



Reactions of MoOCl_4 with 2-Methylpiperidine and 4-Methylpyridine

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Abstract: MoOCl_4 reacts with 2-methylpiperidine & 4-methylpyridine (1:1 molar ratio) in CH_3CN medium to yield: $\text{MoOCl}_4(\text{C}_5\text{H}_9\text{NHCH}_3)\text{CH}_3\text{CN}$ [1] & $\text{MoOCl}_4(\text{C}_5\text{H}_4\text{NCH}_3)$ [3], respectively. MoOCl_4 reacts with 2-methylpiperidine & 4-methylpyridine (1:2 molar ratio) in CH_3CN medium to yield: $\text{MoOCl}_4(\text{C}_5\text{H}_9\text{NHCH}_3)\text{CH}_3\text{CN}$ [2] & $\text{MoOCl}_4(\text{C}_5\text{H}_4\text{NCH}_3)_2$ [4], respectively. Complexes have been characterized by elemental analysis, ^1H NMR, FTIR and Mass (LC-MS).

Keywords: MoOCl_4 ; 2-methylpiperidine; 4-methylpyridine

I. Introduction

Reactions of MoOCl_4 in both polar and non-polar solvents have been reported. Due to better solubility of precursors in polar solvents, polymerization and formation of multinuclear complexes^{1, 2, 3, 4, 5, 6} may take place. Reactions of MoOCl_4 in CH_2Cl_2 medium have been reported^{7, 8, 9, 10, 11} by the author. Products of reactions in CH_3CN medium are mostly soluble in CH_3CN due to better solubility of MoOCl_4 in it, formation of solvent stabilized complexes, like $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

2-Methylpiperidine has catalytic properties¹² used in Baylis-Hillman reaction. 2-Methylpiperidine is used as a food additive¹³ in USA.

4-Methylpyridine¹⁴ is a building block for the synthesis of other heterocyclic compounds. It is a precursor to other commercially significant species, often of medicinal interest. Reactions of 4-Methylpyridine¹⁵ have been reported by the author.

II. Experimental

Materials:

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 of SOCl_2 was evacuated in traps cooled with liquid nitrogen. Dark green crystals thus obtained were dissolved in dry CH_2Cl_2 to get dark red solution. Solution was filtered through filtration unit fitted with G-4 sintered glass crucible to remove unreacted/undissolved MoO_3 . Filtrate on evacuation, gives shining dark green crystals of MoOCl_4 , having m.p. $100^\circ\text{--}102^\circ\text{C}$. 2-Methylpiperidine is a yellowish liquid (Sigma-Aldrich, m.p. -4° to -5°C). It is soluble in water and many polar organic solvents including CH_3CN . 4-Methylpyridine also called 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 colourless liquid. CH_3CN was dried by standard methods.

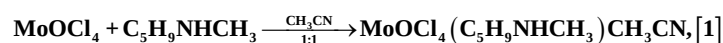
Physical Measurements:

Molybdenum and chlorine were estimated by standard methods¹⁶. 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, ^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 Thermo Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer., at SAIF/CIL Panjab University, Chandigarh (India).

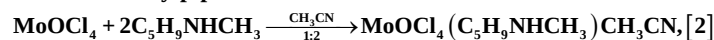
Synthesis of Complexes [1] to [4]:

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 dissolved in dry CH_3CN was taken in round bottomed flask and 1:1 or 1:2 molar amount of 2-methylpiperidine, $\text{C}_5\text{H}_9\text{NHCH}_3$ or 4-methylpyridine $\text{C}_5\text{H}_4\text{NCH}_3$ were dissolved in CH_3CN medium in dropping funnel. The latter was added drop wise to round

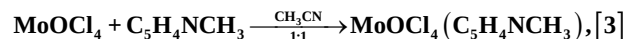
bottom flask with constant stirring, at room temperature. Products were recovered from filtrate by filtration through G-4 bed of a filtration unit, at reduced pressure and under inert atmosphere. All complexes synthesized are very much air and moisture sensitive. They have tendency to turn blue in colour, so all reactions and work ups were handled under dry N₂ gas purged with O₂ using vacuum line and traps cooled with liquid N₂.



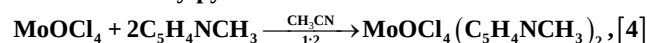
2-Methylpiperidine Filtrate



2-Methylpiperidine Filtrate



4-Methylpyridine Filtrate



4-Methylpyridine Filtrate

III. Results & Discussions

Analytical Measurements:

All complexes are very much moisture and air sensitive. They are insoluble in common organic solvents like CH₂Cl₂, CHCl₃, n-hexane, but soluble in polar solvents like CH₃CN, DMSO and DMF. Formulations of these complexes have been done on basis of their elemental analytical data, mass (LC-MS).

Table-1 (Analytical Data)						
Complexes (Colour/F.W.)	% Composition Observed (Calculated)					
	Mo	Cl	C	H	N	O
MoOCl ₄ (C ₅ H ₉ NHCH ₃)CH ₃ CN, [1] (Green/394.0)	24.70 (24.36)	36.80 (36.04)	23.45 (24.36)	03.96 (04.06)	6.24 (7.10)	04.35 (04.06)
MoOCl ₄ (C ₅ H ₉ NHCH ₃) ₂ CH ₃ CN, [2] (Blackish blue/394.0)	23.50 (24.36)	35.10 (36.04)	25.13 (24.36)	04.98 (04.06)	06.28 (07.10)	03.57 (04.06)
MoOCl ₄ (C ₅ H ₄ NCH ₃), [3] (Greyish blue/347.0)	26.85 (27.66)	40.13 (40.92)	19.89 (20.74)	02.51 (02.02)	03.74 (04.03)	03.57 (04.61)
MoOCl ₄ (C ₅ H ₄ NCH ₃) ₂ , [4] (Light brown/440.0)	21.70 (21.81)	32.10 (32.27)	32.70 (32.72)	03.73 (03.18)	06.26 (06.36)	03.13 (03.63)

FTIR Spectra:

Band at 3392.9 vs cm⁻¹, 3155.5 vs cm⁻¹ show that N-H group is present in complex [1]. Mo-N coordination bond lowers frequency of N-H stretching. (Table-2). Strong band at 984.7 cm⁻¹ shows the presence of terminal Mo=O group^{17, 18} in the complex [1] (Table-2).

Band at 3368.9 vb cm⁻¹, 3134.2 vs cm⁻¹ show that N-H group is present in complex [2]. Mo-N coordination bond lowers frequency of N-H stretching. (Table-2). Strong band at 987.4 cm⁻¹ shows the presence of terminal Mo=O group^{17, 18} in the complex [2] (Table-2).

4-Methylpyridine¹⁹ shows C-H ring stretching at 3072 cm⁻¹ & 3031 cm⁻¹. Bands at 3213.1 s cm⁻¹, 3153.2 s cm⁻¹, 3085.1 s cm⁻¹ show that 4-methylpyridine is present in compound [3]. Strong band at 986.1 cm⁻¹ shows the presence of terminal Mo=O group^{17, 18} in the complex [3] (Table-3).

4-Methylpyridine¹⁹ shows C-H ring stretching at 3072 cm⁻¹ & 3031 cm⁻¹. Bands at 3367.2 vs cm⁻¹, b, 3215.2 s cm⁻¹, 3159.2 s cm⁻¹, 3086 sh cm⁻¹ show that 4-methylpyridine is present in compound [4]. Strong band at 984.3 cm⁻¹ shows the presence of terminal Mo=O group^{17, 18} in the complex [4] (Table-3).

Table-2 (FTIR absorptions in cm ⁻¹)			
Assignments	C ₅ H ₉ NHCH ₃ (2-Methylpiperidine) ^{20, 21}	[1]	[2]
ν _{NH}		3392.9 vs, 3155.5 vs	3368.9 vb, 3134.2 vs
ν _{CH2} , ν _{CH3}	2919 vw	2952.7 s	2946.9 vs
ν _{CH}	2854 m, 2796 m, 2730 m	2869.2 sh	
		1613.3 s	1609.7 s
δ _{HCH}	1445 s, 1376 s	1453.3 m, 1389.5 w	1453.7 m, 1387.5 m
δ _{CCH}	1327 s, 1311 vw, 1263 m, 1224 m, 1157 w		1359.2 vw
δ _{HCH}	1120 s		
ν _{CN}	1085 m	1089.9 w	1090.5 w
ν _{CCH3}	1055 m		
ν _{CC}	1006 w	1023.6 w	1026.1 w
δ _{CCH3}	982 w		

ν_{CCH_3}	908 m	920.9 w	922.5 w
ν_{CC}	804 w		
ν_{CN}	740 vs	742 s	758.1 s
δ_{NCC}	566 m	557.7 w	556.1 w
δ_{CCC}	427 vw		464.7 vw
Terminal Mo=O ^{17, 18} str.	----	984.7 vs	987.4 vs

Table-3 (FTIR absorptions in cm ⁻¹)			
Assignment	4-Methylpyridine ¹⁹	[3]	[4]
ν C-H Ring	3072, 3031	3213.1 s, 3153.2 s, 3085.1 s	3393.9 s, 3214.4 s, 3151.2 s, 3081.0 s
ν C-H Methyl	2993, 2924	2947.6 sh	2939.1 sh, 2842.6 sh
ν Ring	1608, 1562	1635.5 s, 1601.5 s	1637.8 s, 1606.4 m
∂ Ring C-H	1499	1503.4 s	1505.7 s
∂_{as} C-H Methyl	1456, 1446		1439.1 w
∂ Ring C-H	1416		
∂_{s} C-H Methyl	1381		1376.6 w
∂ Ring C-H	1364, 1225	1365.5 w, 1311.0 w, 1245.7 w	1312.4 w, 1249.8 w
ν C-C bond between ring and Methyl	1212		
∂ Ring C-H	1192	1198.7 w	1200.1 w
ν Ring	1116, 1070	1095.8 w, 1036.5 w	1096.4 w, 1038.8 w
∂ Ring	1003	929.4 m	951.0 w,
∂ C-H Ring	874	842.9 s	900.3 w
τ Ring	728	776.8 s	789.9 s, 726.9 w
∂ Ring	522	568.5 w	569.4 w, 518.8 w
∂ C-C bond between ring and Methyl	485	475.7 w	476.7 w
Terminal Mo=O ^{17, 18} str.	----	986.1 s	984.3 m

¹H NMR Spectra:

¹H NMR of 2-methylpiperidine²² in CDCl₃ shows absorptions due to CH₃ protons at 1.04 ppm, C₁-H_e proton on at 2.58 ppm and many other peaks. Spectrum of complex [1] in DMSO-d₆ shows that peak due to CH₃ protons and many other protons have moved downfield (Table-4). Similarly, spectrum of complex [2] in DMSO-d₆ shows that peak due to CH₃ protons and many other protons have moved downfield (Table-4).

Spectrum of 4-methylpyridine^{23, 24} 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 [3] in DMSO-d₆ shows that all of these absorptions have moved downfield (Table-5). Similarly, spectrum of compound [4] in DMSO-d₆ shows that all of these absorptions have moved downfield (Table-5).

Table-4 (¹ H NMR absorptions in ppm)			
Assignments	C ₅ H ₉ NHCH ₃ (2-Methylpiperidine) ²² in CDCl ₃	[1]	[2]
CH ₃	1.04 3H	1.72 3H	1.22 3H
C ₁ H _e	2.58 1H	2.50 1H	2.50 1H
C ₂ H _a	1.05 1H	1.21 1H	
C ₂ H _e	1.61 1H		
C ₃ H _a	1.34 1H	1.42 2H	1.42 2H
C ₃ H _e	1.38 1H		
C ₄ H _a	1.56 1H	2.05 3H	1.69 3H
C ₄ H _e	1.76 1H		
C ₅ H _a	2.65 1H	2.76 1H	2.75 1H
C ₅ H _e	3.04 1H	3.03-3.48 1H	3.14 1H

Table-5 (¹ H NMR absorptions in ppm)			
Assignments	C ₅ H ₄ NCH ₃ in CDCl ₃ (4-Methylpyridine) ^{23, 24}	[3]	[4]
H (CH ₃)	2.34 3H s	2.60 s	2.58 s
H-C ₁ & H-C ₅	8.46 2H d	8.75 s	8.79 s
H-C ₂ & H-C ₄	7.10 2H d	7.90 s	7.89 s

Mass Spectra (LC-MS)²⁵:

Complex [4] has been prepared from MoOCl₄ as the precursor. Mass spectrum (LC-MS) of this complex has [C₅H₄NCH₃]⁺.

Comp.	Table-6 (Fragmentation)
[4]	$\text{MoOCl}_4(\text{C}_5\text{H}_4\text{NCH}_3)_2 \rightarrow [\text{C}_5\text{H}_4\text{NCH}_3]^+$ [4] (F.W. = 440.0) m / z = 93.16

Table-7 (m/z values of some fragments)				
Comp.	Fragment	Calculated ²⁵	Observed	Relative abundance
[4]	[C ₅ H ₄ NCH ₃] ⁺	93.05	93.16	100%

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