
METAL COMPLEXES OF NEW PYRIMIDINE AZODYE LIGANDS SYNTHESIS, SPECTRAL STUDIES, THERMAL ANALYSIS, X-RAY DIFFRACTION AND USES IN INK SYNTHESIS.

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Abstract

Novel azodye ligands 2-Amino-3- (4-chloro phenylazo)-7-(4-fluorophenyl)-5-(thiophen-2-yl)-6,7-dihydropyrazolo (1,5-a) pyrimidine (L₁) and 2-Amino-3- (4-chlorophenylazo)-5,7-Di(thiophen-2-yl)-6,7-dihydropyrazolo(1,5-a) pyrimidine (L₂) and their complexes with Fe (III) , Co (II), Ni (II) and Cu (II) have been synthesized. The stereochemistry and the mode of bonding of the complexes were achieved based on elemental analysis , IR, UV-Vis, ¹HNMR, MS and ESR spectroscopy as well as (TGA). Octahedral structure proposed for geometry of the chelates based on their electronic spectra and magnetic susceptibility. The metal complexes show no bleeding and tinting strength properties for ink synthesis.

1. Introduction

Azo-compounds play an important role in analytical chemistry as metal chromogenic agents [1-4], in industrial dyes [5-6], acid–base indicators and histological stains [7]. Also some azo-compounds possess excellent optical memory and photoelectric properties [8-9]. Various studies have been done on the arylazoheterocycles and their metal complexes [10-20]. The pyrimidine compounds are one of the important classes, so several studies were reported on the structural chemistry of the pyrimidine compounds and their metal complexes [21-25]. In view of these finding and in continuation to our work on the spectral behavior of azodyes and their metal complexes [26-29], this article represents an investigation of the spectral behaviors of amino azodye (L) containing the pyrimidine moiety.

2. Experimental

2.1. Materials:

All the materials were of commercial reagent grade. The 2- acetylthiophene and other compounds for prepared L₁ and L₂ were purified by standard procedures .The purity of them was determined by thin layer chromatography (TLC) and gas chromatography.

2.2. Synthesis of Ligands:

2.2.1 Synthesis of (L₁): (2-Amino-3-(4-chloro phenylazo)-7-(4-fluorophenyl)-5-(thiophen-2-yl)-6,7-dihydropyrazolo (1,5-a)pyrimidine).

2-Acetylthiophene (20 mmol) added to 4-fluorobenzaldehyde (20 mmol) in a porcelain mortar, 200 mg of NaOH was added and the mixture grounded by a pestle for 5 – 20 minutes. the mixture turned to pink color then we add distilled water and filter the suspension then the product was crystallized from 95 % ethanol to produce (E)-3-(4-fluorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one. Into a 10 ml microwave vial was added (20 mmol) (E)-3-(4-fluorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one to (20 mmol) 4-(4-chlorophenylazo)-3,5-diaminopyrazole and a few drops of catalytic amount of pyridine, the mixture was then subjected to microwave irradiation for 3.5 minutes. After cooling at room temperature, the product was crystallized from ethanol/DMF (1 : 1) to give 2-Amino-3-(4-chloro phenylazo)-7-(4-fluorophenyl)-5-(thiophen-2-yl)-6,7-dihydropyrazolo (1,5-a)pyrimidine orange color m.p (236 °C) , %C (found = 60.18 , calc. = 58.60) , %H (found = 3.64 , calc. = 3.58) , %N (found = 17.95 , calc.= 18.64) , %S (found = 6.9 , calc.= 7.11) (C₂₂H₁₆ClFN₆S, MWt = 450.92).

2.2.2 Synthesis of (L₂): (2-Amino-3-(4-chlorophenylazo)-5,7-Di(thiophen-2-yl)-6,7-dihydropyrazolo(1,5-a)pyrimidine):

2-Acetylthiophene (20 mmol) added to thiophene-2-carboxaldehyde (20 mmol) in a porcelain mortar, 200 mg of NaOH was added and the mixture grounded by a pestle for 5 – 20 minutes. the mixture turned to pink color then we add distilled water and filter the suspension then the product was crystallized from 95 % ethanol to produce (E)-1,3-Di(thiophene-2-yl)prop-2-en-1-one. Into a 10 ml microwave vial was added (20 mmol) (E)-1,3-Di(thiophene-2-yl)prop-2-en-1-one to (20 mmol) 4-(4-chlorophenylazo)-3,5-diaminopyrazole and a few drops of catalytic amount of pyridine the mixture was then subjected to microwave irradiation for 8 minutes after cooling at room temperature, the product was crystallized from ethanol/DMF (1 : 1) to give 2-Amino-3-(4-chlorophenylazo)-5,7-Di(thiophen-2-yl)-6,7-dihydropyrazolo(1,5-a)pyrimidine brown color m.p (208 °C) , %C (found= 54.80 , calc. = 54.72) , %H (found = 3.51 , calc. = 3.44) , %N (found = 19.09 , calc.= 19.15) , %S (found = 14.49 , calc.= 14.61) (C₂₀H₁₅ClN₆S₂, MWt = 438.96).

2.3 Synthesis of solid metal complexes:

A warm solution of Nickel acetate $\cdot 4\text{H}_2\text{O}$ (49 mg, 0.2 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L_1 (90 mg, 0.2 mmol) in 20 ml ethanol with continuous stirring and reflux for 2 hours observed change in color from orange to black. The black solid formed filtrated at room temperature m.p(over $300\text{ }^\circ\text{C}$), %C (calc.= 52.52 , found= 50.18), %H (calc. = 3.64 , found = 3.6) , %N (calc. = 15.31 , found =15.9) ,%S (calc. = 5.83 , found 6.9) , %M (calc.=5.35 , found = 4.7). ($\text{C}_{48}\text{H}_{40}\text{Cl}_2\text{O}_5\text{F}_2\text{N}_{12}\text{S}_2$ Ni , MWt = 1096.63)

2.3.2 Synthesis of Cu (II) complex of L_1 :

A warm solution of Cupric acetate $\cdot \text{H}_2\text{O}$ (39 mg, 0.2 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L_1 (90 mg, 0.2 mmol) in 20 ml ethanol with continues stirring and reflux for 2 hours observed change in color from brown to dark brown . The dark brown solid formed filtrated at room temperature m.p(over $300\text{ }^\circ\text{C}$), %C (calc.= 52.34 , found= 49.25), %H (calc. = 3.66 , found = 2.96) , %N (calc. = 15.26 , found =14.71) ,%S (calc. = 5.82, found = 6.44) , %M (calc.=5.77,found = 6.2) ($\text{C}_{48}\text{H}_{40}\text{Cl}_2\text{O}_5\text{F}_2\text{N}_{12}\text{S}_2$ Cu, MWt = 1101.49).

2.3.3 Synthesis of Co (II) complex of L_1 :

A warm solution of cobalt acetate $\cdot 4\text{H}_2\text{O}$ (49 mg, 0.2 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L_1 (90 mg, 0.2 mmol) in 20 ml ethanol with continues stirring and reflux for 2 hours observed change in color from brown to dark brown .

The dark brown solid formed filtrated at room temperature m.p(over $300\text{ }^\circ\text{C}$), %C (calc.= 52.51 , found= 51.63), %H (calc. = 3.64 , found = 4.39) , %N (calc. = 15.31, found =17.64) ,%S (calc. = 5.83, found = 6.75) , %M (calc.=5.37, found = 5.0) ($\text{C}_{48}\text{H}_{40}\text{Cl}_2\text{O}_5\text{F}_2\text{N}_{12}\text{S}_2$ Co, MWt = 1096.87) .

2.3.4 Synthesis of Ni (II) complex of L_2 :

A warm solution of Nickel acetate $\cdot 4\text{H}_2\text{O}$ (62 mg, 0.25 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L_2 (109 mg, 0.25 mmol) in 20 ml ethanol with continuous stirring and reflux for 2 hours observed change in color from brown to dark brown .

The dark brown solid formed filtrated at room temperature m.p(over 300 °C), %C (calc.= 49.27 , found= 49.86), %H (calc. = 3.57 , found = 4.47) , %N (calc. = 15.67, found =15.8) ,%S (calc. = 11.96 , found = 14.5) , %M (calc.=5.47 , found = 6.4) (C₄₄H₃₈Cl₂N₁₂S₄O₅Ni , MWt = 1072.71)

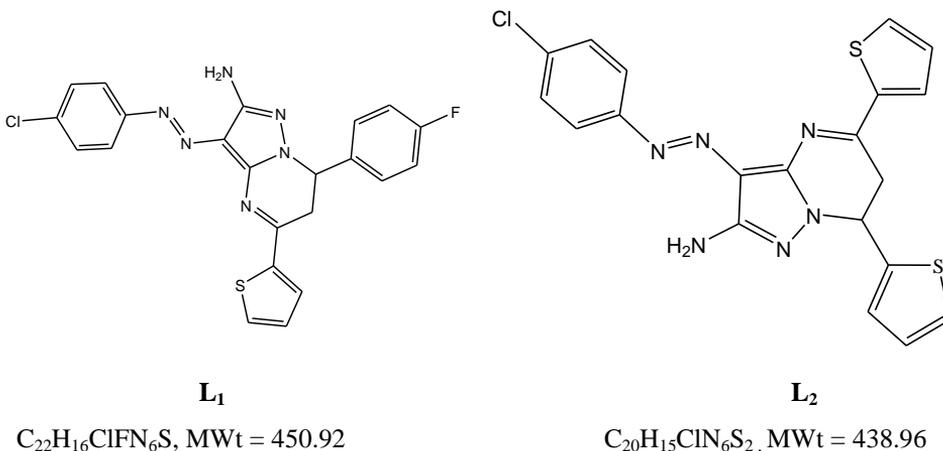
2.3.5 Synthesis of Co (II) complex of L₂:

A warm solution of cobalt acetate .4H₂O (62 mg, 0.25 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L₂ (109 mg, 0.25 mmol) in 20 ml ethanol with continues stirring and reflux for 2 hours observed change in color from brown to dark brown .

The dark brown solid formed filtrated at room temperature m.p(over 300 °C), %C (calc.= 49.25 , found= 47.06), %H (calc. = 3.57 , found = 3.09) , %N (calc. = 15.67 , found =15.37) ,%S (calc. = 11.95, found = 10.95) , %M (calc.=5.49,found = 6.75) (C₄₄H₃₈O₅Cl₂N₁₂S₄Co, MWt = 1072.95)

2.3.6 Synthesis of Fe (III) complex of L₂:

A warm solution of Ferrous Nitrate .9H₂O (101 mg, 0.25 mmol) in 20 ml ethanol dissolved after heating and added drop wise to warm solution of L₂ (109 mg, 0.25 mmol) in 20 ml ethanol with continues stirring and reflux for 2 hours observed change in color from brown to dark brown. The dark brown solid formed filtrated at room temperature m.p(over 300 °C), %C (calc.= 42.19 , found= 43.7) , %H (calc. = 2.81 , found = 3.4) , %N (calc. = 18.45 , found =17.37) , %S (calc. = 11.25 , found = 12.39) , %M (calc.=4.90 , found = 5.4) (C₄₀H₃₂O₁₀Cl₂N₁₅S₄Fe, MWt = 1137.7).



2.4 Instruments

2.4.1 Electronic Spectra:

The absorbance of solutions were measured by UV/Visible in range (190 – 900) nm using Shimadzu 1600 series spectrophotometer at the Faculty of Science Cairo university in Giza , Egypt.

2.4.2 IR spectra:

IR spectra of ligands and metal complexes were recorded in the solid state by Perkin Elmer 3600 and 1650 ratio recording infrared spectrophotometer. IR spectrometer using potassium bromide disc technique at micro analytical center of Faculty of Science, Cairo University, Giza, Egypt.

2.4.3 Thermal Analysis:

Thermal analysis measurements were carried out on Shimadzu TGA in Micro analytical center, Faculty of Science, Cairo University, Giza, Egypt.

2.4.4 ¹H NMR Spectra:

The proton NMR spectra recorded in DMSO-d₆ on varian F.T-300 MHz spectrometer using TMS as internal standard at Cairo University, Giza, Egypt.

2.4.5 Mass Spectra

Mass spectra were recorded at Mass spectroscopy using direct inlet unit (DI-50) of SHIMADZU GC/MS – QP5050A at the Regional center for Mycology & Biotechnology; Al-Azhar University.

2.4.6 Quantitative Analysis of Metal Cations :

All metal cations were determined volumetrically using standard EDTA [30].

2.4.7 Micro analytical analysis:

Carbon, hydrogen, nitrogen and sulpher analysis have been carried out in the Micro analytical center of Faculty of Science, Cairo University, Giza, Egypt.

2.4.8 Electron paramagnetic resonance (ESR) :

The ESR recorded on EMX (x-band), Burker, Germany at the national center for research and radiation technology in Atomic Energy Authority, Egypt .

2.4.9 X-ray diffraction:

The samples were examined using a Philips analytical x-ray diffraction system , type PW 3710 with Cu tube anode in physics department at the Faculty of Science at Al- Azhar University.

2.4.10 Magnetic Susceptibility:

The magnetic susceptibility of prepared complexes was measured in physics department , Faculty of Science Cairo University, Giza, Egypt.

2.5 Materials of bleeding and tinting strength tests:

Polyamide resin, petroleum ether, glass plate and ink knives.

3. Results and discussion:

3.1 Spectral characterization :

3.1.1 IR spectra:

The infrared spectra of the two azodye ligands and their metal complexes obtained as KBr discs in the region of 4000 – 400 cm^{-1} and given in the table (1) .

The $\nu(\text{N}=\text{N})$ of frequency of the ligand appears at 1471(L_1) & 1465(L_2) cm^{-1} , negative shift of the spectra of the complexes take place suggests coordination of one nitrogen of azo group in complexation with metal ions[31] . The $\nu(\text{C}=\text{N})$ observed at 1610 cm^{-1} for (L_1) & (L_2) shift to a lower value occurred in the complexes of L_1 due to the participation of N atom of azo mithine in chelation [31], while the spectra of the complexes of L_2 show the same position of $\text{C}=\text{N} \sim 1610 \text{ cm}^{-1}$ indicate that the azomethine nitrogen did not take part in complexation with metal ions. A broad bands in the 3400 – 3550 cm^{-1} appeared in the spectra of the complexes attributed to $\nu(\text{OH})$ of crystalline water molecules. The $\nu(\text{C-S})$ at (858& 829) cm^{-1} for L_1 & L_2 respectively this band shift to a lower values in complexes indicating (S) sharing in complex formation [32-34]. The $\nu_{\text{ass.}}$ band of NH_2 group appears in the spectra of the complexes as broad due to coupling with νOH of crystalline water molecules which absorbed in the same position on the spectra, confirming this the appearance of new bands in the region 1472 – 1499 cm^{-1} in the complexes which not found in the free ligands which due to $\delta\text{H}_2\text{O}$. The far infrared region shows bands in the range (501 – 552) cm^{-1} assigned to $\nu(\text{M-N})$ [35] and the bands in (409 -471) cm^{-1} region assignable to $\nu(\text{M-S})$ [36].

Table (1): IR spectral data of ligands and metal complexes of L₁ and L₂:

Comp No.	ν OH	ν C-H Ar	ν C-H Al.	ν C=N	ν N=N	δ H ₂ O	ν C-S	ν M-N	ν M-S
L ₁		3165 W	3101 v.w	1610 v.s	1471 S		858 m		
Co-L ₁	3431 Br	2923 M	2852 m	1605 s	1468 W	1478 w	833 m	552 v.w	413 v.w
NiL ₁	3446 Br	2923 v.w	2851 v.w	1606 v.s	1458 m	1472 w	830 m	521 W	409 v.w
Cu-L ₁	3566 Br	2975 W	2924 w	1603 v.s	1458 S	1499 s	827 S	501 M	431 W
L ₂		3156 W	3089 w	1610 v.s	1465 M		829 m		
FeL ₂	3443 Br	3077 W	2921 m	1611 v.s	1461 S	1480 w	807 M	526 M	418 W
CoL ₂	3452 Br	2934 W	2861 w	1610 s	1455 m	1489 S	807 m	527 M	418 W
Ni-L ₂	3419 Br	2952 W	2843 w	1612 v.s	1460 s	1495 w	806 m	520 M	419 S

3.1.2 UV-VIS spectra:

The uv-vis spectral behaviors of azo-metal chelates were investigated in DMF given in table (2). The spectra show a strong absorption maximum at range 200-320 nm and 350 -400 nm due to $\pi - \pi^*$ and n- π^* respectively.

The azo metal chelates of CuL₁ reveals one broad asymmetric ligand field band at 741 and 381 nm assignable to ${}^2E_g \rightarrow {}^2T_{2g}$ transition and charge transfer respectively indicated that distorted octahedral geometry [37] the observed magnetic moment $2.01 \mu_B$ [38].

The azo nickel chelates reveals three bands at 739, 555, 391 nm for NiL₁, 730, 458, 389 nm for Ni L₂ assignable to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ transitions respectively. This is in accordance with the earlier reported values for the octahedral Ni⁺² complexes [35] the magnetic moment $3.14 - 3.16 \mu_B$ confirms its proposed geometry [39]. The azo cobalt chelates shows three d-d transitions at 725, 455, 375 nm for CoL₁, 730, 460, 383 nm for Co L₂ attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$, respectively these transitions suggest an octahedral symmetry around the metal ion [35]. The magnetic moment $4.68 - 4.70 \mu_B$ [39]. The azo iron chelates shows three d-d transition at 735, 450, 396 nm for Fe(III) complex of L₂ attributed to ${}^6A_1 \rightarrow {}^4T_1(G)$, ${}^6A_1 \rightarrow {}^4T_2(G)$, ${}^6A_1 \rightarrow {}^4E(G)$ transitions respectively. The spectra suggest distorted octahedral geometry [40, 41, 42] the magnetic moment $5.84 \mu_B$ [39].

Table (2) UV-Vis data for azo metal chelates in DMF:

Comp.	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	d – d	μ_{eff}
Cu (L ₁) ₂	445	275	741 , 520, 381	2.01
Ni(L ₁) ₂	383	280	739 , 555 , 391	3.14
Co (L ₁) ₂	362	250	725 , 455, 375	4.68
Ni (L ₂) ₂	357	277	730 , 458 , 389	3.16
Fe (L ₂) ₂	378	273	735 , 450, 396	5.84
Co(L ₂) ₂	369	278	730 , 460 , 383	4.70

3.1.3 Mass spectra of solid metal complexes:

The formation of binuclear Co(II) and Cu(II) complexes further evidenced by mass spectral data. The proposed molecular formula of these complexes was confirmed by the mass spectral analysis by comparing its molecular formula weight with m/e values .The molecular ion peaks of ligands and its binuclear Co (II) and Cu (II) complexes shows different m/e values with different intensities. The mass spectra contain molecular ion peaks at m/e (M⁺) 450 (L₁) but the molecular ion peak of its copper complex did not observed due to its high molecular weight than the scale of the mass device and it gives base peak at m/e =149 for C₆H₇N₅ and metal peak at m/e= 63.8 with different peaks m/e :

396,322, 353,322,243,225,161,149,136,121,112,96,84,78,66.....

The mass spectra of CoL₂ complex also gives base peak at m/e=161 for C₆H₅N₆ and metal peak at m/e= 61 with different peaks

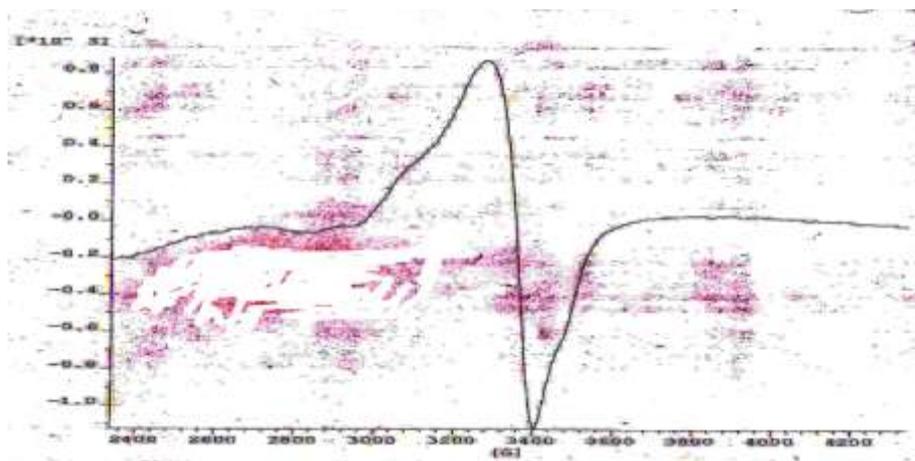
m/e: 438,355,321,245,231,222,161,163,148,121,112,110,96,98,84,78,70,67,66,..... without observing its molecular ion peak due to its high molecular weight than the scale of the mass device. These data is in good agreement with the respective molecular formula.

3.1.4. ESR Spectra :

The ESR (EPR) spectra of Cu (II) of L₁ complex were recorded on X-Band at frequency (9.7) GHz under the magnetic field strength (3480) G , recorded at room temperature. The spectra of the complex exhibit a single anisotropic broad signal. From fig (1). This anisotropic spectrum of ESR Cu (II) shows a $g_{\perp} > g_{\parallel}$ with the following values $g_{\parallel} = 2.06866$ and $g_{\perp} = 2.10975$ in which $g_{\perp} > g_{\parallel} > 2.0023$ calculated for Cu (II) complex, suggest that the unpaired electron is localized in $d_{x^2-y^2}$ orbital $g_{\perp} > g_{\parallel}$. These values indicate that the ground state of Cu (II) is predominately $d_{x^2-y^2}$, which suppose a distorted octahedral. The observed g_{\parallel}

value for Cu (II) complex is less than 2.3, thus, indicating the bonds between the organic ligand and copper ion have a covalent character more than the ionic character [43].

EPR intensity



Magnetic field (G)

Fig (1) ESR spectra of CuL₁

3.1.5.1 ¹HNMR (DmsO-d₆) of L₁:

The ¹HNMR signals of the azodye ligand L₁ are δ3.99 (dd, 1H, J=4.7, 9.8 Hz), 4.18 (dd, 1H, J=4.8, 11.8 Hz), 5.58 (dd, 1H, J=9.8, 11.8 Hz), 6.36 (br's, 2H, NH₂-exchangeable), 7.15-7.92 (m, 11H, ArH's and thiophene protons).

3.1.5.2 ¹HNMR (DmsO-d₆) of L₂:

The ¹HNMR signals of the azodye ligand L₂ are δ3.8 (dd, 1H, J=4.7, 9.8 Hz), 4.30 (dd, 1H, J=4.8, 11.8 Hz), 5.60 (dd, 1H, J=9.8, 11.8 Hz), 5.9 (br's, 2H, NH₂-exchangeable), 7.0-7.8 (m, 11H, ArH's and thiophene protons).

3.2 Thermal analysis of metal complexes:

3.2.1 TGA of CU-L₁:

TGA curve of Cu-L₁, table (3) refers to four steps of mass losses at temperature range 25 – 800 °C. These stages involved mass loss of 55.154 % (calculated 54.8 %) for first, second, third and fourth steps of decomposition respectively. These due to successive loss of C₂₆H₂₂N₆O₅SF molecules as gases at given temperature range

3.2.2 TGA of Ni-L₂:

The thermogram of Ni (II) chelates of ligand L₂, table (3) Show four decomposition steps within temperature range 25 – 800 °C.

The temperature range 25- 270 °C for first and second steps corresponding to losses of one water molecule and one acetate group with mass loss 8.586 % (calcd 7.1 %) For temperature range 270 – 800 °C the third and fourth steps of decomposition corresponding to loss of C₂₈H₂₄N₆S₂Cl₂O₂ with mass loss 56.087 % (calcd 55.83%) overall weight loss 64.673% (calcd 62.93 %).

3.2.3 TGA of Fe-L₂:

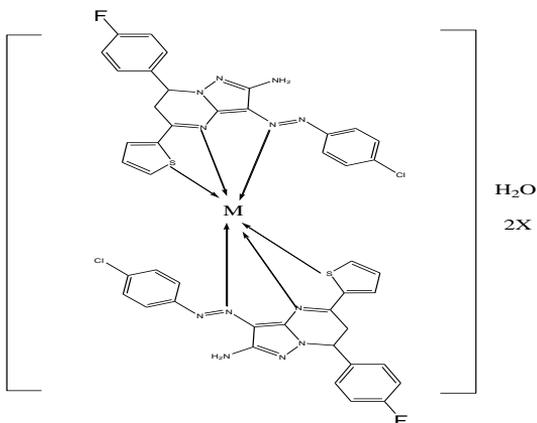
The thermo gram of Fe (III) chelate of ligand L₂, table (3) Show three decomposition steps with temperature range 25 – 800 °C.

The temperature range 25 – 280 °C for the first step corresponding to loss of one molecule of HNO₃ and one H₂O molecule with mass loss 4.921 % (calcd 6.9 %).

The temperature range 280 – 800 °C corresponding to loss of organic molecule of C₄₀H₂₉N₁₄S₂Cl₂O₈ with mass loss 89.564 % (calcd 85.077 %) leaving Fe₂O₃ as residue overall weight loss 94.485 % (calcd 91.977%).

Table (3) : thermal analysis of L₁ and L₂ complexes:

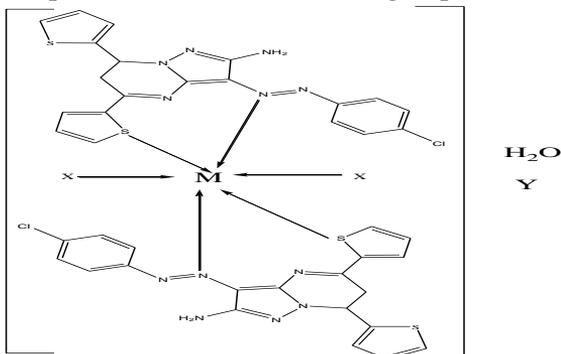
Com No.	TG Range	Mass loss Found/calcd %	Assignment of loss	Residue
Cu-L ₁	25→ 180	1.7/ 1.7	Loss of H ₂ O	
	180→410	14.245/ 13.76	Loss of C ₄ H ₈ O ₄	
	410→580	17.209/ 17.2	Loss of C ₁₂ H ₄ F	
	580→800	22/ 22.15	Loss of C ₁₀ H ₈ N ₆ S	C ₂₂ H ₁₈ N ₆ SFCl ₂ Cu
Ni-L ₂	25→160	1.241/ 1.6	Loss of H ₂ O	
	160→270	7.345/ 5.5	Loss of C ₂ H ₄ O ₂	
	270→480	22.164/ 21.16	Loss of C ₁₀ H ₁₁ S ₂ O ₂	
	480→790	33.923/ 34.67	Loss of C ₁₈ H ₁₃ N ₆ Cl ₂	C ₁₄ H ₈ N ₆ S ₂ Ni
Fe-L ₂	25→280	4.921/ 6.9	Loss of HNO ₃ And H ₂ O	
	280→415	24.586/ 22.677	Loss of H ₉ S ₂ N ₄ O ₈	
	415→800	64.978/ 62.4	Loss of C ₄₀ H ₂₀ N ₁₀ Cl ₂	Fe ₂ O ₃



Complex (1) M= Co, X= acetate group

Complex (2) M= Ni, X= acetate group

Complex (3) M= Cu, X= acetate group



Complex (1) M= Co, X= acetate group, Y=0

Complex (2) M = Ni, X= acetate group, Y=0

Complex (3) M = Fe, X=Y= NO₃

3.3 Bowder X-ray diffraction (XRD) analysis:

It was carried out to identify the phase of samples L₂ reveals the crystalline state containing several different peaks. Fe (III),Co (II) and Ni (II) complexes of L₂ reveals amorphous state .

4.0 Effect of synthesized complexes in ink synthesis :

Most azo-metal complex pigments, have only recently stimulated interest [44, 45] for their commercially interesting properties. It has for a long time maintained an important position as colorants for ink, textiles and paint synthesis there are a number of advantages to complexation. It imparts better weather fastness and light

fastness, bleeding and tinting strength properties which can be used in printing ink by using in printers as well as other areas of applications such as ink synthesis, metallic finishing in industries such as automotives finishing and can be used also in paints .

4.1 Standard test methods for bleeding of pigment [46]:

These test methods cover procedures for determining the bleeding characteristics of dry complexes of L_1 and L_2 (pigments) by direct solvent extraction of the pigment and by over striping a film with a white coating and observing for the color migration from the base coat containing the pigment .

Standard test method for bleeding of pigments :

1- Place 0.50 g of pigment in a 25-mL test tube and add 20-mL of reagent grade petroleum ether 60-80 . Close with a stopper, shake well for 10 s, and let stand 15 min. Repeat the 10-s shake and let stand 45 min.

2- Filter through a glass funnel using double filter paper that has first been wet with petroleum ether and collect approximately 10 mL of filtrate. If the filtrate is cloudy, refilter to get a clear filtrate.

3- Hold the test tube containing the filtrate above a white background and look down through the filtrate for coloration caused by pigment bleed. Describe the degree or severity of bleed according to the following terminology:

None – No perceptible color (that no bleed).

Slight – A faint but distinct coloration.

Moderate – A pronounced but not severe coloration.

Severe – an intense coloration.

We found all complexes give no perceptible color (no bleeding) or slight bleeding as shown in table (4).

Table (4) : The bleeding properties of L_1 and L_2 complexes:

Solvent	Complexes	Bleeding
Petroleum ether 60-80	$Cu (L_1)_2$	No
Petroleum ether 60-80	$Ni(L_1)_2$	Slight
Petroleum ether 60-80	$Co (L_1)_2$	Slight
Petroleum ether 60-80	$Ni (L_2)_2$	Slight
Petroleum ether 60-80	$Fe (L_2)_2$	No
Petroleum ether 60-80	$Co(L_2)_2$	Slight

4.2 Standard test method for relative tinting strength of paste-type ink dispersion [47]:

Tinting strength method by visual evaluation:

Using separate ink knives, gently stir Mix 0.1 gm of complexes of L_1 and L_2 with 0.5 gm of polyamide resin (the test tints). Place a small quantity of each tint, at one end of a small glass plate. Hold the drawdown knife at a low angle (5^0 to 15^0 from horizontal) and using light pressure, draw down the tints in juxtaposition.

Immediately examine the masking degree of the background (from experience) of the drawdown under the standard light as shown in table (5).

Table (5): Tinting strength of L_1 and L_2 complexes:

Complexes	Tinting strength
$Cu(L_1)_2$	Moderate
$Ni(L_1)_2$	Moderate
$Co(L_1)_2$	High
$Ni(L_2)_2$	Moderate
$Fe(L_2)_2$	High
$Co(L_2)_2$	High

4.3 Applications:

All L_1 and L_2 complexes can be used in the ink and paint manufactures.

5.0 Conclusions

The design of the complexes of the two new azodye ligands L_1 and L_2 have been demonstrated. The IR spectra of the complexes indicate that the azo-compounds coordinate to the divalent metal ions $Co(II)$, $Ni(II)$ and $Cu(II)$ and trivalent $Fe(III)$ through the NNS as tridentate ligand with octahedral geometry in L_1 complexes and through the NS as bidentate ligand in L_2 complexes with octahedral geometry also. All of the complexes of L_1 contains one H_2O crystalline water and two non coordinate acetate groups in the outer sphere. Complexes of L_2 have one crystalline water molecule and two coordinated acetate groups in inner sphere while FeL_2 contains one crystalline water molecule and one non coordinated NO_3 molecule in outer sphere while two coordinated NO_3 in inner sphere.

The azodye complexes can be used in the ink and paint synthesis.

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