SPECTRAL, STRUCTURAL AND THERMAL STUDIES OF THE DIVALENT METAL ION COMPLEXES OF PHENYLHYDRAZOETHYLACETOACETATE HYDRAZONE

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Abstract

Metal complexes of phenylhydrazoethylacetoacetate hydrazone derived from phenylhydrazoethyl acetoacetate and thiosemicarbazied (HL) are reported and characterized based on elemental analyses ,IR , electronic spectra, magnetic moment , molar conductance, ESR and thermal analyses . The molar conductance data reveal that the complexes are non-electrolytes while Mn(II) complex is electrolytes.IR spectra show that the ligand (HL) coordinated to the metal ions in a tridentate manner with ONS doner sites . TGA and DTA showed that the complexes are thermally stable. The data of thermal analyses and the calculated activation kinetic parameters of the decomposition of the prepared complexes show that the thermal stability of metal complexes depends essentially on the nature of both the central metal ion and the ligand.

Keywords: Complexes , IR , ESR Spectra , thermal studies , Conductivity , Synthesis

1.Introduction :

Hydrazones were widely applied in the field of insecticides, medicines and analytical reagents for their excellent bioactivity properties(Gup and Kirkan2005). Coordination chemistry of metal complexes of hydrazones (Song1994) has gained a special attraction due to their biological activity and their ability to act as potential inhibitors for many enzymes (Dun1996 and Cunha2002). Hydrazone derivatives possessing anti-inflammatory, analgesic (Murineddu2002 and Sondhi2006), antipyretic (Sridhar2001), antibacterial (Kalluraya2004) and antitumor (Kashar1998) activities are also reported in the literature.Mononuclear and binuclear Zn(lI), Cd(lI) and Hg(II) complexes of orthohydroxybenzeneazoethylacetoacetate isonicotinoyl hydrazone (H_3L), have been synthesized and characterized by elemental analyses, IR, 1H NMR and VlS-UV spectra, conductance and thermal analyses. The ligand behaves as tetradentate in mononuclear complexes and hexadentate in binuclear complexes. The molar conductance of the complexes has been discussed (Bahnasawy1995). Hydrazone ligands can act as bidentate, tridentate or tetradentate ligands depending on the nature of heterocyclic ring substituents attached to the hydrazone unit (Kashar2005and Samus2004). These ligands due to their facile keto–enol tautomerization and the availability of several potential donor sites can coordinate with metals (Kuriakose2007).

In this paper we describe the synthesis, characterization and thermal (DTA and TGA) studies of some divalent metal ion complexes based on hydrazone derived from condensing phenylhydrazoethylacetoacetate with thiosemicarbazide (HL).

2.Experimental:

All compounds and solvents used were pure chemicals from BDH or Aldrich and used as received. The ligand was prepared by mixing ethanolic solutions of thiosemicarbazide (TSC) (0.05mol) and phenylhydrazoethylacetoacetate (0.05mol) with reflux for 3hrs. The resulting product was filtered off and crystallized from ethanol. The complexes were prepared by the following general method. To a hot ethanolic solution of thiosemicarbazone 0.05 ml of metal salts (MCl_2) were added where M= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in (1 : 2) metal : ligand stoichiometric ratio. The reaction mixture was refluxed on a water bath for 5 hours. The formed complexes were filtered off, washed several times with pure dry methanol and dried in vacuo over anhydrous $CaCl_2$.

3.Measurements

Elemental analyses (C, H, N, Cl and S) were carried out at the microanalytical Unit of the University of Cairo. Metal ions were determined using atomic absorption with a Perkin Elmer (model 2380) spectrophotometer. The IR spectra were measured as KBr discs using a Perkin-Elmer 1430 infrared spectrometer (4000-200) cm^{-1}). Electronic absorption spectra in the 200-900 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. The thermal analyses (DTA and TGA) were carried out on a Shimadzu DT-30 and TG-50 thermal analyzers in the 27-800^{o}C range at a heating rate of 10^{o}C.min^{-1}. The magnetic susceptibilities were measured at room temperature using the Gouy method with mercuric tetrathiocyanatocobaltate(II) as magnetic susceptibility standard; diamagnetic corrections were made using Pascal’s constants (El-Tabl1996).

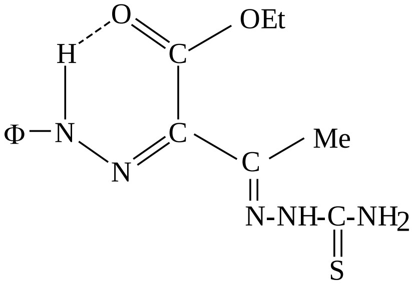
All solid ESR measurements at room temperature were carried out using Joel spectrometer model JES-FE 2XG equipped with an E101 microwave bridge. DPPH was used as a standard material. A Bibby conductimeter MCl was used for conductance measurements.

4.Results and discussion:

The prepared ligand and its metal complexes were subjected to elemental microanalysis; the data are listed in table 1. The results of analysis for the complexes with the ligand phenylhydrazoethylacetoacetate thiosemicarbazone (PHTSC) was found in accordance with the formation of complexes of the composition (MLCl).nH_2O for the divalent metal ions copper, cobalt, nickel and zinc. Whereas, Mn(II) complex was formed as $Mn(HL)_2Cl_2$. All the complexes are brown and orange in color which is common for complexes involving thiosemicarbazone coordination resulting from the sulfur to metal charge transfer bands (Suni2007). The complexes are insoluble in most common organic solvents but soluble in DMF and DMSO. Molar conductance indicates that the complexes are non-electrolytes except manganese complex (Table 1).

4.1.IR spectra

The IR spectrum shows bands at 3320, 3190, 1700 and 1040 cm^{-1} assigned to υNH_2, υNH, υC=O and υC=S respectively. The broadening of the υNH_2 and the shift of υC=O to higher frequency than expected is due to an intramolecular hydrogen bond formed between NH group and C=O group. The spectrum shows also a band at 1630 cm^{-1} assigned to azomethine linkage of the ligand(Kashar2010). The band appears at 925 cm^{-1} is assigned to υN-N vibration (El-Saied2001). Depending on these data the following structure is suggested:



The bonding of the ligand to the metal ions was investigated by IR spectroscopy. The IR spectra for the free ligand differ from those of their complexes and provide significant indications regarding the bonding sites of the ligand. IR spectral assignments of the ligand and the complexes are listed in (Table2). The spectra of the metal complexes compared with that of the free ligand reveals that the presence of water molecules in the prepared divalent complexes is assigned by the presence of the broad band around 3400 cm^{-1} which is usually assigned to OH stretching modes of lattice water and two weaker bands around 950 and 800 cm^{-1} which could be assigned to out of plane deformation modes of OH bands stretching, rocking and wagging modes of vibrations (Srinivasan2004). The IR spectra of the divalent metal complexes except Mn(II) complex show the disappearance of νNH and νC=S at 3260 and 1040 cm^{-1} of the ligand and appearance of new bands around 1595 cm^{-1} and at 1530-1450 cm^{-1} which assigned to azine group νC=N-N=C(Iskender 1976and Patil1981) and νN=C-S(Ghosh1989) respectively. The disappearance of νC=S at 1040 cm^{-1} of the ligand and appearance of νN=C-S in the complexes formation suggest thiolization of the ligand and the reaction of the thiol-form with the elimination of a proton and bonding to the metal through the deprotonated C=S group(Nakamoto1978). The azine group appeared in the spectra of the complexes at lower energy compared to the normal range for vibration of the free ligand results from a decrease in the C=N double bond strength owing to the coordination by one of the two nitrogen atoms of the azine group. This result is in accordance with the expectation that N-coordination to a metal ion having filled π-orbitals should result in a shift towards the lower energy region in the νC=N (Butcher1976). The significant change in the ligand bands upon coordination is the increase of N-N frequency. The band at 980 cm^{-1} assigned to νN-N of the ligand is shifted to higher value of the complexes. Such movement of this band may be explained by the coordination of one of the two nitrogen from each N-N group to the metal ion, this cause the reduction of the lone pair-lone pair repulsive forces in the adjacent nitrogen atom (D. Demertzi 1983, Harison 1984 andPerlepes1985). The appearance of νN=C-S at 1530-1450 cm^{-1} and the shift of νN-N which is observed at higher frequency than that of the free ligand on complexation confirm the coordination of the azomethine nitrogen to the metal ions (Baribanti1968). This shift is due to coordination of nitrogen atom of the azomethine group to the metal ion which reduces the electron density on the azomethine linkage. On the other hand, the shift of the νC=O to the lower frequency confirming that the complexes are formed via thiolized C=S group and azomethine nitrogen indicating that the ligand acts as monobasic tridentate ligand toward metal ions in each complex. In the spectra of the Mn(II) complexes ,the band assigned to νC=S and νC=O are shifted to higher wavenumber. Whereas, the azomethine group νC=N is shifted to lower frequency providing a strong evidence that the ligand coordinated around the Mn ion via carboyl oxygen, thionyl sulfur and azomethine nitrogen (Rapheal2007). These results indicate that the metal ions are bonded to the ligand molecule through covalent bonding and coordination bond to the azomethine nitrogen and carbonyl oxygen in the complexes(Mendes1999and Beraldo 2002). This confirmed by the appearance of medium bands at Ca 510 cm^{-1} corresponding to νM-O (Broomhead 1967)and the bands at 470-450 cm^{-1} and 390–375 cm^{-1} in the spectra of the complexes were attributed to the νM-N and νM-S vibrations (Lima1999).

4.2.Electronic absorption Spectra and magnetic moment .

The electronic absorption spectra of the complexes under study are summarized in Table 3. The electronic spectra of thiosemicarbazone show bands at 245 and 305 nm assigned to π-π∗ and n-π∗ of C=S respectively (Bindu1999). Also, the spectrum show bands at 285, 315, 323 and 335 nm assigned to π-π∗ and n-π∗ of C=O and C=N respectively. The formation of complexes occurs through thiolized form of the ligand and bonding to carbonyl oxygen and azomethine nitrogen. This is confirmed by the disappearance of the bands corresponding to π-π∗ and n-π∗ transitions of C=S and the bands of the π-π∗ and n-π∗ transitions of C=N and C=O bands has shown a blue shift due to donation of lone pair of electrons to the metal and hence the coordination of azomethine and carbonyl group with a reduction of intensity (Philip2006and Kashar2011). In the spectrum of cobalt (II) complex the band observed at 352 nm may assigned to C.T. of intraligand or due to L→Co or Co→L C.T. interaction. The band appears at 420 nm corresponding to $^2B_2g—^2T_2g$ electronic state indicating a square planar geometry (Nishida 1979)for low spin Co^{2+} complex. The observed magnetic moment 1.67 B.M. is slightly lower than the spin only value for one unpaired electron in the d-orbital. The spectrum of Nickel(II) complex shows a band at 347 nm assigned to intraligand C.T. or may be due to L→Ni or Ni→L C.T. interaction. Also, the spectrum shows a band at 389 nm corresponding to $^3A_2g—^3T_1g$ electronic state transition. The magnetic moment value indicates the presence of two unpaired electrons in the d-orbital and show that the complex is present as tetrahedral arrangement (Hammamm1988and Kumar2002). The copper(II) complex shows a band at 382 nm assigned to intraligand M-L C.T. and two bands at 420 and 550 nm due to d-d transitions assigned to $^2B_1g—^2A_1g$ and $^2B_1g—^2E_1g$ electronic state indicating that the complex is formed in square planar arrangement (Lever1984). The μeff value is around the expected for the spin only value of one unpaired electron in the d^9 copper ion. The zinc (II) complex show a band at 400 nm assigned to intra-molecular charge transfer. The electronic absorption spectra and the diamagnetic character of the Zn^{2+} complex show the tetrahedral geometry (Tamel 2002)around the metal ion. On the other hand, the spectra of Mn(II) complex shows a shift of π-π∗and n-π∗ transitions of C=S to higher wave number and shows a band at 420 nm due to d-d transition corresponding to the $^3A_1g—^3T_1g$ electronic state indicating octahedral arrangement (Goodgame1961). The observed magnetic moment value for Mn^{2+} complex is within the expected value for high spin d^5 complex.

4.3.ESR Spectra

The solid state powder X-band ESR spectra for Mn(II), Co(II) and Cu(II) complexes were measured at room temperature. The g_{eff} values are recorded in table 3. The spectrum of Mn^{2+} complex show a strong broad signal with g_{eff} value 2.45 which are characteristic for octahedral high spin Mn^{2+} complex. The positive deviation of g_{eff} from the value of the free electron 2.0023 can be due to partial increased covalent nature of the bonding between the Mn^{2+} ions and the ligand molecule (Findone1959). The spectrum of the Co^{2+} complex is explained a monomeric high spin d^7 configuration. Eight lines were observed in the high field region from the hyper fine interaction of the unpaired electron spin ^{59}Co. The spectrum exhibits two features assigned to $g_{//} = 2.4$ and $g_{\perp} = 2.03$ characteristic for tetrahedral geometry (Mikuriya1997). The values of $g_{//} > g_{\perp} > 2.0023$ indicating $dx^2\text{-}y^2$ ground state(Symons1979). In the spectra of copper (II) complex the greater value of $g_{//}$ compared to $g_{\perp}$ indicate the presence of the unpaired electron in the ground state $dx^2\text{-}y^2$ orbital (Goodwin1970). The g values support a square planar geometry with covalent nature of the metal ligand bonds (Dubey1994). The value of $G = g_{//} -2/g_{\perp}-2$ equals 3.53, being lower than 4 (Hathaway1970). This could be also attributed to square planar geometry around Cu(II) ions with significant exchange coupling is present(Raman2003). The positive deviation of g_{eff} value (2.51) than that of free electron 2.0023 for the Cu(II) complex may be due to increase of the covalent character of the bond between the Cu^{2+} ions and the ligand. according to the above studies the complexes under investigation were found to have the structures in Fig.(1)

4.4.DTA and TGA Thermal Analyses

phenylhydrazoethylacetoacetate thiosemicarbazone shows a weak endothermic peak without weight loss at 40-50 °C due to the cleavage of hydrogen bond and rearrangement of the ligand which shows a thermal stability behavior up to 210 °C, at which a sharp endothermic peak with weight loss of 71% due to melting with cleavage of the (C=N) and loss of the phenylhydrazoethylacetoacetate group ($C_{12}H_{14}N_2O_2$). The ligand shows another endothermic peaks at 360 and 380°C due to successive decomposition and loss of nitrogen as NO_2 followed by further decomposition. The results of the thermogravimetric analysis of the metal complexes under study show that the divalent metal complexes lost their hydration water below 100°C. The anhydrous complexes lost the chloride moiety within the temperature range 120-185^{o}C and then displayed the decomposition of the organic ligand within the temperature range from 270-650^{o}C leading to formation of the metal oxides. The reactions representing the steps of thermal decomposition can be represented as **follows:**

$$[MLCl].nH_2O \xrightarrow[50\text{-}80\ ^oC]{-nH_2O} [MLCl] \xrightarrow[90\text{-}185\ ^oC]{-Cl} ML$$

$$ML \xrightarrow[270\text{-}650\ ^oC]{\text{further decomposition}} MO_2$$

The first step with TGA peak in the range 50-100 ^{o}C range is related to the volatilization of the lattice water molecules. In most complexes an endothermic chloride moieties from the metal complexes. In the third step of decomposition, the organic ligand is lost in the temperature range from 270-650 ^{o}C with the formation of stable metal oxides. The metal contents were determined from the mass of the residual oxides which was found to agree well with the analytical results within appropriate experimental errors. On the basis of the above results one can conclude the following:

a) water molecules and chloride ions were removed from the prepared complexes at 70-185^{o}C in two intermingled steps,
b) the thermal degradation of the chloride free complex takes place by losing phenylhydrazoethyl acetate part,
c) the remainder part of the complexes undergo further decomposition forming metal oxides.

Mn(II) complex shows a weak exothermic peak at 90^{o}C with a weight loss of 9.6% which is due to the loss of the two chloride molecules followed by a thermal stability behavior up to 320^{o}C, at which the melting occurs with decomposition and loss of the remaining organic portion of the complex with the formation of MnO_2 as a final stable form.

The order, n and the energy of activation E* of the decomposition steps were determined using Coats-Redfern equation (Coats 1964 and Zidan2000) in the form:

$$\ln [1-(1-\alpha)^{1-n} /(1-n)T^{2}] = M/T + B \qquad \text{for } n\neq 1 \qquad (1)$$

$$\ln [-\ln(1-\alpha)/T^{2}] = M/T + B \qquad \text{for } n=1 \qquad (2)$$

Where $M = -E^*/R$ and $B = \ln AR/\Phi E^*$; E*, R, A and Φ are the heat of activation, gas constant, pre-exponential factor and heating rate respectively. The correlation factor, r, is computed using the least squares method for equations (1) and (2). Linear curves were drown for values of n ranging from 0-1. The values of n, which gave the best linear plot was chosen as the order parameter for the decomposition stage of interest and the heat of activation was calculated from its slope. The other activation kinetic parameters (ΔH^*, ΔS^*, ΔG^*) were computed using the standard equations (Kandil2001): $\Delta H^* = E^* - RT$, $\Delta S^* = R[\ln(Ah/KT)]$ and $\Delta G^* = \Delta H^* - T\Delta S^*$ where K is Boltzmann's constant and h is the Plank's constant.

The order and the kinetic parameters of the ligand and its complexes are listed in tables (3,4). From which it is clear that:

a) The negative values of ΔS^* for the dehydration step indicate that the complex is more activated than the reactant and /or the thermal decomposition reaction is slower than normal (Frost1961). This can be explained on the premise that the degradation steps involve simultaneous processes. The first one is the volatilization of the water molecules from the solid complex with positive entropy ΔS^* followed by the formation of a more ordered anhydrous complex with negative ΔS^* value. The determined value is the resultant of the two processes (Issa2004). The second step is the loss of the chloride ions with negative entropy change ΔS^*). The third step corresponding to the decomposition of the ligand also has negative entropy changes.

b) There are no obvious trends in the values of E* or the activation enthalpy ΔH^*. However, the values of ΔG^* increase for subsequent decomposition steps of the complexes which means that the second step is slower than the first one(Greisher1964). Actually, the values of ΔG^* for these complexes increase from first step to the third step indicating that for these two complexes the rate of the reaction decrease from the first step to third step. This indicates that in the first step, the free part of the chelated ligand may be subject to partial decomposition then in another step the remainder part is degraded and finally form the representative metal oxide. This may be attributed to the structural rigidity of the chelating ligands which requires more energy for its rearrangement to get the correct order compared with the activated complex(Kandil2001). The values of ΔG^* for these complexes decrease from first step to the third one indicating that for these two complexes the rate of the reaction increase from the first step to third one.

c) The activation energy E* values calculated by the Coats-Redfern method follow the order Mn(II)>Co(II)>Ni(II)>Cu(II)>Zn(II) which is perfectly in agreement with the electropositive character of the metal ions. The activation energy increases with increasing the ionic radius, thus confirming that the stability of the complexes of the ligand increases with the ionic radius.

The data of thermal analysis and the calculated activation kinetic parameters of the decomposition of the prepared complexes show that the thermal stability of metal complexes depends essentially on the nature of both the central metal ion and the ligand.

4.5.Conclusion

The Schiff base ligand has been prepared by condensation phenylhydrazoethyl acetoacetate and thiosemicarbazied in 1: 1 molar ratio . The molecular structures of the resulted complexes are evaluated by physical analyses. The activation kinetic parameters of the decomposition of the prepared complexes show that the thermal stability of metal complexes depends essentially on the nature of both the central metal ion and the ligand

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Table 1 : analytical, physical ,UV and ESR spectral data for the prepared ligand and its divalent metal complexes

Comp.	M.P. °C	Found (Calcd.)%							μ_{eff} B.M.	π-π* (n-π*)			C.T. (d-d)	$g_{//}$	$g_{\perp}$	g_{eff}
		C	H	N	M	S	Cl	H_2O		C=S	C=O	C=N				
H_2L	210	51.1 (50.8)	5.0 (5.5)	22.7 (22.8)	-	11.2 (10.4)	-	-	-	245 (305)	285 (323)	315 (335)	-	-	-	-
$[Mn(HL)_2]Cl_2$	>300	42.7 (42.2)	3.8 (4.6)	19.7 (19.0)	7.0 (7.4)	8.2 (8.6)	9.2 (9.6)	-	5.8	265 (315)	305 (335)	320 (350)	420	-	-	2.452
$[CoLCl].2H_2O$	(285)	37.5 (37.3)	3.6 (4.3)	16.0 (16.7)	13.9 (14.1)	6.9 (7.6)	7.8 (8.5)	4.1 (4.3)	3.6	-	308 (330)	322 (345)	352 (420)	2.4	2.03	2.07
$[NiLCl].2H_2O$	(260)	36.8 (37.3)	4.4 (4.3)	16.1 (16.7)	14.4 (14.0)	7.2 (7.6)	9.2 (8.5)	4.0 (4.3)	dia	-	305 (325)	320 (340)	347 (398)	-	-	-
$[CuLCl].H_2O$	>300	37.1 (36.9)	3.8 (4.3)	15.8 (16.5)	15.3 (15.0)	6.8 (7.5)	7.9 (8.4)	3.9 (4.3)	1.7	-	310 (328)	330 (350)	382 (420,550)	2.77	2.22	2.51
$[ZnLCl].H_2O$	>300	33.9 (33.8)	3.7 (4.1)	15.2 (15.2)	13.8 (14.2)	7.8 (6.9)	8.9 (8.5)	4.2 (3.9)	dia	-	308 (319)	325 (340)	400	-	-	-

Table 2: Characteristic IR spectral data for the prepared ligand and its divalent metal complexes

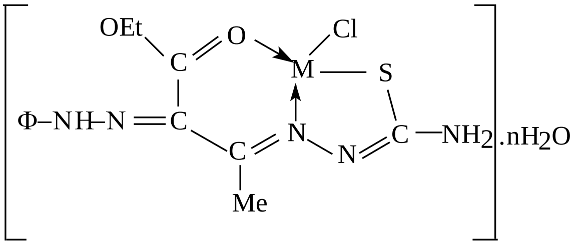
Comp.	υH_2O	υNH_2	υNH	υC=O	υC=N υC=N-N=C*	υC=S	υN-N	υM-O	υM-N	υM-S
HL	-	3320	3190	1700	1630	1040	925	-	-	-
$[Mn(HL)_2]Cl_2$	-	3330	3170	1705	1620	1055	910	510	450	375
$[CoLCl].2H_2O$	3405	3342	-	1685	1585*		935	503	468	390
$[NiLCl].2H_2O$	3390	3325	-	1690	1595*		945	498	450	382
$[CuLCl].H_2O$	3400	3330	-	1685	1600*		950	502	462	378
$[ZnLCl].H_2O$	3402	3315	-	1680	1605*		935	505	470	385

Table 3: DTA and TGA analysis of the prepared ligand and its divalent metal complexes

Assignment	TGA steps			DTA peaks		Complex
	Mass loss %		Temp. range	Peak	Temp.	
	found	calcd				
Cleavage of hydrogen bond and	-	-	40-60	endo	40-	HL
rearrangement	72.5	71.0	200-	endo	50	
Melting with loss of phenyl	14.5	15.0	250	endo	210	
hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)			350-		360,	
Further decomposition			400		380	
loss of two chloride ions and rearrangement	10.3	9.6	80-	endo	90	$[Mn(HL)_2]Cl_2$
Melting with decomposition and loss of	60.2	58.9	120	exo	320	
phenyl hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)	18.9	19.7	300-	exo	460	
further decomposition and formation of		3	350			
MnO_2 as final product			440-			
			600			
loss of two water molecules and one chloride	17.5	16.3	80-	endo	100,	$[CoLCl].2H_2O$
ion	51.5	8	180	exo	150	
Melting with decomposition and loss of	19.0	50.0	250-	exo	260	
phenyl hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)		20.6	320		450	
further decomposition and formation of NiO		2	440-		-	
as final product			550		480	
loss of two water molecules and one chloride	16.10	16.3	80-	endo	90,1	$[NiLCl].2H_2O$
ion	48.9	9	175	exo	65	
Melting with decomposition and loss of	15.4	50.0	250-	exo	285	
phenyl hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)		16.5	320		445	
further decomposition and formation of CoO			440-		-	
as final product			550		470	
loss of water molecule and one chloride ion	13.2	12.6	70-	endo	80,1	$[CuLCl].H_2O$
Melting with decomposition and loss of	52.85	4	190	exo	85	
phenyl hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)	15.8	51.5	280-	exo	315	
further decomposition and formation of CuO		17.0	350		475	
as final product			460-		-	
			600		490	
loss of water molecule and one chloride ion	14.1	12.6	70-	endo	85,1	$[ZnLCl].H_2O$
Melting and loss of phenyl	50.0	51.4	200-	exo	80	
hydrazoethylacetate ($C_{12}H_{14}N_2O_2$)	15.0	16.9	290-	exo	300	
further decomposition and formation of ZnO		6	350		420	
as final product.			400-		-	
			500		450	

Table 4: Thermokinetic parameters of the prepared ligand and its divalent metal complexes

ΔG^* kJ mol^{-1}	ΔS^* kJ mol^{-1}K^{-1}	ΔH^* kJ mol^{-1}	E^* kJ mol^{-1}	T(K)	R	n	Step	complex
71.455	-0.229	-2.68	4.841	323	0.9902	0.33	1	HL
36.505	-0.082	-4.08	11.72	493	0.9962	1	2	
60.629	-0.102	-5.38	4.951	648	0.9984	1	3	
40.447	-0.117	-3.09	2.03	373	0.9994	1	1	$[Mn(HL)_2]Cl_2$
47.074	-0.088	-4.96	9.463	598	0.9829	1	2	
133.962	-0.178	-6.55	34.85	793	0.9829	0.66	3	
41.709	-0.112	-3.35	2.831	403	0.9933	1	1	$[CoLCl].2H_2O$
49.781	-0.098	-4.63	5.951	558	0.9942	1	2	
103.12	-0.143	-6.32	54.63	768	0.9994	0.5	3	
41.708	-0.112	-3.31	2.831	398	0.9933	1	1	$[NiLCl].2H_2O$
44.736	-0.098	-4.63	5.951	558	0.9942	1	2	
50.426	-0.143	-6.32	54.63	768	0.9898	0.5	3	
42.184	-0.112	-3.34	2.831	403	0.9933	1	1	$[CuLCl].H_2O$
44.736	-0.098	-4.63	5.951	588	0.9942	1	2	
50.426	-0.056	-6.62	49.51	803	0.9991	1	3	
42.184	-0.117	-3.39	2.030	408	0.9994	1	1	$[ZnLCl].H_2O$
52.603	-0.087	-4.92	9.462	593	0.9829	0.33	2	
122.69	-0.178	-5.97	34.84	723	0.9892	0.66	3	



M= Co, Ni n = 2
M= Cu, Zn n =1

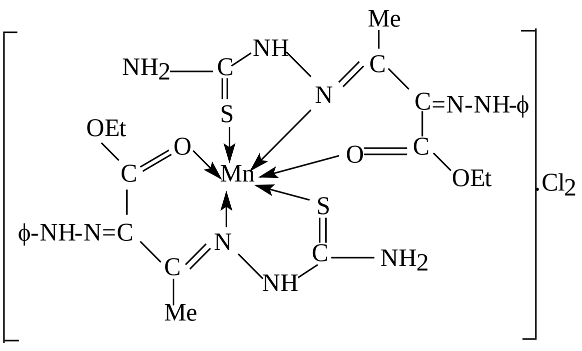


Fig.(1):The structure of the complexes