



Reactions of MoOCl_4 & MoO_2Cl_2 with Imidazole, Pyrazole, Acetamide, Succinimide, Benzamide & 2-Thiazoline-2-thiol

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Abstract: MoO_2Cl_2 reacts with imidazole, pyrazole, acetamide & succinimide in CH_3CN medium to yield multinuclear Mo complexes: $\text{Mo}_4\text{O}_7\text{Cl}_6(\text{CH}_3\text{CN})_4(\text{C}_3\text{H}_4\text{N}_2)\text{Cl}_2$ [1], $\text{Mo}_4\text{O}_7\text{Cl}_6(\text{CH}_3\text{CN})_4(\text{C}_3\text{H}_4\text{N}_2)_4$ [2], $\text{Mo}_4\text{O}_7\text{Cl}_6(\text{CH}_3\text{CN})_4(\text{CH}_3\text{CONH}_2)_2\text{Cl}_2$ [3] & $\text{Mo}_4\text{O}_7\text{Cl}_6(\text{CH}_3\text{CN})_4(\text{C}_4\text{H}_5\text{NO}_2)_2\text{Cl}_2$ [4], respectively. MoOCl_4 reacts with imidazole, pyrazole, benzamide & 2-thiazoline-2-thiol to form $\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})_2(\text{C}_3\text{H}_4\text{N}_2)\text{Cl}_3$ [5], $\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})_2(\text{C}_3\text{H}_4\text{N}_2)\text{Cl}_4$ [6], $\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})_2(\text{C}_6\text{H}_5\text{CONH}_2)_2\text{Cl}_4$ [7] & $\text{Mo}_2\text{O}_3\text{Cl}_2(\text{CH}_3\text{CN})_2(\text{C}_3\text{H}_5\text{NS}_2)_2\text{Cl}_4$ [8], respectively. Compounds have been characterized by elemental analysis, ^1H NMR, FTIR, Mass (LC-MS), electronic spectra and molar conductance studies.

Keywords: MoOCl_4 ; MoO_2Cl_2 ; imidazole; pyrazole; acetamide; succinimide; benzamide, 2-thiazoline-2-thiol.

I. Introduction

Molybdenum is known to form multinuclear complexes.^{1, 2, 3} These complexes may be cyanide bridged^{1, 2}. CH_3CN medium is increasingly used in inorganic reactions, which increases solubility of precursors, otherwise these are not much soluble in less polar solvents, such as, CH_2CH_2 , CHCl_3 , etc. Poor solubility of precursors may lead not only to slowing down of reaction, but also to inhomogeneity of reaction mixture. CH_3CN being a polar solvent (3.92 D), is able to dissolve a wide variety of compounds – both ionic and non-polar. CH_3CN can coordinate to metal via $\text{L} \rightarrow \text{M}$, where terminal $\text{C} \equiv \text{N}$ group is involved in end-on coordination. There may not be $\text{M} \rightarrow \text{L}$ π -back bonding⁴, thus there is increase in $\text{C} \equiv \text{N}$ stretching frequency to $2268 - 2361 \text{ cm}^{-1}$ from 2253 cm^{-1} in free⁵ CH_3CN (thin film in KBr). However, if there is $\text{M} \rightarrow \text{L}$ π -back bonding into ligand π^* orbitals, then there will be a decrease in $\text{C} \equiv \text{N}$ stretching frequency. Sometimes, CH_3CN may not be involved in $\text{L} \rightarrow \text{M}$ end-on coordination, rather it exhibits $\text{L} \rightarrow \text{M}$ coordination through cross-bridging¹. IR band at $1638-1658 \text{ cm}^{-1}$ is assigned to this cross bridged¹ CH_3CN ligand in contrast to terminal CH_3CN stretchings at 2317 cm^{-1} and 2290 cm^{-1} . Effect of cross-bridging of CH_3CN ligand is also seen on ^1H NMR chemical shifts. Terminal¹ CH_3CN ligand shows peak at 1.95 ppm [3H] in CD_3CN medium. However, cross-bridged¹ CH_3CN ligand shows chemical shift at 3.37 – 3.63 ppm [3H] in CD_3CN medium.

The author reported^{6, 7, 8, 9, 10} reactions of MoOCl_4 , MoO_2Cl_2 , MoCl_5 in CH_2Cl_2 medium. Owing to feeble solubility of MoO_2Cl_2 , MoCl_5 and ligands in CH_2Cl_2 medium, above said difficulties were encountered. This stimulated the author to study behaviour of MoOCl_4 , MoO_2Cl_2 & MoCl_5 towards ligands in CH_3CN medium. In reactions reported in this paper, enhanced polarity of CH_3CN medium has plays an important role in reaction process. Products obtained are soluble in CH_3CN . In reactions carried out in CH_2Cl_2 medium, products were obtained as residues. Enhanced solubility of MoOCl_4 , MoO_2Cl_2 & MoCl_5 is due to formation of solvent stabilized complexes, like $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

The compounds reported in this paper are multinuclear as assessed by the fragments detected in mass (LC-MS) spectra. There is some similarity in the fragments formed from the compounds prepared from MoO_2Cl_2 . Similarly, there is some similarity in the fragments formed from the compounds prepared from MoOCl_4 . Pyrazoles and their derivatives exhibit various biological activities including antimicrobial¹¹, anti-cyclooxygenase¹², anticonvulsant¹³, antitubercular¹⁴, antitumor¹⁵, antiinflammatory¹⁶, analgesic¹⁷, antidiabetic¹⁸, antipshycotic^{19, 20, 21}. Many drugs, such as, antifungal drugs and nitroimidazole contain an imidazole^{22, 23} ring.

II. Experimental

Materials:

Molybdenumoxytetrachloride MoOCl_4 has been synthesized in laboratory by reaction of MoO_3 (CDH, AR Grade) with thionyl chloride at reflux temperature for about 6 h. After refluxing, excess thionyl chloride was evacuated in liquid nitrogen traps. Dark green crystals obtained were dissolved in dry CH_2Cl_2 to get a dark red solution. Solution was filtered through filtration unit having G-4 sintered glass crucible to remove any unreacted MoO_3 . On evacuation, filtrate yielded MoOCl_4 shining dark green crystals, having m.p. $100^\circ - 102^\circ \text{ C}$.

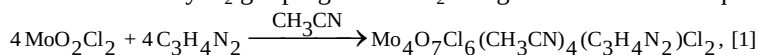
Molybdenumdioxodichloride MoO_2Cl_2 (Sigma-Aldrich, USA) is a light yellow hygroscopic solid. It was purchased from market and used as such. Imidazole is a colourless solid (SD Fine, LR Grade, m.p. $88^\circ\text{--}91^\circ\text{C}$). It is soluble in water and many polar organic solvents including CH_3CN . Pyrazole is a colourless solid (SD Fine, LR Grade, m.p. $66^\circ\text{--}70^\circ\text{C}$). Acetamide (NICE, LR grade, m.p. $79^\circ\text{--}81^\circ\text{C}$) is a colourless solid and was procured from market. It is soluble in CH_3CN , but insoluble in CH_2Cl_2 . Succinimide (CDH, LR Grade, m.p. $125^\circ\text{--}127^\circ\text{C}$) is a white solid, soluble in polar solvents. Benzamide (Loba Chemie, m.p. $127^\circ\text{--}130^\circ\text{C}$) is a white solid, soluble in polar solvents. 2-Thiazoline-2-thiol also called 2-mercapto-2-thiazoline (Sigma-Aldrich, USA, m.p. $100^\circ\text{--}105^\circ\text{C}$) is a white solid, soluble in acetonitrile. 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:

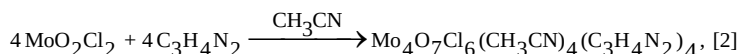
Molybdenum and chlorine were estimated by standard methods²⁴. The elemental analyses (C, H, N and O) were carried out using Organic Elemental Analyzer Series-Flash 2000 Thermo Fisher Scientific (USA), FTIR spectra were recorded in the range $4000 - 400\text{ cm}^{-1}$ using Perkin-Elmer 400 FTIR Spectrometer (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 and UV-VIS spectra in DMSO solvent were recorded using Thermoscientific Genesys 10S Series UV-VIS spectrophotometer (USA), at GZS PTU Campus, Bathinda (India). 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). 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]:

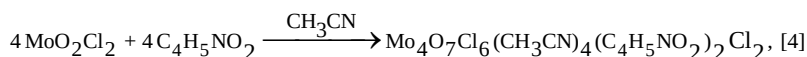
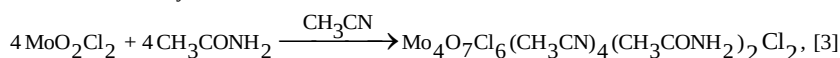
A 100 ml round bottomed flask containing a magnetic bead was attached to a pressure stabilized dropping funnel fitted with a teflon rotaflow stop-cock. Assembly was connected to vacuum line and flame dried under vacuum (10^{-3} torr). Dry N_2 gas purged with O_2 was allowed into assembly at room temperature, through liquid N_2 traps. A known weight of MoOCl_4 or MoO_2Cl_2 dissolved in dry CH_3CN was taken in round bottomed flask. An equimolar amount of $\text{C}_3\text{H}_4\text{N}_2$ (imidazole or pyrazole), CH_3CONH_2 , $\text{C}_4\text{H}_5\text{NO}_2$ (succinimide), $\text{C}_6\text{H}_5\text{CONH}_2$ or $\text{C}_3\text{H}_5\text{NS}_2$ (2-thiazoline-2-thiol) 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 liquid N_2 traps.



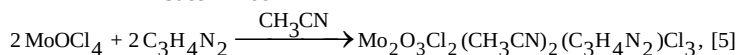
Imidazole



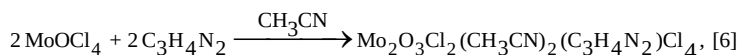
Pyrazole



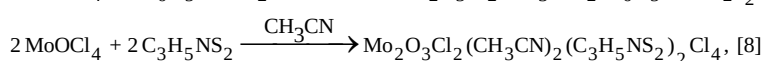
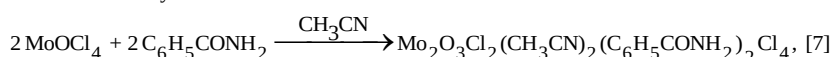
Succinimide



Imidazole



Pyrazole



2 - Thiazoline - 2 - thiol

III. Results & Discussions

Analytical Measurements:

All compounds are 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) and molar conductance

Λ_M measurements. Analytical data and mass (LC-MS) spectra reveal that these compounds are multinuclear. Λ_M of compounds [1] to [8] in DMSO are 2 – 4 cm²ohm⁻¹mol⁻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
Mo ₄ O ₇ Cl ₆ (CH ₃ CN) ₄ (C ₃ H ₄ N ₂)Cl ₂ , [1] (Light blue/1012.0)	2	37.12 (37.94)	21.37 (21.04)	12.48 (13.04)	1.64 (1.58)	07.39 (08.30)	11.9 (11.0)	----
Mo ₄ O ₇ Cl ₆ (CH ₃ CN) ₄ (C ₃ H ₄ N ₂) ₄ , [2] (Light blue/1145.0)	3	33.73 (33.53)	18.93 (18.60)	20.12 (20.96)	2.57 (2.44)	13.78 (14.67)	10.50 (09.7)	----
Mo ₄ O ₇ Cl ₆ (CH ₃ CN) ₄ (CH ₃ CONH ₂) ₂ Cl ₂ , [3] (Light blue/1094.0)	2	35.37 (35.10)	26.17 (25.95)	12.27 (13.16)	2.16 (2.01)	06.77 (07.67)	13.9 (13.1)	----
Mo ₄ O ₇ Cl ₆ (CH ₃ CN) ₄ (C ₄ H ₅ NO ₂) ₂ Cl ₂ , [4] (White/1142.0)	4	32.74 (33.62)	23.95 (24.86)	15.99 (16.81)	2.03 (1.92)	06.82 (07.35)	15.0 (15.4)	----
Mo ₂ O ₃ Cl ₂ (CH ₃ CN) ₂ (C ₃ H ₄ N ₂)Cl ₃ , [5] (Green/567.5)	2	33.04 (33.83)	31.22 (31.37)	15.80 (14.80)	2.06 (1.76)	10.71 (09.86)	09.3 (08.4)	----
Mo ₂ O ₃ Cl ₂ (CH ₃ CN) ₂ (C ₃ H ₄ N ₂)Cl ₄ , [6] (Green/603.0)	3	32.67 (31.84)	36.27 (35.32)	13.04 (13.93)	2.04 (1.65)	09.51 (09.28)	08.6 (07.9)	----
Mo ₂ O ₃ Cl ₂ (CH ₃ CN) ₂ (C ₆ H ₅ CONH ₂) ₂ Cl ₄ , [7] (Green/777.0)	3	24.50 (24.71)	28.32 (27.41)	28.29 (27.89)	2.74 (2.57)	06.59 (07.20)	09.8 (10.2)	----
Mo ₂ O ₃ Cl ₂ (CH ₃ CN) ₂ (C ₃ H ₅ NS ₂) ₂ Cl ₄ , [8] (Light green/773.0)	4	24.17 (24.83)	28.20 (27.55)	16.47 (15.52)	2.32 (2.06)	7.87 (7.24)	06.5 (06.2)	17.2 (16.5)

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

FTIR Spectra:

Imidazole^{25, 26} shows N-H stretchings at 3724-3237 cm⁻¹. Band at 3254.15 cm⁻¹ shows that N-H group is present in compound [1] (Table-2). This peak is broad in the solid state (KBr disk) due to hydrogen bonding. Two medium bands at 943.15 cm⁻¹ & 927.14 cm⁻¹ are attributable to the presence of cis-MoO₂²⁺ core³⁹.

Pyrazole^{27, 28} shows N-H stretching at 3450 cm⁻¹. Band at 3259.2 cm⁻¹ shows that N-H group is present in compound [2] (Table-3). Mo-N coordination bond lowers frequency of N-H stretching. Strong bands at 941.3 cm⁻¹ & 905.3 cm⁻¹ show the presence of cis-MoO₂²⁺ core³⁹.

Acetamide^{29, 30} shows N-H stretchings at 3374 cm⁻¹ & 3302 cm⁻¹. Band at 3348.1 cm⁻¹ shows that N-H group is present in compound [3] (Table-4). Strong bands at 956.6 cm⁻¹ & 916.5 cm⁻¹ show the presence of cis-MoO₂²⁺ core³⁹. Shift in C=O stretching frequency from 1672 cm⁻¹ to 1650.2 cm⁻¹ of acetamide indicates a Mo-O coordination bond.

Succinimide^{31, 32} shows N-H stretchings at 3410 cm⁻¹ & 3223 cm⁻¹. Band at 3332.1 cm⁻¹ shows that N-H group is present in compound [4] (Table-5). Strong bands at 960.4 cm⁻¹ & 921.2 cm⁻¹ show the presence of cis-MoO₂²⁺ core³⁹. There is no shift in C=O stretching frequency from 1771 cm⁻¹, which indicates that there is no Mo-O coordination bond.

Imidazole^{25, 26} shows N-H stretchings at 3724-3237 cm⁻¹. Band at 3291 cm⁻¹ shows that N-H group is present in compound [5] (Table-2). This peak is broad in the solid state (KBr disk) due to hydrogen bonding. A strong band at 977.7 cm⁻¹ shows the presence of terminal Mo=O group^{40, 41}.

Pyrazole^{27, 28} shows N-H stretching at 3450 cm⁻¹. Band at 3366.7 cm⁻¹ shows that N-H group is present in compound [6] (Table-3). Mo-N coordination bond lowers frequency of N-H stretching. A strong band at 977.15 cm⁻¹ shows the presence of terminal Mo=O group^{40, 41}.

Benzamide^{33, 34, 35} shows N-H stretching at 3366 cm⁻¹. Bands at 3426.24 cm⁻¹ & 3329.23 cm⁻¹ show that N-H group is present in compound [7] (Table-6). A strong band at 973.21 cm⁻¹ shows the presence of terminal Mo=O group^{40, 41}.

2-Thiazoline-2-thiol shows N-H stretching at 3145 cm⁻¹. Strong band at 3336.8 cm⁻¹ shows that N-H group is present in compound [8] (Table-7). A strong band at 982.10 cm⁻¹ shows the presence of terminal Mo=O group^{40, 41}.

Table 2 (FTIR absorptions in cm ⁻¹)			
Absorptions	C ₃ H ₄ N ₂ (Imidazole) ^{25, 26}	[1]	[5]
N-H str.	3724 vb, 3656 vb, 3270, 3241, 3237	3254.15 s, br	3291 s, br

C-H str.	3196, 3165	3148.11 s, 2984.20 sh, 2851.24 sh, 2636.36 sh	3151.2 s, 2993.5 sh, 2861.7 sh
cross bridged C≡N str. of CH ₃ CN	----	1621.36 m	1618.7 s
C=C ring str.	1558, 1500	1581.22 s	1584.7 s
N-C ring str.	1434	1423.42 m	1427.15 w
C-H in plane bending	1092, 1074	1093.39 w, 1448.35 m	1093.16 w, 1048.14 m
C-H bending	964	----	----
Ring bending	909	----	----
C-H out of plane bending (wagging), Ring twisting	816, 730	843.3 s, 703.9 s, br	757.10 s, br
Ring twisting	646	621.11 m	623.11 m
Ring twisting, N-H wagging	528	557.19 m	499.19 w
Mo=O ^{40, 41} str.	----	----	977.7 s
Mo=O str. of cis-MoO ₂ ²⁺ core ³⁹	----	943.15 m, 927.14 m	----

Table 3 (FTIR absorptions in cm ⁻¹)			
Absorptions	C ₃ H ₄ N ₂ (Pyrazole) ^{27, 28}	[2]	[6]
N-H, str.	3450	3259.2 vs, b	3366.7 vs, b
C-H str.	3155, 3144	3122 vs, b	3138.7 vs, b
Cross bridged C≡N str. of CH ₃ CN	----	1656.3 vs	1620.17 vs
C=C ring str.	1558	1526.7 m	----
N-C ring str.	1468, 1138	1451.7 sh, 1399.2 s, 1329.1 w, sh, 1240.9 s,	1475.27 sh, 1408.26 w, 1351.2 w, sh, 1119.2 m
C-H in plane bending	1046, 1035	1077.13 sh, 1061.10 s	1053.25 m
C-H bending	938	----	----
Ring bending	918	----	913.29 sh
C-H out of plane bending (wagging), Ring twisting	893, 840, 760	826.5 sh, 771.2 s, b	786.19 m 735.30 m
Ring twisting	656, 619	570.5 m	609.24 w
Ring twisting, N-H wagging	498	475.18 w	497.29 w
Mo=O ^{40, 41} str.	----	----	977.15 vs
Mo=O Str. of cis-MoO ₂ ²⁺ core ³⁹	----	941.3 m, 905.3 m	----

Table 4 (FTIR absorptions in cm ⁻¹)		
Absorptions	CH ₃ CONH ₂ ^{29, 30}	[3]
N-H Str.	3302, 3374	3348.1 s, br
CH ₂ Str.	2820	----
C=O Str., Cross bridged C≡N str. of CH ₃ CN	1672, 1631	1650.2
CH ₃ Deformation	1450	1492.9 m, sh
C-N asym str.	1396	1403.10 w, sh
NH ₂ Deformation	1150	1120.14 m
C-N sym str.	1048	1050.16 w
NH ₂ rocking, twisting and wagging	900	752.3 s, br
N=C=O bending	600	633.8 w, sh, 564.5 s
Mo-N (Strong)	----	481.16 w, sh
Mo=O Str. of cis-MoO ₂ ²⁺ core ³⁹	----	956.6 s, 916.5 s

Table 5 (FTIR absorptions in cm ⁻¹)		
Absorptions	C ₄ H ₅ NO ₂ (Succinimide) ^{31, 32}	[4]
NH str.	3410 s, b, 3223 s, b	3332.1 vb
CH ₂ sym. str.	2964, 2945 w	----
CO sym., HNC in plane bending	1771 m	1771.6 m
CO asym., HNC in plane bending	1713 vs, b	1697.0 vs
CH ₂ sym. scissoring	1431 m	1421.1 vw
CH ₂ asym. scissoring	1400 m	1383.7 s
CNC asym. str., HNC in plane bending	1349 s, 1334	----
CH ₂ bending, ring in plane bending	1294 s	1298.6 m
CH ₂ bending	1241	1249.11 vw
CNC asym. str., HNC in plane bending	1186 s,	1187.3 vs
C ₄ -C ₅ str, CH ₂ bending	998 m	----
Ring in plane bending	901	----
C-C str., CNC sym. str.	849	859.9 vw
CH ₂ bending, ring out of plane bending	817 s	819.5 sh

OCN asym. out of plane bending	632 m	645.5 w
OCN sym. out of plane bending, CH ₂ bending	543 w	562.7 m
CH ₂ bending, ring out of plane bending	528	----
Mo=O Str. of cis-MoO ₂ ²⁺ core ³⁹	----	960.4 s, 921.2 s

Table 6 (FTIR absorptions in cm ⁻¹)		
Absorptions	C ₆ H ₅ CONH ₂ ^{33, 34, 35}	[7]
N-H str. asym.	3366	3426.24 s, 3329.23 s
N-H str. sym.	3170	3154.26 s
CH ₂ str.	2820	----
C=O Str., Cross bridged C≡N str. of CH ₃ CN	1656 s	1634.12 s
NH ₂ Deformation	1624, 1606	1553.22 sh, 1525.17 s
CH ₃ Deformation	1450	1452.24 s
C-N asym. str.	1398 s	1305.38 w
NH ₂ rocking	1142 s, 1122 s	1260.41 w, 1182.41 w, 1162.41 w
C-N sym. str.	1048	1102.99 w, sh, 1082.38 w
C-H out of plane bending	797.7 m	797.33 sh
NH ₂ rocking, twisting and wagging	770.4 m, 700 s, 684 s	710.25 s, 684.25 s
N=C=O bending	600	624.30 sh, 561.26 s
Mo-N (Strong)	----	422.45 w
Mo=O ^{40, 41} str.	----	973.21 s

Table 7 (FTIR absorptions in cm ⁻¹)		
Absorptions	C ₃ H ₅ NS ₂ (2-Thiazoline-2-thiol) ^{36, 37, 38}	[8]
N-H asym. str.	3145	3336.8 vs, very br
C-H str.	2968 s, 2926 s, 2852 s	----
S-H str.	2709	----
Cross bridged C≡N str. of CH ₃ CN	----	1665.13
C=N str.	1518 s	1602.12
C-N ring str.	1260 sh	1256.52 w, sh
C-N sym. str. + C-C str.	1217 sh	1205.13 s
C-S str. + C-SH str.	1160 sh	1155.15 m
Mo=O ^{40, 41} str.	----	982.10 s

¹H NMR Spectra:

Spectrum of imidazole^{42, 43} 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 imidazole⁴⁴ in DMSO-d₆ shows relatively downfield absorptions for CH proton (between two nitrogen atoms) at 9.37 ppm, CH protons on other two carbons at 7.80 ppm.

Spectrum of compound [1] (Table-8) in DMSO-d₆ shows that peaks due to CH proton (between two nitrogen atoms) and CH protons on other two carbons of imidazole have shifted up-field. Two equivalent C-H protons of imidazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of pyrazole⁴⁵ 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 [2] (Table-9) in DMSO-d₆ shows that peaks due to middle CH proton & CH protons on side two carbons have retained their positions in pyrazole. Peaks of C-H protons of pyrazole appears as singlet, because of the tautomerization equilibrium.

Spectrum of compound [3] (Table-10) in DMSO-d₆ shows that peak due to CH₃ in acetamide⁴⁶ has retained its position in the compound.

Spectrum of compound [4] (Table-11) in DMSO-d₆ shows that peak due to CH₂ in succinimide^{47, 48} has moved downfield due to Mo-N coordination.

Spectrum of compound [5] (Table-8) in DMSO-d₆ shows that peaks due to CH proton (between two nitrogen atoms) and CH protons on other two carbons of imidazole have shifted up-field. Two equivalent C-H protons of imidazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of compound [6] (Table-9) in DMSO-d₆ shows that peaks due to middle CH proton & CH protons on side two carbons have moved down field, because of Mo-N coordination. Peaks of C-H protons of pyrazole appear as singlets, because of the tautomerization equilibrium.

Spectrum of compound [7] (Table-12) in DMSO-d₆ shows that peak due to CH₃ in benzamide⁴⁹ has retained its position in the compound.

Spectrum of compound [8] (Table-13) in DMSO- d_6 shows that peak due to CH_2 near N & peak due to CH_2 near sulphur have moved down field due to coordination of 2-thiazoline-2-thiol^{50, 51} with Mo.

Table 8 (^1H NMR absorptions in ppm)			
Absorptions	$C_3H_4N_2$ (Imidazole) ⁴⁴	[1]	[5]
NH	12.4 1H	13.35 (s) 1H	14.59 (s) 1H
CH (between two nitrogens)	9.37 1H	9.07 (s) 1H	9.07 (s) 1H
CH (other carbons)	7.80 2H	7.60 (s) 2H	7.61 (s) 2H
Residual DMSO- d_6	----	2.49 (s)	2.57 (s)

Table 9 (^1H NMR absorptions in ppm)			
Absorptions	$C_3H_4N_2$ in CCl_4 (Pyrazole) ⁴⁵	[2]	[6]
NH	12.64 1H	----	----
Middle CH_2	6.31 (s) 1H	6.30 (s) 1H	6.67 (s) 1H
Side CH_2	7.61(s) 2H	7.67 (s) 2H	8.21 (s) 2H
Residual DMSO- d_6	----	2.52 (s)	2.56 (s)

Table-10 (^1H NMR absorptions in ppm)		
Absorptions	CH_3CONH_2 ⁴⁶	[3]
NH_2	7.04 broad 2H	----
CH_3	2.00 3H	2.06 (s) 3H

Table-11 (^1H NMR absorptions in ppm)		
Absorptions	$C_4H_5NO_2$ (Succinimide) ^{47, 48}	[4]
NH	----	11.06 1H
CH_2	2.73 4H	2.58 4H

Table-12 (^1H NMR absorptions in ppm)		
Absorptions	$C_6H_5CONH_2$ ⁴⁹ in $CDCl_3$	[7]
CH (m & p)	7.34-7.51(s) broad 3H	7.40 (s) broad 2H
CH (o)	7.73-7.80 (s) broad 2H	7.86 (s) broad 2H
NH	6.04 (s) broad 2H	----

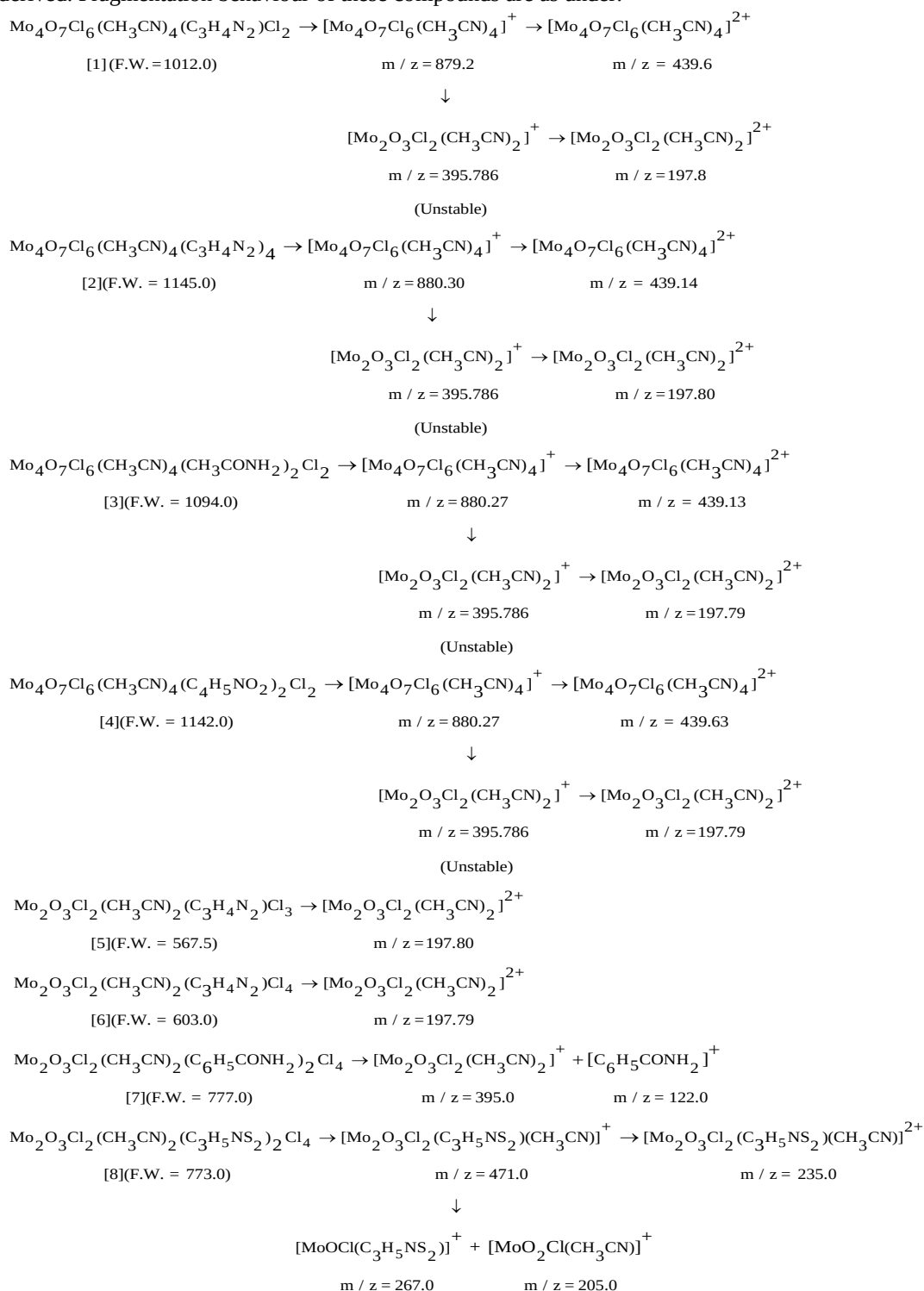
Table-13 (^1H NMR absorptions in ppm)		
Absorptions	$C_3H_5NS_2$ in $CDCl_3$ (2-Thiazoline-2-thiol) ^{50, 51}	[8]
CH_2 near N	3.32 2H	3.40 2H
CH_2 near S	3.55 2H	3.89 2H
NH	7.43 1H	----

Table-14 (m/z values of some fragments)				
Comp.	$[Mo_2O_3Cl_2(CH_3CN)_2]^{2+}$ (m/z = Calc. 197.893)	$[Mo_2O_3Cl_2(CH_3CN)_2]^+$ (m/z = Calc. 395.786)	$[Mo_4O_7Cl_6(CH_3CN)_4]^{2+}$ (m/z = Calc. 438.752)	$[Mo_4O_7Cl_6(CH_3CN)_4]^+$ (m/z = Calc. 877.505)
[1]	197.80 (100.0 %)	----	439.60 (98.12 %)	879.20 (11.97 %)
[2]	197.80 (88.68 %)	----	439.14 (100.0 %)	880.30 (74.04 %)
[3]	197.79 (90.72 %)	----	439.13 (100.0 %)	880.27 (87.15 %)
[4]	197.79 (49.86 %)	----	439.63 (100.0 %)	880.27 (76.76 %)
[5]	197.80 (100.0 %)	----	----	----
[6]	197.79 (100.0 %)	----	----	----
[7]	----	395.00 (35.25 %)	----	----
[8]	----	----	----	----

Mass Spectra (LC-MS):

Compounds [1] to [4] have been prepared from MoO_2Cl_2 and compounds [5] to [8] have been prepared from $MoOCl_4$ as the precursors. Mass spectra (LC-MS) of these compounds have some correlations. Compounds [1] to [4] decompose to form some common fragments (Table-14). Similarly, Compounds [5] to [7] decompose to

form some common fragments (Table-14). Based on the fragments formed, formulae of the compounds have been derived. Fragmentation behaviour of these compounds are as under.



Electronic Spectra:

Imidazole shows a very broad absorption in DMSO at λ_{max} 284 nm. Compound [1] shows two sharp absorptions at λ_{max} 291 nm & λ_{max} 361 nm. Compound [5] shows sharp absorptions at λ_{max} 294 nm, λ_{max} 300 nm & 447 nm. Absorption at 447 nm is due to ligand $\rightarrow$ metal charge transfer transitions $\text{O}(\pi) \rightarrow \text{d}(\text{Mo})$, that is ligand $\rightarrow$ metal charge transfer transitions due to movement of π electron from $\text{Mo} = \text{O}$ to empty d-orbital of molybdenum.

Pyrazole shows a very broad absorption in DMSO at λ_{max} 264 nm. Compound [2] shows a broad absorptions at λ_{max} 300 nm ($\epsilon = 13228$). Compound [6] shows two sharp absorptions at λ_{max} 294 nm ($\epsilon = 10477$) & λ_{max} 300 nm ($\epsilon = 11348$) and a very broad absorption at λ_{max} 457 nm ($\epsilon = 1404$). Absorption at 457 nm is due to ligand $\rightarrow$

metal charge transfer transitions $O(\pi) \rightarrow d(Mo)$, that is ligand $\rightarrow$ metal charge transfer transitions due to movement of π electron from $Mo = O$ to empty d-orbital of molybdenum.

Acetamide shows absorption in DMSO at λ_{max} 267 nm $O(n) \rightarrow C(\pi^*)$ transitions due to presence of $C = O$ group. Compound [3] shows sharp absorption at λ_{max} 292 nm, showing bathochromic shift.

Succinimide shows absorption in DMSO at λ_{max} 259 nm. Compound [4] shows sharp absorption at λ_{max} 299 nm.

Benzamide shows a very broad absorption in DMSO at λ_{max} 273 nm $O(n) \rightarrow C(\pi^*)$ transitions due to presence of $C = O$ group. Compound [7] shows sharp absorptions at λ_{max} 293 nm, 300 nm showing bathochromic shift and at 447 nm. Absorption at 447 nm is due to ligand $\rightarrow$ metal charge transfer transitions $O(\pi) \rightarrow d(Mo)$, that is ligand $\rightarrow$ metal charge transfer transitions due to movement of π electron from $Mo = O$ to empty d-orbital of molybdenum.

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