



Reactions of MoO_2Cl_2 & MoCl_5 with Pyrazole, Imidazole, Pot. Phthalimide, 3-Methylpyridine & Acetamide

Gursharan Singh^{1, #}

¹Professor, Department of Applied Chemistry,
Giani Zail Singh Campus College of Engineering & Technology,
Dabwali Road, Bathinda-151001, Punjab, India
(Constituent College of MRSPTU, Bathinda, India, www.mrsptu.ac.in)

Rakesh Kumar²

Ph.D. Research Scholar

Author to whom correspondence should be addressed

Abstract: MoCl_5 reacts with imidazole, pyrazole, pot. phthalimide and 3-methylpyridine (1:1 molar ratio) in THF medium to yield: $\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_2$ [2], $\text{Mo}_4\text{O}_5\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_4$ [3], $[\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{C}_4\text{H}_8\text{O})]_4$ [4] & $[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_4$ [5], respectively. MoO_2Cl_2 reacts with acetamide (1:1 molar ratio) in THF medium to yield: $[\text{Mo}_2\text{O}_2\text{Cl}_3(\text{CH}_3\text{CONH}_2)_2(\text{C}_4\text{H}_8\text{O})]_4$ [1].

Complexes have been characterized by elemental analysis, ¹H NMR, FTIR, Mass (LC-MS).

Keywords: MoO_2Cl_2 ; MoCl_5 ; acetamide; pyrazole; imidazole; pot. phthalimide; 3-methylpyridine

I. Introduction

Reactions of MoO_2Cl_2 & MoCl_5 with ligands in both polar and non-polar solvents have been reported. One of the difficulties in carrying out reactions in non-polar solvents is that the reactants are feebly soluble in these solvents, so there is possibility of inhomogeneity of the reaction mixture/products. On the other hand, due to better solubility of reactants in polar solvents, the possibility of polymerization and formation of multinuclear complexes increases. Molybdenum multinuclear complexes^{1, 2, 3, 4, 5, 6} have been reported.

Reactions of MoOCl_4 , MoO_2Cl_2 & MoCl_5 in CH_2Cl_2 medium^{7, 8, 9, 10, 11} have been reported by the author. Owing to feeble solubility of MoO_2Cl_2 , MoCl_5 and ligands in CH_2Cl_2 medium, reactions of MoOCl_4 & MoO_2Cl_2 & MoCl_5 were carried out and reported by the author in CH_3CN medium^{4, 5, 12, 13, 14}. In some reactions reported in this paper, enhanced polarity of THF medium leads to extensive polymerization of the products giving rise to sticky materials, which were treated with appropriate solvents to achieve powdered products. Higher solubility of MoO_2Cl_2 , MoCl_5 in THF medium is owing to formation of solvent stabilized¹⁵ precursors, like $\text{MoO}_2\text{Cl}_2(\text{THF})_2$. Mass (LC-MS) spectra show that there is some similarity in the fragments formed from the complexes [1] to [5] prepared from MoO_2Cl_2 & MoCl_5 .

Phthalimide^{16, 17} derivatives have been reported with biological activities like inhibition of tumor necrosis factor- α .

Pyrazoles and their derivatives exhibit various biological activities including antimicrobial¹⁸ anti-cyclooxygenase¹⁹, anticonvulsant²⁰, antitubercular²¹, antitumor²², antiinflammatory²³, analgesic²⁴, antidiabetic²⁵, antipshycotic^{26, 27, 28}. Many drugs, such as, antifungal drugs and nitroimidazole contain an imidazole^{29, 30} ring.

Imidazole³¹ containing drugs have a broad scope in remedying various dispositions in clinical medicine.

3-Methylpyridine³² is a useful precursor to agrochemicals, such as, chlorpyrifos³³. 3-methylpyridine is biodegradable, although it degrades more slowly and volatilize more readily from water samples than either 2-methylpyridine or 4-methylpyridine^{34, 35}.

Acetamide derivatives have been reported to have *in vitro* antinflammatory³⁶ and antioxidant³⁶ activities.

II. Experimental

Materials:

MoO_2Cl_2 (Sigma-Aldrich, USA) is a light yellow hygroscopic solid. It was purchased and used as such. MoCl_5 (Sigma-Aldrich, USA) is a blackish brown hygroscopic solid. It was purchased and used as such. Potassium phthalimide (Sigma-Aldrich, USA) is a pale yellow solid, having m.p. greater than 300° C. Imidazole is a colourless solid (SD Fine, LR Grade, m.p. 88°-91° 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°-70° C). 3-Methylpyridine also

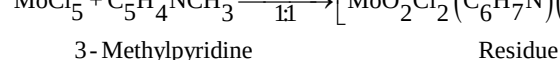
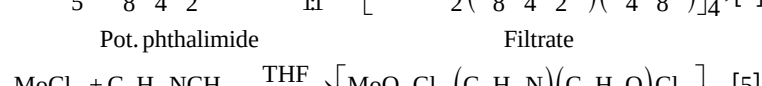
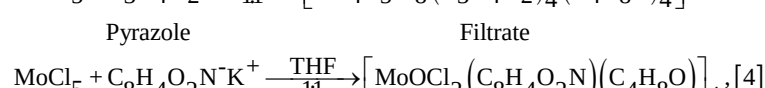
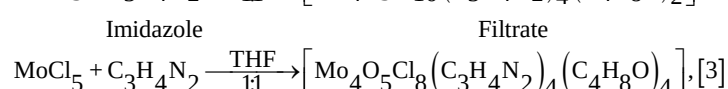
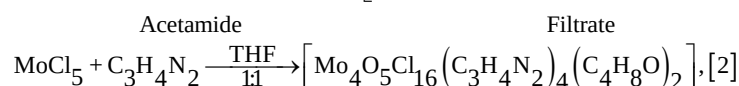
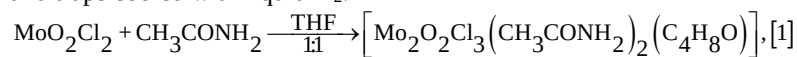
called β -picoline (Sigma-Aldrich, USA, m.p. -18°C , b.p. 141°C) is a colourless liquid. Acetamide (NICE, LR grade, m.p. 79°C – 81°C) is a colourless solid and was procured from market. All ligands were dried under vacuum. SOCl_2 (CDH, LR grade, b.p. 76°C – 78°C) was kept over quinoline for 48 h (50 g SOCl_2 to 10 g quinoline) to remove acid impurities and then fractionally distilled to get colourless liquid. THF was dried by standard methods.

Physical Measurements:

Molybdenum and chlorine were estimated by standard methods³⁷. The elemental analyses (C, H, N) 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, ^1H -NMR spectra were recorded using Bruker Avance-II 400 (Fallanden) NMR, at SAIF/CIL Panjab University, Chandigarh (India), in DMSO-d_6 , LC-MS spectra were recorded in the range $0 - 1100\text{ m/z}$ using WATERS, Q-TOF Micromass LC-MS (UK), at SAIF/CIL Panjab University, Chandigarh (India).

Synthesis of Complexes [1] to [5]:

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 MoO_2Cl_2 or MoCl_5 dissolved in dry THF was taken in round bottomed flask and 1:1 molar amount of $\text{C}_8\text{H}_4\text{O}_2\text{N}^-\text{K}^+$ (potassium phthalimide), $\text{C}_3\text{H}_4\text{N}_2$ (imidazole or pyrazole), acetamide (CH_3CONH_2) or 3-methylpyridine ($\text{C}_5\text{H}_4\text{NCH}_3$) were dissolved in THF medium in dropping funnel. The latter 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 complexes 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 N_2 .



III. Results & Discussions

Analytical Measurements:

All complexes are very much 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 complexes have been done on the basis of their elemental analytical data and mass (LC-MS) measurements (Table-1). Mass (LC-MS) spectra reveal that these complexes have some common fragments.

Table-1 (Analytical Data)					
Complexes (Colour/F.W.)	% Composition Observed (Calculated)				
	Mo	Cl	C	H	N
$[\text{Mo}_2\text{O}_2\text{Cl}_3(\text{CH}_3\text{CONH}_2)_2(\text{C}_4\text{H}_8\text{O})], [1]$ (Black/520.50)	37.62 (37.02)	20.78 (20.54)	17.76 (18.51)	03.23 (03.08)	06.25 (05.40)
$[\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_2], [2]$ (Light green/1448.00)	25.97 (26.51)	40.10 (39.22)	16.91 (16.57)	02.61 (02.20)	07.77 (07.69)
$[\text{Mo}_4\text{O}_5\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_4], [3]$ (Light Brown/1308.00)	28.45 (29.35)	20.84 (20.71)	24.97 (25.68)	03.63 (03.66)	07.73 (08.56)
$[\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{C}_4\text{H}_8\text{O})]_4, [4]$ (Navy Blue/1604.00)	23.10 (23.94)	16.80 (17.70)	35.13 (35.91)	02.16 (02.99)	02.72 (03.35)
$[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_4, [5]$ (Green/870.00)	21.13 (22.06)	31.83 (32.64)	36.73 (25.58)	02.82 (03.44)	03.66 (03.21)

FTIR Spectra:

Acetamide^{38, 39} shows N-H stretchings at 3374 cm⁻¹ & 3302 cm⁻¹. Band at 3294.0 cm⁻¹ shows that N-H group is present in compound [1] (Table-2). Strong bands at 940.2 cm⁻¹ & 913.1 cm⁻¹ show the presence of cis-MoO₂²⁺ core⁴⁰. Shift in C=O stretching frequency from 1672 cm⁻¹ to 1646.0 cm⁻¹ of acetamide indicates a Mo-O coordination bond.

Imidazole^{41, 42} shows N-H stretchings at 3724-3237 cm⁻¹. Broad band at 3287 cm⁻¹ – 3000 cm⁻¹ shows that N-H group is present in complex [2]. This peak is broad in the solid state (KBr disk) due to hydrogen bonding. One band at 984.2 cm⁻¹ is attributable to the presence of terminal Mo=O^{43, 44} str. in complex [2] (Table-3).

Pyrazole^{45, 46} shows N-H stretching at 3450 cm⁻¹. Band at 3200 - 3400 cm⁻¹ shows that N-H group is present in complex [3]. Mo-N coordination bond lowers frequency of N-H stretching. Strong band at 981.3 cm⁻¹ shows the presence of terminal Mo=O^{43, 44} str. in complex [3] (Table-4).

Potassium phthalimide⁴⁷ shows N-H stretchings at 3269 cm⁻¹ and 3154 cm⁻¹. Band at 3200.0 cm⁻¹ shows that N-H group is present in complex [4]. Strong band at 975.0 cm⁻¹ shows the presence of terminal Mo=O group^{44, 45} in the complex [4] (Table-5).

3-Methylpyridine⁴⁸ shows C-H ring stretching at 3060 cm⁻¹ & 3032 cm⁻¹. Bands at 3168.16 cm⁻¹, 3121.16 cm⁻¹, 3053.15 cm⁻¹ show that 3-methylpyridine is present in compound [5]. Strong band at 990.16 cm⁻¹ shows the presence of terminal Mo=O^{43, 44} str. in compound [5] (Table-6).

Table 2 (FTIR absorptions in cm ⁻¹)		
Absorptions	CH ₃ CONH ₂ (Acetamide) ^{38, 39}	[1]
N-H Stretching	3374, 3302	3294.0 sb
CH ₂ Stretching	2820	----
C=O Stretching, NH ₂ Deformation	1672	1646.0 s
NH ₂ Deformation	1631	----
NH ₂ Deformation	1606	1570 s
CH ₃ Deformation	1450	1405.1 s
C-N asym stretching	1396	1358.2 sh
NH ₂ Deformation	1150	1184.6 w, 1129.8 w
C-N sym stretching	1048	1024.5 m
NH ₂ rocking, twisting and wagging	900	747.1 m
N=C=O bending	600	559.2 m
Mo-N (Strong)	----	515.4 w
Mo-Cl Str.	----	----
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴⁰	----	940.2 s, 913.1 s

Table 3 (FTIR absorptions in cm ⁻¹)		
Assignments	C ₃ H ₄ N ₂ (Imidazole) ^{41, 42}	[2]
N-H str.	3724 vb, 3656 vb, 3270, 3241, 3237	3287 vs, 3000 s, vvb
C-H str.	3196, 3165	3146.3 s, 2991.5 s
C=C ring str.	1558, 1500	1601.3 s, 1578.3 s
N-C ring str.	1434	1421.8 s, 1307.1 w, 1246.1 w
C-H in plane bending	1092, 1074	1191.5 m, 1046.5 m, 1050.1 s
C-H out of plane bending (wagging), Ring twisting	816, 730	877.1 w, 792.5 m, 767.2 m
Ring twisting	646	622.4 s
Ring twisting, N-H wagging	528	495.1 m
Terminal Mo=O ^{43, 44} str.	----	984.2 s

Table-4 (FTIR absorptions in cm ⁻¹)		
Assignments	C ₃ H ₄ N ₂ (Pyrazole) ^{45, 46}	[3]
N-H, str.	3450	3200-3400 s, vb
C-H str.	3155, 3144	3138.1 s
C=C ring str.	1558	1621.4 m
N-C ring str.	1468, 1138	1455.6 m, 1408.6 m, 1261.7 m
C-H in plane bending	1046, 1035	1167.9 sh, 1112.3 s, 1050.3 s
C-H out of plane bending (wagging), Ring twisting	893, 840, 760	899.2 s, 781.2 s, 740.2 s
Ring twisting	656, 619	610.5 m
Ring twisting, N-H wagging	498	518.7 w
Terminal Mo=O ^{43, 44} str.	----	981.3 s

Table-5 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_6\text{H}_4\text{O}_2\text{N}^+\text{K}^+$ (Pot. Phthalimide) ⁴⁷	[4]
N-H str	3269 w, 3154 w	3200.0 s, b
In phase C=O str	1704 m, 1687 w, 1665 vvw	1839.19 vw, 1773.2 sh, 1727.0 s
C-C Benzene ring str	1608 s	1604.2 sh
Out of phase C=O str	1593 s, 1588 s, 1552 vw, 1507 vw	1542.2 m
C-C Benzene ring str	1465 vvw, 1449 vvw, 1398 w, 1372 s, 1356 m	1403.0 s
Five membered ring C-C str	1297 s, 1231 w, 1209 vw, 1184 s, 1128 s	1307.1 m, 1259.9 w, 1185.11 sh, 1140.9 w
C-H in plane bending	1091 vvw	1070.7 sh, 1052.3 m
C-C Benzene ring str	769 vw, 756 vw, 743 vw	745.2 sh
C-H out of plane bending	717 s	714.0 s, 647.4 m, 548.1 sh, 534.9 w
Terminal Mo=O ^{43, 44} str.	----	975.0 s

Table-6 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_5\text{H}_4\text{NCH}_3$ IN CDCl_3 (3-Methylpyridine) ⁴⁸	[5]
ν C-H Ring	3060, 3032,	3168.16 m, 3121.16 m, 3053.15 m
ν C-H Methyl	3001, 2957, 2924	2936.20 sh
ν Ring	1598, 1579	1604.25 m, 1542.17 s
δ Ring C-H	1480	---
δ_{as} C-H Methyl	1457, 1450	1467.20 s
δ Ring C-H	1416	---
δ_s C-H Methyl	1386	1387.29 m
δ Ring C-H	1363	1304.38 sh
ν Ring	1249	1251.34 w
ν C-C bond between ring and Methyl	1229	
δ Ring C-H	1192	1180.38 w
ν Ring	1126, 1045	1116.25 m
ν Ring	1031	1044.32 w, 1027.32 w
ν Ring	791	883.2 vs, 786.12 s, 739.19 s
τ Ring	712	722.10 s
δ Ring	636, 538	676.10 s, 512.24
δ C-C bond between ring and Methyl	456	468.38 m
Terminal Mo=O ^{43, 44} str.	----	990.16 s

¹H NMR Spectra:

Spectrum of THF⁴⁹ in CDCl_3 shows multiplets at 3.76 ppm and 1.85 ppm due C-2, 5 protons and C-3, 4 protons, respectively.

Spectrum of DMSO- d_6 ⁴⁹ shows absorption at 2.50 ppm.

Spectrum of acetamide⁵⁰ in CDCl_3 shows singlet due to CH_3 protons at 2.00 ppm and broad absorptions due to N-H protons at 7.04 ppm. Spectrum of complex [1] in DMSO- d_6 shows singlet at 1.84 ppm due to CH_3 protons and at broad absorption at 7.23-7.49 ppm due to N-H protons (Table-7).

Spectrum of imidazole^{51, 52} in CDCl_3 shows absorptions due to C-H proton (between two nitrogen atoms) at 7.73 ppm, C-H protons on other two carbons at 7.15 ppm and due to N-H proton at 11.62 ppm. Spectrum of complex [2] in DMSO- d_6 shows relatively up field absorptions for C-H proton (between two nitrogen atoms) and C-H protons on other two carbon atoms (Table-8). Two equivalent C-H protons of imidazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of pyrazole⁵³ in CCl_4 shows absorptions due to middle C-H proton at 6.31 ppm, C-H protons on side two carbons at 7.61 ppm and due to N-H proton at 12.64 ppm. Spectrum of complex [3] in DMSO- d_6 shows peak that peak due to middle CH proton and on side two carbons have moved downfield (Table-9). Peaks of C-H protons of pyrazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of pot. phthalimide^{54, 55} shows peaks in the range 7.3 ppm-7.8 ppm due to ring protons. Spectrum of complex [4] in DMSO- d_6 shows peaks due to ring protons in the range 7.17 ppm-8.80 ppm, N-H peak at 11.24 ppm (Table-10).

Spectrum of 3-methylpyridine^{56, 57} in CDCl_3 shows absorptions due to H (CH_3), H-C₁, H-C₃, H-C₄ and H-C₅ due at 2.32, 8.44, 7.45 & 7.16 ppm, respectively. Spectrum of compound [5] in DMSO- d_6 show that these absorptions have moved downfield.

Table-7 (¹ H NMR absorptions in ppm)		
Absorptions	CH ₃ CONH ₂ in CDCl ₃ (Acetamide) ⁵⁰	[1]
NH ₂	7.04 broad 2H	7.23-7.49 (t) 2H
CH ₃	2.00 3H	1.86 (s) 3H
Residual DMSO-d ₆	----	2.56 (s)
THF C-2, 5	----	3.65-3.71 (m)
THF C-3, 4	----	1.71-1.77 (m)

Table-8 (¹ H NMR absorptions in ppm)		
Assignments	C ₃ H ₄ N ₂ in CDCl ₃ (Imidazole) ^{51, 52}	[2]
N-H	12.4 1H	14.54 (b) 2H
C-H (between two nitrogen atoms)	9.37 1H	9.07 (s) 1H
C-H (other carbon atoms)	7.80 2H	7.58 (s) 2H
Residual DMSO-d ₆	----	2.50 (s)
THF C-2, 5	----	3.59 (s) 4H
THF C-3, 4	----	1.75 (s) 4H

Table-9 (¹ H NMR absorptions in ppm)		
Assignments	C ₃ H ₄ N ₂ in CCl ₄ (Pyrazole) ⁵³	[3]
N-H	12.64 1H	14.54 3H
Middle CH ₂	6.31 (s) 1H	6.61 (s) 1H
Side CH ₂	7.61(s) 2H	8.14 (s) 2H
Residual DMSO-d ₆	----	2.55 (s)
THF C-2, 5	----	3.35 (s) 4H
THF C-3, 4	----	1.53 (s) 4H

Table-10 (¹ H NMR absorptions in ppm)		
Assignments	C ₈ H ₄ O ₂ NK ⁺ (Pot. phthalimide) ^{54, 55}	[4]
N-H	----	11.24 1H
Ring C-H	7.58 -7.87	7.17-7.80
Residual DMSO-d ₆	----	2.55 (s)
THF C-2, 5	----	3.37-3.66 4H (m)
THF C-3, 4	----	1.78-1.81 4H m

Table-11 (¹ H NMR absorptions in ppm)		
Absorptions	C ₅ H ₄ NCH ₃ in CDCl ₃ (3-Methylpyridine) ^{56, 57}	[5]
H (CH ₃)	2.32 3H Singlet	2.49 (s)
H C ₁	8.44 1H Singlet	8.39 1H (s)
H C ₃	7.45 1H Doublet	8.33
H C ₄	7.16 1H Triplet	7.99
H C ₅	8.42 1H Doublet	8.72-8.77 (d)
Residual DMSO-d ₆	----	2.49 (s)
THF C-2, 5	----	3.58 (m) 4H
THF C-3, 4	----	1.73 (m) 4H

Mass Spectra (LC-MS)⁵⁸:

Complex [1] has been prepared from MoO₂Cl₂ as the precursor. Complexes [2], [3], [4] & [5] have been prepared from MoCl₅ as the precursor. Mass spectra (LC-MS) of these complexes have some correlations and common fragments (Table-13). Based on the fragments formed, formulae of the complexes have been derived. Fragmentation behaviour of these complexes are as under.

Co mp.	Table-12 (Fragmentation)		
[1]	$[\text{Mo}_2\text{O}_2\text{Cl}_3(\text{CH}_3\text{CONH}_2)_2(\text{C}_4\text{H}_8\text{O})] \rightarrow [\text{Mo}_2\text{O}_2\text{Cl}(\text{CH}_3\text{CONH}_2)]^+ + [\text{C}_4\text{H}_8\text{O}]^+ + [\text{CH}_3\text{CONH}_2]^+$ [1] (F.W. = 520.50) m / z = 323.18 m / z = 71.05 m / z = 60.04 ↓ 2[Mo]⁺ m / z = 98.00		

[2]	$[\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_2] \rightarrow [\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_2]^{2+}$ [2] (F.W. = 1448.0) $m/z = 725.57$ ↓ $[\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4]^{2+} + [\text{C}_4\text{H}_8\text{O}]^+$ $m/z = 653.49$ $m/z = 75.00$ ↓ $[\text{MoOCl}_2]^{2+} + [\text{MoOCl}_4(\text{C}_3\text{H}_4\text{N}_2)]^{2+} + [\text{C}_3\text{H}_4\text{N}_2]^+$ $m/z = 91.03$ $m/z = 163.10$ $m/z = 69.03$
[3]	$[\text{Mo}_4\text{O}_5\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_4] \rightarrow [\text{Mo}_4\text{O}_5\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_4]^{2+}$ [3] (F.W. = 1308.00) $m/z = 653.49$ ↓ $[\text{MoOCl}_2(\text{C}_3\text{H}_4\text{N}_2)(\text{C}_4\text{H}_8\text{O})]^{2+} \rightarrow [\text{MoOCl}_2]^{2+} + [\text{C}_3\text{H}_4\text{N}_2]^+ + [\text{C}_4\text{H}_8\text{O}]^+$ $m/z = 163.09$ $m/z = 91.03$ $m/z = 69.03$ $m/z = 73.07$
[4]	$[\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{C}_4\text{H}_8\text{O})]_4 \rightarrow [\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{C}_4\text{H}_8\text{O})]_4^{2+}$ [4] (F.W. = 1604.0) $m/z = 201.10$ ↓ $[\text{C}_4\text{H}_8\text{O}]^+ + [\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})]_4^{2+}$ $m/z = 73.03$ $m/z = 659.33$ ↓ $[\text{C}_8\text{H}_4\text{O}_2\text{N}]^+ + [\text{MoOCl}_2]^{2+} \leftarrow [\text{MoOCl}_2(\text{C}_8\text{H}_4\text{O}_2\text{N})]^{2+}$ $m/z = 149.03$ $m/z = 93.03$ $m/z = 163.10$
[5]	$[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_4 \rightarrow [\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_4^{2+}$ (5) (F.W. = 870.0) $m/z = 869.72$ ↓ $[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_2^{2+}$ $m/z = 437.26$ ↓ $[\text{MoOCl}_2(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]^{2+} + [\text{C}_6\text{H}_7\text{N}]^+$ $m/z = 163.10$ $m/z = 94.07$ ↓ $[\text{MoOCl}_2]^{2+} + [\text{C}_4\text{H}_8\text{O}]^+$ $m/z = 91.03$ $m/z = 74.93$

Table-13 (m/z values of some fragments)				
Comp.	Fragment	Calculated ⁴⁴	Observed	Relative abundance
[1]	$[\text{Mo}_2\text{O}_2\text{Cl}_3(\text{CH}_3\text{CONH}_2)_2(\text{C}_4\text{H}_8\text{O})]^+$	321.80	323.18	100%
	$[\text{CH}_3\text{CONH}_2]^+$	59.03	60.04	20%
	$[\text{C}_4\text{H}_8\text{O}]^+$	72.05	71.05	100%
	$[\text{Mo}]^+$	68.03	98.00	10%
[2]	$[\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_2]^{2+}$	723.68	725.57	1%
	$[\text{Mo}_4\text{O}_5\text{Cl}_{16}(\text{C}_3\text{H}_4\text{N}_2)_4]^{2+}$	651.62	653.49	
	$[\text{Mo}_4\text{O}_4\text{Cl}_{16}(\text{C}_3\text{H}_3\text{N}_2)_4]^+$	1283.22	1276.08	1%
	$[\text{MoOCl}_4(\text{C}_3\text{H}_4\text{N}_2)]^{2+}$	160.90	163.10	100%
	$[\text{MoOCl}_2]^{2+}$	91.91	91.03	89%
	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	69.03	100%
	$[\text{C}_4\text{H}_8\text{O}]^+$	72.05	75.00	26%
[3]	$[\text{MoOCl}_2]^{2+}$	91.91	91.03	100%

	$[\text{MoO}_5\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_4(\text{C}_4\text{H}_8\text{O})_4]^{2+}$	655.86	653.49	
	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	69.00	10%
	$[\text{MoOCl}_2(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_4\text{H}_8\text{O})]^{2+}$	161.46	163.09	87%
	$[\text{C}_4\text{H}_8\text{O}]^+$	72.05	73.07	22%
[4]	$[\text{MoOCl}_2(\text{C}_6\text{H}_4\text{O}_2\text{N})_4]^{2+}$	659.72	659.33	2%
	$[\text{MoOCl}_2(\text{C}_6\text{H}_4\text{O}_2\text{N})(\text{C}_4\text{H}_8\text{O})]^{2+}$	200.95	201.10	15%
	$[\text{MoOCl}_2(\text{C}_6\text{H}_4\text{O}_2\text{N})]^{2+}$	164.93	163.10	29%
	$[\text{C}_6\text{H}_4\text{O}_2\text{N}]^+$	147.02	149.03	17%
	$[\text{MoOCl}_2]^{2+}$	91.91	93.03	100%
	$[\text{C}_4\text{H}_8\text{O}]^+$	72.05	73.07	28%
[5]	$[\text{C}_6\text{H}_7\text{N}]^+$	93.05	94.07	62%
	$[\text{MoOCl}_2]^{2+}$	91.91	91.03	100%
	$[\text{MoOCl}_2(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]^{2+}$	162.91	163.10	47%
	$[\text{C}_4\text{H}_8\text{O}]^+$	72.05	74.93	35%
	$[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_4^{2+}$	869.76	869.72	
	$[\text{MoO}_2\text{Cl}_2(\text{C}_6\text{H}_7\text{N})(\text{C}_4\text{H}_8\text{O})\text{Cl}_2]_2^{2+}$	434.88	437.26	8%

References

- [1] F. Albert Cotton, Lee M. Daniels, Carlos A. Murillo & Xiaoping Wang, *Polyhedron*, **1998**, 17 (17) (pp. 2781-2793).
- [2] <http://worldwidescience.org/topicpages/c/cyanide+bridges+link.html#>.
- [3] A.G. Comrie, A. McVitie and R.D. Peacock, *Polyhedron*, **1994**, 13 (pp. 193).
- [4] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *American International Journal of Research in Science, Technology, Engineering & Mathematics*, **2015**, 9(1) (pp. 25-33).
- [5] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *International Congress on Chemical, Biological and Environmental Sciences*, **2015**, (pp. 930-942) May 7-9, **2015**, Kyoto (Japan).
- [6] Barbara Modec and Jon Zubietta, *Materials*, **2010**, 3 (pp. 150-157).
- [7] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *American International Journal of Research in Science, Technology, Engineering & Mathematics*, **2014**, 8(2) (pp. 131-136).
- [8] S.K. Vasisht, Gursharan Singh, in: VII International Symposium on Organosilicon Chemistry, Kyoto, Japan, **1984** (pp. 40).
- [9] Sham K. Vasisht, Gursharan Singh & (Ms) Sarita Chaudhary, *Indian Journal of Chemistry*, **1985**, 24A (pp. 574-577).
- [10] Sham K. Vasisht, Gursharan Singh & Pawan K. Verma, *Monatshefte fur Chemie*, **1986**, 117 (pp. 177-183).
- [11] S.K. Vasisht & Gursharan Singh, *Z. Anorg. Allg. Chemie*, **1985**, 526 (pp. 161-167).
- [12] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *American International Journal of Research in Science, Technology, Engineering & Mathematics*, **2015**, 10(4) (pp. 299-308).
- [13] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *American International Journal of Research in Science, Technology, Engineering & Mathematics*, **2015**, 11(2) (pp. 158-166).
- [14] Gursharan Singh, Vikas Mangla, Mamta Goyal, Kavita Singla & Deepika Rani, *American International Journal of Research in Science, Technology, Engineering & Mathematics*, **2016**, 16(1) (pp. 56-64).
- [15] Gulsah Kilickaya, Basak Dogan, Nursel Acar, Isil Topaloglu Sozuer, *Turk J. Chem.*, **2009**, 33 (pp. 693-708).
- [16] L.M. Lima, P. Castro, A.L. Machado, C.A.M. Fraga, C. Lugniur, V.L.G. Moraes, *J. Biol. Org. Med. Chem.*, **2002**, 10 (pp. 3067-3073).
- [17] A. Orzeszka, B. Kaminska, G. Orzesko, Starecziak, *J. II Farmaco.*, **2000**, 55 (pp. 619).
- [18] A.A. Bekhit, H.M.A. Ashour, Y.S.A. Ghang, A.E.A. Bekhit, A. Baraka, *Eur. J. Med. Chem.*, **2008**, 43 (pp. 456-463).
- [19] J. Frigola, A. Colombo, J. Pares, L. Martinez, R. Sagarra, R. Rosert, *Eur. J. Med. Chem.*, **1989**, 24 (pp. 435-445).
- [20] M.A. Aziz, G.E.A. Abuorahma, A.A. Hassan., *Eur. J Med. Chem.*, **2009**, 44 (pp. 3480-3487).
- [21] D. Castagnolo, F. Mantti, M. Radi, B. Bechi, M. Pagano, A.D. Logu, *Bioorg. Med. Chem.*, **2009**, 17 (pp. 5716-5721).
- [22] O.M. Ahmed, M.A. Muhamed, R.R. Ahmed, S.A. Ahmed., *Eur. J. Med. Chem.*, **2009**, 44 (pp. 3519-3523).
- [23] A.A. Bekhit, T.A. Azim., *Bioorg. Med. Chem.*, **2004**, 12 (pp. 1935-1945).
- [24] S. Bondock, R. Rabie, H.A. Etman, A.A. Fadda., *Eur. J. Med. Chem.*, **2008**, 43 (pp. 2122-2229).
- [25] S. Gopalakrishnan, T.K. Ravi, P. Manojkumar, *Eur. J. Med. Chem.*, **2009**, 44 (pp. 4690-4694).
- [26] M. Barcelo, E. Ravina, C.F. Masaguer, E. Dominguez, F.M. Areias, J. Brea, *Bioorg. Med. Chem. Lett.*, **2007**, 17 (pp. 4873-4877).
- [27] P. Pospisil, G. Folkers, *FABAD J. Pharm. Sci.*, **2004**, 29 (pp. 81-92).
- [28] A.E. Cho, V. Guallar, B.J. Berne, R. Friesner, *J. computchem.*, **2005**, 26 (pp. 915-931).
- [29] A.F. Pozharskii, *Heterocycles in Life and Society*, Chichester, Newyork, **1997** (pp. 301).
- [30] T.L. Gilchrist, *Heterocyclic Chemistry*, John Wiley & Sons The Bath press, New York, **1985**.
- [31] A. Kleeman, J. Engel, B. Kutscher, and D. Reichert, *Pharmaceutical Substances: Syntheses, Patents, Applications of the Most Relevant APIs*, Thieme Medical, New York, NY, USA, 3rd edition, **1999**.
- [32] <https://en.wikipedia.org/wiki/3-Methylpyridine>.
- [33] Shinkichi Shimizu, Nanao Watanabe, Toshiaki Kataoka, Takayuki Shoji, Nobuyuki Abe, Sinji Morishita, Hisao Ichimura. (2002). 'Pyridine and Pyridine Derivatives'. *Ullmann's Encyclopedia of Industrial Chemistry*. doi:10.1002/14356007.a22_399.
- [34] Sims, G. K. and L.E. Sommers. **1986**. 'Biodegradation of Pyridine Derivatives in Soil Suspensions', *Environmental Toxicology and Chemistry*. 5:503-509.
- [35] Jump up^ Sims, G. K. and L.E. Sommers. **1985**. 'Degradation of Pyridine Derivatives in Soil', *J. Environmental Quality*. 14:580-584.
- [36] Giuseppina Autore, Anna Caruso, Stefania Marzocco, Barbara Nicolaus, Chiara Palladino, Aldo Pinto, Ada Popolo, Maria S. Sinicropi, Giuseppina Tommonaro and Carmela Saturnino, *Molecules*, **2010**, 15 (pp. 2028-2038).
- [37] J.A. Kovacs, R.H. Holm, *Inorg Chem.*, **1987**, 26 (pp.711-718).
- [38] Moamen S. Refat and Khaled M. Elsabawy, *Bull. Mater. Sci.*, **2011**, 34 (pp. 873-881).
- [39] Nakamoto K, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', (New York: Wiley Interscience, 6th Edn.), **2008**.

- [40] V.L. Abramenko, V.S. Sergienko & A.V. Churakov, *Russian J. Coord Chem.*, **2000**, 26(12) (pp. 866-871).
- [41] Spectrochim. Acta A Mol Biomol Spectrosc. **2011** Sep;79(5):1959-68. doi: 10.1016/j.saa.2011.05.100. Epub 2011 Jun 12.
- [42] Chemistry of Heterocyclic Complexs, **1974**, 10, Issue 4 (pp. 471-476).
- [43] A.I. Vogel, A text book of Quantitative Inorganic Analysis; John Wiley and Sons: New York, **1963** (Standard methods).
- [44] Yoshiyuki Hase, *J. Molecular Structure*, **1978**, 48 (pp. 33-42).
- [45] B.A. Stamboliyska et al., *Journal of Molecular Structure*, **2000**, 516 (pp. 237-245).
- [46] Toyozo Uno, Katsunosuke Machida, *Bulletin of the Chemical Society of Japan*, **1962**, 35(2) (pp. 276-283).
- [47] J.R. Rambo, J.C. Huffman, G. Christou, *J. Am. Chem. Soc.*, **1989**, 111 (pp. 8027).
- [48] I. Lo'pez Toco'n, M.S. Woolley, J.C. Otero, J.L. Marcos *Journal of Molecular Structure*, **1998**, 470 (pp. 241-246).
- [49] Gregory R. Fulmer, Alexander J. M. Miller, Nathaniel H. Sherden, Hugo E. Gottlieb, Abraham Nudelman, Brian M. Stoltz, John E. Bercaw and Karen I. Goldberg, *Organometallics*, DOI: 10.1021/om100106e.
http://www.chemicalbook.com/SpectrumEN_109-76-2_1HNMR.htm.
- [50] Editor: Teresa M. V. D. Pinho e Melo, Recent Research Developments in Heterocyclic Chemistry,,: 397-475 ISBN: 81-308-0169-8, **2007**.
- [52] Xinjiao Wanga, Frank W. Heinemann, Mei Yangb, Berthold U. Melcher, Melinda Fekete, Anja-Verena Mudringb, Peter Wasserscheid, Karsten Meyer, Supplementary Material (ESI) for Chemical Communications. This journal is (c) The Royal Society of Chemistry, **2009**.
- [53] Editor: Teresa M. V. D. Pinho e Melo, Recent Research Developments in Heterocyclic Chemistry,,: 397-475 ISBN: 81-308-0169-8, **2007**.
<http://www.sigmaaldrich.com/spectra/fnmr/FNMR001834.PDF>.
- [54] Robertha C. Howell, Selvin H. Edwards, Alison S. Gajadhar-Plummer, Ishenkumba A. Kahwa, Gary L. McPherson, Joel T. Mague, Andrew J. P. White and David J. Williams, *Molecules*, **2003**, 8 (pp. 565-592).
- [55] http://www.hanhonggroup.com/nmr/nmr_en/B61064.html.
- [56] <http://www.sigmaaldrich.com/spectra/fnmr/FNMR003779.PDF>.
- [57] <http://www.sisweb.com/referenc/tools/exactmass.htm>.
- [58]

Acknowledgements

We are thankful to Department of Sophisticated Analytical Instruments Facility/Central Instrumentation Laboratory, Panjab University, Chandigarh (India) for providing us the facility for C, H, N, S analysis, FTIR spectra, Mass (LC-MS/GC-MS) spectra and ¹H-NMR spectra to characterize samples synthesized by us. We are also thankful to Campus Director, Giani Zail Singh Campus College of Engineering & Technology, Bathinda, Punjab (India) (Constituent College of MRSPTU, Bathinda, India, www.mrsptu.ac.in), for providing us all infrastructural facilities and financial assistance out of TEQIP-II grant to execute this project.