“Synthesis, Characterization and microbial studies of transition metal complexes of 2-hydroxy 1, 4 Napthoquinone derrivatives”

Final Report of Minor Research Project

Submitted to

University Grants Commission, New Delhi

Submitted By

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PATIL K.D. THOMBARE A.L.

CONTENTS

List of Abbreviations used

- Phthox - Pthiocolmonoxime
- NCS - N- Chlorosuccinamide
- NBS - N-Bromosuccinamide
- NIS - N- Iodosuccinamide
- Py - Pyridine
- DMSO - Dimethyl sulfoxide
- Ea – Activation Energy
- Fe-1 – Fe(Phthox)2
- Fe-2 – Fe(Phthox)2Cl2
- Fe-3 – Fe(Phthox)2Br2
- Fe- 4 – Fe(Phthox)I2
- Fe-5 – Fe(Phthox)2(py)2
- Fe-6 - Fe(Phthox)4SCN
- Q – Quinone
- SQ – Semiquinone
- NQ – Napthoquinone
- NSQ - Napthosemiquinone
- CAT – Catechol
- SQPL – Square Pyramidal
- SQPL – Square Planer
- SE – Electrophilic Substitution

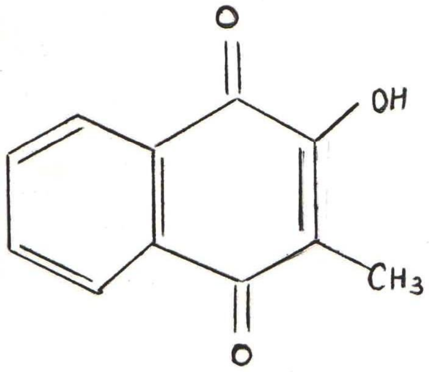
❖ Introduction

The synthesis and antimicrobial activity of metal chelates is of great importance due to their wide applications in laser technology[1], biological Sciences [1,2,3,4,5] and industry. There has been a growing interest in the structural study of the chelates derived from organic compounds containing nitrogen and oxygen donors with antimicrobial activity. The chelates of selective metal ions from first transition series have been found to be more active with promising results than the ligand itself against several types of bacteria[6]. The significant antimicrobial activity has shown by metal complexes with 8- hydroxyquinoline increases their importance in medical and biochemical sciences[7].

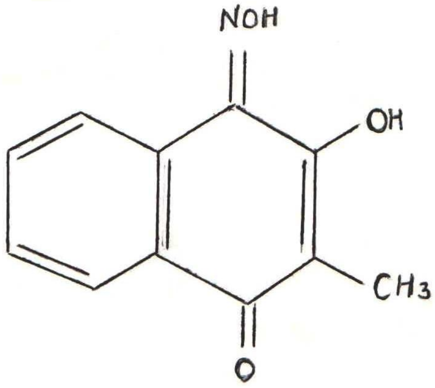
Quinones are naturally occurring materials in soils, plants and animals. Quinones play an important role in many biological electron transfer processes particularly in respiration and photosynthesis. During these processes they are reversibly reduced while divalent metal centers are oxidized.

The derivative of quinine, Lawson (i.e. –hydroxyl-1, 4-napthoquinone) is a coloring material obtained from lawsonia alba which is known as heena. It is also indicated to be useful in the treatment of various ailments, diseases and as disinfectant. Some of the derivatives of quinine show antimicrobial and antimalerial activities due to the formation of metal complexes as intermediates [8-10]. The hydroxyquinone derivatives of 1,4-napthoquinone class have been of interest for sometime due to their mention as therapeutic agents in Indian system of medicine [11-13].

The reactivity of coordinated complex provides a reaction of great versatility when ligands as well as metal centres are prone to redox activity. Hence, it is necessary to see the intramolecular electron transfers probably in redox active ligands viz. phthiocolmonoxime (pthox) (I to IV) having biological releavance. Such electronic transmissions,



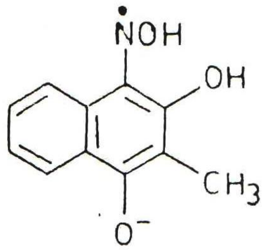
(I) Phth



(II) PhthOX

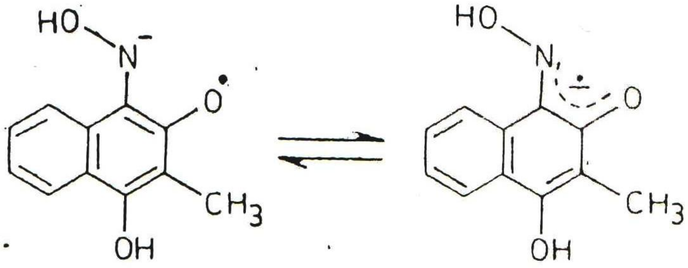
In co-ordinated ligands are well induced in "square planer" complex of nickel when it undergoes through different reactions[14],

(II) NQ

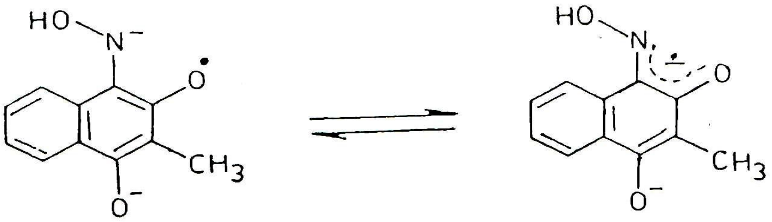


(III) NS$\dot{\bar{Q}}$

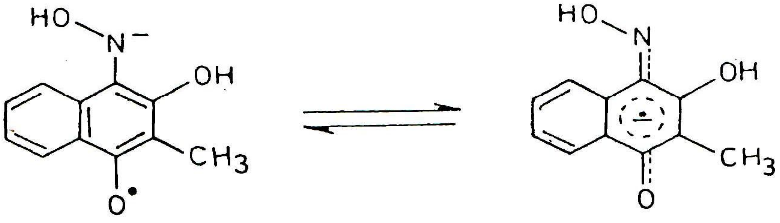
iminoxy radical



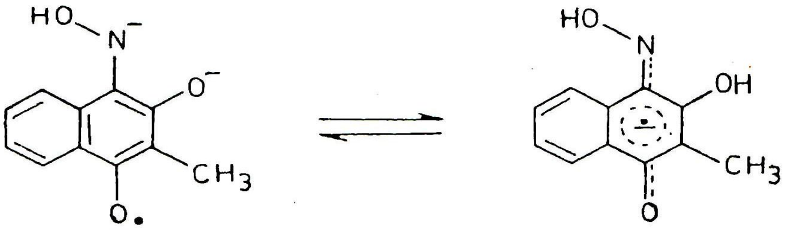
(IIIa) 4-OH-1,2-naphthosemiquinoneoxime



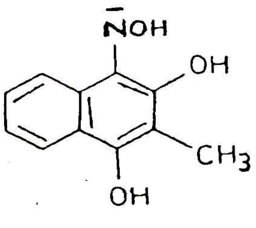
(IIIb) 4-oxido-1,2-naphthosemiquinoneoxime



(IIIc) 2-OH-1,4-naphthosemiquinoneoxime



(IIId) 2-oxido-1,4-naphthosemiquinoneoxime



(IV) CAT

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The interaction of ferrous sulphate with phthiocolmonoxime in the metal; ligand ratio of 1:2 leads to the formation of monomeric complex Fe-1 having general formula ML_2 which is a four co-ordinate compound. It is co-ordinatively unsaturated square planer complex as shown in fig. (II)

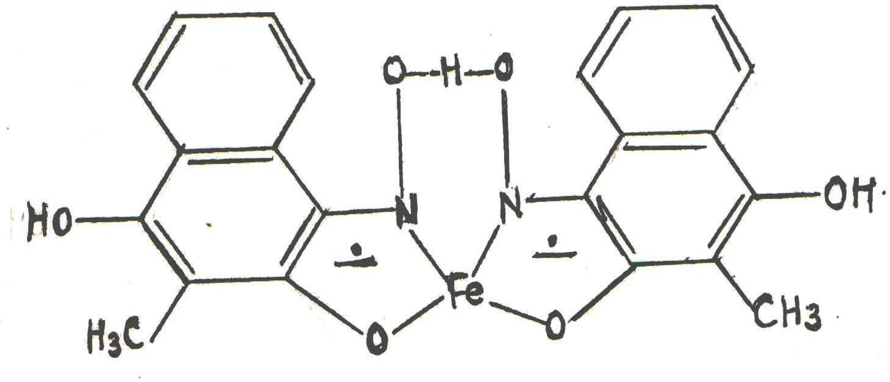


Fig. II Fe- 1

The Fe-1 complex will be susceptible for addition reactions as it is co-ordinatively unsaturated. Although the ligand ratio of syn; amphi forms in phthox is reported to be 30:70, on co-ordination 'syn' form is activated by metal centre and intramolecular hydrogen bonding in oxamino groups leads to large stability in square planar co-ordination.

The chemical reactions of Fe-1 with various reagents were carried out as per the procedures reported in the experimental aspects chapter IV, to prepare the various adduct compounds of Fe-1 complex. It gives the various adduct Fe-2 to Fe-4. All these chelates are anhydrous like parent Fe-1 complex, Table 2-1(a).

Table -2-1 (a) : Analytical data of parent and mixed chelates of iron with phthiocolmooxime.

Compound	Colour	% Yield	Decomposition Temp. (OC)
Fe-1	Dark green	85	260
Fe-2	Pale yellow	90	240
Fe-3	Olive green	87	190
Fe-4	Blackish brown	85	180

Fe-1 :- $Fe(Phthox)_2$

Fe-2 :- $Fe(Phthox)2.Cl_2$

Fe-3 :- $Fe(Phthox)2Br_2$

Fe-4 :- $Fe(Phthox)2.l_2$

The adduct obtained as above from the parent complex may be named as

Fe-2 :- Dichloro-bis- (Pthiocolmonoximato) Iron (III)

Fe-3 :- Dibromo-bis- (Pthiocolmonoximato) Iron (III)

Fe-4 :- Dilodo-bis- (Pthiocolmonoximato) Iron (III)

All these mixed chelates are systematically analysed by elemental analysis, TGA/DTA, magnetic susceptibility measurements, conductivity measurements, IR studies etc. We infer that the halogenated products Fe-2 to Fe-4 have $ML_2 X_2$ type of formulation, where (x=Cl,Br,I) and L = phthox respectively table 2.1(b).

Fig. 2.1 (a) to 2.1(d) TGA Curves for

Fe-1, Fe-2, Fe-3 and Fe-4 Complexes

NETZSCH-Gerätebau GmbH Thermal Analysis

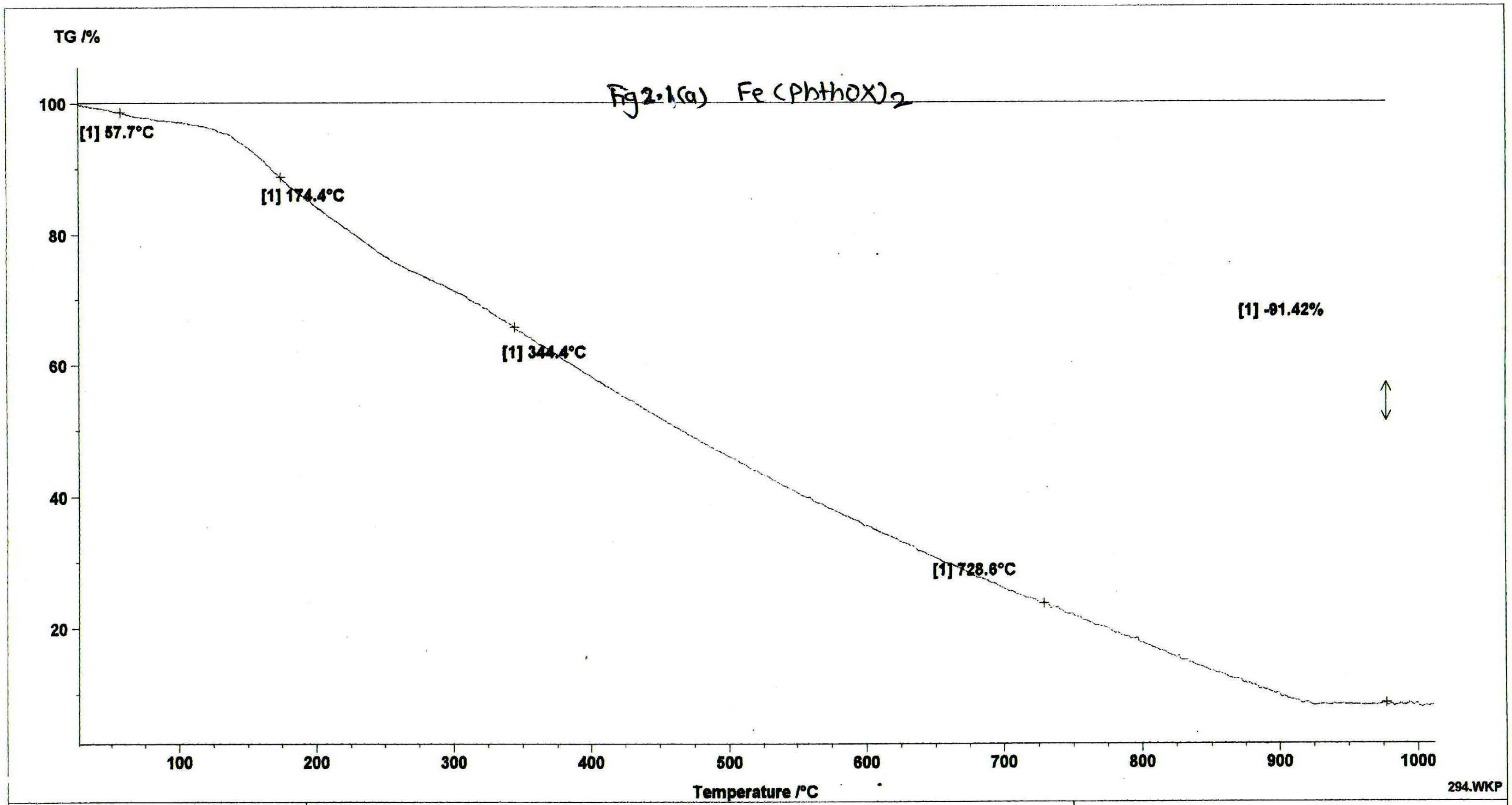


Fig 2.1(a) Fe(phthox)$_2$

INSTRUMENT:	STA 409C	SAMPLE:	YT-1...Ref-294	10.180 mg	MODE/TYPE OF MEAS.:	DTA-TG/samp.+corr.
FILE:	294A.DSS	REFERENCE:	Alumina	22.620 mg	SEGMENTS:	1/1
PROJECT:	External	MATERIAL:	Inorganic		CRUCIBLE:	DTA/TG crucible Al2O3
IDENTITY:	009	CORR / TEMP.CAL.-/SENS-FILE:	NEW10R.BSS/CAL10.TSS/SENSNULL.EXX		ATMOSPHERE:	nitrogen/70
DATE/TIME:	20.11.03 11:15	RANGE:	25 °C/10.0(K/min)/1100 °C		TG-CORR/M.RANGE:	020/50
LABORATORY:	RSIC	SAMPLE CAR./TC:	DTA(/TG) HIGH RG 2/S		DSC-CORR/M.RANGE:	020/500
OPERATOR:	CB	REMARK:				

NETZSCH-Gerätebau GmbH Thermal Analysis

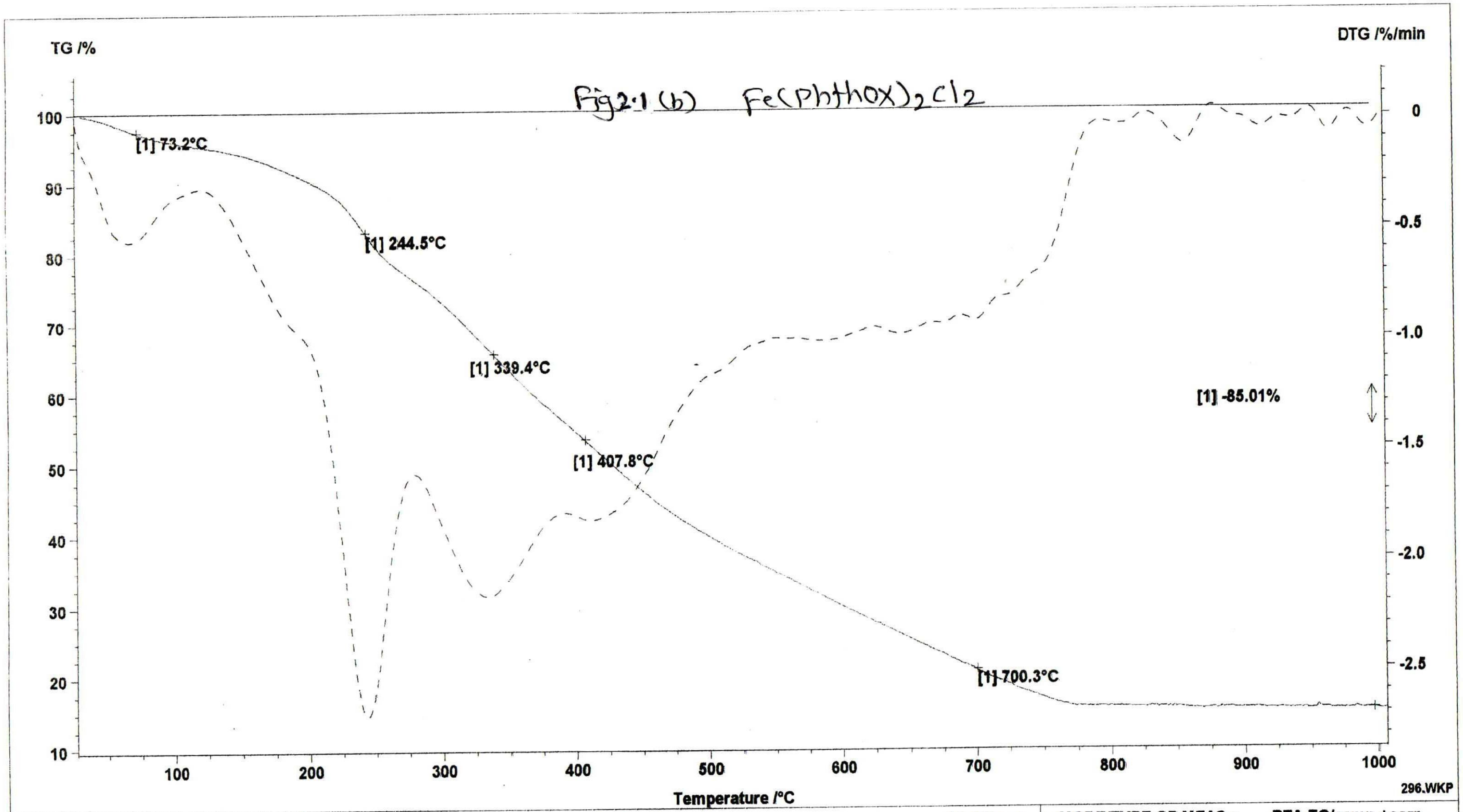


Fig 2.1 (b) Fe(phthox)$_2$Cl$_2$

INSTRUMENT:	STA 409C	SAMPLE:	KT4....REF-296	10.460 mg	MODE/TYPE OF MEAS.: DTA-TG/samp.+corr.
FILE:	296C.DSS	REFERENCE:	Alumina	11.980 mg	SEGMENTS: 1/ 1
PROJECT:	External	MATERIAL:	inorganic		CRUCIBLE: DTA/TG crucible Al2O3
IDENTITY:	009	CORR / TEMP.CAL.-/SENS-FILE:	NEW10R.BSS/CAL10.TSS/SENSNULL.EXX		ATMOSPHERE: nitrogen/70
DATE/TIME:	20.11.00 11:53	RANGE:	25 °C/10.0(K/min)/1100 °C		TG-CORR/M.RANGE: 020/50
LABORATORY:	RSIC	SAMPLE CAR./TC:	DTA(/TG) HIGH RG 2/S		DSC-CORR/M.RANGE: 020/500
OPERATOR:	CB	REMARK:			

NETZSCH-Gerätebau GmbH Thermal Analysis

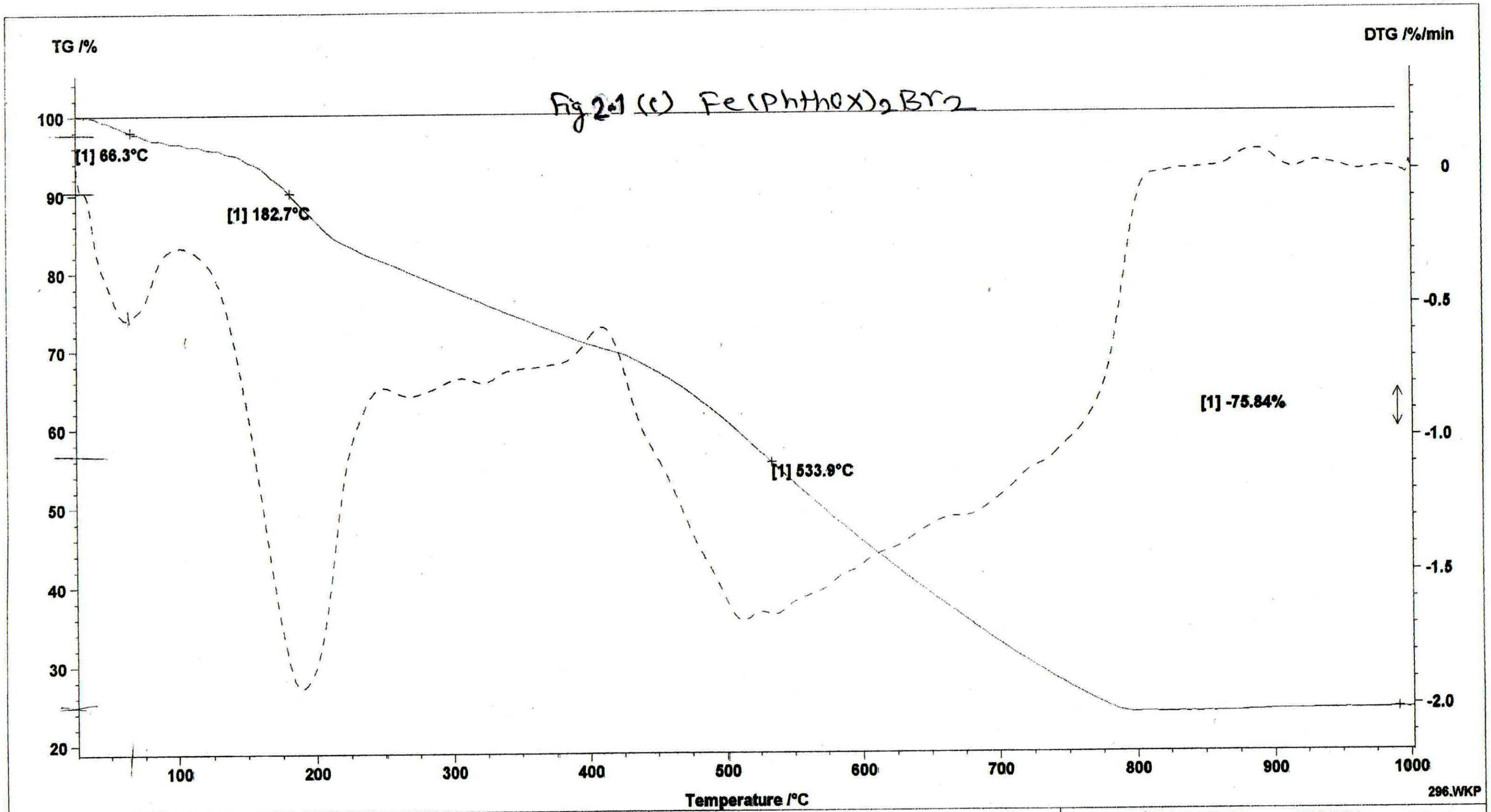


Fig 2.1 (c) Fe(Phthox)$_2$Br$_2$

INSTRUMENT:	STA 409C	SAMPLE:	KT5....REF-296	12.920 mg		MODE/TYPE OF MEAS.:	DTA-TG/samp.+corr.
FILE:	296D.DSS	REFERENCE:	Alumina	11.980 mg		SEGMENTS:	1/ 1
PROJECT:	External	MATERIAL:	inorganic			CRUCIBLE:	DTA/TG crucible Al2O3
IDENTITY:	009	CORR / TEMP.CAL.-/SENS-FILE:	NEW10R.BSS/CAL10.TSS/SENSNULL.EXX			ATMOSPHERE:	nitrogen/70
DATE/TIME:	20.11.09 15:35	RANGE:	25 °C/10.0(K/min)/1100 °C			TG-CORR/M.RANGE:	420/50
LABORATORY:	RSIC	SAMPLE CAR./TC:	DTA(/TG) HIGH RG 2/S			DSC-CORR/M.RANGE:	020/500
OPERATOR:	CB	REMARK:					

NETZSCH-Gerätebau GmbH Thermal Analysis

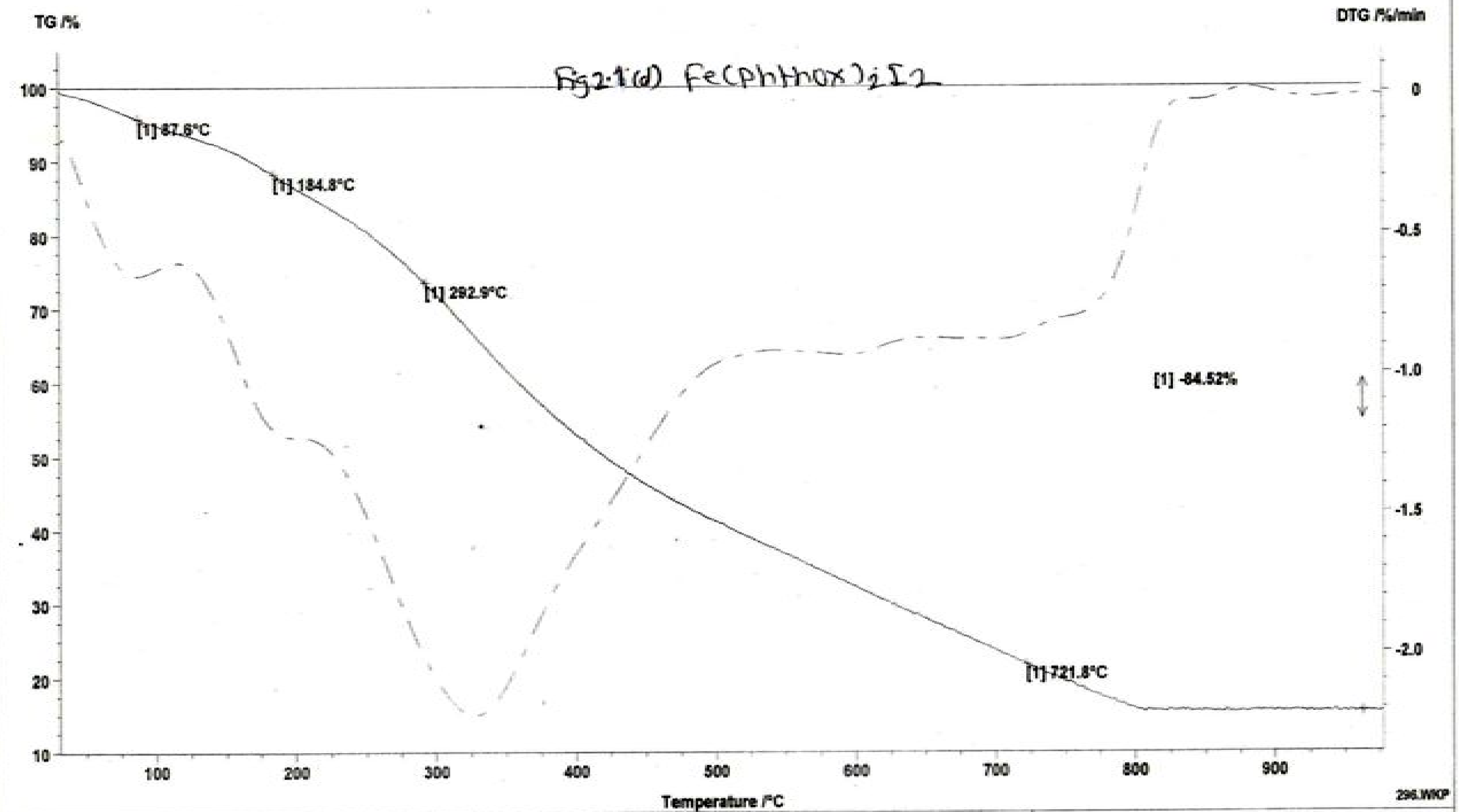


Fig 2.1(d) Fe(phthox)$_2$I$_2$

INSTRUMENT:	STA 409C	SAMPLE:	KT6...Ref-296	11.880 mg	MODE/TYPE OF MEAS.:	DTA-TG/samp.+corr.
FILE:	296E.DSS	REFERENCE:	Alumina	11.980 mg	SEGMENTS:	1/ 1
PROJECT:	External	MATERIAL:	inorganic		CRUCIBLE:	DTA/TG crucible Al2O3
IDENTITY:	009	CORR / TEMP.CAL.-/SENS-FILE:	NEW10R.BSS/CAL10.TSS/SENSNULL.EXX		ATMOSPHERE:	nitrogen/70
DATE/TIME:	21.11.09 12:32	RANGE:	25 °C/10.0(K/min)/1100 °C		TG-CORR/M.RANGE:	020/50
LABORATORY:	RSIC	SAMPLE CAR./TC:	DTA(/TG) HIGH RG 2/S		DSC-CORR/M.RANGE:	020/500
OPERATOR:	CB	REMARK:				

Fig. 2.2 (a) to 2.2(d) DTA Curves for

Fe-1, Fe-2, Fe-3 and Fe-4 Complexes

NETZSCH-Gerätebau GmbH Thermal Analysis

Fig.2.2(a) Fe(Phthox)$_2$

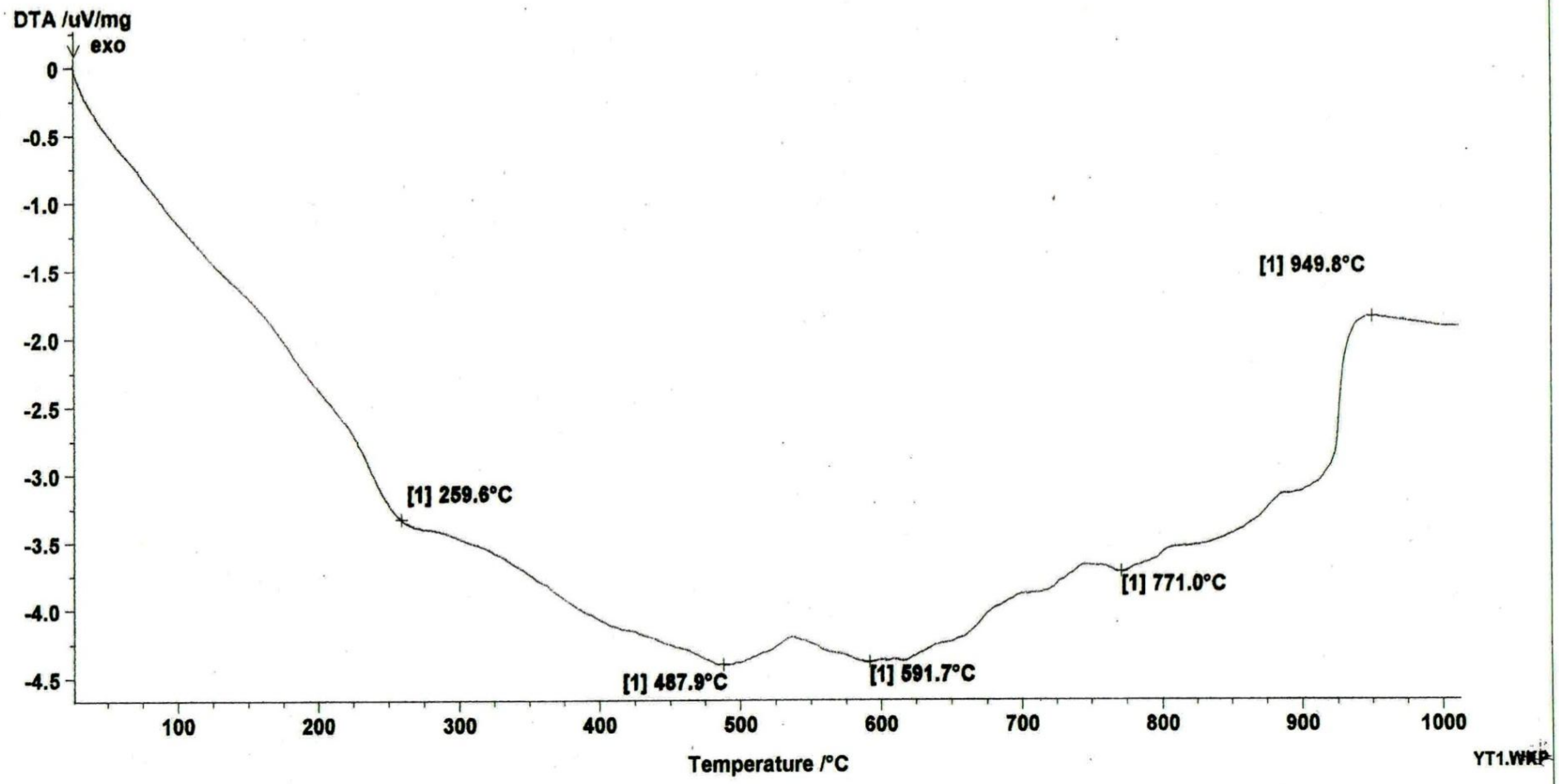
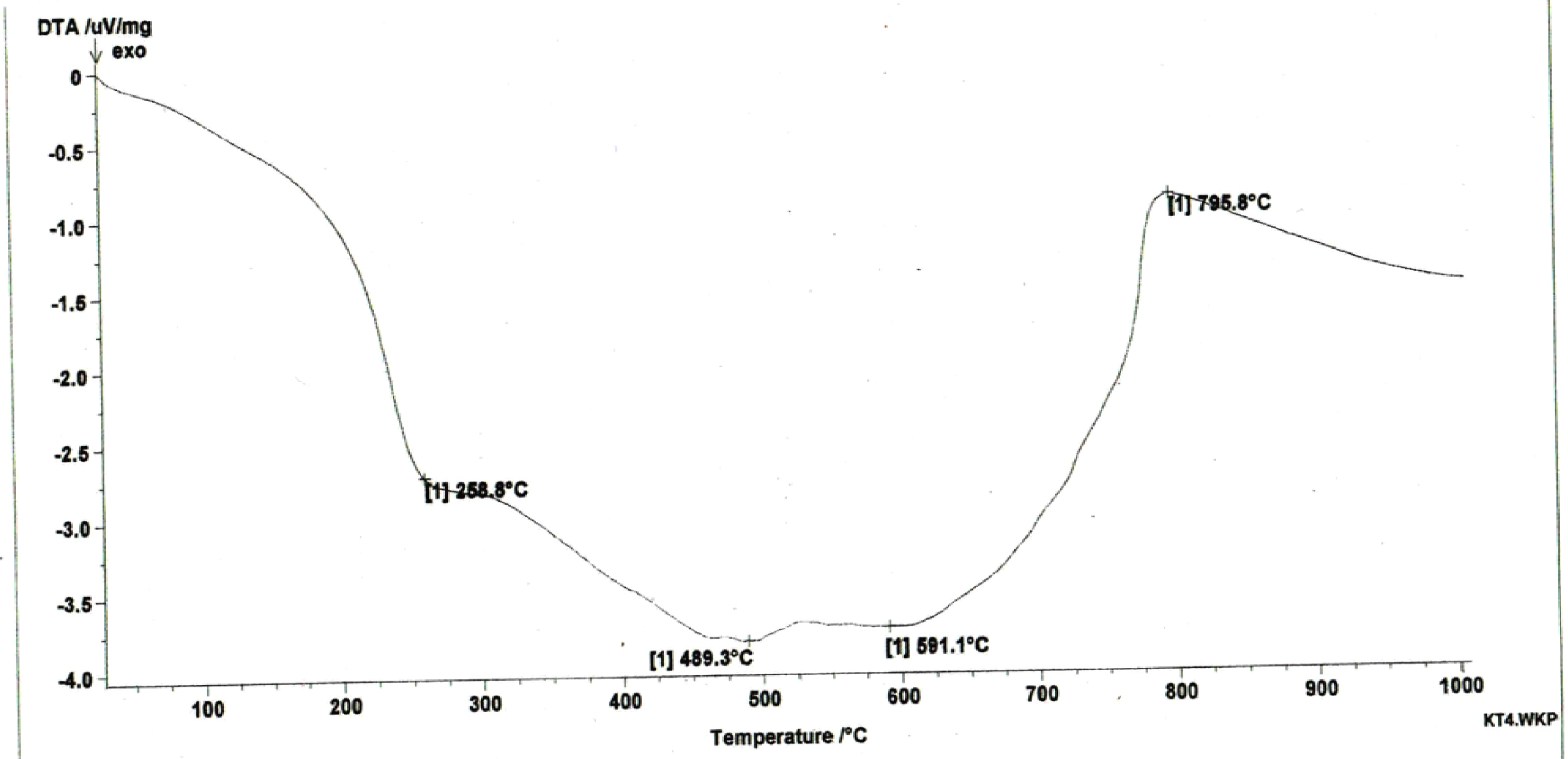
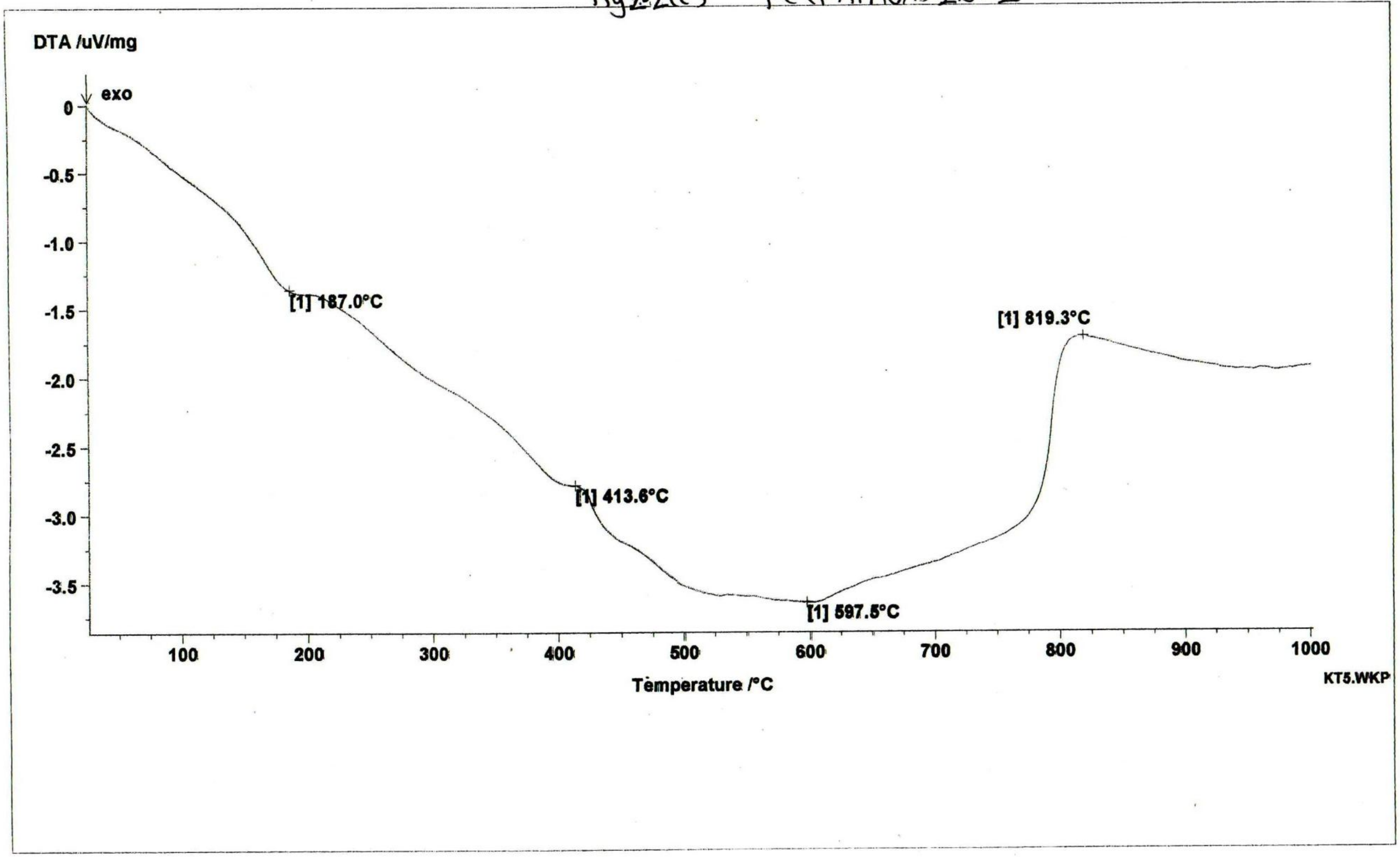


Fig 2:2(b) $Fe(phthox)_2Cl_2$



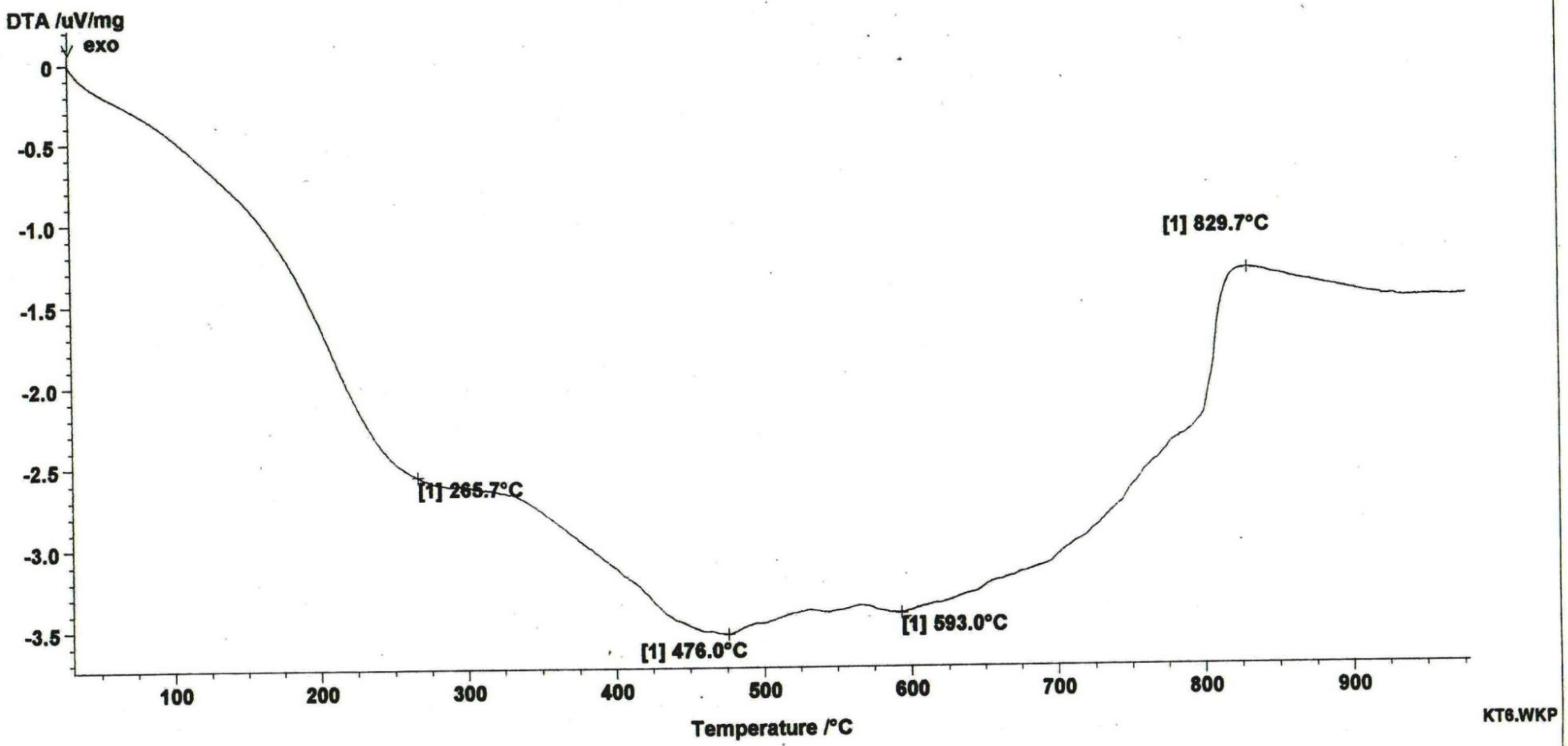
ETZSCH-Gerätebau GmbH Thermal Analysis

Fig 2.2(c) $Fe(Phthox)_2Br_2$



NETZSCH-Gerätebau GmbH Thermal Analysis

Fig2.2(d) $Fe(phthox)_2I_2$



- **Table 2.1 (b)**

Analytical data of parent and mixed chelates of iron with phthiocolmonoxime.

Compound	**Elemental Analysis (%)**				
	C	H	N	Fe	Residue
Fe-1	57.89 (57.39)	3.83 (3.48)	6.10 (6.07)	11.95 (11.29)	16.91 (15.65)a
Fe-2	54.83 (53.91)	3.74 (3.23)	5.00 (5.65)	11.00 (11.29)	15.59 (16.23)a
Fe-3	41.01 (42.8)	2.76 (2.58)	5.11 (4.81)	9.15 (9.02)	13.00 (12.90)b
Fe-4	47.34 (46.09)	3.37 (3.10)	5.22 (4.97)	9.50 (9.55)	13.65 (14.00)

a- Residue – FeO.

b- Residue – Fe + 0.25 Br.

c- Residue - Fe+ 0.5 l

(Figures in parenthesis represent theoretically calculated values).

Apart from all other halogenating agents, NCS, NBS, NIS, in $CHCl_3$ are found to be most suitable for halogenations reactions in metals chelates, which are acid labile. In case of halogenations of Fe-1 chelate all the the other reagents except NCS/NBS/NIS fail to yield undecomposed products. The acid labile nature of metal-quinone oximates has been reported in case of copper oximates.[1]

Generally, Whenever succinamide reagents are used they follow the synthetic route of “electrophilic substitution” by replacing the proton on the chalate rings, As the ractive C-3 site of hydrogen is replaced by CH_3 group substituent in phthox.

SE type mechanism in halogenations reaction is purposefully prevented in formation of Fe-1- to Fe-4 compounds. The halogenating agents has to follow a selective of " Oxidative addition" at metal centre.[2]

Through the composition of halogenated mixed chelates of Fe-1 is ML_2X_2, the Fe-2 to Fe-4 compounds are dihalo in composition, these can be correctly designated according to ion-pair complexes of Copper (II)[3]

such as,

Halo- (2-oxido-1, 4-napthoquinone oximato) ion pair

(4-oxido-halo-1,2-naphtosemiquinone oximato iron (III)

This is because succinamide performs both types of reaction mechanisms viz free radical and nucleophilic substitution. The halide radical, □ and halonium ion, X^+, have to follow two selective paths of addition raction with Fe-1. Although Fe-2 to Fe-4 performs ML_2X_2 composition, the stoichiometry of addition reaction at metal centre is restricted to one X only depending upon nature of the metal ion.[4] Hence Fe(II) in Fe-1 get oxidized to Fe-III during radical □ "oxidative addition", but as Fe(IV) reaction intermediates are rarely reported in literature similar as Co (IV)[5], the second X addition at metal centre is prevented. So only the ML_2X type adduct formation is progressed via "Oxadative addition" of one □ at metal centre, Fe(II) converts to Fe-III, together with oxidation of one NSQ ligand to NQ form. The preventation of second □ addition at same metal site results in second choice of electrophilic substitution path[6] for halogen in the form of X^+ ion at electronegative site on NSQ type co-ordinated ligand.

Finally the attack to X^+ electrophile at 4-Oxido position of second ligand in Fe-1 leads to ion pair formation like O---X^+, to nutrilize charge on organic moiety. The X^+ is not performing finally a strong covalent bond but a weak electrostatic interaction at 4-oxido site of NSQ ligand.

As Fe-2 to Fe-4 fail to show electrolytic nature, also proves that, the second halogen is not is secondary valency of Co-ordination sphere but is in primary valency of co-ordination sphere. It was confirmed form the conductivity measurements carried out for parent as well as the adduct chelates.

❖ Decomposition temperature and thermal stability.

The non-isothermal TG of the compounds Fe-1 to Fe-4 were carried out in air atmosphere. The incipient decomposition temperatures, which are crude measure of thermal stabilities for Fe-1 to Fe-4 compounds show the following order,

Fe-4 < Fe-2 < Fe-3 < Fe-1

The halogenato adducts Fe-2 to Fe-4 show lower thermal stability as compared to parent compound Fe-1.

❖ Summary and Comments

The through investigations thermal decomposition reaction in Fe-2 to Fe-4 compounds reveals the following points;

1. The average Ea for evolution of phthox ligand is □ 20.10 Kj/mole, Which is comparable with the same ligand as reported in its cobalt and nickel analogues.
2. The compound Fe-1 undergo “oxidation addition” reaction which result in Fe-2 to Fe-4 compounds of halogen adducts as follows;

$$\text{Fe-}^{+2}(\text{NS}\dot{\bar{\text{Q}}})\ (\text{NS}\dot{\bar{\text{Q}}})\ \xrightarrow{\text{NCS/NBS/NIS}}\ \text{Fe}^{+3}\ (\text{NQ})\ (\text{NS}\dot{\bar{\text{Q}}}\text{-------X})\ \text{X}$$

Fe-1 Fe-2 to Fe-4

Where X= Cl, Br, I, while for Fe-5 compounds undergo simple addition reaction as follows;

$$\text{Fe-}^{+2}(\text{NS}\dot{\bar{\text{Q}}})\ (\text{NS}\dot{\bar{\text{Q}}})\ \xrightarrow{\text{Py}}\ \text{Fe}^{+2}\ \text{F-}^{+2}(\text{NS}\dot{\bar{\text{Q}}})\ (\text{NS}\dot{\bar{\text{Q}}})\ (\text{Py})_2$$

Fe-1 Fe-5

The synthetic route for Fe-6 is as follows;

$$\text{Fe-}^{+3}(\text{NQ})\ (\text{NS}\dot{\bar{\text{Q}}}\text{----X})\ \text{X}\ \xrightarrow{\text{SCN}^-}\ \mu\text{-SCN-}[\text{Fe}^{+2}(\text{NQ})\ (\text{NS}\dot{\bar{\text{Q}}})]_2$$

Fe-2 Fe-6

3. Fe-1 follows homogeneous decomposition mechanism while, the adduct compounds undergo heterogeneous decomposition mechanism during pyrolysis.
4. The Ea values of “Adduct Ligands” (viz. Cl, Br, I, P_y and SCN) show inverse relation with their crystal field strengths.
5. The lighter rates of decomposition in case of Fe-2 to Fe-4 adducts as compared to Fe-5 and Fe-6 compounds shows effective polarization in Fe-2 to Fe-4 compounds.

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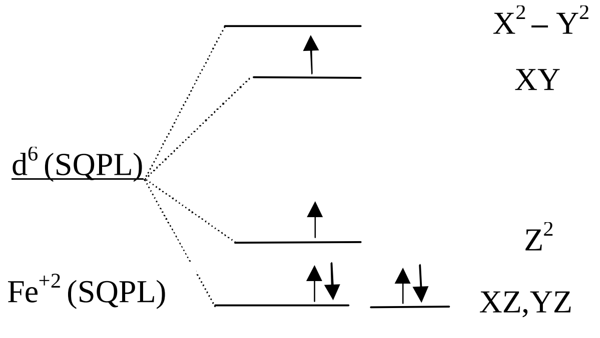
- **Chapter- III**

Magnetic susceptibility Measurements :

The room temperature magnetic susceptibility measurements using faraday technique show paramagnetic properties to all compounds Fe-1 to Fe-4.

Fe-1 is a strong field square planar complex. According to VBT, it possess dsp2 hybridization. With two unpaired electrons on Fe(II) metal centre.

The CFT model (I) leads to electronic configuration containing two unpaired electrons in dz^2 and dxy orbital with empty $dx^2 – y^2$ orbital[1]



However the two paramagnetic ($\mathrm{NS}\overset{\bullet}{\overline{\mathrm{Q}}}$) ligands at equatorial positions may show antiferromagnitic coupling of radical electrons via 6-bonding dx^2-y^2 metal orbital.[2] Hence the observed value of magnetic moment for fe-1 is 2.25 BM.

The Fe-2 to Fe-4 compounds have Fe^{+3} (SQPY) configuration. The dsp^3 hybridization results in one unpaired electron at metal centre. So these compounds show magnetic moments near to 1.79BM with spin only formula. The observation need further refinements.

- **IR Studies**

The IR spectra of phthox ligand, parent chelate Fe-1 and its adduct compounds Fe-1 to Fe-4 are presented in Fig. 3.1 and their significant absorptions are summarized in table 3.1.

A] Hydroxyl stretch region

Except Fe-1 the ligand phthox together with the remaining co-ordination compound show weak broad hydroxyl stretch frequency in the region of 3100-3350 cm. which can be assigned on either C-2 phenolic hydroxyl in ligand or oximino hydroxyl frequency in chelates. As Fe-1 to Fe-4 chelates are anhyfrous one as confirmed from their TG studies, these absorptions are not due to hydroxyl stretch frequency from water molecule.

Strong intramolecular H-bonding effect is seen in case of symmetric SQPL, Fe-1 which leads to absence of (OH) absorption. It also supports that H-bonding giving rise to very stable six-membered ring establishing 'cis' isomer [1] however lower symmetry in Fe-2 to Fe-4 show weak bond (OH) absorption, which may be due to slight rise in polarity of six membered H-bonding.

B] 1700 to 1200 cm^{-1} region

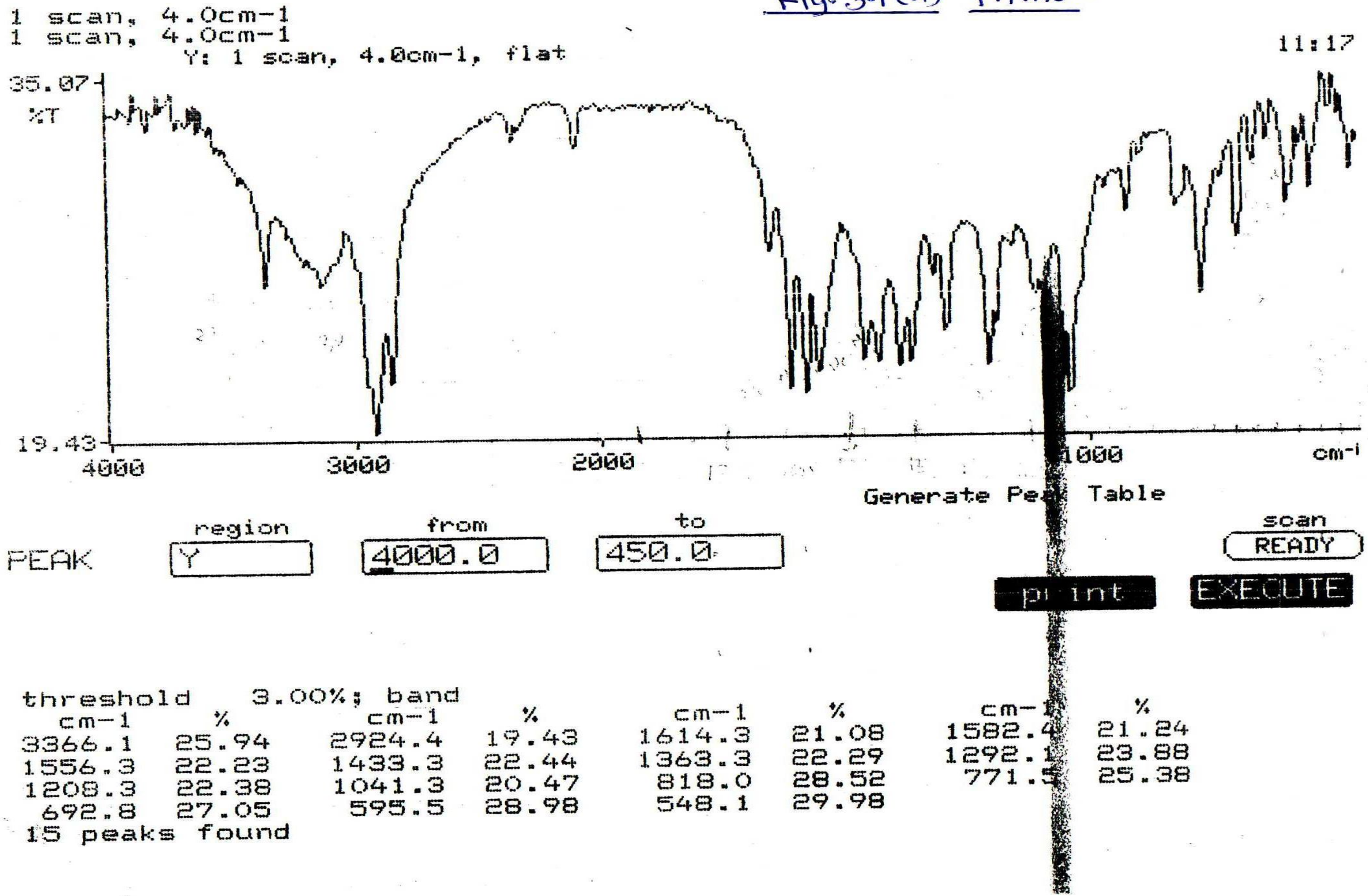
For determining correct oxidation state of "Quinone" the following criteria of IR absorption bands[2] can be used.

1.C=0 stretch : in free quinines it should appear in the range of 1660-1700 cm^{-12} **.** 10 to 65 cm^{-1}. Downwards shift will occur if the quinine co-ordinate as ‘O-quinone’ in its fully oxydised $form^{3}$. Therefore carbonyl bands must be observed as strong absorption above 1650 cm^{-1}.

Fig. 3.1(a) to 3.1 (e): IR Spectra of ligand,

Fe-1,Fe-2, Fe-3 and Fe-4 complexes

Fig-3.1(a) Phthox



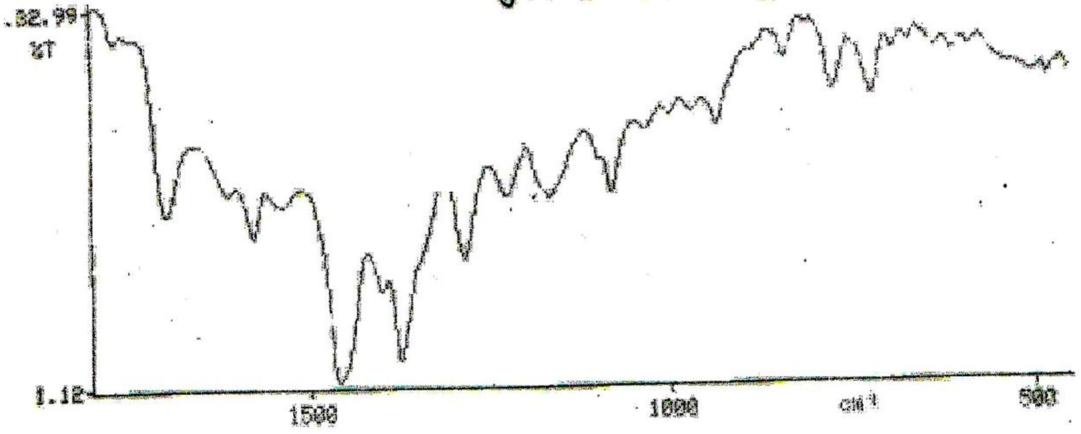
```
1  scan,  4.0cm-1
1  scan,  4.0cm-1
       Y: 1 scan, 4.0cm-1, flat
```

```
threshold    3.00%; band
  cm-1       %        cm-1      %        cm-1      %        cm-1      %
3366.1    25.94     2924.4   19.43     1614.3   21.08     1582.4   21.24
1556.3    22.23     1433.3   22.44     1363.3   22.29     1292.1   23.88
1208.3    22.38     1041.3   20.47      818.0   28.52      771.5   25.38
 692.8    27.05      595.5   28.98      548.1   29.98
15 peaks found
```

X: P-4 Nujol

Fig.3.1(e) Fe(phthox)$_2$Cl$_2$

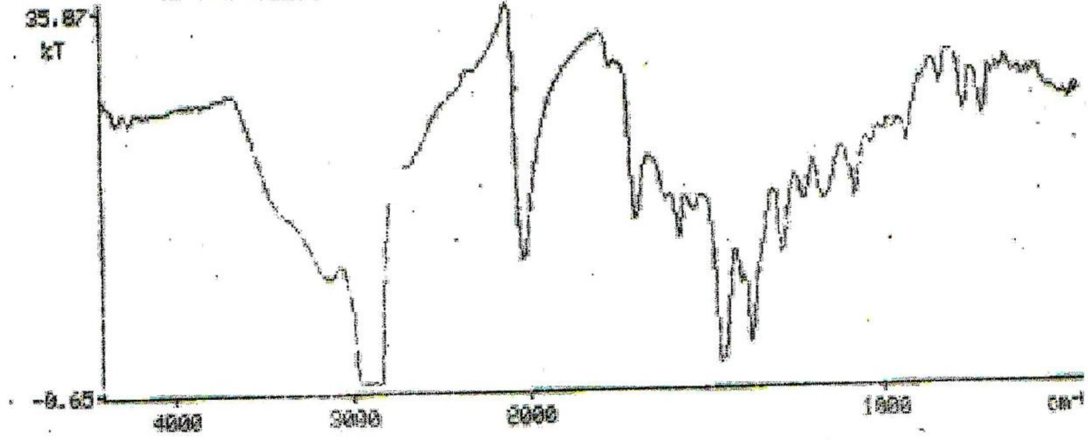
17:02



```
PEAK  X  1800.0  450.0
 threshold   0.60%; band
  cm-1     %       cm-1     %       cm-1     %       cm-1     %
 1700.9  15.58   1578.6  13.66   1536.9  16.17   1460.7   1.60
 1402.2   9.04   1376.9   3.11   1287.8  11.90   1228.5  17.01
 1169.3  16.89   1083.5  17.11   1036.4  22.27    973.3  23.84
  937.9  22.54    843.9  28.13    778.4  25.38    724.0  24.93
  694.3  28.70    612.7  28.57    481.1  26.32
 19 peaks found
```

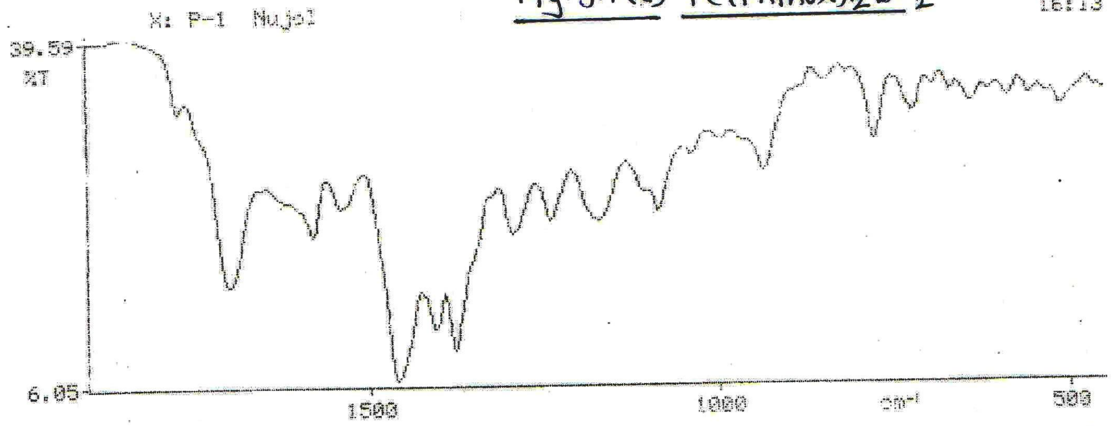
X: P-4 Nujol

17:03

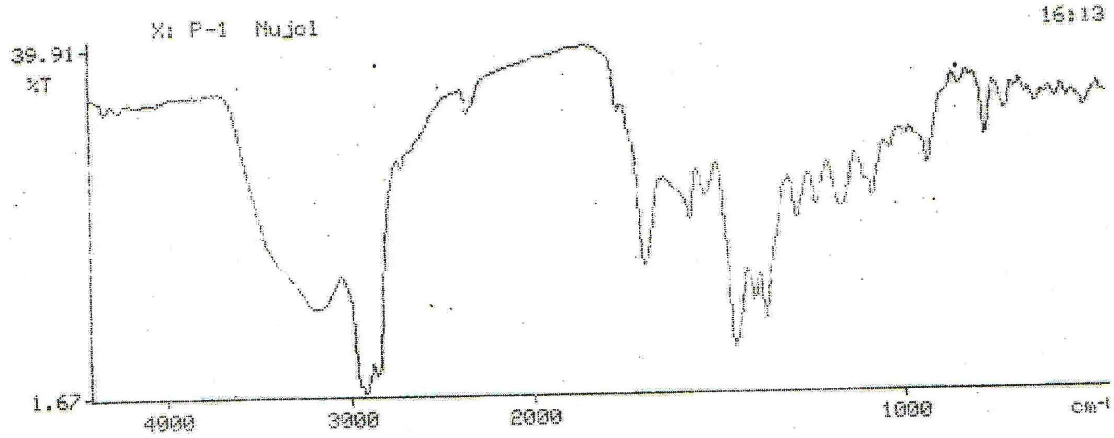


```
PEAK  X  4400.0  450.0
 threshold   2.00%; band
  cm-1     %       cm-1     %       cm-1     %       cm-1     %
 4326.0  25.14   2705.7   0.03   2033.9  11.73   1700.9  15.56
 1578.6  13.66   1460.7   1.60   1376.9   3.31   1287.8  11.90
 1228.5  17.01   1169.3  16.89   1083.5  17.11    937.9  22.54
  843.9  28.13    778.4  25.38    724.0  24.93
 15 peaks found
```

Fig. 3:1 (d) $Fe(phthox)_2Br_2$

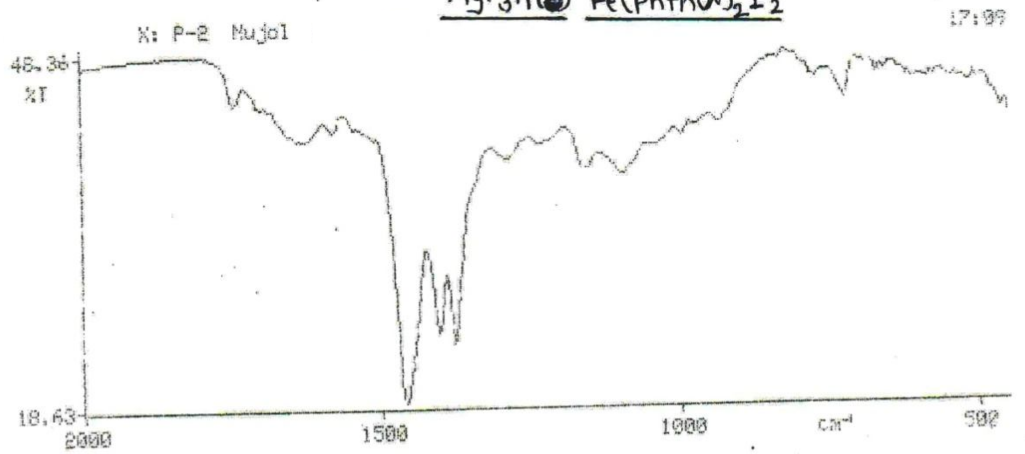


```
PEAK  X  1900.0  450.0
 threshold   0.50%; band
  cm-1     %        cm-1     %         cm-1     %         cm-1     %
 1773.4  32.63    1701.3  15.64     1580.6  20.44     1539.2  23.30
 1460.7   6.53    1405.2  11.42     1377.1   9.34     1292.5  20.63
 1239.4  22.04    1170.1  21.90     1087.5  22.80     1038.9  29.13
  998.6  29.46     936.6  26.45      849.1  35.22      779.2  29.41
  723.7  32.11     695.3  34.69      669.1  33.98      640.5  32.96
  615.6  33.98     586.4  33.37      557.6  33.53      511.7  32.52
 24 peaks found
```

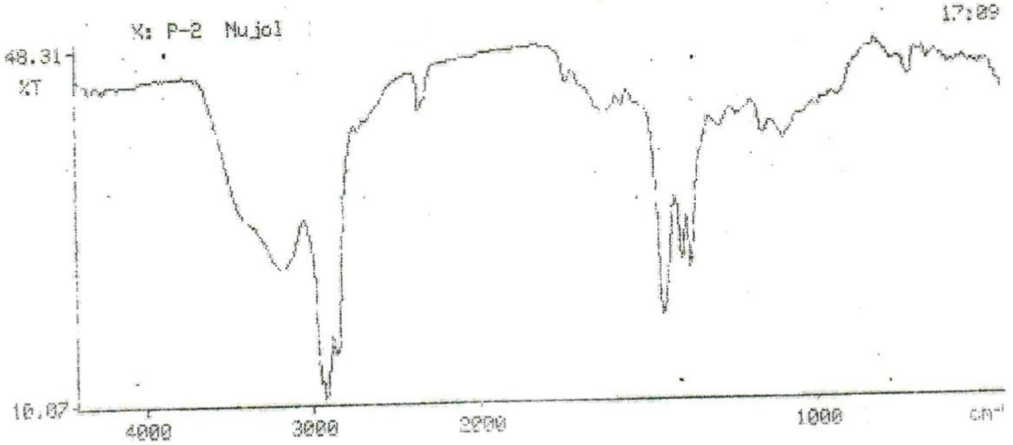


```
PEAK  X  4400.0  450.0
 threshold   3.00%; band
  cm-1     %        cm-1     %         cm-1     %         cm-1     %
 3174.9  11.13    2924.2   1.67     1701.3  15.64     1580.6  20.44
 1460.7   6.53    1405.2  11.42     1377.1   9.34     1292.5  20.63
 1239.4  22.04    1170.1  21.90     1087.5  22.80      936.6  26.45
  779.2  29.41     723.7  32.11
 14 peaks found
```

Fig. 3.1([illegible]) $Fe(phthox)_2I_2$



```
PEAK  X  2000.0  450.0
 threshold   0.50%; band
  cm-1     %       cm-1     %        cm-1     %       cm-1     %
 1746.2  44.12   1628.2  40.99    1579.6  41.70   1460.1  19.06
 1403.6  24.96   1377.4  24.07    1286.5  39.31   1235.7  40.57
 1157.1  38.57   1096.7  37.94     997.5  41.27    934.2  42.25
  770.4  46.04    722.9  44.16     668.9  46.11    586.7  45.73
  515.6  45.38    460.1  43.21
 18 peaks found
```



```
PEAK  X  4400.0  450.0
 threshold   2.00%; band
  cm-1     %       cm-1     %        cm-1     %       cm-1     %
 3181.7  24.47   2925.2  10.07    2854.9  15.20   2360.3  41.03
 1628.2  40.99   1460.1  19.06    1403.6  24.96   1377.4  24.07
 1096.7  37.94    722.9  44.16
 10 peaks found
```

Fig. 3.2 (a) to 3.2 (e) : FAR – IR Spectra of ligand, Fe-1, Fe-2, Fe-3 and Fe-4 Complexes

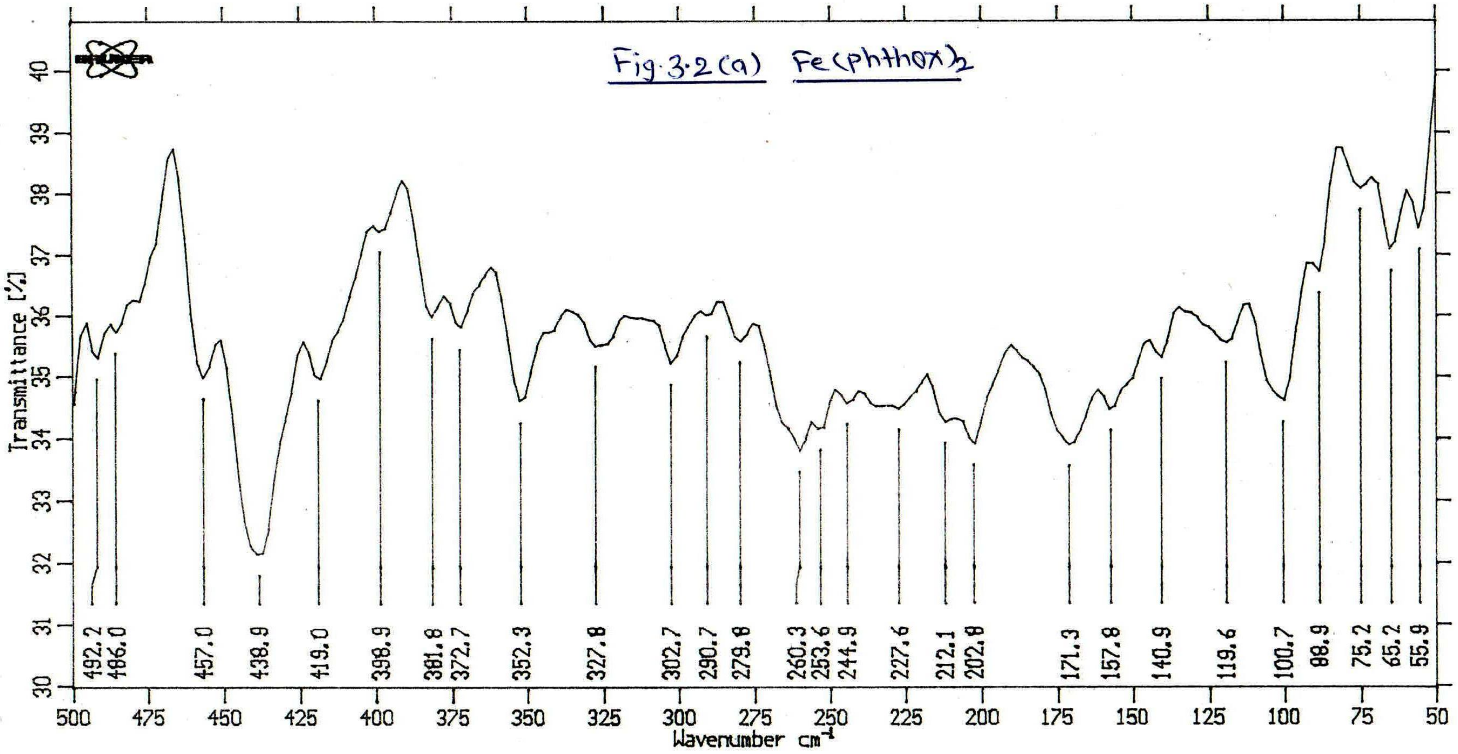


Fig. 3.2 (a) $Fe(phthox)_2$

SPECTRA : WORK.1
DATE : 21/ 9/2009
TIME : 16: 0:29

RSIC. IIT. MADRAS

BRUKER IFS 66v
FT-IR SPECTROMETER

SAMPLE : 296-KI1
TECHNIQUE : polyethypellet
USER : T.LALITHA

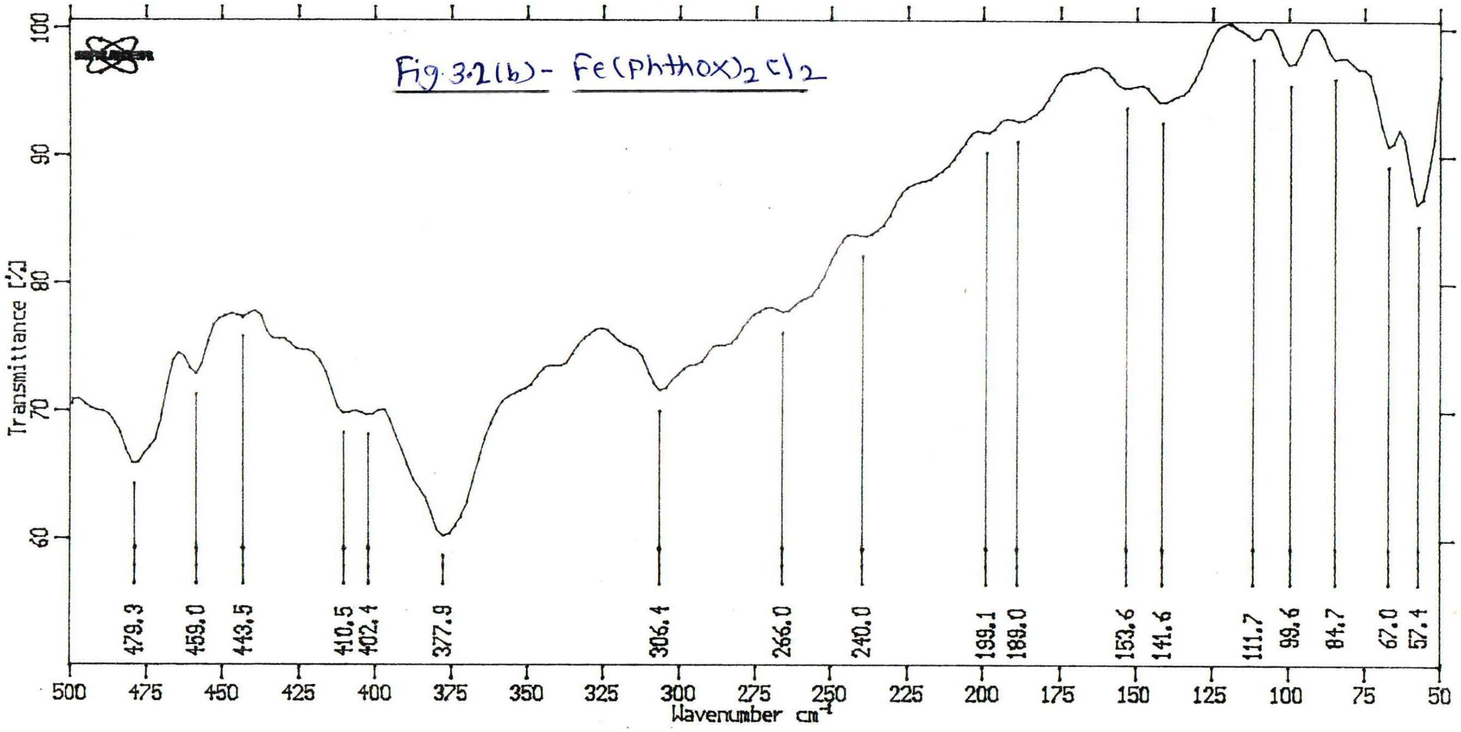


Fig 3.2(b) - Fe(phthox)$_2$Cl$_2$

SPECTRA : WORK.2
DATE : 22/ 9/2009
TIME : 10:54:40

RSIC. IIT. MADRAS

BRUKER IFS 66v
FT-IR SPECTROMETER

SAMPLE : 296-KI4
TECHNIQUE : polyethypellet
USER : T.LALITHA

Ta

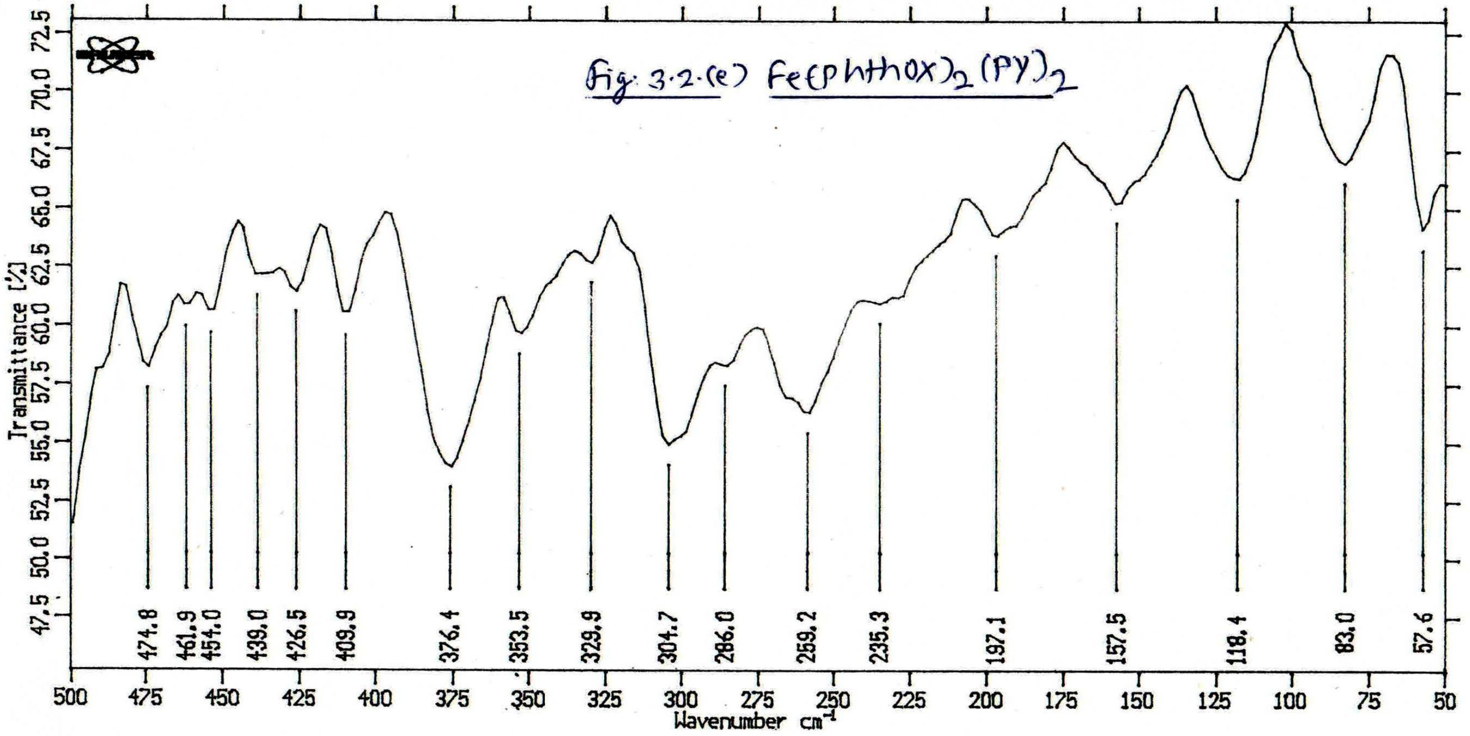


Fig. 3.2.(e) Fe(phthox)$_2$(PY)$_2$

SPECTRA : WORK.3
DATE : 21/ 9/2009
TIME : 14:53:38

RSIC. IIT. MADRAS

BRUKER IFS 66v
FT-IR SPECTROMETER

SAMPLE : 294-YI1
TECHNIQUE : polyethypellet
USER : T.LALITHA

Phthox	Fe-1	Fe-2	Fe-3	Fe-4	Tentative assignments
3350 (s) 3130(mbr)	-	-	3320-3160(wbr)	3320-3160(wbr)	□ (OH) intra
- 1653(s) 1618(s)	- - -	1778(m) 1708(s) 1623(s)	1775(w) 1705(sbr) 1610(mbr)	1730(m) - 1695(sbr)	□ (C=O) - □ (C=N)
1577(s) 1548(m)	1578(sh) 1518(sh)	1583(sh) 1568(sh)	1590(sh) -	1585(mbr) 15309wbr)	□ C=O □ C=N
1470 (s)	1470(s)	1470(s)	1470(s)	1470(s)	Nujol
1380(s)	1375(s)	1385(s)	1375(s)	1370(s)	□ (C-H) + □ (C=O) Activating adjacent C=C
1310(w)	-	1310(w)	1310(w)	-	δ (OH) phenolic
1290(s)	1280(m)	1230(s)	1240(s)	1285(wbr)	Quinone absorption
1200(s)	1200(mbr)	-	-	-	□ (C-O)
1150(w)	-	1180(s)	1180(wbr)	1150(wbr)	δ (C-H) + □ (C-CH_3)
1110(w)	1110(wbr)	1110(s)	1110(s)	-	□ (N-O)
1045(s)	-	1040(wbr)	1040(wbr)	1070(w)	δ □ (-CH_3)
930(m)	940(mbr)	950(s)	945(s)	960(wbr)	δ (OH) oximino
830(m)	850(wbr)	860(wbr)	850(vw)	-	□ (-CH_3)
780(s) 735(wbr) 700(s) 670(m)	800(w) 775(s) 685(mbr) -	830(wbr) 790(mbr) 680(vw) 665(mbr)	760(w) 715(m) 660(vw) -	- - - -	δ (C-H) four adjacent
600(mbr) 585(sh) 550(w)	595(w) 560(w) 530(w) 490(vw)	585(wbr) - - 470(v)	555(mbr) - 425(wbr) 380(wbr)	600(wbr) - 320(wbr) 280(sh)	□ M – O □ M – N □ O - X

S-Strong, m- medium, w-weak , sh- shoulder, br-broad.

2. C------- O stretch : As one electron reduction of quinone Q, to semiquinone , $S\overset{\bullet}{\bar{Q}}$ shifts the carbonyl band about 100-150 cm^{-1} on co-ordination[4], which is assigned as C-------O stretch frequency. So bands in the region 1500 to 1600 cm^{-1}.

probably assigned for “semiguinone” form. Brown[5] had assigned the $S\overset{\bullet}{\bar{Q}}$ coordination in 1450-1500 cm^{-1}. region which may be strongly coupled with ring vibrational mode.

The double bond IR spectral region is a diagnostic tool to detect ‘NQ’ , ‘ ‘$NS\overset{\bullet}{\bar{Q}}$’ CAT’ type co-ordination of phthox ligand. The carbonyl bond shifts towards lower frequency site at about 200 cm^{-1} (1480 cm^{-1}) and an additional strong band at 1250 cm^{-1} is observed on co-ordination . The oxidation of co-ordinate ligand in Fe- ‘$NS\overset{\bullet}{\bar{Q}}$’ to NQ form during adduct formation.

(Fe-2 to Fe-4) together with oxidation of central metal ion, is supported by observation of IR absorptions above 1600cm^{-1} upto 1780 cm^{-1}. these are assigned for □C=O □C=N bonds with decreasing order of frequency showing NQ type of ligation in Fe-2 to Fe-4.

However all compounds including parents Fe-1 show absorptions in the range of 1518 to 1590 □C-------N and C-------O functional group representing $NS\overset{\bullet}{\bar{Q}}$ type of coordinaton and in Fe-2 to Fe-4 adduct show (NQ) ($NS\overset{\bullet}{\bar{Q}}$) coordination from their IR spectra.

For Fe-2 to Fe-4 adducts we come across O--------X absorption (Where X=Cl, Br.I) at lower energy region[6] (300 to 500 cm^{-1}). The least vibronjali coupled metal ligand absorption are assigned in 300-600 cm^{-1} region.

❖ Bactericidal and fungicidal activity of Fe complex:

The activity of fe-1 complex was studied by familiar bio assay type –well method.

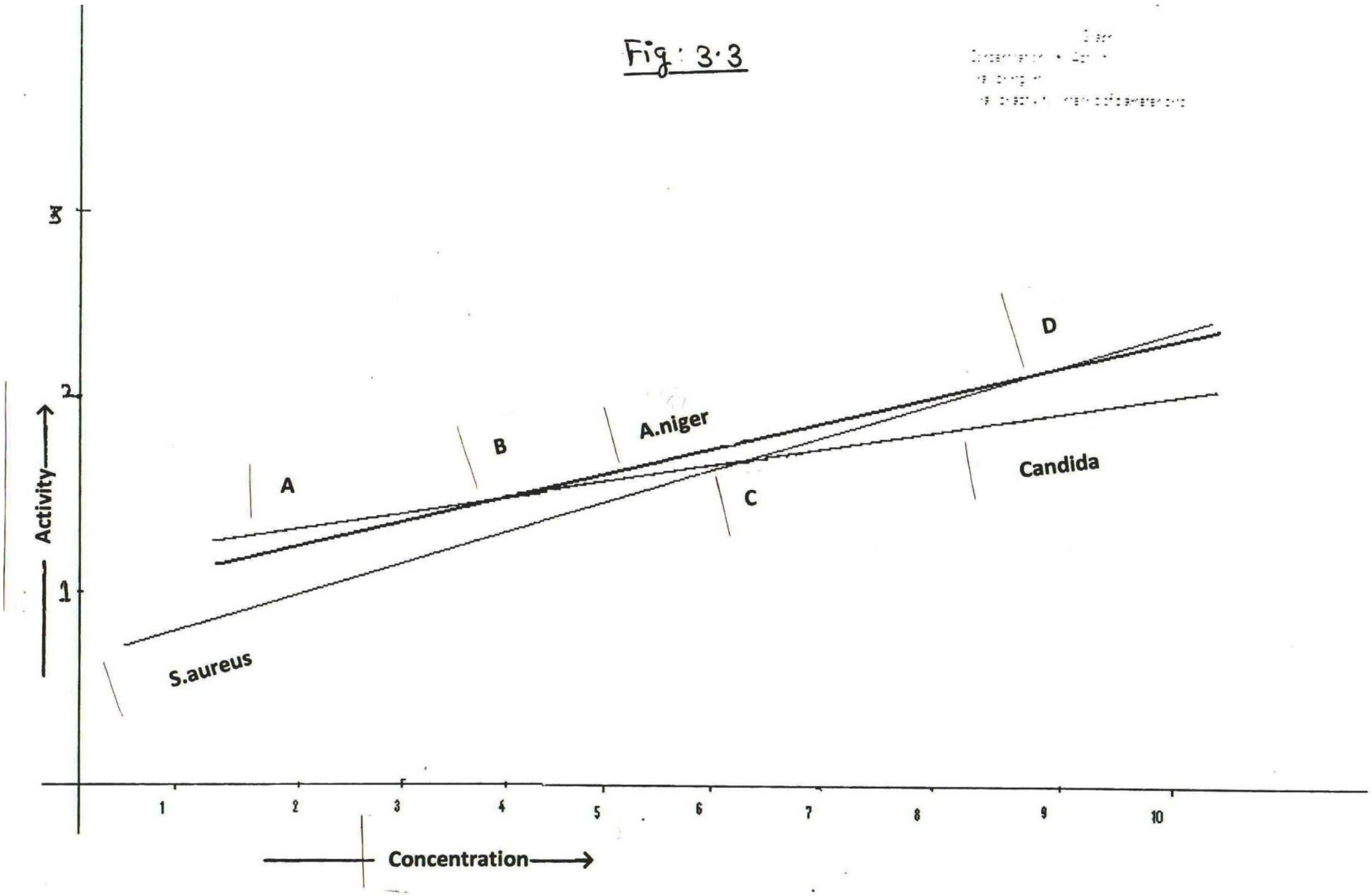
The general nutrient agar (Himedia) was used. After incubation zone of inhibition were observed which are shown in the table given below,

Micro.org.	**Fe-complex Cocn. (mg)**	**Zone of inhibition Diameter (cms).**
Aspergilus niger	2	1,4
	4	1.7
	6	1.8
	8	
S. aureus	3	1.1
	4	1.2
	5	1.5
Candida	2	1.2
	4	1.4
	6	1.6
	8	1.8

The above results indicate that in general the zone of inhibition increases with the increase in concentration of Fe-1 complex.

Fig. 3.3 Graph of concentration V^s Activity of Fe-1 Complexes

Fig: 3·3


3
2
1
Activity
1
2
3
4
5
6
7
8
9
10
Concentration
A
B
A.niger
C
Candida
D
S.aureus

At the initial conc. at point ‘A’ reveals that the Fe-complex was more active on condida (yeast), least effective on S-aureus and effect on A. niger is near to the effect on candida. Fe-complex concentration at point B the effect on A. niger and candida was same and effect on s-aureus was increasing but less as compared to A- niger and candida Fe- complex concentration at point C the fungicidal activety was increasing for A-niger as compared to candida Fe-complex concentration at point D shows that the activity on S-aureeus was more as compared to A-niger and candida.

The above results shows that the Fe metal complex was found to be more active on s-aureus than A –niger and candida at higher conc. While at lower concentration the metal complex activity was more on A-niger and candida while least on S-aureus.

In was observed the on comparison with reference to microtidal and fungicidal activity of the complexes were found to be more effective than ligands. The antimicrobial activity of the compound increases after chelation. Other factors such as solubility, molar conductivity and magnetic susceptibility are also responsible for increasing antimicrobial activity of the complex9 ,10

❖ SUMMARY AND COMMENTS

We can summarize the following points from different spectral studies of Fe-1 to Fe-6 compounds.

1. IR studies help in assigning the redox form of co-ordinated phthox ligands in Fe-2 to Fe-4 compounds.
2. Magnetic susceptibility measurement shows the paramagnetic behavior for all compounds but , to get the more accurate results need more refinements.

❖ References

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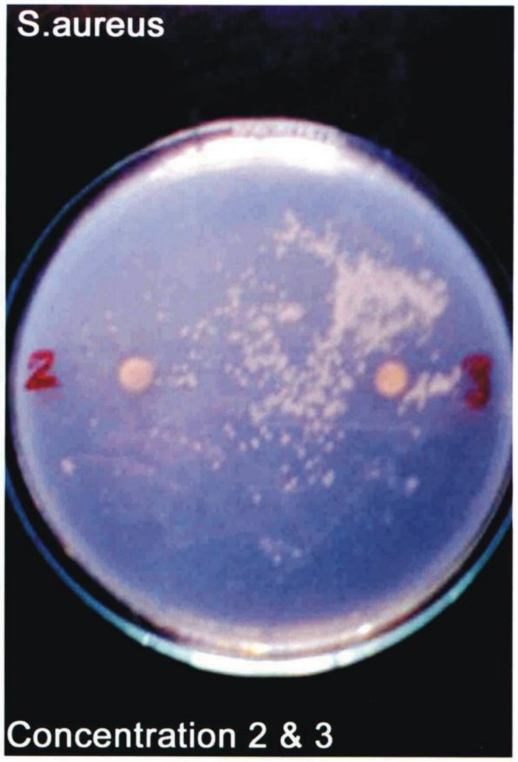
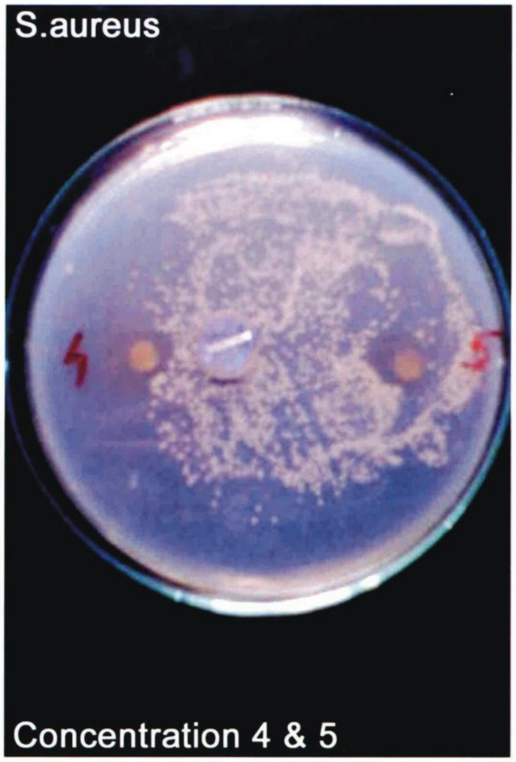
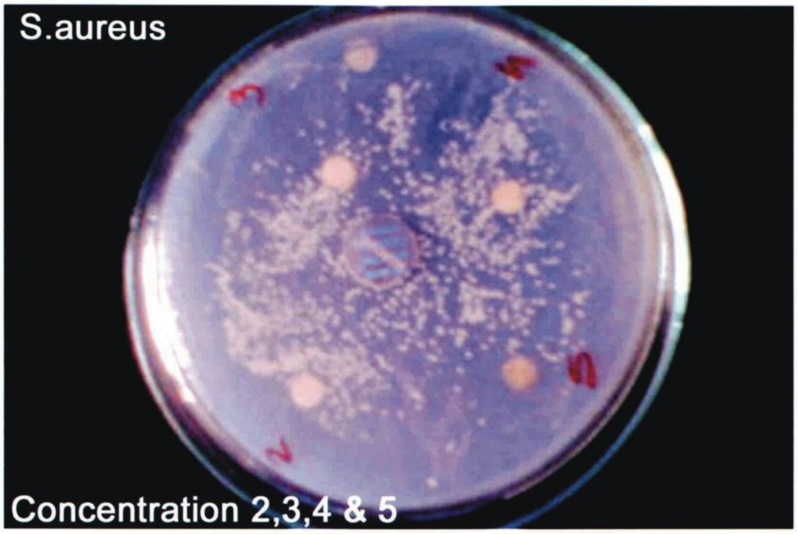
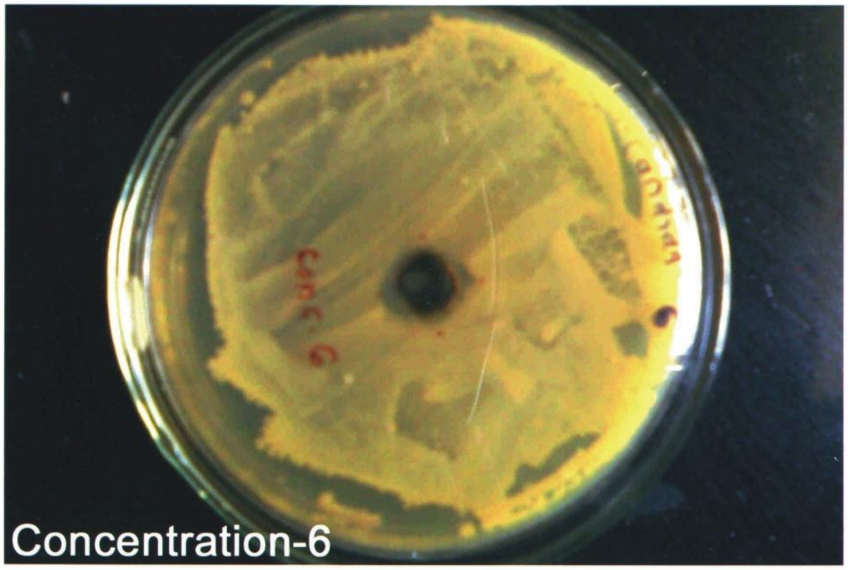
Antibacterial Activity of Fe-Complex

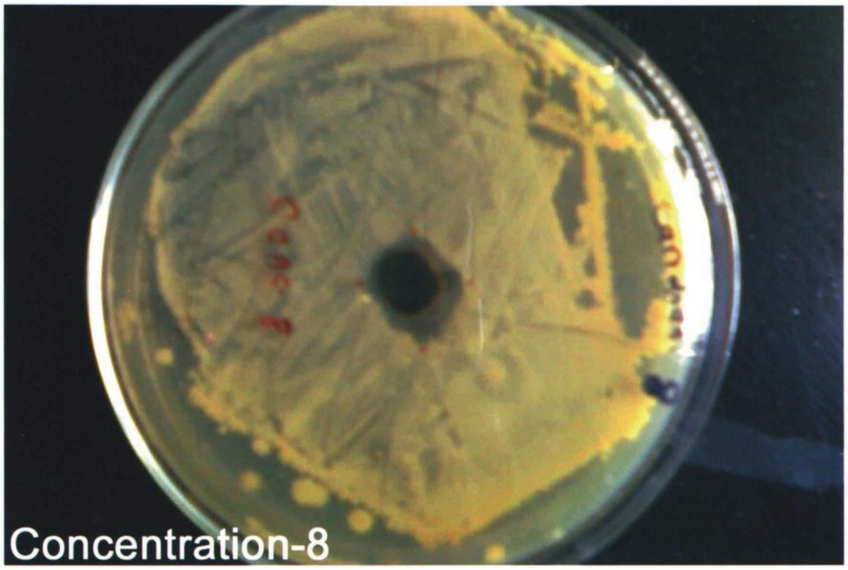




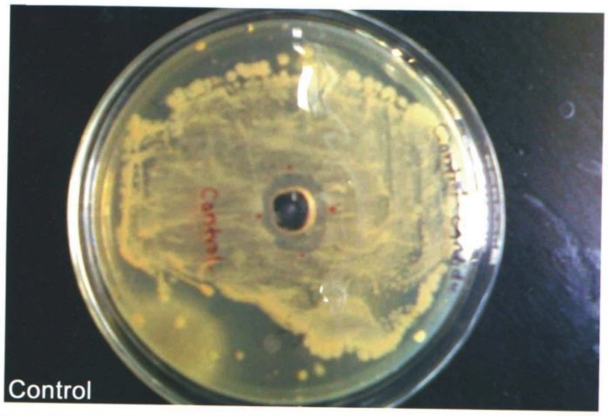


Activity of Fe-Complex against Yeast

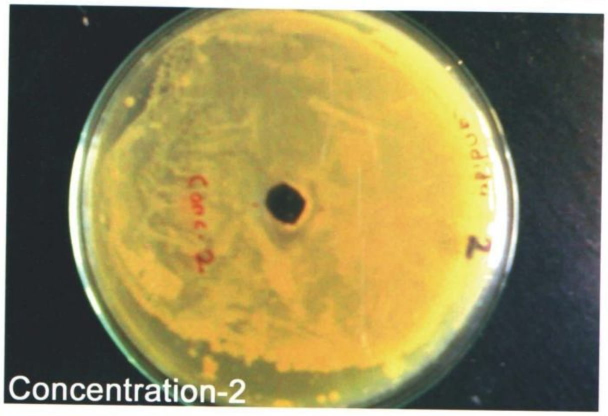

Concentration-6


Concentration-8

Activity of Fe-Complex Against Yeast



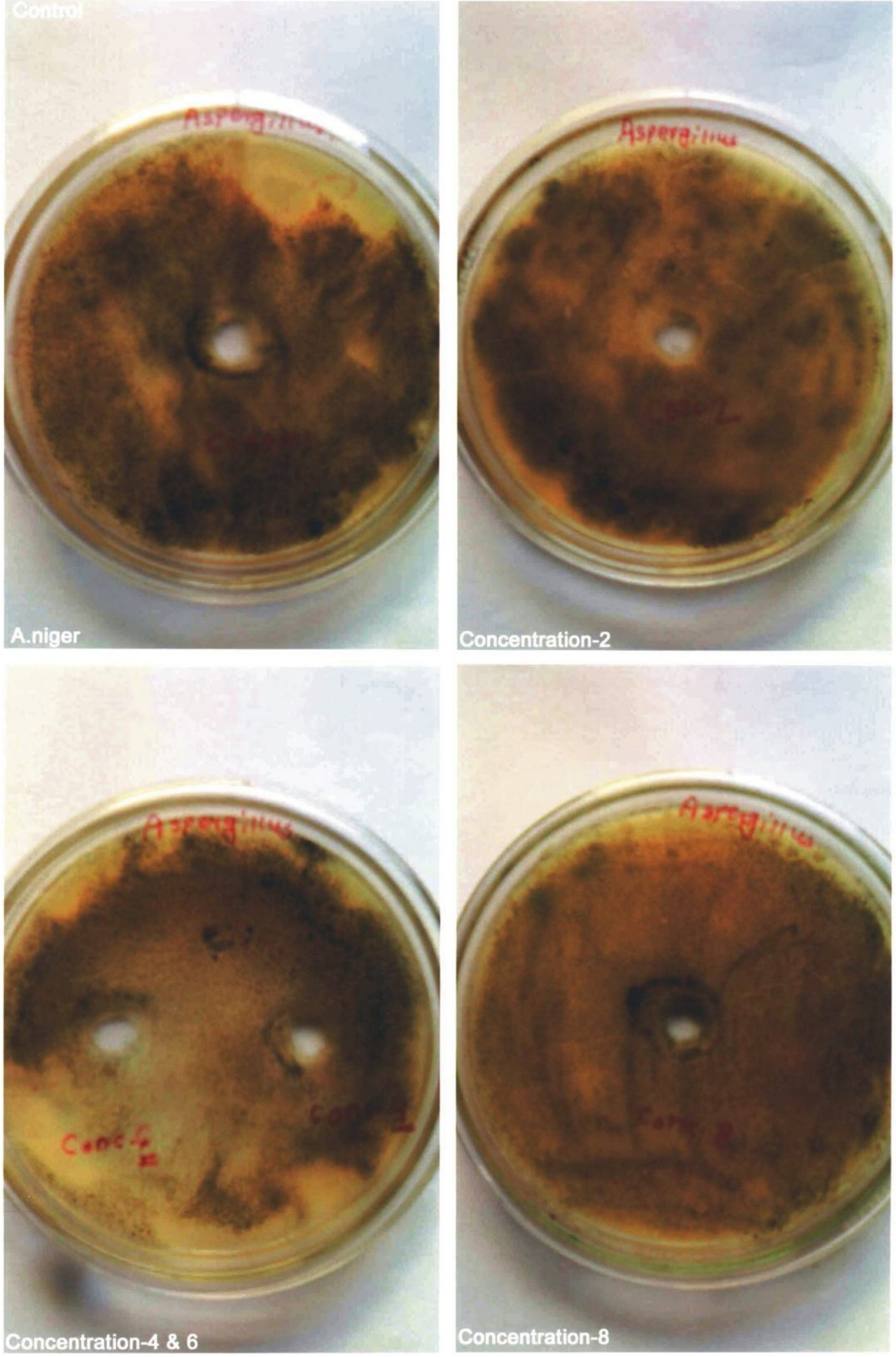
Control



Concentration-2

Concentration-2

Antifungal Activity of Fe-Complex



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4.1 GENERAL

This chapter deals with the experimental aspects of total research work done for this minor Research project. It incorporates method for the ligand (phthiocolmonoxime) its lron (II) Cobalt (II) and Copper (II) complexes as well as the adduct formation reactions such as halogenation, pyridination and thiocyanation here we have also included the details of the physico-chemical measurements and calculations carried out on the samples. Many of the measurements were made in the laboratories other than our own and these are acknowledged at appropriate place this arrangement however put restrictions on the flexibility and ‘on the spot’ modifications during actual measurements.

4.2 SYNTHESIS

All chemicals used in the preparation of ligand, metal complexes and their adducts were of A. R. Grade 2-methyl-1,4naphthoquinone was obtained commercially from Fluka company.

The solvents used for the syntheses and for physico-chemical measurements were of A.R.Grade and further purified according to the literature[1].

(i) Synthesis of Ligand :

a) Preparation of Phthiocol: - Phthiocol was prepared according to Fieser’s procedure[2].

b) Preparation of 1 –monoxime of Phthiocol:

1-monoxime of Phthiocol (phthiocolmonoxime) was synthesized according to the procedure to the literature[1].

(ii) Synthesis of Fe -1, Bis. (Phthiocol monoxmato) Iron (II) : The compound Fe-1 was prepared by using the procedure reported by Previous workers [4] as given below.

Under inert atmosphere the deaerated solution of ferrous sulphate of heptahydrate (1.390gm), 0.005 Mole in anhydrous methanol and 5ml of TEOP was added to the deaerated warm methanolic solution to Pthioncolmonoxime (2.032 gm), 0.01 moles with constant stirring. The reaction mixture was continuously stirred for few hours under nitrogen atmosphere at about 70-80^0 C. The precipitated chelates was then filtered , Washed with cold water then with distilled anhydrous methanol and finally With pet ether. The compound was dried under vacuu room temperature.

(iii) Synthesis of Fe -2 to Fe-6 chelates from parent Fe-1 chelates:

(a)Syntheses of Fe-2 Fe-3 and Fe-4

These chelates were synthesized by doing the halogenations of Fe-1 using NCS, NBS and NIS respectively. It was done according to the procedure followed by E.M.Khan 3 as given below0.00075 (0.3455 gm), chelates was dissolved in 20ml distilled chloroform. It was refluxed in dark with 0.0015 of Mole of NCS, NBS and NIS (0.2003 gm, 0.2670 gm, 0.3372 gm respective solutions made in 20ml chloroform,

on oil bath for about 2-3 hours with constant Stirring. Reaction mixture was then filtered , washed thoroughly with distilled water and finally with ether. The compounds were dried under vacuum at room temperatures all the chelates thus obtained were stored in dark.

(b) Synthesis of Fe-5:

Synthesis of Fe-5 was carried out similar to the reported procedure as given below.

0.00075 Mole of Fe-1 chelates (0.3455gm) in 60ml distilled acetone and 0.00225 Mole of pyridine (0. 1777 gm), were mixed under inert atmosphere and refluxed for about 2 hours th about 70-80^0 C and then allowed to cool slowly. The precipitate was filtered and washed with distilled water and finally with ether . It was dried under vacuum at room timperature and was stored in dark.

(c) Synthesis of Fe-6:

The synthesis of Fe-6 compounds was tried using the procedure reported by Chawala and Jones[9 6]But we failed to get the product. Then thiocyanation was carried out using the procedure followed by Harris and Nholm[10, 7] as given below.

0.00125 Mole of brominated chelates Fe-3 (0.7750gm) was dissolved in hot acetone then it was treated with and aqueous solution 0.0025 Mole of ammonium thiocyanate (0.2153) or 0.0025 Mole of potassium thiocyanate (0.2430gm) in acetone under inter atmosphere. The reaction mixture was refluxed at about 70-80^0 C for 2-3 hours them the chelates was extracted using pet ether It was then filtered washed with distilled water and finally with ether. Dried under vacuum at room temperature and stored in dark.

4.3 PHYSICO MEASUREMENTS:-CHEMICAL

(i) Elemental analyses:

Elemental analyses were performed in micro analytical laboratory of the University of Poona and in the department of chemical sciences of North Maharashtra University , Jalgaon. The results of analyses are depicted in table 2.1. Metal ion estimation was done according to the procedure given in Vogel (8).

The halide estimation was done by the procedure as described below (9).

The complex of known weight (~ 5mg) was burnt on quantitative paper (Whatsman No.41) boat in schoniger flask (8) containing few ml of H_2O_2 and little amount of distilled water and 1 drop of (1N) NaOH. The flask was tightly closed and was dept aside for at least one hour. The solution was then made acidic to Bromophenol blue (pH~3) by using 0.5 N HNO_3. This metal solution was then passed through cation exchanger resin (Amberlite IR-120) which was previously treated with one bed volume Of 2M HNO_3 and then washed with distilled water till neutral to Ph paper and free from bromide. It was tested with $AgNO_3$ solution. The metal solution was then eluted slowly by using thrice bed volume of distilled water. Solution collected from the column was then treated with 20% hexamethylene tetramine to adjust pH~6.5. Then it was acidic by adding 0.5N HNO_3 drop wise till it acquired pH ~3 tested by Bromophenol blue indicator . then about 5ml of isopropanol and 8-10 drops of diphenyl carbazone (0.1% in ethanol) were added. This final solution was then titrated with standard 0.005N Hg $(NO_3)_2H_2O$ solution till pink colour was persisted. Using the exact strength of Hg $(NO_3)_2H_2O$ theamount of halide ion can be determined using the relation;

100 ml. 1N Hg $(NO_3)_2 .H_2O$ = 35.5gm cl^-

1000ml .1N Hg $(NO_3)_2$ H_2O =7904 gm Br^-

100 ml.1N Hg $(NO_3)_2.H_2O$=126.904 gm l^-

(ii) Conductivity measurements:

The molar conductivities of all metal complexes as well as their adduct compounds were obtained in hexane, DMF and DMSO by employing Philips GM 4144 conductivity Bridge. The non-electrolytic behavior was observed for all the complexes and adducts.

(iii) Infrared Spectra:

IR spectra of the ligand (phthox) as well as metal complexes were recorded in nujol mulls on Perkin-Elmer model 1600 FT-IR spectrometer using Csl window in the region 4000-400m^{-1} at university of Poona and on Perkin –Elmer infrared spectrophotometer using KBr pellets at North Maharashtra University, Jalgaon.

The significant peaks in IR spectra of ligand and metal complexes are depicted in table 3.1 and fig 3.1(a) to 3.1(e).

(iv) FAR.IR –IR spectra of the metal complexes and their adduct compounds were recorded on BRVKER IES 66V FT-IR spectrophotometer at regional sophisticated instrumentation centre (RSIC),Indian Institute Of Technology, Madras (India) using polyetelene support in the region 600-50 $cm^{-1.}$ The FAR-IR spectra for metal complexes as well as adducts are presented in fig. 3.2(e).

(v) Magnetic Susceptibility Measurements:

Magnetic susceptibilities of the samples were determined at room temperature (24^0C)on Faraday type magnetic balance with a magnetic field of about 7000 gauss in the department of Chemistry, University of Poona, Pune. The molecular susceptibilities were corrected for diamagnetism of the component atoms by use of Pascal’s constants. The apparatus was calibrated using mercury (II) tetrathiocynato cobaltate[10]. 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 moment were calculated using the following equations[11.]

$$X_{sp} = (\Delta w/m)/K$$

Where, X_{sp}=specific susceptibility of the complex

m = weight in grams of the sample I air

Δw = increase in weight of the sample in magnetic field.

K = tube constant.

$X_M = X_{SP}$ x molecular weight of complex.

$X_{Para} = X_M - (-X_{dia\ (l)})$

Where, X_m =molar susceptibility.

X_{Para} = paramagnetic susceptibility.

$X_{dia\ (L)}$ = diamagnetic correction of the complex.

$\mu = \sqrt{(\,3KT)/N)\ X_{para})}$

$= 2.83 \sqrt{(X_{para}\ X\ T\ )}$

Where, μ = magnetic moment in ergs/gauss.

N = Avogadro’s number.

K = Boltzmann constant.

T= Absolute temperature in degree Kelvin .

$\mu_{bm} = \mu/\beta$

Where μ_{bm} = Effective magnetic moment in Bohr. Magnetron.

B = Bohr Magnetron = 9.273 x 10^{-21} ergs/gauss.

VII) Thermo gravimetric Analysis

The simultaneous TG/DTG and DTA curves were recorded o Netzsch STA 409 simultaneous therma analyzer regional sophisticated instrumentation centre (RSIC) Indian Institute of Technology. Madras(India), about 10-80mgs of sample was heated in Alumina (AI2O3) crucible at the constant rate of 10°C per minute. The heating of sample was carried out in the inert atmosphere 9nitrogen). The TG/TDG curves are presented in fig. 2.1(a) to 2.1 (d) and the DTA curves are presented in fig. 2.2(a) to 2.2(d).

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