



Reactions of MoOCl_4 , MoO_2Cl_2 & MoCl_5 with 1,3-Diaminopropane, 1,4-Diaminobutane, 1,3-Propanediol & Acetamide

Gursharan Singh¹, Vikas Mangla², Mamta Goyal³, Kavita Singla⁴, Deepika Rani⁵

¹Professor, ^{2,3,4,5} Ph.D. Research Scholars

Department of Applied Chemistry, Giani Zail Singh, PTU Campus,
Dabwali Road, Bathinda-151001, INDIA

Abstract: MoOCl_4 reacts with 1,3-diaminopropane, 1,4-diaminobutane & acetamide to yield $\text{MoOCl}_4(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ [1], $\text{MoOCl}_4(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ [2] & $\text{MoOCl}_4(\text{CH}_3\text{CONH}_2)$ [3], respectively. MoO_2Cl_2 reacts with 1,3-diaminopropane, 1,4-diaminobutane & 1,3-propanediol to form $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ [4], $\text{MoO}_2\text{Cl}_2(\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2).0.5\text{HCl}$ [5] & $\text{MoO}_2\text{Cl}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}).0.5\text{HCl}$ [6], respectively. MoCl_5 reacts with 1,4-diaminobutane to provide $\text{MoCl}_5(\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ [7]. Compounds have been characterized by elemental analysis, ¹H NMR, FTIR, electronic spectra and molar conductance studies.

Keywords: MoOCl_4 ; MoO_2Cl_2 ; MoCl_5 ; 1,3-diaminopropane; 1,4-diaminobutane; 1,3-propanediol; acetamide.

I. Introduction

Molybdenum complexes are known to be important catalysts and bioactive materials. The chemistry of MoOCl_4 has been scarcely explored relative to that of MoO_2Cl_2 & MoCl_5 . Within the second series of transition metals only molybdenum represents a biometal, important for microorganisms, plants and animals. The increasing biological applications, namely antibacterial, antifungal, antitubercular, antitumour activities^{1, 2, 3, 4, 5, 6} etc., of the complexes of transition metals with hydrazones have intensified interest in research and analytical studies on these metallic complexes. Molybdenum compounds act as catalysts^{7, 8, 9, 10, 11, 12} in various oxidation reactions, such as, epoxidation and hydroxylation of olefins, oxidation of alcohols and as catalysts for oxygen atom transfer reactions, etc. This stimulated the author to study the behaviour of MoOCl_4 , MoO_2Cl_2 & MoCl_5 towards bidentate ligands containing more than one labile hydrogen atoms. Earlier also the author revealed its interest in the chemistry of MoOCl_4 ^{13, 14, 15, 16}. Such reactions are known to proceed with addition/substitution reactions, which may be accompanied by reductive amination, oxoabstraction, chelation or even dimerization. Polarity of the solvent also plays an important role in the reaction process, especially in case of MoO_2Cl_2 , MoCl_5 and acetamide, which are very slightly soluble in less polar solvents like CH_2Cl_2 , but are fairly soluble in more polar solvents like acetonitrile. This enhanced solubility of MoO_2Cl_2 and MoCl_5 is due to the formation of solvent stabilized complexes, like $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

II. Experimental

A. Materials:

Molybdenumoxytetrachloride MoOCl_4 was prepared in the laboratory by reaction of MoO_3 (CDH, AR Grade) with thionyl chloride at reflux temperature for about 5 hrs. After refluxing, thionyl chloride was evacuated in liquid nitrogen traps. Dark green residue obtained was 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 . Filtrate on evacuation yielded shining dark green crystals of MoOCl_4 . Its melting point was found to be 100° C - 102° C. Molybdenumdioxodichloride MoO_2Cl_2 (Sigma-Aldrich, USA) is a light yellow hygroscopic solid. It was procured from market and used as such. Molybdenumpentachloride MoCl_5 (Sigma-Aldrich, USA) is a brownish black hygroscopic solid. It was procured from market and used as such. 1, 3-Diaminopropane is a colourless liquid with a fishy odour (Alfa Aesar, b.p. 140° - 141° C/760 mm of Hg, 83° C/100 mm of Hg, density 0.880 g/ml). It is soluble in water and many polar organic solvents. It was kept over KOH pellets for 48 hrs and then fractionally distilled under vacuum. 1, 4-Diaminobutane is a colourless and foul-smelling liquid (Aldrich, b.p. 158° C - 160° C, 96° C/100 mm of Hg, density 0.877 g/ml). It was kept over KOH pellets for 48 hrs and then fractionally distilled under vacuum. Acetamide (NICE, LR grade, m.p. 79° C - 81° C) is a colourless solid and was procured from market. It is soluble in acetonitrile, but insoluble in CH_2Cl_2 . 1, 3-Propanediol (Aldrich, b.p. 211° C - 217° C/760 mm of Hg, 119° C/100 mm of Hg, density 1.060 g/ml) was kept over KOH pellets for 48 hrs and then fractionally distilled under vacuum. Thionyl chloride (CDH, LR grade, b.p. 76° - 78° C) was kept over

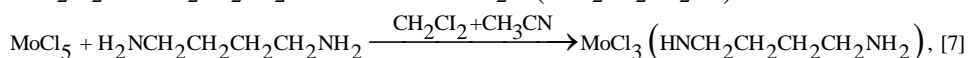
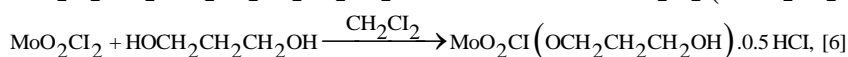
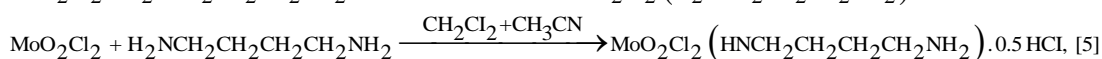
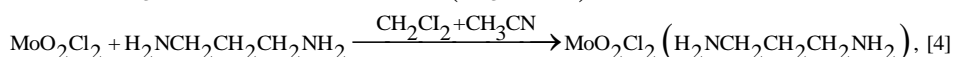
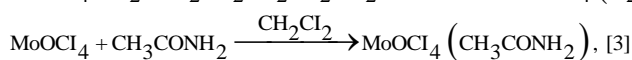
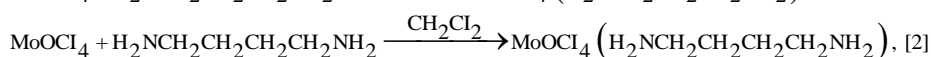
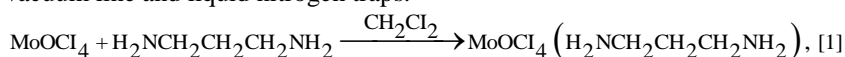
quinoline for 48 hrs (50 g SOCl₂ to 10 g quinoline) to remove acid impurities and then fractionally distilled to get a colourless liquid.

B. Physical Measurements:

Molybdenum and chlorine were estimated by standard methods¹⁷. 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 cm⁻¹ – 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 methanol solvent were recorded using Perkin-Elmer Lambda 750 UV/VIS/NIR Spectrometer (Germany), at SAIF/CIL Panjab University, Chandigarh (India). UV-VIS spectra were also recorded in DMSO solvent using Systronics UV-VIS 2202 Spectrophotometer (India), at GZS PTU Campus, Bathinda (India). Molar conductance measurements of millimolar solutions were carried out on Electronic India Digital Conductivity Meter Model 621 (India) at 30° C.

C. Synthesis of Compounds [1] to [7]:

A 100 ml round bottomed flask with 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 once or twice under vacuum (10⁻³ torr). Dry nitrogen gas purged with oxygen was let into assembly at room temperature through liquid nitrogen traps. A known weight of MoOCl₄, MoO₂Cl₂ or MoCl₅ was dissolved in dry CH₂Cl₂/acetonitrile taken in a flask. An equimolar amount of the H₂N(CH₂)₃NH₂, H₂N(CH₂)₄NH₂, CH₃CONH₂ or HO(CH₂)₃OH dissolved in CH₂Cl₂/acetonitrile was taken in dropping funnel. It was added to the MoOCl₄, MoO₂Cl₂ or MoCl₅ solution in flask drop wise with constant stirring, at room temperature. Products were recovered by filtration through G-4 bed of a filtration unit, at reduced pressure and inert atmosphere. Whenever, acetonitrile was added to reaction mixture to increase solubility of reactants, temperature of reaction mixture got increased. All compounds synthesized are very much air and moisture sensitive. They have the tendency to turn blue in colour. So all reactions and work ups were handled under dry nitrogen gas purged with oxygen using vacuum line and liquid nitrogen traps.



III. Results & Discussions

A. Analytical Measurements:

All complexes are moisture and air sensitive. They are insoluble in common organic solvents like CH₂Cl₂, CHCl₃, acetonitrile, n-hexane, but are soluble in polar solvents like DMSO and DMF. Formulations of these complexes have been done on the basis of their elemental analytical data and molar conductance Λ_M measurements. Analytical data reveal that these complexes are mononuclear. Molar conductances Λ_M of compounds [1] to [7] in DMSO are 2 – 6 cm²ohm⁻¹mol⁻¹, suggesting their non-electrolytic nature (table-1).

B. FTIR Spectra:

Bands at 3153.6 cm⁻¹ & 3390.6 cm⁻¹ show that N-H group is present in compound [1] (table-2). A strong band at 971.12 cm⁻¹ attributable to Mo=O stretching shows that Mo=O bond is a terminal one. NH₂ bending band observed in 1,3-diaminopropane¹⁸ in the range of 1160 cm⁻¹–1183 cm⁻¹ is also shifted to lower wave number 1098.15 cm⁻¹, mainly due to coordination.

Bands at 3010.7 cm⁻¹ & 3412.18 cm⁻¹ show that N-H group is present in compound [4] (table-2). Strong bands at 906.19 cm⁻¹ and 945.12 cm⁻¹ show the presence of cis-MoO₂²⁺ core¹⁹. NH₂ bending band observed in 1,3-diaminopropane¹⁸ in the range of 1160 cm⁻¹–1183 cm⁻¹ is also shifted to lower wave number 1103.22 cm⁻¹, mainly due to coordination.

Bands at 3088.2 cm⁻¹ & 3398.3 cm⁻¹ show that N-H group is present in compound [2] (table-3). A strong band at 973.12 cm⁻¹ attributable to Mo=O stretching shows that Mo=O bond is a terminal one. NH₂ bending band observed in 1,4-diaminobutane²⁰ at 1145 cm⁻¹ is also shifted to lower wave number 1111.17 cm⁻¹, mainly due to coordination.

Bands at 3010.11 cm⁻¹ & 3365.14 cm⁻¹ show that N-H group is present in compound [5] (table-3). Strong bands at 918.16 cm⁻¹ and 980.18 cm⁻¹ show the presence of cis-MoO₂²⁺ core¹⁹. NH₂ bending band observed in 1,4-

diaminobutane²⁰ in the range of 1145 cm⁻¹ is also shifted to lower wave number 1113.15 cm⁻¹, mainly due to coordination.

Bands at 3014.6 cm⁻¹ & 3390.8 cm⁻¹ show that N-H group is present in compound [7] (Table-3). NH₂ bending band observed in 1,4-diaminobutane²⁰ in the range of 1145 cm⁻¹ is also shifted to higher wave number 1189.23 cm⁻¹, mainly due to coordination.

Bands at 3230.10 cm⁻¹ & 3398.9 cm⁻¹ show that N-H group is present in compound [3] (Table-4). A strong band at 973.12 cm⁻¹ attributable to Mo=O stretching shows that Mo=O bond is a terminal one. A shift in ν(C=O) from 1670 cm⁻¹ 1627.23 cm⁻¹ of acetamide^{21,22} indicates a Mo-oxygen bond.

Bands at 3391.40 cm⁻¹ shows that O-H group of 1,3-propanediol²³ is present in compound [6] (Table-5). Strong band at 918.2 cm⁻¹ and weak band at 951.7 cm⁻¹ show the presence of cis-MoO₂²⁺ core¹⁹.

Compounds (Colour/F.W.)	Λ _M *	% Composition Observed (Calculated)					
		Mo	Cl	C	H	N	O
MoOCl ₄ (H ₂ NCH ₂ CH ₂ CH ₂ NH ₂), [1] (Brown/328.0)	5	30.09 (29.26)	43.83 (43.29)	10.23 (10.97)	3.98 (3.04)	8.35 (8.53)	3.98 (4.87)
MoOCl ₄ (H ₂ NCH ₂ CH ₂ CH ₂ CH ₂ NH ₂), [2] (Brown/342.0)	3	27.87 (28.07)	40.88 (41.52)	13.45 (14.03)	4.43 (3.50)	8.70 (8.18)	9.70 (10.22)
MoOCl ₄ (CH ₃ CONH ₂), [3] (Dark green/313.0)	2	29.82 (30.67)	46.30 (45.36)	6.88 (7.66)	2.13 (1.59)	4.34 (4.47)	11.08 (11.72)
MoO ₂ Cl ₂ (H ₂ NCH ₂ CH ₂ CH ₂ NH ₂), [4] (Green/273.0)	2	34.45 (35.16)	25.33 (26.00)	13.03 (13.18)	3.98 (3.66)	8.35 (10.25)	10.98 (11.72)
MoO ₂ Cl ₂ (HNCH ₂ CH ₂ CH ₂ CH ₂ NH ₂). 0.5 HCl, [5] (Blue/305.25)	3	30.87 (31.44)	29.40 (29.07)	14.98 (15.72)	4.18 (4.09)	8.70 (9.17)	9.56 (10.48)
MoO ₂ Cl(OCH ₂ CH ₂ CH ₂ OH).0.5 HCl, [6] (White/256.75)	----	36.72 (37.39)	19.93 (20.74)	14.98 (14.02)	2.13 (1.59)	----	24.08 (24.92)
MoCl ₃ (HNCH ₂ CH ₂ CH ₂ CH ₂ NH ₂), [7] (Dark blue/289.5)	----	32.45 (33.16)	35.83 (36.78)	17.03 (16.58)	3.98 (3.79)	8.95 (9.76)	----

* Molar conductance of millimolar solutions in DMSO at 30° C.

Absorptions	H ₂ N(CH ₂) ₃ NH ₂	[1]	[4]
N-H Str.	3050–3350	3153.6 sb, 3390.6 sb	3010.7 sb, 3412.18 sb
CH ₂ Str.	2875–2960	----	----
NH ₂ Bending	1625	1615.10 s	1601.19 s
CH ₂ Deformation (strong)	1570–1580	1262.16 m, 1406.10 s, 1502.14 mb	1261.37 w, 1408.19 s, 1464.10 s, 1479.14 m
NH ₂ Bending	1160–1183	1098.15 mb	1103.22 s, 1189.25 s, 1216.27 m
C-N sym str. (weak)	1060	1025.16 wb	1029.36 w
CH ₂ Deformation (medium)	743, 840	736.15 mb, 802.13 m	782.20 mb
Mo-N (Strong)	----	497.17 vw	446.31 m
Mo-Cl Str.	----	----	----
Mo=O Str. of monooxo core	----	971.12 s	----
Mo=O Str. of cis-MoO ₂ ²⁺ core	----	----	906.19 s, 945.12 s

Absorptions	H ₂ N(CH ₂) ₄ NH ₂	[2]	[5]	[7]
N-H Str.	3280, 3346	3088.2 sb, 3398.3 sb	3010.11 sb, 3365.14 sb	3014.6 vb sym, 3390.8 vb asym
NH ₂ Bending	1606	1622.10 s	1614.16 s	1616.13 s
CH ₂ Deformation (strong)	1309, 1353, 1390, 1497	1282.20 vw, 1405.10 s, 1448.12 w, 1469.13 vw	1262.25 sh, 1282.19 s, 1343.29 w, 1447.12 s, 1470.14 m	1343.27 vw, 1408.20 m, 1464.12 s, 1479.14 s
NH ₂ Bending	1145	1111.17 m	1113.15 s	1189.23 m
C-N sym str. (weak)	1070	1030.20 w	1025.22 w	1103.21 s
CH ₂ Deformation (medium)	738, 863	739.13 mb, 871.18 w	763.13 mb, 872.14 w	734.13 sb
Mo-N (Strong)	----	497.16 vw	560.15 s	446.24 vw, 498.23 w, 560.16 s
Mo-Cl Str.	----	----	498.23 vw	----
Mo=O Str. of monooxo core	----	973.12 s	----	----
Mo=O Str. of cis-MoO ₂ ²⁺ core	----	----	918.16 m, 980.18 m	----

Absorptions	CH_3CONH_2	[3]
N-H Stretching	3302, 3374	3230.10 sb, 3398.9 sb
CH_2 Stretching	2820	----
C=O Stretching, NH ₂ Deformation	1672	1627.23 s
NH ₂ Deformation	1631	----
NH ₂ Deformation	1606	----
CH_3 Deformation	1450	----
C-N asym stretching	1396	1402.21 s
NH ₂ Deformation	1150	1098.41 vw
C-N sym stretching	1048	----
NH ₂ rocking, twisting and wagging	900	738.30 m
N=C=O bending	600	----
Mo-N (Strong)	----	498.34 w
Mo-Cl Str.	----	----
Mo=O Str.	----	977.26 s

Absorptions	$\text{HO}(\text{CH}_2)_3\text{OH}$	[6]
O-H Str	3376 sb	3391.40 sb
C-H Str	2900 s, 2965 s	2918.35 m, 3000.32 m
CH_2 Deformation	1415 sb	1407.27 s
C-O Str	1070 vs	1034.19 m, 1296.51 m, 1319.38 m
CH_2 Deformation	910 m, 990 m	890.2 s
Mo-O Deformation (Strong)	----	718.31 w
Mo-Cl Str.	----	----
Mo=O Str. of cis-MoO ₂ ²⁺ core	----	918.2 m, 951.7 w
Mo-O Deformation (Strong)	----	437.22s, 454.19 s

¹H NMR Spectra:

Spectrum of compound [1] (table-6) in DMSO-d₆ shows that peaks due to NH₂ and CH₂ protons of 1,3-diaminopropane²⁴ have shifted downfield. This may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum, with subsequent decrease in electron density around CH₂ protons.

Spectrum of compound [4] (table-6) in DMSO-d₆ shows that peaks due to NH₂ and CH₂ protons of 1,3-diaminopropane²⁴ have shifted downfield. This may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum, with subsequent decrease in electron density around CH₂ protons.

Spectrum of compound [2] (table-7) in DMSO-d₆ shows that peaks due to NH₂ protons of 1,4-diaminobutane^{25, 26} have moved downfield, but peaks due to CH₂ protons have shifted up field. It may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum.

Spectrum of compound [5] (table-7) in DMSO-d₆ shows that peaks due to NH₂ protons of 1,4-diaminobutane^{25, 26} have moved downfield, but peaks due to CH₂ protons have shifted up field. It may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum.

Spectrum of compound [7] (table-7) in DMSO-d₆ shows that peaks due to NH₂ protons of 1,4-diaminobutane^{25, 26} have moved downfield, but peaks due to CH₂ protons have shifted up field. It may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum.

Spectrum of compound [3] (table-8) in DMSO-d₆ shows that peaks of NH₂ and CH₃ protons of acetamide²⁷ have moved downfield. It may be due to donation of lone pair by nitrogen atom through coordinate bond formation with molybdenum, with subsequent decrease in electron density around NH₂ and CH₃ protons.

Spectrum of compound [6] (Table-9) in DMSO-d₆ shows that peak due to OH proton of 1,3-propanediol²⁸ has moved downfield. This may be due to donation of lone pair by oxygen atom through coordinate bond formation with molybdenum, with subsequent decrease in electron density around OH proton.

Absorptions	$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$	[1]	[4]
NH ₂	1.21 4H	8.35 (s) 6H	8.13 (s) 6H
Middle CH ₂	1.59 2H	1.99 (s) 2H	1.93 (s) 2H
Side CH ₂	2.76 4H	2.92 (s) 4H	2.87 (s) 4H
Residual DMSO-d ₆	----	2.56 (s)	2.50 (m)

Absorptions	$\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$	[2]	[5]	[7]
NH ₂	1.15 4H	8.16 (s) 4H	7.97 (s) 6H	8.09 (s) 6H
Middle CH ₂	1.74-1.77 4H	1.61 (s) 4H	1.53 (m) 4H	1.61 (s) 4H
Side CH ₂	3.03-3.06 4H	2.75 (s) 4H	2.69-2.71 (m) 4H	2.76-2.78 (d) 4H
Residual DMSO-d ₆	----	2.49 (s)	2.43 (s)	2.49-2.50 (s)

Table-8 (¹ H NMR absorptions in ppm)		
Absorptions	CH ₃ CONH ₂	[3]
NH ₂	7.04 broad 2H	7.23-7.24 (t) 2H
CH ₃	2.00 3H	2.13 (s) 3H
Residual DMSO-d ₆	----	2.59 (s)

Table-9 (¹ H NMR absorptions in ppm)		
Absorptions	HOCH ₂ CH ₂ CH ₂ OH	[6]
OH	4.35 (m) 1H	8.37 1H
Middle CH ₂	1.62 (m) 2H	1.61-1.64 (m) 2H
Side CH ₂	3.51 (t) 4H	3.49-3.53 (t) 4H
Residual DMSO-d ₆	----	2.57-2.61

Electronic Spectra:

1,3-Diaminopropane shows only $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions. The latter occurs as sharp transition at 270.0 nm (absorbance 0.136) in DMSO solvent. An absorptions at 425 nm has been shown by compound [1] dissolved in methanol. This is due to ligand \rightarrow metal charge transfer transitions $O(\pi) \rightarrow d(\text{Mo})$, 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. Similarly, there are ligand \rightarrow metal charge transfer transitions $N(n) \rightarrow d(\text{Mo})$, that is ligand \rightarrow metal charge transfer transitions due to movement of non-bonding electron of nitrogen in 1,3-diaminopropane to empty d-orbital of molybdenum. Electronic spectrum of compound [4] dissolved in DMSO shows peaks at broad 298.0 nm (absorbance 1.172), broad 306.4 nm (absorbance 1.224), broad 334.4 nm (absorbance 1.264) and very broad 704.4nm (absorbance 1.490). Very broad 704.4 nm (absorbance 1.490) band is due to $d \rightarrow d$ transitions from the upper occupied molecular orbitals of Mo to the first vacant molecular orbital of Mo.

1,4-Diaminobutane shows only $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions. Latter is a sharp transition at 278.4 nm (absorbance 0.474) in DMSO solvent. A sharp absorption at 342.6 nm (absorbance 1.389) has been shown by compound [2] dissolved in DMSO. Another very broad absorption at 670.4 nm (absorbance 0.453) has been shown by compound. Electronic spectrum of compound [5] dissolved in DMSO shows peaks at strong 362.4 nm (absorbance 1.741), broad 387.6 nm (absorbance 1.473), very broad 631.2 nm (absorbance 1.554), very broad 648.0 nm (absorbance 1.676) and very broad 695.6 nm (absorbance 1.819). Very broad 695.6 nm (absorbance 1.819) band is due to $d \rightarrow d$ transitions from upper occupied molecular orbitals of Mo to first vacant molecular orbital of Mo. Electronic spectrum of compound [7] dissolved in methanol shows no peak above 400 nm.

Acetamide shows sharp 270.0 nm (absorbance 0.124) $O(n) \rightarrow C(\pi^*)$ transitions due to due to presence of $C = O$ group. An absorptions at 444 nm has been shown by compound [3] dissolved in methanol. This is due to ligand \rightarrow metal charge transfer transitions $O(\pi) \rightarrow d(\text{Mo})$, 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.

References

- [1] P R Mandlik, M B More & A Aswar, *Indian J Chemistry*, vol. 42A (p. 1064) 2003.
- [2] V K Sharma & Shipra Srivastwa, *J Coord Chem.*, vol. 59 (p. 1321) 2006.
- [3] V P Singh, Anshu Katiar & Shaveta Singh, *Biometals*, vol. 21 (p. 491) 2008.
- [4] S S Kanwar, K Lumba, S K Gupta, V M Katoch, P Singh, A K Mishra & S B Kalia, *Biotechnol. Letters*, vol. 30 (p. 677) 2008.
- [5] Z H Chohan, M Arif, Z Shatiq, Yaqub Mohammad & C T Supuran, *J EnzInhib Med Chem*, vol. 21 (p. 95) 2006.
- [6] M L Harikumar Nair & A Sheela, *Indian J Chem*, vol. 47A, (p. 87) 2008.
- [7] J E Bäckvall, 'Modern Oxidation Methods' (Wiley-VCH Ed.), 2004.
- [8] B Meunier, 'Metal-oxo and metal-peroxo species in catalytic oxidations' (Berlin: Springer), 2000.
- [9] J M Bregeault, *Dalton Trans.*, (pp. 3289–3302) 2003.
- [10] C Y Lorber, S.P Smidt & J A Osborn, *Eur. J. Inorg. Chem.*, (pp. 655–658) 2000.
- [11] R H Holm, *Coord. Chem. Rev.*, vol. 100 (pp. 183-221) 1990.
- [12] A Rana, R Dinda, P Sengupta, L R Falvello & S Ghosh, *Polyhedron*, vol. 21 (pp. 1023-1030) 2002.
- [13] S K Vasisht, Gursharan Singh, in: VII International Symposium on Organosilicon Chemistry, Kyoto, Japan, (p. 40) 1984.
- [14] Sham K Vasisht, Gursharan Singh & (Ms) Sarita Chaudhary, *Indian Journal of Chemistry*, vol. 24A (pp. 574-577) 1985.
- [15] Sham K. Vasisht, Gursharan Singh & Pawan K. Verma, *Monatshfte für Chemie*, vol. 117 (pp. 177-183) 1986.
- [16] S K Vasisht & Gursharan Singh, *Z. Anorg. Allg. Chemie*, vol. 526 (pp. 161-167) 1985.
- [17] A I Vogel, A text book of Quantitative Inorganic Analysis; John Wiley and Sons: New York, 1963.
- [18] Seema Yadava, A Mohemana, Abhinav Kumarb, Rajendra Prasadc & K S Siddiqi, *Arabian Journal of Chemistry*, 2013.
- [19] V L Abramenko, V S Sergienko & A V Churakov, *Russian J Coord Chem.*, vol. 26(12) (pp. 866-871) 2000.
- [20] ERGU^{••} N KASAP, SU^{••} LEYMAN & O^{••} ZCELI'K, J. *Inclusion Phenomena and Molecular Recognition in Chem.*, vol. 28 (pp. 259–267) 1997.
- [21] K Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley Interscience, 6th edn.), 2008.
- [22] L Yu Alikberova, D V Al'bov, P S Kibal'nikov, M G Zaitseva, V V Kravchenko, G A Fedorova & N S Rukk, *Russian J Coord Chem.*, vol. 38(4) (pp. 240-244) 2012.
- [23] NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>).
- [24] http://www.chemicalbook.com/SpectrumEN_60-35-5_1HNMR.htm.
- [25] <http://www.ymdb.ca/compounds/YMDB00132>.
- [26] http://www.hmdb.ca/spectra/spectra/nmr_one_d/1703.

- [27] http://www.chemicalbook.com/SpectrumEN_109-76-2_1HNMR.htm.
[28] <http://www.sigmaaldrich.com/catalog/product/aldrich/p50404?lang=en®ion=IN>.

Acknowledgements

We are thankful to Department of Sophisticated Analytical Instruments Facility/Central Instrumentation Laboratory, Panjab University, Chandigarh (India) for providing us the facility for C, H, N, O analysis, UV-VIS spectra, FTIR spectra and ¹H-NMR spectra to characterize samples synthesized by us. We are also thankful to Campus Director, Giani Zail Singh Punjab Technical University Campus Bathinda, Punjab, for providing us all infrastructural facilities and financial assistance out of TEQIP-II grant to execute this project.