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Thermal Analysis of Different Pyrazolone Azo Derivative and Their Complexes with Pd(II), Ni(II) and Ag(I)

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Abstract: ***This study describes thermal analysis of novel azodye reagents, 5-(4-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl)phenyl]-5-ethylpyrimxline-2,4,6(1H,3H,5H)-trione, (L1),1-[(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl]-2,3,7,8-tetrahydroxychromeno(5,4,3-cde) chromene-5,10-dione, (L2), and 4-4-(diazene-1,2-diyl)bis(1,5-dimethyle-2-phenyle-1H-pyrazol-3(2H)-one, (L3), that prepare from 4-aminoantipyrine with (phenoparpetal, ellagic acid and phenazone) respectively as coupling agents and thire complexes with Pd(II), Ni(II) and Ag(I) ions. The thermal measurements were showed that, all the complexes were have good stable compering with the reagents in TG/HDSC curves.***

Keywords: Azodye reagents, Thermal analysis, Pd(II), Ni(II) and Ag(I).

1. Introduction

Azo compounds containing O, N donor atoms act as superior chelating agents for the transition and non-transition metal ions and showed biological activities[1]. Azo dyes are commonly synthesized by coupling a diazonium reagent with an aromatic compound to form an azo reagent[2]. The azo compounds give bright, high intensity colors, much more than the other most common compounds, in addition, they have fair to good fastness properties, their biggest advantage it their cost – effectiveness, which is due to the processes involved in manufacture[3]. The coordinating property of 4-aminoantipyrine ligand has been modified to give a flexible ligand system, formed by condensation with variety reagents like aldehydes, ketones and carbazides[4].

They have been found to have biological[5], clinical[6], pharmacological[7] and anti- inflammatory[8]. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium[9], ink-jet printing[10] and oil-soluble lightfast dyes[11]. Recently, azo metal have also attracted greater than ever attention due to their interesting electronic and geometrical features[12] some of the organic derivatives have shown hypoxia-selective cytotoxicity and they could be potentially useful for the treatment of solid tumors[13].

2. Experimental

2.1. Materials and Apparatus

All chemicals of highest purity were used in this work which supplied by Fluka and BDH. Spectrophotometric measurements were made with Shimadzu UV-Visible 1650 PC double beam. The FTIR measurements were made in Shimadz 8400 Series Japan. ^{1}HNMR spectra were measured on BRUKER AV 400 Avance-III 400MHz instrument. ^{13}CNMR spectra were measured on BRUKER AV 100 Avance-III 100MHz instrument. CE440 CHN/O/S Elemental Analyser was made by EAI. Differential Scanning Calorimeter DSC model STA PT-1000 Linseis. The pH measurements were made with a HANNA pH meter H19841-5 Instrument. Electric molar conductivity measurements were made at room temperature using an Alpha digital conductivity model-UK 9300.

2.2. Synthesis of Reagents

The reagents and solvents were of analytical grade and used without further purification. 4-Aminoantipyrine (0.00492mole) 1.0000 gm was diazotized by dissolving it in 25ml ethanol, then 5ml of HCl was adding keeping the temperature at 0-5^{0}C and then adding $NaNO_2$ solution gradually and left the solution about 15 min[14]. The diazonium salt was spontaneously added slowly drop wise to a well cooled alkaline solution of coupling agents, (phenoparpetal, ellagic acid and phenazone) respectively, Table 1. The mixture was allowed to stand for 1 h. The dark colored mixture was neutralized with HCl and the solid precipitate was filtered off and washed several times with (1:1) (Ethanol:water) mixture then recrystallised from boiling Ethanol and left to dry. To get highest absorbance of complexes formed, it is necessary to get the optimum conditions of forming each complex, which include, the selection of the suitable wavelength (λ_{max}), the effects of time, pH values, sequence of additions, stoichiometry and interferences of strange ions. The general procedure was summarized by taking (0.1–3 mg/L) of Pd(II), Ni(II) and Ag(I) ions with 1×10^{-3} M of reagents after adjusting of optimum pH for each ion, Table 2.

Table 1: Physical Properties of Ligand

Symbol	Formula	Name of Ligand	Color	Percentage yield %	m.p. ^{0}C
L1	$C_{23}H_{22}N_6O_4$	5-(4-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl)phenyl]-5-ethylpyrimxline-2,4,6(1H,3H,5H)-trione	Dark orange	85%	>200
L2	$C_{25}H_{19}N_4O_9$	1-[(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl]-2,3,7,8-tetrahydroxychromeno(5,4,3-*cde*) chromene-5,10-dione	Orange	60.37%	>200
L3	$C_{23}H_{25}N_5O_2$	4-4-(diazene-1,2-diyl)bis(1,5-dimethyle-2-phenyle-1H-pyrazol-3(2H)-one	Dark brown	71.76%	>200

Table 2: Physical Properties of Complexes

Symbol	Formula	M. Wt.	Color	Mole Ratio	Percentageyield%	m.p.^{0}C
L1-Pd	$C_{24}H_{25}N_6O_4Pd$	626.8	Dark brown	1:1	67.46	>350
L1-Ag	$C_{23}H_{27}AgN_7O_8$	637.4	Dark yellow	1:1	76.9	>350
L2-Pd	$C_{50}H_{34}N_8O_{18}Pd$	1141.3	Dark brown	2:1	83.50	>350
L2-Ag	$C_{25}H_{16}AgN_5O_{12}$	686.3	Orange	1:1	71.87	>350
L2-Ni	$C_{51}H_{35}N_8NiO_{18}$	1193.5	Yellow	2:1	73.2	>350
L3-Pd	$C_{44}H_{50}N_{12}O_4Pd$	917.4	Dark brown	2:1	78.84	>350
L3-Ag	$C_{22}H_{24}AgN7O5$	574.3	Dark brown	1:1	64.80	>350
L3-Ni	$C_{44}H_{50}N_{12}NiO_4$	869.6	Yellow	2:1	74.1	>350

3. Results and Discussion

3.1. Thermal Analysis

TG/HDSC analysis are very useful methods for investigating the thermal decomposition of solid substances involving simple metal salts as well as for complex compounds[15]. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature 10^0C min^{-1} up to 400^0C. The decomposition occurs in at least three major detectable steps, each step does not refer in generally to single process, but rather is reflects of two or three overlapping processes and attributed to the ligand alone or companied by chlorine atoms[16]. The aim of the thermal analysis is to obtain information concerning the thermal stability of the investigated complexes as seen in (Fig.1-11), to decide whether water molecules are inside or outside the coordination sphere.

The first mass loss of L1($C_{23}H_{22}N_6O_4$) was observed at 143.6^0Cwith a mass loss of 4% correspond to lose of water molecule and the second decomposition starts at 222^0C correspond to lose of two terminal methyl group and ends decomposition at 392.4^0C with a 60.6% mass loss.

For Pd complex ($C_{23}H_{25}Cl_2N_6O_4Pd$), the TG of this complex reveals a mass loss in the temperature 77.1^0C corresponding to the loss of one terminal methyl groups in 4-aminoantipyrine moieties and one water molecule with a mass loss of 4%. The next decomposition step occurs in the temperature 258^0C a mass loss of 14%, corresponding to the loss of two chloride ions and the last decomposition step occurs in the temperature 393.1^0C with a mass loss of 30% referred to the loss of the 4-aminoantipyrine and intermediate moieties. For Ag(I) complex ($C_{23}H_{27}AgN_7O_8$), this complex is thermally stable up to 173^0C the first step occurs in the temperature 173.2^0C with a mass loss of 1% and the second step occurs in the temperature 288.3^0C with a mass loss of 25.33% and last decomposition step occurs in the temperature 395^0C with a mass loss of 29.33% referred to the loss of the 4-aminoantipyrine and moieties.

For L2 $C_{25}H_{16}N_4O_9$ From the TG curve, it appears that the sample decomposes in two stages. The first stage decomposition occurs at 207.1^0C with a mass loss of 2.0% and the second decomposition at 352.8^0C with a 48% mass loss. For palladium complexes ($C_{50}H_{34}N_8O_{18}Pd$), the data obtained support the proposed structure and indicate that Pd(II) complex undergo three step degradation reaction. The first step occurs at maximum peak lying in 85.6^0C, corresponding to the loss of 2% the weight loss associated with this step agrees quite well with the loss one terminal methyl groups in 4-aminoantipyrine moiety. The second step occurs at T_{max} 150.7^0C, corresponding to the loss of 3% and it referred to loss of chlorine atom. The third decomposition step occurs at $T_{max}354.6^0$C corresponding to the loss of 25% referred to a single process, but it's reflective of two or three overlapping processes and attributed to loss of the 4-aminoantipyrine and moieties. The residual is in agreement with Pd metal.

For Ni complex ($C_{50}H_{34}N_8NiO_{18}$), the data obtained support the proposed structure and indicate that Ni(II) complex undergo three step degradation reaction. The first step occurs at maximum peak lying in 157.7^0C, corresponding to the loss of 2% the weight loss associated with this step agrees quite well with the loss of one water molecule.The second step occurs at T_{max} 189.2^0C, corresponding to the loss of 6% and it referred to loss two terminal methyl groups in 4-aminoantipyrine moiety The third decomposition step occurs at T_{max} (358.3^0C) corresponding to the loss of 35% referred to a single process, but it's reflective of two or three overlapping processes and attributed to loss of the 4-aminoantipyrine and moieties. For Ag complex ($C_{25}H_{16}AgN_5O_{12}$), a mass loss occurred within the temperature 115.6^0C corresponding to the loss of 1% for one molecule of water The temperature 179.7^0C a loss of 5.33%, corresponding to a loss of one NO_3 molecule at the end of the thermogram at higher temperature 356.3^0C.

The first mass loss of L3($C_{22}H_{22}N_6O_2$) was observed at 183.1^0C in the TG profile. From the TG curve, it appears that the sample decomposes in two stages. The first stage decomposition occurs at 183.1^0C with a mass loss of 2.66% and the second decomposition starts at 250^0C and ends at 345.5^0C with a 20% mass loss. Pd(II) complex ($C_{44}H_{50}N_{12}O_4Pd$), the TG of this complex reveals a mass loss in the temperature101.1^0C corresponding to the loss of

four terminal methyl groups in 4-aminoantipyrine and phenazone moieties and four water molecules with intermediate moieties with a mass loss of 15.33%. The next decomposition step occurs in the temperature 250^{0}C a mass loss of 26.66% and the last decomposition step occurs in the temperature 357.3^{0}C with a mass loss of 34% referred to to loss of the 4-aminoantipyrineand intermediate moieties.

Ni(II) complex ($C_{44}H_{50}N_{12}NiO_4$), the TG of this complex reveals a mass loss in the temperature 173.5^{0}C corresponding to the loss of one methyl group and with a mass loss of 2.66%. The next and last decomposition step occurs in the temperature 281.6^{0}C and 360.1^{0}C with a mass loss of 25.33% and 32%, respectively referred to a single process, but it's reflective of two or three overlapping processes and attributed to loss of the 4-aminoantipyrine and moieties.

Ag complex ($C_{22}H_{24}AgN_7O_5$), this complex is anhydrous compounds which decompose in two steps and is thermally stable up to 165^{0}C the first step occurs in the temperature 165.1^{0}C with a mass loss of 2%, and the last decomposition step occurs in the temperature 353.1^{0}C with a mass loss of 43.33% referred to the loss of the 4-aminoantipyrine and moieties.

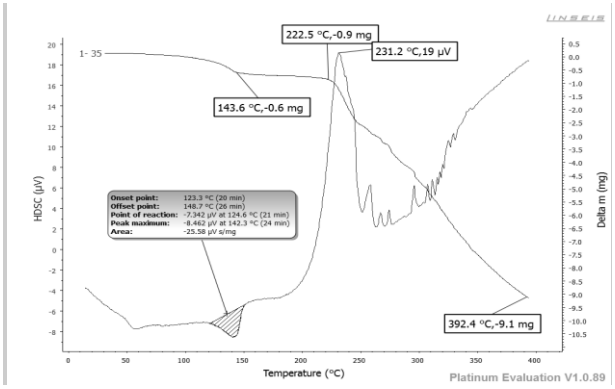

Figure 1: TG/HDSC Thermogram of L1

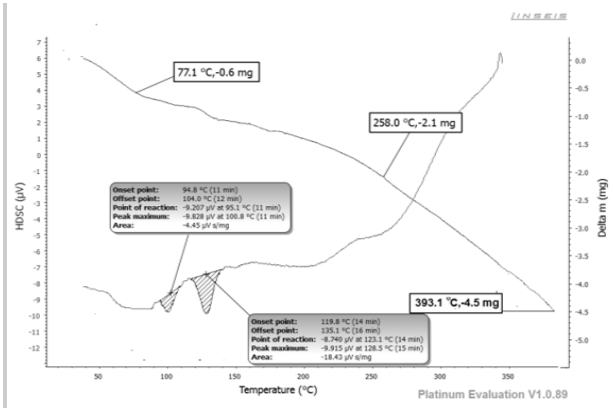

Figure 2: TG/HDSC Thermogram of L1-Pd

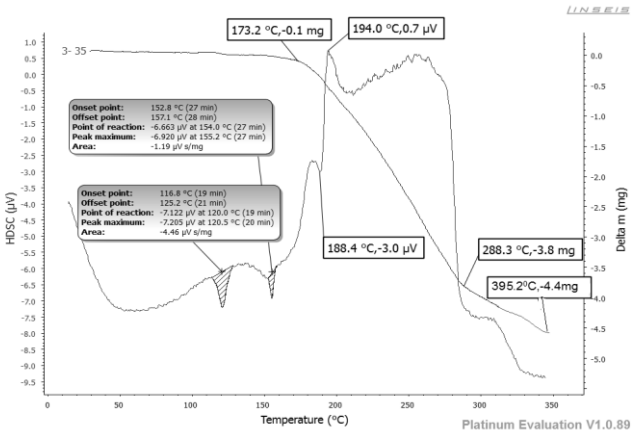

Figure 3: TG/HDSC Thermogram of L1-Ag

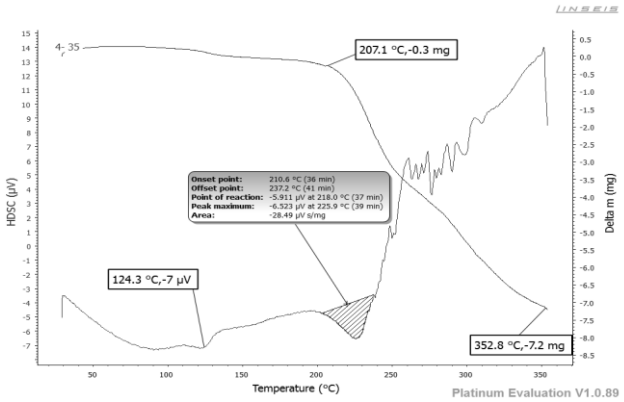

Figure 4: TG/HDSC Thermogram of L2

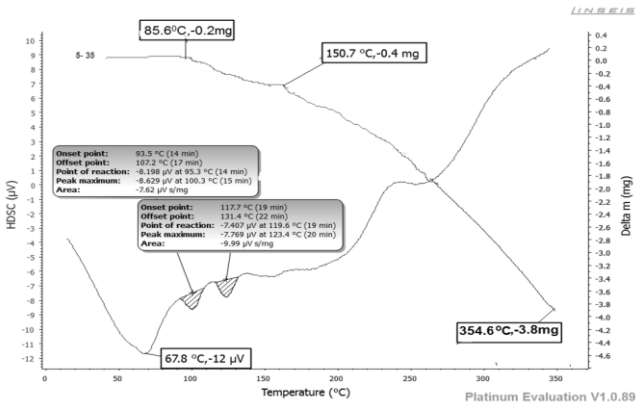

Figure 5: TG/HDSC Thermogram of L2-Pd

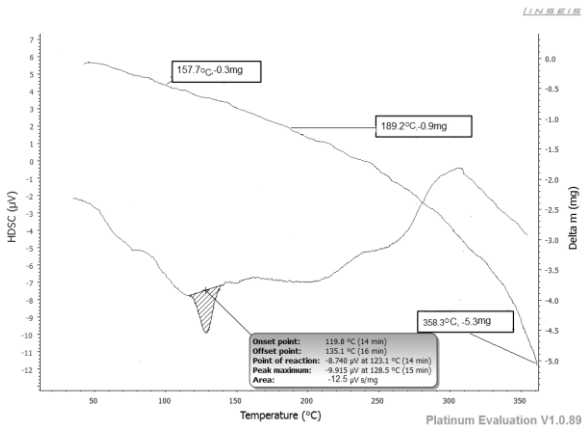

Figure 6: TG/HDSC Thermogram of L2-Ni

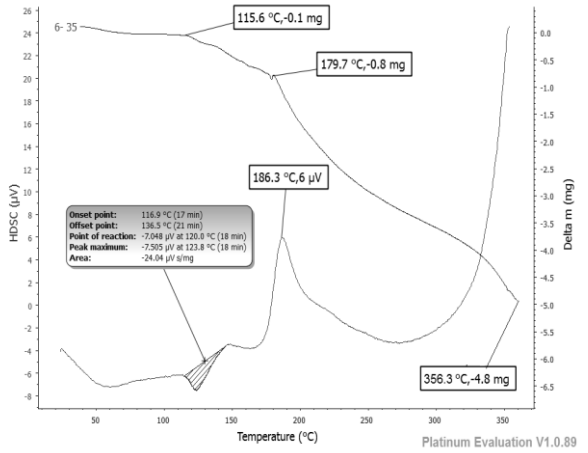

Figure 7: TG/HDSC Thermogram of L2-Ag

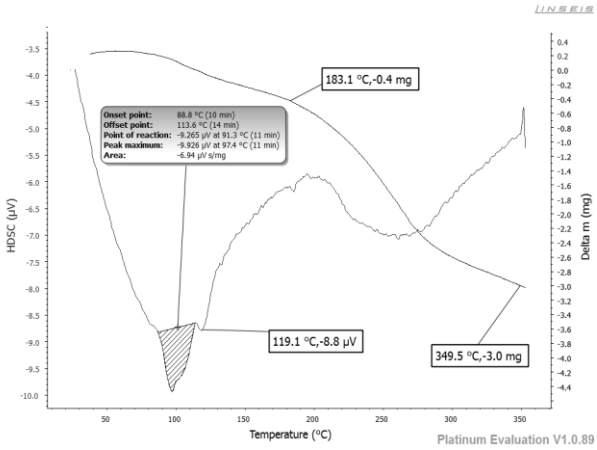

Figure 8: TG/HDSC Thermogram of L3

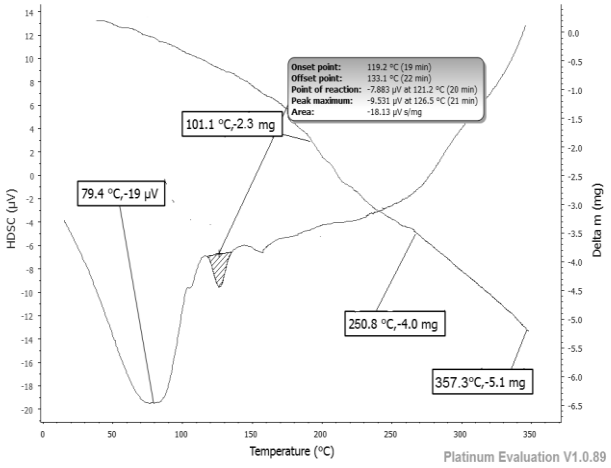

Figure 9: TG/HDSC Thermogram of L3-Pd

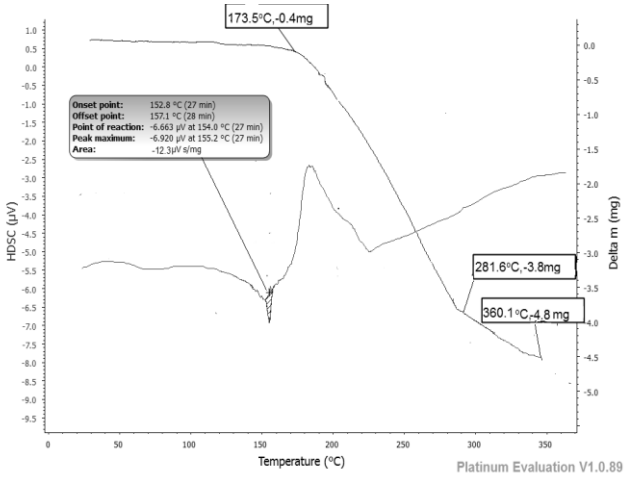

Figure 10: TG/HDSC Thermogram of L3-Ni

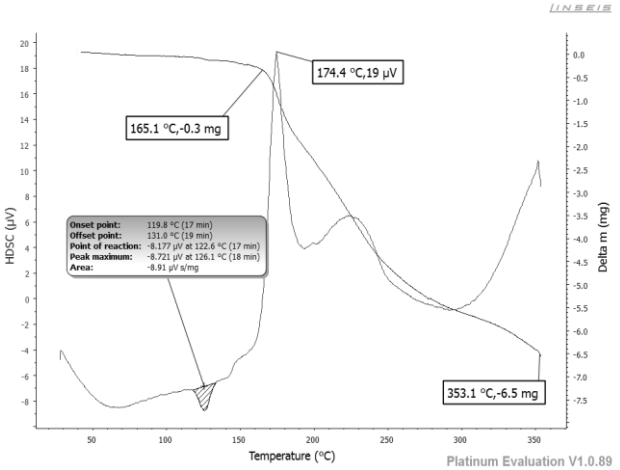

Figure 11: TG/HDSC Thermogram of L3-Ag

4. Acknowledgment

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