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Reactions of $MoOCl_4$ with 1-Methylimidazole, 1,4-Diaminobutane, 2-Methylpyridine, 4-Methylpiperidine, Trimethylsilylimidazole & 1-Methylpyrrolidine

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ABSTRACT

$MoOCl_4$ reacts with 1-methylimidazole, 4-methylpiperidine and trimethylsilylimidazole (equimolar molar amounts) in solvent CH_3CN to provide $MoO_2Cl_4(C_3H_3N_2CH_3)$[1], $MoOCl_4(C_5H_9NHCH_3)$ CH_3CN[4] and $MoO_2Cl_2(C_3H_4N_2)$, [7]. $MoOCl_4$ reacts with twice the moles of 1,4-diaminobutane, 2-methylpyridine, 4-methylpiperidine and 1-methylpyrrolidine in solvent CH_3CN to provide: $MoOCl_4(H_2NC_4H_8NH_2)_2$ [2], $MoOCl_4(C_5H_4NCH_3)$, [3], $MoOCl_4(C_5H_9NHCH_3)_2$, [5], $MoOCl_4(C_5H_9NHCH_3)_2$, [6] and $MoO_2Cl_4(C_4H_8NCH_3)_2$, [8]. Complexes have been studied by techniques: elemental quantitative analysis, FTIR, ^1H NMR, Mass (LC-MS).

Keywords: $MoOCl_4$, 1-methylimidazole, 4-methylpiperidine, trimethylsilylimidazole, 1,4-diaminobutane, 1-methylpyridine, 1-methylpyrrolidine.

INTRODUCTION

Reactions of $MoOCl_4$ with various ligands have been reported. Molybdenum in $MoOCl_4$ being in VI oxidation state, it has the tendency to get reduced during reactions with ligands. Reactions may yield addition, substitution, reduction, rearrangement and polymerization products. Reactions of $MoOCl_4$ in solvent CH_2Cl_2 have been reported[1-5] by the author. Ligands are poorly soluble in solvent CH_2Cl_2 so reactions of $MoOCl_4$ were also carried out and reported[6-11] by the author in CH_3CN medium.

Behavior of saturated N-heterocyclic ligands (4-methylpiperidine, 1-methylpyrrolidine) and unsaturated N-heterocyclic ligands (1-methylimidazole, trimethylsilylimidazole, 1-methylpyridine) towards $MoOCl_4$ in solvent CH_3CN at room temperature have been reported by the author in this paper.

FTIR, ^{1}HNMR and Mass (LC-MS) spectra have helped in identifying the presence of the particular ligands in the compounds [1] to [8] synthesized. Further, Mass (LC-MS) spectra fragmentation pattern of these compounds supported their molecular formulae.

Aim of Investigation

Over the years, there has been increasing applications of Schiff bases and their transition metal complexes in biology, including antifungal, anti-inflammatory, antibacterial, anticancer, antimalarial, antiviral activity. Such studies on complexes of Schiff bases 1-methylimidazole, trimethylsilylimidazole; 1-methylpyridine with transition metals have been scarcely reported. Efforts have been done to prepare such compounds of molybdenum.

Alkylation increases the basic character of piperidine and pyrrolidine. Reactions of simple piperidine and pyrrolidine with $MoOCl_4$ have already been reported[1,2] by the author. Increased basicity of alkylated piperidine and pyrrolidine is expected to impact the substitution/ addition and redox reactions with $MoOCl_4$.

In view of the above, it was decided to carry out the current investigation.

MATERIALS AND METHODS

Precursor $MoOCl_4$ was synthesized in the lab. by refluxing $SOCl_2$ with MoO_3 (CDH, AR Grade) for 5 hours. After the reaction, unreacted $SOCl_2$ was removed with the help of vacuum and collected in in liquid nitrogen traps. Residue thus obtained was dark green in colour. It was treated with dry solvent CH_2Cl_2. Deep red solution was obtained. Red solution was passed through filtration unit having G-4 sintered glass crucible. $MoOCl_4$ dark green crystals were obtained on evaporation of the filtrate.

Sigma-Aldrich ligands were used: 1-Methylimidazole (m.p./b.p.-6°C/124°C), 4-Methylpiperidine (m.p./b.p. 4°C/198°C), Trimethylsilylimidazole (m.p./b.p. -42°C/93°-94°C), 1,4-Diaminobutane (m.p./b.p. 25°-28°C/158°-160°C), 2-Methylpyridine (m.p./b.p. -70°C/128°-129°C), 1-Methylpyrrolidine (m.p./ b.p. -90°C/76°-80°C). These ligands were vacuum dried. LR grade thionyl chloride (b.p. 76°-78°C, CDH) was treated with quinoline for 2 days (250 g $SOCl_2$ to 50 g quinoline) to eliminate acidic impurities. Fractional distillation was carried out to obtain colourless thionyl chloride. Solvent CH_3CN was dried by standard procedure.

Molybdenum and Cl^- were determined by standard procedures[12]. C, H, N, O were determined with Thermo Finnigan Elemental Analyzer, ^{1}H-NMR spectra have been recorded on Brucker Avance-II 400 (Fallanden) NMR in DMSO-d_6, FTIR spectra in the range 4000 – 400 cm^{-1} were taken on Perkin-Elmer 400 FTIR Spectrometer (Germany), in KBr disks, LC-MS spectra were obtained in the range 0 – 1100 m/z using WATERS, Q-TOF Micromass LC-MS (UK), at Panjab University, Chandigarh (India), SAIF/CIL facility.

Preparation of compounds [1] - [8]

One 100 ml R.B. flask was connected to a pressure dropping funnel fitted having teflon stop-cock. A magnetic bead was added in the flask. The whole unit was dried under vacuum flame drying. After cooling the unit, dry nitrogen gas was flushed into it. A known weight of $MoOCl_4$ dissolved in dry CH_3CN was taken in round bottomed flask. Equimolar or 1:2 molar amount of 1-methylimidazole, 4-methylpiperidine trimethylsilylimidazole,1,4-diaminobutane, 2-methylpyridine, 4-methylpiperidine or 1-methylpyrrolidine were dissolved in solvent CH_3CN and taken in dropping funnel. The ligand from the dropping funnel was mixed with $MoOCl_4$ in rb flask at room temperature with constant stirring. Products were filtered through G-4 bed of a filtration unit, under reduced pressure. Compounds prepared are very much sensitive to air and moisture. They tend to turn blue in colour. All reactions were carried out under oxygen free dry nitrogen gas atmosphere in vacuum line. Liquid nitrogen cooled traps were used to get rid of moisture, oxygen.

There seems to be disproportionation/ rearrangement during reactions. Filtrate or residue mentioned below the products, refers to the source from where the product has been isolated.

$$MoOCl_4 + C_3H_3N_2CH_3 \xrightarrow[1:1]{CH_3CN} MoO_2Cl_2.(C_3H_3N_2CH_3)Cl_2, [1]$$
1-Methylimidazole — Filtrate

$$MoOCl_4 + 2H_2NC_4H_8NH_2 \xrightarrow[1:2]{CH_3CN} MoOCl_4.(H_2NC_4H_8NH_2)_2, [2]$$
1,4-Diaminobutane — Residue

$$MoOCl_4 + 2C_5H_4NCH_3 \xrightarrow[1:2]{CH_3CN} MoOCl_4.(C_5H_4NCH_3), [3]$$
2-Methylpyridine — Filtrate

$$MoOCl_4 + C_5H_9NHCH_3 \xrightarrow[1:1]{CH_3CN} MoOCl_4.(C_5H_9NHCH_3)CH_3CN, [4]$$
4-Methylpiperidine — Filtrate

$$MoOCl_4 + 2C_5H_9NHCH_3 \xrightarrow[1:2]{CH_3CN} MoOCl_4.(C_5H_9NHCH_3)_2, [5]$$
4-Methylpiperidine — Residue

$$MoOCl_4 + 2C_5H_9NHCH_3 \xrightarrow[1:2]{CH_3CN} MoOCl_4.(C_5H_9NHCH_3)_2, [6]$$
4-Methylpiperidine — Filtrate

$$MoOCl_4 + (CH_3)_3Si(C_3H_4N_2) \xrightarrow[1:1]{CH_3CN} MoO_2Cl_2.(C_3H_4N_2), [7]$$
Trimethylsilylimidazole — Filtrate

$$MoOCl_4 + 2C_4H_8NCH_3 \xrightarrow[1:2]{CH_3CN} MoO_2Cl_2.(C_4H_8NCH_3)_2\,Cl_2, [8]$$
1-Methylpyrrolidine — Filtrate

RESULTS AND DISCUSSIONS

Analytical Measurements

Compounds are very much sensitive to moisture and air. They are insoluble in less polar solvents like n-hexane, CH_2Cl_2, $CHCl_3$, but are soluble in solvents like CH_3CN, DMSO and DMF of high polarity. These compounds have been formulated on basis of their elemental analysis and LC-MS studies (Table 1).

Table 1: (Elemental Analysis)

Compounds (Color/Formula Mass)	% Observed (Theoretical) Mo	Cl	C	H	N	O
$MoO_2Cl_2.(C_3H_3N_2CH_3)Cl_2$, [1]	27.72	40.92	14.12	2.27	8.11	8.72
(Green/352.0)	-27.27	-40.34	-13.63	-1.7	-7.95	-9.09
$MoOCl_4.(H_2NC_4H_8NH_2)_2$, [2]	21.23	32.23	21.19	6.28	12.34	3.82
(Light blue/434.0)	-22.12	-32.72	-22.12	-6.45	-12.9	-3.68
$MoOCl_4.(C_5H_4NCH_3)$, [3]	26.95	40.45	20.23	2.17	4.74	4.57
(Black/347.0)	-27.66	-40.92	-20.74	-2.02	-4.03	-4.61
$MoOCl_4.(C_5H_9NHCH_3)CH_3CN$, [4]	25.63	36.83	21.92	4.27	6.56	4.17
(Greyish blue/394.0)	-24.36	-36.04	-21.32	-4.06	-7.11	-4.06
$MoOCl_4.(C_5H_9NHCH_3)_2$, [5]	20.6	32.1	32.8	6.28	6.34	3.15
(Dark brown/452.0)	-21.23	-31.42	-31.86	-5.75	-6.19	-3.54
$MoOCl_4.(C_5H_9NHCH_3)_2$, [6]	21.7	30.9	17.81	5.74	5.85	3.13
(Greenish blue/452.0)	-21.23	-31.42	-31.86	-5.75	-6.19	-3.54
$MoO_2Cl_2.(C_3H_4N_2)$, [7]	36.67	27.43	14.36	2.14	10.57	11.23
(Parrot green/267.0)	-35.95	-26.59	-13.48	-1.5	-10.48	-11.98
$MoO_2Cl_2.(C_4H_8NCH_3)_2Cl_2$, [8]	22.33	33.1	27.72	5.15	5.95	6.93
(Blue/440.0)	-21.82	-33.27	-27.27	-5	-6.36	-7.27

FTIR Spectra

Close proximity of vibrational frequencies of 1-methylimidazole[13,14] with that of [1] shows the presence of this ligand in [1]. Nitrogen at position 3 of 1-methylimidazole makes a coordinate bond with molybdenum. On Mo-N coordination, there is increase in ring C=C ring str. recorded at 1584.5 cm^{-1}, 1548.9 cm^{-1}. There is also increase in ring N-C str. observed at 1442.7 cm^{-1}. This increase in frequencies is because of following 2 reasons:

(i) Inductive effect due to coordination with positive metal ion.
(ii) $d\pi$-$p\pi$ interactions dissipate the accumulation of negative charge.

This leads to increase in electron density in the ligand ring system. The greater the increase in ring frequency the stronger is the Mo-N coordinate bond. Presence of cis-MoO_2^{2+} core[15] in [1] is indicated by the presence of strong bands at 983.7 cm^{-1} and 918.1 cm^{-1} (Table 2).

N-H stretching frequencies have been observed at 3413.1 cm^{-1}, 3080.0 cm^{-1} and 3012.5 cm^{-1} in [2] (Table 3). A strong Mo=O stretching[16,17] at 920.0 cm^{-1} shows the presence of terminal Mo=O. Bending mode due to NH_2 observed in 1,4-diaminobutane[18] at 1145 cm^{-1} is lowered to 1116.2 cm^{-1}, because of Mo-N coordination.

Ring C-H stretching in 2-methylpyridine[19-22] are obtained at 3137 cm^{-1} and 3066 cm^{-1}. Ring C-H stretching in [3] are observed at higher frequencies 3296.0 cm^{-1} and 3081.0 cm^{-1}. C=N Str. in [3] was observed at higher frequency at 1625 cm^{-1}. C-N stretching in [3] was observed at lower frequency at 1288.3 cm^{-1} (Table 4). All these observations indicate the presence of 2-methylpyridine in [3]. A strong Mo=O stretching at 980.0 cm^{-1} in [3] shows the presence of terminal Mo=O[16, 17].

There is N-H stretching at 3283 cm^{-1} in 4-methylpiperidine[23-26]. Stretching at 3152.7 cm^{-1} in [4], 3088.7 cm^{-1} in [5] and 3088.7 cm^{-1} in [6] suggest presence of N-H group in these compounds. Decrease in frequency is due to coordination of N-H group through nitrogen atom in these compounds. Stretching at 980.8 cm^{-1}, 975.8 cm^{-1} and 979.2 cm^{-1} in [4], [5] and [6], respectively, refer to Mo=O[16, 17] group in terminal position (Table 5).

N-H stretching in imidazole[27-29] are observed at 3724-3237 cm^{-1}. [7] shows N-H broad

stretching at 3246.0 cm^{-1} due to hydrogen bonding in the solid state (KBr disk). Close proximity of vibrational frequencies of imidazole[27-29] with that of [7] shows the presence of this ligand in [7]. Nitrogen at position 3 of imidazole makes a coordinate bond with molybdenum. On Mo-N coordination, there is increase in ring C=C ring str. recorded at 1615.0 cm^{-1} and 1584.0 cm^{-1}. There is also increase in ring N-C str. observed at 1436.6 cm^{-1}. This increase in frequencies is because of the reasons already explained for [1]. Two bands attributable to the presence of stretching due to cis-MoO_2^{2+} core[15] are observed at 972.9 cm^{-1} and 916.4 cm^{-1} in [7] (Table 6).

Table 2: (FTIR frequencies in cm^{-1})

Mode	$C_3H_3N_2CH_3$ (1-Methylimidazole)[13,14]	[1]
Ring C-H str.	3015 m, 2953 w	3291.8 vs, 3151.0 s
Ring C=C str.	1517 vs	1584.5 m, 1548.9 w
Ring N-C str.	1407 m	1442.7 m
C-H in plane bending	1106 m, 1085 m, 1033 vw	1155.7 w, 1084.9 w
C-H wagging, Ring twisting	813 s, 772 s	752.4 s
Ring twisting	638 s	622.5
N-H wagging, Ring twisting	523	571.5, 504.9 w
υ(Mo=O) of cis-MoO_2^{2+} core[15]	----	983.7 vs, 918.1 w

Table 3: (FTIR frequencies in cm^{-1})

Mode	$H_2NC_4H_8NH_2$ (1, 4-Diaminobutane)[18]	[2]
N-H Str.	3346, 3280	3413.1 s, 3080.0 vs, 3012.5 vs
CH_2 Str.	2960-2875	2946.5 sh, 2881.5 sh
NH_2 Bending	1606	1612.7 m
CH_2 Deformation (strong)	1497, 1390, 1353, 1309	1470.8 m, 1446.5 s
NH_2 Bending	1145	1283.2 s, 1116.2 s
C-N sym str. (weak)	1070	1028.3 m
CH_2 Deformation (medium)	863, 738	872.8 m, 765.0 w
Mo-N (Strong)	----	499.7 m
Terminal υ(Mo=O)16, 17	----	920.0 m

Table 4:(FTIR frequencies in cm^{-1})

Mode	$C_5H_4NCH_3$ (2-Methylpyridine)[19-22]	[3]
Ring C-H Str.	3137 m, 3086 m, 3066 m, 3012 s	3296.0 s, 3081.0 s
Methyl C-H Str.	2958 m	2928.0 s, 2837.0 s
C=N Str.	1596 vs	1625.0 s
Ring C-C Str.	1589 m	1617.0 s
Ring C-H in plane bending	1477 s	1538.1 s
Methyl C-H Asym. bending	1461 s	1469.1 s
Methyl C-H Sym. bending	1377 w	1396.2 m
C-N Str.	1295 s,	1288.3 m
C-CH3 Str.	1237 m	1234.5 w
Ring C-H in plane bending	1148 m,	1165.2 s
Ring C-C Str.	1101 w	1108.5 w, 1096.6 w
Ring breathing	1060 s	1046.4 m
Ring C-H, C-C, C-N out of plane bending	752 vs	770.0 s
Ring C-H out of plane bending	731 m	-
Ring C-C out of plane bending	629 m	627.1 w
Ring C-C-C in plane bending	547 w	566.3
C-CH3 Bending	471	471.3 s
Terminal Mo=O16, 17 Str.	----	980.0 s

Table 5:(FTIR frequencies in cm^{-1})

Mode	$C_5H_9NHCH_3$ (4-Methylpiperidine)[23-26]	[4]	[5]	[6]
N-H Str.	3283 m	3367.2 s, 3152.7 s	3377.1 sh, 3088.7 s	3367.4 sh, 3150.0 s
CH_3 Sym. Str.	2967 s, 2915 s	2957.7 s	2953.0 s	2956.1 s
Ring C-H Asym. Str.	2800 s, 2732 m	2808.1 w	2847.4 s, 2791.5 s	2806.6 sh
Ring C-H Deformation	1456 m, 1448 m 1407.3 w	1610.7 s, 1452.7 m, 1451.8 s	1609.0 sh, 1570.5 s,	1569.3 s, 1452.1 s
Ring C-C Str.	1386 w, 1323 m	1386.8 w, 1301.3 w	1302.0 w	1303.9 w
C-N Str.	1265 w, 1153 m	1223.9 w	1224.7 w, 1178.9 w	1223.5 w
Ring C-H Bending	1007 w, 983 w, 972 w	1065.9 w, 1038.0 w, 917.8 w	1070.6 w, 1038.5 w, 954.9 m	1068.9 w, 1038.1 w
CH2 Rocking	795 m, 771 s	762.4 s	871.6 w, 722.1 s	876.1 w, 839.1 w, 786.5 w, 724.1 m
CNC Deformation	571 m	568.2 m, 444.9 w	569.8 w, 514.7 m, 447.9 w, 410.9 w	567.8 w, 496.3 w, 445.0 w, 407.9 w
Terminal υ(Mo=O)[16, 17]	---	980.8 s	975.8 s	979.2 s

Table 6: (FTIR frequencies in cm^{-1})

Mode	$C_3H_4N_2$ (Imidazole)[27-29]	[7]
υ(N-H)	3724 b, 3656 b, 3270, 3241, 3237	3246.0 b
υ(C-H)	3196, 3165	3149.1 s, 2993.1 sh
Ring υ(C=C)	1558, 1500	1615.0 s, 1584.0 s, 1491.5 sh
Ring υ(N-C)	1434	1436.6 m
δ(C-H) in plane	1092, 1074	1094.0 w, 1069.7 m, 1048.9 w
δ(C-H) (wagging), Ring twisting	816, 730	753.5 vs
Ring twisting	646	643.5 sh, 621.3 w
Ring twisting, N-H wagging	528	562.2 s
υ(Mo=O) of cis-MoO_2^{2+} core[15]	----	972.9 s, 916.4 s

Table 7:(FTIR frequencies in cm^{-1})

Mode	$C_4H_8NCH_3$ (1-Methylpyrrolidine)[30-32]	[8]
C-H Sym. Str.	2973 s	2971.5 s
C-H Asym. Str.	2892 sh, 2833 m, 2782 s	2727.6 s
C-H Deformation	1452 s	1614.1 s, 1459.2 s
C-C Str.	1365 s	1300.8 sh
C-N Str.	1243 s, 1204 m, 1162 s, 1111 m	1205.9 w, 1104.6 w
C-H Bending	1044 s	1069.3 w
CH_2 Rocking	876 s	914.6 s, 851.6 w, 757.6 s
CNC Deformation	577 w	593.3 w
υ(Mo=O) of cis-MoO_2^{2+} core[15]	----	983.7 vs, 914.6 s

1-Methylpyrrolidine[30-32] has C-H symmetric stretching at 2973 cm^{-1} and C-H asymmetric stretching at 2892 cm^{-1}, 2833 cm^{-1}, 2782 cm^{-1}. [8] has C-H symmetric stretching at 2971.5 cm^{-1} and C-H asymmetric stretching at 2727.6 cm^{-1}. Two bands at are attributable to the presence of Stretching due to cis-MoO_2^{2+} core[15] are observed at 983.7 cm^{-1} and 914.6 cm^{-1} in [8] (Table 7).

^{1}H NMR Spectra

1-Methylimidazole,[14,33-35] in solvent $CDCl_3$ has peaks pertaining to CH_3 protons at 3.64 ppm. C_2-H, C_4-H and C_5-H have absorptions at 7.38 ppm, 7.01 ppm and 6.86 ppm, respectively. NMR of [1] in solvent DMSO-d_6 reveals that peaks due to all the protons of 1-methylimidazole have shifted downfield due to decrease in electronic density of imidazole ring. Effect is inversely proportional to distance (Table 8).

1,4-Diaminobutane[36,37] in solvent H_2O has peaks pertaining to N-H protons at 1.15 ppm. NMR of [2] in solvent DMSO-d_6 indicates that peaks due to NH^2 protons and middle CH_2 protons of 1,4-diaminobutane have shifted downfield, but peaks due to side CH_2 protons have shifted up field (Table 9) due to N→Mo lone pair donation.

2-Methylpyridine[21,22,38-40] in solvent $CDCl_3$ has peaks pertaining to CH_3, C_1-H, C_2-H, C_3-H & C_4-H at 2.54, 7.12, 7.53 & 7.08 ppm, respectively. NMR of [3] in solvent DMSO-d_6 reveals that all of these protons have deshielded due to decrease in electron density on N→Mo coordination. There is not much chance of Mo-N π-bonding due to increase of electron density by methyl group on nitrogen (Table 10).

On comparison of NMR of 4-methylpiperidine[41] in solvent $CDCl_3$ with that of [4], [5] and [6] (Table 11), it is found that all peaks in these compounds except that of CH_3 have shifted downfield.

Imidazole[35,42,43] in solvent $CDCl_3$ absorbs at 11.62 ppm due to N-H proton. It absorbs at 7.73 ppm due to C-H proton (between two nitrogen atoms) & at 7.15 ppm due to C-H protons on other two carbons. NMR of [7] in solvent DMSO-d_6 shows that protons have been deshielded due to decrease in electron density on N→Mo coordination (Table 12). Due to tautomerization equilibrium two equivalent C–H protons of imidazole are seen as singlets. N-H proton shows downfield peak.

On comparison of NMR of 1-methylpyrrolidine [30,44,45] with that of [8], it is seen that all absorptions show downfield trend due to decrease in electron density on N→Mo coordination (Table 13).

Table 8: (^{1}H NMR Chemical Shift in ppm)

Protons	$C_3H_3N_2CH_3$ (1-Methylimidazole)[14, 33-35] in solvent $CDCl_3$	[1]
N-CH_3	3.64 3H	3.86
C_2-H	7.38 1H	9.07 1H
C_4-H	7.01 1H	7.91 1H
C_5-H	6.86 1H	7.63 1H

Table 9: (^{1}H NMR Chemical Shift in ppm)

Protons	$H_2NC_4H_8NH_2$ (1, 4-Diaminobutane)[36,37] in solvent H_2O	[2]
NH_2	1.15 4H	7.87 4H
Middle CH_2	1.74-1.77 4H	1.99 4H
Side CH_2	3.03-3.06 4H	2.39-2.41 4H

Table 10: (1H NMR Chemical Shift in ppm)

Protons	$C_5H_4NCH_3$ (2-Methylpyridine)[21,22,38-40] in solvent $CDCl_3$	[3]
CH_3	2.54 3H s	2.79 3H
C_2-H	7.12 1H d	8.07 1H
C_3-H	7.53 1H t	8.43 1H
C_4-H	7.08 1H t	7.87 1H
C_5-H	8.47 1H d	8.70 1H

Table 11: (^{1}H NMR Chemical Shift in ppm)

Protons	$C_5H_9NHCH_3$ (4-Methylpiperidine)[41] in solvent $CDCl_3$	[4]	[5]	[6]
N-H	1.84 1H	8.78-9.02 1H	8.96-9.20 1H	8.89-9.13 1H
C_2-He & C_6-He	3.03 2H	4.15 2H	3.46 2H	3.70 2H
C_2-Ha & C_6-Ha	2.57 2H	3.15 2H	3.14-3.17 2H	3.16 2H
C_3-He & C_5-He	1.61 2H	2.77 2H	2.74-2.82 2H	2.78 2H
C_3-Ha & C_5-Ha	1.08 2H	1.32 2H	1.56-1.71 2H	1.32 2H
C_4-Ha	1.45 1H	2.03 1H	2.50-2.51 1H	2.51 1H
CH_3	0.91 3H	0.88 3H	0.89 3H	0.89 3H

Table 12: (^{1}H NMR Chemical Shift in ppm)

Protons	$C_3H_4N_2$ (Imidazole)[35,42,43]	[7]
N-H	12.4 1H	14.93 1H
C-H between two nitrogen atoms	7.70 1H	9.15 1H
C-H on other carbons	7.03 2H	7.67 2H

Table 13: (^{1}H NMR Chemical Shift in ppm)

Protons	$C_4H_8NCH_3$ (1-Methylpyrrolidine)[30,44,45]	[8]
CH_3	2.3 3H	3.43 3H
C_2-H & C5-H	2.5 4H	2.51-2.89 4H
C_3-H & C4-H	1.6 4H	1.86-1.97 4H

Mass Spectra (LC-MS)[46]

Formulae have been derived from fragmentation obtained as under.

Table 14

$[MoO_2Cl_2{\cdot}(C_3H_3N_2CH_3)Cl_2] \rightarrow [C_3H_3N_2CH_3]^+ + [MoO_2Cl_2]^+$
[1] (F.M. = 352.0) m / z = 82.12 m / z = 199.89

$[MoO_2Cl_2]^+ \rightarrow [MoO_2Cl]^+$
m / z = 199.89 m / z = 164.94

$[MoOCl_4{\cdot}(C_5H_4NCH_3)] \rightarrow [MoOCl_4{\cdot}(C_5H_4NCH_3)]^+ \rightarrow MoOCl_3{\cdot}(C_5H_4NCH_3)]^+$
[3] (F.M. = 347.0) m / z = 347.20 m / z = 311.20

$[MoOCl_2]^+ \xleftarrow{-Cl} [MoOCl_3]^+ + [C_5H_4NCH_3]^+$
m / z = 185.14 m / z = 219.12 m / z = 94.08

$[MoOCl_4{\cdot}(C_5H_9NHCH_3)CH_3CN] \rightarrow [C_5H_9NHCH_3]^+ \xrightarrow{-CH_3} [C_5H_9NH]^+$
[4] (F.M. = 394.0) m / z = 98.20 m / z = 84.17

$[MoOCl_4{\cdot}(C_5H_9NHCH_3)_2] \rightarrow [C_5H_9NHCH_3]^+ \xrightarrow{-CH_3} [C_5H_9NH]^+$
[5] (F.M. = 452.0) m / z = 98.17 m / z = 84.14

$[MoOCl_4{\cdot}(C_5H_9NHCH_3)_2] \rightarrow [C_5H_9NHCH_3]^+ \xrightarrow{-CH_3} [C_5H_9NH]^+$
[6] (F.M. = 452.0) m / z = 98.19 m / z = 84.16

$[MoO_2Cl_2{\cdot}(C_3H_4N_2)] \rightarrow [C_3H_4N_2]^+ + [MoO_2Cl_2]^+ \xrightarrow{-Cl} [MoO_2Cl]^+$
[7] (F.M. = 267.0) m / z = 67.02 m / z = 199.90 m / z = 164.95

$[MoO_2Cl_2{\cdot}(C_4H_8NCH_3)_2Cl_2] \rightarrow [C_4H_8NCH_3]^+ + [MoO_2Cl_2]^+ \xrightarrow{-Cl} [MoO_2Cl]^+$
[8] (F.M. = 440.0) m / z = 82.14 m / z = 199.91 m / z = 164.97

Table 15: (Fragments m/z)

Comp.	Fragment	Theoretical[46]	Obtained	Relative area
[1]	$[MoO_2Cl_2]^+$	199.83	199.89	36%
	$[MoO_2Cl]^+$	164.86	164.94	20%
	$[C_3H_3N_2CH_3)]^+$	82.05	82.12	95%
[3]	$[MoOCl_4(C_5H_4NCH_3)]^+$	346.83	347.20	5%
	$[MoOCl_3(C_5H_4NCH_3)]^+$	311.86	311.20	18%
	$[MoOCl_3]^+$	218.80	219.12	62%
	$[MoOCl_2]^+$	183.83	185.14	84%
	$[C_5H_4NCH_3]^+$	93.05	94.08	100%
[4]	$[C_5H_9NHCH_3)]^+$	99.10	98.20	30%
	$[C_5H_9NH)]^+$	84.08	84.17	10%
[5]	$[C_5H_9NHCH_3)]^+$	99.10	98.17	58%
	$[C_5H_9NH)]^+$	84.08	84.14	14%
[6]	$[C_5H_9NHCH_3)]^+$	99.10	98.19	15%
	$[C_5H_9NH)]^+$	84.08	84.16	6%
[7]	$[C_3H_4N_2]^+$	68.03	67.02	3%
	$[MoO_2Cl_2]^+$	199.83	199.90	8%
	$[MoO_2Cl]^+$	164.86	164.95	5%
[8]	$[C_4H_8NCH_3)_2]^+$	85.08	82.14	100%
	$[MoO_2Cl_2]^+$	199.83	199.91	9%
	$[MoO_2Cl]^+$	164.86	164.97	7%

CONCLUSION

In all the compounds, except [7], molybdenum to chlorine ration remains 1:4, which shows that polar solvent CH_3CN could not solvolyze Mo-Cl bonds, thus leading to formation of adducts/ molecular complexes[47].

[7] is obtained when trimethylsilylimidazole displaces chlorine from $MoOCl_4$ to form trimethylsilylchloride and radical $C_3H_3N_2$. This radical abstracts[2] hydrogen atom from the solvent CH_3CN to form $C_3H_4N_2$ (imidazole).

υ (Mo=O) is reported[48] at 990 cm^{-1} -1010

cm^{-1} in various inert solvents. There is a decrease in υ (Mo=O) in [2]-[6], which shows coordination[49] of ligand in a direction trans to Mo=O bond in these adducts/molecular complexes.

There is increase in υ (C=C) and υ (N-C) in [1] and [7] due to coordination of 1-methylimidazole/ imidazole to Mo through N atom.

Lone pair of N atom in [3] is involved in N→Mo $n\pi$ conjugation as a result there is a shift of υ (C=N) by 29 cm^{-1} on higher frequency side, indicating thereby coordination of ligand[47] to Mo through N atom.

Coordination in [1] and [7] takes place through N-3 of imidazole ring[50].

^{1}H NMR of all compounds show downward shifts on coordination of ligands with Mo through N atom due to decrease in electron density of the rings.

LC-MS spectra of all the compounds synthesized prove the presence of ligands and some of the fragments in them.

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Conflict of interest

We, the authors declare that we have no conflict of interest.

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