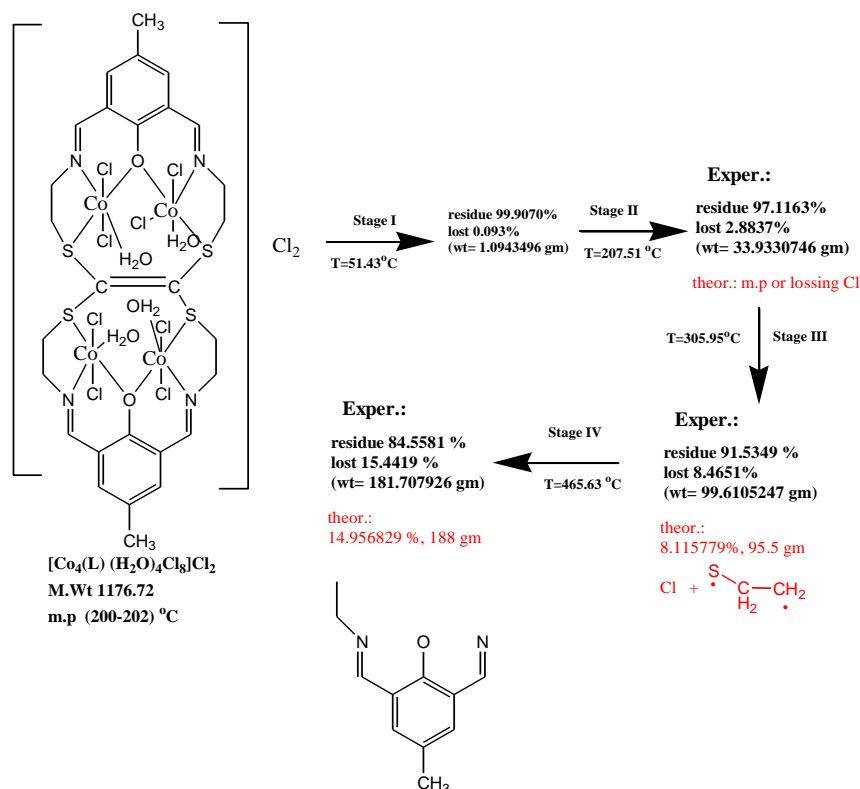


Fig. 5: TG/DTG curve of Co-complex



Scheme. 10: Suggested TG/DTG thermal degradation of Co-complex

From the TG/DTG curves of three endothermic stages for the thermal decomposition of Ni-complex $[\text{Ni}_4\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2\text{S}_4(\text{H}_2\text{O})_8\text{Cl}_4]\text{Cl}_2$ (Table 1, Fig. 6) could be seen that, the dried sample contains no physically absorbed water molecule. The first stage occurs at 121°C with 0.3771% cannot be attributed to melting or loss of any radicals. Also, it was more effective endothermic peak takes place in the second stage at 312.34°C and 8.1860 % due to losing two suggested radicals (Cl and $\text{C}_2\text{H}_4\text{S}$). The third stage displayed a strong endothermic peak at 507.84°C and 18.7907 % attributable to the 2Cl and $8\text{H}_2\text{O}$ as lost fragments as expressed in the most probable thermal decomposition in Scheme (11).

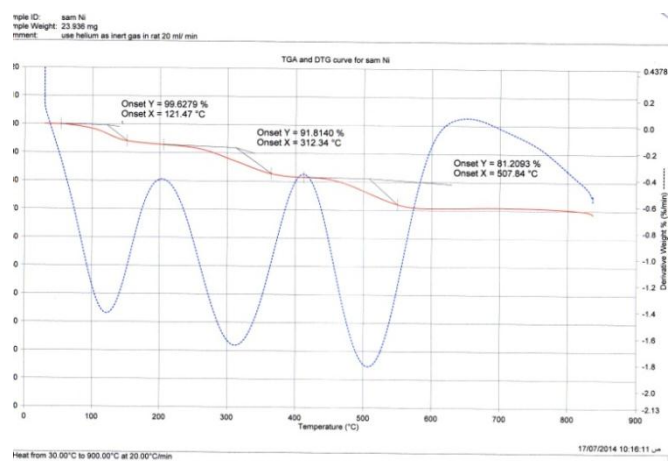
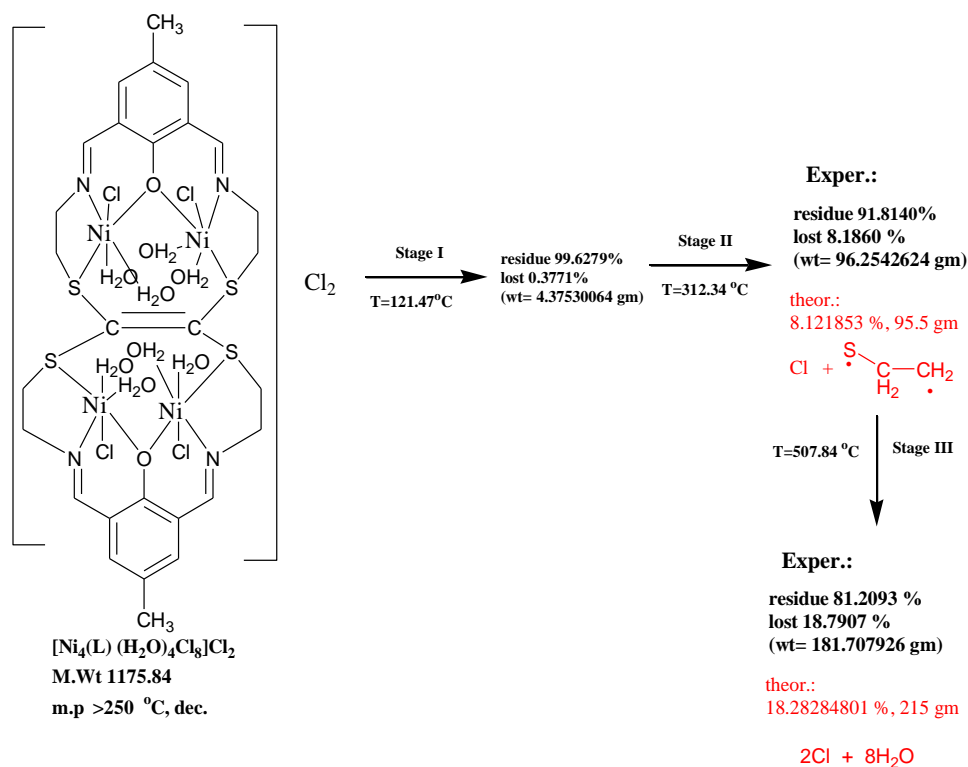


Fig. 6: TG/DTG curve of Ni-complex



Scheme. 11: Suggested TG/DTG thermal degradation of Ni-complex

TG and DTG studies were also carried out for Cu-complex $[\text{Cu}_4\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2\text{S}_4\text{Cl}_4] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$ where it decomposes in three decomposition stages (Table 1, Fig. 7) as indicated by DTG peaks correspond to mass loss of one coordinated water molecule, (Cl and C₂H₄NS), and (C₁₁H₁₁N₂OS) at 194.34 °C (1.2093%), 273.01 °C (9.8605 %), and 580.72 °C (19.9070 %) respectively (Scheme (12)).

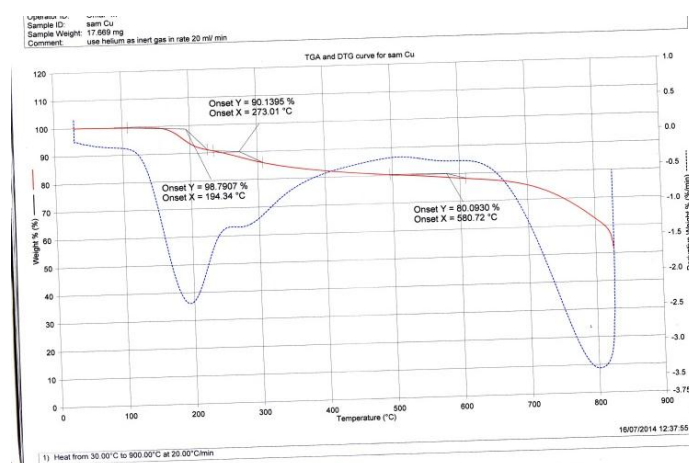
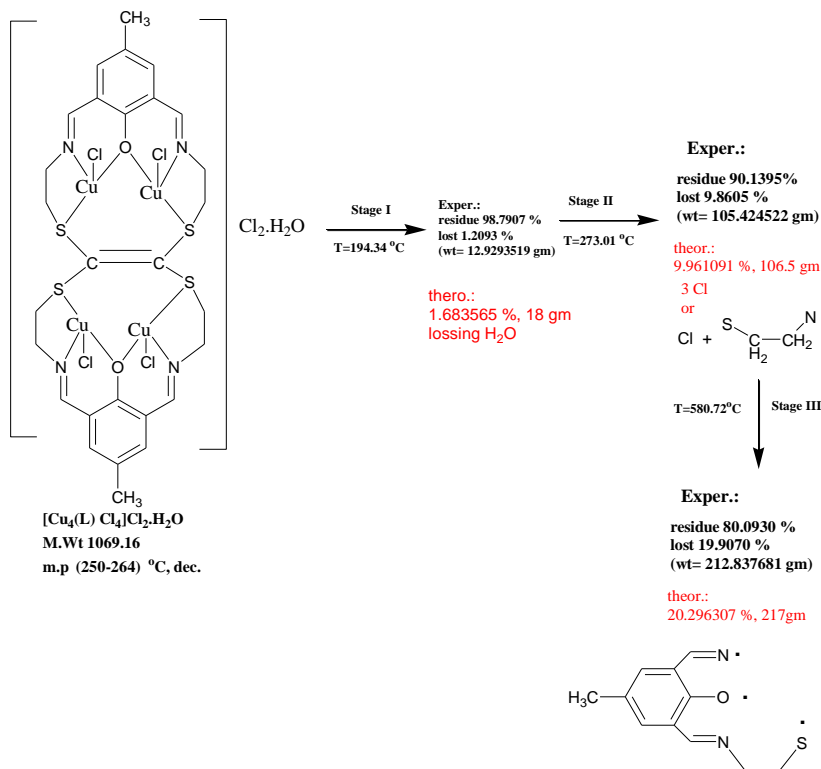


Fig. 7: TG/DTG curve of Cu-complex



Scheme. 12: Suggested TG/DTG thermal degradation of Cu-complex

Zn-complex [Zn₄C₂₈H₃₀N₄O₂S₄ Cl₄]Cl₂.H₂O thermal study by TG/DTG instrument shows three stages (Table1, Fig. 8) graduated from 210.5 °C (0.6512%), 455.78 °C (5.1163 %), to 673.26 °C as maxima decomposition temperature (mass loss%) with suggested losing (Cl and H₂O) and (C₂H₄NS) in the second and third decomposition stages respectively as shown in Scheme (13) .

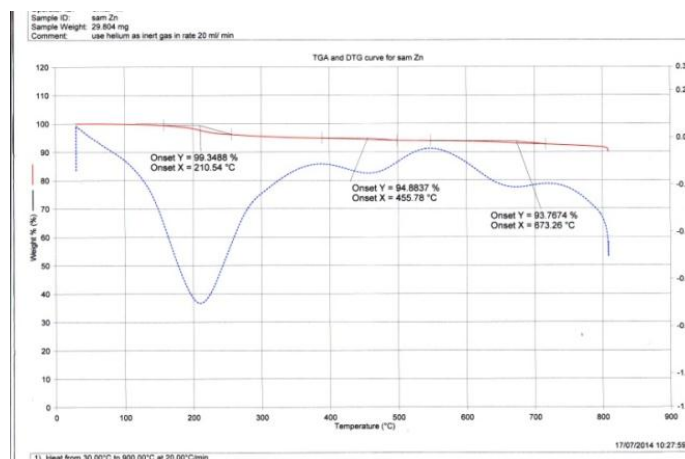
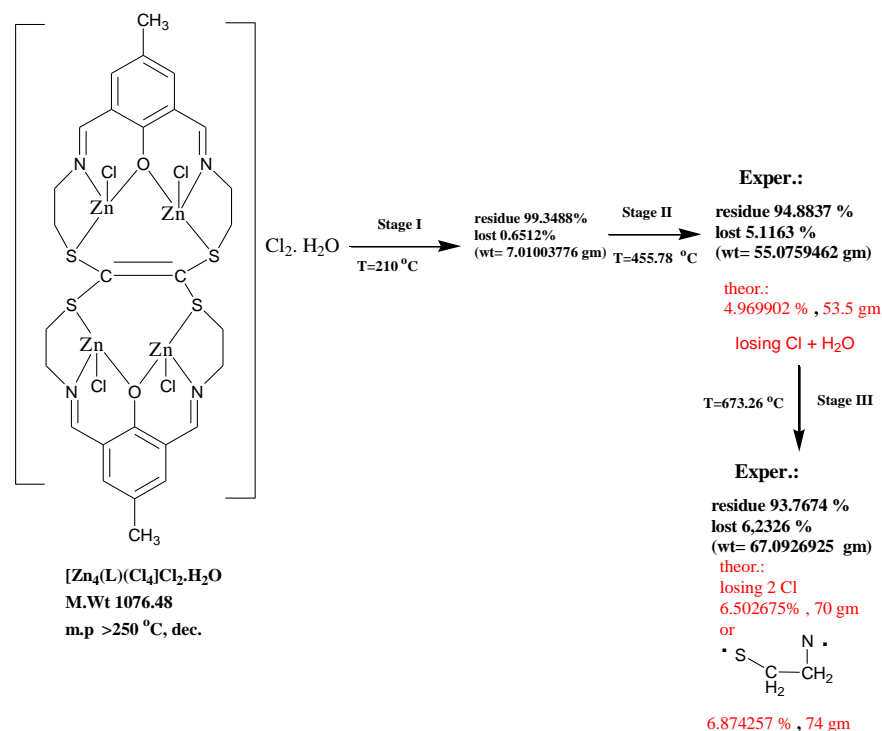


Fig. 8: TG/DTG curve of Zn – complex



Scheme. 13: Suggested TG/DTG thermal degradation of Zn-complex

It can be noticed that the losing of one water molecule in Cu- and Zn - complexes were in the range (194-212) °C as strong endothermic peak.

ACKNOWLEDGEMENT

Our deep grateful thanks are due to Prof. Dr. D. V. Griffith and staff members of the department of Chemistry of Queen Mary, University of London/ United Kingdom for their help.

REFERENCES

1. Cozzi P. Metal–Salen Schiff base complexes in catalysis: practical aspects. *Chem Soc Rev.* 2004;33:410–421.
2. Garnovskii A, Nivorozhkin A and Minkin V. Ligand environment and the structure of Schiff base adducts and tetracoordinated metal-chelates. *Coord Chem Rev.* 1993;126:1-69.
3. Gomez M, Muller G and Rocamora M. Coordination chemistry of oxazoline ligands. *Coord Chem Rev.* 1999;193-195:769-835.
4. Shi P, Liu Y and Peng S. Palladium(II) Complexes Containing P~N~O Donors. Ligand Effect of Tridentate versus Bidentate Coordination on the Oligomerization of Ethylene. *Organomet.* 2002;21(15):3203-3207.
5. Brunner H, Niemetz M and Zabel M. Optically Active Transition Metal Complexes, 122. Synthesis of Palladium(II) Complexes with Schiff Base Ligands - Intramolecular Interactions (In German), *Zeitschrift fur Naturforschung.* 2000;55 B:145-154.
6. Nalik A and Revankarp V. Design, synthesis and physico-chemical investigation of a dinuclearzinc(II) complex with a novel 'end-off' compartmental ligand. *Proc. - Indian Acad. Sci., Chem. Sci.* 2001;113(4):285-290.
7. Kim K, Jung D, Kim D, Choi C, Park K and Byun J. Synthesis and Characterization of Dinuclear Ni(II) complexes with TetraazadiphenolMacrocycle Bearing Cyclohexanes. *Bulletin Korean Chem. Soc.* 2006;27(11):1747-1751.
8. Mistri T, Dolai M, Chakraborty D, Khuda-Bukhshb A, Das K and Ali M. A highly selective and sensitive in vivo fluorosensor for zinc(II) without cytotoxicity. *Org Biomol Chem.* 2012;10: 2380-2384.
9. Al-Jeboori F. Novel acyclic and cyclic polydentate ligands derived from 2,6- diformyl-4-methylphenol and their metal complexes. Synthesis and physico-chemical studies, PhD Thesis, College of Education–Ibn–AL–Haitham, Baghdad University, 2006.

10. Al-Jeboori F, Al-Jeboori M and Al-Haidari A. Synthesis and structural characterization of some transition metal complexes with cyclic N_2OS_2 ligand. *J Chem Pharmaceu Res.* 2013;5(8): 203-216.
11. Al-Jeboori F, Al-Jeboori M, Hammud K, Ashour H and Mohammad J. Synthesis and characterization of polydentate ligand and its metal complexes. *J Chem Pharmaceu Res.* 2013;5(4):160-170.
12. Al-Jeboori F, Hammud K and Al-Jeboori M. Synthesis and characterization of new octadentate ligand and its complexes. *Int J Res Pharm Chem.* 2014;4(1):154-167.
13. Wattedled L and Laschewsky A. New anionic gemini surfactant based on EDTA accessible by convenient synthesis. *Colloid Polymer Sci.* 2007;285(12):1387-1393.
14. Grabke H. Thermogravimetry, Guidelines for Methods of Testing and Research in High Temperature Corrosion: Working Party Report, H. Grabke and D. Meadowcroft, Ed., The Institute of Materials, European Federation of Corrosion, 14, 1995.
15. Keattch C and Dollimore D. An Introduction to Thermogravimetry, 2nd ed., Heydenand Son, Ltd., FL., USA, 1975.
16. Fan Y, Gao Z, Bi C, Xie S and Zhang X. Synthesis and thermal decomposition kinetics of La(III) complex with unsymmetrical Schiff base ligand. *J Therm Anal Calorimet.* 2008;91: 919-923.
17. Aly A, Osman A, Abd El-Mottaleb M and Gouda G. Thermal stability and kinetic studies of cobalt (II), nickel (II), copper (II), cadmium (II), and mercury (II) complexes derived from N-salicyaldine Schiff bases. *J Chilean Chem Soc.* 2009; 54(4): 349-353.