INVESTIGATIONS

ON

THE REACTION OF MOLYBDENUM PENTACHLORIDE AND CHLOROXOMOLYBDENUM COMPLEXES WITH SODIUM AZIDE

by

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D E D I C A T I O N

This piece of work is dedicated to my wife, Hanna Belete, and children, Yishak and Michael.

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ABBREVIATIONS

Ar	aryl
Bu	butyl
dipy	N,N'-dipyridyl
dppe	1,2-bis(diphenyl-phosphine ethane)
EA	elemental analysis
Et	ethyl
m	medium
Me	methyl
Ph	phenyl
py	pyridine
s	strong
thf	tetrahydrafurn
w	weak

ABSTRACT

INVESTIGATIONS ON THE REACTION OF MOLYBDENUM PENTACHLORIDE AND CHLOROOXOMOLYBDENUM COMPLEXES WITH SODIUM AZIDE

The reaction of $MoCl_5$ with NaN_3 in acetonitrile followed by addition of $OPPh_3$ resulted in the formation of impure $MoOCl_3(OPPh_3)_2$ rather than the expected nitrido analogue. NaN_3 acts here as a reducing agent generating a molybdenum(IV) chloride derivative which was trapped as impure $MoCl_4(Py)_2$.

The reaction of $MoOCl_4$ with acetonitrile or NaN_3 produced a green solution containing an $MoOCl_3(MeCN)_2$ complex which could not be isolated but trapped with $OPPh_3$ and identified as $MoOCl_3(OPPh_3)_2$. Addition of NaN_3 to the green molybdenum oxotrichloride intermediate, $MoOCl_3(MeCN)_2$ produced a deep violet solution. The viole product could not be isolated but was inferred to consist of $[Na][MoOCl_3(N_3)(MeCN)]$, a loose adduct of $MoOCl_3(MeCN)_2$ and NaN_3. Thus, addition of $OPPh_3$ to the violet solution resulted in the formation of impure $MoOCl_3(OPPh_3)_2$. The violet intermediate obtained from $MoOCl_3(MeCN)_2$ and NaN_3 is stable in acetonitrile but decomposes in CH_2Cl_2 under evolution of N_2 and reduction yielding $MoOCl_2(MeCN)_3$ as a brown crystalline product which is sensitive to hydrolysis. $MoOCl_3(OPPh_3)_2$ itself reacts slower with NaN_3 in acetonitrile with chloride-azide exchange yielding $MoOCl_2(N_3)(OPPh_3)_2$.

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1. INTRODUCTION

Nitrido complexes of transition metals in general and those of molybdenum in particular have received increasing interest as possbile intermediates in biological nitrogen fixation [1]. Such nitrido complexes are usually conver . to ammonia by addition of alcohols or water, but are sometimes sufficiently reactive to abstract hydrogen even from aprotic solvents such as thf.

Recently it has also been reported that nitrido complexes of manganese can serve as intermediates in the transfer of nitrogen to unsaturated organic substrates [2]. The process may be considered analogues to the well known epoxidation of olefins.

Further attention as to the use of nitrido molybdenum compounds in catalysis came from the finding that they represent an essential constituent of certain homogenous catalyst systems for olefin metathesis [3,4]. Most of the metathesis catalysts published so far of Ziegler-Natta type and based on tungsten, molybdenum or rhenium complexes [5-8]. In contrast to the large number of highly active tungsten containing metathesis systems, there are, surprisingly enough, only a

few molybdenum based systems of comparable activity. Considering the type of molybdenum precatalyst involved in olefin metathesis these can be categorized into the following three major groups [9].

A. Nitrosylmolybdenum complexes

e.g. $MoCl_2(NO)_2L_2/EtAlCl_2$ [10,11]

$MoCl_3(NO)L_2/EtAlCl_2$ [11]

(L = various N-and O-donors)

$MoCl(NO)(CO)_2L_2/EtAlCl_2$ [12]

($L = PPh_3$, $AsPh_3$)

B. Nitridomolybdenum complexes

e.g. $MoNCl_3L_2/RAlCl_2$ [3]

($L= OPPh_3$; $L_2 = Bu_4NCl$; R = Me, Et)

C. Halopentacarbonylmolybdates(0)

e.g. $[Bu_4N][Mo(CO)_5Cl]/EtAlCl_2$ [13]

The use of dinitrosylmolybdenum(0) complexes with $EtAlCl_2$ as a cocatalyst for the homogenous metathesis of olefins was first reported by Zuech in 1967 [10]. Taube and Seyferth found that the mono-nitrosylmolybdenum(II) complexes $Mo^{II}Cl_3(NO)L_2$, and nitrosylcarbonylmolybdenum(0) complexes $Mo^{0}Cl(NO)(CO)_2L_2$, exceed the metathesis activity of the analogous dinitrosyl precatalysts [11,12] and are among the most

Another possible agent to split off the oxygen from the NO group is the Lewis acid, cocatalyst, $EtAlCl_2$.

The above result is further supported by the finding that the nitridomolybdenum(VI) complexes, $MoNCl_3L_2$ (L_2 = Bu_4NCL, L = $OPPh_3$), themselves constitute very efficient metathesis precatalysts [3]. For the homogenous system $MoNCl_3(OPPh_3)_2/EtAlCl_2$, it has been confirmed experimentally that the nitridomolybdenum grouping remains intact throughout the catalytic process. Furthermore, the carbon ligand, being essential for the catalytic alkylidene group rearrangement, was proved to originate from the $EtAlCl_2$ cocatalyst [9]. Incidently, the catalyst formation is very likely to proceed under alkylation of the chloronitridomolybdenum-(VI) precatalyst, $MoNCl_3L_2$, and subsequent α-hydrogen elimination as indicated in equation (3).

$$Mo^{VI}NCl_3L_2+(2+x)C_2H_5AlCl_2 \rightarrow [Mo^{IV}N(CHCH_3)Cl.xAl(Et)Cl_2] + 2L.AlCl_3 + C_2H_6 \qquad (3)$$

A similar process may be operative in transferring the oxonitrido intermediate, $[NMo^{VI}(O)Cl.xAlCl_3.yAl(Et)Cl_2]$ (equation (1)) into a metathetically active nitrido-carbene complex.

Despite the usefulness of the nitridomolybdenum

complexes as catalysts, little is known about their preparation and reactivity. The synthesis of the chloronitridomolybdenum complexes, $MoNCl_3$ and $MoNCl_3L_x$ (x = 1, L = Bu_4NCl, Et_4NCl, dipy; x = 2, L = $OPPh_3$; x = 3, L = py) usually starts with $Mo(CO)_6$, $MoCl_5$, or $MoCl_4L_2$ (L = thf, MeCN) and nitride precursors such as NCl_3 [17], ClN_3 [18], Et_4NN_3 [19] and $(Me)_3SiN_3$ [20]. Very recently a rather safe and convenient synthesis for the compounds, $MoNCl_3L_2$ (L = $OPPh_3$, 1/2 dipy, 1/2 Bu_4NCl) from $MoCl_4(MeCN)_2$ using NaN_3 as a nitrido source was published by Seyferth and Taube [3].

$$MoCl_4(MeCN)_2+NaN_3+2OPPh_3 \rightarrow MoNCl_3(OPPh_3)_2+NaCl+N_2+2MeCN \quad (4)$$

The reaction of $MoCl_5$ with NaN_3 and $OPPh_3$ in acetonitrile has been dealt with by Zewdu Gebeyehu [21].

The only oxonitridomolybdenum compounds known todate are $K_3[Mo(N)O_3]$ [22] and the above mentioned $(C_5H_5)_3Mo_3(N)(O)(CO)_4$ [16,23]. The assumption that oxonitridomolybdenum complexes might be involed in metathesis catalyst systems (see equation (1)) focused our interest on this complex type. A possible preparative entrance should be the reaction of molybdenum oxochlorides with azide, even though oxoazido complexes may also be expected as possbile products. Both

oxonitrido and oxoazidomolybdenum compounds are of general interest as potential metathesis catalysts.

Thus, it is the objective of this project:

1. To study the reaction of $MoCl_5$ with NaN_3 in acetonitrile using $OPPh_3$, Bu_4NCl, and pyridine as auxilary ligands. As possible products nitridomolybdenum(VI) complexes, $MoNCl_3Ln$, may be expected.
2. To investigate the reaction of the oxochloromolybdenum complexes, $MoOCl_4$ and $MoOCl_3(OPPh_3)_2$, with NaN_3 in acetonitrile as a potential route to oxonitrido or oxoazido derivatives of molybdenum.

2. LITERATURE SURVEY: The Reaction of Azides with Molybdenum and Tungsten Complexes

2.1 Reaction Pathways

Nitrogen serves as a donor atom in a great variety of ligands. One of these is the azide ligand, N_3^-. In its behaviour it is quite similar to the chloride anion. Thus, it acts as a moderetely strong δ-donor with some additional π-donor capacity. Even though the azide has a delocalized π-system, the ligand does neither seem to display remarkable π-acceptor properties nor to form π-complexes (side-on bonding). However, a few complexes with bridging azido ligands have been described [38].

The azide ion itself is symmetrical and linear, and its electronic structure may be represented by three mesomeric forms.

$$[\,\overset{\ominus}{\underline{N}} = \overset{\oplus}{N} = \overset{\ominus}{\underline{N}}\,]^- \longleftrightarrow [\,N \equiv \overset{+}{N} - \overset{2\ominus}{\underline{N}}\,]^- \longleftrightarrow [\,\overset{2\ominus}{\underline{N}} - \overset{+}{N} \equiv N\,]^-$$

In covalent azides, the linear symmetry is lost and the structure is best described by the following two resonance hybrids

$$R\text{-}\overset{\oplus}{\underline{N}}\text{=}\overset{\ominus}{N}\text{=}\overset{\ominus}{\underline{N}} \longleftrightarrow R - \overset{\ominus}{\underline{N}} - \overset{\oplus}{N} \equiv N$$

In addition to its role as a ligand, the azide ion, but covalent azides as well, may act as oxidizing or reducing agents. With transition metal complexes the following reactions have been observed so far.

1. Substitution

$$M - X + M' - N_3 \longrightarrow M' - X + M - N_3 \qquad (5)$$

2. Oxidation of the transition metal

   a. Under formation of diazene complexes

$$2M - N_3 \longrightarrow M = N - N = M + 2N_2 \qquad (6)$$

   b. Under formation of alkylimido complexes

$$M + RN_3 \longrightarrow M = N - R + N_2 \qquad (7)$$

   c. Under formation of nitrido complexes

$$M - N_3 \longrightarrow M \equiv N + N_2 \qquad (8)$$

3. Reduction of the transition metal

$$M - N_3 \longrightarrow M + 3/2\ N_2 \qquad (9)$$

4. Nucleophilic addition to unsaturated ligands

$$M - CO + N_3^- \longrightarrow [M - \underset{\underset{O}{\|}}{C} - N_3]^- \longrightarrow [M - NCO]^- + N_2 \qquad (10)$$

The following four sections are meant to deal with a literature survey of the above reactions of azides with molybdenum and tungsten compounds.

2.2 Formation of Azido Complexes

Dehnicke et al. investigated the reaction of $MoCl_5$ and WCl_6 with ClN_3 in order to prepare nitrido complexes of the formula $MNCl_3$. The monoazido intermediates, $MCl_5(N_3)$, were detected but not isolated due to their instability and explosiveness [18,24].

$$MoCl_5 + ClN_3 \xrightarrow{0^\circ C} [MoCl_5(N_3)] + 1/2\ Cl_2 \qquad (11)$$

$$WCl_6 + ClN_3 \xrightarrow{0^\circ C} [WCl_5(N_3)] + Cl_2 \qquad (12)$$

$$[MCl_5(N_3)] \xrightarrow{25^\circ C} MNCl_3 + Cl_2 + N_2 \qquad (13)$$

(M = Mo, W)

With an excess of ClN_3, the $[MoCl_5(N_3)]$ complex could be converted into the more stable but highly explosive, black diazido derivative $MoCl_4(N_3)_2$ [18].

$$[MoCl_5(N_3)] + ClN_3 \longrightarrow MoCl_4(N_3)_2 + Cl_2 \qquad (14)$$

Similar unstable monoazide intermediates have been invoked in the reaction of $MoBr_4$ with IN_3 [25], WBr_6 with IN_3 [26] and $[Ph_4P][WBr_6]$ with IN_3[26]. The treatment of MoI_3 with IN_3 in CCl_4 seems to give a somewhat more stable azido

complex, $MoI_2(N_3)$ [27]. Two other highly explosive but isolable diazido compounds were obtained from $M(CO)_6$ (M = Mo, W) and IN_3 [28].

$$M(CO)_6 + IN_3 \longrightarrow M(CO)_2(N_3)_2 + I_2 \qquad (15)$$

(M = Mo, W)

The reaction of the hexaflourides of molybdenum and tungsten with alkali and tetraalkylammonium azides was investigated in detail by Glavincevski and Brownstein [29,30]. The following three reaction pathways could be detected.

$$MF_6 + N_3^- \longrightarrow [MF_6(N_3)]^- \qquad (16)$$

$$2MF_6 + N_3^- \longrightarrow MF_7^- + MF_5(N_3) \qquad (17)$$

$$MF_6 + N_3^- \longrightarrow MF_6^- + 3/2\ N_2 \qquad (18)$$

Thus, WF_6 is capable of adding one equivalent of $[R_4N][N_3]$ in liquid SO_2 or $CHCl_2$ to give $[R_4N][WF_6(N_3)]$. Excess of azide initiates reaction (16) with slow rate. With alkali azides, $M'N_3$(M' = Li, Na, Cs), in liquid SO_2 pathway (16) predominates, whereas with acetonitrile as a solvent rapid azide addition followed by slow reduction according to equation (18) was observed. $WF_5(N_3)$ and $CsWF_6$ could be isolated as pure compounds.

$$[W(N)(N_3)(dppe)_2] + EtI \longrightarrow [W(NEt)(N_3)(dppe)_2]I \qquad (27)$$

$$[M(N)(N_3)(dppe)_2] + \underset{\diagdown\,S\,\diagup}{CH_2 - CH_2} - CH_3 \longrightarrow [W(NS)(N_3)(dppe)_2] + CH_2{=}CH{-}CH_3 \qquad (28)$$

There is only one example of a bridging azide ligand. Bishop et al.[38] showed that the reaction of $[Ph_4P)[MoO(SCH_2CH_2CH_2S)_3]$ with HN_3 in methanol results in the formation of the unusual triply-bridged complex, $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]$.

$$[Ph_4P][MoO(S(CH_2)_3S)_3] + HN_3 \xrightarrow{MeOH} [Mo_2O_2(\mu\text{-}N_3)(S(CH_2)_3S)_3] \qquad (29)$$

In addition to the μ-N_3 ligand the two molybdenum(V) centers are coupled by two sulphur bridges. The hydrazoic acid in equation (29) is generated in situ from Me_3SiN_3 and methanol.

Another reaction involving in situ formed HN_3 was reported by Dehniche [39]. Thus WCl_6 and IN_3 in CH_2Cl_2 were found to give the tetrameric cyclic HN_3 adduct, $[WNCl_3 \cdot 0.5\ HN_3]_4$.

2.3 Formation of Diazene Complexes

The chemistry of bridging diazene or μ-N_2 complexes of molybdenum and tungsten is not very

extensive. With elements of the VI B group, only a few compounds have been described so far. Thus, the dinitrogen complex $[Re(PMe_2Ph)_4Cl(N_2)]$ reacts with suitable acceptors A (A = $CrCl_3(thf)_2$, $MoCl_3(thf)_2$, $MoCl_4(OMe)$, and $WCl_4(PMe_2Ph)$ to give μ-N_2 derivatives of the formula $[Cl(PMe_2Ph)_4\ Re(\mu\text{-}N_2)A]$ [40]. Also trinuclear species with a $[Re(\mu\text{-}N_2)\ M(\mu\text{-}N_2)Re]$ framework (M = Ti, Mo, W), are known. The best characterized compound of this type is $[\{Cl(PMe_2Ph)_4\ Re(\mu\text{-}N_2)\}_2MoCl_4]$ obtained from $MoOCl_3$ or $MoCl_4(PPh_3)_2$ and $[Re(PPhMe_2)_4Cl(N_2)]$ [41]. Very recently Anderson et al [42] succeeded in isolating the first homometalic binuclear μ-N_2 tungsten complex of this sort, $[\{W(N_2)_2(PEt_2Ph)_3\}_2\ (\mu\text{-}N_2)]$.

There is only one reference concerning the formation of a diazene molybdenum complex employing azide as a source of nitrogen. The reaction of $MoCl_5$ with IN_3 or NCl_3 in CCl_4 yields (μ-diazene)bis(tetrachloromolybdenum), $[MoNCl_4]_2$ [43].

$$2MoCl_5 + 2IN_3 \xrightarrow{CCl_4} [MoNCl_4]_2 + 2N_2 + 2ICl \qquad (30)$$

$$2MOCl_5 + 2NCl_3 \xrightarrow{CCl_4} [MoNCl_4]_2 + 4Cl_2 \qquad (31)$$

Thermal decomposition of $[MoNCl_4]_2$ gives the nitrido complex, $MoNCl_3$.

$$1/2\ [MoNCl_4]_2 \xrightarrow{100^oC} MoNCl_3 + 1/2\ Cl_2 \qquad (32)$$

The reaction is suggested to proceed via the intermediates $MoCl_5$. IN_3 and Cl_5MoNI. In the presence of co-ordinating solvents, e.g. $OPCl_3$, the formation of nitrido complexes is straightforward [43].

$[MoNCl_4]_2$ reacts with water to molybdenum blue, NH_3, and N_2. Nitrogen originates most probably from N_2H_4 as the primary hydrolysis product [43].

The brown diazene complex, $MoNCl_4$ could also be prepared from $Mo(CO)_6$ and NCl_3 in CCl_4, but was isolated only as a crude product [44].

$$Mo(CO)_6 + 2NCl_3 \xrightarrow{CCl_4} \text{"}MoNCl_4\text{"} + 6CO + 1/2\ N_2 + Cl_2 \qquad (33)$$

2.4 Formation of Imido Complexes

The reaction of arylazides with tungsten complexes was found to yield compounds with coordinated RN_3PR_3, RN_3H and RN [45]. One example of such a reaction is shown in equation (34).

$$W(CO)_2(S_2CNEt_2)_2 + ArN_3 \rightarrow W(CO)(NR)(S_2CNEt_2)_2 + N_2 + CO \qquad (34)$$

An analogous complex of molybdenum, $Mo(CO)_2(S_2CNEt_2)_2$, was reported to react with arylazides under formation of a bis(arylimido) derivative, whereas $MoO(S_2CNEt_2)_2$ forms a monoimidoxo complex with the same reagent [46].

$$Mo(CO)_2(S_2CNEt_2)_2 + 2ArN_3 \rightarrow Mo(NAr)_2(S_2CNEt_2)_2 \qquad (35)$$

(Ar = ph)

$$MoO(S_2CNEt_2)_2 + ArN_3 \longrightarrow Mo(O)(NAr)(S_2CNEt_2)_2 \quad (36)$$

(Ar = Ph, p-$C_6H_4NO_2$)

The two NPh groups in monomeric cis-$Mo(NPh)_2(S_2CNEt_2)_2$ are one bent and the secon linear. The bent one has a strong trans-effect [4]. The dumido complex $Mo(NAr)_2$ - $(S_2CNEt_2)_2$ forms a monoimido derivative when treated with either HCl or CH_3Br as shown below [46].

$$Mo(NAr)_2(S_2CNEt_2)_2 + 2HCl \longrightarrow Mo(NAr)Cl_2(S_2CNEt_2)_2 + H_2NAr \quad (37)$$

$$Mo(NAr)_2(S_2CNEt_2)_2 + 2MeBr \longrightarrow Mo(NAr)Br_2(S_2CNEt_2)_2 + Me_2NAr \quad (38)$$

The reaction of the oxoimido complex $MoO(NAr)(S_2CNEt_2)_2$ with HCl leaves the imido group intact if the aryl group is phenyl. However, if the aryl group is p-$C_6H_4NO_2$, the imido group is replaced by chloro ligands [46].

$$MoO(NAr)(S_2CNEt_2)_2 + HCl \longrightarrow Mo(NAr)Cl_2(S_2CNEt_2) + H_2O \quad (39)$$

(Ar = Ph)

$$MoO(NAr)(S_2CNEt_2)_2 + HCl \longrightarrow MoOCl_2(S_2CNEt_2)_2 + H_2NAr \quad (40)$$

(Ar = p-$C_6H_4NO_2$)

Maatta et al. discussed the synthesis of $Mo(NPh)X_2(S_2CNEt_2)_2$ (X = Cl, Br) and the structure of a $CHCl_3$ adduct of this complex [48].

Oxohalo compounds of molybdenum react with Me_3SiN_3 in thf to form oxohaloimido complexes [49].

$$MoOCl_3 + Me_3SiN_3 + 2OPR_3 \xrightarrow{thf} MoCl_2(NH)(O)(OPR_3)_2 + \ldots \quad (41)$$

(R_3 = Ph_3, Ph_2Et, Et_2Ph)

Most probably the solvent is the source of the imido hydrogen in equation (41).

The phenylimidochloro complexes, $W(NPH)Cl_3(PPh_3)_2$ and $W(NPh)Cl_2(PMe_3)_3$ and related compounds were the subject of a recent publication by Bradley et al. [50].

Bridging imido complexes have been synthesized by Korswagen et al. [51].

$$CpM(CO)_3CH_3 + N_3C(=O)OEt \xrightarrow[CH_2Cl_2]{h\nu} [CpMO]_2[\mu\text{-}NCO_2Et]_2 + \ldots \quad (42)$$

(M = Mo, W)

$$[CpMO]_2[\mu\text{-}NCO_2Et](\mu\text{-}O) + \ldots$$

$$CpM(CO)_3Cl + \ldots$$

The preparation of nitrene complexes via acidazides and azidoacid esters was also explored by this group [52].

Chisholm et al, prepared a dimeric diimido complex of molybdenum from $Mo_2(OBu^+)_6$ and RN_3 [53].

../...

$$Mo_2(OBu^t)_6 + ArN_3 \longrightarrow [Mo(NAr)_2(OBu^t)_2]_2 + \ldots \quad (43)$$

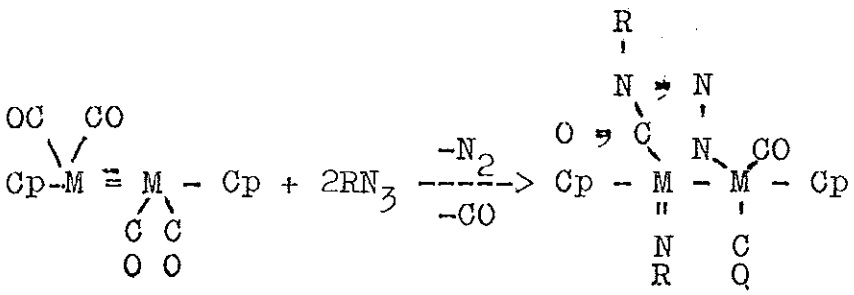
(Ar = Ph, $C_6H_4Me^p$)

Excess of the arylazide produces a dimeric complex that contains bridging and terminal imido groups [54].

$$Mo_2(OBu^t)_6 + \geq 4ArN_3 \longrightarrow [Mo(NAr)(\mu\text{-}NAr)(OBu^t)_2]_2 + 4N_2 + 2[Bu^tO\cdot] \quad (44)$$

(Ar = Ph, $C_6H_4Me^p$)

The alkylazides, RN_3 (R = Me, Et, $CH_3CN = CH_2$), react with the dinuclear molybdenum and tungsten compounds, $[(C_5H_5)M(CO)_2]_2$ (M = Mo, W), at temperatures between 200 and 300 K. In particular, azides add to the metal-metal multiple bond of the precursor with consecutive ring closure via nucleophilic attack of the coordinated azide upon one of the metal carbonyl ligands [55].



(45)

(R = Me, Et, allyl)

2.5 Formation of Nitrido Complexes

The literature on nitrido complexes of molybdenum and tungsten was reviewed by Zewdu Gebeyehu up to 1982 [21]. Here only some recent advances shall be added.

The reaction of WCl_6 and IN_3 in dichloromethane to give the HN_3 adduct $[WCl_3 . O.5HN_3]_4$ has already been mentioned in section 2.2.

Despite the fact that NaN_3 is safe and convenient to handle, it was only recently that Seyferth and Taube [3] used this azide as a source of nitrido-nitrogen.

$$MoCl_4(MeCN)_2 + NaN_3 \xrightarrow{MeCN} [MoNCl_3(MeCN)_x] + NaCl + N_2 \quad (46)$$

$$[MoNCl_3(MeCN)_x] + 2L \longrightarrow MoNCl_3L_2 + xMeCN \quad (47)$$

($L = OPPh_3$; L_2 = dipy, Bu_4NCl)

Other nitrodomolybdenum(VI) and tungsten(VI) complexes, the structure of which was elucidated, are $[Ph_4As]_2[MNCl_3(PO_2Cl_2)]$ [56] and $[PPh_4][MoNCl_4]$ [57].

The reaction of phenyl diazonium chloride with $MoNCl_3$ in $POCl_3$ was investigated by Mueller et al [58] and found to give $[PhN_2][MoNCl_4]$. The compound is unstable in dibutylether yielding the ether adduct $[MoNCl_3 . OBu_2]_4$.

$$PhN_2Cl + MoNCl_3 \xrightarrow{POCl_3} [PhN_2][MoNCl_4] \quad (48)$$

$$[PhN_2][MoNCl_4] + Bu_2O \longrightarrow 1/4\,[MoNCl_3.OBu_2]_4 + N_2 + PhCl \quad (49)$$

A diazo precursor was also employed by Feasey etal.[23] to prepare the oxonitrido complex $[(C_5H_5)_3Mo_3(N)(O)(CO)_4]$.

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$$Mo_2(CO)_4Cp_2 + N_2CHCOOEt \xrightarrow{\Delta} Cp_3Mo_3(N)(O)(CO)_4 \qquad (50)$$

Another synthetic route for the synthesis of this rather unusual cluster compound by thermal splitting of a nitrosyl ligand [16] has already been discussed in the introduction.

A new method for the preparation of the rather rare nitridomolybdenum(V) complexes was published by Schmitte et al [59]. This was prepared from a nitrodomolybdenum(VI) precursor, $[PPh_3Me]I$ which serves as a reducing agent.

$$2[MoNCl_3(MeCn)] + 3PPh_3MeI \xrightarrow{MeCn} [PPh_3Me]_2[MoNCl_4] + PPh_3MeI_3 + MoNCl_2 \cdot nMeCN \qquad (51)$$

Chatt and coworkers [37] continued their work on the reaction of dinitrogen tungsten complexes with Me_3SiN_3, yielding nitridoazidotungsten(IV) derivatives.

$$W(N_2)_2(dppe)_2 + 2Me_3SiN_3 \xrightarrow[\text{slow}]{h\nu} WN(N_3)(drpe)_2 + 2N_2 + 2[Me_3Si\cdot] \qquad (52)$$

The nitrido ligand is basic enough to add proton forming an imido group.

$$WN(N_3)(dppe)_2 + HX \dashrightarrow [W(NH)X(dppe)_2]X + \ldots \qquad (53)$$

(X = F, Cl, Br, I, BF_4)

With strong bases, e.g. LiMe in THF, the process may be reversed again [37].

$$[W(NH)Br(dppe)_2]Br + LiMe \xrightarrow{thf} W(N)Br(dppe)_2 + LiBr + CH_4 \quad (54)$$

The structure of the corresponding molybdenum compounds, $MoN(N_3)(dppe)_2$ and $[Mo(NH)Br(dppe)_2]Br.MeOH$, was investigated by Dilworth et al [36].

The involvement of nitridomolybdenum complexes in biological N_2-fixation and their significance for mimicing the reaction of nitrogenase was pointed out by Hussain et al. [60] and Dilworth et al [61].

Somewhat related to the conversion of azide into nitrido derivatives is the nucleophilic addition of azides to complexes with unsaturated ligands, e.g CO. Thus the reaction of $W(CO)_6$ with NaN_3 proceeds under slow attack of the carbonyl ligand by the azido anion followed by rapid decomposition under libration of N_2 and rearrangment to give an isocyanatopentacarbonyl-tungstate(0) [62].

$$W(CO)_6 + NaN_3 \xrightarrow{slow} [(CO)_5W\text{-}\underset{\underset{O}{\|}}{C}\text{-}N_3][Na] \xrightarrow{-N_2} [(CO)_5W(NCO)][Na] \quad (55)$$

3. RESULTS AND DISCUSSION

3.1 Synthesis of Trichloronitridobis(triphenylphosphineoxide)molybdenum(VI) from Tetrachlorobis(acetonitrile)molybdenum(IV) and Sodium Azide.

In order to become familiar with the inert gas technique, the synthesis of the nitridomolybdenum(VI) complex, $MoNCl_3(OPPH_3)_2$, from $MoCl_4(MeCN)_2$ and NaN_3 in acetonitrile followed by addition of $OPPh_3$ was reproduced according to a procedure described by Seyferth and Taube [3]. For the synthesis of the starting compound, $MoCl_5$ was reacted with an excess of acetonitrile yielding the brown crystalline $MoCl_4(MeCN)_2$ as a sparingly soluble precipitate with 55% yield.

$$2MoCl_5 + 5MeCN \xrightarrow{MeCN} 2MoCl_4(MeCN)_2 + HCl + ClCH_2CN \qquad (56)$$

brown crystals

yield: 55%

IR: V(CN)2285(s),2320(m)cm^{-1}

EA:	% Mo	% Cl	% N
Found:	29.97	43.60	8.21
Calc.:	30.00	44.34	8.76

For the reaction with NaN_3, acetonitrile proved to be the only solvent suitable because it appears to guarantee a

sufficiently high solubility for both, $MoCl_4(MeCN)_2$ and NaN_3. The latter reacts slowly under N_2 evolution yielding purple solution that is supposed to contain an intermediate acetonitrilenitrido complex, $[MoNCl_3(MeCN)_x]$, with x being most probably 2 (see equation (57)). Addition of two equivalents of triphenylphosphine oxide results in the precipitation of light brown crystals of $MoNCl_3(OPPh_3)_2$. The dry compound can be handled in air for a short time.

$$MoCl_4(MeCN)_2 + NaN_3 \xrightarrow{MeCN} [MoNCl_3(MeCN)_2] + N_2 + NaCl \qquad (57)$$

$$[MoNCl_3(MeCN)_2] + 2OPPh_3 \xrightarrow{MeCN} MoNCl_3(OPPh_3)_2 + 2MeCN \qquad (58)$$

light brown crystals

yield: 65%

IR: $\nu(Mo{\equiv}N)$ 1042(w) 1060(w) cm^{-1}

EA:	% Mo	% Cl	% N
Found :	12.72	13.13	1.86
Calc.:	12.41	13.76	1.81

By comparison of the IR-spectrum of $MoNCl_3(OPPh_3)_2$ with the spectrum of the reference compound $MoOCl_3(OPPh_3)_2$, the two weak absorptions at 1042 and 1060 cm^{-1} could be unambigously assigned to the Mo≡N grouping, most probably resulting from the existance of two isomeric forms of the complex. A third band at 1025 cm^{-1} mentioned by Seyferth and Taube obviously belongs to coordinated $OPPh_3$ because it also appears in the spectrum of $MoOCl_3(OPPh_3)_2$ (refer to appendix, Fig. 6 and Fig. 7).

The latter was prepared by a literature method from $MoCl_5$, ethanol, and $OPPh_3$ with 50% yield [62]. $MoOCl_3(OPPh_3)_2$ is a light green substance that is stable to air and moisture. It was characterized by its typical V(Mo = O) frequency at 978 cm^{-1} and elemental analysis (Found (calc.): Mo, 11.98 (12.38); Cl, 14.02 (13.73)%).

3.2 Reaction of Molybdenum Pentachloride with Sodium Azide in Acetonitrile

The reaction of $MoCl_5$ with NaN_3 was found to be vigorous and accompanied by gas evolution yielding a dark violet solution. Subsequent addition of two equivalents of $OPPh_3$ in the same solvent resulted in precipitation of a light brown product in high yield. The compound can be handled in air and was recrystallized from CH_2Cl_2/hexane. Its IR-spectrum does not show any absorption between 1000 and 1100 cm^{-1} which could be assigned to a V(Mo≡N) vibration. In addition to the absorption of the coordinated $OPPh_3$ ligand, there is, however, a new and strong band at 978 cm^{-1} in the region of V(Mo = O) vibrations of oxomolybdenum(V) complexes (refer to appendix, fig 8). Infact, the IR-spectrum of the light brown product is almost identical with that of the reference compound, $MoOCl_3(OPPh_3)_2$ (see section 3.1).

The formation of $MoOCl_3(OPPh_3)_2$ from $MoCl_5$, NaN_3

and $OPPh_3$ in acetonitrile is not a straightforward reaction. The vigorous N_2 evolution on treating $MoCl_5$ with NaN_3 suggests the reduction to $MoCl_4(MeCN)_2$ with the azide acting as a reducing agent. On addition of the phosphine oxide, the intermediate molybdenum(IV) chloride is most probably reoxidized to give $MoOCl_3(OPPh_3)_2$. Similar reactions between molybdenum(IV) halides and oxygen containing ligands under generation of $MoOCl_3$ derivatives have already been described [63]. A possible way for the reaction encountered here is given in equations (59) and (60).

$$MoCl_5 + NaN_3 + 2MeCN \xrightarrow{MeCN} [MoCl_4(MeCN)_2] + 3/2\ N_2 + NaCl \qquad (59)$$

$$[MoCl_4(MeCN)_2] + 3OPPh_3 \xrightarrow{MeCN} MoOCl_3(OPPh_3)_2 + PPh_3 + 2MeCN + 1/2\ Cl_2 \qquad (60)$$

light brown

Yield: 80%

IR: ν(Mo = O) 978(S) cm^{-1}

EA:	% Mo	% Cl
Found:	9.54	19.57
Calc.:	12.38	13.73

Even though the IR-spectrum coincides with that of the reference compound (see appendix, fig. 7 and 8), the product is largely impure. Differences in colour (light brown instead of light green) and the high chlorine content

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suggest other molybdenum chlorides and NaCl as the most likely impurities not being separable by repeated recrystallization from dichloromethane/hexane.

So as to avoid reoxidation of the suggested $[MoCl_4(MeCN)_2]$ intermediate, the reaction was repeated with the oxygen-free ligands tetrabutylammonium chloride and pyridine. On adding Bu_4NCl to the violet solution obtained from $MoCl_5$ and NaN_3 in acetonitrile, the colour changed immediately to brown. Precipitation with diethylether or attempts to crystallize the product from dichloromethane/hexane failed, always yielding a brown oil.

A crystalline product could, however, be obtained with pyridine as a ligand. After addition of two equivalents of pyridine to the solution of the violet intermediate, a light brown crystalline substance precipitated in low yield. The latter is sparingly soluble in acetonitrile and dichloromethane and can be handled in air for a short time. Attempts to recrystallize the compound failed because of its low solubility. Colour, solubility and IR-spectrum of the product are largely identical with those of the reference compound, $MoCl_4(Py)_2$ (see appendix, fig. 9 and 10), which was synthesized directly from $MoCl_4(MeCN)_2$ and pyridine in dichloromethane [63]. Even though the formation of such a complex should also be anticipated from the intermediate, $[MoCl_4(MeCN)_2]$, formed from $MoCl_5$ and

NaN_3 (see equation 61) the

$$MoCl_4(MeCN)_2 + 2Py \xrightarrow{MeCN} "MoCl_4(Py)_2" + 2MeCN \qquad (61)$$

light brown

: Yield: 37%

:EA:	% Mo	% Cl
Found:	10.00	41.39
Calc.:	24.23	35.81

product obtained in this reaction is not pure but considerably contaminated by other chloride containing impurities as indicated by the too high chlorine and the too low molybdenum content. The presence of oxomolybdenum species can also not be excluded because there are two medium broad absorptions at 950 and 910 cm^{-1} i.e. in the range of V(Mo = O) stretching vibrations. The only source of oxygen here can be the inert gas nitrogen, which evidently still contains traces of O_2 capable of reacting with the tetrachloromolybdenum(IV) intermediate in equation (61).

Summing up one can conclude that NaN_3 in its reaction with $MoCl_5$ acts as a reducing agent rather than forming nitridomolybdenum complexes. A tetrachloromolybdenum(IV) intermediate could be trapped with pyridine as grossly impure $MoCl_4(Py)_2$. The oxygen-containing ligand $OPPh_3$ leads to reoxidation of the intermediate and formation of

$MoOCl_3(OPPh_3)_2$. Traces of O_2 in the inert gas may also contribute to the formation of oxomolybdenum compounds. All the products are virtually impure and only identified by their IR-specta.

3.3 Reaction of Molybdenum Oxotetrachloride with Acetonitrile and Sodium Azide

The starting compound $MoOCl_4$ was prepared from MoO_3 and $SOCl_2$ as outlined by Colton et al. [64].

$$MoO_3 + 2SOCl_2 \longrightarrow MoOCl_4 + 2SO_2 \qquad (62)$$

dark green crystals

Yield: 62%

$MoOCl_4$, a dark green crystalline substance, is extremely sensitive to hydrolysis and was used without further purification.

$MoOCl_4$ dissolves in acetonitrile at -40°C to give a dark brown solution. On stirring at room temperature this solution turns green within 2 hours. The green colour indicates the formation of a $MoOCl_3$ derivative, most probably $MoOCl_3(MeCN)_2$. Similar reactions and the reduction of $MoOCl_4$ in other organic solvents have already been described in the literature [65]. The $[MoOCl_3(MeCN)_2]$ intermediate (see equation (63)) could not be isolated but was trapped as $MoOCl_3(OPPh_3)_2$.

$$MoOCl_4 + 2MeCN \xrightarrow[2h]{MeCN} [MoOCl_3(MeCN)_2] + 1/2\ Cl_2 \qquad (63)$$

green solution

$$[MoOCl_3(MeCN)_2] + 2OPPh_3 \xrightarrow{MeCN} MoOCl_3(OPPh_3)_2 + 2MeCN \qquad (64)$$

light green crystals

Yield: 40%

IR: V(Mo = O) 978(s) Cm^{-1}

EA:	% Mo	% Cl
Found:	11.82	13.96
Calc.:	12.38	13.73

Elemental analysis and IR-spectrum are in good agreement with the above formula (see appendix, fig. 11).

The same product was obtained when $MoOCl_4$ was reacted with one equivalent of NaN_3 in acetonitrile. This reaction is, however, very fast and completed within a few minutes. Vigorous gas evolution indicated the oxidation of the azide to nitrogen according to equation (65).

$$MoOCl_4 + NaN_3 + 2MeCN \xrightarrow{MeCN} [MoOCl_3(MeCN)_2] + 3/2\ N_2 + NaCl \qquad (65)$$

green solution

The green intermediate $MoOCl_3(MeCN)_2$ was found to react rapidly with another equivalent of NaN_3 yielding a deep violet solution. Nitrido complex formation can be excluded because there is no N_2 evolution. The violet intermidiate thus formed is stable in acetonitrile at room temperature and is most

The IR-spectrum of the complex does not show any absorption due to an azido group but contains all the bands of coordinated acetonitrile as well as a peak at 960 cm^{-1} characteristic of the V(Mo = O) stretching vibration of dichlorooxomolybdenum(IV) complexes which is expected in the range of 940 and 960 cm^{-1} [66]. Only little is known about this class of oxohalides. A few complexes of the formula $MoOCl_2L_3$ with L being $MePPh_2$, $EtPPh_2$ and Et_2PPh [66] and As Me_2Ph [67] have been described. To the best of our knowledge, the above acetonitrile complex, $MoOCl_2(MeCN)_3$, has not yet been mentioned in the literature.

Attempts to precipitate the violet intermediate from acetonitrile by diethylether were also not successful. The colour of the solution turned instantaneously brown and a slow gas evolution occured. On cooling to $-40^{\circ}C$, yellow crystals precipitated which are extremely sensitive to moisture. The IR-spectrum (see appendix fig. 12 and 13). is quite similar to the one recorded for $MoOCl_2(MeCN)_3$ but exhibits an additional strong absorption at 990 cm^{-1} and another couple of V(CN) peaks at 2260 and 2280 cm^{-1}. The latter absorptions suggest the presence of an oxomolybdenum(V) complex, most probably $MoOCl_3(MeCN)_2$. From the intensity ratio of the two V(Mo = O) absorptions, the latter should be the main product with a part of it obviously already decomposed to $MoOCl_2(MeCN)_3$. The extent of reduction is apparently subtly dependent upon the solvent.

Whereas diethylether causes only partial or slow reduction, dichloromethane as a poor donor solvent is obviously not capable of stabilizing the oxochloromolybdenum(V) intermediate in the presence of NaN_3 and incidentally, rapid reduction takes place. This conclusion was nicely confirmed by reacting the violet intermediate with $OPPh_3$, which is known to be a strong donor ligand.

The deep violet solution obtained from $MoOCl_3(MeCN)_2$ and NaN_3 in acetonitrile reacted with $OPPh_3$ to give a brown mixture from which a light brown crystalline product could be isolated after removal of the solvent, dissolution in dichloromethane, and precipitation with hexane. Gas evolution was not observed.

$$Na[MoOCl_3(N_3)(MeCN)] + 2OPPh_3 \xrightarrow{MeCN} MoOCl_3(OPPh_3)_2 + NaN_3 + MeCN \quad (68)$$

light brown crystals

Yield: 40%

IR: ν(Mo = O) 978(s) cm^{-1}

EA:	% Mo	% Cl
Found:	11.95	13.52
Calc.:	12.38	13.73

Elemental analysis and IR-spectrum (see appendix. fig. 14) of the compound confirm the formula $MoOCl_3(OPPh_3)_2$. The light brown colour suggests the presence of minor impurities. The strong donor ligand $OPPh_3$, does in fact stabilize the oxomo-

lybdenum(V) complex inhibiting any reductive decay. Absorptions at 2070(s) and 2010-2060(sh) cm^{-1} suggest the presence of small amount of an azidooxo complex formed from $MoOCl_3(OPPh_3)_2$ and NaN_3.

3.4 Reaction of Trichlorooxobis(triphenylphosphine oxide)-molybdenum(V) with Sodium Azide in Acetonitrile; Formation of Dichlorooxoazidobis(triphenylphosphine oxide) molybdenum(V)

The oxomolybdenum(V) complex $MoOCl_3(OPPh_3)_2$ was found to be not inert to NaN_3 in acetonitrile but to undergo a slow chlorideazide exchange according to equation (69).

$$MoOCl_3(OPPh_3)_2 + NaN_3 \longrightarrow MoOCl_2(N_3)(OPPh_3)_2 + NaCl \quad (69)$$

dark brown

Yield: 60%

IR: $\nu(N_3)$ 2075(s), 2125(w) cm^{-1}

$\nu(Mo=O)$ 940 cm^{-1}

EA:	% Mo	% Cl
Found:	12.32	9.17
Calc.:	12.28	9.07

The reaction is very slow and goes to complection within 24 hours. Gas evolution could not be observed. $MoOCl_3(OPPh_3)_2$, which is only sparingly soluble in acetonitrile, turns slowly from light green to brown. The dark brown crystalline solid obtained after filtration and

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recrystallization from dichloromethane/hexane can be handled in air for a short time and has similar solubility properties as $MoOCl_3(OPPh_3)_2$. Its composition, $MoOCl_2(N_3)(OPPh_3)_2$, is supported by elemental analysis and IR-spectrum (see appendix fig. 15). In addition to the absorptions of co-ordinated $OPPh_3$, the characteristic $V(N_3)$ frequency of the azido ligand is found at 2075(s) with a shoulder ar 2010 - 2030 cm^{-1}. The position of the V(Mo=O) absorption at 940 cm^{-1} is lower than usually found for Mo(V) oxotrichalide complexes and may be result of the substitution of chloride by the stronger donor azide. The oxoazidomolybdenum complex is stable at room temperature and not explosive. In contrast to simple molybdenum chlorides, the decomposition of azido into nitrido complexes is apparently not favoured in the presence of a strongly π-donating oxoligand and with acetonitrile as a solvent. Neverthless, this result cannot be generalized for other solvents and types of azides. Thus, Chatt et al. [49] reported $MoOCl_3$ to react with Me_3SiN_3 in tetrahydrofuran under formation of oxo-imido complexes of the formula, $MoO(NH)Cl_2L_2$ (L = $OPPh_3$, $OPPhEt_2$ and $OPPh_2Et$). The imido ligand is supposed to be a result of the decomposition of an intermediate azido complex followed by abstraction of proton from the solvent.

4. EXPERIMENTAL PART

4.1 Inert Gas and Solvent Purification

Most of the compounds synthesized were sensitive to hydrolysis and, in some cases, also to air. In order to exclude oxygen and moisture, all operations were performed under nitrogen, inert gas. The nitrogen available in town containes 0.5% oxygen. For purification, nitrogen was first bubbled through two columns (length 100 cm, diameter 5 cm) containing an alkaline pyrogallol solution (63 g pyrogallol/l 5N aqueous NaOH). The inert gas was then further purified by passing it through a $CaCl_2$ column. Traces of oxygen and water were trapped by successively passing the gas through columns packed with a commercial copper catalyst, NaOH, P_2O_5, and molecular sieve (type 4A). The nitrogen thus purified was sufficiently dry and contained less than 0.05% oxygen.

All solvents used were dried and deareated. Acetonitrile and dichloromethane were repeatedly refluxed over P_2O_5 and distilled off under nitrogen before use. Diethylether was repeatedly

refluxed over $LiAlH_4$ and distilled under nitrogen, followed by refluxing over freshly cut Na metal and benzophenon until the solution turned violet. Hexane and pyridine were dried by refluxing over $LiAlH_4$ in an atmosphere of nitrogen. Ethanol was reacted with excess sodium and then distilled under nitrogen.

Molybdenum pentachloride, sodium azide, tetrabutylammonium chloride and N,N'-dipryidyl were commercially available and used without further purification.

Triphenylphosphine oxide, was prepared by oxidizing triphenylphosphine, with $K_2S_2O_8$ and conc. H_2SO_4 according to a procedure by Kennedy et al. [68].

4.2 Preparations and Reactions

4.2.1 Tetrachlorobis(acetonitrile)molbdenum(IV); $MoCl_4(MeCN)_2$

Tetrachlorobis(acetonitrile)molybdenum(IV) was prepared following established procedure [69]. Molybdenum pentachloride (4.15 g, 15.19 mmol) was added to acetonitrile (70 ml) in a shlenk tube under nitrogen. The reaction mixture was stirred over night yielding a light brown solution and a brown crystalline precipitate. The latter was filtered off, washed with three 5 ml portions of

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shaking vigorously, a light brown precipitate began to settle. The mixture was cooled to -30°C, the solid filtered off, followed by washing with three 5 ml portions of a hexane/ether mixture (4:1 ratio) as well as 5 ml of pure hexane, and dried at 50°C in vacuum. The light brown complex is stable in dry air, however, turns bule in contact with moisture. It is very soluble in dichloromethane, soluble in acetonitrile, diethylether, and tetrahydrofuran, but insoluble in hexane. The compound can be recrystallized by dissolution in dichloromethane and precipitating with hxane.

Yield: 2.21 g (65% based on $MoCl_4(MeCN)_2$)

EA: Found (Calc. for $MoNCl_3(OPPh_3)_2$) Mo, 12.72 (12.41); Cl, 13.13 (13.76); N, 1.86 (1.81)%

IR: See appendix, fig. 6.

4.2.3 Reaction of Molybdenum Pentachloride with Sodium Azide in Acetonitrile

To molybdenum pentachloride (1.6 g, 5.86 mmol) dissolved in acetonitrile (30 ml) and cooled to -40°C, sodium azide (0.39 g, 5.99 mmol) was added slowly with stirring in an atmosphere of nitrogen. The reaction proceeds with vigorous gas evolution. Unreacted NaN_3 and NaCl formed were filtered off. The resulting solution has a

violet colour which turns blue-green in contact with air. The mixture was saved for further experiments.

4.2.4 Reaction of Molybdenum Pentachloride with Sodium Azide and Triphenylphosphine Oxide in Acetonitrile

The violet solution prepared in the same manner as above (Cf. 4.2.3) by reacting molybdenum pentachloride (2.4 g, 8.78 mmol) and sodium azide (0.59 g, 9.07 mmol) in acetonitrile, was treated with $OPPh_3$ (5 g, 17.97 mmol) dissolved in acetonitrile (40 ml). The resulting mixture was concentrated to one third of its original volume and then cooled to $-30^{\circ}C$. The light brown crystalline precipitate was filtered off, washed twice with 7 ml hexane, and dried at $50^{\circ}C$ in vacuum. The product is stable in dry air, but turns blue in contact with moisture. It is soluble in dichloromethane and pyridine, sparingly soluble in acetonitrile and diethylether, but insoluble in hexane. It is recrystallizable from a solution in dichloromethane using hexane as a precipitating agent.

Yield: 3.75 g (55.07%, based on $MoCl_5$ and calc. for $MoOCl_3(OPPh_3)_2$)

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EA: Found (calc. for $MoOCl_3(OPPh_3)_2$); Mo, 9.54 (12.38); Cl, 19.57 (13.77)%

IR: See appendix, fig. 8

4.2.5 Reaction of Molybdenum Pentachloride with Sodium Azide and Tetrabutylammonium Chloride in Acetonitrile

Molybdenum pentachloride (2.4 g, 8.78 mmol) and sodium azide (0.59 g, 9.07 mmol) were reacted in the same manner as described in experiment 4.2.4. Excess NaN_3 and NaCl formed during the reaction were filtered off. Addition of Bu_4NCl (2.70 g, 9.73 mmol) in acetonitrile to the violet solution changed its colour to brown without any gas evolution. Treatment of the brown solution with diethylether or hexane resulted in the formation of a dark brown oil. Complete removal of the solvent in vacuum, dissolution of the dark brown tar in dichloromethane and precipitation with hexane failed to give a crystalline product.

4.2.6 Reaction of Molybdenum Pentachloride with Sodium Azide and Pyridine in Acetonitrile

To the violet solution prepared in the same

manner as in experiment 4.2.4 (2.4 g $MoCl_5$ and 0.59 g NaN_3), a solution of pyridine (1.50 g, 18.96 mmol) in acetonitrile (20 ml) was added. No gas evolution was detected. The light brown crystalline precipitate was filtered off, washed twice with 5 ml of hexane, and dried at 50°C in vacuum. The product is stable to air and moisture. It is soluble in pyridine, sparingly soluble in acetonitrile, ethanol, and dichloromethane, but insoluble in hexane. Due to its low solubility in dichloromethane and acetonitrile, the compound could not be recrystallized.

Yield: 1.3 g (37%, based on $MoCl_5$ and calc. for $MoCl_4(Py)_2$),

EA: Found (calc. for $MoCl_4(Py)_2$) Mo; 10.00 (24.23); Cl, 41.39 (35.81)%

IR: See appendix, fig. 9.

4.2.7 Molybdenum Oxotetrachloride; $MoOCl_4$

$MoOCl_4$ was prepared from MoO_3 and $SOCl_2$ according to a procedure outlined by Colton et al. [64]. MoO_3 (17 g, 118.05 mmol) was refluxed in an excess of predistilled $SOCl_2$ for five hours. The dark green crystals formed were separated by distilling off the thionyl chloride at reduced pressure. The oxo-

halide is extremely sensitive to hydrolysis and was used without further purification.

Yield: 18.5 g (61.74%, based on MoO_3).

4.2.8 Reaction of Molybdenum Oxotetrachloride with Acetonitrile and Triphenylphosphine Oxide

A dark brown solution was formed by addition of $MoOCl_4$ (1.4 g, 5.52 mmol) to acetonitrile (30 ml) at -30°C. The reaction was accompanied by gas evolution. The colour of the solution turned green during two hours of stirring at room temperature. The green intermediate could not be isolated in crystalline form by precipitation with ether or from dichloromethane/hexane. Addition of $OPPh_3$ (3.1 g; 11.14 mmol) in acetonitrile to the green solution resulted in the formation of a light green crystalline precipitate. The latter was filtered off, washed three times with 7 ml hexane, and dried at 50°C in vacuum. The product is stable in air and moisture. It is soluble in dichloromethane, moderately soluble in acetonitrile, and insoluble in hexane and diethylether. The product was recrystallized from a solution in dichloromethane by precipitating with hexane.

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Yield: 1.7 g (39.80%, based on $MoOCl_4$, calc. for $MoOCl_3(OPPh_3)_2$)

EA: Found (calc. for $MoOCl_3(OPPh_3)_2$) Mo, 11.82 (12.38); Cl, 13.96 (13.73)%

IR: See appendix, fig 11.

4.2.9 Reaction of Molybdenum Oxotetrachloride with Sodium Azide

NaN_3 (0.38 g, 5.84 mmol) was added to $MoOCl_4$ (1.4 g, 5.52 mmol) dissolved in acetonitrile (30 ml) at -30°C. The reaction was accompanied by gas evolution and completed within few minutes. At the same time the colour of the solution turned from darkbrown to green. The green intermediate could not be isolated (Cf. experiment 4.2.8).

4.2.10 Dichlorooxotris(acetonitrile)molybdenum(IV); $MoOCl_2(MeCN)_3$

$MoOCl_4$ (1.4 g, 5.52 mmol) was reacted with acetonitrile (30 ml) at room temperature to give a green solution (Cf. experiment 4.2.8). Upon addition of NaN_3 (0.38 g, 5.84 mmol) the colour turned immediately dark violet. Gas evolution was not observed. The violet solution

is very sensitive to hydrolysis. Complete removal of the acetonitrile solvent gave a brown oil. Dissolution of this oil in dichloromethane yielded a brown solution with slow gas evolution. A dark brown compound could be isolated by precipitation with hexane. The latter was isolated by suction filtration, washed twice with 5 ml hexance, and dried under vacuum. The product is very sensitive to hydrolysis, soluble in acetonitrile and dichloromethane, but insoluble in hexane. Rcrystallization was brought about by dissolution in dichloromethane and precipitation with hexane.

Yield: 0.51 g (30%, based on $MoOCl_4$, calc. for $MoOCl_2(MeCN)_3$)

EA: Found (calc. for $MoOCl_2(MeCN)_3$); Mo, 29.30 (31.36). Cl, 22.71 (23.17). N, 13.54 (13.73)%

IR: See appendix fig. 12.

On treating the violet solution prepared above with diethylether, the colour changed to brown with concomitant slow gas evolution. After cooling the solution to -40°C, yellow crystals precipitated. They were separated by suction filtration, washed twice with 5 ml diethylether and hexane, and dried under vacuum. The product is extremely sensitive to moisture, exhibits similar solubility properties as $MoOCl_2(meCN)_3$, but is not a pure compound as revealed from its

IR-spectrum (Cf. section 3.3).

Yield: 0.4 g (24.9% based on $MoOCl_4$, calc. for $MoOCl_3(MeCN)_2$)

IR: See appendix, fig. 13

4.2.11 Tricholooxobis(triphenylphosphine Oxide)molybdenum(V); $MoOCl_3(OPPh_3)_2$

The deep violet solution obtained by dissolving $MoOCl_4$ (1.4 g, 5.52 mmol) in acetonitrile (30 ml) followed by addition of NaN_3 (0.38 g, 5.84 mmol) (Cf. experiment 4.2.10) was treated with $OPPh_3$ (3.1 g, 11.14 mmol) in acetonitrile (40 ml). Filtration of the resulting green mixture gave a light brown crystalline substance that was washed with three portions of 7 ml hexane and dried at 50°C under vacuum. The product is stable to air and hydrolysis. It has the same solubility as the compound isolated in experiment 4.2.8, and was recrystallized from dichloromethane/hexane.

Yield: 1.75 (40%, based on $MoOCl_4$, calc. for $MoOCl_3(OPPh_3)_2$.

EA: Found (calc. for $MoOCl_3(OPPh_3)_2$); Mo, 11.95 (12.38); Cl, 13.52 (13.73)%

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2N NaOH. After 30 minutes, dissolution was completed and the solution ready for the molybdenum and chloride determination.

4.3.2 Molybdenum Determination

The molybdenum content was determined gravimetrically by means of the oxinate method [71]. For this purpose, the alkaline molybdate solution was neutralized with respect to methyl orange and acidified with two drops of 2N sulphuric acid. After addition of 5 ml 1N aqueous ammonium acetate, the solution was heated to boiling, removed from the hot plate, and treated with 20 ml 3% oxine acetate solution. The yellow precipitate of molybdenyl oxinate coagulated after 2-3 minutes. The presence of excess reagent is ensured by a distinctly yellow colour of the solution. Then, the mixture was filtered hot, the precipitate washed with hot water until the filtrate remained colourless, and dried at 130-140°C.

4.3.3 Chloride Determination

After neutralizing and acidifying the sample with 2 drops of 2N HNO_3, chloride was determined

by potentiometric titration with a 0.05 N $AgNO_3$ solution [72]. The working electrode was a chloride sensitive electrode and as a reference, a calomel electrode was used.

4.3.4 Kjeldahl Determination of Nitrogen

The Kjeldahl method was successfully employed for the determination of nitrogen in nitrile and nitrido complexes [73]. In particular, ca. 120 mg of the sample ($MoOCl_2(MeCN)_3$) was dissolved in 15 ml of phenol sulphuric acid in a 500 ml Kjeldhal flask followed by addition of 1 g $Na_2S_2O_3$. Then, 10 ml concentrated sulphuric acid and a drop of mercury was added. the mixture was slowly heated to boiling in a hood. After 2 hours the mixture was almost colourless. Then the flask was connected to the Kjeldahl distillation set, diluted with 100 ml. distilled water followed by 150 ml 6N aqueous NaOH. After distilling for 30 minutes, all the ammonia was transferred into the receiver and trapped by 30 ml of 0.1N H_2SO_4. The nitrogen content was finally determined by back-titration with 0.1 N aqueous NaOH against methyl orange.

The estimation of azide nitrogen was not possible by this method.

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4.3.5 IR-Spectra

IR-spectra of the compounds prepared were recorded using an IR-spectrophotometer Pye Unicam SP 2000. The samples were prepared as KI discs. For those compounds tending to hydrolyse, the mull technique was employed. In such cases the sample was ground with nujol and squeezed between NaCl discs. The spectra are collected in appendix, fig. 1 to fig. 15.

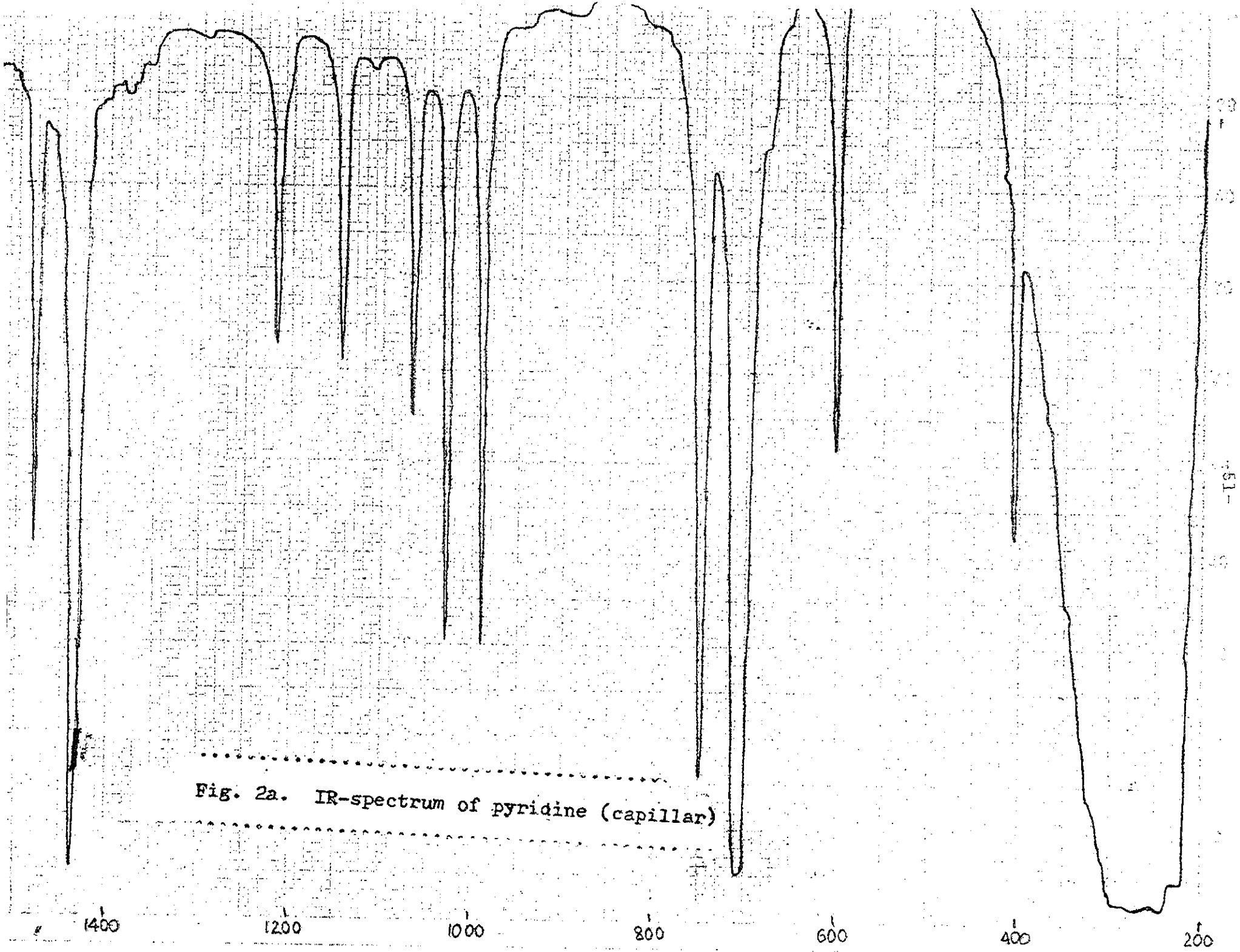


Fig. 2a. IR-spectrum of pyridine (capillar)

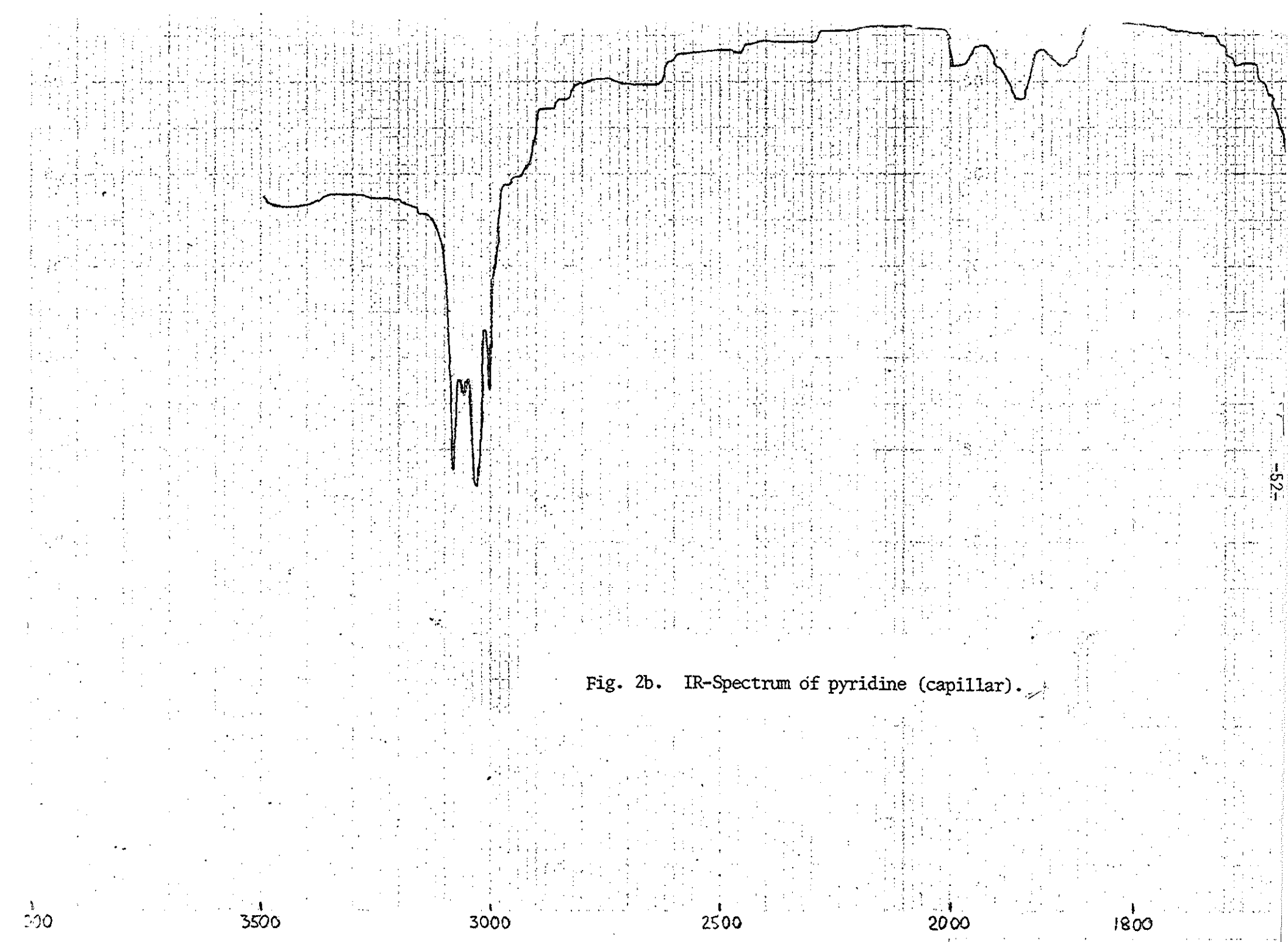


Fig. 2b. IR-Spectrum of pyridine (capillar).

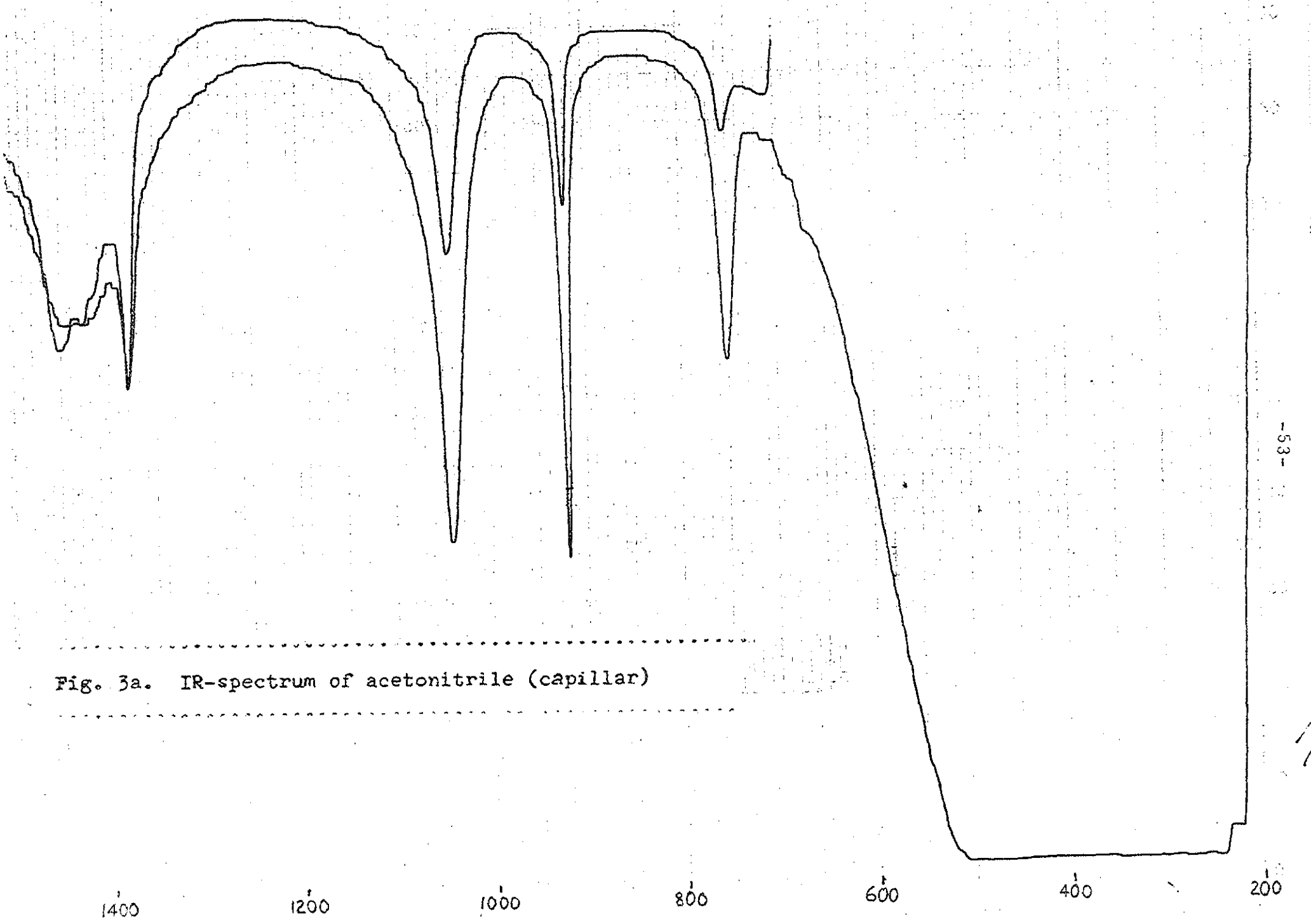


Fig. 3a. IR-spectrum of acetonitrile (capillar)

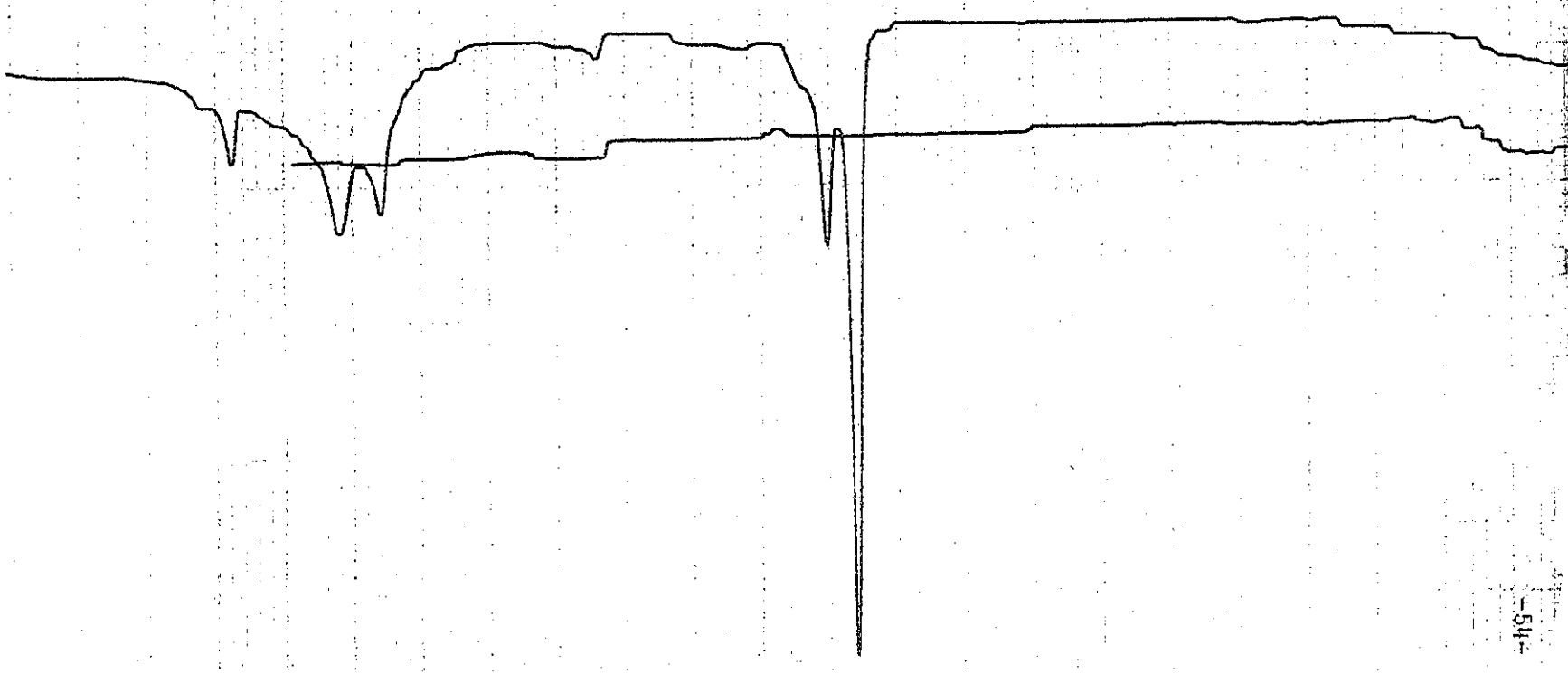


Fig. 3b. IR-spectrum of acetonitrile (capillar)

3500 3000 2500 2000 1800

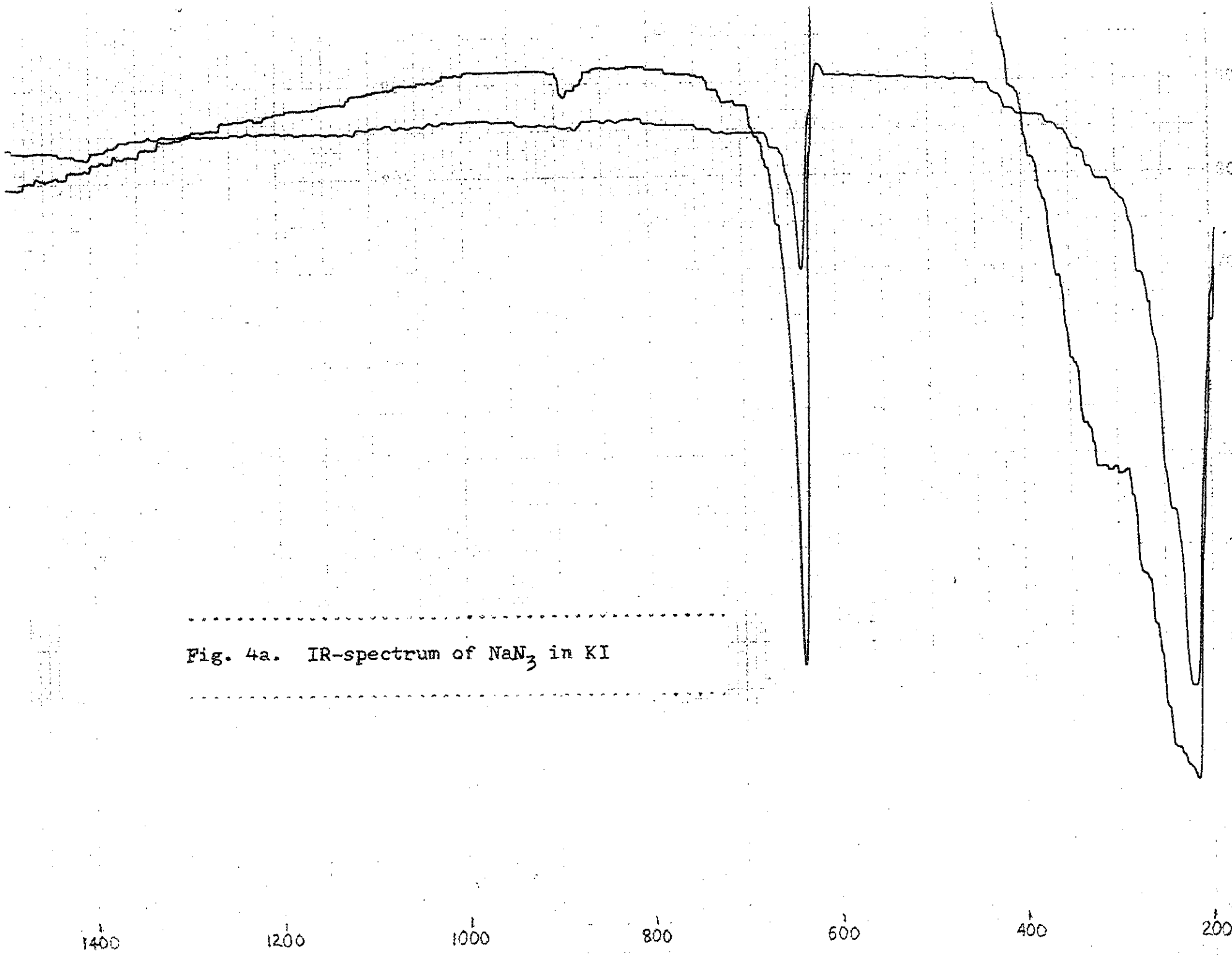


Fig. 4a. IR-spectrum of NaN_3 in KI

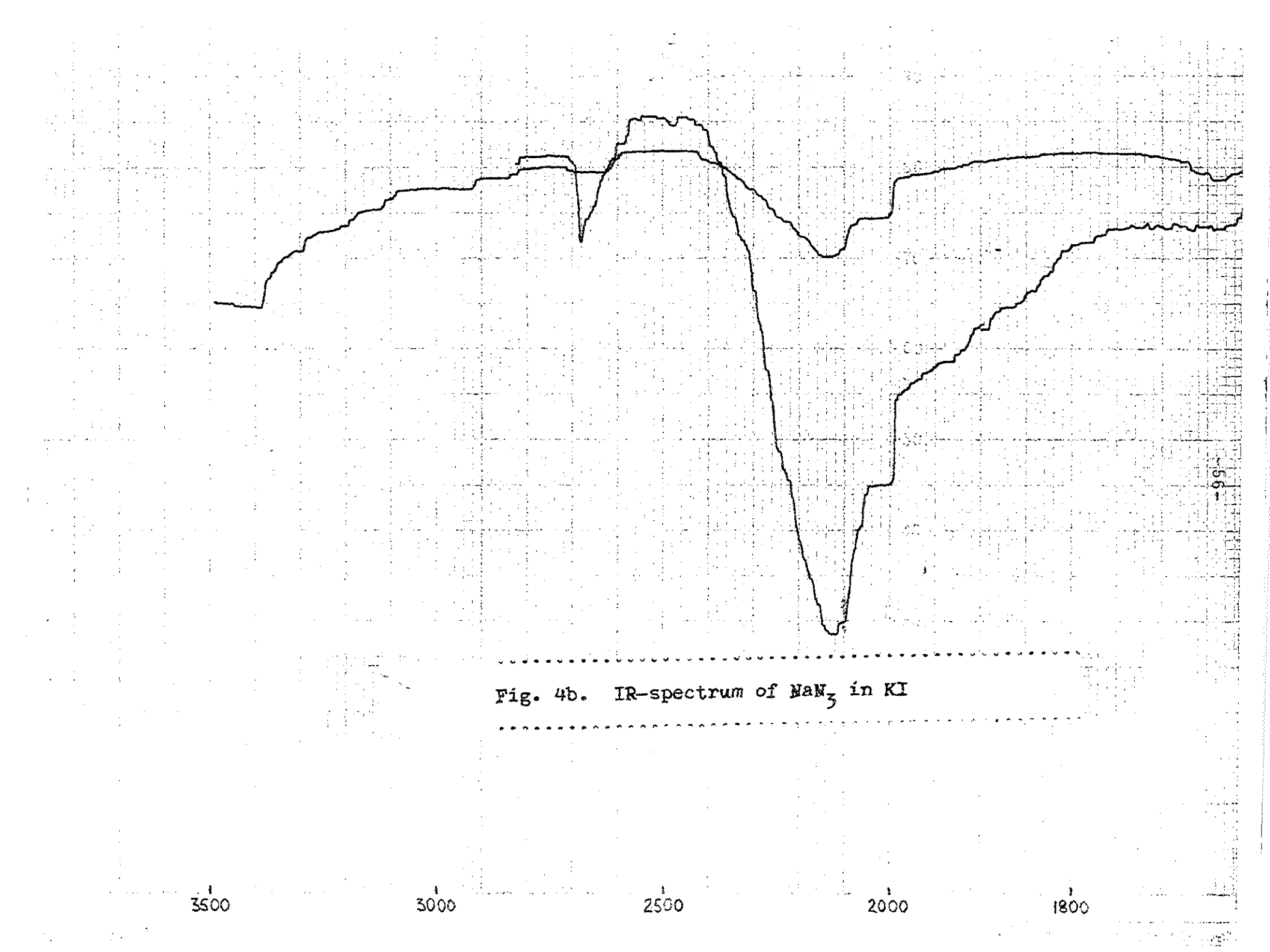


Fig. 4b. IR-spectrum of NaN_3 in KI

Fig. 5a. IR-spectrum of $MoCl_4(MeCN)_2$ (prepared from $MoCl_5$/MeCN) in KI (See sec. 3.1 and 4.2.1.)

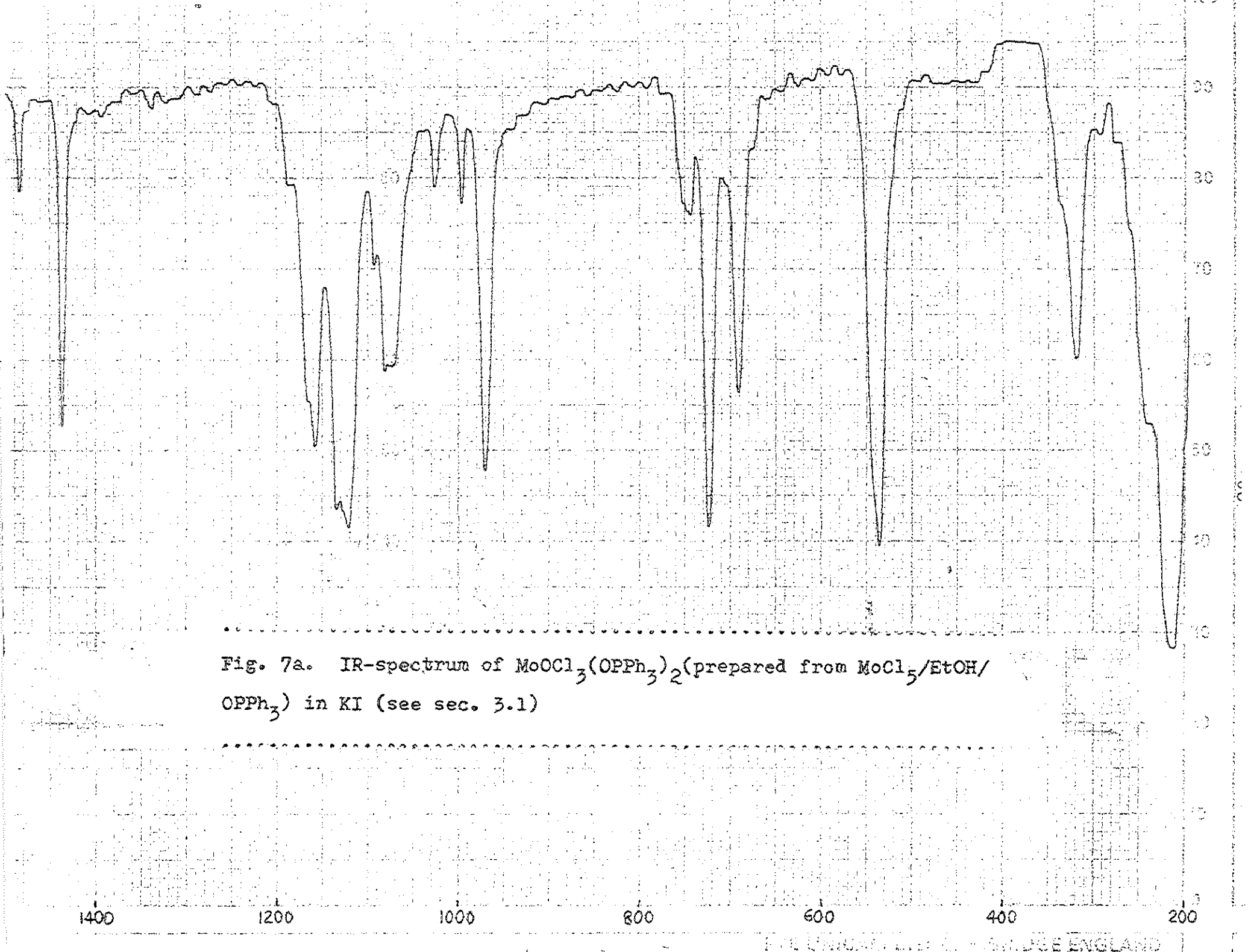


Fig. 7a. IR-spectrum of $MoOCl_3(OPPh_3)_2$(prepared from $MoCl_5$/EtOH/$OPPh_3$) in KI (see sec. 3.1)

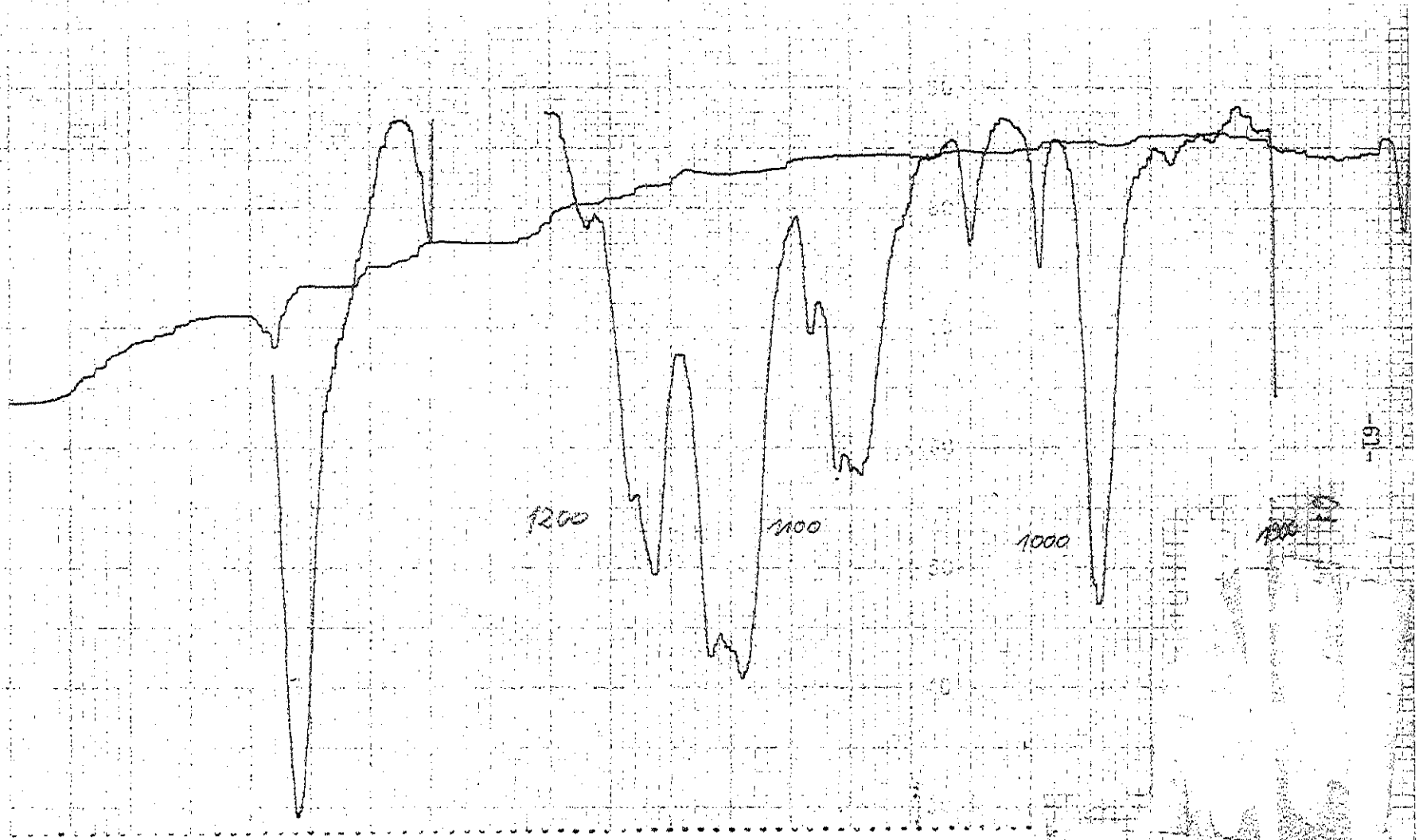


Fig. 7b. IR-spectrum of $MoOCl_3(OPPh_3)_2$ (prepared from $MoCl_5$/EtOH/$OPPh_3$) in KI. (see sec. 3.1)

The green curve is a stretched portion of the spectrum between the indicated wave number

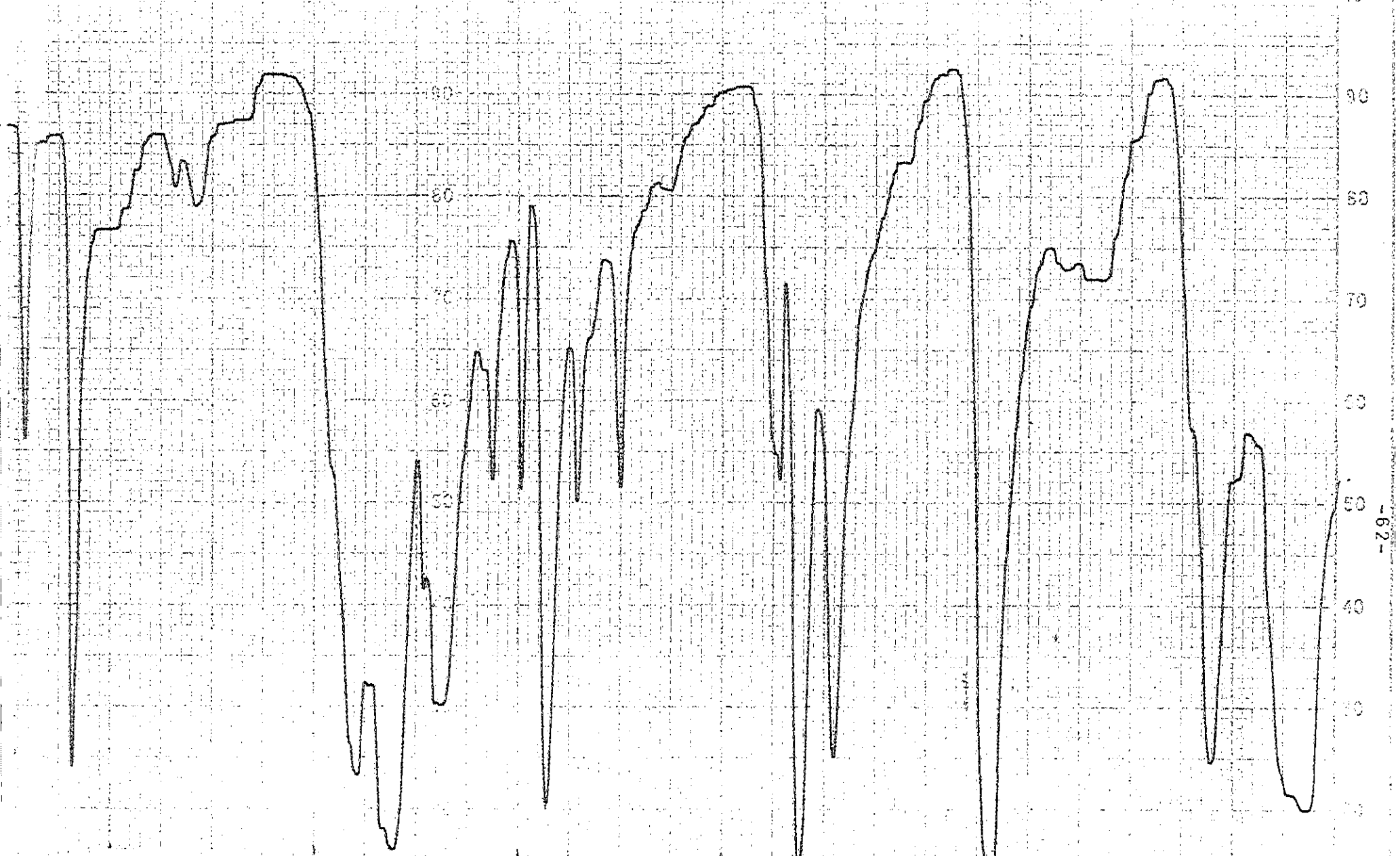


Fig. 8a. IR-spectrum of the product of the reaction of $MoCl_5$ with NaN_3 in acetonitrile followed by addition of $OPPh_3$, in KI; main constituent: $MoOCl_3(OPPh_3)_2$ (see sec. 3.2 and 4.2.4.9)

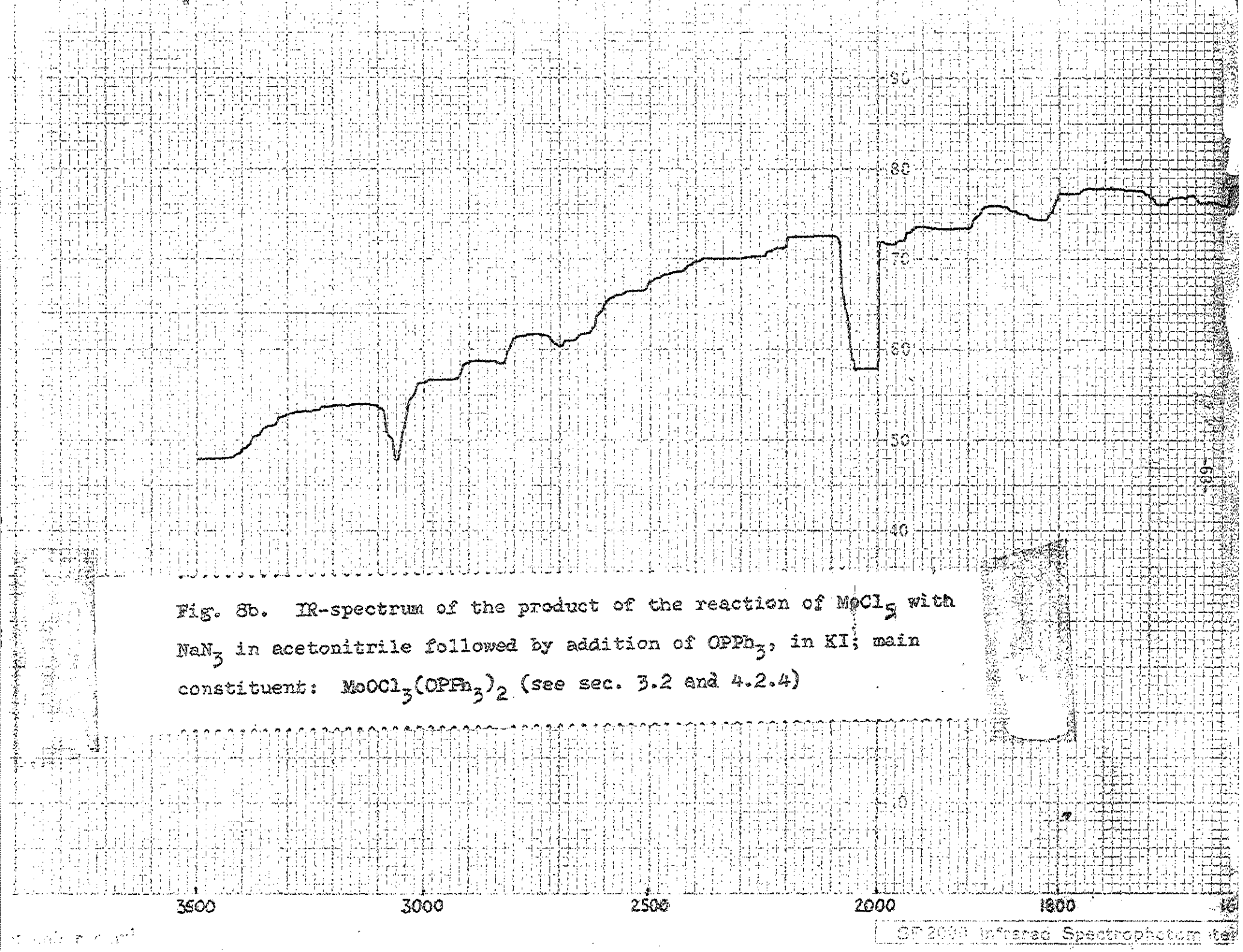


Fig. 8b. IR-spectrum of the product of the reaction of $MoCl_5$ with NaN_3 in acetonitrile followed by addition of $OPPh_3$, in KI; main constituent: $MoOCl_3(OPPh_3)_2$ (see sec. 3.2 and 4.2.4)

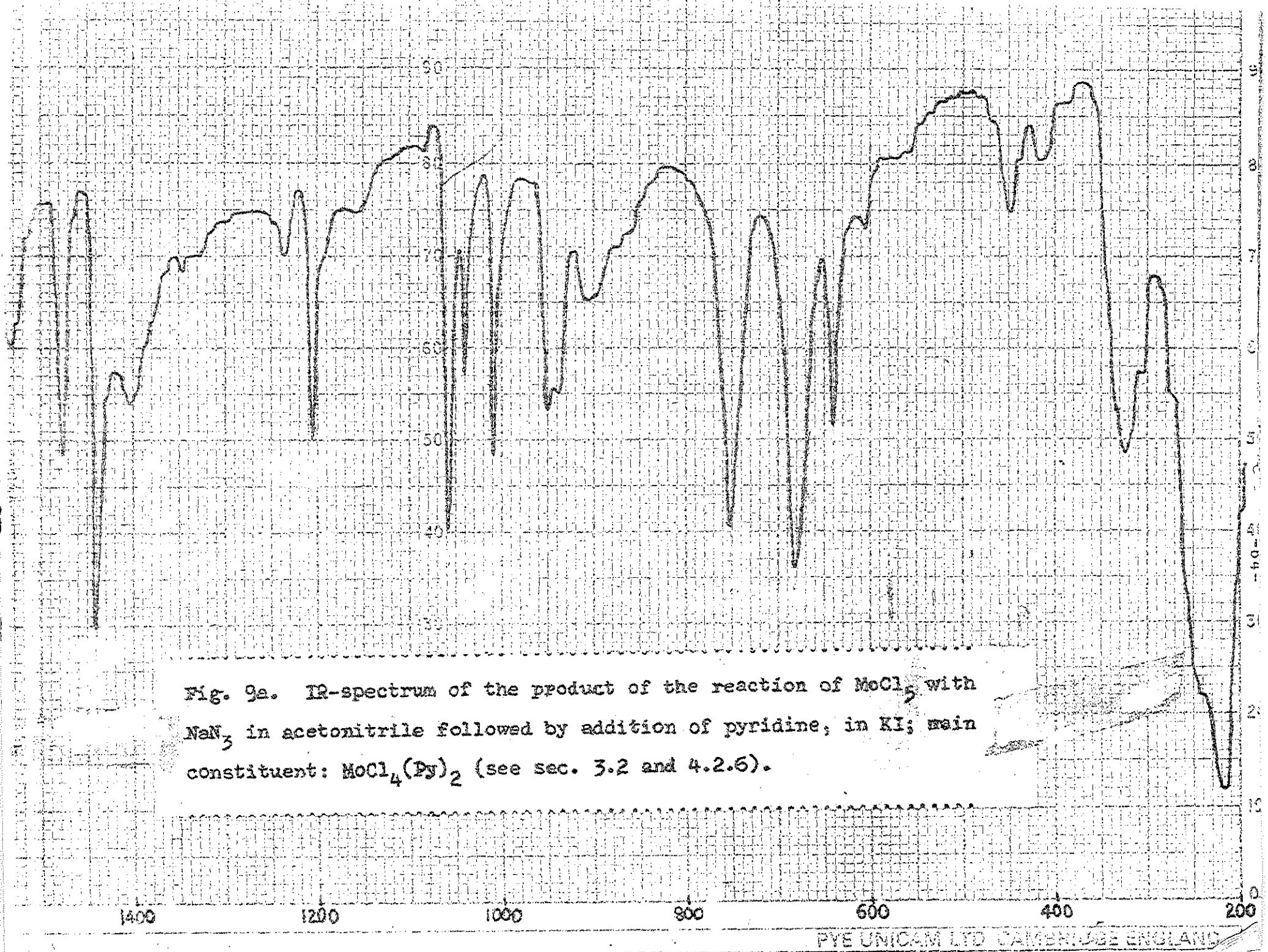


Fig. 9a. IR-spectrum of the product of the reaction of $MoCl_5$ with NaN_3 in acetonitrile followed by addition of pyridine, in KI; main constituent: $MoCl_4(Py)_2$ (see sec. 3.2 and 4.2.6).

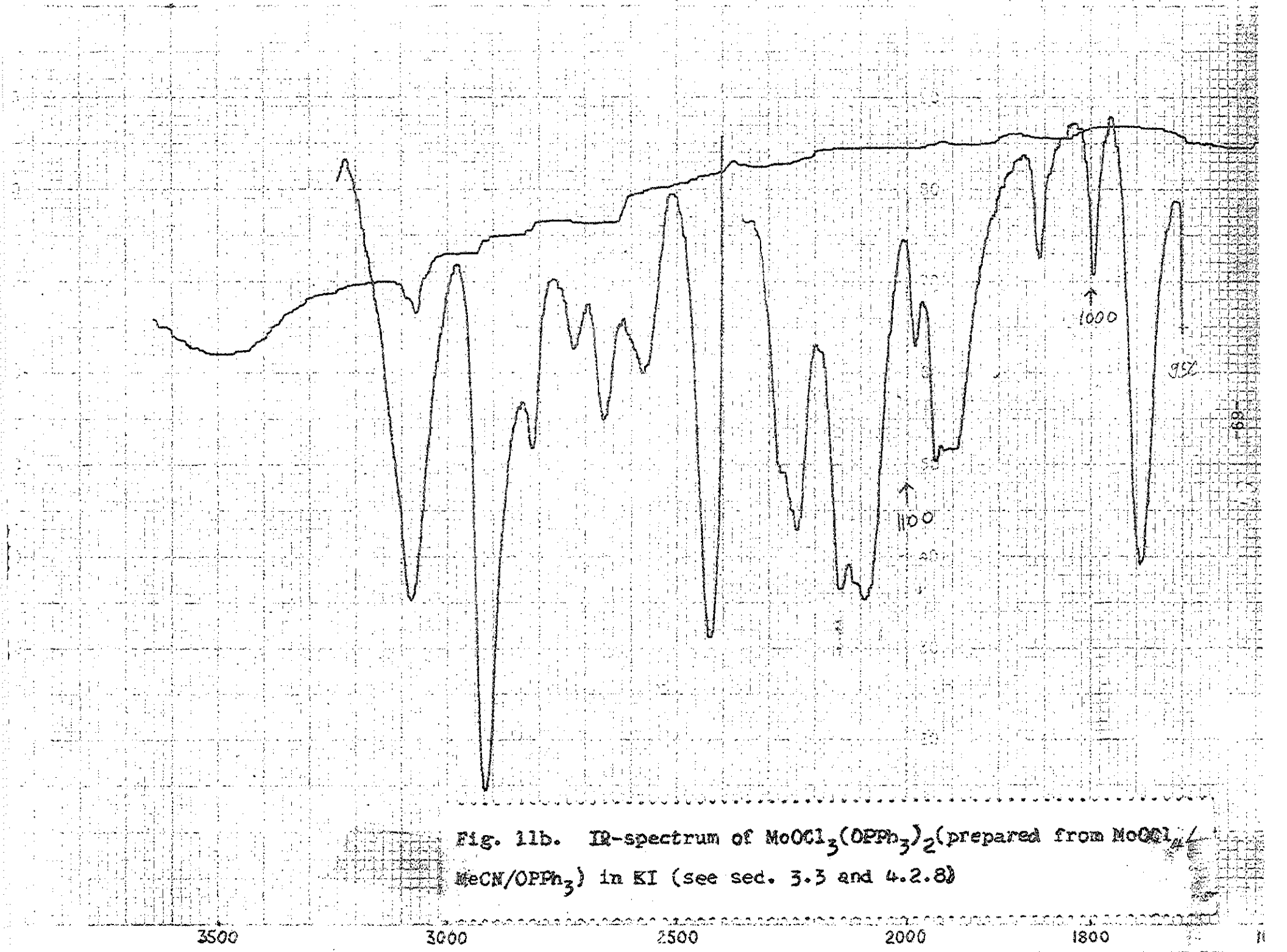


Fig. 11b. IR-spectrum of $MoOCl_3(OPPh_3)_2$ (prepared from $MoOCl_4$/MeCN/$OPPh_3$) in KI (see sec. 3.3 and 4.2.8)

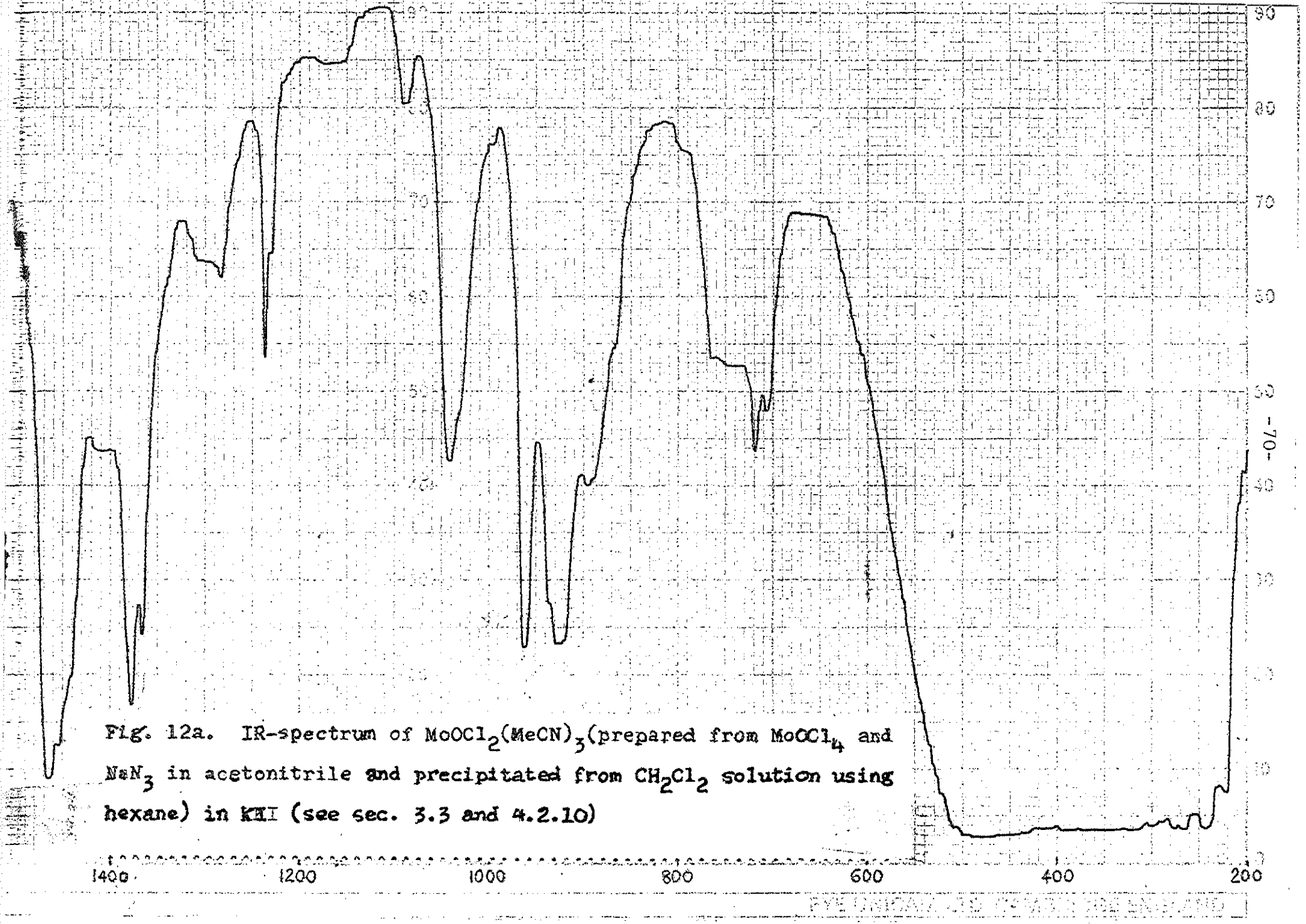


Fig. 12a. IR-spectrum of $MoOCl_2(MeCN)_3$ (prepared from $MoOCl_4$ and NaN_3 in acetonitrile and precipitated from CH_2Cl_2 solution using hexane) in KBr (see sec. 3.3 and 4.2.10)

Fig. 12b. IR-spectrum of $MoOCl_2(MeCN)_3$ (prepared from $MoOCl_4$ and NaN_3 in acetonitrile and precipitated from CH_2Cl_2 solution using hexane) in KI (see sec. 5.3 and 4.2.10)

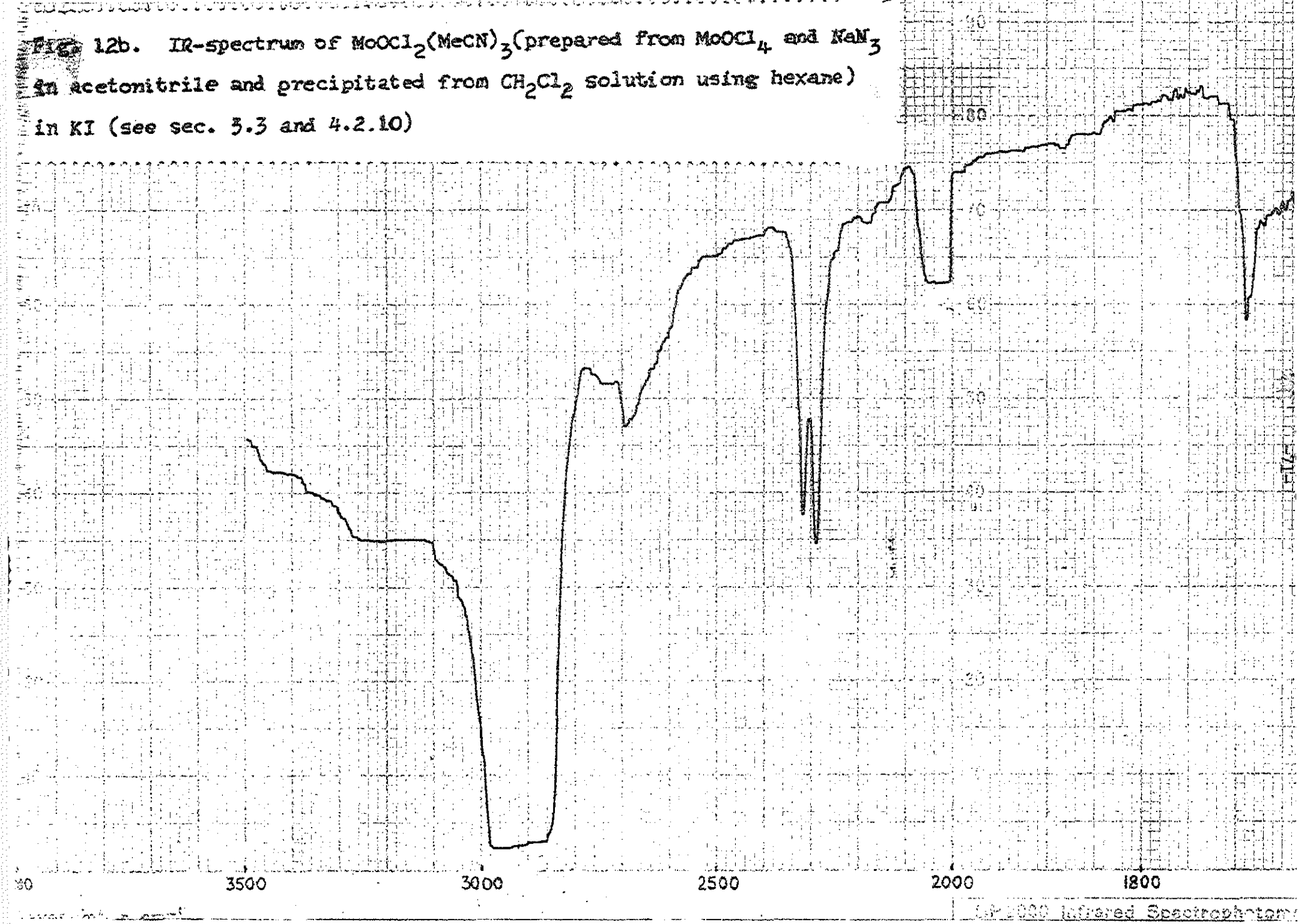
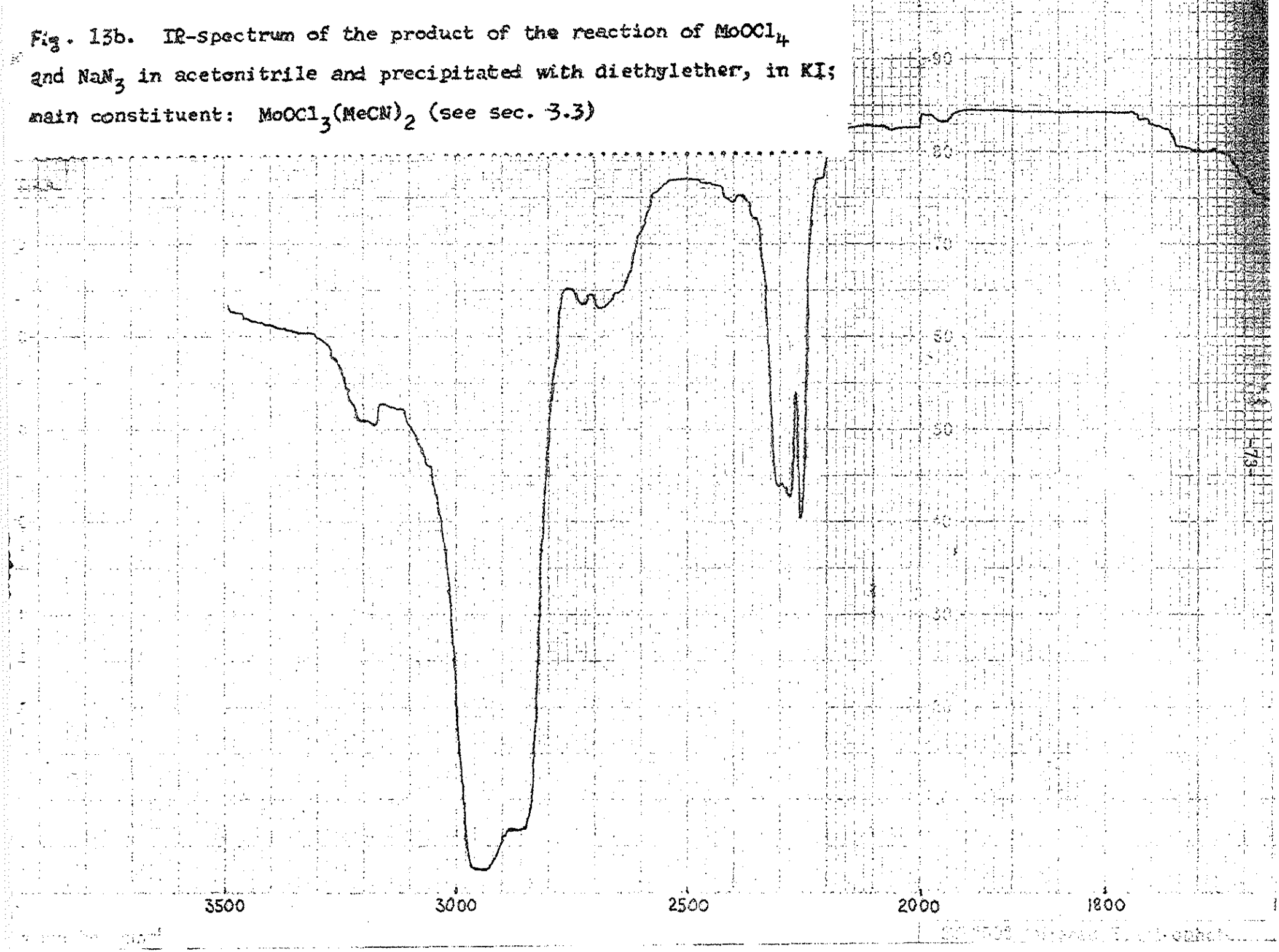


Fig. 13b. IR-spectrum of the product of the reaction of $MoOCl_4$ and NaN_3 in acetonitrile and precipitated with diethylether, in KI; main constituent: $MoOCl_3(MeCN)_2$ (see sec. 3.3)



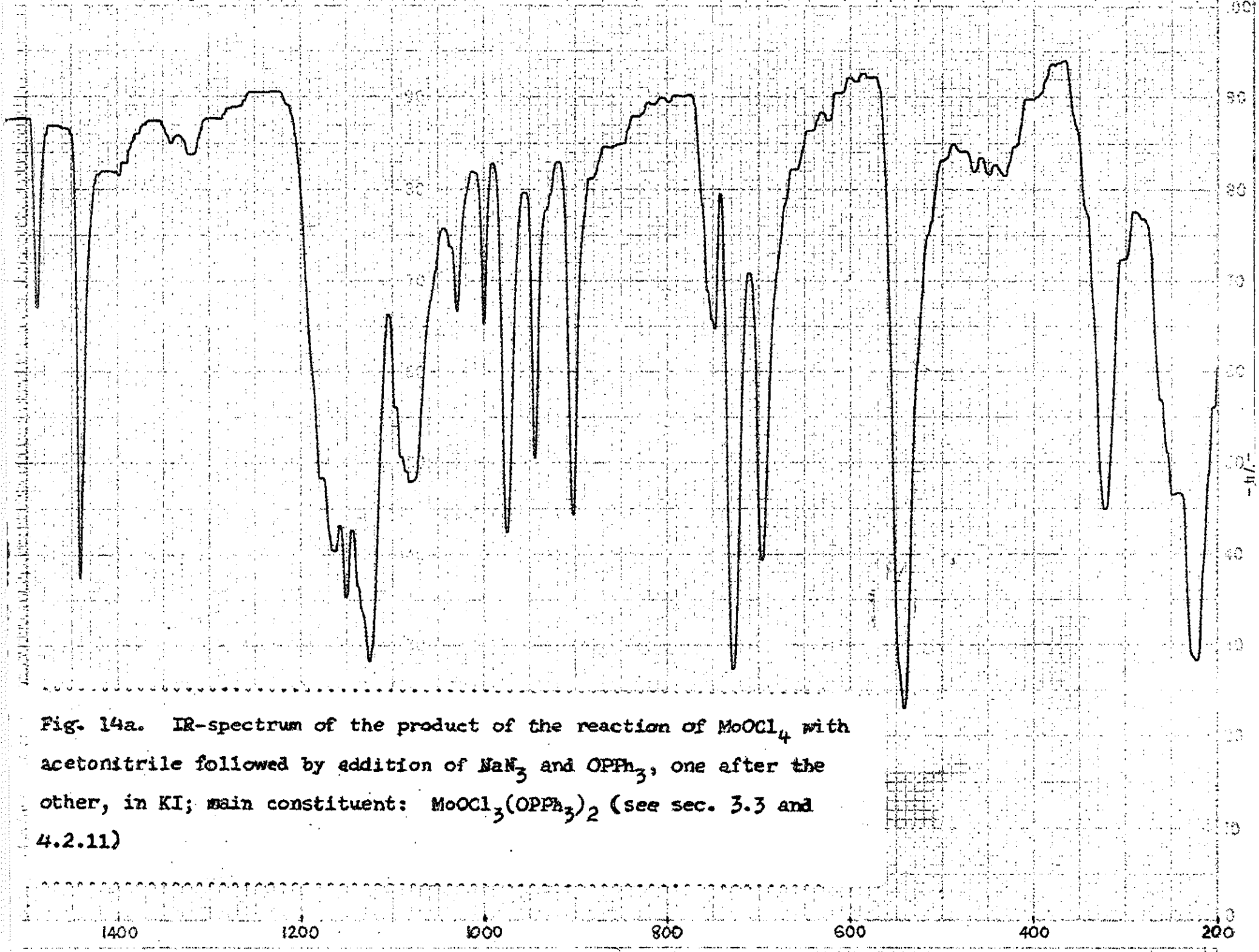
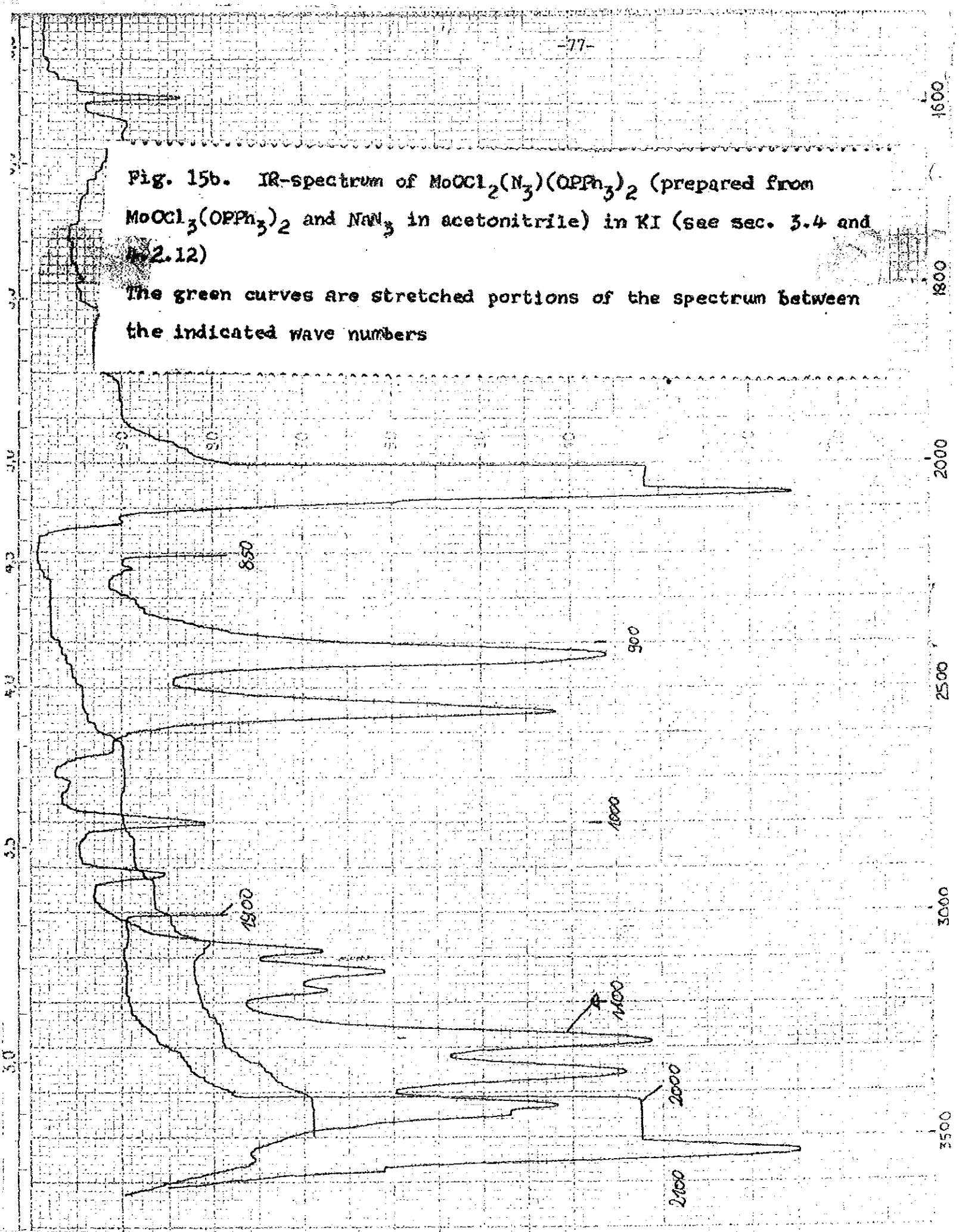


Fig. 14a. IR-spectrum of the product of the reaction of $MoOCl_4$ with acetonitrile followed by addition of NaN_3 and $OPPh_3$, one after the other, in KI; main constituent: $MoOCl_3(OPPh_3)_2$ (see sec. 3.3 and 4.2.11)

Fig. 15b. IR-spectrum of $MoOCl_2(N_3)(OPPh_3)_2$ (prepared from $MoOCl_3(OPPh_3)_2$ and NaN_3 in acetonitrile) in KI (see sec. 3.4 and 4.2.12)

The green curves are stretched portions of the spectrum between the indicated wave numbers



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