179

REACTIVITIES OF DILITHIUM AND DISODIUM TETRAISOPROPOXONICKELATES(II) WITH CARBON DIOXIDE AND CARBON DISULPHIDE

BY
TESFAHUN KEBEDE

A THESIS
SUBMITTED TO THE SCHOOL OF
GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE
REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

JUNE, 1989

179

REACTIVITIES OF DILITHIUM AND DISODIUM TETRAISOPROPOXONICKELATES(II) WITH CARBON DIOXIDE AND CARBON DISULPHIDE

BY
TESFAHUN KEBEDE

A THESIS
SUBMITTED TO THE SCHOOL OF
GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE
REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

JUNE, 1989

REACTIVITIES OF DILITHIUM AND DISODIUM TETRAISOPROPOXONICKELATES(II) WITH CARBON DIOXIDE AND CARBON DISULPHIDE

BY

TESFAHUN KEBEDE

A THESIS
SUBMITTED TO THE SCHOOL OF
GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE
REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

JUNE, 1989

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

REACTIVITIES OF DILITHIUM AND DISODIUM TETRAISOPROPOXONICKELATES(II) WITH CARBONDIOXIDE AND SOME OTHER π-ACIDIC LIGANDS

by

Tesfahun Kebede

Chemistry Department

Science Faculty

Approved by:

Dr. W. Kalies Advisor	Wolfgang Kalies
Dr. Negussie Retta Advisor	
Dr. M.F. Iskander External Examiner	M. Iskander
Dr. B.S. Chandravanshi Examiner	BS Chandravanshi
Dr. Fikru Taffesse Examiner	Fikru Tafesse

To my Wife, Asegedech Kabtimer, for understanding my deepest desire for further education and making it possible.

ACKNOWLEDGEMENT

I am most greatful to my advisors, Dr.W.Kalies And Dr. Negussie Retta for their skillful advices and encouragement throughout the course of the project. I appreciate their special concern and systematic ways of solving problems which were indispensable for the progress of the work. I am particulary indented to Dr. W. Kalies for providing me with reprints of inaccessible journals and other useful materials by making corrspondance.

My deep appreciation also goes to Ato Kiros Habtegabrael for kindly sharing his rich experience in the most difficult job of handling materials in an inert condition.

I am most thankful to Dr.B.S.Chandravanshi; to Ato Ghirma Moges and to Ato Negussie Negash for helpful discussions and analytical services they offered.

My gratitude also goes to Ato Abdu Detango for creative modification of glasswares used for handling moisture sensitive compounds. My thanks are due to Ato Sahle Demei; Ato Naod Kebede; W/t Yordanos Woldu and their colleagues for their services. My thanks are also due to the analysts Ato Fissehaie Derso and his colleagues of plant protection laboratory of the ministry of Agriculture, for recording the infrared spectra; and to W/t Elizabeth Kebede of the Biology Department for running the

flame photometer.

It is a pleasure to thank may heartly friend Ato Demelash Megerssa for encouragement and facilitating success in my studies. My deepest appreciation also goes to Ato Endale Befkadu and W/O Ethiopia Belay for nicely typing and preparing the thesis into a useful document.

I am most greatful to all administrative and academic staff members of Ethiopia Tikdem No. 1 Senior Secondary School for their encouragement. All my friends and colleagues who helped me in any way are also acknowledged.

I also take the opportunity to acknowledge the Swedish Agency for Research Cooperation with Developing countries (SAREC) for the financial assistance obtained through Ministry of Education.

TABLE OF CONTENTS

ABBREVIATIONS

acac	acetylacetonate anion
Bu	butyl
s-Bu	secondary butyl
t-Bu	tertiary butyl
COD	1.5- Cyclooctadiene
cy	cyclo - C_6H_{11}
DME	1.2- dimethoxyethane
dppe	1.2- bis (diphenyl phosphino) ethane
Et	ethyl
Hex	hexyl
OiPr	isopropoxide
iPr	isopropyl
$iPrOCO_2^-$	isopropyl carbonate anion
$iprOCS_2^-$	isopropyldithiocarbonato anion (or isopropylxanthato anion)
m	medium
Me	methyl
M	metal atom
Ph	phenyl
Pr	propyl
R	alkyl group
vs	very strong
s	strong

w	weak
THF	tetrahydrofuran
PPh_3	triphenyl phosphine
VIS	visible spectra
IR	infrared Spectra
NMR	nuclear magnetic resonance
PMe_3	trimethylphosphine
Cp	η^5- C_5H_5
Cp*	η^5-C_5Me_5
tetren	tetraethylene diamine

ABSTRACT

The reactions of the novel alkoxides of nickel (II), $Li_2Ni(OiPr_4.3THF$ and $Na_2Ni(OiPr)_4.2THF$ with CO_2 gave the first alkyl carbonato complexes of NI(II), Viz, $Li_2Ni(O_2COiPr)_4.2THF$ and $Na_2Ni(O_2COiPr)_4.2THF$. The analogous reactions with CS_2 instead of CO_2 gave the corresponding isopropyl xanthato derivatives: $Li_2Ni(S_2COIPr)_4.2THF$ and $Na_2Ni(S_2COiPr)_4.2THF$. The last product was also obtained by reaction of $Na_2Ni(O_2COiPr)_4.2THF$ with CS_2.

These isolated products were characterized on the basis of elemental ananlyses. electronic and IR Spectra. Octahedral sturctures are proposed for nickel (II) compexes containing unidentate and bidentate modes of coordiantions for the isopropyl carbonato ($iPrOCO_2^-$) and isopropyl xanthato ($iPrOCS_2^-$) groups which are expected to be formed by insertion reactions of CO_2 and CS_2, respectively, into the Ni-OR bonds

Reactions of the products with dilute mineral acids resulted in the evolution of CO_2 and CS_2, respectively, indicating that these molecules were indeed inserted. In addition a THF solution of the lithium based CO_2 product was observed to show reversible colour changes under mild condiiton and CO_2 atmosphere suggesting that "insertion-deinsertion" processes can occur repeatedly without any decomposition of the product.

Prelimianry survey was also carried out to tudy the

1. INTRODUCTION

The fixation of carbon dioxide by green plants using solar energy is the most important chemical process observed on Earth. In photosynthesis, CO_2 is reduced by H_2O into Carbohydrates with sun light as the energy source (eq. 1):

$$CO_2 + H_2O \xrightarrow{h\nu} CH_2O + O_2 \qquad (1)$$

It is this photoreduction of CO_2 that serves as the only source of food, there by energy, for the entire world of the animal kingdom and for certain microorganisms which, by themselves, are incapable of utilizing CO_2 as the source of carbon.

The total amount of CO_2 in the atmosphere and in the ocean is estimated to represent 10^{14} tons of carbon while carbonates make up 10^{16} tons of carbon [1]. And nowadays the gas is enormously discharged to the atomsphere as a by-product in several technical processes [2].

Understanding the fact that CO_2 is the major source of carbon in nature scientists began to study actively other types of CO_2 fixation or reduction processes so as to use the gas as a one-carbon precursor of organic chemicals. This was dated back 1828 when F. Woehler [3] prepared the first organic compound, urea, from the inorganic substances, CO_2 and NH_3.

Eversince the time of the sysnthesis of urea, a lot of other similar processes have been widely in use in industrial and organic preparations of a wide variety of products with CO_2 as a C_1 cource.

Ofcourse, the principal reaction possibilities with CO_2 are [4,5]: i) the oxidation to carbonate (CO_3^{2-}); ii) the electyrophilic attack at the oxygen atom (in protonation alkylation and complex formation); iii) the reduction to carbon monoxide, formic acid, oxalic acid, etc.; and iv) the nucleophilic attack at the carbon atom (in alcoholysis, aminolysis, carbanion attack and complex formation).

However, the problem of high thermodynamic stability of the molecule and its kinetic inertness, still remains a permanent challenge to the art of the chemist to 'force' this substrate into selective reactions, particularly at metal centers, under mild conditions.

In its reactions CO_2 is a poor electrophile and needs always to be activated by energy supply. The common means are the chemical, thermal, and photochemical activations and in some cases radio chemical methods are also used [4,5]. Using a chemical means CO_2 can thus be converted into useful forms of organic compounds but only by way of coupling it with an organic substarate. To this effect the CO_2 molecule and/or the organic precurssors have to be primarily activated by forming metal complexes or orgnometallic compounds.

In this regard two of the most important CO_2 chemical

activations are: i) the formation of metal-carbon dioxide coordination complexes and, ii) insertion of CO_2 into metal-heteroatom (H,C,N,O)bond [8]. Catalytic CO_2 insertions into organic precursors (e.g., into sodium phenolate in the Kolbe-Schmidt reaction [7] and reduction by substances like hydrogen are no less important means of CO_2 activations. In addition to these there are still other reactions such as the photochemical and electrochemical reductions of CO_2 which are at present gaining much more interest in the filed, particularly in the recently developed systems involving transition metal complexes as catalysts [3,9].

In its reaction with nucleophiles and bases, CO_2 reacts through addition at its carbon-oxygen double bond. These nucleophilic additions are the most significat CO_2 reactions particularly in the sysnthesis of different carboxylic acids. One of such reactions is the reaction with organomagnesium, compounds (Grignard Compounds [6]) involving the carboxylation of hydrocarbons via an insertion of CO_2 into R-Mg bond which may be given by eq.(2):

$$R\text{-}MgX + CO_2 \longrightarrow RCOOMgX \xrightarrow{H^+} RCOOH + MgX^+ \quad (2)$$

Thus under normal conditions CO_2 is capable of reacting with sufficiently activated groups [5,7] (for an electrophilic attack) to provide stable products. The groups usually are cabonions, or potential carbanions (as metal organylys, CH-acidic compounds); activbated aromatics

(phenols, amines); electron-rich heterocycles; activaed and electron-rich olefins, enamines, enols, endiols or O-, S-, and N-nucleophiles.

Regarding the reactions with metal organyls the overcoming of the kinetic restrictions at metal centers is still a young field of complex and organometallic chemistry. Inspite of this, the development in this field, particualry in the area of investigations of reactions at transition metal centers, which was mainly initiated by Volpin [6], is now making a rapid progress.

Despite the fact that only a few number of studies have been reported until recently, new and suprising results should be expected in this area, including development of new catalytic transformations of CO_2. This applies to both homogeneous and heterogeneous catalytic processes which are now emerging as a promising field of research.

A number of cases are found in the literative [63] concerning the reactions of CO_2 both with trasitional and non-transitional metal compounds leading either to the formation of metal-carbon dioxide coordination compounds or carboxylation products of the organometals. Besides this a comparative number of compounds are reported [1,63] for "normal" type CO_2 insertion reactions into metal-carbon bonds leading to insertion products. In this respect nickel and palladium compounds are well-known representatives of transition metal compounds that are frequently used as the most active CO_3- substrate coupling

catalysts; this behaviour however is more common with main group organometallic compounds.

A number of works have also been devoted to the reactions of CO_2 with metal-hydrides and metal amines. But with metal alkoxo complexes only very few cases are reported.

Nevertheless the reaction with the later is characterized as being a reversible insertion of CO_2 into the M-OR bond to form alkyl carbonato or mixed alkoxo-alkyl carbonato complexes of trasnsition metals such as Ti, Zr, Nb, Fe, Cu, W and No [1Ø]. These alkyl carbonato complexes have been known in their function as a new class of reversible CO_2- carriers in the carboxylation of several organic precurssors [11]. Similar cases are also known for non-transition metal, [5], among which the most prominent is magnesium metal carbonate commonly known as the Stiles-reagent. [12].

Inspite of the fact that most nickel complexes have exceptionally high catalytic activity, as is observed for many nickel containing catalytic systems, there is not even a single case reported so far referring to an alkoxo complex of nickel serving as a metal substrate for insertion of CO_2 into the Ni-OR bond. This holds true also of some other π-acidic ligands with the exception of one particular work, reported by Yamamoto [13] in which reactions occurred between an alkyl-alkoxo complex of nickel (II) (RNi(L)OR) and CO and CS_2. This has been observed for the earlier

types of alkoxides of nickel (II) [14] which are supposed to be providing only less basic centers for an electrophilic attack by the CO_2 molecule and by its likes.

However, later in 1985 a new class of alkoko complexes of nickel (II) based on alkoxo metal alkoko nickleates (II) was reported by Kalies et al [15]. In addition to their relatively more basic nature, which is imparted by the four alkoxo groups coordinated to the nickel center, these novel complexes are observed to show intramolecualr redox property which may result in the reduction of Ni(II) to Ni(I) and Ni(0). This later property of the complexs makes them reactive towards phosphines or phosphites inorder to form hydrido nickel (I) and nickel (0) lignad complexes. These typical and important properties of the new complexes of nickel (II) allow them to act as precatalysts.

Therefore, as part of the investigations on the reactivities of this new class of complexes of nickel towards π-acceptor (elctrophilic) ligands we wish to report in this work the syntheses and charactirzation of some adducts of these complexes by reactions with CO_2 and CS_2 (as π-acceptor substrates).

In view of this the following objective is set:

To investigate the reactivites of $Li_2Ni(OiPr)_4.LiBr.3THF$ and $Na_2Ni(OiPr)_4.2THF$ towards CO_2 and CS_2. To this effect the steps are:

i) Synthesize the starting complexes based on the literature procedure [15]

ii) Synthesize and isolate stable products by reactions of the above compounds with CO_2 and CS_2 and characterize them by elemental analyses and spectroscopic methods (VIS and IR).

(II) LITERATURE REVIEW

1. Transition Metal Alkoxides

1.1 General Features Of "3d" Transition Metal Alkoxides

As reported in some earlier works [14], the alkoxo group (-OR), as a ligand, is capable of forming strong covalent bonds with almost all elements and tends to act as a bridging group between similar as well as different metal atoms.

Bridging in similar atoms gives rise in coordination oligomers $[M(OR)_n]_x$ [16]. Where as bimetallic alkoxides are described as coordination compounds formed by neutralization of basic with acidic (or amphoteric) alkoxides (main group metal alkoxides are more basic than that of transition metals); in these compounds the alkoxo groups act as bridging between the different metal atoms.

A survey of the rapidly growing literature on alkoxide chemistry of the elements in the periodic table had already been compiled in a book Metal Alkoxides [17]. In the book the main focus of attention was on the main group elements and the earlier transition metals (particularly in the d^0 state), except for some work on alkoxides of $3d^{5-9}$ elements, which were investigated mainly from the points of

view of their magnetochemistry and electronic spectra. The recent development in the area of alkoxide chemistry of many other transition metals has also been reviewed in later works [14].

Metal alkoxides have, at least one M-O-C grouping which is strongly polar because of the large electronegativity of oxygen atom. The polarity of the M-O bonds is further enhanced by the type of the metal. Thus, the physical and chemical properties of metal alkoxides are determined by the polarity of their bond, and by the well-developed tendency of the coordinatively unsaturated metal atom to expand its coordination number by intermolecular bonding with oxygen. Indeed, in some circumstances, steric hinderance can preclude intermolecular bonding so that a volatile monomeric alkoxides (or mixed alkoxide-phenoxides) results at low coordination number. Jasunki and his coworkers [19] have reported that all phenoxides and alkoxide-phenoxides of silicon are monomers in benzene. Metal alkoxides are extremely susceptible to hydrolysis and required strictly anhydrous conditions for their handling [1Ø]. They react with a variety of primary, secondary and tertiary alcohols as well as phenols [18]. This property has been utilized extensively for preparing new alkoxide. An example of transition metal alkoxide which interchanges its alkoxy groups readily with primary alcohols at room temperature is[1Ø]:

$$Co(OiPr)_2 + 2ROH \longrightarrow Co(OR)_2 + 2iPrOH \quad (3)$$

R = Me, Bu

An example of transition metal alkoxide which interchanges its alkoxide group with secondary or tertiary alcohols is [14]:

$$Cu(OR)_2 + 2R^1OH \xrightarrow{\text{benzene}} Cu(OR^1)_2 + 2ROH \quad (4)$$

(R = Me, Et or Bu and R^1 = i-Pr, s-Bu, t-Bu or t-Am)

Alkoxides which undergo an interchange reaction with phenol are [14, 18]:

$$Ti(Ot\text{-}Bu)_4 + 4PhOH \longrightarrow Ti(OPh)_4 + 4t\text{-}BuOH \quad (5)$$

$$Cr(OiPr)_3 + 3PhOH \longrightarrow Cr(OPh)_3 + 3iPrOH \quad (6)$$

However, the most direct method of synthesis of alkoxides involves reaction of alcohols with a binary compound of the metal commonly the halide (chloride or bromide) according to (eq (7))

$$MX_2 \; mROH \longrightarrow M(OR)_m X_{2-m} + MRX \quad (7)$$

The other very important method is the reaction of the metal halide with an alkali metal alkoxiode given by the equation

$$MX_n + NLiOr \longrightarrow M(OR)_n + nLiX$$

(Na)

Alcohol exchange reaction and trasestrification in cyclohexane are also two of the alterative sysnthetic routes. eqs (3), (4) and eq (8) [14]

This principle has been exploited for the purpose of synthesis of a wide variety of higher alkoxides and

interesting derivaives by reaction of lower alkoxides with higher alcohols and other hydroxy ligands.

$$M(OR)_n + nCH_3COOR^1 \text{ -------> } M(OR^1)_n + nCH_3COOR \quad (8)$$

The alkoxide usually empoloyed is either i-PrO- or t-BuO- as the separation of isopropyl- and tert-butyl acetate is more readily achieved by azeotropic distitllation,

With many research activities on the alkox o derivatives of '3d' transition metals it has been possible to synthesize quite a lot of alkoxo derivatives by reactions of the alkoxides with hydroxy ligands such as silanols, glycols, β-diketones, β-ketoesters, alkanolamines, oximes, hydroxylamines, and Schiff bases as well as other reagents like organics esters, silyl esters, β-ketoamines, thiols, thio-β-dikatones, acyl halides, acid amides and acid anhydrides [14]

The transition metal alkoxides can also undergo various reactions with molecules such as CO_2, COS, CS_2, and isocynates quantitativ ely to give insertion products [10,14,18] in which the metal center is electrophilic.

1.2 Alkoxides of Nickel(II) And Their Derivatives

1.2.1 Earlier Types of Nickel(II) Alkoxides

The alkoxides of nickel(II) have been studided earlier [14] by classifying them into three types: i) the binary alkoxides of the form $Ni(OR)_2$; ii) nickel (II) tetraalkoxy

aluminates of the form $Ni[Al(OR)_4]_2$, where R=Me, Et, i-Pr, n-Bu; and iii) the mixed alkoxides of the type Ni(OR)X, where X is any other anionic group.

The alkoides of nickel(II) of types $Ni(OR)_2$ ad Ni(OR)X, have been prepared by the following reaction (e. (9) (14):

$$NiCl_2 + 2LiOR \xrightarrow[1,4\ dioxane]{ROH\ or} Ni(OR)_2 + 2LiCl \quad (9)$$

(where R= Me,Et, Pr, Bu, , iPr,s-Bu, t-Bu)

All of these alkoxides of nickel (II) are non-volatile, coloured solids, which are sparingly soluble in common organic solvents.

In the case of the binary alkoxides, the primary alkoxides are light green in colour, where as the secondary and tertiary alkoxides are blue to violet. All of these aloxides are sensitive to moisture, in the presence of which they are hydrolyzed with a sharp colur change from bule (violet) to green. All of the secondary and tertiary alkoxides are unstable towards heat and tend to decompose at around 90-100°C [10].

The spectra of primary alkoxides exhibit three well-defined spin-allowed bands [14] at 8750± 250 (Vi: $^3T_{2g}$), 14,810±115[V_2]; $^3A_{2g}$---> $^3T_{1g}$ (F)]
and 24,980± 125 cm^{-1} [V_3: $^3A_{2g}$---> $^3T_{1g}$ (P)], which are characteristic of an octahedral environment for nickel in these primary alkoxides. On the other hand, the spectra of secondary and tertiary alkoxides of nickel (II) indicate a

tetrahedral geometry with well-defined spin-allowed transitions at 7580± 100 [V_2: $^3T_1$----> $^3A_2$] & 15,850±70 cm^{-1}[v_3: $^3T_1$---> $^3T_1(P)$]

The magnetic moment of the primary alkoxides of nickel(II) fall in the range 3.45± Ø.Ø4 BM (Bohr Magneton) and those of secondary as well as tertiary alkoxides are found in the range 3.65± Ø.Ø5 BM at room temprature. These observations are also in accord with their octahedral and tetrahedal configurations respectively [1Ø,14]

It is interesting to note that nickel alkoxides undergo insertion reaction with substrates like phenyl and naphtyl isocyanates [2Ø]:

$$Ni(OR)_2 + xR^1NCO \longrightarrow (RO)_{2-x}\, Ni[N(R^1)COOR]_x \quad (1Ø)$$

R=Me and i-Pr; R^1= Ph and Naph; X=1,2

All these reactions are exothermic in benzene and their completion was indicated by the disappearance of band at ~ 2250cm^{-1} (due to-N=C=O). The appearance of an intense band~ 17ØØ cm^{-1} (due to C=O) in the addition products suggests that insertion has occured at the C=N site.

Very recently, Yamamoto reported [13] that alkyl alkoxo-nickel(II) complex ($RNi(OR^1)L$) L= phosphine or phosphite, and R,R^1 = alkylgroups) can react with a dative ligand, CO, and with a more elctrophilic reagent CS_2 via insertions into Ni-OR bonds. Regarding the insertion reaction of CO_2 into the Ni-OR bond nothing substantial has been reported to this

date. However, in one particular report [19] there was an attempt to carry out a reaction of CO_2 with $Ni(OMe)_2$ in pyridine which resulted in no possible outcome. But the same reaction in DMF/Py mixture with the corresponding alkoxide of Coper (II), $Cu(OMe)_2$, was found to give copper (II) methyl carbonate. This was assumed, according to the author, to be due to the less basiity of the nickel alkoxide for the electrophilic attack of CO_2.

The binary alkoxides, $Ni(OR)_2$ have also ben observed to undergo reactions with alcohols, halides, Ƀ-diketones and carboxylic acids by ligand exchange reactions.

It was established by Mehrotra et al. [1Ø] that primary alkoxides of Nickel (II) donot undergo alcohol interchange even under forcing condition. Whereas branched alkoxides of nickel e.g,. $Ni(OR)_2$: R=iPr, s-Bu, t-Bu, t-Am undergo facile interchange with primary alcohol even at room temprature.

On the other hand, extensive work [2Ø,21] has been carried out since 1977 on the exchange reaction of nickel alkoxides with alkanolamines, Ƀ-diketones and carboxylic acids to give the corresponding derivatives. And on the basis of IR, electron reflectance, and electron-spin resonance spectra as well as magnetic measurements, all of these derivatives of nickel alkoxides have been shown to have distorted octahedral structures.

In the case of the carboxylic acid derivatives the

monocarboxylates are tetrameric while the dicarboxylate derivatives are trimeric in refluxing benzene. The IR spectra of the later derivatives appear to suggest a bidentate nature of the carboxylate moieties in them. But still the electron reflectance and magnetic measurements indicate the same octahedral environment for nickel in all these derivatives and are non volatile colored solids, soluble in benzene but insoluble in alcohols [10]

1.2.2 The Novel Alkoxides of Nickel (ii): Alkali Metal Alkoxonickelates (II)

The synthesis and characterization of the novel alkoxides of nickel were discussed in the report on the works of Kalies and his coworkers [15]

These new alkoxides are based, according to the authors, on the lithium, sodium and potassium alkoxonickelates (II); and are shown to have different compositions and with a partially good solubility in organic solvents.

The compounds were prepared by the reaction of nickel (II) salts ($NiBr_2.2THF$; $NiBr_2$; $Ni(acac)_2$; or $NiBr_2(PPh_3)_2$) with alkalimetal alkoxides of primary, secondary as well as tertiary monovalent alcohols in aprotic organic sovents like THF and toluene The maximum tempreture for the preparation of the primary and secondary alkoxides is found to be 50°C, but 90°C for the tertiary alkoxides. Above 50°C the

alkalimetal primary and secondary alkoxonickelates (II) are found to decompose giving nickel (o) (metallic nickel), aldelydes or diketones and the corresponding alcohol. This is a result of β-hydrogen transfer from the primary or secondary alkyl group to give a Ni(H) complex and the corresponding aldehyde or Ketone followed by reductive eleimation of hydrogen under the influence of other alkoxide to give Ni(O) and the corresponding alcohol.

Magnetic moment determination using Gouy method on the tetra alkoxonickelate (II) of lithium sodium and potassium show typical tetrahedral as well as octahedral coordination. Where as the sodium isopropoxonickelate (II) is found to be nearly diamagnetic in the gorund state.

The ligand field spectrum of the isopropoxo complexes in THF as well as of the solids in nujol showed tetrahedral coordination with three spin allowed transitions. $^3T_1(F) \longrightarrow {}^3T_2(V_1)$: $^3T_1(F) \longrightarrow {}^3A_2(v_2)$ and $^3T_1(F) \longrightarrow {}^3T_1(p)(v_3)$. Ligand field parameters (Dq= 460cm^{-1}, B=800Cm^{-1}, β = 0.77m further indicted tetrahedral coordination for the isopropoxo complex.

Regarding the chemistry of these novel alkoxides of nickel much more investigation has been carried out for the last five years. The most important thing about these compounds is that they are extremely more reactive towards moisture and are more easily hydrolyzable than the former types of alkoxides of nickel.

The more basic nature of these compounds makes them capable of reacting with electrophilic reagents. Thus they are expected to be prone to the electrophilic attack by CO_2 and other π- acidic ligands. Their internal redox property has been shown to be an advantage by applying them in preperative work as precatalysts.

2.1 Complex Formation of CO_2 with Transition Metal Copmounds

2.1 General

As a linear triatomic molecule of the AB_2 type, CO_2 has a carbon atom forming two equivalent bonds with the oxygen atoms via the σ-and π-bonds, the planes of overlapping π-oribitals of oxygen and carbon being mutually perpendicular.

Carbondioxide molecule has some important functional properties (Carbon is a Lewis acid and Oxygen a Lewis base) that influence its co-ordination to metal centers. Arising from these donor acceptor properties of CO_2, there are several possibilities for complex formation with a transition metal atom [24] as shown in Fig.1.

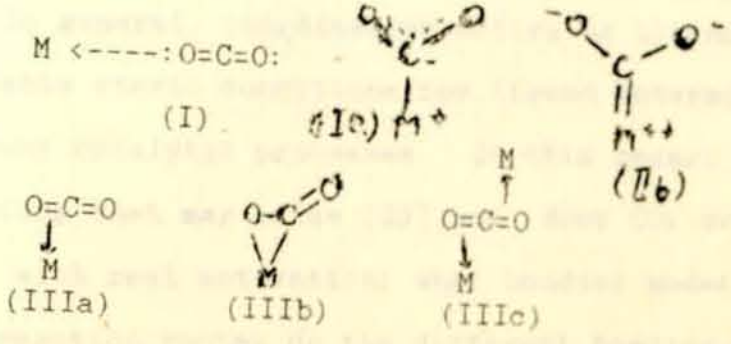


Fig. 1

Since the CO_2 molecule is the poorer electron donor and better acceptor of electrons with respect to its isoelectronic CS_2 molecule, a priori one may expect that less typical for CO_2 would be complexes of type (I) and more typical structures (II) and (III) (Fig 1)

Thus from these bonding modes of CO_2 to the metal M one can see that (Fig.1): In type (I) it is shown that coordination is through M-O bonding by transfer of the Oxygen p electrons (lone-pair) to the metal; and in type (II) a and b there is a M-C bonding through electron donation from the metal to the antibonding orbital ($2\pi u$) of CO_2. Donation of two electrons to the antibonding orbital of CO_2 in a limiting case may result in the formation of carbene-like complexes (IIb). Where as in type (III) a,b and c it is displayed here the possibilities of bonding by π-complex formations (IIIa and IIIc) or by a formation of a three-membered ring in the limiting case (IIIb).

In general, coordination activates ligands and creates favorable steric conditions for ligand interactions and numerous catalytic processes. In this regard possible questions that may arise [19] are: does CO_2 co-ordination agree with real activation: what bonding modes are possible; what reaction routes do the different bonding modes prefer; are these influenced by the nature of the metal complex?

The answers to the above questions have been considered as the basis for the investigations of the different metal-CO_2 complex formation reactions which may be grouped into two major classes: fixation and insertion reactions. However, it is not always possible to distinguish between the two classes, completely since many insertion reactions proceed Via a "fixation" intermediate. Furthermore, Tusuda and co-workers [24] in one side, Chisholm and Extine [25] on the other side separately described many systems as fixation processes but actually they are seen to involve insertion reactions. It follows that all processes in which CO_2 is bound directly to the metal center can, therefore, be described as fixation reactions, and those in which CO_2 is bound Via the breakage of a metal-ligand or internal ligand bond, as insertion reactions.

Generally reversible CO_2 fixations involve the following basic reactions [4]:

(i) Coordination: $LnM + CO_2 \longrightarrow LnM(CO_2)$ (11)

(ii) Insertion: $Ln\ M - X + CO_2 \longrightarrow Ln\ M\text{-}OC(O)X$ (12)

(iii) Oxidative coupling (metal ring closure):

$$LnM(A\text{-}B) + CO_2 \longrightarrow Ln\overbrace{M\text{-}A\text{-}B\text{-}CO}O \quad (13)$$

2.2 Reversible CO_2 Fixation Through Co-Ordination

Coordination of CO_2 to transition metals has long been thought as a reversible initial step in the catalytic conversion of CO_2 [1]. In such a case, metal basicity is an important pre requite to M-CO_2 coordination. Highly basic Ir (I), Rh(I), and Ni(0) complexes [8] have been found to cause CO_2 activation. In several cases, CO_2 seems to require a bifunctional system, i.e. acid-base for its fixation and activation. Therefore, in addition to the basic metal center, the assistance of an acidic partner is needed. For example, in a Co complex, [Co (Salen)$M^1(CO_2)$] [26] (where Salen = O-N-N-O: dianion of Substituted salicylaldehyde ethylene diamine), M^1= Alkali metalion) CO_2 is bonded through a basic (Co) and acidic (M^1) centers.

It is known that Ni(0),in general, forms stable CO_2 complexes. The complex synthesized by Aresta and his co-workers [27], [$Ni(PCy_3)_2(\eta^2\text{-}CO_2)$],was the first structure ever to be reported for a metal-CO_2 complex.

A common reaction could account for the formation of Ni(0) CO_2 complexes [8] and is given by (eg 14)

$$NiL_4 + CO_2 \underset{\longleftarrow}{\longrightarrow} NiL_2(CO_2) + 2L \quad (14)$$

for L = PEt_3, PBu_3, and $P(C_6H_{11})_3$

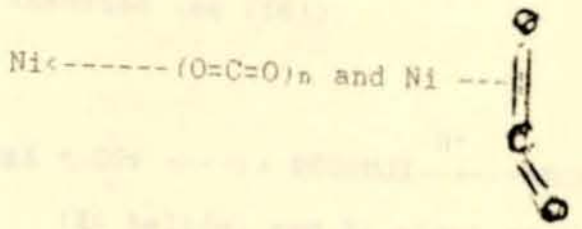
For this the suggested mechanism is (eq 15)

$$NiL_4 \underset{\longleftarrow}{\overset{\text{Toluene}}{\longrightarrow}} NiL_3 + L$$

$$NiL_3 + CO_2 \rightleftharpoons NiL_3(CO_2)$$

$$NiL_3(CO_2) \longrightarrow NiL_2(CO_2) + L \quad (15)$$

In some isolation experiments it was demonstrated that two types of nickel- CO_2 complexes could be detected [6] as shown in Fig-2 as η^1-end-on and as η^2-side-on coordinations.



(as η^1-end-on) Coordination (as η^2- side-on) Coordination

Fig.2: Modes of Coordination Of Ni-CO_2- complexes

For example, the complex $[(Cy_3P)_2Ni(CO_2)]$ [27] has side-on CO_2 coordination (established by X-ray analysis) and reacts at slightly higher temperatures with splitting of CO_2. Intermediate products of the reaction in which the binuclear complex $[(Cy_3P)_2 Ni(CO_2)Ni(PCy_3)_2]$ [28] is also formed with olefin - analogous bonding of bridge-forming CO_2 to give two nickel centers were also studied in which the complex-fixed CO_2 is not, however, active enough to be transferred to organic substractes. This was also confirmed to be true in a number of Co, Ni, Rh and Ir [1] complexes at

which reversible coordination of CO_2 takes place.

2.3. Carbon Dioxide Insertion Reactions

Carbon dioxide is reactive enough to undergo insertion into a series of metal-ligand bonds. The most common insertion reaction is found in the preparation of organic acids Via the Grignard reagent [6]

In this reaction the metal-carbon bond (Mg-R) is broken and CO_2 is inserted (eq (16)).

$$RMgX + CO_2 \longrightarrow RCO_2MGX \xrightarrow{H^+} RCO_2H \quad (16)$$

(X= halide, and R= alkyl group)

Generally, two possible insertion reactions can occur depending on the nature of the metal-ligand bond as described in eqs (17) and (18) [8]:

$$M\text{-}L + O{=}C{=}O \longrightarrow M\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}L \quad (16)$$

$$M\text{-}L + O{=}C{=}O \longrightarrow M\text{-}\overset{\overset{O}{\|}}{C}\text{-}OL \text{ or } M\!<\!\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}\!>\!C\text{-}L \quad (17)$$

L = -H, $-C<$, -O- , $-N<$

In many systems insertion is preceded by a fixation step, eq. (19):

$$M\text{-}\ddot{N}R_2 + O{=}C{=}O \longrightarrow M\text{-}\underset{\ddot{}}{\overset{O{=}C{=}O}{N}}R_2 \longrightarrow M\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\ddot{N}R_2 \quad (19)$$

The following presentation provides a brief look at

some typical insertion reactions involving M-C, M-H and M-N bonds and a detailed discussion on insertion reaction into M-O bonds particularly those reaction with transition metal alkoxides (M-OR)

2.3.1 Insertion Into M-H Bonds

Reacting with a transition metal hydride, CO_2 may insert at a M-H bond to give formato complexes, eq(2Ø). Also depending on polarity of the transition metal-hydrogen bond, a reverse and abnormal insertion may offer metal-formic acid eq (21) [29]

Normal: $Ø=C=O + M-H \longrightarrow M-OOCH$ (2Ø)

Abnormal: $Ø=C=O + M-H \longrightarrow M-COOH$ (21)

Reversible insertions of CO_2 into M-H bonds is essential for homogeneous-catalytic hydrogenation reaction of CO_2 and also plays a role in the water gas shift reaction [3Ø].

Carbon dioxide insertion into transitional metal-hydrogen bond has been studied for a number of examples. The first example was observed by Misono etal. [31] for the cobalt complex $(Ph_3P)_3Co(N_2)H$. Bubbling CO_2 through a

solution of the complex resulted in insertion at the Co-H bond with simultaneous N_2 eleminationa to give the cobalt formato complex $(Ph_3P)_3$ Co(OOCH), and $[(Ph_3P)_3Co(CO)]_2$, the later resulting from formate fragment transformation. The presence of the formate group has been confirmed by the formation of methyl formate upon reaction of the complex with methyl iodide:

$$(Ph^3P)_3Co(N_2)H+CO_2 \text{------} > (Ph_3P)_3Co(OOCH) \xrightarrow{MeI} MeOOCH \qquad (22)$$

Ingeneral, the formation of cobalt-formato complexes has been suggested to involve a CO_2 fixation step for different ligands L [32]:

$$HCoL_4+CO_2 \text{----------} > HCoL_3(CO_2)+L \rightarrow HCOOCoL_3 \qquad (23)$$

The species $HM(CO)_5^-$ (M=Cr, Mo,W) are the most prominent intermediates in the water-gas shift reaction. These complexes react with CO_2 to produce, formate species, [33] and therefore compete with bicarbonate complex formation.

It was referred [8] that a rhodium-carbonyl complex is formed via CO_2 insertion into a Rh-H bond. The over all reaction is

$$Rh(Cl)(PPh_3)_3 \xrightarrow[HMPA,\,100^{o}C]{H_2(20\,atm),\,CO\,(20\,atm)} Rh(Cl)(CO)(PPh_3)_2 + PPh_3 \quad (24)$$

and suggested generalized mechanisms can be formulated as:

$$RhCL_3 \xrightarrow{S} RhClL_2(S) \xrightarrow{H_2} H_2RhClL_2(S) \xrightarrow{CO_2} \xleftarrow{L} HRh(OOCH)ClL_2(S) \xrightarrow{H_2O} S + HCOOH + HRh(OH)ClL_2$$

$$HCOOH \xrightarrow{} H_2O + CO$$

$$RhCl_2(S) + CO \longrightarrow RhCl(CO)L_2 + S$$

L=PPh_3 ; S=HMPA= hexamethylphosphoroamide

In another work [34] it was reported that no formato product (insertion of CO_2 was detected during the reaction of $Rh(H)L_3$ (L=P(i-Pr)3, $PPh(t\text{-}Bu)_2$, $P(C_8H_{14})_3$) with CO_2. Instead a bicarbonate product was isolated. viz., $(H)_2RhL_2(O_2COH)$, and the structure was determined for L=P(i-Pr)3. This shows that there are different possible routes for the reactions considered above. The formation of a bidentate carbonato complex was also reported [35] in the reaction of $[Ru(H)(PMe_2Ph)_5]PF_6$ with CO_2 in MeOH or EtOH. The following mechanism was suggested based on NMR and IR data.

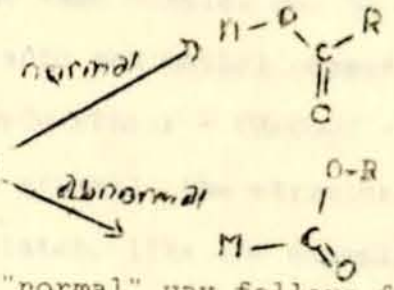
$$Ru\text{-}H + ROH \longrightarrow Ru\text{-}OR + H_2 \xrightarrow{CO_2} Ru\begin{matrix}O\\ \diagdown\diagup\\ C\text{-}OR\\ \diagup\diagdown\\ O\end{matrix} \quad (25)$$

2.3.2 Insertion Into M-C Bonds

In a number of cases the insertion reactions into M-C bonds involve preliminary coordination of CO_2 followed by

insertion [36] to produce a variety of products.

There are two possible path ways for this reaction called the "normal" and the abnormal insertion [27] (eq 26)



(26)

The "normal" way follows for the organometallic compounds giving alkyl carboxylic acid, and the reverse, abnormal ways, with formation of metalloacid ester.

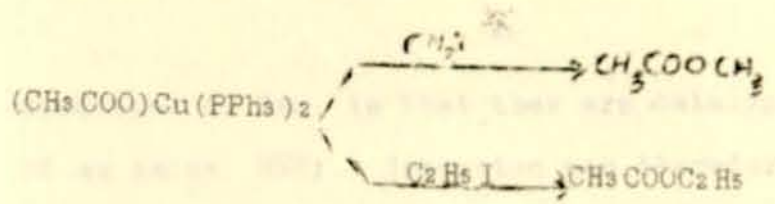
Examples of "normal" reactions with a carbanion transfer to the CO_2 carbon were shown for some titanium and zirconium compounds [36-37]

Carbondioxide inserts comparatively easily into the I-Rhodium-carbon bond by the action of CO_2 on the complexes $(Ph_3P)_3RhR$ (where R=CH_3, Ph) with formation of carboxylates [38]. After esterification of such compounds by means of a solution of BF_3 in methonol or CH_3I, methyl acetate and methyl benzoate form, respectively.

Reversible insertion reactions occur with copper complexes, e.g., the complex $(Ph_3P)_2CuCH_3$ reacts with CO_2 to give the insertion product $(Ph_3P)_2CuOOC\ CH_3$ [39]. Acetic acid is formed in the reaction of HCl with the complex:

$(Ch_3COO)Cu(PPh_3) + 3HCl \rightarrow 2CH_3COOH + CuCl + 2HPPh_3Cl$ (27)

Methyl or ethyl iodides give the corresponding esters:

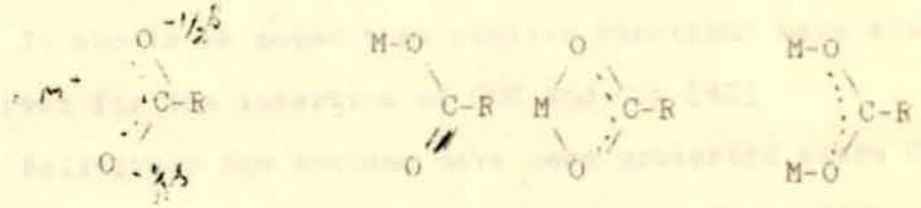


(28)

The same complex can be obtained independently from acetic acid and methyl copper derivatives:

$$CH_3Cu(PPh_3)_2 + CH_3COOH \longrightarrow (CH_3COO)Cu(PPh_3)_2 \quad (29)$$

In general, the structures of various metal carboxylates, like the examples above, may differ cosiderably. For example, the following types of structures are known to date [81]:



It is to be expected that the IR spectra of these types differ substantially [40]

2.3.3 Insertion Into M-N Bonds

Transition metal carbamato complexes are formed as the result of insertion of CO_2 into transition metal-nitrogen bond. These species are observed to be labile towards CO_2 exchange. A mechanism was suggested [41] (Fig.3) in which a step wise formation of carbamato complexes could be observed and various models for CO_2 exchange were also suggested. These insertion reactions differ from the other types

discussed so far, in that they are catalyzed by the presence of an amine, HNR_2. Insertion can therefore follow the normal mode:

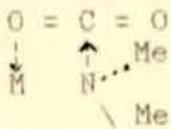


Fig. 3

or proceed according to eq (3Ø)

$$CO_2 + HNR_2 \rightleftharpoons HO_2CNR_2$$

$$M\text{-}NR_2 + HO_2CNR_2 \longrightarrow MO_2CNR_2 + HNR_2 \qquad (3Ø)$$

It should be noted that similar reactions were also observed for the insertion of COS and CS_2 [42]

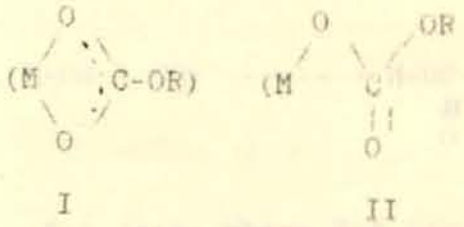
Relatively few systems have been presented where CO_2 insertion into M-N bonds occur. A number of complexes of transition metal dimethyl amides $M(NMe_2)_n$ [M= Ti, Zr, V and n= 4 [43]; M=Nb, Ta and n= 5 [44]; $W_2(NMe_2)_6$ [45]; $W(NMe_2)_6$ [46] and $M_2(NR_2)_4R^1_2$ [M=W, R=Et, R^1=Me [44]; M=W [46], Mo[46,47], R=Me, R^1 =CH_2Ph] have been reported as reacting with CO_2 to give carbamato complexes: $M(O_2CNMe_2)_n$; $W_2(O_2CNMe_2)_6$: $W(NMe_2)_3(O_2CNMe_2)_3$ and $M_2(O_2CNR_2)_4R^1_2$ respectively.

2.3.4 Insertion Into M-O Bonds

Insertion of CO_2 into M-O bonds results generally in the formation of carbonato (CO_3^{2-}) or similar type complexes. The insertion into transition metal-alkoxide bond (M-OR) therefore provides monoalkyl carbonate complexes:

$$M(OR)L_3 + CO_2 \rightleftharpoons M(O_2COR)L_3 \quad (31)$$

The species so obtained may be coordinated as a bidentate (I) or a monodentate (II) Ligands (Fig.4)



I II

Fig. 4: Mode of Coordinations In Alkyl carbonato Complexes.

Similar alkyl carbonato complexes have been obtained [48] from hydrido complexes of transition metals. by reaction with CO_2 in the presence of alcohols. However. the mechanism suggested for such processes (eq (2b) involves formation of an alkoxo complex as an intermediate. This is a result of the attack of the alcohol on the transition metal-hydrogen (M-H) bond. The next step is then the formal insertion of CO_2 into the newly formed M-OR bond [49].

The other version of the insertion of CO_2 into M-O bond is the one observed in transition-metal hydroxo complexes. With these complexes the reaction proceeds via a CO_2 uptake by the hydroxo ligand .

Stability of the alkyl carbonato complexes could be controlled by presence of ancilary ligands such as phoshines or phosphites. In this manner a number of

complexes were synthesized [50]. A series of molybdenum complexes [51] exhibit completely reversible CO_2 insertion reaction, the mechanism in the solid state proceeds via a direct attack on either M or R while the mechanism in solution was suggested to be eq (32):

$$M\text{-}OR + CO_2 \longrightarrow M\text{-}OC(=O)\text{-}OR \text{ or } M\text{-}O\text{-}C(=O)\text{-}OR \qquad (32)$$

(For cases where R=H insertion preferable occurs into the O-H bond)

Fachinetti etal. suggested [52] that the formation of Ti-CO_3 species follow a route that correspond to CO_2 reductive disproportionation [53]:

$$2CO_2 + 2e^- \longrightarrow CO_3^{2-} + CO \qquad (33)$$

In this reaction the two electrons are supplied by oxidation of the metal center from M(0) or M(I) to M(II) or M(III) respectively.

Later on in 1985 Kato and Ito [54] showed that monoalkyl carbonato complexes were formed by reversible reactions of Zinc (II)-tetrazocyclo akane Complexes with CO_2 in the presence of bases in alcohol. The results of structure analysis of these CO_2 adducts [55] confirmed that they are indeed alkyl carbonato complexes.

Schiff-base-chelate complexes with Cu-O bonds likewise

react with reversible insertion of CO_2 into the Cu-O bond [56] similar to a phosphine complex, (HO)C (PR_3)n in which CO_2 reacts with the Cu-OH bond [57]. The later complex being soluble in water is capable of transferring CO_2 to propylene oxide or cyclohexanone to form polypropylene carbonate and the cyclohexanone-2-carboxylic acid which was isolated as a methyl ester [57]. Similarly alkoxolanthanoid complexes can also incorporate CO_2 reversibly with insertion [58]

To conclude this section we would like to include reports on syntheses of transition metal alkyl carbonato complexes following studies of the insertion reaction of the corresponding alkoxides, to mention a few:
$M(OBu)_4$, M^1=Ti,Zr; $M^1(OEt)_4$, M^1=Zr,Nb,Fe[51];
$Mo_2(OCH_2CMe_3)_6$ [51]; $Cu(OMe)_2$ [59]; (t-BuO)Cu(CN-t-Bu) [59];
$[Et_4N][W(CO)_5OR]$[60] where R=Ph, m-$CH_3C_6H_4$;
$Cp^*Ir(Ph_3P)(H)(OEt)$ [61].

3 Carboxylation By Means of Metal Alkyl carbonates and Metal-Carbon Dioxide Complexes

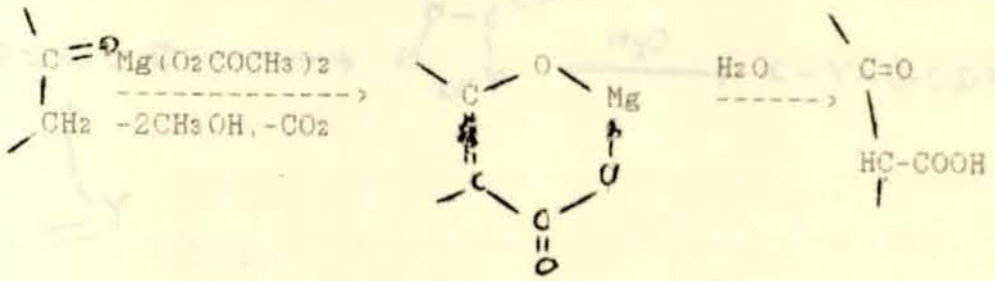
As we have seen in the introduction, the activation of the low-energy CO_2 can be achieved by a "metal phenolate-CO_2-adduct "(metal phenyl carbonate) [5].

It is also of a synthetic significance that main group metal (eg Mg,Li) alkyl carbonates [5] can be used as efficient carboxylating agents instead of CO_2 as it is. To prepare the reagent metal alkoxides of the monovalent

alcohols must react with CO_2. The solution prepared from the species in organic solvents is directly used for carboxylation of an organic substrate.

The very reactive but properly to be handled substance that is frequently used as a carboxylating agent is magnesium methyl carbonate commonly known as Stiles-reagent [62]

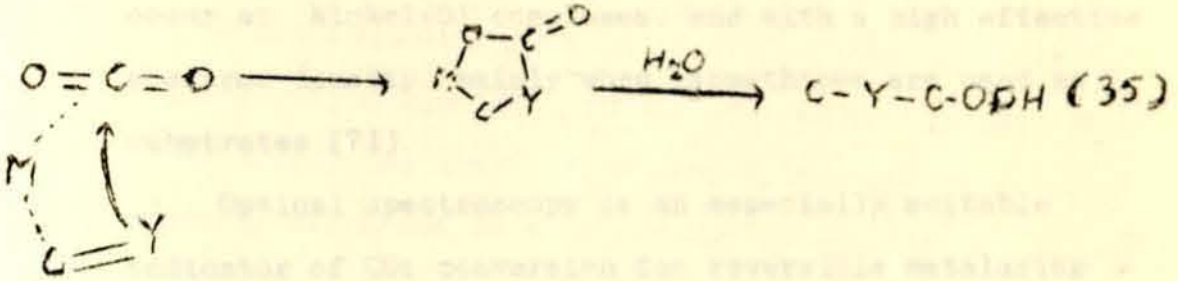
Thus by means of metal alkyl carbonates it is possible to carboxylate numerous substrates specially C-H acidic carbonyl compounds, nitrocompaunds, and also activated aromatic and heterocyclic compounds. A typical reaction is given by eq (34)



(34)

It has also been indicated that [1] other "metal-CO_2-substrate" complexes are active precursors that are the result of formation of a new C-C bond between an organic substrate and CO_2 with retention of both oxygen atoms of CO_2 in the product. Alkynes, alkenes, dienes, strained cycles, and benzene react catalytically with CO_2 to afford pyrones, lactones, esters, and acids in the presence of ruthenium, rhodium, nickel, or palladium complexes. A lot of examples are found in literature [1, 4, 63]

In this connection it should be noted that the activation of CO_2 is caused by the transition metal centers, and this must lead to the coordination of CO_2 at the metal atom in the given complex. The formation of a new C-C bond with an organic substrate, eg.: C=Y, is then catalyzed by the Metal-CO_2- complex. Hydrolysis of the intermediate metal-CO_2-substrate Complex results in the detachment of the metal center from the carboxylated product of C=Y eq (35)



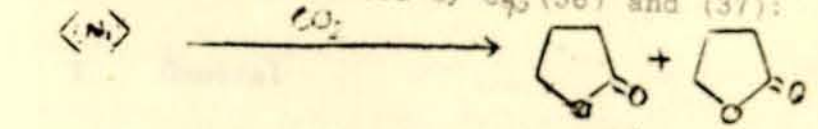
4. Some Useful Applications Of Nickel-Carbon Dioxide Complexes:

Reversible metalaring closure reactions with CO_2 and unsaturated substrate have been observed, by authors such as, Inoue etal [64,65]and Walter etal [80]. These reactions occur at Nickel(0) complexes, and with a high effective electron density, mainly when azomethines are used as substrates [71].

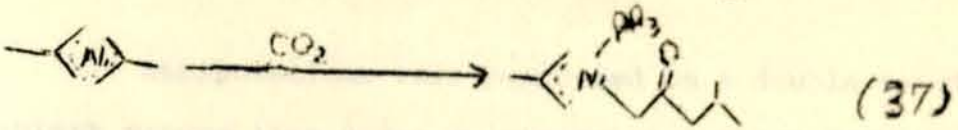
Optical spectroscopy is an especially suitable indicator of CO_2 conversion for reversible metalaring closure reactions. Carbondioxide transfer reactions with the formation of new metalacyclic compounds can also be carried out where nickel heterocycles with N-carboxylate structure are used [62].

Nickel (II) complexes are also known as the most active CO_2-substrate coupling catalysts [23]. For example, carbondioxide insertion into allylic metal complexes has been observed to give several types of products, such as carboxylato species or lactones [1,66] depending on the

nature of the metal and of its ligand. Some of these reactions are described by eqs (36) and (37):

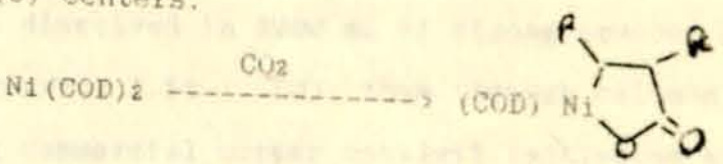


(36)



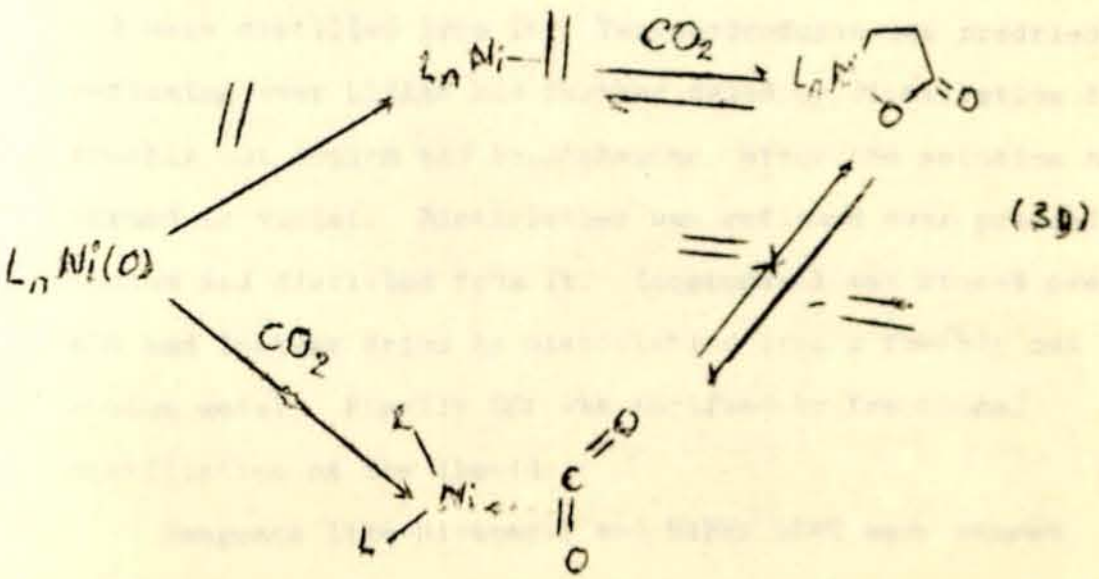
(37)

Very interesting results have also been published on the coupling reactions between alkynes (eq (38) [66]; alkene [67], conjugated dienes [68] or cumulenes [69] and CO_2 on Ni(0) centers.



(38)

No intermediate, such as Ni-CO_2 complexes, could be observed in the formation of the five-membered oxanickela cycles type in eq (38). With alkene, carbon-carbon bonds formating was found to be sometimes reversible eq (39) [67]



(39)

3

III. EXPERIMENTAL SECTION

1. General

All manipulations were performed on a double-manifold Schlenk vacuum line under an atmosphere of dry Nitrogen. Nitrogen with original purity of 99.6% was further purified by passing it through two columns (Length 100cm. diameter 5 cm) each containing an alkaline pyrogallol Solution (30g of pyrogallol dissolved in 3000 mL of strong aqueous KOH of specific gravity 1.54) [70]: then through columns containing commercial copper catalyst (activated at 55°C to absorb oxygen): dry KOH (Pellets): dry P_2O_5 (powder) and Molecular sieve type 4A.

All solvents and reagents were dried and purified according to established procedures [71]. Benzene, toluene, n-hexane and n-haptene were dried over pressed sodium metal and were distilled from it. Tetrahydrofuran was predried by refluxing over $LiAlH_4$ and further dried by distillation from freshly cut sodium and benzophenone, after the solution had turned to violet. Diethylether was refluxed over pressed sodium and distilled from it. Isopropanol was stored over KOH and further dried by distillation from a freshly cut sodium metal. Finally CS_2 was purified by fractional distillation of the liquid.

Reagents like $Ni(acac)_2$ and $NiBr_2.2DME$ were stored

(after synthesized) under nitrogen and transferred into reaction vessels under nitrogen where needed. Moreover, all drying and purifications of solvents were done under nitrogen and deaerated before use.

Carbondioxide gas used in the synthesis was dried and purified following an established procedure [71]. According to this procedure the gas was first passed through a column of conc. H_2SO_4 (A.R.). Possible acid contamination could be neutralized by sodium bicarbonate packed as a powder in a second column in the line. A third column was charged with powdered phosphorous (V) oxide with the aim of removing any water still carried by the gas.

$NiBr_2.2DME$, PPh_3, and diphos used in the synthesis were taken from previously prepared source [72] without further treatment. Other reagents and chemicals needed for the preparations were obtained from commercial sources available in the department store and were directly used with out any further purification.

2. Methods Of Analysis

2.1 Preparation Of Solutions Of The Isolated Products

30 mg of each of the isolated CO_2 reaction product containing nickel was decomposed by a dilute nitric acid solution (1ml of conc. HNO_3 (A.R) dissolved in 30 ml of distilled water). A final solution of 100 ml was made by

adding distilled water. For the same amount of CS_2 reaction products the dissolution was effected with a solution of 10ml conc. HNO_3 IN 20ml distilled water, and the final solution was made to 100 ml by further dilution.

2.2 Determination Of Basic Components In The Isolated Compounds And Determination Of Isopropoxide In LiOiPr And NaOiPr Solutions

By a basic component we mean the substance that would consume a certain equivalent of an acid in an acidimetric titration of the solutions of an isolated compound obtained by reaction of CO_2 or CS_2 with compound (I) or (II).

The Possible reaction are:

$$iPrOCO^{2-} + H^+ \text{-----} > iPrOH + CO_2 \quad (40)$$

$$iPrOCS_2^- + H^+ \text{-----} > iPrOH + CS_2 \quad (41)$$

$$iPrO^- + H^+ \text{-----} > iPrOH \quad (42)$$

For analysis of the basic component in CO_2 reaction products, 30 mg of a given sample was dissolved in 25ml of excess of 0.1 M HCl and the resulting solution was diluted to a final volume of 100 ml. The excess acid was then

determined by titrating a known volume of this solution with Ø.1M NaOH (A.R).

Determination of the base in CS_2 reaction products was impossible in this condition.

For the purpose of defemination of LiOiPr and NaOiPr, exactly measured 1ml of the corresponding solution inTHF was taken from the reaction vessel at a time, and diluted to 5ØmL with distilled water. The resulting solution was then titrated against Ø.1 M HCl in order to determine the equivalent amount of the base (eq.(42)).

2.3 Determination of Nickel

Analysis for the nickel content in solutions prepared according to 5.1 were done based on the procedure given by Vogel[73]. A known volume of a sample solution was taken each time and a known volume of excess of Ø.Ø1M EDTA was added. The mixture was buffered with hexaamine (~1g) to adjust the pH of the solution to 5. The excess EDTA was finally determined by titration with standard Ø.Ø1M $Pb(NO_3)_2$ solution using xylenol orange/NaCl indicator mixture (XO:NaCL = 1:1ØØ).

2.4 Determination Of Bromide

The bromide content of a given sample was determined by using a bromide selective electrode with calomel as

reference electrode. The potential of the solution was recorded by PW 9409 digital PH meter.

Standard solutions were prepared as 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M solutions of KBr. The concentration of Br^- in a given solution was obtained by the direct method as well as by the standard additions method (Gran's plot)

2.5 Determination Of Lithium and Sodium

The content of Li or Na in a given sample was determined by flame photometric technique using Beckmann 652210 KLiNa Flame Photometer.

2.6 Spectroscopic Measurements

IR spectra of the compounds were recorded on a Pye Unicam PU 9512 IR Spectrometer. Samples were handled as mulls with nujol or as KBr pellets and spectra were recorded using NaCl Windows. (range 4000-200 cm^{-1})

Visible Spectra were recorded on Beckman Model 24 UV/Vis Spectrophotometer. (range: 750-350nm)

3. Preparation of Starting Compounds

3.1 Anhydrous Bis (acetyLacetonato)Nickel (II) ($Ni(acac)_2$)

$$NiCl_2.6H_2O + 2Hacac + 2Naac \longrightarrow Ni(acac)_2.2H_2O + 2NaCl + 2Hac + 4H_2O \quad (43)$$

43

For the synthesis of $Ni(acac)_2$ first the dihydrate salt (eq (43)) was prepared according to literature procedure [74]

A solution (25ml) of $NiCl_2.6H_2O$ (59.4g) in distilled water was added to a second solution (100ml) of acetylacetone (50.0g) in methanol while stirring. To the resulting mixture a solution of sodium acetate (41.0g) in 100ml distilled water was added. The final solution was heated to boiling on a hot plate, cooled to room temperature and then placed in a refrigidator for several hours. It was filtered-off on a Buchner funnel as a green solid; washed with ice-cold water and dried in vacuum desiccator for a few days. Finally the anhydrous salt ($Ni(acac)_2$) was obtained by azeotropic distillation of the dihydrated salt in toluene (1:50 by weight). The final product was further dried in vacuum and collected as a dark green solid.

3.2 Lithium Isopropoxide ( )

$$LiH + iPrOH \xrightarrow{\text{reflux}} LiOiPr + H_2 \quad (44)$$

Lithium isopropoxide was prepared by the reaction of an excess of LiH (1.5g) with 10ml of isopropanol in 100ml THF solution. The mixture was refluxed for about 4h and then filtered using G4 sintered funnel to remove the excess LiH. Concentration of the clear solution was determined acidimetrically and found to be in the range 0.9- 1.2M.

3.3 Sodium Isopropoxide

$$2Na + 2iPrOH \xrightarrow{\text{reflux}} 2NaOiPr + H_2 \quad (45)$$

Sodium isopropoxide was prepared by a similar procedure as in 3.2 using sodium metal (2.5g) and isopropanol (10ml) in 100 ml THF solution; refluxed for 3 1/2 h and filtered to remove the excess sodium. Concentration of the clear NaOiPr solution was also determined acidimetrically to be in the same range 0.9-1.2M.

3.4 Dilithium tetraisopropoxo nickelate (II)-Lithium Bromide -3 Tetrahydrafuran.

$(Li_2Ni(OiPr)_4.LiBr.3THF)$ (I)

$$NiBr_2.2DME + 4LiOiPr \xrightarrow{THF} Li_2Ni(OiPr)_4.3THF + LiBr + 2DME \quad (46)$$

Following the procedure given by Kalies etal[17], compound (I) was prepared by reaction of a THF solution (80ml) of excess LiOiPr 72-96 mmol with $NiBr_2.2DME$ 12.7mmol at room temperature in a Schlenk tube under nitrogen. Blue suspension resulted. This suspension was stirred for 1h at room temperature . The blue suspension was then filtered-off by a G3 sintered funnel to separate the blue solid from the deep blue solution. The ligand field spectra of the filtrate (blue) was recorded. The blue crystalline solid was anlysed for its composition and its IR spectra was recorded in Nujol.

Analysis	Exptl Value	Calculated for CPd. (I)
% Li	2.8	3.4
% Ni	9.4	9.5
% (OiPr)-	32.8	38.6
% Br^-	13.5	13.1

IR Spectrum:

ν_{C-H} ($R_2\underline{CH}$) = 2380 cm^{-1} ν_{CO} (R_2C-O) = 1140 cm^{-1}

ν(C-O-C-) as = 1040 cm^{-1} ν_{Ni-O} = 420 cm^{-1}

$\nu(C-O-C)_s$ = 970 cm^{-1}

Vis = Spectra (Observed)	Literature [17]
ν_3: 18,018 cm^{-1}	ν_2 : 18,200 cm^{-1}
16, 950 cm^{-1}	16,900 cm^{-1}

3.5 Disodium Tetraisopropoxonickelate (II)-2-Tetrahydrofuran ($Na_2Ni(OiPr)_4.2THF$). (II)

$$Ni(acac)_2 + 4NaOiPr \xrightarrow[0^\circ C]{THF/toluene} Na_2(OiPr)_4.2THF + 2Naacac \quad (47)$$

To the THF solution (90ml) containing excess of NaOiPr (81-108 m mol), a solution of anhydrous $Ni(acac)_2$ (28 m mol) in 90 ml toluene was added at room temperature. The mixture was stirred for 1h at 0°C. A violet solution and a white precipitate of Naacac were obtained. The white precipitate was filtered-off by a G3 sintered funnel. The

clear violet solution was stored at low temperature under nitrogen in a Schienk tube. Its ligand field spectra was later recorded in an atmosphere of nitrogen.

Vis. Spectra Observed	Literature [17]
18,450 cm^{-1}	18.850 cm^{-1}
16,530 cm^{-1}	16.450 cm^{-1}

4. Reactions Of Carbon dioxide With Alkali Metal Alkoxonickelates.

4.1 With $Li_2Ni(OiPr)_4.LiBr.3THF$ (I)

4.1.1 Reaction In THF Solution

(I) + $4CO_2$ -------> Isopropyl carbonato complex of Ni (II) (III) (48)

Carefully dried CO_2 was slowly bubbled through 80ml of a THF solution containing compound (I) filled in a three-necked flask. The reaction was carried out for 1h at 0°C with continuous stirring.

The blue solution of the starting material (I) first changed to violet then to blue-green and finally to a complete green. The solution was then filtered to remove any solid material. The filtrate (green) was saturated with CO_2 gas and left over night in a refrigidator expecting a precipitate. However, no precipitate was observed in this condition. It was also noticed that the colour change is reversible. i.e, heating upto 50°C results in change of

colour from green to blue and cooling to room temperature in an atmosphere of CO_2 results in a reverse change of colour (from blue to green).

Vis.Spectra of the green solution;

Observed: ν_2: 14,815 cm^{-1}

ν_3: 24,700 cm^{-1}

4.1.2 Reaction In Solid Phase

Compound (I) (blue powder) 6.11g (10 mmol) was packed in a 50 ml sintered funnel under nitrogen. Dry CO_2 gas was slowly generated through the blue charge from the bottom of the funnel. The process continued for a few hours at room temperature. During this time the blue solid gradually became leafy-green probably indicating formation of product (III). This reaction may also be described by the same equation (eg.(47)).

Analysis		Calc.for $Li_2Ni(O_2COiPr)_4.LiBf.2THF$
% Li	2.8	2.9
% Ni	8.2	8.2
% Base:	54.7	57.6
% Br^-:	11.8	11.2

Experimental

Molar ratio. Li: Ni: Br^-: Base = 2.9: 1:1.1 : 3.8

(apprx 3:1:1:4)

Vis.spectra of solution of (III) in THF:

ν_2: 15,528 cm^{-1}

16,260 cm^{-1}

ν_3 : 25,000 cm^{-1}

IR.Spectra of Cpd.(III) in Nujol

ν((C=O)=1612 cm^{-1}(m),1578 cm^{-1} (m): $\nu(C-O-C)^{as}$ =1085 cm^{-1}(s)

$\nu(C-O-C)^{s}$ = 950 cm^{-1}(s)1 ν(c-o)= 1290 cm^{-1} (w)

ν(Ni-O) = 360 cm^{-1}(s)

4.2 Reaction of Carbondioxide with $Na_2Ni(OiPr)_4.2THF$

$$(II) + 4CO_2 \xrightarrow[\text{Ø°C}]{\text{THF/toluene}} \underset{\text{complex of Ni(II)}}{\text{Isopropyl (carbonato}} \quad (IV) \qquad (49)$$

The violet solution of THF/toluene (1:1) (45 ml) containing compound (II) about (11.1 mmol) was filled into a two-necked flask under nitrogen. An adaptor connecting the CO_2-line was suitably fitted to the reaction flask. Carefully dried CO_2 gas was then slowly bubbled into the solution for nearly 2h at Ø°C with continuous stirring. A light-green greasy substance was formed in the solution. After adding an equal volume of THF, the mixture was saturated with CO_2 and was left for a few hours to allow the reaction to be completed. The solid product was filtered-off from the mother laquor by vacuum technique under a condition of an over pressure of CO_2 above the solution.

Finally product (IV) was collected as a light-green solid after it was completely dried in vacuo.

Analysis	Calc for $Na_2Ni(O_2COiPr)_4.2THF$
% Na: 5.4	6.9
% Ni: 8.4	8.9
% Base: 66.2	62.4

Experimental

Molar Ratio Na: Ni: Base === 1.7 : 1 : 4.5

(approx. 2: 1: 4)

Vis. Spectra was difficult since the mother liquor was colorless and the solid product was insoluble in THF, toluene or mixture of the two.

IR spectra of solid in Nujol(cm^{-1})

ν(C=O) 1646(s), 1590 (s); $\nu(C-O)^s$ =1298(s)

$\nu(C-O-C)^{as}$ =1030(s); $\nu(C-O-C)^s$ =922(m) ν(Ni-O)=360(w)

4.3 Qualitative Reactions Of Carbon Dioxide With $Na_2(OiPr)_4.2THF$ In The Presence of Phosphine:

4.3.1 Triphenyl Phosphine (PPh_3)

(II) + PPh_3 + (excess) CO_2 --------> Product (V) (50)

A THF/toluene solution (45 ml) containing compound (II) (6.75 m mol) was taken in a gas-bubbler. Triphenyl phosphine (6.75 m mol) was added to the solution. The

mixture was then stirred at room temperature for 15 min. to give a homogeneous solution. The resulting solution became dark-brown. Dry CO_2 gas was bubbled through this solution with stirring for about 2h at room temperature. A dark-green suspension was obtained. The suspension was then filtered and the residue was washed twice with THF and dried in vacuo. The product (V) was finally collected as a dark-green solid. The filtrate (yellow-green) was used in recording the ligand field spectra.

Vis. spectra of the fiterate:

(No Significant band was observed)

Analysis:

% Ni = 13.5%

4.3.2 1,2-Bis(diphenyL Phosphino)ethane (diphos)

(II) + Ø.5 diphos +(excess) CO_2 ----->Product (VI) (51)

A THF/toluene solution (45 ml) containing compound (II) (6.75 mmol) was taken in a gas bubbler as in section 4.3.1. Diphos (3.375 mmol) was added to the solution and the mixture was stirred for 15 min to make a homogeneous solution. The resulting solution became also dark-brown. Dry CO_2 gas was bubbled through the solution with stirring for a few hours at room temperature. A greenish-brown suspension was forming during this time. The suspension was

allowed to stand for few hours a gray material depositing on the walls of the reaction vessel giving a mirror like apperance.

The final product was dried in vacuo but uncharacterized.

5. Reactions Of Carbon Disulphide With Alkali Metal Alkoxonickelates

5.1 With $Li_2Ni(OiPr)_4.LiBr.3THF$ (I)

(I) + $4CS_2$ --------> Isopropyl Xanthato Nickel (II) (VII) (52)

A THF solution (40 ml) of compound (I) (8.4 mmol) maintained at 0°C was taken in a three-necked flask. To this solution excess of CS_2 (40 ml) was added with stirring . After 1 1/2 h. a dark-yellow brown solution was obtained. The solution was vacuum concentrated to about 1/3 of the initial volume and filtered. The residue was washed with THF and dried in vacuo using vacuum desiccator. A dark brown solid was finally collected as a product; analysed for its composition and the IR spectrum was recorded in nujol. The filtrate first diluted with THF was used in measuring the ligand field spectra of the compound.

Vis. Spectra of the filtrate (diluted eight times)

ν_2 : 15,630 cm^{-1}

ν_3 : 21,280 cm^{-1}

Analysis: Calc. for $Li_2Ni(S_2COiPr)_4.2THF$

5.

58

% Li:	1.85	1.84
% Ni:	7.04	7.74
% Br^- :	6.32	-

Ratio: Li:Ni= 2.3 :1: approx. (2:1)

IR. Spectra of VII in nujol (Cm^{-1})

VC=O = 1720 (m) ; VC-O = 1260 (vs);

VS-C-O(as)= 1080(s) Vc=S= 1020(w)(broad)

VS-C-O(s) = 940(w) VC-S = 720(m)

5.2 With $Na_2Ni(OiPr)_4$. 2THF (II)

(II) + $4CS_2$ ------> Isopropylxanthato nickel (II) (53)

A THF/toluene solution (20 ml) of compound (II) ( ) was taken in a three-necked flask and excess CS_2 (20ml) was added at 0°C with continuous stirring for 2h. A Yellow-brown solution was formed. The solution was then vacuum concentrated to about 1/3 of the initial volume and filtered. The residue (dark-yellow brown) was washed with THF and dried in a vacuum desiccator. The product was collected as yellow-brown solid and analysed for its composition. IR spectra was recorded for the solid while the ligand field spectra was measured from the filtrate (yellow green).

Vis. Spectra of filtrate

ν_2 : 16,600 Cm^{-1}

ν_3 : 22,100 Cm^{-1}

Analysis	calc.for. $Na_2Ni(S_2COR)_4.2THF$
% Na: 6.13	5.82
% Ni: 8.03	7.43

EXPT.ratio Na: Ni=1.9:1, approx = 2.1

IR.Spectra of Solid (VIII) in nujol

ν(C=O) = 1680 (m), 1580(m), ν(C=S)1205(w),1110(s)

ν(C-O) =1280 (ν_s) ν(C-S) = 620(m)

ν(S-C-A)^{as} = 1052 (s) ν(Ni-S) = 340

ν(S-C-O)^{s} = 930(w)

5.3 Displacement Reaction of Carbon Dioxide Reaction Product (IV) With Carbon Disulphide

$$(IV) + nCS_2 \longrightarrow (VIII) + nCO_2 \qquad (54)$$

The product (VIII) was also prepared by stirring a THF/toluene suspension of compound (IV) with equal volume of CS_2 at room temperature for 48h. The compound (IV) was observed to be dissolved with the addition of CS_2. The resulting solution (greenish brown) gradually became yellow-brown. It was then vacuum concentrated to about 1/4 of the initial volume. A dispersion of solid substance appeared in the solution which was then filtered-off as a residue and washed with THF. Product (VIII) was finally collected as a golden-brown solid after being dried in a vacuum desiccator. It was analysed for its composition,

Analysis	calc. for $Na_2Ni(S_2(OiPr)_4.2THF$
% Na: 6.13	5.82
% Ni: 7.7	7.43

Molar ratio: Na: Ni = 2:1

IV RESULTS AND DISCUSSION

4.1. Results of Analyses of Starting Compounds

The starting compounds (I) and (II) were prepared following the general procedure given by Kalies [17], except that $NiBr_2.2THF$ was replaced by $NiBr_2.2DME$ in the synthesis of (I). This change was made following the advice made by a recent report [72] to modify the earlier procedure owing to the fact that $NiBr_2.2DME$ is relatively more stable to air and easy to prepare than its THF analogue. On the other hand a very recent report [75] on the same substance indicated that the previous assignment of its structure (octahedral) was wrong. The new report shows that reinvestigation was carried out on the magnetic moment of the substance and found to be $\mu exp = 3.5\mu_b$ This value suggests that Ni is tetrahedral coordinated. Moreover the authors [90] claimed that the substance contains less than two moles of DME (ca. 1.2 moles). Despite these opposing views on the same material we employed $NiBr_2.2DME$ in our stoichiomeric reaction for the preparation of (I) (See Chapter (III) Section 3.4).

The necessary data in the preparations of (I) and (II) were obtained in a fairly good agreement with those given in the original work [15]. Ligand field spectra measurements indicated the expected tetrahedral coordination in (I) and strongly distorted tetrahedral one in (II).

The colours are observed to be blue for the THF solution of (I) and violet for the THF/toluene solution of (II). A blue stable solid of (I) was also obtained at room temprature.

Like the binary nickel(II) alkoxides [10], compounds (I) and (II) are sensitive to moisture and rapidly hydrolyzed with a sharp colour change from blue (violet) to bright green.

In addition the THF solution of (I) was found to be relatively more stable at room temprature under nitrogen than the THF/toluene solution of (II). The later solution rather undergoes facile decomposition reaction owing to the result of internal redox activity of the substance (II) which may lead to subsequent reduction of NI(II) to Ni(I) and finally to Ni(O) species [15]. This was observed in our solution of (II) with the formation of a dark solution and gray deposit when the former was stored at room temprature even under a nitrogen atmosphere for more than two days.

The IR spectra measurements and results of elemental analyses suggested that the structures and compositions of (I) and (II) are very similar to those reported earlier [15]

2. Reaction Products Of Carbon Dioxide: Lithium And Sodium Isopropyl Carbonatonickelates

2.1 Composition And Structure

From the reactions of $Li_2Ni(OiPr)_4.LiBr.3THF$ (I) and $Na_2Ni(OiPr)_4.2THF$ (II) in THF or THF/toluene at lower temperatures (<Ø°C) isopropylcarbonato complexes (III) and (IV) were formed (Eqs. (48) and (49))

$$(I) + 4CO_2 \xrightarrow[<0°C]{THF} \underset{(III)}{Li_2Ni(O_2COiPr)_4.LiBr.2THF} \quad (48)$$

$$(II) + 4CO_2 \xrightarrow[<Ø°C]{THF/toluene} \underset{(IV)}{Na_2Ni(O_2COiPr)_4.2THF} \quad (49)$$

Although the reactions could also give products with a variety of possible stoichiometries, the products with compositions (III) and (IV) are most probable from the results of the elemental analyses and spectroscopic data provided in the experimental section. This may be explained by the fact that insertion of CO_2 had actually occured in all of the Ni-OiPr bonds of (I) and (II) marking the complexes among the ones that provide more basic centers for an electrophilic attack by CO_2.

The ligand field spectra of (III) in THF indicated an octahedral environment for a metal in the d^6 state. This follows from observation of bands for the spin-allowed transitions:

ν_3: $^3A_{2g}$ -------> $^3T_{1g}(P)$ at ca. 25,000cm^{-1} and

ν_2: $^3A_{2g}$ ---> $^3T_{1g}$ (F) (two splitted bands) at ca. 15,258cm^{-1} and ca. 16,260cm^{-1}.

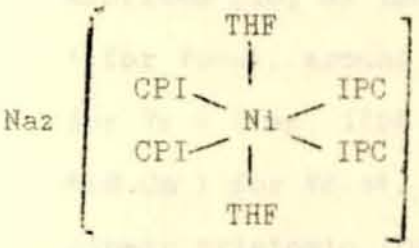
However the band for the transition ν_1 : $^3A_{2g}$->$^3T_{2g}$ did not appear in the spectrum which was measured only for the range 750-350 nm (Section 5 of Chapter III)

The ν_1 band may be expected at ~ 8000 - 1000 Cm^{-1} for octahedral nickel (II) complexes [10]

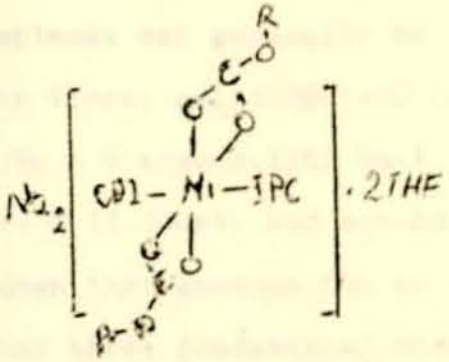
Elemental analysis of (III) suggested that LiBr is found still coordinated in the outer-sphere coordination of the metal as in the starting material (I). This was inferred from the results of Br^- determination which indicated its presence in a 1:1 stoichiometric ratio with nickel. The overall composition of (III) was found to be ca. 2.9: 1:3.8:1.1 corresponding to ratio of Li: Ni: base: Br^- and may be approximated to 3:1 :4:1 to fit the formula $Li_2Ni(CO_2OiPr)_4$ LiBr.2THF. Calculation gives only two coordinated THF (which is three for the starting compound).

Spectroscopic (IR,Vis.) results and analyses of composition of complex (III) may lead us to suggest two structures only owing to the possibility of unidentate

In the same manner structures (C) and (D) [Fig. 2.2] may be suggested for complex (IV) whose composition was given in the experimental section as ca. 1.7:1:4.5 corresponding to the ratio ca.2:1:4 for Na:Ni: base in the formula $Na_2Ni(O_2COiPr)_4.2THF$.



(C) Unidentate Mode



(D) Bidentate Mode

(IPC= $iPrOCO_2^-$; R = iPr^-)

Fig. 2.2.: The possible structures of $Na_2Ni(O_2COiPr)_4.2THF$

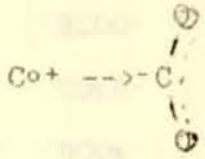
Structure (C) is based on the unidentate mode of coordination of $iPrOCO_2^-$ in all case, while structure (D) implies two bidentate and two unidentate modes for the groups in the octahedral complex of (IV).

A more comprehensive analysis of structure of this type of complex requires additional information from spectroscopic measurements (IR, NMR) and X-rays crystallographic data.

The later method was used, for example, to elucidate structure of $[Ni(CO_2)\{P(C_6H_{11})_3\}].0.75\ MePh$[27] in which CO_2 is co-ordianted to the metal center in a η^2-mode and that of $[Co(Pr\text{-}salen)(CO_2)K(THF)]_n$ [76] (pr-salen = N,N'-ethylenebis (Salicylidenaminato)) in which CO_2 is co-ordianted via the carbon atom to the Co(I) centers

60

as



The IR data for metal-CO_2 complexes can generally be ascribed [10] as 1500-1700 Cm^{-1} for V(oco) as; 1200-1400 Cm^{-1} for $V_{oco}{}^{s}$; around 1750 Cm^{-1} for $V_c = O$ araund 1150 cm^{-1} for $V_c = O$ as, 1750 - 1900 cm^{-1} for M-II (CO_2); and around 820 Cm^{-1} for $V_{c-o}{}^{s}$. It is also known that gaseous CO_2 as a linear triatomic (Dooh) molecule has three fundamental modes of Vibration [77] as depicted in Fig.2.

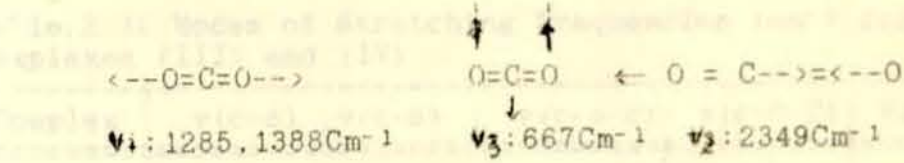


Fig 2. Fundamental Modes of Vibration for CO_2 Molecule

Where, v_1= Symmetric Stretching Mode

v_2= Asymmetric Stretching Mode

v_3= degenerate "C = O" deforamtional Mode.

According to the IR investigations some volues of the prominent band of some selected CO_2 derivatives [78] are summarized in Tabel-1

Anion	IR band, Cm^{-1}
CO_3^{2-}	1665
$HCOO^-$	1633
CO_3^{2-}	1430
HCO_3^-	1697

Table of Prominent IR peaks of anionic derivatives of CO_2

Thus using the complete set of infrared data (Table 2.1) from the spectra of the two complexes (III) and IV) we may discuss the structures of the alkyl carbonato complexes in the following way.

Table.2.1: Modes of Stretching Frequencies (cm^{-1} for Complexes (III) and (IV)

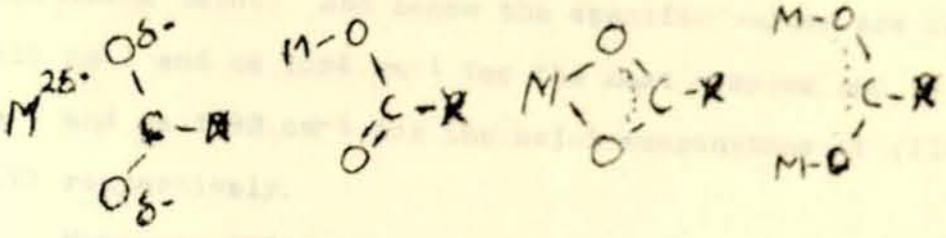
Complex	v(c=o)	v(c-o)	v(c-o-c)	v(c-O-C)	V(Ni-O)
III(Nujol)	1612(m) 1578(m)	1290(w)	1085(s)	950(s)	360(s)
III(Neat)	1615(s) 1575(s)	1270(m)	1070(s)	960(m)	360(s)
IV(Nujol)	1646(s) 1590(s)	1298(s)	1030(s)	922(m)	360(w)
IV(Neat)	1652(m) 1586(vs)	1260(vs)	1020(vs)	925(s)	375(s)

For metal acetate complexes, Holtzclaw and Collman[79] and West and Riley [80] claimed that the order of the carbonyl stretching frequencies is the same as the stability order of the metal complexes, if the highest frequency band near 1600 cm^{-1} is selected as the C=O stretching band. Calculation shows however, that v(c = o) is the C=C stretching frequency. Thus the frequency order of v(C=O) for elements (d^{7-10}) is:

Metal:	Pd	Cu	Zn	Ni	Co
v(C = O) cm^{-1}:	1570	1580	1592	1598	1601

This observation may also be useful for v(C=O) band assignments for other types of metal complexes having the COO,groups.

For metal chelate compounds containing COO, IR studies are useful for distinguishing the un-ionized, the coordinated and the free ionized COO groups in such compounds. The method is based on the simple rule that the un-ionized and uncoordinated COO stretching band occurs at 1750-1700 cm^{-1}, where as the coordinated COO stretching band is at 1650- 1590 cm^{-1}, the exact frequency depends on the nature of the metal [77] . According to Nakamoto [77] metal - COO coordinations in carbonates, acetates, formate and similar complexes the COO group coordinates with the metal in one of the following ways. (as already discussed in the litratrue section):



Where M = metal atom, X = R, H, OR, NR_2, etc.

For any one physical state, the same frequency order for a series of metals is always found, regardless of the nature of the ligand. In other words, when the antisymmentric frequencies increase, the symmetric frequencies decrease, and the separation between the two frequencies increases in the following series of metals: Ni(II) < Zn(II) < Cu (II) < Co (II) < Pd(II) ~Pt(II)<Cr(III)

In general, these results indicate that the effect of coordination is still the major factor in determining the frequency order in a given physical state. This order can best be explained if it is assumed that the covalent character of the M-O bond increases along the series, since an increase of covalent character leads to more asymmetrical carboxyl group and results in an increase in the frequency separation of the two COO stretching bands [93].

In view of the above discussion we may assign the bands very close to the 1600 cm^{-1} in the IR spectra of the two isolated complexes (III) and (IV) for the coordinated COO

stretching bands. And hence the specific values are ca. 1615 cm^{-1} and ca 1586 cm^{-1} for the neat samples and ca. 1612 cm^{-1} and ca 1590 cm^{-1} for the nujol suspensions of (III) and (IV) respectively.

Nakamoto [77] also studied the IR spectra of carbonato (CO_3^{-}) complexes of Co (II) and found that the C - O stretching modes of the monodentate complexes (type (II) above) are observed at 1360 - 1380 cm^{-1} and 1450-1500 cm^{-1} while the corresponding modes of bidentate complexes (type (III)) are at 1260-1290 and 1590-1640 cm^{-1}. For the analogous Ni(II) complexes we expect the corresponding frequency bands at lower values owing to the fact that Ni is lower in the frequency order than Co for similar metal-ligand coordinations.

In particular nickel chelate complexes of amino acids $\nu(COO)_{as}$ are observed at [81] ca. 1589 cm^{-1} 1560 cm^{-1} 1606 cm^{-1} [ ], 1590 cm^{-1} and the corrosponding a $\nu(COO)_s$ are observed at 1420 cm^{-1}, 1402 cm^{-1}, 1418 cm^{-1} and 1430 cm^{-1} respectively. Monica and coworkers [82] also assigned absorption frequencies, $\nu(COO)_{as}$ at 1540 cm^{-1} and $\nu(COO)_s$ at 1320 cm^{-1} for CO_2 groups of carbonate ligands as bands that are always present in metal carbamate complexes. The authors also noted that the higher frequency band (1540 cm^{-1}) lies in the same position as $\nu(C=O)_{as}$ of chelated carboxylato derivatives [83].

Concerning the monoalkyl carbonato complexes of

transition metals such as Cu[58], Pd [48]a the absorption frequency of ν(C=O) were observed above 1600 cm^{-1} upto 1670 cm^{-1} for which the alkyl carbonato moiety behaves as a unidentate ligand.

However, no litrature precedents are found for the synthesis of alkyl carbonato complexes of nickel from which we may draw analogy on the IR data of the prominent frequency bands of the $ROCO_2^-$ group. Therefore our assignment of the characteristic frequency bands for the products (III) and (IV) are indirect i.e., by analogy with similar complex of other metals. Based on the preceding litrature evidences the relatively strong bands of the ν(C=O) for our complexes lie in the range 1575-1652 cm^{-1} suggesting the presence of both monodentate and bidentate mode of coordination for the $iPrOCO_2^-$ groups. This may lead us to conclude that complexes (III) and (IV) have structures (B) and (D) (Fig.2.1 and 2.2) respectively as their most probable structures.

2.2 Properties

An interesting feature of the reaction of CO_2 with compound (I) is its reversibility that was observed under very mild condition. When the green THF solution of product (III) was heated upto 50°C, the blue solution of compound (I) was regenerated. On the other hand, when the blue THF solution of (I) was cooled to room temprature in CO_2

atmosphere the green product (III) was obtained. This "insertion-deinsertion" of CO_2 into the Ni-OR bonds could be repeated several times without any decomposition product being observed.

$$(I) + 4CO_2 \underset{\text{room temp.}}{\overset{50^\circ C}{\rightleftharpoons}} (III)$$

Similar reactions involving CO_2 insertion have been observed for alkyl carbonato complexes of Cu[58]a, W[59], Pa[48a] showing the same behaviour .

The corresponding reversible colour change by reaction of CO_2 with compound (II) was not carried out because of the insolubility of product (IV) in THF, toluene or mixture of the two. Unlike its reactions in solution, CO_2 does not react reversibly with compounds (I) and (II) in solid phase, since the solid products (III) and (IV) are thermally stable upto temperatures between 90-100°C. Above this temprature they would rather be decomposed to unidentified product than to regenerate the starting compounds (I) and (II). Melting of the products was not also possible for the same reason.

Complex (III) was observed to dissolve in solvents like THF, alcohols (ethanol, isopropanol), diethly ether, and organic acids: while complex (IV) was found to be insoluble in most organic solvents. This remarkable properties of the two complexes are attributable to the more solvent

polarizing ability of Li^+ ion than Na^+ ion owing to the small size of the former compared to the later.

Both complexes are affected by the presence of water. The addition of water to the THF solution of (III) caused a bright green substance to begin to form in the solution. Furthermore, slow layering of diethylether and n-hexane to the concentrated solution yielded a final pale green precipitate. This precipitate was insoluble in THF but soluble in more polar solvents like acetone or acetonitrile. This behaviour with water was also indicated in the IR spectrum of an exposed product (III) which happened to show the characteristic OH band.

Following these observations and from the litreture evidences [14,64] we may possibly suggest that bicarbonato complexes could be formed by reactions of (III) and (IV) with water. The pH of the sparingly water soluble products also indicated alkaline property (PH=9-10) of the substances.

Moreover, on the reaction with dilute mineral acids in solid as well as in THF solution of (III), CO_2 gas was evolved according to reaction (64)

$$iPrOCO_2^- + H^+ \text{-------} \rightarrow iPrOH + CO_2 \uparrow \quad (40)$$

A dilute HNO_3 solution of (III) was observed to give a pale yellow precipitate when treated with $AgNO_3$ solution owing to the presence of bromide in the product (III).

Attempts were also made to synthesize complexes (III)

and (IV) by reactions of the corresponding alkoxides (LiOiPr) and (NaOiPr) with CO_2 followed by subsequent addition of $NiBr_2.2OME$ in the former and $Ni(acac)_2$ in the later. However, results of these reactions showed that the products were completely different from those obtained in the earlier reactions. The products were having colours ranging from blue to blue-green and distinct from the light green products (III) and (IV).

2.3 Influence Of Phosphines On The Formation of The Products

Preliminary survey was carried out to study the influence of donor ligands - phosphines in this case, on reaction of CO_2 with compounds (I) and (II). For this purpose 1 mole of PPh_3 and Ø.5 mole of diphos were made to react with 1 mole of compound (II) in THF/toluene solution with subsequent generation of CO_2 into the two solutions. A deep green product was formed in the presence of PPh_3. The ligand field spectrum measured for the mother liquor (filtrate) of PPh_3 product gave no meaningful band assignable to any of the transitions of nickel in the d^8 state. The content of the nickel was also ananlyzed to be ca. 13.5 % and correspond to none of the possible triphenyl phosphino isopropyl-carbonato nickel (II) complex formulas. This may lead us to conclude that a mixture of several possible products might be formed as a result of different

possible reaction routes. Further attempts in the investigation of the products of the reactions could not be made at this stage.

The corresponding reaction of CO_2 with compound (II) in the presence of diphos led to the formation of decomposition products including a deposit of grayish material probably Ni(O) on the walls of the reaction vessel. No attempts were also made to characterize the decomposition products.

3. Reaction Products of Carbon Disulphide: Lithium And Sodium Isopropylxanthato nikelates (II)

3.1 Composition And Structure

The analogous reactions of compounds (I) and (II) with CS_2 were also possible leading to the formation of isopropyl xanthato complexes (VII) and (VIII) according to the equations.

(I) + $4CS_2$ --------> $Li_2Ni(S_2COiPr)_4.2THF$ (52)

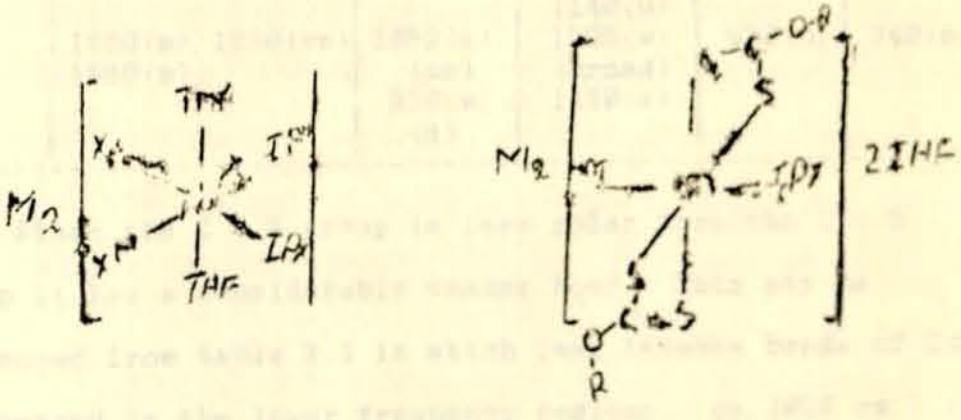
(II) + $4CS_2$ -------> $Na_2Ni(S_2COiPr)_4.2THF$ (53)

The ligand field spectra of the products (VII) and (VIII) have also values for an octahedral environment at the nickel center. This is due to the appearance of bands for the spin-allowed transitions for (VII) at 15,630 cm^{-1} [ν_2: $^3A_{2g}$ -----> $^3T_{1g}$ (F)] and at 21,280 cm^{-1} [ν_3: $^3A_{2g}$---> $^3T_{1g}$ (P)]; and for complex (VIII) the corresponding bands are observed at 16,000 cm^{-1} [ν_2: $^3A_{2g}$-----> $^3T_{1g}$(F)] and at 22,100 cm^{-1} [ν_3: $^3A_{2g}$----> $^3T_{1g}$ (P)]. However, the ν_1 band for the transition [$^3A_{2g}$ ----> $^3T_{2g}$] did not appear in both spectra of (VII) and (VIII) in the range 750-350 nm for the same reason as in 2.1.

Elemental analyses of (VII) indicated the atomic ratio of Ni:Br, ca. 1:0.67 (expected ratio for coordinated Br is 1:1). This leads us to assume that bromide was present in the sample as an impurity. Thus the composition $Li_2Ni(S_2COiPr)_4.2THF$ may be assigned to (VIII) based on the ratio of Ni:Li, ca. 1:2.3 (theoretical value 1:2).

Similarly the formula $Na_2Ni(S_2COiPr)_4.2THF$ may be assigned to (VIII) based on the ratio of Ni:Na.ca.1:1.9 (Theoretical value 1:2).

Regarding the structures of (VII) and (VIII) spectroscopic (vis.IR) measurements and elemental analyses data allow us to suggest similar structures as in section 2.1 These are also based on the assumptions of possible unidentate and bidentate modes of coordination of the isoproyl xanthato ($iPrOCS_2^-$) groups in the same fashion like those of the isopropylcarbonato ($iPrOCO_2^-$) moiety. The suggested structures are given for (VII) and (VIII) in Fig.3.1 as (A) and (B) respectively for the unidentate and bidentate modes for each complex.



(A) Unidentate mode (B) Bidentate mode

M = Li in (VIII) and M= Na in (VIII).
IPX = isopropylxanthato group, R = iPr

Fig.3.1 Possible structures of (VII) and VIII) for non-chelated and chelated modes in each complex.

The infrared data interpretation for band assignments in alkyl xanthato metal complexes and similar other sulphur compounds have been investigated by several workers [83,84]. Our formulation of the isopropylxanthato complexes as having chelated and no-chelated ligands is supported by IR evidence (Table 3.1).

Both complexes show the weak C-S stretching frequency bands in the general region 700-600 Cm^{-1} characteristic of C-S bonds (ca.720(m) for (VII) and ca.620cm^{-1} for VIII).

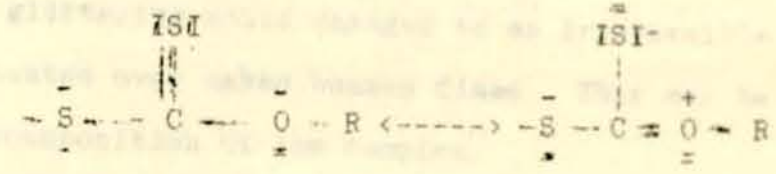
Table.3.1

IR Data For Complexes VII and VIII in Nujol; cm^{-1}

Complex	Vc=O	vC-O	vSC-O	VC=S	VC-S	VM-S
VII	1720(m)	1260(vs)	1080(s) 940(w)	1020(w) (broad) 1140(w)	720(m)	-
VIII	1630(m) 1580(m)	1280(vs)	1052(s) (as) 930(w) (s)	1205(w) (broad) 1110(s)	620(m)	340(m)

Since the C = S group is less polar than the C = O group it has a considerably weaker bond. This may be evidenced from table 3.1 in which less intense bands of C=S appeared in the lower frequency regions, ca. 1020 cm^{-1} (w) for (VII) and ca. 1205 cm^{-1} (w) for (VIII). The existence of the xanthato (dithiocarbonato) groups in the complexes is ascertained by appearance of bands of medium intensity in the C=O stretching frequency region (at ca. 1630 cm^{-1} and 1580 cm^{-1}, for example in complex (VIII)). The occurrence of these bands (more than any other) in this region is

usually attributed to the partial double bond character of the C-O group [85]. Thus we may explain the existence of such bands in the xanthato complexes by occurrence of possible resonance forms as:



In addition several other bands appeared in the broad region 1580 - 600cm^{-1} which can be assigned to vibrations involving interactions between C = S, S - C = S, S - C - O and C - O stretching frequencies [77,85]. Some of these bands, for example, the band at 1280 cm^{-1} (vs) is typical of the Vc-o of the iPrOCS$_2^-$ group of complex (VIII). Similarly the band at 1580 cm^{-1} (m) may be assigned as the Vc-o of the same group indicating a partial double bond nature of the C-O bond. We may cite a litrature evidence [86] for typical Vc-O absorptions of iPrOCS$_2^-$ in similar complexes of osmium:

[OsCl(PMe$_2$Ph)$_2$ (S$_2$COEt)], ca. 1250 cm^{-1} (vs) and cis-[Oss(PMe$_2$Ph)$_2$ (S$_2$CNMe$_2$) (S$_2$COEt)], ca. 1520 cm^{-1} (m), 1230 cm^{-1} (S)

3.2 Properties

Complexes (VII) and (VIII) were obtained as stable solids at room temperature. The colour of the complexes ranges from dark-yellow brown to golden brown. Complex (VIII) was observed to be affected by heat as a result of which the glittering solid changed to an irreversible black tar when heated over naked bunsen flame. This may be due to thermal decomposition of the complex.

Complex (VII) was found to be soluble in polar solvents like acetone, diethylether, isopropanol, THF, forming yellow-brown solutions. Hydrocarbon solvents like benzene, toluene do not dissolve this complex. Unlike complex (IV), the xanthato analogue (VIII) is found to be soluble in the above mentioned polar solvents, but like (VII) it is insoluble in the hydrocarbon solvents. However solutions of these xanthato complexes are quite stable at room temperature under nitrogen.

Both complexes were seen to be affected by water forming a yellowish-green suspension that is insoluble in water and most organic solvents. The pH of the slurry, however, indicates an alkaline pH (8-9).

Both products (VII) and (VIII) were shown also to react with dilute mineral acids with the liberation of CS_2 (recognized by its characteristic smell). The reaction can be described by eq(65):

$$iPrOCS_2^- + H^+ \text{--------} \rightarrow iPrOH + CS_2 \quad (65)$$

3.3. Alterative Routes For Synthesis of Complexes (VII) And (VIII)

More interestingly it was possible for us to react complex (IV) with CS_2 at room temperature with the displacement of CO_2 and the formation of the corresponding xanthato complex derivative (VIII). Our formation of the xanthato complex by this reaction was confirmed by elemental analyses that suggested a similar ratio of the relative number of atoms as in section 3.1 of this Chapter. And this was found to be ca. 1:2 for Ni:Na. The values calculated for the formula $Na_2Ni(S_2COiPr)_4 . 2THF$ 7.4 % Ni, 5.8% Na are very close to the experimental values, 7.7% Ni and 6.13% Na. The ligand field spectra of the product obtained by this reaction indicates transition bands at 16,900 cm^{-1} [ν_2: $^3A_{2g}$ ---> $^3T_{1g}$ (f) and 21,800 cm^{-1} [ν_3: $^3A_{2g}$ ----> $^3T_{1g}$ (P)]. These values are very close to those obtained for the normal CS_2 insertion product (VIII). A similar displacement reaction was reported by Monica [8f] for the preparation of a dithocarbomoto complex of Re(I) by reaction of CS_2 with the corresponding carbamato complex.

V. CONCLUSION

From the results obtained it can be remarked that several points have arisen from this work:

i) Alkalimetal isopropoxonickelates may react reversibly under mild conditions with CO_2 to give the first examples of the alkyl carbonato complexes of nickel (II); and similar reactions are also possible with CS_2 to form the corresponding alkyl xanthato complexes.

ii) There are evidences that CO_2 and CS_2 reaction products with the novel alkoxo complexes are supposed to be octahedral nickel (II) complexes containing monodentate as well as bidentate modes of coordination for the $iPrOCO_2^-$ and $iPrOCS_2^-$ groups.

iii) All products of the reactions with CO_2 and CS_2 are stable in the solid state under nitrogen at room temperature. However, solutions in organic solvents (ethers, alcohols) of these compounds are generally unstable under the same condition. It has been observed for example, that solution of complex (III) in THF gave an insoluble precipitate on prolonged standing. Moreover, the solid isopropyl carbonate derivatives are relatively unaffected by temperature up to 90-

100°C unlike in solutions where reaction was seen to be reversible at (~50°C) for the THF solution of (III). The solids were observed to become pale when heated above 100°C.

However the corresponding isopropyl xanthato complexes are found to be stable both in the solid state as well as in solutions.

The work on the substances formed by reactions of CO_2 with the novel alkoxo complexes of nickel (II) in the presence of phosphine (which may allow a conclusion to be drawn as to what effect they may influence the reactions) is at infantile stage.

However, we may think, in general, that a way to novel complexes of nickel (II) is opened up by the reactions of the alkalimetal alkoxonickelates with CO_2 and CS_2 and it is likely also with SO_2. These new complexes of nickel particularly the alkylcarbonato nickelates may have the potentiality to act as reversible CO_2 carriers by behaving as precatalysts in many catalytic transformations, utilizing CO_2 as a C_1 source. However, to bring these prospective materials for actual services of synthetic chemists a challenging work is awaiting those interested in the field.

79

REFERENCES

[1]. Braunstein, P.; Matt, D.; Nobel, D.; Chem.Rev., 88 (1988)747

[2] Krishina Murthy, K.V.; Harries, G.H.; Sastric, Vis.; Chem.Rev., 70 (1970)171

[3] Ziessel, R.; Nouv.J.Chim., 77, 11 (1983)614

[4] (a) Walther, D.; Coord.Chem.Rev.;79(1987)136-174

(b) Sneeden, R.P.A.; "Comprechensive Organometallic Chemistry, "V.8, Wilkinson, G.,Ed., Pergamon: New York (1982) 225

[5] Mayer, R.;Burgen, H.;Mitt.bl.Chem.Ges.DDR, 3 (1984)74

[6] Huber, H.; Maskovits, M.; Ozin, G.A.; Natura (London) Phys.Sci.; 236(1972)127

[7] Lindsey, A.S ;Jeskey,u H ; Chem.Rev.,57 (1957)583

[8] Palmer, D.A.; van Eldik, R.: Chem.Rev. 83(1983)651

[9] Eisenberg,R.; Hendriken, D.E.; Adv.Catal., 28(1979)79: Chem.Abstr. 90. (1979)P57437K

[10] Mehrotra, R.C.,Adv.Inorg.Chem. Radio Chem. 26(1983)269

[11] Tsuda, T; Sanada, S; Veda, K.; Soegusa, T; Iorg.Chem.,15 (1976)2329

[12] Inoue,S.; Yamazeki, N.:Eds." Organic And Bioorganic Chemistry Of Carbon Dioxide," Kodarsha, John, Wiley, NewYork (1982)

[13] Yamamoto, A.; Orgonometalics,7 (1988) 2182

[14] Mehrotra, R.C.; Coord.Chem., 21(1981) 113-125

[15] Kalies, W.; Witt,B.; Gaube, W.: Wiss.Z.Ernst-Maritz-Arudt Univ. Greinfw.; Math-Naturwiss. Reiche, 34, 1-2 (1985)30-33

[16] (a) Bradley, D.C.: Nature,182(1958) 1211

(b) Bradley, D.C.; "Progress in Inorganic Chemistry,"V.2 303-361, Interscience New York (1960)

[17] Bradley, D.C.; Mehrotra, R.C.; Gaur, D.P.; "Metal Alkoxides," Academic Press, New York, 1978

[18] Malhotra, K.C.; Martin, R.L.; J.Organomet.Chem., 239(1982) 159-187

[19] Rodziewiez, W.; Jasunski, T.; Roczniki Chem., 27(1953)332: Chem.Abstr.49(1953) 2306a

[20] Mehrotra, R.C.; Bharara, P.C.; Branwal, B.P.; Indian J. Chem.; 15A (1977)458

[21] Branwal, B.P.;Mehrotra, R.C.; Trans.Met.Chem.; 3 (1978)320

[22] Krishinamurthy, K.V.; Harris, G.M.; Sastri, Vis.; Chem.Rev., 70 (1970)171 and references there in.

[23] Palmer, D.A.; Haris, G.M.; Inorg. Chem., 17(1974)965

[24] Tsuda, T.; Chujo,Y.; Saeguso, T.; J.Chem.Soc.Chem. Commun.,(1975) 963

[25] Chisholm, M.H.; Extine, M.; J.Chem.Soc. Chem.

Commun., (1975) 438

[26] Fachinetti, G.; Floriani, C.; Inorg. Chem., 18 (1979)3469

[27] Aresta, M.; Nobile, C.F.; Albano, V.G.; J.Chem.Soc Chem. Commun., (1975) 636

[28] Chaffee, E.; Dasgupta, T.P.; Harries, G.M.; J.Am. Chem. Soc., 95 (1973)4169

[29] Vol'pin, M.E.;Kolomin Kov,I.S.;"Organometallic Reactions," V.5, Wiley-Interscience, Ed.; New York (1975)313-386

[30] Jolly, P.W.; Jonas, K.; Krueger, C.; Tsay, Y.H.; J.Organomet. Chem., 33 (1971) 109: Chem. Abstr. 75 (1971) 62712r: 70816t.

[31] Misono, A.; Ushida, G.; Hidai, M.; Kuse, T.; J.Chem.Soc. Chem. Commun..(1968)981

[32] Pu,L.S.; Yamamoto, A.; Ikeda, S.; J.Am.Chem.Soc.; 90(1968)3896

[33] Darensbourg, D.J.; Rokiki, A.; Darensbourg, M,-Y.; J.Am.Chem.Soc.,103(1981)3223

[34] Yoshida, T.; Thorn, D.L.; Okano, T.;Ibers, J.A.; Otsuka, S.; J.Am.Chem.Soc.; 101 (1979)4212

[35] Ashworth, T.V.; Singleton, E.; J.Chem.Soc.; Chem.Commun., (1974)380

[36] (a) Miyshita, A.; Yamamoto, A.; J.Organomet. Chem.; 113(1976)187: Chem. Abstr. 85(1976) 63169c

(b) Beverwijk, C.D.M.; van derKerk,

G.J.M.; J.Organomet. Chem.: 42(1973) C59: Chem. Abstr., 78(1973) 136390v

(c) Yashita, A.M.; Yamamoto, A.; J.Organomet.Chem.; 49(1973)C57: Chem.Abstr., 78(1973)30238m.

(d) Ittel, S.D.; Tolman, C.A.; English, A.D., Jesson, J.P.; J.Am.Chem.Soc., 100(1978)7577

[37] Facchinetti, G.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C.; J.Am.Chem.Soc.; 101(1979)1767

[38] Kolominkov, I.S.; Gusev, A.I.; Belopotapova, T.S.; Grygorjan, M.Ch.; Lysyak, T.V.; Struchkov, Y.T.; Volpin, M.E. J.Organomet. Chem.; 69 (1974) C10: Chem.Abstr.80(1974)13947k

[39] Miyashita, A.; Yamamoto, A.; J. Organomet. Chem.; 49 (1972) C57: Chem. Abstr. 77 (1972) 62107p

[40] (a) Zachariasen, W.H.; J.Am.Chem.Soc.; 62 (1940) 1011

(b) Van NieKerk, J.N.; Schoening, F.R.L.: Nature, 171(1953) 36

[41] Chisholm, M.H.; Extine, M.W.; J.Am.Chem.Soc.; 99(1977) 782

[42] Chistiolm, M.H.; Extine, M.W.; J.Am.Chem.Soc.; 97(1975)5625

[43] Chandra, G.; Jenkins, A.D.; Lappert, M.F.; Srivastava, E.; J.Chem.Soc A.; (1970) 2250

[44] (a) Chisholm, M.H.; Extine, M.W.; J.Am.Chem.Soc.; 96 (1974)6214

(b) Ibid.97 (1975)1623

(c) Ibid. 98 (1975)4683

[45] Chisholm, M.H.; Cotton, F.A.; Extine, M.; Stutt, B.R.; Inorg.Chem.; 16 (1977) 603

[46] Chetcuti, M.J.; Chisholm, M.H.; Folting, K.; Huffman, J.C.; Janos, J.; J.Am.Chem.Soc.; 104 (1982)4684

[47] Chetcuti, M.J.; Chisholm, M.H.; Folting, K.; Heitko, D.A.; Huffman, J.C.; J.Am.Chem.Soc.; 104 (1982)2138

[48] (a) Crutchley, R.J.; Powell, J.; Faggiani, R.; Lock, C.J.; Inorg.Chim. Acta, 24 (1977) L15

(b) Hayward, P.J.; Blake, D.M.; Wilkinson, G.; Nyman, C.J.; J.Am.Chem.Soc.; 92(1970)5873

[49] Ashworth, T.V.; Singleton, E.; J.Chem.Soc.; Chem. Commun.; (1976)204

[50] Hidai, M.; Hikita, T.; Uchida, Y.; Chem.Lett., (1972) 521: Chem. Abstr. 76 (1972) 59713g

[51] (a) Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Reichert, W.W.; J.Am.Chem.Soc.; 100 (1978)1727

(b) Chisholm, M.H.; Reichert, W.W.; Cotton, F.A.; Murillo, C.A.; J.Am.Chem.Soc.; 99 (1977) 1652

[52] Bachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastine, C.; J.Am.Chem.Soc.; 101(1979) 1767

[53] (a) Chatt,J.; Kubota, M.; Leigh, G.J.; March, F.C.; Mason, R.; Yarrow, D.J.;

J.Chem.Soc.;Chem.Commun.: (1974)1033

(b) Ito, T.; Yamamoto, A.;

J.Chem.Soc.; Dalton Trans.,(1975) 1398

[54] Kato, M.; Ito, T.; Inorg.Chem.: 24 (1985) 504

[55] Kato, M.; Ito, T.; Inorg. Chem.: 24(1985)509

[56] Inoue, Y.; Ohao, S.; Hashimoto, H.: Technol. Rep. Tohoku Univ., 41 (1953)1: Chem.Abstr., 100 (1984)28877y

[57] Bochkarev, M.N.; Fedorova, E.A.; Rdkou, Yu.F.; Khorshev, S.Ya.; Galinina, G.S.; Razuvaev, G.N.; J.Organomet. Chem.: 258 (1983) C29

[58] Tsuda, I.; Saegusa, T.;

Inorg.Chem., 11 (1972) 2561

[59] Darensburg, D.J.; Sanchez, K.M.; Kheingold, A.L.; J.Am.Chem.Soc.: 109 (1987)290

[60] Newman, L.J.; Bergman, R.G.:

J.Am.Chem.Soc.: 107(1985) 5314

[61] Ibers, J.A.: Chem. Soc. Reviews 11 (1982)57

[62] (a) Inoue, Y.; Itoh, Y.; Kazama, H.: Chem.Lett.; (1977)855: Chem.Abstr. 88(1978)37564e

(b) Ibid (1978)633: Chem.Abstr., 89(1978) 1089389p

[63] Inoue, Y.; Itoh, Y.; Kazama, H.: Hashimoto, H.; Bull.Chem.Soc.Jpn.: 53(1980) 3329: Chem Abstr., 94(1981) 208404h

[64] Walter, D.; Schonberg, H.; Dinjus, E.;Sielter, J.; J.Organomet.Chem:334(1987) 377

[65] Darensburg, D.J.: Kudaroski, R.A.: Adv.Organomet. Chem.:22 (1983)129: Chem.abstr., 99 (1983) 214459z

[66] (a) Burkhart, G.: Hoberg, H.: Angew.Chem. Int.Ed.Engl., 21(1982)76

(b) Hoberg, H.; Schaefer, D.; Burkhart, G.; J.Organomet.Chem.; 228 (9182)C21

(c) Hoberg, H.: Schaefer, D.: Ibid. 238 (1982)383

[67] (a) Hoberg, H.; Peres, Y.; Kruger, C.: Tsay, J.-H.: Angew.Chem.Int.Ed.Engl.,25(1987)771

(b) Hoberg, H.; Scaefer, D.: J.Organomet.Chem., 236 (1982)C28

[68] Walter, D.: Dinjus, E.: Sieler, J.: Anderson, L.; Lindqvist, O.: J.orgamonet.Chem.266 (1984) 99

[69] Hoberg,h.: Oster, B.W.:J.Organomet.Chem.266(1984)321

[70] Wilson, C.L.;Wilson, D.W.: "Comprehensive Analytical Chemistry," V.1A. Elsevier, London (1959)

[71] Perrin, D.D.; etal.: "Purification Of Laboratory Chemicals."Pergamon New York (1983)

[72] Kiros, H.: Msc.Thesis, Chem.Dept. A.A.U.(1988)

[73] Charles, R.G.: Pawlikowski, M.A.: J.Phys. Chem., 62(958)440: Chem.Abstr.

[74] Vogel, A.: "Textbook Of Quantitative Inorganic Analysis" 4th.Ed., Longman, London (1981)

[75] Private Communication

[76] Fachinetti, G.; Floriani, C.: Zanazzi, P.F.: J. Am.

Chem. Soc., 100 (1978)7405

[77] Nakamot, K.; "Infrared Spectra Of Inorganic and Coordination Compounds," 2nd.ed.; Wiley Interscience: New York (1970)

[78] Becker, E.; Tsutsui, M.; "Organometallic Reactions," V.5.; Wiley- Interscience, New York (1975) P.318

[79] Holtzclaw, H.F.:Collman, J.P.: J.Am.Chem.Soc., 79(1957)3318

[80] West, R.:Riley, R.: J.Inorg. and Nuclear Chem.: 5 (1958)295: Chem.Abstr., 52 (1958) 8732e

[81] Nakamot, K.; Morimoto, Y.; Martell, A.E.: J.Am.Chem.Soc.: 83 (1961) 4528

The anhydrous nickel chelate complexes of amino acids investigated include:

(a) α - alanine, $Ni[NH_2CH(CH_3)COO]$

(b) β - alanine, $Ni[NH_2CH_2CH_2COO]_2$

(c) N - Methylglycine, $Ni[(CH_3)NHCH_2COO]_2$

(d) N - Phenylgynie, $Ni[(Ph)NH\ CH_2COO]_2$

[82] Monica, G.; Ceinini, S.:Porta, F.; Pizzotti, M.: J.Chem.Soc Dalton Trans.: 18(1976)1777

[83] (a) Monica, G.; Ceinini, S.; Albano, V.G.; Forni,F.; Marassero, M.: J.Organomet.Chem.: 112 (1976)297: Chem.Abstr.

[84] Robinson, S.D.; Uttley, M.F.: J.Chem.Soc Dalton Trans.:(1973)1912

[85] Silverstein, R.M.; Baster, G.C.; Morill, C.,
"Spectrometric Identification Of Organic Compounds."
3d ed.-New York: Wiley (1974)

Fig. 1

Absorption Spectra Of
$Li_2Ni(OiPr)_4 \cdot LiBr \cdot 3THF$
(In THF)

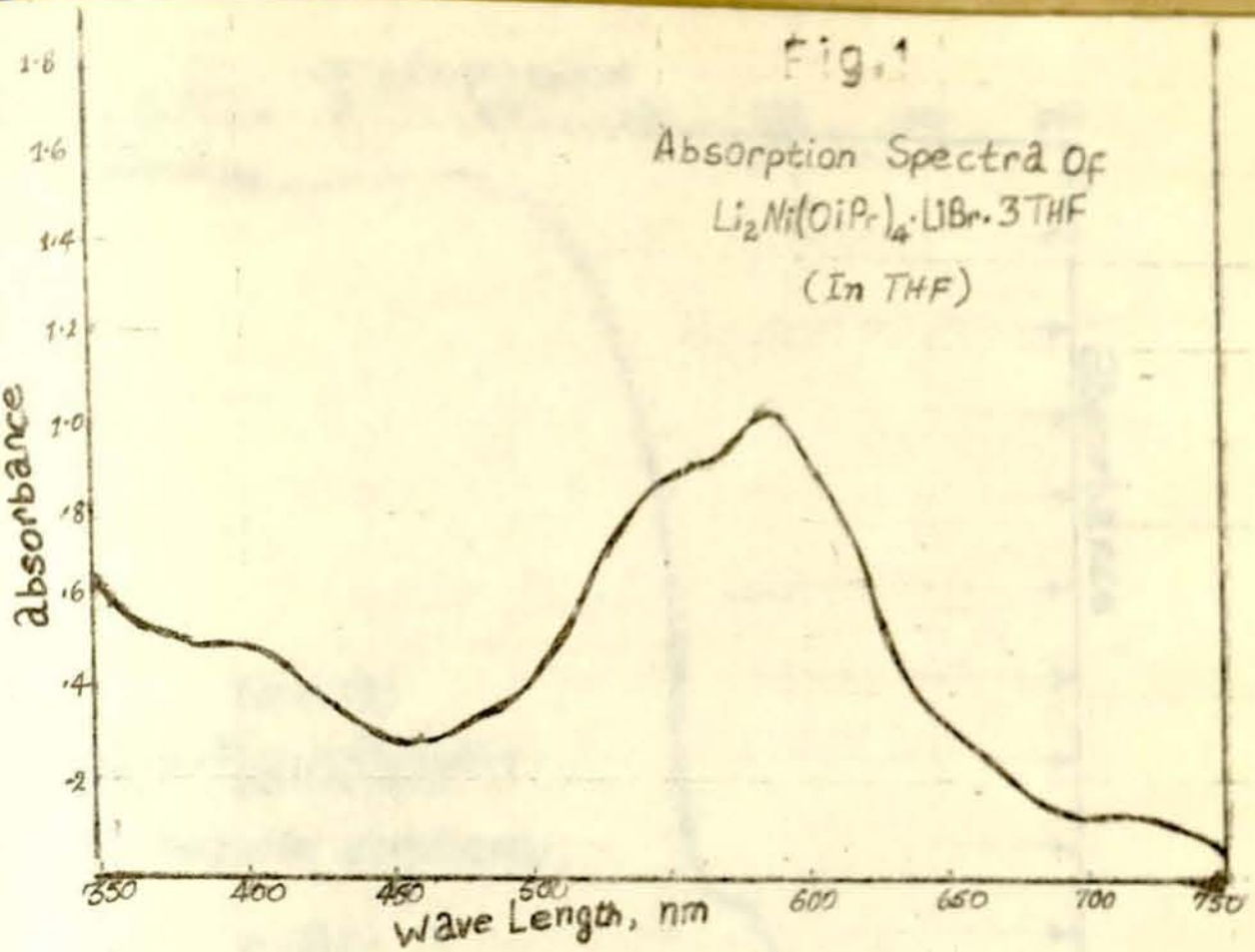


Fig. 2

Absorption Spectra Of
$Li_2Ni(O_2COiPr)_4 \cdot LiBr \cdot 2THF$
(In THF)

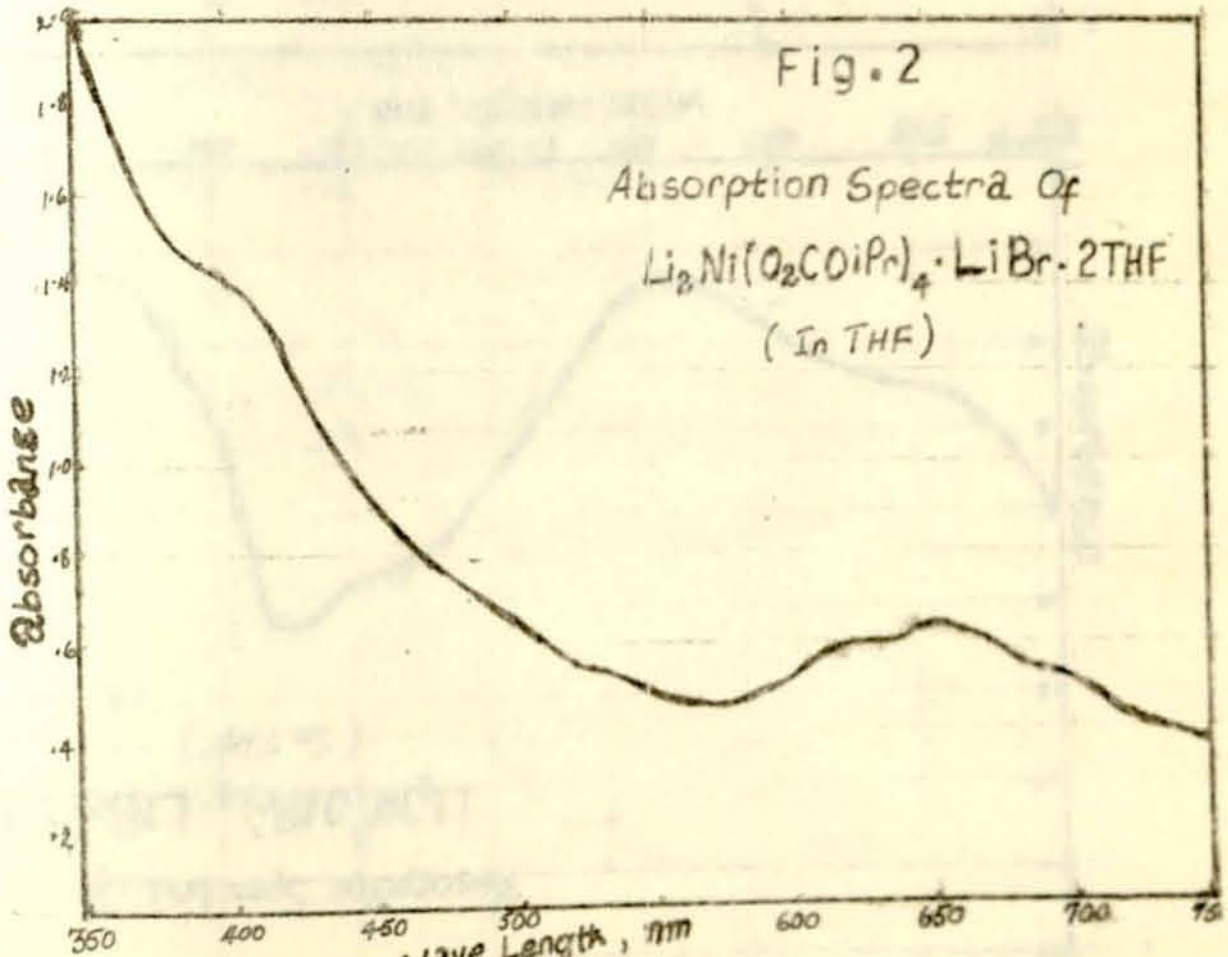


Fig 1

Absorption Spectra Of

$Li_2N[(OiPr)_4 \cdot LiBr \cdot 3THF$

(In THF)

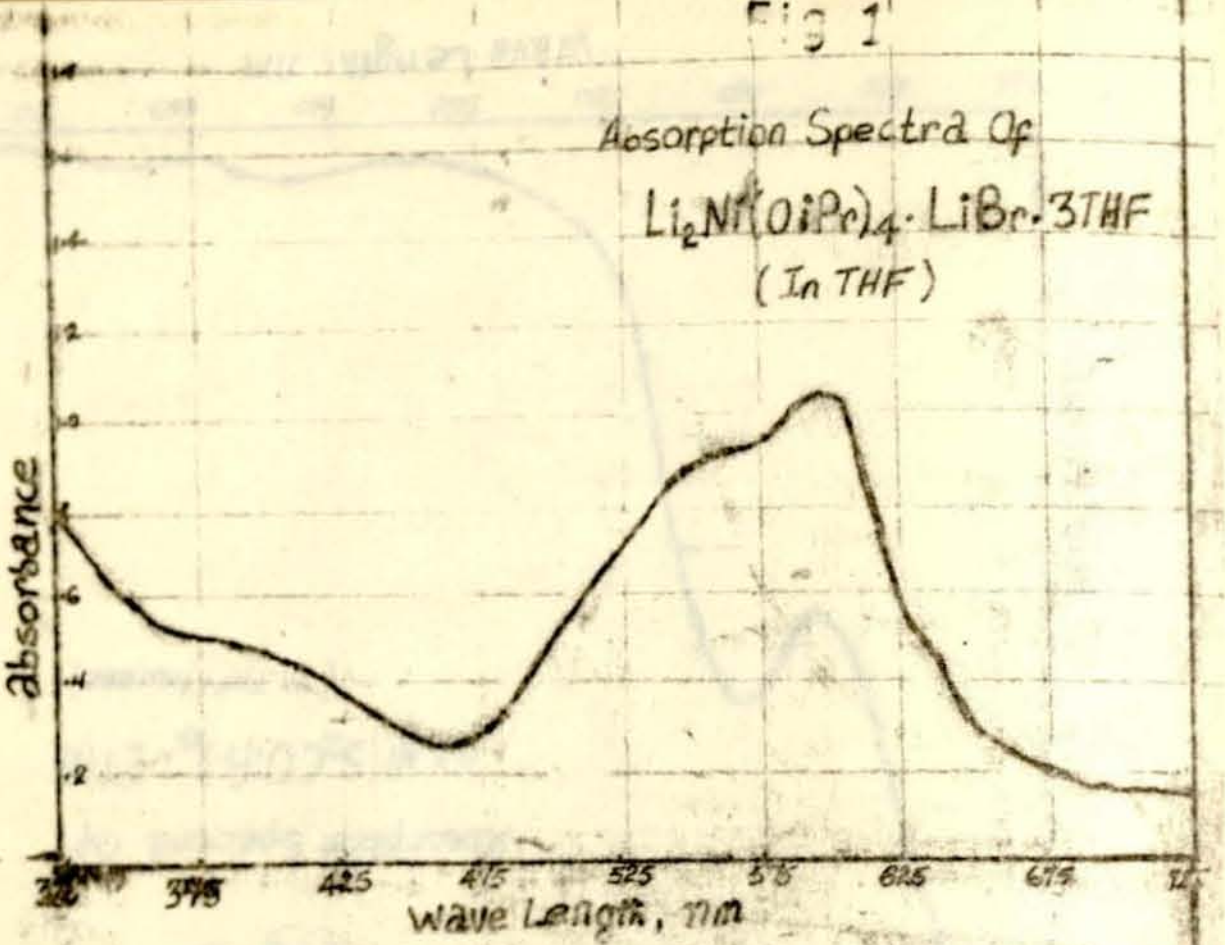


Fig. 3

Absorption Spectra Of

$Li_2N[(S_2COiPr)_4 \cdot 2THF$

(In THF)

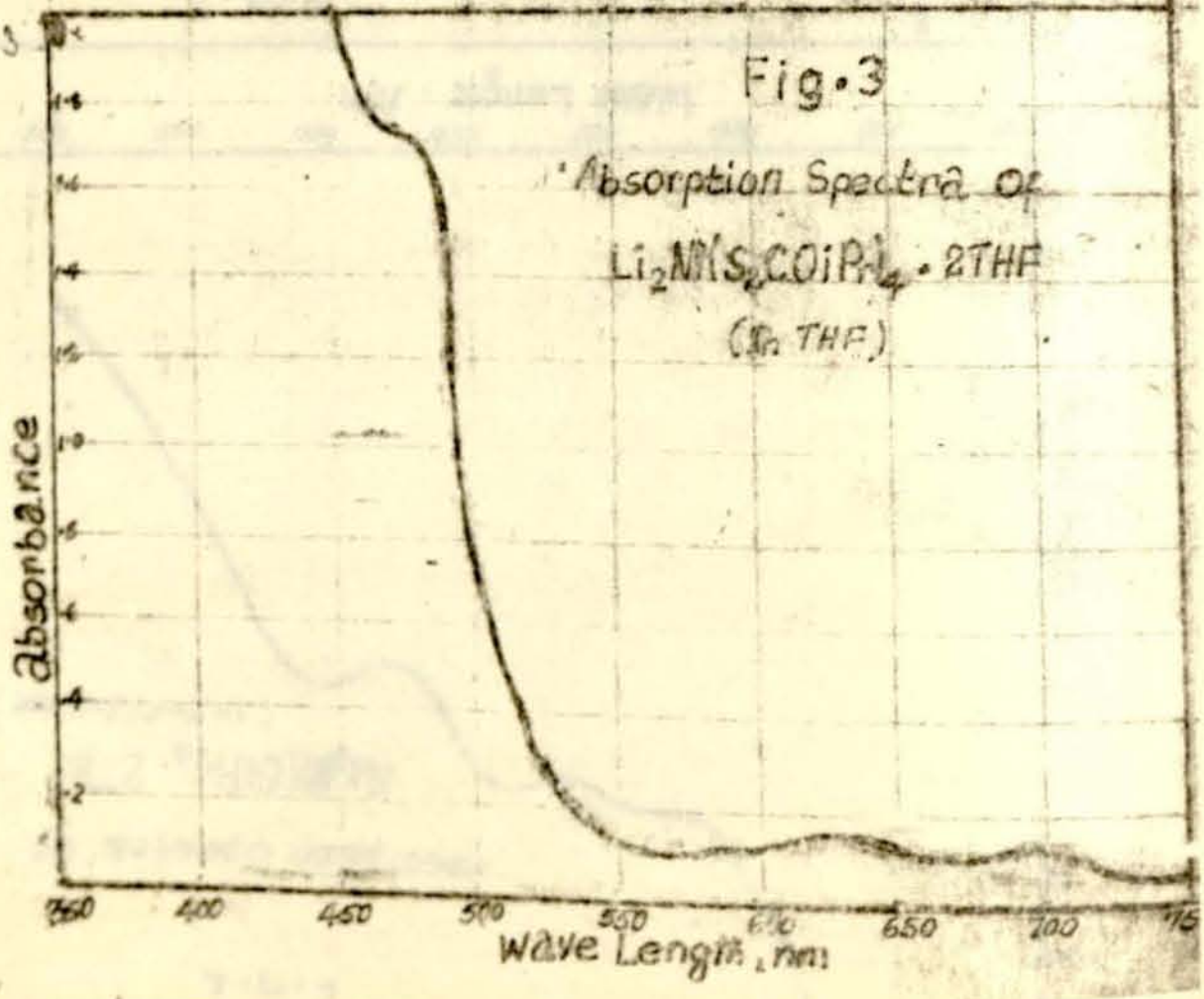


Fig. 4

Absorption Spectra Of

$Na_2Ni(OiPr)_4 \cdot 2THF$

(In THF/Toluene)

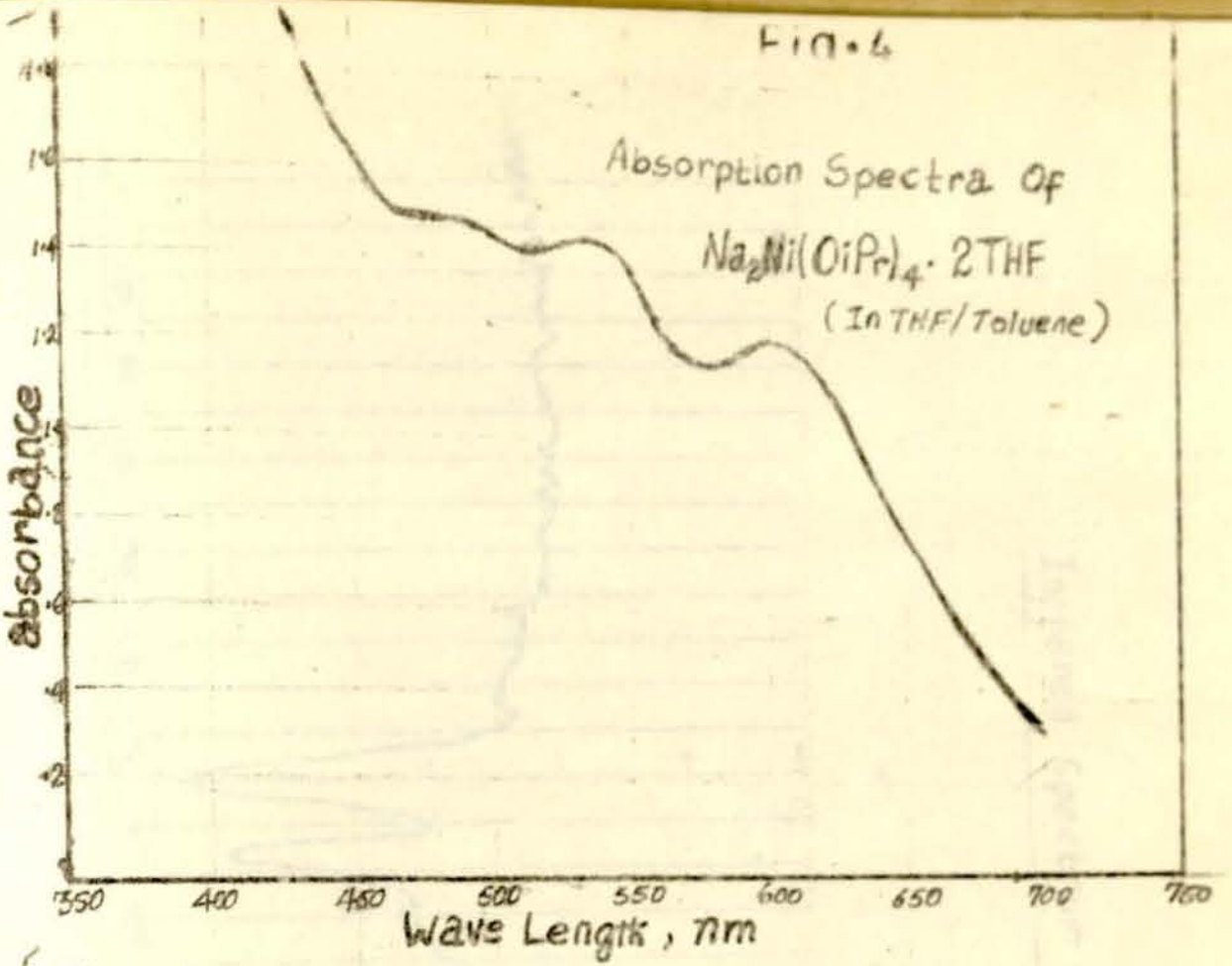
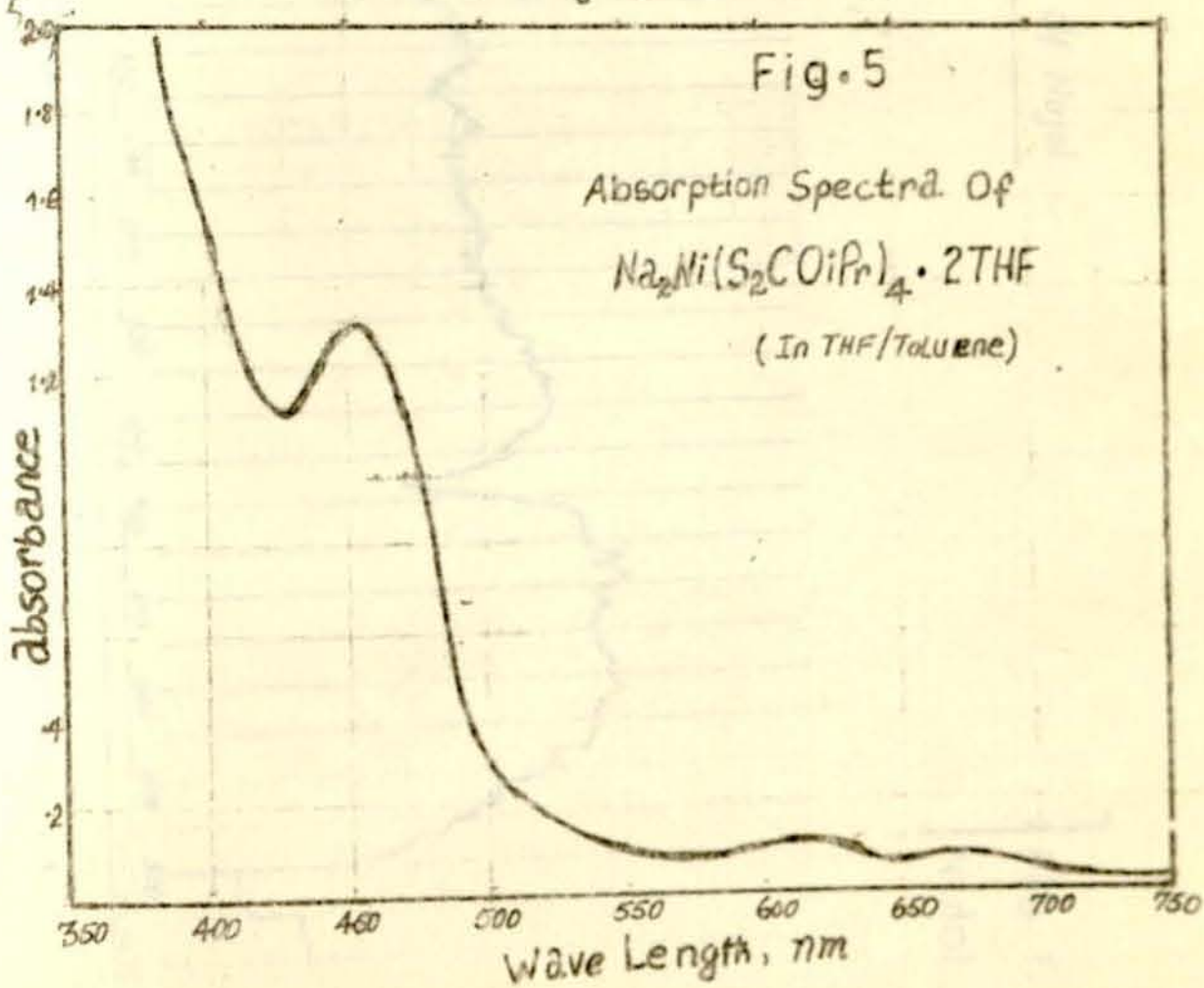


Fig. 5

Absorption Spectra Of

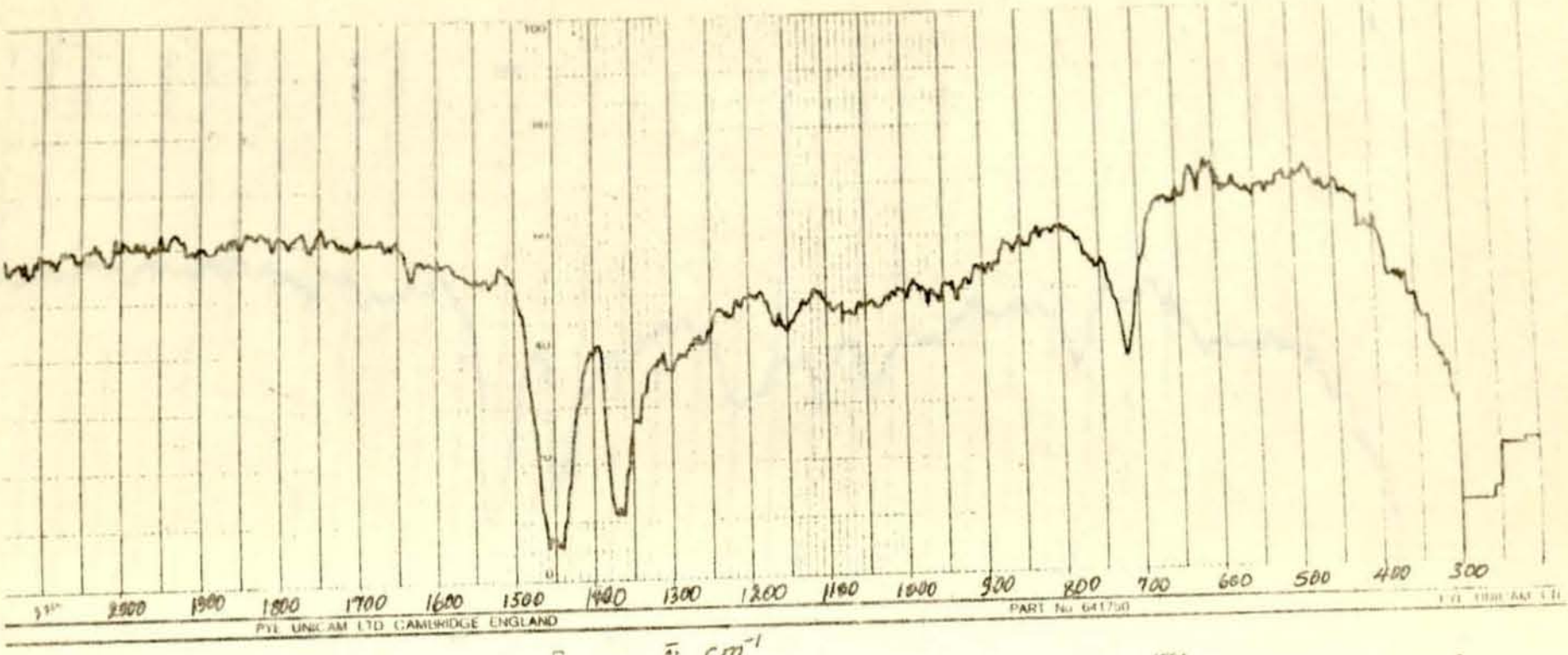
$Na_2Ni(S_2COiPr)_4 \cdot 2THF$

(In THF/Toluene)



Infrared Spectrum Of Nujol

FIG 6
Nujol



$\bar{\nu}$, cm^{-1}

Infrared Spectrum Of

$Li_2Ni(OiPr)_4 \cdot LiBr \cdot 3THF$ (In nujol)

FIG 7

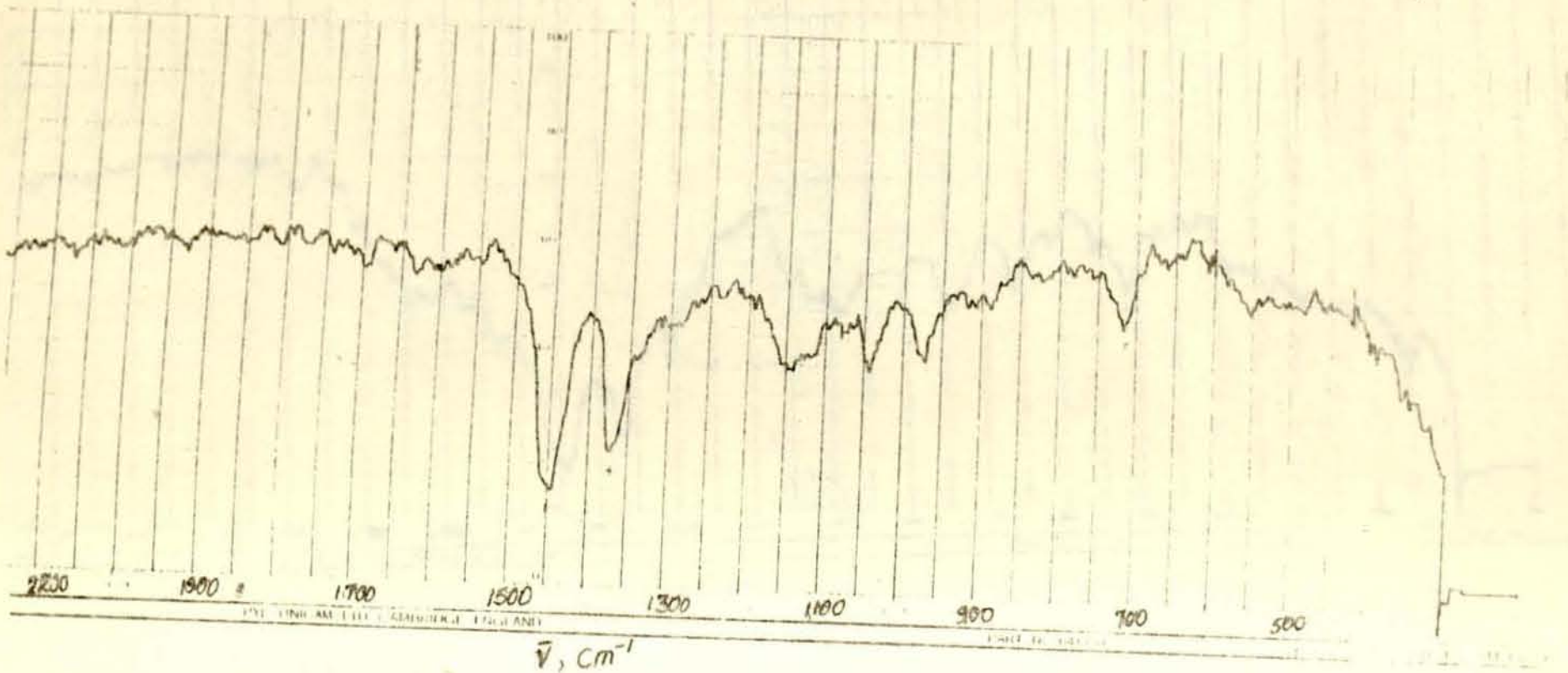
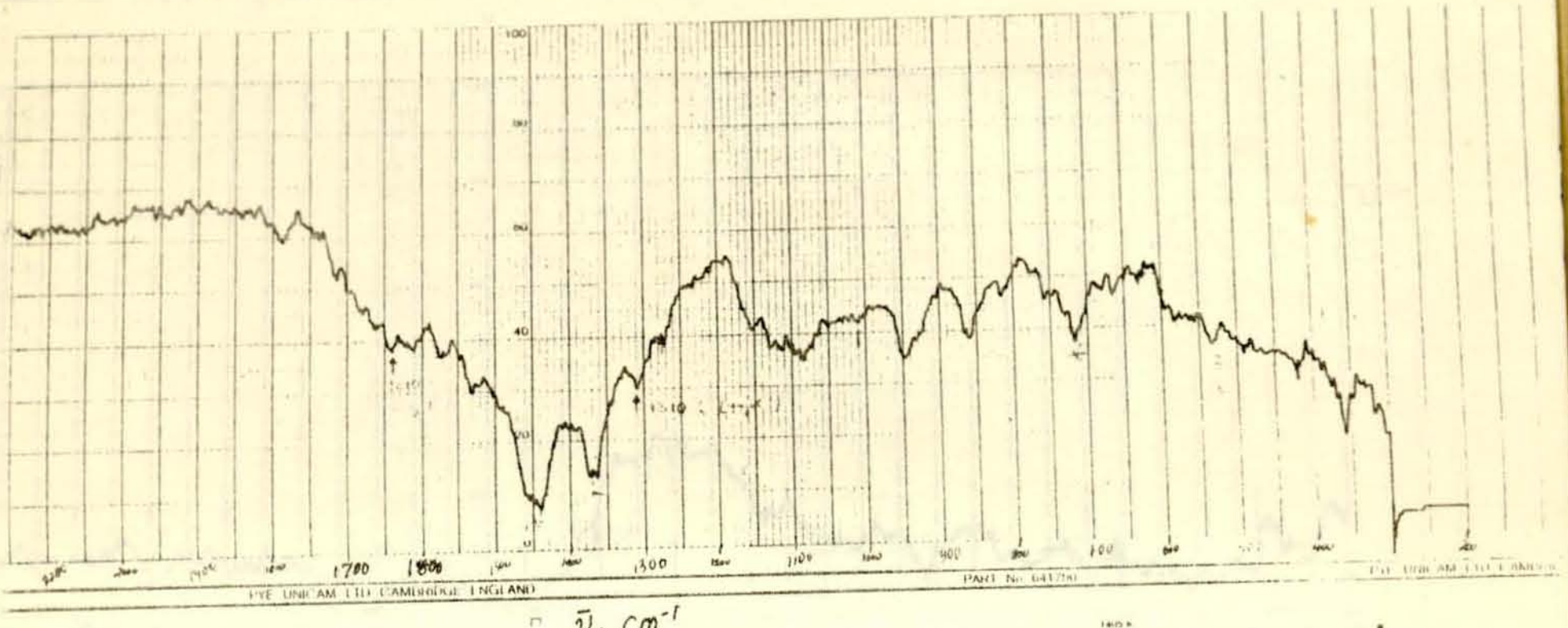


FIG 8

Infrared Spectrum Of

$Li_2Ni[O_2COiPr]_4 \cdot LiBr \cdot 2THF$ (Nujol)



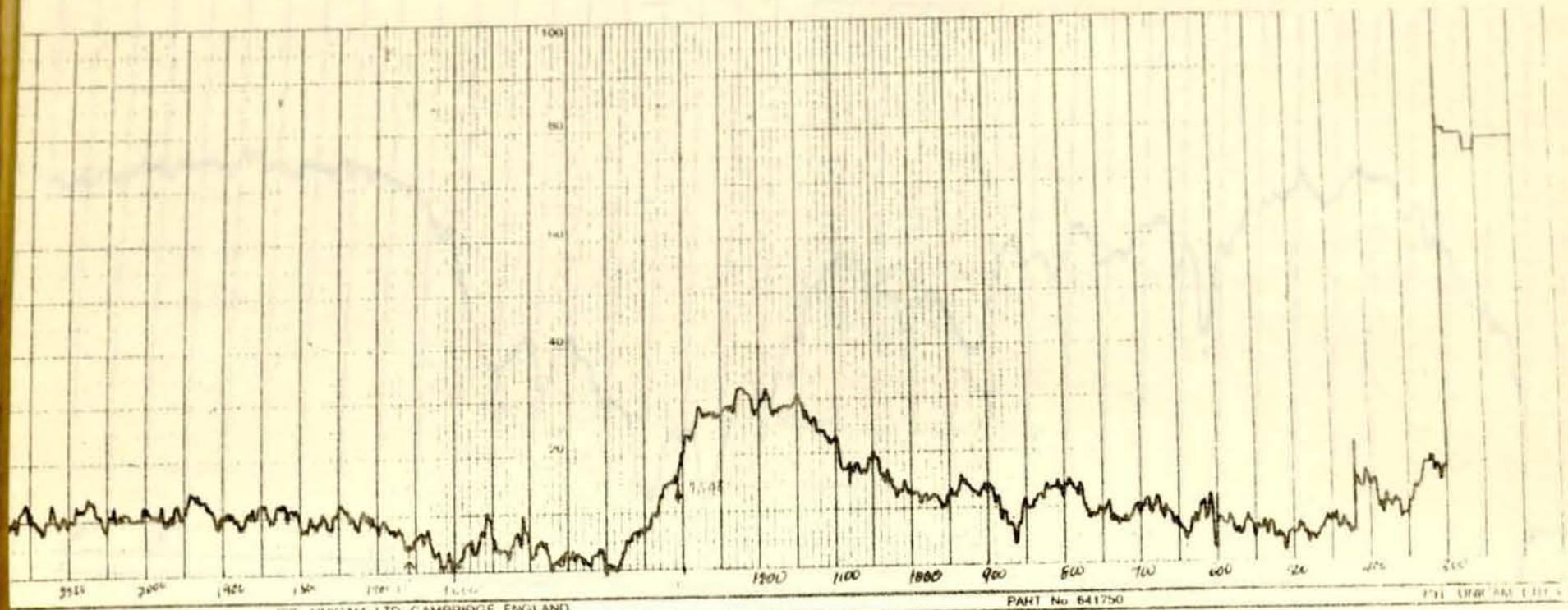
$\bar{\nu}$, cm^{-1}

Infrared Spectrum Of

$Li_2Ni[O_2COiPr]_4 \cdot LiBr \cdot 2THF$ (~~red~~)

(KBr pellet)

FIG 9

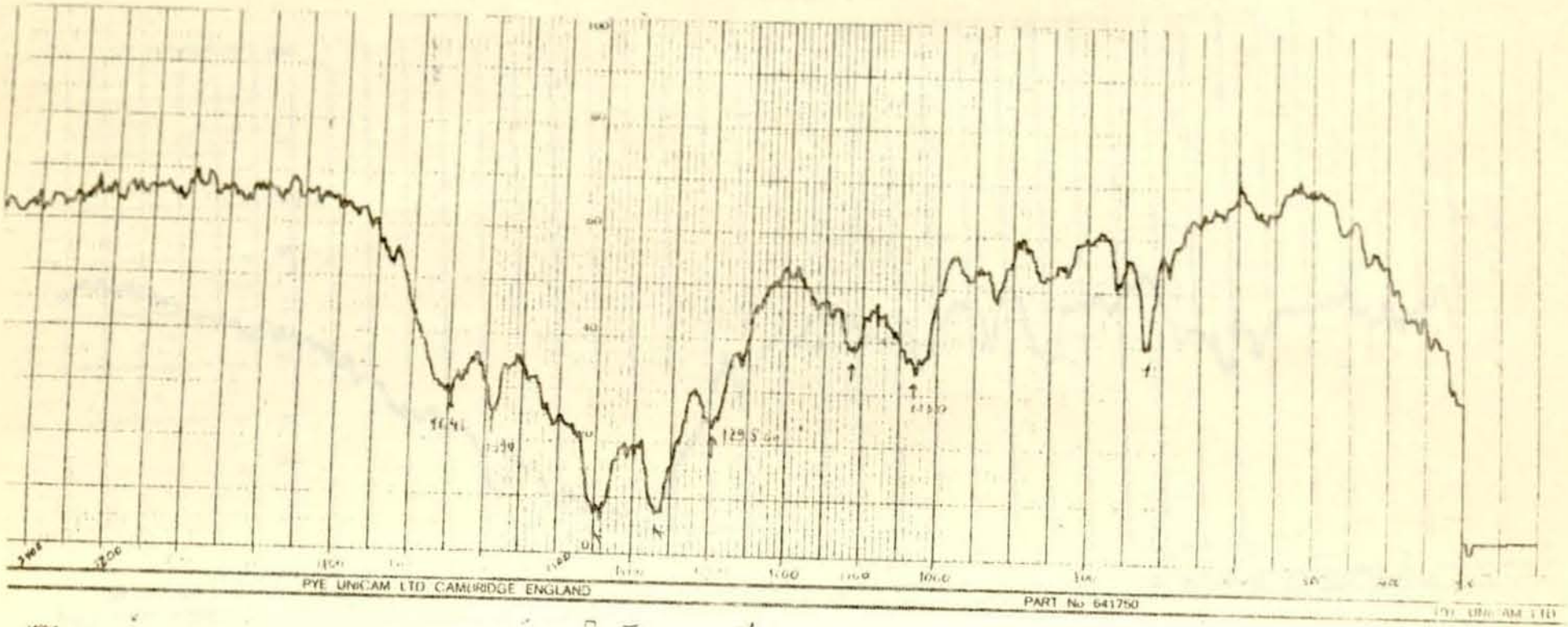


$\bar{\nu}$, cm^{-1}

FIG 10

Infrared Spectrum Of

$Na_2Ni[O_2COiPr]_4 \cdot 2THF$ (In nujol)



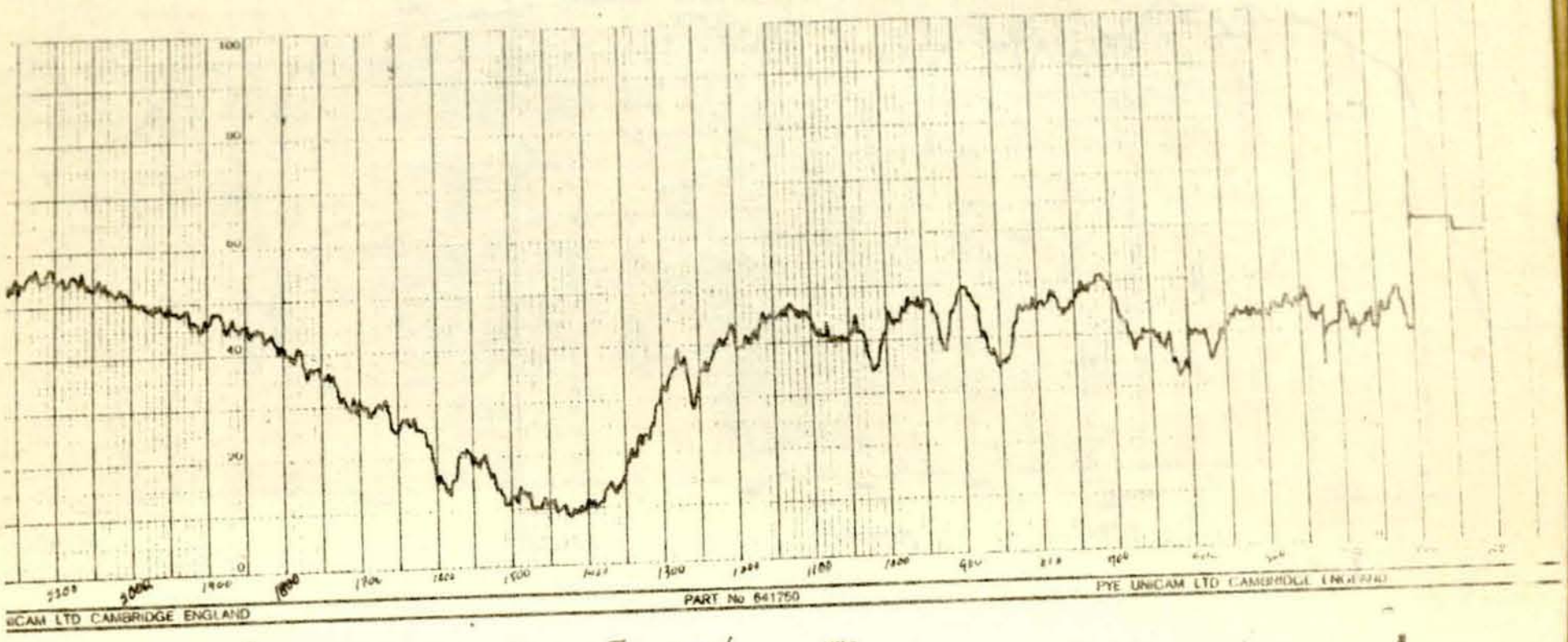
$\bar{\nu}$, cm^{-1}

Infrared Spectrum Of

$Na_2Ni[O_2COiPr]_4 \cdot 2THF$ (mull)

(KBr Pellet)

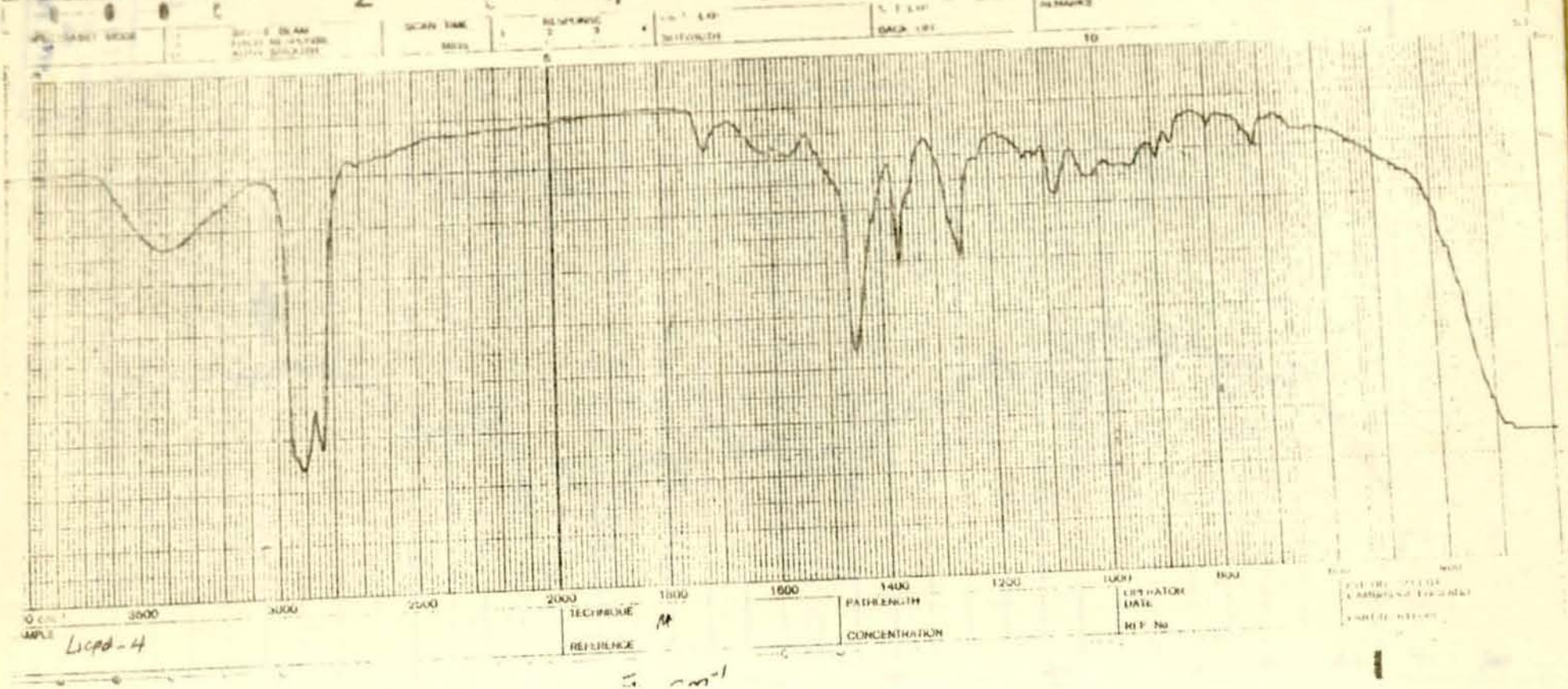
FIG 11



Infrared Spectrum of

$Li_2Ni[S_2COiPr]_4 \cdot 2THF$ (In nujol)

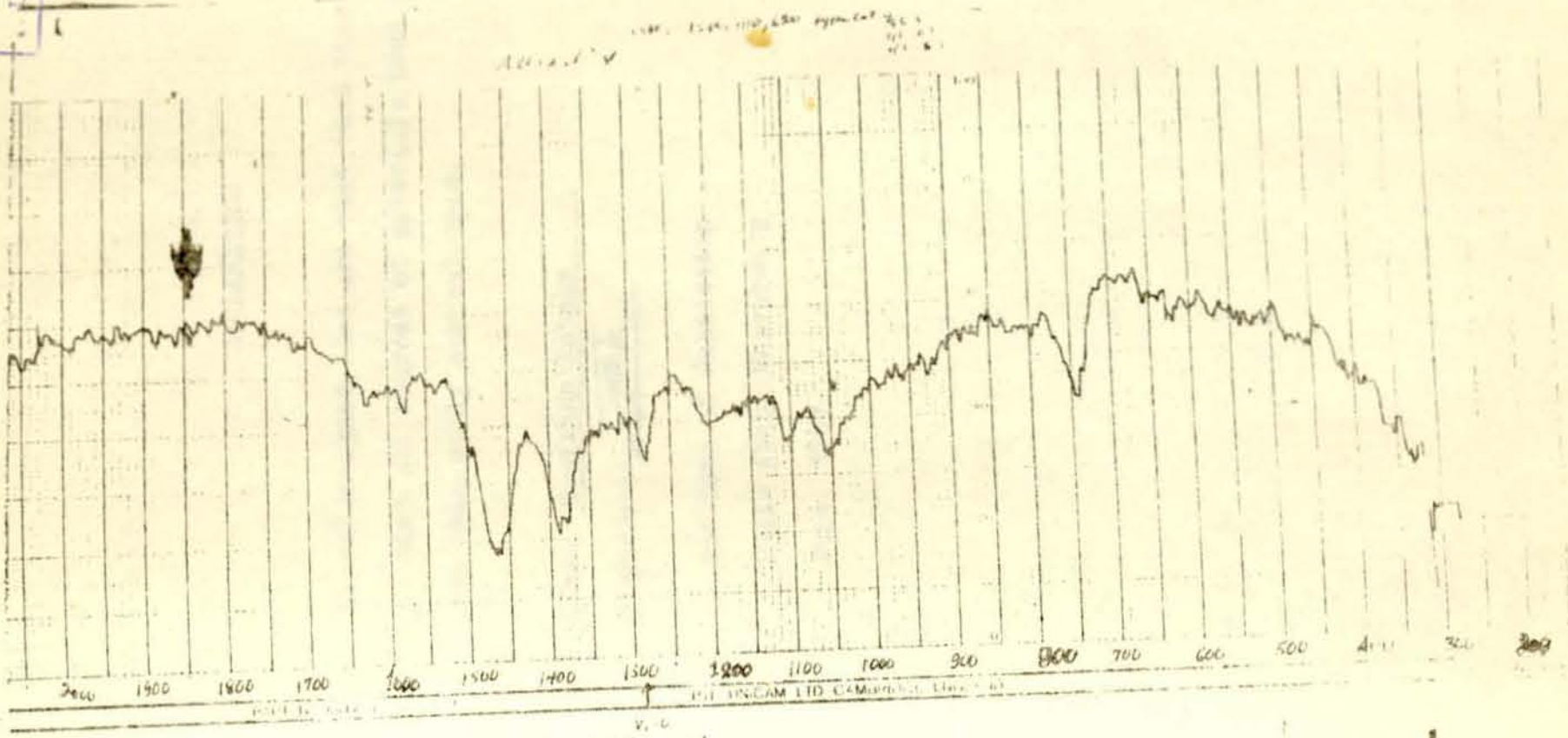
FIG 12



Infrared Spectrum Of

$Na_2Ni(S_2COiPr)_4 \cdot 2THF$ (In nujol)

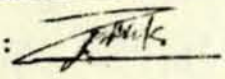
Fig 15



DECLARATION

I, The undersigned, declare that this thesis is my work and that all sources of materials used for the thesis have been dully acknowledged.

Name: Tesfahun Kebede

Signature: 

Place and Date of Submission

Addis Ababa University

June, 1989