



SYNTHESIS, CHARACTERIZATION, THERMOGRAVIMETRIC STUDIES OF BIS-PHTHIOCOLMONOXIMATO IRON III ADDUCTS

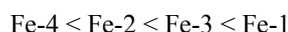
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ABSTRACT

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 Fe-1 complex, which gives the various adduct Fe-2 to Fe-4. All these chelates are anhydrous like parent Fe-1. The halogenated products Fe-2 to Fe-4 have $ML_2 X_2$ type of formulation, where ($x = Cl, Br, I$) and $L = phthox$. 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 from the conductivity measurements carried out for parent as well as the adduct chelates.

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,



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

Key words: Phthox-phthiocolmonoxime, NCS/NBS/NIS-n-halosuccinamides, E_a -Activation energy, Fe-1 to Fe-4-Fe-complex and adduct chelate compounds, NSQ-Naphthosemiquinone, SQPY-squarepyramidal.

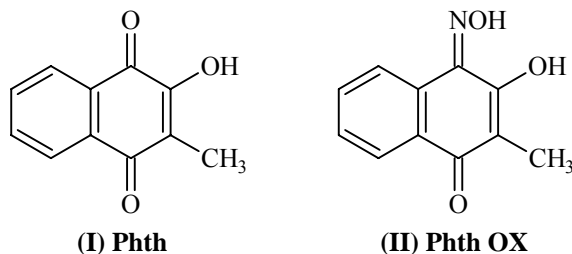
INTRODUCTION

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

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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 bacteria¹. The significant antimicrobial activity has shown by metal complexes with 8-hydroxyquinoline increases their importance in medical and biochemical sciences².

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 (phtox) (I to IV) having biological relevance.



Co-ordinated ligands are well induced in “square planer” complex of nickel when it undergoes through different reactions¹³.

EXPERIMENTAL

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.

Synthesis

(i) Synthesis of ligand

- (a) **Preparation of phthiocol:** Phthiocol was prepared according to Fieser’s procedure⁴.
- (b) **Preparation of 1-monoxime of Phthiocol:** 1-monoxime of Phthiocol (phthiocolmonoxime) was synthesized according to the procedure to the literature⁵.

(ii) Synthesis of Fe-1, Bis. (Phthiocol monoxmato) Iron (II)

The compound Fe-1 was prepared by using the procedure reported by previous workers⁶ as given below.

Under inert atmosphere the deaerated solution of ferrous sulphate of heptahydrate 0.005 mole in anhydrous methanol and 5 mL of TEOP was added to the deaerated warm methanolic solution to Phthioncolmonoxime 0.01 moles with constant stirring. The reaction mixture was continuously stirred for few hours under nitrogen atmosphere at about 70-80°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-4 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 Khan⁷ as given below. 0.00075 moles of chelates was dissolved in 20 mL distilled chloroform. It was refluxed in dark with 0.0015 of mole of NCS, NBS and NIS respective solutions made in 20 mL chloroform, on oil bath for about 2-3 hrs 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.

RESULTS AND DISCUSSION

(i) Elemental analysis

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 1. Metal ion estimation was done according to the procedure reported⁸. The halide estimation was done by the procedure as described.⁹

(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.

It gives the various adduct Fe-2 to Fe-4. All these chelates are anhydrous like parent Fe-1 complex, Table 1.

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Table 1: Analytical data of parent and mixed chelates of iron with phthiocolmooxime

Compound	Colour	% Yield	Decomposition temp. (°C)
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.Cl₂; Fe-3: Fe(Phthox)₂Br₂; Fe-4: Fe(Phthox)₂.I₂

(iii) Thermo gravimetric analysis

The simultaneous TG/DTG and DTA curves were recorded on Netzsch STA 409 simultaneous thermal analyzer regional sophisticated instrumentation centre (RSIC) Indian Institute of Technology, Madras (India). About 10-80 mgs of sample was heated in alumina (Al₂O₃) crucible at the constant rate of 10°C per minute. The heating of sample was carried out in the inert atmosphere (nitrogen). The TG/DTG curves are presented in Fig. 1 (a) to 1 (d) and the DTA curves are presented in Fig. 2 (a) to 2 (d).

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

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

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

Fe-4: Diiodo-bis-(Phthiocolmonoximato) 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 ML₂X₂ type of formulation, where (x = Cl, Br, I) and L = phthox respectively Table 2.

Table 2: 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 I

(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 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.¹⁰

Generally, whenever succinamide reagents are used they follow the synthetic route of “electrophilic substitution” by replacing the proton on the chelate rings, as the reactive 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.¹¹

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)¹² such as –

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

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

This is because succinamide performs both types of reaction mechanisms viz free radical and nucleophilic substitution. The halide radical, X^\bullet and halonium ion, X^+ , have to follow two selective paths of addition reaction 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 ion¹³. 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)¹⁴, the second X addition at metal centre is prevented. So only the ML_2X type adduct formation is progressed via “Oxidative addition” of one at metal centre, Fe(II) converts to Fe-III, together with oxidation of one NSQ ligand to NQ form. The prevention of second addition at same metal site results in second choice of electrophilic substitution path¹⁵ 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 $\text{O}^{\ominus}\text{---}\text{X}^+$, to neutralize 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.

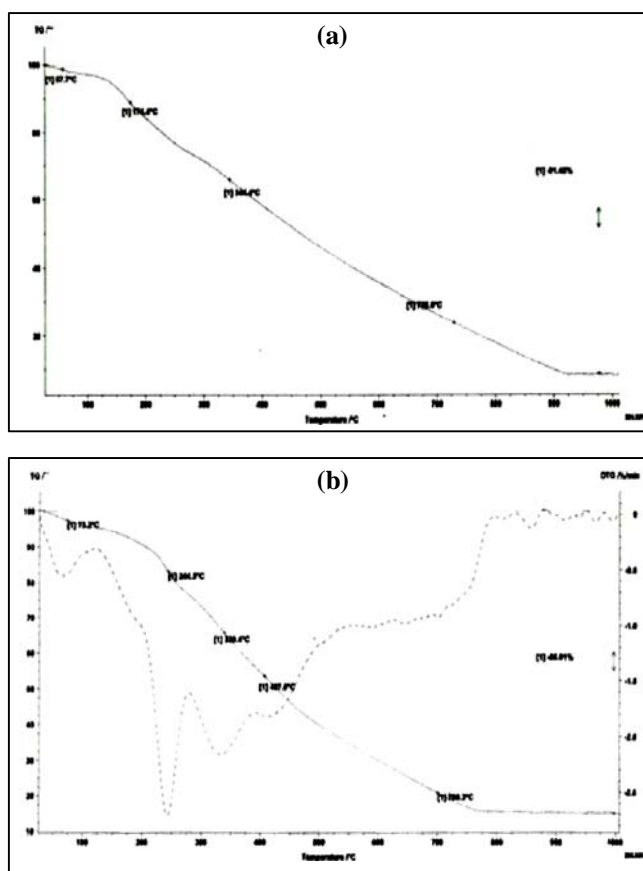
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Decomposition temperature and thermal stability

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,

$$\text{Fe-4} < \text{Fe-2} < \text{Fe-3} < \text{Fe-1}$$

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



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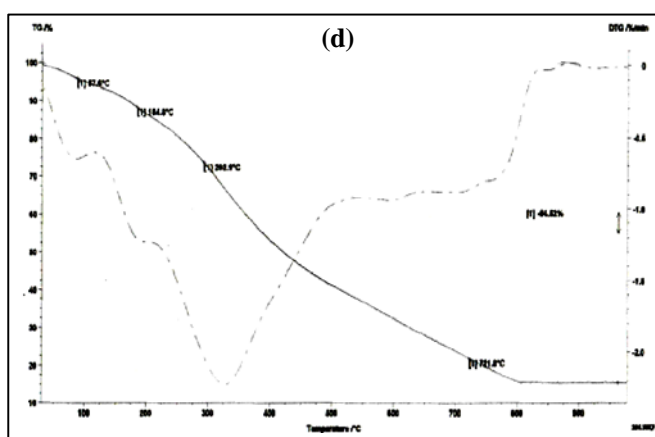
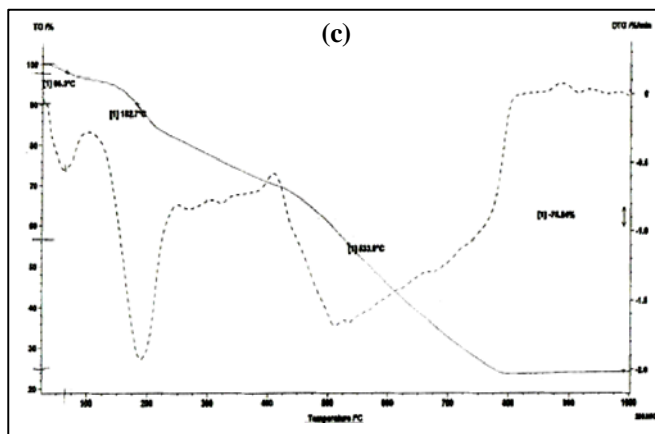
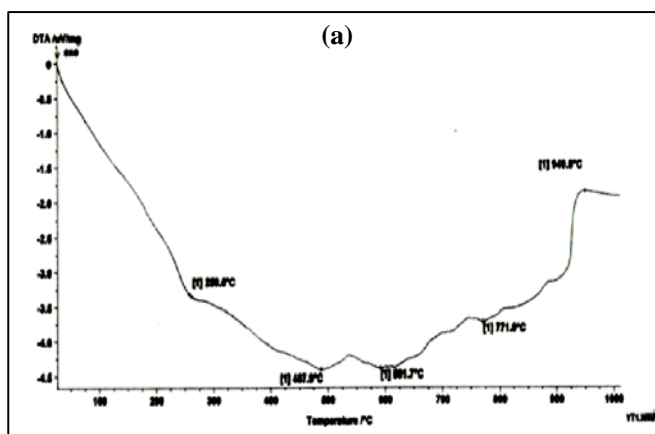


Fig. 1 [(a)-(d)]: TGA Curves for Fe-1, Fe-2, Fe-3 and Fe-4 complexes



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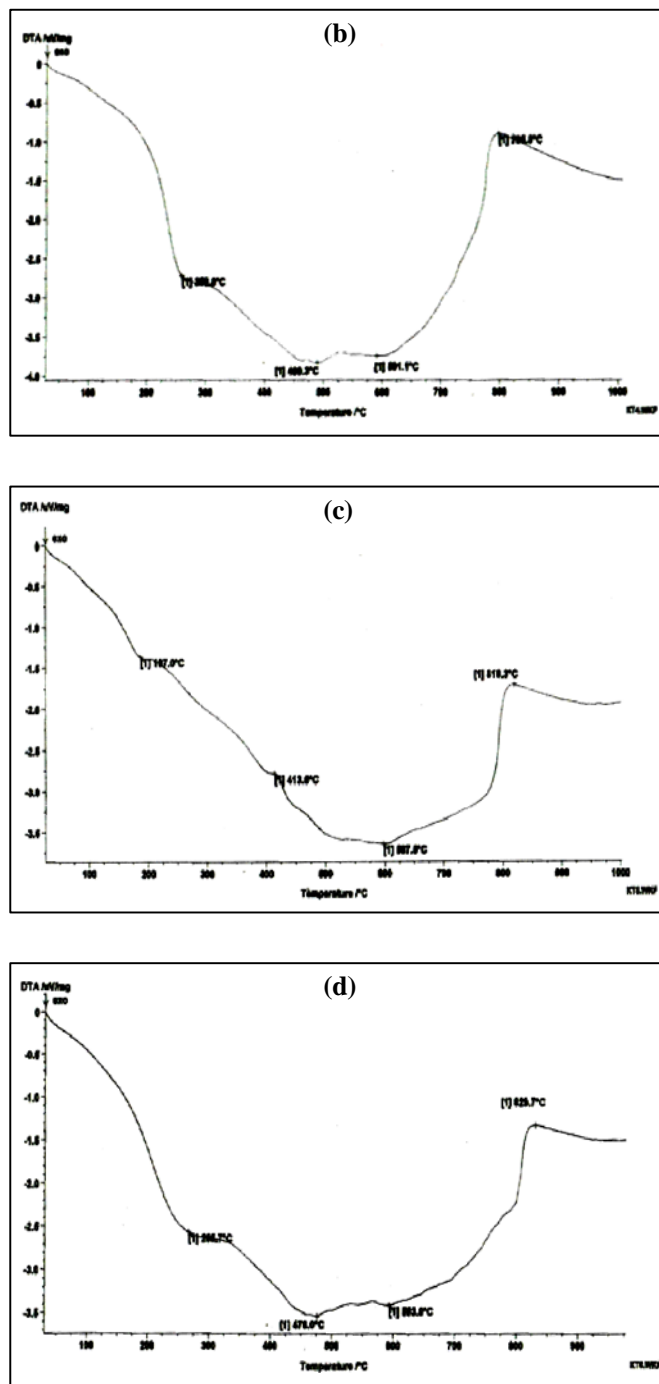
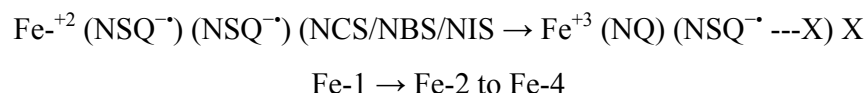


Fig. 2 [(a)-(d)]: DTA Curves for Fe-1, Fe-2, Fe-3 and Fe-4 complexes

Summary and comments

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

1. The average E_a 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 –



Where X = Cl, Br, I. Fe-1 follows homogeneous decomposition mechanism while, the adduct compounds undergo heterogeneous decomposition mechanism during pyrolysis. The E_a values of "Adduct Ligands" (viz. Cl, Br, I, show inverse relation with their crystal field strengths. The lighter rates of decomposition in case of Fe-2 to Fe-4 adducts compounds shows effective polarization in Fe-2 to Fe-4 compounds.

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