



Reactions of MoCl_5 and MoO_2Cl_2 with 4-Phenylimidazole-2-thiol and 2-Thiazoline-2-thiol

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ABSTRACT

Reactions of $\text{MoCl}_5/\text{MoO}_2\text{Cl}_2$ with 4-phenylimidazole-2-thiol/2-thiazoline-2-thiol in CH_3CN solvent in 1:1/1:2 molar ratios have been carried out at room temperature. Products obtained $\text{MoCl}_3(\text{C}_9\text{H}_7\text{N}_2\text{S})(\text{CH}_3\text{CN})$, [1]; $\text{MoCl}_2(\text{C}_9\text{H}_7\text{N}_2\text{S})(\text{CH}_3\text{CN})$, [2]; $\text{Mo}_2\text{OCl}_4(\text{C}_9\text{H}_8\text{N}_2\text{S})_2$, [3] and $\text{Mo}_4\text{O}_2\text{Cl}_{12}(\text{C}_9\text{H}_7\text{N}_2\text{S})_4$, [4]; $\text{MoO}_2\text{Cl}_3(\text{C}_9\text{H}_5\text{NS}_2)_2$, [5] and $\text{Mo}_2\text{O}_4\text{Cl}_6(\text{C}_9\text{H}_5\text{NS}_2)_2$, [6] have been analyzed and characterized by elemental analysis, FTIR, ¹H NMR and LC-MS techniques. Compounds being moisture and air sensitive, these have been prepared in inert atmosphere using vacuum line and liquid nitrogen cooled traps. Fragments obtained in LC-MS spectra support the formulae derived.

Keywords: MoCl_5 , MoO_2Cl_2 , 4-phenylimidazole-2-thiol, 2-thiazoline-2-thiol, FTIR, ¹H NMR and LC-MS, Fragments.

INTRODUCTION

Reactions of MoCl_5 and MoO_2Cl_2 with various ligands have been reported in the literature. Earlier, MoCl_5 reactions with 1,4-diaminobutane, potassium phthalimide, pyrazole, 2-mercaptopyridine-N-oxide sodium, imidazole, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, succinimide, 2-thiazoline-2-thiol have been reported^{1,3-4,6-7} by the author. Reactions of MoO_2Cl_2 with 1,3-diaminopropane, 1,4-diaminobutane, 1,3-propandiol, imidazole, pyrazole, acetamide, succinimide,

potassium phthalimide, 2-thiazoline-2-thiol have also been reported^{1-3,6-7} by the author.

In the current paper, reactions of 4-phenylimidazole-2-thiol/2-thiazoline-2-thiol with $\text{MoCl}_5/\text{MoO}_2\text{Cl}_2$ in CH_3CN solvent at room temperature have been carried out to study addition, substitution, reduction, rearrangement or polymerization processes occurring.

¹H NMR, FTIR of the compounds synthesized have been studied to determine the bonding of the ligands to Mo. Fragmentation pattern



of the compounds observed in LC-MS mass spectra support molecular formulae derived.

AIM of Investigation

Heterocyclic thioamides have N and S-donor ligands which are known to form different types of coordination compounds. They are used in analysis and corrosion control. They are biologically active. N-methylimidazole-2-thione and other thioamides are used as anti-thyroidal agents⁸. Heterocyclic compounds having imidazothiazole structural unit are biologically active⁹. They have the ability to inhibit or activate many enzymes and receptors¹⁰⁻¹³. They act as antitumor¹⁴⁻¹⁹, antimicrobial²⁰⁻²¹, antidiabetic²², diuretic²³, anthelmintic²⁴ and fungicidal²⁵ compounds.

Molybdenum compounds containing 2-thiazoline-2-thiol have been prepared by the author^{2, 5-6}. Metal complexes with sulphur containing ligands have many biochemical applications²⁶⁻²⁸.

MATERIALS AND METHODS

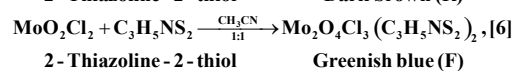
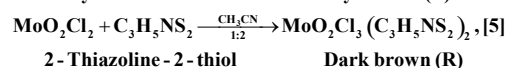
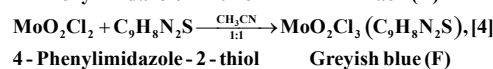
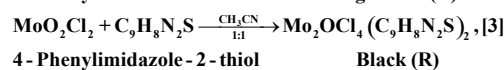
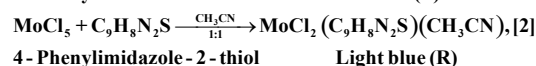
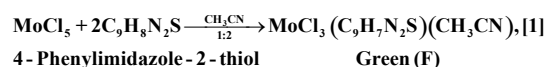
MoO₂Cl₂, MoCl₅ and 2-thiazoline-2-thiol were purchased from Sigma-Aldrich, USA and used as such.

Mo and Cl have been estimated gravimetrically by oxinate method²⁹ and silver chloride method²⁹, respectively. Other elements were analysed using Thermo Finnigan Elemental Analyzer. Perkin-Elmer 400 FTIR Spectrometer, in KBr disks was used to record spectra in the range 4000 – 400 cm⁻¹. Bruker Avance-II 400 NMR in DMSO-d₆ was used for obtaining ¹H-NMR spectra. WATERS, Q-TOF Micromass LC-MS (UK) was used for LC-MS spectra in the range 0 – 1100 m/z. These facilities were availed at SAIF/CIL, Panjab University, Chandigarh (India).

Synthesis of compounds [1]-[6]

Pressure stabilized dropping funnel having teflon stop-cock was connected to a 100 mL flask. For stirring, a magnetic bead was placed in the flask. Apparatus was connected to vacuum line and dried by heating. On cooling, apparatus was flushed with oxygen purged dry nitrogen gas. Known amount of MoO₂Cl₂ or MoCl₅ was placed in the flask along with dry CH₃CN solvent. 4-phenylimidazole-2-thiol or 2-thiazoline-2-thiol was placed in equimolar or 1:2 molar amount along with CH₃CN solvent in dropping funnel. Solution from the dropping funnel was added to MoO₂Cl₂ or MoCl₅ placed in bottom flask at room temperature with continuous stirring. Compounds thus prepared were filtered under reduced pressure through filtration unit. Compounds prepared have sensitivity to air and moisture. On exposure to air and moisture, their colour changes to blue. All procedures and work up have been done in vacuum line using oxygen purged under dry nitrogen gas. Moisture and oxygen were further removed using liquid nitrogen cooled traps.

Rearrangement and disproportionation have occurred during the reactions. F/R means filtrate/residue yielding the product.



Analytical studies

Table 1: (Elemental Analysis)

Compounds	% Observed (Theoretical)					
	Mo	Cl	C	H	N	S
(Colour/Formula Mass)						
MoCl ₃ (C ₉ H ₇ N ₂ S)(CH ₃ CN), [1] (Green/418.5)	23.76 (22.93)	24.76 (25.44)	30.22 (31.54)	3.01 (2.38)	9.41 (10.03)	7.31 (7.64)
MoCl ₂ (C ₉ H ₈ N ₂ S)(CH ₃ CN), [2] (Light blue/383.0)	25.35 (25.06)	17.73 (18.53)	33.66 (34.46)	2.91 (2.61)	10.08 (10.96)	9.21 (8.35)
Mo ₂ OCl ₄ (C ₉ H ₈ N ₂ S) ₂ , [3] (Black/702.0)	28.03 (27.35)	21.00 (20.22)	29.99 (30.76)	2.61 (2.27)	7.32 (7.97)	8.35 (9.11)
Mo ₂ O ₂ Cl ₂ (C ₉ H ₈ N ₂ S) ₂ , [4] (Greyish blue/1546.0)	25.63 (24.83)	28.46 (27.55)	27.07 (27.94)	2.77 (1.81)	6.86 (7.24)	7.50 (8.27)
MoO ₂ Cl ₃ (C ₃ H ₅ NS) ₂ , [5] (Dark brown/472.5)	21.16 (20.31)	22.58 (22.53)	14.56 (15.23)	2.08 (2.11)	5.62 (5.92)	26.99 (27.08)
Mo ₂ O ₄ Cl ₃ (C ₃ H ₅ NS) ₂ , [6] (Greenish blue/600.5)	32.56 (31.97)	17.40 (17.73)	11.32 (11.99)	2.28 (1.67)	4.60 (4.66)	20.47 (21.31)

FTIR Spectra

There is an increase of 145, 149, 150 & 148 cm^{-1} in $\nu(\text{N-H})$ of 4-phenylimidazole-2-thiol³⁰⁻³² in [1], [2], [3] & [4], respectively (Table 2) showing the presence of N-H group. There is no absorption in the region 2550-2600 cm^{-1} of [1], [2], [3] & [4] corresponding to $\nu(\text{S-H})$, conveying absence of S-H group. $\nu(\text{C=S})$ are

absent in these compounds. $\nu(\text{C=S})$ is observed at a lower wave number than $\nu(\text{C=O})$, because C=S bond is weaker and less polar than C=O bond. C=S absorptions are less intense than those of C=O group. Absorption at 762, 761, 762 & 762 cm^{-1} in [1], [2], [3] & [4], respectively is associated with $\nu(\text{C-S})$. Presence of $\nu(\text{C-S})$ may be due to formation of Mo-S bond.

Table 2: (Infrared Absorptions in cm^{-1})

Assignment	$\text{C}_9\text{H}_7\text{N}_2\text{S}$ (4-Phenylimidazole -2-thiol) ³⁰⁻³²	[1]	[2]	[3]	[4]
$\nu(\text{N-H})$	3129, 3248 s	3393.7 v. s.	3396.1 v. s.	3396.6 v. s.	3397.7 v. s.
$\nu(\text{S-H})$		---	---	---	---
$\nu(\text{C=C}), \nu(\text{C=N})$	1558, 1500, 1465	1623.2 s, 1593.2 sh, 1457.2 m	1621.3 s, 1459.1 m	1619.8 s, 1597.3 sh, 1456.9 w	1621.7 s, 1598.2 sh, 1456.6 w
$\nu(\text{C=S})$	1261, 1109	----	----	----	----
$\nu(\text{C-S})$	780	762.4 s	761.7 s	762.9 s	762.2 s
$\nu(\text{Mo-S})$ ³³	421	---	---	---	---
$\nu_{\text{terminal}}(\text{Mo=O})$ ³⁴⁻³⁶	---	---	---	981.3 s	981.7 s

$\nu(\text{Mo=O})$ occurs³³ in the range 990 -1010 cm^{-1} . Absorption at 981 & 981 cm^{-1} in [3] & [4], respectively corresponds to terminal $\nu(\text{Mo=O})$ ³⁴⁻³⁶

Thiol-thione tautomerism is typical of imidazole-2-thiones³². There is a decrease in $\nu(\text{Mo=O})$ which shows S \rightarrow Mo coordination³⁷ of 4-phenylimidazole-2-thiol in a direction trans to Mo=O bond. This shows that 4-phenylimidazole-2-thione reacted in a thiol form.

There is an increase of 285 & zero cm^{-1} in $\nu(\text{N-H})$ of 2-thiazoline-2-thiol in [5] & [6], respectively (Table 3). The spectrum does not show absorption around 2710 cm^{-1} conveying S-H group is absent in [5] & [6]. Presence of $\nu(\text{C=S})$ at 1308 & 1309 cm^{-1} in [5] & [6], respectively and further, absence of

$\nu(\text{C=N})$ indicate that S-H bond is missing in these compounds. Ligand is attached in thio-keto form in them. Bonding of ligand seems to be through S \rightarrow Mo coordinate bond.

Absorption at 963 cm^{-1} in [5] corresponds to terminal $\nu(\text{Mo=O})$ ³⁴⁻³⁶. There is a decrease in $\nu(\text{Mo=O})$ which shows coordination³⁷ of 2-thiazoline-2-thiol to Mo through S atom in a direction trans to Mo=O bond.

Bands at 983 & 960 cm^{-1} in [6] indicate the presence of cis-MoO₂²⁺ core³⁸.

Table 3: (Infrared Absorptions in cm^{-1})

Assignment	$\text{C}_3\text{H}_5\text{NS}_2$ 2-Thiazoline-2-thiol ³⁰⁻³²	[5]	[6]
$\nu(\text{N-H})$ asym.	3145	3429.7 vs	3145.0 s
$\nu(\text{S-H})$	2709	----	----
$\nu(\text{C=N})$	1518 s	----	----
$\nu(\text{C=S})$	1300 m	1308.4 s,	1309.8 sh,
$\nu_{\text{ring}}(\text{C-N})$	1260 sh	1254.8 vw	1256.4 w
$\nu_{\text{sym}}(\text{C-N})$	1218	1202.5 m	1208.6 m
$\nu(\text{Mo-N})$	----	458.6 sh	460.1 sh
$\nu(\text{Mo-S})$	421	---	---
$\nu_{\text{terminal}}(\text{Mo=O})$ ³⁴⁻³⁶	----	963.0 s	---
cis-MoO ₂ ²⁺ core ³⁸ $\nu(\text{Mo=O})$	----	---	984.0 sh, 959.0 vs

¹H NMR Spectra

4-Phenylimidazole-2-thiol^{39,40} has N-H peak at 13.00 ppm. Since -OH, -NH₂, -SH are labile

protons and spectrum is taken in some solvent, so they have no characteristic chemical shift. No N-H peak has been observed in [1], [2], [3] & [4] (Table 4).

Table: 7

Compounds	Fragment	Calculated ³⁵ m/z	Recorded m/z	Rel. abundance
[1]	[C ₉ H ₈ N ₂ S] ⁺	176.04	177.09	40%
	[MoCl ₂ (C ₉ H ₇ N ₂ S)(CH ₃ CN)] ⁺	384.91	383.18	5%
	[MoCl ₂ (C ₉ H ₈)(CH ₃ CN)] ⁺	285.90	286.13	30%
	[MoCl(C ₉ H ₉)(CH ₃ CN)] ⁺	250.93	252.14	10%
	[MoCl ₂ (C ₉ H ₈ N ₂)(CH ₃ CN)] ⁺	352.93	351.14	100%
[2]	[MoCl ₂ (C ₉ H ₇ N ₂ S)(CH ₃ CN)] ⁺	384.91	383.18	6%
	[C ₉ H ₈ N ₂ S] ⁺	176.04	177.09	41%
	[C ₉ H ₈ N ₂] ⁺	144.06	145.12	7%
	[MoCl ₂ (C ₉ H ₈ N ₂)(CH ₃ CN)] ⁺	352.93	351.14	100%
[3]	[MoCl ₂ (C ₉ H ₈ N ₂ S)(CH ₃ CN)] ⁺	285.90	286.13	7%
	[C ₉ H ₈ N ₂ S] ⁺	176.04	177.02	28%
	[Mo ₂ OCl] ⁺	351.68	350.99	100%
	[Mo ₂ OCl ₄ (C ₉ H ₇ N ₂ S)]	526.71	525.01	40%
[4]	[Mo ₂ OCl ₄ (C ₉ H ₇ N ₂ S) ₂] ⁺	701.74	699.00	2%
	[C ₉ H ₈ N ₂ S] ⁺	176.04	177.03	28%
	[Mo ₂ OCl ₄] ⁺	351.68	351.02	78%
	[Mo ₂ OCl ₄ (C ₉ H ₇ N ₂ S)]	526.71	525.01	100%
[5]	[Mo ₂ OCl ₄ (C ₉ H ₇ N ₂ S) ₂] ⁺	701.74	699.06	40%
	[Mo ₄ O ₂ Cl ₈ (C ₉ H ₇ N ₂ S)] ⁺	878.39	873.12	3%
	[Mo ₄ O ₂ Cl ₈ (C ₉ H ₇ N ₂ S) ₂] ⁺	1053.42	1049.14	<1%
	[Mo ₄ O ₂ Cl ₈ (C ₉ H ₇ N ₂ S) ₃] ⁺	1228.46	1223.15	<1%
	[Mo ₄ O ₂ Cl ₈ (C ₉ H ₇ N ₂ S) ₄] ⁺	1403.48	1397.18	<1%
	[MoO ₂ Cl ₃ (C ₃ H ₄ NS ₂) ₂] ⁺	470.75	470.85	4%
	[C ₃ H ₄ NS ₂] ⁺	118.98	119.98	8%
	[MoO ₂] ⁺	129.89	129.03	28%
[6]	[MoO ₂ S] ⁺	161.86	161.01	8%
	[C ₃ H ₄ NS ₂ SNH ₄ C ₃] ⁺	203.98	204.95	100%
	[C ₃ H ₃ NS ₂ Cl ₂] ⁺	188.92	188.99	44%
	[MoO ₂ Cl ₃ (C ₃ H ₄ NS ₂) ₂] ⁺	470.75	470.85	2%
	[C ₃ H ₄ NS ₂] ⁺	118.98	120.00	1%
	[MoO ₂] ⁺	129.89	129.05	25%
	[MoO ₂ S] ⁺	161.86	161.01	20%
	[C ₃ H ₄ NS ₂ Cl ₂] ⁺	188.92	189.00	86%
[C ₃ H ₄ NS ₂ SNH ₄ C ₃] ⁺	203.98	204.97	100%	
[MoO ₂ Cl ₃ (C ₃ H ₄ NS ₂) ₂] ⁺	400.82	399.06	3%	

CONCLUSION

There is no absorption in the region 2550-2600 cm⁻¹ of [1], [2], [3] & [4] corresponding to ν (S-H), showing absence of S-H group. ν (C=S) stretchings are absent in [1], [2], [3] & [4]. Absorptions at 762, 761, 762 & 762 cm⁻¹ in [1], [2], [3] & [4], respectively suggest presence of ν (C-S) of Mo-S bonds.

Presence of ν (C=S) at 1308 & 1309 cm⁻¹ in [5] & [6], respectively and further, absence of ν (C=N) in [5] & [6], respectively indicate that S-H bond is missing. Bonding of ligand seems to be through S→Mo coordinate bond.

No characteristic S-H chemical shift has been observed in all the six compounds, indicating that either C=S is present or Mo-S is present in

these compounds. Presence of CH₃CN in [1] & [2] has been inferred due to presence of ¹H NMR peak of CH₃CN in them.

LC-MS spectra support the presence of particular ligands in these compounds and their proposed formulae.

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Conflict of interest

It is declared that the authors have no conflict of interest.

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