



Reactions of MoOCl_4 , MoO_2Cl_2 & MoCl_5 with Pyrazole, Succinimide, Imidazole, Pot. phthalimide & 2-Thiazoline-2-thiol

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Abstract: MoCl_5 reacts with succinimide, pot. phthalimide & imidazole (1:2 molar ratio) in CH_3CN medium to yield: $\text{MoCl}_3(\text{C}_4\text{H}_4\text{O}_2\text{N})(\text{CH}_3\text{CN})$ [4], $\text{MoO}_2\text{Cl}_3(\text{C}_8\text{H}_4\text{O}_2\text{N})_2$ [5] & $\text{MoCl}_5(\text{C}_3\text{H}_4\text{N}_2)_2$ [6], respectively. MoCl_5 reacts with 2-thiazoline-2-thiol (1:1 molar ratio) in CH_3CN medium to yield: $\text{MoO}_4\text{Cl}_5(\text{C}_3\text{H}_5\text{NS}_2)_2(\text{CH}_3\text{CN})_2$ [8]. MoO_2Cl_2 reacts with imidazole (1:2 molar ratio) in CH_2Cl_2 medium to yield: $\text{MoO}_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)_2$ [3]. MoO_2Cl_2 reacts with 2-thiazoline-2-thiol (1:1 molar ratio) in CH_3CN medium to yield: $\text{Mo}_2\text{O}_3\text{Cl}_2(\text{C}_3\text{H}_4\text{NS}_2)_2(\text{CH}_3\text{CN})_2$ [7]. MoOCl_4 reacts with pyrazole & succinimide (1:2 molar ratio) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ medium to produce: $\text{MoO}_3\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)_2$ [1] & $\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_4$ [2], respectively. Complexes have been characterized by elemental analysis, ^1H NMR, FTIR, Mass (LC-MS/GC-MS), electronic spectra and molar conductance studies.

Keywords: MoOCl_4 ; MoO_2Cl_2 ; MoCl_5 ; pot. phthalimide; succinimide; pyrazole; 2-thiazoline-2-thiol; imidazole

I. Introduction

Reactions of MoOCl_4 , MoO_2Cl_2 & MoCl_5 with ligands in both polar and non-polar solvents have been reported. One of the demerits of carrying out reactions in non-polar solvents is that the precursors are poorly soluble in these solvents, so there is probability of inhomogeneity of the reaction mixture/products. On the other hand, due to better solubility of precursors in polar solvents, the chances of polymerization and formation of multinuclear complexes increase. Molybdenum multinuclear complexes^{1, 2, 3, 4, 5, 6} have been reported. If CH_3CN is used as reaction medium, then these complexes may be cyanide bridged^{1, 2}. Identification of terminal^{4, 5, 7, 8}/cross bridged^{1, 4, 5, 6} CH_3CN ligand can be done by FTIR studies. Cross-bridged¹ CH_3CN ligand can also be identified by ^1H NMR chemical shifts.

Reactions of MoOCl_4 , MoO_2Cl_2 & MoCl_5 in CH_2Cl_2 medium have been reported^{9, 10, 11, 12, 13} 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^{4, 5, 14, 15} by the author in CH_3CN medium. In some reactions reported in this paper, enhanced polarity of CH_3CN medium leads to extensive polymerization of the products giving rise to sticky materials which could not be dried and powdered. To overcome this problem of extensive polymerization, reactions were repeated in $\text{ClCH}_2\text{CH}_2\text{Cl}$ or CH_2Cl_2 medium. Products of reactions in CH_3CN medium are mostly soluble in CH_3CN due to better solubility of MoOCl_4 , MoO_2Cl_2 & MoCl_5 in CH_3CN and formation of solvent stabilized complexes, like $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

Mass (LC-MS/GC-MS) spectra show that there is some similarity in the fragments formed from the complexes [1] to [8] prepared from MoOCl_4 , MoO_2Cl_2 & MoCl_5 .

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

Succinimides¹⁸ are important class of substrates for biological applications.

Pyrazoles and their derivatives exhibit various biological activities including antimicrobial¹⁹ anti-cyclooxygenase²⁰, anticonvulsant²¹, antitubercular²², antitumor²³, antiinflammatory²⁴, analgesic²⁵, antidiabetic²⁶, antipshycotic^{27, 28, 29}. Many drugs, such as, antifungal drugs and nitroimidazole contain an imidazole^{30, 31} ring.

Imidazole³² containing drugs have a broad scope in remedying various dispositions in clinical medicine.

Molybdenum complexes of 2-thiazoline-2-thiol have been reported by the author^{4, 5}. Complexes containing sulphur, as well as their metal complexes exhibit numerous biochemical applications^{33, 34, 35}.

II. Experimental

Materials:

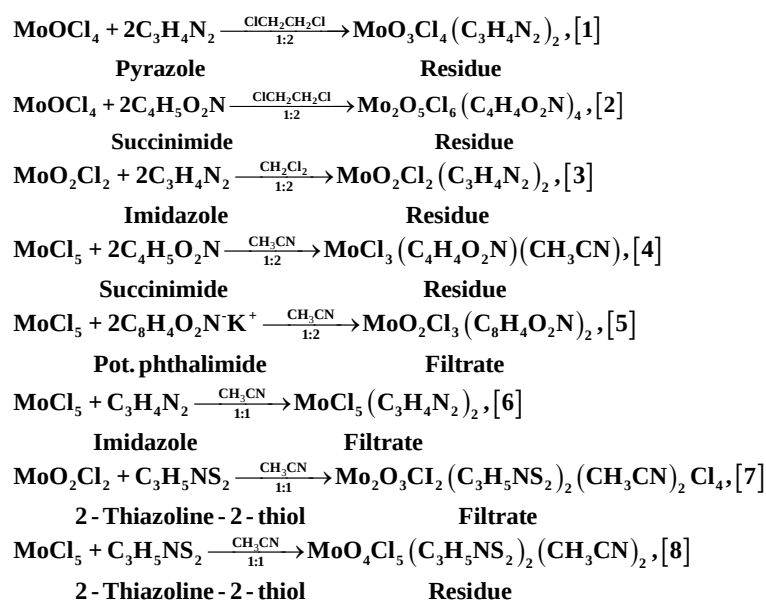
MoOCl₄ has been prepared in laboratory by reaction of MoO₃ (CDH, AR Grade) with SOCl₂ at reflux temperature for about 5 h. After refluxing, excess SOCl₂ was evacuated in traps cooled with liquid nitrogen. Dark green crystals thus obtained were dissolved in dry CH₂Cl₂ to get a dark red solution. Solution was filtered through filtration unit fitted with G-4 sintered glass crucible to remove any unreacted/undissolved MoO₃. Filtrate on evacuation, gives shining dark green crystals of MoOCl₄, having m.p. 100°-102° C. MoO₂Cl₂ (Sigma-Aldrich, USA) is a light yellow hygroscopic solid. It was purchased and used as such. MoCl₅ (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 CH₃CN. Pyrazole is a colourless solid (SD Fine, LR Grade, m.p. 66°-70° C). Succinimide (CDH, LR Grade, m.p. 125°-127° C) is a white solid, soluble in polar solvents. 2-Thiazoline-2-thiol also called 2-mercapto-2-thiazoline (Sigma-Aldrich, USA, m.p. 100°-105° C) is a white solid, soluble in acetonitrile. All ligands were dried under vacuum. SOCl₂ (CDH, LR grade, b.p. 76°-78° C) was kept over quinoline for 48 h (50 g SOCl₂ to 10 g quinoline) to remove acid impurities and then fractionally distilled to get a colourless liquid. CH₃CN was dried by standard methods.

Physical Measurements:

Molybdenum and chlorine were estimated by standard methods³⁶. The elemental analyses (C, H, N, S and O) were carried out using Thermo Finnigan Elemental Analyzer, FTIR spectra were recorded in the range 4000–400 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-d₆ and UV-VIS spectra in DMSO solvent were recorded using Thermoscientific Genesys 10S Series UV-VIS spectrophotometer (USA), at GZS Campus College of Engineering & Technology, Bathinda (India). GC-MS spectra were recorded in the range 0 – 1100 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 Complexes [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 $MoOCl_4$, MoO_2Cl_2 or $MoCl_5$ dissolved in dry CH_3CN was taken in round bottomed flask and 1:1 or 1:2 molar amount of $C_8H_4O_2N^+K^+$ (potassium phthalimide), $C_3H_4N_2$ (imidazole or pyrazole), $C_4H_5NO_2$ (succinimide) or $C_3H_5NS_2$ (2-thiazoline-2-thiol) were dissolved in $ClCH_2CH_2Cl$, CH_2Cl_2 or 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 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 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 fragments of these complexes are common. Λ_M of complexes [1] to [8] in DMSO are 0.1 – 1.9 $\text{cm}^2\text{ohm}^{-1}\text{mol}^{-1}$, suggesting their non-electrolytic nature (Table-1).

Table-1 (Analytical & Molar Conductance Data)								
Complexes (Colour/F.W.)	Λ_M^*	% Composition Observed (Calculated)						
		Mo	Cl	C	H	N	O	S
$\text{MoO}_3\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)_2$, [1] (Parrot green/422.0)	4.0	22.23 (22.74)	33.04 (33.64)	16.22 (17.06)	02.80 (01.89)	12.45 (13.27)	11.03 (11.37)	----
$\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_4$, [2] (Light green/877.0)	6.2	22.03 (21.89)	23.73 (24.28)	21.59 (21.89)	02.82 (01.82)	06.49 (06.38)	22.99 (23.71)	----
$\text{MoO}_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)_2$, [3] (Yellow/335.0)	3.5	27.80 (28.65)	20.43 (21.19)	20.83 (21.49)	03.06 (02.38)	15.97 (16.71)	10.27 (09.55)	----
$\text{MoCl}_3(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{CH}_3\text{CN})$, [4] (Reddish brown/341.5)	0.27	27.34 (28.11)	30.23 (31.18)	21.08 (21.08)	02.33 (02.04)	07.25 (08.19)	08.51 (09.37)	----
$\text{MoO}_2\text{Cl}_3(\text{C}_8\text{H}_4\text{O}_2\text{N})_2$, [5] (Reddish brown/526.5)	0.17	17.45 (18.23)	19.33 (20.22)	35.76 (36.46)	02.19 (01.51)	05.76 (05.31)	17.65 (18.23)	----
$\text{MoCl}_5(\text{C}_3\text{H}_4\text{N}_2)_2$, [6] (Dark brown/409.5)		22.68 (23.44)	42.89 (43.34)	17.81 (17.58)	02.46 (01.95)	13.69 (13.67)	----	----
$\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})_2(\text{C}_3\text{H}_5\text{NS}_2)_2\text{Cl}_4$, [7] (Blackish blue/773.0)		24.13 (24.83)	26.63 (27.55)	14.71 (15.52)	02.02 (02.06)	06.39 (07.24)	07.13 (06.20)	15.63 (16.55)
$\text{MoO}_4\text{Cl}_5(\text{C}_3\text{H}_5\text{NS}_2)_2(\text{CH}_3\text{CN})_2$, [8] (Coffee brown/657.5)		13.75 (14.60)	27.33 (26.99)	17.54 (18.25)	02.09 (02.43)	06.44 (08.51)	07.63 (09.73)	18.57 (19.46)

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

FTIR Spectra:

Pyrazole^{37, 38} shows N-H stretching at 3450 cm^{-1} . Band at 3396.0 cm^{-1} shows that N-H group is present in complex [1]. Mo-N coordination bond lowers frequency of N-H stretching. Strong bands at 976.3 cm^{-1} and 913.7 cm^{-1} show the presence of cis- MoO_2^{2+} core³⁹ in complex [1] (Table-2).

Succinimide^{40, 41} shows N-H stretchings at 3410 cm^{-1} & 3223 cm^{-1} . Band at 3417.2 cm^{-1} shows that N-H group is present in complex [2]. Bands at 980.4 cm^{-1} and 920.6 cm^{-1} show the presence of cis- MoO_2^{2+} core³⁹ in complex [2]. There is no shift in C=O stretching frequency from 1771 cm^{-1} , which indicates that there is no Mo–O coordination bond in complex [2] (Table-3). Band at 3398.22 cm^{-1} shows that N-H group is present in complex [4]. Bands at 989.5 cm^{-1} and 919.9 cm^{-1} show the presence of cis- MoO_2^{2+} core³⁹ in complex [4]. There is no peak near 1771 cm^{-1} which shows that C=O group is involved in coordination in complex [4] (Table-3).

Imidazole^{42, 43} shows N-H stretchings at 3724-3237 cm^{-1} . Broad band at 3500 cm^{-1} – 3000 cm^{-1} shows that N-H group is present in complex [3]. This peak is broad in the solid state (KBr disk) due to hydrogen bonding. Two bands at 949.0 cm^{-1} and 915.0 cm^{-1} are attributable to the presence of cis- MoO_2^{2+} core³⁹ in complex [3] (Table-4). Band at 3253.6 cm^{-1} shows that N-H group is present in complex [6]. This peak is broad in the solid state (KBr disk) due to hydrogen bonding. Band at 988.19 cm^{-1} is attributable to the presence of terminal Mo=O^{44, 45} group in complex [6] (Table-4).

Potassium phthalimide⁴⁶ shows N-H stretchings at 3269 cm^{-1} and 3154 cm^{-1} . Bands at 3400.1 cm^{-1} and 3211.1 cm^{-1} show that N-H group is present in complex [5]. Strong band at 976.7 cm^{-1} shows the presence of terminal Mo=O group^{44, 45} in the complex [5] (Table-5).

2-Thiazoline-2-thiol^{47, 48, 49} shows N-H stretching at 3145 cm^{-1} . Strong band at 3367.10 cm^{-1} shows that N-H group is present in complex [7] (Table-6). Absence of any band in the region of 2709 cm^{-1} shows absence of S-H group in complex. A strong band at 977.13 cm^{-1} shows the presence of terminal Mo=O^{44, 45} group. Strong band at 3367.10 cm^{-1} shows that N-H group is present in complex [8] (Table-6). Absence of any band in the region of 2709 cm^{-1} shows absence of S-H group in complex. Bands at 982.30 cm^{-1} and 916.30 cm^{-1} show the presence of cis- MoO_2^{2+} core³⁹ in complex [8].

Table-2 (FTIR absorptions in cm^{-1})		
Assignments	$\text{C}_3\text{H}_4\text{N}_2$ (Pyrazole) ^{37, 38}	[1]
N-H, str.	3450	3396.0 s, vb
C-H str.	3155, 3144	----
C=C ring str.	1558	1628.2 s
N-C ring str.	1468, 1138	1478.8 sh, 1410.7 w, 1261.10 vw
C-H in plane bending	1046, 1035	1167.7 sh, 1122.6 s, 1053.6 s

C-H out of plane bending (wagging), Ring twisting	893, 840, 760	788.2 m, 736.3 m
Ring twisting	656, 619	610.3 m
Ring twisting, N-H wagging	498	492.5 sh
Mo=O Str. of cis-MoO ₂ ²⁺ core ³⁹	----	976.3 s, 913.7 sh

Table-3 (FTIR absorptions in cm ⁻¹)			
Assignments	C ₆ H ₅ NO ₂ (Succinimide) ^{40, 41}	[2]	[4]
NH str.	3410 s, b, 3223 s, b	3417.2 s, b	3398.2 s, b
CH ₂ sym str	2964, 2945 w	----	2988.4 sh, 2961.4 sh, 2923.3 sh
CO sym., HNC in plane bending	1771 m	1772.3 sh	----
CO asym., HNC in plane bending	1713 vs, b	1695.3 s	1621.4 s
CH ₂ sym. scissoring	1431 m	1478.8 sh	1490.12 sh
CH ₂ asym. scissoring	1400 m	1426.6 sh	1402.8 m
CNC asym. str., HNC in plane bending	1349 s, 1334	1372.3 s	1355.8
CH ₂ bending, ring in plane bending	1294 s	1297.4 m	----
CH ₂ bending	1241	1248.5 sh	----
CNC asym. str., HNC in plane bending	1186 s,	1186.2 s	1025.8 m
C-C str., CNC sym. str.	849	857.7 sh	----
CH ₂ bending, ring out of plane bending	817 s	817.5 w	752.12 m
OCN asym. out of plane bending	632 m	645.4 m	627.15 w
OCN sym. out of plane bending, CH ₂ bending	543 w	551.7 sh	569.14 w
Mo-N Str.	----	431.9 w, 413.8 w	427.10 m, 418.10 m
Mo=O Str. of cis-MoO ₂ ²⁺ core ³⁹	----	980.4 s, 920.6 sh	989.5 s, 919.9 m

Table-4 (FTIR absorptions in cm ⁻¹)			
Assignments	C ₃ H ₄ N ₂ (Imidazole) ^{42, 43}	[3]	[6]
N-H str.	3724 vb, 3656 vb, 3270, 3241, 3237	3500-3000 s, vvb	3253.6 s
C-H str.	3196, 3165	----	3143.5 s, 2981.10 sh, 2849.14 sh
C=C ring str.	1558, 1500	1625.1 sh, 1584.2 s	1698.29 sh, 1609.23 sh, 1580.11
N-C ring str.	1434	1432.2 s, 1316.6 w, 1258.7 w	1420.26 s, 1296.41 w, 1248.41 w
C-H in plane bending	1092, 1074	1194.5 m, 1094.2 m, 1050.1 s	1189.35 w, 1089.24 m, 1045.19 s
C-H out of plane bending (wagging), Ring twisting	816, 730	762.0 b,	884.24 m, 764.13 s, b
Ring twisting	646	624.0 s	621.12 s
Ring twisting, N-H wagging	528	572.1 m	510.37 sh
Mo=O str. of cis-MoO ₂ ²⁺ core ⁴⁰	----	949.0 sb, 915.0 s	----
Terminal Mo=O ^{44, 45} str.	----	----	988.19 s

Table-5 (FTIR absorptions in cm ⁻¹)		
Assignments	C ₈ H ₄ O ₂ NK ⁺ (Pot. Phthalimide) ⁴⁶	[5]
N-H str	3269 w, 3154 w	3400.1 s, b, 3211.1 s, b
In phase C=O str	1704 m, 1687 w, 1665 vvw	1853.11 w, 1764.5 s, 1742.5 s, 1646.5 s
C-C Benzene ring str	1608 s	----
Out of phase C=O str	1593 s, 1588 s, 1552 vw, 1507 vw	----
C-C Benzene ring str	1465 vvw, 1449 vvw, 1398 w, 1372 s, 1356 m	1469.12 sh, 1405.8 s
Five membered ring C-C str	1297 s, 1231 w, 1209 vw, 1184 s, 1128 s	1307.11 m, 1259.9 w, 1141.17 w, 1110.16 w
C-H in plane bending	1091 vvw	1089.1 w, 1053.13 m
C-C Benzene ring str	769 vw, 756 vw, 743 vw	838.16 sh, 793.13 sh, 744.9 sh
C-H out of plane bending	717 s	714.4 s, 647.11 w, 534.11 w
Mo=O Str. ^{44, 45}	----	976.7 s

Table-6 (FTIR absorptions in cm^{-1})			
Absorptions	$\text{C}_3\text{H}_5\text{NS}_2$ (2-Thiazoline-2-thiol) ^{47, 48, 49}	[7]	[8]
N-H asym. str.	3145	3367.10 vs	3393.15 vs
C-H str.	2968 s, 2926 s, 2852 s	----	2960.23 sh, 2899.25 sh
S-H str.	2709	----	----
Cross bridged C-N str. of CH_3CN	----		
C=N str.	1518 s	1694.21 sh, 1592.13 s, 1457.24 sh, 1435.22 w	1609.26 s, 1571.27 s, 1435.38 w, 1402.31 w
C-N ring str.	1260 sh	1371.14 s, 1311.23 w, 1256.22 w	1371.30 w, 1315.32 w, 1257.33 w
C-N sym. str. + C-C str.	1217 sh	1205.18 m	1205.32 w
C-S str. + C-SH str.	1160 sh	1080.27 w, 1049.21 m	1047.33 w, 1027.33 w
No-N str.	----	461.25 sh	422.36 w
$\text{Mo}=\text{O}^{44, 45}$ str.	----	977.13 s	----
$\text{Mo}=\text{O}$ str. of cis- MoO_2^{2+} core ³⁹	----	----	982.30 m, 916.30 w

¹H NMR Spectra:

Spectrum of pyrazole⁵⁰ 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 [1] in DMSO-d_6 shows peak that peak due to middle CH proton and on side two carbons have moved downfield (Table-7). Peaks of C-H protons of pyrazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of succinimide^{51, 52} shows CH_2 peaks at 2.73 ppm. Spectra of complexes [2] & [4] in DMSO-d_6 show that peaks due to CH_2 protons have moved up field (Table-8).

Spectrum of imidazole^{50, 53} 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. Spectra of complexes [3] & [6] in DMSO-d_6 show relatively up field absorptions for C-H proton (between two nitrogen atoms) and C-H protons on other two carbon atoms (Table-9). Two equivalent C-H protons of imidazole 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 [5] in DMSO-d_6 shows peaks due to ring protons in the range 7.74 ppm-8.55 ppm with highest peak at 7.60 ppm, N-H peak at 11.23 ppm & 13.06 ppm and CH_3CN peak at 2.00 ppm. This shows presence N-H group and CH_3CN in the complex [5] (Table-10).

Spectra of complexes [7] & [8] (Table-11) in DMSO-d_6 show that peak due to CH_2 near N & peak due to CH_2 near sulphur have moved down field in [8] due to coordination of 2-thiazoline-2-thiol^{56, 57} with Mo.

Table-7 (¹ H NMR absorptions in ppm)		
Assignments	$\text{C}_3\text{H}_4\text{N}_2$ in CCl_4 (Pyrazole) ⁵⁰	[1]
N-H	12.64 1H	12.05 3H
Middle CH_2	6.31 (s) 1H	6.59 1H
Side CH_2	7.61(s) 2H	8.14 2H

Table-8 (¹ H NMR absorptions in ppm)			
Assignments	$\text{C}_4\text{H}_5\text{NO}_2$ (Succinimide) ^{51, 52}	[2]	[4]
N-H	----	11.01 1H	7.31-7.35 2H
CH_2	2.73	2.54 4H	1.95 4H

Table-9 (¹ H NMR absorptions in ppm)			
Assignments	$\text{C}_3\text{H}_4\text{N}_2$ (Imidazole) ^{50, 53}	[3]	[6]
N-H	12.4 1H	13.85 2H b	14.70 2H
C-H (between two nitrogen atoms)	9.37 1H	9.11 1H	9.15 1H
C-H (other carbon atoms)	7.80 2H	7.59 2H	7.67 2H

Table-10 (¹ H NMR absorptions in ppm)		
Assignments	$\text{C}_8\text{H}_4\text{O}_2\text{N}^+\text{K}^+$ (Pot. phthalimide) ^{54, 55}	[5]
N-H	----	11.23, 13.06
Ring C-H	7.58 -7.87	7.74-8.55
CH_3CN	----	2.00

Table-11 (¹ H NMR absorptions in ppm)			
Assignments	C ₃ H ₅ NS ₂ (2-Thiazoline-2-thiol) ^{56, 57}	[7]	[8]
CH ₂ near N	3.32 2H	3.33	3.51
CH ₂ near S	3.55 2H	3.51	4.06
NH	7.43 1H	----	13.41
CH ₃ CN	----	2.05	2.03

Mass Spectra (LC-MS/GC-MS)⁵⁸:

Complexes [1] & [2] have been prepared from MoOCl₄ as the precursor. Complexes [4], [5], [6] & [8] have been prepared from MoCl₅ as the precursor. Complexes [3] and [7] have been prepared from MoO₂Cl₂ as the precursor. Mass spectra (LC=MS/GC-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.

Comp.	Table-12 (Fragmentation)
[1]	$\text{MoO}_3\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)_2 \rightarrow [\text{MoO}_2\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)]^+ + [\text{C}_3\text{H}_4\text{N}_2]^+ + [\text{O}]^+$ [1] (F.W. = 422.0) m / z = 338.42 m / z = 71.77 ↓ $[\text{MoOCl}_4(\text{C}_3\text{H}_4\text{N}_2)]^+ + [\text{O}]^+$ m / z = 321.43 $[\text{MoO}_2\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)]^+ \rightarrow [\text{MoO}_2\text{Cl}_3(\text{C}_3\text{H}_4\text{N}_2)]^+ + [\text{Cl}]^-$ m / z = 338.42 m / z = 303.45
[2]	$\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_4 \rightarrow 2[\text{C}_3\text{H}_5\text{ON}]^+ + 2\text{CO} + [\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_2]^{2+}$ [2] (F.W. = 877.0) m / z = 71.77 m / z = 338.41 ↓ $[\text{Mo}_2\text{OCl}_3]^{2+} \leftarrow [\text{Mo}_2\text{O}_3\text{Cl}_3]^{2+} \leftarrow [\text{Mo}_2\text{O}_3\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_2]^{2+}$ m / z = 158.06 m / z = 173.85 m / z = 321.43 $[\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N})_2]^{2+} \rightarrow [\text{Mo}_2\text{O}_5\text{Cl}_4(\text{C}_4\text{H}_4\text{O}_2\text{N})_2]^{2+} \rightarrow [\text{MoO}_2]^{2+}$ m / z = 338.41 m / z = 303.45 m / z = 63.01
[3]	$\text{MoO}_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)_2 \rightarrow [\text{C}_3\text{H}_4\text{N}_2]^+ + [\text{MoO}_2\text{Cl}_2]^+$ [3] (F.W. = 335.0) m / z = 68.1 m / z = 199.9 ↓ -Cl $[\text{MoO}_2\text{Cl}]^+$ m / z = 164.9
[4]	$\text{MoCl}_3(\text{C}_4\text{H}_4\text{O}_2\text{N})(\text{CH}_3\text{CN}) \rightarrow [\text{C}_4\text{H}_5\text{O}_2\text{N}]^+ + [\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})]^+$ [4] (F.W. = 341.5) m / z = 99.8 m / z = 241.1 ↓ -HCN ↓ -CH₃CN $[\text{C}_3\text{H}_4\text{O}_2]^+ [\text{MoO}_2\text{Cl}_2]^+$ m / z = 73.1 m / z = 199.9 ↓ -Cl $[\text{MoO}]^+ \xleftarrow{-\text{O}} [\text{MoO}_2]^+ \xleftarrow{-\text{Cl}} [\text{MoO}_2\text{Cl}]^+$ m / z = 113.9 m / z = 129.9 m / z = 164.9
[6]	$\text{MoCl}_5(\text{C}_3\text{H}_4\text{N}_2)_2 \rightarrow [\text{C}_3\text{H}_4\text{N}_2]^+$ [6] (F.W. = 409.5) m / z = 68.1
[7]	$\text{Mo}_2\text{O}_3\text{Cl}_2(\text{C}_3\text{H}_5\text{NS}_2)_2(\text{CH}_3\text{CN})_2\text{Cl}_4 \rightarrow [\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+ \rightarrow [\text{MoO}_2\text{Cl}(\text{CH}_3\text{CN})]^+ \rightarrow [\text{MoO}_2\text{Cl}]^+$ [7] (F.W. = 773.0) m / z = 470.81 m / z = 205.54 m / z = 162.01 ↓ $[\text{MoOCl}(\text{CH}_3\text{CN})]^+ + \text{C}_3\text{H}_5\text{NS}_2 \leftarrow [\text{MoOCl}(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+ \rightarrow [\text{MoOCl}(\text{C}_3\text{H}_4\text{NS}_2)]^+ + \text{CH}_3\text{CN}$ m / z = 189.70 m / z = 308.01 m / z = 267.11

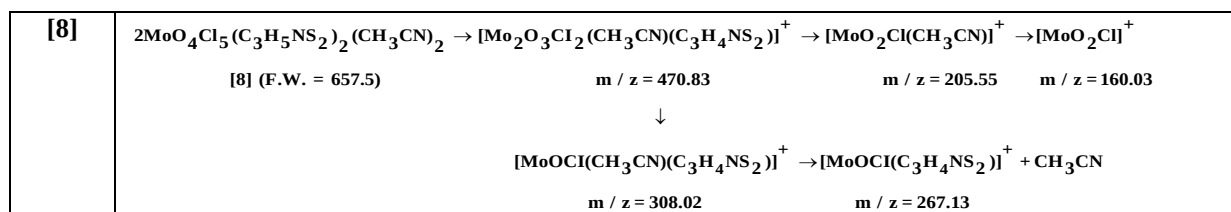


Table-13 (m/z values of some fragments)				
Comp.	Fragment	Calculated ⁴⁴	Observed	Relative abundance
[1]	$[\text{MoO}_2\text{Cl}_4(\text{C}_3\text{H}_4\text{N}_2)]^+$	337.80	338.42	90%
	$[\text{MoOCl}_4(\text{C}_3\text{H}_4\text{N}_2)]^+$	321.81	321.43	15%
	$[\text{MoO}_2\text{Cl}_3(\text{C}_3\text{H}_4\text{N}_2)]^+$	302.83	303.45	8%
	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	71.77	100%
[2]	$[\text{Mo}_2\text{O}_5\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N}_2)]^{2+}$	340.82	338.41	85%
	$[\text{Mo}_2\text{O}_3\text{Cl}_6(\text{C}_4\text{H}_4\text{O}_2\text{N}_2)]^{2+}$	324.82	321.43	22%
	$[\text{Mo}_2\text{O}_5\text{Cl}_5(\text{C}_4\text{H}_4\text{O}_2\text{N}_2)]^{2+}$	305.85	303.46	15%
	$[\text{MoO}_2]^{2+}$	64.94	63.01	100%
	$[\text{Mo}_2\text{O}_3\text{Cl}_3]^{2+}$	174.35	173.85	74%
	$[\text{Mo}_2\text{OCl}_3]^{2+}$	158.35	158.06	28%
	$[\text{C}_3\text{H}_5\text{ON}]^+$	71.03	71.77	52%
[3]	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	199.9	5%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	164.9	2%
	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	68.1	100%
[4]	$[\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})]^+$	240.85	241.1	10%
	$[\text{MoO}_2\text{Cl}_2]^+$	199.83	199.9	100%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	164.9	40%
	$[\text{MoO}_2]^+$	129.89	129.9	10%
	$[\text{MoO}]^+$	113.90	113.9	12%
	$[\text{C}_4\text{H}_5\text{O}_2\text{N}]^+$	99.03	99.8	12%
	$[\text{C}_3\text{H}_4\text{O}_2]^+$	72.02	73.1	10%
[6]	$[\text{C}_3\text{H}_4\text{N}_2]^+$	68.03	68.1	100%
[7]	$[\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+$	472.73	470.81	60%
	$[\text{MoOCl}(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+$	307.87	308.01	58%
	$[\text{MoOCl}(\text{CH}_3\text{CN})]^+$	189.89	189.7	92%
	$[\text{MoO}_2\text{Cl}(\text{CH}_3\text{CN})]^+$	205.89	205.54	35%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	162.01	66%
	$[\text{MoOCl}(\text{C}_3\text{H}_4\text{NS}_2)]^+$	266.84	267.11	100%
[8]	$[\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+$	472.73	470.83	15%
	$[\text{MoOCl}(\text{CH}_3\text{CN})(\text{C}_3\text{H}_4\text{NS}_2)]^+$	307.87	308.02	30%
	$[\text{MoO}_2\text{Cl}(\text{CH}_3\text{CN})]^+$	205.89	205.55	100%
	$[\text{MoO}_2\text{Cl}]^+$	164.86	160.03	55%
	$[\text{MoOCl}(\text{C}_3\text{H}_4\text{NS}_2)]^+$	266.84	267.13	40%
	$[\text{Mo}]^+$	97.90	96.16	10%

Electronic Spectra:

Table-14 (Absorptions in λ_{max} nm)	
Pure Ligand solution in DMSO (Ring $\pi \rightarrow \pi^*$)	Complex solution in DMSO (Ring $\pi \rightarrow \pi^*$)
Pyrazole ⁵⁹ 264 nm	[1] 265 nm (ϵ 0.9x10 ³)
Succinimide ^{4,5} 259 nm	[4] 259 nm (ϵ 3.7x10 ³)
Imidazole ⁶⁰ 284 nm	[3] 260 nm (ϵ 1.3x10 ³)
	[6] 260 nm (ϵ 1.8x10 ³)
Pot phthalimide ^{61, 62, 63, 64} 200-400 nm	[5] 267 nm (ϵ 1.8x10 ³)
2-Thiazoline-2-thiol	[7] 279 nm (ϵ 7.0x10 ³)
	[8] 278 nm (ϵ 7.0x10 ³)

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