Structure and thermal behavior of some transition metal azo and nitroso complexes

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ABSTRACT: Some nitroso gallic acid, p-substituted o-nitroso phenol and azo-barbiturate complexes were prepared and identified. The thermal properties of the prepared complexes were studied under different temperatures using DTA and DSC techniques. The data were explained from different views: the electronic character of the substituent, the chemistry of the transition metal, the stereochemistry of the complexes and the mode of bonding in these complexes. The ΔE_a, ΔH^*, Z and order of reactions were calculated and discussed.

Keywords: azo barbiturate, nitroso phenol, complexes, structure, thermal Analysis

INTRODUCTION

Nucleic acid is related to antimetabolites used in anticarcinogenic chemotherapy. The pyrimidine compounds principally behave as hypnotic drugs and produce depressive effects on the central nervous system. Taken in small doses, barbiturates produce depression of sensory function, and in larger doses cause depression of motor functions. Increasing the dose produces sedation, sleep or anaesthesia, and over produces coma and respiratory cessation. Moreover, certain pyrimidine-pyrazoles are being studied in the fight against cancer(1-12).

Nitroso compounds are biologically active and have antibacterial - antiviral properties. These compounds have been extensively used as analytical reagents and of potential importance to the environment. Most of these compounds are subjected

to the tautomeric equilibria between nitroso phenols and oximes. The study of the cooridinating behavior of these compounds towards the transition metals (e.g. Co^{II}, Ni^{II} and Cu^{II}) is basic to biological molecules and have fundemental roles in catalytic interactions of drugs with biomolecular uptake of ions by living organisms occurs[13-20]. In our laboratory, Masoud et a[21-37]l recently reported a detailed structural chemistry of azo and nitroso metal complexes based on spectral and magnetic susceptibility measurements. Two azo compounds derived from phenyl azobarbituric acid containing o-OH and o-COOH were selected for the studies. These complexes are of variable stereochemistry and of semiconducting properties.
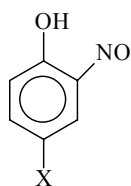
X= COOH, COCH$_3$, OH, CHO

para substituted o-nitrosophenol
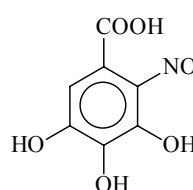
nitroso gallic acid
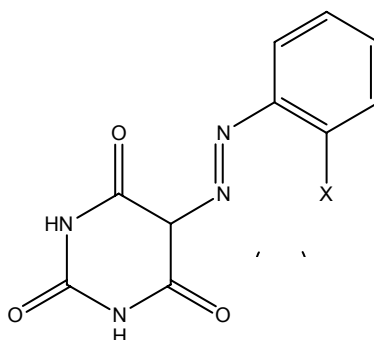
ortho sub-phynyl azo barbiturate ligand: X= -OH, -COOH

In a continuation, the present manuscript aims to study the thermal properties of the entitled compounds based on DTA and DSC techniques. The ΔE_a, Z and n are evaluted and discussed from the structural view piont.

EXPERIMENTAL

Synthesis of nitroso ligands:

Nitroso ligands were prepared by dissolving the required weight of the corresponding phenol (p-hydroxy benzoic acid, p-hydroxy benzaldehyde, p-acetyl phenol and gallic acid) (5g) in a warm solution of NaOH (1.4g) and 60 ml water. The solution was cooled to 0°C (in a bath of ice and salt) and a solution of NaNO$_2$

(2.5g in 20 ml water) was added in small portions with constant stirring. Concentrated sulphuric acid (8.5ml) was added to the above mixture with constant stirring, and the temperature does not exceed 5°C. The mixture was allowed to stand for two days until the nitroso ligands were completely precipitated. The compounds were separated by filtration and washed several times with a mixture of ethanol–ether. The compounds were TLC tested where a simple spot for each was observed, i.e., no isomers exist.

Synthesis of azo ligands:

The o-(substituted phenylazo) barbiturate compounds were prepared according the usual diazodization process[38]. The amines used were o-amino phenol and anthranilic acid as well as barbituric acid behaves as a phenol. The compounds were crystallized using ethanol as a solvent.

Synthesis of nitroso complexes:

The nitroso complexes were prepared by mixing the corresponding phenol (5gm) with glacial acetic acid (30 ml) and sodium acetate (6 g), then treated with a solution of sodium nitrite (6 g in 50 ml water). The metal chloride salt derived from Co^{II}, Ni^{II} and Cu^{II} (2.5gm in 50 ml water) was added to the mixture. The solution was allowed to stand for several days where the metal complexes were formed then separated by filtration, washed several times with water and ethanol and dried in vacuum desiccator over $CaCl_2$. All the prepared metal complexes are of melting points >300°C.

Synthesis of azo complexes:

These complexes were prepared by refluxing 0.01 mole of the organic compound in 30 ml dioxane with 0.01 mole of the metal acetate in 20 ml dioxane. The pH was adjusted at 8.5 by the addition of concentrated ammonia solution. The mixture was left for about three days where the complexes were separated, filtrated off, washed with hot dioxane and dried in vacuum desiccator over anhydrous $CaCl_2$. All the complexes had melting point >300°C. C, H, N contents of the ligands and their complexes were analyzed. The metal contents were determined by EDTA complexometric titration and atomic absorption by the use of Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. The data are given in Table 1. The KBr nfrared spectra of the ligands and their metal complexes were recorded using Perkin-Elmer 710B Infrared Spectrophotometer. The Differential Thermal Analysis (DTA) was measured using a Shimadzu XD-30 thermal analyzer (JPN) with a heating rate of 10°C/ min with a rate of 15m cal sec^{-1}. The Differential Scanning Calorimeter (DSC) data were measured using Perkin-Elmer system Thermal Analysis Microprocessor Controlling covered temperature range from 50 - 400°C

with a rate 20 m cal sec^{-1} and heating rate 20°C/min. High purity indium metal of accurately known enthalpy is used for calibaration[38]. The peak area is determined by weighing method. The calibration constant K calculated from the relation: $K = \dfrac{\Delta H(fusion)m_c}{A_c}$ where ΔH (fusion) is the enthalpy of fusion of the calibrant, where m_c is the mass of calibrant in milligram and A_c is the peak area of the calibration thermogram. The value of K is used to find enthalpy ΔH values for the samples from the relationship: $\Delta H_s = \dfrac{K.C_c.r_c.M.A_s}{C_s.r_s.m_s} \times 10^{-3}$ where C_c and C_s are the chart speeds used for calibration and sample run, respectively, r_c and r_s are the sensitivity (range) used for the calibrant and the sample, respectively. M is the molecular weight of the sample, m_s is the mass of the sample thermogram. Karl-Fischer Autanate, 645 Multi Dosimat instrument was used for water analysis. The loss on drying was achieved using IR heating.

RESULTS AND DISCUSSION

Spectroscopic and magnetochemistry view points are applied to elucidate the structure of the nitroso compounds and their complexes as follows:

1) Multiple IR bands in the region 3800-2350 cm^{-1} indicating the presence of hydrogen bonds involving N-OH group, overlapped with the C-H stretching vibrations beside the possibility of interaction between such compounds and water[39].

2) The nitroso group is identified at 1460, 1550, 1310 and 1500 cm^{-1} in the nitroso hydroquinone, 4-carboxy-2-nitrosophenol, nitroso-m-cresol and 4-acetyl-2-nitrosophenol, respectively[40, 41].

3) In case of carboxy compounds, the band at 940 cm^{-1} is assigned to the presence of dimeric hydrogen bonding.

4) The N-O bending frequency of the aromatic nitroso compounds is assigned at 855cm^{-1}[20].

5) The band at 1108 cm^{-1} in the spectrum of nitroso benzene is assigned to νN=O. This band disappeared upon thermal oxidation of the nitroso-group[39].

6) Nitroso benzene gave two strong IR bands at 1490 and 850 cm^{-1} due to ν and δN-O, respectively[39].

7) The strong bands at 870 cm^{-1} for 2-nitroso gallic acid, 830 and 775 cm^{-1} for 4-carboxy-2- nitrosophenol, 825 cm^{-1} for 4- aldehydo-2- nitrosophenol and 1030cm^{-1} for nitroso-m- cresol, are probably due to N-O bending and stretching

vibrations. All these regions are strongly affected on compelxation. So, the nitroso group coordinates with the transition metal ion.

9) The strong band in the region 1640-1580 cm^{-1} is assigned to the $vC=N$ overlapped with $vC=O$, to increase the bond polarity owing to conjugation[38,39].

10) The δ O---H-O mode of vibration is identified at 1540 cm^{-1} for nitroso gallic acid and 4-carboxy-2-nitrosophenol. For 4-aldehydo-2-nitrosophenol, this region became doublet at 1555 cm^{-1} and 1540 cm^{-1} as well as for nitroso- m- cresol at 1570 cm^{-1} and 1540cm^{-1}. The band appeared in the 1500-1440 cm^{-1} region has been tentatively assigned to the C=N stretching vibration of the C=N-OH group[42]. The change in its position on coordination illustrates its contribution with the metal ion. Such trend explains the formation of a chelate compound of five membered ring structures. Compounds containing carboxyl groups show bands arising from the superposition of C=O, C-O, C-OH and O-H vibrations of five characterisitic bands, three of these (2700, 1300 and 943 cm^{-1}) are associated with vibrations of the –COOH group[43]. Two infrared spectral bands in the vicinity of 1600 and 1450 cm^{-1} are formed due to asymmetric and symmetric vibrations of the carboxyl groups. Such region is affected on complexation where metal - oxygen interaction occurs. On assuming the bonding occurred through the carboxylate site, different skeletons could be suggested.


      A   B   C
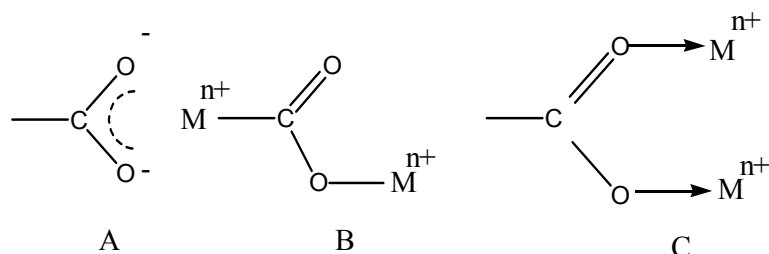
As the covalent character of the M-O bond increased (Structure B) the carboxyl group became more asymmetric in an increase in the frequency separation of the two CO_2- stretching bands, compared to the structure A. Structure C involved coordination of the carboxyl group where the strength of the M-O bond increased with a decrease in the separation between the asymmetric and the symmetric CO_2- vibrations. The broad band in the longer frequency range argued to the presence of hydrogen bonds of the O---H-O type between the carboxyl groups such as:
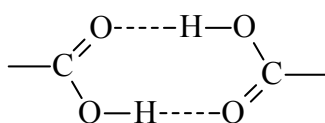
Such scope is verified by the presence of a band at 925 cm^{-1}.

11) Different resonating structure are assigned.
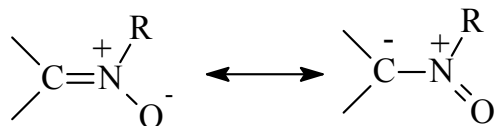
The polarizing effect of the metal ions affects the π electrons of the aromaticity of the ligand. In all these complexes, nitroso - nitrogen mode of interaction favours nitroso - oxygen, due to stability factors[43]. All complexes gave a characteristic band in the frequency range 970-820 cm^{-1}, to justify the existence of nitroso structure. The synthesized nitroso salicylic acid (H$_2$L) nickel complex has the formula Ni(HL)$_2$.2H$_2$O, where both the functional groups –OH and –COOH are affected on complexation[43]. For gallic acid complexes, the carboxy group does not take part through complexation. So, the mode of bonding in these complexes is based on deprotonation of two hydroxyl groups and bonding to nitroso nitrogen where the ligand is of tridentate nature. The insolubility of the complexes suggests their existence in polymeric structures. So, one can suggest the possible structures of the complexes to be as follows:
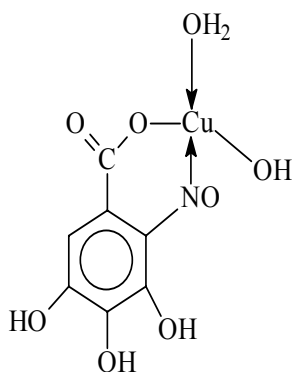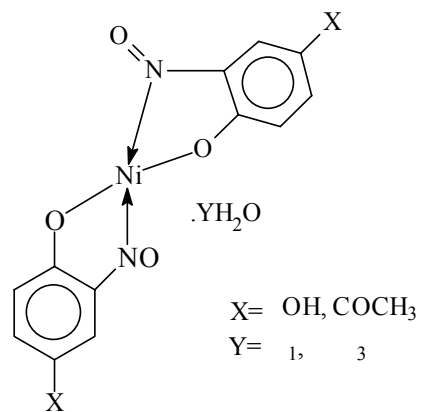

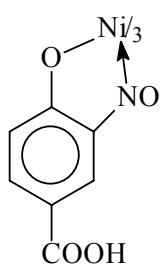1:1Cu nitroso gallic acid complex phenol complexes
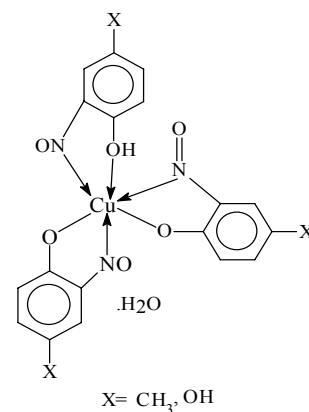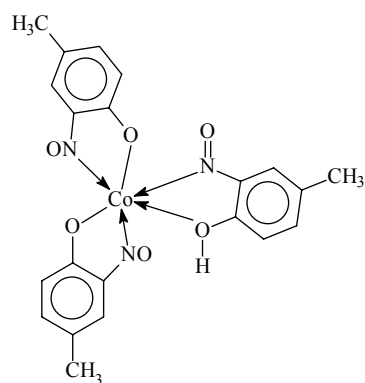
1:3Cu p-OH and p methyl-2-nitroso
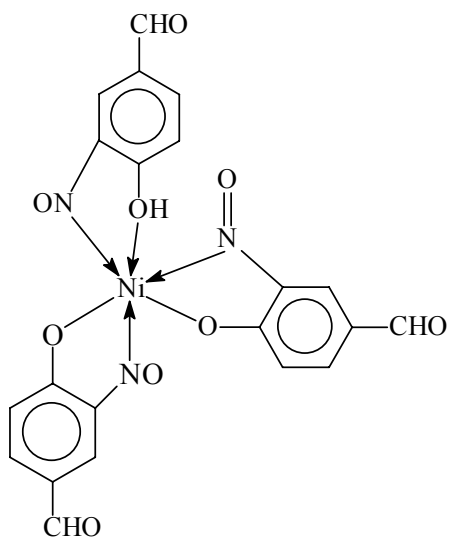
1:3 Ni p- aldehydo-2-nitroso phenol complexes nitrosophenol complex
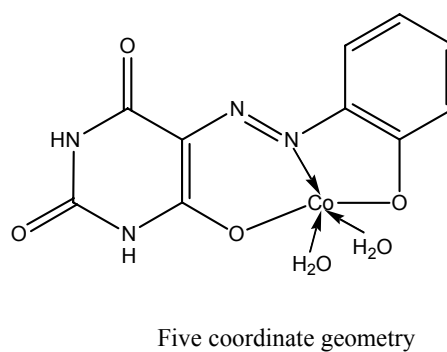

X= OH, COCH₃
Y= 1, 3

1:2 Ni p-OH and p-acetyl -2-

1:3 Ni p- carboxy -2-nitroso phenol cmplex complex

1:3 Co p-CH₃ -2-nitrosophenol

tetrahedral structure

Five coordinate geometry

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M=Ni, Cu

Octahedral structure

M=Ni, Cu   Square planar geometry
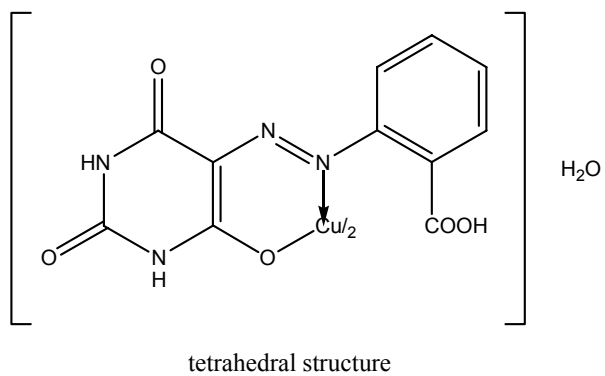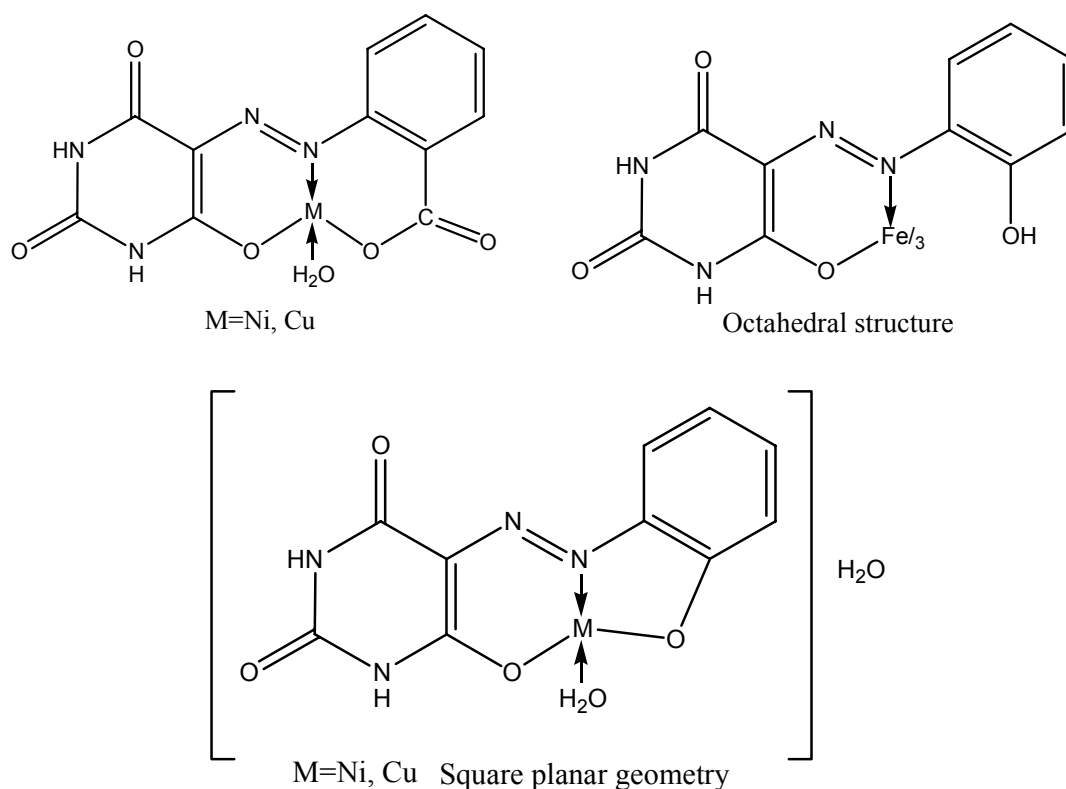
The thermal behaviour of the nitroso and azo compounds
The thermal behaviour of cobalt (II), nickel (II) and copper (II) complexes of 2-nitroso-4-substituted phenol, nitroso gallic acid, and cobalt (II), nickel (II), copper (II) and Fe(III) complexes with 5-(2-carboxy phenylazo) barbituric acid were studied based on DSC and DTA techniques. Also the thermal behaviour of 5-(2-carboxy phenylazo) barbituric acid ligand was studied. The data were explained from different views: the electronic character of the substituted, the chemistry of the transition metal, the streochemistry of the complexes beside the mode of bonding in these complexes. The activation energies (ΔE_a) were evaluated based on Piloyan et al method[44, 45]. The order of reactions (n) were calculated via peak asymmetry method[46,47]. The ΔH values are evaluated.

The DSC curve, Fig. 1 and DTA curve, Fig. 2, is for the octahedral low spin cobalt 4-methyl-2-nitrosophenol where it gave sharp endothermic peak in the temperature range (275-350)°C. The order of reaction is of first order type. The relative higher ΔH value, Table 2, refers to great stability of the complex where the ligand is bidentate and the methyl group gives more stabilization to the complex through its hyperconjugative donating character of electrons. The physical measurements used (DSC, DTA, analytical data, Karl Fischer titration and IR

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measurements) are in favour to suggest the absence of water molecules. In the temperature range (60-175)°C, there is a change in the base line that appeared in DSC and DTA curves. This may refer to the change in the heat capacity without change in ΔH[44]. The DSC and DTA curves for the nickel complexes derived from p-substituted-2-nitrosophenol ligands (substituents: -COOH, -COCH$_3$, -OH, -CHO), are given in Fig. 1and Fig. 2, respectively. The DSC endothermic peak in the temperature range (58.5-200)°C for the (1:3) nickel-4-carboxy-2-nitrosophenol, Fig. 2, and the change in the base line at the same temperature range obtained from DTA measurments. The data illustrated the possible change in the molecule with a little change in ΔH, and may result from the breaking of the hydrogen bond exists in the insoluble dimeric five coordinate structure in an equilibrium between high spin (S=1) and low spin (S=0) states with possible Ni---Ni interaction. The nickel-4-acetyl-2-nitrosophenol 1:2.3H$_2$O complex gave a strong endothermic peak in the temperature range (75-145)°C, Fig. 1, probably due to the release of three molecules of water. The endothermic peak for the nickel-4-hydroxy-2-nitrosophenol 1:2.H$_2$O complex in the temperature range (140-170.6)°C, may be the result from the release of the unique molecule of water in the complex. The relative large area of the dehydration of the acetyl complex compared to that of the hydroxy complex is in harmony with the ΔH values of dehydration of the two complexes, Table 2. However, the DSC curve for the nickel aldehydo complex gave an endothermic peak in the temperature range (120-163)°C, Fig. 1. This is not apparent in the DTA curve, Fig. 2. This peak may be due to tautomerism where there is no change in weight after heating the sample. Meanwhile two consecutive exothermic peaks in the temperature range (330-340)°C and (375-390)°C are obtained. This may be due to dissociation of dimers followed by decomposition. This is supported by a change in weight equivalent to 27% of the molecule. The endothermic peak in the temperature range (216.5-260)°C for the acetyl complex, Fig. 1, may be result from the dissocition of the dimers. The ΔH values for all the transformations were calculated and gathered in Table 2.. The cange in the ΔH of decomposition steps for the tris nickel aldehydo and carboxy complexes may be due to the high electron with drawing character of the carboxylic group rather than the aldehydo group. The higher ΔH values for the tris nickel carboxy and nickel aldehydo complexes compared to the bis nickel acetyl 1:2. 3H$_2$O and nickel hydroxy 1:2. H$_2$O complexes could be related to the number of the ligand molecules. The methyl group of σ and π electron donor property leads to increase the electron density of the phenolic oxygen and decrease the extent of ionization. In

all these complexes, nitroso-nitrogen mode of interaction is more preferable than nitroso-oxygen due to stability factors.

The DSC and DTA curves of the copper complexes derived from 4-hydroxy-2-nitrosophenol, and 4-methyl-2-nitrosophenol and acetophenone oxime ligands are collected in Fig. 1 and Fig. 2. The hydroxo complex gave two consecutive DSC exothermic peaks in the temperature ranges (260-273)°C and (273-287)°C. The first peak is only appeared sharply in the DTA curve, followed by a change in the base line, to assign a change in the heat capacity of the complex. The exothermic decomposition peak is appeared in the DTA and DSC curves in the temperature range (400-455)°C. However, the DSC data of copper methyl complex, Fig. 1, gave two exothermic peaks at the temperature ranges (290-334)°C and (347-370)°C. These two peaks are appeared as a one large exothermic DTA peak, probably due to two consecutive reactions, which may related to decomposition followed by rearrangement of the result complex. This is supported by a loss in weight equals to 31%. The endothermic peak in the temperature range (50-130)°C may be assigned as a dehydration peak. The high electron donor character of the methyl group relative to the other group reflects a higher ΔH value. Inspite of the variation of the ΔH values, the peaks occurred around the same temperature range are due to the breaking of Cu-L system. In some copper complexes, the spin of the two copper ions is strongly coupled where the paramagnetism is completely quenched and the dimer is diamagnetic. The presence of an exothermic peak before the decomposition peak may be due to tautomerism followed by the decomposition. On regarding to the DSC and DTA curves for nitroso gallic acid and its copper complex, gave a sharp endothermic peak in the temperature range (93-128)°C for the ligand that may result from breaking of the intramolecular hydrogen bond. The endothermic peak at the temperature range (242-263)°C may be due to melting of the nitroso gallic acid. The change in the base line at this temperature range may result from the change in the heat capacity, due to the decomposition of gallic acid to pyrogallol and carbon dioxide.

For copper nitroso gallic acid, Karl-Fischer and analytical data refer to the presence of three molecules of water released at the temperature range (225-303)°C, i.e., the water molecules maybe in the inner sphere of the complex. The endothermic peak at the temperature range (308-321)°C maybe due to melting. There is also an exothermic peak at the temperature range (325-326)°C which may be due to oxidative decomposition process. Fig. 3 illustrates the ΔH^* - ΔS^* relation of nitroso phenol compound where a best fit straight line is obtained. The regression data follow the following equation: $\Delta H^{\#} = \Delta H_o^{\#} + \beta \Delta S^{\#}$. In this equation,

$\Delta H_o^{\#}$ illustrates the $\Delta H^{\#}$ at $\Delta S^{\#} = 0$. It will usually have no physical meaning. The slope of the relationship (β) means a quantity having the dimensions of absolute temperature, with a correlation coefficient r = 0.967. The thermal papameters of the dissociation steps for the complexes are collected in Table 2.

For 5-(2- carboxy phenylazo) barbituric acid ligand, Karl-Fisher and the loss on weight using infrared lamp gave that this compound contains one mole of water. The 5-(2-carboxy phenylazo) barbituric acid and its complexes, Fig. (4) is for the DSC data for the transition metal-o-hydroxy complexes Fig. (5), gave an endothermic irreversible peak in the temperature range (115-190)°C which may be due to dehydration process. On further increasing of temperature, the range (280-303)°C is due to the decomposition of irreversible nature. The mechanism of dehydration is first order with ΔE_a and ΔH values equal 4.3 KJ/mole and 4.98 Kcal/mole, respectively. The peaks at the temperature ranges (115-190), (230-270), (230-260) and (150-210)°C for the free ligand and its 1:1 (M:L) complexes, (where M = copper, nickel and cobalt), respectively are of endothermic property. Based on ΔH values, the sequence of these complexes is Co > Ni > Cu to be 14.488, 12.3 and 4.434 Kcal/mole, respectively.

The endothermic peaks in the DTA curves of both the copper and nickel complexes in the temperature ranges (270-320) and (260-300)°C, respectively, may be assigned to polymorphic transformation through desolvation[47]. From weight loss data each of both complexes contains one water molecule, which may be in the inner sphere.

The desolvation process of both the copper and nickel complexes is irreversible as indicated by the disappearance of its DTA peaks. The order of the reactions is 1:1. The ΔE_a value for the mono copper complex is greater than that of the nickel complex, (3.064 KJ/mole for 1:1 Cu, 1.074 KJ/mole for 1:1 Ni complex). This is in accordance with the probability of the presence of the water molecule in the inner sphere of the complexes as a water of crystallization where the electronegativity of copper is more than nickel. However, the DTA data for the Cu 1:2 complex give that the dehydration process is of irreversible nature. All the prepared 1:1 copper and 1:1 nickel complexes of 2-hydroxy complexes gave a similar trend where Karl-Fischer titration in these systems depict the existence of two molecules of water, that released at the temperature ranges (85-120)°C and (120-150)°C for Cu^{II} (58-147)°C and (225-303)°C for Co^{II} and (155-207.5)°C for Ni^{II} complexes.

All the data refer to the absence of water molecules in the iron(III) complex. The ΔH values for dehydration for the 1:1 complexes are 1.02 Kcal/mole at (85-120)°C and 1.95 Kcal/mole at (120-150)°C for Cu^{II}, 2.22 Kcal/mole at (155-207.5)°C for

Ni^{II}, and 1.14 Kcal/mole at (58-147)°C for Co^{II} complex.

Based on ΔH values, the trends follow the following:

a) The William- Irving series.
b) The reciprocals of the ionic radii which measures the electrovalent character of the metal ion.
c) The second ionization potentials (which reflect covalent character of the bonds formed of the metal ion).
d) Increasing electronegativity and crystal field stabilization energy Cu^{II} > Co^{II}.

The ligands are symbolled by H$_3$L. the chemical equation for the 1:1 complexes could be represented as follows:

$$MCl_2 + H_3L \longrightarrow M(HL) + 2HCl$$

(M = Co, Ni, Cu derived from hydroxy and carboxy compounds).

However for the 1:2 Cu-o-COOH complex, the equation is given as follows:

$$CuCl_2 + 2H_3L \longrightarrow Cu(H_2L)_2 + 2HCl$$

Meanwhile the 1:3 Fe-o-OH is represented as follows:

$$FeCl_3 + 3H_3L \longrightarrow Fe(H_2L)_3 + 3HCl$$
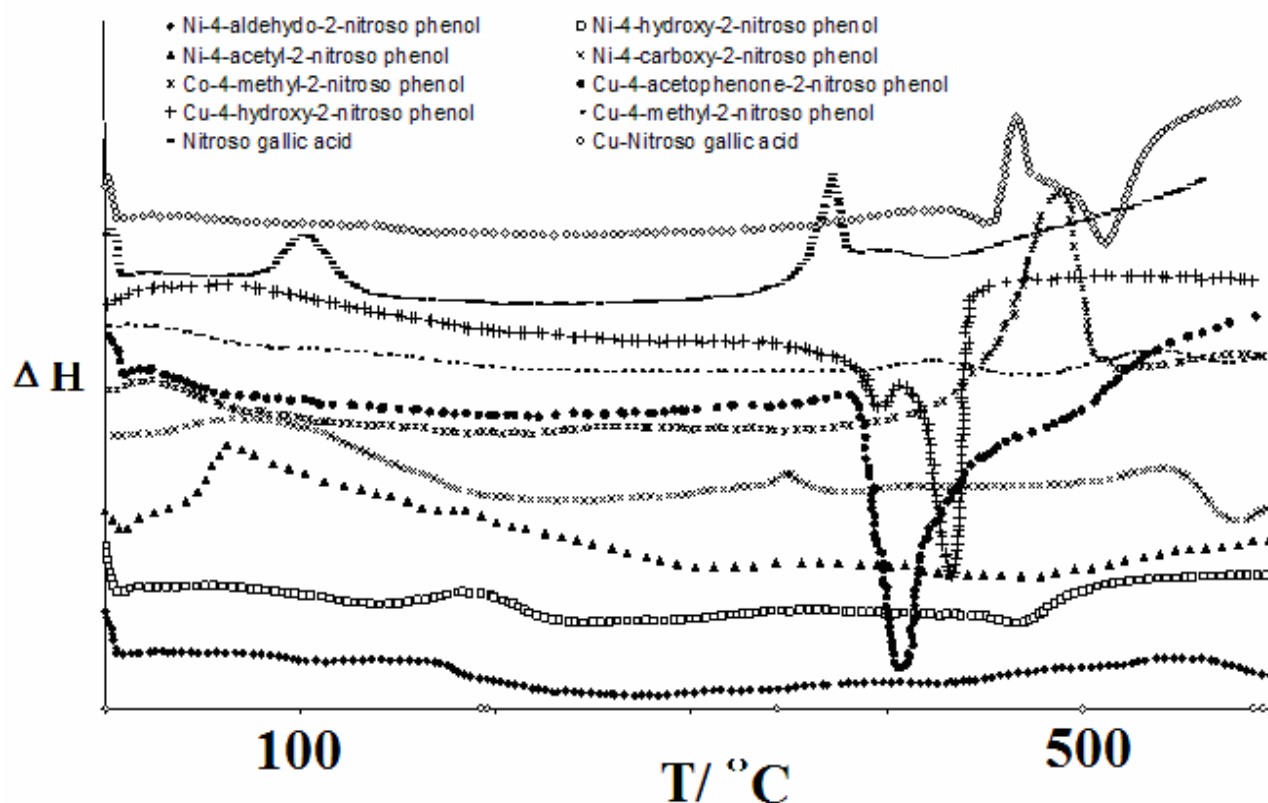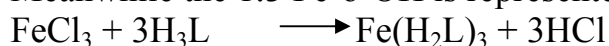
Fig. 1. DSC curves of the investigated nitroso complexes.
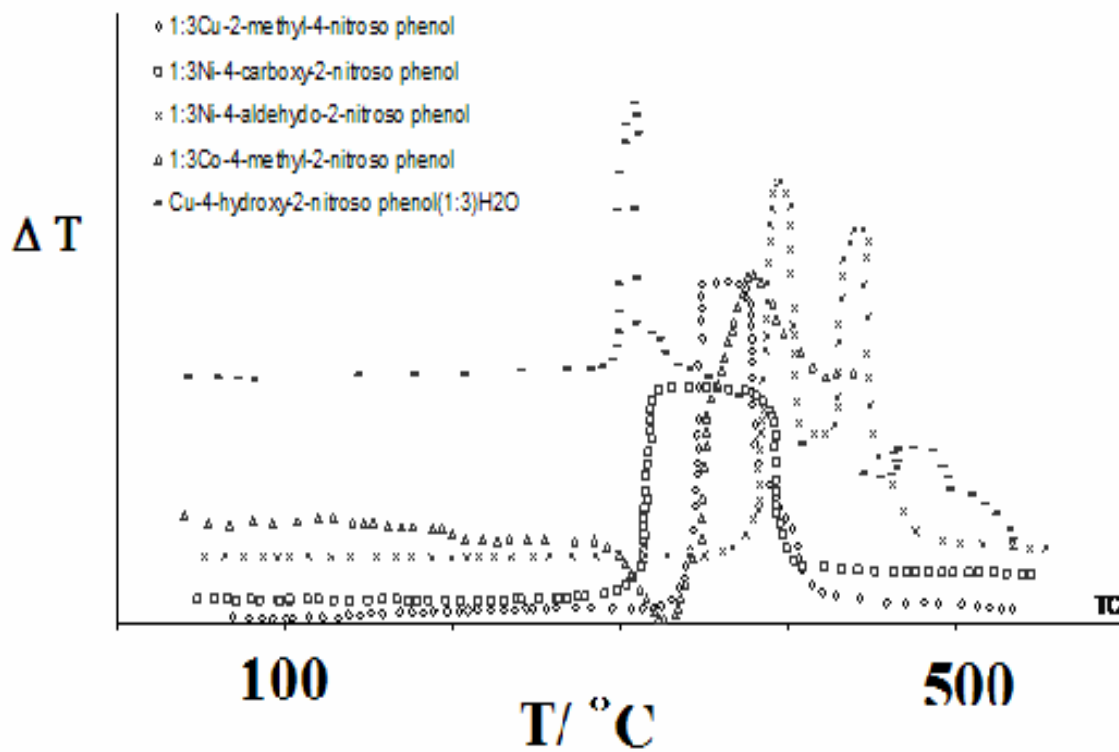
Fig. 2. DTA curves of the investigated nitroso complexes.
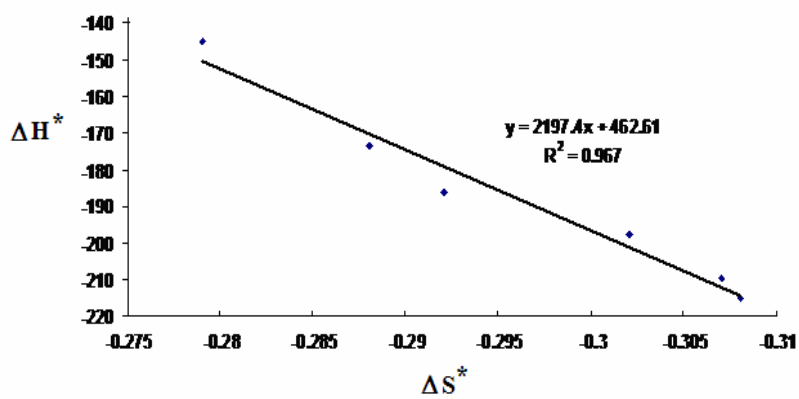
Figure (3): $\Delta H^{\#}$-$\Delta S^{\#}$ relation of nitroso phenol compound

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TABLE 1. Analytical data for the complexes

Complexes	Colour	Calculated/(Found)%			
		C	H	N	M
1:1 Cu-nitroso gallic acid. 3H$_2$O	Brown powder	28.0 (28.1)	3.2 (3.0)	4.5 (4.7)	21.0 (21.3)
1:3 Cu-OH-2-nitroso phenol.H$_2$O	Brownish red powder	43.2 (43.6)	2.7 (2.8)	8.7 (8.5)	12.6 (12.8)
1:3 Cu-CH$_3$-2-nitroso phenol.H$_2$O	Brown powder	53.7 (53.9)	4.7 (3.9)	8.3 (9.0)	12.5 (12.6)
1:3 Ni aldehydo-2-nitroso phenol.	Brown powder	49.0 (49.5)	2.3 (2.4)	8.1 (8.3)	11.1 (11.5)
1:3 Ni carboxy-2-nitroso phenol.	Brown powder	45.4 (45.3)	2.4 (2.2)	7.7 (7.5)	10.6 (10.5)
1:2 Ni-OH-2-nitroso phenol.H$_2$O	Brown powder	40.0 (40.8)	2.6 (2.8)	8.1 (7.9)	16.2 (16.6)
1:2 Ni acetyl-2-nitroso phenol.3H$_2$O	Brown powder	43.4 (43.6)	4.0 (4.1)	6.2 (6.4)	13.6 (13.3)
1:3 Co-CH$_3$-2-nitroso phenol.	Brownish red powder	54.2 (54.0)	3.8 (3.9)	8.7 (9.0)	12.3 (12.6)

All the complexes are with m.p.>300°C

TABLE 2: DTA analysis of 4-substituted-2-nitrosophenol

Complex	Tm °K	ΔE (kJmol^{-1})	n	α_m	ΔS^* (kJK^{1}mol^1)	ΔH^* (kJmol^{-1})	Z (Sec^{-1})
1:3 Cu-4-methyl-2-nitrosophenol	290.0	-1.663	0.86	0.66	0.335	188.605	-3.55x10^{-4}
1:3 Ni-4-carboxy-2-nitrosophenol	295.0	54.170	1.37	0.57	-0.307	-174.380	0.0115
1:3 Ni-4-aldehydo-2-nitrosophenol	602.5	575.700	1.09	0.62	-0.288	-173.460	0.1149
	638.0	403.229	1.16	0.61	-0.292	-186.296	0.0760
1:3 Co-4-methyl -2-nitrosophenol	566.0	95.611	1.28	0.59	-0.302	-170.932	0.0203
1:3 Cu-4-hydroxy -2-nitrosophenol	520.0	1180.588	1.09	0.62	-0.279	-145.08	0.2728
	698.0	70.669	1.78	0.52	-0.308	-214.984	0.0122

n is the order of the thermal reaction, Z is the collision number
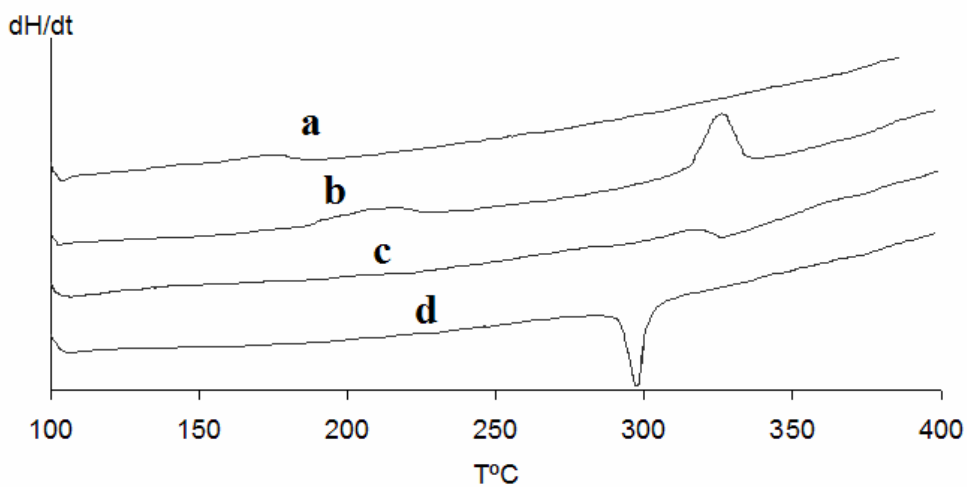
Fig(4): DSC curves for:
a) 1:1Cu-o-Hydroxy phenylazo) barbituric acid
b) 1:1Ni-o-Hydroxy phenylazo) barbituric acid
c) 1:1Co-o-Hydroxy phenylazo) barbituric acid
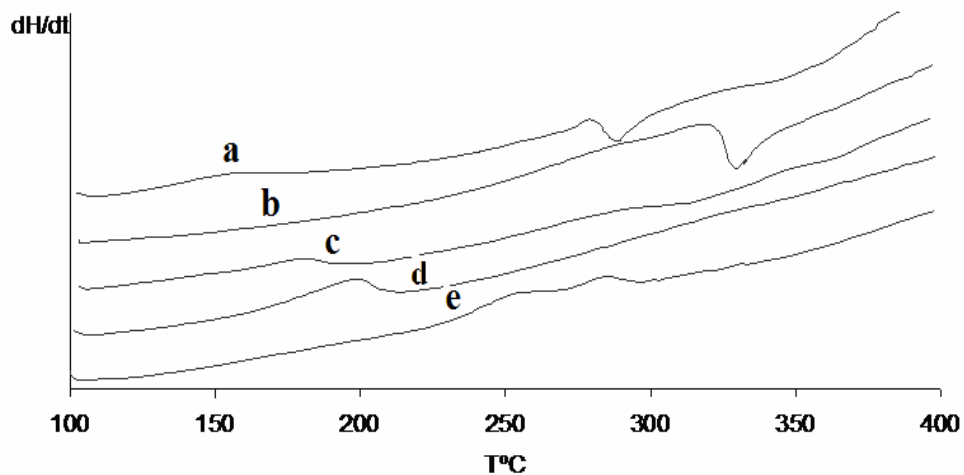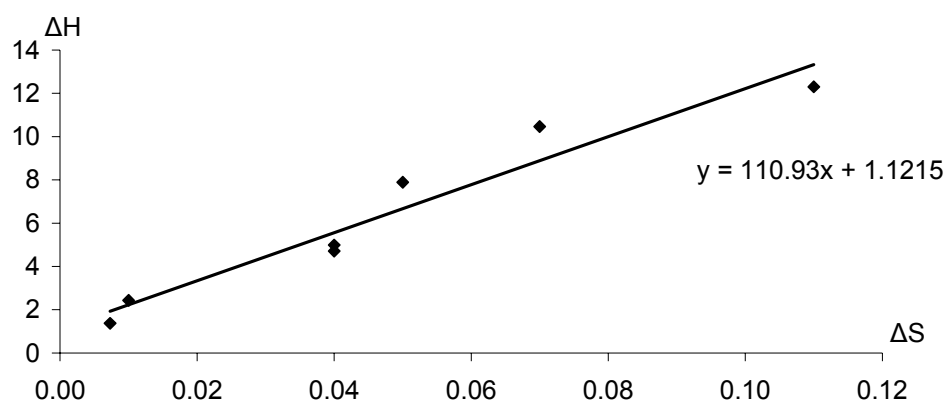d) 1:3Fe-o-Hydroxy phenylazo) barbituric acid

Fig (5) DSC for:
a) 5-(o-carboxy phenylazo) barbituric acid H_2L
b) Cu.L.COOH
c) Cu(HL)$_2$.COOH
d) Ni.L.COOH
e) Co.L.COOH

Figure (6): $\Delta H^{\#}$ - $\Delta S^{\#}$ relation of azobarbiturate compound

Table (3): Analytical data of the complexes

Complexes	Colour and appearance	%Found (%Calculated)			
		C	H	N	M
1:1 Ni-o-OH.2H$_2$O	Reddish brown powder	35.1 (35.2)	3.0 (2.9)	16.8 (16.4)	17.4 (17.2)
1:1 Co-o-OH. 2H$_2$O	Brown powder	35.4 (35.2)	3.2 (2.9)	17.0 (16.4)	17.5 (17.3)
1:1 Cu-o-OH. 2H$_2$O	Brown powder	34.3 (34.7)	2.6 (2.9)	16.1 (16.2)	18.3 (18.4)
1:3 Fe-o-OH	Brown powder	45.2 (45.2)	3.2 (2.6)	20.3 (21.1)	6.8 (7.0)
1:1 Ni-o-COOH. H$_2$O	Reddish brown powder	37.8 (37.6)	3.1 (2.3)	14.7 (16.0)	16.6 (16.7)
1:1 Co-o-COOH.2H$_2$O	Brown powder	35.6 (35.8)	2.2 (2.7)	14.9 (15.2)	15.6 (16.0)
1:1 Cu-o-COOH. H$_2$O	Green powder	37.2 (37.1)	2.6 (2.3)	15.2 (15.8)	17.8 (17.9)
1:2 Cu-o-COOH. H$_2$O	Dark green powder	41.5 (41.8)	2.8 (2.5)	17.1 (17.7)	10.0 (10.1)

Table (4): Order of reaction and activation energy of barbituric acid and 5-(carboxyazo) barbituric acid (H₂L) complexes using DTA and DSC techniques at different temperatures[*].

Compound	T°C	N	α	Z	ΔE_a (KJ.mol⁻¹)	ΔH (Kcal. mol⁻¹)	ΔS (KJ.mol⁻¹K⁻¹)	ΔG (KJ.mol⁻¹)
(H₂L)	115-180	1.33	0.58	0.005	4.30	4.989	0.04	3.12
	240-300	1.63	0.54	0.002	2.25	4.711	0.04	3.919
1:1 Cu-H₂L	230-270	1.10	0.62	0.003	3.06	2.434	0.01	2.978
	300-350	1.30	0.58		----	15.189	-----	-----
1:2 Cu-H₂L	110-160	1.40	0.57	0.0008	0.67	-----	-----	-3.28
	160-200	1.00	0.63	0.0011	1.03	7.653	-0.07	-3.3
	300-350	1.10	0.62	0.0006	0.70	10.463	0.07	1.983
1:1 Ni-H₂L	70-90	1.10	0.62	0.0019	1.34	1.372	0.0073	3.16
	230-260	1.10	0.62	0.0010	1.07	12.3	0.11	3.178
	260-300	1.22	0.50	0.0002	0.268	7.89	0.05	3.633

- All the reactions are of endothermic type.

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