

GROUP VI PRECURSOR COMPOUNDS

Field of the Invention

The present invention relates to certain precursors for the vapor deposition of certain
5 Group VI -containing materials and to a method for their preparation.

Background of the Invention

In consequence of its characteristics of extremely high melting point, low coefficient
of thermal expansion, low resistivity, and high thermal conductivity, Group VI metals such as
10 molybdenum, chromium, and tungsten are increasingly utilized in the manufacture of
semiconductor devices, including use in diffusion barriers, electrodes, photomasks, power
electronics substrates, low-resistivity gates, flat-panel displays, and interconnects.

Such utility has motivated efforts to achieve deposition of molybdenum, chromium,
and tungsten films for such applications that is characterized by high conformality of the
15 deposited film and high deposition rate to accommodate efficient high-volume manufacturing
operations. This in turn has enabled efforts to develop improved molybdenum and tungsten
source reagents useful in vapor deposition operations, as well as improved process
parameters utilizing such reagents.

Summary of the Invention

The invention provides a facile process for preparing various Group VI precursor
compounds useful in the vapor deposition of certain Group VI metals onto solid substrates,
especially microelectronic semiconductor device substrates. The process provides an
effective means to obtain and isolate such volatile solid or liquid materials, which can then be
25 sources of molybdenum, chromium, or tungsten-containing materials to be deposited on such
substrates. Additionally, the invention provides a method for vapor deposition of such
compounds onto microelectronic device substrates.

Brief Description of the Drawings

30 Figure 1 is a three-dimensional solid-state crystal structure depiction of
 $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

Figure 2 is a three-dimensional solid-state crystal structure depiction of
 $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

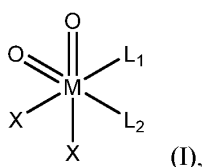
Figure 3 is a plot of molybdenum deposition rate ($\text{\AA}/\text{cycle}$) versus on substrate temperature ($^{\circ}\text{C}$) on a titanium nitride substrate using $\text{MoO}_2\text{Cl}_2(\text{dimethoxyethane})$ as precursor.

Figure 4 is a plot of XRF Carbon (X-ray fluorescence analysis for carbon) ($\mu\text{gm}/\text{cm}^2/100\text{\AA Mo}$) versus substrate temperature ($^{\circ}\text{C}$) on a titanium nitride substrate using $\text{MoO}_2\text{Cl}_2(\text{dimethoxyethane})_2$ as precursor. Figures 3 and 4 thus illustrate the process parameters under which Mo is preferentially deposited versus MoC.

Figure 5 is a three-dimensional solid-state crystal structure depiction of $\text{MoO}_2\text{Cl}_2(\text{tetrahydrofuran})_2$.

Detailed Description of the Invention

In a first aspect, the invention provides a process for preparing compounds of the Formula (I)



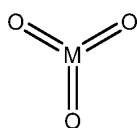
wherein M is chosen from molybdenum, chromium, and tungsten, X is chosen from fluoro, chloro, bromo, and iodo, and each L_1 and L_2 are the same or different and constitute:

(i) a monodentate hydrocarbyl ligand coordinated with M, or

(ii) are taken together to form a bidentate hydrocarbyl ligand coordinated with M;

which comprises:

(A) contacting a compound of the formula



with (a) water containing about 0.1% (w/w) to about 48% (w/w) of a compound of the formula HX , and (b) a compound of the formula L_1 and/or L_2 ; followed by (B) isolation of the compound of Formula (I) as a solid or liquid.

As used herein, the term "hydrocarbyl" represents a $\text{C}_2\text{-C}_{16}$ group comprising carbon and hydrogen atoms and optionally containing at least one nitrogen, sulfur, or oxygen atom. Such hydrocarbyl groups may comprise straight- or branched-chain saturated, unsaturated,

and polyunsaturated alkylene and cycloalkylene groups and may be substituted, for example, with one to five groups selected from C₁-C₆ alkoxy, carboxyl, nitro, amino, C₂-C₆ aminocarbonyl, C₂-C₆ amido, cyano, C₂-C₇-alkoxycarbonyl, C₂-C₇-alkanoyloxy, hydroxy, aryl, heteroaryl, thiol, thioether, C₂-C₁₀ dialkylamino, C₃-C₁₅ trialkylammonium, and halogen. The terms "C₁-C₆ alkoxy", "C₂-C₇-alkoxycarbonyl", and "C₂-C₇-alkanoyloxy" are used to denote groups corresponding to the structures --OR³, --CO₂R³, and --OCOR³, respectively, wherein R³ is C₁-C₆ alkyl or substituted C₁-C₆ alkyl. The terms "C₂-C₁₆ aminocarbonyl" and "C₂-C₁₆ amido" are used to denote groups corresponding to the structures --NHCOR⁴, --CONHR⁴, respectively, wherein R⁴ is C₁-C₇ alkyl. As noted above, L₁ and L₂ comprise such hydrocarbyl groups, and contain at least one nitrogen, sulfur, or oxygen atom.

L₁ and L₂ are chosen independently and represent monodentate ligands or are taken together to form bidentate ligands. In general, L₁ and L₂ comprise a hydrocarbyl group having at least one oxygen, sulfur, or nitrogen atom. Such ligands may, for example, be chosen from t-butyl nitrile, toluene, tetrahydrofuran, and acetonitrile, and such groups optionally substituted by one or more groups chosen from halo, cyano, nitro, C₁-C₆ alkyl, C₁-C₆ alkoxy, tetrahydrofuran, C₁-C₆ alkoxycarbonyl, and phenyl. Further examples include 1,2-dimethoxyethane; 1,2-diethoxyethane; 1,2-dimethoxypropane; N,N-dimethylacetamide; N,N-dimethylformamide; N,N-dimethylcyanoacetamide; diamines and triamines such as N,N,N',N'-tetramethylethylenediamine, ethylenediamine, hexaethylene diamine, diethylene triamine, and diethylenetriamine; dimethylsulfoxide; and glycols such as ethylene glycol, propylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol.

The step (B) isolation of the compound of Formula(I) may be effected by extraction of the compound from the aqueous reaction mixture with a water-immiscible solvent, followed by evaporation of solvent or crystallization. Alternately, a water-miscible solvent such as an alcohol (*e.g.*, ethanol) may be added to the aqueous solution to induce precipitation of the desired compound of Formula (I). The solid compounds of Formula (I) may be purified if desired, by crystallization and/or vacuum sublimation.

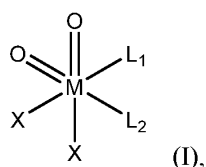
It will be appreciated that the structure above depicting the compounds of the invention is drawn in a two-dimensional format, not necessarily representing its three-dimensional orientation.

Additionally, the compounds of Formula (I) once formed, may be reacted with additional/different compound(s) of formula L₁ and/or L₂ to form a different compound of

Formula (I) via a displacement reaction. Accordingly, in a further embodiment, the invention provides the above process, further comprising the step of contacting the compound of the Formula (I) with a compound chosen from t-butyl nitrile, toluene, tetrahydrofuran, and acetonitrile, and such groups optionally substituted by one or more groups chosen from halo, cyano, nitro, C₁-C₆ alkyl, C₁-C₆ alkoxy, tetrahydrofuran, C₁-C₆ alkoxy carbonyl, and phenyl; 1,2-dimethoxyethane; 1,2-diethoxyethane; 1,2-dimethoxypropane; N,N-dimethylacetamide; N,N-dimethylformamide; N,N-dimethylcyanoacetamide; N,N,N',N'-tetramethylethylenediamine, ethylenediamine, hexaethylene diamine, diethylene triamine, and diethylenetriamine; dimethylsulfoxide; and ethylene glycol, propylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol,

to afford a compound of Formula (I) having a different ligand of formula L₁ and/or L₂.

In a further embodiment, the invention provides a compound of Formula (I)



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wherein M is chosen from molybdenum, chromium, and tungsten, X is chosen from fluoro, chloro, bromo, and iodo, and each L₁ and L₂ are the same or different and constitute:

(i) a monodentate hydrocarbyl ligand coordinated with M, or

(ii) are taken together to form a bidentate hydrocarbyl ligand coordinated with M;

20 in solid or liquid form. In certain embodiments the compound of Formula (I) possesses less than about 3 weight percent impurities. In other embodiments, the compound of Formula (I) possesses less than 1 weight percent impurities. In other embodiments, the compound of Formula (I) is isolated in crystalline form. Particular examples of such crystalline forms of the compounds of Formula (I) include MoO₂Cl₂(CH₃CN)₂ and WO₂Cl₂(CH₃CN)₂ and MoO₂Cl₂(tetrahydrofuran)₂. In a further embodiment, the invention provides a compound having the formula MoO₂Cl₂(CH₃CN)₂ in crystalline form and having the x-ray crystallographic structure as shown in Figure 1. In a further embodiment, the invention provides a compound having the formula WO₂Cl₂(CH₃CN)₂ in crystalline form and having the x-ray crystallographic structure as shown in Figure 2. In a further embodiment, the invention provides a compound having the formula MoO₂Cl₂(tetrahydrofuran)₂ in crystalline

form and having the x-ray crystallographic structure as shown in Figure 5. These crystalline forms are further characterized in the Experimental Section below.

In a further embodiment, the invention provides a compound having the formula $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$, and having an orthorhombic crystal system, and unit cell dimensions of about

$$\begin{array}{ll} a = 12.0350(8) \text{ \AA} & \alpha = 90^\circ \\ b = 11.5956(9) \text{ \AA} & \beta = 90^\circ \\ c = 26.5807(15) \text{ \AA} & \gamma = 90^\circ. \end{array}$$

In a further embodiment, the invention provides a compound having the formula $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$, and having an orthorhombic crystal system, and unit cell dimensions of about

$$\begin{array}{ll} a = 8.7091(6) \text{ \AA} & \alpha = 90^\circ \\ b = 8.2536(7) \text{ \AA} & \beta = 90^\circ \\ c = 12.8021(8) \text{ \AA} & \gamma = 90^\circ. \end{array}$$

In a further embodiment, the invention provides a compound having the formula $\text{MoO}_2\text{Cl}_2(\text{tetrahydrofuran})_2$, and having an orthorhombic crystal system, and unit cell dimensions of about

$$\begin{array}{ll} a = 7.4048(4) \text{ \AA} & \alpha = 90^\circ \\ b = 12.5437(6) \text{ \AA} & \beta = 90^\circ \\ c = 13.7487(7) \text{ \AA} & \gamma = 90^\circ. \end{array}$$

As used herein the term "unit cell" refers to the smallest and simplest volume element of a crystal that is completely representative of the unit of pattern of the crystal. The dimensions of the unit cell are defined by six numbers: dimensions a, b, and c and angles α , β , and γ . A crystal is an efficiently packed array of many unit cells.

As used herein, the term "orthorhombic unit cell" refers to a unit cell wherein $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$.

As used herein, "crystal lattice" refers to the array of points defined by the vertices of packed unit cells, as determined by single-crystal x-ray diffraction analysis.

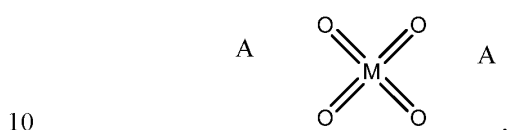
As used herein, "space group" refers to the symmetry of a unit cell. In a space group designation (*e.g.*, C2) the capital letter indicates the lattice type and the other symbols

represent symmetry operations that can be carried out on the unit cell without changing its appearance.

In the process of the invention, suitable water-immiscible solvents include dichloromethane, ethyl acetate, diethyl ether, toluene, benzene, pentane, and the like.

- 5 In one embodiment, the process is conducted at elevated temperatures, for example from about 20 °C to about 100 °C.

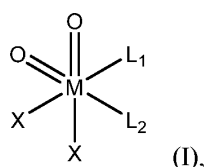
The compounds of Formula (I) may also be prepared by utilizing a starting material of the formula



i.e., compounds of the general formula A_2MO_4 , wherein M is chosen from chromium, molybdenum, or tungsten, and A is chosen from group I and II metal or ammonium cations. Examples of such cations include Li^+ , Na^+ , K^+ , NH_4^+ , alkylammonium compounds, and the like. Such compounds can be similarly reacted with HX in the presence of a compound of

15 the formula L_1 and/or L_2 to afford the desired precursor compounds.

- The process of the invention affords certain compounds which are in turn useful in the vapor deposition of certain Group VI metals onto various substrates, including microelectronic semiconductor device substrates. Thus, in another aspect, the invention provides a process for forming a material on a substrate, comprising contacting the substrate
- 20 with a compound of the Formula (I)



wherein M is chosen from molybdenum, chromium, and tungsten, X is chosen from fluoro, chloro, bromo, and iodo, and each L_1 and L_2 are the same or different and constitute:

- (i) a monodentate hydrocarbyl ligand coordinated with M, or
- 25 (ii) are taken together to form a bidentate hydrocarbyl ligand coordinated with M;
- depositing the molybdenum, chromium, or tungsten-containing material onto the substrate, under vapor deposition conditions.

The substrate utilized in the deposition process of the invention may be of any suitable type, and may for example comprise a semiconductor device substrate, *e.g.*, a silicon

substrate, a silicon dioxide substrate, or other silicon-based substrate. In various embodiments, the substrate may comprise one or more metallic or dielectric substrates, for example, Co, Cu, Al, W, WN, WC, TiN, Mo, MoC, SiO₂, W, SiN, WCN, Al₂O₃, AlN, ZrO₂, HfO₂, SiO₂, lanthanum oxide (La₂O₃), tantalum nitride (TaN), ruthenium oxide (RuO₂), iridium oxide (IrO₂), niobium oxide (Nb₂O₃), and yttrium oxide (Y₂O₃).

In certain embodiments, for example in the case of an oxide substrate such as silicon dioxide, or alternatively a silicon or polysilicon substrate, the substrate may be processed or fabricated to include a barrier layer thereon, *e.g.*, titanium nitride, for subsequently deposited material.

In one embodiment, the molybdenum, chromium, or tungsten-containing layer deposited on the substrate surface may for example be formed by pulsed chemical vapor deposition (CVD) or atomic layer deposition (ALD) or other vapor deposition technique, without the prior formation of a nucleation layer and thus directly with vapor derived from the compounds of Formula (I). The respective Formula (I) vapor contacting steps may be carried out alternately and repetitively for as many cycles as are desired to form the desired thickness of the molybdenum, chromium, or tungsten film. In various embodiments, the contact of the substrate (*e.g.*, titanium nitride) layer with such vapor is conducted at temperature as low as 350°, and in other embodiments in a range of from 300° C to 750° C.

With vapor derived from compounds of Formula (I), the molybdenum, chromium, or tungsten-containing material can be deposited directly onto the substrate to form a bulk deposit of elemental molybdenum, chromium, or tungsten or their corresponding oxides. The concentration of H₂ is critical towards the formation of metal or oxide, as greater than four molar equivalents or an excess of H₂ is required for metal formation. Less than four (4) molar equivalents of H₂ will result in the formation of varying amounts of an oxide of such metals, and thus will require further exposure to H₂ in order to reduce the metal oxide thus formed.

In various embodiments, the molybdenum, chromium, or tungsten-containing material is deposited on the substrate surface at temperature in a range of from 300° C to 750° C. The process may be carried out so that the vapor deposition conditions produce deposition of elemental molybdenum, chromium, or tungsten as the metal-containing material on the substrate. The vapor deposition conditions may be of any suitable character, and may for example comprise presence of hydrogen or other reducing gas, to form a bulk layer of elemental molybdenum, chromium, or tungsten on the substrate.

More generally, the broad method of forming a molybdenum, chromium, or tungsten - containing material on a substrate in accordance with the present disclosure may comprise vapor deposition conditions comprising presence of hydrogen or other reducing gas. The molybdenum, chromium, or tungsten--containing material may be deposited on the barrier layer or surface in the presence or absence of hydrogen. For example, the barrier layer may be constituted by titanium nitride, and the titanium nitride layer may be contacted with vapor derived from the compounds of Formula (I) in the presence of hydrogen.

In another embodiment, an oxidizing co-reactant such as oxygen may be added to the process when using compounds of Formula (I) as a means of depositing a metal oxide thin film, such as MoO₂, WO₃, and Cr₂O₃.

It will be appreciated that the method of the present invention may be carried out in numerous alternative ways, and under a wide variety of process conditions. The process of the invention may for example be carried out in a process for making a semiconductor device on the substrate. The semiconductor device may be of any suitable type, and may for example comprise a DRAM device, 3-D NAND device, or other device or device integrated structure. In various embodiments, the substrate may comprise a via in which the molybdenum-containing material is deposited. The device may, for example, have an aspect ratio of depth to lateral dimension that is in a range of from 10:1 to 40:1. In still other embodiments, the device may be a film used in a flat-panel display or mobile device.

The process chemistry for depositing molybdenum-containing material in accordance with the present invention may include deposition of elemental molybdenum, Mo(0), by the reaction $2 \text{MO}_2\text{Cl}_2[(\text{L}_1)(\text{L}_2)] + 6\text{H}_2 \rightarrow 2\text{M}(\text{wherein M} = \text{molybdenum, chromium, or tungsten}) + 4\text{HCl} + 4\text{H}_2\text{O}$. The molybdenum, chromium, or tungsten -containing material (M) deposited in accordance with the method of the present invention may be characterized by any appropriate evaluation metrics and parameters, such as deposition rate of the molybdenum, chromium, or tungsten -containing material, film resistivity of the deposited molybdenum, chromium, or tungsten -containing material, film morphology of the deposited molybdenum, chromium, or tungsten -containing material, film stress of the deposited molybdenum, chromium, or tungsten -containing material, step coverage of the material, and the process window or process envelope of appropriate process conditions. Any appropriate evaluation metrics and parameters may be employed, to characterize the deposited material and correlate same to specific process conditions, to enable mass production of corresponding semiconductor products. Advantageously, the process of the invention is capable of depositing a film of high purity molybdenum, chromium, or tungsten onto a semiconductor

device. Accordingly, in a further aspect, the invention provides a semiconductor device having a molybdenum film deposited thereon, wherein said film comprises greater than 99% molybdenum, chromium, or tungsten.

5 In certain embodiments, the disclosure relates to a method of forming a molybdenum, chromium, or tungsten -containing material on a substrate, comprising depositing molybdenum, chromium, or tungsten on the substrate surface by a chemical vapor deposition (CVD) process utilizing precursor compounds of Formula (I), to produce the molybdenum, chromium, or tungsten -containing material on the substrate.

Such process may be carried out in any suitable manner as variously described herein.

10 In specific embodiments, such method may be conducted with a vapor deposition process comprising chemical vapor deposition, *e.g.*, pulsed chemical vapor deposition. The method may be carried out so that the resulting molybdenum, chromium, or tungsten--containing material is composed essentially of elemental molybdenum, chromium, or tungsten, and in various embodiments the molybdenum, chromium, or tungsten may be deposited on the

15 substrate surface in the presence of hydrogen or other suitable reducing gas. In other embodiments of the invention, the precursors of Formula (I) and reducing gas may be pulsed sequentially to deposit the molybdenum film on pulsing with the pulse sequence being optimized for film conformality and film resistivity. The method may be carried out in the manufacture of a semiconductor device product, such as a DRAM device, or a 3-D NAND, a

20 logic device, a flat-panel display, or an IC packaging component.

Generally, the methods of the present disclosure for forming molybdenum, chromium, or tungsten -containing material on a substrate may be carried out to achieve deposition of the molybdenum, chromium, or tungsten--containing material at high levels of step coverage, *e.g.*, step coverage ranging from about 75% to about 100%.

25 This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

30 Experimental Section

Using the following general procedure, the compounds of Formula (I) may be prepared:

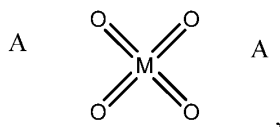
Synthetic Procedure No. 1.

MoO₃ (20.0 g, 138 mmol) was loaded into a 500 mL round bottom flask equipped with a magnetic stir bar. HCl (200 mL, 37%) was added directly to the MoO₃, the reaction flask outfitted with a water-cooled condenser (5 °C), and the resulting light-green suspension was heated to near reflux (95 °C) using an oil bath. After ~ 2 hours the reaction presented as a clear light-green solution. The reaction was cooled to room temperature before being placed in an ice bath. At this point, DME (50 mL) was added directly to the cooled solution and the reaction was warmed to room temperature and stirred overnight. The following morning the light-green solution was poured into a 1L separation funnel and extracted with DCM (2 x 200 mL). The organic layers were combined, dried using MgSO₄, filtered, placed in a 1L round-bottom flask equipped with a magnetic stir bar, and the solvent removed under reduced pressure to yield MoO₂Cl₂(dimethoxyethane) as an off-white solid. Mass = 12.68g, Yield = 31.8%. The product may be purified by vacuum sublimation (80 °C @ 25 mTorr). ¹H NMR (400 MHz, C₆D₆, 298K): δ 3.29 (s, 6H); 2.78 (s, 4H) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆, 298K): δ 70.68, 64.13 ppm.

Synthetic procedure No. 2

Of the general formula A₂MO₄, where M = chromium, molybdenum, or tungsten and A = lithium, sodium, or potassium.

Here, the general synthetic procedure and workup are very similar to procedure No. 1.



i.e., compounds of the general formula A₂MO₄, wherein M is chosen from chromium, molybdenum, or tungsten, and A is chosen group I and II metals, or ammonium cations. Examples include Li⁺, Na⁺, K⁺, NH₄⁺, alkylammonium compounds, and the like.

Synthetic Procedure No. 3

Ligand substitution can be utilized to synthesize the compounds of Formula (I). For example; the MoO₂Cl₂(N,N-dimethylformamide)₂ complex can be made using Procedure No.

1 above, and then the N,N-dimethylformamide ligands substituted for dimethoxyethane via solvolysis to generate MoO₂Cl₂(dimethoxyethane).

5

As noted above, Figure 1 is a three-dimensional solid-state crystal structure depiction of MoO₂Cl₂(CH₃CN)₂. This compound was subjected to x-ray crystallographic analysis and
10 yielded the following data:

Table 1. Crystal data and structure refinement for MoO₂Cl₂(CH₃CN)₂.

	Identification code	NB00618-002	
15	Empirical formula	C ₄ H ₆ Cl ₂ Mo N ₂ O ₂	
	Formula weight	280.95	
	Temperature	100.0 K	
	Wavelength	0.71073 Å	
	Crystal system	Orthorhombic	
20	Space group	Pnma	
	Unit cell dimensions	a = 12.0350(8) Å	α = 90°.
		b = 11.5956(9) Å	β = 90°.
		c = 26.5807(15) Å	γ = 90°.
	Volume	3709.4(4) Å ³	
25	Z, Z'	16, 4	
	Density (calculated)	2.012 Mg/m ³	
	Absorption coefficient	1.945 mm ⁻¹	
	F(000)	2176	
	Crystal size	0.24 x 0.19 x 0.18 mm ³	
30	Theta range for data collection	1.857 to 26.718°.	
	Index ranges	-15 ≤ h ≤ 15, -14 ≤ k ≤ 14, -33 ≤ l ≤ 32	
	Reflections collected	22254	
	Independent reflections	4134 [R(int) = 0.0475]	
	Completeness to theta = 25.242°	99.9 %	
35	Absorption correction	Semi-empirical from equivalents	
	Max. and min. transmission	0.7454 and 0.6516	
	Refinement method	Full-matrix least-squares on F ²	
	Data / restraints / parameters	4134 / 0 / 222	
	Goodness-of-fit on F ²	1.008	
40	Final R indices [I > 2σ(I)]	R1 = 0.0258, wR2 = 0.0518	
	R indices (all data)	R1 = 0.0388, wR2 = 0.0558	
	Extinction coefficient	0.00013(2)	
	Largest diff. peak and hole	0.492 and -0.462 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

		x	y	z	U(eq)
5	Mo(4)	7248(1)	2500	4414(1)	10(1)
	Mo(2)	2330(1)	7500	3151(1)	10(1)
	Mo(1)	2455(1)	2500	3069(1)	11(1)
	Mo(3)	7667(1)	7500	4464(1)	12(1)
10	Cl(2)	4372(1)	2500	2868(1)	17(1)
	Cl(3)	1038(1)	7500	2486(1)	19(1)
	Cl(4)	4104(1)	7500	3531(1)	15(1)
	Cl(5)	5845(1)	7500	4786(1)	20(1)
	Cl(7)	7535(1)	2500	3536(1)	17(1)
15	Cl(8)	7804(1)	2500	5264(1)	16(1)
	Cl(1)	877(1)	2500	3592(1)	19(1)
	Cl(6)	9054(1)	7500	3833(1)	19(1)
	O(1)	2102(2)	3651(1)	2715(1)	19(1)
	N(2)	3254(2)	6256(2)	2597(1)	13(1)
20	N(1)	3109(2)	3737(2)	3706(1)	16(1)
	N(3)	6849(2)	8742(2)	3887(1)	16(1)
	O(4)	6389(2)	1350(2)	4438(1)	18(1)
	O(3)	8142(2)	6347(2)	4788(1)	21(1)
	C(2)	3871(2)	5026(2)	4428(1)	17(1)
25	C(1)	3436(2)	4302(2)	4022(1)	13(1)
	C(4)	4342(2)	4940(2)	1977(1)	18(1)
	C(7)	9534(2)	4320(2)	4355(1)	10(1)
	N(4)	8773(2)	3745(2)	4367(1)	15(1)
	C(8)	10517(2)	5057(2)	4342(1)	15(1)
30	O(2)	1813(2)	8648(2)	3461(1)	19(1)
	C(3)	3728(2)	5680(2)	2325(1)	13(1)
	C(6)	5822(2)	10073(2)	3259(1)	17(1)
	C(5)	6407(2)	9324(2)	3608(1)	12(1)

Table 3. Bond lengths [Å] and angles [°] for MoO₂Cl₂(CH₃CN).

	Mo(4)-Cl(7)	2.3601(9)
	Mo(4)-Cl(8)	2.3561(9)
5	Mo(4)-O(4)	1.6885(17)
	Mo(4)-O(4)#1	1.6885(17)
	Mo(4)-N(4)#1	2.338(2)
	Mo(4)-N(4)	2.338(2)
	Mo(2)-Cl(3)	2.3547(9)
10	Mo(2)-Cl(4)	2.3623(9)
	Mo(2)-N(2)	2.343(2)
	Mo(2)-N(2)#2	2.343(2)
	Mo(2)-O(2)	1.6846(17)
	Mo(2)-O(2)#2	1.6846(17)
15	Mo(1)-Cl(2)	2.3672(10)
	Mo(1)-Cl(1)	2.3534(10)
	Mo(1)-O(1)#1	1.6867(17)
	Mo(1)-O(1)	1.6867(17)
	Mo(1)-N(1)	2.355(2)
20	Mo(1)-N(1)#1	2.355(2)
	Mo(3)-Cl(5)	2.3528(10)
	Mo(3)-Cl(6)	2.3671(10)
	Mo(3)-N(3)	2.323(2)
	Mo(3)-N(3)#2	2.323(2)
25	Mo(3)-O(3)#2	1.6885(17)
	Mo(3)-O(3)	1.6885(17)
	N(2)-C(3)	1.137(3)
	N(1)-C(1)	1.135(3)
	N(3)-C(5)	1.134(3)
30	C(2)-C(1)	1.462(3)
	C(4)-C(3)	1.462(3)
	C(7)-N(4)	1.133(3)
	C(7)-C(8)	1.461(3)
	C(6)-C(5)	1.453(3)
35	Cl(8)-Mo(4)-Cl(7)	155.09(4)
	O(4)#1-Mo(4)-Cl(7)	97.26(6)
	O(4)-Mo(4)-Cl(7)	97.26(6)

	O(4)#1-Mo(4)-Cl(8)	97.95(6)
	O(4)-Mo(4)-Cl(8)	97.94(6)
	O(4)#1-Mo(4)-O(4)	104.33(13)
	O(4)#1-Mo(4)-N(4)#1	165.97(8)
5	O(4)-Mo(4)-N(4)	165.97(8)
	O(4)-Mo(4)-N(4)#1	89.70(8)
	O(4)#1-Mo(4)-N(4)	89.70(8)
	N(4)-Mo(4)-Cl(7)	80.39(5)
	N(4)#1-Mo(4)-Cl(7)	80.39(5)
10	N(4)-Mo(4)-Cl(8)	80.08(5)
	N(4)#1-Mo(4)-Cl(8)	80.08(5)
	N(4)-Mo(4)-N(4)#1	76.27(11)
	Cl(3)-Mo(2)-Cl(4)	156.61(3)
	N(2)-Mo(2)-Cl(3)	80.86(5)
15	N(2)#2-Mo(2)-Cl(3)	80.86(5)
	N(2)-Mo(2)-Cl(4)	80.76(5)
	N(2)#2-Mo(2)-Cl(4)	80.76(5)
	N(2)#2-Mo(2)-N(2)	76.03(10)
	O(2)#2-Mo(2)-Cl(3)	97.08(6)
20	O(2)-Mo(2)-Cl(3)	97.08(6)
	O(2)-Mo(2)-Cl(4)	97.18(7)
	O(2)#2-Mo(2)-Cl(4)	97.18(7)
	O(2)#2-Mo(2)-N(2)	89.75(8)
	O(2)-Mo(2)-N(2)#2	89.75(8)
25	O(2)-Mo(2)-N(2)	165.78(8)
	O(2)#2-Mo(2)-N(2)#2	165.78(8)
	O(2)#2-Mo(2)-O(2)	104.47(12)
	Cl(1)-Mo(1)-Cl(2)	156.82(4)
	Cl(1)-Mo(1)-N(1)#1	81.08(6)
30	Cl(1)-Mo(1)-N(1)	81.08(6)
	O(1)-Mo(1)-Cl(2)	96.88(6)
	O(1)#1-Mo(1)-Cl(2)	96.88(6)
	O(1)#1-Mo(1)-Cl(1)	97.24(6)
	O(1)-Mo(1)-Cl(1)	97.24(6)
35	O(1)#1-Mo(1)-O(1)	104.56(12)
	O(1)-Mo(1)-N(1)#1	165.24(8)
	O(1)#1-Mo(1)-N(1)#1	90.19(8)
	O(1)-Mo(1)-N(1)	90.20(8)

	O(1)#1-Mo(1)-N(1)	165.24(8)
	N(1)#1-Mo(1)-Cl(2)	80.59(6)
	N(1)-Mo(1)-Cl(2)	80.59(6)
	N(1)#1-Mo(1)-N(1)	75.05(10)
5	Cl(5)-Mo(3)-Cl(6)	156.17(4)
	N(3)#2-Mo(3)-Cl(5)	81.11(6)
	N(3)-Mo(3)-Cl(5)	81.11(6)
	N(3)-Mo(3)-Cl(6)	80.24(6)
	N(3)#2-Mo(3)-Cl(6)	80.24(6)
10	N(3)#2-Mo(3)-N(3)	76.59(10)
	O(3)#2-Mo(3)-Cl(5)	97.49(7)
	O(3)-Mo(3)-Cl(5)	97.49(7)
	O(3)-Mo(3)-Cl(6)	97.00(7)
	O(3)#2-Mo(3)-Cl(6)	97.00(7)
15	O(3)#2-Mo(3)-N(3)	89.38(8)
	O(3)-Mo(3)-N(3)	165.95(8)
	O(3)-Mo(3)-N(3)#2	89.38(8)
	O(3)#2-Mo(3)-N(3)#2	165.95(8)
	O(3)#2-Mo(3)-O(3)	104.65(13)
20	C(3)-N(2)-Mo(2)	177.7(2)
	C(1)-N(1)-Mo(1)	177.7(2)
	C(5)-N(3)-Mo(3)	177.0(2)
	N(1)-C(1)-C(2)	179.3(3)
	N(4)-C(7)-C(8)	179.7(3)
25	C(7)-N(4)-Mo(4)	177.4(2)
	N(2)-C(3)-C(4)	179.7(3)
	N(3)-C(5)-C(6)	178.8(3)

Symmetry transformations used to generate equivalent atoms:

30 #1 x,-y+1/2,z #2 x,-y+3/2,z

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})$. The anisotropic

displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

		U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
5							
	Mo(4)	9(1)	9(1)	13(1)	0	2(1)	0
	Mo(2)	9(1)	10(1)	10(1)	0	3(1)	0
	Mo(1)	13(1)	10(1)	10(1)	0	-3(1)	0
10	Mo(3)	15(1)	9(1)	11(1)	0	-4(1)	0
	Cl(2)	16(1)	18(1)	17(1)	0	3(1)	0
	Cl(3)	12(1)	23(1)	22(1)	0	-4(1)	0
	Cl(4)	13(1)	18(1)	13(1)	0	-1(1)	0
	Cl(5)	20(1)	19(1)	21(1)	0	3(1)	0
15	Cl(7)	19(1)	20(1)	13(1)	0	0(1)	0
	Cl(8)	19(1)	17(1)	13(1)	0	2(1)	0
	Cl(1)	15(1)	20(1)	23(1)	0	4(1)	0
	Cl(6)	17(1)	20(1)	21(1)	0	2(1)	0
	O(1)	21(1)	16(1)	21(1)	5(1)	-4(1)	1(1)
20	N(2)	11(1)	12(1)	17(1)	1(1)	-1(1)	2(1)
	N(1)	18(1)	14(1)	17(1)	-2(1)	0(1)	-1(1)
	N(3)	18(1)	13(1)	17(1)	-2(1)	-1(1)	1(1)
	O(4)	17(1)	15(1)	21(1)	-1(1)	3(1)	-5(1)
	O(3)	25(1)	16(1)	22(1)	4(1)	-2(1)	4(1)
25	C(2)	20(2)	16(2)	17(2)	-5(1)	0(1)	1(1)
	C(1)	11(1)	13(1)	15(1)	5(1)	4(1)	4(1)
	C(4)	21(2)	16(2)	16(1)	-2(1)	4(1)	2(1)
	C(7)	16(1)	9(1)	6(1)	1(1)	1(1)	3(1)
	N(4)	17(1)	14(1)	13(1)	-1(1)	0(1)	2(1)
30	C(8)	14(2)	16(2)	15(1)	3(1)	-3(1)	-4(1)
	O(2)	17(1)	21(1)	20(1)	-4(1)	5(1)	3(1)
	C(3)	12(1)	13(1)	13(1)	3(1)	-4(1)	-2(1)
	C(6)	18(2)	15(2)	18(1)	7(1)	-3(1)	-1(1)
	C(5)	13(1)	10(1)	14(1)	-2(1)	2(1)	-2(1)
35							

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{MoO}_2\text{Cl}_2(\text{CH}_3\text{CN})$.

		x	y	z	U(eq)
5					
	H(2A)	3835	5837	4327	26
	H(2B)	4645	4814	4496	26
	H(2C)	3425	4910	4732	26
10	H(4A)	3937	4884	1658	27
	H(4B)	4422	4169	2124	27
	H(4C)	5080	5270	1916	27
	H(8A)	10874	4995	4012	22
	H(8B)	11040	4812	4604	22
15	H(8C)	10298	5860	4402	22
	H(6A)	6256	10150	2949	26
	H(6B)	5722	10835	3412	26
	H(6C)	5094	9740	3181	26

As noted above, Figure 2 is a three-dimensional solid-state crystal structure depiction of $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

5 Table 6. Crystal data and structure refinement for $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

	Identification code	NB00666-001	
	Empirical formula	$\text{C}_4\text{H}_6\text{Cl}_2\text{N}_2\text{O}_2\text{W}$	
10	Formula weight	368.86	
	Temperature	100.0 K	
	Wavelength	0.71073 Å	
	Crystal system	Orthorhombic	
	Space group	Pbcn	
15	Unit cell dimensions	$a = 8.7091(6)$ Å	$\alpha = 90^\circ$.
		$b = 8.2536(7)$ Å	$\beta = 90^\circ$.
		$c = 12.8021(8)$ Å	$\gamma = 90^\circ$.
	Volume	920.23(12) Å ³	
	Z	4	
20	Density (calculated)	2.662 Mg/m ³	
	Absorption coefficient	13.088 mm ⁻¹	
	F(000)	672	
	Crystal size	0.37 x 0.35 x 0.33 mm ³	
	Theta range for data collection	3.183 to 28.277°.	
25	Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 6, -16 ≤ l ≤ 16	
	Reflections collected	5168	
	Independent reflections	1139 [R(int) = 0.0281]	
	Completeness to theta = 25.242°	99.9 %	
	Absorption correction	Semi-empirical from equivalents	
30	Max. and min. transmission	0.6035 and 0.3693	
	Refinement method	Full-matrix least-squares on F ²	
	Data / restraints / parameters	1139 / 0 / 52	
	Goodness-of-fit on F ²	1.133	
	Final R indices [I > 2σ(I)]	R1 = 0.0183, wR2 = 0.0431	
35	R indices (all data)	R1 = 0.0256, wR2 = 0.0459	
	Extinction coefficient	n/a	
	Largest diff. peak and hole	0.641 and -1.611 e.Å ⁻³	

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

5

	x	y	z	$U(\text{eq})$
W(1)	5000	3420(1)	2500	7(1)
Cl(1)	7382(1)	4003(1)	3276(1)	14(1)
10 O(1)	5680(3)	2149(3)	1552(2)	12(1)
N(1)	4324(4)	5646(4)	3495(2)	12(1)
C(2)	3798(5)	8375(4)	4431(3)	14(1)
C(1)	4080(4)	6841(4)	3911(3)	11(1)

Table 8. Bond lengths [Å] and angles [°] for $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

	W(1)-Cl(1)#1	2.3502(9)
	W(1)-Cl(1)	2.3502(9)
5	W(1)-O(1)#1	1.710(3)
	W(1)-O(1)	1.710(3)
	W(1)-N(1)#1	2.312(3)
	W(1)-N(1)	2.312(3)
	N(1)-C(1)	1.141(5)
10	C(2)-H(2A)	0.9800
	C(2)-H(2B)	0.9800
	C(2)-H(2C)	0.9800
	C(2)-C(1)	1.452(5)
	Cl(1)-W(1)-Cl(1)#1	156.36(4)
15	O(1)-W(1)-Cl(1)	96.89(9)
	O(1)#1-W(1)-Cl(1)	97.55(9)
	O(1)-W(1)-Cl(1)#1	97.55(9)
	O(1)#1-W(1)-Cl(1)#1	96.89(9)
	O(1)-W(1)-O(1)#1	104.30(17)
20	O(1)-W(1)-N(1)	165.20(12)
	O(1)-W(1)-N(1)#1	90.48(11)
	O(1)#1-W(1)-N(1)	90.48(11)
	O(1)#1-W(1)-N(1)#1	165.20(12)
	N(1)-W(1)-Cl(1)#1	81.11(8)
25	N(1)#1-W(1)-Cl(1)#1	80.15(8)
	N(1)#1-W(1)-Cl(1)	81.11(8)
	N(1)-W(1)-Cl(1)	80.15(8)
	N(1)-W(1)-N(1)#1	74.75(15)
	C(1)-N(1)-W(1)	172.6(3)
30	H(2A)-C(2)-H(2B)	109.5
	H(2A)-C(2)-H(2C)	109.5
	H(2B)-C(2)-H(2C)	109.5
	C(1)-C(2)-H(2A)	109.5
	C(1)-C(2)-H(2B)	109.5
35	C(1)-C(2)-H(2C)	109.5
	N(1)-C(1)-C(2)	178.8(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

5

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W(1)	8(1)	5(1)	7(1)	0	-1(1)	0
10 Cl(1)	11(1)	14(1)	16(1)	-1(1)	-4(1)	-1(1)
O(1)	12(1)	11(1)	14(1)	-1(1)	-2(1)	1(1)
N(1)	10(2)	12(2)	12(2)	0(1)	0(1)	-1(1)
C(2)	21(2)	8(2)	12(2)	-3(1)	-3(2)	2(1)
C(1)	11(2)	11(2)	11(2)	1(1)	-4(2)	-2(1)

15

Table 10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{WO}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$.

20

	x	y	z	U(eq)
H(2A)	3864	9258	3921	16
25 H(2B)	4569	8540	4979	16
H(2C)	2772	8363	4744	16

As noted above, Figure 5 is a three-dimensional solid-state crystal structure depiction of $\text{MoO}_2\text{Cl}_2(\text{THF})_2$. (THF = tetrahydrofuran) This compound was subjected to x-ray crystallographic analysis and yielded the following data:

35

Table 11. Crystal data and structure refinement for MoO₂Cl₂(THF)₂.

	Empirical formula	C ₈ H ₁₆ Cl ₂ Mo O ₄	
	Molecular formula	C ₈ H ₁₆ Cl ₂ Mo O ₄	
	Formula weight	343.05	
5	Temperature	200 K	
	Wavelength	0.71073 Å	
	Crystal system	Orthorhombic	
	Space group	P2 ₁ 2 ₁ 2 ₁	
	Unit cell dimensions	a = 7.4048(4) Å	□ = 90°.
10		b = 12.5437(6) Å	□ = 90°.
		c = 13.7487(7) Å	□ = 90°.
	Volume	1277.03(11) Å ³	
	Z	4	
	Density (calculated)	1.784 Mg/m ³	
15	Absorption coefficient	1.437 mm ⁻¹	
	F(000)	688	
	Crystal size	0.15 x 0.15 x 0.1 mm ³	
	Crystal color, habit	clear colourless block	
	Theta range for data collection	2.198 to 26.382°.	
20	Index ranges	-9<= <i>h</i> <=9, -15<= <i>k</i> <=13, -17<= <i>l</i> <=17	
	Reflections collected	11549	
	Independent reflections	2611 [R(int) = 0.0731]	
	Completeness to theta = 25.242°	99.9 %	
	Absorption correction	Semi-empirical from equivalents	
25	Max. and min. transmission	0.4652 and 0.3891	
	Refinement method	Full-matrix least-squares on F ²	
	Data / restraints / parameters	2611 / 0 / 136	
	Goodness-of-fit on F ²	1.065	
	Final R indices [I>2sigma(I)]	R ₁ = 0.0332, wR ₂ = 0.0838	
30	R indices (all data)	R ₁ = 0.0361, wR ₂ = 0.0858	
	Absolute structure parameter	0.00(5)	
	Extinction coefficient	n/a	
	Largest diff. peak and hole	0.360 and -0.510 e.Å ⁻³	

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

For Example 11, $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

		x	y	z	U(eq)
5	Mo(1)	5728(1)	5036(1)	4146(1)	36(1)
	Cl(2)	6796(2)	6222(1)	2947(1)	42(1)
	Cl(1)	5665(2)	3642(1)	5296(1)	59(1)
10	O(3)	7484(4)	3874(3)	3290(2)	33(1)
	O(4)	8555(5)	5286(3)	4799(3)	37(1)
	O(2)	3868(5)	4641(4)	3542(4)	60(1)
	O(1)	4986(7)	6018(4)	4890(3)	63(1)
	C(6)	10956(8)	5056(5)	5895(4)	56(2)
15	C(1)	7073(9)	2746(4)	3220(4)	44(1)
	C(8)	9173(9)	6336(5)	5068(4)	54(2)
	C(2)	8331(10)	2315(4)	2433(4)	52(2)
	C(4)	9009(8)	4133(5)	2657(4)	45(1)
	C(7)	10698(10)	6210(6)	5705(8)	97(3)
20	C(3)	9888(9)	3099(5)	2452(5)	53(2)
	C(5)	9912(11)	4520(5)	5131(5)	64(2)

Table 13. Bond lengths [Å] and angles [°] for MoO₂Cl₂(THF)₂.

Mo(1)-Cl(2)	2.3575(14)
Mo(1)-Cl(1)	2.3576(15)
Mo(1)-O(3)	2.280(3)
Mo(1)-O(4)	2.300(4)
Mo(1)-O(2)	1.683(4)
Mo(1)-O(1)	1.692(4)
O(3)-C(1)	1.451(6)
O(3)-C(4)	1.462(6)
O(4)-C(8)	1.442(6)
O(4)-C(5)	1.463(8)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.483(9)
C(6)-C(5)	1.469(8)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(1)-C(2)	1.526(8)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(8)-C(7)	1.438(9)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(3)	1.516(9)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(3)	1.478(8)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
Cl(1)-Mo(1)-Cl(2)	160.67(6)
O(3)-Mo(1)-Cl(2)	81.43(9)
O(3)-Mo(1)-Cl(1)	83.31(10)
O(3)-Mo(1)-O(4)	76.68(12)
O(4)-Mo(1)-Cl(2)	83.21(10)
O(4)-Mo(1)-Cl(1)	81.78(10)
O(2)-Mo(1)-Cl(2)	96.61(17)
O(2)-Mo(1)-Cl(1)	95.55(17)
O(2)-Mo(1)-O(3)	91.38(18)

O(2)-Mo(1)-O(4)	167.97(18)
O(2)-Mo(1)-O(1)	104.3(2)
O(1)-Mo(1)-Cl(2)	94.13(16)
O(1)-Mo(1)-Cl(1)	97.36(16)
O(1)-Mo(1)-O(3)	164.1(2)
O(1)-Mo(1)-O(4)	87.7(2)
C(1)-O(3)-Mo(1)	122.6(3)
C(1)-O(3)-C(4)	109.8(4)
C(4)-O(3)-Mo(1)	127.3(3)
C(8)-O(4)-Mo(1)	120.9(3)
C(8)-O(4)-C(5)	107.6(5)
C(5)-O(4)-Mo(1)	131.1(4)
H(6A)-C(6)-H(6B)	108.9
C(7)-C(6)-H(6A)	110.8
C(7)-C(6)-H(6B)	110.8
C(5)-C(6)-H(6A)	110.8
C(5)-C(6)-H(6B)	110.8
C(5)-C(6)-C(7)	104.7(5)
O(3)-C(1)-H(1A)	110.7
O(3)-C(1)-H(1B)	110.7
O(3)-C(1)-C(2)	105.4(5)
H(1A)-C(1)-H(1B)	108.8
C(2)-C(1)-H(1A)	110.7
C(2)-C(1)-H(1B)	110.7
O(4)-C(8)-H(8A)	110.2
O(4)-C(8)-H(8B)	110.2
H(8A)-C(8)-H(8B)	108.5
C(7)-C(8)-O(4)	107.8(5)
C(7)-C(8)-H(8A)	110.2
C(7)-C(8)-H(8B)	110.2
C(1)-C(2)-H(2A)	111.2
C(1)-C(2)-H(2B)	111.2
H(2A)-C(2)-H(2B)	109.1
C(3)-C(2)-C(1)	102.9(5)
C(3)-C(2)-H(2A)	111.2
C(3)-C(2)-H(2B)	111.2
O(3)-C(4)-H(4A)	110.7
O(3)-C(4)-H(4B)	110.7
O(3)-C(4)-C(3)	105.0(4)
H(4A)-C(4)-H(4B)	108.8
C(3)-C(4)-H(4A)	110.7
C(3)-C(4)-H(4B)	110.7

C(6)-C(7)-H(7A)	110.0
C(6)-C(7)-H(7B)	110.0
C(8)-C(7)-C(6)	108.4(6)
C(8)-C(7)-H(7A)	110.0
C(8)-C(7)-H(7B)	110.0
H(7A)-C(7)-H(7B)	108.4
C(2)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3B)	111.0
C(4)-C(3)-C(2)	103.7(5)
C(4)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3B)	111.0
H(3A)-C(3)-H(3B)	109.0
O(4)-C(5)-C(6)	106.4(5)
O(4)-C(5)-H(5A)	110.4
O(4)-C(5)-H(5B)	110.4
C(6)-C(5)-H(5A)	110.4
C(6)-C(5)-H(5B)	110.4
H(5A)-C(5)-H(5B)	108.6

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{MoO}_2\text{Cl}_2(\text{THF})_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	30(1)	33(1)	44(1)	-1(1)	12(1)	0(1)
Cl(2)	47(1)	32(1)	46(1)	7(1)	-1(1)	0(1)
Cl(1)	77(1)	48(1)	52(1)	10(1)	30(1)	-8(1)
O(3)	35(2)	24(2)	38(2)	-4(1)	9(2)	-2(1)
O(4)	43(2)	25(2)	42(2)	-5(2)	-5(2)	0(2)
O(2)	31(2)	63(3)	87(3)	5(3)	1(2)	-6(2)
O(1)	65(3)	52(3)	72(3)	-10(2)	32(3)	12(2)
C(6)	43(3)	66(5)	59(4)	2(4)	4(2)	-6(3)
C(1)	53(3)	28(3)	50(3)	-8(2)	-2(3)	-7(3)
C(8)	75(4)	31(3)	56(4)	-6(3)	-11(3)	-12(3)
C(2)	80(4)	33(3)	42(3)	-8(3)	-7(3)	16(3)
C(4)	49(3)	39(3)	46(3)	-3(3)	19(3)	0(3)
C(7)	73(5)	45(4)	172(9)	-34(5)	-58(6)	10(4)
C(3)	58(3)	42(4)	59(4)	-1(3)	20(3)	10(3)
C(5)	70(4)	43(4)	78(5)	-5(3)	-24(4)	13(3)

Table 15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{MoO}_2\text{Cl}_2(\text{THF})_2$.

	x	y	z	U(eq)
H(6A)	12249	4862	5854	67
H(6B)	10496	4862	6548	67
H(1A)	5794	2636	3035	52
H(1B)	7299	2385	3848	52
H(8A)	9528	6741	4481	64
H(8B)	8197	6730	5404	64
H(2A)	8745	1584	2591	62
H(2B)	7731	2309	1790	62
H(4A)	9857	4623	2988	54
H(4B)	8586	4471	2048	54
H(7A)	10480	6593	6324	116
H(7B)	11794	6512	5398	116
H(3A)	10766	2913	2968	64
H(3B)	10521	3115	1817	64
H(5A)	10710	4310	4586	76
H(5B)	9322	3872	5392	76

The table below illustrates the various physical properties for certain compounds of Formula (I):

<u>Compound</u>	<u>M.P.</u>	<u>STA-DSC</u>		<u>Example Number</u>
		<u>T₅₀ (°C)</u>	<u>Residual Mass (%)</u>	
MoO ₂ Cl ₂ (DME)	128.4	184.4	1.69	1
MoO ₂ Cl ₂ (DMM)		200.4	46.36	2
MoO ₂ Cl ₂ (1,2-DMP)	131.8	185.0	40.89	3
MoO ₂ Cl ₂ (DMA) ₂	124.7	238.3	17.06	4
MoO ₂ Cl ₂ (DMF) ₂	162.6	232.0	9.93	5
MoO ₂ Cl ₂ (MeCN) ₂	112.4	143.5	2.61	6
MoO ₂ Cl ₂ (tBuCN) _x	95.3	135.7	4.55	7
MoO ₂ Cl ₂ (iPrCN) _x	69.9	134.1	3.15	8
MoO ₂ Cl ₂ (DMCA)		n/a	64.45	9
MoO ₂ Cl ₂ (TMEN)		n/a	57.12	10
MoO ₂ Cl ₂ (THF) ₂		138.1	18.77	11

Abbreviations:

DME = 1,2-dimethoxyethane
DMM = 1,2-dimethoxymethane
1,2-DMP = 1,2-dimethoxypropane
DMA = N,N-dimethylacetamide
DMF = N,N-dimethylformamide
DMCA = N,N-dimethylcyanoacetamide
TMEN = N,N,N',N'-tetramethylethylenediamine
CN = nitrile
THF = tetrahydrofuran

STA-DSC:

simultaneous thermal analysis - differential scanning calorimetry