The Study of Thermal and Magnetic properties of Fe (II), Co (II), Ni (II) and Cu (II) Metal Complexes with 3-Aminolawsone oxime

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ABSTRACT

Recent trade is found to be of great interest in structural study of complexes which are derived from organic compounds containing oxygen and nitrogen donar atom. The ligand 3-aminolawoneoxime was synthesized and its complexes with some of the transition metal Fe, Co, Ni, and Cu were prepared by usual method. The complexes of Fe, Co and Ni are found to be paramagnetic while that of copper complex shows diamagnetic behavior. The experimental values of magnetic moments for Fe, Co and Ni complexes when compared with the magnetic moments of Fe, Co and Ni complexes in literature these values are found more close to the values of tetrahedral type of the complexes. The slight lower values of magnetic moment may be attributed to anti ferromagnetic exchange interaction between paramagnetic transition metal ion and the ligand mostly in the semi-quinone form. The observed magnetic moment values for the complexes are closer to the values of tetrahedral type of structures. In copper complex the value lowers to such an extent that it shows diamagnetism probably due to anti ferromagnetic interaction via d-orbitals of two Cu centers present in stacked type square planar structure.

Keywords: Metal complexes, thermal studies, magnetic studies metal-oximes, 1, 4-naphthoquinone complexes
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INTRODUCTION

The co-ordination chemistry of transition metal ions has expanded rapidly during the last three decades. Transition metal complexes of o-quinone ligands have been reported by Pierpoint and Buchanan [1]. Compared to o-quinone ligands no summarized account of p-quinone ligands is available except a brief account provided by Foster and Foreman [2]. The majority of available results on transition metal complexes of p-quinone in case of 1, 4-benzoquinone but a few deal with derivatives of 1, 4-naphthoquinone and 9,10 anthroquinone. The development of co-ordination chemistry of metal p-quinone compounds has been slow and has picked up momentum in recent years due to biomimetic potential. Thus oxidation and reduction of iron porphyrin by quinone and hydroquinone has been studied by several workers [3-5] in the recent years to find out the influence of a protein upon the reactivity of its heme in variety of hemoproteins. Dimetric [6] and tetrametic [7] manganese quinone complexes have also been considered as viable models for the photo-synthetic manganese cofactor.

Co-ordination polymers of copper (II) with tetrahydroxy anthroquinone are reported by Coble and Haltzclaw [8] while Day and Banerjie [9] have prepared such polymers in case of nickel (II), cobalt (II) manganese (II), iron (II) and uranium (IV) ions. These were synthesized by refluxing an equimolar mixture of ligand and hydrated metal acetate in N, N-dimethyl formamide at $140^{\circ}C$. The monomeric unit of the polymer consists of an octahedral complex of the central metal atom with two co-ordinated water molecules filling the vacant sites.

Although formation of coloured co-ordination compounds is used as diagnostic test for the presence of hydroxyl naphthoquinone in natural products, [10-12] very few studies have been devoted in the past to the structural characterization of these compounds. Many of these earlier studies were concerned with either synthesis or isolation

of these compounds via salt formation reactions with alkali metal, alkaline earths and heavier metals like lead and silver. The precipitated metal complexes were at the most evaluated for their metal contents or the decomposition temperature.

Definitive studies towards structural characterization of metal complexes of hydroxynaphthoquinones were probably initiated by Bottle and Mc Eachern [13] in 1970 who examined the IR spectra and thermal stabilities of metal chelates of lawsone (2-hydroxy-1,4-naphthoquinone), juglone (5-hydroxy-1,4-naphthoquinone) and naphthazarin (5,8-dihydroxynaphthoquinone).Another study [14] has involved Mossbauer spectra of iron (II) and iron (III) complexes of C-3 alkyl derivatives of lawsone where it was shown that although the isomer shift of complexes of different ligands is nearly the same, the quadrapole split and its temperature dependence varies with ligand structure. Systematic investigation on ortho and para-hydroxy-naphthoquinone derivatives were initiated in the Department of Chemistry, University of Poona around 1970, initial studies were concerned with the comparison of the pair of metal chelates of both the series with and without substituents and confirmed the anticipated expectation that five member unsaturated chelates rings are generally less stable [15-17] than corresponding six membered chelate rings.

The transition metal complexes of the semicarbazone and thiosemicarbazone derivatives [18] are essentially low spin type and the participation of sulphur in co-ordination is a function of the substitution on the sulphur. Some first row transition metal chelates of o-acyl derivatives of 3-iodolawsone monoxime bearing O→N→O ligating system which has been reported by Durwas [19]. There is obviously a tendency toward dimerisation in the resulting complexes promoted through the bridge intermediates composed of the anions of metal salt used or the hydroxyl group generated probably through hydrolysis of metal salts. Thermal and magnetic properties of transition metal complexes of nitrolawsone and aminolawsone was studied by Kolhe [20] and lanthanide complexes of aminolawsone by Bajaj [21].The thermogravimertic studies of bis-Phthicol monoximato Fe (III) adduct was reported by Patil et al [22]. On the other thermal, spectral and magnetic properties of 2-hydroxy-1,4-naphtho quinone monoximates of Ho(III), Er (III) and Yb(III) by Jagtap et al [23] reported the ligating system for these complexes is $[ML_3(H_2O)_2]$.

In present study the thermal and magnetic moment measurement of Fe (II), Co (II), Ni (II) and Cu (II) metal complexes with 3- Amino-2- hydroxy, 4-keto 1-naphthoxime (3-Aminolawsoneoxime) were studied.

EXPERIMENTAL SECTION

Synthesis of ligand:
The ligand 3- Amino-2- hydroxy, 4-keto 1-naphthoxime was prepared from 3-Amino-2-hydroxy-1,4-Naphthoquinone (3A2HNQ) by general method of preparation of oxime. In this method carbonyl group at position 1 is replaced by oxime group. The compound 3-Amino-2-hydroxy-1,4- Naphthoquinone was synthesized from 3-Nitro-2-hydroxy-1,4- Naphthoquinone by method of Nagase, Matsumoto and others [24].

In a small beaker 0.005 mole (0.945 gms) of 3- aminolawsone was dissolved in 10 ml of 2N solution of sodium hydroxide and was mixed with 0.75 mole (0.500 gms) of hydroxylamine hydrochloride in 10 ml. distilled water. The mixture was maintained at 50-60°C for about half an hour with constant stirring [25].The reaction mixture was allowed to cool and was neutralized by 2N solution of glacial acetic acid when amino-lawsone oxime was precipitated as yellow crystals. The precipitated mass was then filtered, washed with ice cold water and dried under vacuum at room temperature, C, H- Analysis for $C_{10}H_8O_3N_2$ gave observed values for C=58.81%, H=3.97% and theoretically calculated values are C=58.80%, H=3.82% Decomposition temperature 224°C.

Preparation of Metal complexes:
The most common procedure was adopted for the preparation of metal complexes. 0.002 moles ethanolic solution of ligand (3-Aminolawsoneoxime) and (0.001 mole in each case, Ferrous sulphate hepta hydrate, Cobalt chloride hexa hydrate, Nickel sulphate hexa hydrate, Copper chloride di hydrate) aqueous solution of metal chloride were de-aerated by passing dry and oxygen free nitrogen gas for about five minutes before mixing the solutions.

The metal solutions were added to ligand solution drop wise under nitrogen atmosphere in Schlenk: assembly with constant stirring. The reaction mixture was stirred for about two and half hours under the nitrogen atmosphere. The pH of the final reaction mixture was adjusted between 5 - 6.5 using 2N solutions of sodium hydroxide for above complexes so that solid complex appears in the mixture. The reaction mixture was kept overnight in a refrigerator for maximum precipitation of the complex. The precipitated complexes were separated by filtration and were washed with distilled water and then with ethanol. They were dried under vacuum at room temperature.

Magnetic Susceptibility Measurement:

Magnetic susceptibilities of transition metal complexes (Fe, Co, Ni and Cu) in solid state were carried out using Faraday method at room temperature. The molecular susceptibilities were corrected for diamagnetism of the component atoms by use of Pascal's Constants. The apparatus was calibrated with mercury (II) tetrathiocynato cobaltate [26]. The compound in the form of fine powder was packed densely in weighing tube and weights were recorded at various field strengths. The room temperature magnetic susceptibilities and magnetic moments were calculated using following equations:

$$\chi \, sp = \frac{\Delta\omega/m}{k}$$

Where, χ_{Sp} = Specific susceptibility of the sample.
m = Weight in grams of the sample in air.
$\Delta\omega$ = Increase in weight of sample in magnetic field.
k = Tube constant, Tube i) 6.367×10^4 cm^3/gm.
Tube ii) 1.6×10^4 cm^3/gm.

χ_M = χ sp x Molecular weight of sample.

χ_{Para} = $\chi_M - (-\chi \, dia)$
Where, χ_M = Molar susceptibility
χ_{Para} = Paramagnetic susceptibility
χ dia = Diamagnetic susceptibility

$$\mu = \frac{3 \, K \, T}{N} \quad x \quad \chi \, para = 2.83 \sqrt{\chi \, para \, x \, T}$$

Where, μ = Effective magnetic moment in ergs/gauss,
N = Avogadro's number, k = Boltzmann constant
T = Absolute temperature in degree kelvin
μ_{BM} = μ / β
Where, μ_{BM} = magnetic moment in Bohr magneton
β = Bohr magneton
= 9.267×10^{-21} ergs/gauss

Thermogravimetry:

Simultaneous TG and DTG were recorded at University of Pune , Pune (India) Perkin Elmer model No. 3700 TGA-7 thermal analyzer using about 15 mgm sample in platinum crucible. The rate of heating the sample holder was fairly constant at 10^0C per minute. The thermo-balance was calibrated using calcium oxalate. The heating was done in presence of inert atmosphere. The thermocouple used for recording the temperature was Pt-Rh -10 %

RESULTS AND DISCUSSION

The molar magnetic susceptibility χ_M and magnetic moment (μ_{BM}) for these metal complexes are depicted in Table 1

The complexes of Fe, Co and Ni are found to be paramagnetic while copper complex shows diamagnetic behavior. The experimental values of magnetic moments for Fe, Co and Ni complexes when compared with the magnetic moments of Fe, Co and Ni complexes in literature, [27] (Table 2) these values are found more close to the values of tetrahedral type of the complexes. The slight lower values of magnetic moment may be attributed to anti-ferromagnetic exchange interaction between paramagnetic transition metal ion and the ligand mostly in the semiquinone form

Table 1: Magnetic Susceptibility Data of Transition Metal complexes of 3-Aminolawsoneoxime

Complex	χ_{Sp} x 10^{-6} cgs unit	χ_M x 10^{-6} cgs unit	χ_{Para} x 10^{-6} cgs unit	$\mu_{eff \, (BM)}$ (obs)	$\mu_{cal \, (BM)}$
[Fe (NH$_2$LwOx) (H$_2$O)$_2$]	38.33	11307.0	11181.5	5.1	5.91
[Co (NH$_2$LwOx) (H$_2$O)$_2$]	23.12	6091.4	6217.2	3.8	3.87
[Ni (NH$_2$LwOx) (H$_2$O)$_2$]	9.73	2899.0	302.0	2.7	2.82
[Cu (NH$_2$LwOx) (H$_2$O)$_2$]	D	-	-	0.0	1.73

χ_{Sp} = Specific susceptibility χ_M = Molar susceptibility

χ_{Para} = Paramagnetic susceptibility, $\mu_{eff \, (BM)}$ = Effective magnetic moment in Bohr Magneton

Table 2 : Magnetic Moments of Complexes of Some Transition Metal Ions

Sr. No	Complex	Stereochemistry	μ_{cal} (BM)	μ_{obs} (BM)
1	$K_3[Fe(CN)_6]$	Octahedral	1.73	2.25
2	$(Et_4N)_2[FeCl_4]$	Tetrahedral	4.90	5.40
3	$Cs_2[CoCl_4]$	Tetrahedral	3.87	4.59
4	$[Co(BigH)_2]SO_4$	Square planer	1.73	2.49
5	$(EtN)_2[NiCl_4]$	Tetrahedral	2.83	3.89
6	$[Ni(BigH)_2]Cl_2$	Square planer	0.00	0.00
7	$[Cu(BigH)_2]Cl_2$	Square planer	1.00	1.73
8	$Cs_2[CuCl_4]$	Tetrahedral	1.73	2.00

BigH = Protonated biguanide

In copper complex the values of magnetic moment is lowered to such as extent that it shows diamagnetism at room temperature and needs VTMS, ERP studies for revealing the magnetic interaction. The diamagnetic nature of copper complex may be either due to the anti-ferromagnetic interaction via d-orbitals of copper centers in the stacked type of square planer diametric complex or diametric interaction as reported by Yerande [28]. The diametric nature of copper complex is also supported by ESR of analogous copper complex of parent ligand aminolawsone and low solubility of this complex in most of the common organic solvents.

Thermo gravimetric Studies:
Thermo gravimetric analysis (TGA) is an important supportive analytical tool to reveal the thermal behavior of the metal complexes. The close examination of TG curve of metal complexes gives an idea about their probable chemical composition. The thermal behavior of metal complexes (Fe, Co, Ni and Cu) and ligand in the form of TG Curve is shown in Fig. 3.11 to 3.15 and the data is presented in Table 3.

Table 3 : TG data of some transition metal complexes 3ALwOx in air atmosphere

Complex	Decomposition Temperature ^0C	Decomposition steps	Probable Composition of group lost	% Residue observed.
Fe L(H_2O)_2	379	I II	2H_2O L	27.24
Co L(H_2O)_2	354	I II	2H_2O L	23.5
Ni L(H_2O)_2	403	I II	2H_2O L	26.66
Cu L(H_2O)_2	290	I II III	2H_2O L	30.55

L = 3ALwOx

A careful inspection of TG curves shows that the metal decomposition while copper complex undergo three stage decomposition. The first stage of the decomposition in the complexes of Fe, Co and Ni indicates the loss of two co-ordinated water molecules and the second stage indicates the breaking of M – L bond and loss of ligand molecule.

In case of copper complex the decomposition is complex process. The first step of thermal decomposition corresponds to loss of water molecules while the second and third stages together are indicative of loss of ligand molecule. The end product of thermal decomposition in all four metal complexes of Fe, Co, Ni and Cu is found to be divalent metal oxide.

The thermal analysis of metal complexes thus suggests the probable chemical composition for these metal complexes to be ML (H_2O)_2.

Electronic Spectra:
This is secondary diagnostic tool used by researchers [29-32] to reveal metal quinone interactions in terms of electronic transitions.

The electronic spectra of ligand and metal complexes in DMSO solutions were recorded in the range 200 nm to 800 nm and are presented in Fig. 3.16 to 3.20. The data obtained from these electronic spectra are depicted in Table 4.

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Table 4 : Electronic Spectral frequencies in cm⁻¹ for some transition metal complexes of 3ALwOx

Frequencies in cm⁻¹					Tentative assignment
Ligand 3ALwOx	Fe-Complex	Co-Complex	Ni-Complex	Cu-Complex	
37735	38461	38461	38461	38461	$\Pi \rightarrow \Pi^*$
35714	36363	36363	36363	36383	$\Pi \rightarrow \Pi^*$
21739	25000	25000	25000	24390	CT

The electronic spectra of transition metal quinone complexes are usually dominated by charge transfer transitions. These transitions may be localized within the ligand molecule (For example, $\Pi \rightarrow \Pi^*$) or they may involve electron transfer between the metal ion and the ligand (M→L, L→M) [33-34].

A comparison of electronic spectra of free ligand and those of the corresponding metal complexes in DMSO solution shows the shifts in the positions of the bands on lower side. In free ligand the absorption appears at 265 (37735 cm⁻¹). 280 (35724 cm⁻¹) and 460 nm (21739 cm⁻¹) and 480 nm (21739 cm⁻¹) while in metal complexes the absorption appears at 260, 275 and 400 nm.

The two bands around 265 and 280 nm are assigned to ligand based localized $\Pi \rightarrow \Pi^*$ transitions while the third band around 400 nm may be due to charge transfer [35-36]. The shift of the charge transfer band toward the lower wave number side (400 nm) in metal complexes may be due to co-ordination of the 3ALwOx to the metal atom.

In the present work new 3-aminolawsoneoxime ligand was used in synthesize four metal complexes of divalent metals viz. Fe, Co, Ni and Cu. These metal complexes were characterized by using various physicochemical techniques.

The observed magnetic moment values for the complexes are closer to the values of tetrahedral type of structures. In copper complex the value lowers to such an extent that it shows diamagnetism probably due to anti-ferromagnetic interaction via d-orbitals of two Cu centers present in stacked type square planar structure.
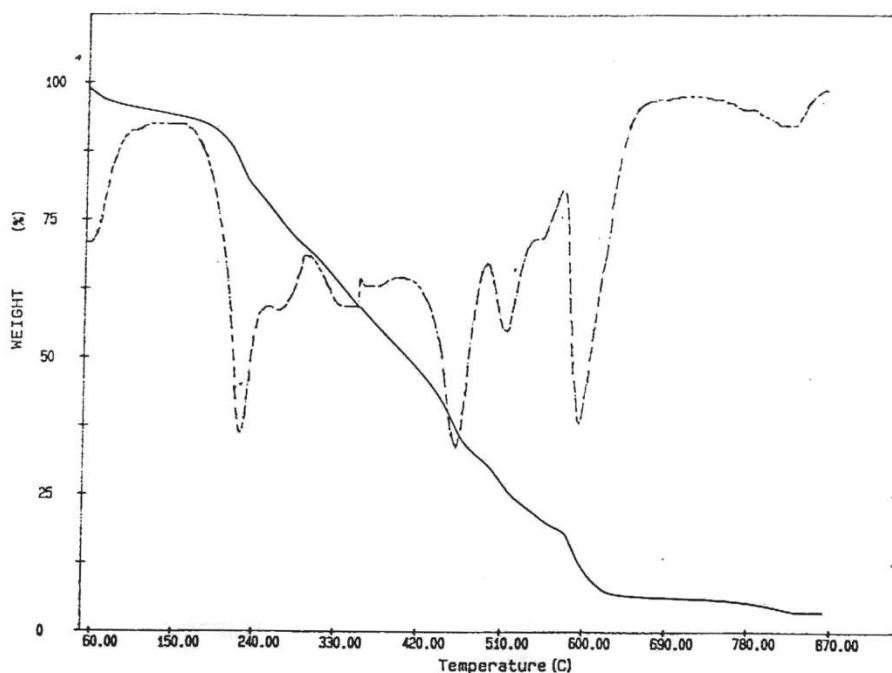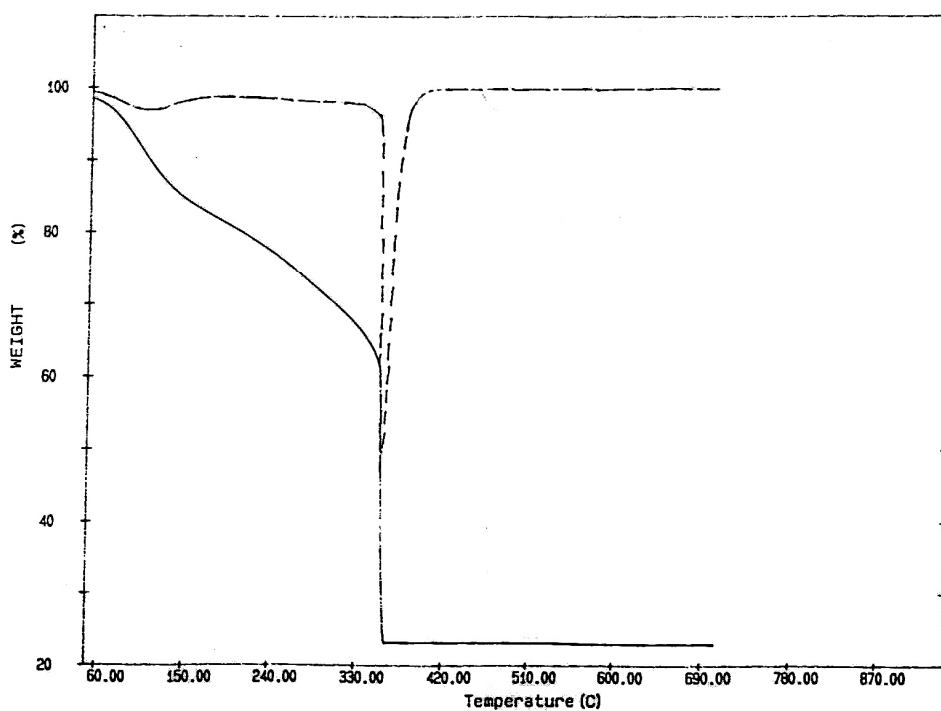

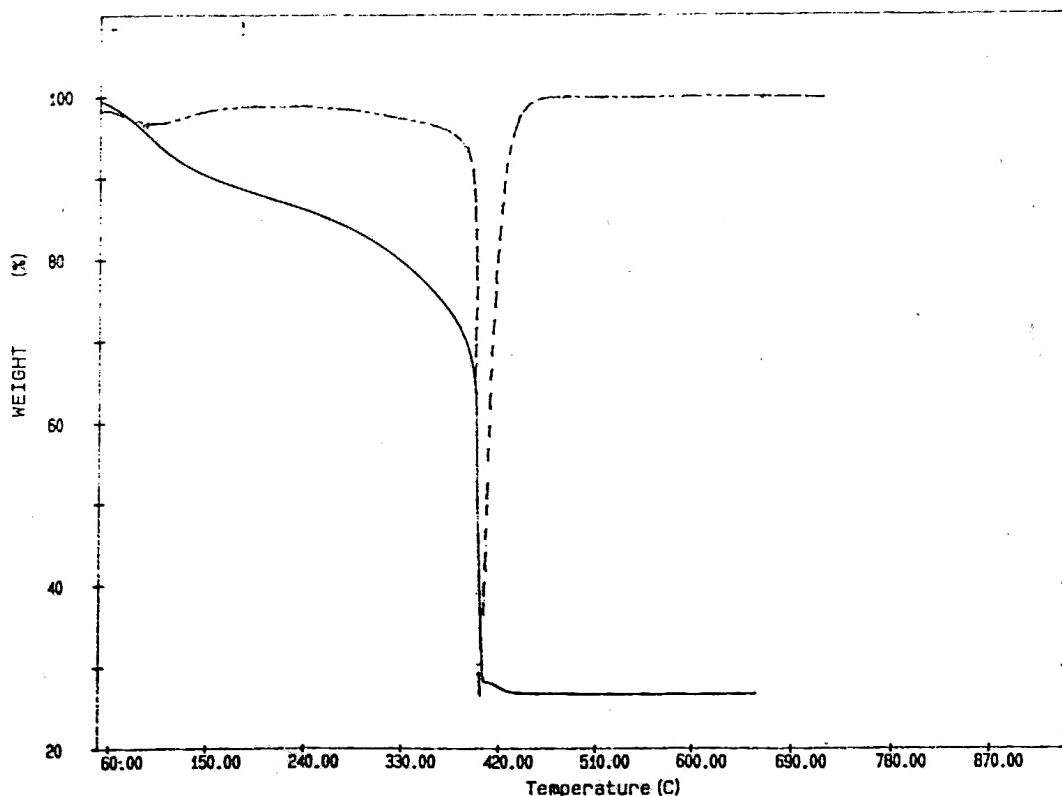*DELTA SERIES TGA7*
Fig. 3.11 : Thermogram of 3ALwOx
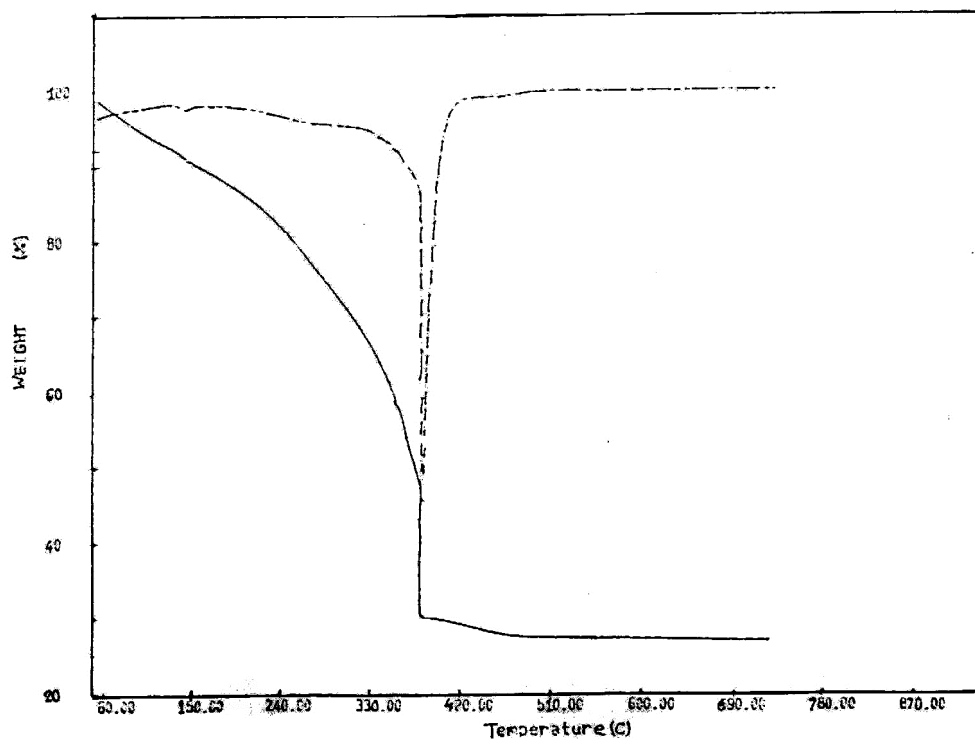
DELTA   SERIES   TGA7

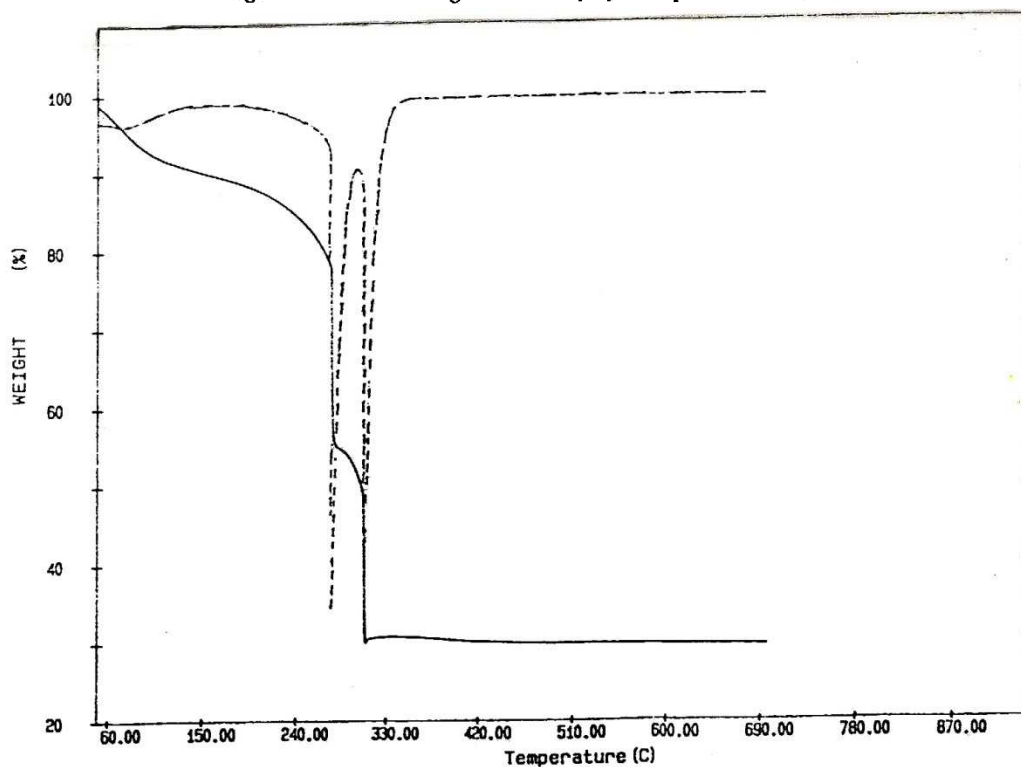**Fig. 3.12 : Thermogram of Fe(II) Complex with 3ALwOx**

DELTA SERIES TGA7

Fig. 3.13 : Thermogram of Co(II) Complex with 3ALwOx

DELTA SERIES TGA7

Fig. 3.14 : Thermogram of Ni(II) Complex with 3ALwOx

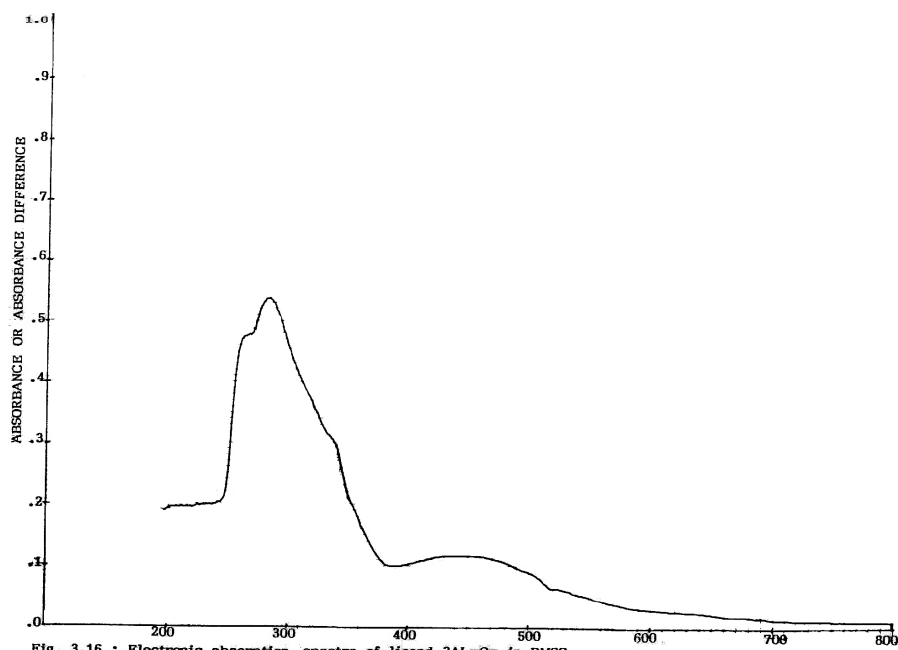DELTA SERIES TGA7

Fig. 3.15 : Thermogram of Cu(II) Complex with 3ALwOx

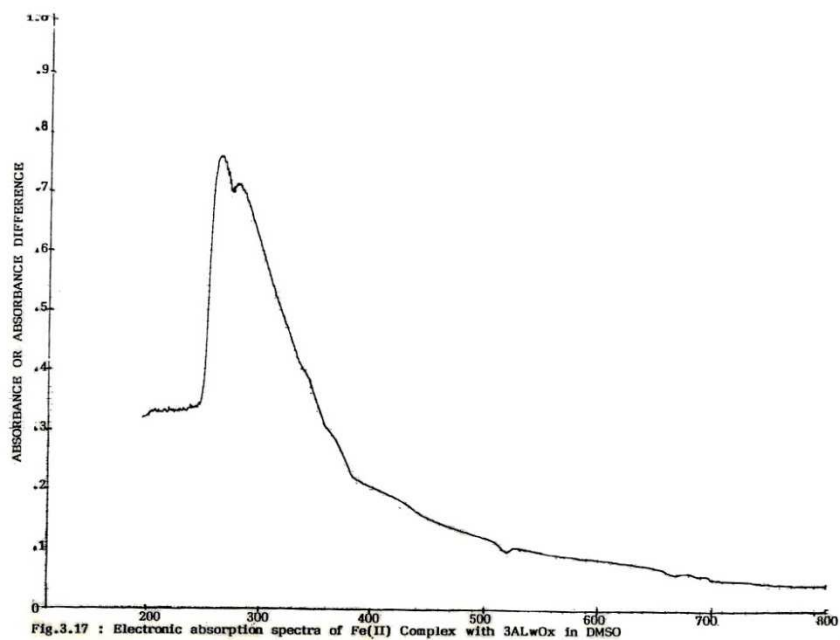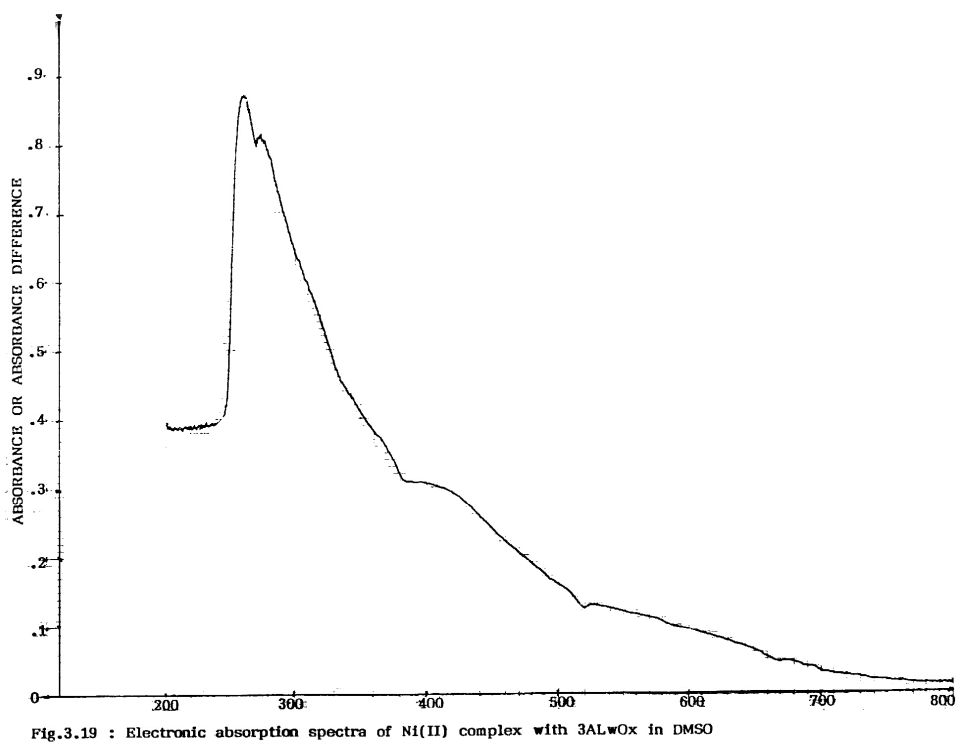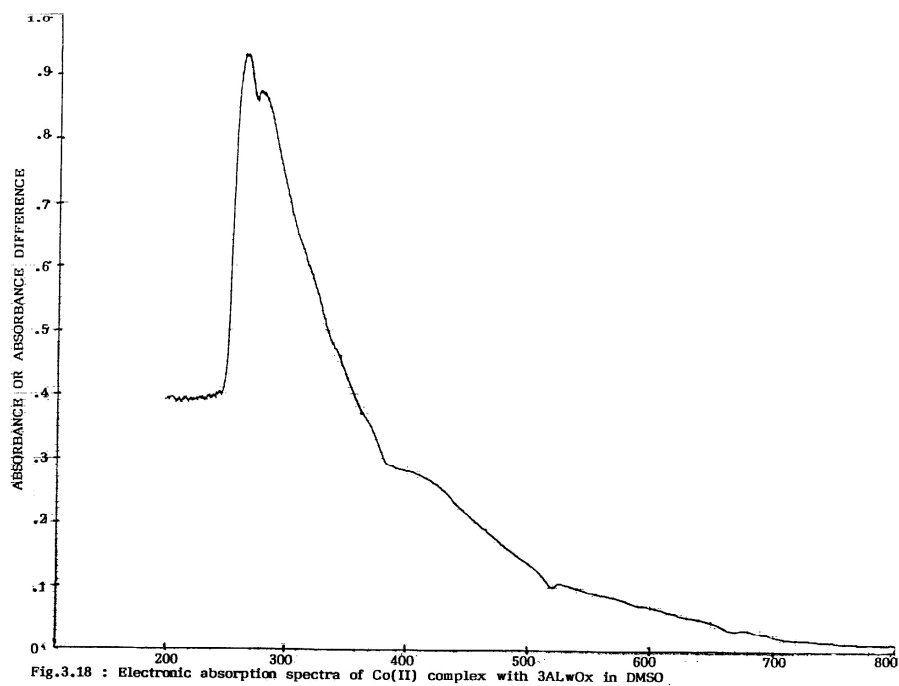Fig. 3.16 : Electronic absorption spectra of ligand 3ALwOx in DMSO

Fig.3.17 : Electronic absorption spectra of Fe(II) Complex with 3ALwOx in DMSO

Fig.3.18 : Electronic absorption spectra of Co(II) complex with 3ALwOx in DMSO

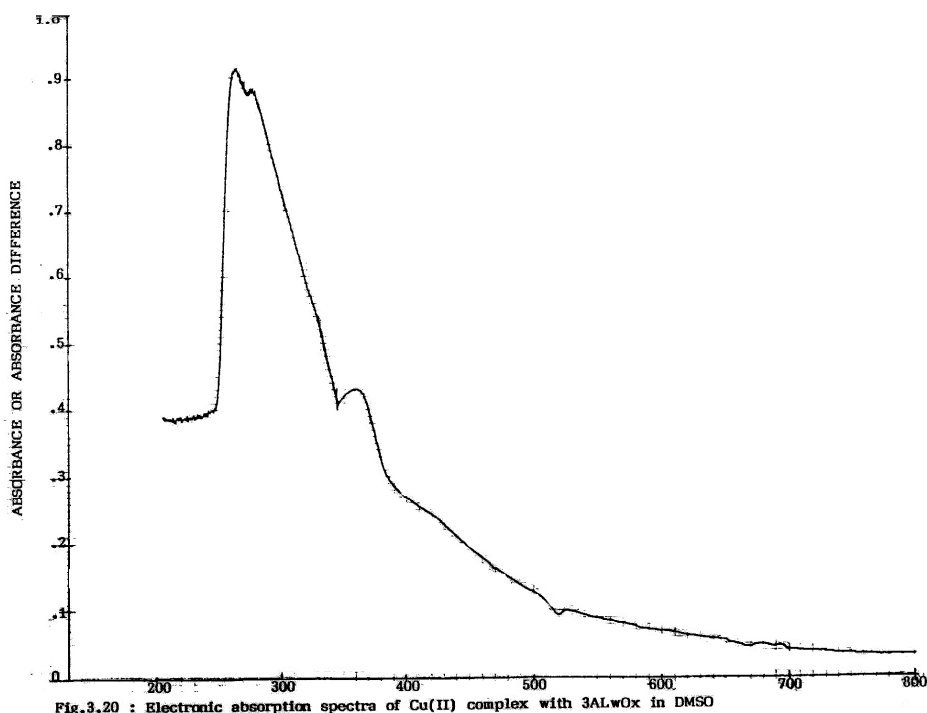Fig.3.19 : Electronic absorption spectra of Ni(II) complex with 3ALwOx in DMSO

Fig.3.20 : Electronic absorption spectra of Cu(II) complex with 3ALwOx in DMSO

On the basis of the electronic spectra for the complexes coupled with the magnetic studies for these complexes distorted tetrahedral structures are proposed for Fe, Co, and Ni complexes while square planar structure may be for copper complex.

Thermal studies for the complexes shows that two water molecules are coordinated to the metal ion. After decomposition of the complexes the final residue is fitted as the divalent metal oxides. The probable composition for all the metal complexes is thus, $ML (H_2O)_2$.

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