



Reactions of MoOCl_4 & MoCl_5 with Pyrazole, Imidazole, 2-Methylpyridine, 3-Methylpyridine, 4-Methylpyridine & 2-Mercaptopyridine-N-oxide sodium

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Abstract: MoCl_5 reacts with pyrazole, 2-mercaptopyridine-N-oxide sodium, imidazole, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine in CH_3CN medium to yield multinuclear Mo complexes: $\text{MoOCl}_3(\text{C}_3\text{H}_4\text{N}_2)(\text{CH}_3\text{CN})\text{OCl}$ [1], $\text{Mo}_2\text{O}_4\text{Cl}_4(\text{C}_5\text{H}_4\text{SN-NSH}_4\text{C}_5)$ [2], $\text{MoO}_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)\text{Cl}$ [3], $\text{Mo}_2\text{Cl}_7\text{O}_4(\text{C}_6\text{H}_7\text{N})_2$ [6], $\text{Mo}_2\text{Cl}_7\text{O}_4(\text{C}_6\text{H}_7\text{N})_2$ [7] & $\text{MoCl}_4\text{O}_3(\text{C}_6\text{H}_7\text{N})_2$ [8], respectively. MoOCl_4 reacts with 2-methylpyridine & 3-methylpyridine producing $\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_6\text{H}_7\text{N})_2(\text{CH}_3\text{CN})_2$ [4] & $\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_6\text{H}_7\text{N})_2(\text{CH}_3\text{CN})_2$ [5], respectively.

Compounds have been characterized by elemental analysis, ^1H NMR, FTIR, Mass (LC-MS/GC-MS), electronic spectra and molar conductance studies.

Keywords: MoOCl_4 ; MoCl_5 ; pyrazole; 2-mercaptopyridine-N-oxide sodium; imidazole; 2-methylpyridine; 3-methylpyridine; 4-methylpyridine.

I. Introduction

Molybdenum is known to form multinuclear complexes.^{1, 2, 3, 4, 5, 6} When CH_3CN is used as reaction medium, these complexes may be cyanide bridged^{1, 2}. CH_3CN may act as terminal or cross bridged ligand. Identification of terminal^{4, 5, 7, 8}/cross bridged^{1, 4, 5, 6} CH_3CN ligand can be done by FTIR studies. Cross-bridging¹ of CH_3CN ligand can also be identified by ^1H NMR chemical shifts.

The author reported^{9, 10, 11, 12, 13} reactions of MoOCl_4 , MoO_2Cl_2 , MoCl_5 in CH_2Cl_2 medium. The author reported^{4, 5, 14} reactions of MoOCl_4 & MoO_2Cl_2 & MoCl_5 in CH_3CN medium. In the reactions reported in this paper, enhanced polarity of CH_3CN medium has played an important role in reaction process. Products obtained are mostly soluble in CH_3CN due to good solubility of MoOCl_4 & MoCl_5 in CH_3CN due to formation of solvent stabilized complexes.

Some compounds reported in this paper are multinuclear as assessed by the fragments detected in mass (LC-MS/GC-MS) spectra. There is some similarity in the fragments formed from the compounds prepared from MoOCl_4 & MoCl_5 .

Pyrazoles and their derivatives exhibit various biological activities including antimicrobial¹⁵, anti-cyclooxygenase¹⁶, anticonvulsant¹⁷, antitubercular¹⁸, antitumor¹⁹, antiinflammatory²⁰, analgesic²¹, antidiabetic²², antipshycotic^{23, 24, 25}. Many drugs, such as, antifungal drugs and nitroimidazole contain an imidazole^{26, 27} ring.

Imidazole²⁸ containing drugs have a broad scope in remedying various dispositions in clinical medicine.

Compounds containing N-oxides and Sulphur, such as 2-mercaptopyridine and 2-mercaptopyridine-N-oxide, possess important biological activity^{29, 30}. Compounds containing sulphur, as well as their metal complexes exhibit numerous biochemical applications^{31, 32, 33}.

2-Methylpyridine³⁴ is used in a variety of agrochemicals and pharmaceuticals, such as, nitrapyrin; to prevent loss of ammonia from fertilizers³⁵; picloram, a herbicide; and amprolium, a coccidiostat.

3-Methylpyridine³⁶ is a useful precursor to agrochemicals, such as, chlorpyrifos³⁵. 3-methylpyridine is biodegradable, although it degrades more slowly and volatilize more readily from water samples than either 2-methylpyridine or 4-methylpyridine^{37, 38}.

4-Methylpyridine³⁹ is a building block for the synthesis of other heterocyclic compounds. It is a precursor to other commercially significant species, often of medicinal interest.

II. Experimental

Materials:

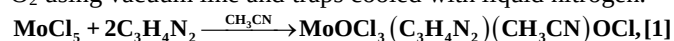
Molybdenumoxytetrachloride MoOCl_4 has been prepared in laboratory by reaction of MoO_3 (CDH, AR Grade) with SOCl_2 at reflux temperature for about 5 h. After refluxing, excess SOCl_2 was evacuated in traps cooled with liquid nitrogen. Dark green crystals thus obtained were dissolved in dry CH_2Cl_2 to get a dark red solution. Solution was filtered through filtration unit fitted with G-4 sintered glass crucible to remove any unreacted/undissolved MoO_3 . On evacuation of filtrate, shining dark green crystals of MoOCl_4 were obtained, having m.p. $100^\circ\text{--}102^\circ\text{C}$. Molybdenumpentachloride MoCl_5 (Sigma-Aldrich, USA) is a blackish brown hygroscopic solid. It was purchased and used as such. Imidazole is a colourless solid (SD Fine, LR Grade, m.p. $88^\circ\text{--}91^\circ\text{C}$). It is soluble in water and many polar organic solvents including CH_3CN . Pyrazole is a colourless solid (SD Fine, LR Grade, m.p. $66^\circ\text{--}70^\circ\text{C}$). 2-Mercaptopyridine-N-oxide sodium (Sigma-Aldrich, USA, m.p. 250°C) is a deep brown solid, soluble in acetonitrile. 2-Methylpyridine also called α -picoline (Sigma-Aldrich, USA, m.p. -66.7°C , b.p. 129.4°C) is a colourless liquid. 3-Methylpyridine β -picoline (Sigma-Aldrich, USA, m.p. -18°C , b.p. 141°C) is a colourless liquid. 4-Methylpyridine γ -picoline (Sigma-Aldrich, USA, m.p. 3.6°C , b.p. 145.4°C) is a colourless liquid. All ligands were dried under vacuum. SOCl_2 (CDH, LR grade, b.p. $76^\circ\text{--}78^\circ\text{C}$) was kept over quinoline for 48 h (50 g SOCl_2 to 10 g quinoline) to remove acid impurities and then fractionally distilled to get a colourless liquid. CH_3CN was dried by standard methods.

Physical Measurements:

Molybdenum and chlorine were estimated by standard methods⁴⁰. The elemental analyses (C, H, N and O) were carried out using Thermo Finnigan Elemental Analyzer, FTIR spectra were recorded in the range $4000 - 400\text{ cm}^{-1}$ using Perkin-Elmer 400 FTIR Spectrometer (Germany), in KBr disks, $^1\text{H-NMR}$ spectra were recorded using Bruker Avance-II 400 (Fallanden) NMR, at SAIF/CIL Panjab University, Chandigarh (India), in DMSO-d_6 and UV-VIS spectra in DMSO solvent were recorded using Thermoscientific Genesys 10S Series UV-VIS spectrophotometer (USA), at GZS PTU Campus, Bathinda (India). GC-MS spectra were recorded in the range $0 - 1100\text{ m/z}$ using Thermo Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer., at SAIF/CIL Panjab University, Chandigarh (India). Molar conductance measurements of millimolar solutions were carried out on Electronic India Digital Conductivity Meter Model 621 (India) at 25°C .

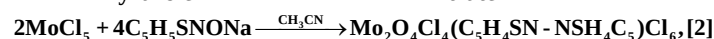
Synthesis of Compounds [1] to [8]:

A 100 ml round bottomed flask containing a magnetic bead was attached to a pressure stabilized dropping funnel fitted with a teflon rotaflow stop-cock. Assembly was connected to vacuum line and flame dried under vacuum (10^{-3} torr). Dry N_2 gas purged with O_2 was allowed into assembly at room temperature, through traps cooled with liquid nitrogen. A known weight of MoOCl_4 or MoCl_5 dissolved in dry CH_3CN was taken in round bottomed flask. 1:1 or 1:2 molar amount of $\text{C}_3\text{H}_4\text{N}_2$ (imidazole or pyrazole), $\text{C}_5\text{H}_4\text{NSO}^-\text{Na}^+$ (2-mercaptopyridine-N-oxide sodium), 2-methylpyridine, 3-methylpyridine or 4-methylpyridine dissolved in CH_3CN in dropping funnel, was added drop wise to round bottom flask with constant stirring, at room temperature. Products were recovered from filtrate by filtration through G-4 bed of a filtration unit, at reduced pressure and under inert atmosphere. All compounds synthesized are very much air and moisture sensitive. They have tendency to turn blue in colour. So all reactions and work ups were handled under dry N_2 gas purged with O_2 using vacuum line and traps cooled with liquid nitrogen.



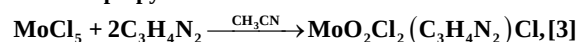
Pyrazole

Filtrate



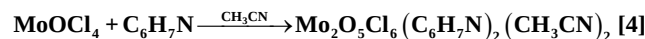
2-Mercaptopyridine - N - oxide sodium

Filtrate



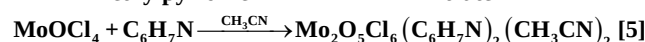
Imidazole

Filtrate



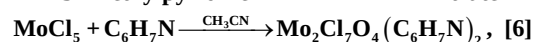
2-Methylpyridine

Filtrate



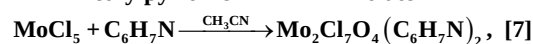
3-Methylpyridine

Filtrate



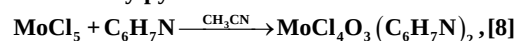
2-Methylpyridine

Filtrate



3-Methylpyridine

Filtrate



4-Methylpyridine

Filtrate

III. Results & Discussions

Analytical Measurements:

All compounds are very moisture and air sensitive. They are insoluble in common organic solvents like CH_2Cl_2 , CHCl_3 , n-hexane, but soluble in polar solvents like CH_3CN , DMSO and DMF. Formulations of these compounds have been done on basis of their elemental analytical data, mass (LC-MS/GC-MS) and molar conductance Λ_M measurements. Analytical data and mass (LC-MS/GC-MS) spectra reveal that some of these compounds are multinuclear. Λ_M of compounds [1] to [8] in DMSO are $0.27 - 1.34 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}$, suggesting their non-electrolytic nature (Table-1).

Table-1 (Analytical & Molar Conductance Data)								
Compounds (Colour/F.W.)	Λ_M^*	% Composition Observed (Calculated)						
		Mo	Cl	C	H	N	O	S
$\text{MoOCl}_3(\text{C}_3\text{H}_4\text{N}_2)(\text{CH}_3\text{CN})\text{OCl}$ (Light brown/379.0)	0.30	25.95 (25.32)	37.29 (37.46)	16.41 (15.83)	2.56 (1.84)	11.98 (11.08)	08.1 (08.4)	----
$\text{Mo}_2\text{O}_4\text{Cl}_4(\text{C}_5\text{H}_4\text{SN-NSH}_4\text{C}_5)$ (Light brown/831.0)	1.21	22.44 (23.10)	42.99 (42.71)	14.94 (14.44)	01.82 (00.96)	04.18 (03.36)	07.1 (07.7)	08.0 (07.7)
$\text{MoO}_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)\text{Cl}$ (Dark brown/302.5)	0.06	30.93 (31.73)	34.88 (35.20)	12.85 (11.90)	1.95 (1.32)	10.20 (09.25)	09.6 (10.5)	----
$\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_6\text{H}_7\text{N})_2(\text{CH}_3\text{CN})_2$ (Bright green/753.0)	0.34	24.78 (25.49)	29.13 (28.28)	24.77 (25.49)	3.05 (2.65)	06.49 (07.43)	10.21 (10.62)	----
$\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_6\text{H}_7\text{N})_2(\text{CH}_3\text{CN})_2$ (Dark green/753.0)	1.34	24.67 (25.49)	28.94 (28.28)	24.78 (25.49)	02.86 (25.49)	06.55 (25.49)	09.82 (25.49)	----
$\text{Mo}_2\text{Cl}_7\text{O}_4(\text{C}_6\text{H}_7\text{N})_2$ (Henna green/690.5)	0.30	27.04 (27.80)	35.13 (35.98)	21.73 (20.85)	02.96 (02.02)	04.88 (04.05)	09.19 (09.26)	----
$\text{Mo}_2\text{Cl}_7\text{O}_4(\text{C}_6\text{H}_7\text{N})_2$ (Light green/690.5)	0.27	26.98 (27.80)	35.13 (35.98)	21.67 (20.85)	02.72 (02.02)	04.98 (04.05)	08.27 (09.26)	----
$\text{MoCl}_4\text{O}_3(\text{C}_6\text{H}_7\text{N})_2$ (Dark green/472.0)	0.27	19.40 (20.33)	29.13 (30.08)	29.67 (30.52)	02.94 (02.96)	04.95 (05.93)	09.33 (10.16)	----

* Molar conductance of millimolar solutions in DMSO at 25°C .

FTIR Spectra:

Pyrazole^{41, 42} shows N-H stretching at 3450 cm^{-1} . Band at 3208 cm^{-1} shows that N-H group is present in compound [1]. Mo-N coordination bond lowers frequency of N-H stretching. Strong band at 975.27 cm^{-1} shows the presence of $\text{Mo}=\text{O}^{44, 45}$ str. in compound [1] (Table-2).

2-Mercaptopyridine-N-oxide sodium^{46, 47, 48, 49, 50, 51} shows N-H stretching above 3100 cm^{-1} . Bands at 3392.36 cm^{-1} & 3101.41 cm^{-1} show the presence of N-H group in compound [2] (Table-3). Bands are missing in the range of 2700 cm^{-1} showing the absence of S-H group. Two bands at 944.43 cm^{-1} and 908.35 cm^{-1} are attributable to the presence of cis-MoO_2^{2+} core⁴³ in compound [2] (Table-3).

Imidazole^{52, 53} shows N-H stretchings at $3724-3237 \text{ cm}^{-1}$. Band at 3278.1 cm^{-1} shows that N-H group is present in compound [3]. This peak is broad in the solid state (KBr disk) due to hydrogen bonding. Two bands at 979.9 cm^{-1} and 921.23 cm^{-1} are attributable to the presence of cis-MoO_2^{2+} core⁴³ in compound [3] (Table-4).

2-Methylpyridine⁵⁴ shows C-H ring stretching at 3406 cm^{-1} , 3137 cm^{-1} , 3086 cm^{-1} . Band at 3390.3 cm^{-1} shows that 2-methylpyridine is present in compound [4]. Strong band at 956.7 cm^{-1} & 917.7 cm^{-1} shows the presence of cis-MoO_2^{2+} core⁴³ in compound [4] (Table-5). Band at 3397.4 cm^{-1} shows that 2-methylpyridine is present in compound [6]. Strong band at 979.14 cm^{-1} shows the presence of $\text{Mo}=\text{O}^{44, 45}$ str. in compound [6] (Table-5).

3-Methylpyridine⁵⁵ shows C-H ring stretching at 3060 cm^{-1} & 3032 cm^{-1} . Band at 3366.4 cm^{-1} shows that 3-methylpyridine is present in compound [5]. Strong band at 955.10 cm^{-1} & 916.10 cm^{-1} shows the presence of cis-MoO_2^{2+} core⁴³ in compound [5] (Table-6). Band at 3088.16 cm^{-1} shows that 3-methylpyridine is present in compound [7]. Strong band at 983.14 cm^{-1} shows the presence of $\text{Mo}=\text{O}^{44, 45}$ str. in compound [7] (Table-6).

4-Methylpyridine⁵⁵ shows C-H ring stretching at 3072 cm^{-1} & 3031 cm^{-1} . Bands at 3367.2 cm^{-1} , 3215.2 cm^{-1} , 3159.2 cm^{-1} & 3086 cm^{-1} show that 3-methylpyridine is present in compound [8]. Strong band at 984.6 cm^{-1} & 919.18 cm^{-1} shows the presence of cis-MoO_2^{2+} core⁴³ in compound [8] (Table-7).

Table 2 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_3\text{H}_4\text{N}_2$ (Pyrazole) ^{41, 42}	[1]
N-H str.	3450	3208 vs, b
C-H str.	3155, 3144	3136.22 s, 2856.29 sh
C=C ring str.	1558	1621.35 m, 1552.40 m
N-C ring str.	1468, 1138	1472.41 m, 1404.38 m, 1350.45 w, 1265.49 w, 1205.59 vw, 1165.47 w,
C-H in plane bending	1046, 1035	1111.9 s, 1051.32 s
C-H bending	938	-----
Ring bending	918	-----
C-H out of plane bending (wagging), Ring twisting	893, 840, 760	783.27 s, 734.32 s
Ring twisting	656, 619	609.36 m, 565.4 m
Ring twisting, N-H wagging	498	494.44 w
Mo=O ^{44, 45} str.	-----	975.27 s

Table 3 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_5\text{H}_5\text{NS}$ ^{46, 47, 48, 49, 50, 51} (2-Mercaptopyridine)	[2]
N-H str	3176	3392.36 s, 3101.41 sh
C-H str	3054, 2927, 2879	2928.48 sh
S-H str	2709 m	---
Ring breathing modes & Hydrogen in plane wagging	1613 s, 1576 vs, 1504 s, 1446 s, 1418 s	1607.41 s, 1528.54 w, 1464.47 w, 1428.48 w, 1381.54 w
C=N ring	1275 m	1277.53 m
C-H in plane bending	1246 m	1246.56 w
C-S str	1188 vs, 1145 vs	1199.46 m
C=S str, Hydrogen out of plane bending out of plane	745, 613	828.41 m, 770.31 vs, 621.49 sh, 566.46 m
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴³	-----	944.43 m, 908.35 s

Table 4 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_3\text{H}_4\text{N}_2$ (Imidazole) ^{52, 53}	[3]
N-H str.	3724 vb, 3656 vb, 3270, 3241, 3237	3271.8 sb
C-H str.	3196, 3165	3150.8 s, 2993.9 sh, 2869.11 sh,
C=C ring str.	1558, 1500	1747.18 sh, 1614.10 s, 1585.10 s
N-C ring str.	1434	1426.18 sh
C-H in plane bending	1092, 1074	1192.23 w, 1093.20 w, 1048.17 m
C-H bending	964	-----
Ring bending	909	-----
C-H out of plane bending (wagging), Ring twisting	816, 730	757.12 s
Ring twisting	646	623.13 s
Ring twisting, N-H wagging	528	498.19 sh
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴³	-----	979.9 s, 921.23 sh

Table 5 (FTIR absorptions in cm^{-1})			
Assignment	2-Methylpyridine ⁵⁴	[4]	[6]
ν C-H Ring	3406 mb, 3137 m, 3086 m, 3066 m, 3012 s	3390.3 vs, b	3397.4 vs, b
ν C-H Methyl	2958 m	-----	-----
ν Ring	1596 vs, 1589 m	1633.5 s, 1621.5 s, 1540.9 sh	1627.11 s, 1539.24 sh,
∂ Ring C-H	1477 s	1473.9 sh	1474.25 sh
∂_{as} C-H Methyl	1461 s	-----	-----
∂_{s} C-H Methyl	1377 w	1399.10 w	1399.27 sh
∂ Ring C-H	1295 s,	1294.10 w	1294.28 w
ν C-C bond between ring and Methyl	1237 m	1242.11 w	1254.29 w
∂ Ring C-H	1148 m,	1167.10 w	1165.28 w
ν Ring	1101 vw, 1060 s	1108.11 w, 1047.11 w	1108.29 w, 1047.28 w
∂ C-H Ring	752 vs, 731 m	762.5 s	766.16
τ Ring	629 m	629.8 sh	628.22
∂ Ring	547 w	565.8 sh	-----
∂ C-C bond between ring and Methyl	471 m	471.9 sh	499.24 w, 470.23 w
Mo=O ^{38, 39} str.	-----	-----	979.14 s

Mo=O str. of cis-MoO ₂ ²⁺ core ⁴³	----	956.7 m, 917.7 m	----
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Table 6 (FTIR absorptions in cm ⁻¹)			
Assignment	3-Methylpyridine ⁵⁶	[5]	[7]
ν C-H Ring	3060, 3032,	3366.4 vs, b	3088.16 vs, b
ν C-H Methyl	3001, 2957, 2924	2844.7 sh	----
ν Ring	1598, 1579	1630.7 s, 1615.7 s, 1555.8 s	1615.14 s, 1554.15 s
δ Ring C-H	1480	1474.11 s	1474.18 s
δ _{as} C-H Methyl	1457, 1450	----	----
δ Ring C-H	1416	1386.15 w, 1354.16 w	1387.21 sh
δ _s C-H Methyl	1386	1262.14 w	1261.20 m
δ Ring C-H	1363	----	----
ν Ring	1249	----	----
ν C-C bond between ring and Methyl	1229	----	----
δ Ring C-H	1192	1184.17 w	1185.23 w
ν Ring	1126, 1045	1118.15 w, 1047.16 w	1118.21 w, 1047.22 m
ν Ring	1031	881.13 sh	879.21 m
ν Ring	791	789.7 s, 737.10 sh, 678.7 s, 630.14 sh, 564.15 sh, 461.16	786.16 s, 738.18 sh, 677.14 s, 630.20 w, 498.22
Mo=O ^{38, 39} str.	----	----	983.14 s
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴⁰	----	955.10 m, 916.10 m	----

Table 7 (FTIR absorptions in cm ⁻¹)		
Assignment	4-Methylpyridine ⁵⁶	[8]
ν C-H Ring	3072, 3031	3367.2 vs, b, 3215.2 s, 3159.2 s, 3086 sh,
ν C-H Methyl	2993, 2924	2948.6 sh
ν Ring	1608, 1562	1637.4 s, 1607.7 sh, 1505.9 s
δ Ring C-H	1499	1474.11 s
δ _{as} C-H Methyl	1456, 1446	----
δ Ring C-H	1416	----
δ _s C-H Methyl	1381	1374.19 m
δ Ring C-H	1364	1309.20 m
δ Ring C-H	1225	1248.20 m
ν C-C bond between ring and Methyl	1212	----
δ Ring C-H	1192	1196.17 m
ν Ring	1116, 1070	1109.22 w, 1094.22 w, 1037.21 w
δ Ring	1003	881.13 sh
δ C-H Ring	874	,
τ Ring	728	778.6 s, 702.13 sh, 648.16 w
δ Ring	522	567.15 sh, 518.16 w
δ C-C bond between ring and Methyl	485	475.13 m
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴³	----	984.6 s, 919.18 m

¹H NMR Spectra:

Spectrum of pyrazole⁵⁷ in CCl₄ shows absorptions due to middle CH proton at 6.31 ppm, CH protons on side two carbons at 7.61 ppm and due to N-H proton at 12.64 ppm. Spectrum of compound [1] in DMSO-d₆ shows peak that peak due to middle CH proton and on side two carbons have moved downfield (Table-8). Peaks of C-H protons of pyrazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of 2-mercaptopyridine⁵⁸ shows peaks at 7.33 ppm, 6.80 ppm, 7.46 ppm and 7.70 ppm due to C₃-H, C₄-H, C₅-H and N-C-H protons, respectively. Spectra of compound [2] shows that absorptions move downfield (Table-9). N-H peaks were not observed.

Spectrum of imidazole⁵⁹ in CDCl₃ shows absorptions due to CH proton (between two nitrogen atoms) at 7.73 ppm, CH protons on other two carbons at 7.15 ppm and due to N-H proton at 11.62 ppm. Spectrum of compound [7] in DMSO-d₆ shows relatively up field absorptions for CH proton (between two nitrogen atoms), CH protons on other two carbons (Table-10). Two equivalent C-H protons of imidazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of 2-methylpyridine^{60, 61} in CDCl₃ shows absorptions due to H (CH₃), H-C₁, H-C₂, H-C₃ and H-C₄ due at 2.54, 7.12, 7.53 & 7.08 ppm, respectively. Spectra of compounds [4] and compound [6] in DMSO-d₆ show that all of these absorptions have moved downfield.

Spectrum of 3-methylpyridine^{62, 63} in CDCl₃ shows absorptions due to H (CH₃), H-C₁, H-C₃, H-C₄ and H-C₅ due at 2.32, 8.44, 7.45 & 7.16 ppm, respectively. Spectra of compounds [5] and compound [7] in DMSO-d₆ show that all of these absorptions have moved downfield.

Spectrum of 4-methylpyridine^{64, 65} in CDCl₃ shows absorptions due to H (CH₃), H-C₁ & H-C₅, H-C₃ & H-C₄ at 2.34, 8.46 & 7.10 ppm, respectively. Spectrum of compound [8] in DMSO-d₆ shows that all of these absorptions have moved downfield.

Assignments	C ₃ H ₄ N ₂ in CCl ₄ (Pyrazole) ⁵⁷	[1]
N-H	12.64 1H	----
Middle C-H	6.31 1H	6.62 1H
Side C-H	7.61 2H	8.16 2H

Table-9 (¹ H NMR absorptions in ppm)		
Assignments	C ₈ H ₅ O ₂ NS ⁵⁸ (2-Mercaptopyridine)	[2]
N-H	---	---
C ₃ -H	7.33 1H	7.58
C ₄ -H	6.80 1H	7.21
C ₅ -H	7.46 1H	7.71
NC-H	7.70 1H	8.40

Table-10 (¹ H NMR absorptions in ppm)		
Assignments	C ₃ H ₄ N ₂ (Imidazole) ⁵⁹	[3]
N-H	12.4 1H	14.22 1H
C-H between two nitrogen atoms	9.37 1H	8.69 1H
C-H on other carbons	7.80 2H	7.26 2H

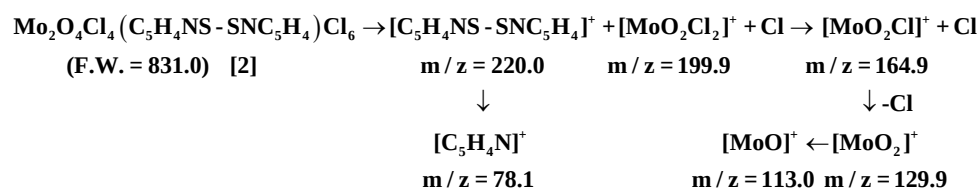
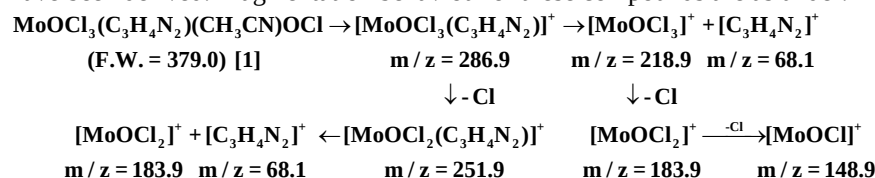
Assignments	C ₆ H ₇ N in CDCl ₃ (2-Methylpyridine) ^{60, 61}	[4]	[6]
H (CH ₃ (	2.54 3H s	2.83	2.76
H-C ₂	7.12 1H d	8.48	8.43
H-C ₃	7.53 1H t	----	----
H-C ₄	7.08 1H t	7.93	7.88
H-C ₅	8.47 d	8.73	8.66

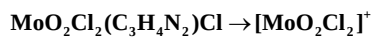
Assignments	C ₆ H ₇ N in CDCl ₃ (3-Methylpyridine) ^{62, 63}	[5]	[7]
H (CH ₃ (	2.32 3H s	2.55 3H	2.57 3H
H-C ₁ & H-C ₅	8.44 1H s	8.85 2H	8.82 1H, 9.18 1H
H-C ₃	7.45 1H d	8.01 1H	7.99 1H
H-C ₄	7.16 1H t	8.49 1H	8.49 1H

Assignments	C ₆ H ₇ N in CDCl ₃ (4-Methylpyridine) ^{64, 65}	[8]
H (CH ₃ (	2.34 3H s	2.68 3H
H-C ₁ & H-C ₅	8.46 2H d	8.78 2H
H-C ₃ & H-C ₄	7.10 2H d	7.95 2H

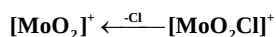
Mass Spectra (LC-MS/GC-MS)⁶⁶:

Compounds [1], [2], [3], [6], [7] and [8] have been prepared from MoCl₅ as the precursor. Compounds [4] and [5] have been prepared from MoOCl₄ as the precursor. Mass spectra (GC-MS) of these compounds have some correlations and common fragments (Table-14). Based on the fragments formed, formulae of the compounds have been derived. Fragmentation behaviour of these compounds are as under.





(F.W. = 302.5) [3] $m/z = 199.9$



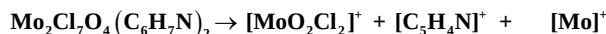
$m/z = 129.9$ $m/z = 164.9$



(F.W. = 753.0) [4] $m/z = 198.6$ $m/z = 77.48$ $m/z = 96.16$



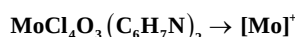
(F.W. = 753.0) [5] $m/z = 198.6$ $m/z = 77.49$ $m/z = 96.16$



(F.W. = 690.5) [6] $m/z = 198.62$ $m/z = 77.49$ $m/z = 96.16$



(F.W. = 690.5) [7] $m/z = 96.16$



(F.W. = 472.0) [8] $m/z = 96.16$

Table-14 (m/z values of some fragments)				
Comp.	Fragment	Calculated ⁶⁶	Observed	Relative abundance
[1]	$[\text{MoOCl}_3(\text{C}_3\text{H}_4\text{N}_2)]^+$	286.84	286.9	55%
	$[\text{MoOCl}_2(\text{C}_3\text{H}_4\text{N}_2)]^+$	251.87	251.9	55%
	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	68.1	100%
	$[\text{MoOCl}_3]^+$	218.80	218.9	90%
	$[\text{MoOCl}_2]^+$	183.83	183.9	15%
	$[\text{MoOCl}]^+$	148.86	148.9	10%
[2]	$[\text{C}_5\text{H}_4\text{NS-SNC}_5\text{H}_4]^+$	220.01	220.0	75%
	$[\text{C}_5\text{H}_4\text{N}]^+$	78.03	78.1	100%
	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	199.9	85%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	164.9	60%
	$[\text{MoO}_2]^+$	129.89	129.9	18%
	$[\text{MoO}]^+$	113.90	113.0	60%
[3]	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	199.9	100%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	164.9	30%
	$[\text{MoO}_2]^+$	129.89	129.9	5%
[4]	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	198.6	18%
	$[\text{C}_5\text{H}_4\text{N}]^+$	78.03	77.48	40%
	$[\text{Mo}]^+$	97.90	96.16	100%
[5]	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	198.6	5%
	$[\text{C}_5\text{H}_4\text{N}]^+$	78.03	77.49	15%
	$[\text{Mo}]^+$	97.90	96.16	100%
[6]	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	198.62	25%
	$[\text{C}_5\text{H}_4\text{N}]^+$	78.03	77.49	8%
	$[\text{Mo}]^+$	97.90	96.16	100%
[7]	$[\text{Mo}]^+$	97.90	96.16	100%
[8]	$[\text{Mo}]^+$	97.90	96.16	100%

Electronic Spectra:

Absorptions (λ_{max} nm) Pure Ligand	Absorptions (λ_{max} nm) Compound (solution in DMSO)
Pyrazole ⁶⁷ (solution in DMSO) 264 nm pyrazole ring $\pi \rightarrow \pi^*$	[1] 259 nm (ϵ 1.8x10 ³) ring $\pi \rightarrow \pi^*$
2-Mercaptopyridine-N-oxide sodium ^{69,70} below 300 nm ring $\pi \rightarrow \pi^*$	[2] 273 nm (ϵ 8.8x10 ³) ring $\pi \rightarrow \pi^*$
Imidazole ⁶⁸ (solution in DMSO) 284 nm imidazole ring $\pi \rightarrow \pi^*$	[3] 260 nm (ϵ 0.9x10 ³) ring $\pi \rightarrow \pi^*$
2-Methylpyridine (solution in DMSO) 273 nm ring $\pi \rightarrow \pi^*$	[4] 264 nm (ϵ 5.6x10 ³) ring $\pi \rightarrow \pi^*$
3-Methylpyridine (solution in DMSO) 272 nm ring $\pi \rightarrow \pi^*$	[5] 325 nm (ϵ 6.8x10 ³) ring $\pi \rightarrow \pi^*$
2-Methylpyridine (solution in DMSO) 273 nm ring $\pi \rightarrow \pi^*$	[6] 266 nm (ϵ 6.9x10 ³) ring $\pi \rightarrow \pi^*$
3-Methylpyridine (solution in DMSO) 272 nm ring $\pi \rightarrow \pi^*$	[7] 268 nm (ϵ 5.2x10 ³) ring $\pi \rightarrow \pi^*$
4-Methylpyridine (solution in DMSO) 268 nm ring $\pi \rightarrow \pi^*$	[8] 261 nm (ϵ 4.1x10 ³) ring $\pi \rightarrow \pi^*$

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