SYNTHESIS AND CHARACTERIZATION OF SOME NITRIDC MOLYBDENUM AND TUNGSTEN COMPLEXES

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To my parents, my wife Roman Hegash

and my dhild Hiwot Zewdu

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ABSTRACT

The nitridomolybdenum(VI) complexes $MoNOI_3(OPPh_3)_2$ and $[Bu_4N][MoOCl_4]$ were synthesized from $MoOCl_3(CH_3CN)_2$, sodium azid, triphenylphosphine oxide and totrabutylaromonium chloride respectively in acetonitrile. The reaction of $MoOCl_3$ with sodium azide and triphenylphosphine oxide also gave $MoNCl_3(OPPh_3)_2$ which is found to be anew way of preparing nitridomolybdenum complexes. The nitridomolybdenum complexes obtained were analytically pure.

Attempts to synthesize nitridotungsten(VI) complexes by reaction of WCl_6 with sodium azide in acetonitrile gave impure $WNCl_3(CH_3ON)_3$ complex. Reaction of the recrystallized and decomposition product of $WNCl_3(CH_3OH)_2$ with triphenylphosphine oxide in methylenechloride gave pure $VOCl_3(OPPh_3)_2$ in low yield. Similar reaction of $VOCl_3(CH_3CN)_2$ with tetrabutylammonium chloride and 2,2'-dipyridyl in acetonitrile gave only impure products.

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ABBREVIATIONS

THF	Tetrahydrofuran
Et	Ethyl
Me	Methyl
st$_2$O	Diethyl ether
Bu	Butyl
d:ipy	2,2'-dipyridyl
py	Pyridine
EtOH	Ethylalcohol
cliphos	1,2-Bis(diphenylphosphino)-ethane
Hptpp	Tetraphenylporphyrin
dtc	Dithioearbamate
oqn	Equation
Ir	Infra-red
w	**Weak**
vs	Very strong
El	Medium

IM!3tODUCO?:1OK

The olefin metathesis reaction which represents a versatile and novel teclinique in alkene and alkyne chemistry$_5$ is a catalytic reaction with outstanding scientific interest and considerable industrial significance« The reaction was discovered by BATIKS and BAILEY in 1964, who found that propene is selectively converted into ethene and 2-butene, in the presence of a heterogeneous catalyst consisting of ilO(CO)$_\Lambda$ supported on aluminium oxide[1]„

Olefin metathesis can be defined as the exchange of alleylidene units between one or several olefins via cleavage and reformation of tbe carbon-carbon double bonds» This is illustrated by equation (l) for the general case ox on acyclic, asymmetric olefin[2-9]„

$$2\ \mathrm{IL_1\text{-}CH = CII\text{-}R_P} \xrightarrow{\text{rrtl}} \mathrm{1'_1\text{-}CH\text{-}CH\text{-}R_1} + \mathrm{R_2\text{-}CH{=}CH\text{-}R_2} \quad (1)$$

90% 25% 25%

As the above reaction is nearly thermoneutral, the metathesis equilibrium is mainly governed by the change of reaction entropy, leading to a statistical distribution of the alkylidene moieties[0]„ The catalytically active species itself is a transition metal carbene complex as has been proved recently[7-10]„

At present numerous heterogeneous and homogeneous metathesis catalysts are known, mainly consisting of tungsten, molybdenum and rhenium compounds as the essential constituents„ The heterogeneous catalysts in most cases contain oxides or carbonyls of the above transition metals supported on Al_2O_3 or SiO[14].

Most of the homogeneous catalysts are of ZIEGLER - MATTA typeo The first and one of the most active catalyst system described by CALDERON in 1967 consists of WCl_6/EtOH / EtAlCl$_2$ (1:1:4)[15]„ In the mean time, plenty of other more or less effective tungsten based systems have been published. However, the number of highly active Mo-containing homogeneous catalysts has remained restricted to only a few that may be classified into three major groups as shown below,

1) [illegible] / R_4AlCl_2, $R_3Al_2Cl_3$[16]

2) $HOCl_2(HO)_2L_2$ / LAlCl$_2$[17]

   $HOCl_2(HO)_2L_2$ / RAlCl$_2$[18-19]

   L = various H - or O - donor ligands

   $Mo(NO)(CO)_2L_2$ / RAlCl$_2$[20]

   (L = PPh_3, $AsPh_3$)

3) [illegible] / RAlCl$_2$[21]

   (R = Me, Et; L = $OPPh_3$, 2,2' dipy, Bu_4NCl)

   (X = Halide).

Groups 1 and 2 contain certain carbonyls and nitrosyl Molybdenum complexes in combination with a cocatalyst.

As shown by DOYLE for group 1 and by SEYEEKTH and TAUBE for group 2 the Mo-base systems exhibit a significantly higher metathesis activity than their tungsten counterparts. Moreover, the two groups contain Mo in a low oxidation state. On the contrary, the nitrido complexes in group 3 are the only active Mo-containing catalyst precursors with the metal in the high oxidation number +6. Up to now the corresponding nitridotungsten complexes have not yet been investigated extensively. There is only scarce information as to their preparation and nothing is known about their catalytic properties with respect to olefin metathesis.

The synthesis of chloronitridomolybdenum complexes MoNCl and MoNCl$_3$Lp (L = donor ligand) usually starts with Mo(CO)$_6$ or MoCl$_5$ and such nitride precursors as NaN, ClN$_3$, Et$_4$NN, and (CH$_3$)$_3$SiN$_3$. In a similar way few derivatives of timgsten, WNCl$_3$ (see next chapter) have been obtained from W(CO)$_6$. Very recently a rather safe and convenient synthesis for the compounds MoNCl$_2$L$_2$ (L = OPh, py, dipy) and [^{n}Bu$_4$N][MoNCl$_4$] using NaN$_3$ as a nitrido source has been published by SEYEERTH and TAITBE. Although, already mentioned by CHATT et al. sodium aside has never been used for the synthesis of analogous nitridotungsten derivatives.

Therefore it is the objective of this project to investigate the reaction of various molybdenum and tungsten chlorides with sodium aside and to develop a convenient method for the synthesis of chloronitrido complexes of these transition elements. The complexes synthesized have to be characterized analytically and spectroscopically and may serve as catalysts for metathesis experiments.

2. LITERATURE SURVEY

2.1. transition Metal Nitrido Complexes

At present nitrido compounds are intensively investigated because of their possible occurrence as intermediates in the biologically important nitrogen fixation[28]. Attempts to simulate and modelize this important catalytic process have directed the interest to the nitrogen transition metal bond, its synthesis, and reactivity. Additional importance might come from the application of nitridomolybdenum complexes as highly active precatalysts in olefin metathesis[21]. Above all it is a current topic of research to look more thoroughly into complexes containing TQotalnitrogen multiple bonds.

2.2 The Nitrido Ligand

The nitrogen atom serves as the donor atom in a great variety of ligands. One of these is the nitride ion N^{3-} which is not only a stronger π-donor but also one of the strongest σ-donors known. In contrast to the oxides and fluorides, it is only the nitrido lignad which has the capacity of forming metal-ligand triple bonds, due to the comparatively low electronegativity of nitrogen

and, incidently, an optimal overlap between nitrogen-p and metal d-orbitals. As for the central atom, high electronegativity and high oxidation states should obviously favor the formation of nitrido complexes encouraging a substantial electron transfer from the nitrido ligand to the metal[28-29].

Only a limitted number of transition metals have been found to form nitrido complexes, especially those in the middle of the d-series. Among these, Mo, W, Re, Ru and Os are the most common and properly studied partly due to their providing apparently favorable conditions for metal nitrogen multiple bond formation[28,30].

In most cases the nitrido ligand occurs as a terminal ligand. Well known are the tetragonal pyramidal complex anions $[MNCl_4]^-$. (M = Mo, W, Re, Ru, Os) which contain an extremely short M≡N bond. The triple bond arises from overlap of one σ- and two degenerate π - type orbitals of the nitride ligand with empty d - orbitals of the metal. The non bonding electron pair remaining on the nitrogen makes the nitrido ligand only a poor Lewis base[28, 31-33].

In addition to the terminal mode of bonding there are also complexes with some types of nitrido bridges,
Asymmetrical $M = \overset{+}{N} - M$ bridges, e.g. in $[Re\ NCl_4]^-$ [34]
Symmetrical $M = \overset{+}{N} = M$ bridges, e.g. in $[Ta_2NBr_{10}]^{3-}$ [35]
Nitrido M_3N bridges, e.g. in $[Ir_3N(SO_4)(H_2O)_3]^{4-}$ [36]

2.3 Synthesis of Nitrido Complexes

There are various ways leading to nitrido complexes. These are briefly compiled here and illustrated by selected examples. Complete reviews on this topic are given by GRIFFITH[37], DEHNICKE and STRAEHLE[28].

1. Ammonolysis Reaction

Nitridoosmate $[OsO_3N]^-$ was the first complex to be prepared by FRITSCHE and STRUVE in 1847[38] by treatment of OsO_4 in KOH solution with strong ammonia

$$OsO_4 + KOH + NH_3 \longrightarrow K[OsO_3N] + 2H_2O \qquad (2)$$

2. Reaction with Hydrazine[39-42]

$$NaReO_4 + PR_3 + N_2H_4 \cdot 2HCl \xrightarrow{EtOH} ReNCl_2(PR_3)_2 \qquad (3)$$

$$ReO(OEt)Cl_2(PPh_3)_2 + N_2H_4 \cdot 2HCl + H_2O \longrightarrow ReNCl_2(PPh_3)_2 + EtOH + Ph_3PO + NH_4Cl \qquad (4)$$

3. Reaction of Vanadium Nitride with Chlorine[43]

$$VN + 2Cl_2 \xrightarrow{120 - 140^\circ C} Cl_3VNCl \qquad (5)$$

4. Reaction with Nitrogen Trichloride[23]

$$ReCl_5 + NCl_3 \xrightarrow{\text{high temp.}} ReNCl_3 + 2.5Cl_2 \qquad (6)$$

$$ReCl_5 + NCl_3 \xrightarrow{0^\circ C} ReNCl_4 + 2Cl_2 \qquad (7)$$

5. Decomposition of Azides

The most effective preparative method is the reaction of azides with transition metal halides. The halogen azides ClN_3[24], Et_4NN_3[25], Me_3SiN_3[26], and NaN_3[21] have been employed so far.

$$ReCl_5 + ClN_3 \xrightarrow{CCl_4} [ReCl_5N_3] + \tfrac{1}{2}Cl_2 \quad (8)$$

$$[ReCl_5N_3] \xrightarrow{CCl_4} ReNCl_3 + N_2 \quad (9)$$

2.4 Nitrido Complexes of Molybdenum and Tungsten

2.4.1 Preparation of Nitrido Molybdenum(VI) and Tungsten(VI) Compounds.

The first nitrido complexes of molybdenum and tungsten were prepared by DEHNICKE and STRAEHLE by converting either $MoCl_5$ or WCl_6 with ClN_3 in CCl_4.[24]

$$MoCl_5 + ClN_3 \xrightarrow{CCl_4} [MoCl_5N_3] + \tfrac{1}{2}Cl_2 \quad (10)$$

$$WCl_6 + ClN_3 \xrightarrow{CCl_4} [WCl_5N_3] + Cl_2 \quad (11)$$

$$[MCl_5N_3] \xrightarrow[RT]{CCl_4} MNCl_3 + Cl_2 + N_2 \quad (12)$$

M = Mo, W

The unstable azido intermediate $[MCl_5N_3]$ decomposes at room temperature to give the nitrido complex $MNCl_3$. The intermediate monoazide can, however, react with a second ClN_3 to form highly explosive shiny black crystals of $MoCl_4(N_3)_2$.[24]

$$[MoCl_5N_3] + ClN_3 \xrightarrow{CCl_4} MoCl_4(N_3)_2 + Cl_2 \quad (13)$$

DEHNICKE and KRUEGER used IN_3 or NCl_3 in trapping another intermediate the bis(tetrachloromolybdenum)diazene, $(MoNCl_4)_2$, which splits off Cl_2 to give $MoNCl_3$ at 100°C or on refluxing.[44,45]

$$MoCl_5 + 2IN_3 \xrightarrow{CCl_4} (MoNCl_4)_2 + N_2 + Cl_2 \quad (14)$$

$$2MoCl_5 + 2NCl_3 \xrightarrow{CCl_4} (MoNCl_4)_2 + 4Cl_2 \quad (15)$$

$$(MoNCl_4)_2 \xrightarrow{100^oC} 2MoNCl_3 + Cl_2 \quad (16)$$

In a similar way $MoNBr_3$ has been obtained from $MoBr_4$ and IN_3[45] whereas MoI_3 gives the azido derivative MoI_2N_3 under these conditions[46].

$$MoBr_4 + IN_3 \longrightarrow MoNBr_3 + IBr + N_2 \quad (17)$$

$$MoI_3 + IN_3 \longrightarrow MoI_2N_3 + I_2 \quad (18)$$

WBr_6 and IN_3 react via an explosive azido intermediate WBr_5N_3 to give $WNBr_3$[47].

$$WBr_6 + IN_3 \xrightarrow{-IBr} WBr_5N_3 \longrightarrow WNBr_3 + Br_2 + N_2 \quad (19)$$

Instead of using tungsten and molybdenum halides one may as well start with the hexacarbonyls of these elements and NCl_3[27,48].

$$M(CO)_6 + NCl_3 \xrightarrow{CCl_4} MNCl_3 + 6CO \quad (20)$$

M = Mo, W

Reaction (20) is more complex and very probably proceeding via a $[MNCl_4]$ intermediate by liberating N_2 and Cl_2 in addition to CO[27]. With IN_3 and $M(CO)_6$ the explosive $M(CO)_2(N_3)_2$ could be isolated[49].

A rather uncommon method to prepare $MNCl_3$ (M = Mo, Re) is the transfer of the nitrido group from $[Cl_3VNCl]$ which has recently been described by DEHNICKE and LIESE[23].

$$Cl_3V{\equiv}N\text{-}Cl + MCl_5 \longrightarrow MNCl_3 + VCl_4 + Cl_2 \quad (21)$$

Complex halonitrido compounds with Mo and W in the oxidation number + 6 may be obtained either by conversion

of the appropriate transition metal halide complexes with various azides or by ligand addition to MNX_3 (M = Mo, W; X = Cl, Br). The first method has been used by BERMAN[25] for the preparation of $[Et_4N][MoNCl_4]$ from $MoCl_5$ and $[Et_4N]N_3$.

$$MoCl_5 + [Et_4N]N_3 \xrightarrow{CH_2Cl_2} [Et_4N][MoNCl_4] \qquad (22)$$

Starting with $MoCl_4L_2$ complexes (L = MeCN, THF) and Me_3SiN_3 a straight forward method to nitrido molybdenum (VI) complexes was proposed by CHATT and DILWORTH in 1974[26].

$$MoCl_4L_2 + Me_3SiN_3 \xrightarrow{CH_3CN} [MoNCl_3L_x] + N_2 + Me_3SiCl \qquad (23)$$

(L = CH_3CN, THF)

$$[MoNCl_3L_x] + 2L' \longrightarrow MoNCl_3L'_2 + xL \qquad (24)$$

(L'= ½ dipy $OPPh_3$, Et_4NCl)

$$[MoNCl_3L_x] + 3\,Me_3Si(dtc) \longrightarrow MoN(dtc)_3 + 3Me_3SiCl + xL \qquad (25)$$

(dtc = $Et_2NCS_2^-$, $Me_2NCS_2^-$, $C_5H_{10}NCS_2^-$)

As reaction (25) does not give a good yield of $MoN(S_2CNEt_2)_3$, an alternative pathway is recomended which includes the introduction of the dithiocarbamate ligand prior to the nitrido one[26].

$$MoCl_4L_2 + 3Me_3Si(S_2CNEt_2) \longrightarrow MoCl(S_2CNEt_2)_3 + 3Me_3SiCl + 2L \qquad (26)$$

$$MoCl(S_2CNEt_2)_3 + Me_3SiN_3 \longrightarrow MoN(S_2CNEt_2)_3 + Me_3SiCl + N_2 \qquad (27)$$

If Me_3SiN_3 is added in excess, more than one chloro ligand may be substituted as shown by SCHWEDA and STRAEHLE [50,51]

$$MoCl_4(dipy) + 4Me_3SiN_3 \xrightarrow{Cl(CH_2)_2Cl} MoN(N_3)_3(dipy) + N_2 + 4Me_3SiCl \quad (28)$$

$$MoCl_4(Py)_2 + 4Me_3SiN_3 \xrightarrow{Cl(CH_2)_2Cl} MoN(N_3)_3(Py) + N_2 + 4Me_3SiCl + Py \quad (29)$$

$$MoCl_4(Py)_2 + 2Me_3SiN_3 \xrightarrow{Cl(CH_2)_2Cl} MoN(N_3)Cl_2(Py) + 2Me_3SiCl + N_2 + Py \quad (30)$$

All the azido complexes are highly explosive and sensitive to hydrolysis.

Although already mentioned by CHATT et al. in 1974[26], it is somewhat strange that, the use of sodium azide as the simplest nitrogen source for nitrido complexes has only been explored very recently by SEYFERTH and TAUBE[21].

$$MoCl_4(CH_3CN)_2 + NaN_3 \xrightarrow{CH_3CN} [MoNCl_3(CH_3CN)_x] + NaCl + N_2 \quad (31)$$

$$[MoNCl_3(CH_3CN)_x] + 2L \longrightarrow MoNCl_3L_2 + xCH_3CN \quad (32)$$

(L_1 = ½ dipy, $OPPh_3$; L_2 = Bu_4NCl)

This reaction is, however, limitted to acetonitrile as a solvent and permits only one chloro ligand to be substituted.

Regarding the synthesis and reaction of similar tungsten complexes there are only few reports. RUSCHKE and DEHNICKE[47] obtained $[PPh_4][WNBr_4]$ as an impure compound, starting with WBr_5 and Ph_4PN_3 in CH_2Cl_2.

$$WBr_5 + Ph_4PN_3 \xrightarrow{CH_2Cl_2} [Ph_4P][WNBr_4] + N_2 + \tfrac{1}{2}Br_2 \quad (33)$$

The same product still more impure could also be isolated after converting $[Ph_4P][WBr_6]$ with IN_3.

$$[Ph_4P][WBr_6] + IN_3 \longrightarrow [Ph_4P][WNBr_4] + IBr + \tfrac{1}{2}Br_2 + N_2 \quad (34)$$

The IBr formed in this process attacks, the nitrido complex to give $[Ph_4P][IBr_2]$ and $WNBr_3$.

$$[Ph_4P][WNBr_4] + IBr \longrightarrow [Ph_4P][IBr_2] + WNBr_3 \quad (35)$$

In many cases nitrido complexes of Mo(VI) and W(VI) have been prepared from tetrameric parent compound $[MNX_3]_4$ (M = Mo, W; X = Cl, Br) by ligand addition reaction without and with cleavage of the eight-membered planar $[M \equiv N]_4$ ring[53] Up to now it is only the $OPCl_3$ ligand that has proved to be unable to cleave the cyclic $[MNX_3]_4$ moiety because of its rather modest Lewis basicity[53-55].

$$[MNCl_3]_4 + 6OPCl_3 \longrightarrow [MNCl_3(OPCl_3)]_4 \cdot 2OPCl_3 \quad (36)$$

The analogous bromonitrido molybdenum compound has also been characterized[56]. $[MoNCl_3 \cdot OPCl_3]_4$ may be likewise obtained from $MoCl_5 \cdot OPCl_3$[44].

Stronger Lewis bases lead to a complete rupture of the N-M single bonds in the tetrameric units and give rise to monomeric complexes of the type MNX_3L_n (n = 1-3). Complexes with n = 1 are normally formed with Me_4NCl[57], Et_4NCl[57-58], Bu_4NCl[21], Ph_4PCl[57], Ph_4AsCl[31,58] and Ph_4PBr[56] to yield the corresponding tetrachloronitridometalates (VI).

$$MNX_3 + ER_4X \longrightarrow [ER_4][MNX_4] \qquad (37)$$

E = N, P, As; M = Mo, W; X = Cl, Br; R = Me, Et, Bu, Ph

If the complex cation used is not too bulky, even a second chloride may be accomodated by the molybdenum central atom as found by KOHLITSCH and DENNICKE[57].

$$[Et_4N][MoNCl_4] + Et_4NCl \xrightarrow{CH_2Cl_2} [Et_4N]_2[MoNCl_5] \qquad (38)$$

$MNCl_3$ (M = Mo, W) and 2,2' - dipyridyl give the octahedral complexes $MNCl_3(dipy)$[59] which are rather unstable and tend to decompose by reduction[50, 59-60].

$$MNCl_3 + dipy \longrightarrow MNCl_3(dipy) \qquad (39)$$

With pyridine the seven coordinate complexes $MNCl_3(Py)_3$ have similarly been obtained[24].

$$MNCl_3 + 3Py \longrightarrow MNCl_3(Py)_3 \qquad (40)$$

2.4.2. Preparation of Nitrido Molybdenum (V) and Tungsten (V) Complexes.

In principle, nitridomolybdenum (V) complexes may be obtained by intramolecular reduction of the corresponding Mo (VI) derivatives. This can be achieved either by heating or by addition of ligands which are capable of stabilizing lower oxidation states. According to CHATT and DILWORTH, $MoCl_4(THF)_2$ reacts with Me_3SiN_3 and PPh_3, Ph_2PMe, or dipy respectively in CH_2Cl_2 to give the complexes $MoNCl_2L_2$ [26,60].

The dipryidyl complexes $MoNX_2(dipy)$ (X = Cl, Br) have been found indopendently by DEHNICKE et. al.[50,59]

$$MoCl_4(THF)_2 + Me_3SiN_3 + 2L \xrightarrow{CH_2Cl_2} MoNCl_3L_2 + N_2 + Me_3SiCl + 2THF \quad (41)$$

$$MoNCl_3L_2 \longrightarrow MoNCl_2L_2 + \tfrac{1}{2}Cl_2 \quad (42)$$

(L = Ph_3P, Ph_2PMe, ½ dipy; X = Cl; L = dipy, X = Br)

$$MoCl_3(THF)_3 + Me_3SiN_3 + 2PPh_3 \xrightarrow{CH_2Cl_2} MoNCl_2(PPh_3)_2 + N_2 + 3THF + Me_3SiCl \quad (43)$$

The nature of the product was confirmed by a direct synthesis starting from $MoCl_3(THF)_3$ and Me_3SiN_3.

The only W(V) containing nitrido complex known so far is the binuclear ion $[AsPh_4]_2[W_2NCl_{10}]$ containing a slightly asymmetric $W^{(VI)} \equiv N - W^{(V)}$ unit [61].

2.4.3 Preparation of Nitrido Molybdenum (IV) and Tungsten (IV) complexes

Hitherto no attempts have been made to obtain nitrido complexes of Mo (IV) and W (IV) by reduction. A direct route for this type of compounds is, however, the oxidation of $M(N_2)_2(diphose)_2$ published by CHATT et al.[51,52]

$$M(N_2)_2(diphose)_2 \xrightarrow[THF,\ PhMe]{Me_3SiN_3} MN(N_3)(diphose)_2$$

M = Mo, W

The azido ligand in $MN(N_3)(diphose)_2$ may be substituted by bromide to give $MNBr(diphose)_2$[52]. CHATT et al.[52] have

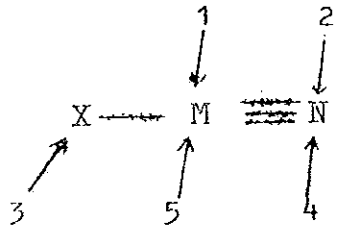
also obtained nitridotungsten (IV) complexes by the reaction of LiMe with a tungsten compound.

$$[W(NH)Br(diphos)_2]Br + LiMe \xrightarrow{THF} WNBr(diphos)_2 + LiBr + CH_4 \quad (45)$$

2.5 Reactivity of Nitrido Molybdenum and Tungsten Compounds

2.5.1 Modes of Reaction

In considering a nitrido transition metal complex, five modes of reaction, supported experimentaly are conceivable.



1. Nucleophilic addition to M
2. Electrophilic addition to N
3. Nucleophilic substitution of X
4. Substitution of N
5. Reduction of M

2.5.2 Nucleophilic Addition to the Metal

Addition of the Lewis base, $OPCl_3$ to the tetrameric nitrido halides $MNCl_3$ (M = Mo, W) and $MoNBr_3$ takes place under retention of its structure to give $[MNX_3.OPX_3].2OPX_3$ complexes (see eqn.(36)). Stronger ligands such as Cl^-, Br^-, dipy, py, cleave the eight membered ring into monomeric unts, (see eqn.(37) to (40))[56-59].

2.5.3 Electrophilic Addition to the Nitrido Ligand

In contrast to the strongly electrophilic central atom the nitrido ligand has got only little nucleophilic character in most cases. Thus, even such a strong Lewis acid as $SbCl_5$ does not undergo complex formation with $MoNCl_3$ or $MoNCl_4^-$. Only if strongly II - basic fluoro ligands weaken the MoN bond and thus, increase the electron density on N, adduct formation at the nitrido ligand is possible[28].

$$[MoNCl_4]^- + SbCl_5 \not\longrightarrow \quad (46)$$

$$[MoNF_4]^- + BF_3 \longrightarrow [F_4MoN - BF_3]^- \quad (47)$$

A sufficient level of nucleophilicity of the nitrido ligand also seems to be necessary for the formation of thionitrosyl[26,52,60], imido[52] and alkylimido[52,60] complexes from nitrido compounds. The addition of oxygen to give nitrosyl complexes has not been managed so far, but leads only to oxo-complexes.

$$MoN(S_2CNR_2)_3 + S \xrightarrow{CH_3CN} Mo(NS)(S_2CNR_2)_3 \quad (48)$$

R = Me, Et, $(CH_2)_5$

$$WNBr(diphos)_2 + HBr \longrightarrow [W(NH)Br(diphos)_2]Br \quad (49)$$

$$WNBr(diphos)_2 + CH_3\text{-}CH\text{-}CH_2 \longrightarrow W(NS)Br(diphose)_2 + CH_3\text{-}CH = CH_2 \quad (50)$$

(S)

$$MoN(S_2CNR_2)_3 + [Ph_3C]^+ BF_4^- \longrightarrow [Mo(NCPh_3)(S_2CNR_2)]BF_4 \quad (51)$$

An interesting reaction is the conversion of $WN(N_3)(diphos)_2$ with ethyl iodide in THF, leading to the ethylimido complex

$[W(NEt)(N_3)(diphose)_2]I$[52]

$$WN(N_3)(diphose)_2 + EtI \xrightarrow{THF} [W(NEt)(N_3)(diphos)_2]I \quad (52)$$

2.5.4 Nucleophilic Substitution of the Ligand X

Substitution reactions of this sort with X being neutral or charged are quite common and may be considered as a synthetical route for new nitrido complexes. In exchange reaction taking place in $[MoNCl_4]^-$ and related ions, the sixth coordination site trans to the nitrido ligand is normally left vacant.

$$[AsPh_4][MoNCl_4] + 4AgN_3 \xrightarrow{CH_2Cl_2} [AsPh_4][MoN(N_3)_4] + 4AgCl \quad (53)$$

$$[AsPh_4][MoNCl_4] + 4AgF \xrightarrow{CH_2Cl_2} [AsPh_4][MoNF_4] + 4AgCl \quad (54)$$

With chelate ligands such as dipyridyl or tetraphenyl porphyrin H_2tPP[59] and also with CH_3CN[47] substitution may take place.

$$[MNCl_4]^- + dipy \xrightarrow{slow} MNCl_3(dipy) + Cl^- \quad (55)$$

(M = Mo, W)

$$2[Ph_4P][WNBr_4] + 2CH_3CN \longrightarrow [WNBr_3(CH_3CN)]_2 + 2Ph_4PBr \quad (56)$$

$$MoNBr_3 + H_2tPP \longrightarrow [MoN(tPP)]^+[Br_3]^- + H_2 \quad (57)$$

Though unusual Mo(VI) is reduced here to Mo(V) with oxygen acting as a reducing agent. This process is not reversible.

2.5.6 Reduction of the Central Metal

The few examples for the reduction of nitrido complexes of Mo(VI) and W(VI) under retention of the nitrido group have already been mentioned in section 2.4.2 The reactions proceed via $MNCl_3L_x$ intermediates containing M(VI) which by subsequent addition of the phosphine or dipy decomposes reductively to give complexes of the type MNX_2L_2 (M = Mo, W; X = Cl, Br; L = Ph_3P, Ph_2PMe, ½ dipy) Although there is no proof at the moment, one may assume that the catalyst formation reaction in the homogeneous metathesis system $MoNCl_3(OPPh_3)_2$/ $EtAlCl_2$ in chlorobenzene[21], very well may involve reduction of the nitrido Mo(VI) complex by the aluminum organic cocatalyst.

3. RESULTS AND DISCUSSION

3.1. Preparation of Nitridomolybdenum (VI) Complexes

3.1.1. Preparation of Trichloronitridobis(triphenylphosphine oxide)molybdenum (VI) from $MoCl_4(CH_3CN)_2$ and Sodium Azide

In order to become familiar with the inert gas techniques and also for comparison with other nitrido compounds attempts were made first to reproduce the synthesis of $MoNCl_3(OPPh_3)_2$ from $MoCl_4(CH_3CN)_2$, sodium azide and triphenylphosphine oxide in acetonitrile as recently described by SEYFERTH and TAUBE[21]

The starting compound $MoCl_4(CH_3CN)_2$ was easily prepared by stirring molybdenum pentachloride in an excess of acetonitrile for two days at room temperature according to a procedure outlined by CHOI et al[62].

$$2MoCl_5 + 5CH_3CN \longrightarrow 2MoCl_4(CH_3CN)_2 + [CH_3CNH]^+ [HCl_2]^- + 2[\cdot CH_2CN] \qquad (61)$$

The reaction proceeded with formation of a black brown solution from which the dark-brown crystalline product precipitated in 72% yield. Although not recrystallized due to its insolubility in most solvents, the compound was found to be analytically pure as confirmed by elemental analysis (see section 4.2.1)

For the synthesis of $MoNCl_3(OPPh_3)_2$, $MoCl_4(CH_3CN)_2$ was treated with one equivalent of sodium azide in acetonitrile. Accompained by nitrogen evaluation a

red-brown solution was formed within one hour. The white solid residue consisted of sodium chloride and unreacted sodium azide. The reaction presumably involves the formation of an azido intermediate which immediately docomposes to give nitrogen and a nitrido acetonitrile complex such as $[MoNCl_3(CH_3CN)_x]$.

$$MoCl_4(CH_3CN)_2 + NaN_3 \xrightarrow{CH_3CN} [MoNCl_3(CH_3CN)_x] + NaCl + N_2 \quad (62)$$

(1)

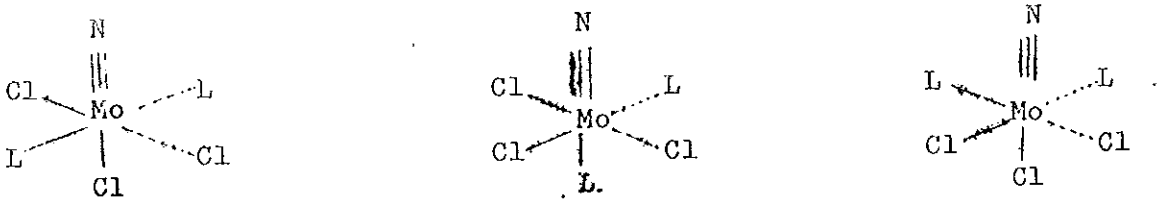
The latter is stable under nitrogen at room temperature but hydrolyses rapidly to green and blue decomposition products (presumbly oxo--complexes) on exposure to wet air[63]. As the compound failed to recrystallize from suitable solvents such as methylenechloride or acetonitrile, a thorough characterization was impossible. However, its composition was deduced from the ligand exchange reaction with triphenylphosphine oxide which gave a lightbrown precipitate in 65% yield. The analytical result (table 6) and the IR - spectrum (table 7) confirmed the compound to be the nitridomolybdenum (VI) complex, $MoNCl_3(OPPh_3)_2$, the formation of which may be expressed by the following equation.

$$[MoNCl_3(CH_3CN)_x] + 2OPPh_3 \xrightarrow{CH_3CN} MoNCl_3(OPPh_3)_2 + xCH_3CN \quad (63)$$

(2)

In contrast to (I) this triphenylphosphine oxide adduct(2) crystallized very well and was more stable to hydrolysis. It could be handled in dry air, was soluble in CH_2Cl_2, ether , THF, but did not dissolve in benzene and hexane. On treating the complex with water it turned blue due to reduction to Mo(V) complexes[31]. Treatment of the reduced product with conc.H_2SO_4 and then refluxing for some time on air caused re-oxidation to a colourless soluble molybdate(VI). Subsequent addition of a strong base liberated ammonia, used to measure the nitrogen content by the KJELDAHL method.

$MoNCl_3(OPPh_3)_2$ exhibits an IR-spectrum which contains all the absorptions expected for the ligand triphenylphosphine oxide, such as the intense ν(P=O) band at 1120 cm^{-1}. Furthermore, there are strong bands in the region 230-400cm^{-1} which correspond to the various Mo-Cl stretching and bending vibrations. Important for the characterization of the complex are three medium absorptions in the region 1100-1000 cm^{-1}, which can be assigned to the ν(Mo≡N) vibrations. The fact that there are three absorptions at 1053 cm^{-1}, 1035 cm^{-1} and 1026 cm^{-1} may be interpreted by the three possible stereoisomers, which are possible for an octahedral complex $MoNCl_3L_2$.



2a 2b 2c

Fig 1. Stereoisomers of an octahedral complex, $MoNCl_3L_2$.

The chloride ligand trans to the nitrido group in (2a) and (2c) competes with the nitrido ligand for the d_{xz} and d_{yz} acceptor orbitals of the central metal by the virture of its being a strong π-donor as depicted by Fig.2.

As $OPPh_3$ ligand is supposed to be a weaker π-donor than the chloride, the Mo≡N bond in (2b) should be strongest and therefore, give rise to that absorption with the highest frequency at 1053 cm^{-1}.

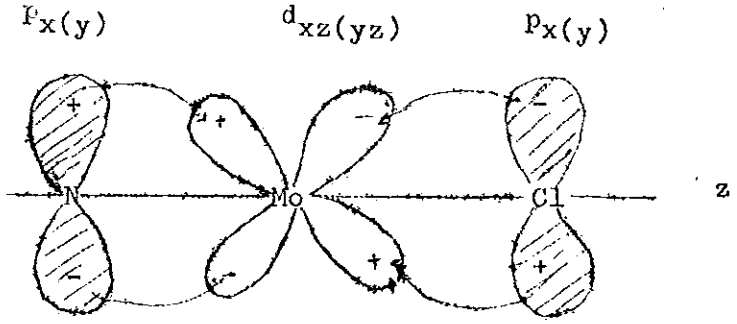


Fig. 2. Orbital overlap scheme between metal and ligand

3.1.2 Preparation of Tetrabutylammonium Tetrachloronitridomolybdate(VI) from $MoCl_4(CH_3CN)_2$ and Sodium Azide.

Treatment of the red-brown solution (1) obtained from $MoCl_4(CH_3CN)_2$ and sodium azide in acetonitrile (see eqn.(62)) with one equivalent of tetrabutylammonium chloride dissolved in the same solvent gave red-brown, shiny, sheet like crystals. The analytical values for Mo, Cl, and N-content (see table 6) and the IR-spectrum (table 7) confirm the composition $[Bu_4N][MoNCl_4]$ for the compound which was formed by the following reaction.

$$[MoNCl_3(CH_3CN)_x] + Bu_4NCl \xrightarrow[(3)]{CH_3CN} [Bu_4N][MoNCl_4] + xCH_3CN \qquad (64)$$

The complex could be handled in air for a short time, but tended to hydrolyse when in contact with moisture yielding a blue decomposition product probably containing Mo(V). Hydrolysis with conc. H_2SO_4 under oxidizing conditions (addition of $CuSO_4$ or Se-KJELDAHL catalyst), followed by treatment with excess sodium hydroxide gave ammonia.

The IR-spectrum of the compound apart from the bands due to the ligand, shows a medium absorption at 1067 cm^{-1} which can be assigned to the ν(Mo≡N) stretching vibration. This is in agreement with the IR-spectra reported for other tetrachloronitridomolybdate(VI) complexes (see table 1).

Nitrido complexes	(Mo≡N in cm^{-1}	Lit
$[Me_4N][MoNCl_4]$	1054	58
$[Et_4N][MoNCl_4]$	1060	58
$[Et_4N][MoNCl_4]$	1030	51
$[Et_4N][MoNCl_4]$	1052	25

Table 1. (Mo≡N) frequencies of $[R_4N][MoNCl_4]$

The relatively high value of the (Mo≡N) frequency may be explained by the absence of any donor ligand in trans position to the Mo≡N grouping. Characteristic but not very conclusive are the various poorly resolved absorptions in the range of 230-400 cm^{-1} due to various ν(Mo-Cl) and δ(Mo-Cl) vibrations[58].

3.1.3 Preparation of Trichloronitridobis(triphenylphosphine oxide)molybdenum(VI) from $MoCl_5$ and Sodium Azide

We found that nitrido molybdenum complexes could be prepared directly from molybdenum pentachloride and sodium azide in acetonitrile. The reaction of $MoCl_5$ with NaN_3 in CH_3CN resulted in the formation of a dark violet solution with some white precipitate (proved to be sodium chloride by potentiometric titration with $AgNO_3$) and concomitant gas evolution. In addition to nitrogen, the evolved gas contained chlorine detected qualitatively by

reaction with a KI / starch mixture. The violet solution was not stable but changed to red-brown on stirring for one hour. Addition of two equivalents of triphenylphosphine oxide dissolved in acetonitrile to this solution gave a light brown precipitate. Both the analytical values for the Mo, Cl, and N content as well as the IR-spectrum were consistent with the structure, $MoNCl_3(OPPh_3)_2$, formed in 70% yield by the following reaction:

$$MoCl_5 + NaN_3 + 2OPPh_3 \xrightarrow{CH_3CN} MoNCl_3(OPPh_3)_2 + NaCl + N_2 + \tfrac{1}{2}Cl_2 \quad (65)$$

(4)

By analogy to a similar conversion of $MoCl_5$ with ClN_3 investigated by DEHNICKE et al.[24], the violet intermediate, though not isolated or characterized may be an unstable azido complex such as $[MoCl_4(N_3)(CH_3CN)]$ which slowly decomposes to the red-brown but stable intermediate $[MoNCl_3(CH_3CN)_x]$ nitrogen, and chlorine. The latter obviously reacts with triphenylphosphine oxide according to equation(63).

Both $MoNCl_3(OPPh_3)_2$ complexes, (2) and (4) exhibit identical properties (see section 3.1.1). The IR-spectrum of complex (4), however, shows one remarkable difference in the ν(Mo≡N) region. In contrast to complex (2), only one ν(Mo≡N) absorption at 1027 cm^{-1} is observed. This value is identical with the lowest

ν(Mo≡N) frequency of (2), having been assigned to one of the two $MoNCl_3(OPPh_3)_2$ isomers in which chlorine is trans to the nitrido ligand.

3.2 Attempts to Prepare Nitridotungsten (VI) Complexes,

3.2.1 Reaction of $WCl_4(CH_3CN)_2$ with Sodium Azide in Acetonitrile.

Unlike $MoCl_4(CH_3CN)_2$, $WCl_4(CH_3CN)_2$, does not react with NaN_3 in CH_3CN. Neither colour change nor evolution of gas was observed upon stirring at room temperature or upon refluxing. The reason for the inertness of $WCl_4(CH_3CN)_2$ with respect to NaN_3 is unclear. In contrast to the Mo derivative, $WCl_4(CH_3CN)_2$ is soluble in acetonitrile, suggesting a monomeric structure in solution rather than a polymeric one as expected for the sparingly soluble $MoCl_4(CH_3CN)_2$. Therefore, subtle differences in the balance of lattice, solvation, (M-Cl) and ($M-N_3$) bond energies may be responsible for the different reactivities of the two chloro-complexes.

3.2.2 Reaction of Tungsten Hexachloride with Sodium Azide in Acetonitrile.

In contrast to the unreactive $WCl_4(CH_3CN)_2$, tungsten hexachloride reacted slowly with sodium azide in acetonitrile with liberation of a mixture of nitrogen and chlorine. When the gas evolution was complete, a red-brown

solution with a white precipitate of sodium chloride and excess sodium azide was obtained. On reducing the volume of this solution in vacuum, and cooling down to -30°C, dark-brown, needle like crystals precipitated. Even though this extremely moisture sensitive, dark-brown complex (5) was recrystallized from CH_3CN and dried at room temperature in vacuum for several hours, the analytical results were not in good agreement with the composition of the most likely product $WNCl_3(CH_3CN)_2$ (see table 2). The most reasonable interpretation of the composition of (5) is to regard it as a mixture of $WNCl_3(CH_3CN)_2$ and reduced chloroacetonitriletungsten complexes. The latter is formed in a side reaction of WCl_6 with CH_3CN that finally results in the formation of $WCl_4(CH_3CN)_2$ according to equation(66).

$$WCl_6 + 5CH_3CN \longrightarrow WCl_4(CH_3CN)_2 + [CH_3CNH]^+ [HCl_2]^- + 2[\cdot CH_2CN] \qquad (66)$$

CH_3CN by RUSCHKE and DEHNICKE. The existence of the corresponding chloro-derivatives of tungsten and molybdenum has only been mentioned[47]. As both compounds, (5) and (6) are highly sensitive to hydrolysis and the appropriate instruments (glove box, etc.) were not at hand, it was impossible to support the above interpretation by the IR-spectra of the complexes.

3.2.3 Reaction of Tungsten Hexachloride with Sodium Azide and Triphenylphosphine Oxide.

Since the reaction of $MoCl_5$, NaN_3, and $OPPh_3$ in CH_3CN gave the well defined nitrido complex, $MoNCl_3(OPPh_3)_2$, there was good reason to expect the formation of the corresponding tungsten derivative by reaction of WCl_6 with NaN_3 and the same ligand. After adding two equivalents of triphenylphosphine oxide to the red-brown acetonitrile solution obtained from WCl_6 and NaN_3 the colour turned yellow-brown. On reducing the volume a yellow crystalline precipitate was obtained. This compound (7) was recrystallized from CH_2Cl_2 and hexane. A decrease in yield was always observed because of the formation of an oily product if an excess of hexane was added. The complex is stable in dry air but hydrolysed rapidly in the presence of moisture to form a green decomposition product, most probably an oxo-derivative. It dissolves in CH_2Cl_2,

CH_3CN and THF, but is not soluble in ether and hexane. The analytical values are not in good agreement with a complex $WNCl_3(OPPh_3)_2$. Though the reaction was expected to proceed as follows the chlorine content was found to be too high and the tungsten content too low (see table 3 and 6).

$$WNCl_3(CH_3CN)_2 + 2OPPh_3 \xrightarrow{CH_3CN} WNCl_3(OPPh_3)_2 + 2CH_3CN \quad (69)$$

(7)

Complex	Content in %		
	W	Cl	N
(7)	18.02	17.05	0.66
$WNCl_3(OPPh_3)_2$	21.37	12.38	1.61
$WNCl_4(OPPh_3)$	29.37	22.97	2.62
$WNCl_2(OPPh_3)_2$	22.29	8.60	1.70

Table 3. W, Cl^- and N^- content found for (7) and calculated for some hypothetrical products, $WNCl_x(OPPh_3)_y$

The impurities may again be reduced tungsten (IV) chlorides as indicated by the high chloride content. The nitrogen value obtained by the KJELDAHL method and the IR-spectrum (table 7) suggest the presence of a

nitrido tungsten complex, $WNCl_3(OPPh_3)_2$. The IR-spectrum shows the various absorptions of the $OPPh_3$ ligand such as the typical $\nu(P = O)$ frequency at 1120 cm^{-1} and is quite similar to the analoguous Mo complex. In the $\nu(W \equiv N)$ region there is a weak, but chracteristic band at 1027 cm^{-1} indicating the presence of only one $WNCl_3(OPPh_3)_2$ isomer. The absorptions between 230 and 400 cm^{-1} due to W-Cl stretching and bending modes are not very well resolved.

In another attempt, the recrystallized $WNCl_3(CH_3CN)_2$ complex (5) itself was treated with $OPPh_3$ in CH_2Cl_2. A yellow complex (8) was separated in 24% yield having the same properties as the above compound (7). As confirmed by elemental analysis (table 6) its composition is in good agreement with the formula $WNCl_3(OPPh_3)_2$. The IR-spectrum is identical with that of the impure product (7). The isolation and characterization of (8) also provides direct evidence for the reaction of tungsten hexachloride and sodium azide to give a $WNCl_3(CH_3CN)_2$ derivative in acetonitrile as discussed in the previous section. The preparation of pure nitrido complexes seems to be considerably complicated by the need to separate the ubiquitous tungsten chloride impurities and the tendency to form oily products.

In another attempt to prepare $WNCl_3(OPPh_3)_2$, the brownish-black decomposition product (6), was reacted with triphenylphosphine oxide. Thus (6) was suspended in methylenechloride followed by addition of two equivalents of $OPPh_3$. From the brown solution a light brown compound (9) was precipitated. The analytical values for W, Cl and N of the recrystallized complex agreed well with those calculated for $WNCl_3(OPPh_3)_2$ (see table 6). The IR-spectrum (table 7) shows clearly all the characteristic absorptions including a $\nu(W \equiv W)$ band at 1035 cm^{-1}. Unfortunately in a second attempt to synthesize this compound no crystalline product could be obtained but only a brown oil, indicating once more the poor crystallizability observed for the $OPPh_3$ derivatives. The results support without doubt the interpretation of the thermal degradation of $WNCl_3(CH_3CN)_2$ (5) to a $WNCl_3(CH_3CN)$ complex (6), rather than a nitrido tungsten (V) complex formed by an intramolecular reduction as described for $WNBr_3(dipy)$[59].

3.2.4 Reaction of Tungsten Hexachloride with Sodium Azide and Tetrabutylammonium Chloride.

Addition of one equivalent of tetrabutylammonium chloride to the red brown solution prepared from WCl_6 and NaN_3 in acetonitrile gave yellow, sheet like crystals,

The IR-spectrum shows absorptions in the region 235-400 cm^{-1} which correspond to the bending and stretching modes of the metal-chlorine bond. A band at 1033 cm^{-1} seems to be the $\nu(W \equiv N)$ frequency but could not be assigned unambiguously because of its weakness and interference of the tetrabutylammonium cation (see table 7). For the complexes $[Me_4N][WNCl_4]$ and $[Ph_4As][WNCl_4]$, 1036 and 1032 cm^{-1}, respectively, have been reported as the $\nu(W \equiv N)$ frequencies[58],

3.2.5 Reaction of Tungsten Hexachloride with Sodium Azide and 2,2'-Dipridyl.

The dark-brown crystalline compound (5) prepared from WCl_6 and NaN_3 in CH_3CN was dissolved in CH_2Cl_2 and treated with one equivalent of 2,2'-dipyridyl. On concentrating the resulting brown solution a brown-product . (11) was obtained. The latter, however, decomposed immediately and turned greenish-gray after removing the solvent completely. In the presence of CH_2Cl_2 or CH_3CN as a solvent, the same decomposition was found to take place after several days. As the grey final product (12) proved to be insoluble in most solvents, recrystallization could not be accomplished. The compound is stable in air and has no tendency to hydrolyse. Th IR-spectrum exhibits the absorptions expected for dipyridyl and, furthermore,

some bands in the ν(W-Cl) and δ(W-Cl) region, i.e. between 230-400 cm^{-1}. The ν(W≡N) region is not conclusive because a characteristic ν(W≡N) absorption could not be located.

A complex with the composition $WNCl_3$(dipy) has already been synthesized from $WNCl_3$ and dipyridyl in CH_2Cl_2 by DEHNICKE et al.[59] Therefore, the brown substance observed in the reaction discussed above should have been formed in the following way.

$$WNCl_3(CH_3CN)_2 + \text{dipy} \xrightarrow{CH_2Cl_2} WNCl_3(\text{dipy}) + 2CH_3CN \quad (71)$$

Complex	Content in %		
	W	Cl	N
(12)	29.94	27.43	3.31
$WNCl_3$(dipy)	39.76	23.00	9.09
$WNCl_2$(dipy)	43.06	16.61	9.84
$WNCl_4$(dipy)	36.93	28.48	8.43

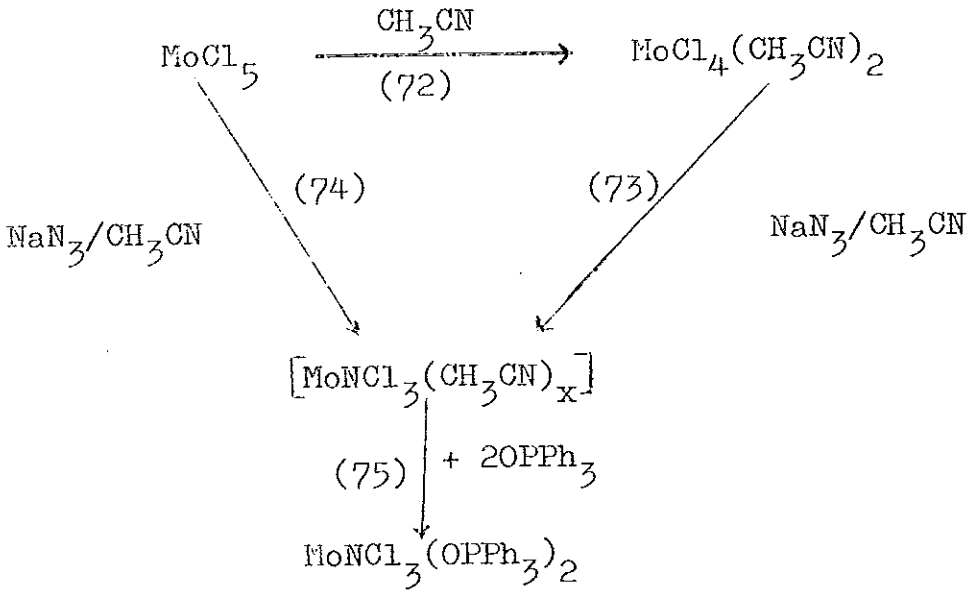
Table 5. W, Cl and N-contents found for (12) and calculated for some hypothetical products.

The grey final product (12) has been analyzed, but the analytical values obtained for W, Cl and N are not conclusive (see table 5 and 6). Though the decomposition

of (11) appears to be in contradiction to the stable complex $WNCl_3(dipy)$ mentioned in the litrature, the use of acetonitrile as a solvent and the different starting compound, $WNCl_3(CH_3CN)_2$ (5) may be responsible for the different course of reaction observed. A similar decomposition product has been obtained in synthesizing the molybdenum analogue from $[MoNCl_3(CH_3CN)_x]$ and diprydyl in acetonitrile[21]. Therefore, the assumption of a reductive decay under formation of $WNCl_2(dipy)$, as reported for the analogous bromo derivative[59], seems to be responsible, but there is no evidence so far in this case.

3.3 Conclusions

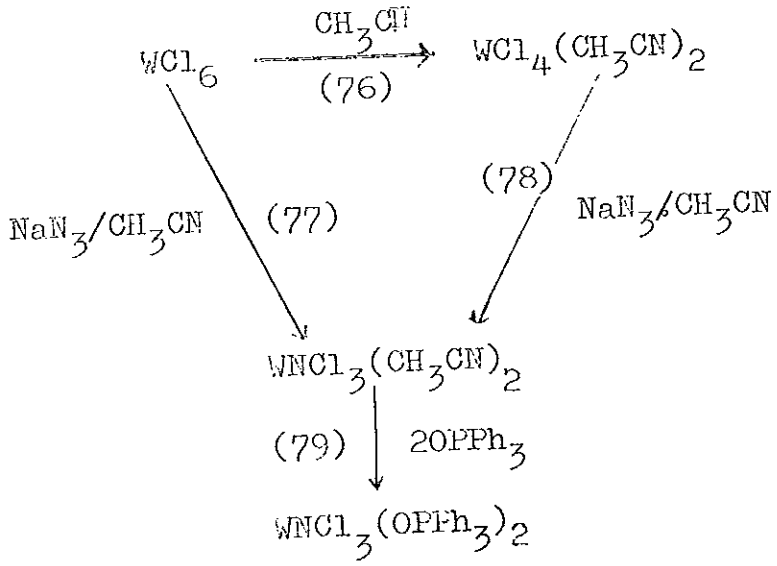
The use of sodium azide for the synthesis of nitrido complexes of Mo(VI) and W(VI) has been described in the previous sections. In the case of molybdenum both $MoCl_5$ and $MoCl_4(CH_3CN)_2$ may be used as starting compounds, where as for tungsten only WCl_6 reacts with NaN_3 in acetonitrile. The processes taking place in the synthesis of nitridomolybdenum(VI) complexes can be summerized as shown in the following scheme.



It should be noted that the reactions (73) and (74) proceed via different azide intermediates but result in the same stable $[MoNCl_3(CH_3CN)_x]$ complex. Moreover (74) seems to be stereospecific whereas (73) leads to a mixture

of stereoisomeric nitrido complexes as shown for $MoNCl_3(OPPh_3)_2$.

For the synthesis of nitridotungsten(VI) complexes a similar reaction scheme can be outlined.



Scheme 2.

Although, the formation of nitridotungsten(VI) complexes has been proved by the synthesis of $WNCl_3(OPPh_3)_2$, there is a parallel reaction (76) that produces $WCl_4(CH_3CN)_2$ which has proved to be inert to NaN_3 and thus represents an ubiquitous source of impurities.

The colours and the corresponding W, Cl, and N -contents of the compounds attempted to be synthesized are listed in table 6. For the impure tungsten complexes, the most likely main constituent is indicated in brackets. The high chlorine content and the low tungsten values found

for (5), (7), (10) and (12) confirm the presence of tungsten(IV) chlorides as source of impurities.

The essential IR-spectroscopic data are collected in table 7. The presence of one or several $\nu(M \equiv N)$ absorptions in the range of 1100-1000 cm^{-1} is characteristic for all nitrido complexes of Mo(VI) and W(VI). For the tungsten adducts with dipy and Bu_4NCl a definite assignment of the $(M \equiv N)$ frequency is not possible. The characteristic absorptions in the $\nu(M-Cl)$ and $\delta(M-Cl)$ region are badly resolved (see Fig. 1 to 7) and not conclusive for structural elucidation.

In conclusion, the reaction of $MoCl_5$ or $MoCl_4(CH_3CN)_2$ with NaN_3 in CH_3CN is a reliable method for the preparation of nitridomolybdenum complexes. The corresponding reaction of WCl_6 and NaN_3 in CH_3CN seems, however, to be unselective and cumbersome, and is therefore limited in its applicability.

Complex[1]	Colour	Content in % found (calcd.)		
		Mo/W	Cl	N
$MoNCl_3(OPPh_3)_2^2$ (2)	light brown	12.72(12.41)	13.13(13.76)	1.86(1.81)
$[Bu_4N][MoNCl_4]$ (3)	red-brown, shiny sheet like	18.82(19.1)	28.11(28.69)	6.68(5.76)
$MoNCl_3(OPPh_3)_2^3$ (4)	light brown	12.36(12.41)	13.66(13.77)	1.35(1.81)
$\{WNCl_3(CH_3CN)_2\}$ (5)	dark-brown	44.39(47.59)	31.15(27.53)	11.40(10.88)
$\{WNCl_3(OPPh_3)_2\}^4$ (7)	yellow	18.02(21.37)	17.61(12.38)	0.66(1.61)
$WNCl_3(OPPh_3)_2^5$ (8)	yellow	19.94(21.37)	12.46(12.38)	1.03(1.61)
$WNCl_3(OPPh_3)_2^6$ (9)	brown	20.71(21.39)	20.71(21.38)	1.13(1.61)
$\{[Bu_4N][WNCl_4]\}$ (10)	yellow, shiny sheet like	28.69(31.58)	29.44(24.36)	4.26(4.81)
$\{WNCl_3(dpy)\}$ (12)	grey	29.94(39.01)	27.43(23.00)	3.31(9.13)

Table 6. colour and analytical results of nitrido complexes synthesized.

1. If impure the most likely constituent is put into brackets { }
2. From $MoCl_4(CH_3CN)_2$ and NaN_3
3. From $MoCl_5$ and NaN_3
4. From (5) and $OPPh_3$ in CH_3CN
5. From (5) and $OPPh_3$ in CH_2Cl_2
6. From decomposition product of (5) and $OPPh_3$ in CH_2Cl_2

Complex		(M ≡ N) in cm^{-1}	(M-Cl), (M-Cl) in cm^{-1} (VS)
$MoNCl_3(OPPh_3)_2$	(2)	1026, 1035, 1053 (m)	318
$[Bu_4N][MoNCl_4]$	(3)	1067 m	349
$MoNCl_3(OPPh_3)_2$	(4)	1027 m	319
$\{WNCl_3(OPPh_3)_2\}$	(7)	1027 w	--
$WNCl_3(OPPh_3)_2$	(8)	1030 m	--
$WNCl_3(OPPh_3)_2$	(9)	1032 m	308
$\{[Bu_4N][WNCl_4]\}$	(10)	1033[1] w	310
$\{WNCl_3(dpy)\}$	(12)	not clear	--

Table 7. Characteristic ν(M ≡ N) and $\nu(\delta)$ (M-Cl) absorptions of the nitrido complexes of Mo and W synthesized in KI.

1. Cannot be assigned an unambiguously

4. EXPERIMENTAL PART

4.1 General

The majority of the compounds synthesized were senstive to hydrolysis and in some cases, to oxidation. Thus complete exclusion of air and moisture was necessary in most of the experiments. For this purpose nitrogen gas produced locally by the SEDE factory was used as an inert gas. Unfortunately this gas was proved to contain about 4% of oxygen. Subsequent attempts by the SEDE factory to produce a purer nitrogen gas resulted in a maximum content of 0.5% oxygen. The need to remove even this 0.5% of oxygen was a challenging problem. Various trials were made to remove this oxygen. Thus, copper foil activated by a concentrated solution of NH_3/NH_4Cl in water was packed in two five liter containers. After bubling the impure nitrogen gas through, the oxygen content was lowered to about 0.2%. A more effective method, however, seemed to be the use of an alkaline pyrogallol solution (65 g pyrogallol/L of 5N aqueous NaOH solution). This was found to absorb oxygen very fast and with a high capacity. The nitrogen bubbled through two such pyrogallol containing columns (length 100 cm and diameter 5 cm.) was first dried over $CaCl_2$. For further purification the gas was allowed to pass over columns packed with a commercial catalyst to trap traces

of oxygen and coloumns filled with NaOH, P_2O_5 and molecular sieve (Type 4A). The nitrogen purified in this manner was sufficiently dry and the oxygen content found to be less than 0.05%.

All solvents used had to be dry and deaerated. Acetonitrile and dichloromethane were repeatedly refluxed over P_2O_5 in an atmosphere of nitrogen and distilled off when required. Diethyl ether was first refluxed over $LiAlH_4$ and then distilled under nitrogen gas. The distillate was again refluxed over freshly cut Na metal and benzophenone until the solution adopted a violet color. Hexane was dried by refluxing with $LiAlH_4$ under nitrogen.

Molybdenum pentachloride, tungsten hexachloride, and sodium azide were commercial products and used without further purification.

Tetrabutylammonium chloride and 2,2' -dipyridyl were also available in the Department. Triphenylphosphine oxide was prepared by oxidation of triphenylphosphine with $K_2S_2O_8$ and conc. H_2SO_4 according to a procedure outlined by KENNEDY et al.[64]

Various glasswares for the inert gas (SCHLENK) technique were either modified or made in the glass blowing section of the Department of Chemistry.

4.2 Preparations and Conversions

4.2.1 Tetrachlorobis(acetonitrile)molybdenum(IV); $MoCl_4(CH_3CN)_2$ [62].

To a Schlenk tube with 40 ml of acetonitrile 2.25 g (8.24 mmol) of molybdenum pentachloride was slowly added under nitrogen. The reaction mixture was stirred for 48 hours. The brown precipitate formed was filtered, washed with three 5 ml portions of acetonitrile, and dried in vacuum at 50°C. The brown crystalline solid is sensitive to hydrolysis but can be handled in dry air for a short time. The compound is sparingly soluble in acetonitrile, dichloromethane, and insoluble in ether and hexane.

Yield: 1.91 g (72.3% based on $MoCl_5$)

Analysis: Found(calc.for $MoCl_4(CH_3CN)_2$); Mo, 29.5% (29.99); Cl, 44.10(44.33)%.

4.2.2 Trichloronitridobis(triphenylphosphine oxide)molybdenum(VI), $MoNCl_3(OPPh_3)_2$.

4.2.2.1 From Tetrachlorobis(acetonitrile)molybdenum(IV) [21].

1.38 g (4.31 mmol) of $MoCl_4(CH_3CN)_2$ was added to a schlenk tube containing 0.34(5.23 mmol) of NaN_3 and 25 ml of CH_3CN under nitrogen. The mixture was stirred until the evolution of gas was completed. The NaCl formed during the reaction and excess NaN_3 was filtered off. To the

red purple filterate 2.68 g (9.63 mmol) of triphenyl phosphine oxide dissolved in 30 ml of CH_3CN was added while shaking vigorously. A light brown precipitate was formed. The mixture was cooled to - 30°C then filtered off, followed by washing with small portions of a hexane / ether mixture (4:1 ratio) and dried at 50°C in vacuum. The light brown complex is stable in dry air, however, turns blue when in contact with moisture. It dissolves well in CH_2Cl_2 moderately in CH_3CN, ether and THF, but is not soluble in hexane. It can be recrystallized by dissolving in CH_2Cl_2 and then precipitating with hexane.

Yield: 2.21g (65.1% based on $MoCl_4(CH_3CN)_2$).

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

4.2.2.2 From Molybdenum(V) Chloride

In Schlenk tube filled with nitrogen and containing 30 ml of CH_3CN, 1.4g(5.12 mmol) of $MoCl_5$ and 0.37g(5.69 mmol) of NaN_3 was added. The mixture was stirred until no more gas was evolved. The resulting violet solution was filtered and then treated with 3g(10.78 mmol) of $OPPh_3$ dissolved in 25 ml of CH_3CN . After decreasing the volume of the dark brown solution to one fourth of the original volume a brown crystalline product precipitated which after cooling to -30°C was filtered, washed with hexane, and dried at 50°C in vacuum. The product is stable in dry air, but turns blue in color when in contact with moisture. It is well soluble in

CH_2Cl_2, moderately in CH_3CN, ether and THF , but not in hexene. Recrystallization by dissolving in CH_2Cl_2 and then precipitating with hexane gave a light brown product.

Yield: 2.19 (69.8% with respect to $MoCl_5$)

Analysis: Found (calc. for $MoNCl_3OPPh_3)_2$: Mo, 12.36 (12.41); Cl, 13.66 (13.77); N 1.35 (1.81)%

4.2.3 Tetrabutylammonium Tetrachloronitridomolybdate(VI) $[Bu_4N^+][MoNCl_4^-]$[21]

4.5g (14.07 mmol) of $MoCl_4(CH_3CN)_2$ and 1.0g (15.38 mmol) NaN_3 were stirred under nitrogen in 110 ml of acetonitrile until the evolution of nitrogen was completed. The red-purple solution was filtered and further reacted with a solution of 3.2g (14.8 mmol) tetrabutylammonium chloride in 50 ml of CH_3CN. After filtering the resulting mixture once more, the solvent was completely removed in vacuum. The residue was dissolved in CH_2Cl_2 and precipitated by hexane (Precipitate slowly because of danger of oil formation!) to give red-brown, shiny, sheet like crystals. This was filtered off, washed with little CH_2Cl_2/hexane(1/3) mixture, followed by pure hexane, and dried in vacuum at 50°C. The compound is moisture sensitive, readily soluble in CH_2Cl_2, CH_3CN, and THF, sparingly soluble in ether, and insoluble in hexane. Recrystallization is carried out by dissolving in CH_2Cl_2 and precipitating with hexane.

4.2.6 Reaction of Tungsten(VI) Chloride with Sodium Azide in Acetonitrile

3.73 g (9.41 mmol) of WCl_6 and 0.67g(10.31 mmol) of NaN_3 was suspended in 35 ml of CH_3CN under nitrogen. The mixture was stirred until no more gas was evolved. After filtering off the NaCl formed and excess NaN_3, the dark brown filtrate was reduced by vacuum to one-fourth of the original volume. The dark brown needlelike crystals the precipitatinn of which was completed by coolling to -30°C were filtered, washed three times with 7 ml portions of CH_3CN (cooled to -30°C), and finally sucked dry in vacuum at room temperature. The complex is extremly sensitive to moisture, changes blue on exposure to air, and was found to decompose to a black - product when heated to 50°C. The compound is highly soluble in CH_2Cl_2 moderately soluble in acetonitrile, but insoluble in hexane and ether. It can be recrystalized from aceto-nitrile.

Yield: 2.96 g (81.5% with respect to WCl_6 and the formula $WNCl_3(CH_3CN)_2$).

Analysis: Found (calc. for $WNCl_3(CH_3CN)_2$): W, 44.39 (47.59); Cl 31.15 (27.53); N, 11.40 (10.88)

2.3 g (8.30 mmol) of Bu_4NCl dissolved in 25 ml of CH_3CN was then added dropwise to the dark brown solution while agitating vigorously. In doing so yellow, shiny, sheet-like crystals were formed. Precipitation was completed by decreasing the volume of the solution to one-third. The yellow solid was filtered off, washed three times with 5 ml portions of ether and dried at 50°C in vacuum. The compound dissolves well in CH_3CN and CH_2Cl_2, but is insoluble in hexane and ether. It can be handled in dry air for a short time but turns blue in contact with moisture. Recrystallization by dissolving in CH_2Cl_2 and then precipitating with hexane gave a nicely crystallized yellow product.

Yield: 3.21 g (73.0% with respect to WCl_6 and the formula $[Bu_4N][WNCl_4]$).

Analysis: Found (calc. for $[Bu_4N][WNCl_4]$): W, 28.69 (31.58); Cl, 29.44 (24.36); N, 4.26 (4.81)%.

4.2.9 Reaction of Tungsten(VI) Chloride with Sodium Azide and 2,2'- Dipyridyl in Acetonitrile

2.1 g (6.30 mmol) of WCl_6 and 0.4 g (6.15 mmol) of NaN_3 was converted in 25 ml of CH_3CN in the same manner as above. The dark brown solution was filtered and the solvent sucked off completely in vacuum. The brown crystalline solid resulting was dissolved in 20 ml

of CH_2Cl_2 and treated with 0.9 g (5.76 mmol) of 2,2' -depyridyl dissolved in 20 ml CH_2Cl_2 under vigorous shaking. On reducing the volume of the solution, a brown precipitate was formed that decomposed to a greyish product after complete removal of the solvent. The same thing happend if the product was isolated from acetonitrile solution. The precipitate was filtered off, washed with three portions of 5 ml hexane, and dried at room temperature in vacuum. The greyish product could not be recrystallized as it is insoluble in CH_3CN, CH_2Cl_2, hexane, and ether.

Yield: 2.2 g (89.8% with respect to WCl_6 and the formula $WNCl_3$(dipy))

Analysis: Found (calc. for $WNCl_3$(dipy)): W, 29.94 (39.91) Cl 27.43 (22.00); N 3.3 (9.13) %.

4.2.10 Reaction of the Nitrido Acetonitrile Tungsten Complex (5) with Triphenylphosphine Oxide in Methylenechloride.

1.17 g (3.03 mmol calculated for $WNCl_3(CH_3CN)_2$) of the nitrido acetonitrile tungsten complex (5) was dissolved in 15 ml of CH_2Cl_2 followed by addition of 1.8 g (6.47 mmol) of triphenylphosphine oxide in 10 ml of the same solvent. The resulting yellow solution was filtered. Precipitation with about 25 ml of hexane gave a yellow

crystalline solid. The latter was filtered off, washed twice with 5 ml portions of hexane, and dried in vacuum. Properties and recrystallization are the same as described for compound (7) (see section 4.2.7).

Yield: 0.62 g (23.9% with respect to $WNCl_3(CH_3CN)_2$ and $WNCl_3(OPPh_3)_2$).

Analysis: Found (calc. for $WNCl_3(OPPh_3)_2$): W, 19.94 (21.37); Cl, 12.46 (12.38); N, 1.03 (1.61)%.

4.2.11 Thermal Decomposition of the Nitrido Acetonitrile Tungsten Complex (5)

The nitrido acetonitrile tungsten complex (5) was heated at 50°C in vacuum for two hours. In doing so the dark-brown starting compound turned black. This degradation product (6) is only slightly sensitive to moisture. It is moderately soluble in CH_2Cl_2, acetonitrile, but insoluble in ether.

4.2.12 Reaction of the Decomposition Product (6) with Triphenylphosphine Oxide in Methylenechloride.

2.05 g (5.94 mmol calculated for $WNCl_3(CH_3CN)$) of the decomposition product (6) was dissolved in 25 ml of CH_2Cl_2. The brown solution was treated with 3.4 g (12.23 mmol) of triphenylphosphine oxide dissolved in 20 ml of the same solvent. The latter was filtered and its volume decreased

by vacuum to one-third. Precipitation with 15 ml of hexane gave a light-brown solid. This was filtered, washed twice with 5 ml portions of hexane, and dried in vacuum. The light brown product is stable in dry air for a short time, but changes blue in contact with moisture. It is soluble in CH_3CN and CH_2Cl_2, little in ether and benzene, and insoluble in hexane. Recrystallization can be achieved by dissolving the product in CH_2Cl_2 and precipitating with hexane (Danger of oil formation!). A second attempt to prepare this complex failed because of its poor crystallizability.

Yield: 1.4g (27.4% with respect to $WNCl_3(CH_3CN)$ and $WNCl_3(OPPh_3)_2$).

Analysis: Found (calc. for $WNCl_3(OPPh_3)_2$): W, 20.71 (21.37); Cl, 11.81 (12.38); N, 1.13 (1.61)%

4.3 Analysis

4.3.1 Determination of Oxygen in Nitrogen Gas

4.3.1.1 Sodium Benzophenone Method

1.82 g (10 mmol) of benzophenone and 0.5g (22 mmol) Sodium were shaken in 100 ml of dry ether under nitrogen until the mixture became dark violet. This violet solution resulting from the formation of disodium benzophenone was introduced drop by drop into a one litre flask filled with nitrogen gas. When the colour remains blue all the oxygen in the flask is chemically absorbed. 1 mmol of oxygen decolorizes 4 mmol of disodium benzophenone.

4.3.1.2 Copper-Ammonia-Ammonium Chloride Method

Nitrogen filled in a gas burette is introduced to a container packed with copper foil and NH_3/NH_4Cl aqueous solution. After a while the nitrogen is allowed to flow back into the burette. The difference in the gas volume is due to the amount of oxygen absorbed.

4.3.2 Elemental Analysis

4.3.2.1 Determination of Chloride

The complexes containing 20 to 40 mg chloride were either dissolved in strong NaOH solution and a few drops of H_2O_2 or oxidized by the SCHÖENIGER method and absorbed

in 50 ml of 2N NaOH solution. These solutions were acidified with 2N HNO_3 and the chloride content determined by potentiometric titration with 0.1 N $AgNO_3$[66].

4.3.2.2 Determination of Molybdenum and Tungsten

Both elements were determined gravimetrically by the oxinate method[67]. Solutions containing 5-50 mg of Mo or W were prepared in a similar manner as for the chloride determination. The solutions containing molybdate were acidified with 2N acetic acid, followed by addition of 10% ammonium acetate, then heated to boiling, and precipitated with an excess of a solution of 3g 8-hydroxyquinoline in 100 ml of conc. acetic acid. The solution was boiled and filtered hot through a G4 frit. The molybdenyl oxinate was dried at 120-140°C. Similarly the tungstate solution was made slightly basic precipitated with 4% alcoholic solution of 8-hydroxyquinoline, boiled, and filtered through a G4 frit. The tungstenyl oxinate was dried at 120°C.

4.3.2.3 Determination of Nitrogen

Each determination was carried out with quantities of the substance containing 2 to 5 mg of nitrogen. The samples were transfered into a KJELDAHL flask and then digested by 25 ml of conc. H_2SO_4 in the presence of 0.1 g of a commercial KJELDAHL catalyst, containing $CuSO_4$ or Se[68].

When the solution had turned light yellow digestion was completed. The content was diluted to 250 ml and mixed with 25 ml 4% Na_2S solution. This was made basic by 15 M aqueous NaOH solution, boiled, and the ammonia liberated absorbed by 50 ml of 0.05N H_2SO_4. The distillation was stopped when half of the water had been distilled into the receiver. The acid was back titrated with 0.1N NaOH solution. From the volume of NaOH solution consumed, the amount of NH_3 and the percentage of nitrogen in the compound was calculated.

4.3.3 IR-Spectra

The IR-spectra of the compounds were measured using the IR-spectrometers Perkin Elmer 727B and Pye Unican SP 2000. The samples were prepared as KBr(> 600 cm^{-1}) or KI discs (200 -600 cm^{-1}). For the compounds tending to hydrolyse KI was preferred. The spectra are collected in Appendix, Fig. 1 to 7.

SUMMARY

It was the objective of this project to synthesize and characterize some nitridomolybdenum and tungsten complexes. The results obtained are summerized as follows.

1. In accordance to the literature the nitridomolybdenum(VI) complexes $MoNCl_3(OPPh_3)_2$ and $[Bu_4N][MoNCl_4]$ were prepared from $MoCl_4(CH_3CN)_2$ and sodium azide in acetonitrile followed by addition of the appropriate ligands. The compounds were characterized by elemental analysis and IR-spectrum. The latter confirmed $MoNCl_3(OPPh_3)_2$ (2) to consist of a mixture of three stereoisomers.

2. Molybdenum pentachloride was found to react directly with sodium azide in acetonitrile. Subsequent addition of triphenylphosphine oxide gave the complex $MoNCl_3(OPPh_3)_2$ (4) which consists of only one stereoisomer.

3. Tungsten hexachloride and sodium azide reacted in acetonitrile to give a dark brown, but impure nitrido acetonitrile tungsten (VI) complex (5) mainly consisting of $\{WNCl_3(CH_3CN)_2\}$ which decomposes at about 50°C to give an acetonitrile depleted black compound $\{WNCl_3(CH_3CN)\}$ (6).

4. The reaction of $WNCl_3(CH_3CN)_2$ (5) with triphenylphosphine oxide gave yellow, impure $\{WNCl_3(OPPh_3)\}$ (7). From the recrystallized complex (5) and triphenylphosphine

oxide in methylenechloride a yellow compound with 23% yield was obtained. The elemental analysis and the IR-spectrum are consistent with the formula $WNCl_3(OPPh_3)_2$. The decomposition product (6) reacted with triphenyl-phosphine oxide to form a light brown complex $WNCl_3(OPPh_3)_2$ (9) also characterized by elemental analysis and IR-spectrum. This reaction, however, could not be reproduced.

5. The reaction of $\{WNCl_3(CH_3CN)_2\}$ (5) with Bu_4NCl gave a yellow complex. Though the product is likely to contain $\{Bu_4N\}[WNCl_4]\}$ neither elemental analysis nor IR-spectrum are conclusive.

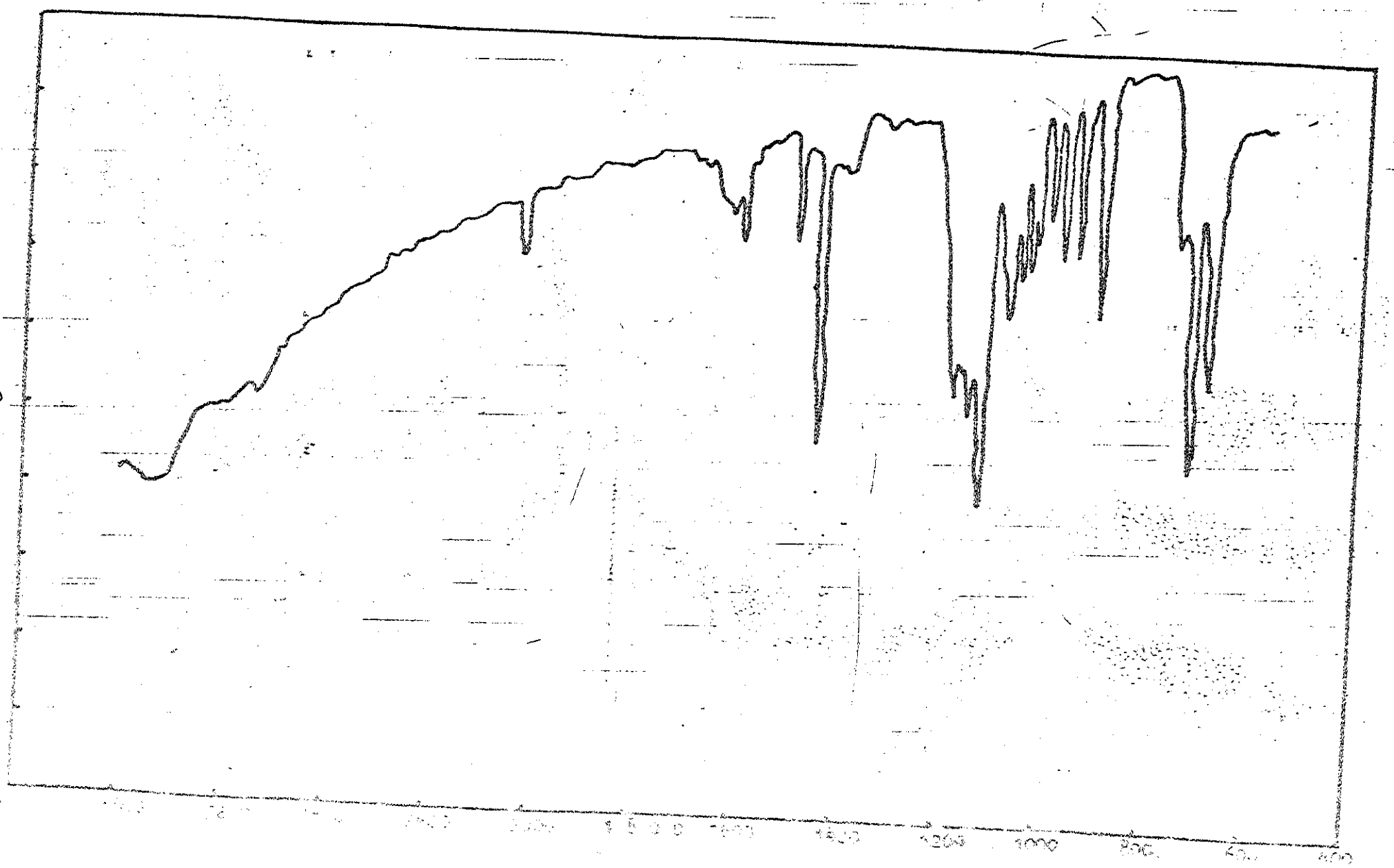
6. The reaction of (5) with 2,2'-dipyridyl gave a brown complex that decomposed at room temperature. The nature of the decomposition product could not be understood.

7. The source of impurity in the nitridotungsten complexes (5), (7), (10) and (12) is suggested to be a side reaction of WCl_6 with acetonitrile eventually leading to $WCl_4(CH_3CN)_2$ which in contrast to its Mo analogue is inert to sodium azide.

Thus, it is possible to conclude that, sodium azide can be used for the synthesis of nitridomolybdenum complexes either from $MoCl_4(CH_3CN)_2$ or $MoCl_5$ in acetonitrile. Though

the reaction of WCl_6 and NaN_3 gives nitridotungsten complexes, its applicability is limited due to the difficulty of obtaining pure product.

Fig. 1a. IR-spectrum of $MoNCl_3(OPPh_3)_2$ (2) /on KBr



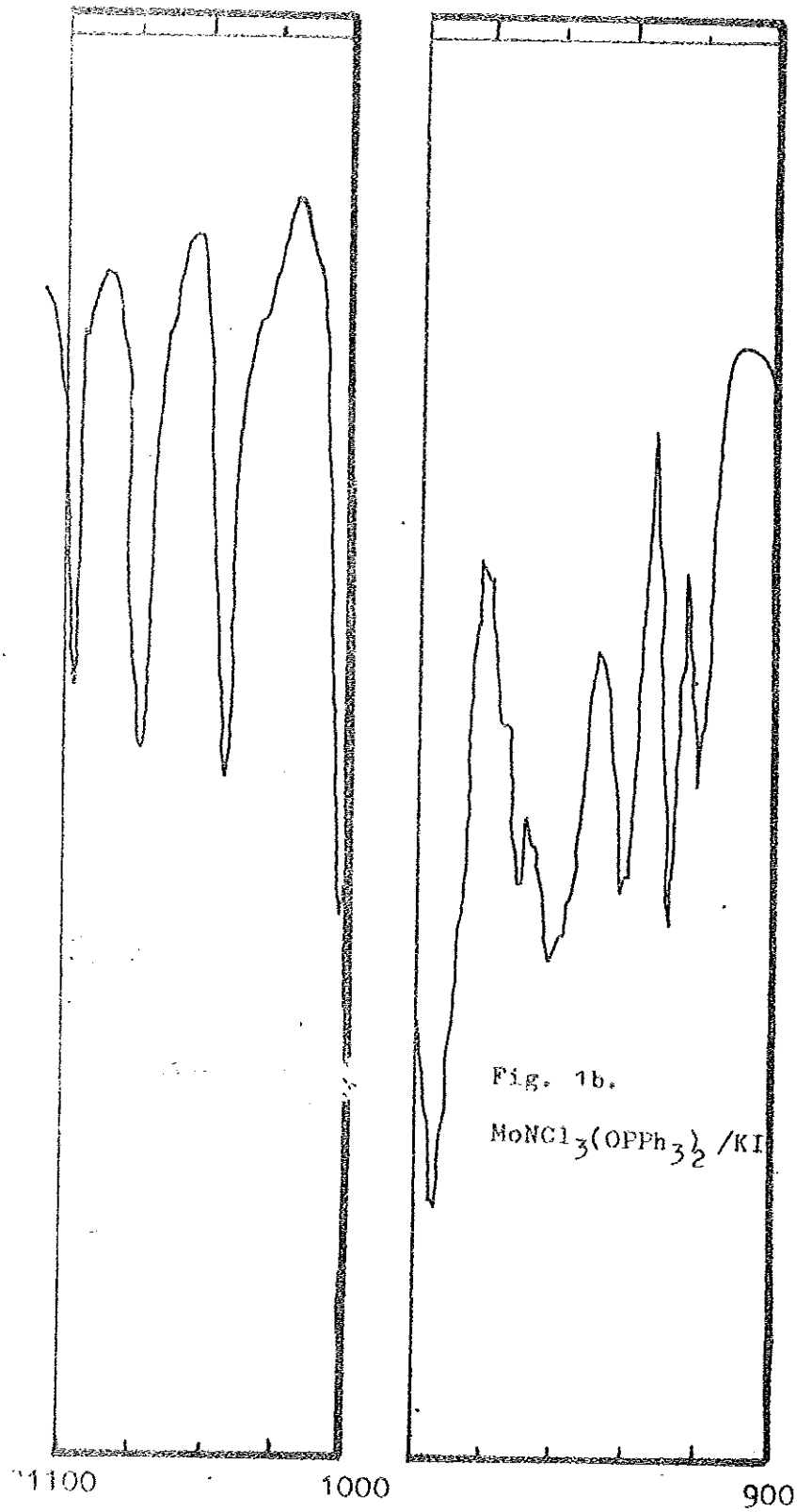


Fig. 1b.

$MoNCl_3(OPPh_3)_2$ /KI

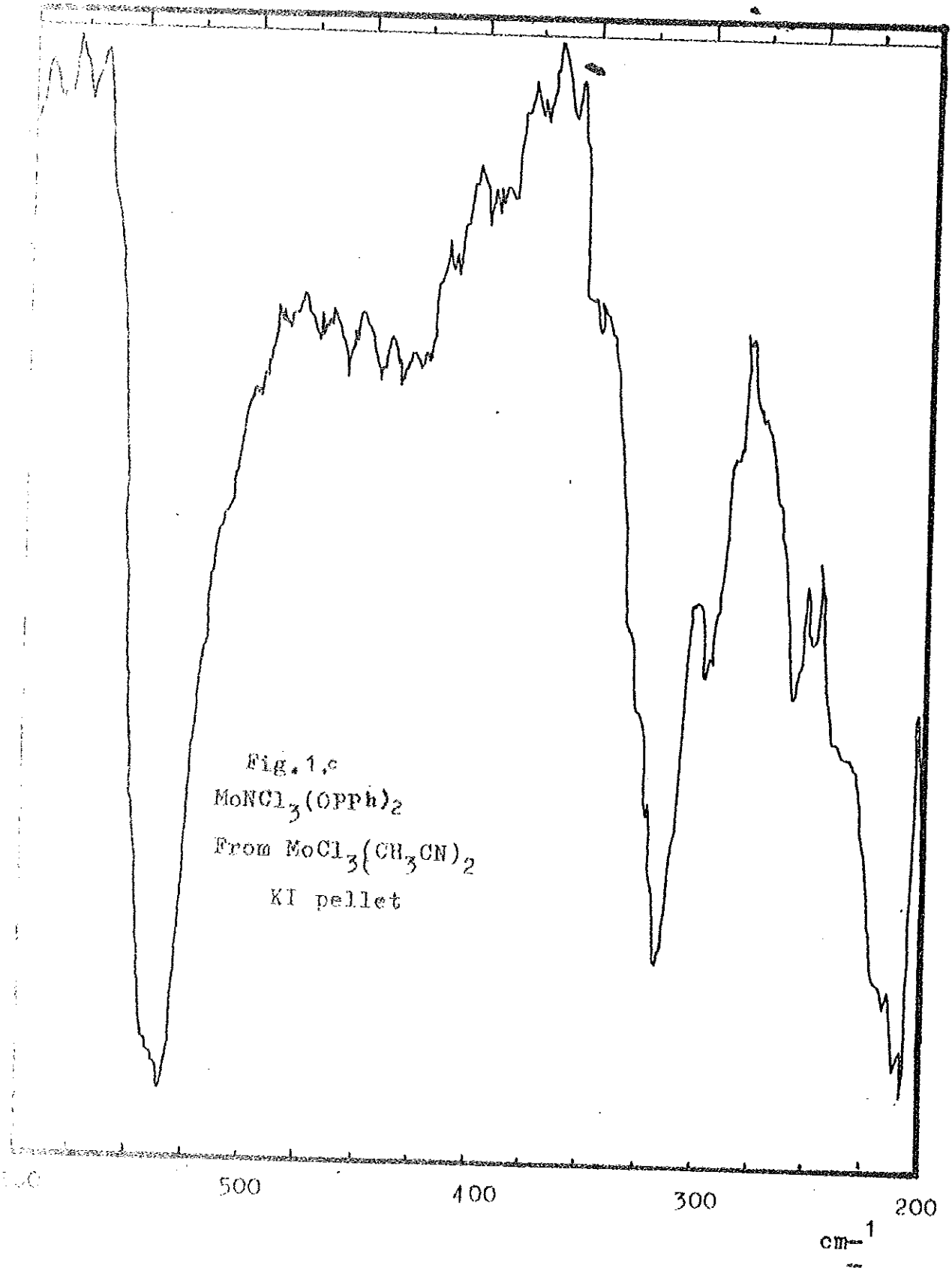
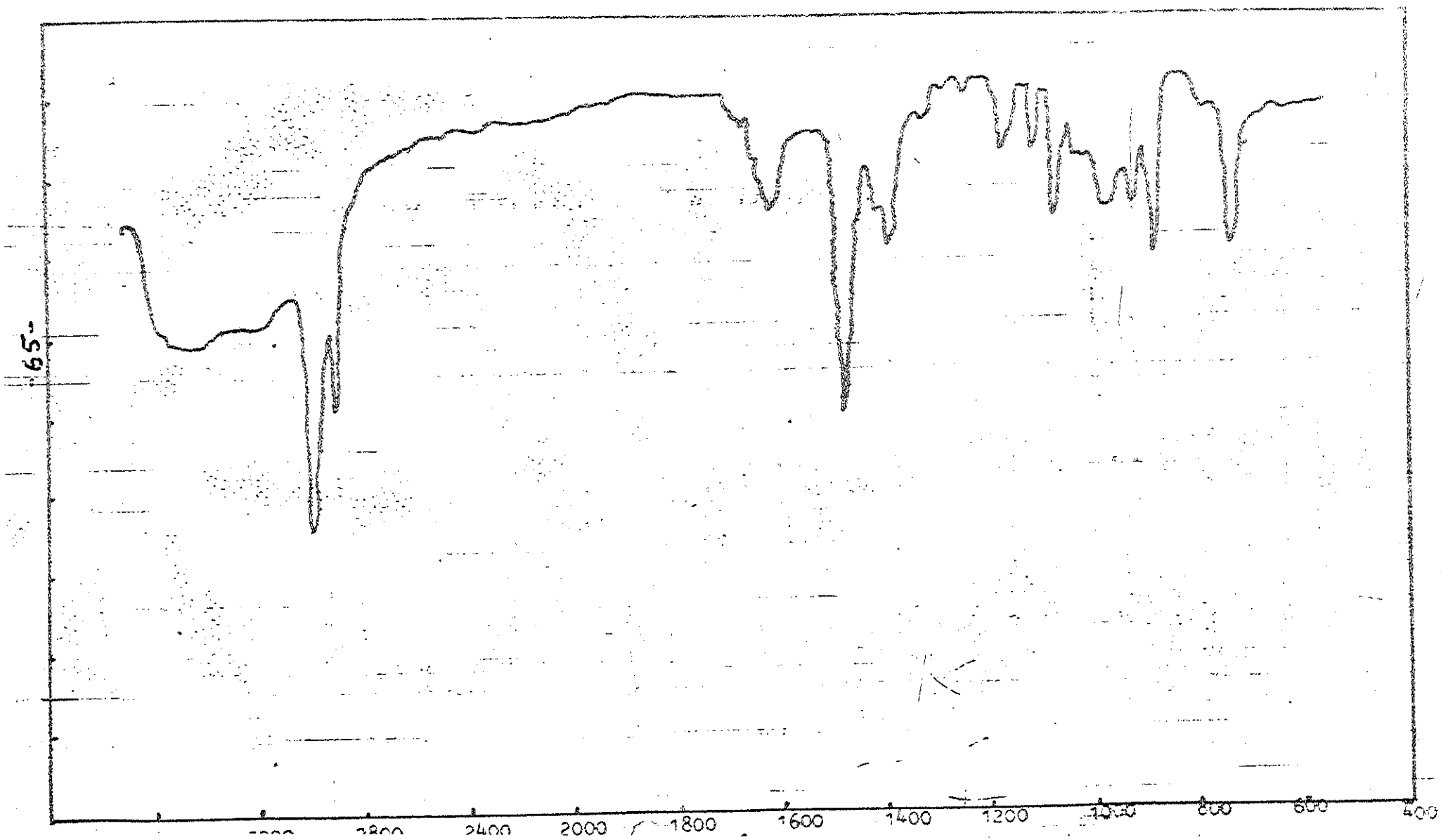


Fig. 1,c
$MoNCl_3(OPPh)_2$
From $MoCl_3(CH_3CN)_2$
KI pellet

Fig. 2a. IR-spectrum of [illegible] (2) [illegible]



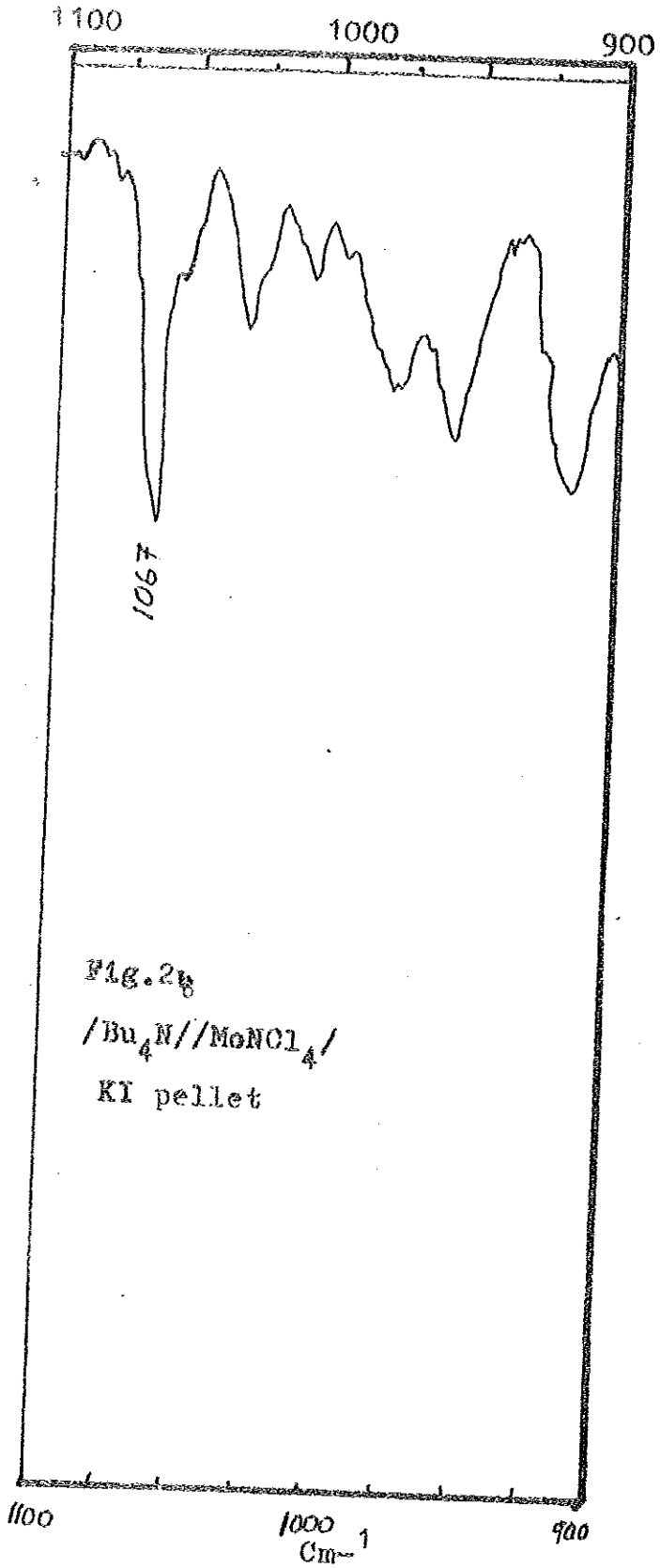


Fig.2b

/Bu_4N//$MoNCl_4$/

KI pellet

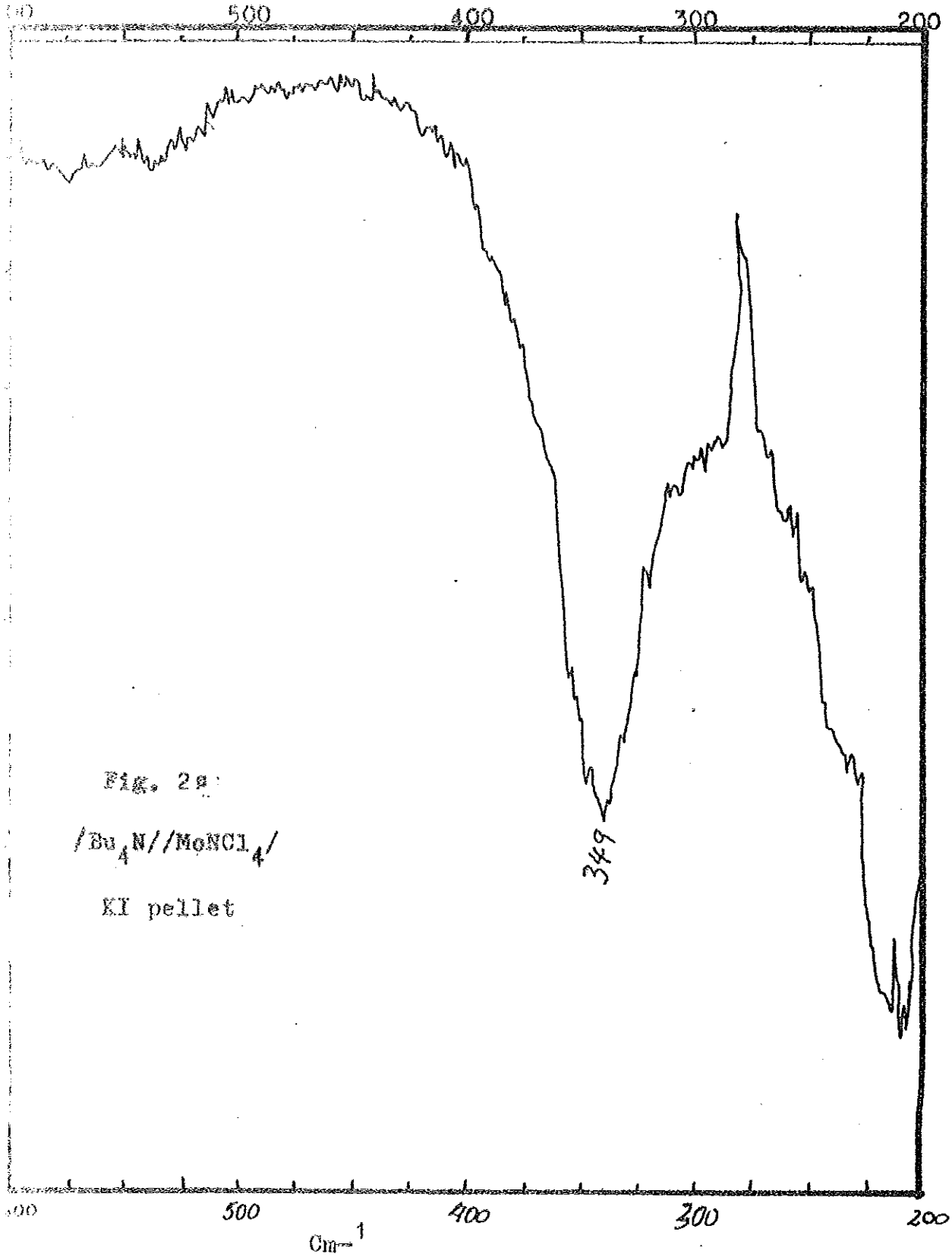
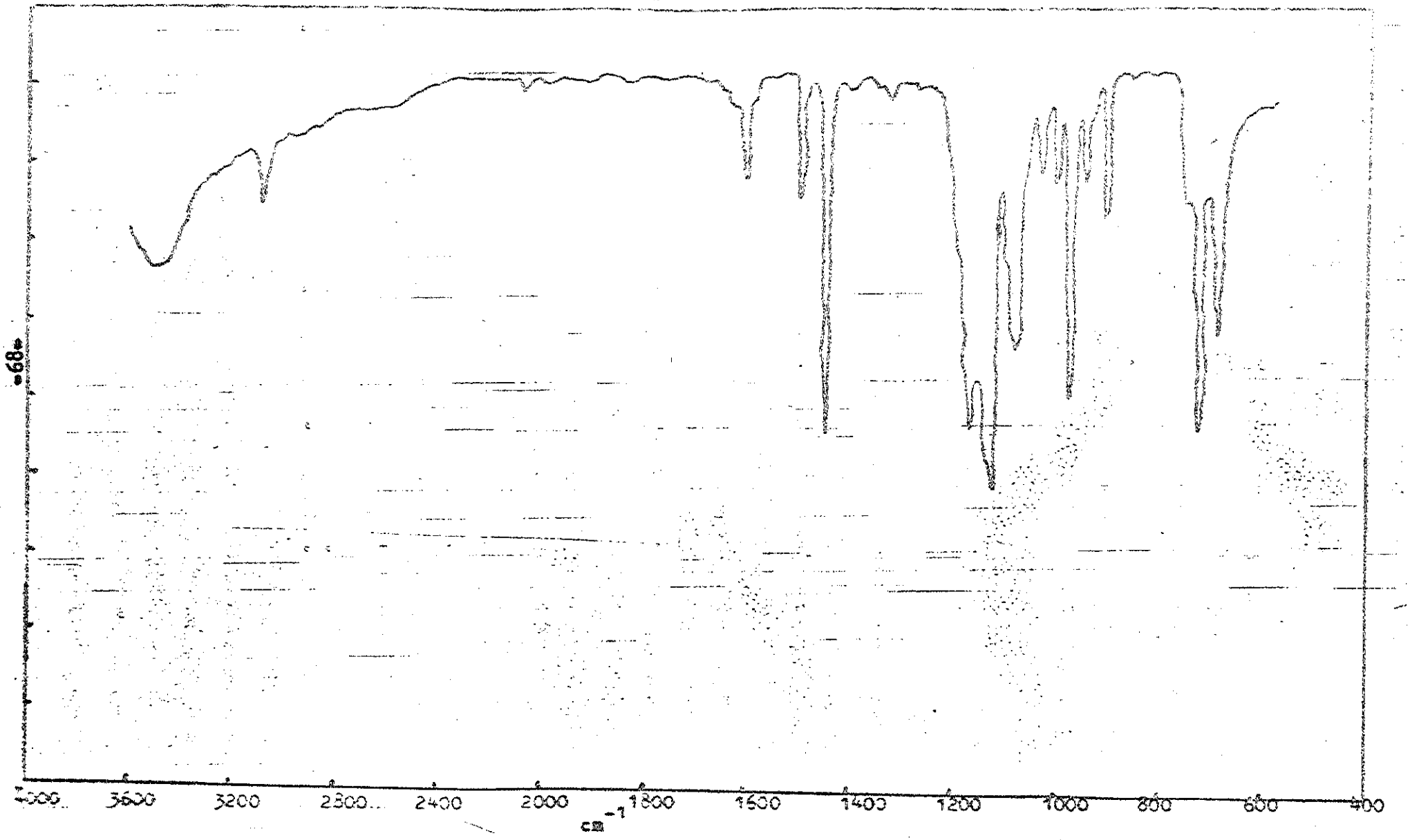


Fig. 2a:

$/Bu_4N//MoNCl_4/$

KI pellet

Fig. 3a. IR-spectrum of $NbOCl_3(OPPh_3)_2$ (2) for KBr



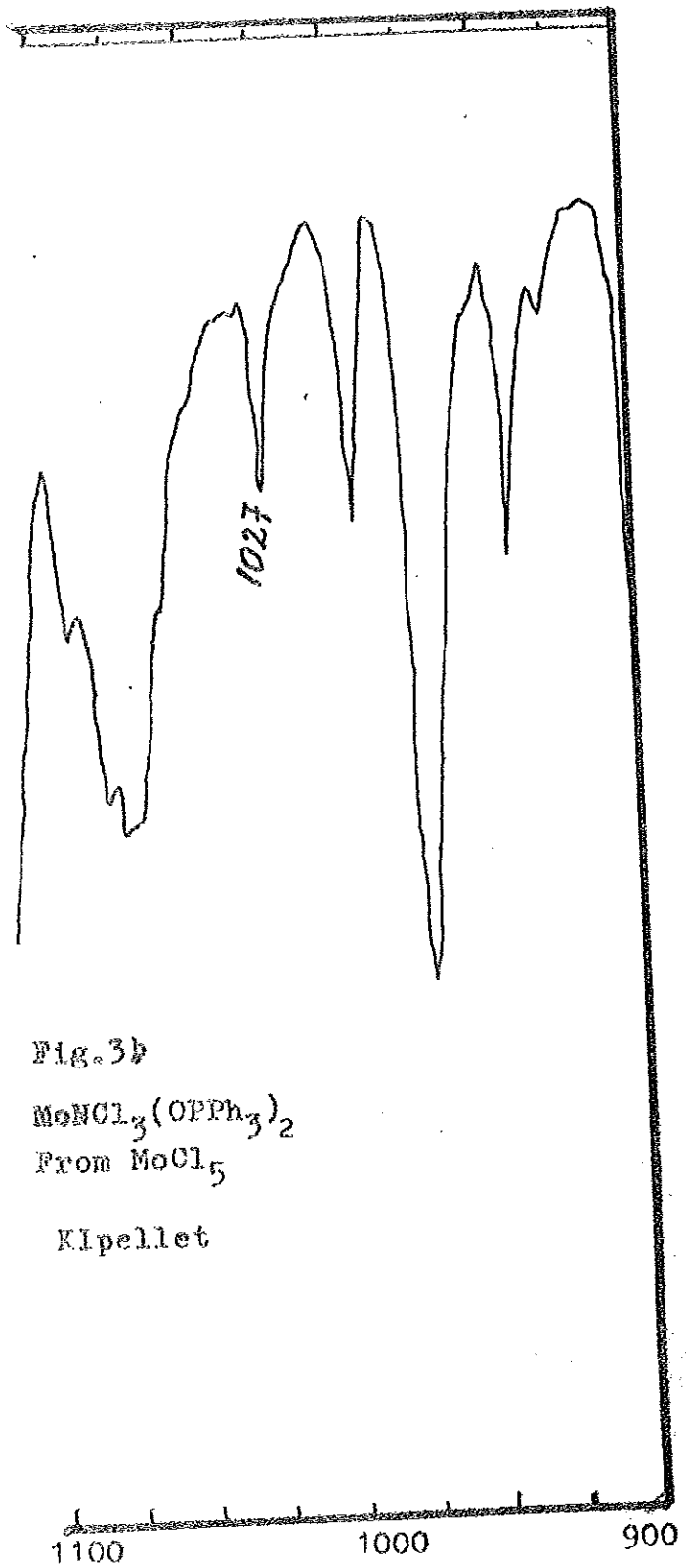


Fig. 3b

$MoNCl_3(OPPh_3)_2$
From $MoCl_5$

KI pellet

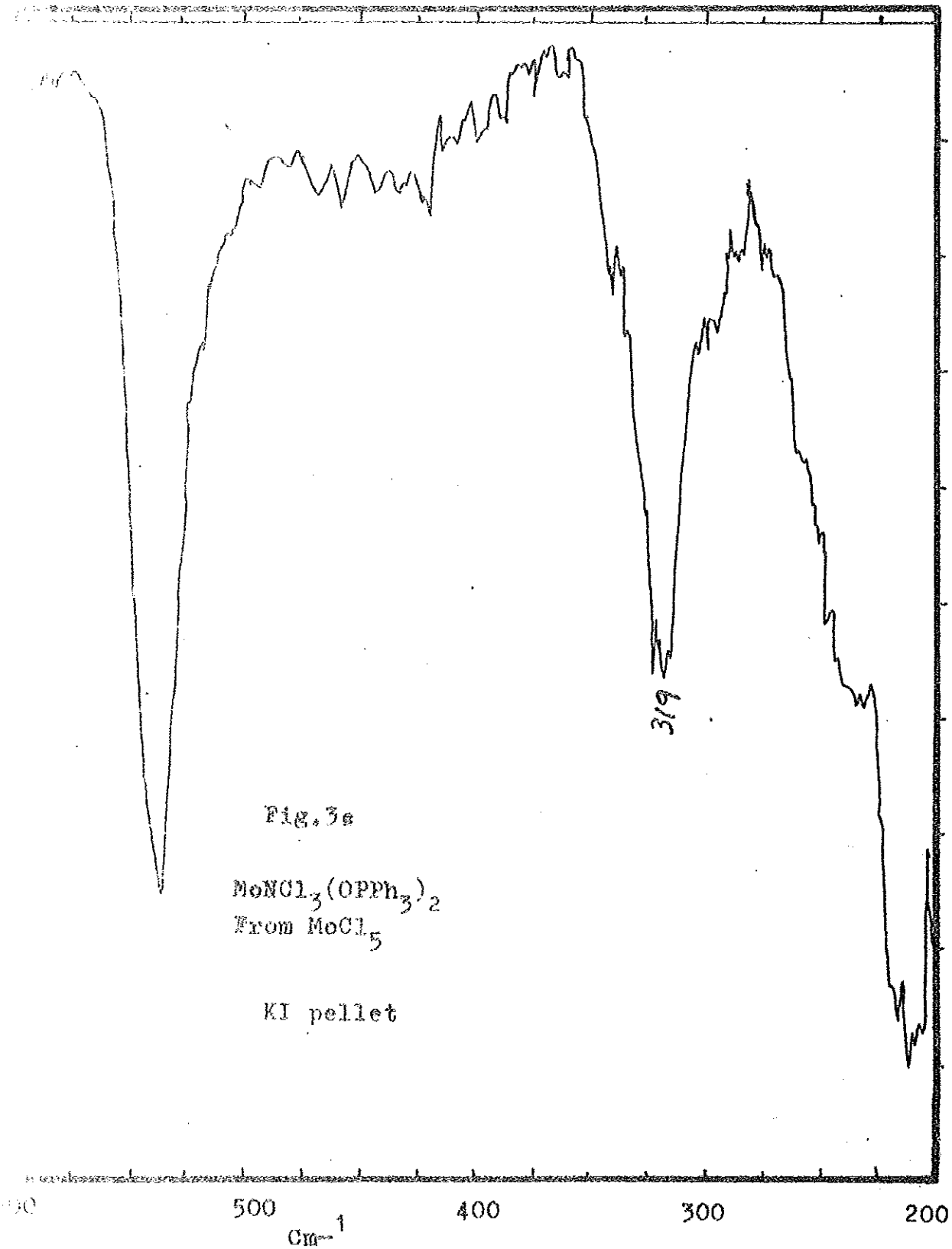


Fig. 3a

$MoNCl_3(OPPh_3)_2$
From $MoCl_5$

KI pellet

4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
cm⁻¹

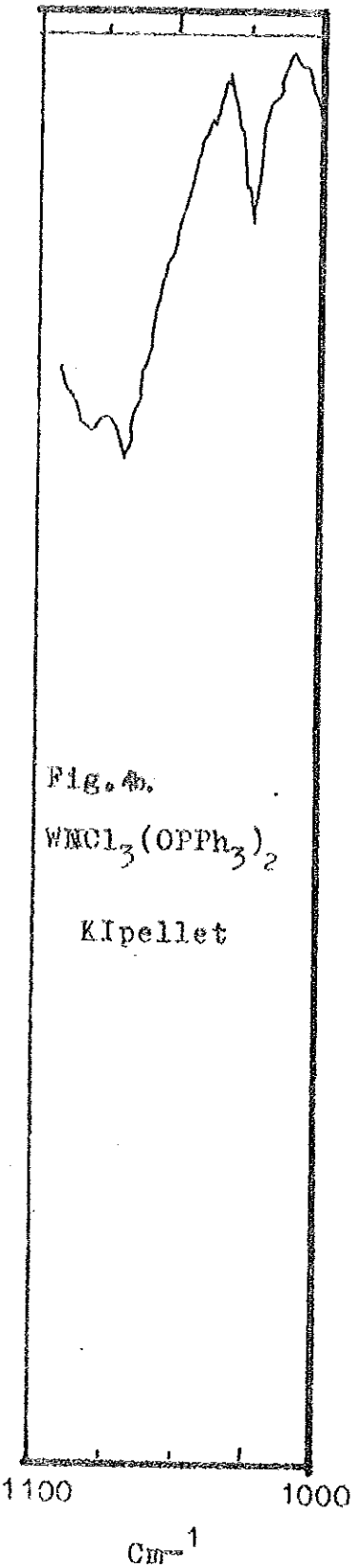


Fig. 4.

$WNCl_3(OPPh_3)_2$

KIpellet

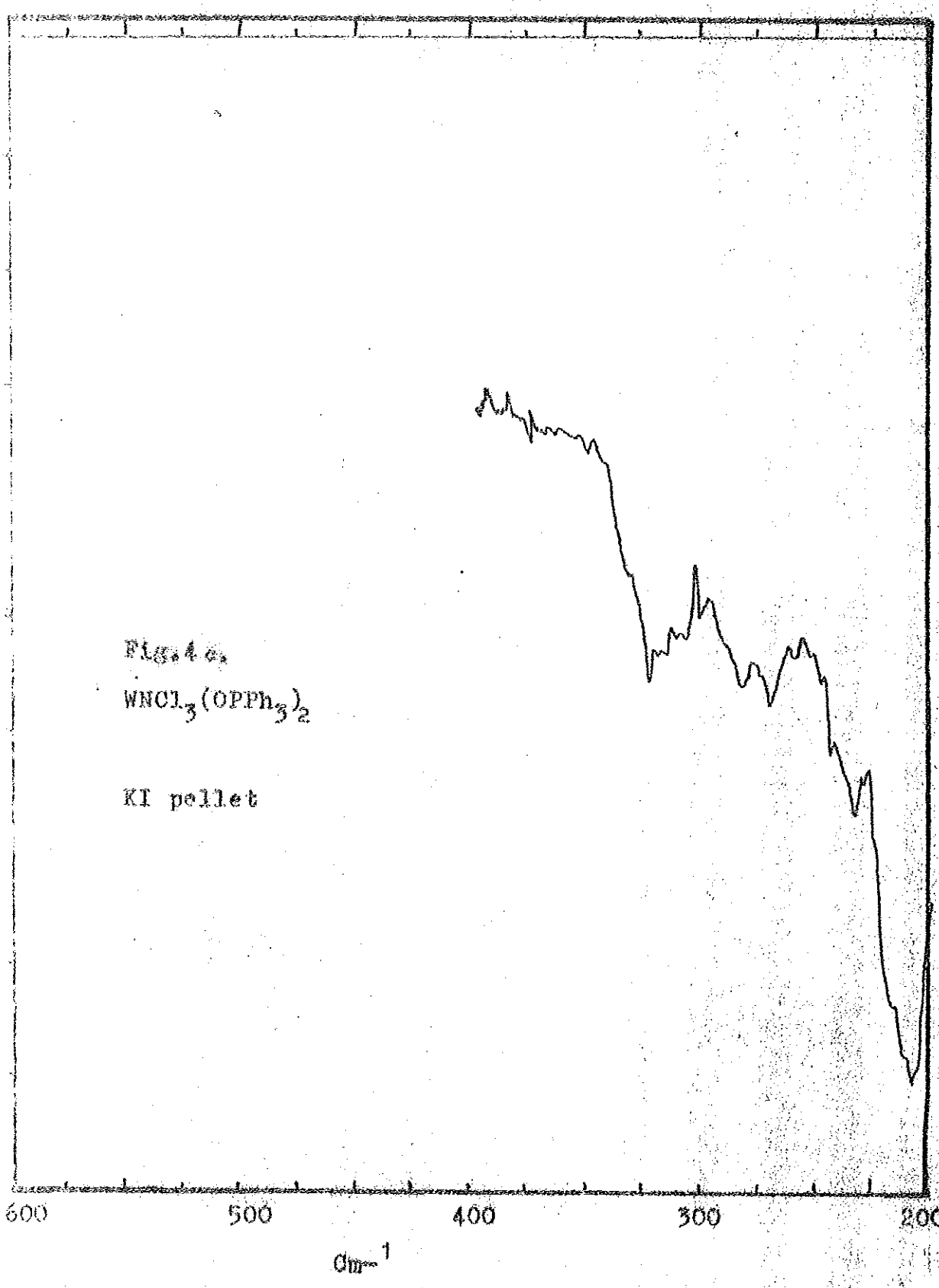
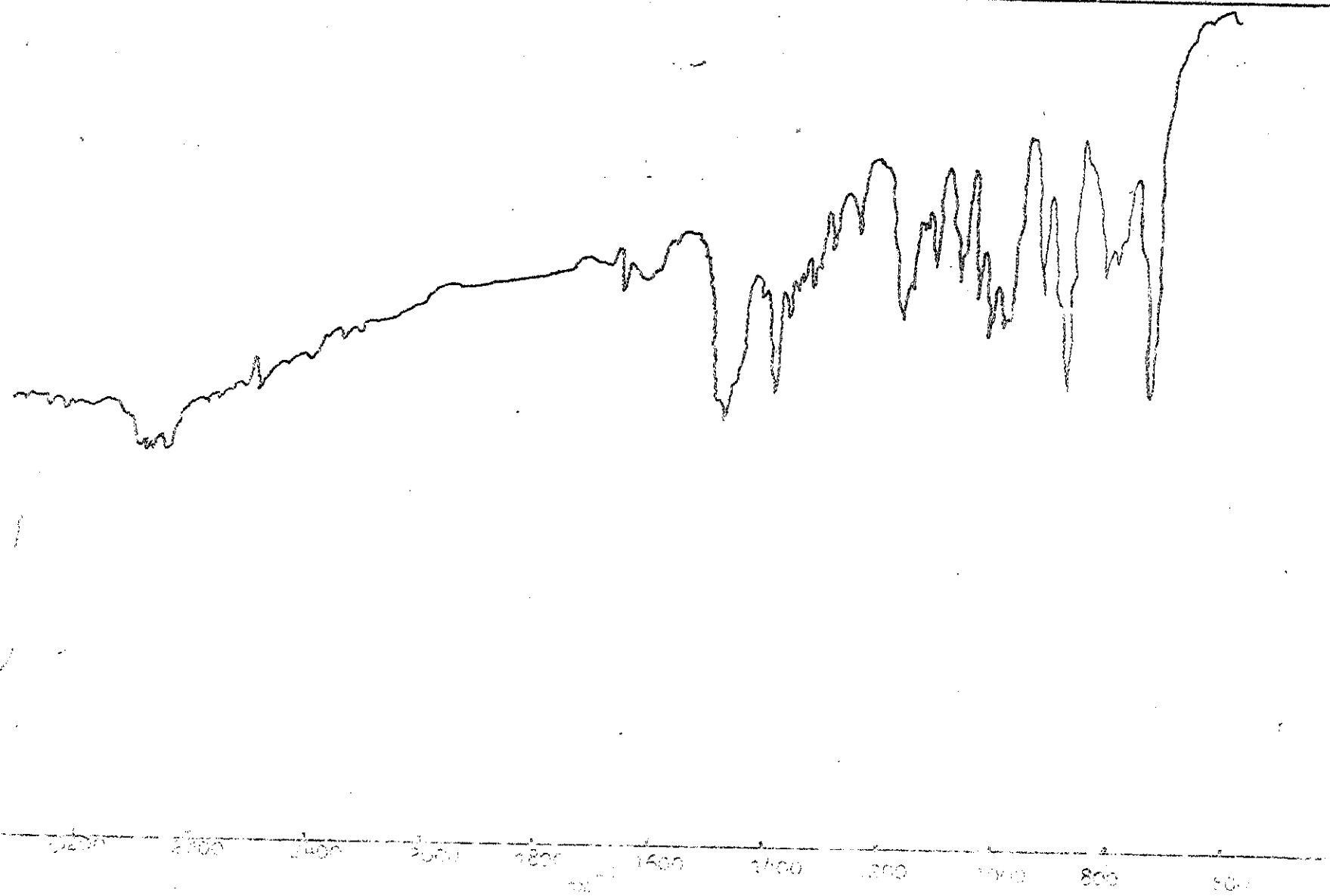


Fig.4a.

$WNCl_3(OPPh_3)_2$

KI pellet

Fig. 5a. IR-spectrum of $[Bu_4][WNCl_4]$ (10) /on KBr



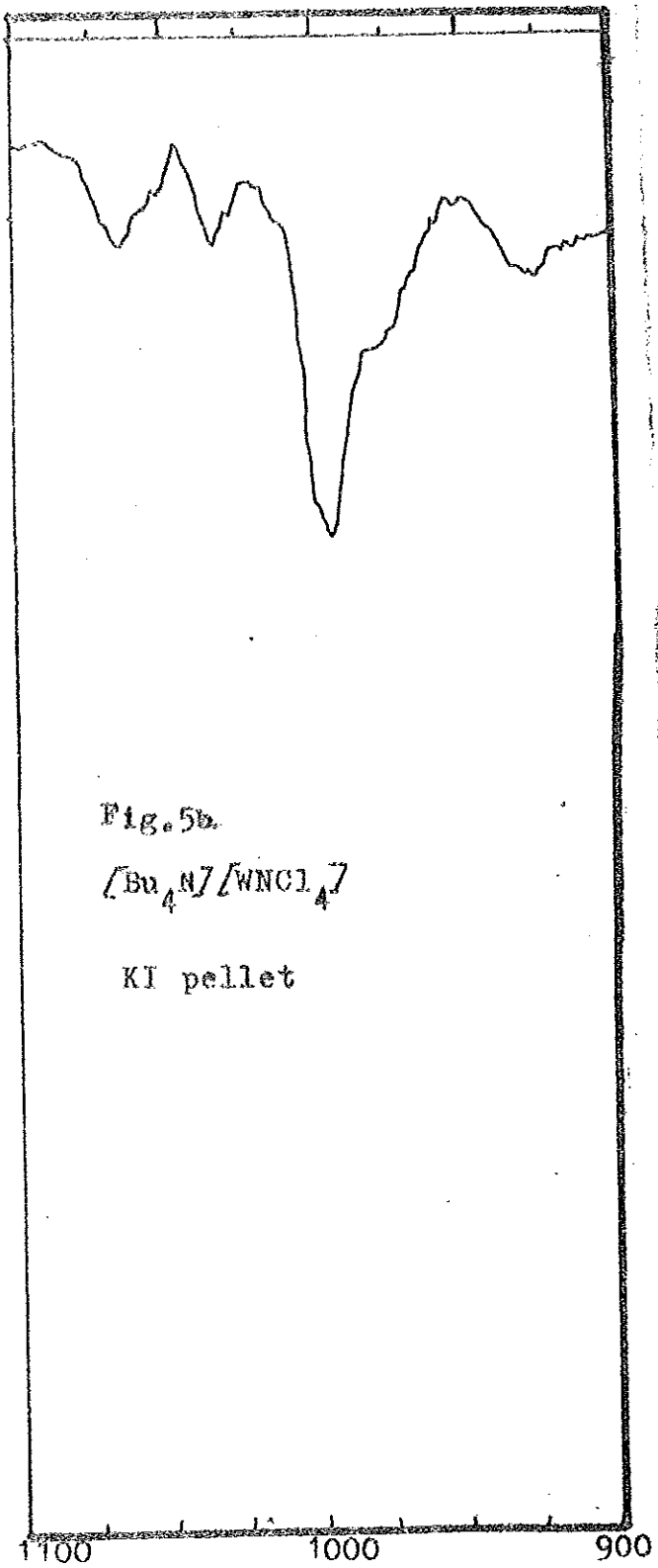


Fig.5b.

$[Bu_4N][WNCl_4]$

KI pellet

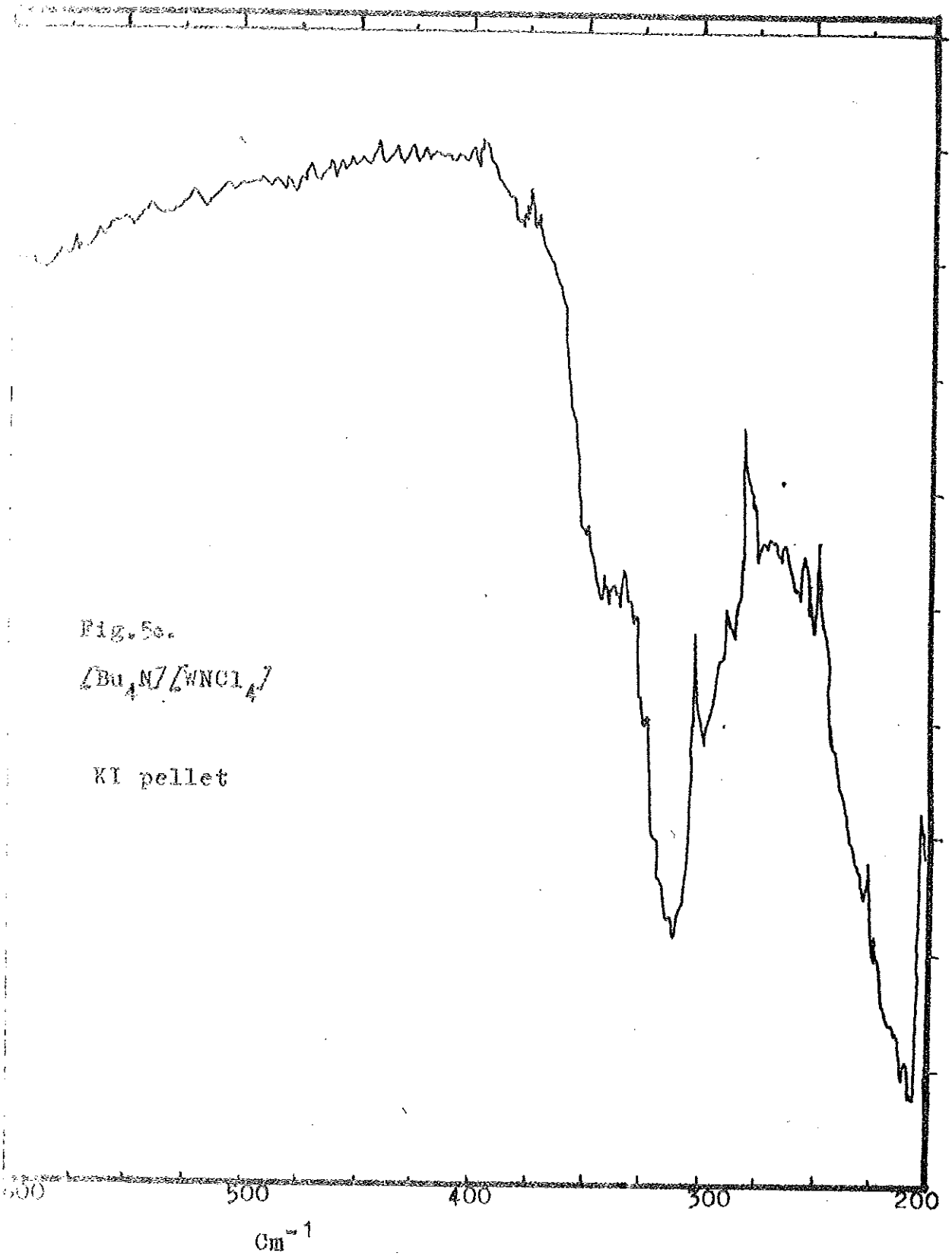
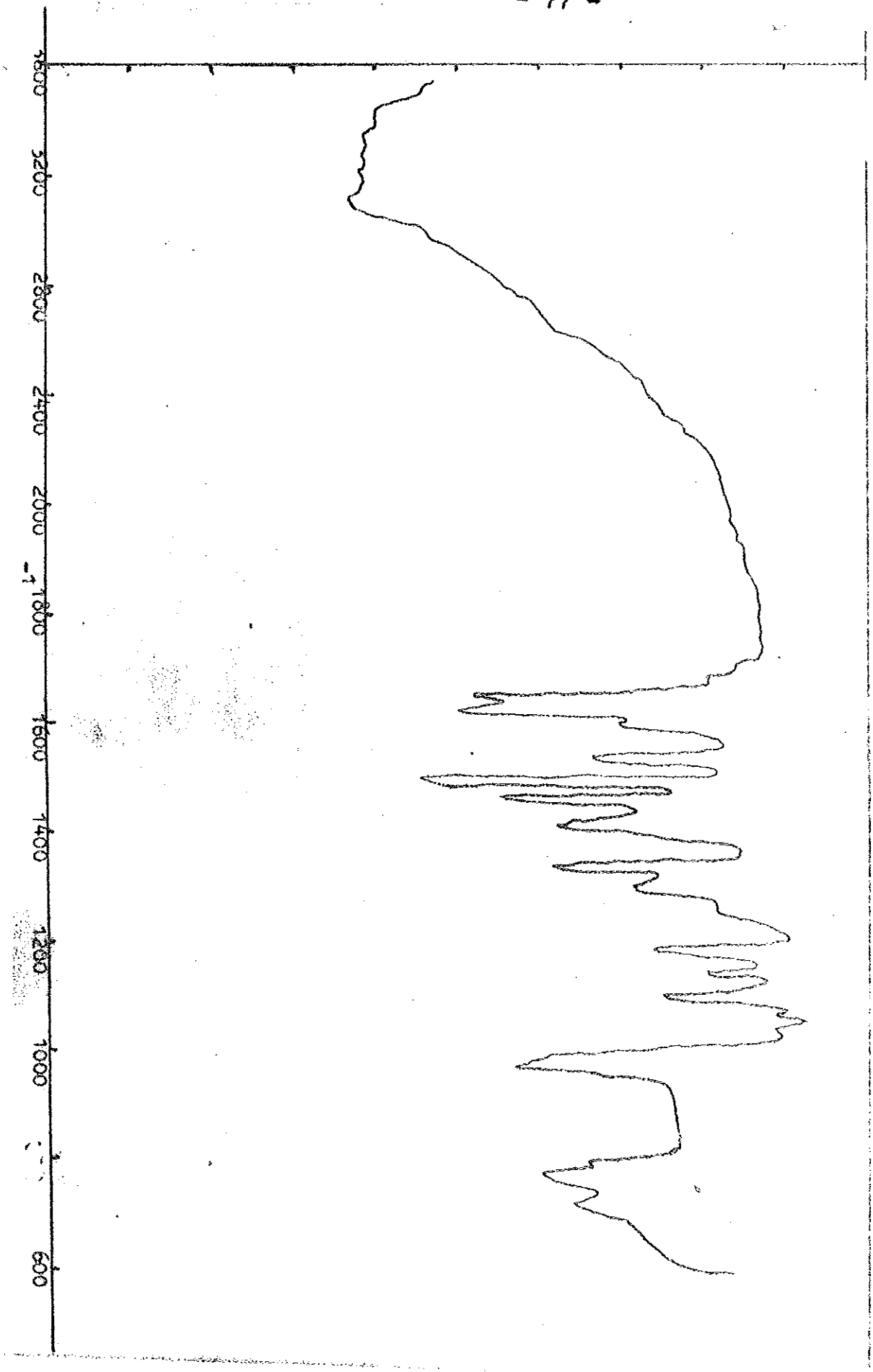


Fig. 5e.

$[Bu_4N][WNCl_4]$

KI pellet


3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
600

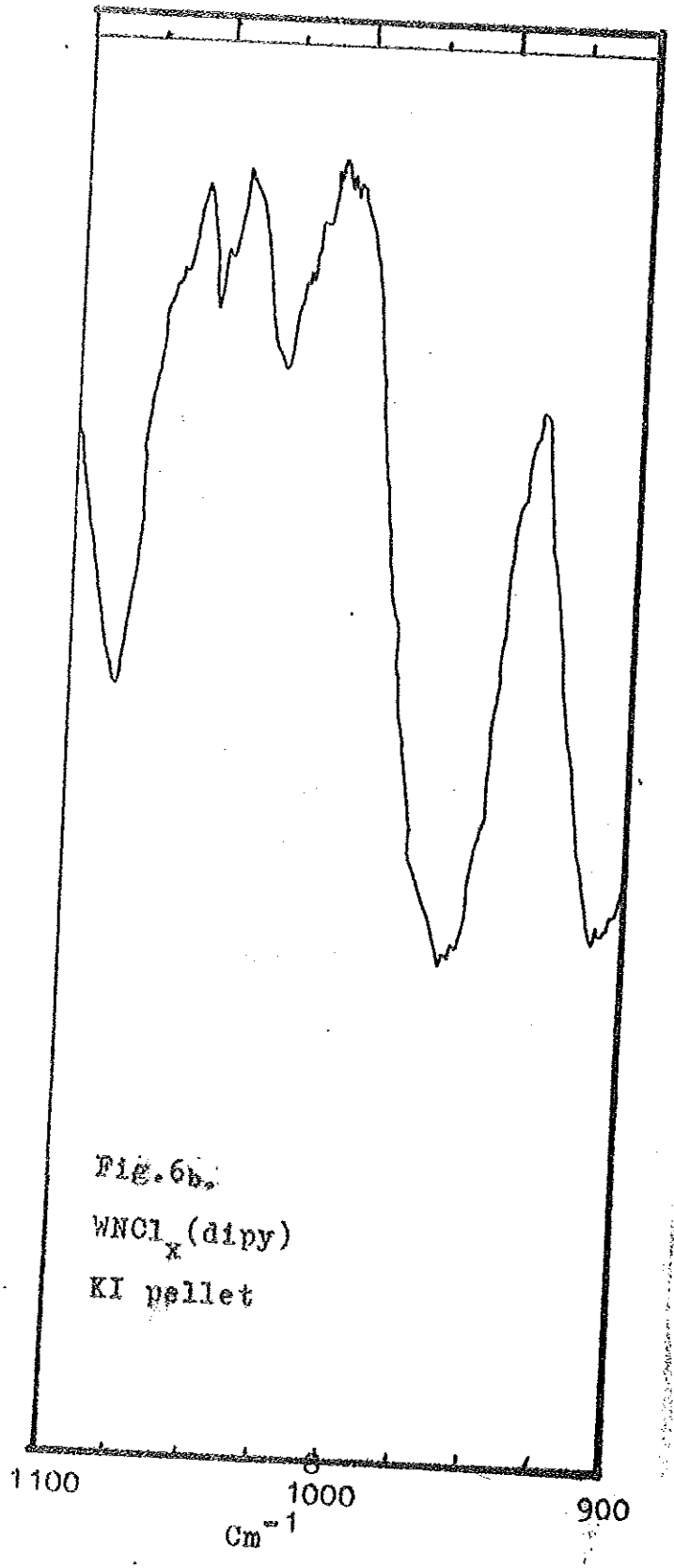


Fig.6b.

$WNCl_x$(dipy)

KI pellet

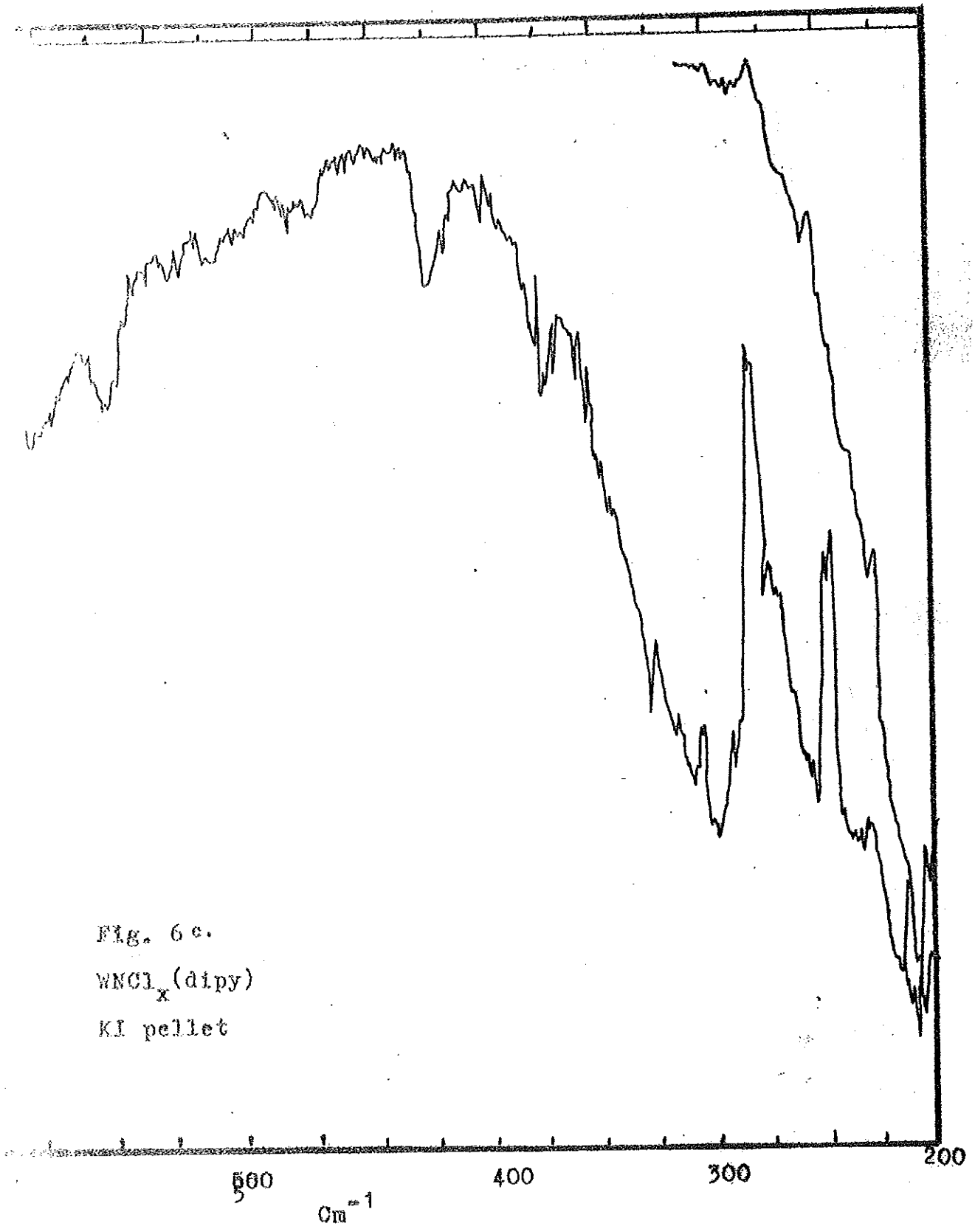
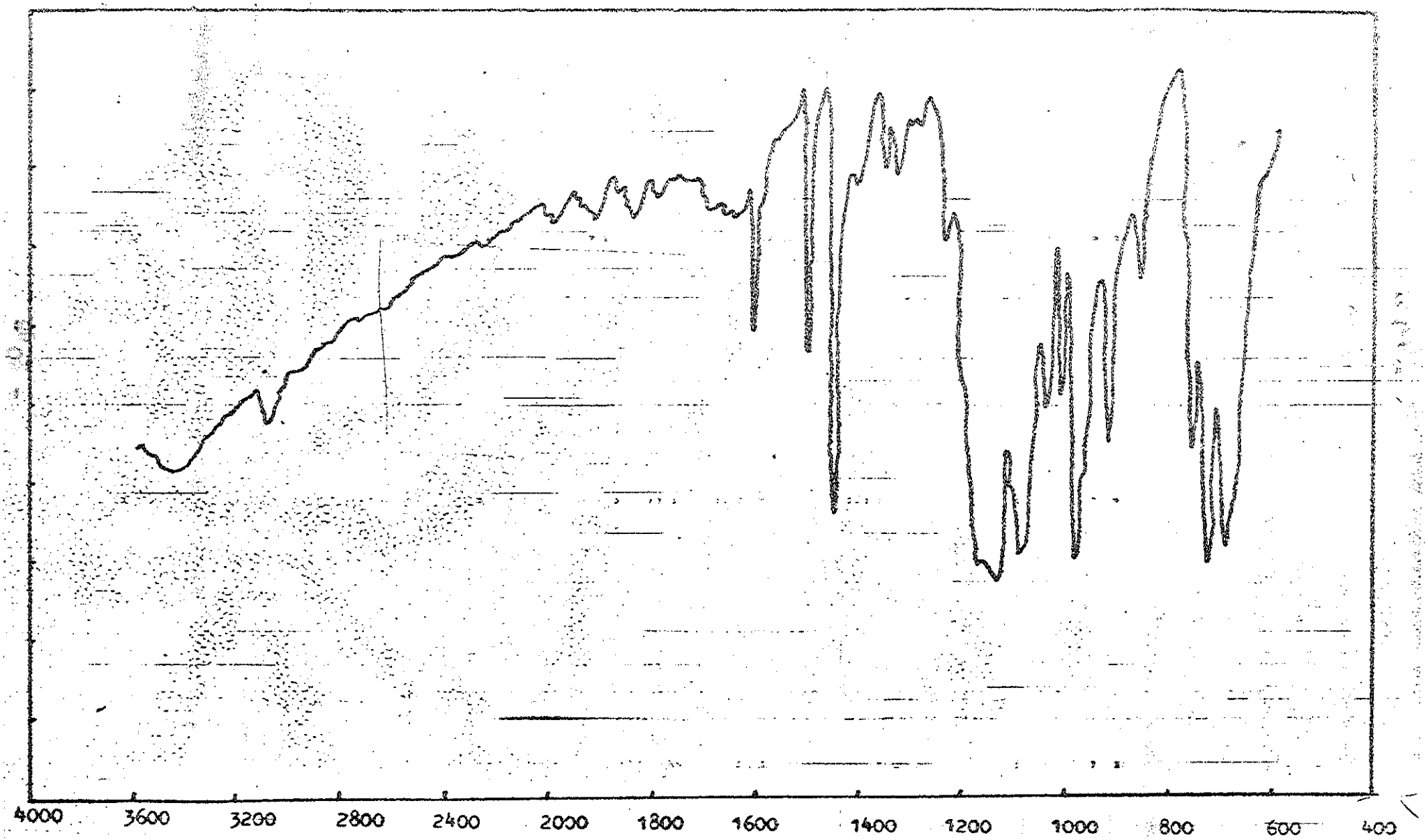


Fig. 6 c.

$WNCl_x$(dipy)

KI pellet

Fig. 7a. IR-spectrum of $RhCl_3(OPPh_3)_2$(2) /cm KBr



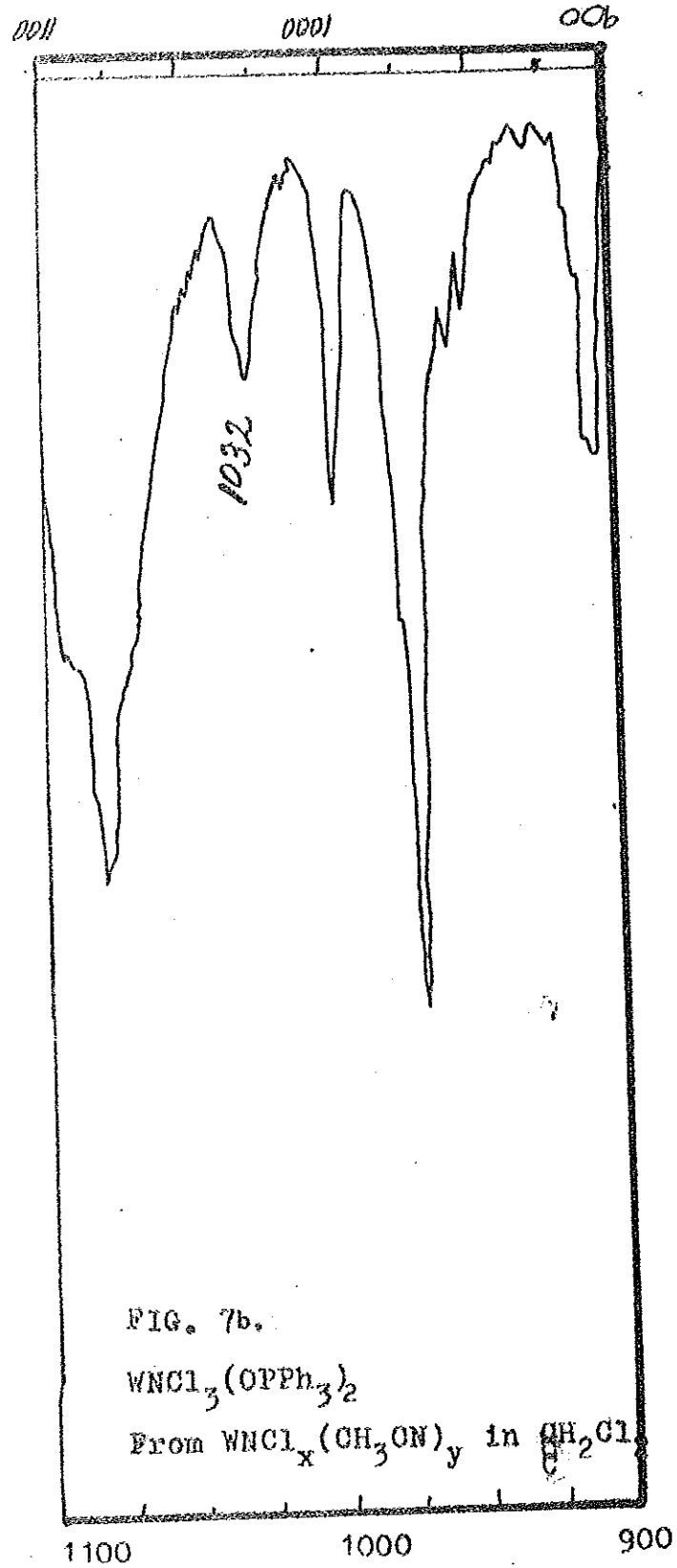


FIG. 7b.

$WNCl_3(OPPh_3)_2$

From $WNCl_x(CH_3ON)_y$ in CH_2Cl_2

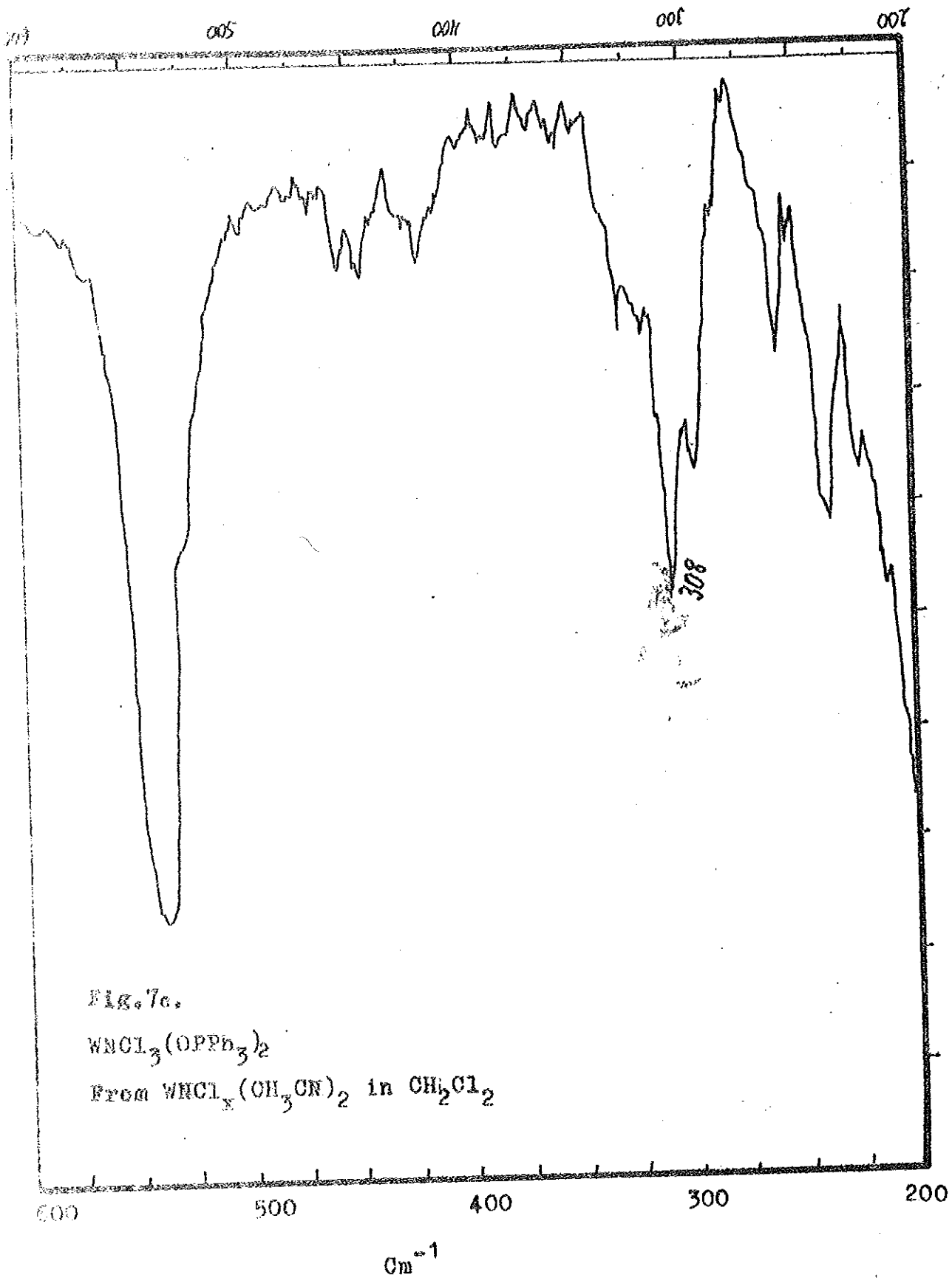


Fig.7a.

$WNCl_3(OPPh_3)_2$

From $WNCl_x(CH_3CN)_2$ in CH_2Cl_2

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