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Reactions of $MoCl_5$ with 4-Methylpyridine, 2-Methylpyridine and 1-Methylimidazole in Tetrahydrofuran

RAKESH KUMAR[1] and GURSHARAN SINGH[2]*

[1]Research Scholar registered with Punjab Technical University, Kapurthala, India.
[2]Department of Applied Chemistry, Giani Zail Singh Campus College of Engineering & Technology, Dabwali Road, MRSPTU Bathinda-151001, India.
*Corresponding author E-mail: gursharans82@gmail.com

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ABSTRACT

$MoCl_5$ reactions with 4-methylpyridine/2-methylpyridine/1-methylimidazole in THF in 1:1/1:2 stoichiometric ratios, at room temperature were carried out. The following products were synthesized: $MoO_2Cl(C_6H_7N)$,[1]; $Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2$,[2]; $Mo_4O_4Cl_4(C_6H_7N)_3(C_4H_8O)_2$,[3] and $Mo_2O_4Cl_4(C_4H_6N_2)_2(C_4H_8O)$,[4]. These compounds have been investigated by FT-IR (transmission mode), FT-^{1}H NMR, FT-^{13}C NMR, microbiological, LC-MS and elemental (C, H, N, Mo, Cl) studies. In view of the sensitivity of all the reactants and products towards oxidation/hydrolysis by air/moisture, all the reactions and products were handled using dry nitrogen atmosphere in vacuum line. LC-MS and elemental studies agree with the formulae of compounds.

Keywords: 4-Methylpyridine, 2-Methylpyridine, 1-Methylimidazole, $MoCl_5$, Microbiological.

INTRODUCTION

Pyridine derivatives have a number of biological activities, like antimycobacterial[1], antimicrobial[2,3], analgesic[4], anticonvulsant[5], antitumoral[6], antimalarial[7], antiparkinsonian[8], cytotoxic[9], pesticidal[10], antidiabetic[11], antibacterial[12], inhibitory[13] and receptor[14] antagonists. Electron donating groups[15] in pyridine derivatives increase the biological activity of transition metal-pyridine derivative compounds.

4-Methylpyridine

4-Methylpyridine[16] is used as a precursor for the preparation of a number of heterocyclic compounds. It is used for the preparation of many compounds of medicinal interest, like 'isoniazid' used as antituberculosis drug[17].

2-Methylpyridine

2-Methylpyridine[18] acts as an intermediate for the manufacture of drugs, like picoplatin, amprolium, encainide and dimethindene. It is used as a precursor for the preparation of 2-vinylpyridine. It is used to manufacture nitrapyrin[19] which controls loss of NH_3 from fertilizers. It is also used to prepare herbicide piclorand.

1-Methylimidazole

Azoles[20] are widely used in antibiotics and

antifungal agents, because cytochrome P450 sterol 14α-demethylase of the pathogens are inhibited by them. Azole action mechanism involves,

a) Coordination of imidazole non-protonated nitrogen and enzyme heme-iron,
b) π-cation interaction,
c) Hydrogen binding.

Only a few antifungal agents are available: azoles, allylamines, polyenes, fluoropyrimidines and thiocarbamates[21]. Among these agents, azoles are the most important because of their high therapeutic index. Effectiveness of the azole drug depends on the strength of the coordinate bond[22].

Imidazole drugs have many applications[23-35] as antifungal, 20-carboxypeptidase inhibitors, hemeoxygenase inhibitors, anticancer, anti-inflammatory, antibacterial, antimalarial, antitubercular, antiviral agents. They are also anticoagulants, antidiabetic HETE (20-Hydroxy-5, 8,11,14-eicosatetraenoic acid) synthase inhibitors, β-lactamase inhibitors and antiaging agents.

Metal chelates drugs are more effective than ligands themselves[36-41].

AIM of investigation

$MoCl_5$ reactions with imides, diaminoalkanes, aromatic azoles, thiols like 4-phenylimidazole-2-thiol, 2-thiazoline-2-thiol, alkylpyridines and mercaptopyridine-N-oxide have been reported[42-51] by the author.

Since applications of transition metal compounds with pyridine and imidazole derivatives are widening very fast, so $MoCl_5$ compounds of 4-methylpyridine, 2-methylpyridine and 1-methylimidazole have been prepared and investigated. These complexes were studied with elemental analysis, FT-IR, LC-MS, FT-^{1}H NMR, FT-^{13}C NMR and microbiological studies.

MATERIALS AND METHODS

4-Methylpyridine, 2-methylpyridine, 1-methylimidazole and $MoCl_5$ used were of Sigma-Aldrich.

Reactants and products being prone to oxidation by air/moisture, so all reactions were carried out and products handled in vacuum line in dry nitrogen atmosphere.

4-Methylpyridine/2-methylpyridine/1-methylimidazole was added to the dropping funnel and dissolved in 10 mL dry THF. It was added dropwise to $MoCl_5$ solution in THF with continuous agitation in 100 mL B-14 flask. Contents were stirred for 7-8 hours. Filtration was carried out. Products from both the residue and filtrate were isolated and studied.

Molybdenum was estimated using 8-hydroxyquinoline gravimetrically[52]. Chlorine was estimated using silver nitrate gravimetrically[52]. Other elements were determined quantitatively by Thermo Finnigan Elemental Analyser. Proton/^{13}C nuclear magnetic resonance spectra were recorded in DMSO-d_6 with Multinuclear Brucker Avance-II 400 NMR spectrometer. Vibrational peaks have been studied using Perkin-Elmer 400 FTIR Spectrometer. LC-MS studies have been carried out in the span 0-1100 m/z. P. U. Chandigarh, India provided the instrumental support.

Molybdenum compounds activity against bacteria and fungi was investigated by 'Agar Well Diffusion Assay' method. Various strains used are: fungi *Candida albicans* and *Aspergillus niger*, *Gram -positive* bacteria *Staphylococcus aureus* and *Gram -negative* bacteria *E. coli*. The Microbial Type Culture Collection and Gene Bank, Chandigarh, India cultures were used. Amoxicillin and ketoconazole for bacteria and virus, respectively were used as standard drugs for comparison. Studies were performed at Indo Soviet Friendship College of Pharmacy, Moga, Punjab, India.

REACTIONS

All the products have been isolated from filtrate (F).

$$MoCl_5 + C_6H_7N \xrightarrow[1:2]{THF} MoO_2Cl(C_6H_7N), [1]$$

4-Methylpyridine Light brown (F)

$$MoCl_5 + C_6H_7N \xrightarrow[1:1]{THF} Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2, [2]$$

4-Methylpyridine Black (F)

$$MoCl_5 + C_6H_7N \xrightarrow[1:1]{THF} Mo_4O_4Cl_4(C_6H_7N)_3(C_4H_8O)_2, [3]$$

2-Methylpyridine Grey (F)

$$MoCl_5 + C_4H_6N_2 \xrightarrow[1:1]{THF} Mo_2O_4Cl_4(C_4H_6N_2)_2(C_4H_8O), [4]$$

1-Methylimidazole Coffee brown (F)

RESULTS AND DISCUSSIONS

Elemental Studies

Table 1: (observed (theoretical) percentage)

Compounds	Chlorine	Molybdenum	Hydrogen	Carbon	Nitrogen
$MoO_2Cl(C_6H_7N)$, [1]	13.74	36.96	3.13	27.65	4.85
(Light brown/256.5)	(13.84)	(37.42)	(2.72)	(28.07)	(5.45)
$Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2$, [2]	23.57	25.53	04.00	31.93	3.16
(Black/731.5)	(24.26)	(26.24)	(4.10)	(32.80)	(3.82)
$Mo_4O_4Cl_4(C_6H_7N)_3(C_4H_8O)_2$, [3]	13.23	37.11	3.82	30.09	3.27
(Grey/1013.0)	(14.01)	(37.90)	(3.65)	(30.79)	(4.14)
$Mo_2O_4Cl_4(C_4H_6N_2)_2(C_4H_8O)$, [4]	21.78	29.67	03.09	21.92	7.13
(Coffee brown/634.0)	(22.39)	(30.28)	(3.15)	(22.71)	(8.83)

FT-IR Spectra

Ring υ(C-H) of 4-methylpyridine[50,53-60] occurs at 3072 cm^{-1} and the corresponding str. in [1] has been noted at 3090 cm^{-1}. Ring υ(C=N) and torsion show upward shift, but ring δ(C-H) shows downward shift, showing Mo(dπ)→N(pπ). 976 cm^{-1} peak suggests the presence of terminal Mo=O[45,61,62] in [1]. υ(Mo=O) decreases on N→Mo coordination[63]. Coordinate bond and Mo=O are trans to each other. Molybdenum abstracts[64,65] oxygen from THF to form Mo=O (Table-2).

Ring υ(C-H) has not been noticed in [2]. It has been observed that ring υ(C=N) and torsion show upward shift, but ring δ(C-H) has decreased, as a result of Mo(dπ)→N(pπ). 975 cm^{-1} str. of Mo=O[45,61,62] group at terminal position is observed. υ(Mo=O) decreases on N→Mo coordinate bond[63] formation. Coordinate bond is trans to Mo=O. Molybdenum abstracts[64,65] oxygen from THF forming Mo=O (Table 2).

Ring υ(C-H) in 2-methylpyridine[58,59,66,67] is noted at 3065 cm^{-1}, but [3] does not show this vibration. υ(C=N) in [3] has been noted at 1632 cm^{-1} showing an upward shift[47] by 36 cm^{-1} and torsion was observed at 571 cm^{-1} showing an upward shift[47] by 24 cm^{-1}. This upshift is because of Mo(dπ)→N(pπ). υ(Mo=O) at 979 cm^{-1} in [3] has been recorded because of Mo=O[45,61,62] group at terminal position. υ(Mo=O) drops on N→Mo coordination[63]. Coordinate bond and Mo=O are trans to each other. Molybdenum abstracts[64,65] oxygen from THF to form Mo=O (Table 3).

Unprotonated nitrogen of 1-methylimidazole[68] coordinates with molybdenum. Ring υ(C=C) has been noted at 1553 cm^{-1} showing an increase of 36 cm^{-1}. Ring υ(N-C) is located at 1446 cm^{-1} showing an increase of 39 cm^{-1}. This increase in wave numbers on N→Mo coordination is caused by,

(i) Inductive effect on ligand-molybdenum cation coordination.
(ii) dπ-pπ back bonding which changes the electron density on the ligand.

It causes electron density to increase in the ring which increases N→Mo coordinate bond strength. 978 cm^{-1} str. of Mo=O[45,61,62] group at terminal position is observed. υ(Mo=O) decreases on N→Mo coordinate bond[63] formation. Coordinate bond is trans to Mo=O. Molybdenum abstracts[64,65] oxygen from THF forming Mo=O (Table 4).

Table 2: (FT-IR absorptions in cm^{-1})

Assignments	4-Methylpyridine[50,53-60]	[1]	[2]
Ring υ(C-H)	3034,3072	3403 b, 3090 sh	3399 s
Methyl υ(C-H)	2927, 2990	2951 sh	
Ring υ(C=N)	1564,1611	1640 s	1640 s
Methyl$\delta(C\text{-}H)_{asym}$	1499	1507 m	1508 w
Ring δ(C-H)	1365, 1418, 1445, 1458, 1194	1445 sh, 1316 w	
ethyl$M\delta_{sym}$(C-H)	1383	1380 w	1381 w
Ring υ(C-N)	1227	1256 w	
$\upsilon(_3CH\text{-}C)$	1210	1203 w	1204 sh
Methyl ρ(C-H)	1114	1099 w	1111 sh
Ring breathing	1072	1039 w	
Ring out of plane bending	877,994	870 sh	
Ring ω(C-H), ω(C-C), ω(C-N)	730	794 m, 734 m	791 w, 735 w
Ring torsion	524	619 sh , 566 w, 521 w	570 w
$\delta(_3CH\text{-}C)$	486	476 w	476 w
Terminal Mo=O[45,61,62] str.		976 s	975 m

Table 3: (FT-IR absorptions in cm^{-1})

Assignments	2-Methylpyridine[58,59,66,67]	[3]
Ring υ(C-H)	3135 m, 3087 m, 3065 m	3379 s
Methyl υ(C-H)	2960 m	
Ring υ(C=N)	1596 vs	1632 s
Methyl δ_{asym}(C-H)	1463 s	
Ring δ(C-H)	1475 s, 1148 m,	1477 sh
Methyl δ_{sym}(C-H)	1375 w	1404
Ring υ(C-N)	1297 s,	1297 w
υ(C-CH_3)	1235 m	
Methyl ρ(C-H)	1075	
Ring breathing	1059 s	1050 w
Ring ω(C-H),	750 vs, 730 m	762 s
ω(C-C), ω(C-N)		
Ring υ(C-C)	630 m	
Ring torsion	547 w	571 sh
δ(C-CH_3)	471	
Terminal Mo=O[45,61,62] str.		979 s

Table 4: (FT-IR absorptions in cm^{-1})

Assignments	1-Methylimidazole68	[4]
Ring υ(H-C)	3017 m, 2955 w	3398 s
Ring υ(C=N)		1630 s
Ring υ(C=C)	1519 vs	1553 sh
Ring υ(N-C)	1409 m	1446 w
Ring δ(H-C)	1107 m, 1087 m, 1035 vw	1086 w
Ring υ(H-C),	814 s, 774 s	740 s
Ring τ(H-C)		
Ring τ(H-C)	640 s	624 m
υ(N-H), Ring twisting	525	569 m
Terminal Mo=O[45,61,62] str.		978 s

FT-^{1}H NMR Spectra

Compounds were dissolved in DMSO-d_6 to take spectrum. DMSO-d_6[69] residual peak appears at 2.5 ppm. THF[69] solution in DMSO-d_6 shows CH_2 peak at 1.7 ppm and O-CH_2 peak at 3.6 ppm. ↑ and ↓ signify upfield/downfield shift.

When spectra of 4-methylpyridine[50,58,59,70] and [1] are compared, it is observed that absorptions show deshielding due to flow of π-electron density towards molybdenum cation on N→Mo coordinate bond formation (Figure 1, Table 5).

4-Methylpyridine[50,58,59,70] and [2] spectra on comparison show that absorptions go downfield in [2]. This results from flow of π-electrons towards molybdenum on coordination (Figure 2, Table 5).

2-Methylpyridine[58,59,70] and [3] spectra reveal that all of the protons resonances occur at lower field due to delocalisation of ring π-electron density when ligand coordinates with molybdenum through nitrogen (Figure 3, Table 6).

[4] spectrum shows that all the protons of the 1-methylimidazole[67,68,71] have deshielded on account of flow of π-electrons towards molybdenum on coordination (Figure 4, Table 7).

Table 5: (^{1}H-NMR absorptions in ppm)

Assignments	4-Methylpyridine[50,58,59,70] in $CDCl_3$	[1]	[2]
H-C_2 & H-C_6 (Ortho),	8.4 2H d	8.8 ↓	8.7 ↓
H-C_3 & H-$C)_5$ (Meta),	7.1 2H d	7.8 ↓	7.9 ↓
CH_3 attached to C_4	2.3 3H s	2.5 ↓	2.5 ↓
Residual[69] DMSO-d_6		2.5	2.5
THF[69] O-CH_2			3.5
THF[69] CH_2			1.7

Table 6: (^{1}H-NMR absorptions in ppm)

Assignments	2-Methylpyridine[58,59,70] in $CDCl_3$	[3]
CH_3 attached to C_2	2.5 3Hs	2.8 ↓
H-C_5 (Meta)	7.0 1H t	7.9 ↓
H-C_3 (Meta)	7.2 1H d	7.9 ↓
H-C_6 (Ortho)	8.4 1H d	8.8 ↓
H-C_4 (Para)	7.5 1H t	8.5 ↓
Residual[69] DMSO-d_6		2.5
THF[69] O-CH_2		3.6
THF[69] CH_2		1.8

Table 7: (^{1}H-NMR absorptions in ppm)

Assignments	1-Methylimidazole[67,68,71] in D_2O	[4]
H-C_4	7.0 1H	7.6 ↓
H-C_5	7.0 1H	7.6 ↓
H-C_2 (between two N)	7.5 1H	9.1 ↓
CH_3 attached to N	3.6 3H	3.8 ↓
Residual[69] DMSO-d_6		2.5
THF[69] O-CH_2		3.6
THF[69] CH_2		

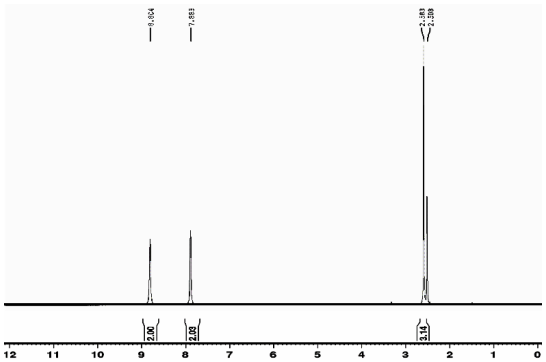

Fig. 1. FT-^{1}H NMR of $MoO_2Cl(C_6H_7N)$, [1]

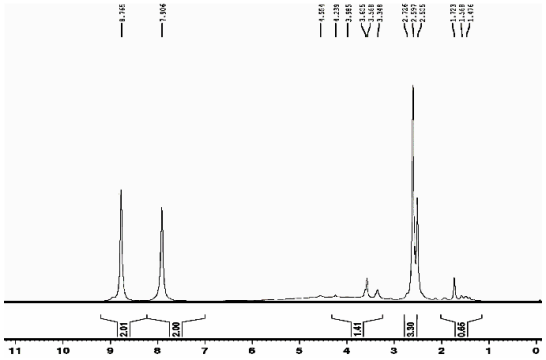

Fig. 2. FT-^{1}H NMR of $Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2$, [2]

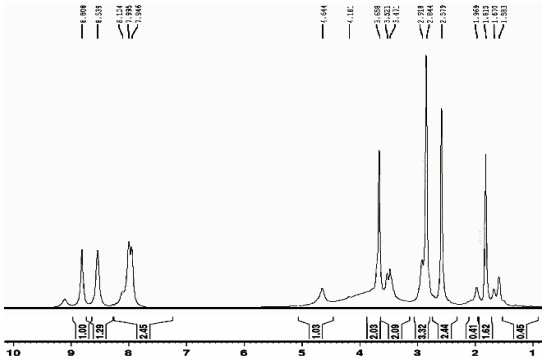

Fig. 3. FT-^{1}H NMR of $Mo_4O_4Cl_4(C_6H_7N)_3(C_4H_8O)_2$, [3]

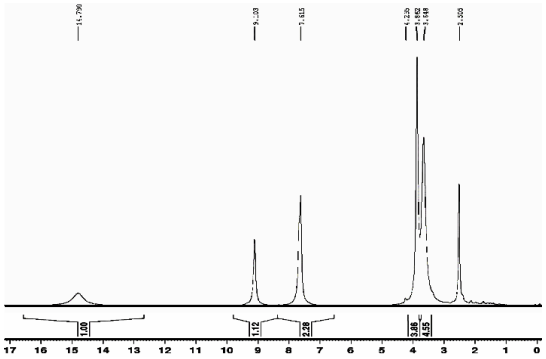

Fig. 4. FT-^{1}H NMR of $Mo_2O_4Cl_4(C_4H_6N_2)_2(C_4H_8O)$, [4]

FT-^{13}C NMR Spectra

Compounds were dissolved in DMSO-d_6 to take spectrum. DMSO-d_6[69] residual peak occurs at 39.52±0.06 ppm. ↑ and ↓ represent upfield/ downfield shift.

Spectrum of [2] reveals that all carbons of 4-methylpyridine[72] show resonances at lower field except meta carbons on ligand-metal coordination (Figure 5, Table 8).

Microbiological Activity

Potency of molybdenum compounds synthesized against *Gram-positive* bacteria *Staphylococcus aureus*, *Gram-negative* bacteria *E. coli*, fungi *Candida albicans* and *Aspergillus niger* has been investigated. Amoxicillin and ketoconazole have been used as reference drugs against bacteria and fungi, respectively. Efficiency of molybdenum compounds have been tested by 'Zone of inhibition' method[73]. Potency of molybdenum compounds has been found to be good to control bacteria and fungi (Table 9). It is to be noted that,

1. Compounds 1, 2, 3 and 4 are more potent against *E. coli* than amoxicillin.
2. Compound 4 is more potent against *C. albicans* than ketoconazole.

Table 8: (^{13}C NMR absorptions in ppm)

Assignments	4-Methylpyridine[72] in $CDCl_3$	[2]
C-2 C-6 (ortho)	149.6	157.6
C-3 C-5 (meta)	146.9	139.8
C-4 (para)	124.6	127.5
CH_3 attached to C-4	20.8	22.1
Residual[69] DMSO-d_6		39.4

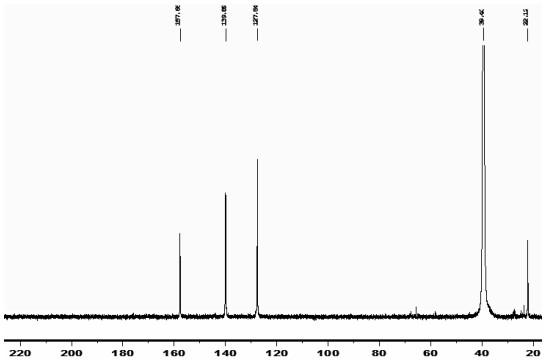

Fig. 5. ^{13}C-NMR of $Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2$, [5]

Table 9: (Microbiological Study)

Compound (100 μg/mL)	Zone of inhibition73 (mm)			
	S. aureus	*E. coli*	*C. albicans*	*A. niger*
Reference Drug	24.99	17.85	21.37	27.88
[1]	21.36	21.58	19.57	19.63
[2]	21.28	23.14	19.87	18.54
[3]	22.31	21.56	18.38	19.88
[4]	19.87	21.32	22.17	21.38

Mass (LC-MS) Spectra

Masses of the most abundant isotopes have been used to calculate theoretical m/z values[74] of the ions (Tables 10, 11).

Table 10: (LC-MS Ionization)

Compound	
[1]	$MoO_2Cl(C_6H_7N) \rightarrow [C_6H_7N]^+$ [1] M.W. = 256.5 94.06
[2]	$Mo_2O_2Cl_5(C_6H_7N)_2(C_4H_8O)_2 \rightarrow [MoO_2Cl_3(C_6H_7N)]^+ \rightarrow [MoO_2Cl(C_6H_7N)]^+$ [2] M.W. = 731.5 328.25 256.18 ↓ ↓ $[MoO_2Cl_3(C_6H_7N)]^{2+} \rightarrow [C_6H_7N]^+$ 166.14 94.06 ↓ $[MoO_2Cl_3]^+$ 238.21
[3]	$Mo_4O_4Cl_4(C_6H_7N)_3(C_4H_8O)_2 \rightarrow [MoO_2Cl_3(C_6H_7N)]^+ \rightarrow [MoO_2Cl(C_6H_7N)]^+$ [3] M.W. = 1013.0 328.25 256.15 ↓ ↓ $[MoO_2Cl_3(C_6H_7N)]^{2+} \rightarrow [C_6H_7N]^+$ 166.14 94.06
[4]	$Mo_2O_4Cl_4(C_4H_6N_2)_2(C_4H_8O) \rightarrow [MoOCl_2(C_4H_6N_2)(C_4H_8O)]^+ \rightarrow [MoOCl_2(C_4H_8O)]^+$ [4] M.W. = 634.0 338.39 256.19 ↓ ↓ $[C_4H_6N_2]^+$ $[MoOCl]^+$ 83.06 149.05

Table 11: (m/z values of ions)

Compound	Ion	Calculated[74]	Observed	Relative abundance
[1]	$[C_6H_7N]^+$	93.05	94.06	100%
[2]	$[MoO_2Cl(C_6H_7N)]^+$	257.92	256.18	58%
	$[MoO_2Cl_3(C_6H_7N)]^+$	327.85a	328.25	3%
	$[MoO_2Cl_3(C_6H_7N)]^{2+}$	163.92	166.14	2%
	$[MoO_2Cl_3]^+$	234.8	238.21	4%
	$[C_6H_7N]^+$	93.05	94.06	100%
[3]	$[MoO_2Cl(C_6H_7N)]^+$	257.92	256.15	92%
	$[MoO_2Cl_3(C_6H_7N)]^+$	327.85	328.25	34%
	$[MoO_2Cl_3(C_6H_7N)]^{2+}$	163.92	166.14	25%
	$[C_6H_7N]^+$	93.05	94.06	100%
[4]	$[MoOCl]^+$	148.86	149.05	1%
	$[MoOCl_2(C_4H_8O)]^+$	255.89	256.19	8%
	$[MoOCl_2(C_4H_8O)(C_4H_6N_2)]^+$	337.94	338.39	1%

CONCLUSION

There is an increase in υ(C=N) and torsion and decrease in ring δ(C-H) due to Mo(dπ)→N(pπ) in [1]. 976 cm^{-1} peak reveals that Mo=O is in terminal position. υ(Mo=O) decreases on N→Mo coordination. Mo=O and the coordinate bond are trans to each other. Molybdenum abstracts oxygen from THF to form Mo=O. Presence of N→Mo coordinate bond is further supported by the ^1H NMR in which all absorptions move to lower field, due to flow of π-electron density towards molybdenum. [1] is very much active against microbes. Ions detected in LC-MS suggest the formula presented.

υ(C=N) and torsion show upward shift and ring δ(C-H) shows downward shift owing to Mo(dπ)→N(pπ) in [2]. Mo=O is a terminal group is inferred by the observation of 975 cm^{-1} peak. N→Mo coordination leads to decrease of υ(Mo=O). Coordinate bond and Mo=O are trans to each other. Molybdenum abstracts oxygen from THF forming Mo=O. N→Mo coordinate bond is further supported by the fact that all ^1H NMR absorptions show deshielding, because of depletion of ring π-electron density. Deshielding is further supported by ^{13}C NMR in which absorptions move downfield. Compound is very much potent against microbes. LC-MS fragments noted are in tune with the formula suggested.

υ(C=N) shows an upward shift by 36 cm^{-1} and torsion shows an upward shift by 24 cm^{-1} in [3] due to metal to ligand back bonding. υ(Mo=O) at 980 cm^{-1} refers to Mo=O group in terminal position.

υ(Mo=O) declines on coordinate bond formation. Mo=O and the coordinate bond are trans to each other. Molybdenum abstracts oxygen from THF leading to formation of Mo=O. N→Mo coordination is further evident from ^{1}H NMR which shows that all the protons have deshielded on account of decrease in ring π-electron density. Compound can control microorganisms. Fragments observed in mass spectrum conform to the formula.

υ(C=C) shows an increase of 36 cm^{-1} and υ(N-C) also shows an increase of 39 cm^{-1} in [4]. This increase is due to inductive effect on coordination of ligand with molybdenum cation and dπ-pπ interactions. Increase in electron density increases the coordinate bond strength. υ(Mo=O) is observed at 978 cm^{-1} indicating Mo=O being terminal one. N→Mo coordination is further supported by ^{1}H NMR which shows that all the protons have deshielded. Compound has been found to be potent against microbes. Ions observed in LC-MS agree with the formula derived.

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Conflict of interest

There is no conflict of interest among the authors.

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