Synthesis, Characterization and X-Ray Structure of *N'*-(2-Hydroxy-5-methylbenzylidene)-4-trifluoromethylbenzohydrazide and Its Dioxidomolybdenum(VI) Complex with Catalytic Property

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Abstract

A new hydrazone compound *N'*-(2-hydroxy-5-methylbenzylidene)-4-trifluoromethylbenzohydrazide (H_2L) was prepared. Based on H_2L, a new dioxidomolybdenum(VI) complex [*cis*-$MoO_2L(MeOH)$], was obtained. Single crystals of H_2L and the complex were obtained by slow evaporation of methanolic solution containing the compounds, and were characterized by elemental analysis, infrared spectroscopy, and single crystal X-ray diffraction techniques. The geometry around the molybdenum center is distorted octahedral in which the tridentate benzohydrazone ligand with two anionic oxygens and one neutral imine nitrogen occupies meridional position. The octahedral geometry of the *cis*-dioxomolybdenum center is additionally completed by a coordinated methanol solvent molecule. The complex was tested for the homogeneous oxidation of various olefins.

Keywords

molybdenum dioxido complex, synthesis, X-ray structure, catalytic property

INTRODUCTION

Hydrazones prepared by the condensation of salicylaldehydes with hydrazides are an important class of versatile ligands.[1-3] Transition metal complexes derived from such ligands have been widely investigated due to their interesting properties, such as magnetic exchange,[4] biological activities,[1, 5, 6] as well as catalytic materials.[7, 8] Molybdenum is an important metal that is capable of forming various complexes with organic ligands,[8-10] and usually show essential catalytic properties.[11-19] Epoxides are very important and versatile intermediates for manufacturing a range of important commercial products such as pharmaceuticals and polymers. In addition, it can be easily transformed to a variety of functional groups.[20] Many transition metal complexes including molybdenum complexes have been reported for oxidation of olefins.[8, 11, 21-23] As a continuation of the work, in this report, a new hydrazone compound *N'*-(2-hydroxy-5-methylbenzylidene)-4-trifluoromethylbenzohydrazide (H_2L) and its dioxidomolybdenum(VI) complex [*cis*-$MoO_2L(MeOH)$] are reported.

EXPERIMENTAL

Materials and Methods

5-Methylsalicylaldehyde, 4-trifluoromethylbenzohydrazide, and $MoO_2(acac)_2$ of AR grade were purchased from Aldrich and used as received. CHN elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. I.r. spectra (KBr disks) were recorded on a Perkin-Elmer 257 spectrophotometer. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 mm × 320 mm × 0.25 mm) and a flame ionization detector. ^{1}H NMR spectrum was obtained in DMSO-d^6 solution with a Bruker 300 MHz spectrometer.

Preparation of H_2L

5-Methylsalicylaldehyde (0.68 g, 5 mmol) and 4-trifluoromethylbenzohydrazide (0.10 g, 5 mmol) were dissolved in 30 mL methanol. The mixture was heated to reflux for 1 h, and cooled to room temperature. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. Yield: 77%; ^{1}H NMR (DMSO-d^6, 300 MHz): δ = 2.34 (s, 3H, CH_3), 6.93 (d, 1H, ArH), 7.07 (d, 1H, ArH), 7.49 (s, 1H, ArH), 7.78 (d, 2H), 7.99 (d, 2H), 8.65 (s, 1H, -CH=N-), 11.27 (s, 1H, NH). IR (KBr pellet): ν(OH) 3366; ν(NH) 3226; ν(C=N) 1657 cm^{-1}. Anal. calcd. for $C_{17}H_{17}F_3N_2O_3$: C, 57.63; H, 4.84; N, 7.91. Found: C, 57.51; H, 4.92; N, 7.98%.

Preparation of the Complex

H_2L (0.16 g, 5 mmol) and $MoO_2(acac)_2$ (1.63 g, 5 mmol) were mixed in methanol (20 mL). the mixture was stirred at room temperature for 30 min to give a yellow solution. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. Yield: 45%; ^{1}H NMR (DMSO-d^6, 300 MHz): δ = 2.32 (s, 3H, $PhCH_3$), 3.13 (s, 3H, CH_3), 6.91 (d, 1H, ArH), 7.13 (d, 1H, ArH), 7.45-7.72 (m, 3H, ArH), 8.13 (d, 2H, ArH), 8.45 (s, 1H, -CH=N-). IR (KBr pellet): ν(OH) 3460; ν(C=N) 1628 cm^{-1}; ν(MoO_2) 951, 860 cm^{-1}. Anal. calcd. for $C_{17}H_{15}F_3MoN_2O_5$: C, 42.52; H, 3.15; N, 5.83. Found: C, 42.40; H, 3.32; N, 5.71%.

Crystal Structure Determination

Crystals suitable for X-ray measurement were grown from methanol by slow evaporation method. The single crystals of H_2L and the complex were chosen and glued to thin glass fibers by epoxy glue in air for data collection. The diffraction data were collected on a Bruker Apex2 CCD with Mo *Kα* radiation (λ = 0.71073 Å) at 298(2) K using the ω scan method. An empirical absorption correction was applied. The structures were solved by direct methods and difference

Fourier synthesis. Crystal data collection, parameters, and refinement statistics for the compounds are listed in Table 1. All of the non-H atoms were refined anisotropically. The methanol H atoms were located from electronic density maps and refined with O···H distances restrained to 0.85(1) Å. All other H atoms of the compounds were included in calculated positions, and assigned isotropic thermal parameters which were set to ride on the parent atoms. The CF_3 group of H_2L is disordered over two sites, with occupancies of 0.602(3) and 0.398(3). All calculations were performed using the SHELXTL-97.[24]

Catalytic Oxidation Procedure

Catalytic experiments were carried out in a 50 mL glass reaction flask fitted with a water condenser. In a typical procedure, 0.032 mmol dioxidomolybdenum(VI) complex was dissolved in 10 mL CH_2Cl_2. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

RESULTS AND DISCUSSION

The hydrazone ligand used for the preparation of the dioxidomolybdenum complex was derived from condensation of 5-methylsalicylaldehyde and 4-trifluoromethylbenzohydrazide. The complex was prepared by simple ligand exchange reaction of the hydrazone ligand with $MoO_2(acac)_2$ in methanol (Scheme 1). Single crystals of the compounds were successfully grown by slow evaporation of methanolic solution at room temperature. The molar conductance of the complex is 22 Ω^{-1} cm^2 mol^{-1}, indicating the non-electrolytic nature.

IR Spectra

The compounds were characterized by IR spectroscopy. The free hydrazone showed stretching bands attributed to C=O, C=N, C–OH and NH at 1657, 1636, 1153 and 1232, and 3317 cm^{-1}, respectively. The sharp band at 3226 cm^{-1} for H_2L is absent in the spectrum of the complex, indicating the coordination of the hydrazone ligand through enolate form. The molybdenum complex showed two prominent bands at 951 and 860 cm^{-1} attributed to *cis*-dioxomolybdenum (MoO_2) group.[14] The bands due to $\nu_{C=O}$ and ν_{NH} are absent in the complex, but a new C–O stretch appeared at 1272 cm^{-1}. This suggest occurrence of *keto*-imine tautomerization of the ligand during complexation. The C=N stretching band at 1657 cm^{-1} in the free hydrazone shifted to 1628 cm^{-1} upon coordination to Mo atom. A broad and weak band centered at 3460 cm^{-1} in the spectrum of the complex is also appeared, which may be attributed to the coordinate methanol O–H group.

Crystal Structure Description of H_2L and the Complex

The molecular structure of H_2L is shown in Fig. 1 and the bond parameters are given in Table 2. There is a hydrazone molecule and a methanol molecule in the compound. The bond distances and angles are normal.[25] The dihedral angle between the two benzene rings is 138.8(3)°. The molecule of the compound displays an *E* geometry about the C=N bond. The hydrazone molecules are linked by methanol molecules through hydrogen bonds (Table 3) into chains along *a* axis (Fig. 2).

The molecular structure of the complex is shown in Fig. 3 and the bond parameters are given in Table 2. The mononuclear complex has a distorted octahedral geometry with one nitrogen atom and five oxygen atoms. Three atoms, O(1), N(1) and O(2) (from the tridentate ligand), and one terminal oxo atom, O(4), occupy the meridional plane. The Mo(1) atom lies 0.709(2) Å out from this plane in the direction of the other terminal oxygen atom O(4). Both O(4) and O(3), the latter from the coordinated methanol molecule, occupy the axial positions forming an O(4)–Mo(1)–O(3) angle of 170.76(8)° which indicate the distorted octahedral nature of the donor environment around the Mo(VI) center. The MoO_2 moiety has a *cis* configuration. The Mo(1)–O(3) bond *trans* to the terminal oxygen atom O(4) is significantly longer compared to the length of other molybdenum oxygen bonds, indicating that the methanol molecule is weakly coordinated to the metal center and can behave as a substrate-binding site. The coordinate bond parameters are consistent with those reported in the literature.[13, 14] In the crystal, the molecules are linked *via* intermolecular hydrogen bonds (Table 3), forming dimers, as shown in Fig. 4.

Catalytic Results

The catalytic property of the complex was investigated in the epoxidation of cyclooctene, as a model substrate, and *tert*-butyl hydroperoxide as the oxygen donor. In the absence of catalyst, the reactions did not proceed even under reflux. The results are presented in Table 4. Oxidation of 4-fluorostyrene, 4-chlorostyrene, 4-methylstyrene, and 4-methoxystyrene gave the corresponding epoxide as the sole product, while in the oxidation of styrene some benzaldehyde was were detected as a by-product. From the results, it can be seen that the electron donating group in the salicylidene ring can decrease the activity of the catalyst, which results from the decreasing Lewis acidity of the molybdenum center and therefore the deduction of TBHP activation.[11] In the proposed catalytic cycle (Scheme 2), at first step, TBHP will be activated by coordination to the molybdenum center and formation of hepta-coordinated molybdenum intermediate **I**. It seems that heterolytic cleavage of the TBHP occurs. Therefore catalysts with higher lewis acidity character increase the efficiency of the coordinated peroxo group. Then olefin as a nucleophile will attack to the electrophile oxygen atom of the coordinated TBHP. A comparison of the results obtained for this work with those reported in the literature which used TBHP as oxidizing agent reveals that reaction time is lower than other systems and higher conversion for epoxide formation will be achieved. In addition, the catalytic oxidation property of the complex is comparable to those reported in the literature.[26,27]

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TABLE 1 Crystallographic and experimental data for H_2L and the complex

	H_2L	The complex
Empirical Formula	$C_{17}H_{17}F_3N_2O_3$	$C_{17}H_{15}F_3MoN_2O_5$
Formula weight	354.33	480.25
Temperature/K	298(2)	298(2)
Wavelength (Mo$K\alpha$) /Å	0.71073	0.71073
Crystal shape/colour	Block/colorless	Block/yellow
Crystal size/mm	0.15 × 0.13 × 0.13	0.31 × 0.29 × 0.28
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a /Å	6.7399(5)	8.0778(5)
b /Å	35.0990(12)	9.4758(6)
c /Å	7.6570(7)	12.4185(8)
α /°	90	90.1490(10)
β /°	108.517(2)	92.9880(10)
γ /°	90	91.0060(10)
V /Å^3	1717.6(2)	949.11(10)
Z	4	2
Calculated density/g cm^{-3}	1.370	1.680
Absorption coefficient/mm^{-1}	0.116	0.750
Theta range for data collection	3.04-25.50	2.53-25.50
Index ranges/h, k, l	-8, 8; -42, 34; -8, 9	-9, 9; -9, 11; -15, 14
T_{min}	0.9828	0.8007
T_{max}	0.9851	0.8174
Reflections/parameters	8349/261	4974/258
Unique reflections	3021	3479
Observed reflections [$I \geq 2\sigma(I)$]	2350	3251
Restraints	61	1
F(000)	736	480
Goodness of fit on F^2	1.039	1.080
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0851, 0.1689	0.0251, 0.0676
R_1, wR_2 (all data)^a	0.1065, 0.1831	0.0275, 0.0699
Largest diff. peak and hole/e Å^{-3}	0.215, -0.224	0.448, -0.450

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

TABLE 2 Selected bond lengths (Å) and bond angles (°) for the compounds

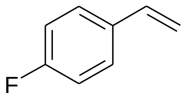
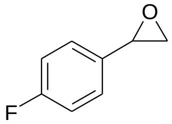
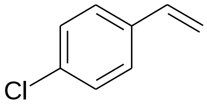
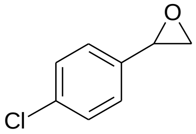
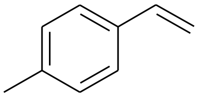
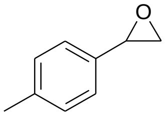
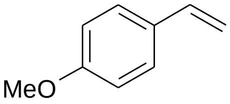
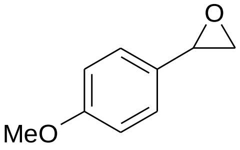
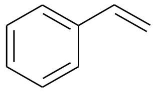
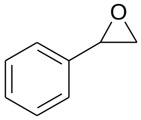
H_2L			
C(7)–N(1)	1.283(4)	N(1)–N(2)	1.387(4)
N(2)–C(8)	1.342(4)	C(8)–O(2)	1.232(4)
The complex			
Mo(1)–O1	1.9170(18)	Mo(1)–O(2)	2.0183(17)
Mo(1)–O(3)	2.3618(17)	Mo(1)–O(4)	1.6928(19)
Mo(1)–O(5)	1.6930(17)	Mo(1)–N(1)	2.2495(18)
O(4)–Mo(1)–O(5)	106.43(10)	O(4)–Mo(1)–O(1)	98.68(10)
O(5)–Mo(1)–O(1)	102.23(8)	O(4)–Mo(1)–O(2)	96.89(9)
O(5)–Mo(1)–O(2)	98.26(8)	O(1)–Mo(1)–O(2)	149.49(7)
O(4)–Mo(1)–N(1)	95.57(8)	O(5)–Mo(1)–N(1)	156.78(8)
O(1)–Mo(1)–N(1)	81.21(7)	O(2)–Mo(1)–N(1)	71.28(7)
O(4)–Mo(1)–O(3)	170.76(8)	O(5)–Mo(1)–O(3)	82.32(7)
O(1)–Mo(1)–O(3)	81.99(7)	O(2)–Mo(1)–O(3)	78.60(7)
N(1)–Mo(1)–O(3)	75.38(6)		

TABLE 3 Hydrogen bond distances (Å) and bond angles (°) for the compounds

H_2L				
O(1)–H(1)···N(1)	0.82	2.04	2.728(3)	141(3)
O(1)–H(1)···O(3)^{i}	0.82	2.55	3.051(4)	120(3)
O(3)–H(3)···O(2)^{ii}	0.82	1.89	2.679(3)	162(3)
N(2)–H(2)···O(3)	0.90(1)	1.95(1)	2.849(4)	177(5)
The complex				
O(3)–H(3A)···N(2)^{iii}	0.84(1)	1.96(1)	2.796(2)	170(4)

Symmetry codes for i: –1 + *x*, *y*, *z*; ii: 1 + *x*, *y*, *z*; iii: 1 – *x*, 1 – *y*, – *z*.

TABLE 4 Epoxidation of olefins using TBHP catalyzed by the complex in CH_2Cl_2[b]

Alkene	Conversion (%)[c]	Product	Selectivity to epoxides (%)	Time (h)	TOF (h^{-1})
	41		100	1	97.0
	38		100	1	82.5
	23		100	1	41.7
	15		100	1	28.2
	26		100	1	72.1

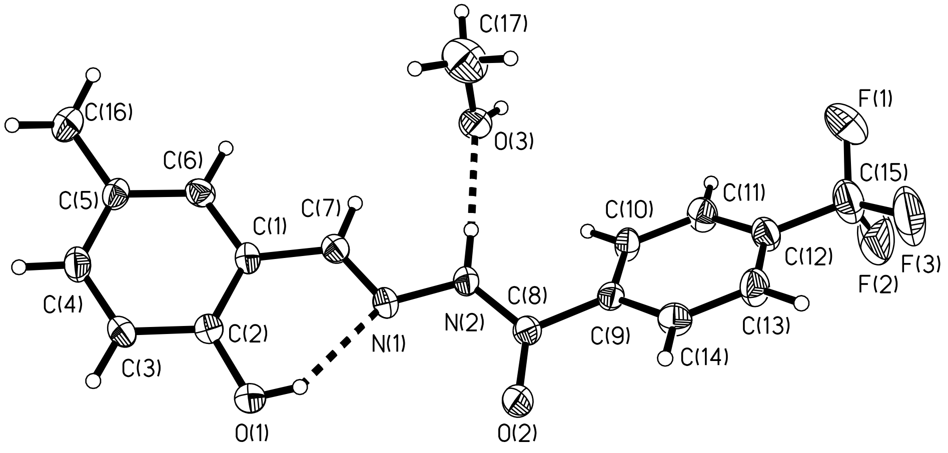


Fig. 1. ORTEP diagram (30% thermal ellipsoid) of H_2L with atom labeling scheme. Only the major component of the CF_3 group is shown. Hydrogen bonds are drawn as dashed lines.

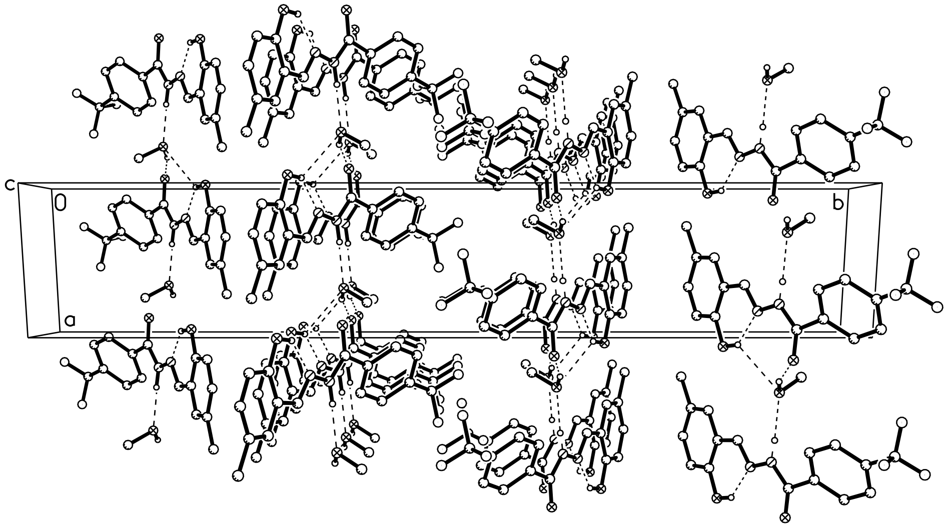


Fig. 2. Intermolecular hydrogen bonds (dotted lines) linked structure of H_2L.

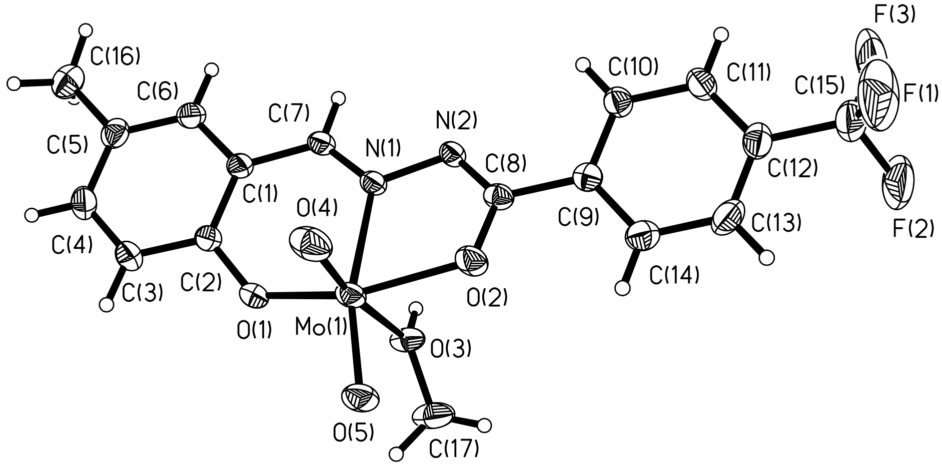


Fig. 3. ORTEP diagram (30% thermal ellipsoid) of the complex with atom labeling scheme.

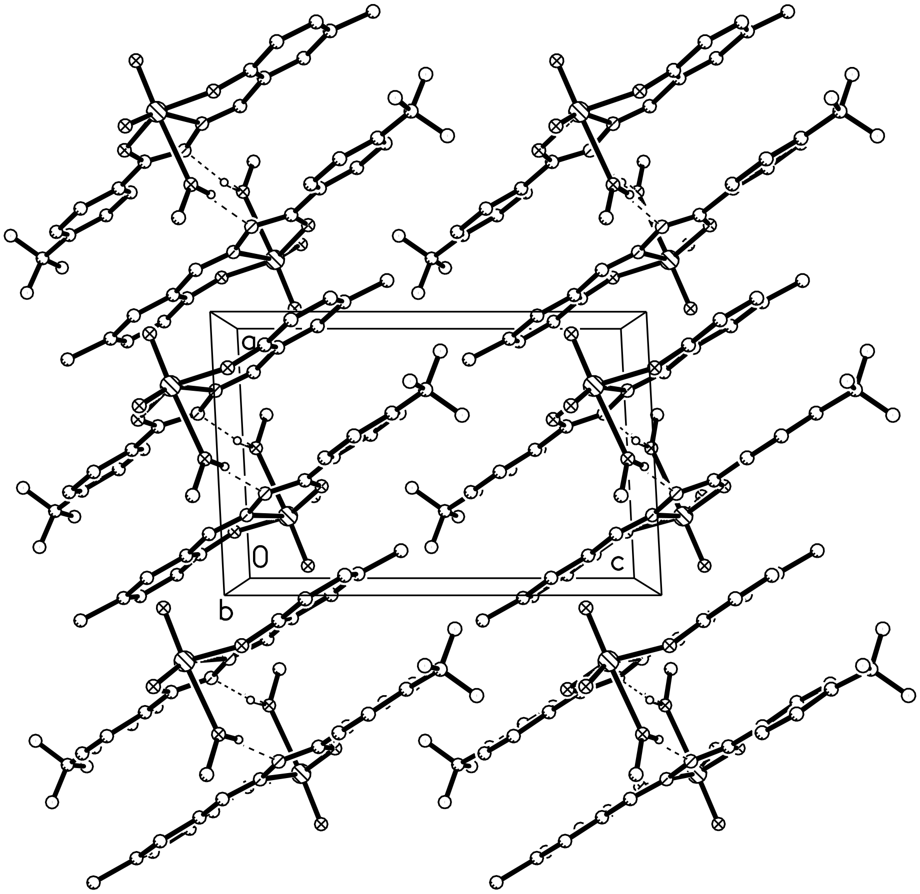
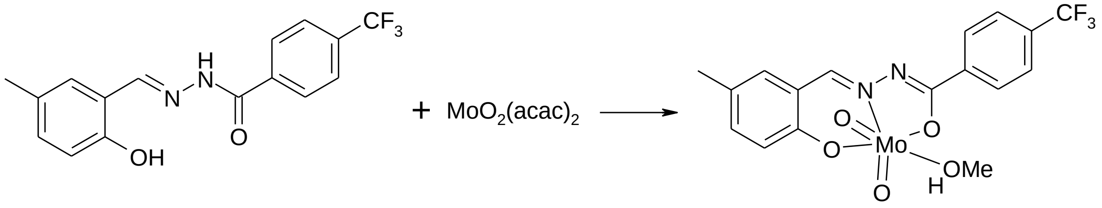
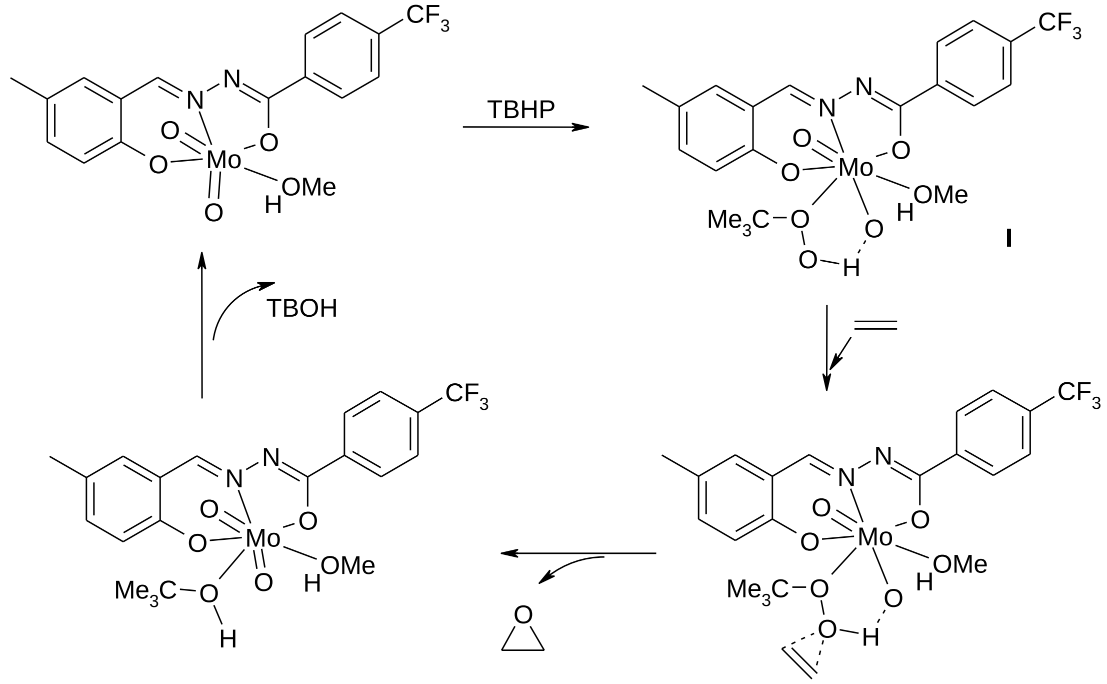


Fig. 4. Intermolecular hydrogen bonds (dotted lines) linked structure of the complex.



Scheme 1. The synthesis procedure of the complex



Scheme 2. The catalytic procedure of the oxidation.