BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE OF ARTS, SCIENCE AND COMMERCE, PUNE-411038

Final Report

1st May 2013 to 30th April 2017

File No.42-235/2013 (SR), Date 12th March, 2013

MAJOR RESEARCH PROJECT

Project Title

"Chemical, structural and biological investigations of the metal chelates of 1, 2 Naphthoquinone oximes."

Principal Investigator

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SUBMITTED TO
THE SECRETARY
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BAHDUR SHAH ZAFAR MARG
NEW DELHI-110002

Tenure: May 2013 to April 2017

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FINAL REPORT

MAJOR RESEARCH PROJECT IN CHEMISTRY (SCIENCE)

Title: “Chemical, structural and biological investigations of the metal chelates of 1, 2-naphthoquinone oximes.”

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Dr. Vishwas V. Dhapte
Principal Investigator

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FINAL REPORT

MAJOR RESEARCH PROJECT IN CHEMISTRY (SCIENCE)

Title: *“Chemical, structural and biological investigations of the metal chelates of 1, 2 Naphthoquinone oxime”.*

Dedication

Dedicated to original innovative researchers

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CHAPTER I

INTRODUCTION

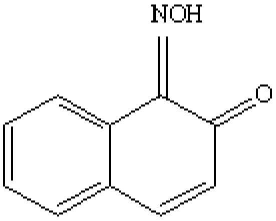
1.1 1, 2-naphthoquinone-1-oxime

1.1.1 General

In 1, 2-naphthoquinone-1-oxime is versatile derivatives of 1, 2-naphthoquinone which finds important application in the field of co-ordination chemistry, analytical chemistry and industrial chemistry. It is also known as to possess significant biological activity. This oxime is known since last more than 150 years and has been studied in detail from various aspects.

Exploration of the structural and stereochemical features of lanthanide 1, 2-naphthoquinone-oximates is a complicated and challenging task for coordination chemists. This is mainly due to the structural multiplicity of the 1, 2-naphthoquinone monoximates as well as 1, 2- naphthoquinone-dioximate.
Thus for 1, 2-naphthoquinone-1-oxime there are two alternative tautomerism forms. One of these is oxime form (I) and other is nitroso form (II).

1.1.2. Molecular structure

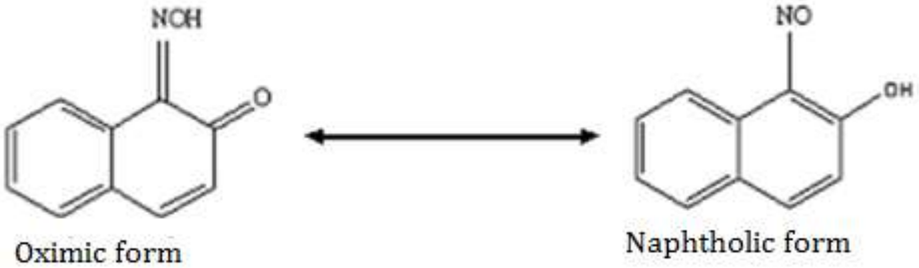


1, 2- naphthoquinone -1-oxime

In accordance with experimental conditions it can be seen that the ligands exist in two forms that is naphtholic form and oximic tautomeric form. 1, 2-naphthoquinone-1-oxime is the key reagent in the production of azo dyes. It possess good chelating property, hence it is used as fungicides insecticides for protecting seeds, plants and fruits. The action prevents and controls the fungi and insects to an unusual degree by the use different composition containing such active agents. Glenworth Lamb et. al. patented a method of protecting organic materials against fungi [1]. Krazan A. et. al. have studied tautomeric equilibrium of 1-nitroso, 2 naphthol and 1,2-naphthoquinone -1-oxime by using molecular orbital (MO) calculations using Hartree – Fock method [2]. They have reported values for 1, 2-naphthoquinone-1-oxime such as dipole moments, energy and some bond length values. The nitrosooxime tautomeric equilibrium was extensively studied by spectroscopic methods including UV [3], IR [4-5] and NMR [6-8]. Intramolecular hydrogen bonding interactions as in 1-nitroso-2-naphthol and their monoxime tautomers were investigated density functional theory (DFT) levels by A. E. Shchavlev et. al. [9]. Many organic molecules, containing conjugated π electrons were characterized by the large values of molecular friesthy perpolarizabilities and were analyzed by means by vibrational spectroscopy [10]. Presently ab-initio quantum mechanical method is widely used for simulating the IR spectrum. Hartree-Fock and density functional theory at different levels have been used to simulate NMR spectrum. Such simulations are indispensible to perform normal co-ordinate analysis so that modern vibrational NMR and electronic spectroscopy is unimaginable without involving them. In the present study, the theoretical calculation of wave numbers, chemical shifts of proton NMR and ^{13}C NMR as well as electronic transitions of the title compounds are reported and compared with the data obtained from experimental work [11].

For 1, 2-naphthoquinone-monoxime (1-nitroso-2-naphthol) it is now recognized that both 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinone-2-oxime exist in two tautomeric forms known as quinine oxime form and naphtholic form.

Isomeric tautomerism



The nature of this tautomerism and the relative dominance of a particular form (oxime or naphtholic) depends on the physical state as well as experimental conditions. Both these have following aspects

i) Historically important in analytical chemistry.

ii) Powerful chelating agents due to which their coordination chemistry has been subject of interest in research field.

iii) Biologically active, possessing powerful antimicrobial activity, many research workers are interested in the structural investigation of these monoximes as well as their metal chelates.

iv) However an examination of the previous work shows that, the structural chemistry of these ligands is a challenging. Thus in literature these ligands are recognized as 1, 2-naphthoquinone 1-oxime or 1, 2-naphthoquinone-2-oxime by one group where their oxime form is assumed to be predominant and as 1-nitroso-2-naphthol or 2-nitroso-1-naphthol by other group where its ‘nitroso’ ‘naphthol’ form is belived to be dominant. Argument in favour of both these form on the basis of experimental evidence obtained under specific condition are reported in literature. Birca et. al. based on the IR and UV spectroscopy gave wider support for the dominance of oxime form [12-13]. The same is also provided by Hadzi, Norris and Charalambous et. al. using same techniques [4, 6 and 14]. Dominance of the oxime form in quinine monoximes is also largely supported by X-ray crystallographic studies of these ligands as well as their metal chelates.

1.2 1, 2-Naphthoquinone-2-oxime

1.2.1 General

This compound is known for about more than 100 years ago. Now more information is available regarding its physical constant, absorption spectra in different organic solvents, thermogravimetric parameters, dissociation constants, electric conductance and electric dipole moments.

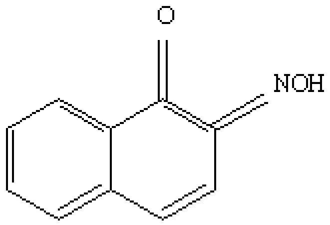
Also for 1, 2-naphthoquinone-2-oxime, there exist two quinine tautomeric forms, oxime form and nitroso form. Both these forms (quinone based oxime form) and (naphthol based nitroso form) are in equilibrium and the relative abundance of either of these forms depends on different factors which include physical /chemical state, medium (solution state), temperature etc.

When any of these monoxime enters into coordination state especially with a metal ion, the multiplicity of the resulting metal chelates increases. Wadekar - Kulkarni has predicted six alternative stereochemical configurations for the metal chelates of each of 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinone-2-oxime.

The compound 2-nitroso-1-naphthol is reported to be synthesized from 1-hydroxy-2-naphtholic acid on treatment with sodium nitrite and dilute H_2SO_4 at room temperature.

2-nitroso-1-naphthol on treatment with $SnCl_2$ and HCl gets reduced to 2-amino 1-naphthol. On treatment with $FeCl_3$, it is partially converted into 2-Nitro-1-naphthol. On treatment with bromine in cold glacial acetic acid, it gives 3-bromo-1, 2-naphthoquinone-2-oxime.

1.2.2 Molecular structure

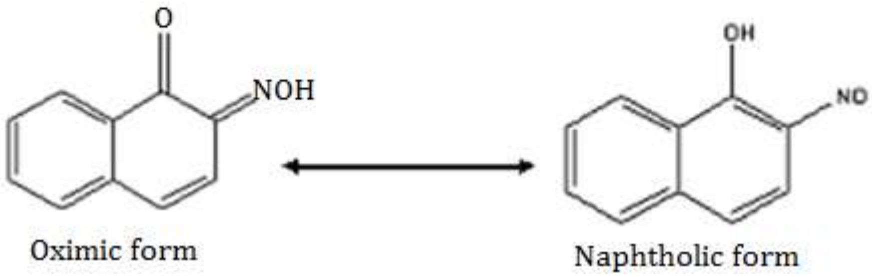


1, 2-naphthoquinone-2-oxime

1, 2-naphthoquinone-2-oxime is an isomer of 1, 2-naphthoquinone-1-oxime having different properties. Hence it will be another interesting ligand for investigating the position isomerism in metal chelates. By using X-ray diffraction technique, nitroso naphthol and there chelates with various elements have been studied.

Similar to 1, 2-naphthoquinone1-oxime, this isomer is also expected to exhibit tautomeric forms namely naphthol form and oximic form which exist in equilibrium.

Isomeric tautomerism



It is known 2-Nitrosophenol exhibits tautomerism with the corresponding monoxime. 2-nitroso-1-naphthol has great ability to form metal chelates and it is a sensitive and specific reagent for fluorimetric determinations of tyrosine residues in protein and peptides [15]. It also shows good cytotoxic action [16]. This compound makes part of noxious substances in the different industries such as pharmaceutical preparations and pesticides [17]. Proton transfer in a hydrogen bond is an elementary process presenting many systems of biological interest. Recent studies on proton dynamics in hydrogen bond is appearing in literature [18-21]. The nitroso-oxime tautomeric equilibrium was extensively studied by employing spectroscopic methods including UV [3, 22] and NMR [6-8, 23-24]. A systematic abs initio MO study of various structures is done based on 2 nitroso-1-naphthol to elucidate different factors [2]. The results of Hartree-Fock MO calculations on 2-nitroso-1-naphthol for IR in solid state and the data is compared with experimental values. UV and NMR calculations were carried out in solutions i.e. for 1,2 Naphthoquinone-2-oxime and the data is verified with the experimental data have been published by N. R. Gonewar et. al. [25]. According to the results of infra red, proton NMR and carbon13 NMR spectral data, all the complexes in the solid state exists in the quinone oxime form [26]. The Fe (III) complex of 1, 2-naphthoquinone-2-oxime has been reported and its IR spectra were explained along with electronic spectra [27]. The stability of the metal chelates was assigned to the fact that the oxygen of a resonating have better basic centre [28]. The complexes of 1, 2-naphthoquinone-2-oxime have been synthesized and their infra red absorption frequencies and electronic transitions have been reported by Gurrieri and Siracus [29].

1.3 1, 2-Naphthoquinone-dioxime

1.3.1. General

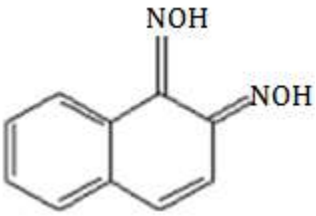
The ligand 1, 2-naphthoquinone-dioxime has been reported about 100 years ago and its physical properties, dipole moments and absorption spectra also reported long back. But it seems that its ability as an important ligand was not properly explored and therefore its co-ordination chemistry was not developed as compared to 1, 2-naphthoquinone-1-oxime from which it is synthesized. The main advantage of this ligand in the 1, 2-naphthoquinone-oxime series is that it does not shows the type of tautomerism that is shown by monoxime due to which their stereochemistry becomes too complicated. At the same time it retain the important characteristic of both 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinone-2-oxime. Also it provides N-N donar system. Therefore, there is an equal interest in the synthesis and structural investigation of its metal chelates for comparative studies with monoximates.

It has been found that biological systems have great influence by dioxime such as vitamin B12 [30-32]. Many oxime compounds and their metal chelates have shown notable bioactivity as chelating therapeutres, as drug, as inhibiters of enzymes as well as intermediates in the bio synthesis of nitrogen oxides and other important biomaterials [33-34].

Dioxime, generally forms chelates of anti isomers but it has been stated that aromatic rings destroy such action and no scarlet coloured chelates is formed by the dioxime of 1,2 naphthoquinone [35] for which stable amphi configuration could be expected.

Antimicrobial activity of transition metal complexes of 3-hydroxyimino-5-methyl-2-hexanone and 5-methyl-2, 3-hexanedionedioxime have been reported by Donde et. al.[36]. Among the 3 isomers, namely anti, amphi and syn, the first is more liable to form N, N coordinated planner chelates stabilized by hydrogen bonding [37]. In the research area of bioinorganic chemistry, transition metal chelates can probe nucleic acids with oxime and dioxime bases is a prominent one [38-40].

1.3.2. Molecular structure



1, 2-naphthoquinone-dioxime

1, 2-naphthoquinone-dioxime belongs to the vicinal dioxime type of ligands derived from aromatic nuclei. For such ligands, it is well known that, the complexing ability of C (=NOH)-C (=NOH) - group is strongly influenced by the special arrangement of the two oxime group. From the theoretical point of view, there are three alternative stereochemical configurations. Out of theses configurations the syn configurations are out of consideration for chelating purpose due to the steric factor. Therefore, for the chelation process, the remaining two configurations should be taken into consideration.

Now the most important and well known example of vic-dioxime chelates is bis Ag (II) dimethyl glyoximate which is widely used in the gravimetric estimation of Ag (II). This specific reactivity of DMG towards Ag (II) and formation of stable chelates has been attributed to the anti isomer. For 1, 2 Naphthoquinone Dioxime, formation of its stable chelates has been attributed to the anti isomers. [41-44]

1.4 Analytical application

Most of analytical applications of 1, 2-naphthoquinone-1-oxime are related with detection of amino acids. An alcoholic solution of 1, 2-naphthoquinone-1-oxime when treated with tyrosine containing Na_2CO_3 and HNO_3 gives dark purple coloration. This test is very sensitive and tyrosine concentration can be detected up to mg per litre. As far as amino acid is concerned this is very specific test. The sex hormone mixture folliculin can be analyzed by similar test. Tyrosine content the urine and serum can be analyzed by a spot test using 1, 2-Naphthoquinone-1-oxime is treated with H_2SO_4 determines color shade. Generally the technique like amperometry, nephlelometry and spectrographometry are employed for the micro determination of tyrosine using 1, 2-naphthoquinone-1-oxime as the analytical reagent.

1.5 Biological activity

1, 2-naphthoquinone-1-oxime is known to possess significant biological activity and this property is established long ago. Several workers recognized the significant physiological and biological properties. 1Nitroso-2-naphthol has bactericidal action in vitro against *Escherichia coli*. It also inhibits the growth of grafted tumors in mice. It can also employed for activating the alcoholic fermentation and has general paralyzing action on dogs and frogs.

Alkaline Earth Metal

Magnesium and calcium are ubiquitous and essential to all known living organism. They are involved in more than one role. Magnesium or Calcium ion play a role in some enzyme and calcium salts playing a structural role most notably in bones.

1.6 Ability to form complexes

Alkaline earth metal ion can form numerous coordinate compounds, when in solution either with water, or any other molecules or ions. They have small, highly charged metal ions.

1.6.1 Chelation chemistry

The word chelates derives from the Greek word “chel”, meaning a crab’s claw and refers to the pincer-like manner in which the metal is bound. Chemically a chelates is a compound from complexing of cations with organic compounds resulting in a ring structure.

1.6.2 Chelating agents: their structure and properties

Chelating agents can be defined as compound which sequesters metal ions. The word chelate derives from the greek root “chela” meaning the claw of a lobster. The chelating agent removes a metallic ion from a solid salt and holds it in solution. By forming a soluble complex from an insoluble compound it is possible to remove unwanted material, washing it away with water.

1.7 Colour

Metal complexes often have spectacular colors caused by electronic transition by the absorption of light. Most transition that is related to colored metal complexes is either d-d transition or charge transfer bands. In d-d transition, an electron in an orbital on the metal is excited by a proton to another d orbital of higher energy. A charge transfer band entails promotion of an electron from a metal based orbital into an empty ligands based orbital. The converses also occur.

1.8 Trends in coordination chemistry of transition metal

1.8.1. Co-ordinate compounds

A coordinate compound is complex compound in which the number of bonds formed by central atom or ions is greater than the expected from the usual valency consideration. The spectra or ion are attached to metal by coordination bond.

1.8.2. Central atoms

It is metal atom generally present in the central coordination compound to which two or more neutral molecules or anions are attached.

1.8.3. Ligand

Any atom, ion or molecule which is capable of donating a pair of electron to central metal atom or ion is called as ligand or coordinating group.

1.8.4. Co-ordinate bonds

A coordination bond is a special type of covalent bond in which two shared electrons are contributed by only one of the two atoms linked together, and the atom which accepts the electron pair is known as acceptor.

The presence of partially filled d-orbital which is supposed to be the basic requirement for complexing ability. Chemistry of transition of metal may be regarded as the chemistry of coordinate compounds or complexes. The ability to form complex arise due to special properties associated with the transition metals.

The properties are given below:

a) Transition metal atoms have small atomic size.
b) They have comparatively higher nuclear charge.
c) They are moderately basic.
d) They exhibit variables oxidation states.
e) The electronic structure is suitable for bonding.
f) They have vacant or partially filled (n-1) d orbital of suitable energy to accept lone pair of electron to establish coordinate covalent bond.

The bond involved in coordination complexes are coordinate, hence complexes are termed as coordinate complexes.

The structure of complexes is commonly found as linear, square planer, tetrahedral or octahedral and geometries depends upon nature of hybridization of the metal.

S Block Elements

Sr. No.	Physical properties	Calcium	Magnesium
1.	Atomic number	20	12
2.	Electronic configuration	[Ar] $4s^2$ 2, 8, 8, 2	[Ne] $3s^2$ 2, 8, 2
3.	Group, periodic block	group 2, period 4 (alkaline earth metals), s-block element	group 2, period 3 (alkaline earth metals), s-block element
4.	Atomic weight	40.078	24.305
5.	Melting point (^{0}C)	1115 K (842 °C,1548 °F)	923 K (650 °C, 1202 °F)
6.	Boiling point (^{0}C)	1757 K (1484 °C, 2703 °F)	1363 K (1091 °C, 1994 °F)
7.	Electronegativity	Pauling scale: 1.00	Pauling scale: 1.31
8.	Density (near RT)	1.55 g/cm^3	1.738 g/cm^3

d block elements

Sr.No.	Physical properties	Copper	Nickel
1.	Atomic number	29	28
2.	Electronic configuration	[Ar] $3d^{10}$ $4s^{1}$ 2, 8, 18, 1	[Ar] $3d^{8}$ $4s^{2}$ 2, 8, 16, 2 *or* 2, 8, 17, 1
3.	Group, periodic block	group 11,d-blockperiod 4	group 10, d-block period 4
4.	Atomic weight	63.546	58.693
5.	Melting point (^{0}C)	1357.77 K (1084.62°C,1984°F)	1728 K (1455°C, 2651°F)
6.	Boiling point (^{0}C)	2835 K (2562 °C, 4643 °F)	3003 K (2730 °C, 4946 °F)
7.	Electronegativity	Pauling scale: 1.90	Pauling scale: 1.91
8.	Density (near RT)	8.96 g/cm^{3}	8.908 g/cm^{3}

f block elements

Sr.No.	Physical properties	Samarium	Gadolinium
1.	Atomic number	62	64
2.	Electronic configuration	[Xe] $4f^6$ $6s^2$ 2, 8, 18, 24, 8, 2	2, 8, 18, 25, 9, 2
3.	Group, periodic block	group n/a, f-block period 6	group n/a, f-block period 6
4.	Atomic weight	150.36	157.25
5.	Melting point (^{0}C)	1345 K (1072 °C, 1962 °F)	1585 K (1312 °C, 2394 °F)
6.	Boiling point (^{0}C)	2173 K (1900 °C, 3452 °F)	3273 K (3000 °C, 5432 °F)
7.	Electronegativity	Pauling scale:1.17	Pauling scale:1.20
8.	Density (near RT)	7.52 g/cm^3	7.90 g/cm^3

1.9 Metal Organic framework (MOF)

Formation of 1, 2-naphthoquinone oximates of Mg (II), Ca (II), Cu (II), Ni (II), Sm (III) and Gd (III) takes place by following general reaction between the methanolic solution of 1,2-naphthoquinone-1-oxime with the aqueous solutions of the alkaline earth metal salts.

Chapter II

REVIEW WORK

2.1 Ligands

Due to the predominance of ionic or electrostatic characters with majority of ligands, the most abundant and stable complexes are formed with ligands having a negatively charged oxygen atom. Large number of complexes containing the carboxylate group is isolated and characterized, complexes with neutral ligands containing oxygen atoms such as alcohol, ethers and ketones do exist but are less stable than those containing anionic oxygen donars. This may be due to weak coordinating ability of these ligands as compared to water molecule present as reaction medium. These weak donar molecules can formed adducts with coordinately unsaturated complexes like $R(fod)_3$ in non coordinating solvents such as hexane or carbon tetrachloride. Complexes containing aliphatic nitrogen donars must be synthesized under inert media and should be kept in moisture free atmosphere. However, the tendency of these aliphatic nitrogen donar can be enhanced by coupling it with oxygen donars such as the carboxylate ion usually found in the aminopoly-carboxylates which results in better complexation with lanthanides ions and such bonds can persist even in the presence of water.

A variety of ligands having heterocyclic nitrogen atom are known to form complexes with the lanthanides ions. These ligands are weakly basic in nature and their complexes often are prepared under alcoholic conditions. The electrostatic factors which usually stabilize complexes of these ligands are not present. A particularly common type of complex is the one in which some of the coordinating sites are occupied by the heterocyclic nitrogen ligands while at the remaining positions, one or more of the anion are present.

Complexes of the halides, oxygen or nitrogen containing anions also exist. As expected from their hard acid character, the lanthanides are more readily and strongly complexed by the fluorides compared to the other halides. In addition, there are a few compounds known that contain ligands possessing donar sulfur atom.

The final class of ligands is the anions of compounds such as cyclopentadiene and cycloosctetraene. Compounds containing these ligands must be synthesized in anhydrous and oxygen free systems since the compounds have tendency to get hydrolyzed and to catch fire on contact with air. These complexes might perhaps be the best examples for observed covalence in the metal ligands bonding.

2.1.1 Nature of metal –ligands bonding

During past few years, there is a tremendous progress in the coordination chemistry of the transition metals both from theoretical as well as applied point of view. The earlier valence bond approach outlined by Pauling was gradually replaced by the simple crystal field approach which itself has been supplemented by the ligand field and molecular orbital theories. It has been recognized that there is a varying amount of covalent character in the metal ligand bonding depending primarily on the type of donar atom present in the ligand molecules and the nature of the bonds within the molecule.

The limitations of the crystal field theory for transition was realized due to developments of experimental evidences where in it has been established that there is appreciable delocalization of electron between the ligands and the metal ion; even with fluoride complexes. Recognition of this has led to the preparation of large number and variety of complexes with different types of ligands.

The lanthanides, on the other hand form large ions in which the ns, np and (n-1) d orbital are empty while 4f orbital are partially filled. Earlier, the attempts have been made to utilize these 4f orbital in chemical bonding with ligand molecules. However in all the cases, the extent of involvement of the 4f orbitals was found to be quite minimal; as expected from the effective shielding of the 4f orbital. The satisfactory explanations for the results obtained are substantiated by NMR, ENDOR, ESR and optical measurements. The findings based on overlap and covalency effects are clearly reflected in better understanding of observed and calculated parameters, even though magnetic neutron scattering clearly demonstrated appreciable covalent bonding for transition metals compounds. Similar studies with lanthanide compounds suggested very lesser covalency effects involving the 4f orbitals.

In the case of lanthanides an important factor is the possibility of involving outer 6s, 6p and 5d orbitals in chemical bonding for the lanthanides has also been considered. Although there are evidences for the gaseous halides, MX_3, they can be better interpreted by a covalent model rather than an ionic model. The majority of observations suggest that the bonding in the lanthanide complexes may be ionic, however certain complexes have some degree of covalency. The substantial covalence is observed for o- or n- bonded organometallic complexes.

2.2 Application of Naphthoquinone

The chemistry as well as biochemistry of animals in general and naphthoquinone and their derivatives in particular have been the subject of interest for organic, bio and analytical chemists during past one or two centuries. But the specifically importance and role of hydroxyl and oxime derivatives of 1, 4-naphthoquinone and 1,2-naphthoquinone in coordination chemistry is brought into picture since last forty years by the research school established in Pune University. Around 1971, Kulkarni and coworkers from the department of Chemistry of the University of Pune came across three isomeric pairs derived from hydroxyl 1, 4-naphthoquinone and 1, 2-naphththoquinone monoximes. There were Lawsone-Juglone, Phthiocol-Plumbagin and 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinone-2-oxime. They firstly realized that, there is a tremendous research potential manifested in these apparently simple ligands which constitute isomeric series of unique characteristics [45].

All these parent ligands and their derivatives were found to be characteristic chelating ligands. They not only possess powerful chelating ability but also possess several other aspects of special interest in coordination chemistry and bioinorganic chemistry. Some of these include i) exhibition of an interesting type isomerism exhibited by isomeric hydroxyl 1, 4-naphthoquinone derivatives which results exclusively due to difference in ring size. This has been recognized as ring isomerism which involved five membered and six membered chelates. ii) Exhibition of equally interesting and another type of isomerism caused due to exchange of oxime and carbonyl groups isomeric 1, 2-naphthoquinone monoximes. iii) Significant effects of these two types of isomerism on biological and medicinal activities of isomeric parent ligands as well as their metal chelates. iv) New and appreciable analytical applications of these naphthoquinone derivatives.

Out of the types of naphthoquinone referred above extensive as well as intensive work on hydroxyl 1,4-naphthoquinone derivatives and their metal chelates with most of the s, p, d and f block metals has been carried out by our research group as well as researchers from abroad [46]. Large number of Ph. D theses and research publications related to this class of metal chelates are reported and voluminous work in this area is in progress even at present. Since this class of metal chelates derived from 1, 4-naphthoquinone base ligand is not the subject of our current interest, detail review of the work in this area is not reviewed here.

2.3 Work related to 1, 2-naphthoquinone-oximates

Out of the three 1, 2-naphthoquinone-oximes, maximum work is reported on 1, 2-naphthoquinone-1-oxime (popularly known as α-nitroso-β- naphthol). Next to this on 1, 2-naphthoquinone-2-oxime and least amount of work is knows on 1, 2-naphthoquinone dioxime. When an up-to-date literature survey is done, it was rather surprising to note that more extensive and significant work on various aspects of metal chelates of all these three oxime derivatives has been carried out by the research group from Pune. Thus synthesis, characterization and structural as well as antimicrobial investigations of many metals from periodic table are carried out systematically by different researchers since last 30 years. This foundation work has created more interest for advance research work in coordination chemistry of these three derivatives.

The chemical and biochemical properties of naphthoquinone and their derivatives have interested research scientists on the global level for past two centuries. Several new applications of these naphthoquinone in the different branches of science have been invented in the past six decades.

Numerous Publications related the synthesis characterization and Varity of applications of new naphthoquinone derivatives appeared in reputed journals at international level.
Hydroxyl derivatives of 1, 4-naphthoquinone and oxime derivatives of 1, 2-naphthoquinones are having significance in coordination and analytical chemistry as well as biological sciences. Our research group was first to identify a specific series of isomeric ligands based on these 1, 2-naphthoquinones-oximes [47].

The above-mentioned naphthoquinone derivatives have been named as 1, 2-naphthoquinones-monoximes. Two isomeric series are derived from 1, 2-naphthoquinones-1-oxime and 1, 2-naphthoquinones-2-oxime. Extensive work on the coordination chemistry of these isomeric ligands was carried out by the research scientist working in our group for last thirty years. This work is presented in the form of Ph.D. theses, research publications in international journals and numerous presentations in national as well as international conferences.

The extensive research work done by this group as well as survey of current literature related to this subject has encouraged undertaking more advanced work, which is expected to be appreciated by scientific community.

It is worth mentioning that we are the pioneers in the development of naphthoquinone Chemistry and its extensions to various branches of science. The importance and various aspects of naphthoquinone chemistry have been portrayed through national conferences and research journals published in India.

1, 2 Naphthoquinone1-oxime is versatile derivatives of 1, 2 Naphthoquinone oxime which finds important applications in the field of coordination chemistry and analytical chemistry [48].

All this significant work is being done in University of Pune (UOP) and Bharati Vidyapeeth Deemed University (BVDU). There are few other Universities in India from Rajasthan, Madhya Pradesh and Uttar Pradesh where such a type of work related to Naphthoquinone has been carried out.

It is utmost needed to have an emphasize on relevance of juglone chemistry from the point of view of an advance research programmes in this area. Therefore, aptly the present research project is planned in the desired direction.

1, 2-naphthoquinone1-oxime and 1, 2 Naphthoquinone 2-oxime are equally important for their structural investigations as well as their metal chelates [49]

In 1986, Vainiotalo Anto et. al. reported that proton and carban C13 NMR studies on nitroso-naphthol and their complexes with the dioxouranium(IV) ion Nitrosophenol exist predominantly in the oxime form and the quinonoid oxygen does not take part in bonding [50].

In 1976 P. Lingaih and Sundaram prepared 1, 2-naphthoquinone-2-oxime complexes of Mn, Co and Zn. He reported that 1, 2-naphthoquinone 2-oxime complexes of Co crystal data [28]. In 1994 V. V. Dhapte reported that La (III), Ce (III) and Nd (III) metal chelates have shown antimicrobial activity. Substances containing the nitroso-hydroxy moiety are associated with antimicrobial activity [51].

In 1996, G. S. Jagtap prepared 1, 2-naphthoquinone-2-oxime complexes of Thorium (IV), Zirconium (IV) and Uranium (VI) chelates of some naphthoquinone derivatives [52].

Stefan Wirth et. al. reported Rhodium (III) and Iridium (III) complexes of 1, 2-naphthoquinone 1-oxime and characterized as potential anticancer agents, in respect to their neurotoxicity, to induce programmed cell death and their impact on double strand DNA [53]. Fischer and Burger prepared 1, 2-naphthoquinone-1-oxime and 2, 1-naphthoquinone-2-oxime complexes of Mn, Fe, Co and reported the IR and UV spectra [23, 54]. Glenworth and Clapp prepared metal chelates of 1, 2-naphthoquinone-1-oxime containing Mn, Fe, and Zn. These complexes can be used for the prevention and control of fungal infections of agricultural [1]. In 2002, Karzan et. al. have studied tautomeric equilibrium of 1-nitroso-2-naphthol and 1, 2-naphthoquinone-1-oxime by abinito molecular orbital (MO) calculations using HF method. They have reported for 1, 2-naphthoquinone-1-oxime the value of dipole moment energy and some bond length [55].

R. G. Sarawadekar and V. B. Jadhav and other reported by theoretical calculations of Mid, Far infrared, NMR, Electronic spectra of 1, 2-naphthoquinone-1-oxime, 1,2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime and its comparison with experimental data. He concluded that 1-nitroso-2-naphthol exists in solid state and due to tautomerism it shows oxime form in solution [11, 25, and 56].

Pankaj Kumar et. al. [57] explained synthesized, purified and characterized spectroscopic studies such as UV, FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis of substituted 1, 2-naphthoquinones. He explained compounds for cytotoxicity against a panel of human cancer celllines.

Elucidation of molecular structures of three 1, 2-naphthoquinone oximes selected for the present study has been subject of special interest of coordination chemists since past several decades. The techniques employed for this purpose mainly include infrared ultraviolet spectroscopy and NMR spectroscopy.

A careful study of the literature published in this connection shows that there is controversy in the interpretation of the experimental data, results and conclusions based on the research investigations carried out by different researchers. Dhapte has summarized the earlier work related to the structural investigations up to 1994 which is published in international journals. The subsequent additions of the recent work are reviewed by Kulkarni-Wadekar and attempts are made to update the knowledge to understand the current status of this challenging problem.

Vandana Kadam, from our research group; who firstly selected this area for investigations; synthesized some transition metal chelates of isomeric 1,2-naphthoquinone-monoximes and characterized these through elemental analysis [58]. The structural investigations were carried out with the help of infrared spectra, electronic spectra in different solvents and magnetic susceptibility measurements. Some important conclusions of this work are i) IR spectra support bonding through carbonyl oxygen and oximic nitrogen ii) electronic spectra of the isomeric pairs of chelates show significant difference in band position, band shape and band intensity and they may serve as diagnostic tools for differentiating position isomerism iii) magnetic moments of the metal chelates are closer to each other, but lower than spin only moment with an exception of cobalt chelates. Both the isomeric cobalt oximates were diamagnetic indicating that during chelates formation; Co (II) is oxidized to Co (III). The next significant work in this area was carried out by Dhapte. He carried out the synthesis, characterization and structural investigations of some lanthanide 1, 2-naphthoquinone-oximates. The main object of his work was to examine the effect of position isomerism exhibited by isomeric 1,2-naphthoquinone-1-oximates and 1,2-naphthoquinone-2-oximates and change of donar system from $\overset{\frown}{O\,N}$ (provided by monoximes) to $N \frown N$ (provided by 1, 2-naphthoquinone dioximate) on physical, chemical, structural and antimicrobial properties.

The techniques employed by Dhapte for structural investigations included IR and UV spectroscopy, TG/DTG and magnetic susceptibility measurements. For antimicrobial studies, disc assay technique was employed.

The important conclusion of this work may be summarized as follows:

i) 1, 2-naphthoquinone monoximates of the selected lanthanides are greenish brown while the corresponding 2-oximates are dark brown. The dioximate are brownish black.

ii) Magnetic moments of the chelates are closed to the moments of corresponding tri positive lanthanide ion except those of La(III) which are diamagnetic as expected.

iii) The solid state IR spectra in KBr pellets in the region (4000-400) cm^{-1} support the bonding through carbonyl oxygen and oximic nitrogen. The effect of isomerism and change of donar system, on the relevant infrared frequencies was also studied.

iv) The electronic spectra of the three series of the lanthanides 1, 2-naphthoquinone-oximates in methanol and chloroform are interpreted in terms of benzenoid electronic transition, quinonoid electronic transition and n-π* transitions. The spectra of these three series are well resolved and remarkably different from one another as well as from the spectra of the parent ligands. This work carried out for seven lanthanide metal was further extended for five other lanthanide Eu(II), Tb(III), Er(III) and Yb(III) by kulkarni-wadekar to explore the molecular structures of the three series of 1, 2-naphthoquinone oximates [59]. Some techniques used by Dhapte were employed. The results and conclusion of this work were consistent with the finding of Dhapte, supporting that a) these lanthanides chelates possess brownish colors with greenish or blackish shades. b) The chemical composition of all these oximates correspond to ML_3nH_2O (where n varies from 2 to 4 c) the bonding through both the oximic nitrogen in dioximates. d)

Magnetic moments do not show significant effect of isomerism or change of the donar system and e) electronic spectra of the three series are different indicating the effect of isomerism.

2.4 Summary of the previous work

Most of the previous work in connection of the 1, 2-naphthoquinone-oximes may be classified into three main categories of our interest as follows

(a) Analytical aspects
(b) Synthetic and structural investigations
(c) Antimicrobial activities

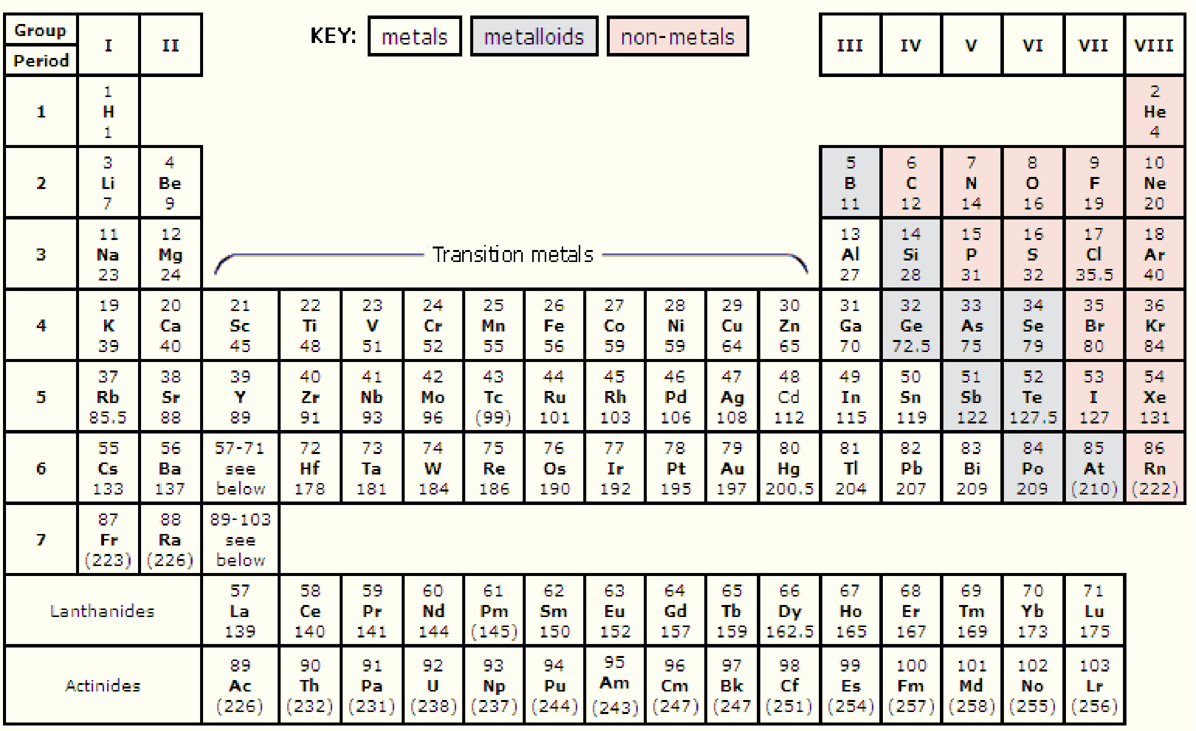
Large number of metals are covered in the coordination chemistry of these three 1, 2-naphthoquinone oximes. Similarly there are huge numbers of publications during past more than one hundred years. Therefore, it will not be possible here to describe the reported work even briefly. However, with the help of the periodic table and citation of relevant references, this work may be pointed out with reference to above referred three major categories.

2.4.1. Analytical aspects

Among three oxime derivatives of 1, 2-naphthoquinone, 1, 2-naphthoquinone-1-oxime (which is also popularly known as (α-nitroso-β-naphthol) is the most famous reagent recognized in analytical chemistry. It was found to possess widest analytical applications as a spot test reagent, colorimetric/spectrophotometric reagent and also as a gravimetric precipitant. It is still used on a wider scale in most of the analytical laboratories all over the world. It is relatively much cheaper readily available and possesses maximum utility. Another ligand 1, 2-naphthoquinone-2-oxime (i.e β-nitroso-α-naphthol) is used in the similar areas less widely. The third ligand 1, 2-naphthoquinone-dioxime is not used for analytical purpose although it has appreciable analytical potential. This may be mainly due to the fact that, it is not commercially available and so it must be synthesized on laboratory scale for its practical use. Also not any appropriate research is done to test its analytical utility.

The analytical utility of 1, 2-naphthoquinone-1-oxime in terms of the large number of metals from the periodic table which can be qualitatively identified and quantitatively estimated by this reagent is proven. Similar applicability is possible for the other two oximes, but well planned and systematic work is necessary to test as well as established their practical utility.

Periodic table



KEY: metals metalloids non-metals

Group Period	I	II											III	IV	V	VI	VII	VIII
1	1 H 1																	2 He 4
2	3 Li 7	4 Be 9											5 B 11	6 C 12	7 N 14	8 O 16	9 F 19	10 Ne 20
3	11 Na 23	12 Mg 24	Transition metals										13 Al 27	14 Si 28	15 P 31	16 S 32	17 Cl 35.5	18 Ar 40
4	19 K 39	20 Ca 40	21 Sc 45	22 Ti 48	23 V 51	24 Cr 52	25 Mn 55	26 Fe 56	27 Co 59	28 Ni 59	29 Cu 64	30 Zn 65	31 Ga 70	32 Ge 72.5	33 As 75	34 Se 79	35 Br 80	36 Kr 84
5	37 Rb 85.5	38 Sr 88	39 Y 89	40 Zr 91	41 Nb 93	42 Mo 96	43 Tc (99)	44 Ru 101	45 Rh 103	46 Pd 106	47 Ag 108	48 Cd 112	49 In 115	50 Sn 119	51 Sb 122	52 Te 127.5	53 I 127	54 Xe 131
6	55 Cs 133	56 Ba 137	57-71 see below	72 Hf 178	73 Ta 181	74 W 184	75 Re 186	76 Os 190	77 Ir 192	78 Pt 195	79 Au 197	80 Hg 200.5	81 Tl 204	82 Pb 207	83 Bi 209	84 Po 209	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89-103 see below															
Lanthanides			57 La 139	58 Ce 140	59 Pr 141	60 Nd 144	61 Pm (145)	62 Sm 150	63 Eu 152	64 Gd 157	65 Tb 159	66 Dy 162.5	67 Ho 165	68 Er 167	69 Tm 169	70 Yb 173	71 Lu 175	
Actinides			89 Ac (226)	90 Th (232)	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (255)	103 Lr (256)	

2.4.2. Synthetic and structural investigations

As compared to analytical applications for chemical analysis of all types metals, the work on synthesis and characterization of 1, 2-naphthoquinone-oximates is much less and relatively it is of recent origin. It is since last 50-60 years, work on synthesis and elucidation of molecular or solid structures of transition metal oximates (of mainly 1, 2-naphthoquinone-1-oximes) is reported in literature. Most of such work is related to Cu (II), Co (II) and Ni (II) and some other transition metals. The techniques employed for structural elucidations were infrared and electronic Spectroscopy (UV) and thermodynamics studies. Some work on the formation of metal chelates in solution state and structural studies is also reported. Similarly wok on mixed ligand complexes in which 1, 2-naphthoquinone-oxime is one of the ligands are also reported. Due to the possibility of alternative configuration involves naphtholic and oximic forms and cis-trans configuration of oxime groups, attempts are mainly centered to throw light on these aspects. No systematic work to study the effect of position isomerism or change of donar system from $O \frown N$ to $\overset{\frown}{NN}$ is known. It seems that the work in this area needs to be more systematic and extensive.

Although the work is on metal oximates shown for the group of three oximes, maximum work is done for 1,2-naphthoquinone-1-oxime. Relatively less work is found in case of 1, 2-naphthoquinone-2-oxime while very less work is reported for 1,2-naphthoquinone-dioxime.

2.4.3. Antimicrobial and other biomedical aspects

The antimicrobial activity of α-nitroso-β-naphthol has been established about one hundred years ago. Subsequently, several workers have recognized its biological properties which include antimicrobial activities against gram positive and gram negative microorganisms, pharmacological actions and biotechnological applications. Also for its isomer β-nitroso-α-naphthol, significant antimicrobial activity has been identified long ago. For the dioxime not much work on antimicrobial activity is reported except its fungicidal activity. Most of this previous work is related to the three oximes, but no significant work in this area seems to be reported on activity of metal chelates. But during recent years some remarkable work on antimicrobial and fungicidal activity of metal chelates of the isomeric monoximes is reported.

2.5 Present work

From the survey of previous work reported in literature and the work carried out in our laboratory, it is clear that complete elucidation of the molecular or solid state structures of 1, 2-naphthoquinone metal oximates is not an easy task. More experimental evidences based on different instrumental techniques with logical interpretation supported by theoretical base are necessary to arrive at some definite conclusions and their confirmations

The present work is an attempt to provide some more experimental evidences based on available techniques which will help to throw light on the solid state as well as molecular structures of the metal oximates of the selected 1,2-naphthoquinone-oximes. For this purpose lanthanide chelates of the three 1,2-naphthoquinone-oximes with Gadolinium(III) and Samarium (III) are synthesized and characterized by standard procedures.

By examining carefully the previous work and critically analyzing the data and information reported in literature, it will reveal that the synthetic and structural chemistry of 1, 2 naphthoquinone-oximates is quite complicated. For coordination chemists, it is a challenging task to explore the exact nature and unambiguous structures of the metal chelates of 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime. This is mainly due to the structural multiplicity of each of these oxime derivatives and different claims by different research workers which are based on their own experimental evidences. Therefore more and more experimental work related to structural investigations employing new and advanced techniques will be appreciable to arrive at more meaningful and fruitful conclusions. The present work is an attempt in this direction to provide some new and additional experimental evidences for elucidation of the structural aspects of lanthanide 1, 2 naphthoquinone oximates.

The selection of the two lanthanide elements for this work, gadolinium (III) and samarium (III) is arbitrary and preferred mainly due to the practical convenience. This work is an extension of the previous work done by Dhapte using the traditional techniques like mid IR spectroscopy, UV spectroscopy in different solvents and magnetic susceptibility measurements. Therefore some synthetic procedure is employed for the preparation of the lanthanide chelates of the three series of 1, 2 naphthoquinone oximates as well as methods for their chemical characterization.

Three new techniques have been employed for the structural investigations. There are powder diffraction X-ray spectrometry (XRD); scanning electron microscopy (SEM) and solid state electron spectroscopy. The other two techniques namely thermogravimetry and infrared spectroscopy have been also used to confirm the previous findings.

Apart from structural investigations, another equally important aspect of this work is detail and systematic study of antimicrobial activities of the parent ligands and their metal chelates with the Gram positive bacteria and Gram negative bacteria. The well diffusion technique has been used for quantitative measurements. Also effect of concentration and time has been examined.

The central object of this work is to employ the data to examine the effect of position isomerism exhibited by the selected isomeric 1, 2-naphthoquinone-monoximates on the structural and antimicrobial properties. Similarly another important object is to study the effect of change of donor system from $\overset{\frown}{O\,N}$ (for 1, 2 naphthoquinone monoximates) to $N \frown N$ (for 1, 2-naphthoquinone-dioximates).

CHAPTER III

OBJECTIVES

3.1 Objectives

- To develop a new series of isomeric 1, 2-naphthoquinone monoximates this will exhibit a special type of isomerism.
- To explore the nature of this type of isomerism, and study of its consequences. A series of isomeric pairs of metal chelates will be synthesized and characterized for this purpose.
- To examine the effect of position isomerism on various physical, chemical and biological properties. A comparative study of the general physical properties, TG/DTG patterns, XRD patterns, IR and UV spectra and other structural aspects will be investigated in this regard. Antimicrobial activities of the compounds for selected microorganisms will be studied by using standard established procedures.
- Oxime derivatives of 1, 2-naphthoquinone and their metal complexes will be synthesized. Their possible nanometric nature will be explored with the help of SEM/TEM. Further structural investigations will be carried out by using other modern analytical techniques.

3.2 Significance of the study

Naphthoquinone derivatives have significant pharmacological properties. They are cytotoxic; they have significant antibacterial, antifungal, antiviral, insecticidal, anti-inflammatory and antipyretic properties. Plants with naphthoquinone contents are widely used in China and the countries of South America, where they are used to treat malignant and parasitic diseases.

The important aspects of the coordination chemistry of juglones include different physical, chemical and biological properties.

A) Structure- Activity co relationships: the effect of position isomerism on different physical, chemical and biological properties.

B) Preparation of nanosized metal chelates from oxime derivatives.

C) Formation of intense colored chelates with non transition elements in absence of d or f electrons. These colors are found to be very stable for several years. But the stability is found only in solid state. The color intensity is reduced or lost in solution state. These colors show all the colors of visible spectrum as well as intermediate shades. Since there are no d-d transitions, the anticipated mechanism may be ligand to metal charge transfer.

The metal chelates of non transition elements belonging to s and p block of periodic table or pseudo non transition metals like Zn (II), Cd (II), Ti (IV), La (III), Y(III) etc. may be regarded as typical examples of said type of charge transfer complexes.

Synthesis and characterization of such solid state charge transfer complexes along with their application will be our advanced research as elucidation of the origin of these visible colors is itself an interesting research area.

Also naphthoquinone possess biological importance and several biochemical reactions are involved in non-aqueous media, the acid base indicator properties of juglone is yet another significant and useful applications in non-aqueous media.

CHAPTER IV

OBSERVATIONS RESULTS AND DISCUSSIONS

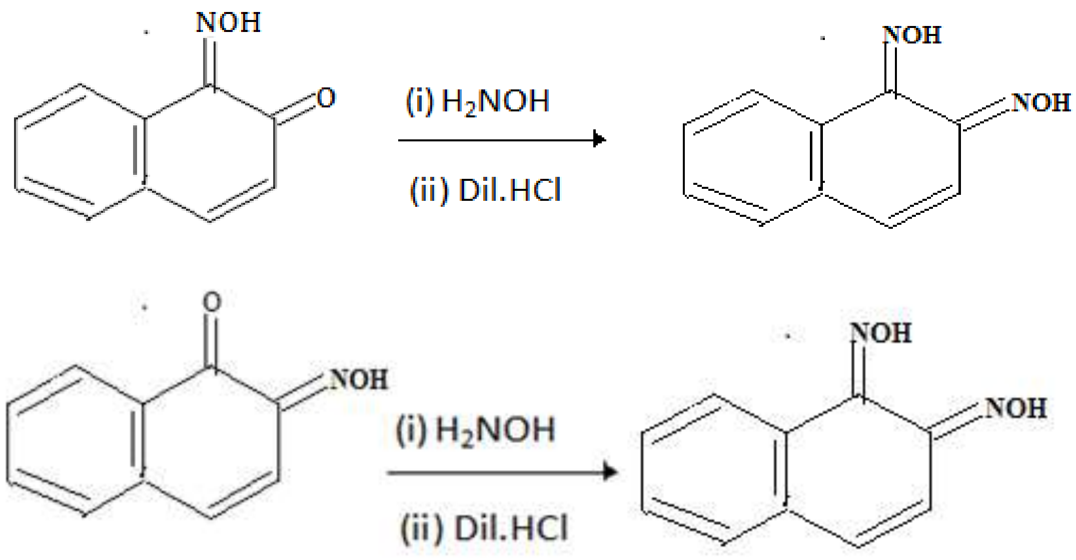
4.1 Ligands:

Out of three ligands 1,2-naphthoquinone-1-oxime and 1,2-naphthoquinone-2-oxime are commercially available in pure state. These are called as 1-Nitroso 2-naphthol and 2-Nitroso 1-naphthol and were purchased from Aldrich.

4.1.1 1,2-naphthoquinone-dioxime

Out of three ligand, 1, 2-naphthoquinone-1-Oxime and 1, 2-naphthoquinone-2-oxime are commercially available in pure state. These are sold as 1-Nitroso-2-Naphthol and were purchased from Aldrich.

The third ligand 1, 2-naphthoquinone-dioxime is not commercially available but can be synthesized either from 1, 2-naphthoquinone-1-oxime or 1, 2-naphthoquinone-2-oxime by the following reaction.



In the present work, this ligand was prepared from methanolic solution 1, 2-naphthoquinone-1-oxime by heating it with hydroxyl amine hydrochloride in presence of dil.HCl by the method suggested by Goldschmidt [60]. The detail procedure followed is given below.

A solution of 1, 2-naphthoquinone-1-oxime corresponding to 5 mmol was prepared by dissolving 0.94 g in minimum quantity of methanol in a round bottom flask to which a solution of hydroxylamine hydrochloride (0.33 g dissolved in minimum quantity of distilled water) was added along with a few drop of dilute HCl (2N). The reaction mixture was heated on a water bath for half an hour when yellow product was isolated after addition of distilled water. This crude product was filtered and washed with cold water and then dissolved in dilute NaOH (2N) solution. The solution obtained was filtered and then acidified with dilute 2N H_2SO_4, when yellow colored dioxime was precipitated which was filtered, washes with cold water and then with Methanol (Yield 90%).

The isolated Dioxime was finally recrystallized from benzene and Ligroin in the form of yellow needles (M.P. 149^0C).

4.2 Preparation of metal chelates

General all three ligands, 1, 2-naphthoquinone-1-oxime, 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime were prepared as has been described as above. They were freshly recrystallized from the respective solvent before use.

4.2.1. Preparation of the metal solutions

Aqueous solutions of the four alkaline earth metal ions which include Magnesium (II), Calcium (II), Copper (II), and Nickel (II) corresponding to $1*10^{-3}$ M were prepared by dissolving the necessary quantities of each rare alkaline earth metal in distilled water. It was necessary to add 2-3 drop of concentrated hydrochloric acid (A.R. grade) to prevent the precipitation of hydroxides and to obtain clear solutions.

4.2.2. Preparation of the ligands solutions

The ligands stock solutions corresponding to $1*10^{-3}$ M were prepared by dissolving the properly weighed quantity of recrystallized 1, 2-naphthoquinone-1-oxime in distilled methanol and dilute the solution to 250 ml by methanol.

4.2.3. Preparation of the chelates

Similar procedure were adopted for preparing the stock solution of another two ligands (i.e. 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime) corresponding to $1*10^{-3}$ M.

Aqueous ammonia solution (1M) was prepared by diluting the liquor ammonia (A. R. grade) by distilled water and this was used to adjust the desired pH.

Metal chelates of the 1, 2-naphthquinone-1-oxime 1, 2-naphthoquinone-2oxime and 1, 2-naphthoquinone-dioxime were prepared by the general procedure given below.

For the preparation of metal chelates, a three necked flask provided with a magnetic stirrer was used for each chelate. The 1, 2-naphthoquinone-1-oxime, 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime were precipitated by mixing the corresponding metal ion solution. The solution of 1,2 naphthoquinone 2-oxime in methanol corresponding to the concentration of $3*10^{-3}$ M was taken to which the particular rare earth metal ion solution corresponding to the concentration of $1*10^{-3}$ was added drop by drop while constant stirring the mixture by the magnetic stirrer. After addition of all metal chloride solution drop wise, the pH of the reaction mixture was adjusted to about 6-7 with the help of 1M aqueous ammonia by adding it drop by drop till the desired pH is reached. The rare earth chelate was precipitated. After ensuring the complete precipitation the entire mixture was kept stirring for about three hours in an oil bath at 60^0C temperature. The precipitate was then kept overnight in a refrigerator and was filtered next day at room temperature under vacuum. Each precipitate was thoroughly washed by distilled water, followed by little methanol. After cooling the product were filtered by using Whatmann filter paper No.42 and washing with cold water and then with ethanol, and finally dried in a vacuum desiccators.

4.3 Color of metal chelates

Metal complexes often have spectacular colors caused by electronic transition by the absorption of light. Most of transitions related to colored metal complexes are d-d transition or charge transfer bands. In d-d transition, an electron in a d orbital on the metal is excited by a photon to another d orbital of higher energy. A charge transfer band in valves promotion of an electron from a metal based orbital into an empty ligand based orbital. The converse also occurs. Excitation of an electron in ligand based orbital into an empty metal based orbital (ligand to metal charge transfer or LMCT). These phenomena can be observed with the aid of electronic spectroscopy also known as UV-Vis.

Sr. No.	Compound	Colour
1.	Mg-1-oximate	Green
2.	Mg-2-oximate	Brown
3.	Mg-dioximate	Brown
4.	Ca-1-oximate	Green
5.	Ca-2-oximate	Brown
6.	Ca-dioximate	Brown
7	Cu-1-oximate	Chocolate
8.	Cu-2-oximate	Chocolate
9.	Cu-dioximate	Dark brown
10.	Ni-1-oximate	Light Brown
11.	Ni-2-oximate	Light brown
12.	Ni-dioximate	Black

13.	Sm-1-oximate	Brown yellow
14.	Sm-2-oximate	Pale brown
15.	Sm-dioximate	Brown
16.	Gd-1-oximate	Green
17.	Gd-2-oximate	Dark brown
18.	Gd-dioximate	Brown black

Colour in alkaline earth metal compounds is generally due to electronic transition of two types.

Charge transfer transition: An electron may jump from a predominantly ligand orbital to a predominately metal orbital, giving rise to a ligand to metal charge transfer (LMCT) transition. These can most easily occur when the metal is in high oxidation state.

An electron from one d-orbital to another. In complexes the d-orbital do not have same energy as pattern of the other d-orbital. This can be calculated by crystal field theory. The extent of the splitting depends on the particular metal.

4.4 CHEMICAL CHARACTERIZATION

I. Elemental analysis
II. IR Spectroscopy
III. SEM
IV. XRD
V. Antimicrobial activity
VI. TGA
VII. Electronic spectra
VIII. Magnetic susceptibility
IX. Catalytic activity

The chemical identity of 1, 2-naphthoquinone-oximes was checked by using their melting points and TLC. The 1, 2-naphthoquinone-oximates were chemically characterized by using the elemental analysis and thermogravimetric technique.

4.4.1. Elemental Analysis

The microanalysis of the compounds was performed for the percentage of carbon, hydrogen and residue on Hosli carbon-hydrogen microanalysis instrument. The residue obtained in the above elemental analysis was considered to possess a general formula M_2O_3 for the respective metal complexes.

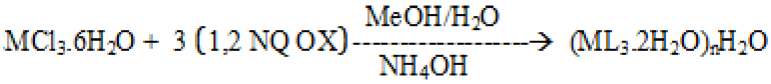
The percentage of metal (from its metal oxide residue) and the number water molecules associated with the metal chelate (as either lattice, absorbed or coordinated) was further determined from thermogravimetric data.

The interactions of aqueous solutions of hydrated metal chlorides and methanolic solution of 1, 2-naphthoquinone oximes under inert atmosphere led to yield amorphous products, possessing a general formula $(ML_2).nH_2O$ or $(ML_3).nH_2O$.

An aqueous solution of metal chlorides hexahydrate reacts with methanolic solution under refluxing condition in a 1:2 molar ratio to yield dark coloured products for the metal chelates.

The aqueous solution of copper chloride and alcoholic solution of the oxime ligand led to formation of amorphous product with general formula $ML_2.2H_2O$.

An aqueous solution of metal chloride hexahydrate reacts with methanolic solution under refluxing condition in 1:3 mole ratios to yield dark coloured products for the lanthanides chelates.



$$MCl_3.6H_2O + 3\,(1{,}2\ NQ\ OX) \xrightarrow[NH_4OH]{MeOH/H_2O} (ML_3.2H_2O)_nH_2O$$

Where M: Lanthanide L= 1, 2 NQ OX: 1, 2 Naphthoquinone oxime.

The results of the elemental analysis are shown in Table 1.

Sr. No.	Ligands	Melting point
1.	1,2-naphthoquinone 1-oxime	111^0C
2.	1,2-naphthoquinone 2-oxime	163^0C
3.	1,2-naphthoquinone dioxime	153^0C

The colour, yield elemental analysis and molecular composition of Mg (II), Ca (II), Ni(II), Cu (II), Sm (III) and Gd (III) complexes of 1,2-naphthoquinone-1-oxime

Complexes	**Colour**	**Yield**	**% Analysis (calculated)**			**Molecular Composition**
			C	**H**	**Residue**	
Mg(II) 1,2 NQ-1-ox	Green	70%	58.99 (59.07)	4.49 (4.46)	9.94 (9.91)	$ML_2.2H_2O$
Ca (II) 1,2 NQ-1-ox	Green	55%	62.22 (62.16)	3.68 (3.65)	14.57 (14.51)	$ML_2.2H_2O$
Cu(II) 1,2 NQ-1-ox	Chocolate	84%	56.40 (54.88)	3.28 (2.80)	6.57 (5.89)	$ML_2.2H_2O$
Ni (II) 1,2 NQ-1-ox	Light Brown	70%	53.33 (51.68)	3.62 (2.87)	6.33 (5.74)	$ML_2.2H_2O$
Sm (III) 1,2 NQ-1-ox	Brown yellow	79%	51.48 (50.74)	2.69 (2.89)	15.20 (12.16)	$ML_3.2H_2O$
Gd(III) 1,2 NQ-1-ox	Yellow green	75%	50.97 (50.08)	2.69 (2.89)	14.20 (12.58)	$ML_3.2H_2O$

The colour, yield elemental analysis and molecular composition of Mg(II), Ca(II), Ni (II), Cu (II), Sm (III) and Gd(III) complexes of 1,2-naphthoquinone-2-oxime

Complexes	**Colour**	**Yield**	**% Analysis (calculated)**			**Molecular Composition**
			C	**H**	**Residue**	
Mg(II) 1,2 NQ-2-ox	Brown	68%	59.10 (59.07)	4.42 (4.46)	9.94 (9.91)	$ML_2.2H_2O$
Ca (II) 1,2 NQ-2-ox	Brown	55%	57.01 (56.86)	4.23 (4.29)	12.57 (12.67)	$ML_2.2H_2O$
Cu(II) 1,2 NQ-2-ox	Chocolate	83%	56.40 (54.88)	3.28 (2.20)	16.57 (15.89)	$ML_2.2H_2O$
Ni (II) 1,2 NQ-2-ox	Light brown	69%	53.33 (51.68)	3.62 (2.87)	16.33 (11.50)	$ML_2.2H_2O$
Sm (III) 1,2 NQ-2-ox	Pale brown	66%	51.48 (51.77)	2.72 (2.89)	13.55 (11.19)	$ML_3.2H_2O$
Gd (III) 1,2 NQ-2-ox	Dark brown	70%	59.97 (50.67)	2.69 (2.83)	14.57 (14.62)	$ML_3.2H_2O$

The colour, yield elemental analysis and molecular composition of Mg(II), Ca(II), Ni (II), Cu (II), Sm(III) and Gd(III) complexes of 1,2-naphthoquinone-dioxime

Complexes	**Colour**	**Yield**	**% Analysis (calculated)**			**Molecular Composition**
			C	**H**	**Residue**	
Mg(II) 1,2 NQ-Diox	Brown	62%	55.21 (55.01)	4.67 (4.61)	9.18 (9.22)	$ML_2.2H_2O$
Ca (II) 1,2 NQ-Diox	Brown	58%	52.98 (53.09)	4.41 (4.44)	12.31 (12.39)	$ML_2.2H_2O$
Cu(II) 1,2 NQ-Diox	Dark brown	31%	54.50 (52.78)	3.63 (2.93)	12.71 (11.61)	$ML_2.2H_2O$
Ni (II) 1,2 NQ-Diox	Black	75%	52.54 (50.92)	3.94 (2.95)	12.64 (11.49)	$ML_2.2H_2O$
Sm (III) 1,2 NQ-Diox	Brown	71%	48.36 (47.82)	2.92 (3.08)	16.33 (11.50)	$ML_3.2H_2O$
Gd(III) 1,2 NQ-Diox	Brown black	68%	47.92 (48.24)	2.93 (3.08)	14.20 (12.89)	$ML_3.2H_2O$

4.4.1.1 Result and discussion

The analytical data is presented for the chelates. All these chelates are sparingly soluble in non polar solvents like n-hexane, carbon tetrachloride etc, moderately soluble in polar solvents and appreciably soluble in strongly coordinating solvents like DMSO and DMF. Yield of these chelates are in between 50-84%. These metal chelates are comparatively less soluble in Methanol, ethanol and chloroform while sparingly soluble in n-heptane.

The analytical data form microanalysis confirms the presence of 1:2 stiochiometry for Mg, Ca, Cu and Ni chelates with inclusion of water in coordination sphere. The number of coordinated with water molecule is observed to be two for all the complexes.

The elemental analysis of lanthanides metal chelates differs from the other metal chelates in the sense that they have higher percentage of hydrogen and lower percentage of carbon and residue. For these cases, the observed percentage of residue is lower than the expected values the observed percentage of water is higher than the expected value. It indicates that the presence of absorbed water in these chelates. Hence the elemental analysis was corrected accordingly considering this kind of possibility. Thus the molecular composition for the complexes is modified to (ML_3.2 (H_2O) 2.H_2O)

All these chelates are expected to be associated with two coordinated water molecules. This is also supported by thermogravimetric analysis. This observation is further confirmed by observing broad band in the region 3500 – 3100 cm^{-1}.

The microanalysis of the compounds was performed for the percentage of carbon; Hydrogen residue on Hosli carban-hydrogen microanalysis instrument. The residue obtained in the above elemental analysis was considered to possess a general formula M_2O_3.

Mg (II) metal chelates have green –brown color. Ca (II) chelates observed green – brown color and Ni (II) metal chelates showed light brown -black in color. Cu (II) metal chelates of 1, 2-naphthoquinone-oxime derivatives showed brown - chocolate color. All these chelates were highly soluble in DMSO. Elemental analysis indicated that observed percentages of carbon, hydrogen and residue are much closer to the theoretical values shown in the parentheses. Cu (II) dioximate has very low yield as compared to Cu (II) 1-oximate and Cu (II) 2-oximate. The molecular composition of Ca (II), Mg (II), Cu (II) and Ni (II) metal chelates has $ML_2.2H_2O$, the composition of lanthanide metal chelates of Sm (III) and Gd (III) has $ML_3.2H_2O$.

4.4.2. Infrared spectroscopy

4.4.2.1. General

Infra red spectroscopy also known as vibrational spectroscopy. It is an important and regularly used technique for research investigations. It's important appreciable aspect is that, it is applicable to all of the three physical states, gaseous, liquid and solid state of the matter. It provides very useful data and information for structural elucidations.

Infrared spectroscopy has played significant role in drug discoveries and drug research. For practical purpose IR spectroscopy is divided in three classes as a) Near infrared spectroscopy b) Mid infrared spectroscopy c) Far infrared spectroscopy.

4.4.2.2. Principle of Infrared Spectroscopy

The fundamental equation on which infrared spectroscopy based is as follows:

$$\overline{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$$

Where,

$\overline{\nu}$ =frequency of vibrating masses m_1 and $m_2$in cm^{-1}

f = Force constant

c= Velocity of light

μ = Reduced mass of the two bonded atoms

The above equation is valid for vibrating masses m_1 and m_2 from infrared absorption point of view, only if certain rules are obeyed. These are a) the energy (or wavelength) of incident radiation must be equal to the energy difference between the excited and ground state of the molecules. b) The vibration must be accompanied by a change of dipole moment. In infrared spectroscopy, the concept of vibration of diatomic system having masses m_1 and m_2 is extended to other kind of vibration or oscillations exhibited by polyatomic systems. These include i) bending vibrations in angular molecules like H_2O, NH_3, NO_2 etc. ii) twisting vibration or oscillations, wagging oscillations and iv) lattice vibrations where lattices formed by constituent atoms are vibrating as a whole.

Therefore infrared spectra of polyatomic compounds should be carefully analyzed for absorption peaks related to i) vibration of linear molecule ii) bending vibrations iii) twisting vibrations iv) wagging oscillations v) lattice vibrations (for solid samples).

4.4.2.3. Experimental

All the samples were dried completely prior to their use for recording IR spectra. The solid state infrared spectra of the ligands as well as their chelates. We were taken determine in KBr pallets. The KBr pellets were prepared by mixing about 1.0 to 2.0 mg of the finely powdered samples with 100mg of KBr and the transparent pellets were obtained by following the standard technique. The spectra recorded in the region of 4000 to 400 cm^{-1}on Nicolet iS5 model. Simultaneously transparent plate of pure KBr pellets was also prepared in the same way and this was used as the reference.

The solid state infrared spectra of the all three ligands and their metal chelates under investigations were recorded in KBr pellets.

4.4.2.4. Results

Nature of the IR spectra of Ligands and their metal chelates from the point of view molecular structures were studied. Their IR spectra are composed of the following infrared frequencies.

i) C-H stretching (3000-2800) cm^{-1}
ii) C=C stretching (1500-1450) cm^{-1}
iii) Ring vibration (1500-1400) cm^{-1}
iv) O-H stretching (3600-3000) cm^{-1}
v) N-O stretching (1150-950) cm^{-1}
vi) C=N stretching (1580-1520) cm^{-1}
vii) O-H bonding (1400-1300) cm^{-1}
viii) Other ring vibration (800-500) cm^{-1}

In addition, the IR spectra of the metal complexes will involve,

ix) M-O stretching (600-200) cm^{-1}
x) M-N stretching (600-200) cm^{-1}
xi) O-H vibration modes from co-ordinate water

All these frequencies are not of equal importance for the present work because here, the principal object is to explore the effect of a) chelation b) position isomerism c) change of donar system. Therefore, the IR spectra will be analyzed here with special reference to the following relevant frequencies. a) O-H Stretching b) C=O stretching c) C=N Stretching d) N-O Stretching e) M-O and M-N Stretching.

The IR spectra are shown in figures and the relevant IR absorption frequencies are given in table.

These spectra are analyzed with reference to O-H stretching, C=O stretching, C=N stretching, N-O stretching and M-N, M-O stretching frequencies which are directly involved in the process of chelation. Further the peak corresponding to these stretching frequencies will be examined to assess the effect of chelation, position isomerism and change of donar system on the molecular structures.

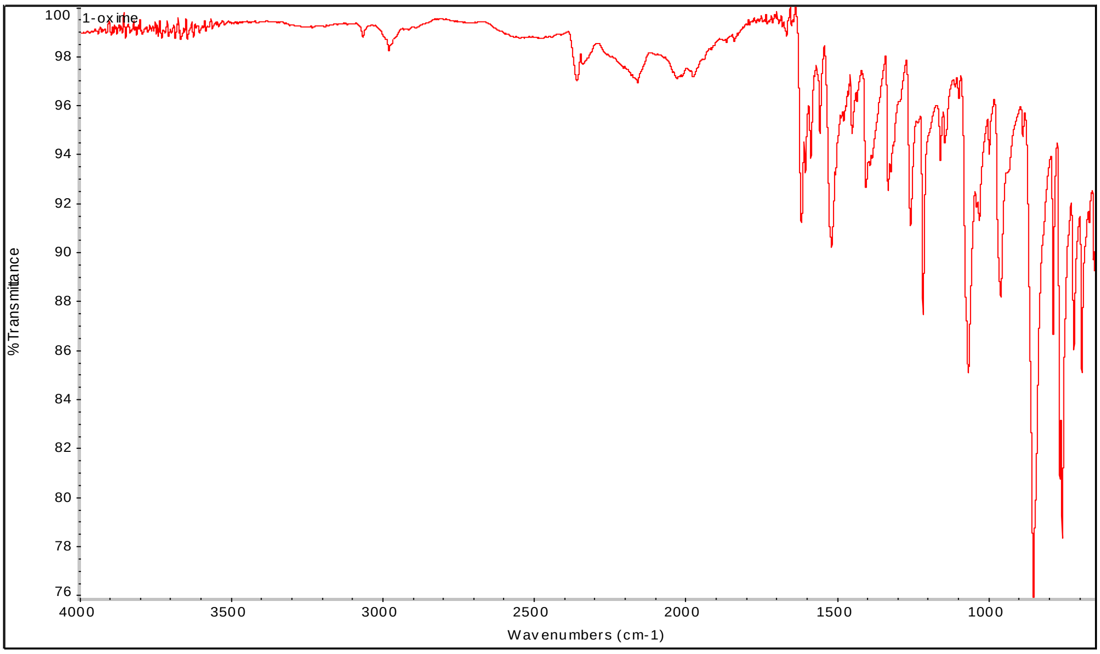
Effect of chelation:

Such comparison among the three series seems to be difficult and challenging from quantitative point of view. Because a) the general trends of the selected IR frequencies for the three series are apparently same b) the spectra of three ligands as well as their chelates consist of a large number of closely spaced sharp lines whose appropriate assignments is a challenging task.

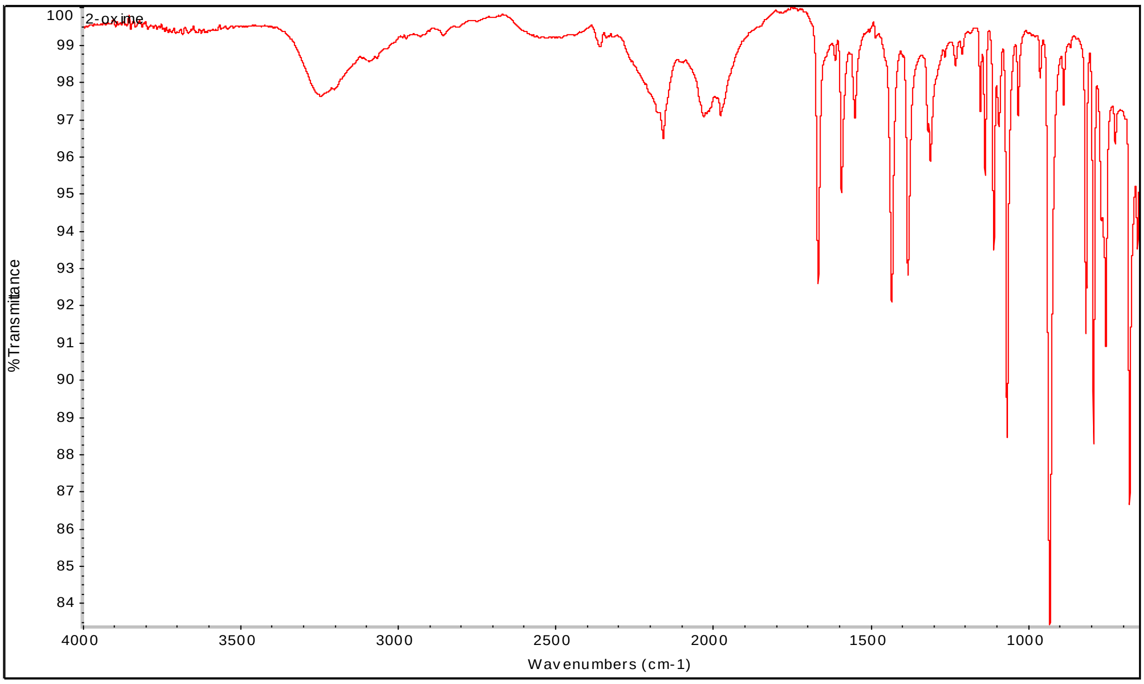
Even then, when such comparison is attempted carefully, it is found that, although it is difficult to make quantitative assessments for such effects, some remarkable observations useful for qualitative assessments are possible. Because there are several significant changes in the band, shape and band intensities indicative of the effect of position isomerism and change of donar system on these three series. These may be summarized in brief in the following way:

The significant differences in band shape and band intensities with special reference to O-M, C=O, C=N and N-O stretching frequencies and other peaks also clearly indicate that the isomeric chelates retain their identity ever after chelation which can be recognized in terms of their IR spectra.

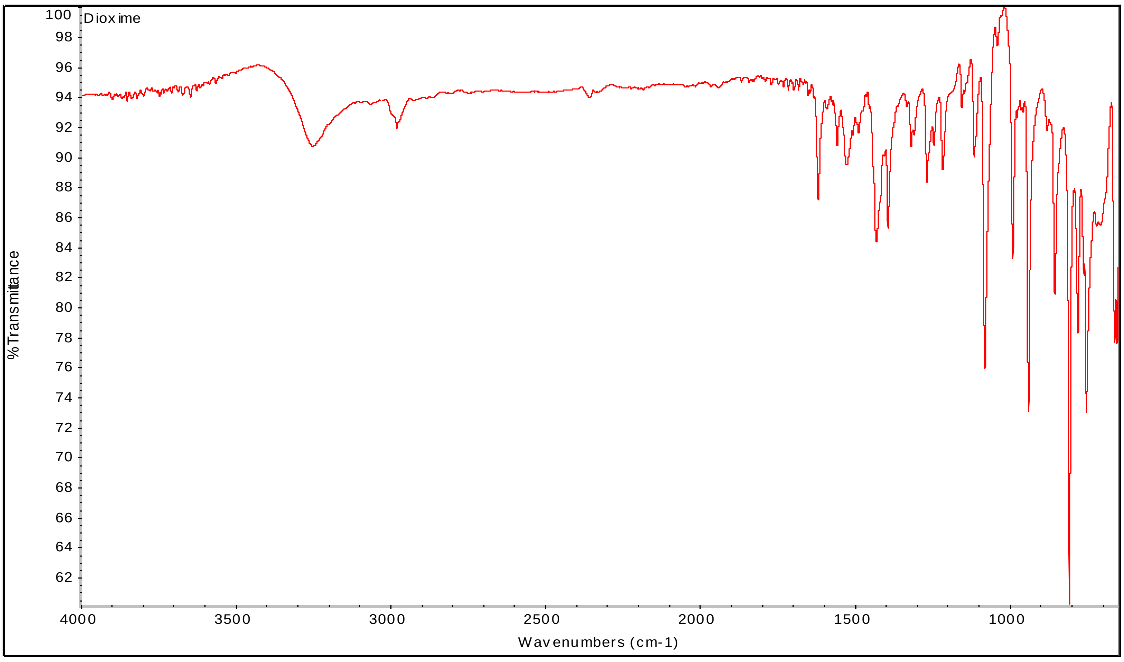
Secondly the effect of change of donor system from ($\overset{\frown}{O\ N}$) associated with the two monoximes to ($\overset{\frown}{N\ N}$) associated with the dioxime, is reflected by a) absence of the characteristic C=O stretching frequency into two adjacent group due to two adjacent but non-equivalent-CN groups and c) splitting of the N-O stretching frequency into a doublet due to the presence of two nonequivalent-NO groups.



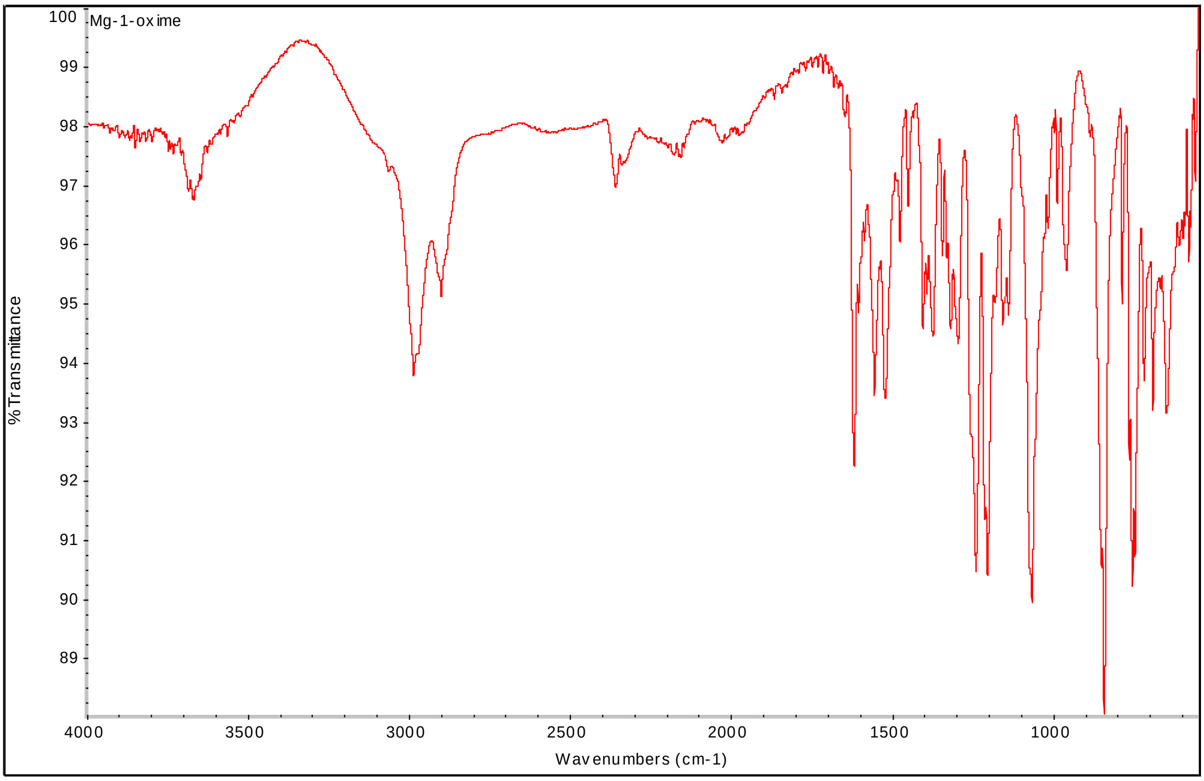
1, 2-naphthoquinone-1-oxime



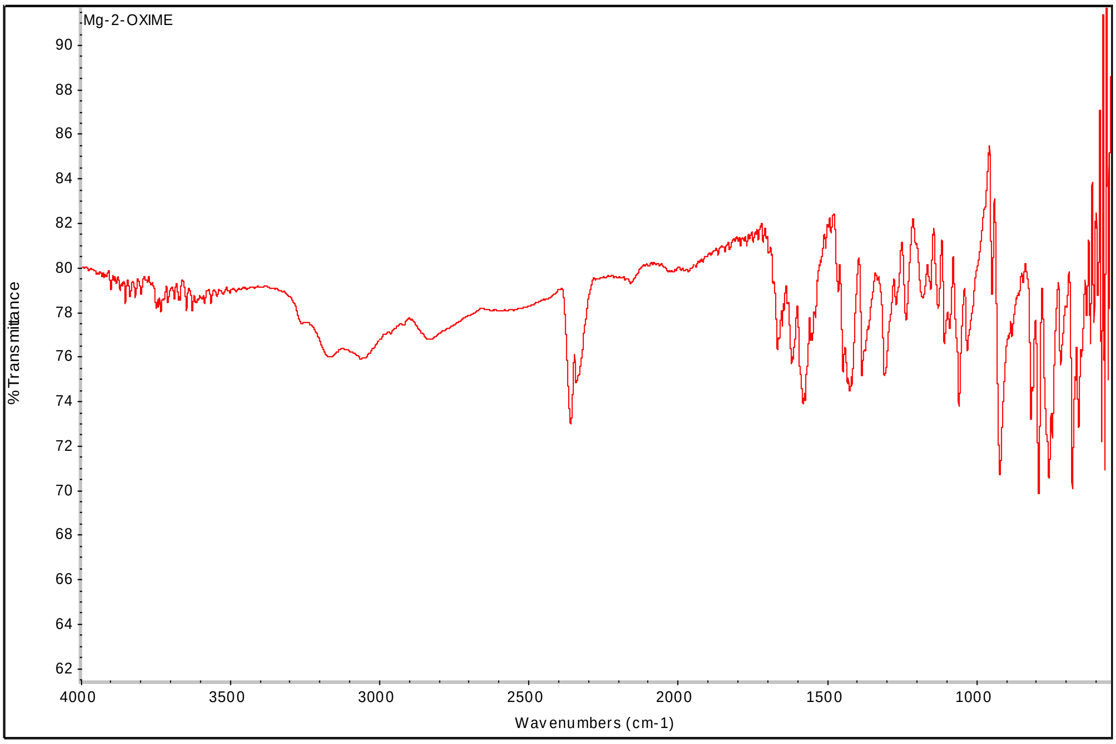
1, 2-naphthoquinone-2-oxime



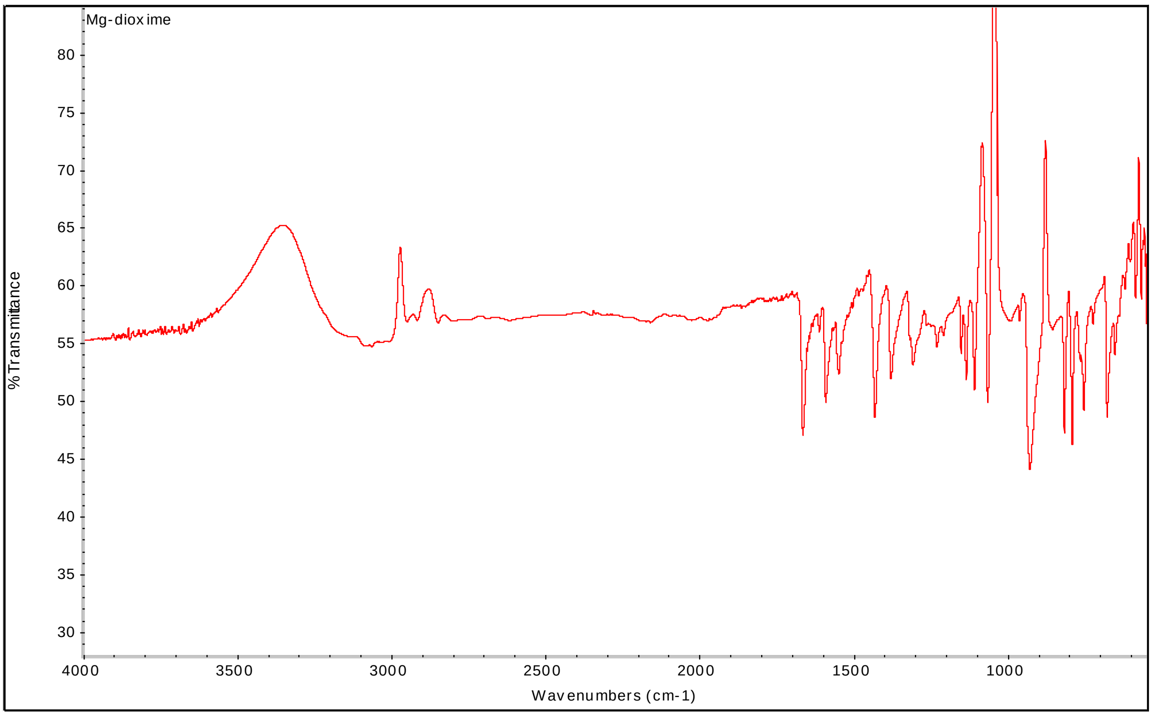
1, 2-naphthoquinone-dioxime



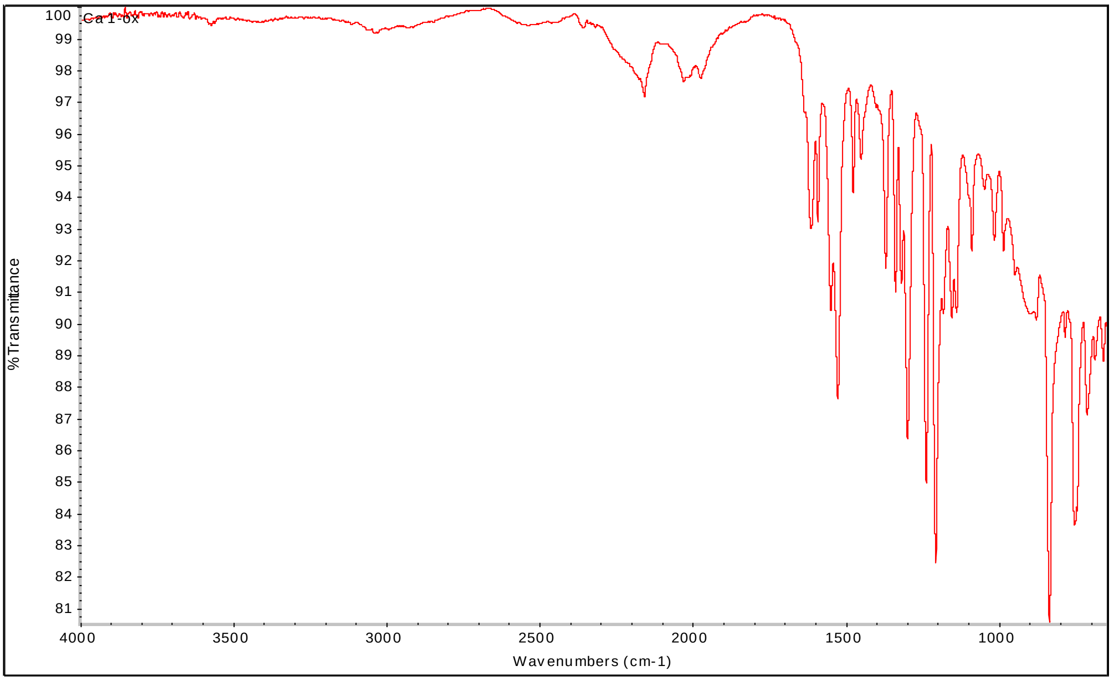
1, 2-NQ Mg (II)-1-oximate



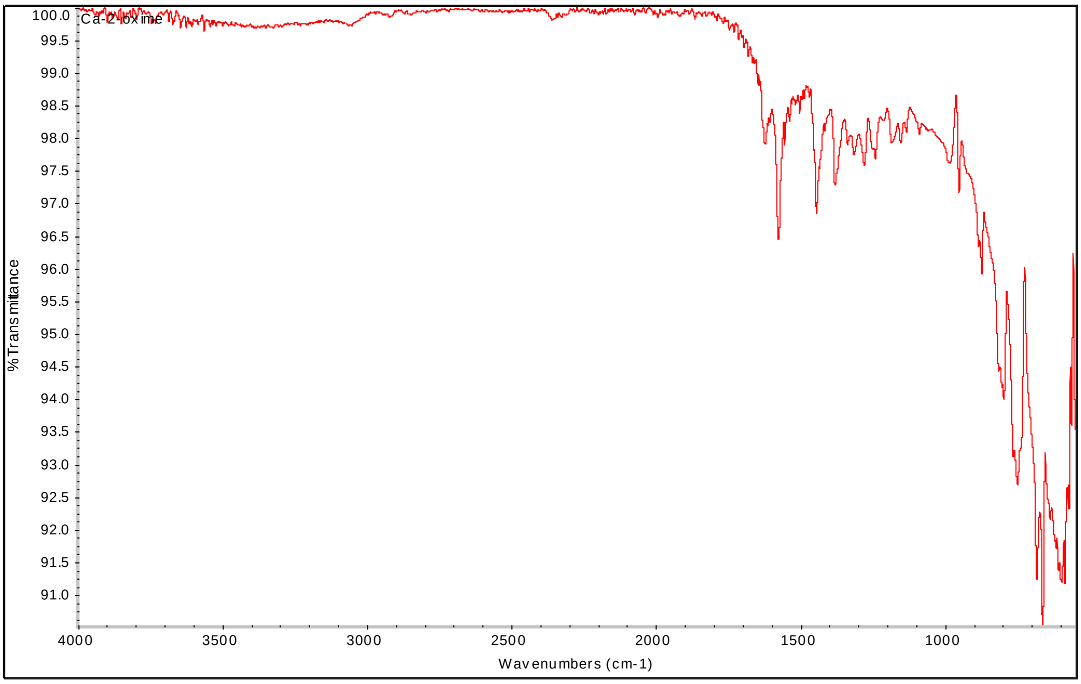
1, 2-NQ Mg (II)-2-oximate



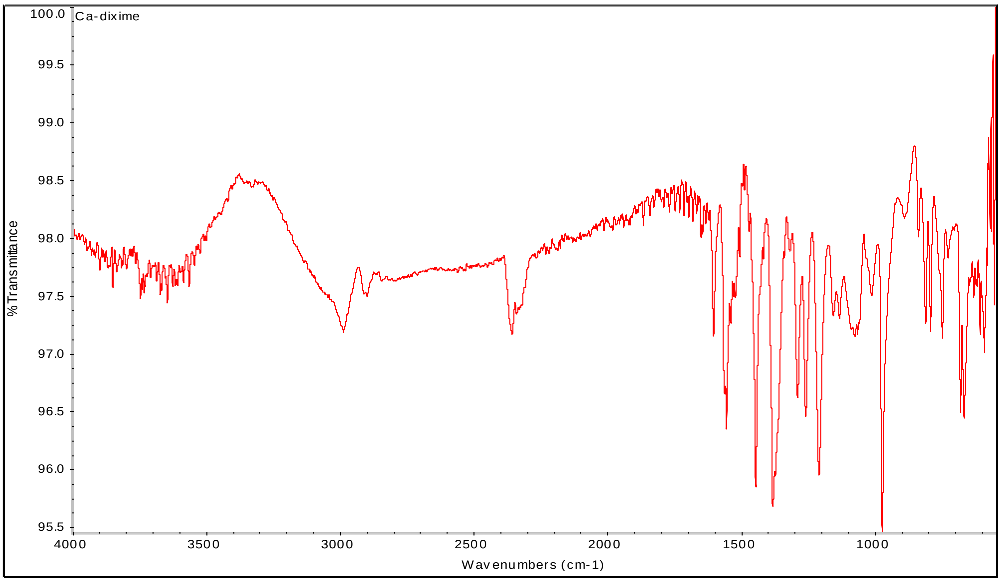
1, 2-NQ Mg (II)-dioximate



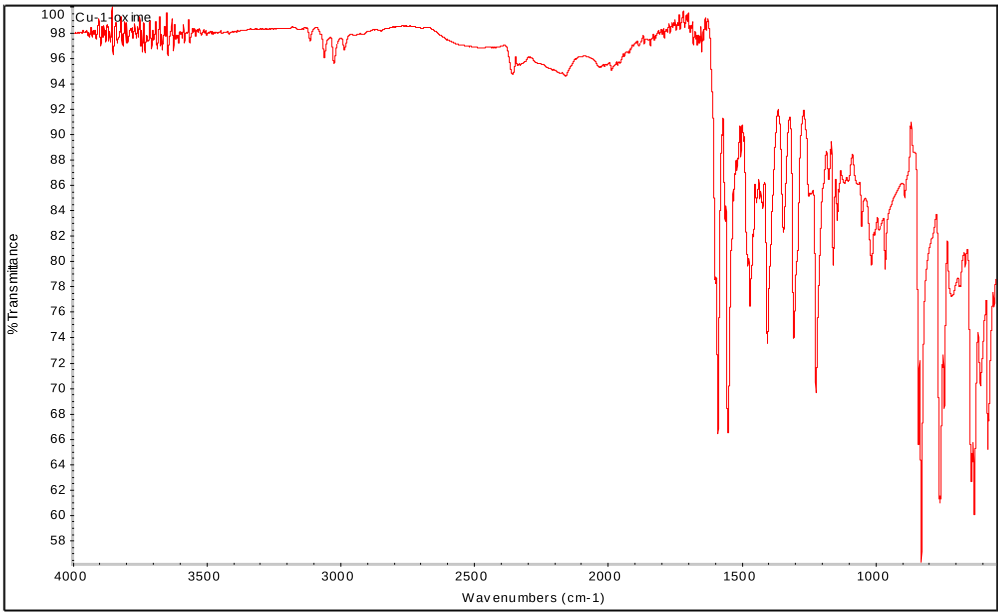
1, 2-NQ Ca (II)-1-oximate



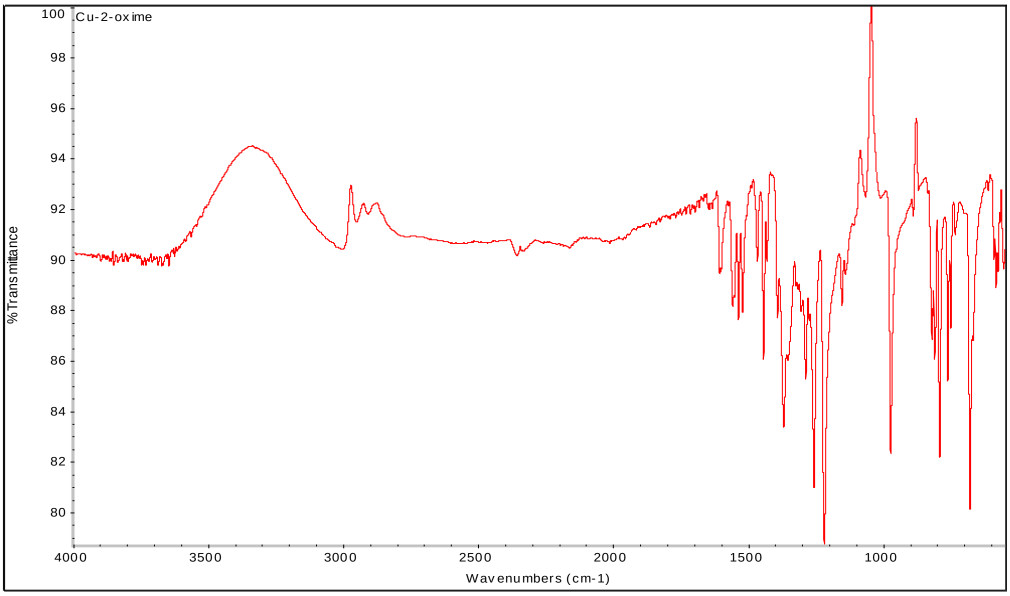
1, 2-NQ Ca (II)-2-oximate



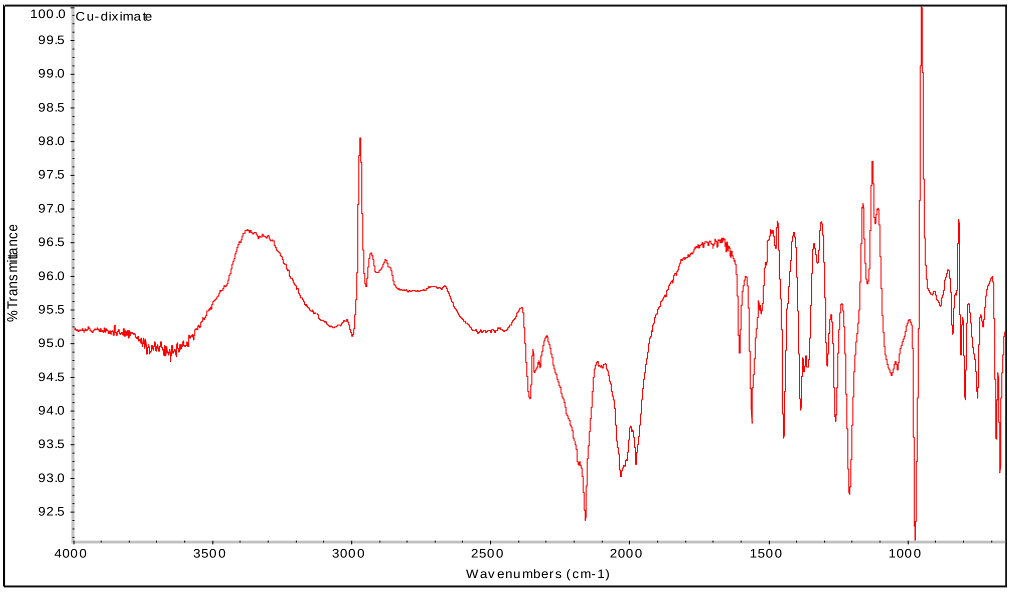
1, 2-NQ Ca (II)-dioximate



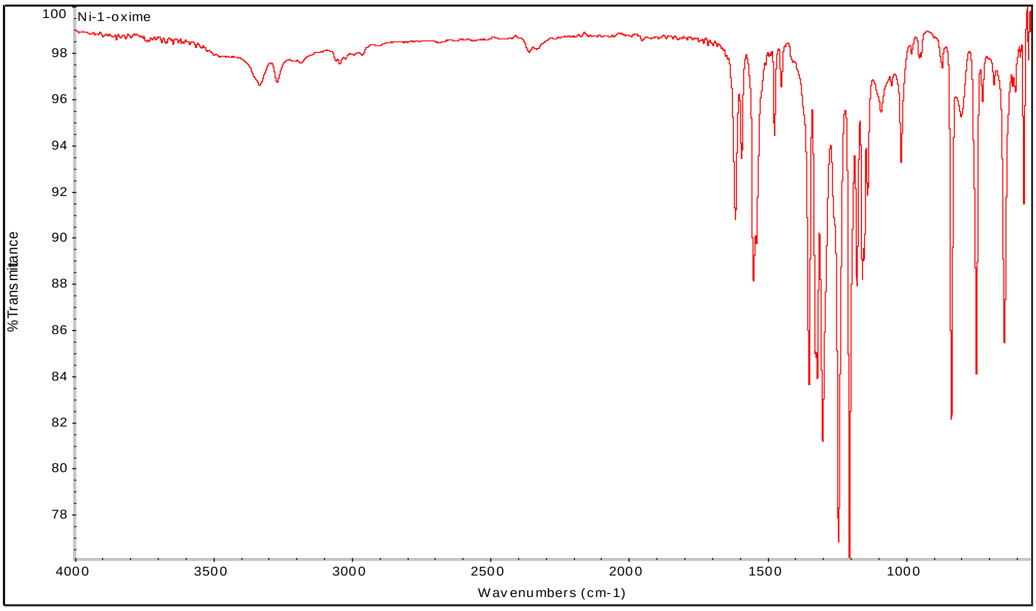
1, 2-NQ Cu (II)-1-oximate



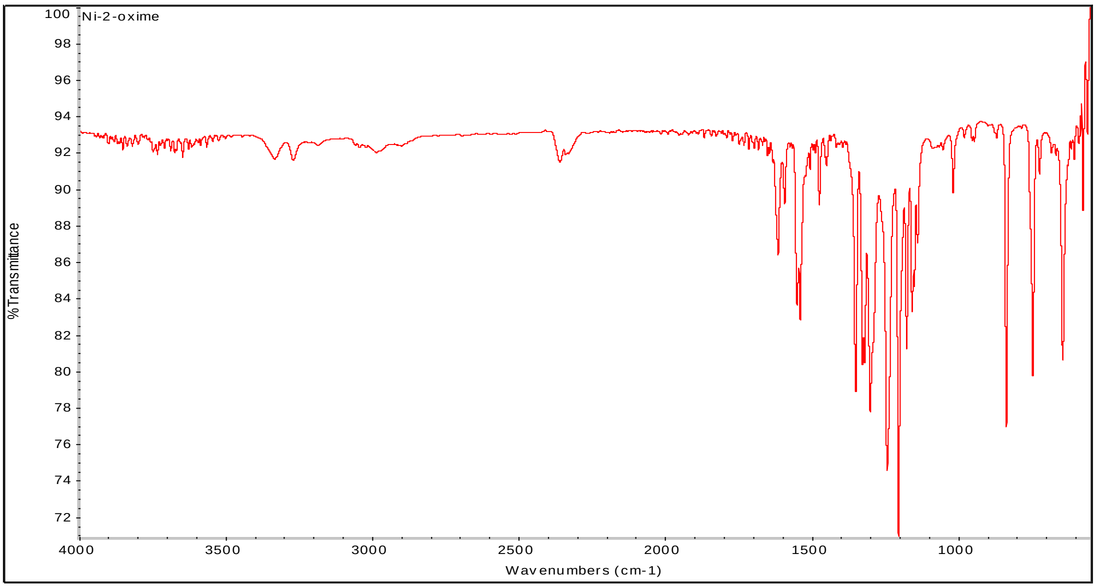
1, 2-NQ Cu (II)-2-oximate



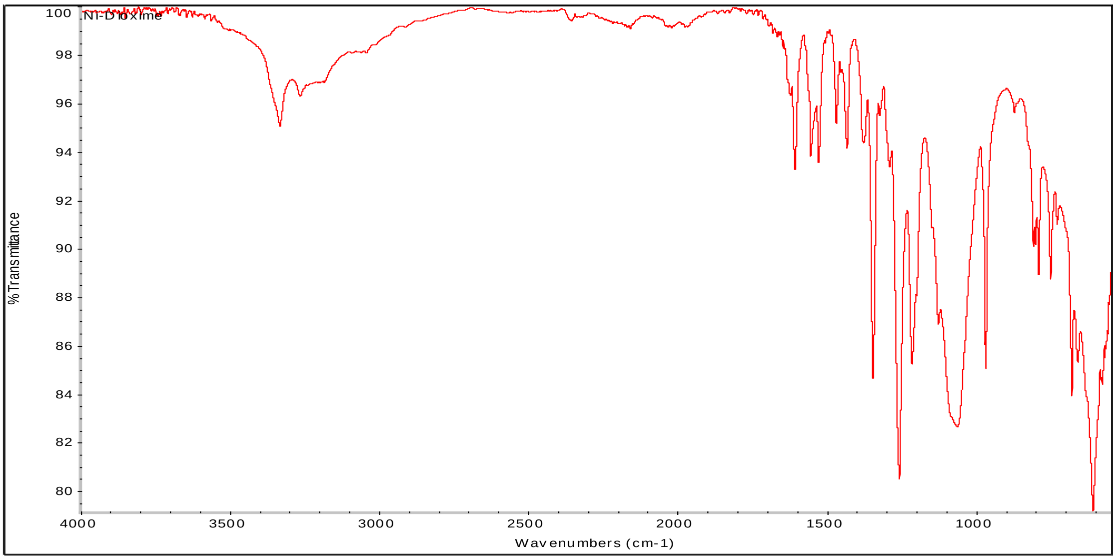
1, 2-NQ Cu (II)-dioximate



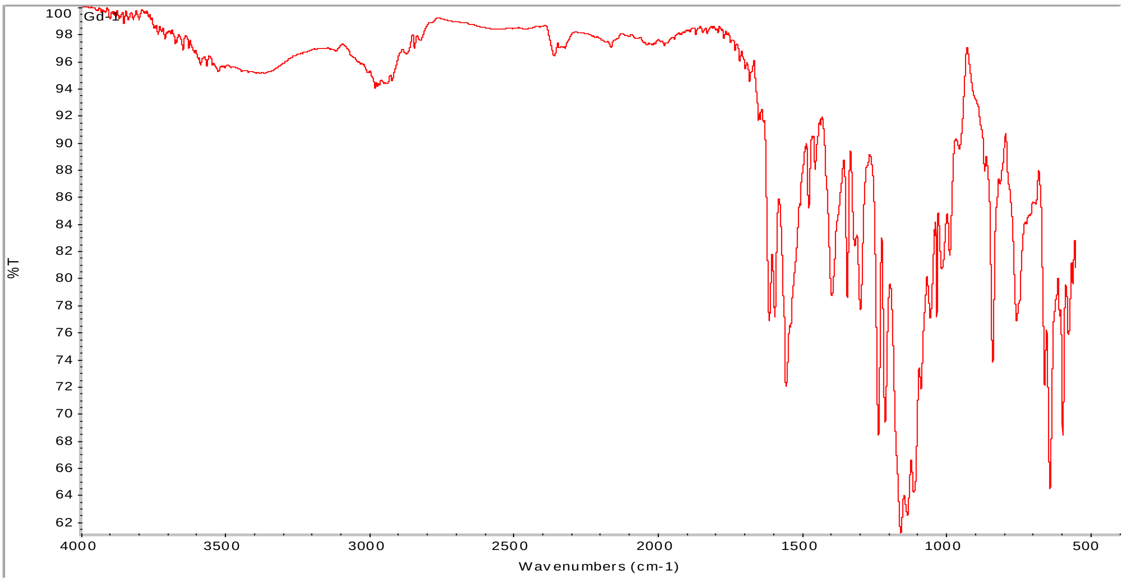
1, 2-NQ Ni (II)-1-oximate



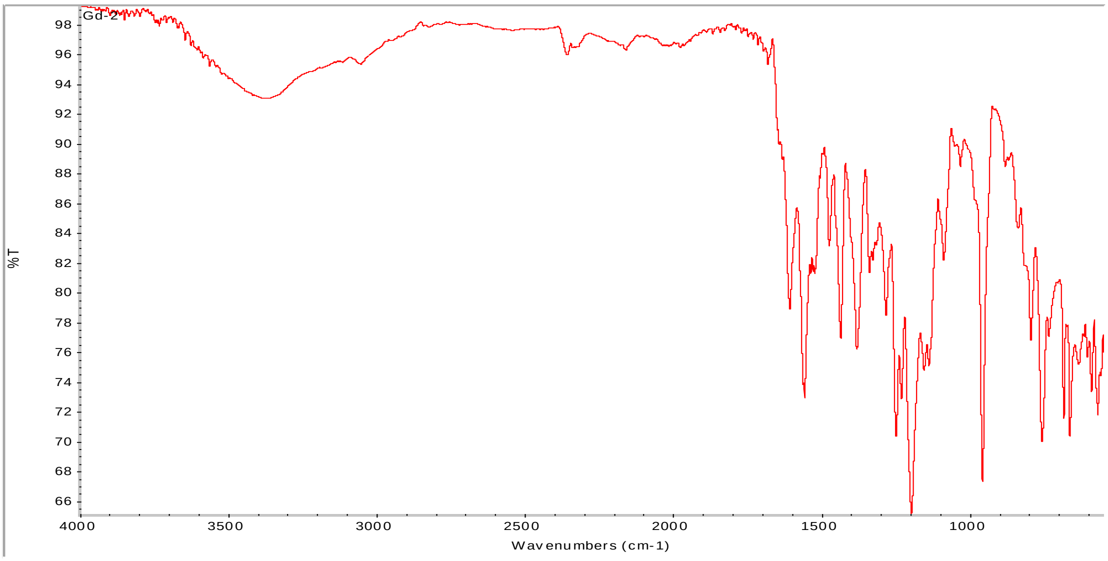
1, 2-NQ Ni (II)-2-oximate



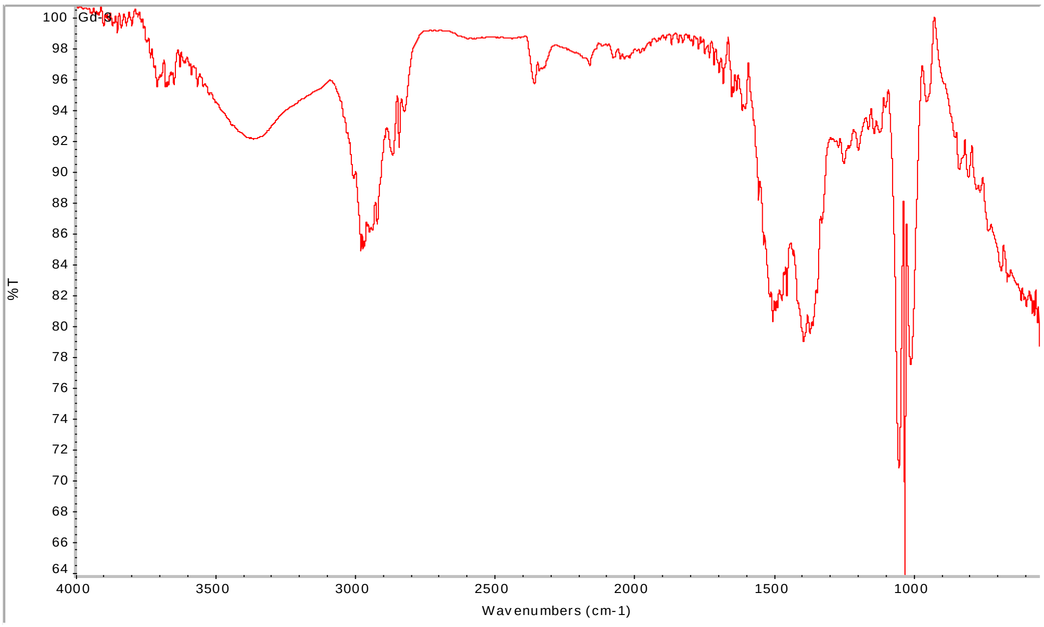
1, 2-NQ Ni (II)-dioxime



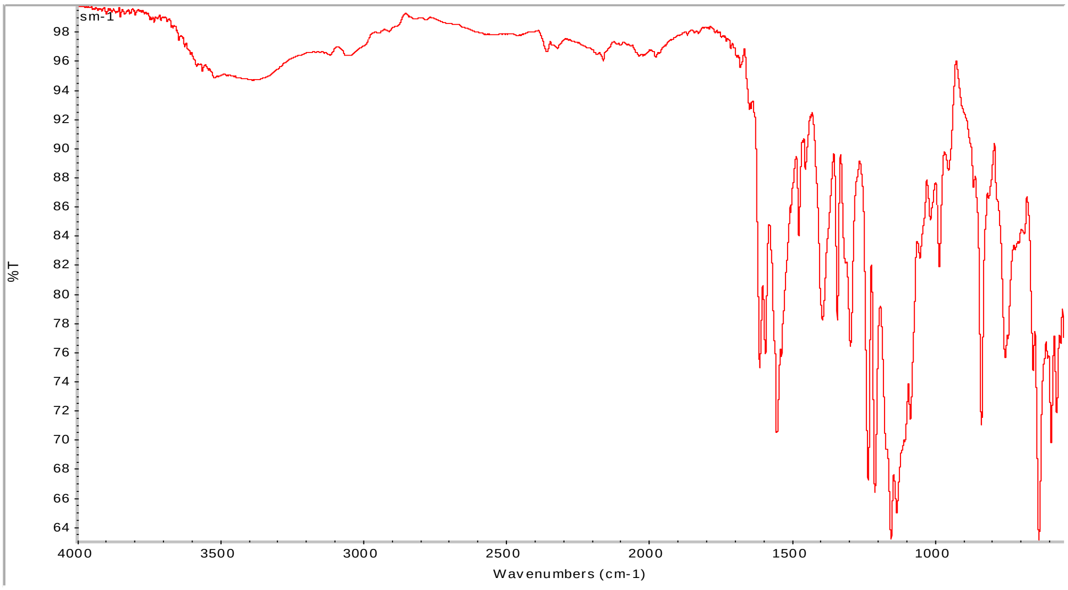
1, 2-NQ Gd (III)-1-oximate



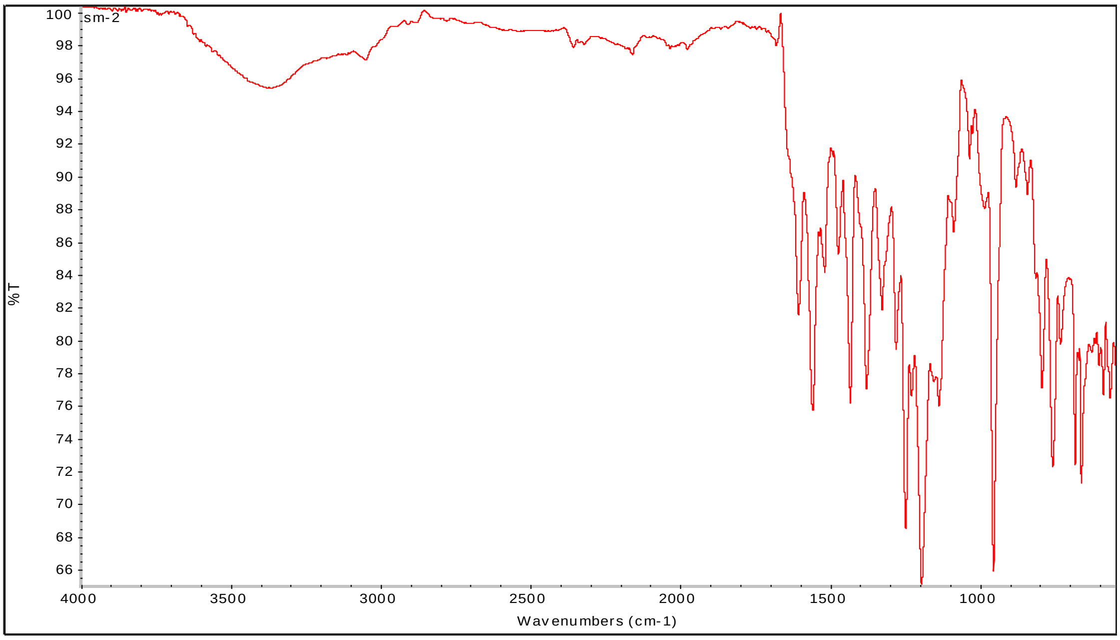
1, 2-NQ Gd (III)-2-oximate



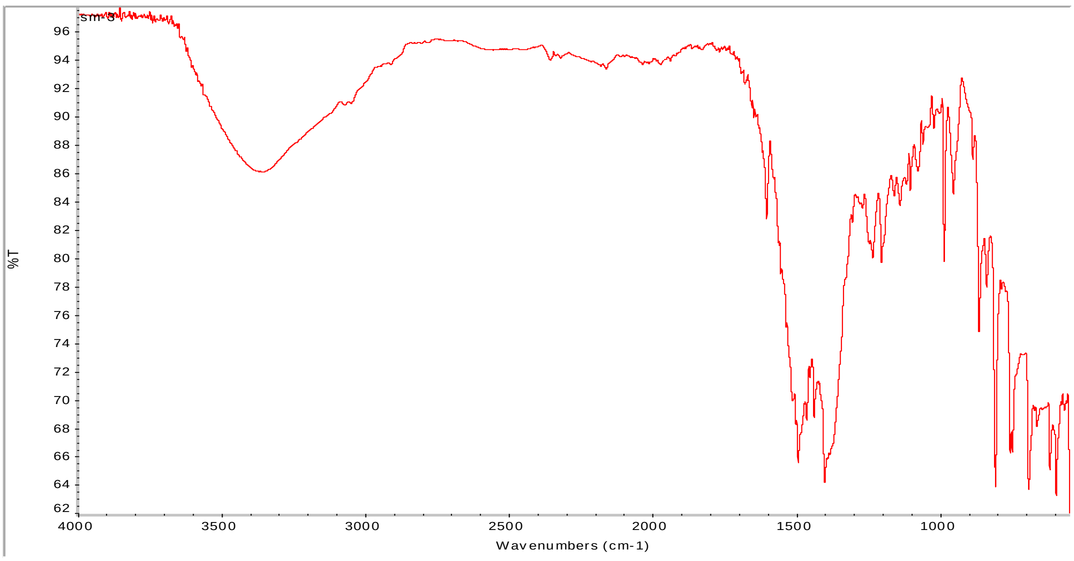
1, 2-NQ Gd (III)-dioximate



1, 2-NQ Sm (III)-1-oximate



1, 2-NQ Sm (III)-2-oximate



1, 2-NQ Sm (III)-dioximate

Sr. No	Name of compound	O-H frequency	C=N frequency	C=O frequency	N-O frequency	M-O & M -N frequency
1	1-oxime	3088	1557	1630	1518	692
2	2-oxime	3255	1558	1669	1067	679
3	Dioxime	3250(ss)	1592, 1620(s)	1667	1080	780
4	Ca-1-ox	3030(w)	1551	1616	1208	688
5	Ca-2-ox	3565(m)	1579(vs)	1622(m)	953(s)	684(s)
6	Ca-diox	3734	1557(vs)	1605(s)	974(vs)	663(s)
7	Mg-1oxi	3069	1558	1619(vs)	1067(vs)	692
8	Mg-2-0x	3063(w)	1580	1667	951(vs)	720
9	Mg-diox	3065(w)	1549	1666	1066(vs)	653
10	Cu-1-ox	3061	1552	1590	1016	717
11	Cu-2-ox	3002	1558	1607	974	735
12	Cu-diox	3650	1559	1605	1145	749
13	Ni-1ox	3335	1552	1617	1019	725
14	Ni-2-ox	3271	1551	1616	1140	724

15	Ni-diox	3334	1556	1668	1065(vs)	730
16	Sm-1-ox	3350	1480	1340	1205	630
17.	Sm-2-ox	3400	1470	1335	1250	670
18.	Sm-diox	3400	1610	--	1205	660
19.	Gd -1-ox	3350	1480	1340	1205	640
20	Gd -2-ox	3300	1470	1330	1240	670
21	Gd–diox	3300	1610	--	1205	640

a) O-H stretching frequency

Sr.no	**Name of compound**	**O-H frequency**
1	1-oxime	3088
2	2-oxime	3255
3	Dioxime	3250(ss)
4	Ca-1-ox	3030(w)
5	Ca-2-ox	3565(m)
6	Ca-diox	3734
7	Mg-1oxi	3669
8	Mg-2-0x	3063(w)
9	Mg-diox	3065(w)
10	Cu-1-ox	3061
11	Cu-2-ox	3002
12	Cu-diox	3650
13	Ni-1ox	3335
14	Ni-2-ox	3271
15	Ni-diox	3334

16	Sm-1-ox	3350
17.	Sm-2-ox	3400
18.	Sm-diox	3400
19.	Gd -1-ox	3350
20	Gd -2-ox	3300
21	Gd -diox	3300

All the metal chelates are aqauted and at least two water molecules enter into coordination sphere of each metal ion. In the present case the coordination number of all the eighteen chelates is shown to be eight cubic geometry in which two water molecules function as ligands. The presence of a broad peak in the region (i.e. absence of the sharp peak) 3450-2850cm^{-1} in the spectrum of 1, 2- naphthoquinone-1-oxime supports strong intra molecular hydrogen bonding.

The IR spectra of all the eighteen chelate show a broad band of medium intensity in the region 3400-3000 cm^{-1} and provide strong experimental evidence in favour of the proposed aqauted molecular structures

The presence of a broad peak but with multiple structures in the region 3400-3200 cm^{-1} in the spectra of 1, 2-naphthoquinone-2-oxime indicates the absence of strong intra-molecular hydrogen bonding. The multiple structure may be attributed to (1) free OH (2) overtones of C=O, C=N, O-H stretching frequencies (3) predominance of oxime form.

The presence of unique intense peak at 3100 cm^{-1} as well as two other doublet peaks at 1490-1480 attributed to two non equivalent C=N groups and 1080-1050 cm^{-1} attributed to two non equivalent N-O groups support the anti structure of 1,2 Naphthoquinone dioxime.

b) C=N frequency

Sr. no	**Name of compound**	**C=N frequency**
1	1-oxime	1557
2	2-oxime	1558
3	Dioxime	1592, 1620(s)
4	Ca-1-ox	1551
5	Ca-2-ox	1579(vs)
6	Ca-diox	1557(vs)
7	Mg-1oxi	1558
8	Mg-2-0x	1580
9	Mg-diox	1549
10	Cu-1-ox	1552
11	Cu-2-ox	1558
12	Cu-diox	1559
13	Ni-1ox	1552
14	Ni-2-ox	1551
15	Ni-diox	1556
16	Sm-1-ox	1480
17.	Sm-2-ox	1470
18.	Sm-diox	1610
19.	Gd -1-ox	1480
20	Gd -2-ox	1470
21	Gd –diox	1610

This is another important frequency related to chelate formation for all the three series. In the present work C=N stretching frequency for 1-oxime and 2-oxime is assigned at 1557cm^{-1} and 1558 cm^{-1} respectively. On chelation this frequency also shows large red shift indicating that the other mode of L→M bonding is through oximic nitrogen providing an additional support to oxime form as well as five membered ring.

In the case of 1, 2-naphthoquinone dioxime, due to the presence of two non-equivalent but adjacent oximic group, the C=N frequency is expected to split into doublet. But due to identical bond length (reported in literature), a clear splitting is not observed and two adjacent peaks at 1592 cm^{-1} and 1620 cm^{-1} seem to be overlapped as indicated from the shape of the peak in this region. These are therefore assigned for the two adjacent C=N groups. These red shifts indicate the bonding through oximic nitrogen and gives supporting evidenced in favour of five membered ring chelates.

c) C=O stretching frequency

Sr. No	**Name of compound**	**C=O frequency**
1	1-oxime	1630
2	2-oxime	1669
3	Dioxime	1667
4	Ca-1-ox	1616
5	Ca-2-ox	1622(m)
6	Ca-diox	1605(s)
7	Mg-1oxi	1619(vs)
8	Mg-2-0x	1667
9	Mg-diox	1666
10	Cu-1-ox	1590
11	Cu-2-ox	1607
12	Cu-diox	1605
13	Ni-1ox	1617
14	Ni-2-ox	1616

15	Ni-diox	1668
16	Sm-1-ox	1340
17.	Sm-2-ox	1335
18.	Sm-diox	--
19.	Gd -1-ox	1340
20	Gd -2-ox	1330
21	Gd -diox	--

This is important frequency involved in the chelate formation by both the monoximes. In the case 1, 2-naphthoquinone and their derivatives the region lying between1700-1300 cm^{-1} is shown to be important for the 1, 2-naphthoquinone dioxime. C=O stretching frequency is out of consideration due to the absence of C=O bond. Accordingly, the C=O stretching frequency is assigned at 1630 cm^{-1} for 1, 2-naphthoquinone-1-oxime and at 1669 cm^{-1} for 1, 2-naphthoquinone-2-oxime. As the effect of chelation, this frequency is found to be shifted to lower frequency region for both the isomeric series. The extent of shift is about 30-40cm^{-1}. These large shifts are due to the bonding through carbonyl oxygen. This also supports the oxime from of the monoximes. 1, 2-naphthoquinone oximes showed higher frequency than all the metal chelates of respective ligands. In this case blue shift observed.

d) N-O frequency

Sr. No	**Name of compound**	**N-O frequency**
1	1-oxime	1518
2	2-oxime	1067
3	Dioxime	1080
4	Ca-1-ox	1208
5	Ca-2-ox	953(s)

6	Ca-diox	974(vs)
7	Mg-1oxi	1067(vs)
8	Mg-2-0x	951(vs)
9	Mg-diox	1066(vs)
10	Cu-1-ox	1016
11	Cu-2-ox	974
12	Cu-diox	1145
13	Ni-1ox	1019
14	Ni-2-ox	1140
15	Ni-diox	1065(vs)
16	Sm-1-ox	1205
17.	Sm-2-ox	1250
18.	Sm-diox	1205
19.	Gd -1-ox	1205
20	Gd -2-ox	1240
21	Gd–diox	1205

This is the third important frequency involved in the process of chelation indirectly. For 1, 2-naphthoquinone 1-oxime this is assigned for the peak at 1518 cm^{-1} and for the 2-oxime at 1067 cm^{-1}. This N-O stretching frequency is shifted to higher frequency region as shown in above table. The remarkable blue shifts indicate that N-O bond becomes stronger on chelation. Such blue shifts have literature support also.

For 1, 2-naphthoquinone dioxime due to the non-equivalent of the NOH groups, the two N-O stretching frequencies are expected to be different. But actually due to the overlapping of these two adjacent peaks, they are not well resolved and from the nature of the peak in the region 1045 cm^{-1} and 1040 cm^{-1}. Here also, as a result of chelation both these peaks show blue shift indicating that the N-O bond becomes stronger.

e) M-O stretching and M-N stretching frequencies

Sr.no	**Name of compound**	**M-O &** **M -N frequency**
1	1-oxime	692
2	2-oxime	679
3	Dioxime	780
4	Ca-1-ox	688
5	Ca-2-ox	684(s)
6	Ca-diox	663(s)
7	Mg-1oxi	692
8	Mg-2-0x	720
9	Mg-diox	653
10	Cu-1-ox	717
11	Cu-2-ox	735
12	Cu-diox	749
13	Ni-1ox	725
14	Ni-2-ox	724
15	Ni-diox	730
16	Sm-1-ox	630
17.	Sm-2-ox	670
18.	Sm-diox	660
19.	Gd -1-ox	640
20	Gd -2-ox	1240
21	Gd –diox	1205

In the present work, these are assigned only tentatively because the region in which these frequencies are likely to occur is not resolved properly in Mid IR region.

Thus the M-O stretching frequency has been tentatively assigned for the broad and weak peaks in the region 430-420 cm^{-1} while the M-N stretching frequencies are assigned to similar peaks in the region 670-640cm^{-1} for more definite assignments FAR IR spectra will be more useful.

Both these aspects (position isomerism and change of donar system), although are very important as well as interesting are very difficult to assess on the basis of infra red spectroscopy. Because for assessing any of these two aspects it will be necessary to examine carefully the spectra of the three ligands and their lanthanide chelates as a whole from comparative point of view.

4.4.3. Scanning Electron Microscope

4.4.3.1. General

Scanning electron microscopy is one of the modern instrumental techniques that are commonly employed for examination of particle size and surface structures. When used in combination with EDEX attachment (Energy dispersion analysis by X ray) it can be used to determine the percentages (both weight percentages and atomic number percentage) of constituent elements of the sample. This technique is non destructive and rapid in providing very useful information within short time. Since it is applicable for solid state samples and the original sample is recoverable, it is found to be very convenient and excellent technique.

4.4.3.2. Principle

A scanning electron microscope generating an electron beam scanning forth and back over a sample. Due to the interaction of the beam and the sample several different signals are produced providing details information about the surface structure, differences of atomic number within the sample as well as quantitative information about the constituent elements. The only limitations are very low atomic number elements and amorphous solid cannot be scanned.

4.4.3.3. Applications

Following are the important application of this technique:

i) It throws good light on the topography of an object where the surface features of the object and its texture can be seen within a very small area of few nanometers.

ii) Information regarding the shape, size and arrangement of the particles making up the object is provided from the SEM photographs.

iii) Composition of the object in terms of the percentage of constituent elements in small area of the order of 1 micrometer in diameter is readily provided through computerized program.

iv) Crystallographic information about the arrangement of atoms in the sample and their of order is obtained in the case of micro sized crystals.

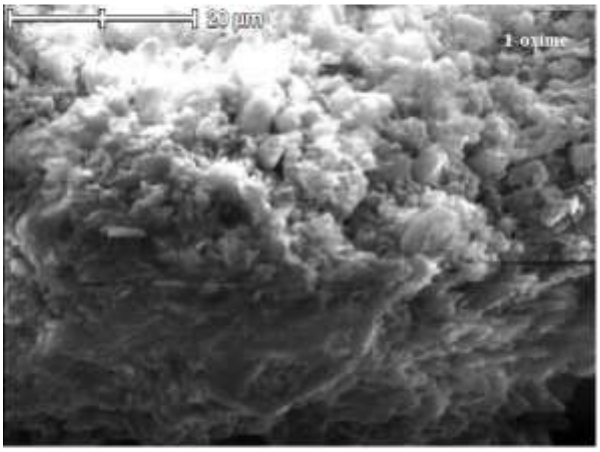
4.4. 3.4. Experimental

The scanning electron microscopy (SEM) of the two isomeric ligands 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinone-2-oxime and their isomeric chelates were carried out on a JEOL-3SM-5200 scanning electron microscope in collaboration with University Department of physics University of Pune and National Chemical Laboratory, Pune.

The samples under study (ligand and metal chelates) were dispersed in a n-hexane solution and there were cast on to a carbon coated copper grid sample holder followed by evaporation at room temperature. The thin uniform film formed in this way was subjected to scanning electron microscopy. The SEM photographs were obtained for all the samples by following this procedure.

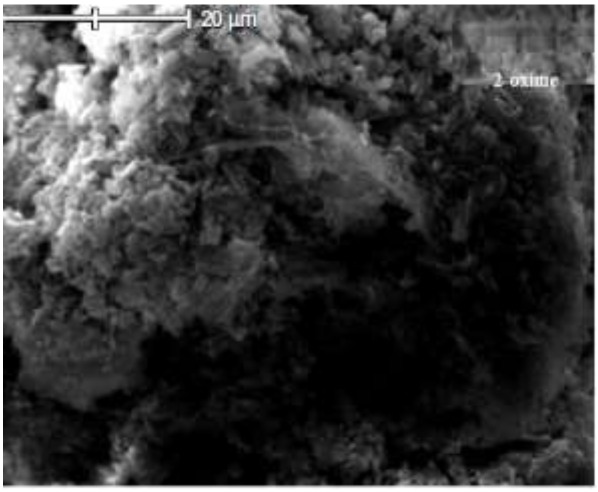
4.4.3.5. Results

The results of SEM investigation are presented in terms of SEM photographs and these photographs are shown below.



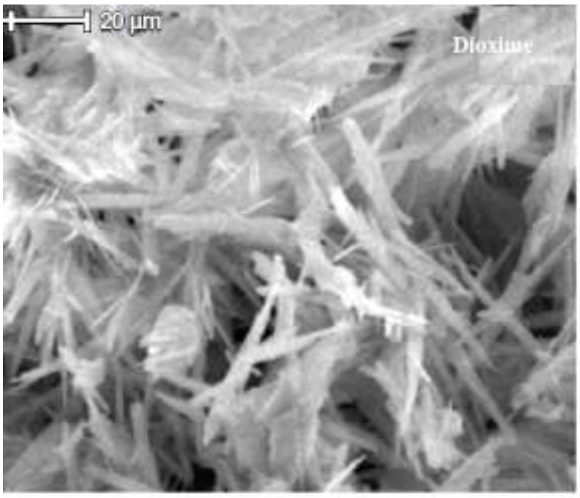
1,2-naphthoquinone-1-Oxime

The sample shows nanocrystals bound together forming cloud like structure. The cloudy structure is formed by very thin hair like threads firmly woven together.



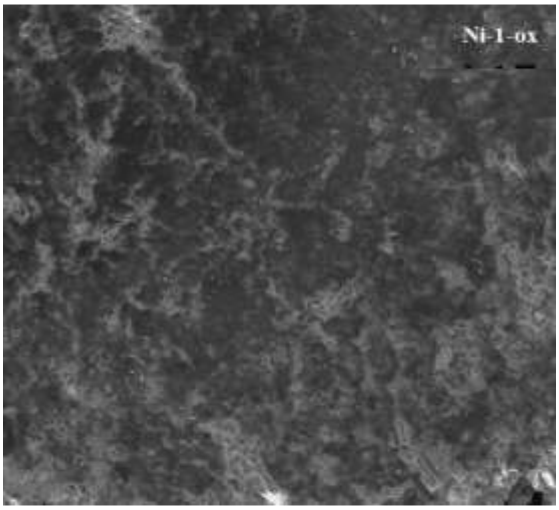
1,2 Naphthoquinone-2-Oxime

It is a crystalline particulate matter holding on to form micro groups of particles.



1,2 Naphthoquinone-dioxime

The sample shows needle like crystallite structure. Needles are entangled with each other.



1, 2-NQ Ni(II)-1-oximate

It is a continuous phase planer structure with grain boundaries merged together. The phase shows distribution of Ni phase in a heterogeneous pattern.

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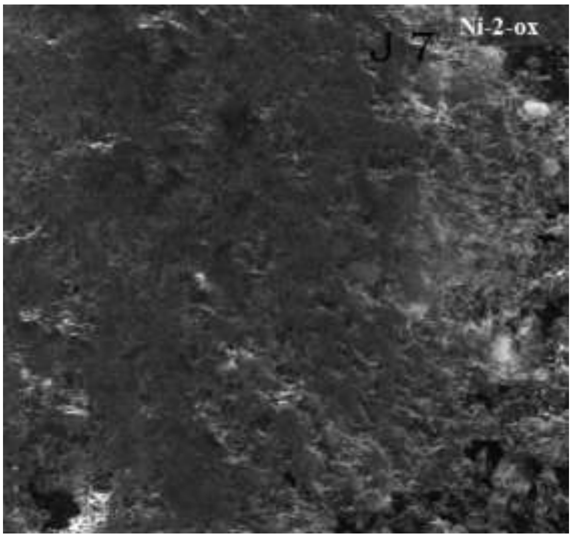
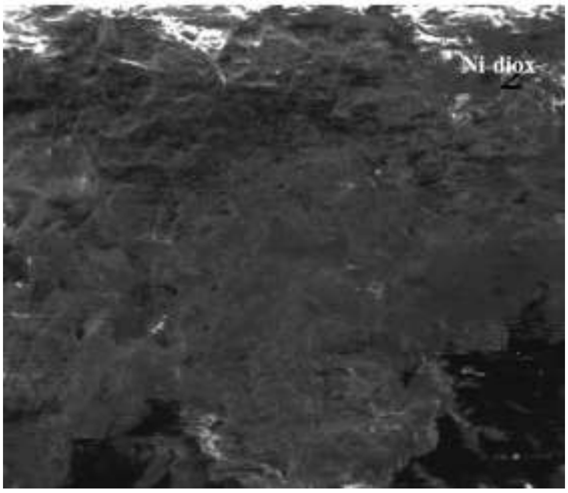


1,2-NQ Ni(II) 2 Oximate

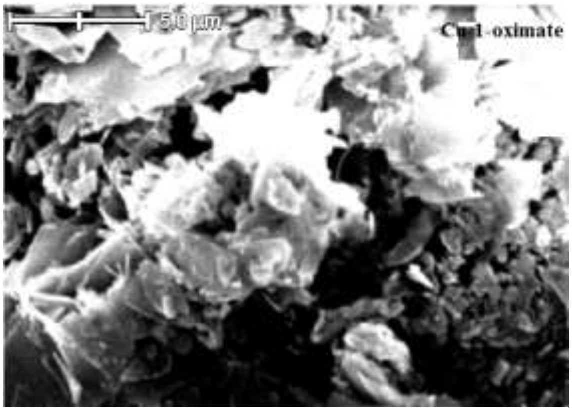
It is a continuous phase planer structure with grain boundaries merged together

.



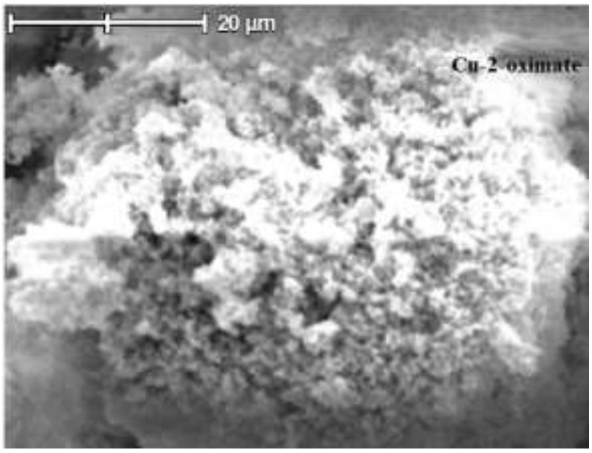
1,2-NQ Ni(II) Dioximate

The sample shows continuous amorphous phase with Ni homogeneously dispersed



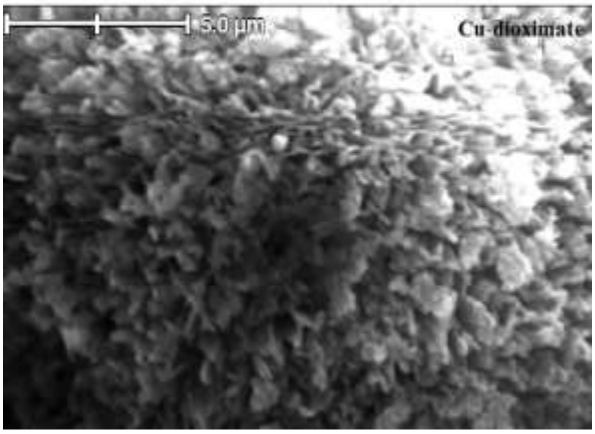
1,2-NQ Cu(II)-1-Oximate

It shows platelet like structure grouping together to form a multilayered leafy structure resembling cabbage leaves like appearance.



1,2-NQ Cu(II) 2 Oximate

The sample shows continuous amorphous phase with Cu homogeneously dispersed**.**



1,2 NQ-Cu(II) Dioximate

A cluster of well defined crystals grouped in a bunch grape like structure.

4.4.3.6. Summary and conclusion from SEM studies

1. The scanning electron microscopy (SEM) of the following isomeric ligands and their metal chelates were carried out at department of Physics, University of Pune.
    - i) 1, 2-naphthoquinone-1-oxime
    - ii) 1,2-naphthoquinone-2-oxime
    - iii) 1,2-naphthoquinone-dioxime
    - iv) Ni (II) 1, 2-naphthoquinone- 1-oximate
    - v) Ni (II) 1, 2-naphthoquinone-2-oximate
    - vi) Ni (II) 1, 2-naphthoquinone-dioximate
    - vii) Cu (II) 1, 2-naphthoquinone-1-oximate
    - viii) Cu (II) 1, 2-naphthoquinone-2-oximate
    - ix) Cu (II) 1, 2-naphthoquinone-dioximate
2. In general the average crystallite size of the metal chelates is smaller than the crystallite size of the parent ligands 1, 2-naphthoquinone-1-oxime, 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone-dioxime.

   These results of SEM investigations support the results obtained from XRD investigations. The XRD patterns were found to be composed of overlapped sharp line as well as broad bands indicative of both small crystalline of nano crystalline type and extremely small crystallite size tending to amorphous nature. These SEM results were compared with literature and confirm the agglomeration was observed in the metal chelates.

   Secondly a careful examination of the SEM photographs of the two isomeric ligands and their six isomeric metal chelates reveals that all the samples are heterogeneous mixture of different particle size.

4.4.4. X ray powder diffractometry

4.4.4.1. Principle and Utility of the technique

X ray diffractometry is based on the fundamental relation, between wavelength of electromagnetic radiation(λ), interplanar distance in the crystal lattice (d) and angle of diffraction (θ) established by Bragg equation.

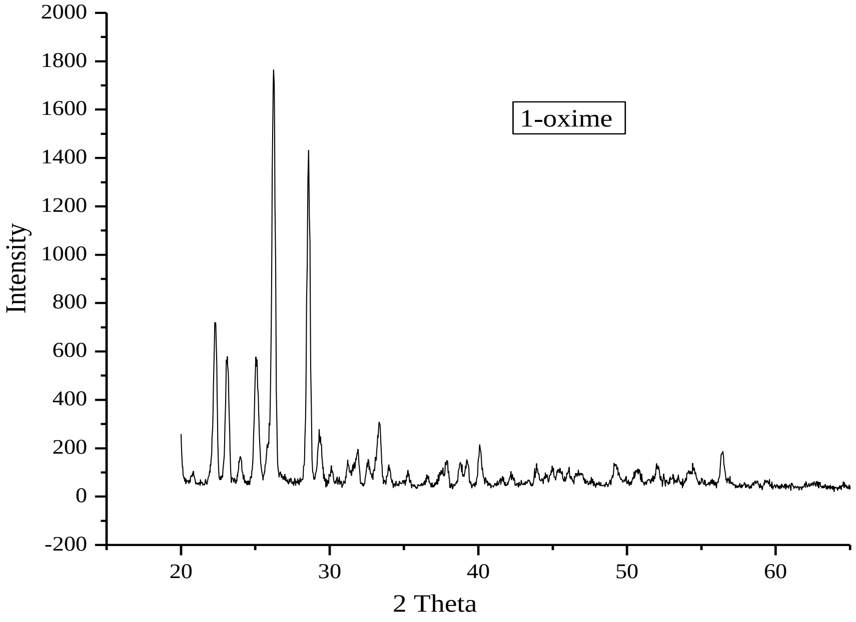
$$n\lambda=2d\mathrm{Sin}\theta$$

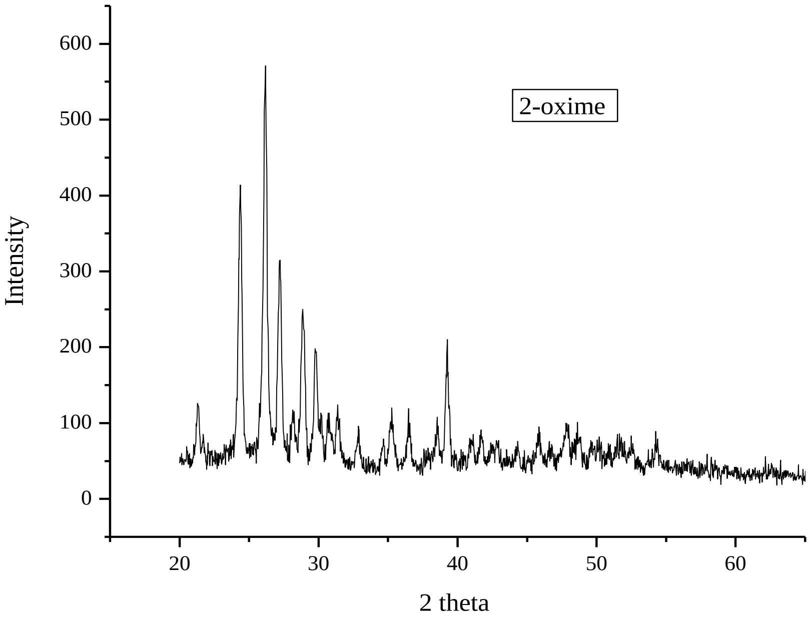
Where n is the order of reflection.

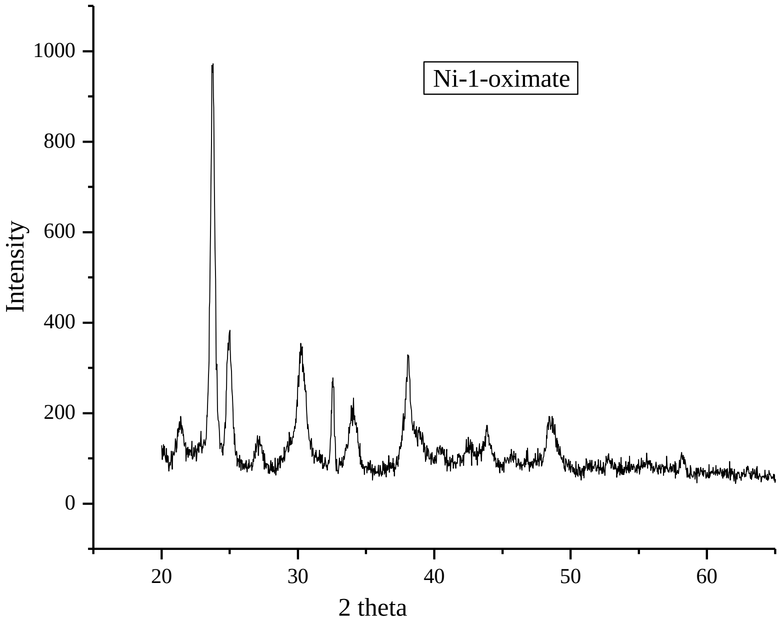
When an X-ray beam strikes a crystal surface at some angle θ, a portion is scattered by the layer of the atoms at the surface. The unscattered portion of the beam penetrates to the second layer of the atoms where again a fraction is scattered and the remaining possess to the third layer. The cumulative effect of this scattering from the regular spaced centers of the crystal is diffraction of the beam. The requirements for diffraction are (a) the spacing between the layers of the atoms must of roughly the same as the wave length of radiation. (b) The scattering centers must be spatially distributed in a highly regular way.

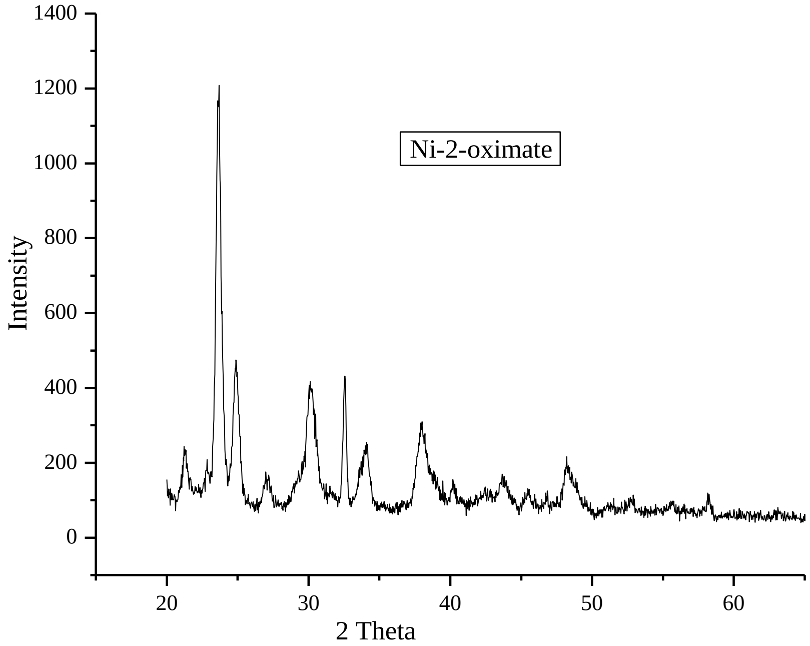
4.4.4.2. Experimental

The XRD patterns of all samples are recorded on Philips X. pert. Pro powder diffractometry in the diffraction angle range $(1\text{-}90)^0 2\ \theta$ finely powdered and dried samples were spread in the form of thin layer on cavity mounts. Monochromatic Cu Kα X rays of wavelength $1.5405A^0$was used for diffraction studies.


2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
Intensity
1-oxime
20
30
40
50
60
2 Theta


600
500
400
300
200
100
0
Intensity
2-oxime
20
30
40
50
60
2 theta


Ni-1-oximate
Intensity
0
200
400
600
800
1000
20
30
40
50
60
2 theta


Ni-2-oximate
Intensity
0
200
400
600
800
1000
1200
1400
20
30
40
50
60
2 Theta

4.4.4.3.Summary and conclusion from XRD investigations

The XRD patterns of the following Ni chelates are examined.

Conclusion

A careful examination of these patterns leads to following important conclusions:

1. These Ni Metal chelates seem to be amorphous as indicated by the non crystalline patterns.
2. As against this, 1, 2-naphthoquinone-1-oxime seems to be crystalline.

4.4.5. Antimicrobial activity

4.4.5.1. Microorganism and their characteristics

General:

Microorganisms are exceptionally attractive models for studying fundamental life processes. They can be grown conveniently in test tube or flask, thus requiring less space and maintenance than large plants and animals. They grow rapidly and reproduce at an unusually high rate. Some species of bacteria undergo almost 100 generations in a 24h period. The metabolic processes of microorganisms follow patterns that occur among higher plants and animals. For example, yeast utilizes glucose in essentially the same manner as cell of mammalian tissue. The same system of enzyme is present in these diverse and made available for the work to be performed by the cells, whether they be bacteria , yeasts, protozoa, or muscle cells. In fact, the mechanism by which organism utilize energy is fundamentally the same throughout the biological world. The plants are characterized by their ability to use radiant energy, whereas animals require chemical substances as their fuel. In this respect some microorganism are like animals and some have the unique ability of using either radiant energy or chemical energy and thus are plants and animals. Furthermore, some microorganism, the bacteria in particular, are able to utilize a great variety of chemical substances as their energy source ranging from simple inorganic substances to complex organic substances.

Definition of Antimicrobial activity and antimicrobial agents

Antimicrobial activity:-

Antimicrobial activity may be defined as the property possessed by a chemical and biological agent who destroys or inhibits the growth of a microorganism.

Antimicrobial agents:-

Chemical or biological agents possessing antimicrobial activity are called as antimicrobial agents. These agents interfere with the growth and metabolism of microbes. The term antimicrobial agents denoted the ability to kill or inhibit the growth of microorganisms, with reference to specific groups of organisms, specific terms like antibacterial or antifungal are also employed. Some antimicrobial agents are used to treat infections and these are called chemotherapeutic agents.

Some representative examples of Gram positive and Gram negative bacteria

Sr. No.	Gram positive bacteria	Gram negative bacteria
1.	*Bacillus substilus*	*Escherichia coli*
2.	*Bacillus magaterium*	*Salmonella paratyphi*
3.	*Sarchialuta*	*Salmonella pullorum*
4.	*Bacillus anthracis*	*Pasterurellamultocida*
5.	*Staphylococcus aureus*	*Pseudomonas aeruginusa*

Techniques Employed For Measuring Antimicrobial Activity:

There are several techniques established for measuring antimicrobial activity. Among these, following Well diffusion Assay Method technique has been used for the antimicrobial investigations naphthoquinone derivatives and their metal chelates.

Well Diffusion Assay Method:

In this method, well of 8-10 mm diameter are bored in an agar layer in a Petri dish which is previously mixed with known volume containing cultures of test organisms. These wells are loaded with known concentrations of test compounds. The Petri dishes are pre-incubated for about two hours at lower temperature (eg.40^0C) and then incubated for 48 hours at 37^0C, after incubation, the zone of inhibition is measured in terms of its diameter. This is then compared with that of control (like dichlone) as well as blanks if necessary (containing other materials than the antimicrobial agent under investigations)

4.4.5.2.Experimental

Microorganisms:

Following microorganisms are selected.

a) *Bacillus subtilis (Gram-positive)*
b) *Escherichia Coli (Gram-negative)*
c) *Salmonella typhi (Gram negative)*
d) *Proteus vulgaris (Gram negative)*
e) *Pseudomonas aeruginosa.(Gram negative)*
f) *Staphylococcus aureus (Gram positive)*

Media:

Following media components were from MERK India.

Nutrient agar (Peptone: 5 gm, Yeast extract: 5 gm, NaCl: 1 gm, Agar: 2.5%, D/W: 1000 ml.) Saline (Normal Saline)

Materials and Methods:

Microorganisms and compounds:

The antimicrobial investigations of Calcium chloride, Magnesium chloride, Cupper chloride, Nickel chloride, 1, 2-naphthoquinone-oxime and their chelates with Ca(II), Mg(II), Cu(II) and Ni(II) with their corresponding metal chelates were carried out against four Gram negative bacteria i. e *Escherichia coli* (NCIM – 2065), *Pseudomonas aeruginosa*, *Salmonella typhi* and *Proteus vulgaris* and two Gram positive bacteria which are *Bacillus subtilis* (NCIM –2063), *Staphylococcus aureus* (NCIM –2079). These were obtained from National collection of Industrial Microorganisms division of National Chemical Laboratory, Pune. Metal salt purchased by Aldrich was used for comparative purpose of antimicrobial activities. Well diffusion method was employed for the measurement of the activities. The effect of chelation and effect of ring isomerism on the selected compounds is studied in the present work.

Concentration of compounds under test:

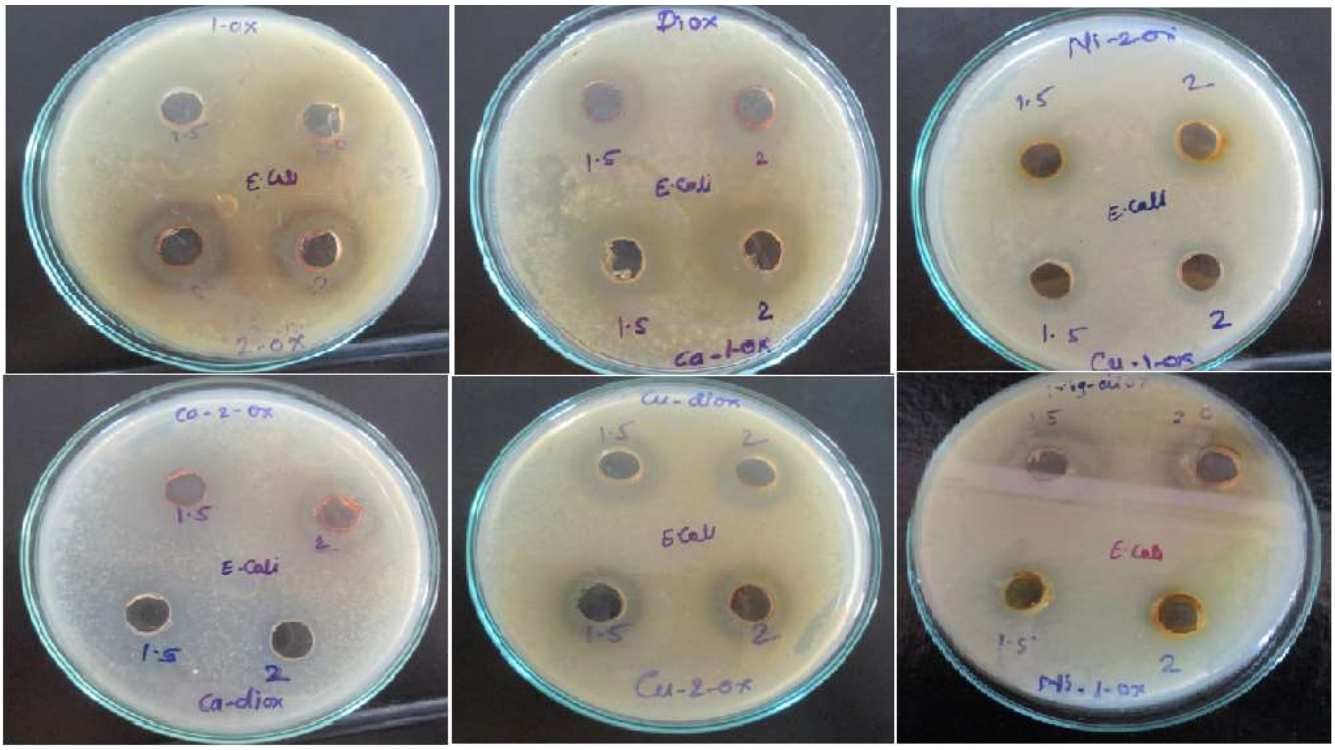
The compound was tested for three concentrations 1mg/ml, 1.5mg/ml, and 2mg/ml dissolved in DMSO. The concentration (1.5mg/ml) at which all ligands and all chelates show significant activity are taken for the comparison.

Experimental Procedure:

Fresh cultures of the bacteria organisms are taken. Suspension of the organisms was prepared in sterile peptone water. Prepared suspension was aseptically seeded in Nutrient Agar for bacterial cultures. Seeded agar was poured in sterile petriplates. After cooling, four wells of 8 mm diameter were bored in each plate. Each well was marked with the sample name and with the help of micropipette, 0.1 ml of sample dilution was added in respective well. (0.1 ml of sample dilution correspond to 500 µ g Concentration per well). The bacterial plates were incubated at 37^{0}C for 48 hrs. After incubation the organisms which are sensitive are inhibited by the test sample and inhibition zone is developed. The diameters of these inhibition zones were measured in mm [61-62].

Results and discussion of antimicrobial activity:

4.4.5.3. Antimicrobial activity against *Escherichia coli*

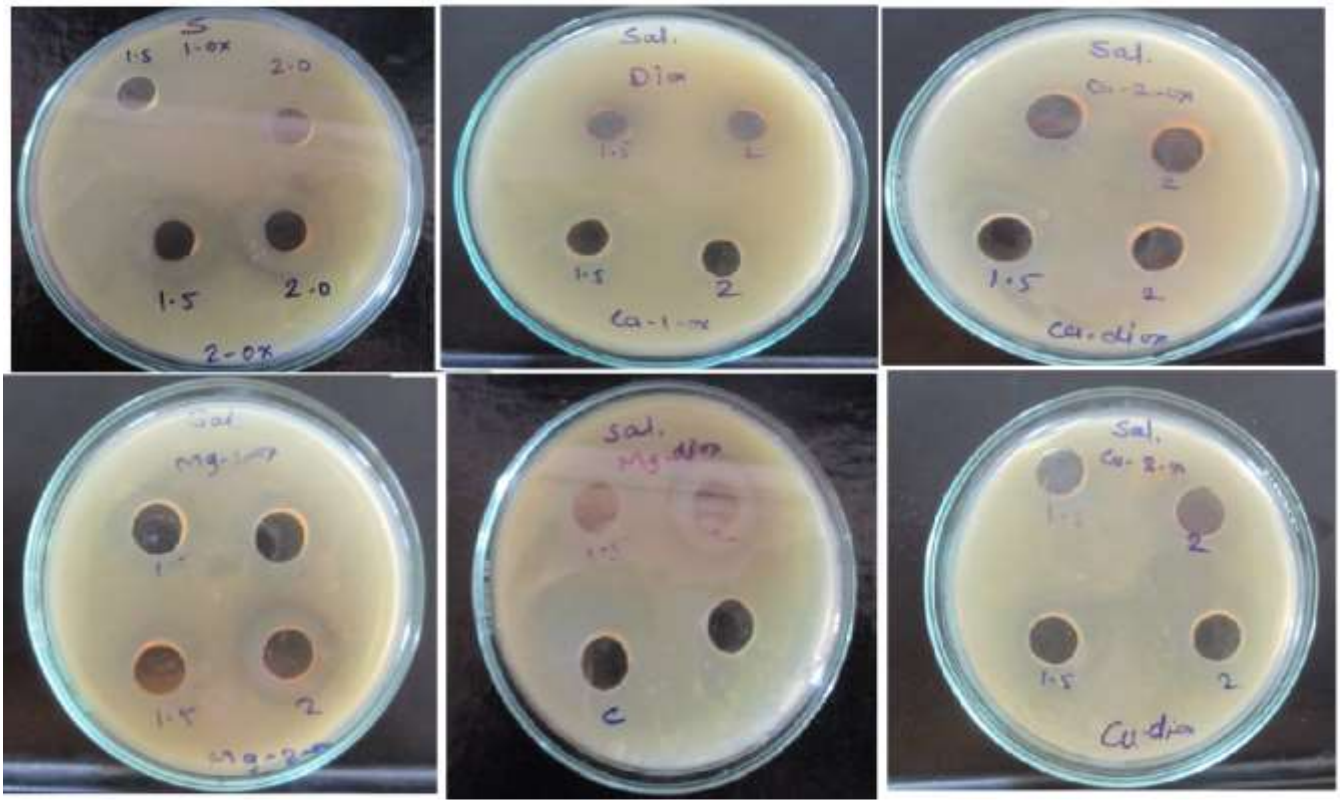


Sr. No	Name of Compound	Concentration mg/ml	Zone of inhibition in mm
1.	1-oxime	1.5	11
2.	2-oxime	1.5	20
3.	Dioxime	1.5	20
4.	Ca-1-Oximate	1.5	22
5.	Ca-2-oximate	1.5	26
6.	Ca-dioximate	1.5	16
7.	Cu-1-oximate	1.5	17
8.	Cu-2-oximate	1.5	18
9.	Cu-dioximate	1.5	21
10.	Ni-1-oximate	1.5	17
11.	Ni-2-oximate	1.5	19
12.	Ni-dioximate	1.5	11

Conclusion from above table

- Maximum inhibition activity was showed in Ca-2-oximate against *Escherichia coli.*
- The range of inhibition activity was 11 to 26 mm showed ligand and metal complexes.
- Minimum inhibition activity was 11mm in ligand 1-oxime.
- Metal complex showed more inhibition activity than ligand due to the effect of chelation for 1-oximate.
- Metal complex showed no definite trend on chelation for 2-oximate and dioximate.

4.4.5.4. Antimicrobial activity against *Salmonella typhi*.



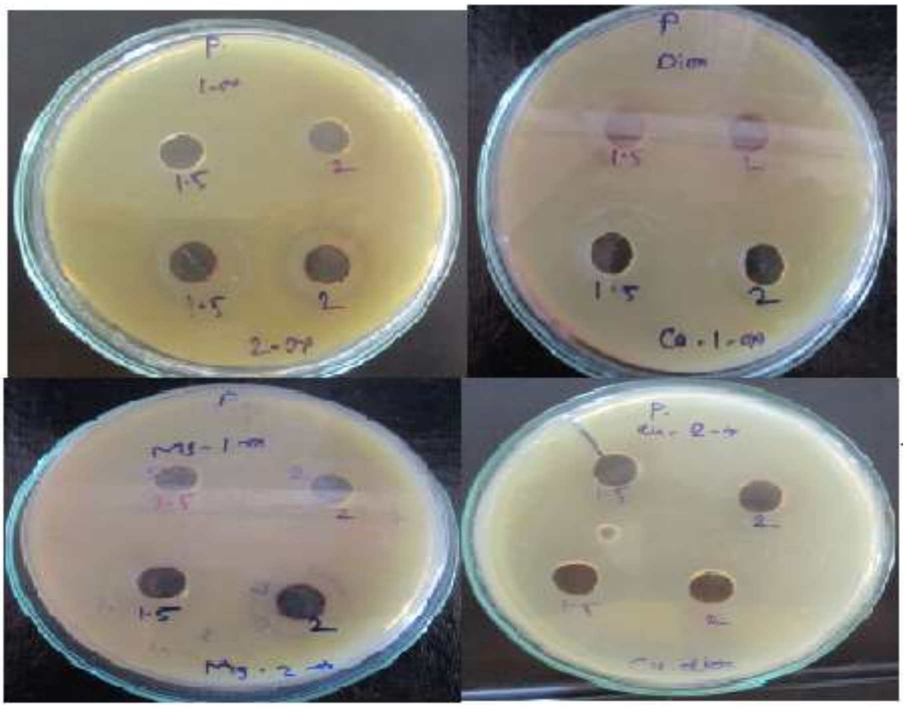
Sr. No	Name of Compound	Concentration mg/ml	Zone of inhibition in mm
1.	1-oxime	1.5	13
2.	2-oxime	1.5	19
3.	Dioxime	1.5	27
4.	Ca-1-Oximate	1.5	18
5.	Ca-2-oximate	1.5	14
6.	Ca-dioximate	1.5	16
7.	Cu-1-oximate	1.5	14
8.	Cu-2-oximate	1.5	14

9.	Cu-dioximate	1.5	14
10.	Mg-1-oximate	1.5	18
11.	Mg-2-oximate	1.5	15
12.	Mg-dioximate	1.5	17

Conclusion from above table

- Maximum inhibition activity 27mm was showed in dioxime ligand against *Salmonella typhi.*
- The range of inhibition activity was 13 to 27 mm shown by ligand and metal complexes
- Minimum inhibition activity shown by ligand 1-oxime.
- Metal complex 1-oxime showed more inhibition activity than ligand due to the effect of chelation.
- Metal complexes of oxime and dioxime showed less inhibition activity on chelation.

4.4.5.5. Antimicrobial activity against *Proteus vulgaris.*

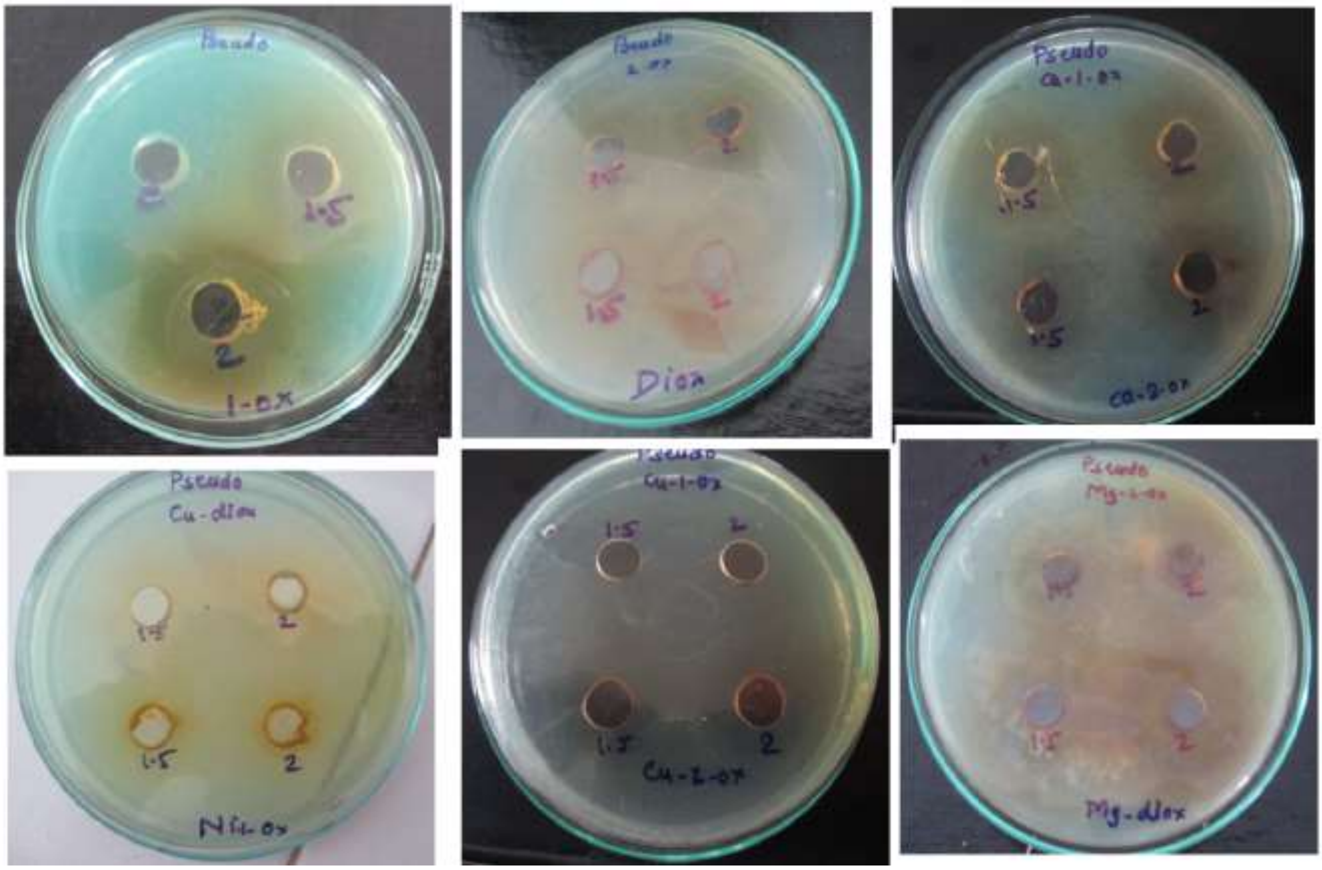


Sr. No	**Name of Compound**	**Concentration mg/ml**	**Zone of inhibition in mm**
1.	1-oxime	1.5	16
2.	2-oxime	1.5	19
3.	Dioxime	1.5	20
4.	Ca-1-Oximate	1.5	21
5.	Ca-2-oximate	1.5	20
6.	Ca-dioximate	1.5	16
7.	Mg-1-oximate	1.5	18
8.	Mg-2-oximate	1.5	18
9.	Mg-dioximate	1.5	17

Conclusion from above table

- Maximum inhibition activity was showed in Ca-1-oximate (21mm) against *Proteus vulgaris.*
- The range of inhibition activity was 14 to 21 mm shown by ligand and metal complexes
- Minimum inhibition activity shown in ligand Cu1-oximate.
- Metal complex showed more inhibition activity than ligand due to the effect of chelation.
- 2-oxime metal complex showed on particular trend on chelation.
- Dioxime metal complex showed low inhibition activity on chelation.

4.4.5.6. Antimicrobial activity against *Pseudomonas aeruginosa*.



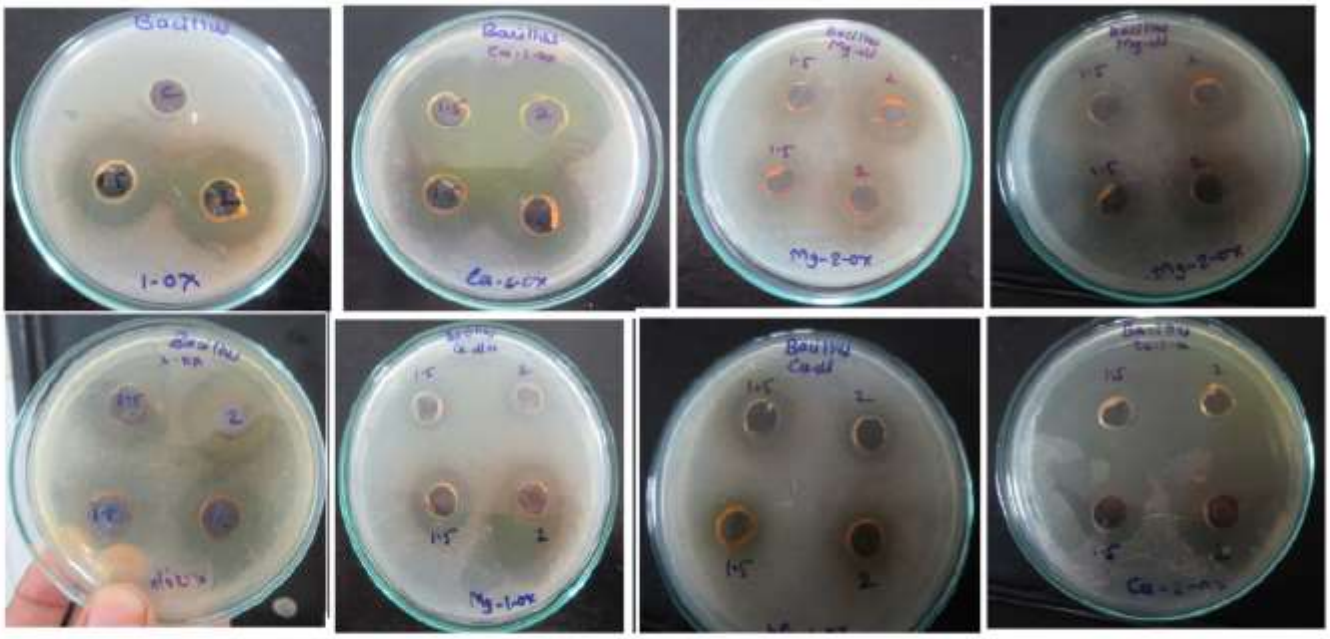
Sr. No	Name of Compound	Concentration mg/ml	Zone of inhibition in mm
1.	1-oxime	1.5	18
2.	2-oxime	1.5	19
3.	Dioxime	1.5	22
4.	Ca-1-Oximate	1.5	25
5.	Ca-2-oximate	1.5	21
6.	Ca-dioximate	1.5	16
7.	Cu-1-oximate	1.5	21
8.	Cu-2-oximate	1.5	21
9.	Cu-dioximate	1.5	20

10.	Mg-1-oximate	1.5	22
11.	Mg-2-oximate	1.5	20
12.	Mg-dioximate	1.5	22

Conclusion from above table

- Maximum inhibition activity (25 mm) was shown in Ca-1-oximate against *Pseudomonas aeruginosa.*
- The range of inhibition activity was 16 to 25 mm shown in ligand and metal complexes
- Minimum inhibition activity 16 mm is shown in Ca-dioximate.
- 1-oximate and 2-oximate metal complex showed more inhibition activity than ligand due to the effect of chelation.
- Metal chelates of dioxime showed less inhibition activity on chelation.

4.4.5.7. Antimicrobial activity against *Bacillus substilus.*

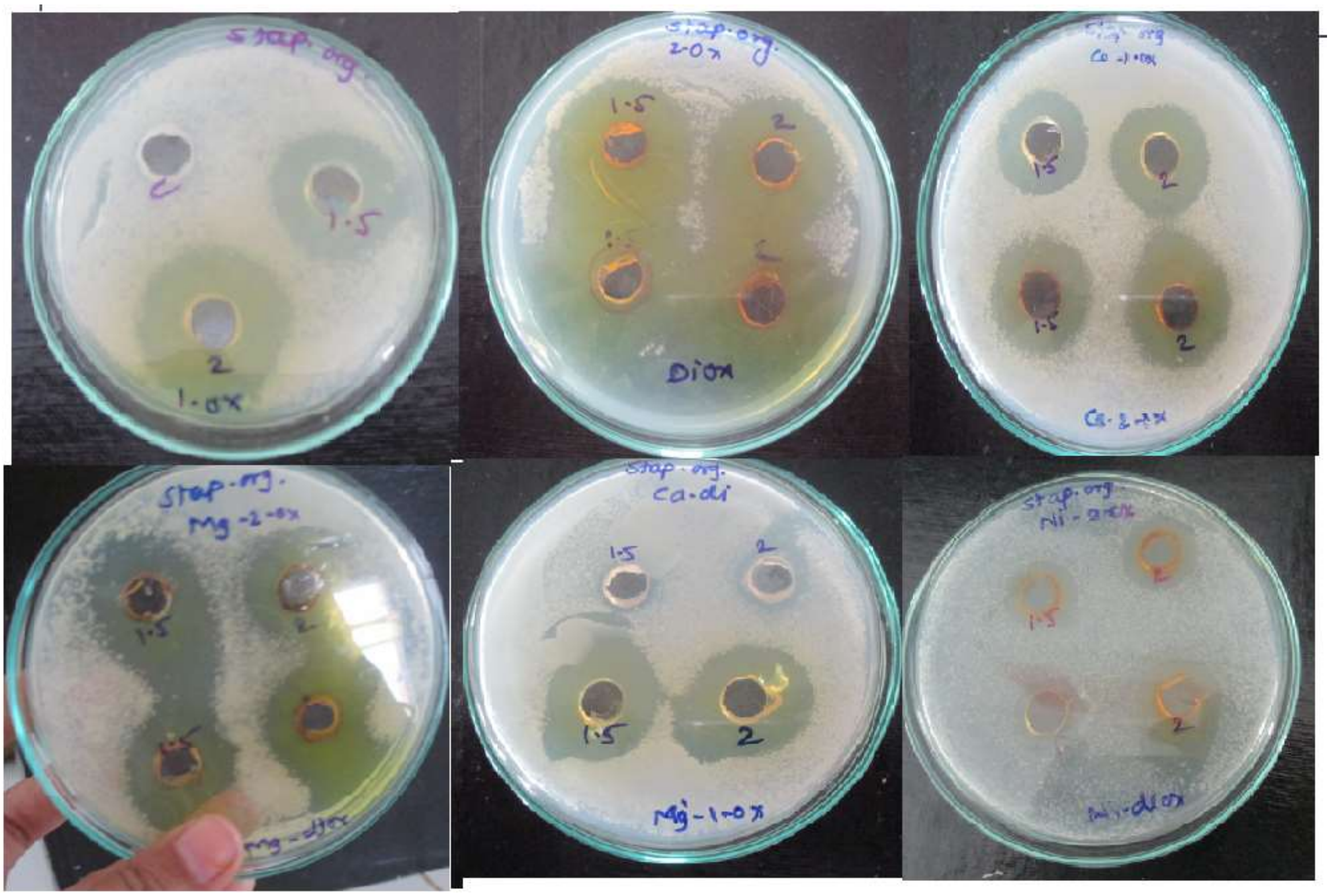


Sr. No	**Name of Compound**	**Concentration mg/ml**	**Zone of inhibition in mm**
1.	1-oxime	1.5	21
2.	2-oxime	1.5	21
3.	Dioxime	1.5	19
4.	Ca-1-Oximate	1.5	23
5.	Ca-2-oximate	1.5	24
6.	Ca-dioximate	1.5	18
7.	Cu-1-oximate	1.5	28
8.	Cu-2-oximate	1.5	21
9.	Cu-dioximate	1.5	19
10.	Mg-1-oximate	1.5	20
11.	Mg-2-oximate	1.5	18
12.	Mg-dioximate	1.5	18

Conclusion from above table

- The range of inhibition activity was 18 to 28 mm showed ligand and metal complexes against *Bacillus substilus*.
- Maximum inhibition activity is shown in ligand Cu-1-oximate.
- Metal complex of 1-oximate showed more inhibition activity than ligand due to the effect of chelation.
- Metal complexes of 2-oximate and dioximate showed no trend in inhibition activity on chelation.

4.4.5.8. Antimicrobial activity against *Staphylococcus aureus*



Sr.No	Name of Compound	Concentration mg/ml	Zone of inhibition in mm
1.	1-oxime	1.5	25
2.	2-oxime	1.5	28
3.	Dioxime	1.5	28
4.	Ca-1-Oximate	1.5	22
5.	Ca-2-oximate	1.5	23
6.	Ca-dioximate	1.5	25
7.	Ni-1-oximate	1.5	23
8.	Ni-2-oximate	1.5	18

9.	Ni-dioximate	1.5	19
10.	Mg-1-oximate	1.5	26
11.	Mg-2-oximate	1.5	16
12.	Mg-dioximate	1.5	25

Conclusion from above table

- Maximum inhibition activity (28 mm) was shown for ligands 2-oxime and dioxime against *Staphylococcus aureus*.
- The range of inhibition activity was 18 to 28 mm shown ligand and metal complexes
- In case of metal complexes of 1-oxime, 2-oxime and dioxime, there is a lowering in inhibition activity on chelation.

4.4.6. Thermo gravimetric Analysis (TGA)

4.4.6.1. Introduction

Thermo gravimetric analysis or thermal gravimetric method (TGA) is a method of thermal analysis in which change in physical and chemical properties of material are measured a as function of increasing temperature (with constant heating rate), or as a function of the time (with constant temperature and /or constant mass loss).

TGA can provide information about physical phenomenon, such as second order phase transition, including vaporation, sublimation, absorption, adsorption and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition and solid gas reaction (e.g. oxidation or reduction)

TGA is commonly used to determine selected characteristic of material that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture)

Common application

1. Material characterization through analysis of characteristic decomposition patterns,

2. Studies of degradation mechanisms and reaction kinetics,

3. Determination of organic content in a sample and

4. Determination of inorganic (e.g. Ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coating and paints. Discussion of the TGA apparatus, method and trace analysis will be elaborated upon below. Thermal stability, oxidation, and combustion, all of which are possible interpretations of TGA traces, will also be discussed.

4.4.6.2. Instrumental apparatus

Thermo gravimetric analysis relies on a high degree of precision in three measurements: mass change, temperature and temperature change. Therefore, the basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample, and a programmable furnace. The furnace can be programmed either for constant heating rate, or for heating to acquire a constant mass loss with time.

Though a constant heating rate is more common, a constant mass loss rate can illuminate specific reaction kinetic. For example, the kinetic as parameters of the carbonization of polyvinyl butyral were found using a constant mass loss rate of 0.2 weight%/min. regardless of the furnace programming, the sample is placed in a small, electrically heated furnace equipped with a thermocouple to monitor accurate measurement of the temperature by comparing its voltage output with that of the voltage versus temperature table stored in the computer’s memory. A reference sample may be placed on another balance in a separate chamber. The atmosphere in the sample chamber may be purged with as inert gas to prevent oxidation or other undesirable reactions. A different process using a quartz crystal microbalance has been devised for measuring smaller samples in the order of a microgram (versus milligram with conventional TGA).

4.4.6.3. Methods

The TGA instrument continuously weighs a sample as it is heated to temperature of up to 2000^0C for coupling with FTIR and Mass spectroscopy gas analysis. As the temperature increases, various components of the sample are decomposed and the temperature on the X-axis and Mass loss on the Y-axis. The data can be adjusted using curve smoothing and first derivatives are often also plotted to determine points of inflection for more in-depth interpretations.

TGA instruments can be temperature calibrated with melting point standards or Curie point materials becomes paramagnetic which nullifies the apparent weight change effect of the magnetic field.

The thermograms of the rare earth complexes were recorded in Department of chemistry, University of Poona, on laboratory constructed thermogravimetric instrument. About with the heating rate of 3-5^{0}C per minute.

4.4.6.4 Trace analysis

If the identity of the product after heating is known, then the ceramic yield can be found from analysis of the ash content. By taking the weight of known product and dividing it by the initial mass of the starting, materials, the mass percentage of all inclusions can be found. Knowing the mass of the starting materials and the total mass of inclusions, such as ligands, structural defects, or side products of reaction, which are liberated upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample.

The results from thermo gravimetric analysis may be presented by 1. Mass versus temperature (or time) curves, referred to as the thermo gravimetric curve, or 2. Rate of mass loss versus temperature curve, referred to as the differential thermogravimetric curve see in figure. Though this is by no means an exhaustive list, simple thermogravimetric curves may contain the following features:

- A horizontal portion, or plateau that indicates constant sample weight
- A curved portion; the steepness of the curve indicates the rate of mass loss.
- An inflection at which dw/dt is a minimum, but not zero.

Certain features in the TGA curve that are not readily seen can be more clearly discerned in the first derivative TGA curve. For example, any change in the rate of weight loss can immediately be seen in the first derivative TGA curves also can show considerable similarity to differential thermal analysis (DTA curves, which can permit easy comparisons to be made.

The thermogravimetric profiles for the solid phase thermal decomposition of metal chelates are presented in figure. The data are summarized in table

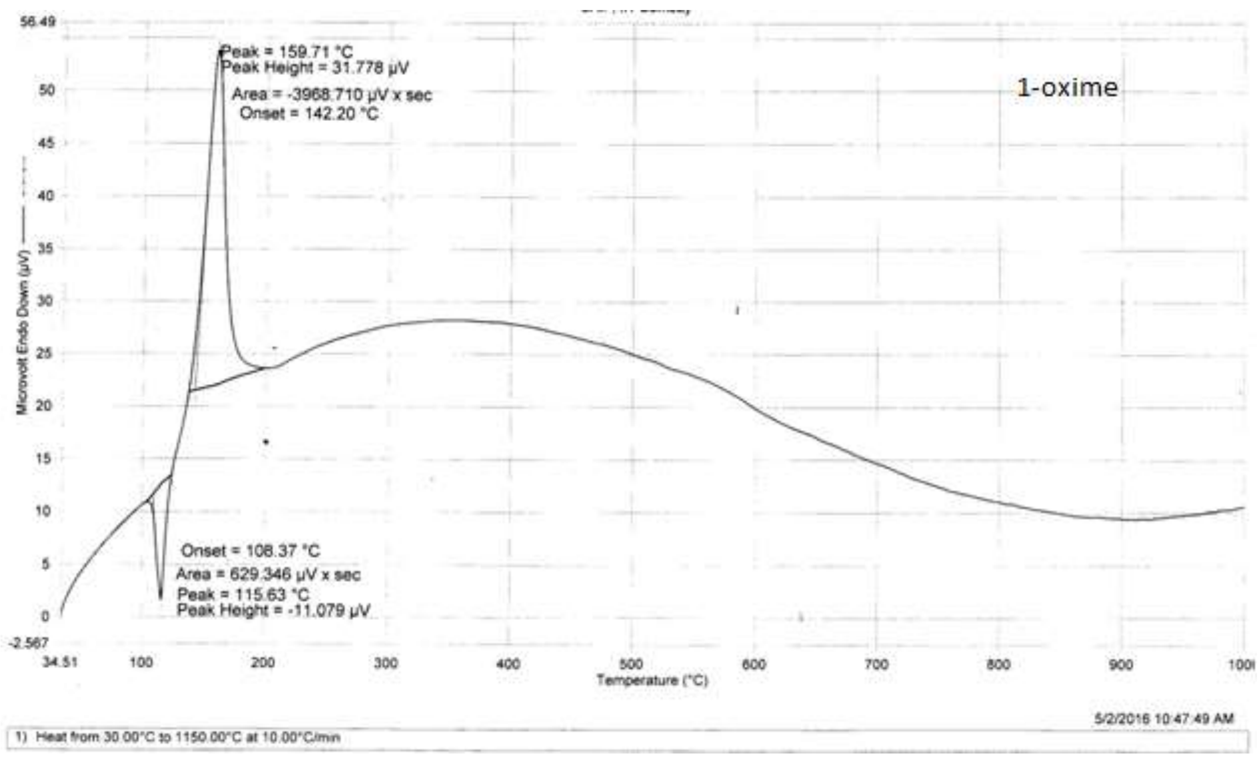
The pyrolysis of all the metal chelates in air has resulted in three step weight loss pattern. The central metal ion is eight coordinated with three ligands and two water molecules All these thermogravimetric curves indicate that the chelates are stable up to 80^0C.

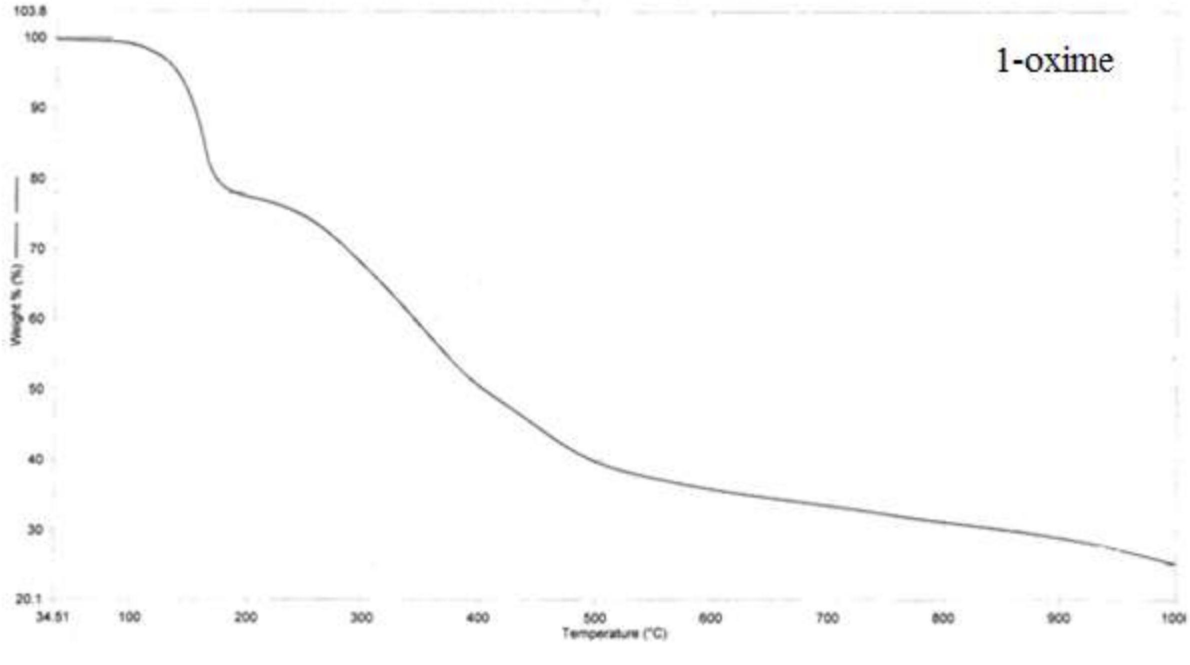
The first step is attributed to loss of the absorbed or lattice water. The second step of pyrolysis is attributed to dehydration reaction along with decomposition of some part of ligand. This step can be divided into two parts out of which the initial weight loss pattern below 15% (8-15%) is attributed to dehydration of the chelates followed by accelerated weight loss pattern which is due to partial decomposition of ligand. The third step shows accelerated weight loss pattern within very narrow temperature range due to oxidative decomposition of remaining ligand. The nature of this step may suggest free radical induced decomposition mechanism.

4.4.6.5. Results

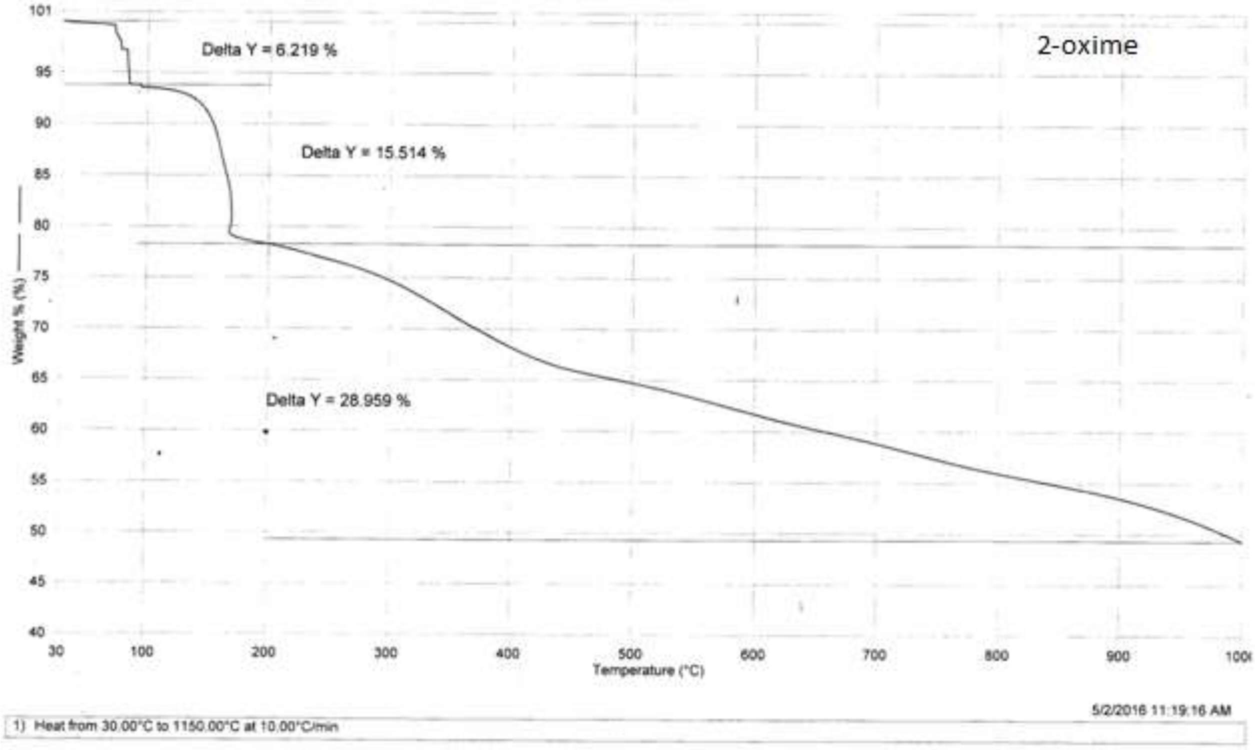
Thermogravimetric analysis of Ligands and metal chelates

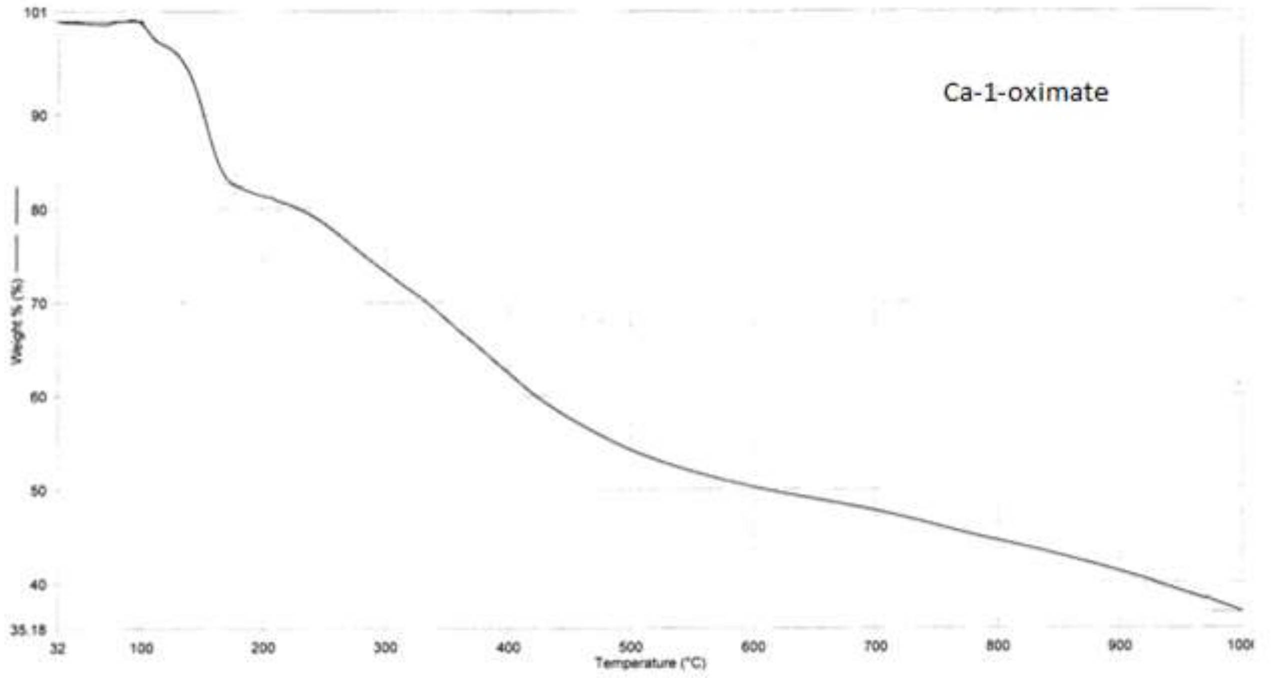
The thermal analysis investigate TGA of the synthesized complexes of Ca(II), Mg (II), Cu(II) and Ni (II)were carried out in the temperature range from room temperature to 1000^0C under nitrogen atomsphere. About 3.0 to 9.0 mg sample was used with heating rate 10^0C per minute. For differential thermal analysis purpose indium powder(10mg) was used as the reference material. The thermogravimetric curvess (TG) are illustrated in Figure. These are representative thermographs

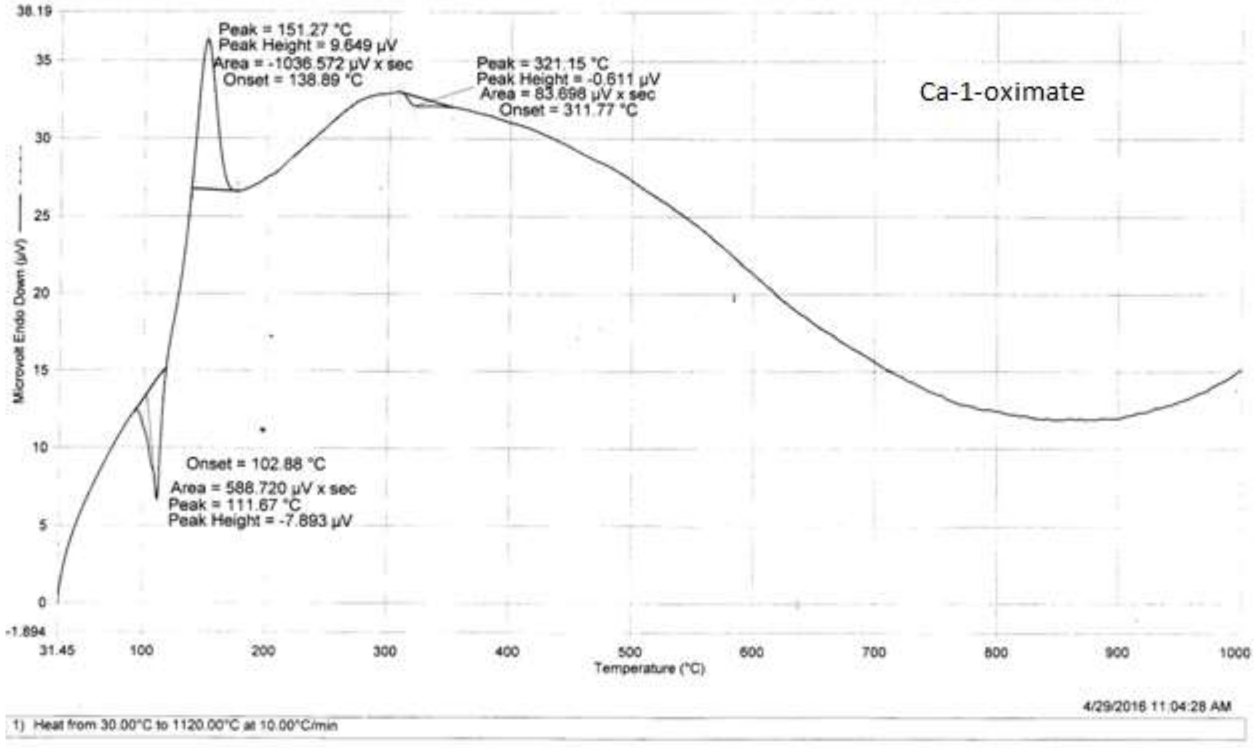

56.49
50
45
40
35
30
25
20
15
10
5
0
-2.567
Microvolt Endo Down (µV)
Peak = 159.71 °C
Peak Height = 31.778 µV
Area = -3968.710 µV x sec
Onset = 142.20 °C
1-oxime
Onset = 108.37 °C
Area = 629.346 µV x sec
Peak = 115.63 °C
Peak Height = -11.079 µV
34.51
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)
5/2/2016 10:47:49 AM
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min

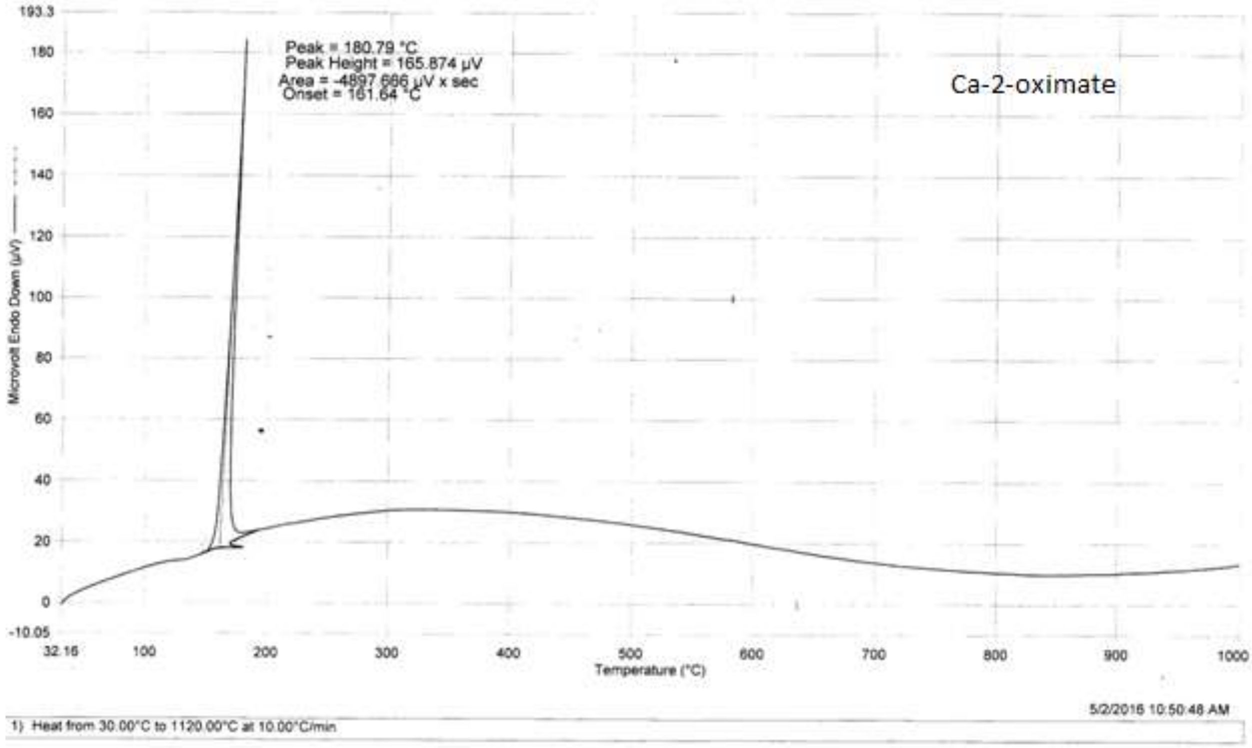

103.8
100
90
80
70
60
50
40
30
20.1
Weight % (%)
1-oxime
34.51
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

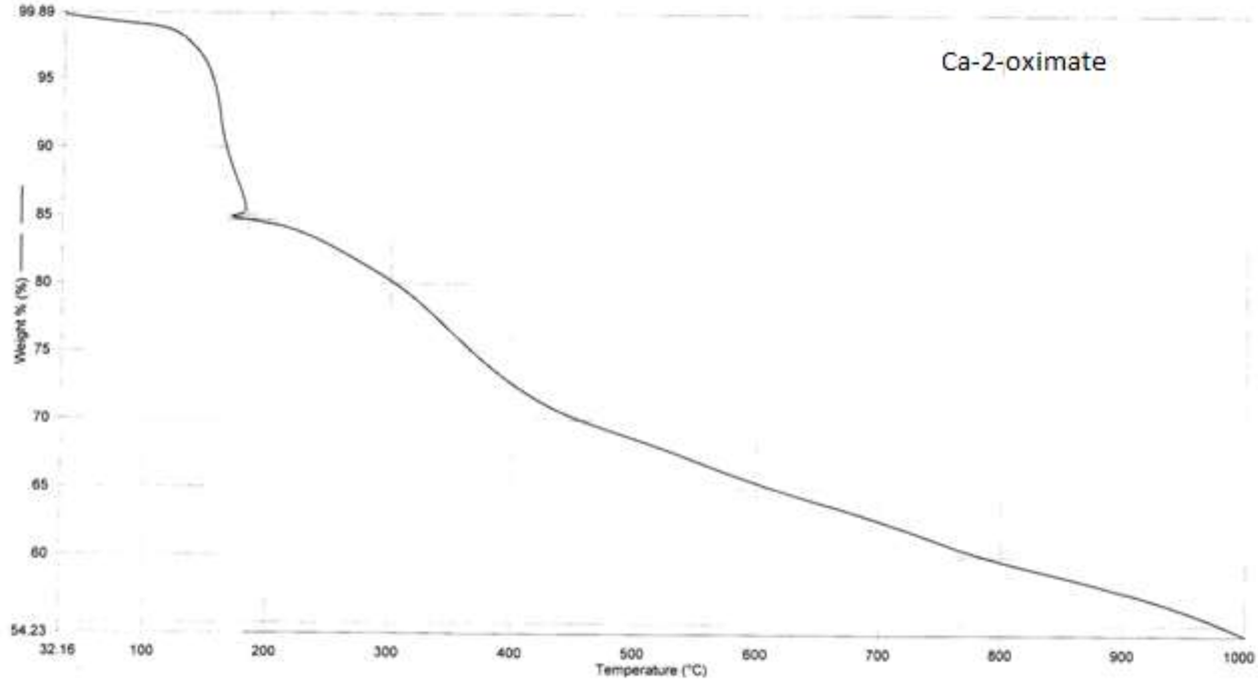

Peak = 169.67 °C
Peak Height = 79.443 µV
Onset = 159.98 °C
Area = -3226.455 µV x sec
2-oxime
Microvolt Endo Down (µV)
104.2
100
90
80
70
60
50
40
30
20
10
0
-5.102
31.3
100
200
300
400
500
600
700
800
900
Temperature (°C)
5/2/2016 11:20:47 AM
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min

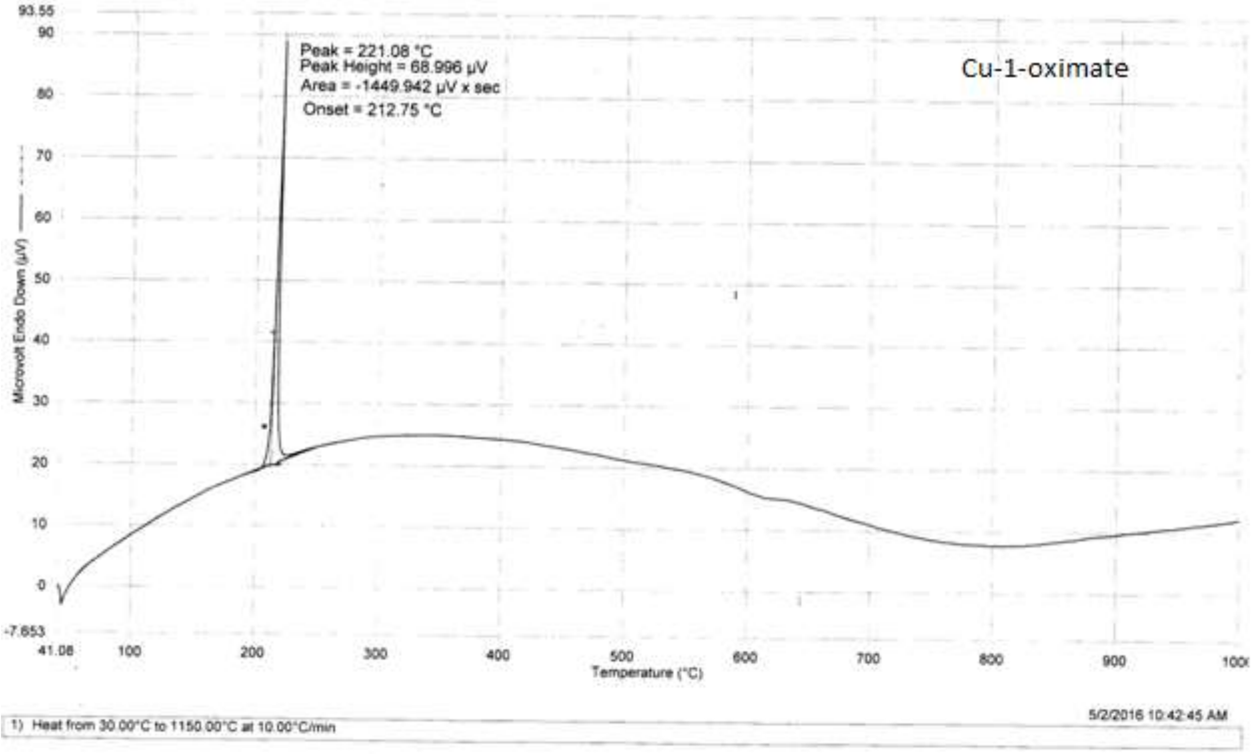

Delta Y = 6.219 %
Delta Y = 15.514 %
Delta Y = 28.959 %
2-oxime
Weight % (%)
101
95
90
85
80
75
70
65
60
55
50
45
40
30
100
200
300
400
500
600
700
800
900
Temperature (°C)
5/2/2016 11:19:16 AM
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min

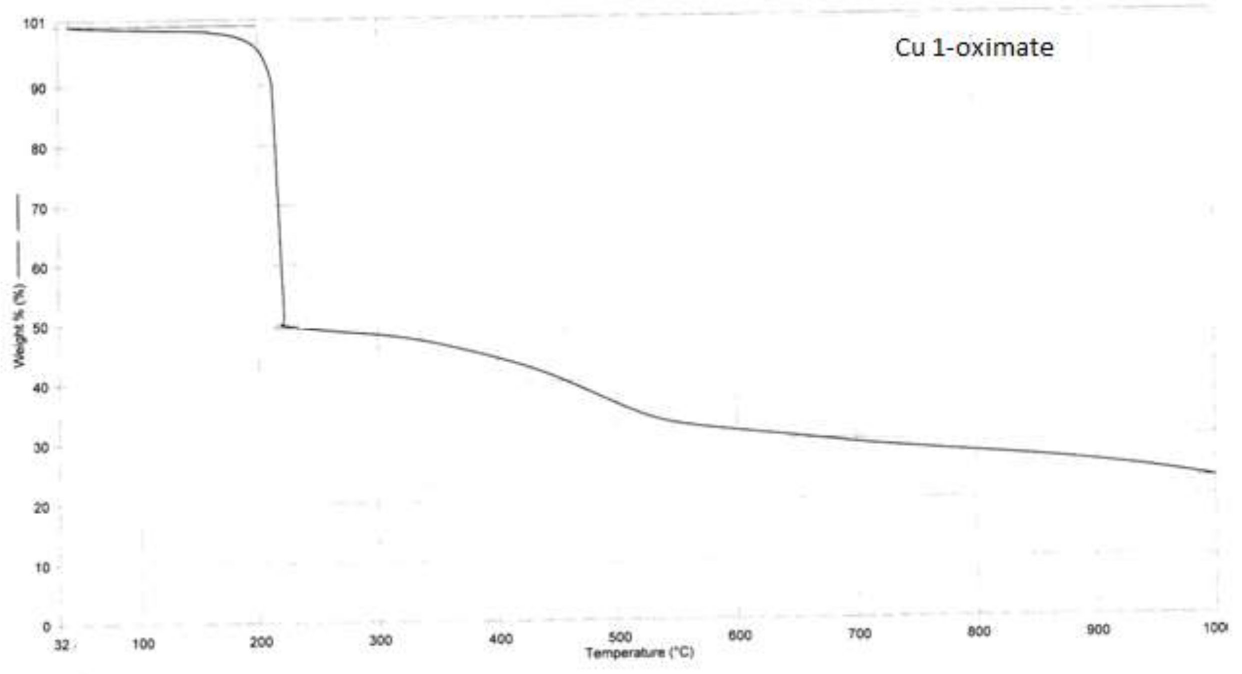

Ca-1-oximate
Weight % (%)
101
90
80
70
60
50
40
35.18
32
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

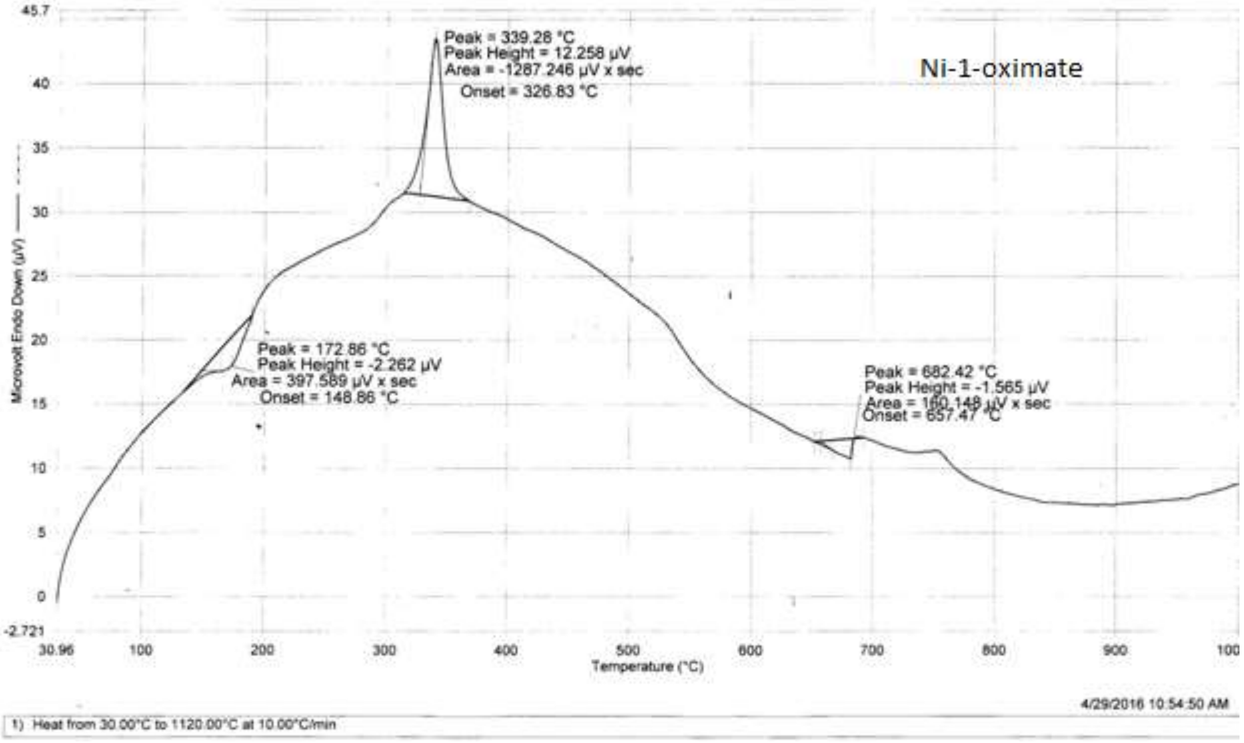

Ca-1-oximate
Microvolt Endo Down (µV)
38.19
35
30
25
20
15
10
5
0
-1.894
31.45
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)
Peak = 151.27 °C
Peak Height = 9.649 µV
Area = -1036.572 µV x sec
Onset = 138.89 °C
Peak = 321.15 °C
Peak Height = -0.611 µV
Area = 83.698 µV x sec
Onset = 311.77 °C
Onset = 102.88 °C
Area = 588.720 µV x sec
Peak = 111.67 °C
Peak Height = -7.893 µV
4/29/2016 11:04:28 AM
1) Heat from 30.00°C to 1120.00°C at 10.00°C/min

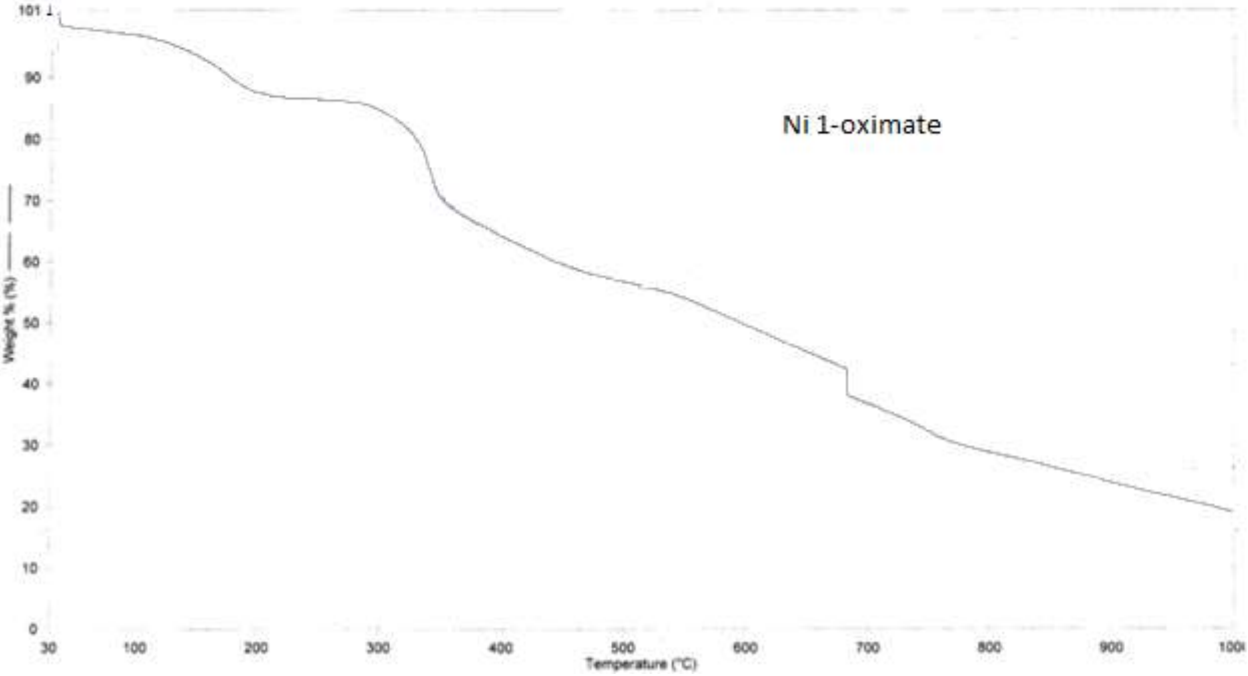

Ca-2-oximate
Peak = 180.79 °C
Peak Height = 165.874 µV
Area = -4897.666 µV x sec
Onset = 161.64 °C
Microvolt Endo Down (µV)
193.3
180
160
140
120
100
80
60
40
20
0
-10.05
32.16
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)
5/2/2016 10:50:48 AM
1) Heat from 30.00°C to 1120.00°C at 10.00°C/min

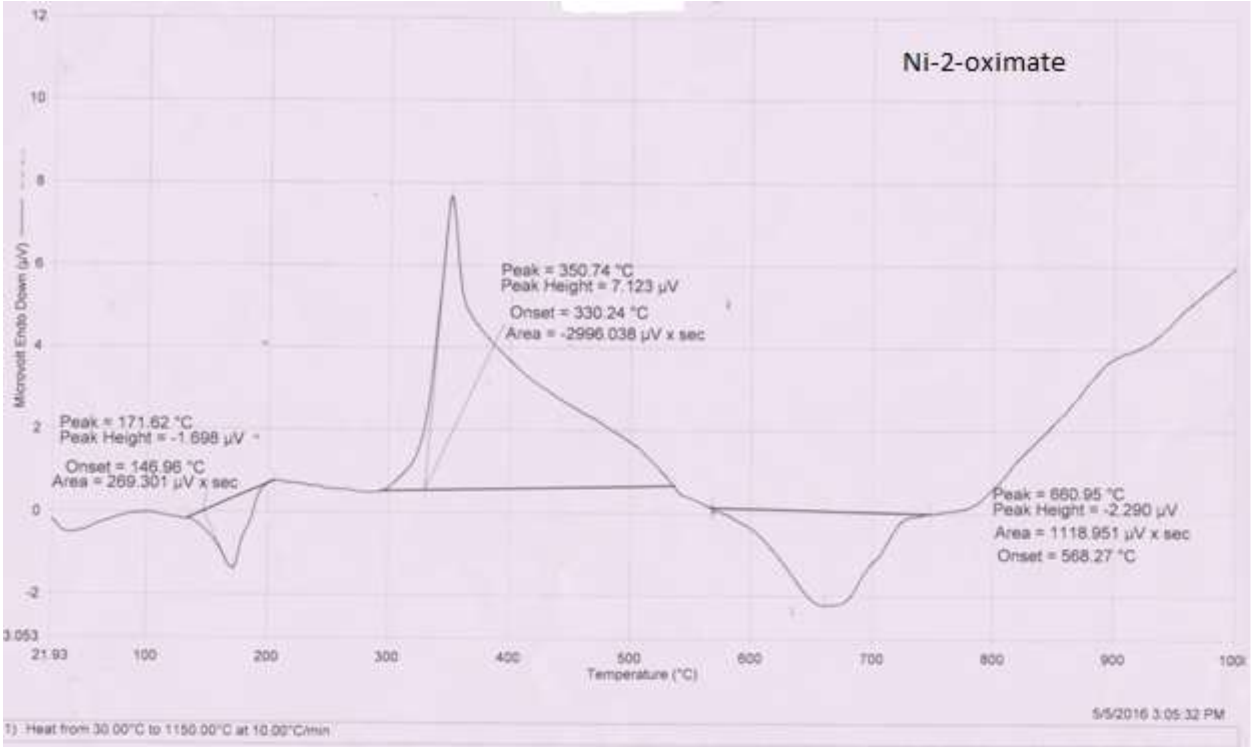

Ca-2-oximate
Weight % (%)
99.89
95
90
85
80
75
70
65
60
54.23
32.16
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

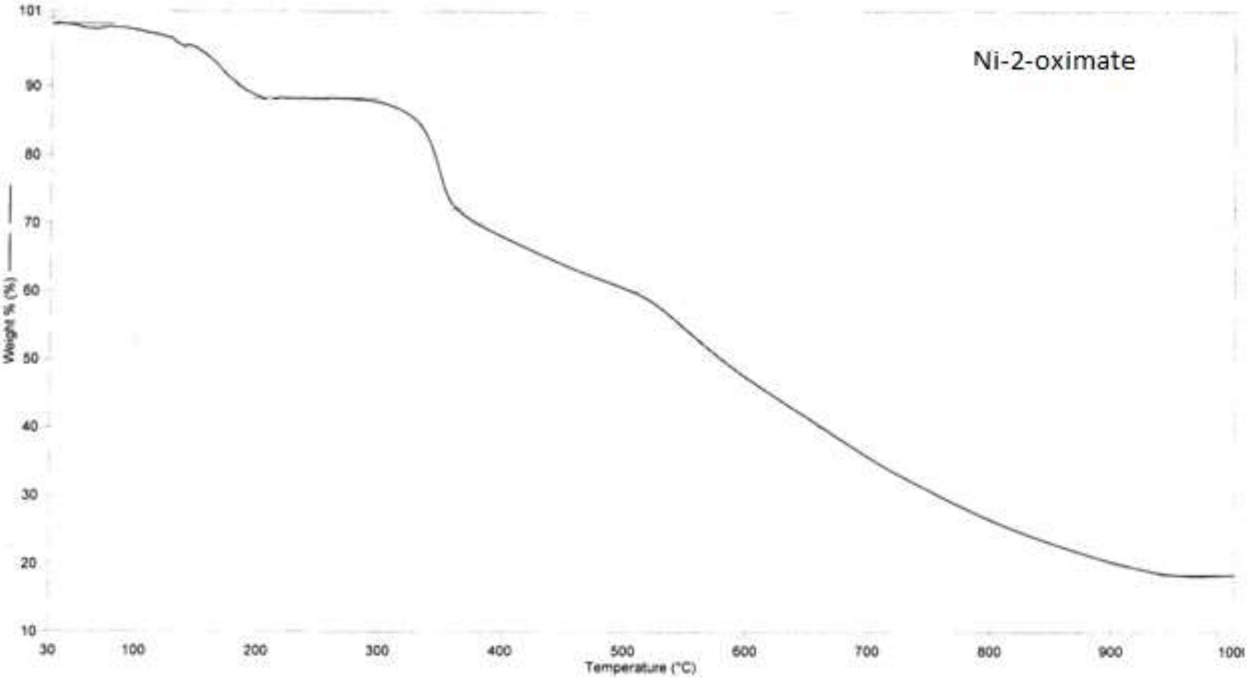

Cu-1-oximate
Peak = 221.08 °C
Peak Height = 68.996 µV
Area = -1449.942 µV x sec
Onset = 212.75 °C
Microvolt Endo Down (µV)
93.55
90
80
70
60
50
40
30
20
10
0
-7.653
41.08
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min
5/2/2016 10:42:45 AM

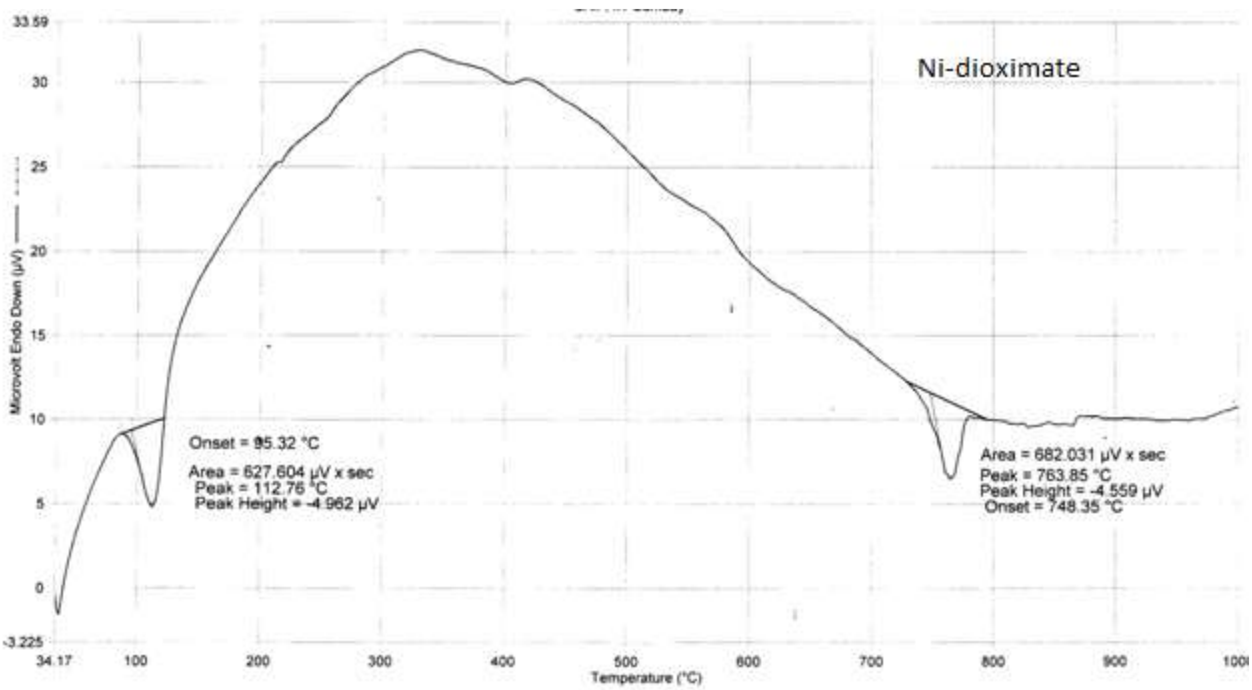

Cu 1-oximate
Weight % (%)
101
90
80
70
60
50
40
30
20
10
0
32
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

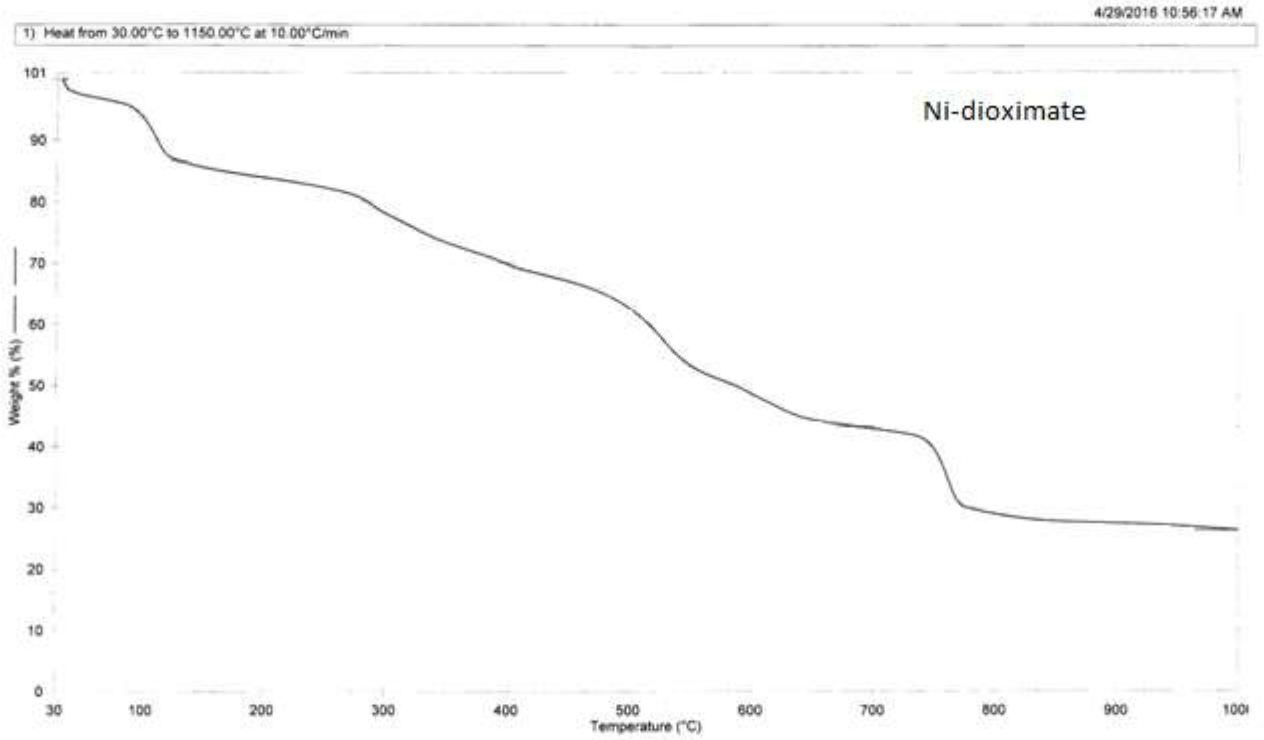

Ni-1-oximate
Peak = 339.28 °C
Peak Height = 12.258 µV
Area = -1287.246 µV x sec
Onset = 326.83 °C
Peak = 172.86 °C
Peak Height = -2.262 µV
Area = 397.589 µV x sec
Onset = 148.86 °C
Peak = 682.42 °C
Peak Height = -1.565 µV
Area = 160.148 µV x sec
Onset = 657.47 °C
Microvolt Endo Down (µV)
45.7
40
35
30
25
20
15
10
5
0
-2.721
30.96
100
200
300
400
500
600
700
800
900
Temperature (°C)
4/29/2016 10:54:50 AM
1) Heat from 30.00°C to 1120.00°C at 10.00°C/min

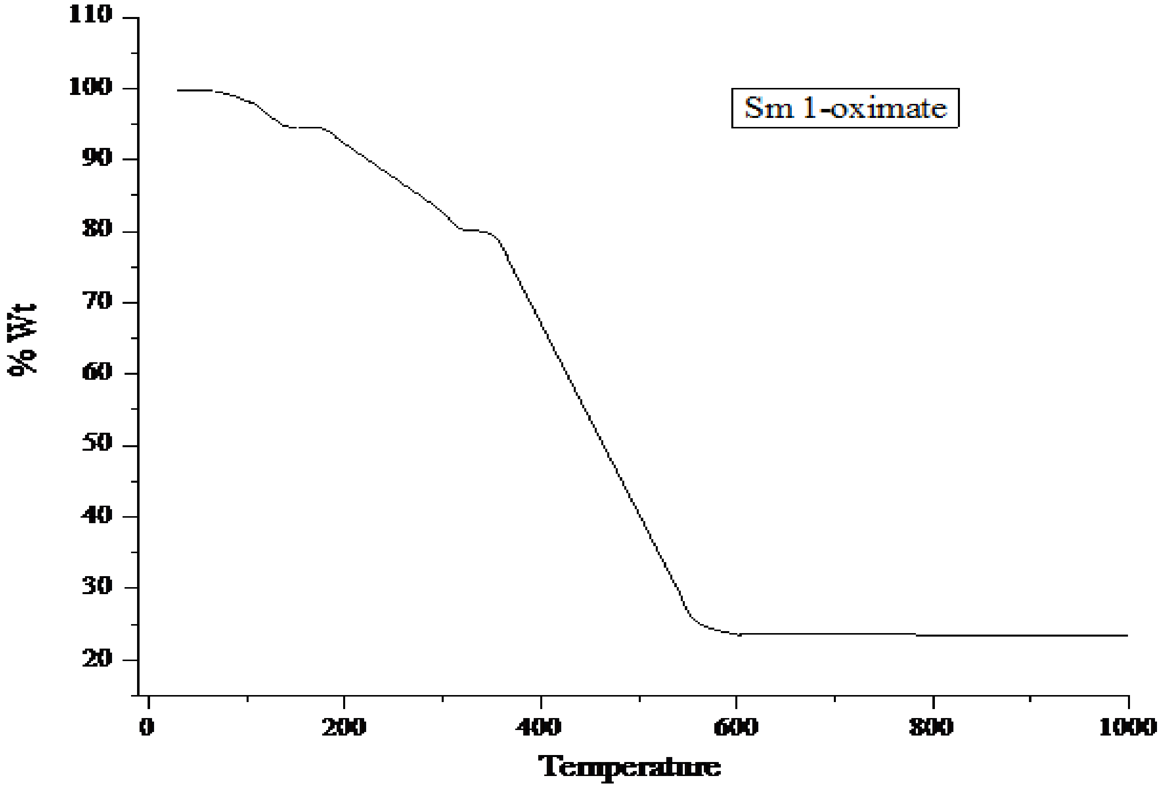

Ni 1-oximate
Weight % (%)
101
90
80
70
60
50
40
30
20
10
0
30
100
200
300
400
500
600
700
800
900
Temperature (°C)

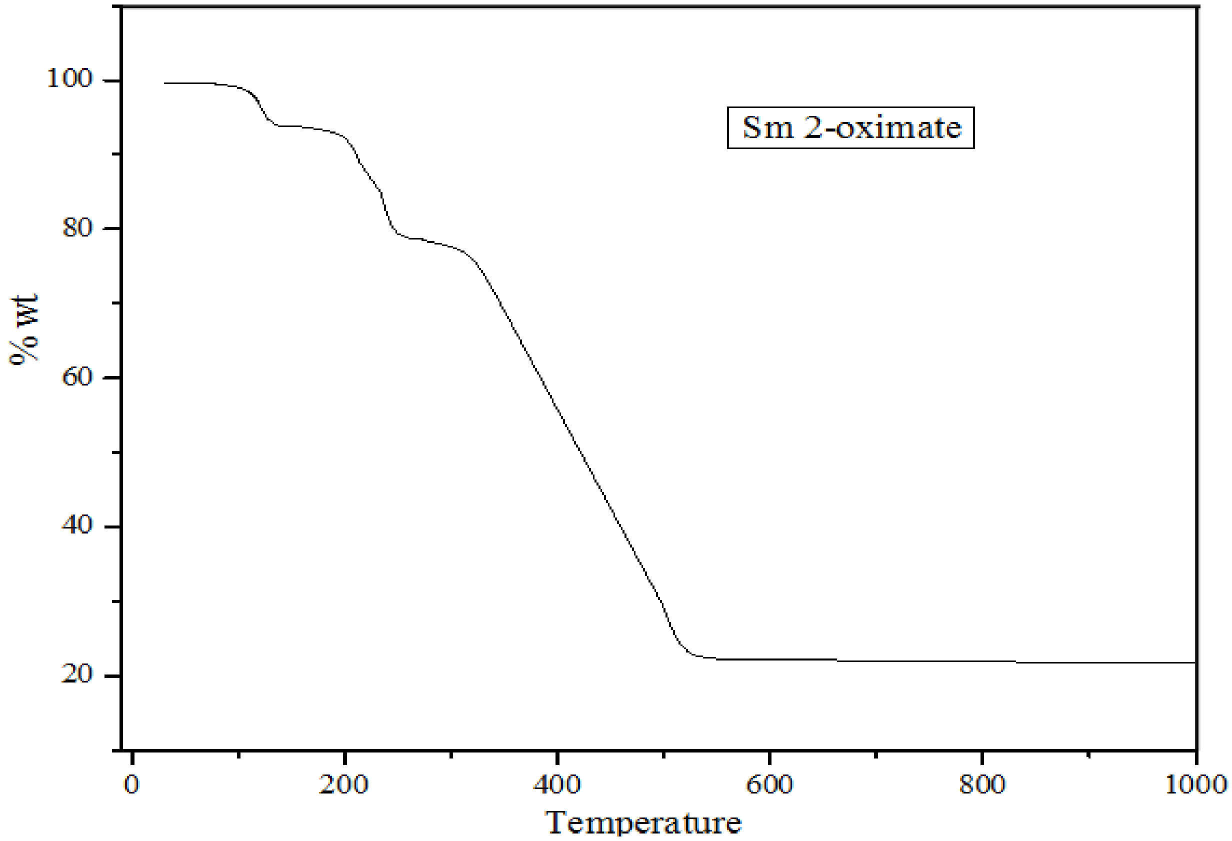

Ni-2-oximate
12
10
8
6
4
2
0
-2
3.053
Microvolt Endo Down (µV)
Peak = 350.74 °C
Peak Height = 7.123 µV
Onset = 330.24 °C
Area = -2996.038 µV x sec
Peak = 171.62 °C
Peak Height = -1.698 µV
Onset = 146.96 °C
Area = 269.301 µV x sec
Peak = 660.95 °C
Peak Height = -2.290 µV
Area = 1118.951 µV x sec
Onset = 568.27 °C
21.93
100
200
300
400
500
600
700
800
900
100
Temperature (°C)
5/5/2016 3:05:32 PM
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min

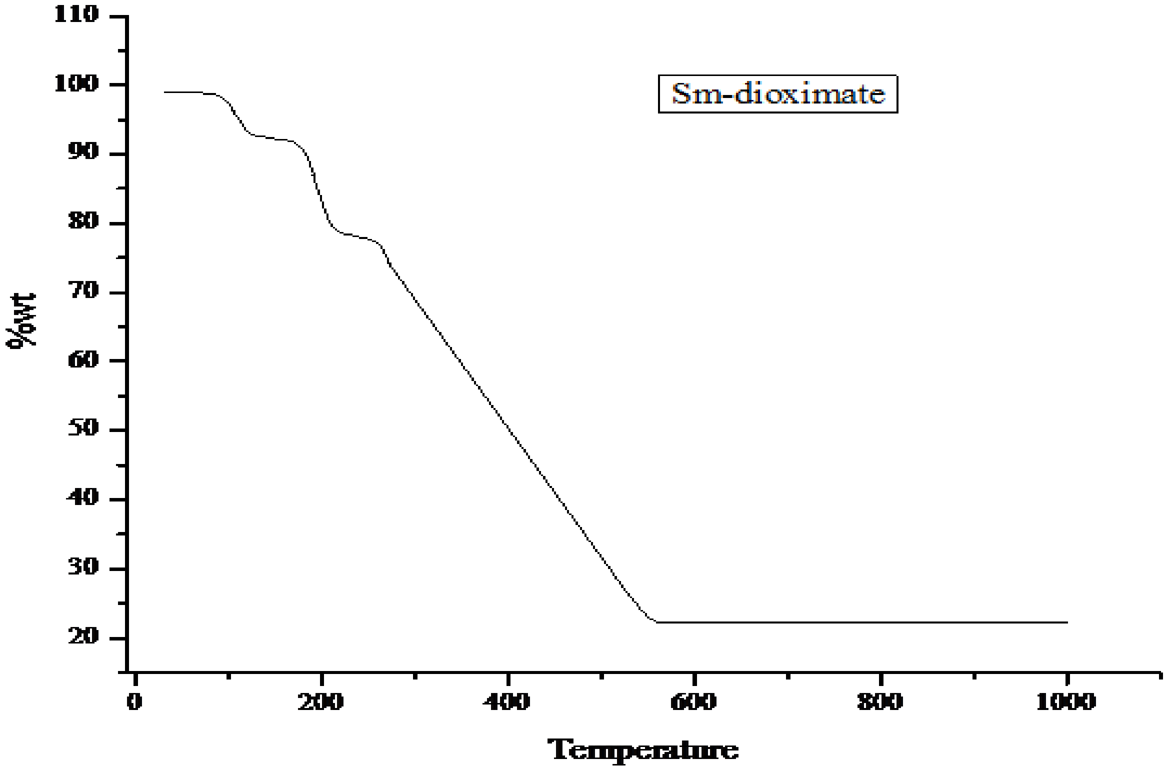

Ni-2-oximate
101
90
80
70
60
50
40
30
20
10
Weight % (%)
30
100
200
300
400
500
600
700
800
900
100
Temperature (°C)


Ni-dioxamate
Microvolt Endo Down (µV)
33.59
30
25
20
15
10
5
0
-3.225
34.17
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)
Onset = 95.32 °C
Area = 627.604 µV x sec
Peak = 112.76 °C
Peak Height = -4.962 µV
Area = 682.031 µV x sec
Peak = 763.85 °C
Peak Height = -4.559 µV
Onset = 748.35 °C


4/29/2016 10:56:17 AM
1) Heat from 30.00°C to 1150.00°C at 10.00°C/min
Ni-dioxamate
Weight % (%)
101
90
80
70
60
50
40
30
20
10
0
30
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)


Sm 1-oximate
% Wt
110
100
90
80
70
60
50
40
30
20
0
200
400
600
800
1000
Temperature


Sm 2-oximate
% Wt
100
80
60
40
20
0
200
400
600
800
1000
Temperature



Compounds	Stages of decomposition	Temperature range in ^{0}C	%Weight loss	Tentative assignment
Ca-1-oximate	Stage I	90-125^{0}C	3.12	Loss of coordinated water
	Stage II	125-180^{0}C	17.366	Loss related to release of one ligand
	Stage III	180-600^{0}C	45.609	Loss related to release of remaining ligands
Ca-2-oximate	Stage I	40-120^{0}C	0.209	Loss of coordinated water
	Stage II	120-185^{0}C	15.199	Loss related to release of one ligand
	Stage III	185-600^{0}C	30.455	Loss related to release of remaining ligands

Ni-1-oximate	Stage I	80-190^{0}C	11.456	Loss of coordinated water
	Stage II	270-345^{0}C	15.879	Loss related to release of one ligand
	Stage III	34-680^{0}C	44.428	Loss related to release of remaining ligands
Ni-2-oximate	Stage I	97-200^{0}C	10.872	Loss of coordinated water
	Stage II	306-352^{0}C	16.132	Loss related to release of one ligand
	Stage III	510-900^{0}C	53.611	Loss related to release of remaining ligands
Ni-dioximate	Stage I	35-97^{0}C	13.224	Loss of coordinated water
	Stage II	280-580^{0}C	43.342	Loss related to release of one ligand
	Stage III	590-800^{0}C	16.915	Loss related to release of remaining ligands
Sm 1-oximate	Stage I	88-138^{0}C	5.0	Loss of coordinated water
	Stage II	176-326^{0}C	14.23	Loss related to release of one ligand
	Stage III	351-563^{0}C	56.57	Loss related to release of remaining Ligands

Sm 2-oximate	Stage I	101-138^{0}C	4.98	Loss of coordinated water
	Stage II	188-263^{0}C	15.22	Loss related to release of one ligand
	Stage III	313-526^{0}C	56.50	Loss related to release of remaining ligands
Sm dioximate	Stage I	88-126^{0}C	6.70	Loss of coordinated water
	Stage II	176-213^{0}C	14.26	Loss related to release of one ligand
	Stage III	251-551^{0}C	55.90	Loss related to release of remaining ligands

4.4.6.6. Conclusions:

1. From the procedural and final decomposition temperatures thermal stability of the complexes is studied.
2. In the temperature range R.T to 1000^{0}C, two water molecules are lost which could be either lattice or coordinated water molecules.
3. The second and third stage of decomposition gives partial weight loss of the ligands to give respective metal oxides.

The thermogravimetric profile of all these synthesized metal chelates indicates that the thermolysis of metal complexes of 1, 2-naphthoquinone oximes takes place in several distinct stages as summarized in table

It is essential to mention here that the TG profile of all the present complexes were derived at a very slow heating rate of about 3-5^{0}C/min in order to locate the losses corresponding to lattice held and the coordinated water molecules. The losses are found to be overlapped and individual distinction becomes extremely difficult if the heating rates are faster.

The weight losses in the temperature range 80-176^{0}C are noticed for all the complexes. These weight losses can be attributed to coordinate and lattice held water molecules. These weight losses correspond to two water molecules which are considered to be coordinated water molecules except in the case of lanthanides metal chelates where higher weight losses are recorded. These higher weight losses in the case of metal chelates can be attributed to the presence of one lattice or adsorbed water molecule.

In the second stage of thermal degradation (temperature range from 176-326^{0}C) and the third range (temperature range from 251-563^{0}C exhibit weight losses corresponding to the partial decomposition of organic ligand molecule.

At the end of the third stage, the residue oxides are obtained which reasonably well within the limits of experimental error to the composition M_2O_3.

The presence of 1:3 and 1:2 stiochiometery which was maintained during the synthesis (Metal to Ligand ratio as 1:3 and 1:2) is shown to be present in all the complexes. The above stiochiometry is also confirmed by the non electrolytic nature of all these complexes in 10^{-3} M DMF solution.

4.4.7. Electronic Spectra

4.4.7.1. Introduction

General nature of the electronic spectra

The electronic absorption spectra of 1, 2-naphthoquinone (which is the basic nucleus of 1, 2-naphthoquinone-1-oxime, 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone dioxime) and its derivatives has been extensively studied and it has been proposed that these structures are conveniently explained on the basis of what are termed as benzenoid and quinonoid electron transfer bands. These spectra are new recognized by their following characteristic features.

(i) Most of the electronic spectra using common ultraviolet solvent show two intense bands in the 240-290 nm (13,000-25000) region and these are attributed to benzenoid and quinonoid electron transfer. These bands are shown to be due to $\pi \rightarrow \pi^*$ transitions.

(ii) In addition, one medium intensity band is always found at 335 nm (26000-32000) which corresponds to benzenoid electron transfer.

(iii) In the region 330-340 nm, a low intensity band is observed for some derivatives. The band is attributed to quinonoid electron transfer which involves $n \rightarrow \pi^*$ transitions.

(iv) One broad local excitation band of very low intensity is also observed in the 400-500 nm region which is attributed to the low energy $n \rightarrow \pi^*$ transitions of the quinonoid carbonyls.

4.4.7.2. Objectives

The main objective of our study related to the electronic spectra of the metal chelates is to obtain appropriate and useful data to throw light on the electronic structure of the chelates in the following respects.

(i) To find the structural changes in the ligand due to their chelation.

(ii) To study the effect of positional isomerism on the electronic spectra of the isomeric chelates, and

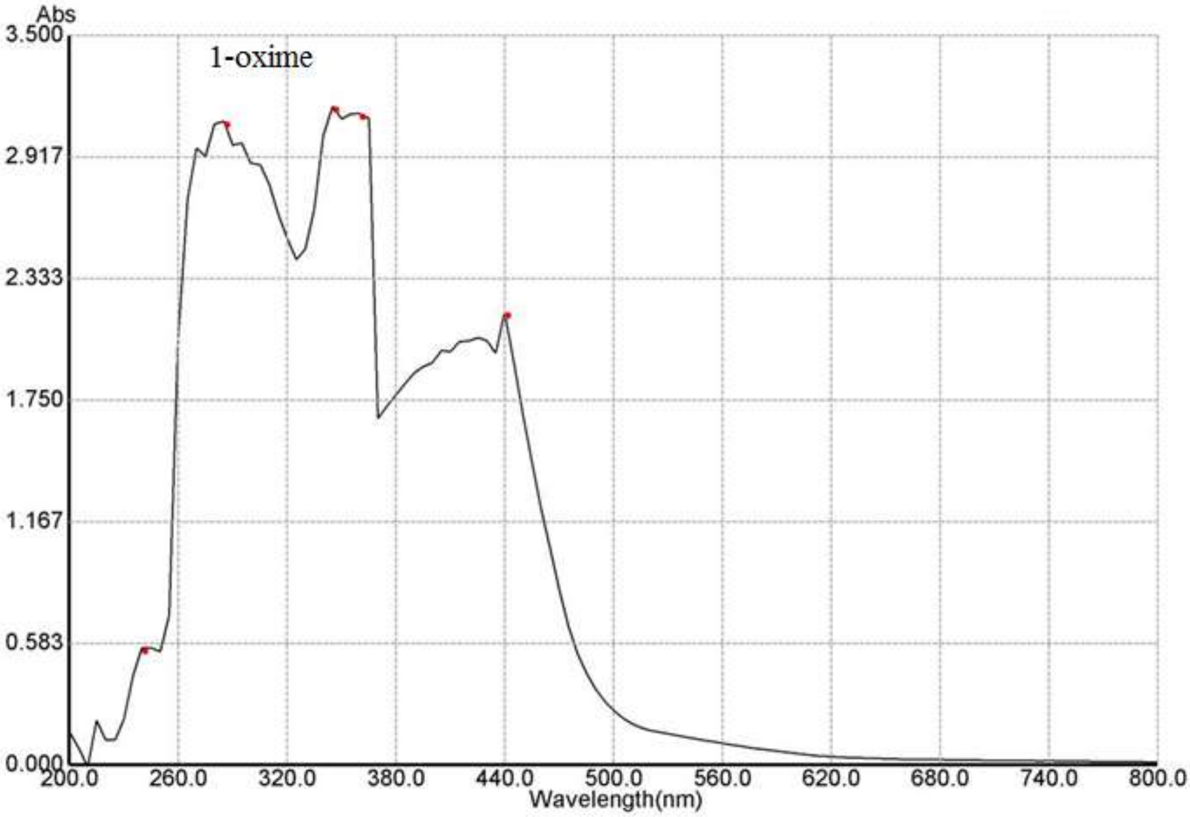
(iii) To examine the ligand field effect on the electronic energy levels of the rare earth ions trough the knowledge of f-f transitions which can be recognized as ligand field spectra.

However, it was not possible to investigate the ligand field spectra involving f-f transitions most probably due to insufficient solubility of the chelates in the suitable ultraviolet solvents and therefore we are in a position to discuss the spectra only with reference to the effect of positional isomerism on the electronic spectra of two isomeric series and effect of chelation on the electronic energy levels of 1,2-naphthoquinone-1-oxime, 1,2-naphthoquinone-2-oxime and 1,2-naphthoquinone dioxime.

Electronic spectra of the six metal chelates of 1, 2 Naophthoquinone-1-oxime (1,2 NQ 1-oxime), 1,2 Naphthoquinone 2-oxime (1,2 NQ 2-oxime) and 1,2 Naphthoquinone dioxime (1,2 NQ dioxime) are studied in detail to investigate manly the effect of i) chelation ii) position isomerism and iii) solvent on the electronic energy level of the 1, 2-naphthoquinone dioxime.

Electronic spectra

Electronic spectra of all the chelates are recorded in solid state. The electronic spectra were recorded on Shimadzu Model-UV 160. A spectrophotometer in the region 200-700nm. Some of the representative spectra are shown below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2.333
1.750
1.167
0.583
0.000
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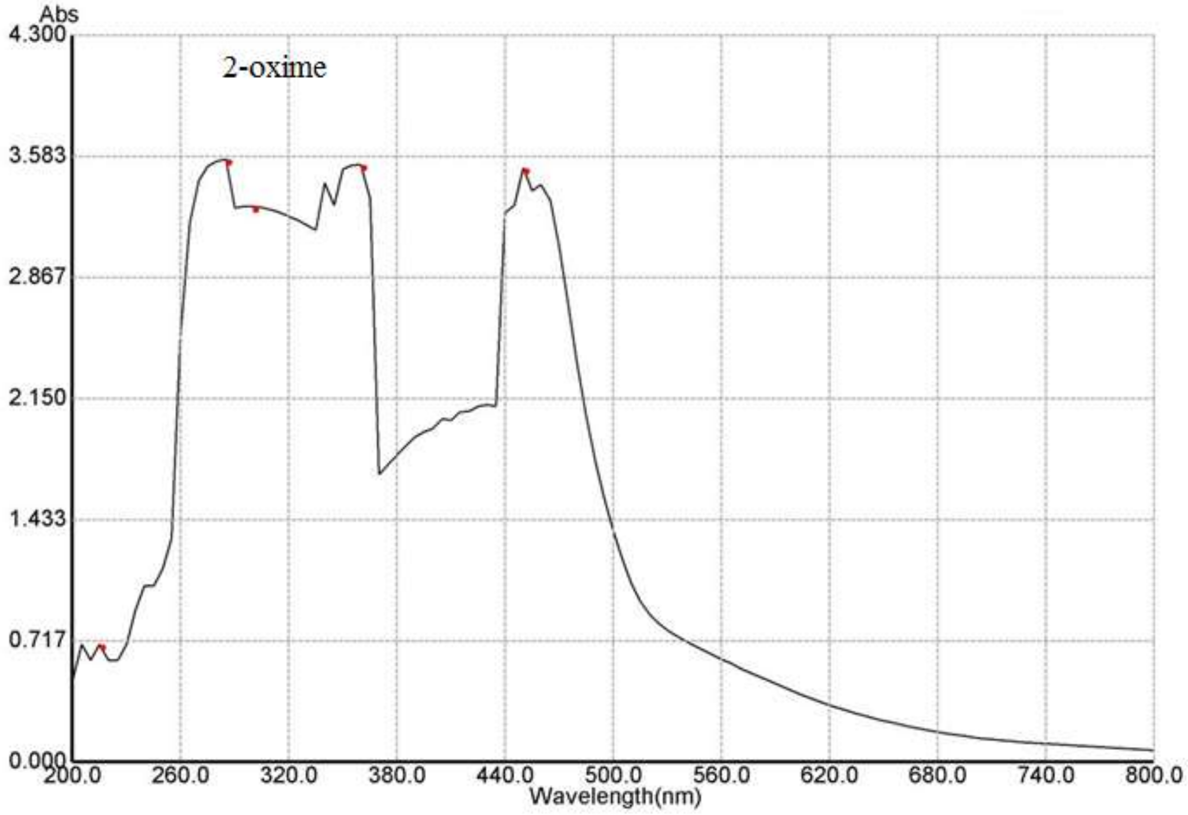
380.0
440.0
500.0
560.0
620.0
680.0
740.0
800.0
Wavelength(nm)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0.717
0.000
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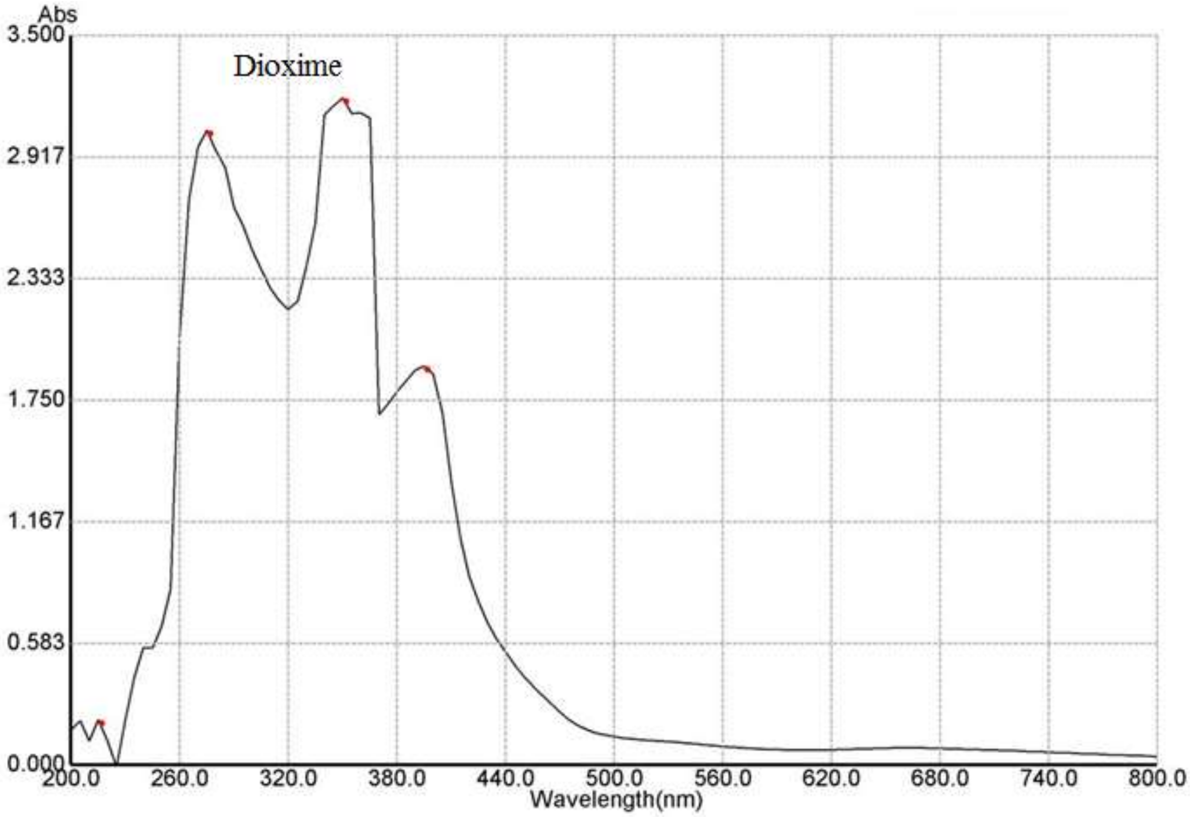
Wavelength(nm)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0.000
Dioxime
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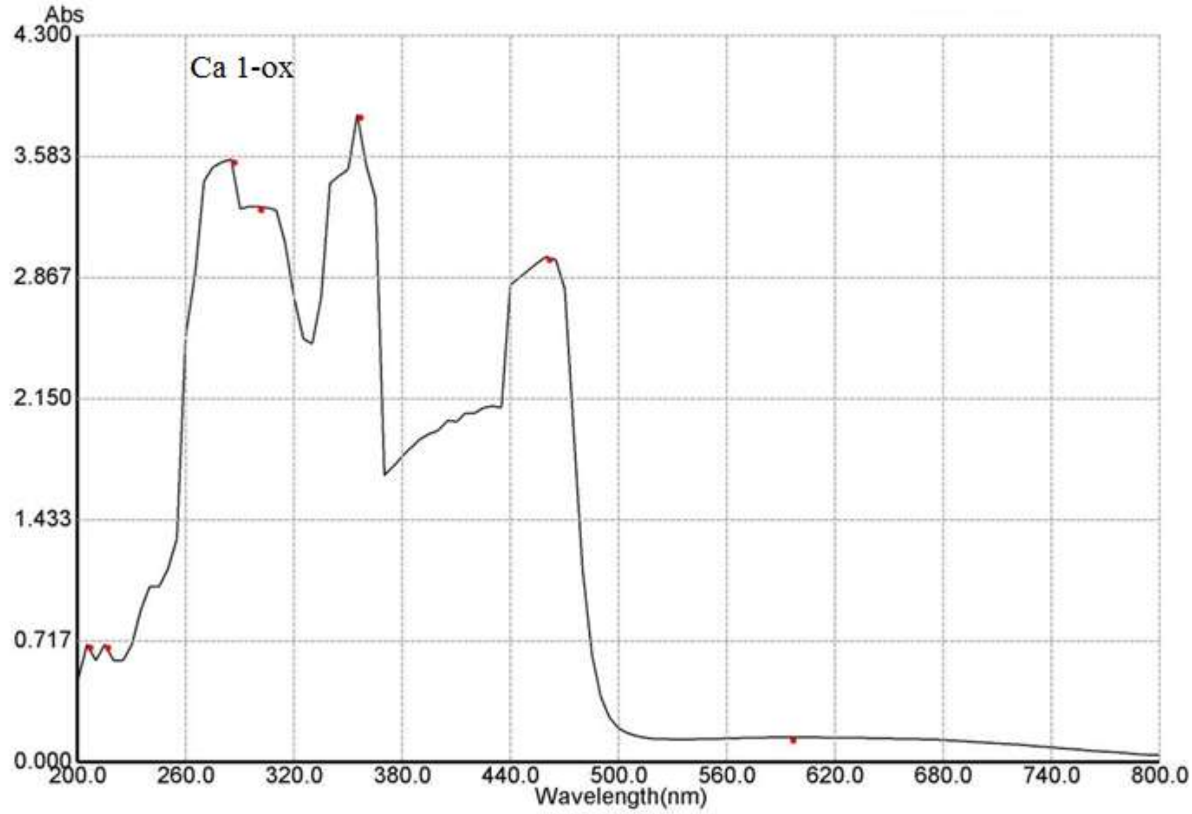
740.0
800.0
Wavelength(nm)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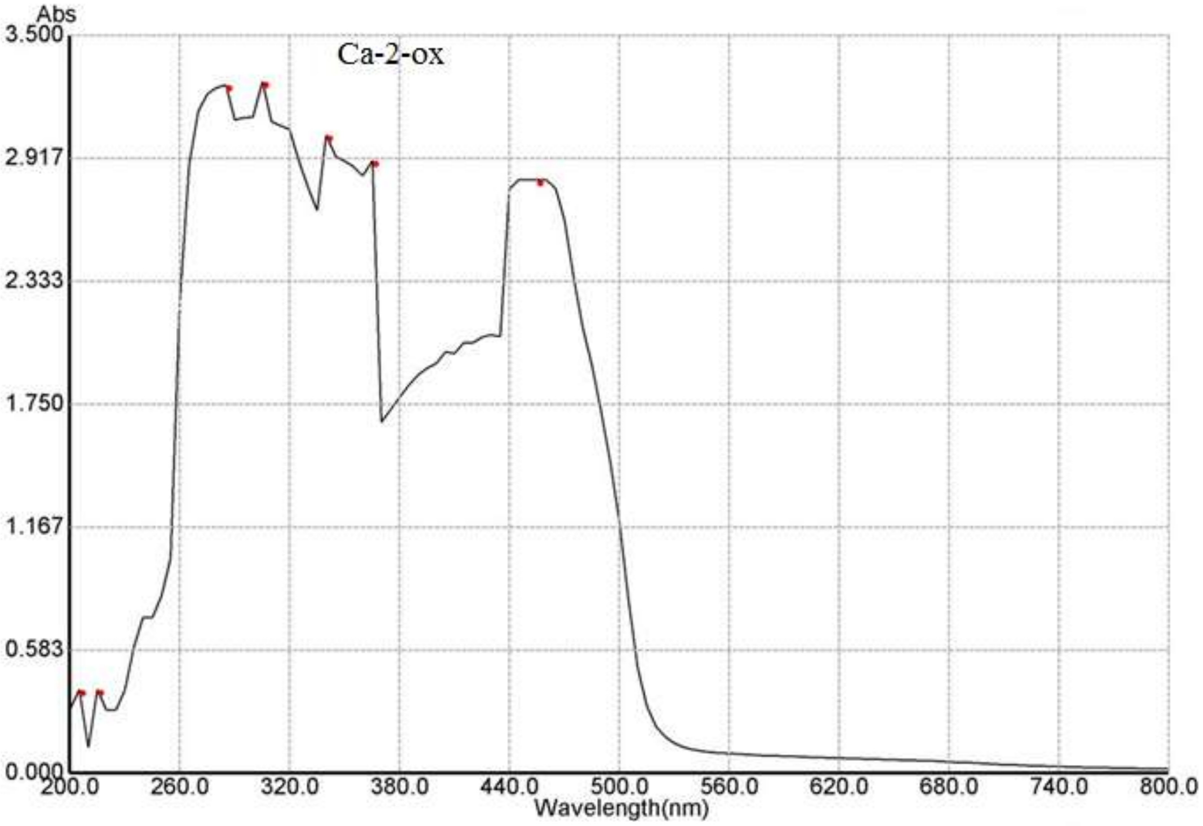
740.0
800.0
Wavelength(nm)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0.000
Ca-2-ox
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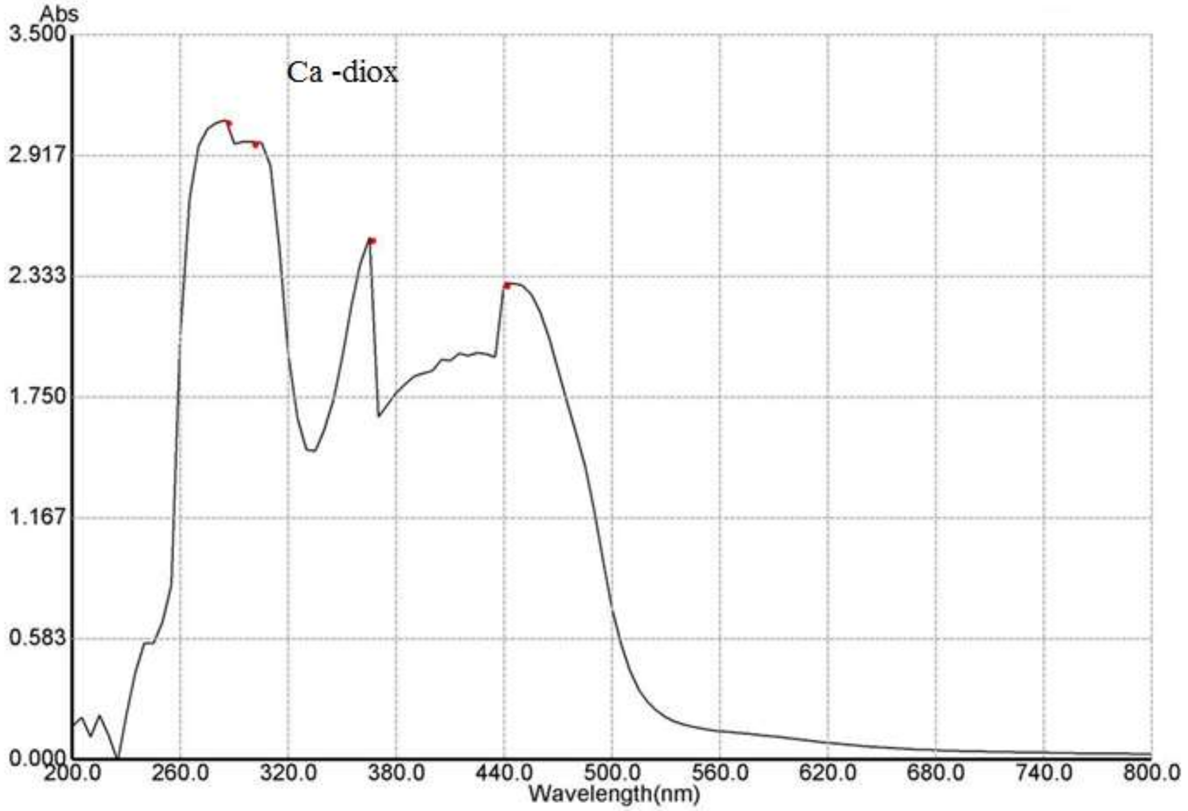
740.0
800.0
Wavelength(nm)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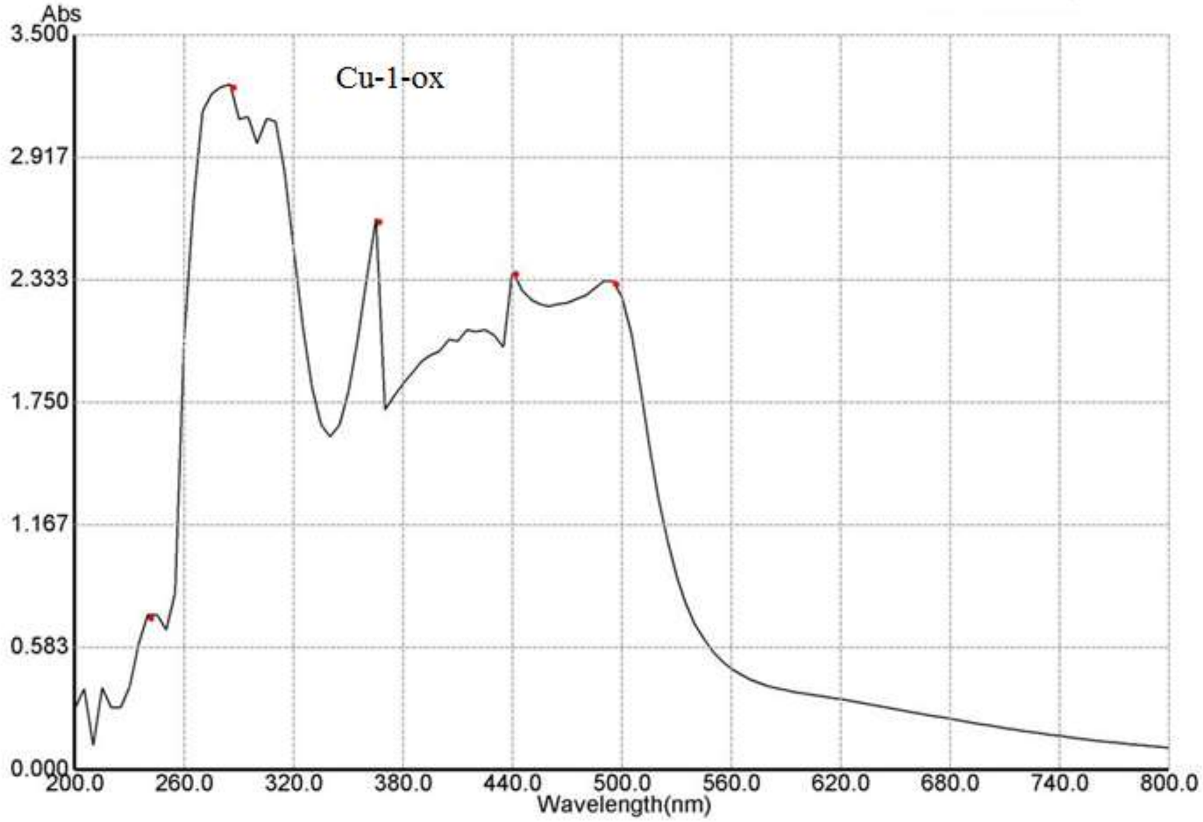
740.0
800.0
Wavelength(nm)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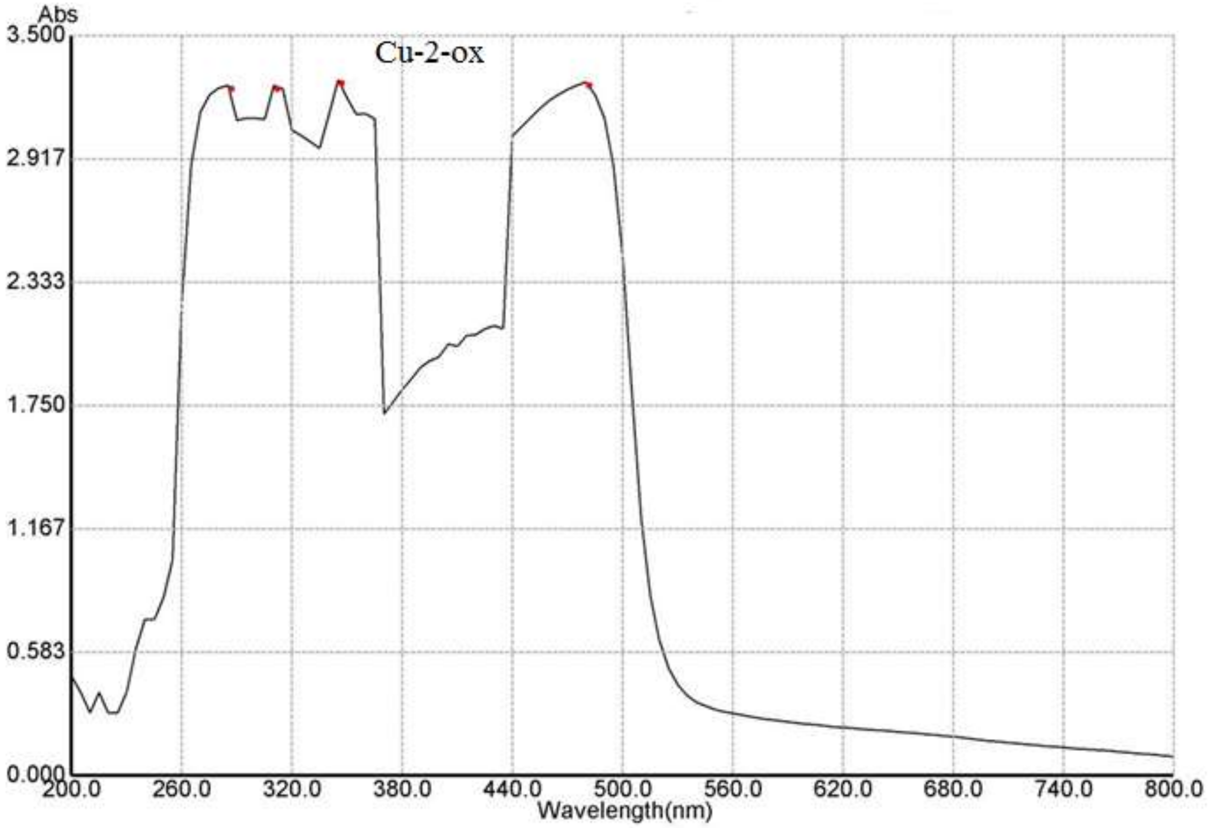
500.0
560.0
620.0
680.0
740.0
800.0
Wavelength(nm)
Cu-1-ox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200.0
260.0
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500.0
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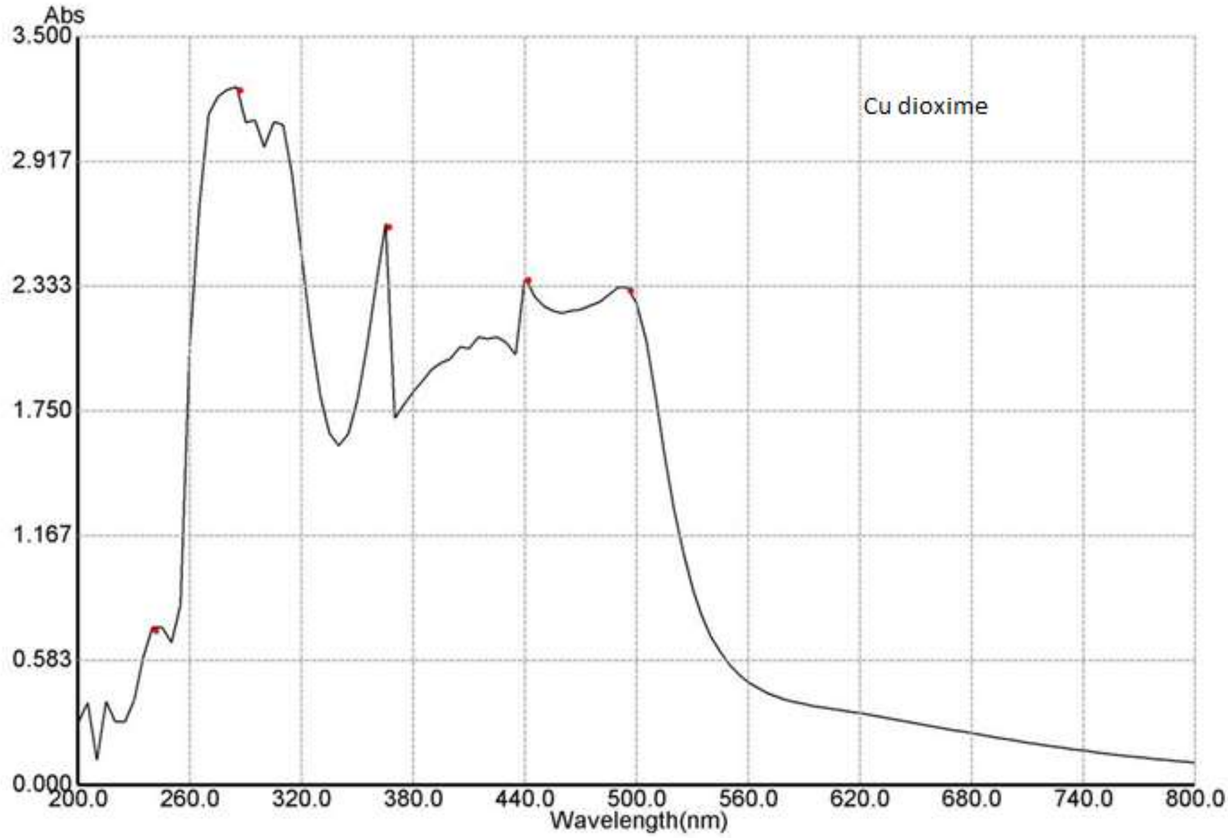
680.0
740.0
800.0
Wavelength(nm)
Cu-2-ox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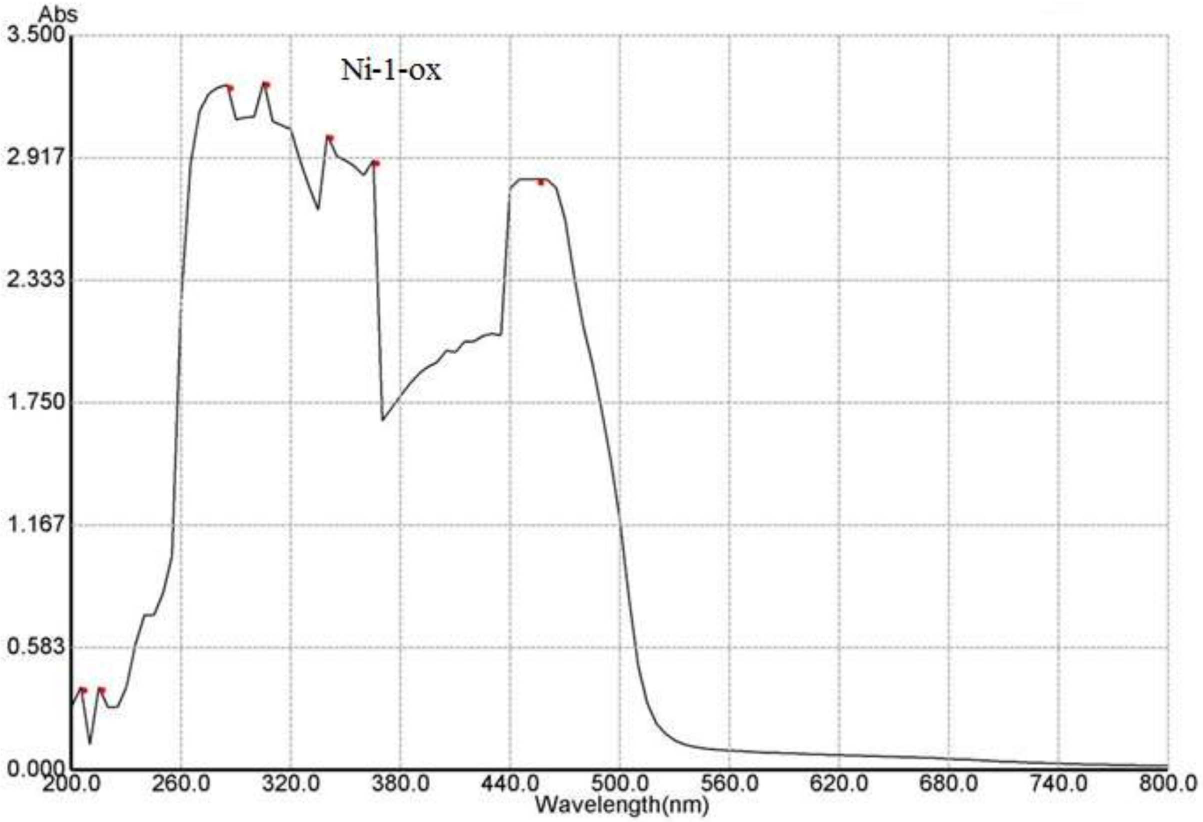
440.0
500.0
560.0
620.0
680.0
740.0
800.0
Wavelength(nm)
Cu dioxime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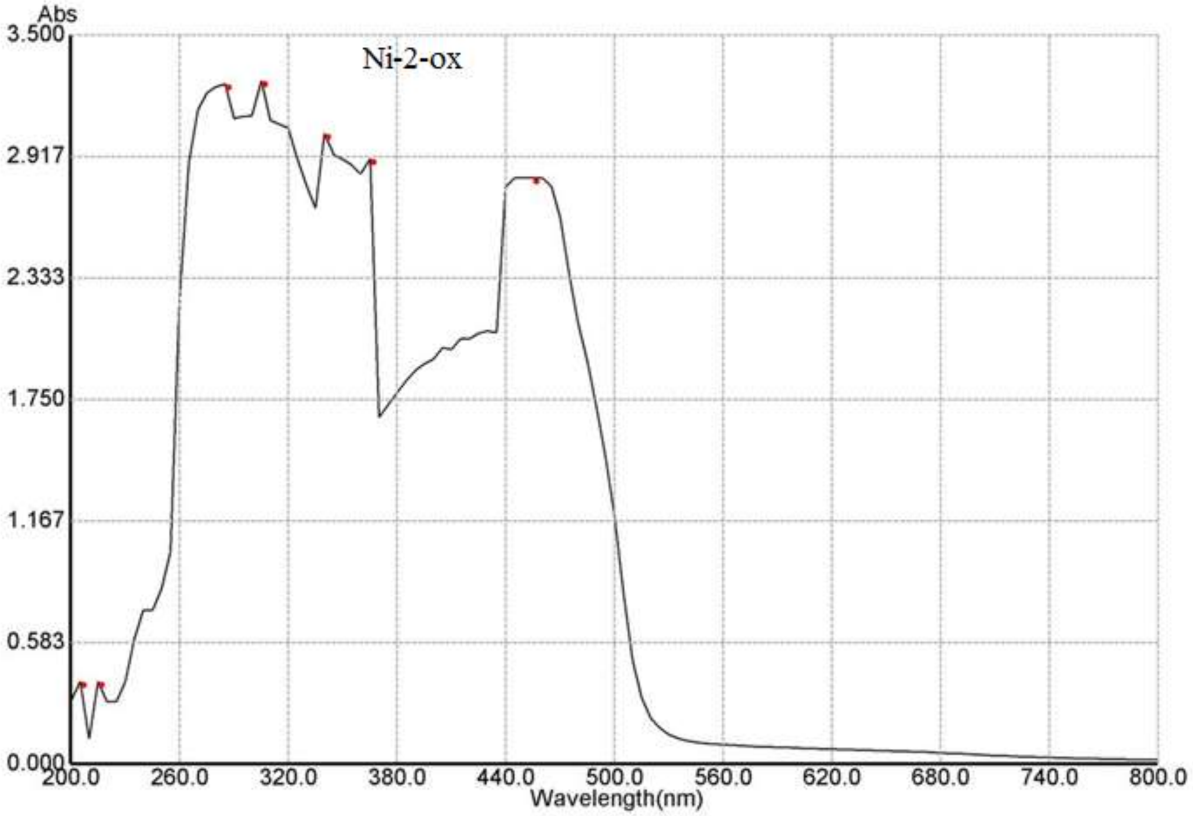
500.0
560.0
620.0
680.0
740.0
800.0
Wavelength(nm)
Ni-1-ox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0.000
Ni-2-ox
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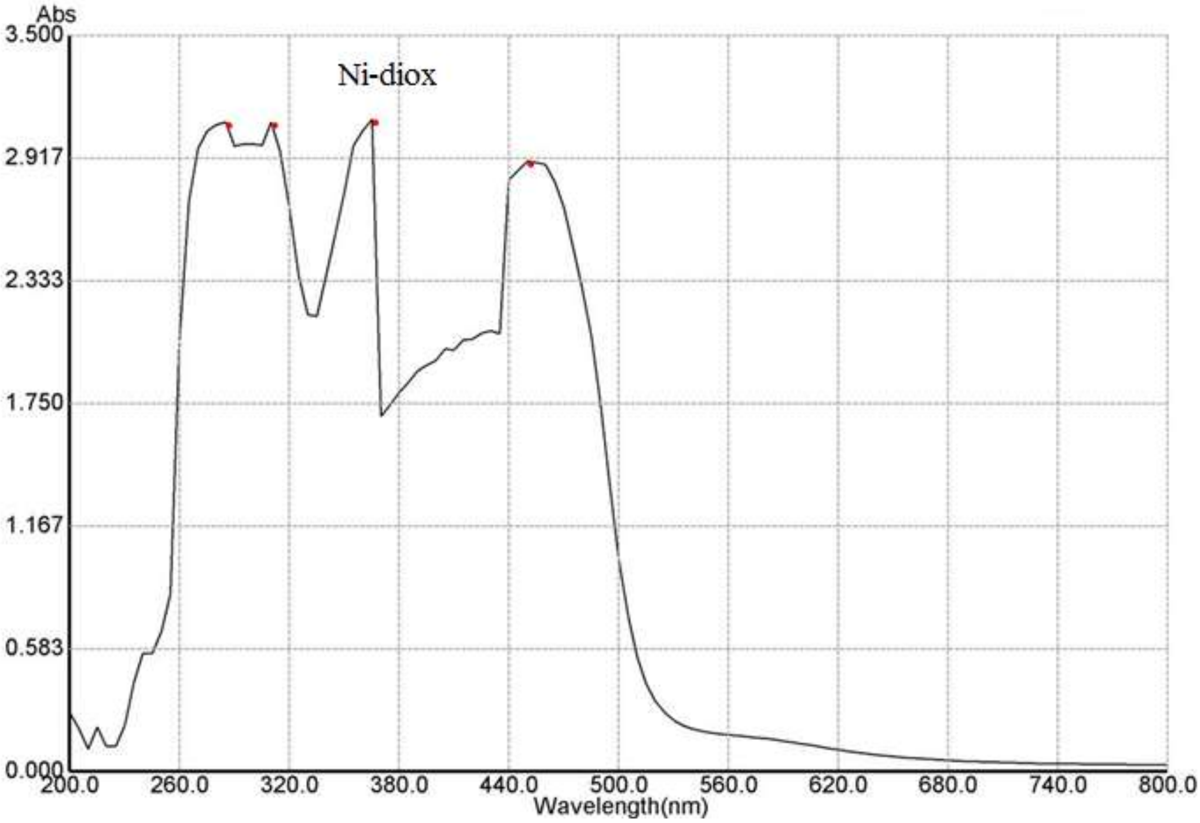
740.0
800.0
Wavelength(nm)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Ni-diox
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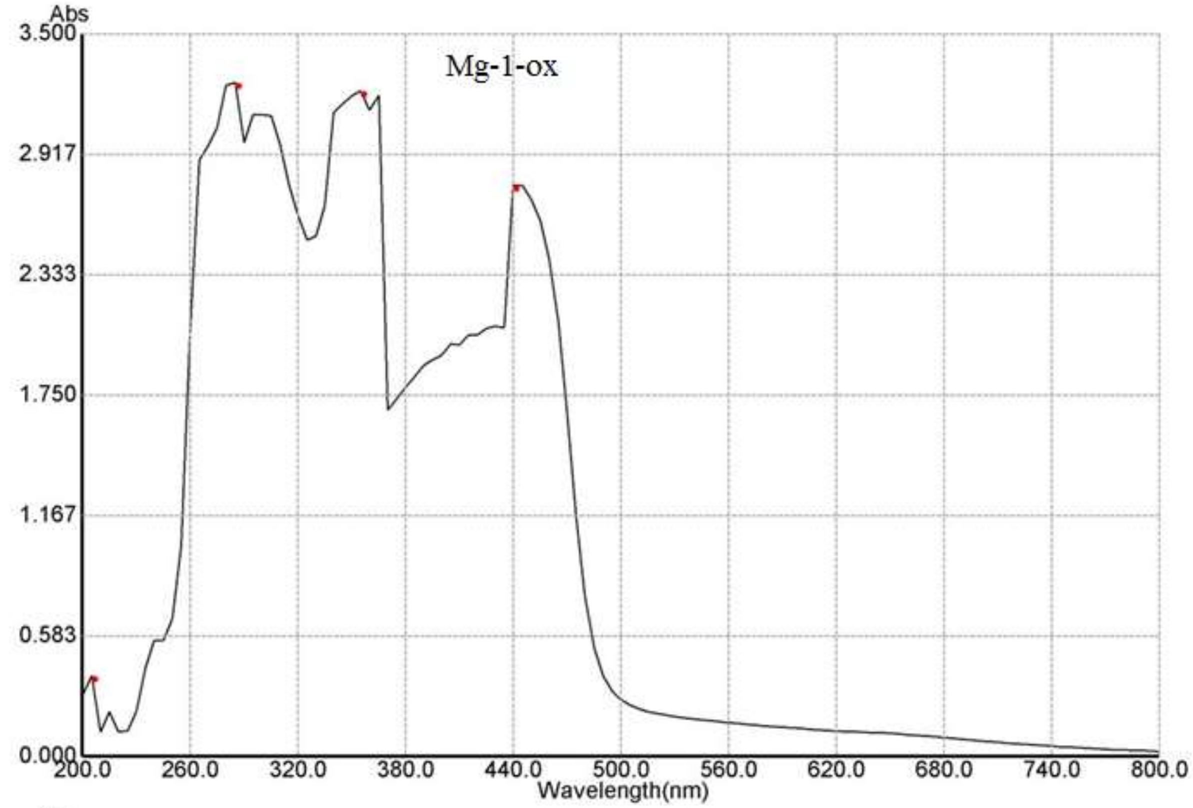
740.0
800.0
Wavelength(nm)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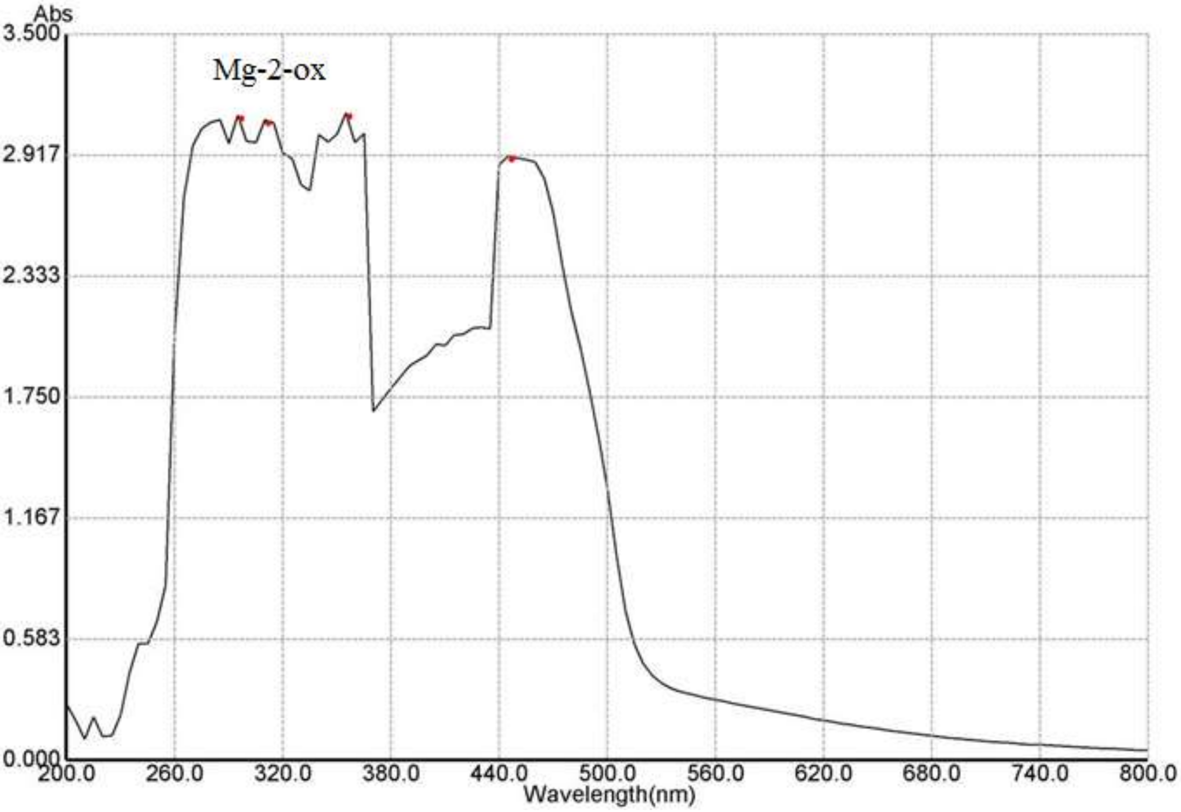
Wavelength(nm)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Mg-2-ox
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740.0
800.0
Wavelength(nm)

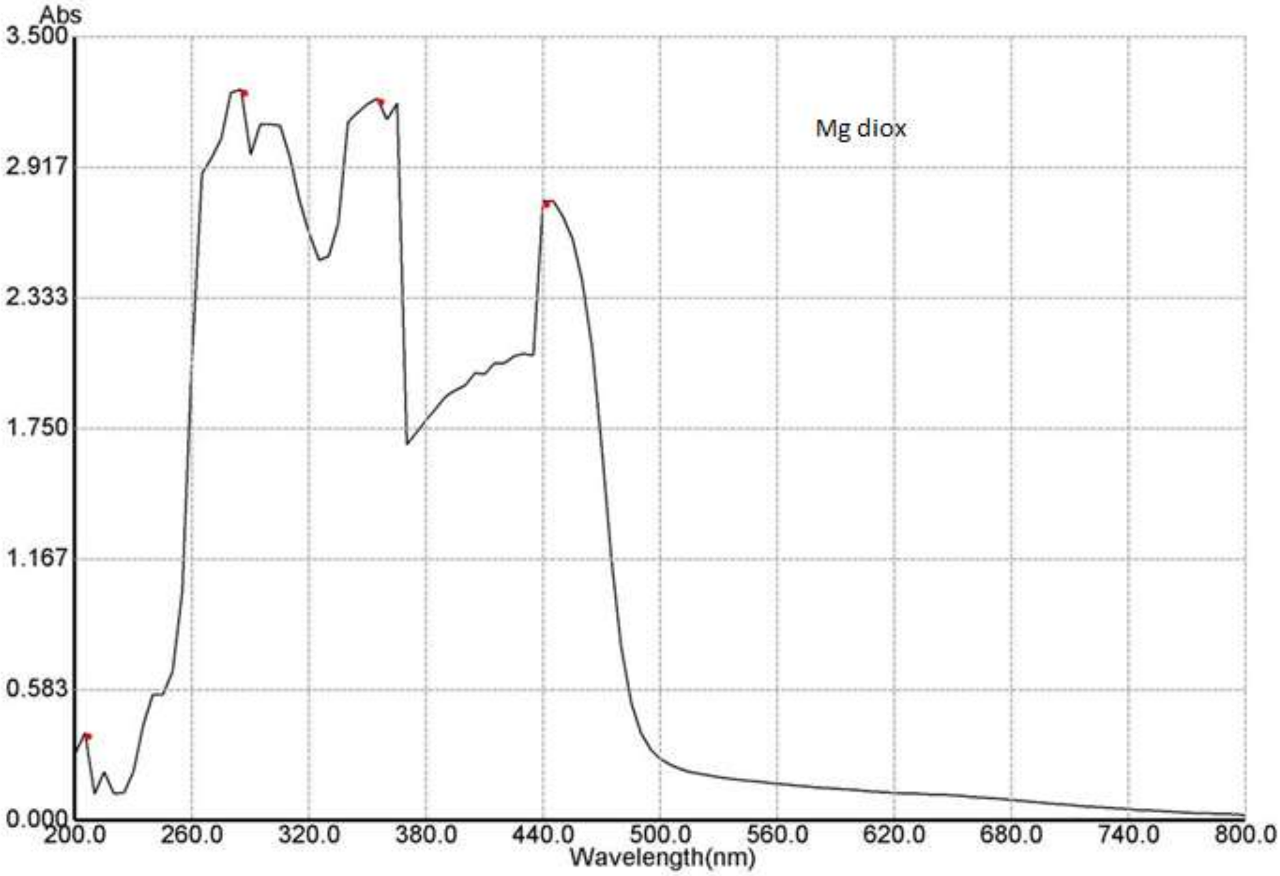


Table showing BET,QET and n-π* transition

Sr. No.	Name of Compound	B.E.T	Q.E.T.	π-π*/ n-π* transition
1.	1-oxime	240	285, 360	440
2.	2-oxime	215	285, 360	450
3.	Dioxime	215	275, 350	395
4.	Ca 1-ox	215	285, 305	375, 460
5.	Ca 2-ox	--	285, 350	450
6.	Ca- diox	215	285, 365	450
7.	Mg 1-ox	205	285,365	440
8.	Mg 2-ox	--	295, 365	445
9.	Mg diox	240	285	435
10.	Cu-1-ox	240	280, 365	495

11.	Cu 2-ox	--	285,345	445
12.	Cu diox	240	280	480
13.	Ni 1-ox	---	365	380
14.	Ni 2-ox	--	365	439
15.	Ni diox	--	360	300

Spectra of ligands

It is convenient interpret the electronic spectra of the naphthoquinone derivatives as well as their metal chelates in terms of BET, QET and n-π* transitions. Therefore these are discussed under three categories:

i) Benzenoid Elecronic Transitions (BET)

These are given in as expected this BET is the first intense band which is region of 200-240 nm. This band is closer to 1, 2-naphthoquinone-2-oxime and in case of 1, 2-naphthoquinone-dioxime and 1, 2-naphthoquinone-1-oxime is observed at 240 nm.

ii) Quinonoid Electronic Transitions (QET)

These are given in the second important band attributed to QET is showing surprisingly unexpected trend. This band is observed at 285 nm in 1, 2-naphthoquinone-1-oxime and 1, 2-naphthoquinne-2-oxime.

iii) n-π* transitions

This is most important and significant bands observed in the spectra of the three oximes. They show maximum variation as a result of isomerism as well as change of donar system.

A comparison of spectra of chelate the spectra of their ligand show that there is a general resemblance between the spectra. Thus all these spectra consist of three principle bands. The first being due to the BET, the second due to the QET and last band expected to occur due to mixing of n-π*, d-d transition and charge transfer transition as a result of chelation with the metal ions. Following are comparable changes observed.

Spectra of the chelates

A) Ca (II) 1, 2NQ oximates

In ca-1-oximate, the BET band is observed at 215nm. This band was shifted to lower wavelength, hence blue shift was observed. QET band was observed at 285nm in Ca-1-oximate. The broad band n-π* is observed at 460 nm which was shifted to higher wavelength (440 nm) after chelation and red shift observed.

In Ca-2-oximate, BET was not observed. QET band is observed at 350nm. This band is shifted to lower wavelength (360nm), blue shift observed. n-π* band was observed at 450nm in ca-2-oximate.

Ca (II)-dioximate, BET band observed at 215nm, bands was shifted to lower wavelength. In case QET band was observed at 365nm, it shifted to higher wavelength. n-π* bands also showed red shift.

b) Mg (II) 1, 2 NQ oximates

In Mg-1-oximate, the BET band is observed at 205 nm. This band was shifted to lower wavelength, hence blue shift was observed. QET band was observed at 365nm in Mg-2-oximate, hence showed red shift after chelation. The broad band n-π* was observed 440nm at in Mg-1-oximate.

Mg (II) 2-Oximate, the BET band was not observed. In Mg (II) 2-Oximate, the QET band at 365 nm was changed after chelation. This band was also shifted to lower wavelength (360 nm). Hence there is a blue shift as a result of chelation.

Mg (II)-dioximate, BET band observed at240nm, there is no effect after chelation. In case of QET band was observed at 285nm, it shifted to lower wavelength. n-π* bands no change after chelation.

c) Cu (II) 1, 2-NQ oximates

As BET was observed at 240 nm, in Cu (II) -1-oximate, hence that no change after chelation. QET and n- π* bands were found in ligand and Cu (II) 1-oximate suggesting change after chelation. The broad band formation takes place due to d-d and L-M overlapping.

In Cu (II) 2-Oximate, the BET band is not observed. In Cu (II) 2-Oximate, the QET band at 345 nm was changed after chelation. This band was also shifted to lower wavelength (341nm). Hence there is a blue shift as a result of chelation.

In Cu (II) 2-Ox, a band of medium intensity was observed at nm and for 1, 2 Naphthoquinone 2-oxime it is at 472nm, which was attributed due to n-π*, d-d transition .This band is shifted to higher wavelength. Hence red shift was observed after chelation.

In Cu (II)-Dioximate, BET band was observed at 240 nm. The QET band observed in 1, 2-naphthoquinone-dioximate at 280 nm which was shifted to lower wavelength after chelation. Hence change in band position after chelation and red shift was observed.

The broad band is observed at 440 nm for Dioxime and is shifted to 480 nm for Cu (II) dioximate. It is again due to mixing of n-π* transition, d-d transition and L-M charge transfer.

d) Ni (II) 1, 2 NQ oximates

BET band was not observed in Ni (II)-1-oximate. In case of QET band 1, 2-naphthoquinone-1-oxime showed at 360nm and Ni (II)-1-oximate observed at 365nm. There is slight change is observed. It showed red shift.

Ni (II)-2-oximate, the BET band is not seen. The QET band is observed at 365nm in Ni (II)-2-oximate. Higher wavelength observed in oximates after chelation.

Ni (II) dioximate, BET band is not observed. There is no change is observed in QET and n-π* band after the chelation.

4.4.7.3. Conclusions

The important conclusion of this work may be summarized as follows:

i. Effect of chelation as well as position isomerism is clearly seen on the band position, intensity and shape of the BET, QET and n-π* transition and hence on the molecular energy level of the chelates.

ii. As the chelates are insoluble in water but soluble in aprotic solvent like DMSO and DMF.

iii. After chelation, in addition to π-π*, n-π* transition, new bands due to d-d and L-M are also added in the third band. Since they are overlapping on each other, it is difficult to differentiate from each other.

4.4.8. Magnetic measurement

4.4.8.1. General

The measurement of para magnetic susceptibilities of the synthesized rare earth chelates; in solid state, where done at room temperature by using Faraday's technique.

All the chelates were carefully dried before the measurement and these were taken in a glass tube (10cm height and 0.3 cm diameter.). The measurement of apparent change in weight of glass tube after applying the magnetic field from the magnet were taken on Faraday's magneto-chemical balance with a permanent magnetic field of 7000 gases. The glass tube used for this purpose was calibration and the tube constant was determined by using Tris (Ethylene diamine)-nickel (II) Thiosulphate ($Ni\ (en)_3$). S_2O_3) as the standard solid. The appearent change in the weight was measured for three different packing of about 1.2 mm height each time. The average mean value $\Delta w/m$ was used for calculating the magnetic susceptibilities.

The molecular paramagnetic susceptibilities were finally corrected for demagnetization of the atom present in the ligands by use of literature value of the pascal constant.

The molar paramagnetic suspcetibilies were determined from molar magnetic susceptibility. Using the value of molar paramagnetic susceptibility, the corresponding value of the paramagnetic moment has been calculated. Magnetic moments of all the chelates are calculated from the paramagnetic susceptibilities after applying the necessary corrections for diamagnetism. The experimental paramagnetic susceptibilities obtained in this way and the magnetic moments obtained from it are given in tables

4.4.8.2. Observations

Magnetic susceptibilities of the rare earth chelate of Gd (III) and Sm (III) 1, 2-naphthoquinone oximes. The given is representative example.

Table 1

Name of the chelate	Weight of sample(g)	Weight of sample in magnetic field	Change in weight Δw	Mean Δw
Sm(III) 1,2-naphthoquinone- 1-oximate	0.00895	0.01040	0.00145	0.00175
	0.01370	0.01515	0.00145	
	0.01665	0.01900	0.00235	
Sm(III) 1,2-naphthoquinone- 2-oximate	0.00570	0.00695	0.00125	0.00115
	0.00620	0.00705	0.00085	
	0.00710	0.00845	0.00135	
Sm(III) 1,2-naphthoquinone dioximate	0.01400	0.01615	0.00215	0.00215
	0.01705	0.01905	0.00200	
	0.02225	0.02455	0.00230	
Gd (III) 1,2-naphthoquinone-1-oxime	0.00350	0.01265	0.00915	0.00960
	0.00380	0.01245	0.00865	
	0.00475	0.01575	0.01100	
Gd (III) 1,2-naphthoquinone-2-oxime	0.00265	0.01155	0.00890	0.01058
	0.00315	0.01375	0.01060	
	0.00375	0.01600	0.01225	
Gd (III) 1,2-naphthoquinone-dioxime	0.00350	0.01615	0.01265	0.01532
	0.00440	0.02005	0.01565	
	0.00560	0.02325	0.01765	

Table 2

Magnetic moment (in B.M.) of the rare earth chelates of 1, 2-naphthoquinone-1-oxime at room temperature

Name of chelates	Molecular weight (M)	(X10^{-6})	(X10^{-6})	(X10^{-6})	B.M.
Sm(III) 1,2-naphthoquinone-1-oximate	666.35	1.513	1008.18	1314.89	1.77
Sm(III) 1,2-naphthoquinone -2-oximate	666.25	2.06	1377.34	1684.05	1.812
Sm(III) 1,2-naphthoquinone-dioximate	708.35	1.39	980.56	1323.00	1.776
Gd(III) 1,2-naphthoquinone-1-oximate	673.25	25.609	17241.25	17544.96	6.45
Gd(III) 1,2 – naphthoquinone-2-oximate	673.25	36.97	24896.25	25193.96	7.75
Gd(III) 1,2-naphthoquinone-dioximate	715.25	37.97	27160.04	27499.48	8.10

5.4.8.3. Result and discussion:

The two rare earth metal under the present study

i. The chelates of Sm (III) with 1, 2-naphthoquinone-1-oximates, 1, 2-naphthoquinone-2-oximates and 1, 2-naphthoquinone-dioximates show nearly the same value of magnetic moment. Thus there is no significant impact of isomerism and donar system.

ii. The chelates of Gd (III) with 1, 2-naphthoquinone-1-oxime, 1, 2-naphthoquinone-2-oxime and 1, 2-naphthoquinone dioxime showed quite different value of magnetic moment. This indicates significant impact of isomerism as well as donar system.

4.4.9. Catalytic activity

Traditionally, industrial catalysts have been classified as homogeneous and heterogeneous. Metal complexes and organometallic compounds are the important homogeneous catalysts. The development of the science and practice of catalysis has opened up new vistas for the fast and selective production of desired chemical molecules [63-64]. Catalyst technology has become all pervasive in our society and includes in its domain enzymes (biocatalysts), pharmaceuticals, petrochemicals, energy, plastics and fibers [65-66].For this reason, immobilization of metal Schiff base complexes on organic or inorganic polymers and inorganic supports has been widely reported [67-68].

Oxidation of benzyl alcohol to benzaldehyde is an industrially important reaction. Benzaldehyde is a versatile chemical intermediate widely used in the manufacture of pharmaceuticals, perfume and flavoring chemicals [69].

Several research groups have developed different catalytic methods for oxidation of benzyl alcohol to benzaldehyde. However, only few references with useful heterogeneous catalysts for oxidation procedures have been reported [70-71]

Copper(II) complex with a tridentate imine, was revealed an efficient catalyst for oxidation of phenol, cyclohexene, styrene and benzyl alcohol using hydrogen peroxide and tert-butyl hydroperoxide as oxidant in homogeneous reaction [72-74].The Schiff base complexes have been used as catalysts in the epo-oxidation reaction [75-79].

The simple method for the preparation of heterogeneous Schiff base catalyst consisting metal complexes heterogenized on silica matrix. The prepared material was tested as a catalyst on oxidation of benzyl alcohol to benzaldehyde and benzoic acid (Dagade et. al.).

.4.4.9.1. Preparation of silica composites

One mole TEOS was mixed with 4 mol of ethanol, 4 mol of distilled water and stirred for 0.5 hrs, 0.01mol hydrochloric acid (HCl, 37 wt % in water) was added into the solution and then the solution was stirred at room temperature for 1 hrs and dried in 600°C for 2hrs.

4.4.9.2. Preparation of heterogenized 1, 2-naphthoquinone oxime complex catalyst:

Silica composite was activated by refluxing in concentrated hydrochloric acid and then washed thoroughly with deionised water and dried before undergoing chemical surface modification. Hydrated silica was then added to metal complex solution (1 gm in 10 ml of DMSO) and the mixture was stirred over night. The solvent was removed by water bath at 70ºC temperature. Then resulting product was washed with alcohol and water until the colourless filtrate obtained. Further drying of solid product was carried out in an oven at 80ºC for 8 hrs [80].

4.4.9.3. Catalytic reaction on silica based ligand and metal complexes:

Oxidation of alcohol was performed at various parameters in presence of catalyst (ligand/ complexes) and hydrogen peroxide as an oxidant. To the catalyst (0.1mmol) was added the substrate benzyl alcohol (1mmol) and then hydrogen peroxide (10mmol) (30%) was slowly added. Reaction mixture was stirred until the TLC pointed out the reaction was completed. Reaction mixture was also analyzed by using Gas Chromatography.

Reaction was studied at different parameters such as effect of temperature, effect of different catalysts, effect of molar ratio, effect of catalyst, and reuse of catalyst.

We were studied varied different parameter with oxidation reaction such as effect of temperature, Effect of Molar ratio, Effect of Different catalyst, Effect of amount of catalyst and effect of reuse and recycle of catalyst.

4.4.9.4. Effect of temperature

Sr. No.	**Temperature**	**% Conversion**	**%Selectivity for Benzaldehyde**	**% selectivity for Benzoic acid**
1.	100^0C	25.31	67.16	32.75
2.	120^0C	39.37	74.49	25.50
3.	140^0C	29.89	63.26	36.70

Benzyl alcohol= 1mmol, catalyst 0.1mmol, 30 % H_2O_2= 10mmol. Ren. time=4h

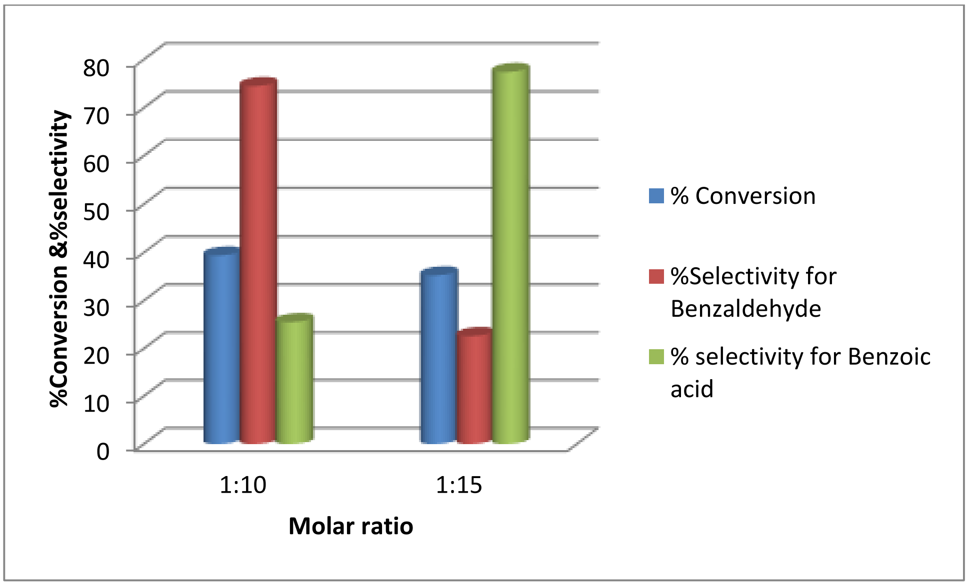
Here, conversion of benzyl alcohol was varied at different temperature as shown in table. As the temperature increased from 100^0C to 140^0C, the conversion increases and after temperature 140^0C it start decreasing with formation of by-products and other unidentified product in traces. The results of oxidation of benzyl alcohol with copper 1, 2 Naphthoquinone oxime metal complexes supported over silica using hydrogen peroxide (30%) as an oxidant at various temperatures with Benzaldehyde as a major product and Benzoic acid as a minor product. It showed that at 120^0C the conversion and selectivity were higher with no other by products, but at lower temperature it showed low conversion. The optimum temperature for benzyl alcohol oxidation with hydrogen peroxide catalysed by silica supported Schiff base complexes was 120^0C.

4.4.9.5. Effect of Molar ratio

To determine the effect of H_2O_2 (30%) on the oxidation of benzyl alcohol to Benzaldehyde, benzyl alcohol : H_2O_2 molar ratio varied from 1:10 and 1:15 mmol and keeping other parameter fixed such as catalyst, temperature 393K and reaction time (4h). The results were shown below in the form of bar diagram. A benzyl alcohol to H_2O_2 molar ratio of 1:10 resulted with conversion 39.37%, with increase in selectivity of Benzaldehyde and when benzyl alcohol to H_2O_2 molar ratio was changed to 1:20, conversion increased to nearly 35.24%, but selectivity of Benzaldehyde deceases. This indicated that as the concentration of H_2O_2 increases it oxidises benzyl alcohol to higher selectivity for benzoic acid and less selectivity for Benzaldehyde.

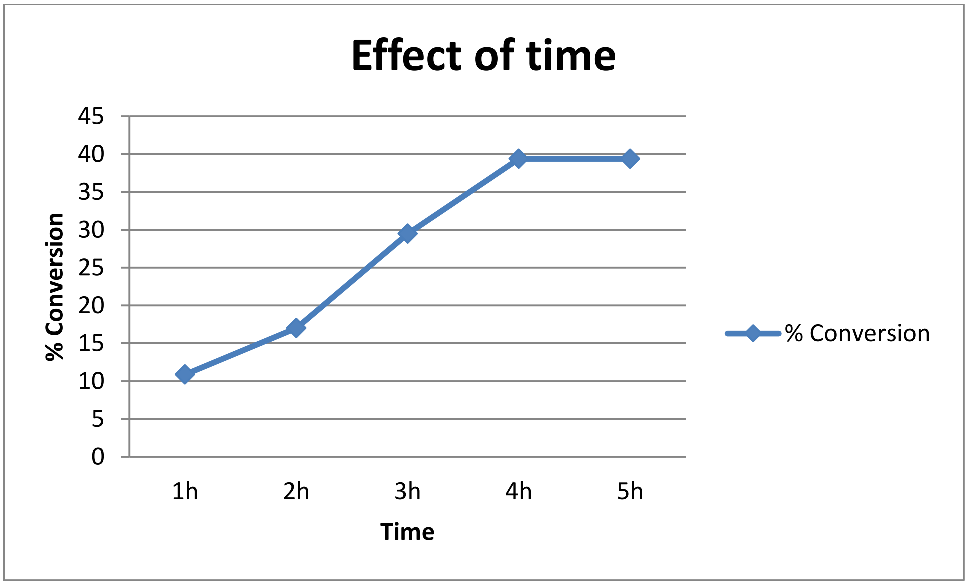
Sr. No.	**Molar ratio**	**% Conversion**	**%Selectivity for Benzaldehyde**	**% selectivity for Benzoic acid**
1.	1:10	39.37	74.49	25.50
2.	1:15	35.24	22.60	77.40

Catalyst 0.1mmol, Temperature-120^{0}CRen.time=4h



4.4.9.6. Effect of time

The reaction profile during the oxidation of benzyl alcohol with hydrogen peroxide over Copper 1, 2 Naphthoquinone 1-oximate catalysts has been studied. The variations of reaction products with time are measured and the results are shown in Fig. The conversion rate of Benzyl alcohol in the first 3 h has low, it was observed from Figure 3 that with an increase in period of reaction, the conversion of benzyl alcohol also increased and the selectivity towards the three products is varied with reaction time. Initially the selectivity to benzaldehyde and benzoic acid was high. The formation of benzaldehyde increased substantially at prolonged reaction and at the same time selectivity of benzoic acid is decreases. These results suggest that further oxidation of alcohol is taking place with time to yield more benzaldehyde, a stable oxidation product.



Benzyl alcohol= 1mmol, 30 % H_2O_2= 10mmol. , Catalyst 0.1mmol, Temperature-120^0C.

4.4.9.7. Effect of Different catalyst

Sr. No.	**Catalyst**	**% Conversion**	**%Selectivity for Benzaldehyde**	**% selectivity for Benzoic acid**
1.	1-oxime	15.83	48.06	51.88
2.	Ca-1-oximate	28.01	63.25	36.38
3.	Mg -1-oximate	24.34	50.94	23.50
4.	Cu-1-oximate	39.37	74.49	25.50
5.	Ni-1-oximate	30.37	66.90	33.05

Benzyl alcohol= 1mmol, 30 % H_2O_2= 10mmol. , Catalyst 0.1mmol, Temperature-120^{0}CRen.time=4h

In oxidation reaction of benzyl alcohol, we were use as a catalyst i.e., 1-oxime, Ca-1-oximate, Mg-1-oximate, Cu-1-oximate and Ni-1-oximate. A ligand used as catalyst which gave the lower conversion of benzyl alcohol with benzoic acid as major product and Benzaldehyde as minor product, while reaction with metal complexes as catalyst gave Benzaldehyde as major product. The metal complexes showed higher catalytic activity as compare to the ligand. The results were shown in table 1.

The conversion of the benzyl alcohol with Copper 1, 2-naphthoquinone-1-oximate complex supported on silica catalyst showed 39.37% and selectivity for Benzaldehyde was 75%, comparatively higher than other catalysts. These results indicated that among all the 1, 2-naphthoquinone-1-oxime catalyst, Copper 1, 2 naphthoquinone-1-oximate catalyst was an effective catalyst for oxidation of benzyl alcohol by using hydrogen peroxide as an oxidant. The activity of Naphthoquinone oxime complexes of these transition metals showed significant improvements on their immobilization on silica support.

4.4.9.8. Effect of amount of catalyst

The reaction of oxidation of benzyl alcohol to benzaldehyde was carried out by using various amounts of catalyst using H_2O_2 as oxidant and following table showed the results.

Sr. No.	**Amount of catalyst**	**% Conversion**	**% Selectivity for Benzaldehyde**	**% Selectivity for Benzoic acid**
1.	Without catalyst	9.38	44.13	55.65
2.	0.2 gm	39.37	74.49	25.50
3.	0.4 gm	39.36	74.49	27.90

Benzyl alcohol= 1mmol, 30 % H_2O_2= 10mmol. , Temperature-120^0CRen.time=4h

Oxidation of benzyl alcohol was carried over various amounts of copper 1,2 Naphthoquinone 1-oxime complexes with molar ratio was 1:10 mmol of benzyl alcohol to aqueous H_2O_2 at 120^0C. The effect of amount of catalyst was studied over Copper 1, 2 Naphthoquinone 1-oxime complex catalyst which increases conversion of benzyl alcohol. The selectivity of Benzaldehyde also depends upon the amount of catalyst used in catalytic reaction. The maximum conversion was 39.37 % with 0.2 gm of catalyst. As the amount of catalyst was increased the conversion of benzyl alcohol decreases, selectivity was also decreased. It is concluded that the best result of oxidation of benzyl alcohol were obtained with 0.2 gm of catalyst.

On the other hand, in the presence heterogeneous 1, 2-Naphthoquinone oxime catalyst the catalytic performance for the reaction was effectively improved.

4.4.9.9. Reuse and recycle of the catalyst

We were use of 1, 2-naphthoquinone oxime and complex catalyst twice of reaction, more environmental friendly method for the use of catalyst. In a typical experiment, the solid catalyst was washed several times with acetone. The procedure was repeated several times and then the catalyst was recovered, catalyst was reused under same conditions as the first reaction.

The stability of the supported catalyst was monitored using multiple sequential oxidation of benzyl alcohol with hydrogen peroxide. After the catalysts were reused, the benzaldehyde yield was still 75%. These supported complexes can be reusable and active heterogeneous catalyst in the oxidation of primary and secondary alcohols with hydrogen peroxide. An efficient catalytic oxidation procedure that allows the transformation of simple alcohol onto carbonyl compounds has been described in this study.

4.4.9.10. Conclusion:

- We have successfully prepared 1, 2-naphthoquinone oxime complexes impregnated on silica and investigated their performance as catalysts in the oxidation of Benzyl alcohol to benzaldehyde and benzoic acid using H_2O_2 as oxidant.
- These studies have clearly demonstrated that 1,2-naphthoquinone oxime complexes of transition metals supported on silica were versatile and efficient catalysts for reactions of commercial importance and suitable to catalyze various acid catalyzed reactions under mild conditions.
- Among, with other catalysts, Copper 1, 2-naphthoquinone- 1-oximate complex catalyst gave good conversion with higher selectivity, has been successfully utilized for the catalytic oxidation of benzyl alcohol.
- The imperative role played by various reaction parameters has optimum value in order to acquire maximum activity.
- The present catalytic system is environmentally benign, economical and non-corrosive. Catalytic activity of the complex indicated that Copper 1, 2-naphthoquinone oximates complex gave maximum conversion, was carried out by changing the different parameter like reaction time, reaction temperature and amount of oxidant. Further research and developments in the area of 1, 2-naphthoquinone oxime complexes transition metal ions would be highly useful to industries and academia.

5.0 References

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Publication

1. Comparative study of 1, 2 Naphthoquinone oximes and their Cu (II) metal chelates
   V. V. Dhapte*, J. M. Deshmukh, S. P. Dagade, Vividha Dhapte
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5. Synthesis, characterization and antimicrobial investigation of Zinc (II) 1, 2-naphthoquinone oximates
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   ICC 2013 Dharwad, International Chemistry Section