

# Molybdenum(V) and Molybdenum(IV) Coordination Compounds from the Reactions of MoCl<sub>5</sub> with Sulfones

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## Abstract

The mononuclear complexes  $\text{MoCl}_5\text{L}$  ( $\text{L} = 2,5\text{-dihydrothiophene-1,1-dioxide}$ ), **1**, and  $\text{MoCl}_4\text{L}_2$  ( $\text{L} = \text{dimethylsulfone}$ , **2**;  $\text{diethylsulfone}$ , **3**;  $\text{diphenylsulfone}$ , **4**) were obtained by the reactions of  $\text{MoCl}_5$  with the corresponding sulfones at room temperature in dichloromethane, and were characterized by analytical and magnetic data, and by X-ray crystallography in the cases of **1** and **2**. The X-ray structure of **1** is the first one ever reported for an adduct of  $\text{MoCl}_5$  with a carbon-containing species.

*Keywords:* Molybdenum pentachloride, Coordination complexes, Metal reduction, Sulfones, X-ray structure

## 1. Introduction

Molybdenum pentachloride [1] is a versatile, oxophilic, cheap and environmentally acceptable chemical [2], that has been effectively employed as catalytic precursor for a large variety of organic reactions [3]. These features have triggered the exploration and the advance in the knowledge of the coordination chemistry of  $\text{MoCl}_5$  [4]. In this context, possible drawbacks are represented by the high moisture sensitivity of  $\text{MoCl}_5$  and the variety of reaction pathways that may proceed when  $\text{MoCl}_5$  is allowed to contact with potential ligands [4b-h, 5, 6]. In particular, the two main pathways observed in the reactions of  $\text{MoCl}_5$  with oxygen donors are the oxygen abstraction by the metal centre to give oxido-molybdenum complexes [4, 5, 7] and the  $\text{Mo(V)}$  to  $\text{Mo(IV)}$  reduction resulting in the formation of  $\text{MoCl}_4$  adducts [4]. This mono-electron reduction is usually accompanied by the release of elemental chlorine [4b]. As a consequence of such a high reactivity, simple derivatives of  $\text{MoCl}_5$  with formula  $\text{MoCl}_5\text{L}$  are extremely rare [4a, 8]: the only crystallographic characterization refers to  $\text{MoCl}_5(\text{OPCl}_3)$  [8].

Studies on the interaction of MoCl<sub>5</sub> with compounds containing the S–O functionality are rather sparse in the literature. The chemistry of MoCl<sub>5</sub> with dimethylsulphoxide was tentatively described in the sixties [9], while we have recently reported the synthesis of the polynuclear oxido complexes Mo<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>[μ-κ<sup>2</sup>-1,4-Me(SO<sub>3</sub>Me)C<sub>6</sub>H<sub>4</sub>] and Mo<sub>4</sub>O<sub>4</sub>Cl<sub>8</sub>[μ<sub>3</sub>-1,4-Me(SO<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>4</sub> [10].

In the present paper, we present the results of our investigation on the reactivity of MoCl<sub>5</sub> with a series of sulfones, R<sub>2</sub>SO<sub>2</sub>, including the first X-ray characterization of a MoCl<sub>5</sub> adduct with a carbon-containing species. It is remarkable that sulfones have been rarely used as ligands in general; fully characterized examples of sulfone metal complexes are limited to mono- and dinuclear group 4 derivatives [11], Co<sub>2</sub>Cl<sub>4</sub>(μ-Et<sub>2</sub>SO<sub>2</sub>-O,O')<sub>2</sub> [12], Rh<sub>2</sub>(CF<sub>3</sub>COO)<sub>4</sub>(Me<sub>2</sub>SO<sub>2</sub>)<sub>2</sub> [13], and Cu<sub>3</sub>Cl<sub>6</sub>(C<sub>4</sub>H<sub>8</sub>SO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub> [14].

## 2. Results and Discussion

Molybdenum pentachloride reacts with sulfones R<sub>2</sub>SO<sub>2</sub> [R<sub>2</sub> = –CH<sub>2</sub>CH=CH–CH<sub>2</sub>–, Me<sub>2</sub>, Et<sub>2</sub>, Ph<sub>2</sub>], in dichloromethane at room temperature, affording mononuclear Mo(V) or Mo(IV) complexes, depending on R (Scheme 1).

**Insert Scheme 1 about here.**

The new complexes **1-4** could be isolated in 45-55% yields. They are readily soluble in chlorinated solvents and are rapidly hydrolyzed by moisture with release of the sulfone. It is plausible that the formation of **1-4** proceeds with initial, symmetric cleavage of the dinuclear structure of molybdenum pentachloride [1], to give MoCl<sub>5</sub>L adducts. The same feature is frequently observed in the coordination chemistry of MCl<sub>5</sub> (M = Nb, Ta), which are isostructural with MoCl<sub>5</sub> [15]. Moreover, we previously proposed, on the basis of DFT calculations, that the formation of MoCl<sub>5</sub>L from Mo<sub>2</sub>Cl<sub>10</sub> and cyclic ethers (L) is a strongly exothermic process [4b].

We were not able to detect intermediates in the course of the synthesis of **2-4**, therefore the conversion of  $\text{MoCl}_5\text{L}$  and unreacted L (L =  $\text{Me}_2\text{SO}_2$ ,  $\text{Et}_2\text{SO}_2$ ,  $\text{Ph}_2\text{SO}_2$ ) into **2-4** should be a fast process. The complexes **2-4** were obtained as the prevalent products even when using a sulfone/Mo = 1 molar ratio. On the other hand, the yield of the reaction affording **1** did not substantially change when using a two-fold molar excess of the sulfone.

The unusual outcome of the reaction of  $\text{MoCl}_5$  with the cyclic compound 2,5-dihydrothiophene 1,1-dioxide might be the consequence of the peculiar electronic and steric properties of the latter, stabilizing **1**. It is possible that  $\text{R}_2\text{SO}_2$  (R = Me, Et, Ph), due to higher steric demand compared to 2,5-dihydrothiophene 1,1-dioxide, favor the release of one chlorine from the  $\text{MoCl}_5(\text{R}_2\text{SO}_2)$  intermediates, thus leading to the formation of **2-4**.

The magnetic moments ( $\mu_{\text{eff}}$ ) (1.57 BM for **1** and 2.20 - 2.37 BM for **2-4**) are significantly lower than the spin only value calculated for one or two unpaired electrons, respectively. This is true especially for the Mo(IV) complexes **2-4**, in view of the spin-orbit coupling for the triplet ground state derived from the  $t_{2g}^2$  electronic configuration. All of the observed values fall in within the ranges typical of  $\text{MoCl}_5\text{L}$  and  $\text{MoCl}_4\text{L}_2$  complexes, respectively [4b,c,e,f, 16].

Complexes **1** and **2** were crystallized from dichloromethane/heptane mixtures and the crystals were studied by X-ray diffraction methods (Figures 1 - 2, Tables 1 - 2). **1** represents the first example of a structurally characterized Mo(V) complex of the type  $\text{MoCl}_5\text{L}$  (L = organic molecule), and also the first example of a transition metal complex containing the  $[\text{O}_2\text{S}-\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2-]$  ligand. The C(2)–C(3) distance [1.327(12) Å] is typical for a double bond, whereas C(1)–C(2) and C(3)–C(4) [1.499(11) and 1.508(11) Å] are single bonds [17]. As a consequence of the coordination of O(1) to Mo(1), the S(1)–O(1) bond [1.482(5) Å] is slightly longer than S(1)–O(2) [1.436(5) Å].

Complex **2** contains a Mo(IV) centre coordinated to four chloride and two  $\text{Me}_2\text{SO}_2$  ligands, the latter being in relative *cis* position. **2** adds to the family of  $\text{Mo}^{\text{IV}}\text{Cl}_4\text{L}_2$  complexes, which may

adopt both the *cis* and the *trans* configurations [4d-f, h]. As observed in **1**, the S(1)–O(1) [1.482(5) Å] and S(2)–O(3) [1.482(3) Å] contacts are slightly elongated compared to S(1)–O(2) [1.435(4) Å] and S(2)–O(4) [1.435(4) Å], as a consequence of the coordination of O(1) and O(3) to Mo(1). The structural parameters of the dimethyl sulfone ligand are comparable to those previously reported for the zirconium(IV) and rhodium(II) complexes *cis*-ZrCl<sub>4</sub>(Me<sub>2</sub>SO<sub>2</sub>)<sub>2</sub> [S–O 1.430 Å, av.; O–S–O 115.0(4)°] [11b] and Rh<sub>2</sub>(CF<sub>3</sub>COO)<sub>4</sub>(Me<sub>2</sub>SO<sub>2</sub>)<sub>2</sub> [S–O 1.453 Å, av.; O–S–O 115.48(6)°] [13], respectively, and for uncoordinated Me<sub>2</sub>SO<sub>2</sub> [S–O 1.448 Å, av.; O–S–O 117.2(6)°] [18]. The C–S–C angles in **2** [105.8(3) ° and 106.0(3) °] are larger than the corresponding angle in **1** [C(1)–S(1)–C(4) = 97.2(4) °], accounting for the different steric properties of the respective ligands in the two complexes (see above).

**Insert Table 1 and Figure 1 about here.**

In Table 3, the experimental values of the asymmetric [ $\nu_{\text{as}}(\text{OSO})$ ] and symmetric [ $\nu_{\text{s}}(\text{OSO})$ ] stretching vibration wavenumbers are reported for **1-4** and the sulfones treated in the present study. In agreement with the expected reduction of the sulfur-oxygen bond order on coordination, the OSO stretching modes are shifted to lower wavenumbers on going from each sulfone to the corresponding Mo complex. Furthermore, similarly to carboxylato complexes [19], the separation  $\Delta\nu$  between the asymmetric [ $\nu_{\text{as}}(\text{OSO})$ ] and symmetric [ $\nu_{\text{s}}(\text{OSO})$ ] stretching vibrations of the ligands should provide information about the type of coordination. In particular, bridging bidentate coordination of a sulfone is expected to result in smaller  $\Delta\nu$  with respect to the non coordinated molecule, due to S–O bond order decrease and consequent lowering of OSO vibrational coupling [20]. Also in the case of chelation, vibrational coupling is expected to be lower, thus producing a further decrease of  $\Delta\nu$  due to constrained O–S–O angle. Conversely, a greater  $\Delta\nu$  is expected for a monodentate sulfone, essentially reflecting the larger redshift of the symmetric stretching mode [ $\nu_{\text{s}}(\text{OSO})$ ] (pseudo single-bond order of the coordinated S–O bond). In

the present work, the observed large  $\Delta\nu$  separations (Table 3) confirm the monodentate coordination of the sulfone, as found by X-ray for **1** and **2**.

**Insert Table 3 about here**

### 3. Conclusions

This paper describes the preparation and the structural characterization of **molybdenum derivatives** containing sulfone ligands, representing rare examples of coordination compounds of transition elements with sulfones. Both 1:1 and 2:1 adducts have been isolated, depending on the nature of the sulfone but not on the stoichiometry employed. The formation of the 2:1 adducts is accompanied by monoelectron reduction of the Mo centre, i.e. a feature commonly observed in the context of the reactivity of  $\text{MoCl}_5$ . On the other hand, the isolation of the 1:1 adduct, obtained from  $\text{MoCl}_5$  and 2,5-dihydrothiophene 1,1-dioxide, is a much more unusual event. In all of the new complexes, monodentate coordination of the sulfones has been ascertained by IR spectroscopy and, in two cases, by X-ray diffraction.

### 4. Experimental

#### 4.1. General procedures

*Warning:* All the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at  $150^\circ\text{C}$  prior to use, evacuated ( $10^{-2}$  mmHg) and then filled with argon.  $\text{MoCl}_5$  was purchased from Strem (99.6% purity) and stored in sealed tubes under argon atmosphere. Once isolated, the metal products were conserved in sealed glass tubes under argon. The organic reactants were commercial products (Sigma Aldrich) stored under argon atmosphere as received. Solvents (Sigma Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. The chloride content was determined by the Mohr

method [21] on solutions prepared by dissolution of the solid samples in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of diluted HNO<sub>3</sub> up to neutralization. Molybdenum was analyzed according to the method proposed by Crouthamel and Johnson [22], upon dissolution of the solid samples (30-60 mg) into 100 mL of 4 M HCl; the calibration curve was obtained using (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O as standard ( $R^2 = 0.999$ ).

*4.2. Synthesis and isolation of MoCl<sub>5</sub>[OS(O)CH<sub>2</sub>CHCHCH<sub>2</sub>], 1.* A mixture of MoCl<sub>5</sub> (380 mg, 1.39 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL), in a Schlenk tube, was treated with 2,5-dihydrothiophene 1,1-dioxide (166 mg, 1.40 mmol). The mixture was stirred for 18 h at room temperature. The final red-brown solution was concentrated to ca. 3 mL and added of hexane (30 mL), thus affording a brown solid which was dried in vacuo. Yield: 0.279 mg, 51%. Crystals suitable for X-ray analysis were collected by slow diffusion of heptane into a dichloromethane solution, at -30°C. Anal. calcd for C<sub>4</sub>H<sub>6</sub>Cl<sub>5</sub>MoO<sub>2</sub>S: C, 12.28; H, 1.55; Cl, 45.29; Mo, 24.51. Found: C, 12.39; H, 1.43; Cl, 44.96; Mo, 24.30. IR (solid state):  $\nu = 3083w, 2971m, 2926m, 1615w, 1393m, 1387m, 1339m, 1281s, 1243vs$  [ $\nu_{\text{asym}}(\text{OSO})$ ],  $1128s, 1038m, 1049vs$  [ $\nu_{\text{sym}}(\text{OSO})$ ],  $991vs, 968s, 943m, 915m, 902w-m, 855w, 736w, 702m$ . Magnetic measurement:  $\chi_M^{\text{corr}} = 1.02 \times 10^{-3}$  cgsu ( $1.28 \times 10^{-8}$  SI units),  $\mu_{\text{eff}} = 1.57$  BM.

*4.3. Synthesis and isolation of MoCl<sub>4</sub>[OS(O)R<sub>2</sub>]<sub>2</sub> (R = Me, 2; Et, 3; Ph, 4).* Complexes **2-4** were synthesized by using a procedure analogous to that described for **1**. Crystals of **2** suitable for X-ray analysis were collected from a CH<sub>2</sub>Cl<sub>2</sub>/heptane mixture at -30 °C.

*MoCl<sub>4</sub>[OS(O)Me<sub>2</sub>]<sub>2</sub>, 2.* From MoCl<sub>5</sub> (500 mg, 1.83 mmol) and Me<sub>2</sub>SO<sub>2</sub> (350 mg, 3.72 mmol). Yield 366 mg, 47%. Anal. calcd for C<sub>4</sub>H<sub>12</sub>Cl<sub>4</sub>MoO<sub>4</sub>S<sub>2</sub>: C, 11.28; H, 2.84; Cl, 33.29; Mo, 22.52. Found: C, 11.40; H, 2.73; Cl, 33.12; Mo, 22.66. IR (solid state):  $\nu = 3013m, 2916m, 1393m, 1327m-s, 1312s, 1264s$  [ $\nu_{\text{asym}}(\text{OSO})$ ],  $1242m, 1214m-s, 1189w, 1092w-sh, 1059vs$  [ $\nu_{\text{sym}}(\text{OSO})$ ],

1008m-s, 945vs, 770s, 696w. Magnetic measurement:  $\chi_M^{\text{corr}} = 2.09 \times 10^{-3}$  cgsu ( $2.63 \times 10^{-8}$  SI units),  $\mu_{\text{eff}} = 2.24$  BM.

*MoCl<sub>4</sub>[OS(O)Et<sub>2</sub>]<sub>2</sub>*, **3**. From MoCl<sub>5</sub> (520 mg, 1.90 mmol) and Et<sub>2</sub>SO<sub>2</sub> (466 mg, 3.81 mmol). Yield 441 mg, 48%. Anal. calcd for C<sub>8</sub>H<sub>20</sub>Cl<sub>4</sub>MoO<sub>4</sub>S<sub>2</sub>: C, 19.93; H, 4.18; Cl, 29.41; Mo, 19.90. Found: C, 19.84; H, 4.25; Cl, 29.58; Mo, 20.02. IR (solid state):  $\nu = 2971\text{w}, 2927\text{w}, 2881\text{w}, 2119\text{w}, 1452\text{m}, 1404\text{m}, 1381\text{w}, 1276\text{s}, 1259\text{s}$  [ $\nu_{\text{asym}}(\text{OSO})$ ],  $1225\text{s}, 1082\text{s}, 1029\text{vs}$  [ $\nu_{\text{sym}}(\text{OSO})$ ],  $992\text{vs}, 789\text{s}, 730\text{s}, 661\text{w}$ . Magnetic measurement:  $\chi_M^{\text{corr}} = 2.34 \times 10^{-3}$  cgsu ( $2.95 \times 10^{-8}$  SI units),  $\mu_{\text{eff}} = 2.37$  BM.

*MoCl<sub>4</sub>[OS(O)Ph<sub>2</sub>]<sub>2</sub>*, **4**. From MoCl<sub>5</sub> (483 mg, 1.77 mmol) and Ph<sub>2</sub>SO<sub>2</sub> (773 mg, 3.54 mmol). Yield 668 mg, 56%. Anal. calcd for C<sub>24</sub>H<sub>20</sub>Cl<sub>4</sub>MoO<sub>4</sub>S<sub>2</sub>: C, 42.75; H, 2.99; Cl, 21.03; Mo, 14.23. Found: C, 42.53; H, 3.07; Cl, 21.17; Mo, 14.09. IR (solid state):  $\nu = 3067\text{w}, 1579\text{w}, 1475\text{w}, 1448\text{s}, 1288\text{vs}$  [ $\nu_{\text{asym}}(\text{OSO})$ ],  $1183\text{w}, 1151\text{s}, 1101\text{vs}$  [ $\nu_{\text{sym}}(\text{OSO})$ ],  $1045\text{s}, 1018\text{m}, 993\text{vs}, 840\text{w}, 756\text{s}, 728\text{vs}, 681\text{s}$ . Magnetic measurement:  $\chi_M^{\text{corr}} = 2.03 \times 10^{-3}$  cgsu ( $2.56 \times 10^{-8}$  SI units),  $\mu_{\text{eff}} = 2.20$  BM.

#### 4.4. X-ray Crystallographic Studies.

Crystal data and collection details for **1** and **2** are listed in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-K $\alpha$  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [23]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$  [24]

**Insert Table 4 about here.**



**Appendix A. Supplementary data.** CCDC 1410031 (**1**) and 1410032 (**2**) contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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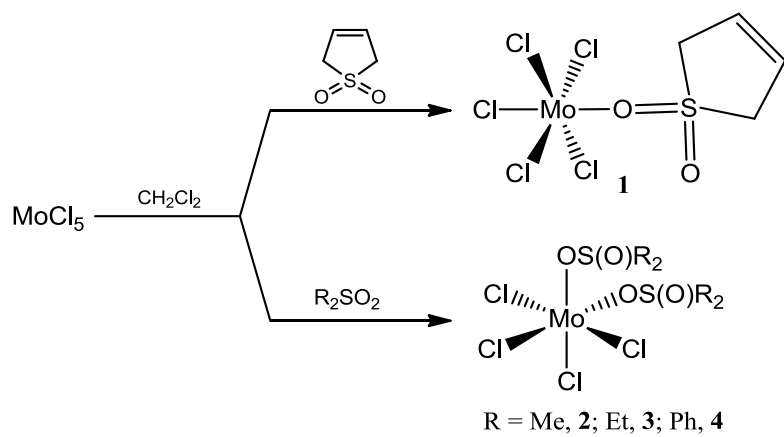
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**Scheme 1** Preparation of Mo sulfone complexes.

## Captions for Figures and Tables

Figure 1. Molecular structure of **1**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level.

Figure 2. Molecular structure of **2**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level.

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Table 3. Asymmetric and symmetric stretching vibrations of coordinated and non coordinated sulfones

Table 4. Crystal data and experimental details for **1** and **2**.

## TABLES

**Table 1.** Selected bond distances (Å) and angles (°) for **1**.

Mo(1)-Cl(1)	2.2321(19)	Mo(1)-Cl(2)	2.2682(19)
Mo(1)-Cl(3)	2.3384(18)	Mo(1)-Cl(4)	2.2782(19)
Mo(1)-Cl(5)	2.3163(18)	Mo(1)-O(1)	2.169(5)
S(1)-O(1)	1.482(5)	S(1)-O(2)	1.436(5)
S(1)-C(1)	1.789(7)	S(1)-C(4)	1.798(7)
C(1)-C(2)	1.499(11)	C(3)-C(4)	1.508(11)
C(2)-C(3)	1.327(12)		
O(1)-Mo(1)-Cl(1)	176.48(14)	Cl(2)-Mo(1)-Cl(4)	166.92(7)
Cl(3)-Mo(1)-Cl(5)	175.09(6)	Mo(1)-O(1)-S(1)	134.7(3)
O(1)-S(1)-O(2)	117.0(3)	S(1)-C(1)-C(2)	102.0(5)
C(1)-C(2)-C(3)	116.9(7)	C(2)-C(3)-C(4)	117.1(7)
C(3)-C(4)-S(1)	101.3(5)	C(1)-S(1)-C(4)	97.2(4)

**Table 2.** Selected bond distances (Å) and angles (°) for **2**.

Mo(1)-Cl(1)	2.2488(15)	Mo(1)-Cl(2)	2.3347(14)
Mo(1)-Cl(3)	2.3148(14)	Mo(1)-Cl(4)	2.3410(14)
Mo(1)-O(1)	2.150(3)	Mo(1)-O(3)	2.153(3)
S(1)-O(1)	1.482(3)	S(2)-O(3)	1.482(3)
S(1)-O(2)	1.435(4)	S(2)-O(4)	1.435(4)
S(1)-C(1)	1.751(5)	S(2)-C(3)	1.756(5)
S(1)-C(2)	1.751(5)	S(2)-C(4)	1.748(5)
O(1)-Mo(1)-O(3)	82.61(13)	Cl(3)-Mo(1)-Cl(4)	168.47(5)
O(1)-Mo(1)-Cl(1)	172.99(10)	O(3)-Mo(1)-Cl(2)	174.56(10)
Mo(1)-O(1)-S(1)	137.5(2)	Mo(1)-O(3)-S(2)	136.4(2)
O(1)-S(1)-O(2)	115.6(2)	O(3)-S(2)-O(4)	116.3(2)
C(1)-S(1)-C(2)	106.0(3)	C(3)-S(2)-C(4)	105.8(3)

**Table 3.** Asymmetric and symmetric stretching vibration wavenumbers ( $\text{cm}^{-1}$ ) of the [OSO] moiety.

Species	$\nu_{\text{asym}}$	$\nu_{\text{sym}}$	$\Delta\nu$
2,5-dihydrothiophene-1,1-dioxide	1263	1144	119
$\text{MoCl}_3[\text{OS}(\text{O})\text{CH}_2\text{CHCH}_2]$	1243	1049	194
$\text{Me}_2\text{SO}_2$	1281	1131	150
$\text{MoCl}_4[\text{OS}(\text{O})\text{Me}_2]_2$	1264	1059	205
$\text{Et}_2\text{SO}_2$	1279	1121	158
$\text{MoCl}_4[\text{OS}(\text{O})\text{Et}_2]_2$	1259	1029	230
$\text{Ph}_2\text{SO}_2$	1308	1152	156
$\text{MoCl}_4[\text{OS}(\text{O})\text{Ph}_2]_2$	1288	1101	187

**Table 4.** Crystal data and experimental details for **1** and **2**.

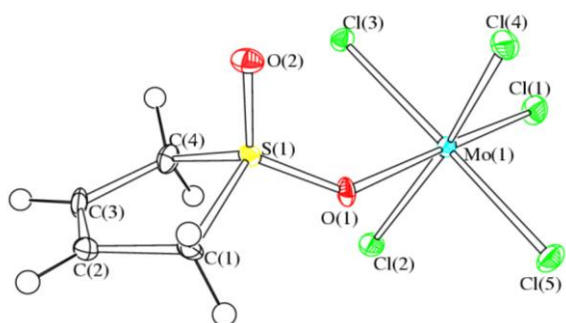
	<b>1</b>	<b>2</b>
Formula	$\text{C}_4\text{H}_6\text{Cl}_3\text{MoO}_2\text{S}$	$\text{C}_4\text{H}_{12}\text{Cl}_4\text{MoO}_4\text{S}_2$
$F_w$	391.34	426.00
$T$ , K	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space Group	$P\bar{1}$	$P2_1/n$
$a$ , Å	5.8024(14)	6.3648(10)
$b$ , Å	9.217(2)	14.228(2)
$c$ , Å	11.479(4)	15.352(2)
$\alpha$ , °	67.231(3)	90
$\beta$ , °	88.163(4)	98.858(2)
$\gamma$ , °	82.224(3)	90
Cell Volume, Å <sup>3</sup>	560.7(3)(3)	1373.7(4)
$Z$	2	4
$D_x$ , g cm <sup>-3</sup>	2.318	2.060
$\mu$ , mm <sup>-1</sup>	2.510	2.027
$F(000)$	378	840
Independent reflections	1909 [ $R_{\text{int}} = 0.0277$ ]	2680 [ $R_{\text{int}} = 0.0591$ ]

Data / restraints / parameters	1909 / 0 / 119	2680 / 0 / 136
Goodness on fit on $F^2$	1.159	1.020
$R_1$ ( $I > 2\sigma(I)$ )	0.0426	0.0434
$wR_2$ (all data)	0.1611	0.1058
Largest diff. peak and hole, $e \text{ \AA}^{-3}$	1.221 / -1.077	0.948 / -0.644

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**Figure 1**



**Figure 2**

