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THERMAL ANALYSES (DTA AND TGA) FOR PREPARED NEW ETHER HYDRAZONE LIGANDS AND ITS METAL COMPLEXES Cu(II), Co(II), Mn(II)

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ABSTRACT
In this paper we study the thermal analyses (DTA and TGA) of metal complexes: Cu(II), Co(II), Mn(II) as: $C_{35}H_{34}N_4O_8$ Cu_2, $C_{31}H_{57}N_4O_{26}S_2$ Cu_2, $C_{35}H_{42}N_4O_{12}Co_2$, $C_{43}H_{48}N_4O_{14}Mn_2$. The thermal curves in the 27-800°C temperature range indicated that, the metal complexes are thermally stable up to 40°C. The weight losses recorded in the Cu(II) complex (2) are due to the endo-thermic peak which observed at 200°C, with 7.52% weight loss (Calc. 7.6%) is due to loss of one coordinated acetate group, whereas, the loss of the other coordinated acetate group, was accompanied by an endothermic peak appeared at 230°C with 8.26% weight loss (Calc. 8.38%). The endothermic peak observed at 315°C, is corresponding to melting point of the complex.

KEYWORDS: Metal, complexes, DTA, TGA.

INTRODUCTION

The solid complexes of Cu(II), Co(II), Mn(II), La(III) and Ce(III) were prepared from bidentate Schiff base, N-benzylidene-2-hydroxy benzohydrazide. The Schiff base ligand was synthesized from 2- hyhdroxy benzohydrazide and benzaldehyde. These metal complexes were characterized by molar condu-ctivity, magnetic susceptibility, thermal analysis, X-ray diffraction, FTIR, ^{1}H-NMR, UV-Vis and mass spectro-scopy.[1]

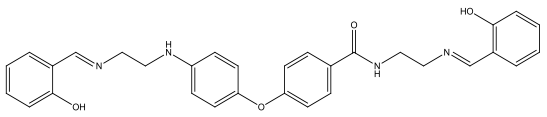
The X-ray diffraction data suggest monoclinic crystal system for these complexes. Thermal behavior (TG/DTA) and kinetic parameters calculated by Coats-Redfern method are suggestive of more ordered activated state in complex formation. The ligand and their metal complexes were screened for antibacterial activity against Staphy-lococcus aureus and Escherichia coli and fungicidal activity against Aspergillus niger and Trichoderma.[2]

Schiff's bases (2(1-hydrazono-ethyl)phenol), (2, 4-dibromo 6-(hydraz-onomethyl)phenol) and (2 (hydrazono-methyl) phenol). The structures of were characterized by elemental analysis (EA), mass (MS), FT-IR and 1H NMR spectra, and thermal analyses (TG, DTG, and DTA). The activation thermodynamic parameters, such as, DE⁄, DH⁄, DS⁄ and DG⁄ were calculated from the TG curves using Coats–Redfern method. It is important to investigate their molecular structures to know the active groups and weak bond responsible for their bio-logical activities. Consequently in the present work, the obtained thermal (TA) and mass (MS) practical results are confirmed by semiempirical MO-calc-ulations (MOCS) using PM3 proc-edure.[3]

EXPERMENTAL

A. Preparation of Ligand (1)

4-Chlorophenol (1.28 g, 1mol) was added to 30 cm^3 of ethyl alcohol containing sodium salt of methyl 4-hydroxy benzoate (1.74 g, 1.0 mol). Stirring the suspension at 70 ^oC for one hour, The product obtained is filtered off to remove sodium chloride then take solution (a starting material). Ethylene diamine (1.2 g, 2.0 mol) was added to above solution, heating to 60 ^oC with stirring for an hour. The product obtained reacted with salicyaldehyde (2.44 g, 2.0 mol) by heating to 60 ^oC with stirring for an hour was filtered off to give crude product which was crystallized in water to yield pure yellow ligand **(1)** as shown below:



Ligand (1): N-(2-((E)-(2-hydroxybenzylidene) amino) ethyl)-4-(4-((2-((E)-(2 hydroxy benzylidene) amino) ethyl)amino) phenoxy) benzamide.

Preparation of Metal Complexes[4]

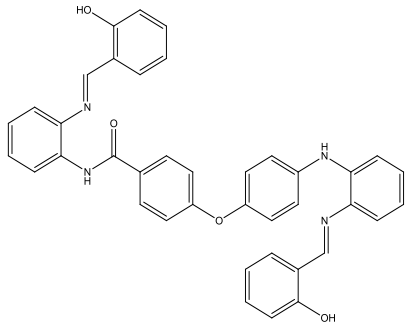
Complex (1): Copper(II) acetate mono hydrate (4 g, 2.0 mol) dissolved in ethanol 30 cm^3 was added to (L_1) (5.22 g, 1.0 mol) dissolved in ethanol 25 cm^3. The mixture was warmed at 60 ^oC with stirring for 1 hour, then the solution was cooled at room temperature filtered off and glossy green precipitate was obtained.

Complex (2): Copper(II) sulfate penta hydrate (5 g, 2.0 mol) was added to ligand **(1)** (5.22 g, 1.0 mol) using the above procedure.

Complex (3): cobalt(II) acetate tetra hydrate (4.98 g, 2.0 mol) was added to ligand **(1)** (5.22 g, 1.0 mol) using the above procedure.

Preparation of Ligand (2) (9)

4-Chlorophenol (1.28 g, 1.0 mol) was added to 30 cm^3 of ethyl alcohol containing sodium salt of methyl 4-hydroxy benzoate (1.74 g, 1.0 mol). Stirring the suspension at 70 ^oC for one hour, The product obtained is filtered off to remove sodium chloride then take the solution (a starting material). O- phenylene diamine (2.16 g, 2.0 mol) was added to above solution, heating to 60 ^oC with stirring for another an hour. The product obtained reacted with salic-yaldehyde (2.44 g, 2.0 mol) by heating to 60 ^oC with stirring for an hour was filtered off to give crude product. The crude was dissolved in 30 cm^3 ethyl alcohol then added 0.5g charcoal) by heating to 60 ^oC with stirring for an hour was filtered off to give pure deep yellow ligand **(2)** as shown below:



Ligand (2): N-(2-((E)-(2-hydroxybenzylidene)amino) phenyl)-4-(4-((2-((E)-(2-hydroxy benzylidene) amino) phenyl)amino) phenoxy)benzamide.

Complex (4): manganese(II) acetate tetra hydrate (4.9 g, 2.0 mol) dissolved in ethanol 30 cm^3 was added to (L_2) (6.18 g, 1.0 mol) dissolved in ethanol 25 cm^3. The mixture was warmed at 60 C^o with stirring for 1 hour, then the solution was cooled at room temperature filtered off and glossy green precipitate was obtained.

Thermal Analyses

DTA and TGA were carried out on a Shimadzu DT-30 thermal analyzer in nitrogen atmosphere, from room temperature to 600 °C at a heating rate of 10 °C per minute.

RESULT AND DISCUSSION

Thermal Analyses (DTA AND TGA)

The thermal data of complex (1) figures (1) and (2), complex (2) figures (3) and (4), complex (3) figures (5) and (6) and complex (4) figures (7) and (8) were presented in (**Table 1**). The thermal curves in the 27-800°C temperature range indicated that, the metal complexes are thermally stable up to 40 °C. The weight losses recorded in the Cu(II) complex (1) are due to the endo-thermic peak which observed at 200°C, with 7.52% weight loss (Calc. 7.6%) is due to loss of one coordinated acetate group, whereas, the loss of the other coordinated acetate group, was accompanied by an endothermic peak appeared at 230°C with 8.26% weight loss (Calc. 8.38%). The endothermic peak observed at 315°C, is corresponding to melting point of the complex. Finally, the complex showed several exothermic peaks observed at 420, 485, 510 and 530°C, with total 20.7% weight loss (Calc. 20.7%) corresponding to thermal decomposition with eventually formation of 2CuO molecules. The thermogram of Cu(II) complex (2) shows the loss of four hydrated water molecules was acco-mpanied with endothermic peak at 80°C with 3% weight loss (Calc. 3.15%). The endothermic peak observed at 135°C, with 4.99% weight loss (Calc. 5.2%) is due to loss of five coordinated water molecules. The endothermic peak observed at 155°C, with 5.29% weight loss (Calc. 5.35%) is due to loss of five coordinated water molecules. The endothermic peak observed at 230°C, with 9.89% weight loss (Calc. 10.13%) is due to loss of one coordinated sulfate group, whereas, the loss of the other coordinated sulfate group, was accompanied by an endothermic peak appeared at 250°C with 11.2% weight loss (Calc. 11.24%). The endothermic peak observed at 310°C, is corresponding to melting point of the complex. Finally, the complex showed several exothermic peaks which observed at 420, 485, 510 and 530°C, with total 20.97% weight loss (Calc. 21.26%) corresponding to thermal decomposition with eventually formation of 2CuO molecules. The thermogram of Co(II) complex (3) showed endothermic peak observed at 135°C, with 3.15% weight loss (Calc. 3.21%) is due to loss of two coordinated water molecule. The endothermic peak observed at 155°C, with 3.26% weight loss (Calc. 3.34%) is due to loss of two coordinated water molecules. The endothermic peak observed at 200°C, with 11.2% weight loss (Calc. 11.29%) is due to loss of one coordinated acetate group, whereas, the loss of the other coordinated acetate group, was accompanied by an endo-thermic peak which observed at 230°C with 12.74% weight loss (Calc. 12.8%). The endothermic peak observed at 315°C, is corresponding to melting point of the complex. Finally, the complex showed several exothermic peaks which appeared at 420, 485, 510 and 530°C, with total 19.2% weight loss (Calc. 19.32%) corresponding to thermal decomposition with eventually formation of 2CoO molecules. The thermogram of Mn(II) complex (4) showed the loss of two hydrated water molecule was accompanied with endothermic peak at 80°C with 3.3% weight loss (Calc.

3.4%). The endothermic peak observed at 135°C, with 5.1% weight loss (Calc. 5.29%) is due to loss of two coordinated water molecules. The endothermic peak observed at 155°C, with 5.29% weight loss (Calc. 5.31%) is due to loss of two coordinated water molecule.

Table (1): Thermal analyses for complexs (1), (2), (3) and (4).

Complex No. Molecular formula	Temp. (°C)	DTA (peak)		TGA (Wt.loss %)		Assignments
		Endo	Exo	Calc.	Found	
complex (1) $C_{35}H_{34}N_4O_8Cu_2$	50	Endo	-	-	-	Broken of H-bondings
	200	Endo		7.6	7.52	Loss of coordinated (OAc) group
	230	Endo		8.38	8.26	Loss of coordinated (OAc) group
	315	Endo	-	-	-	Melting point
	420	-	Exo	20.7	20.7	Decomposition process with the formation of 2CuO
Complex (2) $C_{31}H_{57}N_4O_{26}S_2Cu_2$	50	Endo	-	-	-	Broken of H-bondings
	80	Endo	-	3.15	3	Loss of ($4H_2O$) hydrated water molecules
	135	Endo	-	5.20	4.99	Loss of ($5H_2O$) coordinated water molecules
	155	Endo		5.35	5.29	Loss of ($5H_2O$) coordinated water molecules
	230	Endo		10.13	9.89	Loss of coordinated SO_4 group
	250	Endo		11.24	11.2	Loss of coordinated SO_4 group
	310	Endo	-	-	-	Melting point
	420	-	Exo	21.26	20.97	Decomposition process with the formation of 2CuO
complex (3) $C_{35}H_{42}N_4O_{12}Co_2$	50	Endo	-	-	-	Broken of H-bondings
	135	Endo	-	3.21	3.15	Loss of ($2H_2O$) coordinated water molecule
	155	Endo		3.34	3.26	Loss of ($2H_2O$) coordinated water molecule
	200	Endo		11.29	11.2	Loss of coordinated (OAc) group
	230	Endo		12.8	12.74	Loss of coordinated (OAc) group
	315	Endo	-	-	-	Melting point
	420	-	Exo	19.32	19.2	Decomposition process with the formation of 2CoO
Complex (4) $C_{43}H_{48}N_4O_{14}Mn_2$	45	Endo	-	-	-	Broken of H-bondings
	80	Endo	-	3.4	3.3	Loss of ($2H_2O$) hydrated water molecules
	135	Endo	-	5.29	5.1	Loss of ($2H_2O$) coordinated water molecules
	155	Endo		5.31	5.29	Loss of ($2H_2O$) coordinated water molecules
	230	Endo		10.16	9.99	Loss of coordinated (OAc) group
	250	Endo		11.34	11.2	Loss of coordinated (OAc) group
	310	Endo	-	-	-	Melting point
	420	-	Exo	19.26	19.16	Decomposition process with the formation of 2MnO

Acetate group. Another endothermic peak was observed at 250°C, with 11.2% weight loss (Calc. 11.34%), which is assigned to loss of coordinated acetate group. The endo-thermic peak observed at 310°C, is corresponding to the melting point of the complex. Finally, the complex showed several exothermic peaks which observed at 370, 420 and 430, with total 19.16% weight loss (Calc. 19.26%) corres-ponding to thermal decomposition with the final formation of 2MnO molecules.

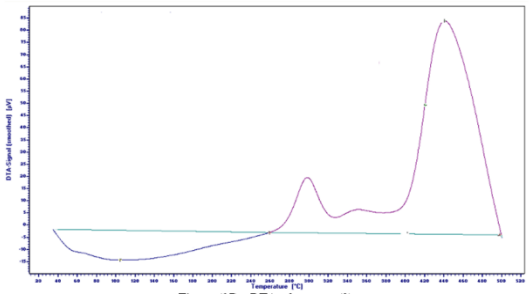


Figure (1):- DTA of complex (1)

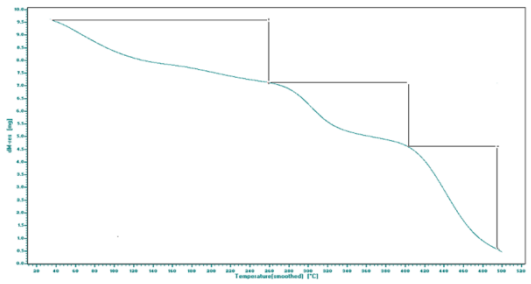


Figure (2):- TGA of complex (1)

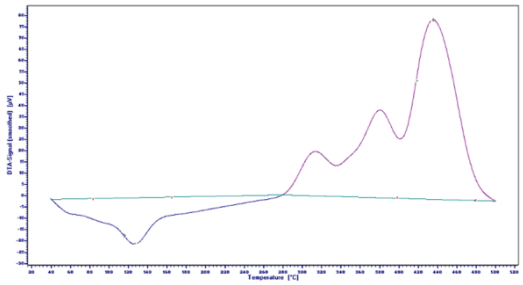


Figure (3):- DTA of complex (2)

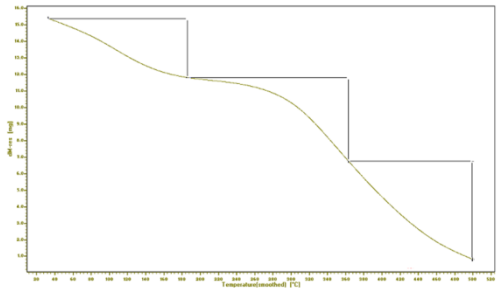


Figure (4):- TGA of complex (2)

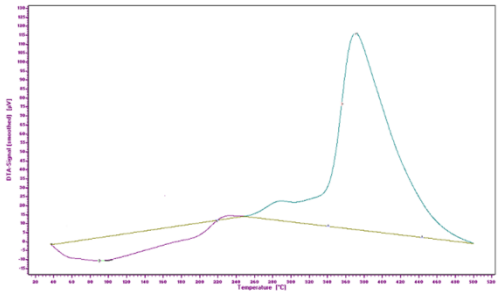


Figure (5):- DTA of complex (3)

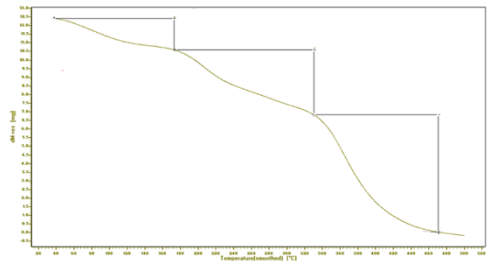


Figure (6):- TGA of complex (3)

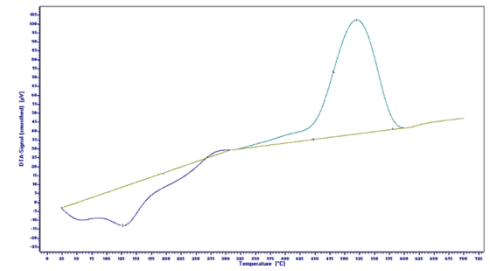


Figure (7):- DTA of complex (4)

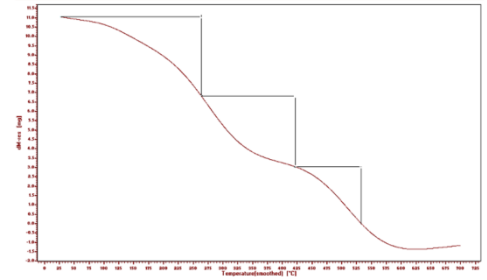


Figure (8):- TGA of complex (4)

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