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Synthesis , Spectral Characterization and photo Thermal Decomposition Studies of New Hetrocyclic Azo Dye Compound Derived From Imidazole with Some Transition Metal Complexes.

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ABSTRACT

New heterocyclic azo dye ligand 2-[2$^-$- (4,5- dimethoxy carboxy phenyl) azo]- Imidazole, (DMCPAI=HL) was prepared by coupling between a diazonium chloride solution of 2- amino - 4,5- dimethoxy benzoic acid with imidazole in alkaline ethanolic solution. Eight complexes with Cr(III), Mn(II) , Co(III) ,Ni(II) ,Cu(II) ,Zn(II) ,Cd(II) and Hg(II) ions were prepared and characterized using available techniques such as elemental analysis , Mass spectral, ^{1}H- NMR, FT- IR, UV-Visb.,X- ray, TGA, SEM, molar conductance measurments and magnetic susceptibility. The analytical data show that the ligand behaves as neutral tridentate (N, N,O) ligand forming chelates with 1:2 ; [Metal : ligand] in all metal Complexes. The molar conductance data for all complexes are nonelectrolyte expected Cr(III) and Co(III) Complexes are 1:1 electrolyte. Octahedral geometry is suggested for metal complexes and d^2sp^3 or sp^3d^2 hybridization. Decomposition kinetics was studies photochemical for metal complexes through irradiation solution at wavelength 365 nm at 25 °C for 1 hour in ethanol was found to be the reaction from first order also. The calculated rate constant photolysis (k_d) mediated follow spectral changes during the process of irradiation. The thermal analysis (TGA), SEM and X-ray diffraction are explained and discussed.

Keywords: Azo imidazole (DMCPAI), Metal Complexes , Irradiation , X- ray diffraction ,TGA and SEM

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INTRODUCTION

Azo imidazole derivatives ligands have important roles in coordination chemistry because of formation stable complexes with most transition metal [1-3]. Azo imidazole derivatives are very important class of chemical compounds receiving attention scientific research [4,5].The azo imidazole ligands and its metal complexes are highly colored and have been used as dyes and pigments for along time [7]. Azo containing compounds are used in dyeing processes cotton [8],wool [9] silk [10],Rubber [11],plastic [12],print [13], cosmatics [14] and biological activites in cluding antibacterial [15], discouraging the growth of germs [16], Azo imidazole derivatives dyes are known as excellent analytical reagents in spectrophotometric determination of most transition metal ions[17،18] The coupling of diazonium salt occurs in position 2 of imidazole molecule in alkaline medium to give shining azo imidazole dyes[19], More literature survey regarding the imidazole drivatives focuses them as an important drug that selectivety inhibition endothelial cell growth and suppress angingenes in vitro and in vivo[20]. In this work we report the synthesis and characterization of new heterocyclic azo dye derived from imidazole [DMCPAI] and its metal complexes with Cr(III), Mn(II), Co(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions and study the thermal decomposition of the complexes , irradiation the solutions of this complexes, SEM and X-ray diffraction.

EXPERIMENTAL

Materials and Measurments

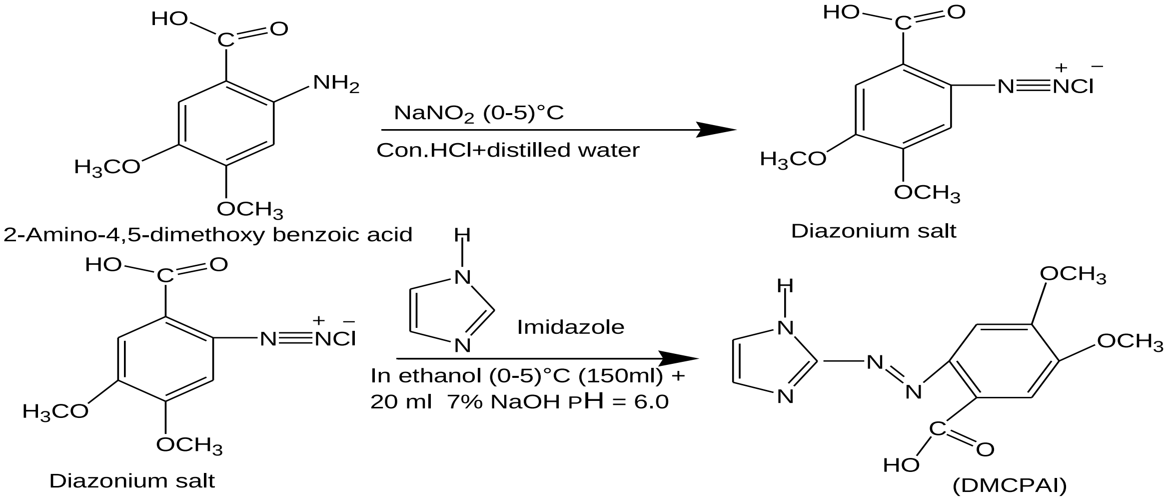
All chemicals and solvents were highest purity obtained from multiple companys such as Fluk, B.D.H, Merck, J.T.Baker, Scharian , Segma and Alderich. Elemental analysis of azo dye ligand ant its metal complexes were carried out by mean of micro analytical unit of EA 300 C.H.N Element analyzer (Isfahan university, Iran). ^{1}H- NMR spectra were recorded with a model Bruker 500 MHZ spectro photometer using DMSO as a solvent and TMS as an internal standard (Isfahan university, Iran). Mass spectra was obtained unsing a shimadzu Agilent Technologies 5973C at 70^e and MSD energy using a direct insertion probe (Acq method 10 W energy) at temperature 90-110 °C (Isfahan university, Iran). Infared spectra were recorded in KBr medium as dics using a shimadzu 8400 S FT-IR spectrophotometer in wave number at range (4000-400) cm^{-1}. Electronic spectra were measured in absolute ethanol as a solvent (10^{-3}M) in the range (200-1100) nm by using a UV-Visb. T80-PG spectrophotometer. The metal content of the complexes was measurmed using atomic absorption technique by shimadzu AA-6300. X-ray diffraction were measured using Bestec Germany Alminium anode model X pertpro, wavelength of X-ray beam(Cu k_α) 1.54 angstrom, Anod material=Cu, the Voltage = 40KV and current = 30mA (Isfahan university, Iran). TGA analysis were measured with England PL- TG using Rheometric scientific TGA-1000 (Tarbbit modars university, Iran).SEM images of ligand and its complexes, were taken using micrograph kyky 3200 (Isfahan university, Iran) The magnetic susceptibility for the prepared complexes were measured at room temperature using faraday method. For this purpose, Burker Magnet (B.M) had been employed and the diamagnetic correction were made by pascals constants. Electric molar conductivity measurments were carried out at room temperature in DMF (10^{-3} M) solution by using conductivity bridge model 31A.The melting points of ligand and its complexes were measured by using electro thermal melting point 9300.The PH measurments were determinted using a Philips pw 9421 PH meter (±0.001). .The chlorid ions in Cr(III) and Co(III) complexes was estimated by more method [21] and $AgNO_3$ solution.

Synthesis of Azo Dye Ligand (DMCPAI)

The new heterocyclic azo dye ligand (DMCPAI),(Scham1) has been synthesized by the diazotization coupling by flowing methods proposed by shibate *etal* [21] and Al-Adilee *etal* [8,15,22] with some modification.

A diazonium solution was prepared by dissolving 2-amino - 4,5- dimethoxy benzoic acid 1.9 gm (0.01 mol) in 30 ml distilled water containing 3ml concentrated hydrochloric acid. The filtered solution was cooled to 0 °C, To this mixture a solution of 0.75 gm (0.01 mol) of sodium nitrate in 25ml distilled water was added dropwise at (0-5) °C and stirred for 30 min. This diazonium chloride solution was added dropwise into a 500 ml beaker containing 0.68gm (0.01 mol) of imidazole was dissolved in 150 ml of ethanol and 20 ml of 7% sodium hydroxide with cooling and stirring continuously for one hour at(0-5) °C in ice- bath and allowed to stand over night and acidified with dilute hydrochloric acid to PH= 6.0 . The precipitate was filtered off and washed several times with cold distilled water and recrystallized twice from hot ethanol and then dried in oven at 60 °C for several hours and stored in a desiccator over anhydrous calcium chloride.The yield was 83% of red crystals and melting point found to be 152 °C. The purity was confirmed by the elemental analysis and TLC techniques.

The structural of the ligand (DMCPAI) as shown below:



2-[2^- - (4,5-Di methoxy carboxy phenyl) azo]-Imidazole, (DMCPAI)
Scheme(1):- Synthesis of hetrocyclic azo dye ligand (DMCPAI)

Synthesis of Metal Complexes

The metal complexes were prepared adding 0.55gm(0.002 mol) of ligand (DMCPAI) dissolved in 50 ml hot ethanol which then added dropwise with stirring continuously to (0.001 mol),1:2 [M:L] molar ratio,for Cr(III),Mn(II),Co(III),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II) chloride salt dissolved in 30 ml hot buffer solution (ammonium acetate) at PH=7.0 for each metal ions. The mixture was heated to (50-60) °C for 30 mints, then left over night. The solid complexes formed was filtered off ,washed with distilled water and washed with 5 ml ethanol to remove any traces of unreacted materials and dried in oven at 60 °C to several hours and preserved in a desiccators over anhydrous calcium chloride. The % yield, m.p, PH, color, molecular formula, M.wt and element analysis data (C.H.N) of ligand and its metal complexes are collected in table 1.

Table (1):- Analytical and physical data of ligand (DMCPAI) and its metal complexes

compound	color	m.p °C	Yield %	Molecular Formula (Mol.wt)	Found (calc.)%			
					C	H	N	M
HL= DMCPAI	red	152	76	$C_{12}H_{12}O_4N_4$ (276.24)	52.35 (52.17)	4.45 (4.38)	20.39 (20.28)	---------
$[Cr(L)_2].Cl$	purple	175	68	$C_{24}H_{22}O_8N_8CrCl$ (637.93)	45.47 (45.19)(	3.59 (3.47)	17.73 (17.56)	8.38 (8.15)
$[Mn(L)_2]$	Reddish purple	182	73	$C_{24}H_{22}O_8N_8Mn$ (605.42)	47.82 (47.61)(	3.75 (3.66)	18.70 (18.51)	9.31 (9.07)
$[Co(L)_2].Cl$	Dark purple	185	61	$C_{24}H_{22}O_8N_8CoCl$ (644.87)	44.92 (44.70)	3.55 (3.44)	17.48 (17.38)	9.32 (9.14)
$[Ni(L)_2]$	Light purple	215	64	$C_{24}H_{22}O_8N_8Ni$ (609.19)	47.59 (47.32)(	3.73 (3.64)	18.52 (18.39)	9.82 (9.64)
$[Cu(L)_2]$	purple	210	83	$C_{24}H_{22}O_8N_8Cu$ (614.03)	47.18 (46.95)	3.72 (3.61)	18.38 (18.25)	10.54 (10.35)
$[Zn(L)_2]$	Reddish purple	224	72	$C_{24}H_{22}O_8N_8Zn$ (615.86)	47.02 (46.81)	3.68 (3.60)	18.32 (18.19)	10.84 (10.61)
$[Cd(L)_2]$	Brown	235	78	$C_{24}H_{22}O_8N_8Cd$ (662.89)	43.69 (43.48)	3.46 (3.34)	17.12 (16.90)	---------
$[Hg(L)_2].H_2O$	Reddish brown	205	59	$C_{24}H_{24}O_9N_8Hg$ (769.09)	37.67 (37.48)	3.23 (3.14)	14.81 (14.57)	--------

HL=ligand (DMCPAI)

RESULT AND DISCUSSION

Characterization of azo dye ligand (DMCPAI) and its metal complexes

The hetrocyclic azo dye ligand (DMCPAI) was red crystals but the metal complexes of this ligand vary in colar from purple, reddish purple, dark purple, light purple,brown to reddish brown. The azo dye ligand and its metal complexes were soluble in most organic solvents such as ethanol, methanol DMSO, acetone and DMF but insoluble in water. The purity and structure of azo dye ligand and its metal complexes were tested by elemental analysis (C.H.N) and several techniques.

Metal:Ligand Ratio

The composition of metal complexes were determined by the methol of molor ratio a fixed wavelength of maximum absorption and concentration of metal ion and increasing a mount of ligand. The solutions of prepared metal complexes increase the intensity of the colours when access to point intersection [M:L] ratio and continuation color constant at after crossing the intersection point , which indicat that the complexes formed in constant solution . The matel:ligand [M:L] ratio in all metal complexes it was 1:2 mole ratio. The results are in agreement with the values reported for some aryl aso imidazole complexes [23,24].

Conductivity measurments

The conductivity measurments of the prepared metal complexes are shown in table (2) were measured in DMF solvent (10^{-3}M) at room temperature. The high values of molare conductivity of the Cr(III) and Co(III) complexes indicate that the complexes are 1:1 electrolyte type with ionic nature and suggest that Cl^- ion present outside the coordination spheres[25,26]. But the low values of molar conductivity of metal complexes of the Mn(II),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II) ions indicate these complexes are non- electrolytes nature and no anions outside the coordination spheres [24,25,27].

Calculation of the Metal Complexes Stability Constant (β)

Stability constants (β) are obtained spectrophotometrically by measuring the absorbance of solution azo dye ligand and metal ions at fixed wavelength (λ_{max}) and PH values.

The degree of formation of the metal complexes is obtained according to the relationship , $\beta= (1- \alpha) /4\alpha^3c^2$,$\alpha=A_m- A_s /A_m$ where A_m and A_s are the absorbance of the fully and partially formed metal complexes respectively at optimum concentration[28]. The calculated β and Log β values for the prepared metal complexes are included in table(2). The stability constant of metal complexes according to the following sequence:- Cu(II)> Ni(II)> Zn(II)> Co(III) > Cd(II)> Cr(III) > Mn(II)> Hg(II) . The sequence of metal ions of the first row transition metal agree with Irving- williams series of stability constant [29].

Table (2):- Molar conductivity, optimization concentration, stability constant values (β and Log β), maximum wavelength (λ_{max}) and molar absorptivity (ϵ) of metal complexes

Ligand	Metal ion	Optimal Conc. $\times10^{-4}$M	Maximum Wavelength nm)λ_{max} (	Molar Absorptivity $\times10^3$ (ϵ) $L.mol^{-1}.cm^{-1}$	Molar Conductivity $S.Cm^2.Mol^{-1}$	Stability Constant (β) $L^2.mol^{-2}$	Log β
Ligand=HL (DMCPAI) λ_{max} = 413nm 8.69×10^3 ϵ = Conc.=1.5×10^{-4}M	Cr(III)	1.25	520	4.12	73.82	1.11×10^9	9.046
	Mn(II)	1.50	468	12.27	9.18	9.74×10^8	8.988
	Co(III)	1.75	527	1.73	69.73	1.37×10^9	9.135
	Ni(II)	1.50	479	8.25	11.07	1.84×10^{10}	10.264
	Cu(II)	1.75	505	3.54	12.42	1.61×10^{11}	11.206
	Zn(II)	2.00	475	4.22	10.36	4.51×10^9	9.654
	Cd(II)	1.25	432	10.82	9.58	1.13×10^9	9.054
	Hg(II)	1.50	447	1.75	11.19	4.11×10^8	8.614

Mass spectra of new azo dye ligand and its Ni(II) – complex

The mass spectral data fragmentation of the azo dye figand (DMCPAI) and Ni(II) - complex are shown in schems 2 and 3 and figures 1 and 2 . The mass spectrum of azo dye ligand displays a base peak at m/z^{+}=276.1 attributed to the original molecular weight of ligand (DMCPAI) (276.2) , [$C_{12}H_{12}O_4N_4$] [16,24]. The peak at m/z^{+}=231.1 due to loss of carboxyl group (COOH) [$C_{11}H_{11}O_2N_4$]$^{+}$ ion, while the peak at m/z^{+}=203.1 corresponding to [$C_{11}H_{11}O_2N_2$]$^{+}$ ion due to loss azo group (-N=N-). The peaks at m/z^{+}=173.0 and 144.0 attributed to loss methoxy groups (-OCH_3) corresponding to [$C_{10}H_9ON_2$]$^{+}$and [$C_9H_7N_2$]$^{+}$ ions respectively. The loss of imidazole molecule give peak at m/z^{+}= 77.0 is due to [C_6H_5]$^{+}$ ion [15,25]. The peak at m/z^{+}=68.0 corresponding to imidazole ring [C_3H_4] [15.24]. The sam specbram show a peak at m/z^{+}=53.0 attributed to [C_4H_5]$^{+}$ ion [15]. The mass spectrum of Ni(II) - complex give base peak at m/z $^{+}$= 608.5 is attributed to the original molecular weight of the [Ni(L)$_2$] complex (609.21), [$C_{24}H_{22}O_8N_8Ni$]. The spectrum of this complex give a peak at m/z^{+}=244.1 due to [$C_{11}H_8O_3N_4$] because of loss methoxy group (OCH_3) and one atom hydrogen.The loss of carbonyl group (CO) give a peak at m/z^{+}=216.9 attributed to [$C_{10}H_8O_2N_4$]. The peak at m/z^{+}=110.1 due to loss azo group , imidazole molecule and one oxygen atom attributed to [C_7H_7O]$^{+}$ ion [25]. The spectrum of Ni(II)-complex give two peaks at m/z^{+}= 96.0 and 68.0 due to [$C_3H_4N_4$] and imidazole molecules respectively. The peak at m/z^{+} = 77.1 due to [C_6H_5]$^{+}$ ion while the peak at m/z^{+} = 64.0 and 52.1 attributed to [C_5H_4]$^{+}$ ion and cyclobutadine [C_4H_4] respectively [15,25]

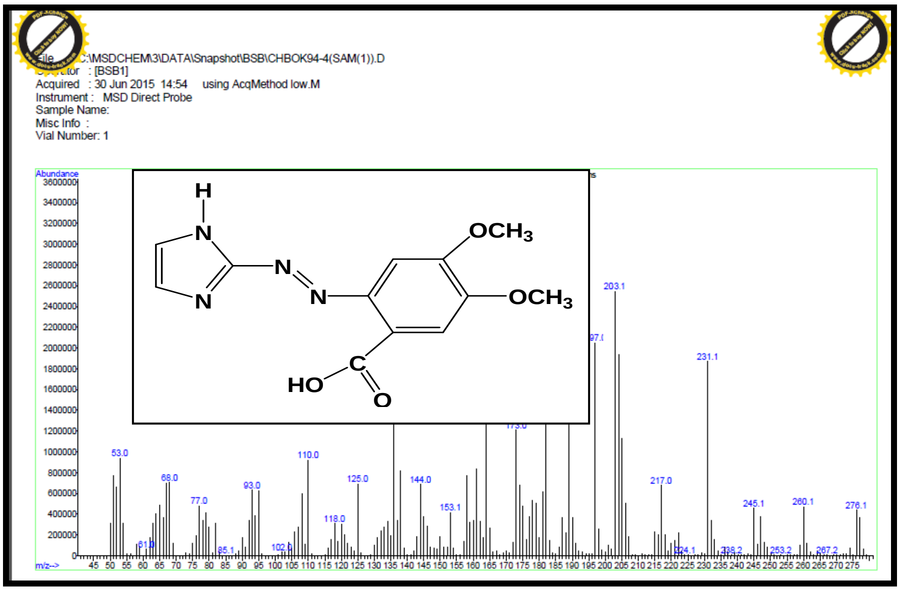


Figure (1):- Mass spectrum of azo dye ligand (DMCPAI)

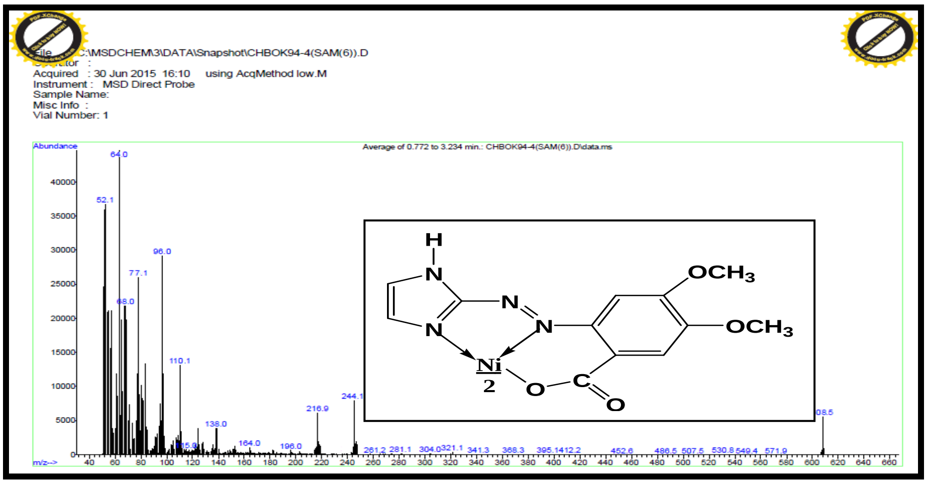
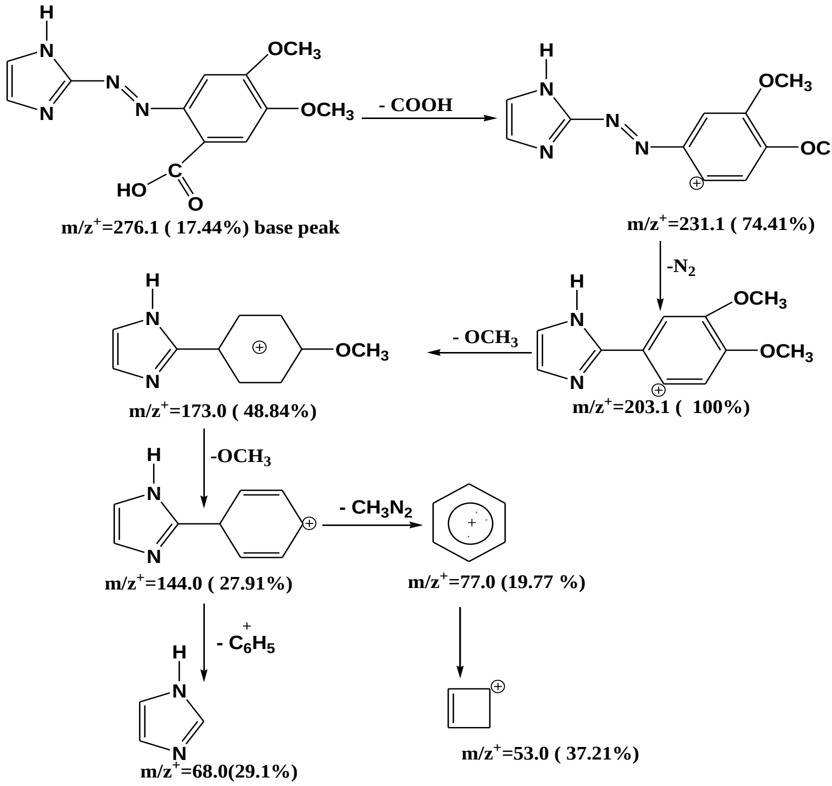
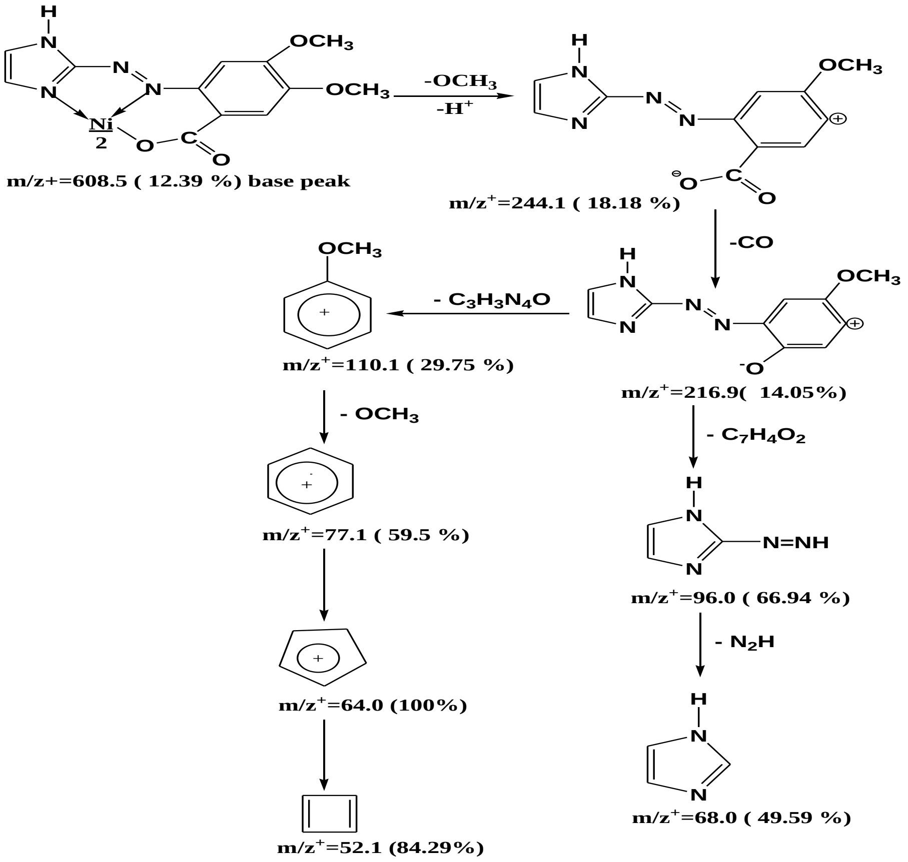


Figure (2):- Mass spectrum of Ni-Complex:[Ni(L)$_2$]



Schem (2):- Mass spectrum fragmentation of azo dye ligand (DMCPAI)



Scheme (3):-Mass spectrum fragmentation of Ni- complex; $[Ni(L)_2]$

^{1}H-NMR Spectra [15,16,25]

The signals of ^{1}H-NMR spectra of azo dye ligand (DMCPAI) and Hg(II) - complex, figures 3 and 4 respectively, was measured in d^6 – DMSO as asolvent with TMS as an internal reference and characterized by presence of a low- field. The spectrum of free ligand showed a doublate peak at 3.78- 3.80 ppm due to methoxy groups (-OCH_3). The single peak at 7.24 ppm attributed to H_4 and H_5 protons of imidazole ring , while the doublate peak at 7.40- 7.48 ppm which are assigned to the H_3 and H_6 proton in phenyl ring. Single peak at 8.02 ppm due to NH group in imidazole ring . The ^{1}H-NMR spectrum of free ligand give single peak at 9.82 ppm attributed to the proton of carboxylic group (COOH).

The ^{1}H-NMR spectrum of Hg(II) – complex, the proton of hydroxylic group disappeared indicate hydrogen atom carboxylic group replacement by Hg(II) ion during coordination with ligand. The doublate peak at 3.88- 3.94 ppm in Hg(II) - complex due to methoxy group, while the single peak at 7.25 ppm attributed to the H_4 and H_5 of imidazole ring. The proton of NH group appear at 8.12 ppm in complex. The different in position and intensity of signals between free ligand and Hg(II) - complex agree well with complex formation.

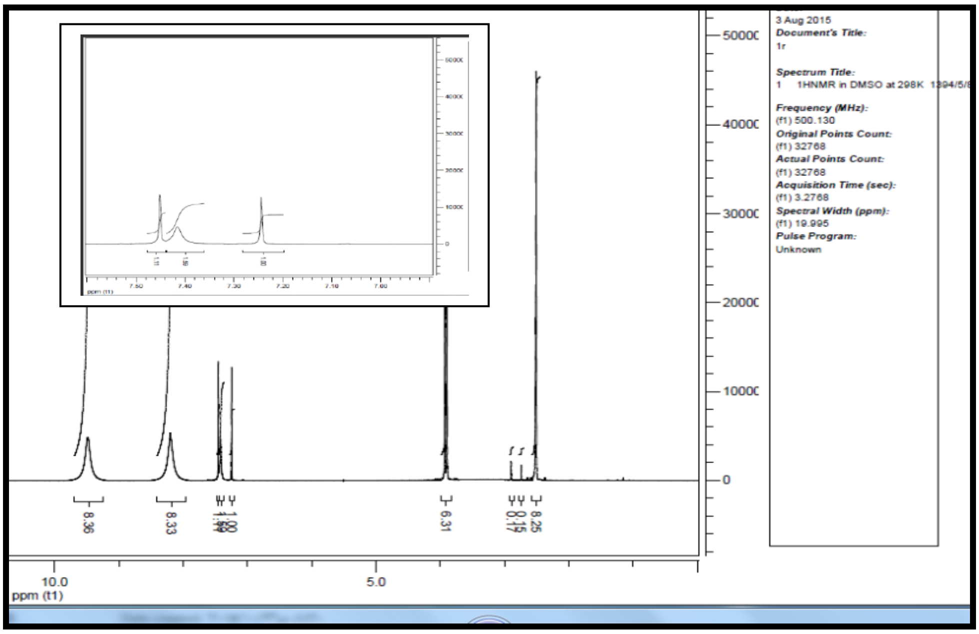


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Figure (3):-^{1}H-NMR spectrum of azo dye ligand (DMCPAI)

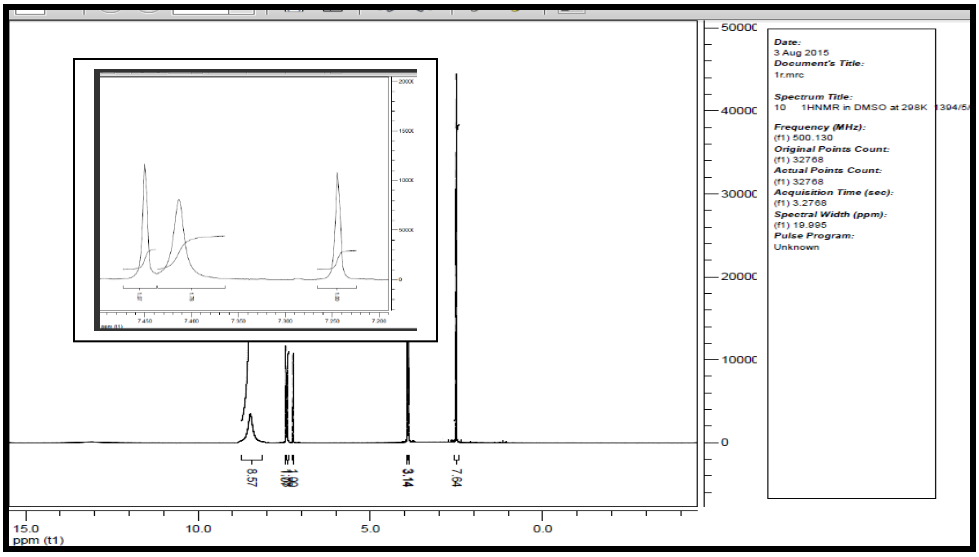

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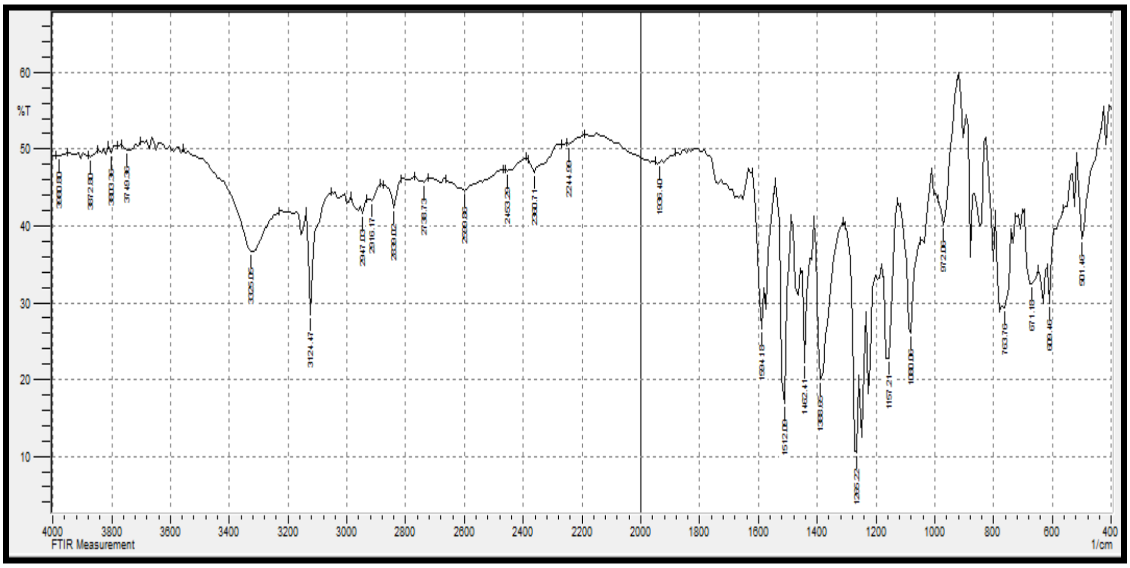
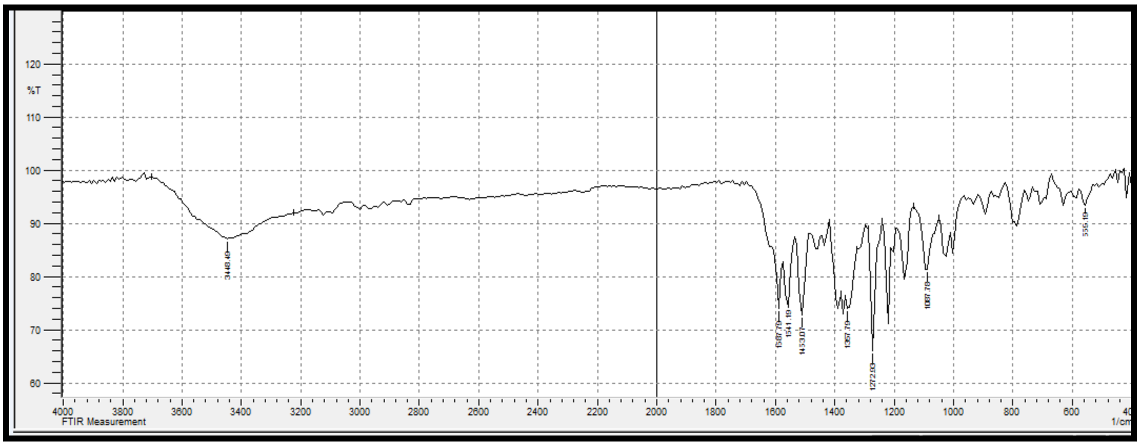
Figure (4):-^{1}H-NMR spectrum of Hg- complex; $[Hg(L)_2]. H_2O$

Infrared spectra of azo dye ligand and their metal complexes

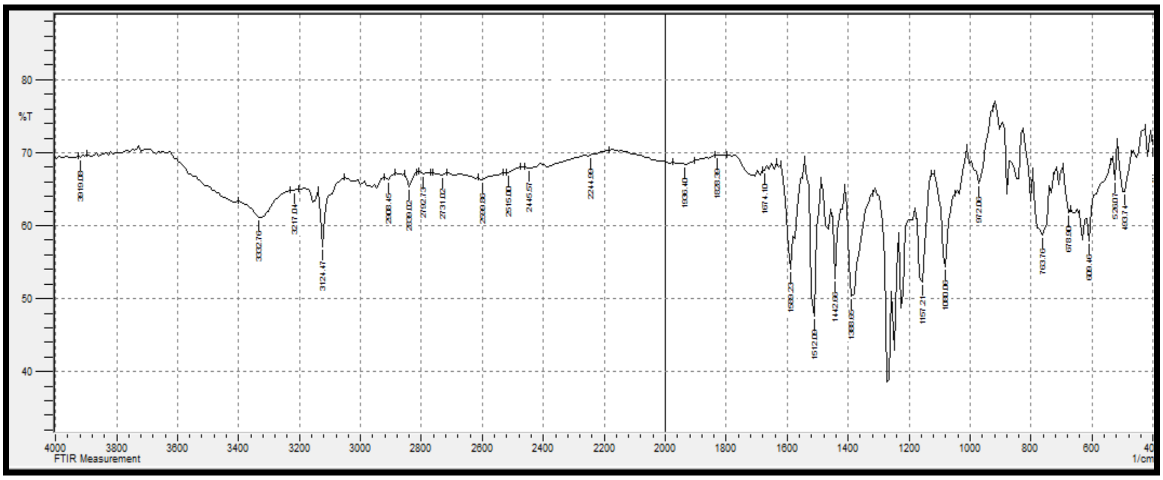
Infrared spectra data of the azo dye ligand (DMCPAI) and their metal complexes are listed in table (3). The IR spectra are comparison between the free ligand with those of there metal complexes have revealed certion characteristic differences. Some of these main shifts and conclusion are given below. The spectrum of the azo dye ligand showed a broad absorption around 3325 cm^{-1} assignable to the amine hydrogen and hydroxyl of carboxylic group [30]. This band is change in position and intensity in all metal complexes indicat of the coordination through the deprotonated carboxylic group. In the spectrum of Hg(II)- complex the broad band around 3332cm^{-1} indicat the presence of water molecule in this complex. But the spectra of rest metal complexes weak band observed at (3217-3448 cm^{-1}) due to υ(NH) group in imidazole ring does not participate in coordantion [16,22]. The medium band at 3124 cm^{-1} and weak band at 2947 cm^{-1} in the ligand spectrum which is due to υ(C-H) aromatic and aliphatic respectively. These bands are stable in position as well as intensity in both free ligand and their metal complexes spectra. spectrum of ligand shows a single strong absorption band at 1589 cm^{-1} assignable to the υ(COOH) group.This absorption band in the spectral of metal complexes disappears and asplit band of asymmetrical (COO^-) vibration at (1558-1512) cm^{-1} region as well as bands of symmetrical vibration in the (1389- 1373) cm^{-1} respectively appear. The spilt band of υ_{as} (COO^-) and υ_s (COO^-) as well as the separation ($\Delta\upsilon$) of υ_{as} and υ_s of (169- 139) cm^{-1} suggest that the carboxylate group coordinated with metal ions as a mono denate ligand [31]. The infrared spectrum of azo dye ligand (DMCPAI) revealed a strong band at 1594 cm^{-1} due to υ (C=N) of imidazole molecule. This band decrease in position and intensity in all metal complexes indicate that the imine nitrogen atom (N_3) in imidazole ring coordination with metal ions [32,33]. The azo group, υ (N=N) appear at 1462 cm^{-1}, this band it is observed with a little change in shape, intensity and shifted to lower frequencies at (1458-1438) cm^{-1} in the spectra of all metal complexes suggests its due to complex formation because of participation the nitrogen atom (N3) of azo group nearst to phenyl ring with metal ions [34].Metal complexes spectra show new weak bands in the region of (563-442) cm^{-1} which are not present in the spectrum of the free ligand may be attributed to the υ (M-O) and υ (M-N) bands [35-37]. Based on the above infrared spectra data lead to suggest that the azo dye ligand (DMCPAI) behaves as a trident chelating agent coordinating through the position of nitrogen of azo group which is the farthest of hetrocyclic ring (N3), nitrogen atom of imidazole ring (N3) and ahydroxyl oxygen of carboxylic group to give five and sixe membered chelate ring. The infrared spectra of azo dye ligand (DMCPAI) and some metal complexes are shown in figures 5,6 and 7.



Figure(5) :- IR Spectrum of azo dye ligand (DMCPAI=HL)



Figure(6):- IR Spectrum of the $[Co(L)_2]$ Cl complex



Figure(7):-IR Spectrum of the $[Hg(L)_2]$ H_2O complex

Table (3):- selected infrared absorption bands (4000-400) cm^{-1} for azo dye ligand (DMCPAI) and its metal complexes (KBr disc).

Group	Ligand	Cr(III)	Mn(II)	Co(III)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)
ν(OH)	3325[(a)] m.br	------	------	------	------	-----	------	------	3332[(b)] w.br.
ν(NH)	3325[(a)] m.br	3333 m.br	3425 w.	3448 w.br.	3441 w.br	3418 w.br	3394 w.	3425 w.br.	3217 w.
ν(C=N)	1594 s.sh.	1589 S.	1565 m.	1587 m.	1582 m.	1589 S.	1588 m.	1558 S.	1589 m.
ν(COO^-) asym.	---------	1512 S.	1512 m.	1541 m.	1512 S.	1520 Vs.	1512 S.	1512 m.	1512 S.
ν(COO^-) sym.	---------	1381 m.	1381 S.	1358 w.sh.	1381 S.	1373 m.	1381 S.	1373 S.	1389 m.
ν(N=N)	1462 m.	1443 m.	1442 m.	1453 m.	1458 m.	1438 w.	1438 m.	1458 m.	1443 m.
Imid.rde.	1080 m.	1080 m.	1080 m.	1088 m.	1088 S.	1087 S.	1088 m.	1087 S.	1080 m.
ν(M-0)	---------	525 w.	548 w.	556 w.	555 w.	563 w.	548 w.	547 w.	526 w.
ν(M-N)	---------	501 w.	501 w.	442 w.	491 w.	493 w.	487 w.	481 w.	494 w.

HL=ligand (DMCPAI) ,Vs = very strong , S = strong , m= medium , w = weak, sh = sholder,
b = H_2O molecule , a= the bands interface between COOH and NH groups

Electronic spectra and magnetic susceptibility measurments

The electronic spectra of azo dye ligand (DMCPAI) and all the metal complexes were recored in absolute ethanol in the range (200-1100) nm (10^{-3}M) at room temperature. The data obtained from the measurments of magnetic susceptibility and UV-Visb. spectra of the ligand and their metal complexes are given in table (4) and figures 8 and 9. The electronic spectrum of free ligand show three bands at 222 nm (45045 cm^{-1}), 259 nm (38610 cm^{-1}) and which may be attributed to the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ respectively [38,39]. The characteristic third visible band accurred at 413 nm (24213 cm^{-1}) may be assigned $\pi \rightarrow \pi^*$ charge transfer transition due to presence of conjugation in the imidazole ring [40]. This band (413nm) showed a red shift on coordination with metal ion. These observations respresent a further indicat for the coordination of the azo dye ligand with metal ions [24,32]

Chromium(III) - Complex

The electronic spectrum of Cr(III) - complex was studied in 10^{-3}M absolute ethanol show three absorption bands at520 nm (19231cm^{-1}) , 409 nm (24450 cm^{-1}) and 261 nm (38314 cm^{-1}) which may be d-d transition of chromium(III) ion , $^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g_{(F)}$ and center ligand transitions respectively. The magnetic susceptibility measurments of this complex has been found to be a parmagnetic porparties and $\boldsymbol{\mu}_{eef}$ value is 3.56 B.M this value is too close to the theortical of magnetic moment for the Cr(III) ion (t_2g^3 eg^0) and the $\boldsymbol{\mu}_{eef}$ =3.87 B.M depend on the data we conculed that the Cr(III) - complex takes hexa coordinate indicate octahedral geometry and d^2sp^3 hybrdization[25].

Manganes(II) – Complex

The electronic absorption spectrum of Mn(II) - complex show four bands , the first and second bands at 979 nm (10214 cm^{-1}) and 468 nm (21367 cm^{-1}) which my be attributed to $^2A_1g \rightarrow {}^4T_1g_{(p)}$ and $^2A_1g \rightarrow {}^4T_1g_{(G)}$ transitions respectively whil the third and foure bands located at 274 nm (36496 cm^{-1}) and 237 nm(42194 cm^{-1}) which are assigned to ligand centered transition. The magnetic moment for this complex was found to be 1.83BM. This values refers that the Mn(II) - complex has a low spin distorted octahedral geometry (z-out) due to a presence of one electron unpaired and configuration the electrons as (t_2g^5 eg^0) because of the strong ligand. The hybridization is d^2sp^3[25,41].

Cobalt(III) – Complex

The electronic spectrum of this complexes show two absorption bands , the first band located at 527 nm (18975 cm^{-1}) due to $^1A_1g \rightarrow {}^1T_1g_{(F)}$ transition while the second band appear at 424 nm (23585 cm^{-1}) attributed to $^1A_1g \rightarrow {}^1T_2g$ transition. The absorpation band 221 nm (45249 cm^{-1}) du to ligand centrated transition . The Co(III) - complex was found to be diamagnetic with low spin behavior. The magnetic moment of this complex has been found to be 0.08 B.M. This may also indicate that Co(II) ion is oxidized to Co(III) ion during complexation. The change of oxidation state a greement with earlier observation that show the a queaous solution of Co(II)salt is spontaneously oxidized to Co(III) in the presence of strong ligand such as azo imidazole compounds which may be suggest an arguler structer (t_2g^6 eg^0) and d^2 sp^3 hybridization [24,32,42].

Nickel (II) – Complex

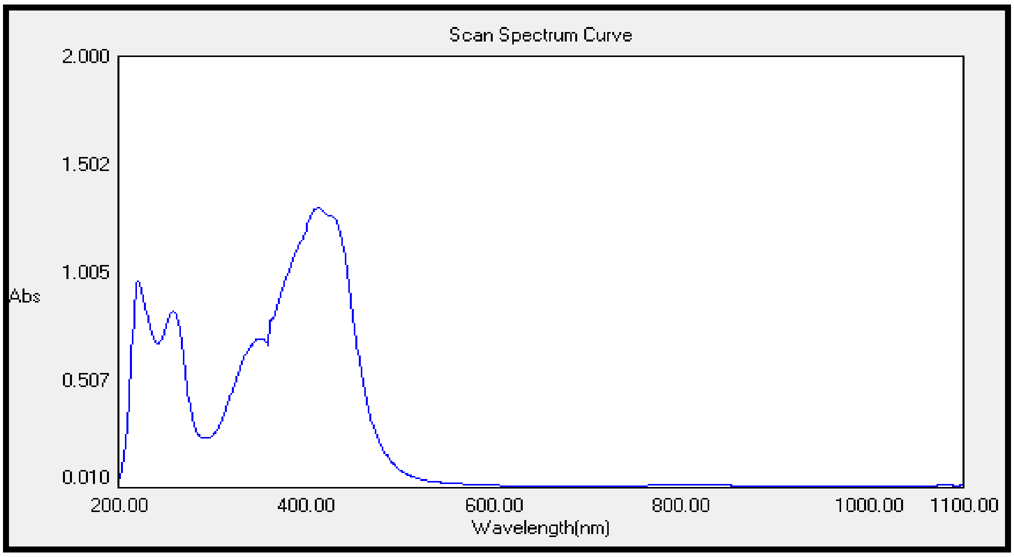
The electronic spectrum of Ni(II) - complex show tow absorption bands , spin allowed transitions at 479 nm (20877 cm^{-1}) and 281 nm (35587 cm^{-1}) corresponding to $^3A_2g \rightarrow {}^3T_1g_{(F)}$ and ligand centered respectively. There are the υ_2 and υ_3 bands [43]. The third spin allowed absorption band υ_1 was not observed but were calculated by using υ_2 and υ_3 bands positions , the calculated value is 1092 nm (9157 cm^{-1}).The magnetic moment measurement was found to be 3.16 B.M whach can be anormal value because of presence two unpaired electrons which may be suggests octahedral high spin a rgular geometry (t_2g^6 eg^2) and sp^3d^2 hybridization [44].

Copper(II) – Complex

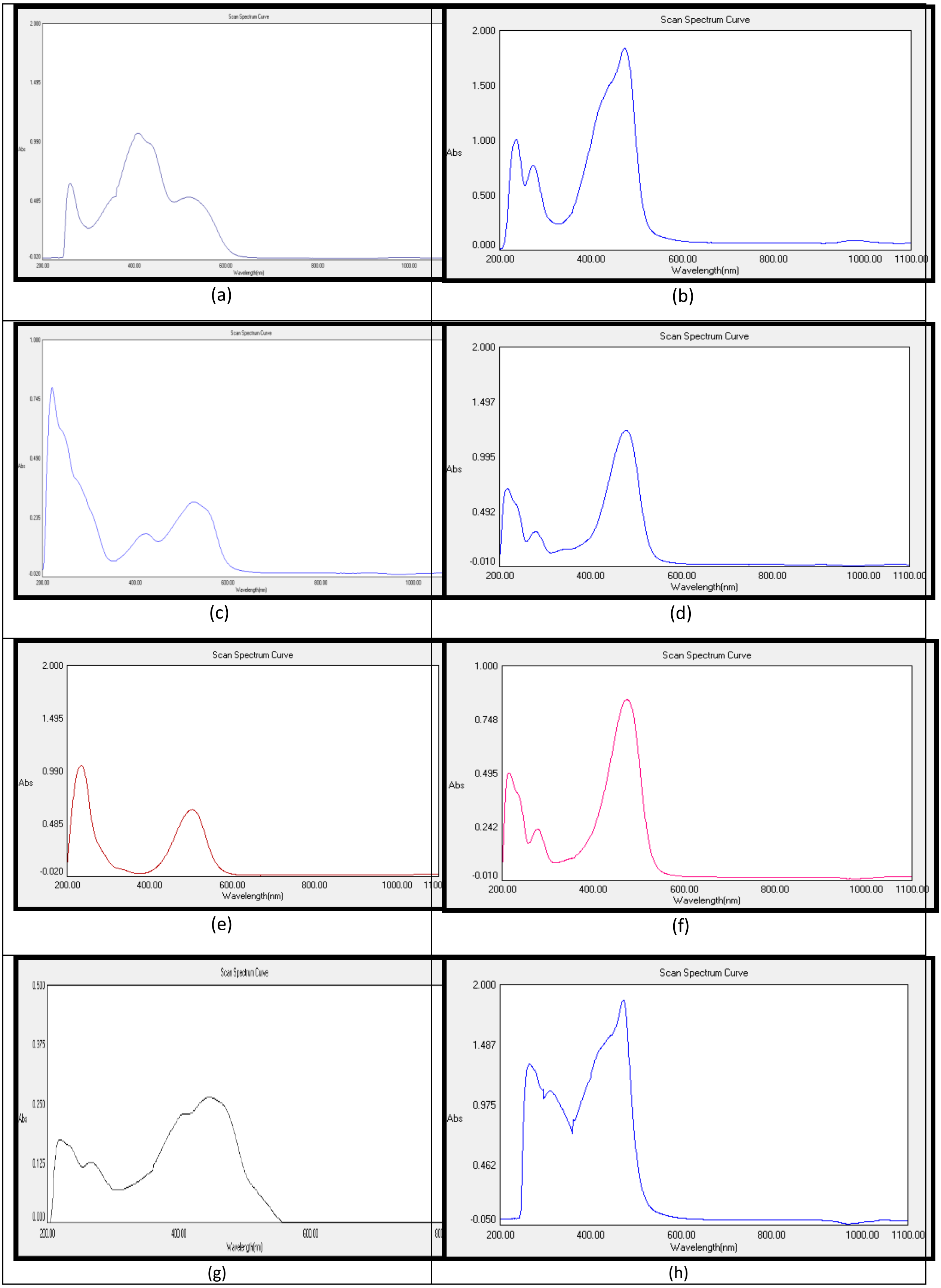
The UV-Visb. spectrum of Cu(II) – complex show a broad absorption band around at 505 nm (19802 cm^{-1}) in 10^{-3}M absolute ethanol attributed to $^2B_2g \rightarrow {}^2A_2g$ transtion . The absorption band at 235 nm (42553 cm^{-1}) assigned to ligand centered transition . The value of magnetic moment for this complex is found to be 1.76 B.M due to presence one electron un paired which may be suggest a distorted octahedral geometry (z-in or z-out) and sp^3d^2 hyhridization .

Zinc(II) , Cadmium (II) and Mercury (II) Complexes

The solution electronic spectra of these complexes do not show any d-d transition because are saturated with electrons (d^{10}). The absorption bands at longer wave length 475 nm (21053 cm^{-1}) , 432 nm (23148 nm) and 447 nm (22371 cm^{-1}) these are due to a charge transfer (M→ L,CT) transtions to Zn(II), Cd(II) and Hg (II) complexes respectively. These transition may be referred to the combination of MLCT[$d\pi(M^{+2}) \rightarrow \pi^*$ (L)] transitions where π^* (L) is believed to be primarily dominated by the LUMO of the azoimine chromophore[45,46]. The magnetic susceptibility measurments show that all complexes have diamagnetic moments with the d^{10} configuration and sp^3d^2 hybridization for these complexes.



Figure(8) :- Absorption spectrum of ligand (DMCPAI)



(a) (b) (c) (d) (e) (f) (g) (h)

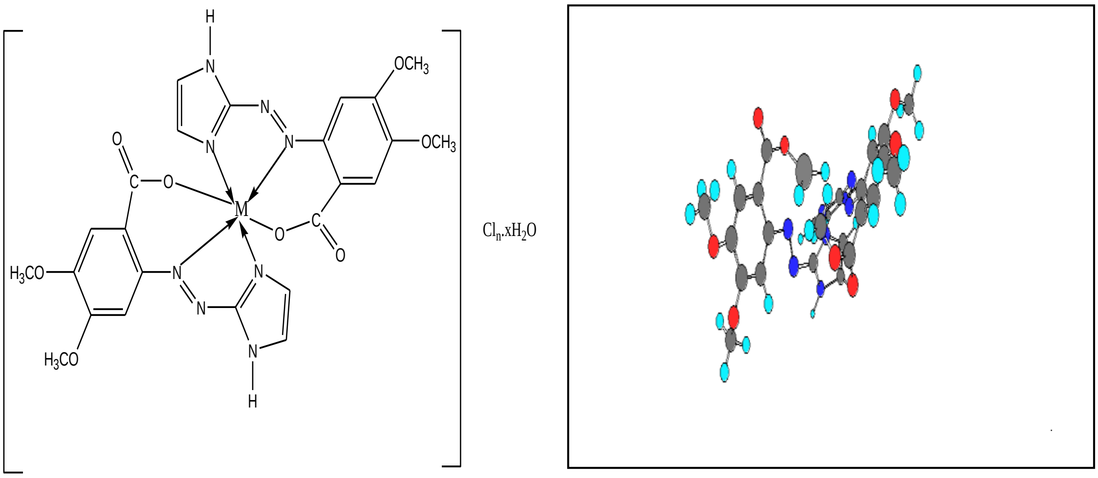
Figure(9):- Absorption spectra (a) Cr(III)- Complex, (b) Mn(II) -Complex (c) Co(III) – Complex , (d)Ni(II) -Complex, (e) Cu(II) - Complex, (f) Zn(II) - Complex, (g) Cd(II) - Complex and (h) Hg(II) – Complex

Table(4):- Electronic spectra (nm , cm^{-1}), magnetic moments, geometry and hybridization

Compounds	λ_{max} (nm)	Absorption bands(cm^{-1})	Transitions	μ_{eff} (B.M)	Geometry	Hybridization
Ligand=HL (DMCPAI)	222	45045	$\pi \rightarrow \pi^*$	-------	-----------	--------------
	259	38610	$n \rightarrow \pi^*$			
	413	24213	$\pi \rightarrow \pi^*$			
$[Cr(L)_2].Cl$	261	38314	Center ligand	3.56	Octahedral regular	d^2sp^3
	409	24450	${}^4A_2g \rightarrow {}^4T_1g_{(F)}$			
	520	19231	${}^4A_2g \rightarrow {}^4T_2g$			
$[Mn(L)_2]$	237	42194	Center ligand	1.83	distorted (Z-out)	d^2sp^3 (Low spin)
	274	36496				
	468	21367	${}^2A_1g \rightarrow {}^4T_1g_{(G)}$			
	979	10214	${}^2A_1g \rightarrow {}^4T_1g_{(P)}$			
$[Co(L)_2].Cl$	221	45249	Center ligand	0.08	Octahedral regular	d^2sp^3 (Low spin)
	424	23585	${}^1A_1g \rightarrow {}^1T_2g$			
	527	18975	${}^1A_1g \rightarrow {}^1T_1g_{(F)}$			
$[Ni(L)_2]$	281	35587	Center ligand	3.16	Octahedral regular	Sp^3d^2 (high spin)
	479	20877	$A_2g \rightarrow {}^3T_1g_{(F)}{}^3$			
	1092	9157	$A_2g \rightarrow {}^3T_2g^3$			
$[Cu(L)_2]$	235	42553	Center ligand	1.75	distorted (Z-in or Z-out)	Sp^3d^2
	505	19802	$B_2g \rightarrow {}^2A_2g$ ^{2}			
$[Zn(L)_2]$	475	21053	$d\pi(Zn)^{+2} \rightarrow \pi^*(L)$	Dia	Octahedral regular	Sp^3d^2
$[Cd(L)_2]$	432	23148	$d\pi(cd)^{+2} \rightarrow \pi^*(L)$	Dia	Octahedral regular	Sp^3d^2
$[Hg(L)_2].H_2O$	447	22371	$d\pi(Hg)^{+2} \rightarrow \pi^*(L)$	Dia	Octahedral regular	Sp^3d^2

B.M= Bohr magneton

According to these results and discussed the data through different techniques suggest the structural formula of prepared metal complexes in this work may be proposed in figure(10) , shown below :-

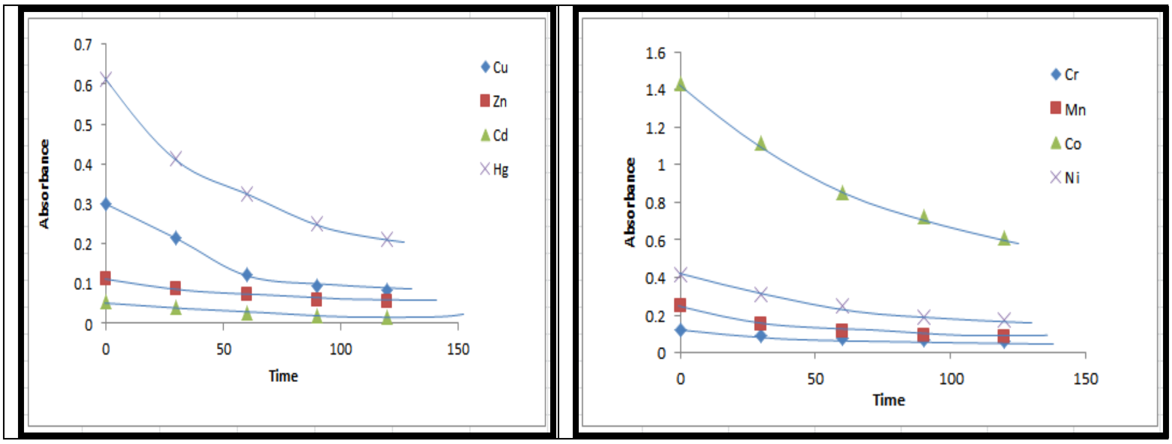


M= Cr(III) and Co(III) ; n=1 ; x=0, M= Mn(II) ;Ni(II) ; Cu(II) ; Zn(II) and Cd(II) ; n=0 ; x=0
M=Hg(II) ; n=0 ; x=1
Figure(10):-The suggest structural formula of Cr(III) , Mn(II) , Co(III) , Ni(II) , Cu(II) , Zn(II) , Cd(II) and Hg(II) complexes.

Photo decomposition of complex

The effect of irradiation time

This study showes the effects of irradiation time on the decomposes rate of the complexes during the periods of time confined to extent of between 0-120 min and the absorbance was measured at that time,noting that the absorption spectrum complexes when all wavelength was below with an increase of the irradiation time the result are shown in figure.(11),which shows the absorption spectrum.

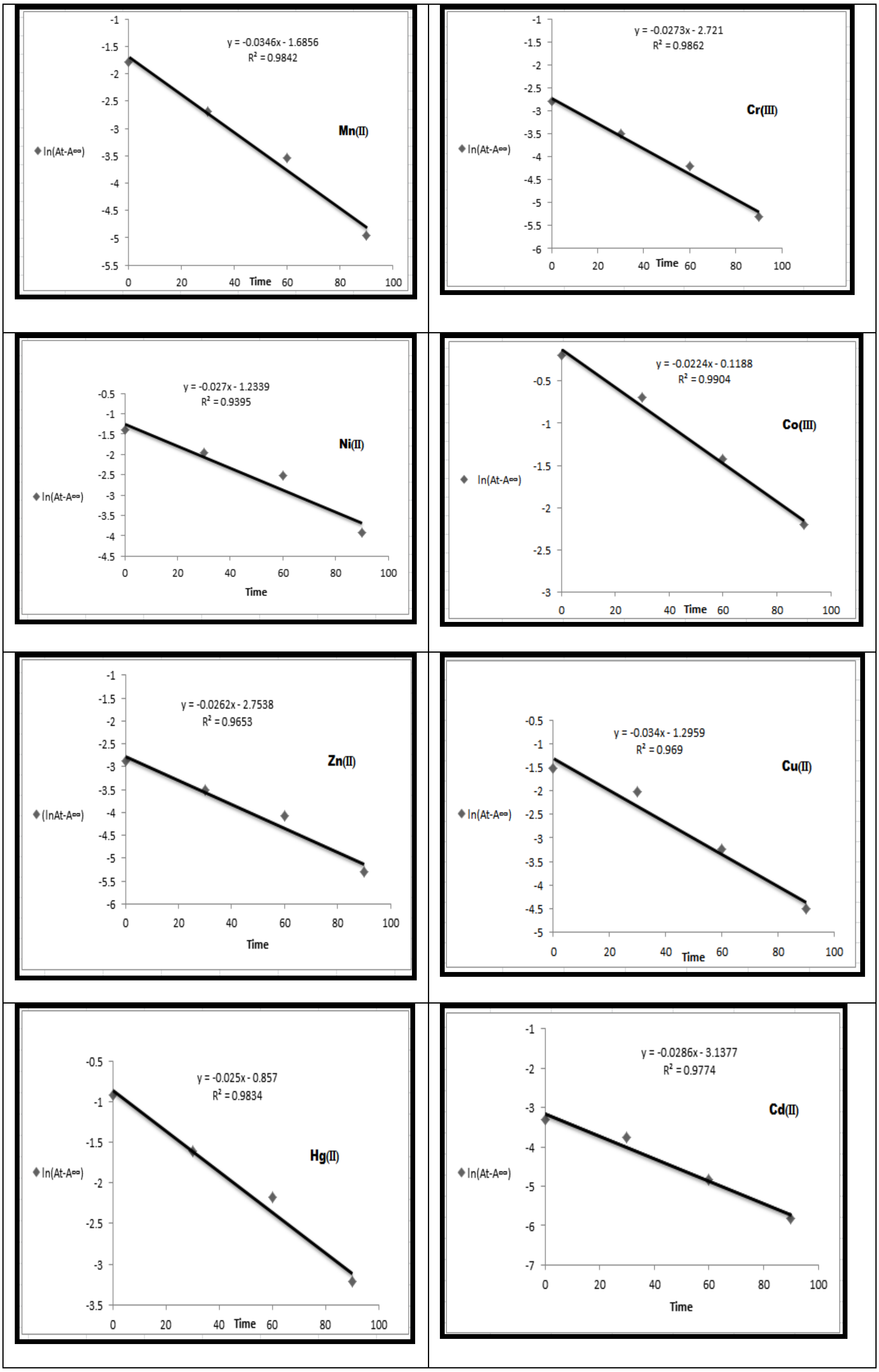


Figure(11) :- Effect of irradiation time on the decomposition rate of the complexes

A ppointed as rate constant to the decomposition of the metal complexes k_d mediated reaction rate equation of the first order $\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_d t$ the result are shown in figure (12) and table(5) [47].

Table(5) :- values k_d of metal complexes.

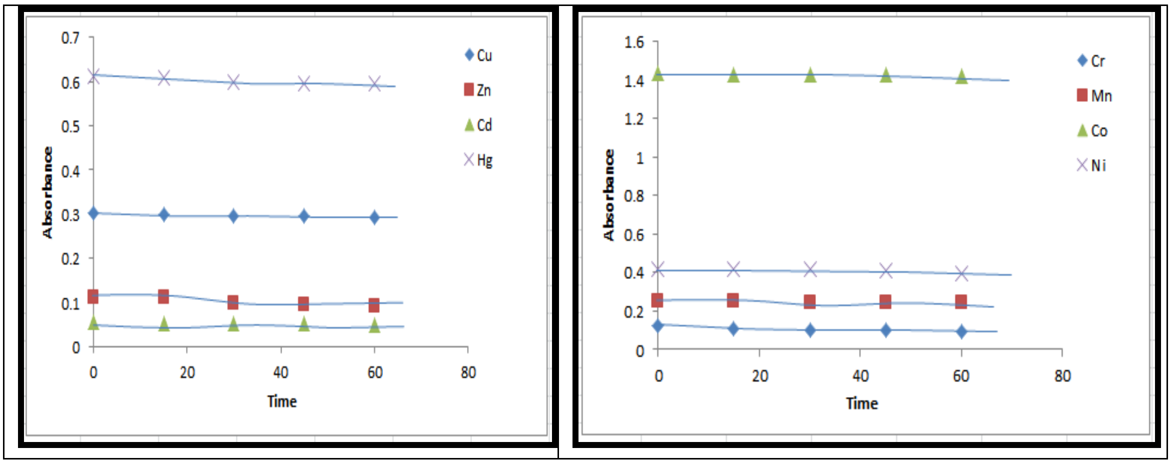
complex	k_{d} (s^{-1})
$[Cr(L)_2].Cl$	0.024
$[Mn(L)_2]$	0.030
$[Co(L)_2].Cl$	0.016
$[Ni(L)_2]$	0.019
$[Cu(L)_2]$	0.017
$[Zn(L)_2]$	0.021
$[Cd(L)_2]$	0.015
$[Hg(L)_2].H_2O$	0.023



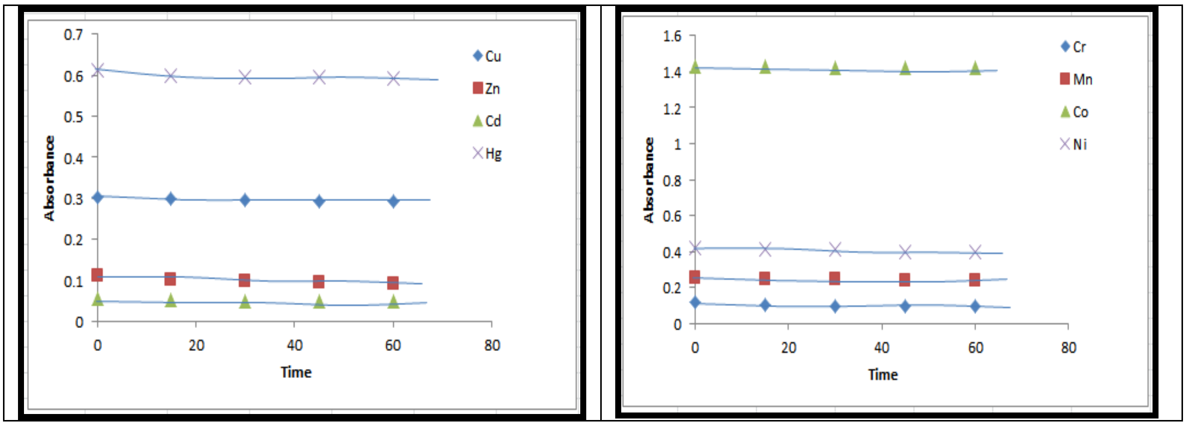
Figure(12):-Values k_d of metal complexes

Dark decomposition

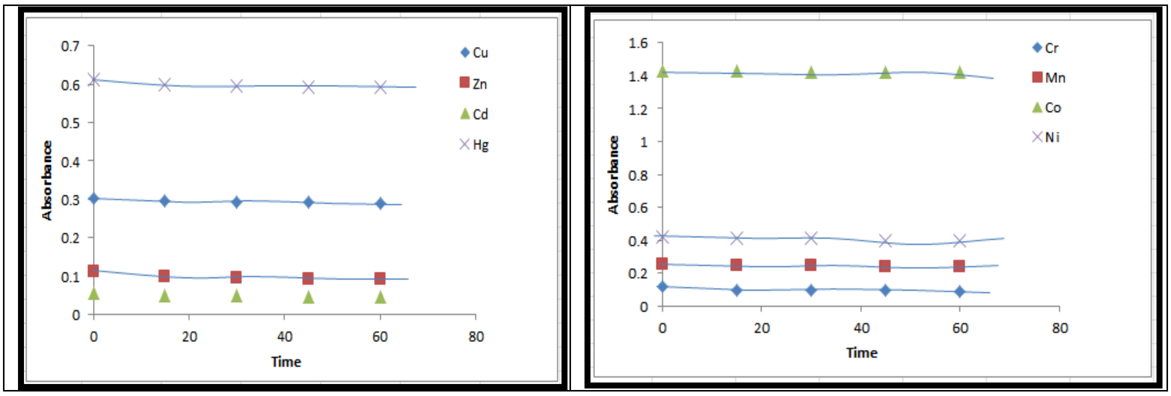
The study includes impact of the change in temperature rang [40 - 70] °C on the decomposition rate of the metal complexes during the periods of the time confined to extent of between 0-60 min and the absorbance was measured at that time noting that the absorption spectrum complexes when all wavlenght was smoll chang with an increase of the time result the metal complexes is high stability of and the result are shown in figures 13, 14, 15 and 16 .



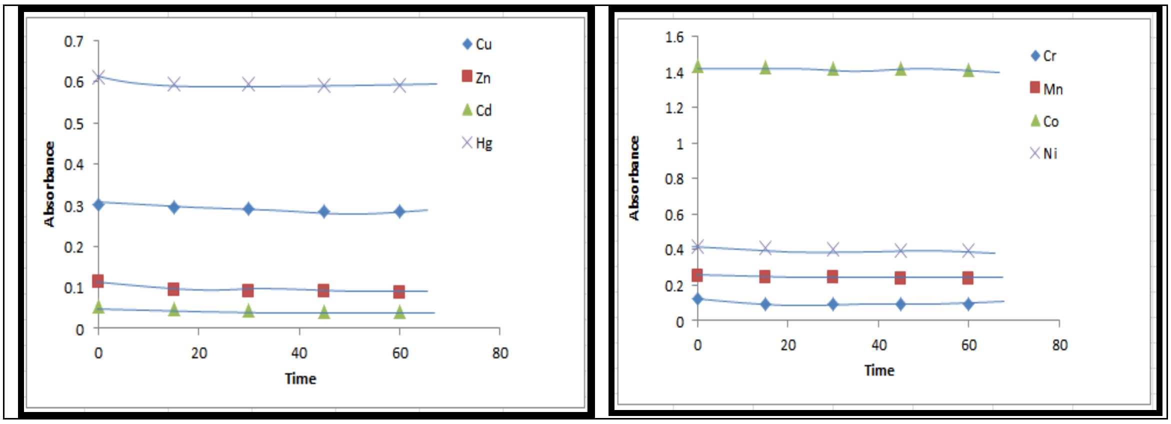
Figur(13) :- Values absorption of metal complexes versus time in 40 °C , PH =7.0



Figur(14) :- Values absorption of metal complexes versus time in 40 °C , PH =7.0



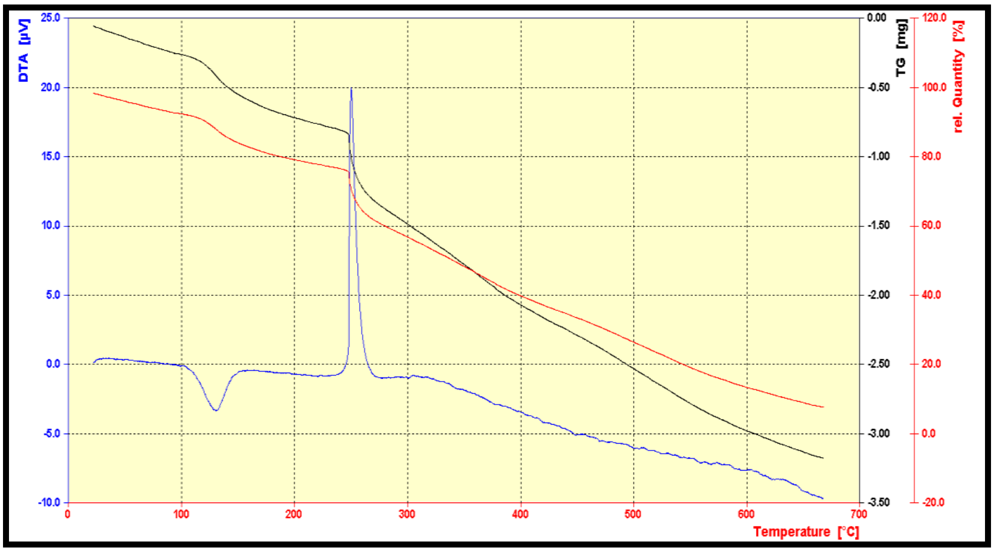
Figur(15) :- Values absorption of metal complexes versus time in 60 °C , PH =7.0



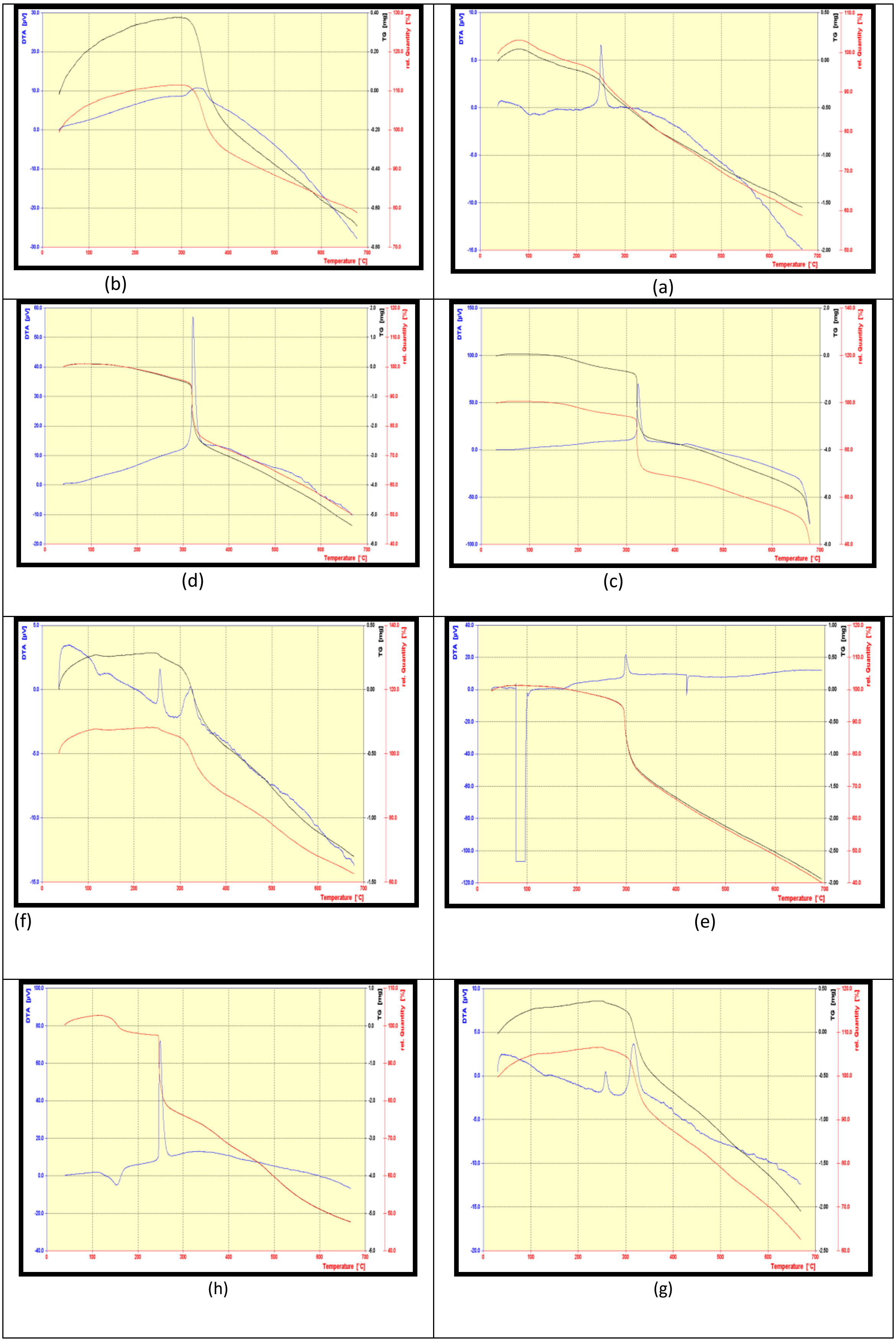
Figur(16) :- Values absorption of metal complexes versus time in 60 °C , PH =7.0

Thermal studies

The thermal properties of ligand and transition metal complexes were examined from ambient temperature up to 700 °C by thermogravimetric (TGA) and deferential thermal analysis (DTA) in nitrogen atmosphere as illustrated in figures 17 and 18 [48,49,50] . The temperature , percentage weight loss and expected decomposition compounds were listed in table(6). The TGA Gurve reveals the ligand of the decompose in to steps shows in figure(17), in the temperature rang 100-200 °C in the first step which is rapid ligand losses at 124 °C volatile matel CO_2 and moisture,DTA Gruve shows endothermic peak in second step at temperature rang 200-300 °C The ligand losses carboxyl group (COOH) in temperature 251 °C with an estimated mass loss 16.31% then the thermogram of ligand showed stability then decomposes every up to 700 °C. The thermogram of Cr- complex showed stability up to 248 °C the complex decomposes the losses methoxy group and one hydrogen atom with enestimated mass loss 5.02% , DTA Gurve shows exothermic peak then chromium oxid Cr_2O_3 was produced up to 700 °C. The thermogram of Mn- complex showed stability up to 332 °C the complex decomposes the losses methoxy group and one hydrogen atom with enestimated mass loss 5.3% , DTA Gurve shows exothermic peak then Manganese oxid Mn_3O_4 was produced up to 700 °C. The thermogram of Co- complex showed stability up to 324 °C the complex decomposes the losses methoxy group and one hydrogen atom with enestimated mass loss 4.96% , DTA Gurve shows exothermic peak then Cobalte oxid Co_3O_4 was produced up to 700 °C. The thermogram of Ni- complex showed stability up to 321 °C the complex decomposes the losses methoxy group and one hydrogen atom with enestimated mass loss 5.25% , DTA Gurve shows exothermic peak then Nickel oxid NiO was produced up to 700 °C. The thermogram of Cu-complex showed stability up to 298 °C the complex decomposes the losses methoxy group and one hydrogen atom with enestimated mass loss 5.22% , DTA Gurve shows exothermic peak then Cupper oxid CuO was produced up to 700 °C. The Zn- complex decompose in two step in the temperature rang 200-300 °C in the first step , the complex decompose at 260 °C the losses methoxy group and one hydrogen atom enestimated mass loss 5.02% , DTA Gurve shows exothermic peak. in second step at temperature rang 300-400 °C The complex losses carbonyl group (CO) in temperature 327 °C with an estimated mass loss 4.54% DTA Gurve shows exothermic peak then Zink oxid ZnO was produced up to 700 °C. The Cd- complex decompose in two step in the temperature rang 200-300 °C in the first step , the complex decompose at 260 °C the losses methoxy group and one hydrogen atom enestimated mass loss 4.83% , DTA Gurve shows exothermic peak. in second step at temperature rang 300-400 °C The complex losses carbonyl group (CO) in temperature 312 °C with an estimated mass loss 4.23% DTA Gurve shows exothermic peak then Cadmium oxid CdO was produced up to 700 °C. The Hg- complex decompose in two step in the temperature rang 100-200 °C in the first step , the complex decompose at 153 °C the losses H_2O molecule enestimated mass loss 2.34% , in second step at temperature rang 200-300 °C The complex losses methoxy group and one hydrogen atom in temperature 254 °C with an estimated mass loss 4.16% DTA Gurve shows exothermic peak then Mercury oxid HgO was produced up to 700 °C.



Figure(17) :-TG-DTA diagramof ligand (DMCPAI)



(b) (a) (d) (c) (f) (e) (h) (g)

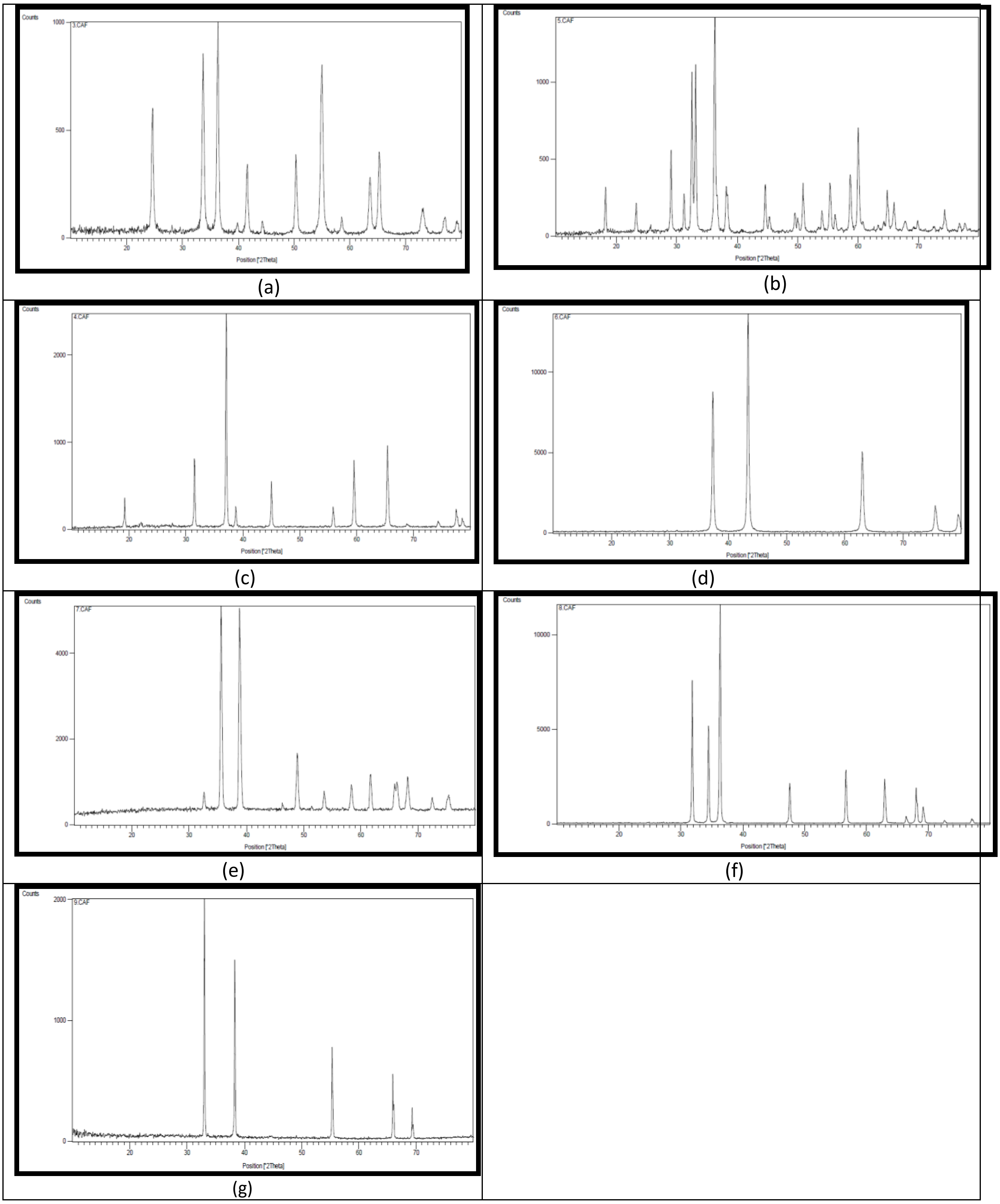
Figure(18):-TG-DTA diagram of (a) Cr(III)- Complex, (b) Mn(II)-Complex (c) Co(III) - Complex, (d) Ni(II) - Complex, (e) Cu(II) - Complex, (f) Zn(II) - Complex, (g) Cd(II) - Complex and (h) Hg(II) – Complex

Table (6):-Thermal analysis result of the complexes

Compound	TGA Reang °C	Mass Loss %	Assiment
$C_{12}H_{12}O_8N_8$	100-200	----------	Volatiles matrial
(DMCPAI)	200-300	16.31	COOH group
$[Cr(C_{12}H_{11}O_8N_8)_2].Cl$	200-300	5.02	H Atom and CH_3O
$[Mn(C_{12}H_{11}O_8N_8)_2]$	300-400	5.3	H Atom and CH_3O
$[Co(C_{12}H_{11}O_8N_8)_2].Cl$	300-400	4.96	H Atom and CH_3O
$[Ni(C_{12}H_{11}O_8N_8)_2]$	300-400	5.25	H Atom and CH_3O
$[Cu(C_{12}H_{11}O_8N_8)_2]$	200-300	5.22	H Atom and CH_3O
$[Zn(C_{12}H_{11}O_8N_8)_2]$	200-300	5.02	H Atom and CH_3O
	300-400	4.54	C=O group
$[Cd(C_{12}H_{11}O_8N_8)_2]$	200-300	4.83	H Atom and CH_3O
	300-400	4.23	C=O group
$[Hg(C_{12}H_{11}O_8N_8)_2].H_2O$	100-200	2.34	H Atom and CH_3O
	200-300	4.16	C=O group

XRD Analysis of product thermal analysis

The diffractograms of metal oxides were illustrated in figure(19). The X-ray diffractogram of metal oxids Cr(III), Mn(II), Co(III), Ni(II), Cu(II), Zn(II) and Cd(II) were scanned in the rang $2\theta=(18\text{-}80)°$ the diffractogram and associated data depict 2θ values for each peak ,relative intensity.The diffractogram of Cr_2O_3 had ten reflection with maxima at 2θ =36.3062.The diffractogram of Mn_3O_4 had thirteen reflection with maxima at 2θ =36.2787.The diffractogram of Co_3O_4 had eight reflection with maxima at 2θ =37.0511.The diffractogram of NiO had five reflection with maxima at 2θ =43.3792. The diffractogram of CuO had Nine reflection with maxima at 2θ = 35.6184.The diffractogram of ZnO had eight reflection with maxima at 2θ = 36.3027. The diffractogram of CdO had five reflection with maxima at 2θ = 33.0210 [51, 52].



(a)

(b)

(c)

(d)

(e)

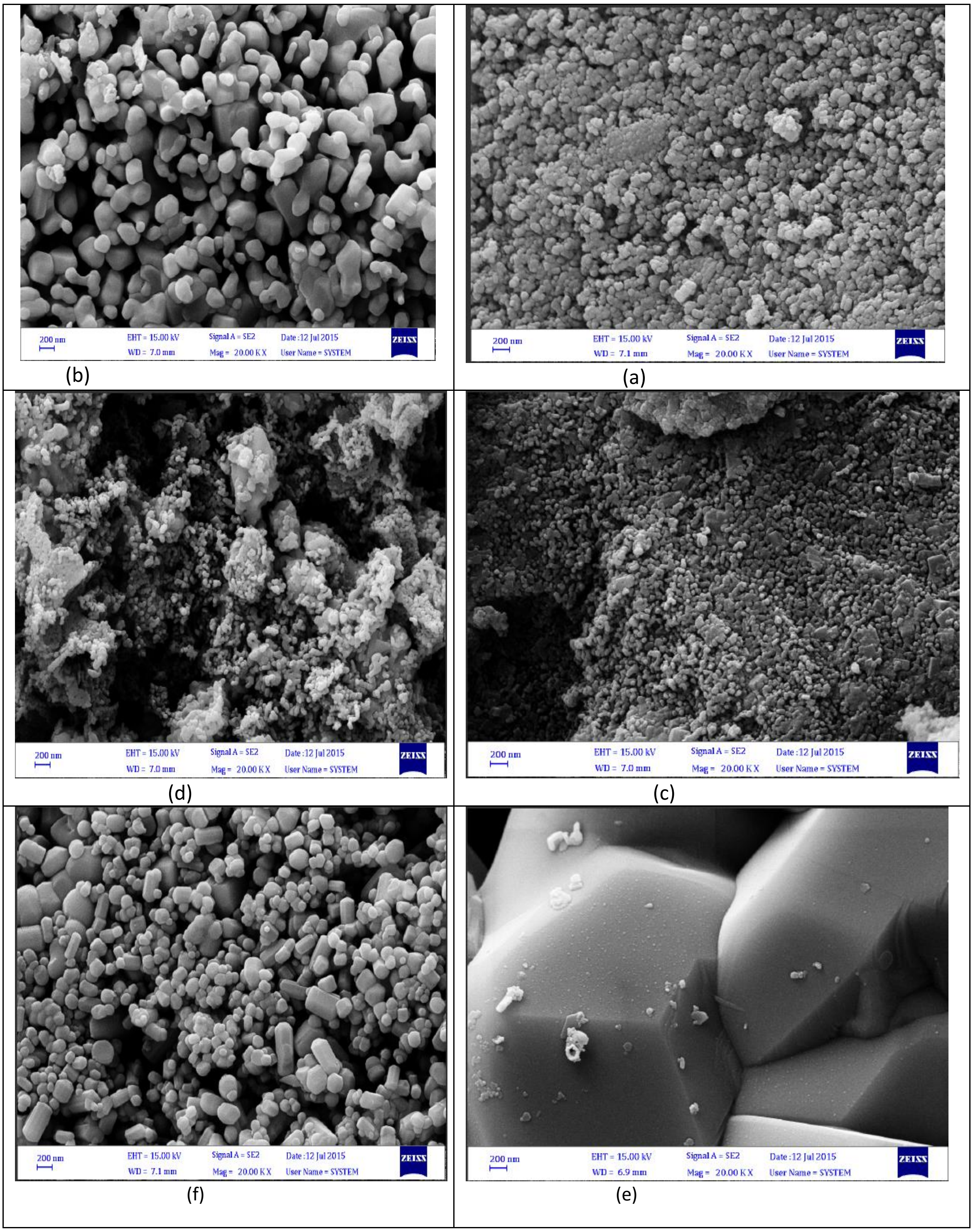
(f)

(g)

Figur(19):- X-RD patterns of (a) Cr_2O_3 , (b) Mn_3O_4 , (c) Co_3O_4 , (d) NiO , (e) CuO , (f) ZnO , (g) CdO

SEM Analysis

The oxids show different morphologies as illustrated in figure (20) .The SEM of Cr_2O_3 seemed homogeneous surfaced type with average size 59 nm.The SEM of Mn_3O_4 seemed homogeneous surfaced type with average size 50 nm. The SEM of Co_3O_4 seemed homogeneous surfaced type with average size 125 nm. The SEM of NiO seemed homogeneous surfaced type with average size 67 nm. The SEM of CuO seemed hetrogeneous surfaced type with average size 250 nm. The SEM of ZnO seemed homogeneous surfaced type with average size 59 nm[53,54,55].



(b) (a)

(d) (c)

(f) (e)

Figure(20) :- SEM images of (a) Cr_2O_3 , (b) Mn_3O_4 , (c) Co_3O_4 , (d) NiO , (e) CuO and (f) ZnO

CONCLUSIONS

In this work we report synthesis , spectra charactercterization and photo thermal decomposition of new tridentate hetrocyclic azo dye ligand (DMCPAI) derived from imidazole and its metal complexes with Cr(III) , Mn(II) , Co(III) , Ni(II) , Cu(II) , Zn(II) , Cd(II) and Hg(II) metal ions. The isolation sold metal complexes were characterization by available techinques and having octahedral geometry. The azo dye ligand (DMCPAI) behaves as a tridentate agent coordination through the postion of carboxylic oxygen , nitrogen of azo group (N_3) which is the farthest of imidazole ring and nitrogen of imidazole ring (N_3) to form five and six memberd metal ring. The molare conductivity measurments suggest the presence of chloride ion outside the coordination ring in Cr(III) and Co(III) complexes and 1:1 electrolyte nature but non electrolyte nature in rest metal complexes. The ligand and its complexes different morphologies as appeared in XRD and SEM studies. The thermal stability of ligand and its metal complexes had good thermal stability.The prepared metal complexes showed important application in photo reaction when using them as sensitizers.

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