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Reactions of $MoCl_5$ and MoO_2Cl_2 with Succinimide, 1,4-Diaminobutane, 3-Methylpyridine, 1,3-Diaminopropane, Pyrazole and 1-Methylpyrrolidine in Tetrahydrofuran

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ABSTRACT

It has been reported that molybdenum may extract oxygen from oxygen containing ligands. Oxo complexes of above bases with transition metals show numerous applications and are biologically active. So to study the biological activity of molybdenum complexes and to study oxo abstraction reactions by molybdenum, reactions of succinimide/1,4-diaminobutane/ 3-methylpyridine/1, 3-diaminopropane/pyrazole/1-methylpyrrolidine with $MoCl_5$/MoO_2Cl_2 have been carried out, in THF medium using equimolar/bimolar quantities of the ligand, at normal temperature. The products thus obtained are: $Mo_2O_3Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2$,[1]; $Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2$,[2]; $MoO_2Cl_2(HNCH_2CH_2CH_2CH_2NH_2)_2$,[3]; $Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2$, [4]; $Mo_3Cl_6(C_6H_7N)_6(C_4H_8O)_6$,[5]; $MoO_2Cl_3(HNCH_2CH_2CH_2NH_2)_2$,[6]; $Mo_2O_4Cl_4(C_3H_4N_2)_4$, [7] and $Mo_2O_6Cl_8(C_5H_{11}N)_4$, [8]. There is oxygen abstraction by molybdenum during the reaction from the oxygen containing solvent THF. Formulations of these compounds were made and their properties were studied with FTIR (transmission mode), ^{1}H NMR/^{13}C NMR, microbiological studies, elemental analysis (Mo, Cl, C, H, N) and LC-MS. All preparations, separations and isolations were executed in vacuum line and inert atmosphere (dry nitrogen) to eliminate any oxidation/hydrolysis of products by air/moisture. The formulations proposed have been supported by the above characterization studies.

Keywords: Succinimide, 1, 4-diaminobutane, 3-methylpyridine, 1, 3-diaminopropane, pyrazole, 1-methylpyrrolidine.

INTRODUCTION

Succinimide

Succinimides[1] are involved in various biological applications. Succinimide is a constituent of various biologically active compounds having significance as: CNS depressant[2], hypotensive[3], antitumour[4], cytostatic[5], bacteriostatic[6], nerve conduction blocking[7], muscle relaxant[8], anorectic[9], antibacterial[10], analgesic[11], anti-convulsant[12], anti-tubercular[13], antispasmodic[14] and antifungal[15].

Succinimide can form complex through oxygen atom. Deprotonated succinimide (on removal of hydrogen from nitrogen) can form complex through the nitrogen atom. In deprotonated succinimide, the

CN bond length lies between single and double bond, because the new free electron pair of nitrogen gets delocalized and is spread on both CN bonds due to conjugation between lone pair of nitrogen and π-electrons of C=O bonds[16]. This conjugation reduces chances of availability of this lone pair for coordination. So coordination in succinimide through oxygen is more likely.

1, 4-Diaminobutane

1, 4-Diaminobutane[17-19] has a variety of applications in agrochemicals, paint additives, pharmaceuticals, surfactants and micronutrients. It is used as starting material in some biological systems and amido-ureas. It is used in the preparation of nylon 46. It acts as corrosion inhibitor of mild steel in 1N H_2SO_4.

3-Methylpyridine

3-Methylpyridine[20] has application in agrochemical industry as chlorpyrifos[21]. 3-Methylpyridine degrades/evaporates slowly from water samples as compared to 2-methylpyridine/4-methylpyridine[22,23]. 3-Methylpyridine is precursor to prepare antidote for organophosphate poisoning[24]. It is used as waterproofing agent[25] in textile industry.

1,3-Diaminopropane

1, 3-Diaminopropane[26] has a variety of industrial applications, such as, in epoxy resin and cross-linking agents. It is used as precursor for preparation of pharmaceuticals, organic chemicals and agrochemicals. It is used[27] in the synthesis of heterocycles used in coordination complexes and textile finishing. It is a potential inhibitor[28,29] against neoplasia and ornithine decarboxylase enzyme protein on rat urinary bladder carcinogenesis.

Pyrazole

Pyrazoles as well as their derivatives have a lot of biological properties, like antipshycotic[30-32], antimicrobial[33], anticonvulsant[34], antitumor[35], anti-cyclooxygenase[36], analgesic[37], antitubercular[38], antidiabetic[39], antiinflammatory[40], etc.

1-Methylpyrrolidine

1-Methylpyrrolidine[41] has numerous applications in agrochemicals, pharmaceuticals, colourants, organic synthesis, photographic chemicals, plasticizers, emulsifiers, rubber chemicals, curing agent for epoxy resins, corrosion inhibitors, etc. It is used in PU manufacture as a catalyst. In cosmetics, it acts as a powerful surfactant. It is present in cigarette smoke. It is part of cefepime[42]: broad-spectrum cephalosporin antibiotic capable to treat bacteria causing pneumonia, infections of the skin and urinary tract.

Transition metals complexes on coordination with ligands undergo deep change in physiological properties of the metals and ligands. Desired properties[27,43] on transition metals for particular applications can be incorporated by coordination of metals with certain ligands. It involves modification of properties, like stability of oxidation states, electrophilic/nucleophilic properties and solvophilicity of the metal ions. We have to choose a suitable metal and the ligand after various trials. On coordination, metal and ligand properties undergo a desired change. Many drugs containing metal chelates have higher biological activity than the uncoordinated ligands themselves[44-49].

Aim of Investigation

$MoCl_5$ reacts with a variety of bases. The author has investigated[50-55] the reactions of $MoCl_5$ with 4-phenylimidazole-2-thiol, aromatic azoles, imides, diaminoalkanes, alkylpyridines, 2-thiazoline-2-thiol, thiols and mercaptopyridine-N-oxide sodium. MoO_2Cl_2 reacts with various bases. The author has investigated[50-58] the reactions of MoO_2Cl_2 with aromatic azoles, alkanediols, diaminoalkanes, imides, amides, thioamides, purine and thiols.

It has been reported that molybdenum may extract[59,60] oxygen from oxygen containing ligands. Oxo complexes of above bases with transition metals show numerous applications and are biologically active. So to study the biological activity of molybdenum complexes and to study oxo abstraction reactions by molybdenum, reactions of succinimide/1,4-diaminobutane/3-methylpyridine/1,3-diaminopropane/pyrazole/1-methylpyrrolidine with $MoCl_5$/MoO_2Cl_2 have been carried out. Formulations of these compounds were made and their properties were studied with FTIR, ^{1}H NMR/^{13}C NMR, microbiological studies, elemental analysis and LC-MS.

MATERIALS AND METHODS

Succinimide, 1,4-diaminobutane, 3-methylpyridine, 1,3-diaminopropane, pyrazole,

1-methylpyrrolidine, $MoCl_5$ and MoO_2Cl_2 were procured from Sigma-Aldrich.

The reactants and products are sensitive to air/moisture, so all preparations, separations and isolations were executed in vacuum line and dry atmosphere (dry nitrogen) to eliminate any oxidation/ hydrolysis of reactants/products by air/moisture.

Ligand solution in dry THF was dropped from dropping funnel with continuous agitation to $MoCl_5/MoO_2Cl_2$ solution in THF taken in 100 mL round bottom flask. The reaction was carried out for about 7 hours. The products were isolated after filtration through filtration unit fitted with G-4 sintered glass crucible.

Oxinate gravimetric method[61] was used for molybdenum estimation. Mixture of sodium carbonate and sodium peroxide was fused with a known weight of the sample by using nickel crucible. Contents were fused in muffle furnace for 1 hours. at 400ºC. Fused mixture was extracted with distilled water and content was filtered through fine filter paper. Discarded the residue and only filtrate was retained. Added methyl red indicator to the filtrate. 2 N sulphuric acid was added to it dropwise to make it acidic. Added 2N ammonium acetate solution dropwise until colour of solution became faint. Solution was heated to boiling. Added 3% oxine solution (in glacial acetic acid) dropwise until yellow precipitates obtained. Boiled gently with stirring until the precipitation was complete. Filtered the yellow precipitate with G-4 sintered glass crucible. Precipitate were washed with hot water, dried at 130-140°C and weighed as $MoO_2(C_9H_6NO)_2$.

Estimation of chlorine was carried out gravimetrically as silver chloride[61]. A known weight of the sample was taken in distilled water. Added 10-12 pallets of sodium hydroxide in it. Content was boiled, cooled and filtered through a fine filter paper. Acidified the solution with dilute nitric acid. Added excess of N/10 aqueous solution of $AgNO_3$ until white precipitate of AgCl were obtained. Boiled the solution until precipitation and coagulation were complete. Filtered the precipitate through G-4 sintered glass crucible, washed with acetone, dried at 130-140°C and weighed as AgCl.

Carbon, hydrogen and nitrogen were estimated by Thermo Finnigan Elemental Analyser. Perkin-Elmer 400 FTIR Spectrometer was used for obtaining infrared spectra (transmission mode). Multinuclear Brucker Avance-II 400 NMR spectrometer was used for recording $^1H/^{13}C$ NMR in DMSO-d_6 solvent. LC-MS spectra in the range 0-1100 m/z have been attained. These studies were executed in SAIF at P. U. Chandigarh.

Molybdenum compounds prepared were tested using agar well diffusion assay method for their antibacterial and antifungal potential on the strains: *Staphylococcus aureus* (*Gram-positive* bacteria) (MTCC-737), *E. coli* (*Gram-negative* bacteria) (MTCC-1687), *Candida albicans* (fungus) (MTCC-227) and *Aspergillus niger* (fungus) (MTCC-282). Standard drugs amoxicillin and ketoconazole were used for bacteria and virus, respectively as reference. Cultures of MTCC (The Microbial Type Culture Collection and Gene Bank, Chandigarh, India) were used. Drug testing at ISF Analytical Laboratory (ISF College of Pharmacy), Ferozepur Road, Moga, Punjab (India) was carried out. R (Residue)/ F (Filtrate) refer to product source.

REACTIONS

$$MoCl_5 + C_4H_5NO_2 \xrightarrow[1:1]{THF} Mo_2O_3Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2, [1]$$

Succinimide — Black (F)

$$MoCl_5 + C_4H_5NO_2 \xrightarrow[1:2]{THF} Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2, [2]$$

Succinimide — Dark Black (F)

$$MoO_2Cl_2 + H_2NCH_2CH_2CH_2CH_2NH_2 \xrightarrow[1:1]{THF} MoO_2Cl_2(H_2NCH_2CH_2CH_2CH_2NH_2)_2, [3]$$

1, 4 - Diaminobutane — Coffee brown (R)

$$MoCl_5 + C_6H_7N \xrightarrow[1:1]{THF} Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2, [4]$$

3 - Methylpyridine — Coffee red (F)

$$MoCl_5 + C_6H_7N \xrightarrow[1:2]{THF} Mo_3O_6Cl_6(C_6H_7N)_6, [5]$$

3 - Methylpyridine — Light brown (R)

$$MoO_2Cl_2 + H_2NCH_2CH_2CH_2NH_2 \xrightarrow[1:1]{THF} MoO_2Cl_3(HNCH_2CH_2CH_2NH_2)_2, [6]$$

1, 3 - Diaminopropane — Black (R)

$$MoCl_5 + C_3H_4N_2 \xrightarrow[1:2]{THF} Mo_2O_4Cl_4(C_3H_4N_2)_4, [7]$$

Pyrazole — Black (F)

$$MoCl_5 + C_5H_{11}N \xrightarrow[1:2]{THF} Mo_2O_6Cl_8(C_5H_{11}N)_4, [8]$$

1 - Methylpyrrolidine — Brick red (R)

RESULTS AND DISCUSSIONS

Elemental Estimation

Percentage of the observed (theoretical) values of the elements has been depicted in Table-1.

Table 1: Analytical data of Mo halide derivatives with succinimide

Compounds	Cl	Mo	H	C	N
$Mo_2O_3Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2$,[1]	22.87	24.73	3.23	24.67	4.13
(Black/759.5)	(23.37)	(25.27)	(3.42)	(25.27)	(3.68)
$Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2$,[2]	11.55	29.42	3.68	29.87	4.74
(Dark black/637.0)	(11.14)	(30.14)	(4.08)	(30.14)	(4.39)
$Mo_2O_2Cl_2(H_2NCH_2CH_2CH_2CH_2NH_2)_2$,[3]	18.23	24.73	6.48	24.79	14.27
(Coffee brown/375.0)	(18.93)	(25.6)	(6.4)	(25.6)	(14.93)
$Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2$,[4]	25.33	25.69	3.39	34.67	4.64
(Coffee red/1088.0)	(26.1)	(26.47)	(4.04)	(35.29)	(5.14)
$Mo_3O_6Cl_6(C_6H_7N)_6$,[5]	17.73	24.69	3.93	36.78	6.98
(Light brown/1055.0)	(18.44)	(24.93)	(3.63)	(37.4)	(7.27)
$MoO_2Cl_3(HNCH_2CH_2CH_2NH_2)_2$,[6]	27.02	24.67	5.13	17.98	14.13
(Black/380.5)	(27.98)	(25.22)	(4.73)	(18.92)	(14.71)
$Mo_2O_4Cl_4(C_3H_4N_2)_4$,[7]	20.68	27.93	2.71	20.98	16.04
(Black/670.0)	(21.19)	(28.65)	(2.38)	(21.49)	(16.71)
$Mo_2O_6Cl_8(C_5H_{11}N)_4$,[8]	30.47	20.28	5.36	27.11	5.84
(Brick red/912.0)	(31.14)	(21.05)	(4.82)	(26.31)	(6.14)

FTIR Spectra

N-H stretching of succinimide[62,63] have been noted at 3409 cm^{-1} & 3221 cm^{-1}. Strong absorption at 3294 cm^{-1} indicates that [1] contains N-H group. Bands at 980 cm^{-1} and 919 cm^{-1} support the availability of cis-MoO_2^{2+} core[64,65] in [1]. Occurrence of cis-MoO_2^{2+} core is due to oxo abstraction[59,60] by molybdenum from THF. There is some decrease in C=O sym and asym absorptions. There is decrease in C=O bond order, referring to the presence of O→Mo coordination[16] in [1] (Table 2).

Strong absorption at 3433 cm^{-1} indicates that [2] contains N-H group. Bands at 984 cm^{-1} and 923 cm^{-1} support the availability of cis-MoO_2^{2+} core[64,65] in [2]. Occurrence of cis-MoO_2^{2+} core is due to oxo abstraction[59,60] by molybdenum from THF. There is some decrease in C=O sym and asym absorptions. There is decrease in C=O bond order, referring to the presence of O→Mo coordination[16] in [2] (Table-2).

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

Assignments	Succinimide[62,63]	[1]	[2]
N-H str.	3409 sb, 3221 sb	3509.6 sh, 3381.5 sh, 3294.4 s, 3152.4 s,b	3433.5 sb
CH_2 sym. str.	2960, 2947 w	2983.7 sh	
C=O sym., H-N-C in plane bending	1774 m	1776.9 m, 1756.0 m	1772.8 w
C=O asym., H-N-C in plane bending	1710 vs, b	1686.0 s 1705.2 s,	1637.2 m
CH_2 sym. scissoring	1430 m	1415.1 sh	
CH_2 asym. scissoring	1401 m	1399.1 sh	1399.8 sh
C-N-C asym. str., H-N-C in plane bending	1347 s, 1337	1373.7 m, 1358.9 sh	1373.3 w
CH_2 bending, ring in plane bending	1298 s	1297.9 s	1298.1 w
CH_2 bending	1240	1248.1 m	1247.1 sh
C-N-C asym. str., H-N-C in plane bending	1189 s,	1183.2 s	1189.9 m
C-C str., CNC sym. str.	849	857.2 w	
CH_2 bending, ring out of plane bending	820 s	817.1 s	
OCN asym. out of plane bending	632 m	645.9 s	642.4 m
OCN sym. out of plane bending, CH_2 bending	539 w	552.2 w	563.2 m
Mo-N str.			418.0 sh
Mo=O str. of cis-MoO_2^{2+} core[64,65]		980.6 s, 919.1 w	984.7 w, 923.5 sh

N-H stretching of 1,4-diaminobutane[66] has been detected at 3345 cm^{-1} & 3278 cm^{-1}. Strong N-H absorptions have been recorded at 3391 cm^{-1}, 3077 cm^{-1} and 3010 cm^{-1} in [3] (Table 3). Terminal Mo=O stretching occurs[67] at 990 cm^{-1} -1010 cm^{-1} in various inert solvents. A medium Mo=O stretching[64,67,68] at 921 cm^{-1} conforms to the presence of terminal Mo=O group. There is a decline in Mo=O stretching to 921 cm^{-1} showing Mo coordination[69] to 1,4-diaminobutane through N

atom, in a direction trans to Mo=O bond. Bending mode due to NH_2 observed in 1,4-diaminobutane[66] at 1146 cm^{-1} is declined to 1116 cm^{-1}, because of N→Mo coordination.

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

Assignments	1,4-Diaminobutane[66]	[3]
N-H str.	3345, 3278	3391.2 s, 3077.1 s, 3010.1 s
CH_2 str.	2961-2874	2881.1 sh
NH_2 bending	1608	1614.2 s
CH_2 deformation (strong)	1498, 1391, 1355, 1310	1519.3 m,1470.7 m, 1448.1 s, 1403.3 w, 1344.4 w
NH_2 bending	1146	1184.4 w, 1116.2 s
C-N sym str. (weak)	1071	1025.3 m
CH_2 deformation (medium)	862, 736	817.1 s
Mo-N (strong)		498.3 m
Terminal Mo=O[64,67,68] str.		921.2 m

3-methylpyridine[70-73] shows ring C-H absorptions at 3060 cm^{-1} and 3032 cm^{-1}. Strong bands at 3119 cm^{-1} and 3054 cm^{-1} have been noticed in [4]. Ring C=N stretching & ring C=N torsion wave numbers have increased and ring C-H bending mode wave numbers have declined due to Mo(dπ)→N(pπ) back bonding. A strong band at 989 cm^{-1} reveals the presence of terminal Mo=O[64,67,68] group in [4] (Table 4).

Strong band at 3391 cm^{-1} has been noticed in [5]. Ring C=N stretching & ring C=N torsion wave numbers have increased and ring C-H bending mode wave numbers have declined due to Mo(dπ)→N(pπ) back bonding. A medium band at 989 cm^{-1} reveals the presence of terminal Mo=O[64,67,68] group in [5] (Table 4). Occurrence of terminal Mo=O is due to oxo abstraction[59,60] by molybdenum from THF.

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

Assignments	3-Methylpyridine[70-73]	[4]	[5]
C-H ring str.	3060, 3032	3168.9 s, 3119.9 s, 3054.8 s	3391.0 s b
C-H methyl str.	3002, 2958, 2928	2937.5 sh, 2866.8 sh	
Ring str.	1600, 1578	1629.1 m, 1607.1 m, 1543.1 s	1630.7 s,1554.6 s
Ring C-H bending	1478		
C-H methyl assym bending	1458, 1452	1469.1 m	1474.2 m
Ring C-H bending	1415		
C-H methyl sym. bending	1388	1387.1 w	1386.2 w
Ring C-H bending	1361	1306.2 w	
Ring str.	1250	1258.1 w	1264.3 w
C-C bond between ring and methyl str.	1228		
Ring C-H bending	1190	1180.2 w	1186.2 sh
C-H methyl rocking	1127, 1044	1116.9 s	1119.2 w
Ring out of plane bending	1030	1044.1 sh, 1019.1 sh	1048.5 w
Ring C=N str.	792	883.1 vs, 785.7 s, 738.7 m	891.1 s, 788.1 s
Ring C=N torsion	710	722.7 m	721.9 m
Ring bending	635, 540	676.6 s, 511.1 m	678.0 s, 630.3 sh, 568.4 sh, 513.8 sh
∂ C-C bond between ring and methyl	458	463.1 m	463.3 w
Terminal Mo=O[64,67,68] str.		989.9 s	949.9 m

1,3-Diaminopropane[74] shows N-H absorption bands in the range 3052-3351 cm^{-1}. Absorptions at 3427 cm^{-1} & 3014 cm^{-1} suggest the presence of N-H group in [6] (Table 5). A strong band at 944 cm^{-1} is attributed to terminal Mo=O[64,67,68] stretching. NH_2 bending absorption in the range 1159 cm^{-1}-1182 cm^{-1} is also shifted to lower wave number 1108 cm^{-1}, mainly due to coordination with molybdenum. Occurrence of terminal Mo=O is due to oxo abstraction[59,60] by molybdenum from THF.

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

Absorptions	1, 3-Diaminopropane[74]	[6]
N-H str.	3052–3351	3427.1 m, 3014.1 v s
CH_2 str.	2873–2961	2898.3 sh, 2787.7 sh, 2701.1 sh
NH_2 bending	1627	1609.1 s
CH_2 deformation	1571–1582	1481.1 m, 1464.5 s, 1409.1
NH_2 bending	1159–1182	1193.2 m, 1108.2 m
C-N sym str.	1062	1031.3 sh
CH_2 deformation	742, 841	887.1 s, 786.1 m
Mo-N		449.3 w
Terminal Mo=O[64,67,68] str.		944.9 s

N-H stretching of pyrazole[75,76] occurs at 3452 cm^{-1}. Band at 3386 cm^{-1} reflects that [7] contains N-H group. N-H stretching is declined due to N→Mo coordination. Medium band at 969 cm^{-1} shows the existence of terminal Mo=O[64,67,68] in [7] (Table 6). Occurrence of terminal Mo=O is due to oxo abstraction[59,60] by molybdenum from tetrahydrofuran.

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

Absorptions	Pyrazole[75,76]	[7]
N-H, str.	3452	3386.9 s
C-H str.	3153, 3142	3149.9 sh
C=C ring str.	1560	1631.0 m, 1519.0 sh
N-C ring str.	1467, 1140	1474.5 w, 1402.2 sh, 1350.3 w
C-H in plane bending	1047, 1037	1126.0 w, 1052.2 w
C-H out of plane bending (wagging), ring twisting	891, 841, 762	777.0 m, 760.1 sh, 740.8 sh
Ring twisting	658, 620	675.4 sh, 605.2 sh, 581.8 sh
Mo-N		437.7 sh
Ring twisting, N-H wagging	501	518.7 w
Terminal Mo=O[64,67,68] str.		969.6 m

1-Methylpyrrolidine[77-79] shows strong C-H symmetric stretching at 2971 cm^{-1} and C-H asymmetric stretching at 2890 cm^{-1}, 2832 cm^{-1}, 2780 cm^{-1}. C-H asymmetric stretching of [8] is found at 2750 cm^{-1}. Weak band corresponding to the presence of terminal Mo=O[64,67,68] str. is observed at 976 cm^{-1} in [8] (Table 7). A peak at 3410 cm^{-1} may be due to 1-methylpyrrolidinium cation. Occurrence of terminal Mo=O is due to oxo abstraction[61,62] by molybdenum from tetrahydrofuran.

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

Absorptions	1-Methylpyrrolodine[77-79]	[8]
N+-H		3410.6 v s,
υ_sC-H sym. str.	2971 s	
υ_{as}C-H asym. sym. str.	2890 sh, 2832 m, 2780 s	2750.3 sh
(C-H) deformation	1450 s	1634.0 m, 1462.0 w
υ(C-C) str.	1364 s	1383.7 sh
υ(C-N) str.	1245 s, 1202 m,	1163 s, 1113 m, 1108.6 w
(C-H) bending	1046 s	1004.6 sh
CH_2 rocking	877 s	734.9 m b
CNC deformation	575 w	
Terminal Mo=O[64,67,68] str.		976.1 w

^{1}H NMR Spectra

Spectra were taken in DMSO-d_6 solvent. Solvent residual peak of DMSO-d_6[80] occurs at 2.50 ppm. THF[80] spectrum in DMSO-d_6 shows O-CH_2 peak and CH_2 peak at 3.60 ppm and 1.76 ppm, respectively. In the spectra given below, ↑ and ↓ represent upfield/downfield shift.

Succinimide[51,53] CH_2 absorb at 2.73 ppm. Spectrum of [1] in DMSO-d_6 shows CH_2 absorption at 3.63 ppm showing downfield shift due to decrease in electron density around these protons on coordination with molybdenum through carbonyl group (Fig.1, Table 8).

Spectrum of [2] in DMSO-d_6 shows CH_2 absorption at 3.42 ppm showing downfield shift due to decrease in electron density around these protons on coordination with molybdenum through carbonyl group (Fig. 2, Table 8).

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

Assignments	Succinimide[51,53] in $CDCl_3$	[1]	[2]
N-H	8.9	11.06↓	10.97↓
CH_2	2.73	3.63↓	3.42↓
Residual[80] DMSO-d_6		2.54	2.48

1,4-Diaminobutane[81] in H_2O shows N-H peak at 1.15 ppm. NMR of [3] in DMSO-d_6 suggests that NH_2 peak has shifted downfield. Peak of side CH_2 (attached to N which coordinates) as well as peak of middle CH_2 (attached to outer CH_2 on the side in which N coordinates) have shifted down field due to decrease in electron density around these protons on N→Mo coordination (Fig. 3, Table 9).

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

Assignments	1, 4-Diaminobutane[81] in H_2O	[3]
NH_2	1.14 4H	8.23↓
Side CH_2 (attached to N which coordinates)	3.02-3.05 4H	3.52↓
Middle CH_2 (attached to outer CH_2 on the side in which N coordinates)	1.75-1.78 4H	2.66↓
Residual[80] DMSO-d_6		2.43

Comparison of 3-methylpyridine[71,72,82] spectrum with that of [4], shows that there is downfield shift for all protons. This is due to reduction in ring π-electron density around these protons on sharing of lone pair by nitrogen with molybdenum (Fig. 4, Table 10).

Further, in the spectrum of [5], it is found that there is downfield shift for all protons. This is due to reduction in ring π-electron density around these protons on sharing of lone pair by nitrogen with molybdenum (Fig. 5, Table 10).

Table 10: (^{1}H NMR absorptions in ppm)

Absorptions	3-Methylpyridine[71,72,82] in $CDCl_3$	[4]	[5]
H (CH_3)	2.32 3H Singlet	3.27↓	2.56↓
H-C_1	8.44 1H Singlet	8.77↓	8.80↓
H-C_3	7.45 1H Doublet	8.40↓	8.23↓
H-C_4	7.16 1H Triplet	7.92↓	7.82↓
H-C_5	8.42 1H Doublet	8.70↓	8.74↓
Residual[80] DMSO-d_6		2.46	2.49
THF[80] C-2, 5 (attached to N)		3.53	
THF[80] C-3, 4		1.69	

Comparison of spectrum of 1, 3-diaminopropane[83] with that of [6] (Fig. 6, Table 11) in DMSO-d_6 suggests that NH_2 and CH_2 absorptions of 1,3-diaminopropane have downfield shift. This is because of decrease in electron density around these protons on N→Mo coordination.

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

Assignments	1, 3-Diaminopropane[83] in $CDCl_3$	[6]
NH_2	1.21 4H	7.89↓
Middle CH_2	1.59 2H	2.87↓
Side CH_2 (attached to N which coordinates)	2.76 4H	3.56↓
Residual[80] DMSO-d_6		2.50

Spectrum of pyrazole[72,84] in CCl_4 shows absorptions due to middle C-H proton at 6.31 ppm, C-H protons on other two carbons at 7.61 ppm and due to N-H proton at 12.64 ppm. Spectrum of [7] shows that all the pyrazole CH protons have moved downfield (Fig. 7, Table 12). This is because of decrease in electron density around these protons on N→Mo coordination. Due to keto-enol tautomerization equilibrium, peaks of CH protons of pyrazole appear as singlets.

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

Assignments	Pyrazole[72,84] in CCl_4	[7]
N-H	12.64 1H	9.42↑
Middle CH	6.31 (s) 1H	6.51↑
Side CH	7.61(s) 2H	7.96↑
Residual[80] DMSO-d_6		2.57

Spectrum of [8] shows that all the CH absorptions of 1-methylpyrrolidine[77] have moved downfield, referring to decline in electron density of the ring on N→Mo coordination (Fig. 8, Table 13). There is a broad peak at 11.10 ppm indicating formation of 1-methylpyrrolidinium ion.

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

Assignments	1-Methylpyrrolidine[77]	[8]
N+.H		11.10
CH_3	2.3 3H	3.43-3.51↓
C_2-H & C_5-H (attached to N)	2.5 4H	2.73-2.91↓
C_3-H & C_4-H	1.6 4H	1.85-1.98↓
Residual[80] DMSO-d_6		2.50

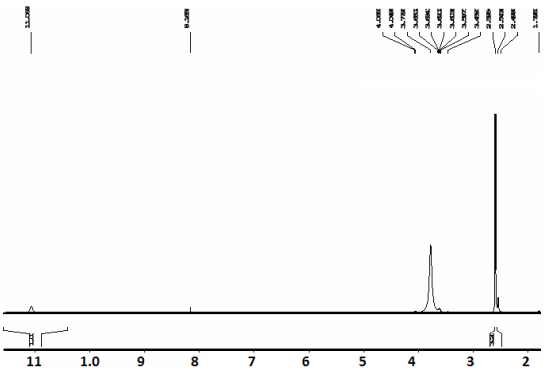

Fig. 1. ^{1}H-NMR of $Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2$, [1]

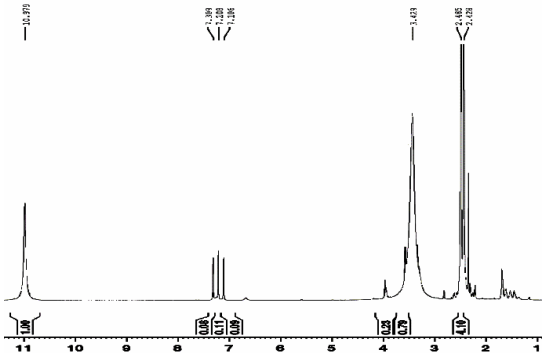

Fig. 2. ^{1}H-NMR of $Mo_2O_3Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2$, [2]

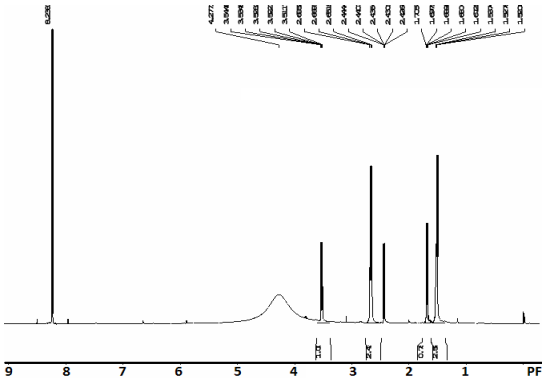

Fig. 3. ^{1}H-NMR of $Mo_2O_2Cl_2(H_2NCH_2CH_2CH_2CH_2NH_2)_2$, [3]

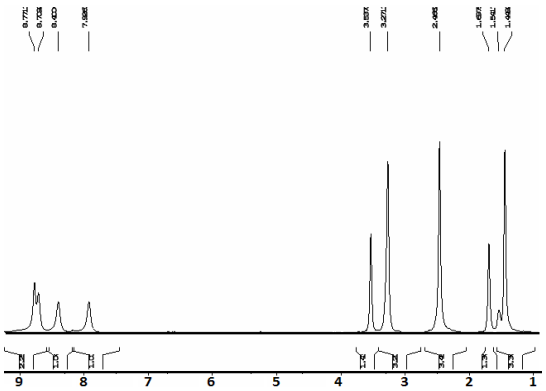

Fig. 4. ^{1}H-NMR of $Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2$, [4]

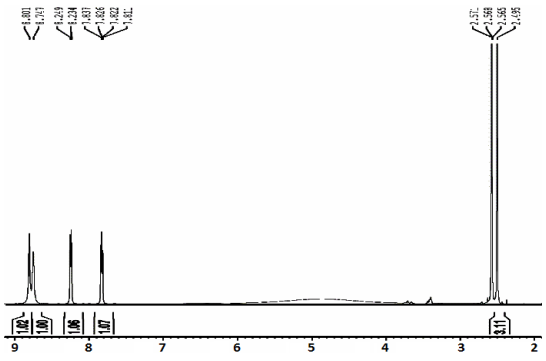

Fig. 5: ^{1}H-NMR of $Mo_3O_6Cl_6(C_6H_7N)_6$, [5]

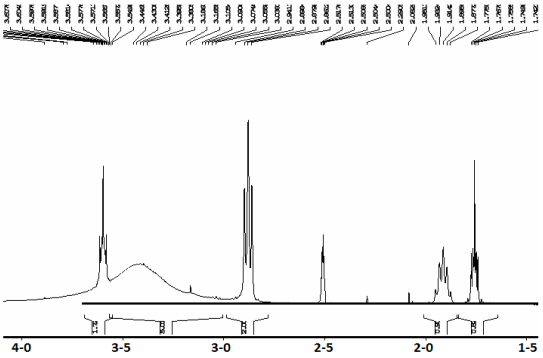

Fig. 6. ^{1}H-NMR of $MoO_2Cl_3(HNCH_2CH_2CH_2NH_2)_2$, [6]

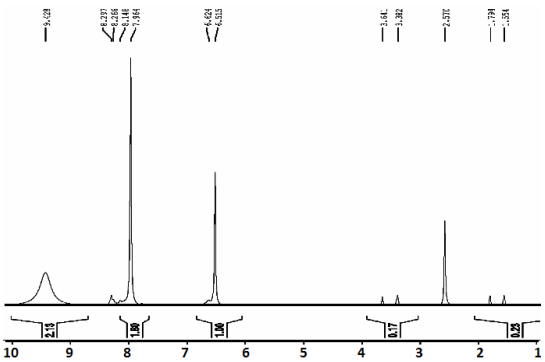

Fig. 7. ^{1}H-NMR of $Mo_2O_4Cl_4(C_3H_4N_2)_4$, [7]

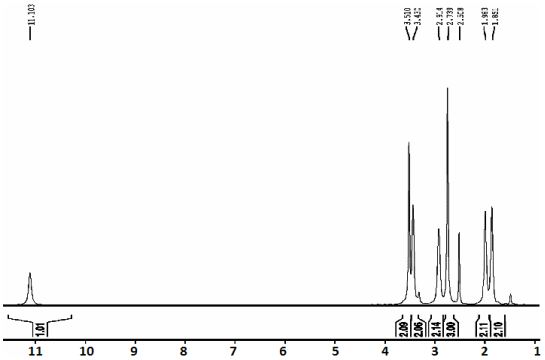

Fig. 8. ^{1}H-NMR of $Mo_2O_6Cl_8(C_5H_{11}N)_4$, [8]

^{13}C NMR Spectra

Spectra were taken in DMSO-d_6 solvent. Solvent residual peak of DMSO-d_6[80] occurs at 39.52 ± 0.06 ppm. THF[87] spectrum in DMSO-d_6 shows O-CH_2 peak and CH_2 peak at 67.03 ppm and 25.14 ppm, respectively. In the spectra given below, ↑ and ↓ represent upfield/ downfield shift.

Spectrum of [3] shows that there is slight upfield shift of all absorptions of 1,4-diaminobutane[85]. This may be due to change of solvent from $CDCl_3$ to DMSO-d_6 (Fig. 9, Table 14).

Table 14: (^{13}C NMR absorptions in ppm)

Assignments	1,4-Diaminobutane[85] in $CDCl_3$	[3]
C attached to nitrogen	41	38.24↑
Other C	29	25.04↑
Residual[80] DMSO-d_6		39.50

Spectrum of [4] shows that there is slight upfield shift of C-2 and C-6 of 3-methylpyridine[86], whereas there is slight downward shift of C-3, C-4 and C-5. This is due to flow of π-electron density from C-3, C-4 and C-5 to N through C-2 and C-6, when N coordinates with Mo (Fig. 10, Table 15).

Table 15: (^{13}C NMR absorptions in ppm)

Assignments	3-Methylpyridine[86] in $CDCl_3$	[4]
C-2 (attached to CH_3)	150.27	146.14↑
C-3	133.08	136.27↓
C-4	136.40	138.77↓
C-5	123.16	126.43↓
C-6	146.93	140.83↑
CH_3	18.36	17.94↑
Residual[80] DMSO-d_6		39.42
THF[87] C-2,5 (attached to N)		65.88
THF[87] C-3,4		23.97

Spectrum of [7] shows that there is practically no change in chemical shift of pyrazole[88] on N→Mo coordination (Fig. 11, Table 16).

Table 16: (^{13}C NMR absorptions in ppm)

Assignments	Pyrazole[88] in $CDCl_3$	[7]
Carbons attached to N atoms	134.0	133.12↑
Remaining carbona	105.1	104.81↑
Residual[80] DMSO-d_6		39.42

Spectrum of [8] shows that there is slight upfield shift of all absorptions of 1-methylpyrrolidine[89]. This may be due to change of solvent from $CDCl_3$ to DMSO-d_6 (Fig. 12, Table 17).

Table 17: (^{13}C NMR absorptions in ppm)

Assignments	1-Methylpyrrolidine[89] in $CDCl_3$	[8]
C-1,C-4 (attached to N)	58.8	54.24 ↑
C-2, C-3	23.3	22.66 ↑
CH_3	46.6	40.12 ↑
Residual[80] DMSO-d_6		39.42

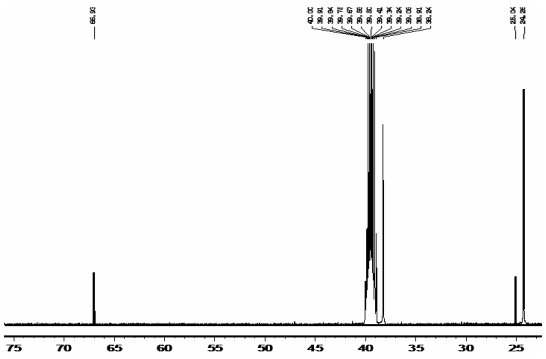

Fig. 9. ^{13}C-NMR of $Mo_2O_2Cl_2(H_2NCH_2CH_2CH_2CH_2NH_2)_2$, [3]

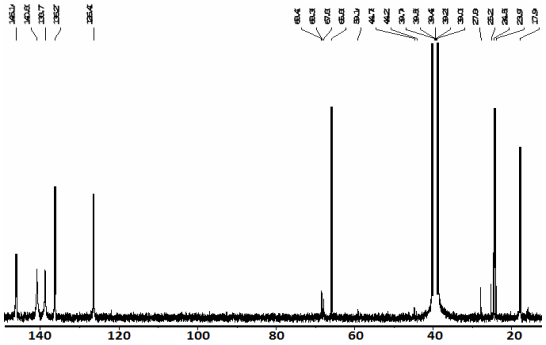

Fig. 10. ^{13}C-NMR of $Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2$, [4]

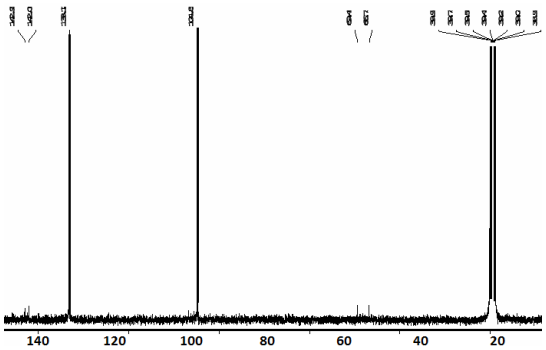

Fig. 11. ^{13}C-NMR of $Mo_2O_4Cl_4(C_3H_4N_2)_4$, [7]

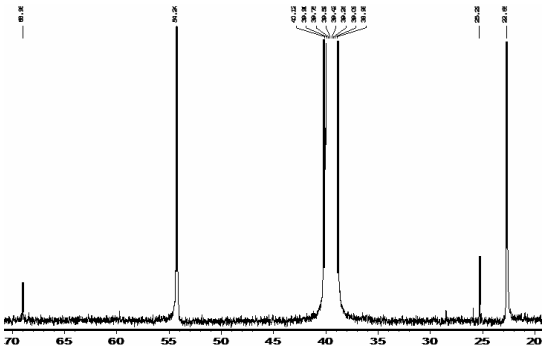

Fig. 12. ^{13}C-NMR of $Mo_2O_6Cl_8(C_5H_{11}N)_4$, [8]

Microbiological Activity

Molybdenum compounds prepared were tested using agar well diffusion assay method for their antibacterial and antifungal potential on the strains: *Staphylococcus aureus* (*Gram-positive* bacteria) (MTCC-737), *E. coli* (*Gram-negative* bacteria) (MTCC-1687), *Candida albicans* (fungus) (MTCC-227) and *Aspergillus niger* (fungus) (MTCC-282). Standard drugs amoxicillin and ketoconazole were used for bacteria and virus, respectively as reference. Zone of inhibition[90] for a strain of bacteria/fungi was estimated to ascertain the amount of resistance of bacteria/fungi to the drug used as reference. Molybdenum compounds synthesized have been noted as potentially active against the above said bacteria and fungi (Table 18). Especially,

1. Compounds 1,2,4,5 and 8 have greater antibacterial activity against *E. coli* than the reference drug (amoxicillin).
2. Compounds 1,2 and 5 have greater antifungal activity against *C. albicans* than the reference drug (ketoconazole).

Mass Spectra (LC-MS)

Theoretical m/z values of the fragments have been calculated[91] on the basis of the most abundant isotopes of the individual elements. Fragments detected (Tables 19,20) reinforce the formulae,

Table 18: (Microbiological Study)

Compound (100 μg/mL)	Zone of inhibition[90] (mm)			
	Gram-positive	*Gram-negative*	Antifungal	
	S. aureus	*E. coli*	*C. albicans*	*A. niger*
Reference Drug	25.69	18.35	21.37	28.21
[1]	24.12	19.56	21.74	21.56
[2]	19.28	22.51	23.12	21.58
[4]	19.84	22.21	19.52	21.69
[5]	21.54	49.62	21.47	19.87
[8]	23.11	22.61	19.85	18.72

Conclusion and results: These compounds can kill and inhibit the growth of microbes

Table 19: (LC-MS Ionization)

Compounds	
[1]	$[Mo_2O_3Cl_3(C_4H_5NO_2)_2(C_4H_8O)_2] \rightarrow [Mo_2O_3Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+} \rightarrow [Mo_2O_2Cl_2(C_4H_5NO_2)(C_4H_8O)_2]^{+}$ M.W. = 759.50 [1] m/z = 380.40 m/z = 448.25 ↓ $[MoOCl_3(C_4H_5NO_2)_2(C_4H_8O)]^{+} + [MoO_2Cl_2]^{+}$ m/z = 490.35 m/z = 197.04 ↓ $[MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)]^{2+}$ m/z = 230.08 $[MoOCl_2]^{2+} \leftarrow [MoOCl_2(C_4H_8O)_2]^{+}$ m/z = 91.03 m/z = 324.17
[2]	$[Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2] \rightarrow [Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+} \rightarrow [MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+}$ M.W. = 637.0 [2] m/z = 321.11 m/z = 263.13 ↓ ↓ $[Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)]^{+}$ $[MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)]^{2+}$ m/z = 471.24 m/z = 230.09 ↓ ↓ $[MoO_2Cl]^{+} \leftarrow [Mo_2O_2Cl_2(C_4H_5NO_2)]^{+} \leftarrow [Mo_2O_2Cl_2(C_4H_5NO_2)_2]^{+}$ $[MoOCl_2]^{2+} + [C_4H_5NO_2]^{+} + [C_4H_8O]^{+}$ m/z = 163.10 m/z = 299.18 m/z = 397.23 m/z = 91.04 m/z = 100.05 m/z = 73.07
[3]	$[MoO_2Cl_2(H_2NCH_2CH_2CH_2CH_2NH_2)_2] \rightarrow [H_2NCH_2CH_2CH_2CH_2]^{+} + [MoO_2Cl_2]^{+} \rightarrow [MoO_2Cl]^{+} \rightarrow [MoO_2]^{+}$ M.W. = 375.0 [3] m/z = 71.0 m/z = 199.8 m/z = 164.9 m/z = 130.0 ↓ ↓ $[H_2NCH_2CH_2CH_2]^{+}$ $[MoOCl]^{+}$ m/z = 59.0 m/z = 147.0
[4]	$[Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2] \rightarrow [Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2]^{2+} \rightarrow [Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)]^{2+}$ M.W. = 1088.0 [4] m/z = 544.46 m/z = 509.34 ↓ ↓ $[MoCl_6(C_6H_7N)]^{+}$ $[Mo_3Cl_8(C_6H_7N)_4]^{2+} + [C_4H_8O]^{+}$ m/z = 400.0 m/z = 472.84 m/z = 73.07 ↓ $[MoCl_4(C_6H_7N)]^{+}$ m/z = 329.11 ↓ $[MoCl_4]^{+} + [C_6H_7N]^{+}$ m/z = 235.17 m/z = 94.07
[5]	$[Mo_3O_6Cl_6(C_6H_7N)_6] \rightarrow [Mo_3O_6Cl_6(C_6H_7N)_6]^{2+} \rightarrow [Mo_3O_6Cl_4(C_6H_7N)_6]^{2+} \rightarrow [Mo_3O_5Cl_4(C_6H_7N)_5]^{2+}$ M.W. = 1055.0 [5] m/z = 581.38 m/z = 545.49 m/z = 472.38 ↓ $[MoO_2Cl_3(C_6H_7N)]^{2+} \leftarrow [MoO_2Cl_3(C_6H_7N)]^{+} \leftarrow [MoO_2Cl_3(C_6H_7N)_3]^{2+} \leftarrow [Mo_3O_2Cl_3(C_6H_7N)_4]^{2+}$ m/z = 163.0 m/z = 328.25 m/z = 256.18 m/z = 400.31 ↓ $[MoOCl_2]^{2+} + [C_6H_7N]^{+}$ m/z = 91.04 m/z = 94.06
[6]	$[MoO_2Cl_3(HNCH_2CH_2CH_2NH_2)_2] \rightarrow [MoOCl(HNCH_2CH_2CH_2NH_2)]^{+} \rightarrow [MoO(HNCH_2CH_2CH_2NH_2)]^{+}$ M.W. = 380.5 [6] m/z = 220.0 m/z = 187.0 ↓ ↓ $[HNCH_2CH_2CH_2]^{+}$ $[MoO(HNCH_2CH_2CH_2NH_2)]^{2+}$ m/z = 59.0 m/z = 93.10
[7]	$[Mo_2O_4Cl_4(C_3H_4N_2)_4] \rightarrow [Mo_2O_3Cl_4(C_3H_4N_2)_2]^{+} \rightarrow [Mo_2O_3Cl_2(C_3H_4N_2)_2]^{+}$ M.W. = 670.0 [7] m/z = 519.42 m/z = 447.36 ↓ $[MoO_2Cl_3(C_3H_4N_2)_2]^{+} \rightarrow [MoO_2Cl_3]^{+} + [MoO_2Cl]^{+} + [C_3H_4N_2]^{+} + [MoOCl_2]^{2+}$ m/z = 375.30 m/z = 235.17 m/z = 163.11 m/z = 69.05 m/z = 91.04
[8]	$[Mo_2O_6Cl_8(C_5H_{11}N)_4] \rightarrow [Mo_2O_6Cl_4(C_5H_{11}N)_2]^{+} \rightarrow [Mo_2O_5Cl_4(C_5H_{11}N)]^{+} \rightarrow [Mo_2O_3(C_5H_{11}N)]^{2+}$ M.W. = 912.0 [8] m/z = 596.19 m/z = 503.10 m/z = 207.19 ↓ $[MoO_2Cl]^{+} + [MoOCl_2]^{2+} + [C_5H_{11}N]^{+}$ m/z = 163.12 m/z = 91.04 m/z = 86.09

Table 20: (LC-MS Ion m/z values)

Compounds	Fragment	Calculated[91]	Detected	Relative intensity
[1]	$[MoOCl_2(C_4H_8O)_2]^+$	327.95	324.17	30%
	$[MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)]^{2+}$	226.97	230.08	58%
	$[MoOCl_3(C_4H_5NO_2)_2(C_4H_8O)]^+$	488.92	490.35	8%
	$[MoO_2Cl_2]^+$	199.83	197.04	34%
	$[MoOCl_2]^{2+}$	91.91	91.03	25%
	$[Mo_2O_2Cl_5(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+}$	372.41	376.20	100%
	$[MoO_2Cl_2(C_4H_5NO_2)(C_4H_8O)_2]^+$	442.99	448.25	10%
[2]	$[MoOCl_2]^{2+}$	91.91	91.04	100%
	$[C_4H_5NO_2]^+$	99.03	100.05	21%
	$[C_4H_8O]^+$	72.05	73.07	11%
	$[MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)]^{2+}$	226.97	230.09	8%
	$[MoOCl_2(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+}$	263.00	263.13	52%
	$[Mo_2O_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)_2]^{2+}$	319.95	321.11	20%
	$[MoO_2Cl_2(C_4H_5NO_2)_2(C_4H_8O)]^+$	469.95	471.24	12%
	$[MoO_2Cl_2(C_4H_5NO_2)_2]^+$	397.89	397.23	18%
	$[MoO_2Cl_2(C_4H_5NO_2)]^+$	298.86	299.18	14%
	$[MoO_2Cl]^+$	164.86	163.10	15%
[3]	$[MoO_2Cl_2]^+$	199.83	199.8	100%
	$[MoO_2Cl]^+$	164.86	164.90	40%
	$[MoOCl]^+$	148.86	147.00	92%
	$[MoO_2]^+$	129.89	130.00	10%
	$[H_2NCH_2CH_2CH_2CH_2]^+$	72.08	71.0	22%
	$[H_2NCH_2CH_2CH_2]^+$	58.06	59.0	36%
[4]	$[C_6H_7N]^+$	93.05	94.07	44%
	$[MoCl_4]^+$	237.78	235.17	17%
	$[MoCl_4(C_6H_7N)]^+$	330.83	329.11	5%
	$[Mo_3Cl_8(C_6H_7N)_4]^{2+}$	472.84	472	1%
	$[MoCl_6(C_6H_7N)]^+$	400.77	400	3%
	$[Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)_2]^{2+}$	544.90	544.46	5%
	$[Mo_3Cl_8(C_6H_7N)_4(C_4H_8O)]^{2+}$	508.87	509.34	5%
	$[C_4H_8O]^+$	72.05	73.07	20%
[5]	$[C_6H_7N]^+$	93.05	94.06	100%
	$[MoO_2Cl_3(C_6H_7N)]^+$	327.85	328.25	10%
	$[MoO_2Cl_3(C_6H_7N)]^{2+}$	163.92	163.0	1%
	$[MoO_2Cl_3(C_6H_7N)_3]^{2+}$	256.98	256.18	5%
	$[Mo_3O_2Cl_3(C_6H_7N)_4]^{2+}$	401.40	400.31	5%
	$[Mo_3O_5Cl_3(C_6H_7N)_5]^{2+}$	471.94	472.38	3%
	$[MoOCl_2]^{2+}$	91.91	91.04	3%
	$[Mo_3O_6Cl_4(C_6H_7N)_6]^{2+}$	543.95	545.49	2%
	$[Mo_3O_6Cl_6(C_6H_7N)_6]^{2+}$	578.92	581.38	<1%
[6]	$[MoO(HNCH_2CH_2CH_2NH_2)]^+$	186.97	187.00	15%
	$[MoO(HNCH_2CH_2CH_2NH_2)]^{2+}$	93.48	93.10	60%
	$[MoOCl(HNCH_2CH_2CH_2NH_2)]^+$	221.94	220.0	100.0%
	$[H_2NCH_2CH_2CH_2]^+$	58.06	59.0	4%
[7]	$[C_3H_4N_2]^+$	68.03	69.05	100%
	$[MoOCl_2]^{2+}$	91.91	91.04	27%
	$[MoO_2Cl]^+$	164.86	163.11	24%
	$[MoO_2Cl_3(C_3H_4N_2)_2]^+$	370.87	375.30	5%
	$[MoO_2Cl_3]^+$	234.80	235.17	8%
	$[Mo_2O_3Cl_4(C_3H_4N_2)_2]^+$	519.74	519.42	3%
	$[Mo_2O_3Cl_2(C_3H_4N2)_2]^+$	449.80	447.36	5%
[8]	$[C_5H_{11}N]^+$	85.08	86.09	100%
	$[MoOCl_2]^{2+}$	91.91	91.04	3%
	$[Mo_2O_3(C_5H_{11}N)_2]^{2+}$	206.98	207.19	6%
	$[Mo_2O_6Cl_4(C_5H_{11}N)_2]^+$	601.83	596.19	2%
	$[MoO_2Cl]^+$	164.86	163.12	2%
	$[Mo_2O_5Cl_4(C_5H_{11}N)]^+$	500.74	503.10	7%

CONCLUSION

Band at 3294 cm^{-1} indicates that [1] contains succinimide N-H group. Bands at 980 cm^{-1} and 919 cm^{-1} support the availability of cis-MoO_2^{2+} core in [1]. Occurrence of cis-MoO_2^{2+} core is due to oxo abstraction by molybdenum from THF. There is decrease in C=O sym and asym absorptions due to decrease in C=O bond order on O→Mo coordination in [1]. Succinimide CH_2 absorb at 2.73 ppm. Spectrum of [1] shows CH_2 absorption at 3.63 ppm showing downfield shift due to decrease in electron density around these protons on coordination with molybdenum through carbonyl group. Microbiological studies reveal that [1] is effective against the bacteria/fungi tested for, especially *E. coli* and *C. albicans*, where [1] is more effective than the reference drugs themselves. Elemental analysis and LC-MS fragmentation support the proposed formula.

Band at 3433 cm^{-1} indicates that [2] contains succinimide N-H group. Bands at 984 cm^{-1} and 923 cm^{-1} support the availability of cis-MoO_2^{2+} core in [2]. Occurrence of cis-MoO_2^{2+} core is due to oxo abstraction by molybdenum from THF. There is decrease in C=O sym and asym absorptions due to decrease in C=O bond order on O→Mo coordination in [2]. Spectrum of [2] shows CH_2 absorption at 3.42 ppm showing downfield shift due to decrease in electron density around these protons on coordination with molybdenum through carbonyl group. Microbiological studies reveal that [2] is effective against the bacteria/fungi tested for, especially *E. coli* and *C. albicans*, where [2] is more effective than the reference drugs themselves. Elemental analysis and LC-MS fragmentation support the proposed formula.

Strong 1,4-diaminobutane N-H absorptions have been recorded at 3391 cm^{-1}, 3077 cm^{-1} and 3010 cm^{-1} in [3]. Terminal Mo=O stretching occurs at 990 cm^{-1}-1010 cm^{-1} in various inert solvents. A medium Mo=O stretching at 921 cm^{-1} conforms to the presence of terminal Mo=O group. There is a decline in Mo=O stretching to 921 cm^{-1} showing Mo coordination to 1,4-diaminobutane through N atom, in a direction trans to Mo=O bond. Bending mode due to NH_2 observed in 1,4-diaminobutane at 1146 cm^{-1} is declined to 1116 cm^{-1}, because of N→Mo coordination. 1, 4-Diaminobutane shows N-H peak at 1.15 ppm. NMR of [3] suggests that NH_2 peak has shifted downfield. Peak of side CH_2 (attached to N which coordinates) as well as peak of middle CH_2 (attached to outer CH_2 on the side in which N coordinates) have shifted down field due to decrease in electron density around these protons on N→Mo coordination. ^{13}C NMR spectrum of [3] shows that there is slight upfield shift of all absorptions of 1,4-diaminobutane. This may be due to change of solvent from $CDCl_3$ to DMSO-d_6. Elemental analysis and LC-MS fragmentation support the proposed formula.

Strong bands at 3119 cm^{-1} and 3054 cm^{-1} have been noticed in [4] which show presence of 3-methylpyridine ring C-H absorptions. Ring C=N stretching & ring C=N torsion wave numbers have increased and ring C-H bending mode wave numbers have declined due to Mo(dπ)→N(pπ) back bonding. A strong band at 989 cm^{-1} reveals the presence of terminal Mo=O in [4]. Comparison of 3-methylpyridine spectrum with that of [4], shows that there is downfield shift for all protons. This is due to reduction in ring π-electron density around these protons on sharing of lone pair by nitrogen with molybdenum. ^{13}C NMR spectrum of [4] shows that there is slight upfield shift of C-2 and C-6 of 3-methylpyridine, whereas there is slight downward shift of C-3, C-4 and C-5. This is due to flow of π-electron density from C-3, C-4 and C-5 to N, through C-2 and C-6, when N coordinates with Mo. Microbiological studies reveal that [4] is effective against the bacteria/fungi tested for, especially *E. coli* where [4] is more effective than the reference drug itself. Elemental analysis and LC-MS fragmentation support the proposed formula.

Strong band at 3391 cm^{-1} has been noticed in [5] which shows presence of 3-methylpyridine ring C-H absorption. Ring C=N stretching & ring C=N torsion wave numbers have increased and ring C-H bending mode wave numbers have declined due to Mo(dπ)→N(pπ) back bonding. A medium band at 949 cm^{-1} reveals the presence of terminal Mo=O group in [5]. Comparison of 3-methylpyridine spectrum with that of [5], shows that there is downfield shift for all protons. This is due to reduction in ring π-electron density around these protons on sharing of lone pair by nitrogen with molybdenum. Microbiological studies reveal that [5] is effective against the bacteria/fungi tested for, especially *E. coli* and

C. albicans, where [5] is more effective than the reference drugs themselves. Elemental analysis and LC-MS fragmentation support the proposed formula.

Absorptions at 3427 cm^{-1} & 3014 cm^{-1} in [6] suggest the presence of 1,3-diaminopropane N-H group in the compound. A strong band at 944 cm^{-1} is attributed to terminal Mo=O stretching. NH_2 bending absorption in the range of 1159 cm^{-1}-1182 cm^{-1} is also shifted to lower wave number 1108 cm^{-1}, mainly due to coordination with molybdenum. Occurrence of terminal Mo=O is due to oxo abstraction by molybdenum from THF. Comparison of spectrum of 1,3-diaminopropane with that of [6] suggests that NH_2 and CH_2 absorptions of 1,3-diaminopropane have downfield shift. This is because of decrease in electron density around these protons on N→Mo coordination. Elemental analysis and LC-MS fragmentation support the proposed formula.

Band at 3386 cm^{-1} reflects that [7] contains pyrazole N-H group. N-H stretching is declined due to Mo-N coordination. Medium band at 969 cm^{-1} shows the existence of terminal Mo=O in [7]. Occurrence of terminal Mo=O is due to oxo abstraction by molybdenum from THF. Spectrum of pyrazole shows absorptions due to middle C-H proton at 6.31 ppm, C-H protons on other two carbons at 7.61 ppm and due to N-H proton at 12.64 ppm. Spectrum of [7] shows that all the pyrazole CH protons have moved downfield. This is because of decrease in electron density around these protons on N→Mo coordination. Due to keto-enol tautomerization equilibrium, peaks of CH protons of pyrazole appear as singlets. ^{13}C NMR spectrum of [7] shows that there is practically no change in chemical shift of pyrazole. Elemental analysis and LC-MS fragmentation support the proposed formula.

Absorption at 2750 cm^{-1} in [8] shows presence of 1-methylpyrrolidine C-H asymmetric the stretching. Weak band corresponding to the presence of terminal Mo=O is observed at 976 cm^{-1}. A peak at 3410 cm^{-1} may be due to 1-methylpyrrolidinium cation. Occurrence of terminal Mo=O is due to oxo abstraction by molybdenum from THF. Spectrum of [8] shows that all the CH absorptions of 1-methylpyrrolidine have moved downfield, referring to decline in electron density of the ring on N→Mo coordination. There is a broad peak at 11.10 ppm indicating formation of 1-methylpyrrolidinium ion. ^{13}C NMR spectrum of [8] shows that there is slight upfield shift of all absorptions of 1-methylpyrrolidine. This may be due to change of solvent from $CDCl_3$ to DMSO-d_6. Microbiological studies reveal that [8] is effective against the bacteria/fungi tested for, especially *E. coli* where [8] is more effective than the reference drug itself. Elemental analysis and LC-MS fragmentation support the proposed formula.

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Conflict of interest

There is no conflict of interest among the authors.

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