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Reactions of MoO_2Cl_2 and $MoOCl_4$ with 2-Mercaptopyridine, 4-Phenylimidazole-2-thiol and 6-Mercaptopurine monohydrate

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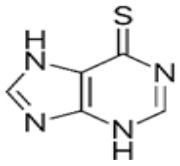
ABSTRACT

MoO_2Cl_2/$MoOCl_4$ have been reacted with 4-phenylimidazole-2-thiol/6-mercaptopurine monohydrate/2-mercaptopyridine in acetonitrile solvent in unimolar/bimolar proportions at room temperature. The products thus obtained are: $MoOCl_3(C_9H_8N_2S)$,[1]; $Mo_2O_3Cl_6(C_9H_7N_2S)(CH_3CN)_2$,[2]; $Mo_2O_3Cl_8(C_9H_7N_2S)_2(CH_3CN)_2$,[3] and $Mo_2O_4Cl_4(C_5H_4NS\text{-}SN_4C_5)$,[4]. These products were studied by various techniques: infrared, proton NMR, liquid/gas chromatography-mass spectrometry, elemental analyses. Owing to the sensitivity of the products to air and moisture, the reactions and work ups were performed in vacuum line purged with oxygen by flushing dry nitrogen in it. Ions observed in mass spectrum are concurrent with the depicted formulae.

Keywords: MoO_2Cl_2, $MoOCl_4$, 2-mercaptopyridine, 4-phenylimidazole-2-thiol, 6-mercaptopurine monohydrate, Acetonitrile solvent, Infrared, proton NMR, DMSO-d_6, Liquid/gas chromatography-mass spectrometry.

INTRODUCTION

6-Mercaptopurine ring system may be considered as if a pyrimidine ring has been fused to an imidazole ring. Electrons of 6-mercaptopurine are highly delocalized. The ring is susceptible to both electrophilic and nucleophilic attacks. 6-Mercaptopurine[1-2] is used as chemotherapy drugs for treatment of autoimmune diseases and cancer like leukemia, ulcerative colitis and Crohn's disease. Mercaptopurine is sold as purinethol. It is a class of medication known as purine antagonists and works by stopping the growth of cancer cells. Many transition metal complexes of 6-mercaptopurine are reported[3-4]. Some of transition metal complexes of 6-mercaptopurine have higher anticancer activity than that of 6-mercaptopurine[5-8]. Divalent transition metals coordinate[5,7,9] through S and N atoms of 6-mercaptopurine.



Heterocyclic thioamides like 4-pheny -limidazole-2-thiol having N and S-donor ligands are biologically active and are used as anti-thyroidal agents[10]. Imidazothiazole structural unit containing heterocyclic compounds are biologically active[11]. Many enzymes and receptors[12-15] can be inhibited by them. They are used in diuretic[16], fungicidal[17], antihelmintic[18], antitumor[19-24], antidiabetic[25] and antimicrobial[26-27] drugs.

There are many biochemical applications[28-30] of metal complexes with thioligands.

AIM of investigation

MoO_2Cl_2 and $MoOCl_4$ are known to react with a variety of ligands. The author earlier investigated[31-37] reactions of MoO_2Cl_2 with various diaminoalkanes, alkanediols, amides, imides, thiols and aromatic azoles.

The author earlier also investigated[31-33,38-39] reactions of $MoOCl_4$ with various diaminoalkanes, amides, imides, alkylpyridines, mercaptopyridine, mercaptopyridine-N-oxide sodium, 2-thiazoline-2-thiol, alkylpyrrolidine, alkylpiperidine and aromatic azoles.

The author has reported earlier also molybdenum compounds containing 4-pheny -limidazole-2-thiol, 6-mercaptopurine monohydrate and 2-mercaptopyridine.

In view of the wide applications of the transition metal complexes, now author has prepared molybdenum complexes of 2-Mercaptopyridine, 4-Phenylimidazole-2-thiol and 6-Mercaptopurine monohydrate on reaction with MoO_2Cl_2 and $MoOCl_4$. The complexes have been characterised by elemental analysis, Mass, IR and NMR techniques. All preparations and work ups have been done under rigorous moisture/air free environment.

MATERIALS AND METHODS

MoO_2Cl_2, $MoOCl_4$, 4-phenylimidazole-2-thiol, 6-mercaptopurine monohydrate and 2-mercaptopyridine used were manufactured by Sigma-Aldrich. We used them without any further treatment. Owing to the sensitivity of the products to air and moisture, the reactions and work ups were performed in vacuum line purged with oxygen by flushing dry nitrogen in it. The reactions were carried out for 6-8 h with continuous stirring using pressure stabilised dropping funnel. The products were filtered through filtration unit fitted with G-4 crucible and isolated.

Molybdenum was determined by oxinate[40] gravimetric method. Chlorine was determined by silver chloride[40] gravimetric method. Thermo Finnigan Elemental Analyser was used to determine other elements. Perkin-Elmer 400 FTIR Spectrometer, in the range 4000–400 cm^{-1} was used to obtain spectra using KBr disks. ^{1}H-NMR spectra were recorded in solvent DMSO-d_6 using Brucker Avance-II 400 NMR. Liquid Chromatography-Mass spectra were obtained in the range 0–1100 m/z. These facilities were provided by Panjab University, Chandigarh (India).

Preparation of compounds[1-4]

Disproportionation/rearrangement might have occurred during the course of reactions. The source of the products is indicated below the products.

$$MoOCl_4 + C_9H_8N_2S \xrightarrow[1:1]{CH_3CN} MoOCl_3\left(C_9H_8N_2S\right), [1]$$

4-Phenylimidazole-2-thiol Black

$$MoOCl_4 + C_5H_4N_4S.H_2O \xrightarrow[1:2]{CH_3CN} Mo_2O_3Cl_6\left(C_5H_2N_4S\right)\left(CH_3CN\right)_2, [2]$$

6-Mercaptopurine monohydrate Blackish brown

$$MoOCl_4 + C_5H_4N_4S.H_2O \xrightarrow[1:1]{CH_3CN} Mo_2O_3Cl_8\left(C_5H_2N_4S\right)_2\left(CH_3CN\right)_2, [3]$$

6-Mercaptopurine monohydrate Coffee brown

$$MoO_2Cl_2 + C_5H_5NS \xrightarrow[1:1]{CH_3CN} Mo_2O_4Cl_4\left(C_5H_4NS\text{-}SNH_4N_5\right), [4]$$

2-Mercaptopyridine Black

RESULTS AND DISCUSSIONS

Analytical Measurements

Estimation of elements (percentage) are given in Table 1. Theoretical values are given in parenthesis.

Table 1: (Elemental Analysis)

Products	Mo	Cl	C	H	N	S
$MoOCl_3(C_9H_8N_2S)$,[1]	23.66	26.78	28.13	2.78	6.13	7.23
(Black/394.5)	-24.33	-27	-27.38	-2.03	-7.1	-8.11
$Mo_2O_3Cl_6(C_9H_7N_2S)(CH_3CN)_2$,[2]	27.53	30.13	14.95	1.65	12.78	4.54
(Blackish brown/685.0)	-28.02	-31.09	-15.76	-1.16	-12.26	-4.67
$Mo_2O_3Cl_8(C_9H_7N_2S)_2(CH_3CN)_2$,[3]	20.78	30.73	17.66	1.17	15.14	3.23
(Coffee brown/906.0)	-21.19	-31.34	-18.54	-1.1	-15.45	-3.53
$Mo_2O_4Cl_4(C_5H_4NS\text{-}SN_4C_5)$,[4]	31.67	22.6	18.54	1.48	4.34	9.55
(Black/618.0)	-31.06	-22.97	-19.41	-1.29	-4.53	-10.35

FTIR Spectra

Absorption at 3137 cm^{-1} in[1] refers to N-H stretching of 4-phenylimidazole-2-thiol[37,41-43] (Table 2). There is no υ(S-H) in the range 2551-2602 cm^{-1} of[1] indicating S-H group is not present it. Peaks at 1261 cm^{-1} and 1106 cm^{-1} in [1] correspond to C=S stretching. υ(C=O) is higher than υ(C=S), because carbonyl bond is stronger and more polar than thiocarbonyl bond. Carbonyl bond absorptions are more intense than that of thiocarbonyl bond. C-S stretching is detected at 761 cm^{-1}. C-S stretching observed points out to the existence of Mo-S bonds. υ(Mo-S)[9,49] appears at 498 cm^{-1}. Terminal Mo=O group absorbs[44] in the span 991 cm^{-1} -1008 cm^{-1}. Mo=O stretching[45-47] was observed at 986 cm^{-1}. There is thiol-thione tautomerism in imidazole-2-thiones[37,43]. Mo=O stretching shows downward shift owing to S→Mo coordination[37,48] of 4-phenylimidazole-2-thiol. Ligand coordination is trans to Mo=O. It implies that 4-phenylimidazole-2-thione reacts in thiol form. This fact is further evident by the higher value of υ(C=N).

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

Mode	(4-Phenylimidazole-2-thiol)[37,41-43]	[1]
υ(N-H)	3129, 3248 s	3137.28 v s
υ(S-H)		
υ(C=N), υ(C=C)	1560, 1502, 1463	1621.30 s, 1597.31 s, 1505.38 m, 1457.37 m
υ(C=S)	1261, 1109	1261 m, 1106 m
υ(C-S)	780	761.27 v s
υ(Mo-S)[9,49]		498.44 v w
Terminal υ(Mo=O)[45-47]		986.30 v s

Absorptions at 3400 cm^{-1} in [2] and 3407 cm^{-1} in [3] suggest υ(N-H) of pyrimidine ring of 6-mercaptopurine[9,50,58]. υ(N-H) of imidazole ring are missing due to absence of N-H bond of imidazole ring (Table 3). This shows that there is Mo-N bond formation. No υ(S-H) peak has been observed in [2] and [3]. This means that 6-mercaptopurine has participated in thiol form. This is further supported by higher C=N stretching in these complexes. Lower N-H stretching implies coordination[50] of 6-mercaptopurine to molybdenum. υ(Mo-S)[9,49] appears at 729 cm^{-1} and 728 cm^{-1} in [2] and [3], respectively. υ(Mo=O) absorptions at 973 cm^{-1} in [2] and 970 cm^{-1} [3], reveal terminal (Mo=O)[45-47] in them.

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

Mode	6-Mercaptopurine monohydrate[9,50,58]	[2]	[3]
υ(N-H) Imidazole	3523		
υ(N-H) Pyrimidine	3376	3400.5 v s	3407.1 v s
υ(C-H)	3095.0, 2993.8		
υ(S-H)	2671.5		
υ(C=C)	1669.7		
υ(C=N) Imidazole	1620	1626.8 v.s.	1626.1 v.s.
υ(C=N) Pyrimidine	1393	1402.1 m	1401.6 m
υ(C-N)	1343.8	1335.2 w	1334.9 w
υ(N-H)	1526.6	1504.1 sh	1504.6 sh
υ(C=S)	1193	1027.24 w	1027.1 w
υ(Mo-S)[9,49]		729.1 m	728.6 m
υ(Mo-N)[9]		496.2 w	496.9 w
Terminal υ(Mo=O)[45-47]		973.1	970.4 s

2-Mercaptopyridine[33, 51-55] shows υ(N-H) at 3177 cm^{-1} and υ(S-H) at 2708 cm^{-1} (Table 4). Bands at 3383 cm^{-1} shows that [4] has N-H group. υ(S-H) around 2708 cm^{-1} is missing pointing to S-H group absence in [4]. υ(Mo=O) peak at 983 cm^{-1} reveals presence of terminal Mo=O group[45-47] [4].

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

Mode	(2-Mercaptopyridine)[33,51-55]	[4]
υ(N-H)	3177	3383 vs
υ(C-H)	3053, 2928, 2880	3128.2 s, 2889.1 m
υ(S-H)	2708 m	
Ring breathing modes & Hydrogen in plane wagging	1614 s, 1577 vs, 1503 s, 1447 s, 1419 s	1604.1s, 1578.2 s, 1496.2 m
υ(C=N) ring	1274 m	1273.2 w
υ(C-H) in plane bending	1247 m	1227.4 w
υ(C=S)	1187 vs, 1144 vs	1177.3 w
υ(C-S), Hydrogen out of plane bending out of plane	746, 614	767 vs, 707.3 w
Terminal υ(Mo=O)[45-47]		983.2 s

^{1}H NMR Spectra

Chemical shift of 4-phenylimidazole-2-thiol[37,56-57] N-H occurs at 12.9 δ. alcoholic, phenolic, amino and thiolic protons have no specific chemical shift, because these are labile and. Spectrum is generally recorded in a solvent, N-H chemical shift (Table 5) is missing in [1]. S-H in 4-phenylimidazole-2-thiol has chemical shift at 12.14 δ. S-H peak is missing in [1]. S-H group does not exist in [1]. [1] shows upfield chemical shift of ring protons and H-5.

Table 5: (^{1}H NMR absorptions in ppm)

Protons	(4-Phenylimidazole-2-thiol)[37,56-57]	[1]
N-H	12.99	
S-H	12.14	
H-5	7.51	7.39
Aromatic H-2 and H-6	8.13	7.72
Aromatic H-3 and H-5	7.51	7.39
Aromatic H-4	7.41	

6-Mercaptopurine monohydrate[58] aromatic N-H absorption shits to 7.8 δ, 7.15 δ in [2] and [3], respectively showing that this N-H is not involved in bonding (Table 6). S-H peak is missing in [2] and [3], indicating presence of Mo-S bond in them.

Table 6: (^{1}H NMR absorptions in ppm)

Protons	6-Mercaptopurine monohydrate[58]	[2]	[3]
N-H (Arom)	7.2	7.15	7.92
S-H	1.2		
N-H	1.4	1.85	1.84
CH_3CN		2.05	2.01

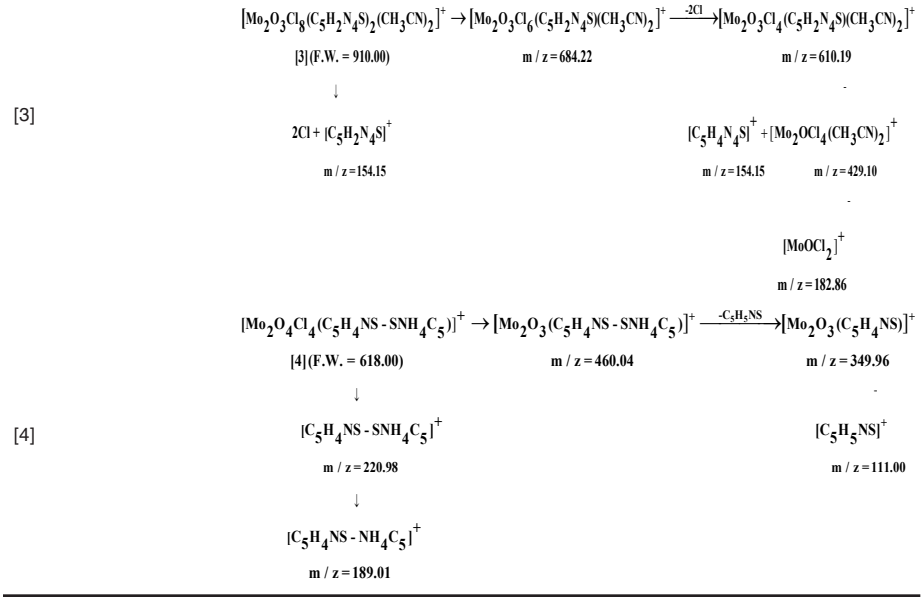
Comparison of 2-mercaptopyridine[33,53] spectrum with that of [4] shows that absorptions move downfield (Table 7). There is no N-H peak. Deshielding is due to an increase in π electron density on coordination in the C–N bond.

Table 7: (^{1}H NMR absorptions in ppm)

Protons	(2-Mercaptopyridine)[3,53]	[4]
N-H		
C_3-H	7.32	7.67
C_4-H	6.81	7.28
C_5-H	7.47	7.81
NC-H	7.69	8.48

Table 8: (Fragmentation)

Comp.	
[1]	$[MoOCl_3(C_9H_7N_2S)] \rightarrow [SOCl_2]^+ \rightarrow [SOCl]^+$ [1] (F.W. = 394.5) m / z = 118.9 m / z = 84.0
[2]	$[Mo_2O_3Cl_6(C_5H_2N_4S)(CH_3CN)_2]^+ \xrightarrow{-2Cl} [Mo_2O_3Cl_4(C_5H_2N_4S)(CH_3CN)_2]^+$ [2] (F.W. = 684.21) m / z = 610.19 ↓ $[C_5H_4N_4S]^+ + [Mo_2OCl_4(CH_3CN)_2]^+$ m / z = 154.14 m / z = 429.10 ↓ $[C_5H_4N_4S]^{2+}$ $[MoOCl_2]^+$ m / z = 77.51 m / z = 182.85



Mass Spectra (LC-MS)[59]

There is formation of $[SOCl_2]^+$ and $[SOCl]^+$ on fragmentation[60] of [4]. Ions observed in mass spectrum are concurrent with the depicted formulae (Tables 8, 9),

Table 9: (m/z values of some fragments)

Comp.	Fragment	Calculated[52]	Observed	Relative abundance
[1]	$[SOCl_2]^+$	117.9	118.9	100%
	$[SOCl]^+$	82.93	84.0	17%
[2]	$[C_5H_4N_4S]^+$	152.01	154.14	100%
	$[C_5H_4N_4S]^{2+}$	76.00	77.51	26%
	$[MoOCl_2]^+$	183.83	182.85	66%
	$[Mo_2OCl_4(CH_3CN)_2]^+$	433.73	429.	3%
	$[Mo_2O_3Cl_4C_5H_2N_4S(CH_3CN)_2]^+$	615.72	610.19	8%
	$[Mo_2O_3Cl_6C_5H_2N_4S(CH_3CN)_2]^+$	685.66	684.21	4%
[3]	$[C_5H_4N_4S]^+$	152.01	154.15	100%
	$[MoOCl_2]^+$	183.83	182.86	20%
	$[Mo_2OCl_4(CH_3CN)_2]^+$	433.73	437.21	5%
	$[Mo_2O_3Cl_4C_5H_2N_4S(CH_3CN)_2]^+$	615.72	610.19	6%
	$[Mo_2O_3Cl_6C_5H_2N_4S(CH_3CN)_2]^+$	685.66	684.22	3%
	$[Mo_2O_3Cl_8(C_5H_2N_4S)_2(CH_3CN)_2]^+$	--	--	--
[4]	$[C_5H_5NS]^+$	111.01	111.00	4%
	$[C_5H_4NS\text{-}SN_4C_5]^+$	220.1	220.98	93%
	$[C_5H_4N\text{-}SN_4C_5]^+$	188.04	189.01	100%
	$[Mo_2O_3(C_5H_4NS\text{-}SN_4C^5)]^+$	463.80	460.04	4%
	$[Mo_2O_3(C_5H_4NS)]^+$	353.80	349.96	3%

CONCLUSION

[1] does not have any absorption in the region 2548-2602 cm^{-1} due to absence of S-H group in it. C=S stretching at 1261 and 1109 wave numbers are concurrent with presence of C=S group. 761 cm^{-1} absorption due to C-S stretching support formation of Mo-S bonds. Terminal υ(Mo=O) at 986 cm^{-1} is observed. S-H peak has not been observed in ^1H NMR of [1]. This indicates that S-H group is absent in [1]. Fragmentation pattern in GC-MS is compatible with the proposed formula.

[2] and [3] do not have any absorption around 2670 cm^{-1} because there is no S-H group in them. S-H bond does not exist because of presence of υ(C=S) at 1027 cm^{-1} in both of them. Ions observed in mass spectrum are concurrent with the depicted

formulae. S→Mo coordinate bond is likely to be present. Terminal υ(Mo=O) absorbs at 973 cm^{-1} in [2] and at 970 cm^{-1} in [3]. S-H peak is missing in ^1H NMR of [2] and [3]. LC-MS supports the predicted formulae. CH_3CN is present in in [2] and [3] as verified by the presence of its peak in ^1H NMR.

N-H group absorbs at 3383 cm^{-1} in [4]. Absence of any peak around 2708 cm^{-1} is because of missing S-H group it. C=S stretching at 1261 cm^{-1}, 1109 cm^{-1} are due to C=S group. C-S stretching at 767 cm^{-1}, 707 cm^{-1} depict Mo-S bond existence. υ(Mo=O) absorption at 983 cm^{-1} in [4] suggests presence of terminal Mo=O group it. Fragmentation pattern in LC-MS support the proposed formula.

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Conflict of interest

The authors do not have any conflict of interest.

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