Reactions of MoCl$_5$ and MoO$_2$Cl$_2$ with 4-Phenylimidazole-2-thiol and 2-Thiazoline-2-thiol

DEEPIKA RANI$^1$, GURSHARAN SINGH$^2*$ and SEEMA SHARMA$^3$

$^1$Research Scholar Registered with Punjab Technical University, Kapurthala, India.

$^2$Department of Applied Chemistry, Giani Zail Singh Campus College of Engineering and Technology, MRSPTU, Dabwali Road, Bathinda-151001, India.

$^3$Department of Chemistry, Maharaja Ranjit Singh Punjab Technical University’, Dabwali Road, Bathinda-151001, India.

*Corresponding author E-mail: gursharans82@gmail.com

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ABSTRACT

Reactions of MoCl$_5$/MoO$_2$Cl$_2$ with 4-phenylimidazole-2-thiol/2-thiazoline-2-thiol in CH$_3$CN solvent in 1:1/2 molar ratios have been carried out at room temperature. Products obtained MoCl$_3$(C$_9$H$_7$NS)(CH$_3$CN)$_2$, [1]; MoCl$_2$(C$_9$H$_7$NS)(CH$_3$CN), [2]; MoOCl$_2$(C$_9$H$_8$NS)$_2$, [3] and Mo$_2$OCl$_4$(C$_3$H$_5$NS)$_2$, [4]; MoO$_2$Cl$_3$(C$_3$H$_5$NS)$_2$, [5] and Mo$_2$O$_2$Cl$_2$(C$_3$H$_5$NS)$_2$, [6] have been analyzed and characterized by elemental analysis, FTIR, $^1$H 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$_2$Cl$_2$, 4-phenylimidazole-2-thiol, 2-thiazoline-2-thiol, FTIR, $^1$H NMR and LC-MS, Fragments.

INTRODUCTION

Reactions of MoCl$_5$ and MoO$_2$Cl$_2$ with various ligands have been reported in the literature. Earlier, MoCl$_5$ reactions with 1,4-diaminobutane, potassium phthalimide, pyrazole, 2-mercaptopypyridine-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$_2$Cl$_2$ with 1,3-diaminopropane, 1,4-diaminobutane, 1,3-propanediol, 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 MoCl$_5$/MoO$_2$Cl$_2$ in CH$_3$CN solvent at room temperature have been carried out to study addition, substitution, reduction, rearrangement or polymerization processes occurring.

$^1$HNMR, 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 formulæ 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 agents. Heterocyclic compounds having imidazoazole structural unit are biologically active. They have the ability to inhibit or activate many enzymes and receptors. They act as antitumor, antimicrobial, anti-diabetic, diuretic, antihelminthic, and fungicidal compounds.

Molybdenum compounds containing 2-thiazoline-2-thiol have been prepared by the authors, 5-6. Metal complexes with sulphur containing ligands have many biochemical applications.

**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 oximate method and silver chloride method, 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. Brucker Avance II 400 NMR in DMSO-d₆ was used to record spectra in the range 0 – 1100 m/z. These facilities were availed from SAIF/CIL, Panjab University, Chandigarh (India). Micromass LC-MS (UK) was used for LC-MS spectra using Thermo Finnigan Elemental Analyzer. Rearrangement and disproportionation have occurred during the reactions. F/R means filtrate/residue yielding the product.

![Chemical equations and structures]

**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.

**Analytical studies**

Table 1: (Elemental Analysis)

| Compounds | Mo | Cl | C | H | N | S |
|-----------|----|----|---|---|---|---|
| MoCl₂(C₂H₅N₂S)(CH₃CN), [1] | 23.76 | 24.76 | 30.22 | 3.01 | 9.41 | 7.31 |
| (Green/418.5) | (22.93) | (25.44) | (31.54) | (2.38) | (10.03) | (7.64) |
| MoCl₅(C₂H₅N₂S)(CH₃CN), [2] | 25.35 | 17.73 | 33.66 | 2.91 | 10.08 | 9.21 |
| (Light blue/383.0) | (25.06) | (18.53) | (34.46) | (2.61) | (10.96) | (8.35) |
| MoCl₂(C₂H₅N₂S)₂, [3] | 28.03 | 21.00 | 29.99 | 2.61 | 7.32 | 8.35 |
| (Black/702.0) | (27.35) | (20.22) | (30.76) | (2.27) | (7.97) | (9.11) |
| MoO₂Cl₂(C₂H₅N₂S)₂, [4] | 25.63 | 28.46 | 27.07 | 2.77 | 6.86 | 7.50 |
| (Greyish blue/1546.0) | (24.83) | (27.55) | (27.94) | (1.81) | (7.24) | (8.27) |
| MoO₂Cl₂(C₂H₅N₂S)₃, [5] | 21.16 | 22.58 | 14.56 | 2.08 | 5.62 | 26.99 |
| (Dark brown/472.5) | (20.31) | (22.53) | (15.23) | (2.11) | (5.92) | (27.08) |
| MoO₂Cl₂(C₂H₅N₂S)₄, [6] | 32.56 | 17.40 | 11.32 | 2.28 | 4.60 | 20.47 |
| (Greenish blue/600.5) | (31.97) | (17.73) | (11.99) | (1.67) | (4.66) | (21.31) |
FTIR Spectra

There is an increase of 145, 149, 150 & 148 cm\(^{-1}\) in \(\nu(N-H)\) of 4-phenylimidazole-2-thiol\(^{30-32}\) 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 \([1, 2, 3, \& 4]\), respectively corresponding to \(\nu(S-H)\), conveying absence of S-H group. \(\nu(C=S)\) are absent in these compounds. \(\nu(C=S)\) is observed at a lower wave number than \(\nu(C=O)\), 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 \(\nu(C-S)\). Presence of \(\nu(C-S)\) may be due to formation of Mo-S bond.

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

| Assignment          | C\(_2\)H\(_5\)N\(_2\)S (4-Phenylimidazole-2-thiol)\(^{30-32}\) |
|---------------------|--------------------------------------------------------------|
| \(\nu(N-H)\)        | 3129, 3248 s                                                |
| \(\nu(S-H)\)        | ---                                                          |
| \(\nu(C=C), \nu(C=N)\) | 1558, 1500, 1465                                            |
| \(\nu(C=S)\)        | 1261, 1109                                                  |
| \(\nu(C=S)\)        | 780                                                          |
| \(\nu(Mo=S)\)\(^{33}\) | 421                                                          |
| \(\nu_{terminal}(Mo=O)\(^{34-36}\) | ---                                                          |

\(\nu(Mo=O)\) occurs\(^{33}\) in the range 990 -1010 cm\(^{-1}\). Absorption at 981 & 981 cm\(^{-1}\) in \([3, \& 4]\), respectively corresponds to terminal \(\nu(Mo=O)\(^{34-36}\)

Thiol-thione tautomerism is typical of imidazole-2-thiones\(^{32}\). There is a decrease in \(\nu(Mo=O)\) which shows S\(\rightarrow\)Mo coordination\(^{37}\) of 4-phenylimidazole-2-thiol in a direction trans to MoO bond. This shows that 4-phenylimidazole-2-thione reacted in a thiol form.

There is an increase of 285 & zero cm\(^{-1}\) in \(\nu(N-H)\) 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 \(\nu(C=S)\) at 1308 & 1309 cm\(^{-1}\) in \([5, \& 6]\), respectively and further, absence of \(\nu(C=N)\) 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(Mo=O)\(^{34-36}\). There is a decrease in \(\nu(Mo=O)\) which shows coordination\(^{37}\) of 2-thiazoline-2-thiol to Mo through S atom in a direction trans to MoO bond.

Bands at 983 & 960 cm\(^{-1}\) in \([6]\) indicate the presence of cis-MoO\(^{2+}\) core\(^{38}\).

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

| Assignment          | C\(_2\)H\(_5\)N\(_2\)S 2-Thiazoline-2-thiol\(^{30-32}\) |
|---------------------|--------------------------------------------------------------|
| \(\nu(N-H)\) asym.  | 3145                                                          |
| \(\nu(S-H)\)        | 2709                                                          |
| \(\nu(C=N)\)        | 1518 s                                                        |
| \(\nu(C=S)\)        | 1300 m                                                        |
| \(\nu(C=N)\)        | 1260 sh                                                       |
| \(\nu(C=N)\)        | 1218                                                          |
| \(\nu(Mo=N)\)       | 458.6 sh                                                      |
| \(\nu(Mo=S)\)       | 421                                                           |
| \(\nu_{terminal}(Mo=O)\(^{34-36}\) | ---                                                          |
| cis-MoO\(^{2+}\) core\(^{38}\) \(\nu(Mo=O)\) | ---                                                          |

\(^1\)H NMR Spectra

4-Phenylimidazole-2-thiol\(^{39,40}\) has N-H peak at 13.00 ppm. Since -OH, -NH\(_2\), -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).
4-Phenylimidazole-2-thiol has S-H peak at 12.15 ppm. No S-H peak has been observed in [1], [2], [3] & [4]. This indicates the absence of S-H group in [1], [2], [3] & [4]. There has been upfield shift of H-5 in all the four compounds. All the ring protons of phenyl group have also shown up field shift in all the four compounds. Presence of CH$_3$CN in [1] & [2] has been inferred by the absorptions at 2.05 & 1.98 ppm, respectively.

Table 4: (1'H NMR absorptions in ppm)

| Assignment | C$_7$H$_5$N$_2$ (4-Phenylimidazole-2-thiol) | [1] | [2] | [3] | [4] |
|------------|------------------------------------------|-----|-----|-----|-----|
| N-H        | 13.00                                    | --- | --- | --- | --- |
| S-H        | 12.15                                    | --- | --- | --- | --- |
| H-5        | 7.51                                     | 7.47| 7.41| 7.33| 7.39|
| Phenyl H-2, H-6 | 8.13                                   | 7.90| 7.86| 7.76| 7.77|
| Phenyl H-3, H-5 | 7.51                                    | 7.47| 7.41| 7.33| 7.45|
| Phenyl H-4 | 7.41                                     | --- | --- | --- | --- |
| CH$_3$CN   | ---                                      | 2.05| 1.98| --- | --- |

N-H absorptions have not been observed in [5] & [6] (Table 5). Other protons have shown downfield shift in them showing S→Mo coordination.

Table 5: (1'H NMR absorptions in ppm)

| Assignment | C$_7$H$_5$N$_2$S 2-Thiazoline-2-thiol | [5] | [6] |
|------------|---------------------------------------|-----|-----|
| CH$_2$ attached to N | 3.33 (2H) | 3.27| 3.41|
| CH$_2$ attached to S | 3.56 (2H) | 3.88| 3.83|
| N-H | 7.43 (1H) | --- | --- |
| S-H | --- | --- | --- |

LC-MS MASS Spectra

Fragmentation pattern obtained below has been used to derive the formulae (Table 6,7). m/z values have been given below of the fragments.

Table 6: (Fragmentation)
that either C=S is present or Mo-S is present in all the six compounds, indicating the absence of S-H bond in [5] & [6], respectively and further, absence of S-H group in [1], [2], [3] & [4]. Absorptions at 762, 761, 762 & 762 cm⁻¹ in [1], [2], [3] & [4], respectively indicate that S-H bond is missing. Bonding of ligand seems to be through S-Mo coordinate bond.

Presence of υ(C=S) at 1308 & 1309 cm⁻¹ in [5] & [6], respectively and further, absence of υ(C=N) in these compounds. Presence of CH₂CN 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.

Table: 7

| Compounds | Fragment | Calculated m/z | Recorded m/z | Rel. abundance |
|-----------|----------|----------------|--------------|---------------|
| [1]       | [C₃H₇N₃S]⁺ | 176.04         | 177.09       | 40%           |
|           | [MoCl₂(C₃H₇N₃S)(CH₂CN)]⁺ | 384.91         | 383.18       | 5%            |
|           | [MoCl₂(C₃H₇)](CH₂CN)⁺ | 285.90         | 286.13       | 30%           |
|           | [MoCl₂(C₃H₇)](CH₂CN)⁺ | 250.93         | 252.14       | 10%           |
|           | [MoCl₂(C₃H₇N₃S)(CH₂CN)]⁺ | 352.93         | 351.14       | 100%          |
| [2]       | [MoCl₂(C₃H₇N₃S)(CH₂CN)]⁺ | 384.91         | 383.18       | 6%            |
|           | [C₃H₇N₃S]⁺ | 176.04         | 177.09       | 41%           |
|           | [C₃H₇N₃Cl]⁺ | 144.06         | 145.12       | 7%            |
|           | [MoCl₂(C₃H₇N₃S)(CH₂CN)]⁺ | 352.93         | 351.14       | 100%          |
|           | [MoCl₂(C₃H₇)](CH₂CN)⁺ | 285.90         | 286.13       | 7%            |
| [3]       | [C₃H₇N₃S]⁺ | 176.04         | 177.02       | 28%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 351.68         | 350.99       | 100%          |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 256.71         | 255.01       | 40%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 701.74         | 699.00       | 2%            |
| [4]       | [C₃H₇N₃S]⁺ | 176.04         | 177.03       | 28%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 351.68         | 350.99       | 78%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 256.71         | 255.01       | 100%          |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 701.74         | 699.06       | 40%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 878.39         | 873.12       | 3%            |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 1053.42        | 1049.14      | <1%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 1228.46        | 1223.15      | <1%           |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 1403.48        | 1397.18      | <1%           |
| [5]       | [MoCl₂](C₃H₇N₃S)⁺ | 470.75         | 470.85       | 4%            |
|           | [C₃H₇N₃Cl]⁺ | 118.98         | 119.98       | 8%            |
|           | [MoCl₂]⁺ | 129.89         | 129.03       | 28%           |
|           | [MoCl₂]⁺ | 161.86         | 161.01       | 8%            |
|           | [C₃H₇N₃Cl]⁺ | 188.92         | 188.99       | 44%           |
|           | [C₃H₇N₃Cl]⁺ | 203.98         | 204.95       | 100%          |
| [6]       | [MoCl₂](C₃H₇N₃S)⁺ | 470.75         | 470.85       | 2%            |
|           | [C₃H₇N₃Cl]⁺ | 118.98         | 119.98       | 1%            |
|           | [MoCl₂]⁺ | 129.89         | 129.05       | 25%           |
|           | [MoCl₂]⁺ | 161.86         | 161.01       | 20%           |
|           | [C₃H₇N₃Cl]⁺ | 188.92         | 189.00       | 86%           |
|           | [C₃H₇N₃Cl]⁺ | 203.98         | 204.97       | 100%          |
|           | [MoCl₂](C₃H₇N₃S)⁺ | 400.82         | 399.06       | 3%            |

CONCLUSION

There is no absorption in the region 2550-2600 cm⁻¹ of [1], [2], [3] & [4] corresponding to υ(S-H), showing absence of S-H group. υ(S-H) 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 υ(C-S) of Mo-S bonds.

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 CH₂CN in [1] & [2] has been inferred due to presence of ¹H NMR peak of CH₃CN in them.
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