REACTIVITY OF DISODIUM AND DILITHIUM TETRAISOPROPOXONICKELATES (II) WITH SOME SELECTED π - ACIDIC LIGANDS

BY

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DEDICATION

To my mother, Silas Tesfamariam.

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ABBREVIATIONS

acac	acetylacetonate anion
Am	amyl
μ_B	Bohor Magneton
Bu	butyl
sBu	secondary butyl
tBu	tertiary butyl
δ	chemical shift
Cy	Cyclo-C_6H_{11}
COD	1,5-cyclooctadiene
DME	1,2-dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
Hex	hexyl
OiPr	isopropoxide
iPr	isopropyl
m	medium
M	metal
Ph	phenyl
Pr	propyl
R	alkyl group
s	strong
w	weak
t,c,c	trans, cis, cis
t,t,c	trans, trans, cis
t,t,t	trans, trans, trans

Abbre. Contd.

thf	tetrahydrofuran
$P(OPh)_3$	triphenyl phosphite
PPh_3	triphenylphosphine
Vis	visible spectra
χ_g	gram susceptibility
χ_{mol}	molar susceptibility

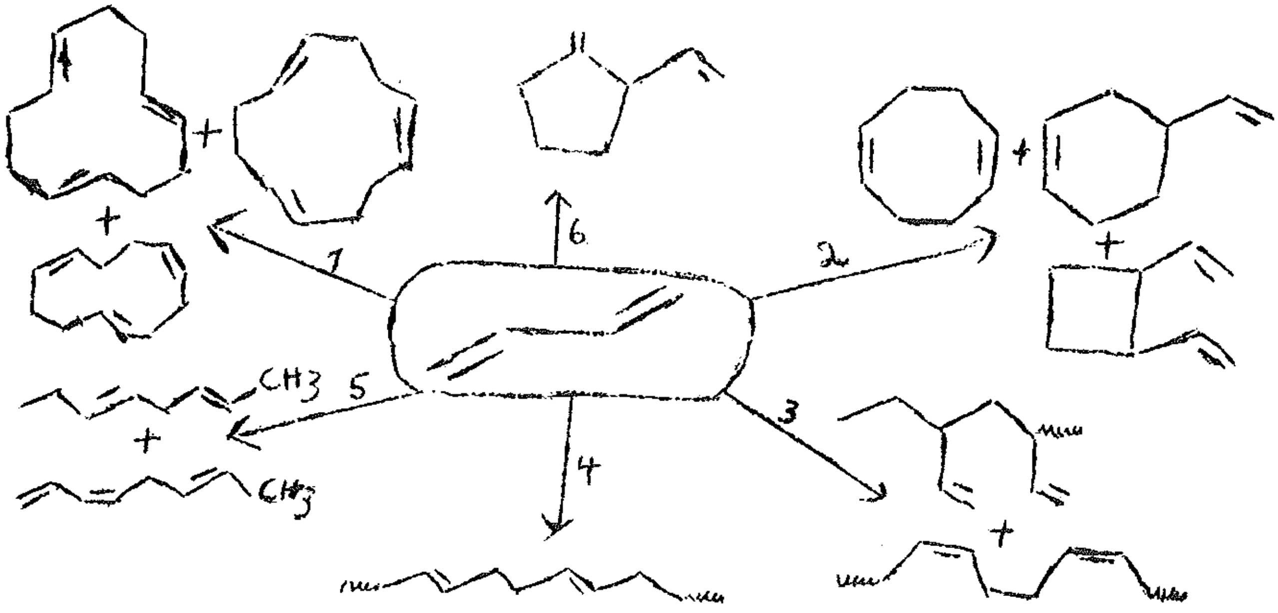
ABSTRACT

The syntheses of dilithium and disodium tetraisopropoxonickelate(II) were achieved using a novel starting compound, $NiBr_2.2DME$. This nickel(II) compound was found to be easy to prepare and a relatively stable compared to the commonly used starting analogue, $NiBr_2.2thf$, which was difficult to prepare and easily hydrolized on exposure to air. Electronic spectra and magnetic moment of $NiBr_2.2DME$ indicate an octahedral type coordination of nickel(II) in solution. The two alkoxonickelates synthesized from $NiBr_2.2DME$ were found to be identical with those prepared using $NiBr_2.2thf$. Using intramolecular redox properties of the above isopropoxonickelates, a series of low valent nickel complexes were synthesized. A yellow-brownish complex, $Ni(PPh_3)_2(COD)$ was synthesized starting from $Na_2Ni(OiPr)_4.2thf$. White, tetrakis complexes of Ni(o) with friallyl phosphite, triphenyl phosphite, and orange to yellow-brownish bis complex of 1,2-bis(diphenylphosphino)ethane were synthesized from either alkoxonickelates. In every case, the complexes synthesized from lithium and sodium derivatives were found to be the same. All the above complexes were observed to be unstable in air. The results obtained support the assumption of zero-valent nickel species to be active in catalytic systems consisting of Ni(II); PR_3, and primary and primary and secondary alkoxides which can be used to transfer 1,3-dienes into dimers and oligomers.

1. INTRODUCTION

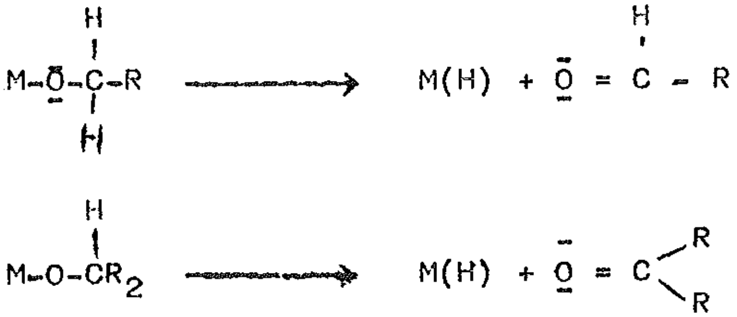
Catalyst systems based on transition metal complexes of Group VIII in general, and nickel complexes in particular, provide a fascinating field of research for the last 30 years both from academic and industrial point of views. Most of the catalytic processes of such complexes are related to dimerization, oligomerization, isomerization and cyclization of olefins (1-4). Particular interest is attached to nickel containing catalysts, due to their exceptionally high catalytic activity and the ease with which the course of the reaction can be directed by tailoring them. The properties of these nickel complexes are perhaps without parallel among other transition metal complexes (4).

The various catalytic possibilities, involving nickel containing complexes, may be shown with catalytic transformations of butadiene (3).



Scheme 1: 1:t, C,C; t,t,t and t,t,C-1, 5,9-cyclododecatriene with $Ni(COD)_2$; 2:1,5-cyclooctadiene, 4-vinylcyclohexen, C-12-divinylcyclobutane with $Ni(COD)_2 + PR_3$; 3:1,4-polybutadiene with $(C_3H_5NiCF_3COD)_2$; 4:1,4-t-polybutadiene with $(C_3H_5NiI)_2$; 5:t,t and C,t-1,3,6-octatriene with $Ni(COD)_2 + PR_3 + (CH_2)_5\ NH$; 6: 1-Methylene-2-vinylcyclopentane with $Ni[P(OEt)_3]_4 + CF_3COOH$.

Various methods are available for the preparation of nickel containing catalysts. Wilke, Heimbach and co-workers developed efficient classes of catalysts by reducing nickel(II) salts, using organo-metallic ligands, such as, phosphines, phosphites and olefins (5). Organo and hydrido compounds of main group metals (Group I-III) were also used as reducing agents. Reducing agents like sodium naphthalide, potassium graphite, sodium dithionite, hydrazinehydrate, hydrogen and electric current were also reported to be efficient (6). Catalysts, active for dimerization of dienes, were discovered by Gaube and co-workers (7). These catalysts are produced in situ in a system containing Ni(II), alkali metal alkoxide (MOR), phosphines, and the substrate. Best results with such systems were achieved with a molar ratio of $Ni(II):PR_3:MOR = 1:2:4$, in the temperature range 60°C - 100°C. Even though the system was known to work properly, the identity, mechanism of formation of the catalytically active species and the part played by the alkoxide was not known. The product formed by the alkoxide activated systems have been shown to be similar to those formed by nickel(o) containing systems. From that the following mechanism was suggested (8).



$$M-\underline{\overline{O}}-\overset{H}{\underset{H}{C}}-R \longrightarrow M(H) + \underline{\overline{O}}=\overset{H}{C}-R$$

$$M-O-\overset{H}{C}R_2 \longrightarrow M(H) + \underline{\overline{O}}=CR_2$$

(1a)

$$M(H) + {}^{-}OR \longrightarrow M(O) + ROH \qquad (1b)$$

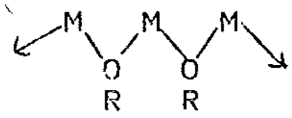
The mechanism involves β-hydrogen transfer from the α-carbon of the alkoxide to nickel(II) with formation of aldehyde or ketone, followed by reductive elimination to give an alcohol and the nickel(o) species. Detailed investigations of the primary interaction between the components of the catalytic system led to the discovery of a novel type of alkali metal alkoxocomplexes of nickel(II) as well as the synthesis of $Ni(H)Br(PCY_3)_2$. These alkoxides containing α-CH bonds were found to undergo facile intramolecular redox reactions, at temperatures between $65^{\circ}C$ and $90^{\circ}C$. Once the identity of the alkoxides and their intramolecular redox behavior was established, their synthetic advantage in the formation of low valent nickel complexes was shown in the presence of stabilizing neutral ligands (8). In view of the cost and handling problems of Ziegler - Natta type reducing systems, the use of alkali metal alkoxides of nickel as a source of low valent nickel is of a synthetic advantage.

Nickel is known to form complexes with formal oxidation state of zero. In such type of complexes, the σ-donor ligands have a low energy π-aceptor orbital (LUMO), while the σ-acceptor metal has filled π-donor orbitals (HOMO) . Nickel(o) has its π-orbitals (t_{2g}) filled. The stabilization is synergistic, i.e., the more electron density that the π-system can transfer from the metal to the ligand, the more the metal can accept via the σ-system. In turn, the more the σ-system removes from the ligand, the more readily the ligand can accept electron density through the π-system. Upto a certain point, then, each system can augment the bonding possibilities of the other. Such is the case with ligands such as phosphines and phosphites, which can bond by both mechanisms (60). Olefins bond to a metal through their π-electron density directed to a metal orbital of σ-symmetry, where the metal back donates electron density to the empty anti-bonding π^* orbital of the olefin (61).

2. LITERATURE SURVEY

2.1 Alkoxo Complexes of Later 3d Transition Metals

The alkoxide ion RO^-, is known to act as strong ligand with almost all metals giving a wide range of compounds, monomeric to polymeric; soluble to insoluble. The variety in coordination chemistry arises from the tendency of the metal to form rather covalent bonds than ionic ones with alkoxides, Furthermore, the diversity in the coordination chemistry arises from a balance, between the tendency of the metal to expand its coordination number by utilizing the bridging properties of alkoxide, and the tendency of the coordination number of the metal to be reduced by the steric effects of the alkyl groups. The polymeric nature of the metal alkoxide arises by the covalent character of intermolecular bonds involving the metal and oxygen atoms, namely:



(2)

which increases for metals in the same subgroup with increasing size, and the degree of hydrolysis decreasing (9a).

Most alkoxides of early transition and main group elements are volatile and soluble in organic solvents, with notable exceptions of methoxides. In contrast, alkoxides of later 3d metals are non-volatile and insoluble in organic solvents, with the exception of iron(III) alkoxides and chromium(IV) ter-butoxide. Most alkoxides of transition metals of the type $M(OR)_n$ were commonly prepared by alcoholysis of their corresponding metal dialkylamides, $M(NR_2)_n$ (9b). Primary alkoxides of Cr(III) were also synthesized by novel UV irradiation of tricarbonyl arene chromium complexes (10). The synthesis of bis(aryloxo)iron(II) and bis(alkoxo)iron(II) with 2,2'-bipyridine were reported by the reaction of diethylbis(2,2'-bipyridine)iron(II) with p-substituted phenols and alcohols, respectively((11). Mehrotra and co-workers (12) developed simple and systematic procedures for the syntheses of alkoxides of later 3d transition metals from their soluble halides in solvents like benzene, tetrahydrofuran and dioxane.

$$MCl_n + nLiOR \longrightarrow M(OR)_n + nLiCl \qquad (3)$$

n = 3 or 4 for Cr; R = Me, Et, Bu, tBu
n = 2 for Co; R = Me, Et or iPr, sBu
n = 2 for Ni; R = Pr, Bu, Hex, iPr
n = 2 for Cu; R = Me, Et, iPr or tBu

Bimetallic isopropoxides of the above elements with aluminium have been prepared as in the following reaction:

$$MCl_n + nK\left[Al(OiPr)_4\right] \longrightarrow M\left[Al(OiPr)_4\right]_n + nKCl \qquad (4)$$

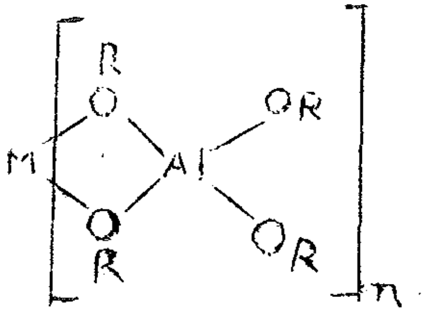
n = 3 for Fe(III), Cr(III), and n = 2 for
Mn(II), Fe(II), Co(II), Ni(II) or Cu(II)

As part of an investigation of ligands with large steric requirements, a series of first and second row transition metal alk oxides of 1-adamantanol, 2-admantanol and 1-adamantylmethanol have been synthesized from their dialkylamides by Wilkinson et al. (13a). In addition, the synthesis of neutral alkoxides and lithium alkoxometallate of the sterically demanding, bis(ter-butyl)methanol for Cr(IV), Mn(II), Fe(II), and Cu(II) were reported by the same research group (13b). Electronic (visible) spectra measurements and magnetic property determinations were made on most of the simple alkoxocomplexes by Mehrotra and co-workers (12). Primary and secondary alkoxides of chromium(III) are polymeric solids with octahedrally coordinated chromium, where as the ter-butoxide of Cr(IV) is a volatile blue liquid and has tetrahedral geometry. Co(II) alkoxides are in general octahedral. Spectra of Ni(II) primary alkoxides arecharacteristic of octahedral derivatives which exhibit three well defined spinallowed bands at 8750 $\pm$ 250 cm^{-1} ($\nu_1 = {}^3A_{2g} \longrightarrow {}^3T_{2g}$); 14810 $\pm$ 115 cm^{-1} (ν_2 = ${}^3A_{2g} \longrightarrow {}^3T_{1g}$ (F)) and 24980 $\pm$ 125 cm^{-1} ($\nu_3 = {}^3A_{2g} \longrightarrow {}^3T_{1g}$ (P)).

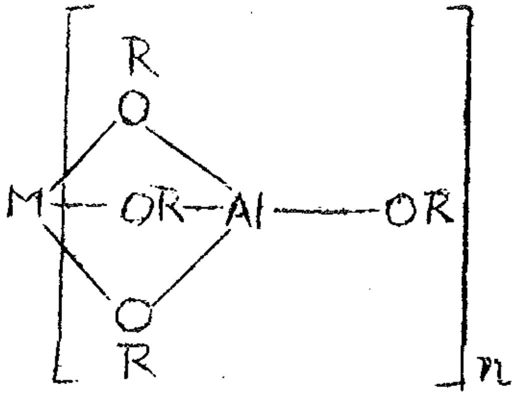
The spectra of the blue secondary and tertiary alkoxides of Ni(II) clearly indicate a tetrahedral geometry with well defined spinallowed transitions at 7580 $\pm$ 100 cm^{-1} ($\nu_2 = {}^3T_1$ ---- ${}^3A_2$) and 15850 $\pm$ 70 cm^{-1} ($\nu_3 = {}^3T_1$ ---- ${}^3T_1$ (P).

The magnetic moment (μ_B) of the primary alkoxides of nickel(II) fall in the range of 2.9 - 3.3, and those of secondary as well as tertiary alkoxides are found in the range of u_B = 3.2 - 3.9 at room temperature. These observations are in accord with their octahedral and tetrahedral geometries, respectively. Primary alkoxides of Cu(II) have a distorted octahedral geometry and the branched analogues are tetragonal. Most octahedral alkoxides of the above metals (with the exception of alkoxides of Cu(II)) are found to be inert towards alcoholyses with branched chain alcohols. This might be due to the extra stability associated with octahedral geometry, as compared to the lower thermal stability of the tetrahedral geometry. Moreover, when the alkoxide is bulky, the octahedral configuration may not be stable for steric reasons. The stability of $Cr(OtBu)_4$ might be due to the absence of α-CH bonds in addition to extra stability from two singly occupied lower e_g orbitals (14).

Even though there are variations in alcoholyses, most of them are found to goby facil interchange with chelating hydroxy ligands, such as silanols, glycols, β-diketones, alkanolamines etc. In contrast to the polymeric, insoluble nature of the simple alkoxides of the later transition metals, the bimetallic analogues are found to be coloured liquids or solids, which are miscible with organic solvents, and appear to be monomeric in refluxing solvents like benzene. These bimetallic alkoxides are found to have structure (I) with tetraisopropoxoaluminate acting as a bidentate ligand. But data for a few cobalt, nickel and copper derivatives appear to be more easily understood on the basis of a structure of the type(II) (15).



(I)



(II)

n = 3 for Cr(III) or Fe(III), n =2 for Ni(II), Co(II), Mn(II), Cu(II)

Prior to 1985, three different types of alkoxides of nickel(II) were known:

a. The simple binary nickel(II) alkoxides of the type, $Ni(OR)_2$

b. Bimetallic nickel(II), tetraalkoxoaluminates of the type, $Ni[Al(OR)_4]_2$, R = Me, Et, Bu, Pr, iPr.

c. The mixed alkoxides of nickel(II) of the type Ni(OR)X, where X is an anion beside the alkoxide ion (16). In 1985, W. Kalies and W. Gaube reported (8) the discovery of new alkoxides of nickel, based on lithium, sodium and potassium alkoxonickelates(II), having different compositions and with partially good solubility in organic solvents. These new types of alkoxides of nickel(II) are prepared by the reaction of nickel(II) compounds ($NiBr_2.2thf$, $NiBr_2$, $Ni(acac)_2$ or $NiBr_2$ $(PPh_3)_2$ with alkalimetal alkoxides of primary, secondary and tertiary univalent alcohols in aprotic organic solvents like, tetrahydrofuran or toluene. The maximum temperature for preparing primary and secondary alkoxides of nickel(II) is found to be 50°C, but 90°C for tertiary alkoxides, which do not have α-CH bonds for ß-hydrogen transfer. When the temperature is raised above 50°C, the alkalimetal primary and secondary alkoxonickelates(II) are found to decompose, giving metalic nickel, aldehydes or ketones, and an alcohol corresponding to the particular alkoxide group. The proposed mechanism is by β-hydrogen transfer from α-CH of the alkoxide ion to nickel(II) to give Ni(H) species, followed by reductive elimination of Ni(H) by an alkoxide group to form an alcohol and the nickel(o) species. The mechanism is supported by the separation of an equivalent amount of alcohol. The LiBr incorporated in the alkoxide derivatives of lithium. The LiBr is found to be undissociated during conductivity measurement in thf (45). Similar complexes containing lithium and solvent molecules are reported by Wilkinson et al (13), where the lithium ion is found to serve as a bridge between two alkoxide oxygens.

Magneticmoment determination using Gouy method on the tetraalkoxonickelates(II) of lithium and potassium in solid state showed typical of tetrahedral coordination with ground state term $^3T_1(F)$. The ligan ieldspectrum in nujol suspension showed tetrahedral coordination of nickel with three spinallowed transitions: $^3T_1(F)$--- $^3T_2(\ _1)$, $^3T_1(F)$--- $^3A_2(V_2)$, $^3T_1(F)$--- $^3T_1(P)$. Ligandfield-parameter further indicate tetrahedral coordination of the alkoxonickelates. D_q = 460 cm^{-1}, B = 800 cm^{-1} and ß = 0.77. From magneticmoment determination in nujol suspension, sodium derivative is found to have values of octahedral coordination.

	u_{exp}/u_B			
Compound	Solid state		Solution in thf	
Li_2 $Ni(OiPr)_4$ .LiBr.3thf	2934k	80-293k	293k	(Mass%)
Li_2 $Ni(OiPr)_4$ .LiBr.3thf	3,46	3,33-3,45	3,27	(1,27)
			3,48	(3,57)
Li_2 $Ni(OiPr)_4$ .LiBr	3,26	2,46-3,25		
Li_2 $Ni(OsBu)_4$ .LiBr-3thf	3,35		3,46	(6,9)
			3,45	(22,7)
Na_2 $Ni(OiPr)_4$. 2thf	1,44	1,15-1,44		
	0,75		2,71	(3,00)
			2,56	(5,29)
	0,78			
	0,96			
	1,03		2,30	(3,5)
	1,33		2,38	(3,03)
K $Ni(OiPr)_3$. thf	3,23			

2.2 Syntheses of Low Valent Nickel Complexes

Wilke and co-workers (5) developed an efficient method of reducing nickel(II) salts, such as $Ni(acac)_2$ using organometallic compounds of main group metals in the presence of suitable ligands like phosphines, phosphites, and olefins. In the absence of such ligands, reduction of the nickel(II) to metallic nickel was observed. The mechanism of reduction is thought to occur via unstable nickel alkyl or nickel hydride intermediate species.

$$Ni(acac)_2 + 4P(C_6H_5)_3 + AlR_3 \longrightarrow Ni\left[P(C_6H_5)_3\right]_4 + RAlacac_2 + 2R^\bullet \qquad (5)$$

Reducing agents, like sodiumborohydride and hydrazinehydrate, have also been used by Chatt and co-workers (17) to reduce nickel(II) salts in the presence of various ligands. Sodium dithionate is also found to be effective in reducing nickel(II) in the presence of carbon monoxide. It is itself oxidized to sulfite. Other reducing agents which have been used are sodium naphthalide, potassium graphite, metal powders and hydrogen (6).

Step-wise electrochemical reduction of nickel(II) in the presence of the ligand using a controlled reduction potential is also widely used (18 -- 21)-

$$Ni(II) \longrightarrow Ni(I) \longrightarrow Ni(o) \qquad (6)$$

The step-wise reduction process is found to depend mainly on the type of ligand involved and the geometry of the complex (19). Nickel(II) is found to be reduced step-wise to nickel(I) and nickel(o) only in the presence of smaller ligands, such as, PEt_3 and PEt_2Ph, i.e., those which give $[NiL_4]^+$ or NiL_4 species having the same coordination number as the corresponding nickel(II) complex. In fact, in the case of diphosphines like $Ph_2P(CH_2)_n PPh_2$, the diphosphine is found to be less suited as a bidentate ligand when $n > 2$, allowing only comnolexes like $NiLS_2$ (S = solvent molecule, L = diphosphine) to be obtained for nickel in +2 and +1 oxidation states (20). In agreement with the above facts, nickel(II) is found to be reduced to nickel(o) by irreversible two electron reduction in the presence of bulkier ligands like, PPh_3, PCY_3 and relatively good $\overline{II}$-aceptor ligands such as $P(OPh)_3$. The existence of $[Ni(PPh_3)_4]^+$ is attributed to conproportionation of nickel(o) with nickel(II).

$$Ni(o) + Ni(II) \longrightarrow 2Ni(I) \qquad (7)$$

NiL_4 complexes, where L = triphenyl phosphite; tricyclohexyl phosphite, bis(o-phenylene)phenyl phosphite have been synthesized by carbon monoxide displacement from $Ni(CO)_4$ (22 - 24). Nickel(o) complexes of triphenylphosphite and 1,2-bis(diphenylphosphino)ethane or propane have been also synthesized by ligand exchange with nickelocene or dimethylnickelocene (25 - 26).

The equilibrium,

$$NiL_4 + 4L' \rightleftharpoons L'NiL_{(4-n)} + nL \qquad (8)$$

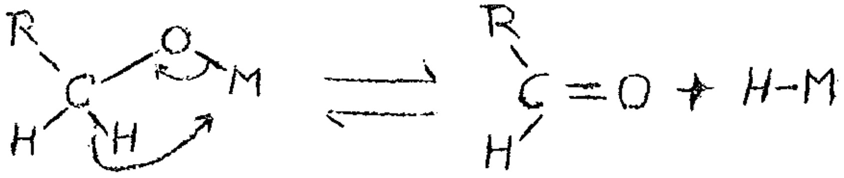
has been studied for wide variety of phosphorus containing ligands using ^{31}P nmr by Tolman (27) on the basis of competition experiments. The degree of substitution is found to be governed by the steric and electronic effects of the ligand.

The reduction of nickel(II) by the ligand is sometimes found to occur as in the reduction of nickel(II) halides by diphenylphosphine (22) and triethyl phosphite (29).

$$NiBr_2+5HP(C_6H_5)_2+H_2O \longrightarrow Ni\left[HP(C_6H_5)_2\right]_4+HPO(C_6H_5)_2 + 2HBr \qquad (9)$$

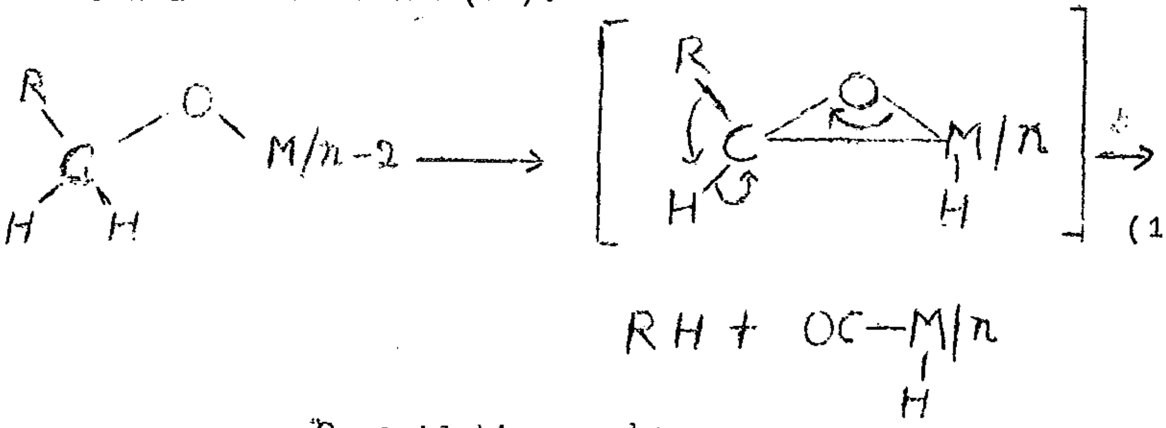
$$NiBr_2+5P(OEt)_3+2(Et)_2NH+H_2O \longrightarrow Ni\left[P(OEt)_3\right]_4 +2(Et)_2NH_2Br + OP(Et)_3 \qquad (10)$$

Lower yields (5 - 10%) of $NiL_2(CO)_2$ were produced by novel photo-irradiation process on $L_2Ni(S_2C_2O_2)$ (L = dppe) (30). Transition metal compounds, especially their halides, are reduced using a system consisting of a basic-alcohol in the presence of stabilizing ligands (L) such as phosphines, (ROH + L + KOH). This method was principally developed by Malatesta and co-workers. Chatt, Shaw and Vaska used the method for the synthesis of hydrometal complexes of Group VIII transition metals, in the presence of phosphines or arsines (31 - 34). With isotopic techniques, the above workers showed that the initial step was coordination of an alkoxide to the metal center, where an α-hydrogen of thealkoxide is transfered to the metal (β-hydrogen shift) (32). Primary alcohol is oxidized to an aldehyde and secondary alcohol to a ketone, as in reactions involving a β-hydrogen shift in metal alkyl systems (35).



(11)

The reverse of the above reaction is the Meerwein-Ponndorf - Verly (MPV) reduction of an aldehyde or ketone by transition metal hydride (36). A second type of transfer to form hydrido-metal carbonyl complexes by a similar route was also observed. This type of transfer involves the transfer of both hydrogen and α-carbon of the alkoxides to the metal which is coordinatively unsaturated, through intramolecular oxidative addition (37).



(12)

n = Oxidation number

M = Rh(I), Ir(I)

The hydrido metal carbonyl formation by coordinative unsaturation is reinforced by the observation that the process occurs for just those metals whose complexes are found to participate in oxidative addition (38). The process of hydride transfer is found to be facilitated in part by increasing bascity of the phosphorus ligands. In fact, there is a report on theisolation of stable rhodium-hydrides from halides in the presence of phosphines and in the absence of organic solvents at refluxing temperature (39).

$$RhX_3 \cdot 3H_2O + 3L \longrightarrow HRhX_2L_2 + R_3PO + HX + 2H_2O$$

$$(L = PPh_3 \text{ or } PEtPh_2)$$

Though the above method of reduction was applicable to other Group VIII transition metals, it was assumed in general to be non-feasible to iron, cobalt and nickel. In fact, Chatt, Shaw and Duncanson, expressed the view as, "These are general reactions of Group VIII metals, except iron, cobalt and nickel ..." (32). But the syntheses of $NiCl(H)(PCY_3)_2$ changed the prevailing view (45). The stability of $(R_3P)_2M(H)X$, $(X = Br)$, is found to decrease in the order of Pt > Pd > Ni. This fact has been in part attributed to the change in the energy (ΔE) between the highest occupied orbital and lowest unoccupied orbital, which decreases in the same order. The stability of hydridonickel(II) complexes of PCY_3 and $P(iPr)_3$ is attributed mainly to the steric bulk of these ligands, which increases ΔE, restricts the conversion of the trans-square-planar to tetrahedral geometry and the approach of other groups along the out-of-plane axis (40).

Lindenlaub (41) showed the syntheses of stable nickel(O) carbonyl complexes, $NiL_2(CO)_2$ and $NiCl_2L_2$ in the presence of 4 moles of LiOiPr in a carbon monoxide atmosphere in boiling toluene. The same products can also be obtained at higher pressure of carbon monoxide in 2-propanol at room temperature. The mechanism is again postulated as a ß-hydrogen transfer from the alkoxide, since acetone and isopropanol were shown to be present in solution. In the absence of carbon monoxide, nickel metal was deposited quantitatively. This shows that the carbonyl complex is not formed by the second type of transfer. In excess PPh_3, under an inert atmosphere the paramagnetic Ni(1) complex, $Ni(PPh_3)_3Br$ was isolated.

Stolze and Wetzel (42 - 43) were also able to characterize hexene, hexane and acetone from the solution obtained by the reaction of $Ni(acac)_2$ with hexyl - lithium in the presence of LiOiPr, showing ß-hydrogen transfer from an alkyl and alkoxide to the metal. Catalytic oligomerization of isoprene by the complex $NiCl(H)(PCY_3)_2$ in alkalimetal alkoxide media was noted by Sachse (44) indicating that the catalytically active Ni(o) species which is responsible to oligomerization of isoprene is produced in situ.
It was also possible to synthesize $Ni(dppe)_2$, $Ni(PPh_3)Br$, $Ni[P(OiPr)_3]_4$ from $Li_2Ni(OiPr)_4.LiBr.3thf$, and $Ni(PPh_3)_4$

from $Na_2Ni(OiPr)_4$.2thf, in the presence of dppe, PPh_3 and $P(OiPr)_3$ at temperatures between 70°C and 100°C in either thf or toluene (45).

Objective of the Project

1. To reproduce the synthesis of $Li_2Ni(OiPr)_4$.LiBr.3thf using a new starting compound; $NiBr_2$.2DME.
2. To develop and reproduce the work by W. Kalies (8) and confirm the formation of nickel(o) species in the $Ni(II)-PR_3$-alkoxide system by stoichiometric reaction.
3. To supplement further examples by taking new ligands, such as triallyl phosphite.
4. To compare the products formed from $Na_2Ni(OiPr)_4$.2thf and $Li_2Ni(OiPr)_4$.LiBr.3thf with different chemical compositions.

3. EXPERIMENTAL

3.1 General

All reagents and solvents used for syntheses were handled by Schlenk tube technique under nitrogen. Nitrogen with original purity of 99.6% was further purified by passing through two columns (length 100 cm, diameter 5 cm) each containing an alkline pyrogallol solution (30 g of pyrogallol) dissolved in 300 ml of strong aqueous KOH of specific gravity 1.54) (50), then through columns containing commercial copper catalyst (activated at 55°C to absorb oxygen), KOH, P_2O_5 and molecular sieve type 4A. All solvents and reagents were dried and purified according to literature procedures (51). Hydrocarbon solvents, like benzene, toluene, n-hexane, n-heptane were dried over pressed sodium metal and were distilled from it. Tetrahydrofuran and 1,2-dimethoxyethane were predried by refluxing over $LiAlH_4$ and further dried by distillation from freshly cut sodium and benzo-phenone, after the solution had turned violet. Diethyl ether was refluxed over pressed sodium and distilled from it. Pyridine was refluxed over $LiAlH_4$ and distilled from it. Allyl alcohol was dried by storing over magnesium sulfate, distilled from it, and further stored over molecular sieve type 5A. Isopropanol was stored over KOH, and distilled from wire. It was further dried by storing over molecular sieve type 5A. PCl_3 was purified by distillation . 1,5-

cyclooctadiene was purified by distillation. Reagents like $Ni(acac)_2$ and dppe were stored permanently under nitrogen and transfered to reaction tubes under nitrogen when needed. All drying, purification of solvents were done under nitrogen, and solvents were deaerated before use.

3.2 Prepararation of Starting Compounds

3.2.1 Dibromonickel(II)2-dimethoxyethane, $NiBr_2.2DME$ (52)

100 m mol of Analar bromine was added dropwise to a mixture containing 100 m mol of powdered nickel in 100 ml of DME. The exothermic reaction was left overnight with stirring. An orange complex was filtered off, washed with 60 ml of DME and vacuum dried at room temperature.

$$Ni + Br_2 \xrightarrow{DME} NiBr_2.2DME \qquad (13)$$

Yield: 34 g (85% based on nickel)

Analysis	Found	Calc. for $NiBr_2.2DME$
%Ni	15.06	14.72
%Br	40.70	40.60

IR: V_{asy} (C-O-C) = 1095 cm^{-1} (s)

Vis: ν_1= 11,521 cm^{-1}, $\mathcal{E}$= 6.7 $M^{-1}cm^{-1}$; 21,186 cm^{-1}(ν_2) = 11.2 $M^{-1}cm^{-1}$

$\chi_g.10^{-6}$ = 9.12 cgs; $\chi_m.10^{-6}$ =3843.7 cgs, μ_B = 3.02

3.2.2 Lithium Isopropoxide (LiOiPr) and Sodium Isopropoxide (NaOiPr) (45)

Both were prepared in thf solution. LiOiPr and NaOiPr were prepared by using an excess (100 mm 01-130 m mol) of LiH and Na with 100 m mol of isopropanol in 100 ml of thf solution, and refluxing for 3 and $3^1/2$ hrs respectively . The solutions were filtered using G-4 sintered funnels to remove excess LiH and Na.

$$\begin{aligned} &\text{LiH} + \text{iPrOH} \longrightarrow \text{LiOiPr} + H_2 \\ &\text{Na} + \text{iPrOH} \longrightarrow \text{NaOiPr} + 1/2\ H_2 \end{aligned} \qquad (14)$$

3.2.3 Dilithium Tetraisoproxo-nickelate (II): $Li_2Ni(OiPr)$. LiBr.3thf

7 m mol of $NiBr_2$.DME was taken with 35.13 m mol (41.2 ml) of LiOiPr/thf at room temperature. The solution was stirred for 1 hr and deep blue crystals were obtained, after filtering and drying in vacuum for 1 hr.

$$\text{NiBr}_2\text{.2DME} + 4\text{LiOiPr} \xrightarrow{\text{thf}} \text{Li}_2\text{Ni(OiPr)}_4\text{.LiBr.3thf} + \text{LiBr} + 2\text{DME} \qquad (15)$$

Analysis	Found	Calc. for $Li_2Ni(OiPr)_4$.LiBr.3thf
%Li	3.38	3.40
%Ni	9.37	9.54
$\%(OiPr)^-$	38.58	38.61
%Br	12.89	13.05

IR: $V_{(Ni-O)}$ = 410 cm^{-1} (m), V_{asy} (C-O-C) = 1052 cm^{-1} (s)

V_{C-H} ($R_2\underline{CH}$) = 2620 cm^{-1} (m), V_{sy}(C-O-C) = 900 cm^{-1} (m)

V_{C-O} (R_2C-O) = 1150 cm^{-1} (s)

Vis:	Obs. (cm^{-1})	Lit. (cm^{-1}) (45)
	18282, $\varepsilon(M^{-1}cm^{-1})$ = 136.8	18215, $\varepsilon(M^{-1}cm^{-1})$ = 152.6
	16863, ε = 79.4	16835, ε = 117.7

Yield: 3.64 g (85% based on $NiBr_2.2DME$)

3.2.4 Disodium Tetraisopropoxonickelate(II), $Na_2Ni(OiPr)_4.2thf$ (45)

The complex was prepared in solution. 8.4 m mol of anhydrous $Ni(acac)_2$ dissolved in 50 ml of toluene was treated with 33.6 m mol of NaOiPr (26 - 74 ml) in thf. The reaction mixture was stirred for 1 hr at 0°C. A voilet solution was obtained after filtering off the Na acac.

$$Ni(acac)_2 + 4\ NaOiPr \xrightarrow[thf]{toluene} Na_2Ni(OiPr)_4.2thf + 2Na\ acac \qquad (16)$$

Vis:	Obs. (cm^{-1})	Lit. (cm^{-1}) (45)
	18904 ε = 102.2 $M^{-1}cm^{-1}$	18850, ε = 141.3 $M^{-1}cm^{-1}$
	16502 ε = 40.6 $M^{-1}cm^{-1}$	16450, ε = 89.2 $M^{-1}cm^{-1}$

Since the complex is formed in a mixture of toluene and thf, the spectra was taken against a blank of toluene and thf in the same proportion as in the complex mixture.

3.2.5 Triallyl phosphite and Triphenyl phosphite

Triallyl phosphite was synthesized according to the established procedure (53).

Yield: 22.90 gm, 68% based on PCl_3

$$PCl_3 + 3CH_2{=}CHCH_2OH + C_5H_5N ---- P(OCH_2CH{=}CH_2)_3 + 3C_5H_5NHCl \quad (17)$$

Triphenyl phosphite was also prepared according to the procedure given by Gottlieb (54).

Yield: 32 gm, 94% based on PCl_3

$$PCl_3 + 3C_6H_5OH ---- P(OC_6H_5)_3 + 3HCl \quad (18)$$

3.3 Syntheses of Nickel(0) Complexes

3.3.1 Syntheses of (η^4-1,5-Cyclooctadiene)bis-(triphenylphosphine)nickel(o); $Ni(PPh_3)_2(COD)$

9.8 m mole of $Na_2Ni(OiPr)_4 \cdot 2thf$ was heated with 19.7 m mol of PPh_3 and an excess of COD (98 m mol) for 5 hrs at 65°C-68°C, with stirring. the violet colour disappeared and the solution turned yellow-brownish. After a further 5 $^1/2$ hrs the colour had become deep brown. The heating was discontinued and the solution was cooled to room temperature, and vaccum concentrated. A six fold excess of n-hexane was added as precipitating agent. No precipitation was observed at room temprature. Instead glittering metallic-yellow crystals were precipitated after storing the solution in a freezer (-20°C) for 12 hrs. After washing the crystals with n-hexane and vacuum drying at room temprature, the colour of the complex became yellow-brown.

Yield: 1.12g (26.6% based on $Na_2Ni(OiPr)_4$ 2thf.)

Analysis	Found	Calc. for $Ni(PPh_3)_2(COD)$
Ni%	8.5%	8.48%

IR: V(C=C) = 1515 cm^{-1}(m), 1187 cm^{-1}(s); V(C-H) = 3030 cm^{-1}(w), 3040 cm^{-1}(w); V(Ph-ring) = 1072 cm^{-1} (m), 745 cm^{-1}(s), 700 cm^{-1}(s), V(P-C) 1115 cm^{-1}(s)

^{31}P nmr: = 30.04 ppm; δ = -4.7

^{1}H nmr: = 7.40 ppm; δ = 7.60 ppm; δ = 3.87 ppm
= 5.51 ppm; δ = 2.08 ppm

3.3.2 Syntheses of Bis[1,2-bis(diphenylphosphino)ethane]-nickel(o), $Ni(dppe)_2$.

a. Dppe (7.78 m mol) was added to 3.89 m mol of $Na_2Ni(OiPr)_4$.2thf (13.4 ml). The colour of the solution changed to brown-yellowish at room temperature. The solution was stirred for 1 hr at room temperature, concentrated, and sixfold excess n-heptane was added as precipitating agent. After cooling the solution overnight in a freezer, brownish-orange crystals were obtained. These were filtered off and washed with 30 ml of n-heptane and vacuum dried at room temperature.

Yield: 1.51 g (71% based on $Na_2Ni(OiPr)_4$.2thf)

IR: $V(P-CH_2)$ = 1438 cm^{-1} (w); V (P-Ph) = 1122 cm^{-1}(m), 1000 cm^{-1} (m), 730 cm^{-1}(s), 695 cm^{-1}(s).

^1H nmr: δ = 1.65 ppm, triplet

^{31}P: δ = 32.8 ppm

b. The same complex was synthesized using a similar procedure for $Li_2Ni(OiPr)_4$.LiBr.3thf. Dppe (3.05 m mol) was added to 1.52 m mol of $Li_2Ni(OiPr)_4$LiBr. 3thf dissolved in 25 ml of thf. Reaction occurred at room temperature with stirring for 1 hr. Precipitation was facilitated by adding 5 fold excess volume of isopropanol. After cooling the solution in a deep freezer for 8 hrs, orange crystals were obtained. They were filtered off and washed with isopropanol.

Yield: 1.23g (94.6% based on $Li_2Ni(OiPr)_4$.LiBr.3thf)

IR: $V(P-CH_2)$ = 1435 cm^{-1} (w); V(P-Ph) = 1135 cm^{-1}(m), 1000 cm^{-1}(s), 700 cm^{-1}(s).

^1H nmr: δ = 1.65 ppm, triplet

^{31}P nmr: δ = 32.84 ppm.

the first time by Wilke and co-workers (5) by the reduction of $Ni(acac)_2$ with diethylaluminiumethoxide in the presence of the ligands.

The synthesis of $Ni(PPh_3)_2$ (CD) using $Na_2Ni(OiPr)_4$. 2thf was attempted in the presence of 2 moles of PPh_3 and excess COD, as discussed in the experimental section. IR spectra measurements of the complex indicated two new bonds at 1515 cm^{-1}(m) and 1189 cm^{-1}(s), which are absent in the free COD and PPh_3. These are correlated with the stretching frequencies of C=C, observed for metal-olefin complexes. Most metal-olefin complexes are seen to absorb at around 1500 cm^{-1} and 1200 cm^{-1}(s), as a result of strong coupling between $V_{C=C}$ and $V_{C=C-H}$. The 1200 cm^{-1}(s) is assumed to be predominantly C=C stretching vibration by comparison with the spectra of unsubstituted olefinic complexes of silver and platinum (18). The absorption of 1189 cm^{-1} may be assigned to the metal-olefinic of the complexes synthesized. The decrease in stretching frequency of the complexed olefin (1189 cm^{-1}) from that of the free olefin (1645 cm^{-1}), is related to the decrease in electron density in the olefinic $p\overline{II}$ orbitals and increased density in the antibonding $p\overline{II}^*$ orbital due to complex formation, ultimately weakening the olefinic bond. To check the presence of COD in the complex, a proton nmr spectrum was obtained without sealing the tube. This showed broad signals, indicating the presence of paramagnetic nickel(II) which might be the result of decomposition (oxidation) of the complexes solution. The measurement was made only after adding few crystals of KCN in order to change paramagnetic Ni(II) to diamagnetic, tetracyanonickelate(II). Less intense signals (^{31}P at -4.7 ppm and ^{1}H at 5.51 ppm) further indicate the presence of free PPh_3 and COD. The intense signal at 30.4 ppm, in the ^{31}P spectrum downfield from the free PPh_3 (-4.47 ppm) may be assigned to bonded PPh_3. The downfield shift is correlated with the decrease of electron density around phosphorus which is generally observed in phosphines without strong electron withdrawing substituents. The decrease of electron density might arise for phosphines which are more of σ-bonding type (49). A signal at 3.87 ppm in the ^{1}H spectrum is assigned to the bonded COD where the upfield shift is expected from the electron density decrease in the olefinic bond due to complex formation (18). Attempts to analyse the phosphine content in the complex failed, mainly to lack of appropriate oxidizing system which breaks the P-C bond of PPh_3.

4.2.9. Tetrakis(triallyl phosphite)nickel(o);$Ni[P(OCH_2-CH=CH_2)_3]_4$

The complex was synthesized from $Li_2Ni(OiPr)_4.LiBr.3thf$ in the presence of the ligand as in the procedure given in the experimental section. The complex was white. The analysis indicated a tetrakis complex, where Ni:P ratio was found 1:4. In addition the presence of triallyl phosphite was confirmed by comparing the IR spectrum of the free ligand with the spectrum of the complex. Absorption frequencies at 1638 cm^{-1} ($V_{C=C}$), 3090 cm^{-1} (w)) and 917 cm^{-1} (s) ($V_{C=C-H}$), and 995 cm^{-1} (s) (V_{P-O-C}) clearly indicate triallyl phosphite in the complex. A white complex was also obtained from $Na_2Ni(OiPr)_4$.2thf with triallyl phosphite. The IR spectrum of this complex was found to be identical in the range of 4000 cm^{-1} to 200 cm^{-1} with that obtained from $Li_2Ni(OiPr)_4$.LiBr.3thf, showing the same complex was obtained from either starting materials.

4.2.3 Bis[1,2-bis(diphenylphosphino)ethane]nickel(o); $Ni(dppe)_2$

The compound $Ni(dppe)_2$ was synthesized by W. Kalis from $Li_2Ni(OiPr)_4$.LiBr.3thf. The complex was characterized by a molecular weight determination. The same complex was produced by us from the same starting material. The complex was orange; precipitation is best accomplished using isopropanol. IR absorptions at 1435 cm^{-1} (w) ($P-CH_2$), 1135 cm^{-1}(m), and 100 cm^{-1}(m) ($V_{P-phenyl}$), and the proton signal at 1.65 ppm (triplet) and the ^{31}P signal at 32.84 ppm, clearly indicate the presence of dppe and the absence of other ligands. The proton nmr was run in non-deuterated benzene, where the phenyl protons of dppe overlap with free benzene protons at 6.52 ppm. The magnetic propeties where studied in benzene solution with a capillary filled with benzene (46). If the solution was paramagnetic a downfield shift of the signal from the benzene protons in the capillary should have been observed. No shift was observed, indicating that the substance is diamagnetic and a bis-complex in agreement with the synthesis from other starting materials (17).

The same complex was synthesized by us starting from $Na_2Ni(OiPr)_4.2thf$ in the presence of dppe. The complex was yellow-brownish. The complex was precipitated in good yield using non-polar solvents like n-hexane and n-heptane. The IR spectrum of the complex showed same frequency of absorption in the range of 4000 cm^{-1} to 200 cm^{-1} as the spectrum from the complex prepared above. Similarly, the proton nmr spectrum indicated a triplet at 1.65 ppm assigned to the $-CH_2-CH_2-$ group. The ^{31}P nmr spectrum showed a signal at 32.8 ppm. The shift from -12.4 ppm for free dppe in benzene to 32.8 ppm is similar to that observed to the complex formation of phosphines in general. Magnetic susceptibility measurements gave the same result as that for the above complex. Both complexes are relatively stable to air; they can be handled in open air for periods upto 30 minutes. But fast decomposition with deposition of a white substance was observed in solution. Similar observations were made by Chatt (17). From the data and observations, we may conclude, the same complex is produced using either of the alkoxonickelates.

4.2.4 Tetrakis(triphenyl phosphite)nickel(o); $Ni[P(OPh)_3]_4$

$Ni[P(OPh)_3]_4$ was synthesized by W. Kalies (45), who characterized the complex by elemental analysis. He synthesized the complex from $Li_2Ni(OiPr)_4$.LiBr.3thf in the presence of the ligand. We repeated the synthesis of the complex from the same starting material. The complex formation of $P(OPh)_3$ was confirmed by the IR spectra, where frequencies of absorption at 1200 cm^{-1} (s) (V_{C-O}), 887 cm^{-1}(s) (V_{P-O}) and absorption frequencies typical of a phenyl–ring where observed. The analysis indicated a ratio of Ni to P of 1:4. The same white complex was synthesized by us starting from $Na_2Ni(OiPr)_4$.2thf in the presence of excess ligand. The IR spectra showed the same frequencies of absorption as above. In addition ^{31}P nmr spectrum of the complex showed a signal at 128.8 ppm in agreement with that reported by Tolman (12). From the data of analysis and spectra indicate the formation of tetrakis complex in both cases.

5. Conclusion

The synthesis of $Li_2Ni(OiPr)_4$ LiBr 3thf was best accompanied using $NiBr_2$ 2DME, which is relatively easy to prepare and more stable to hydrolysis than $NiBr_2$ 2thf. Electronic spectra and magneticmoment determination of $NiBr_2$ 2DME indicated octahedral geometry of nickel(11).

Using the intermolocular redox properties of the isopropoxonickelates of lithium and sodium, a series of nickel(o) complexes were synthesized. Complexes synthesized from either of them using dppe, triallyl phosphite triphenyl phosphite were found to be identical. Eventhough, the isopropropoxonickelates of sodium and lithium are chemically different, the results indicated the same reaction pathway way followed, i.e nickel(11) is reduced to nickel(o). Furthermore the results obtained strengthen the proposed mechanism.

The syntheses of low valent nickel complexes in the presence of stabilizing ligands, using primary or secondary alkoxonickelates of alkalimetals may have a synthetic advantage as compared to the syntheses using organo or hydrido compounds of main group metals in being easy to prepare and handle.

Specta Positions in Appendix (Figure Numbers)

Compound	Vis	IR	^1H nmr	^{31}P nmr
1. $Li_2Ni(OiPr)_4$.LiBr. 3thf	1	2	-	-
2. $NiBr_2$2DMe	3	4	-	-
3. $NiBr_2$.2thf	6	-	-	-
4. $Na_2Ni(OiPr)_4$.2thf	8	-	-	-
5. $Ni(PPh_3)_2)_2(COD)$	-	7,9	10	11
6. $Ni(dppe)_2$ from 4	-	12	13	14
7. $Ni(dppe)_2$ from 1	-	15	16	17
8. $Ni\ P(OCH_2CHCH_2)_{3\ 4}$ from 1	-	18	-	-
9. $Ni\ P(OCH_2CHCH_2)_{3\ 4}$ from 4	-	19	-	-
10. $Ni\ P(OPh)_{3\ 4}$ from 1	-	20	-	-
11. $Ni\ P(OPh)_{3\ 4}$ from 4	-	21	-	22

Calibration Curve for Bromide Determination: 5

1: $Li_2Ni(OiPr)_4$.LiBr.3thf

4: $Na_2Ni(OiPr)_4$.2thf

3.3.3 Syntheses of Tetrakis(triallyl phosphite)nickel(o); $Ni[P(OCH_2-CH=CH_2)_3]_4$

a. 3.4 m mol of $Li_2Ni(OiPr)_4.LiBr.3thf$ in 30 ml of benzene was mixed with an excess of triallyl phosphite (17.1 m mol). The solution was refluxed for 2 hrs, and the colour of the solution changed to brown. The solution was cooled to room temperature, with n-heptane added as precipitating agent. The solution was stored in deep freezer for 6 hrs, where white crystals were formed. These were filtered off and washed with n-heptane and dried in vacuum at room temprature.

Yield: 2.72 g (93% based on $Li_2Ni(OiPr)_4.$
LiBr.3thf.)

IR: $V_{(P-O-C)}$ = 995 cm^{-1}(s); $V_{(C=C)}$=1638 cm^{-1} (m); $V_{(C-H)}$≃3090 cm^{-1} (w), 917 cm^{-1} (s).

Analysis	Found	Calc. for $Ni[P(OCH_2-CH=CH_2)_3]_4$
%Ni	6.95	6.76
%P	14.01	14.26

b. The same complex was prepared by a similar procedure by mixing 3.89 m mol((15 ml) of $Na_2Ni(OiPr)_4.2thf$ with excess triallyl phosphite (15.56 m mol). The reaction mixture was heated for $2^1/2$ hrs at 50°C - 65°C. The colour of the solution turned from violet to brown-red. It was cooled to room temperature and concentrated. Sixfold excess of n-heptane was added to facilitate precipitation. After storing the solution in a deep freezer for 8 hrs, white crystals were obtained. These were filtered off, washed with n-heptane, and dried in vacuum at room temperature.

Yield: 1.74 g (79% based on $Na_2Ni(OiPr)_4.2thf$)

IR: Identical in the range of 4000 cm^{-1} to 200 cm^{-1} with the complex prepared from $Li_2Ni(OiPr)_4.LiBr.3thf$.

3.3.4 Syntheses of Tetrakis(triphenyl phosphite)nickel(o); $Ni[P(OPh)_3]_4$

a. 2.88 m mol of $Li_2Ni(OiPr)_4.LiBr.3thf$ in 30 ml of benzene was mixed with an excess (1440 m mol) of $P(OPh)_3$. The blue colour of the solution disappeared after refluxing for 3 hrs. The solution was cooled to room temperature, and isopropanol was added to give a milky mixture. After cooling in a freezer for 10 hrs white crystals were obtained. These were filtered, washed with 30 ml of isopropanol, and vacuum dried at room temperature.

Yield: 2.57 g (80% based on $Li_2Ni(OiPr)_4LiBr.3thf$).

IR: $V(C-O) = 1165\ cm^{-1}(s)$; $V(P-O) = 8.87\ cm^{-1}(s)$

Analysis	Found	Calc. for $Ni[P(OPh)_3]_4$
%Ni	4.75	4.51
%P	9.15	9.54

b. The same complex was synthesized by mixing 5.25 m mol (22 ml) of $Na_2Ni(OiPr)_4.2thf$ with 25 m mol (excess) of $P(OPh)_3$. The reaction mixture was heated for 3 hrs at 55°C - 65°C with stirring. The brown-red solution was cooled to room temperature and concentrated under vacuum. Sixfold excess of n-hexane was added as precipitating agent. The solution turned milky and after 8 hr in a deep freezer a white precipitate was filtered off washed with n-hexane and dried under vacuum at room temprature.

Yield: 4.12 g (63.9% based on $Na_2Ni(OiPr)_4.2thf$).

IR: V(C-O) 1165 cm^{-1}(s); V(P-O) = 885 cm^{-1}(s)

^{31}P nmr: 128.8 ppm

The two complexes prepared from $Li_2Ni(OiPr)_4.LiBr.3thf$ and $Na_2Ni(OiPr)_4.2thf$ were found to have the same absorbtion frequencies in the range of 4000 cm^{-1} 200 cm^{-1}.

3.4 Analysis

3.4.1 Dissolution of Nickel Complexes

Dissolution of those complexes containing nickel(II) was affected by treating 30 - 40 mg samples with a known volume of water (50 ml) and

0.5 ml of Analar nitric acid (%) . The solution was ready for analyses for nickel and lithium after such treatment.

For complexes containing nickel(o), dissolution was affected by treating the known amounts (50 - 80 mg) with 0.5 ml of fuming nitric acid and evaporating the resulting solution. After three such treatments, the solutions were diluted with water to known volumes and ready for analyses.

For the analysis of the isopropoxide anion, 20 - 30 mg of the complex was treated with a known excess volume of 0.1 HCl and the excess acid was determined by 0.1 M NaOH. The concentrations of the thf solutions containing LiOiPr and NaOiPr were determined in the same manner by taking 1 ml of samples by microsyringe and diluting them to 50 ml with water. The equivalent amounts of NaOH and LioH were determined acidimetrically (55).

3.4.2 Nickel Determination

Analyses for nickel in solutions prepared from complexes containing nickel(II) were done according to the procedure given by Vogel (55). Thus, the pH of the solution was adjusted to 6 by adding two grames of hexamethylenetetraamine, and a known excess volume of 0.01 MEDTA was added. The excess of EDTA was determined by titrating with standard 0.01 M $Pb(NO_3)_2$ solution using xylenol orange as indicator. The nickel content of solutions prepared from complexes containing nickel(o) was determined by atomic absorption spectroscopy.

3.4.3 Lithium and Bromide Determination

The content of lithium was determined by atomic emission spectroscopy (Mekanissa Mining Laboratory) after preparing the solutions with known volume.

Bromide was determined using a bromide selective electrode with calomel as reference electrode and Pw 9409 digital pH meter.

Standard (M)	Voltage (mv)
10^{-1}	- 126
10^{-2}	- 67.3
10^{-3}	- 29.3
10^{-4}	+ 20.6
Sample: B	52.4
A	61

3.4.4 Phosphorus Determination

Phosphorus in the phosphite complex was determined by first oxidizing the phosphite to phosphate. The complex was decomposed by treating it with 5 ml fuming nitric acid. The decomposed complex was further heated with fuming nitric acid and potassiumpermanganate (59). For complete oxidation the process was repeated three times by adding 5 ml of fuming nitric acid and evaporating after each addition. The phosphate was precipitated as $MgNH_4PO_4.6H_2O$ and the phosphorus content was determined by dissolution the precipitate in basic solution (pH = 10) volumetrically as in the procedure given by Flaschka (56). The results of the analyses were compared with the results obtained from the determination of the phosphorus content of the phosphite ligands by the same procedure.

3.4.5 Spectra and Magnetic Susceptibility Measurements

IR spectra of the compounds prepared and ligands used were recorded using a Pye Unicam Pu 9512 IR spectrometer (obtained from Shola Crop Protection Laboratory). The samples were prepared as mulls with nujol for solid complexes and ligands, and the spectra were run in between KBr discs.

Visible spectra were recorded on a Philps Pu-8600-UV/Vis spectrophotometer (obtained from Shola Crop Protection Laboratory).

Proton nmr spectra were recorded either on Varian-s 60T spectrometer or JNM FX 90Q FT-NMR spectrometer (obtained from the Department of Chemistry, A.A.U.)

Phosphorus spectra were recorded at JNM FX-90Q FT NMR spectrometer relative to 85% H_3PO_4. Positive shifts indicate deshielding. Magnetic susceptibility measurements were done by Evans's method (46).

4. RESULTS AND DISCUSSION

4.1 Lithium and Sodium Isopropoxonickelate(II)

The syntheses of dilithium tetraisoproposonickelate(II) was accomplished according to the procedure given by [illegible]. W. Kalies (45), except that $NiBr_2.2thf$ was replaced by $NiBr_2.2DME$. $NiBr_2.2DME$ is found to be a very suitable and novel starting material as compared to $NiBr_2.2thf$, which is difficult and time consuming to prepare, and relatively unstable to ingredients of air. $NiBr_2.2thf$ is prepared by first dehydrating $NiBr_2.6H_2O$ and later extracting with thf. That the same alkoxonickelate is obtained using $NiBr_2.2DME$ is ascertained by elemental analysis and electronic and IR spectra measurements. In addition, the electronic spectra of $NiBr_2.2DME$ in thf shows it to be identical with that of $NiBr_2.2thf$ shows it to be identical with that of $NiBr_2.2thf$ in the same solvent.

Vis:	λ(nm), $\bar{\nu}$(cm^{-1})	ε($M^{-1}cm^{-1}$)	transitions
$NiBr_2.2DME$ in thf	493;20283	12.6	$\nu_3 = {}^3A_{2g} --- {}^3T_{1g}(P)$
$NiBr_2.2thf$ in thf	492;20325	13.4	$\nu_3 = {}^3A_{2g} --- {}^3T_{1g}(P)$
$NiBr_2$(58)	1470;6800 847;11,800 485;20,600		$\nu_1 = {}^3A_{2g} --- {}^3T_{1g}(P)$ $\nu_2 = {}^3A_{2g} -- {}^3T_{1g}(F)$ $\nu_3 = {}^3A_{2g} -- {}^3T_{1g}(P)$

This results indicates the two molecules of DME are replaced by thf molecules.

As $NiBr_2.2DME$ is only briefly mentioned in literature (52), attempts were made to characterize it. Visible spectra measured in DME indicate; two bands at 11,521 cm^{-1} (868 nm) and 21,186 cm^{-1} (472 nm). The frequencies of absorption are in the range of absorption frequencies in solution for $NiBr_2$ (58). The extinction coefficients calculated are: 6.7 $M^{-1}cm^{-1}$ and 11.2 $M^{-1}cm^{-1}$ respectively. These results are similar to those for octahedrally coordinated nickel(II) (57).

Magnetic property of $NiBr_2.2DME$ was measured by Evans's method (46,47). The results support the electronic spectra measurement.

Electronic spectra data on the two alkoxonickelates of lithium and sodium are found to be in good agreement with the reported values (45). In the case of $Li_2Ni(OiPr)_4.LiBr.3thf$, IR spectra measurements clearly indicate the presence of thf. In addition, elemental analyses are in good agreement with the calculated values of $Li_2Ni(OiPr)_4.LiBr.3thf$. Both alkoxonickelates are rapidly hydrolized when exposed to air. In fact, the violet complex, $Na_2Ni(OiPr)_4.2thf$, formed in solution is seen to decompose, depositing nickel metal even under nitrogen, if stored more than two days.

4.2 Nickel(o) Complexes

The main principle of syntheses is based on the intramolecular redox properties of an alkoxo complexes of nickel(II) with primary and secondary alkoxides discovered by Gaube and co-workers (7). When primary and secondary alkoxides of nickel(II) are heated in the range of 50°C - 90°C, elemental nickel is seen to be deposited, ie., nickel(II) is reduced to nickel(o). The mechanism was proposed as β-hydrogen transfer from α-Ch bond of the alkoxide to the metal, followed by reductive elimination of it by an alkoxo onion to form an alcohol. The proposition of mechanism was based on the isolation study made. Thus, the use of these alkoxocomplexes may provide a novel way to easy and simple reduction methods for the preparation of nickel(o) complexes in the presence of stabilizing ligands.

4.2.1 (η^4-1,5-Cyclooctadiene)bis(triphenylphosphine)-nickel(Co); Ni(PPh$_3$)$_2$(COD)

During an attempt to synthesize Ni(COD)$_2$ from Na$_2$Ni(OiPr)$_4$.2thf and COD, deposition of elemental nickel was observed (45). This was attributed to the instability of Ni(COD)$_2$ at the temperature of the reduction of Na$_2$Ni(OiPr)$_4$.2thf. In fact, Ni(COD)$_2$ is found to decompose above 60°C (48). The low thermal stability of Ni(COD)$_2$ is mainly because, it does not have low lying empty molecular orbitals. With this in mind, we tried to synthesize nickel-COD complex in the presence of stabilizing ligands like PPh$_3$.

The complex, Ni(PPh$_3$)$_2$(COD) was synthesized for

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Fig. 1 $Li_2Ni(OiPr)_4 \cdot LiBr \cdot 5thf$

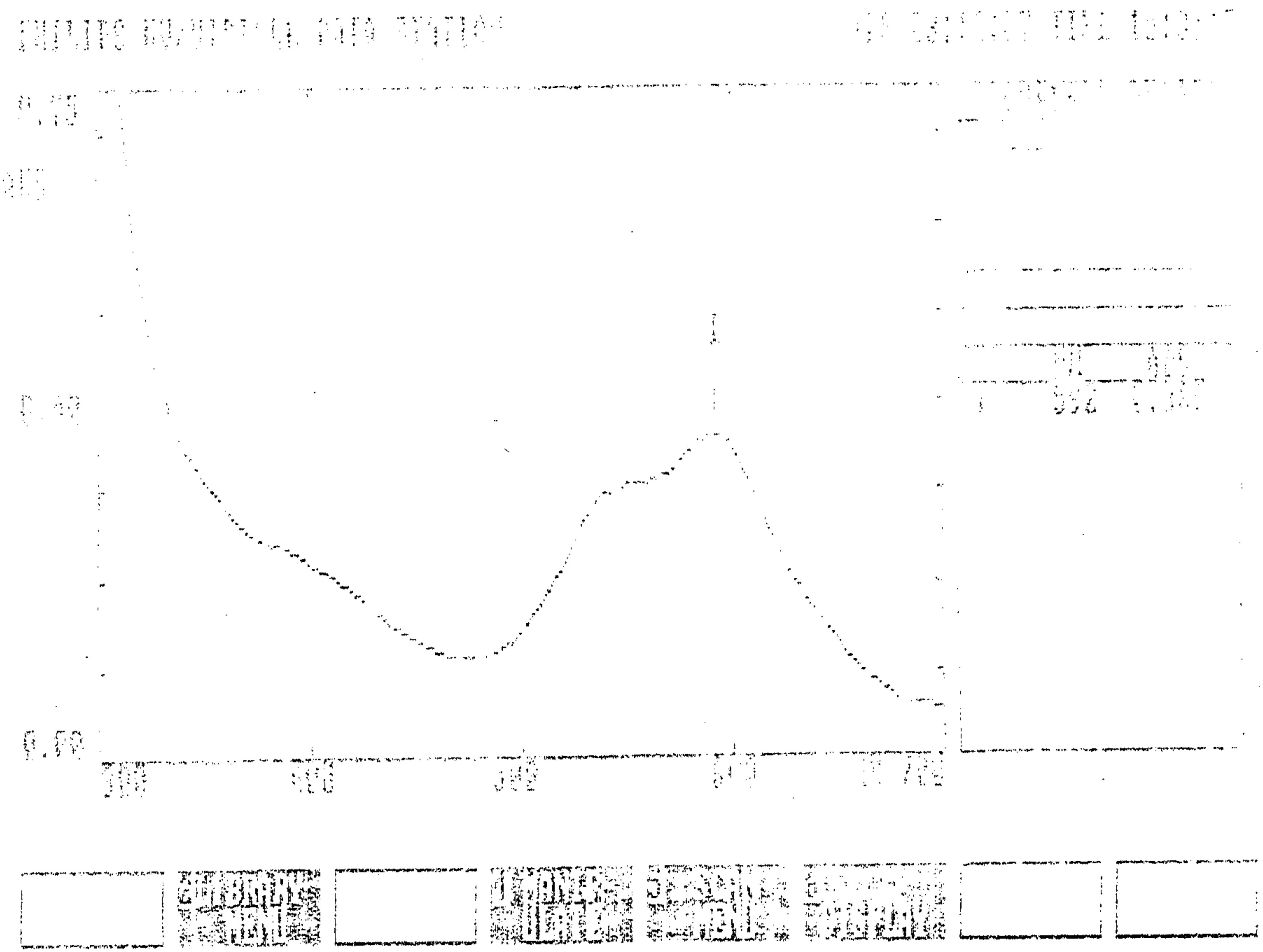


FIG. 2. $Li_2Ni(OiPr)_4 \cdot LiBr \cdot 3thf$

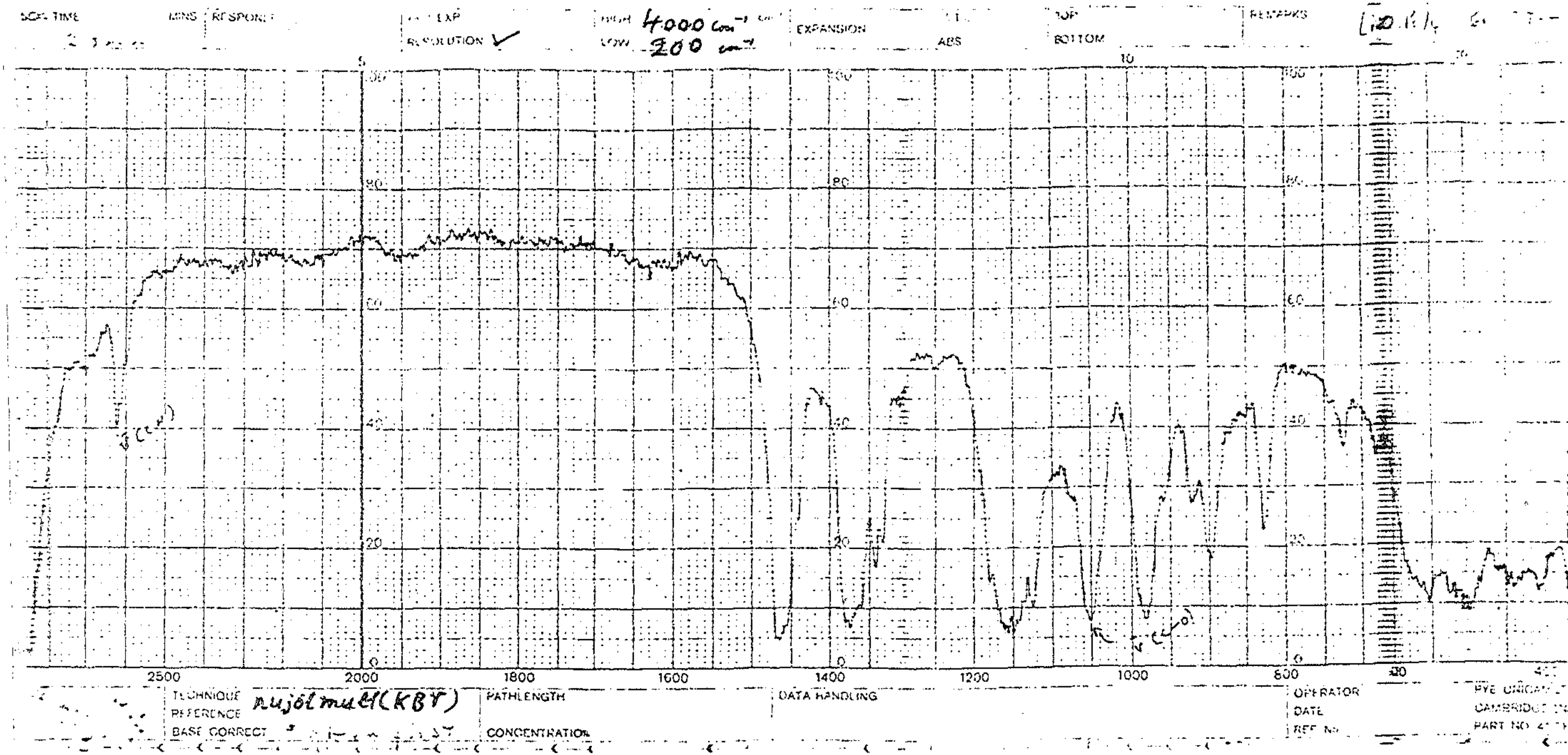


FIG 3. $NiBY_2 \cdot 2DME$

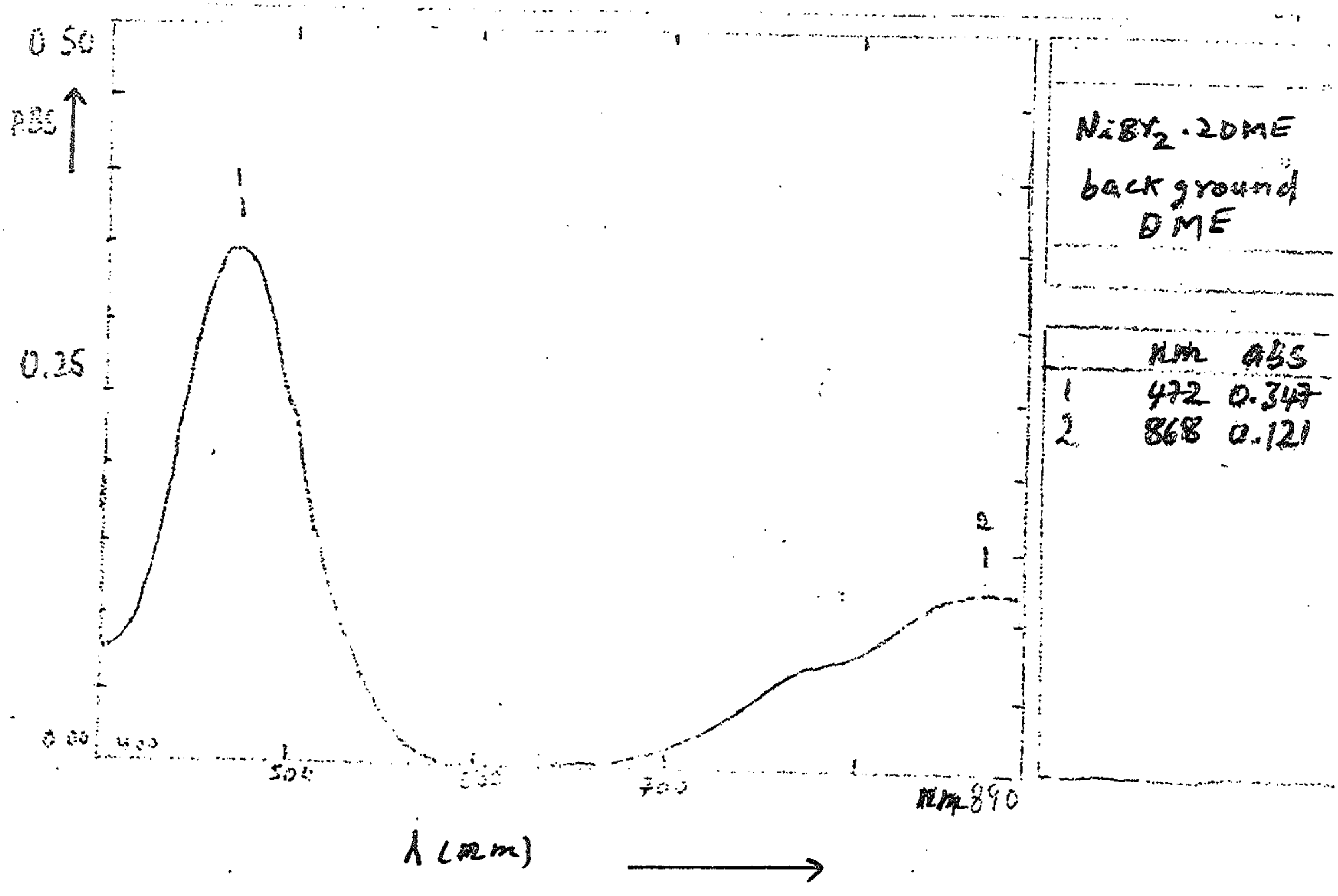


FIG. 4 $NiBr_2 \cdot 2DME$

SCAN TIME 2.5 MINS RESPONSE

EXP

RESOLUTION ✓

HIGH 4000 cm⁻¹

LOW 200 cm⁻¹

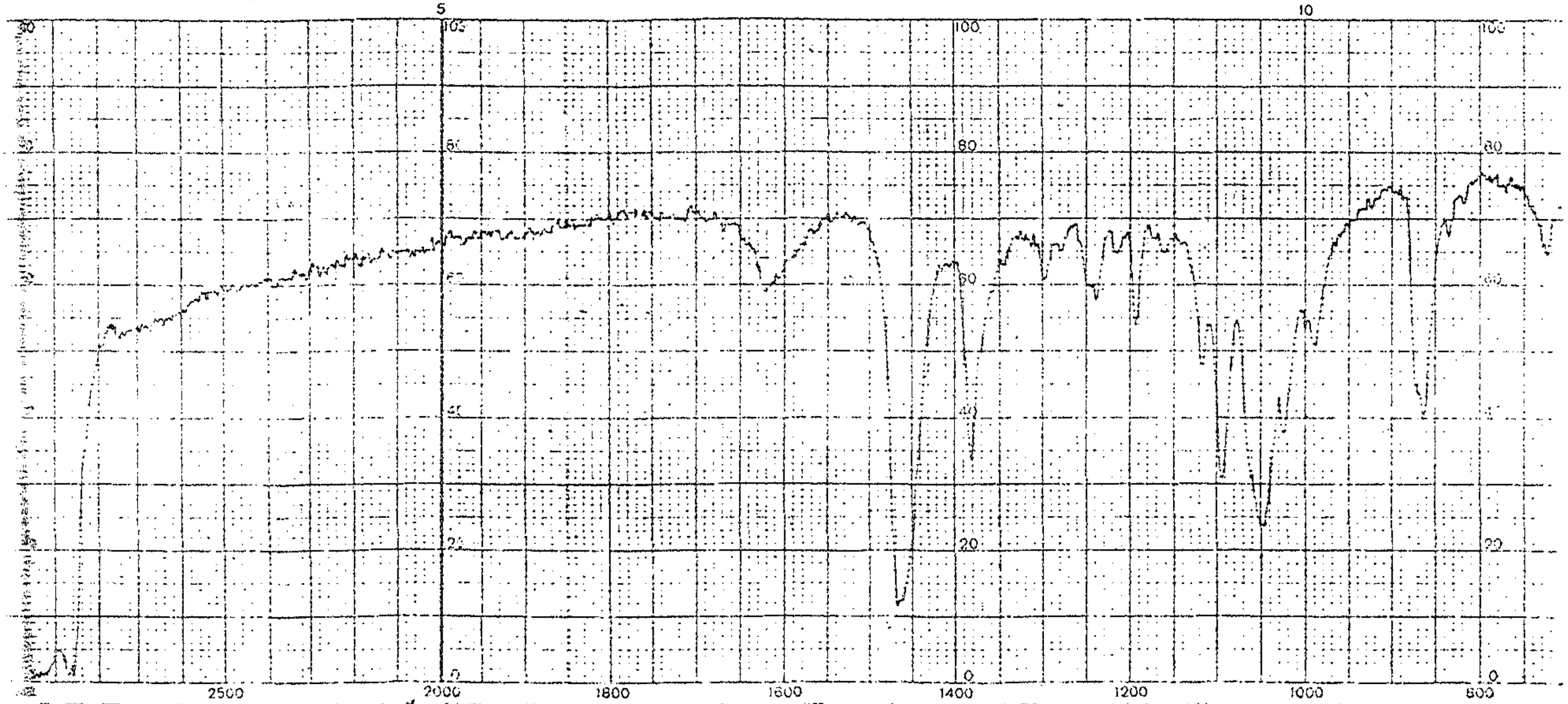
EXPANSION

ABS

TOP

BOTTOM

REMARKS



$NiBr_2 \cdot 2DME$

TECHNIQUE KBr disc (nujol mull)

REFERENCE

BASE CORRECT

PATHLENGTH

CONCENTRATION

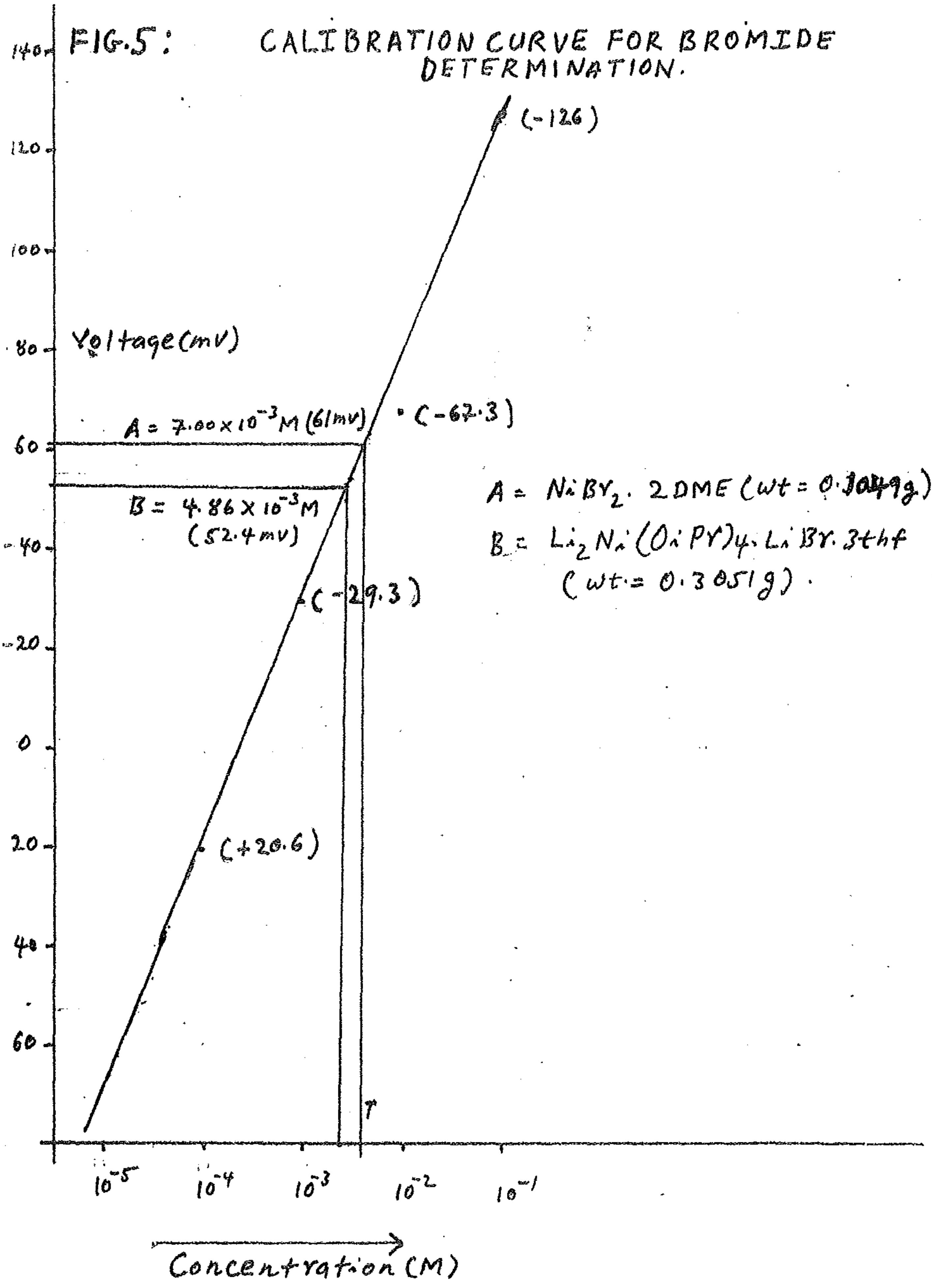
DATA HANDLING

OPERATOR

DATE

REF No

FIG.5: CALIBRATION CURVE FOR BROMIDE DETERMINATION.



A = $NiBr_2 \cdot 2DME$ (wt = 0.3049g)

B = $Li_2Ni(OiPr)_4 \cdot LiBr \cdot 3thf$ (wt = 0.3051g).

Fig. 6 $NiBr_2$. 2DME/thf

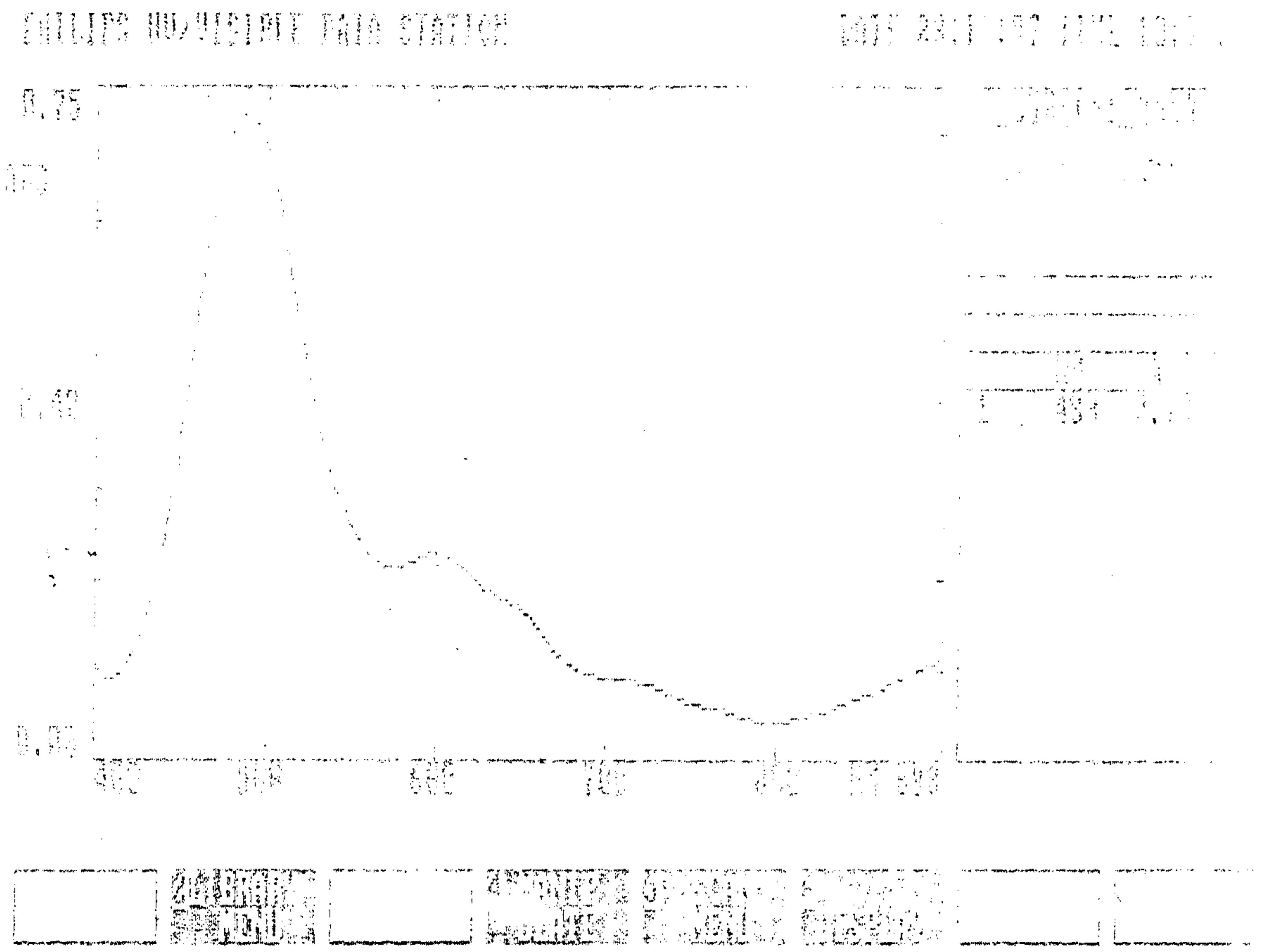
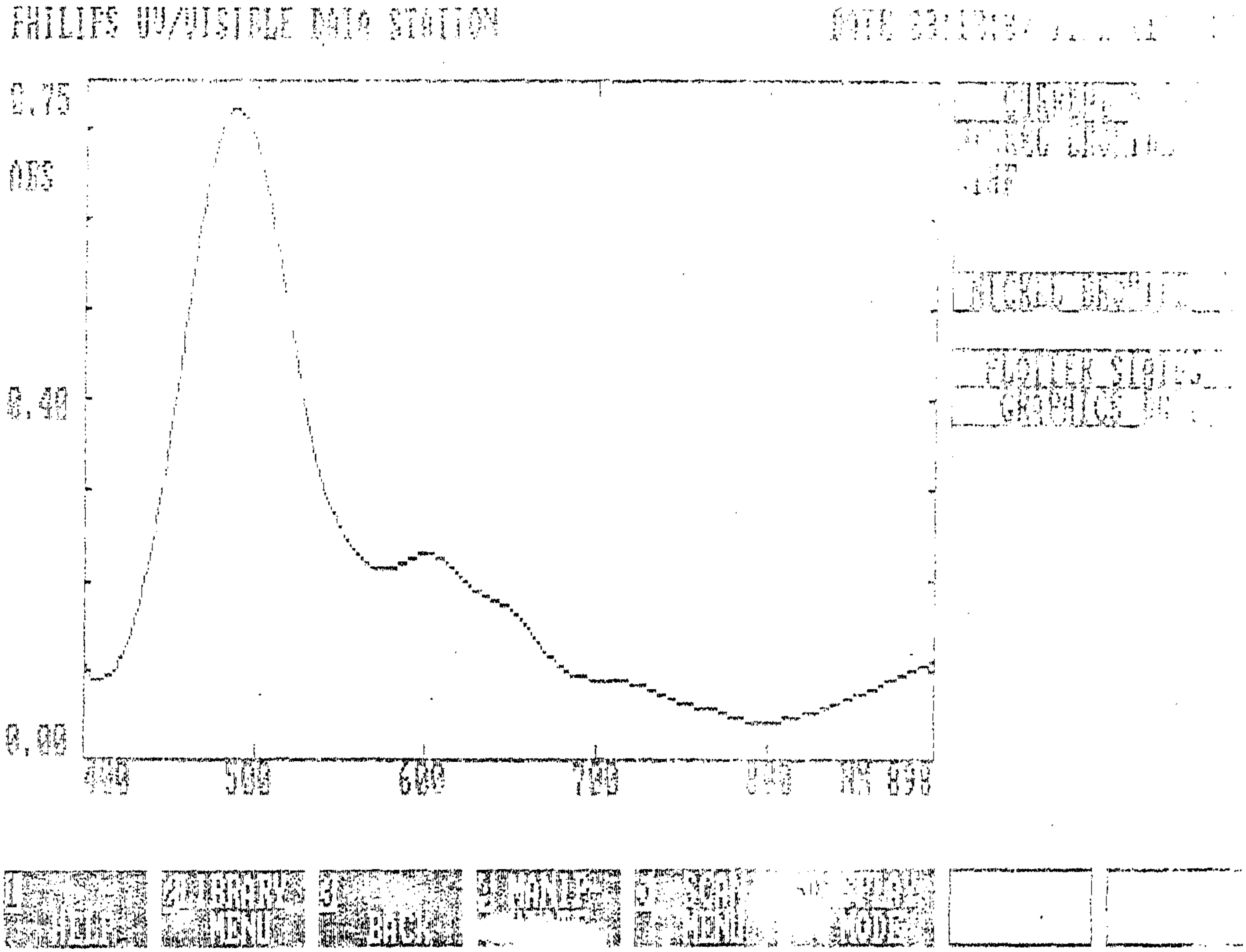


Fig 6. $NiBr_2$. 2thf/thf



compound-1
Spectra-2

Fig. 8 $Na_2Ni(OiPr)_4 \cdot 2thf$

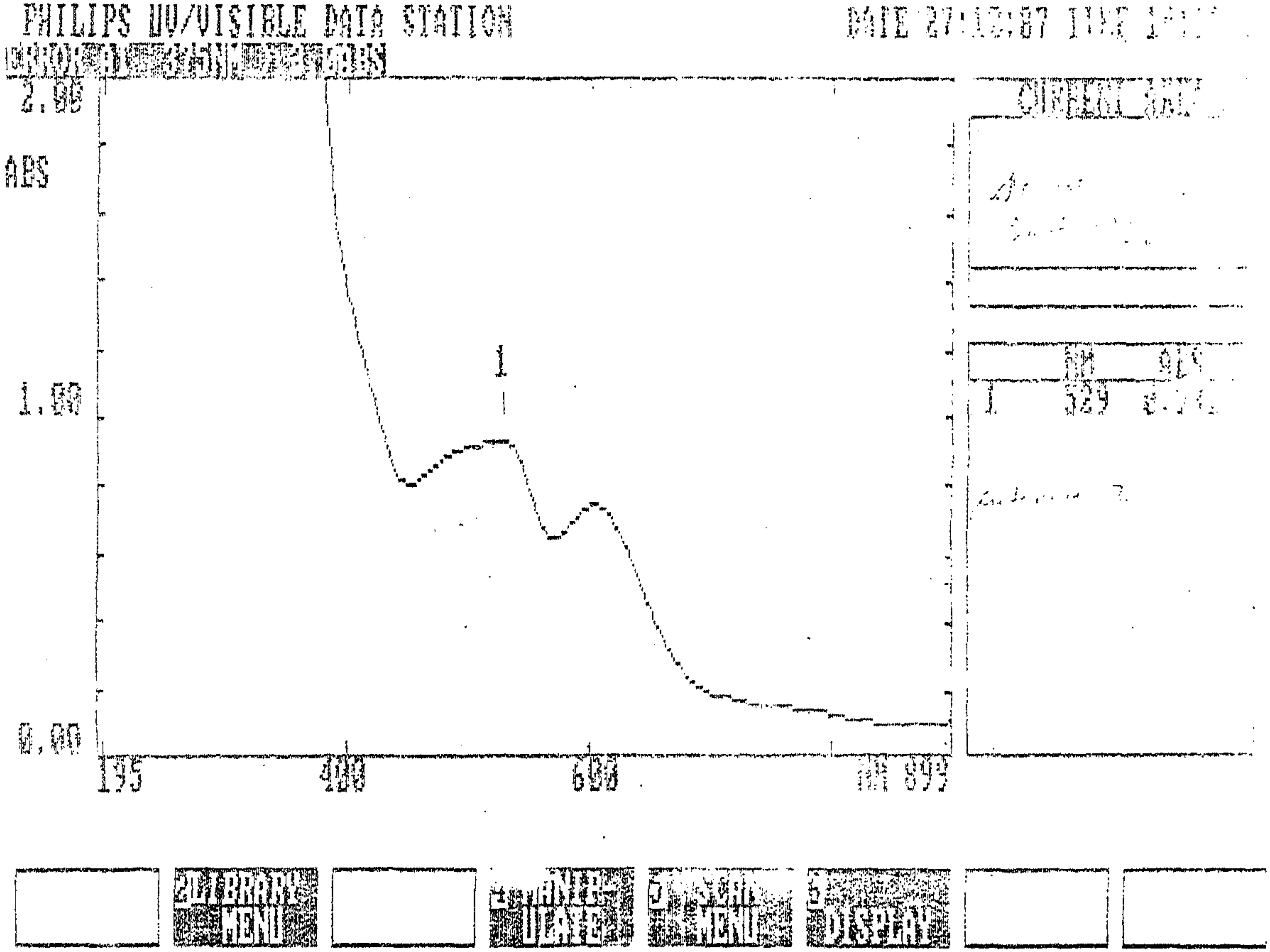
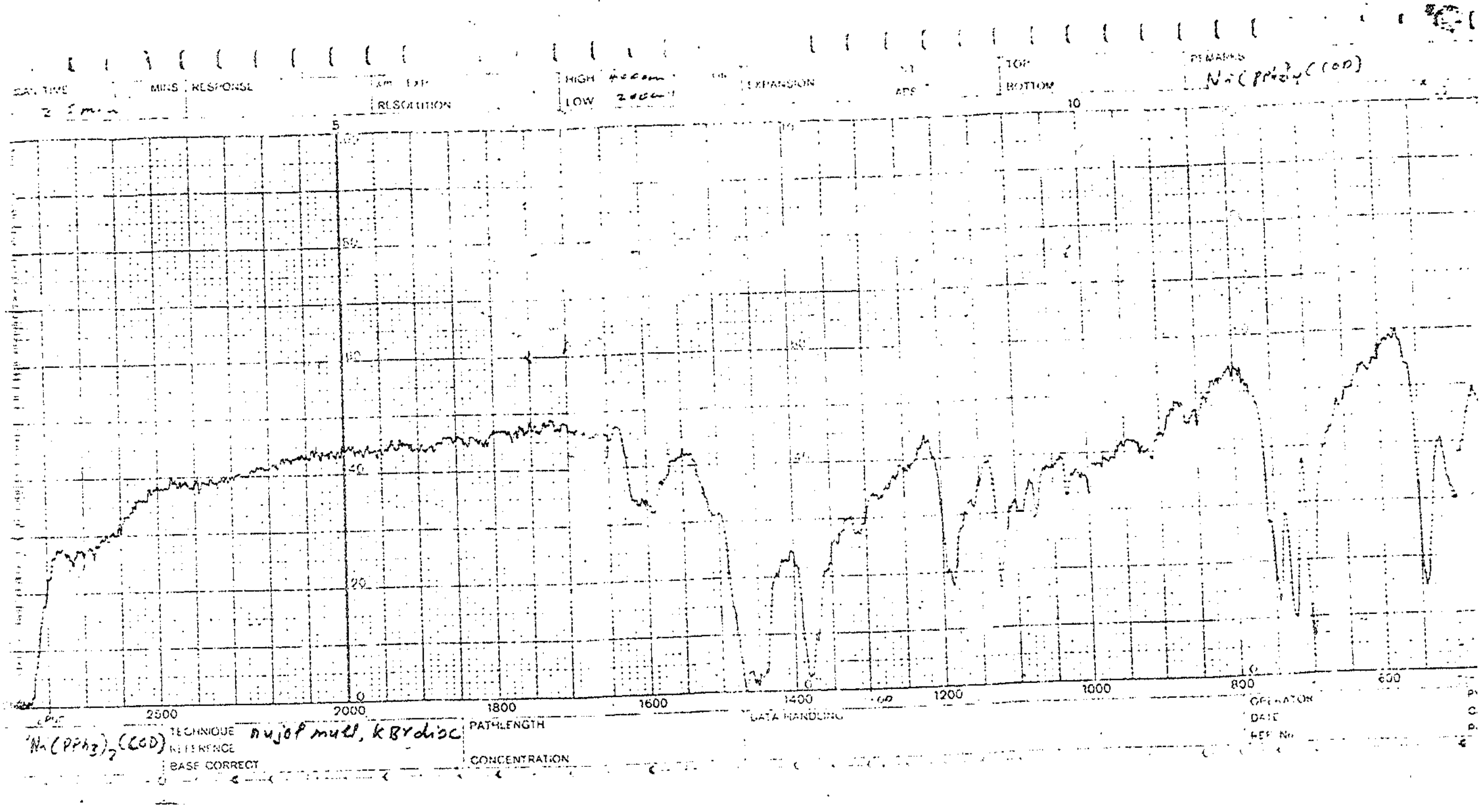


FIG. 9 $Ni(PPh_3)_2(COD)$



[FIG. 9b Ni(PPh$_3$)$_2$CCl$_2$]

CONCENTRATION

CAL ☐ SAMPLE Ni(PPh$_3$)$_2$CCl$_2$

PHASE Nujol mull

RESOLUTION ☐

REMARKS

OPERATOR K. R. J. DATE 20 · 11 · 87

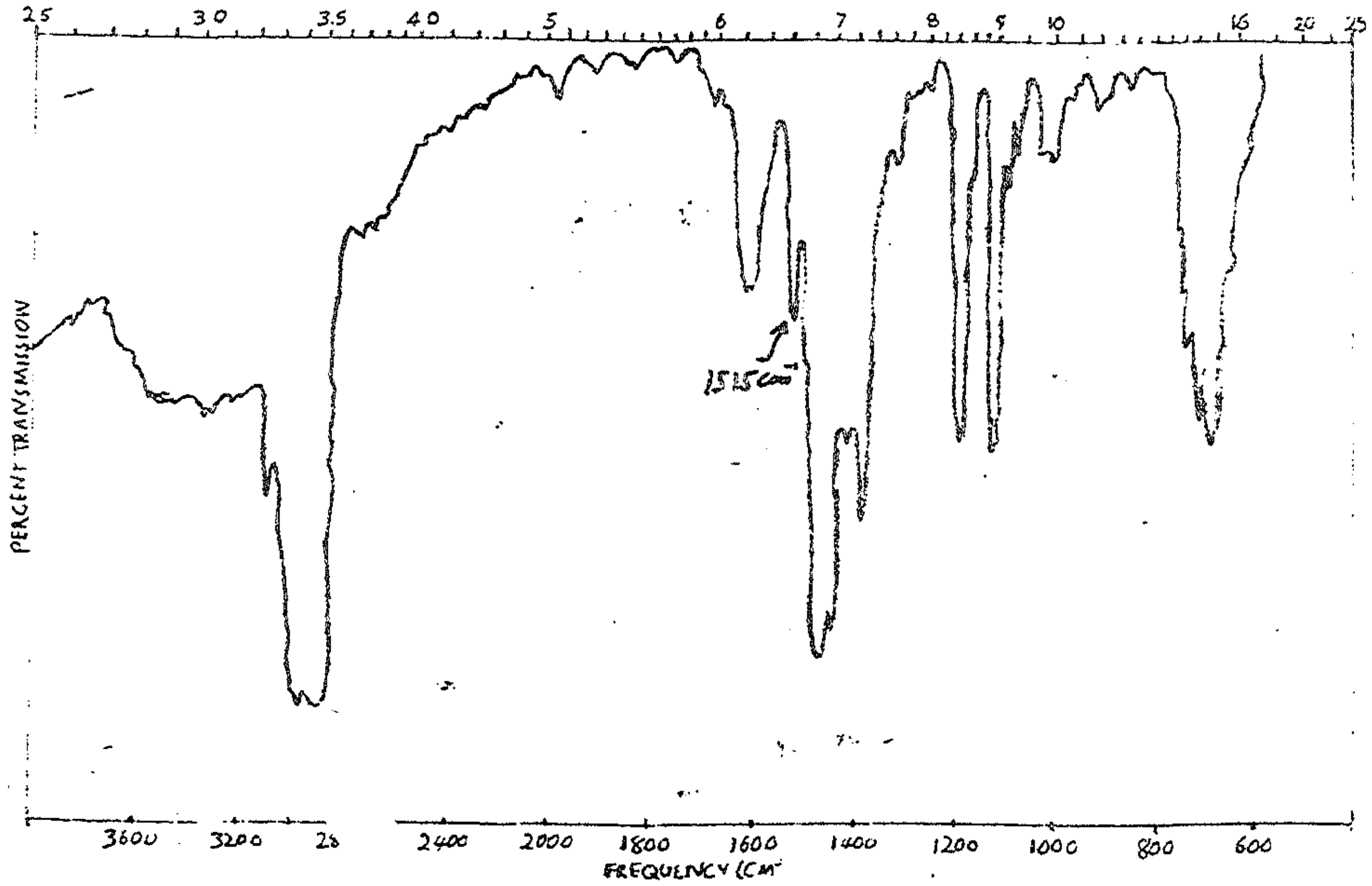
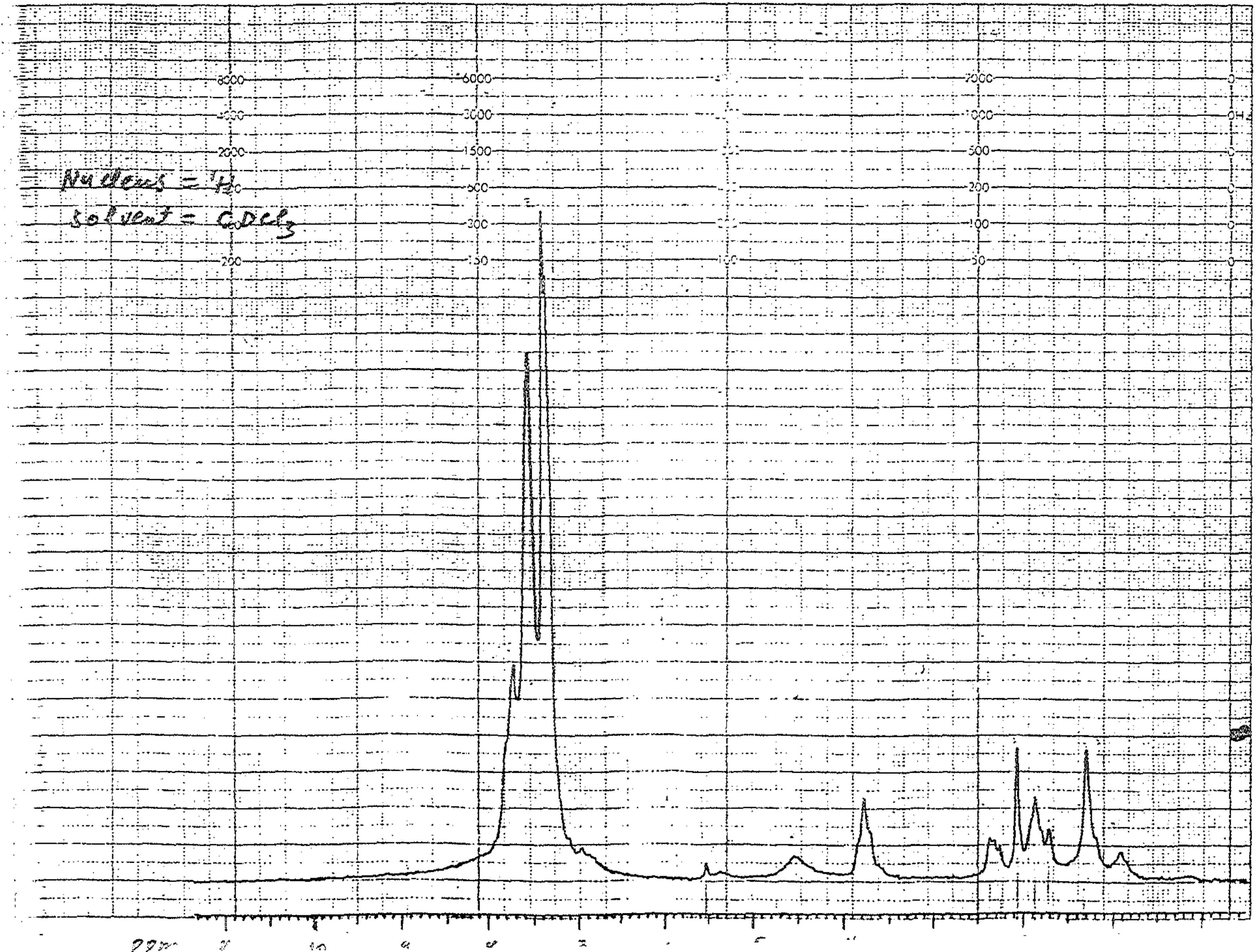
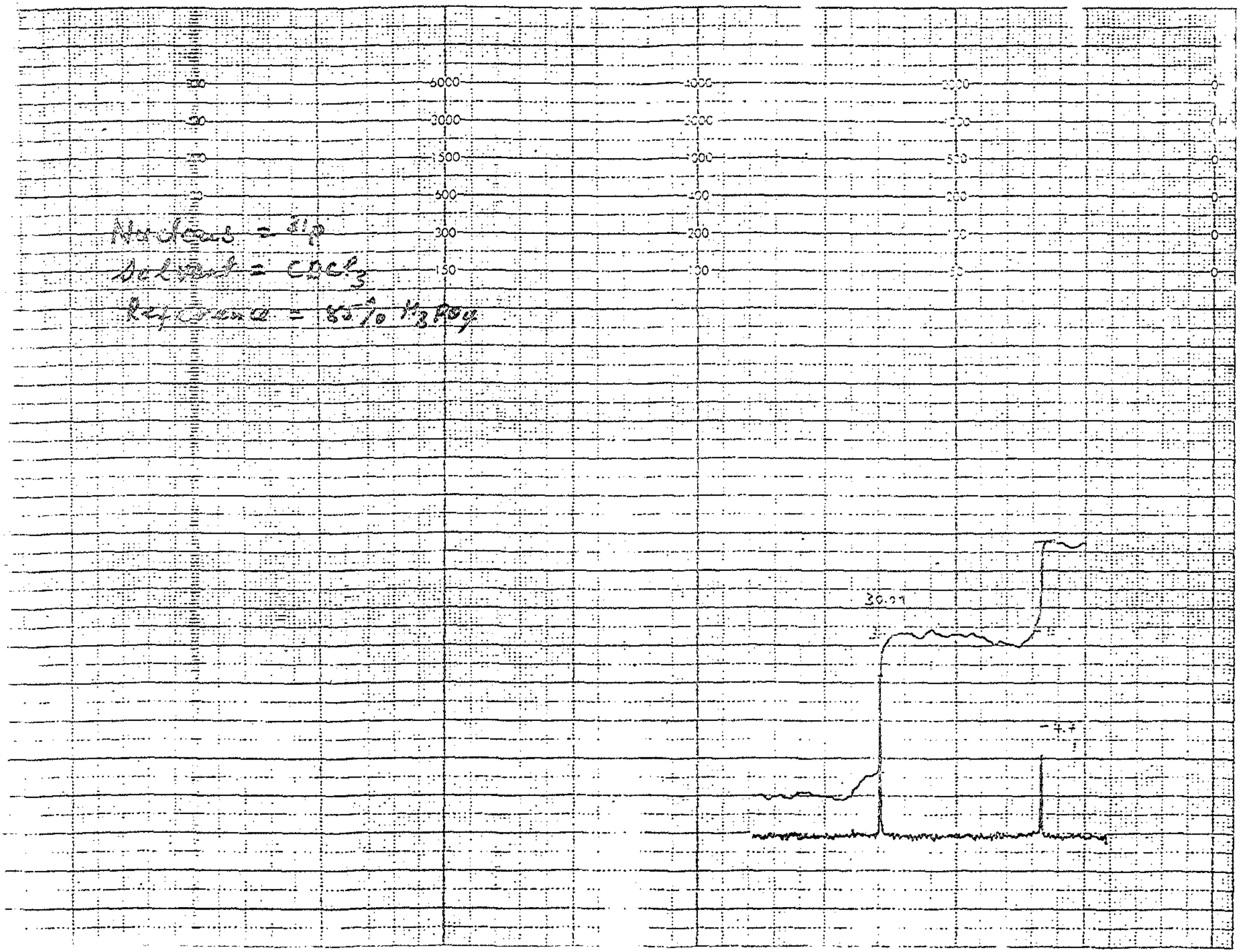


FIG-1. - $Ni(PPh_3)_2(CO)_2$



FX 100
SPECTRUM NO.
SAMPLE
G₂-1"
¹H
NUCLEUS
OBS MHz
$Ni(PPh_3)_2$
LOCK
IRR
SOLVENT CDCl₃
CONCENTRATION
REFERENCE
TEMPERATURE
OFFSET
OBS AF
IRR
PULSE
WIDTH PW
INTERVAL
REPETITION
DATA POIN
WINDOW
NO. OF PULSE
SPECTRAL WIDTH
AMPLITUDE
DECOUPLING
NON COM
INNE HOMO
NOISE
DATE
OPERATOR
REMARKS: ACRES

FIG [illegible] (PPh$_3$)$_2$C [illegible]



Nucleus = ^{31}P
Solvent = $CDCl_3$
Reference = 85% H_3PO_4

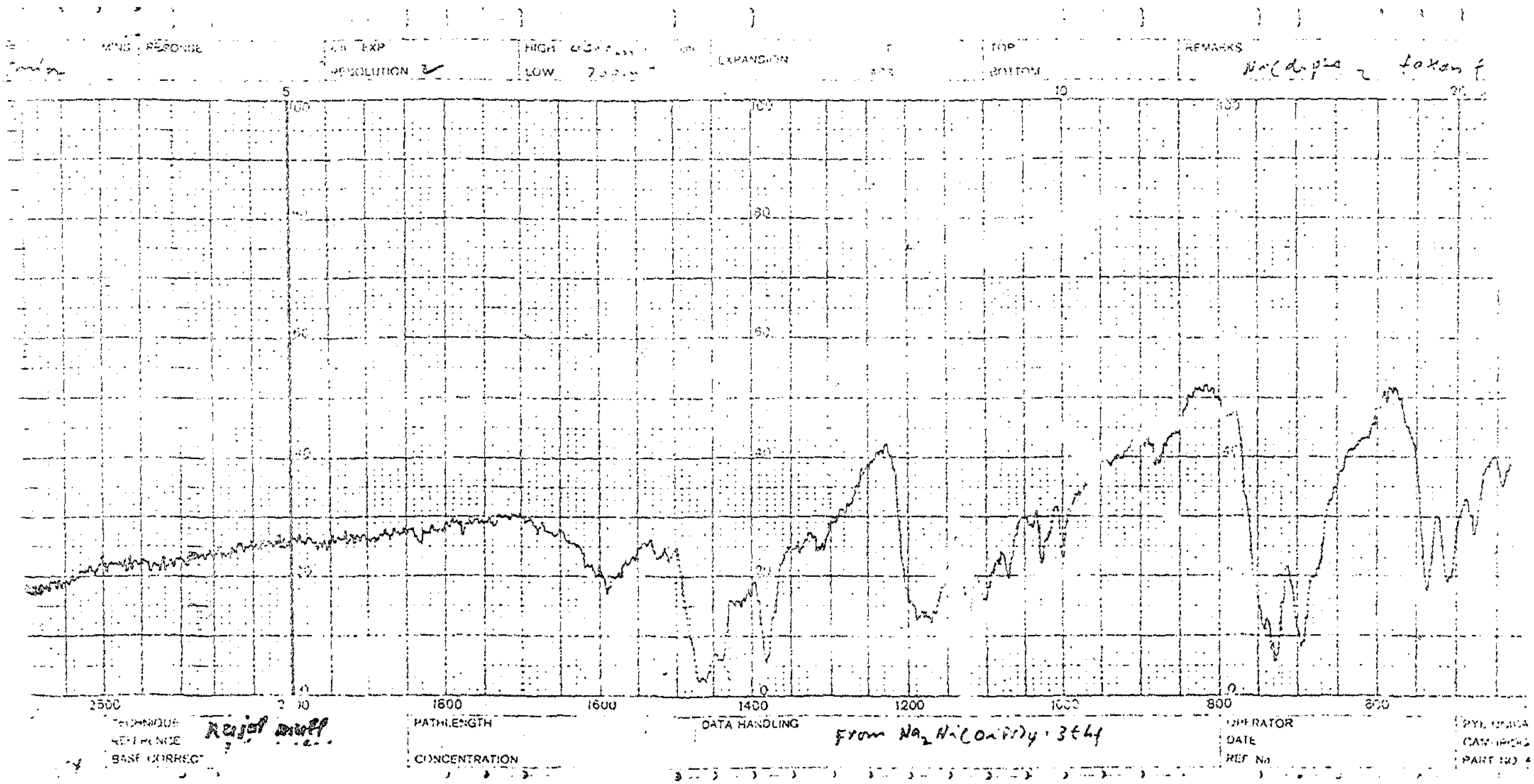
F(100 900 50C
SPECTRUM NO
SAMPLE
[illegible] Sample
taken

^{31}P

NUCLEUS
OBS MHz
C 25.05 22.53
H 99.50 89.50

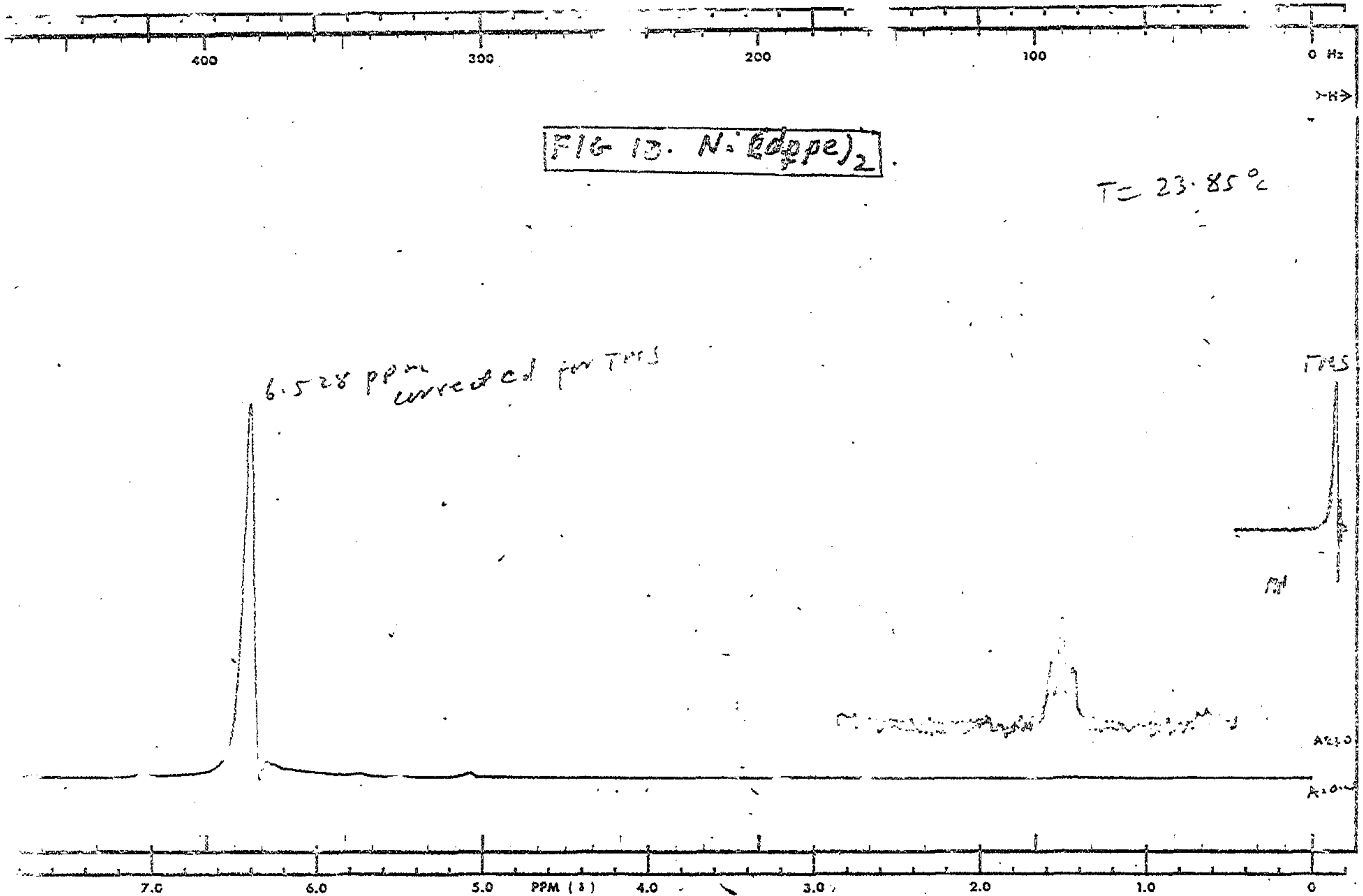
LOCK
INT EXT
IRR.
SOLVENT $CDCl_3$ TUBE
CONCENTRATION
REFERENCE H_3PO_4
TEMPERATURE
OFFSET
OBS AF KHz RF
IRR. 5+5
PULSE SINGLE
MULTI
WIDTH PW 12 μSEC
PW 24 μSEC
INTERVAL
REPETITION
DATA POINTS (FID)
WINDOW EX.
NO. OF PULSES 256
SPECTRAL WIDTH 10,00
AMPLITUDE 28
DECOUPLING
NON COM OFR
NNE HOMO HMD
NOISE KHz POWER
DATE
OPERATOR
REMARKS: ADRES

FIG. Ni(dppe)$_2$



From Na$_2$Ni(CaFs)y · 3t4f

FIG 13. Ni(dppe)$_2$



	MANUAL	AUTO ☑
SWEEP TIME (SEC):	50 250	(250)
SWEEP WIDTH (Hz):	25 50 100 250 500	(500)
FILTER:	1 2 3 4 5 6 7 8	(2)
RF POWER LEVEL:		(.05)

S): 60

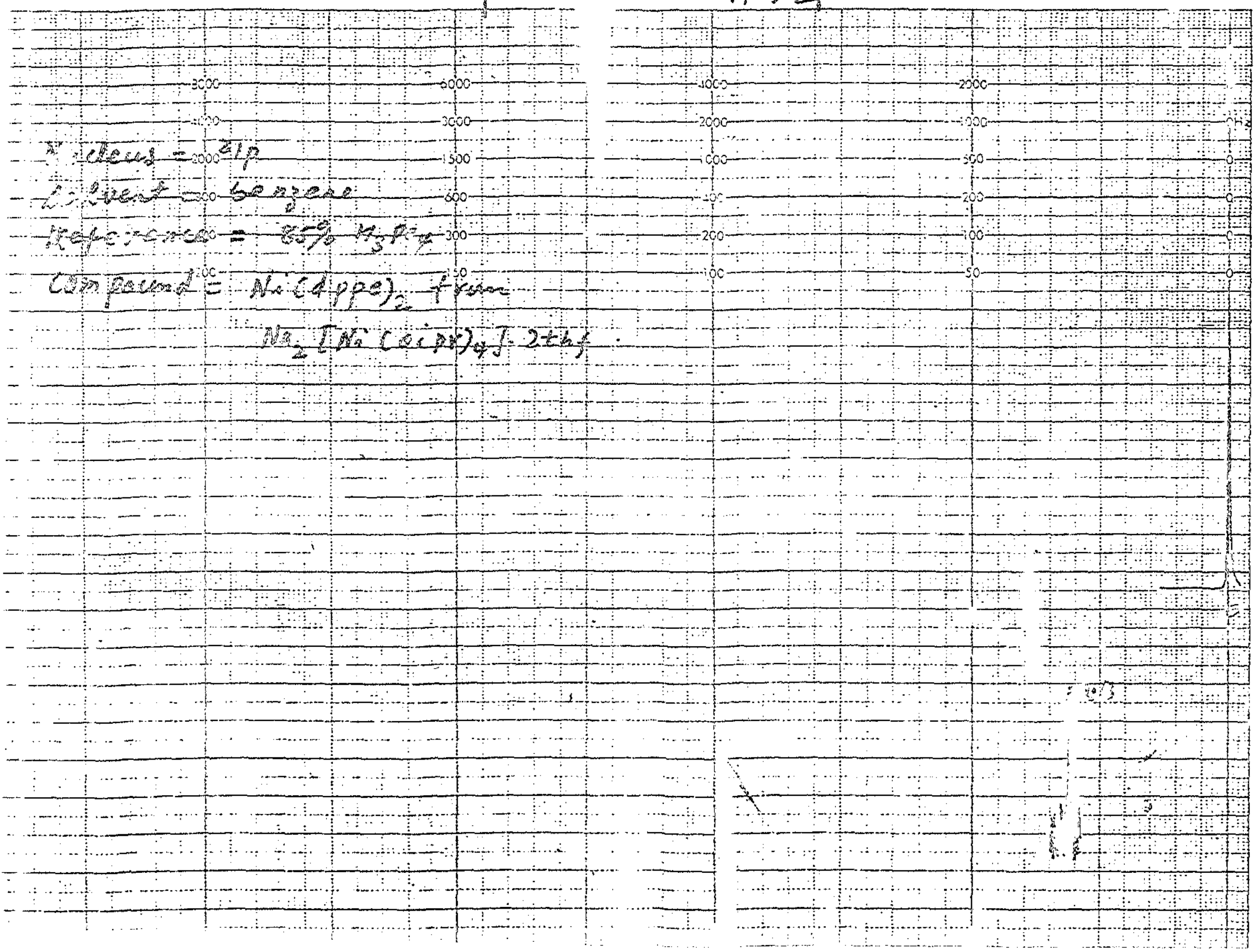
SAMPLE: Ni(dppe)$_2$

SOLVENT: benzene

REMARKS: From $Na_2Ni(OiPr)_4$ · 2THF, with capillary filled w. benzene

60 MHz NMR

FIG. $Ni(dppe)_2$



Nucleus = 31P
Solvent = benzene
Reference = 85% H_3PO_4
Compound = $Ni(dppe)_2$ from
$Na_2[Ni(C_2H_4)_4] \cdot 2thf$.

FX-100 . 900

SPECTRUM NO.
SAMPLE
$Ni(dppe)_2$
$Na_2 Ni(C_2H_4)$

NUCLEUS 31P
OBS MHz

LOCK
IRR.
SOLVENT TUBE
CONCENTRATION
REFERENCE H_3PO_4
TEMPERATURE
OFFSET
OBS
IRR 545
PULSE
WIDTH 12
24
INTERVAL
REPETITION
DATA POINTS
WINDOW EX-
NO. OF PULSES 75
SPECTRAL WIDTH
AMPLITUDE
DECOUPLING
NON
NOISE
DATE
OPERATOR
REMARKS

FIG. 15. Ni(ppe)$_2$

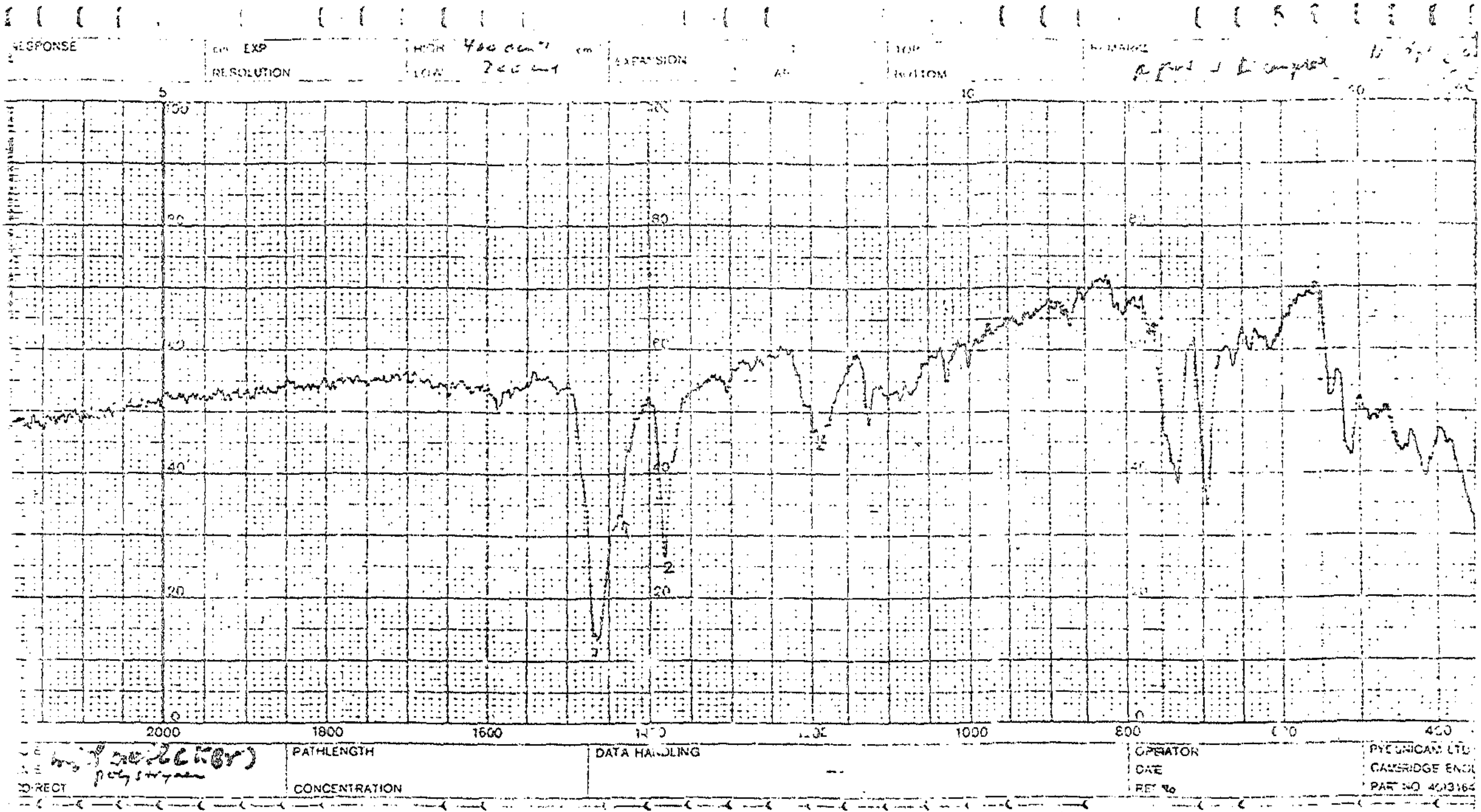
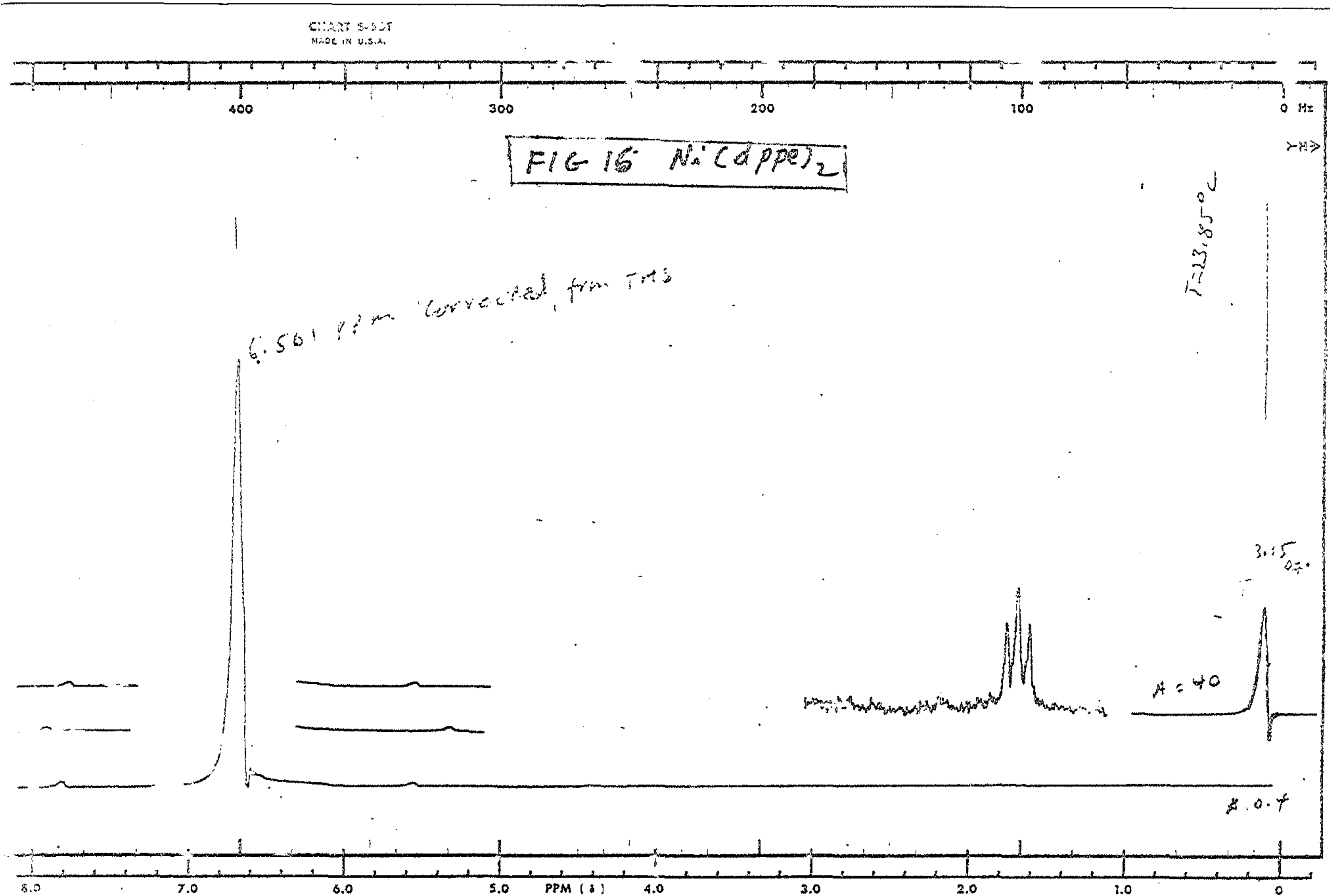


FIG 16 Ni(dppe)$_2$



MANUAL

ET (Hz): -------

MPLITUDE: 40----

MPLITUDE: -------

ATS (RPS): -------

SWEEP TIME (SEC): 50 | 250

SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500

FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8

RF POWER LEVEL: ------------

AUTO ☐

(250)

(500)

(2)

(.05)

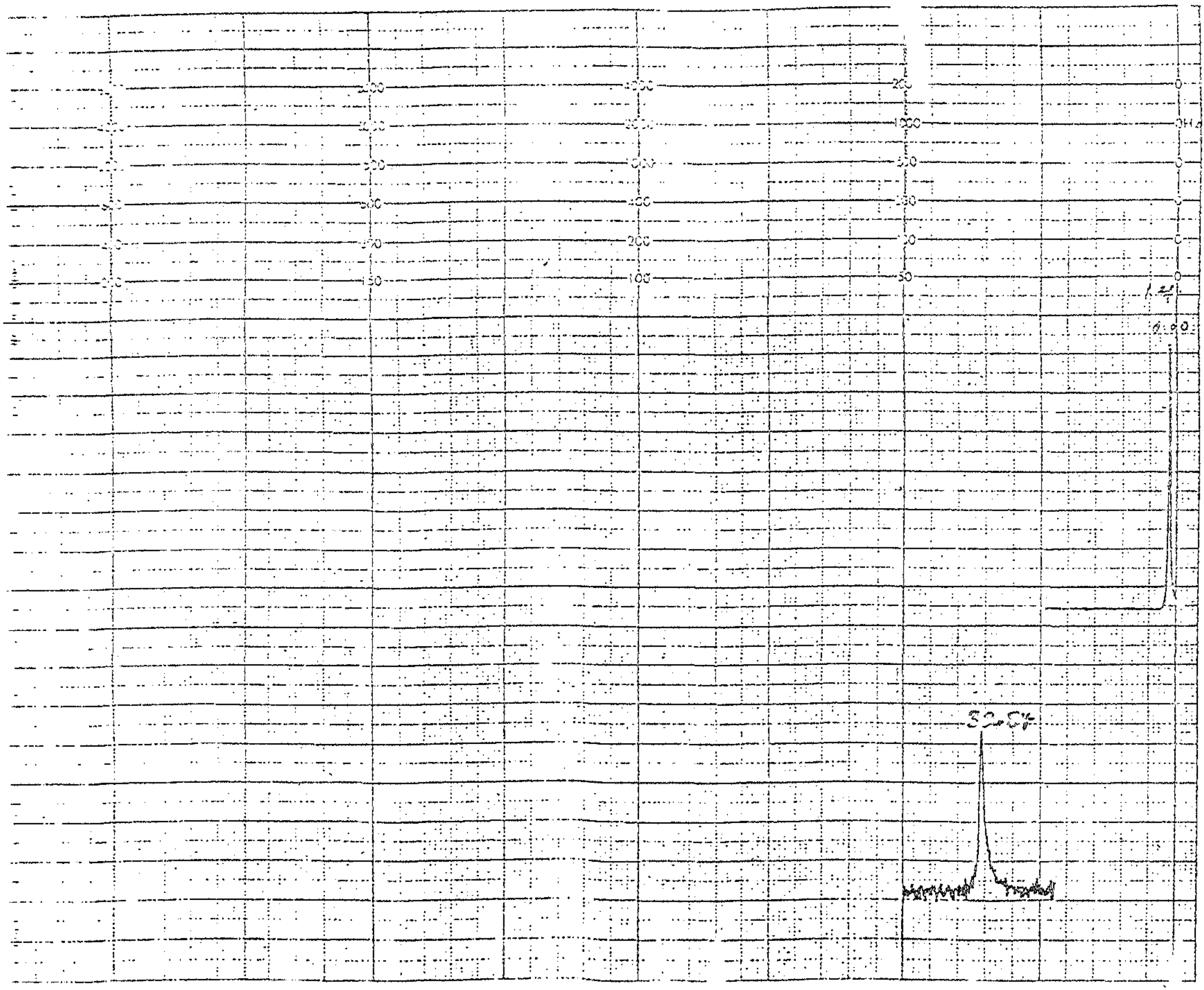
SAMPLE: Ni(dppe)$_2$

Benzene

REMARKS:

From $Li_2Ni(OiPr)_4$·LiBr·3THF
with capillary filled with Benzene

60 MHz NMR



FX

SPECTRUM NO

SAMPLE

Ni(dppe)$_2$

from Li$_2$Ni(COD)$_4$ + LiBr THF

NUCLEUS ^{31}P

LOCK

IRR

SOLVENT C_6D_6 TUBE 5 mm

CONCENTRATION

REFERENCE H_3PO_4

TEMPERATURE

OFFSET

OBS (AF) 95.7 KHz

IRR 58.5 KHz

PULSE SINGLE

MULTI

WIDTH (PW) 12 μSEC

(PW) 24 μSEC

INTERVAL (PI) SEC

REPETITION (TR) SEC

DATA POINTS FID

WINDOW EX Hz

NO. OF PULSES 256

SPECTRAL WIDTH 10,000 Hz

ppm

AMPLITUDE 18

DECOUPLING

NON OFR NOE

INNE HOMO HMG

NOISE KHz POWER

DATE 21/5/81

OPERATOR Terrie

REMARKS: ACRES

FIG. 18 $Ni[P(OCH_2CH=CH_2)_3]_4$

SCAN TIME 2.5

RESPONSE

EXP

RESOLUTION ✓

HIGH 4000 cm⁻¹

LOW 250 cm⁻¹

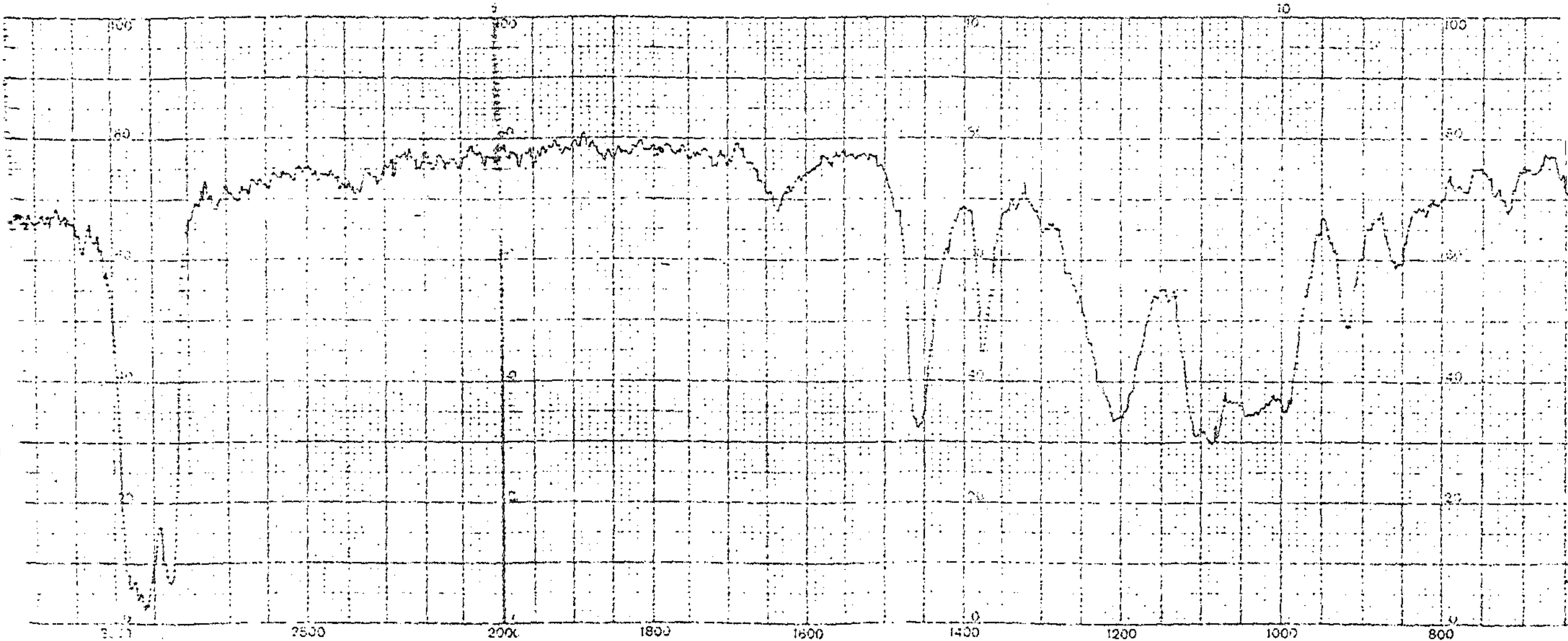
EXPANSION

ABS

TOP

BOTTOM

REMARKS



$Ni[P(OCH_2-CH=CH_2)_3]_4$

TECHNIQUE nujol mull

REFERENCE

BASE CORRECT

PATHLENGTH

CONCENTRATION

DATA HANDLING

OPERATOR

DATE

REF. NO.

FIG. 19 $Ni[P(OCH_2-CH=CH_2)_3]_4$

SCAN TIME 2.5 MINS

RESPONSE

cm EXP

RESOLUTON ✓

HIGH 4000cm⁻¹ cm

LOW 200cm⁻¹

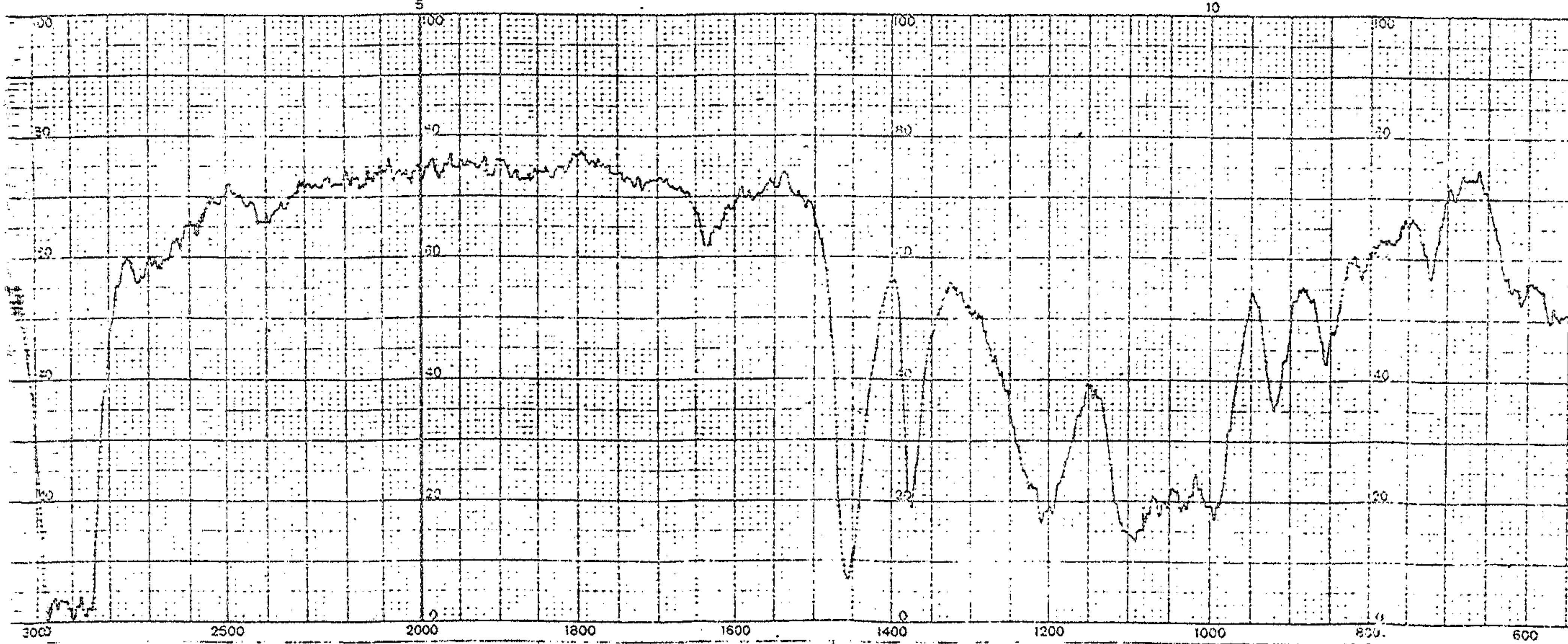
EXPANSION

ABS

TOP

BOTTOM

REMARKS



$Ni[P(OCH_2-CH=CH_2)_3]_4$

$Na_2Ni(OC(PT))_4 \cdot 2Haf$

TECHNIQUE

REFERENCE

BASE CORRECT

PATHLENGTH

CONCENTRATION

DATA HANDLING

OPERATOR

DATE

FIG. 20 $Ni[P(OPh)_3]_4$

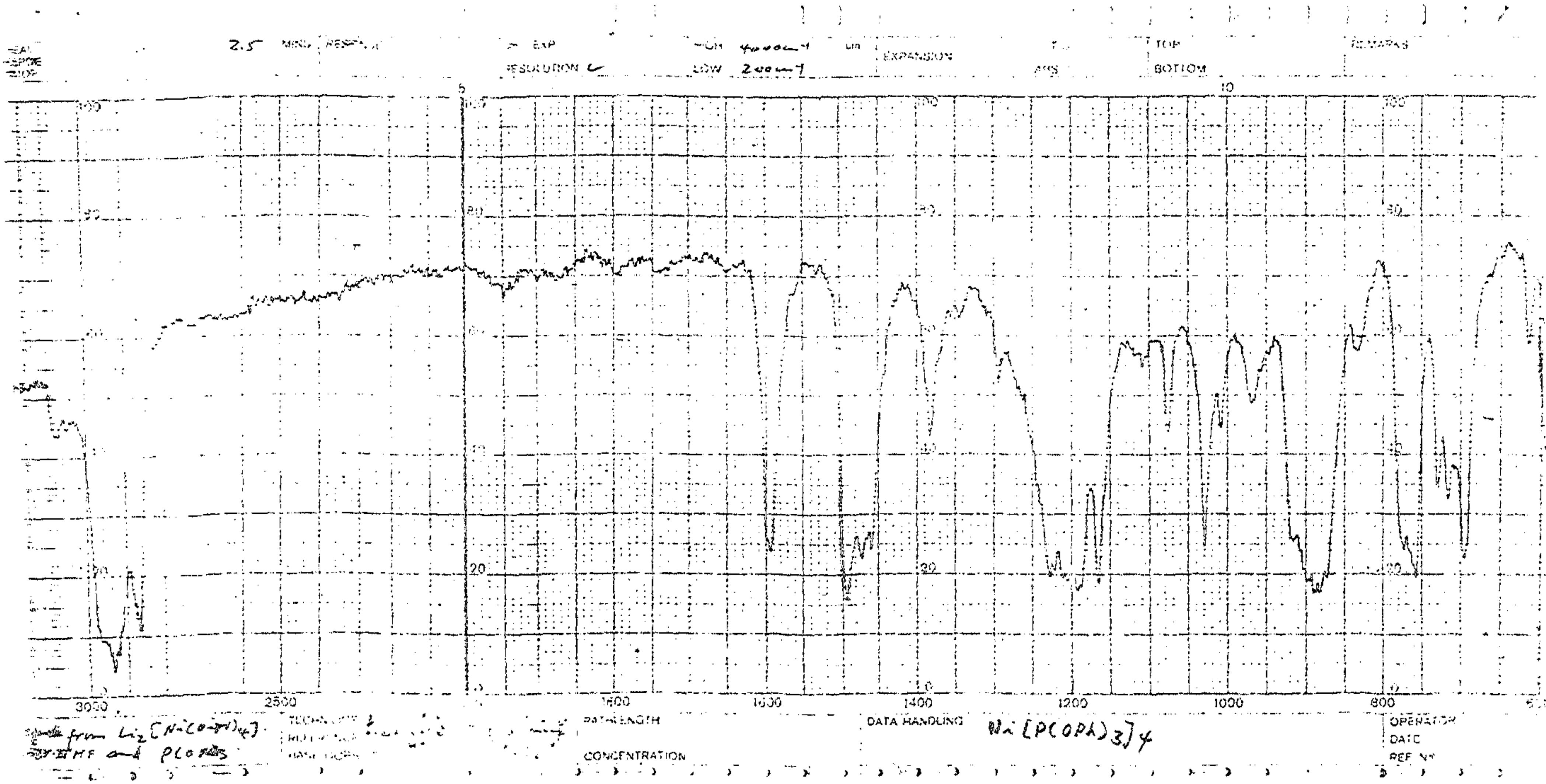
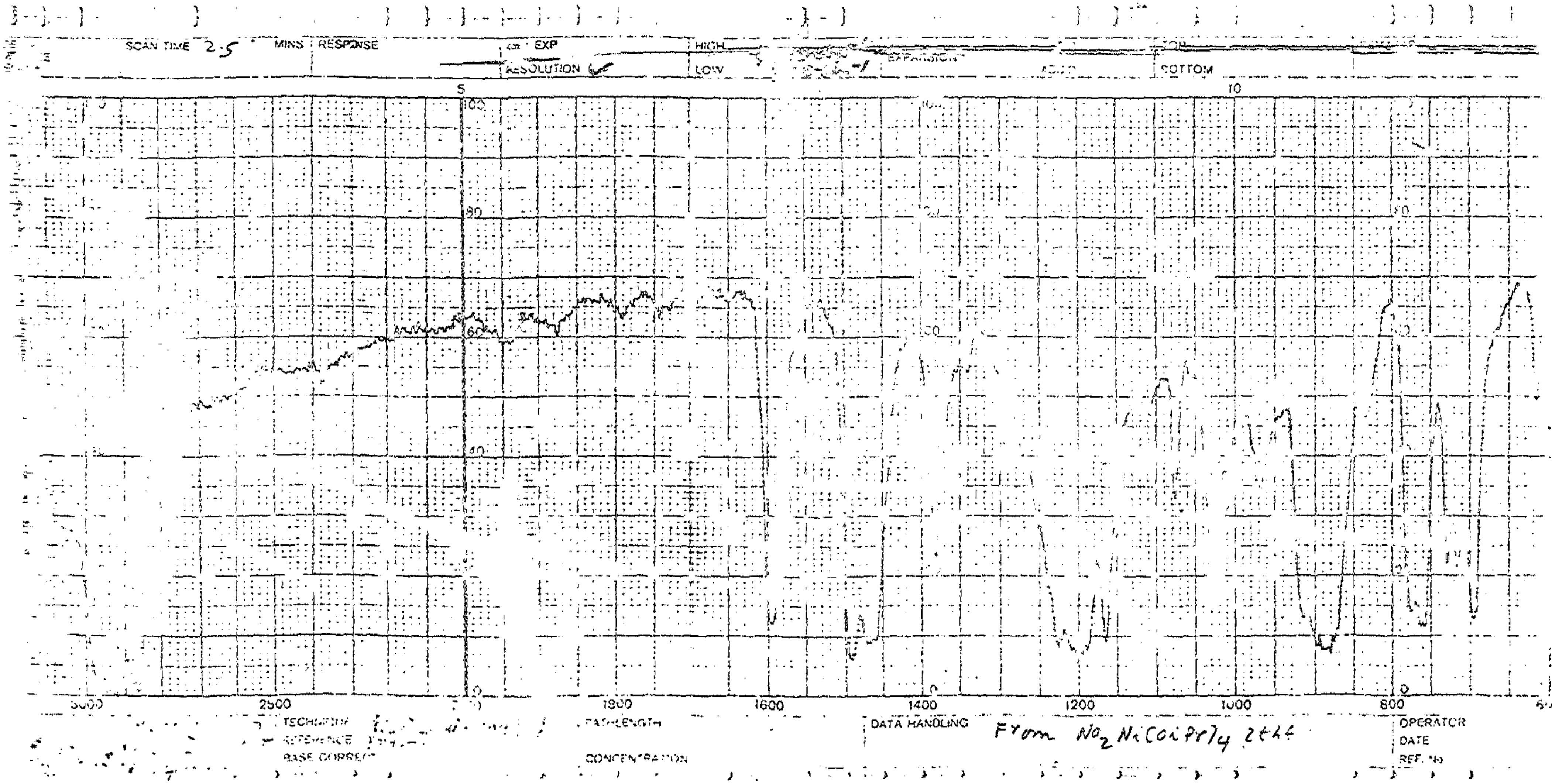
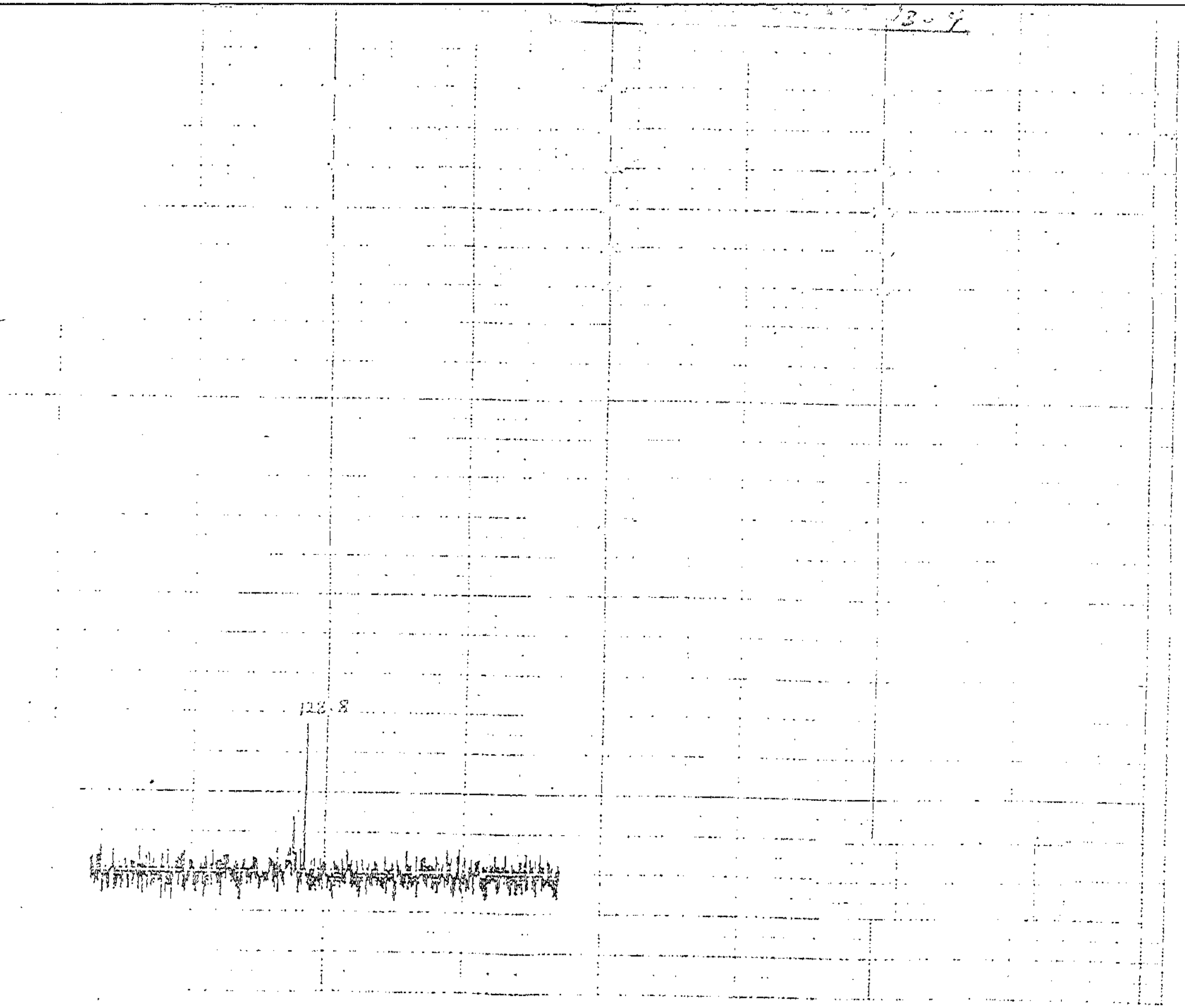


FIG. 2: $Ni[P(OPh)_3]_4$



From $Na_2Ni(OiPr)_4$ 2thf



G - 6

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