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Synthesis, structural characterization, and catalytic reactivity of a new molybdenum(VI) complex containing 1,3,4-thiadiazole derivative as a tridentate NNO donor ligand

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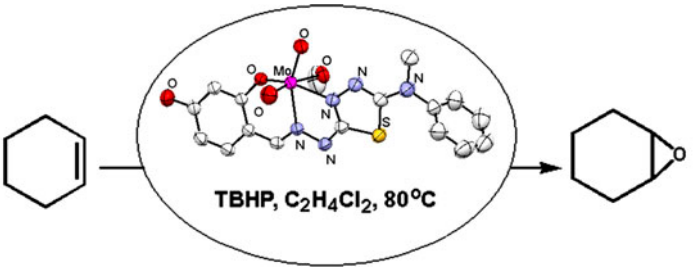

A new *cis*-dioxo molybdenum(VI) complex was obtained by reaction of 2,4-dihydroxybenzylidene (5-N,N-methylphenylamino-1,3,4-thiadiazol-2-yl)hydrazone as ligand and $[MoO_2(acac)_2]$ in methanol and was characterized by elemental analyses, ^{1}H NMR, IR, and electronic spectroscopic studies. The complex was also analyzed by single-crystal X-ray diffraction. The structure determination revealed a distorted octahedral coordination geometry around molybdenum in which the tridentate NNO donor (L^{2-}) is bonded to $[MoO_2]^{2+}$ through phenolic oxygen, hydrazinic nitrogen, and thiadiazole nitrogen. The sixth coordination site is occupied by a weakly bonded methanol. The complex was tested as a catalyst for homogeneous epoxidation of olefins using *tert*-butyl hydrogen peroxide as an oxidant. In the homogeneous catalytic system, the reactions are efficiently carried out with high yields and selectivity.

Keywords: Molybdenum(VI) complex; Thiadiazole; Olefin epoxidation

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1. Introduction

Oxomolybdenum(VI) complexes attract interest because of their relevance to both biological and industrial systems [1]. It is well known that the biological redox process of molybdoenzymes involves the transfer or abstraction of oxygen to or from generalized substrate X or XO, respectively [2]. To demonstrate the viability of catalytic oxo transfer reactions high-valent oxo-molybdenum complexes have been examined because of their possible relationship to redox-active molybdoenzymes [3, 4].

Catalytic oxo transfer properties of monomeric dioxomolybdenum complexes are also important in industrial processes such as the epoxidation of olefins [5, 6]. Subsequently, various ligands with different donor properties have been used to produce dioxomolybdenum complexes which serve as catalysts in biological and industrial processes [3, 7].

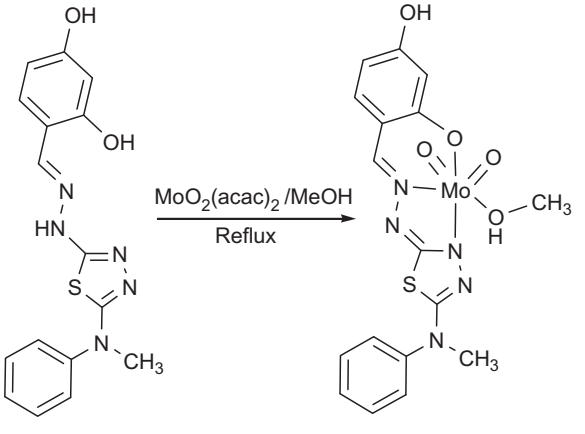
Antimicrobial, antiviral, anti-inflammatory, and antitumor activities of 1,3,4-thiadiazole derivatives, which belong to an important group of heterocyclic bioactive compounds, and their metal complexes, have inspired numerous investigations concerning their synthesis, characterization, and bioinorganic relevance [8–13].

This report thus describes preparation and characterization of the new *cis*-dioxo molybdenum (VI) complex of a 1,3,4-thiadiazole derivative, $[MoO_2(L)(CH_3OH)]$ which crystallizes with weakly bound CH_3OH and disordered water, in which L^{2-} supplies a tridentate NNO donor set to molybdenum (scheme 1). In addition, the catalytic behavior of dioxomolybdenum(VI) complex, $[MoO_2(L)(CH_3OH)]$, toward the epoxidation of olefins using *tert*-butyl hydrogen peroxide (TBHP) have been also investigated. The catalyst shows excellent catalytic efficiency in epoxidation reactions with various olefinic compounds including linear and cyclic alkenes.

2. Experimental

2.1. Materials and methods

All reagents employed were purchased commercially and used without purification. 4-Methyl-4-phenyl-3-thiosemicarbazide [14] and bis(acetylacetonato)dioxomolybdenum



Scheme 1. Synthesis of $[MoO_2(L)(CH_3OH)]$.

(VI), $[MoO_2(acac)_2]$ [15] were prepared as described. Elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400 CHNS/O elemental analyzer. Infrared spectra (4000–400 cm^{-1}) of solid samples were taken in KBr pellets using a Unicam Matson 1000 FT-IR spectrophotometer. NMR spectra were obtained on a Bruker 500-DRX Avance Spectrometer in DMSO-d6. UV–vis spectra were recorded with a CARY 100 Bio VARIAN UV–vis spectrophotometer using quartz cells having 1.0 cm path lengths. Melting points of the products were monitored on a BUCHI Melting Point Model B-540.

2.2. *Synthesis of H_2L*

Solution of 2,4-dihydroxybenzaldehyde (0.138 g, 1 mM) in 20 mL methanol was added to a 20 mL 4-methyl-4-phenyl-3-thiosemicarbazide (0.091 g, 1 mM) methanolic solution. Three drops of acetic acid were added. The reaction mixture was refluxed with vigorous stirring for 8 h. A precipitate was formed when the solution was allowed to cool at room temperature overnight. The orange–yellow precipitate was filtered, washed with cold methanol, and dried in air. Yield: 0.156 g (46%). M.p.: 204–205 °C. Anal. Calcd for $C_{16}H_{15}N_5O_2S$ (%): C, 56.29; H, 4.43; N, 20.51. Found: C, 56.38; H, 4.63; N, 19.81.

2.3. *Synthesis of $[MoO_2(L)(CH_3OH)]$*

A solution of H_2L (0.172 g, 0.5 mM) dissolved in 5 mL of methanol was added to a solution of $[MoO_2(acac)_2]$ (0.164 g, 0.5 mM) in 5 mL methanol. The reaction mixture was then refluxed for 4 h and the solution was allowed to stand at room temperature. Brown crystals were formed after slow evaporation for one week. The product was filtered, washed with ether, and dried in air. Yield: 0.080 g (32%). M.p.: 165 °C. Anal. Calcd for $C_{17}H_{17}N_5O_5SMo$ (%): C, 40.89; H, 3.43; N, 14.02. Found: C, 40.05; H, 3.26; N, 13.87.

2.4. *Crystal structure determination and refinement*

Diffraction data were collected at room temperature, by the ω-scan technique, on an Oxford Diffraction SuperNova diffractometer (Atlas detector) with mirror-monochromated CuKα radiation (λ = 1.54178 Å). The data were corrected for Lorentz-polarization and empirical absorption correction (multi-scan) using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [16]. Accurate unit-cell parameters were determined by a least-squares fit of 27,523 reflections of highest intensity, chosen from the whole experiment. The structure was solved with SIR92 [17] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [18]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms (with the exception of disordered water, vide infra) were refined anisotropically. Hydrogens involved in hydrogen bonds were found in difference Fourier maps. All other hydrogens were put in idealized positions, and refined as riding, with their isotropic thermal parameters set at 1.2 (1.5 for methyl groups) times Ueq's of appropriate carrier atoms. The relatively large residual electron density near the twofold axis (at 0, y ,1/4) was interpreted as disordered C_2-symmetrical water. The oxygen of this molecule was refined isotropically, position of hydrogens was calculated on the basis of potential hydrogen bonding; the O–H and H···N distances were restrained at 0.90(1) and 2.20(2) Å, respectively (O···N distance is 3.010(8) Å). Relevant crystal data are listed in table 1, together with refinement details.

Table 1. Crystal data, data collection, and structure refinement.

Formula	$(C_{17}H_{17}MoN_5O_5S)_2{\cdot}CH_3OH{\cdot}1/4(H_2O)$
Formula weight	1035.28
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	27.1334(3)
b (Å)	12.0889(2)
c (Å)	27.5632(3)
α (°)	90
β (°)	108.951(2)
γ (°)	90
V (Å^3)	8551.0(3)
Z	8
d_x (g cm^{-3})	1.61
F (0 0 0)	4196
μ (mm^{-1})	6.31
Θ range (°)	3.39–75.61
hkl range	$-33 < h < 29$
	$-15 < k < 14$
	$-34 < l < 34$
Reflections	
collected	40,612
unique (R_{int})	8717 (0.041)
with $I > 2\sigma(I)$	8233
$R(F)$ [$I > 2\sigma(I)$]	0.033
$wR(F^2)$ [$I > 2\sigma(I)$]	0.091
$R(F)$ [all data]	0.035
$wR(F^2)$ [all data]	0.093
Goodness-of-fit	1.04
Max/min $\Delta\rho$ (e Å^{-3})	0.84/−0.57

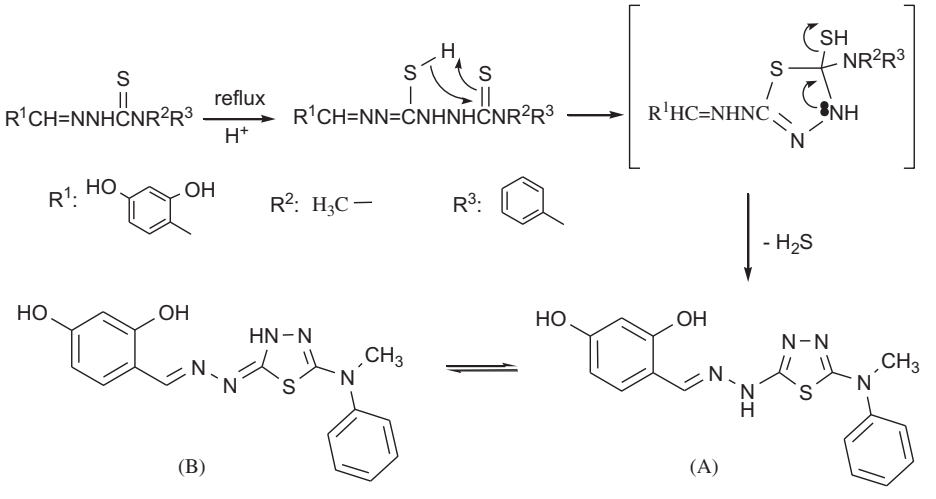
2.5. *Catalytic experiments*

To a solution of olefin (1 mM), chlorobenzene (1 mM) as internal standard, and $[MoO_2(L)(CH_3OH)]$ (0.003 mM) in 1,2-dichloroethane (1 mL) was added TBHP (1 mM) as oxidant. The mixture was vigorously stirred at reflux under air for the required time, and the course of the reaction was monitored using a gas chromatograph. Assignments of the products were made by comparison with authentic samples. All reactions were run at least in duplicate.

3. Results and discussion

3.1. *Synthesis and spectral analysis of $[MoO_2(L)(CH_3OH)]$*

H_2L has been synthesized following the same procedure as for 1-(2,4-dihydroxybenzylidene)-N-methyl-N-phenylthiosemicarbazone [19], except that the reaction was performed in the presence of acetic acid and the reaction mixture was refluxed for 8 h. The formation of the product, (2,4-dihydroxybenzylidene(5-N,N-methylphenylamino-1,3,4-thiadiazol-2-yl) hydrazone), via self-cyclization of thiosemicarbazone (scheme 2) may be rationalized as explained by J.P. Scovill *et al.* [20, 21]. The dioxomolybdenum(VI) complex, $[MoO_2(L)(CH_3OH)]$, was obtained by reaction of bis(acetylacetonato)dioxomolybdenum(VI) with a stoichiometric amount of H_2L in refluxing methanol. Brown crystals of the complex were isolated from the reaction mixture by slow evaporation of solvent at room temperature. The chemical formula is in accord with the data of elemental analysis and physicochemical



Scheme 2. Ligand synthesis and tautomer forms.

measurements. A single-crystal X-ray diffraction study of $[MoO_2(L)(CH_3OH)]$ shows it to be a six-coordinate monomeric complex in which the central Mo is coordinated by a tridentate NNO-donor ligand and the sixth coordination site is occupied by a methanol.

The characteristic IR frequencies of the complex confirmed the proposed molecular formula shown in scheme 1. The complex shows strong absorption bands at 916 and 887 cm^{-1} which can be assigned to symmetric and anti-symmetric stretches of $[MoO_2]^{2+}$, respectively [22]. The sharp band at 1628 cm^{-1}, assigned to ν(C=N) in the free ligand, has a bathochromic shift to 1605 cm^{-1} in the spectrum of the complex suggesting coordination of azomethine nitrogen to molybdenum [23–25]. The ν(N–N) of the hydrazone is found at 1112 cm^{-1}. The increase in the strength of this band in the spectrum of the complex again confirms coordination via azomethine nitrogen [26]. IR spectrum of the complex shows a sharp band at 1550 cm^{-1} due to the newly formed (N=C) bond, also indicating that thiadiazole nitrogen is coordinated. A slight shift with decreasing intensity of the (O–H) band at 3200 cm^{-1} [27] further agreed with coordination to the central metal ion through deprotonated phenolic oxygen.

The ^{1}H NMR spectrum of the ligand exhibits phenolic OH resonances at 9.86 and 10.86 ppm. Upon coordination to Mo, one signal disappeared and the second was observed at 10.36, indicating deprotonation of one phenolic OH and coordination [28]. The hydrazone NH in the ligand at $\delta = 9.86$ ppm is absent in the complex, suggesting tautomerization of ligand to form B in scheme 2 consistent with deprotonation of the amide NH in the thiadiazole ring [29]. The azomethine C–H signal in ligand at 8.25 ppm shifted to 8.51 ppm in the complex. The downfield shift of this signal might be attributed to removal of electron density from the nitrogen of the azomethine to the Mo [30]. The methyl protons of ligand were observed at $\delta = 3.34$ ppm. The ^{1}H NMR data for ligand and complex are consistent with interpretation of the IR spectra.

Electronic absorption spectra of the ligand and complex were recorded in 10^{-4} M DMF solution between 250 and 700 nm (figure 1). The absence of a d–d transition absorption band in the visible region confirms the $4d^0$ electronic configuration of Mo(VI). The compounds display several common absorption maxima at 200–350 nm assigned to

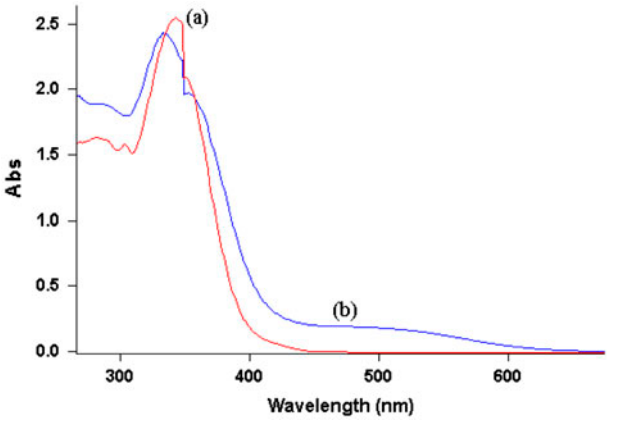


Figure 1. UV–vis spectroscopy of (a) ligand (10^{-4} M) and (b) $[MoO_2L(CH_3CN)]$ (10^{-4} M) in DMF.

intra-ligand transitions. Electronic absorption of the complex exhibits one shoulder at 500 nm (in the region 450–550 nm) which may be assigned as ligand to metal charge transfer transition.

3.2. *Description of the crystal structure of $[MoO_2(L)(CH_3OH)]$*

The asymmetric unit of the crystal consists of two symmetry-independent, but structurally very similar, Mo(VI) species denoted as **A** and **B**, one uncoordinated methanol and one disordered water (at special position, on the twofold axis). Both Mo(VI) ions have similar six coordination in which *cis*-$[MoO_2]^{2+}$ species are meridionally coordinated by doubly deprotonated L^{2-} via ONN donors, phen-2-ol-oxygen, imine- and thiadiazole-1-nitrogens, forming six- and five-membered chelate rings around *cis*-$[MoO_2]^{2+}$. The sixth site is occupied by oxygen from methanol. The molecular geometry and atom numbering of one of the structurally similar $[MoO_2L(CH_3OH)]$ molecules is presented in figure 2. Selected bond lengths and angles with their standard deviations for $[MoO_2(L)(CH_3OH)]$ are given in table 2.

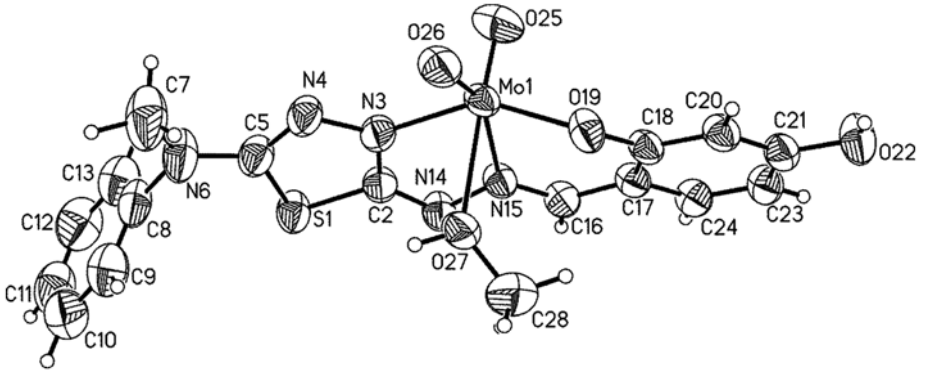


Figure 2. One of the symmetry independent molecules of $[MoO_2(L)(CH_3OH)]$; ellipsoids are drawn at the 50% probability level with hydrogens shown as spheres of arbitrary radii.

Table 2. Selected bond distances (Å) and angles (°) for $[MoO_2(L)(CH_3OH)]$; numerical values for **B** are given in square brackets.

Bond distance	
Mo1–O19	1.922 (2) [1.935(2)]
Mo1–O25	1.675(2) [1.703(2)]
Mo1–O26	1.703 (2) [1.698(12)]
Mo1–O27	2.427(2) [2.380(2)]
Mo1–N3	2.086(2) [2.067(2)]
Mo1–N15	2.246(2) [2.236(2)]
N3–C2	1.346(3) [1.351(3)]
N4–C5	1.291(3) [1.293(3)]
N14–C2	1.310(3) [1.310(3)]
N15–C16	1.292(3) [1.298(3)]
Bond angle	
O19–Mo1–O25	100.99(1) [99.23(8)]
O19–Mo1–O26	106.29(1) [105.90(8)]
O19–Mo1–O27	78.24(7) [77.25(7)]
O19–Mo1–N15	81.99(7) [81.54(7)]
O25–Mo1–O26	106.29(1) [105.58(9)]
O25–Mo1–O27	169.33(9) [170.93(8)]
O25–Mo1–N3	100.10(1) [101.69(9)]
O25–Mo1–N15	94.86(1) [94.96(8)]
O26–Mo1–O27	84.02(8) [83.47(8)]
O27–Mo1–N3	76.32(8) [78.00(7)]
O27–Mo1–N15	74.47(7) [76.32(8)]
N3–Mo1–N15	70.91(7) [70.68(7)]

As both complexes are structurally very similar, we will discuss them jointly giving the appropriate numerical values for **B** in square brackets. The coordination geometry around molybdenum can be described as distorted octahedral. For example, the *cis* angles range from 70.91(7)° [70.68(7)°] for N(3A)-Mo(1A)-N(15A) to 106.29(1)° [105.58(9)°] for O (25)–Mo(1A)–O(26).

Bond lengths N14–C2 and N3–C2, 1.310(3) [1.310(3)] and 1.346(3) [1.351(3)] Å, respectively, indicate partial double-bond character, while N4–C5 and N15–C16 are pure double-bonds with 1.291(4) [1.293(3)] and 1.292(3) [1.298(3)] Å, respectively [31–34]. This suggests that during complexation the ligand undergoes tautomerization to the B tautomeric form shown in scheme 2.

The Mo–O25 and Mo–O26 bond lengths, 1.675(2) [1.703(2)] and 1.703(2) [1.698(12)] Å, respectively, are mostly as expected, indicating they are double-bonds [35–37]. The corresponding O=M=O angle 106.29(1) [105.58(9)] is significantly larger than 90° because of the repulsion between the π-electrons of the terminal oxos. This event is accompanied by a contraction of the opposite angle N3–Mo–N15, 70.91(7) [70.68(7)], in accord to literature data for *cis*-dioxo molybdenum(VI) complexes [24, 34]. In the coordination sphere of molybdenum, the distances of 2.086(2) [2.067(2)] Å to thiadiazole-1-nitrogen N3 and of 1.922(2) [1.935(2)] Å to the phenolate oxygen O19 represent rather normal single-bond values [25, 27, 29, 38], whereas the bonds from molybdenum to the azomethine nitrogen N15, 2.246(2) [2.236(2)] Å and to O27 of the solvent molecule, 2.427(2) [2.380(2)] Å are longer than the normal single-bond length due to the strong *trans* influence of the essentially doubly bonded terminal oxo ligands O25 and O26 [23, 39–41]. Other structural parameters for ligand framework are comparable with previously reported Mo(VI) complexes, containing tridentate ONN-donor ligands [29, 42–44].

Crystal packing diagram of $[MoO_2(L)(CH_3OH)]$ is shown in figure 3. As shown in this figure, there are several O–H···O, O–H···N, and C–H···O hydrogen bonds which stabilize the structure of the complex (table 3). Only in intermolecular interactions are two symmetry-independent molecules essentially different. The principal structural motif is the infinite chains along the b-direction of alternating **A** and **B** complexes connected by O27–H···N14 hydrogen bonds. The chains are connected by hydrogen bridges through solvent methanol and by direct hydrogen bonds between symmetry-related complex molecules. Two molecules **A** and two methanols are connected into centrosymmetric tetramers by O22–H···O1S–H···N4, while **B** molecules are connected into centrosymmetric dimers by O22–H···O25.

3.3. *Homogeneous catalytic epoxidation of olefins*

In order to find the optimized conditions for oxidation of alkenes with TBHP catalyzed by $[MoO_2(L)(CH_3OH)]$, cyclooctene is used as the model substrate. The molar ratio 3 : 1000 : 1000 of the catalyst : cyclooctene : TBHP is the optimum molar ratio for the catalytic system. The effect of various solvents on the progress of the reactions was investigated on catalytic epoxidation of cyclooctene (table 4). Efficiency of the catalyst in different solvents decreases in the order dichloroethane > chloroform > dichloromethane > acetonitrile > methanol.

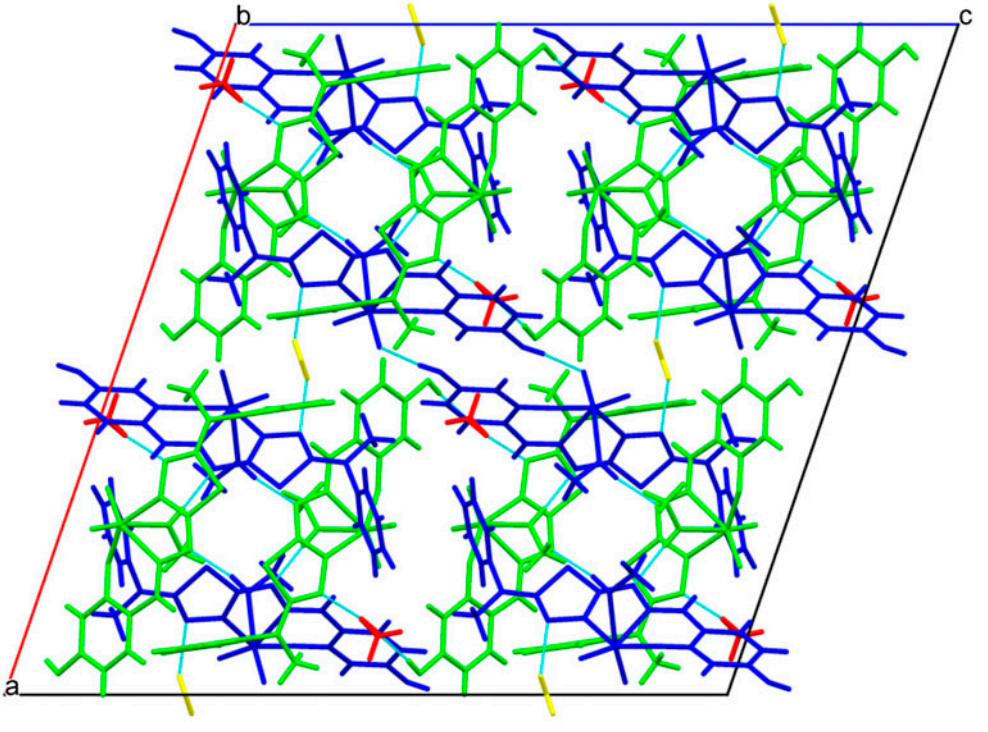


Figure 3. A fragment of the crystal packing of $[MoO_2(L)(CH_3OH)]$ as seen along the *b*-direction (along ~ABAB~ chains). Hydrogen bonds are shown as dashed lines; one can realize the different modes of connecting A and B (cf. text). Color codes: green – molecule A, blue – molecule B, red – methanol, yellow – water (see http://dx.doi.org/10.1080/00958972.2014.993321 for color version).

Table 3. Geometry of the hydrogen bonds (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O1S–H1S···N4A[i]	1.00	1.87	2.835(3)	161
O22A–H22A···O1S	0.87	1.80	2.652(3)	169
O22B–H22B···O25B[ii]	0.91	1.86	2.764(3)	174
O27A–H27A···N14B	0.82	1.97	2.786(3)	169
O27B–H27B···N14A[iii]	0.87	1.91	2.765(3)	169
C16B–H16B···O26A	0.93	2.38	3.271(3)	161
O1 W–H1 W···N4B	0.90	2.21	3.010(8)	148

Symmetry operations: i = 1/2 − *x*, 1/2 − *y*, −*z*; ii = –*x*, 1 − *y*, −z; iii = 1/2 − *x*, 1/2 + *y*, 1/2 − *z*.

Apparently, highly coordinating solvents such as CH_3OH cause a significant decrease in the catalytic activity, since they compete with TBHP to bind to molybdenum. The best solvent was 1,2-dicholoroethane. In the next step, the effect of the catalyst amount on the conversion and selectivity is illustrated in table 4. Five different amounts of catalyst, 0.005, 0.004, 0.003, 0.002, 0.001 mM, were examined while keeping a fixed amount of cyclooctene (1 mM) and TBHP (1 mM). The results show that decreasing of the catalyst from 0.005 to 0.003 mM does not have an effect on the percent of conversion under the reaction condition in this study (table 4, entries 5 and 6), but further decreasing the catalyst amount to 0.001 mM causes conversion of cyclooctene to 84%.

Table 4. Optimized reaction condition in oxidation of cyclooctene with TBHP catalyzed by $[MoO_2(L)(CH_3OH)]$[a].

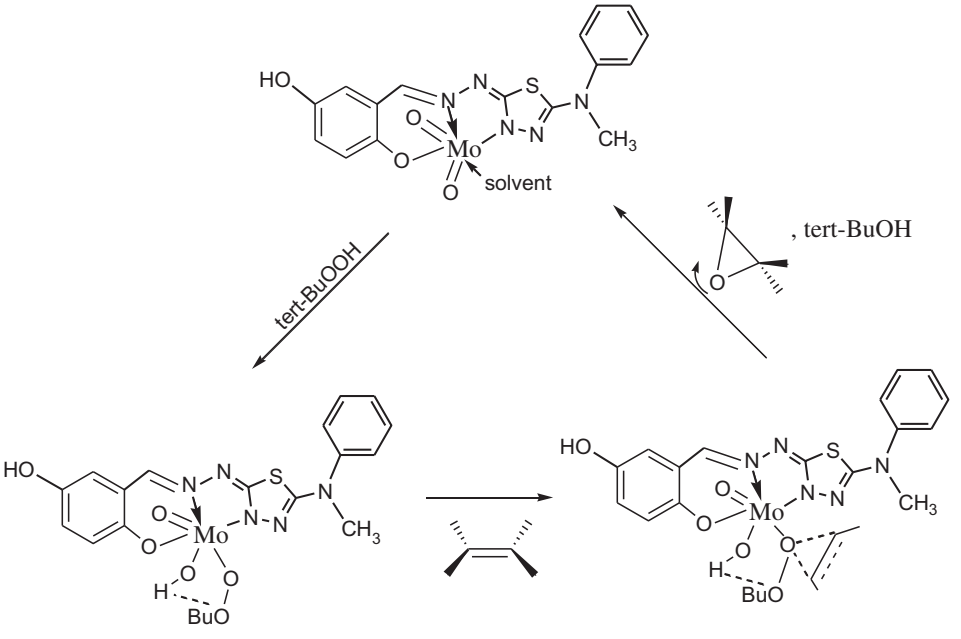
Entry	Catalyst (mM)	Solvent	Conversion (%)	Selectivity (%)
1	0.005	CH_3CN	55	100
2	0.005	CH_2Cl_2	83	95
3	0.005	CH_3OH	38	99
4	0.005	$CHCl_3$	96	99
5	0.005	$C_2H_4Cl_2$	99	99
6	0.004	$C_2H_4Cl_2$	99	99
7	0.003	$C_2H_4Cl_2$	99	99
7	0.002	$C_2H_4Cl_2$	96	99
8	0.001	$C_2H_4Cl_2$	84	99

[a]Reaction condition: 1 mM cyclooctene, 1 mM TBHP.
The reactions were run in reflux for 30 min.

Table 5. $[MoO_2(L)(CH_3OH)]$ catalyzed epoxidation of different olefins by TBHP[a].

Entry	Substrate	Conversion %[b]	Time (h)	Selectivity to epoxide %[b]
1	cyclohexene	98	1	>99
2	cyclooctene	99	0.5	99
3	styrene	96	4	6 (72[c], 22[d])
4	1-octene	90	3	>99
5	1-heptene	85	3	>99
6	*trans*-stilbene	92	3	89[e] (11)[c]
7	*cis*-stilbene	95	2	65[f] (35)[c]

[a]Reaction condition: The molar ratios for catalyst : alkene : TBHP are 3 : 1000 : 1000. The reactions were run in reflux and in 1 mL dichloroethane. [b]GC yield based on starting alkene. The by-product is: [c]benzaldehyde, [d]benzoic acid, [e]*trans*-stilbene epoxide, [f]*cis*-stilbene epoxide.



Scheme 3. Proposed mechanism for oxidation of alkenes catalyzed by $[MoO_2(L)(CH_3OH)]$ in the presence of TBHP.

In order to establish the general applicability of the method, various alkenes were subjected to the oxidation protocol with $[MoO_2(L)(CH_3OH)]$ (table 5). The most reactive cyclic alkenes were oxidized in high yield and excellent selectivity. The data for oxygenation of cyclohexene show no product from allylic attack, indicating that catalytic reaction occurs via non-radical processes [45]. High epoxide yields and selectivities were observed for aliphatic terminal alkenes such as 1-octene and n-heptene. The epoxidation of styrene with TBHP gave styrene oxide, benzaldehyde, and benzoic acid. Styrene oxide has been obtained only in poor yield, while the yield of benzaldehyde is the highest. Additionally, the epoxidation reaction is stereoselective. Epoxidation of *trans*-stilbene led to the *trans* epoxide, while epoxidation of *cis*-stilbene under similar conditions gave exclusively the *cis* epoxide.

Based on the results of this study, we suggest a general pathway (scheme 3), as proposed by Thiel [46], for this catalytic reaction, involving transfer of one TBHP proton to one oxo group of dioxo complex and coordination of TBHP anion to the Lewis acidic metal center. The six-coordinate species is subsequently activated for oxygen transfer to the olefin.

Recently, we reported the structures and catalytic activities of complexes of the form $[MoO_2L'(solv)]$ (solv = C_2H_5OH, CH_3OH and L′ = ONO donor Schiff-base ligand) [47–49]. The complexes catalyzed epoxidation of olefins using TBHP. The comparison of the catalytic activity of these complexes and $[MoO_2(L)(CH_3OH)]$ presented here indicates that replacing an oxygen donor with a nitrogen donor in the structure of chelating ligand does not significantly affect the catalytic activity of the complexes in epoxidation.

4. Conclusion

$[MoO_2(L)(CH_3OH)]$ was synthesized by reaction of a new Schiff base having a 1,3,4-thiadiazole moiety with $[MoO_2(acac)_2]$. Crystallographic investigation reveals that the ligand is tridentate via phenolic oxygen, azomethine nitrogen, and thiadiazole nitrogen. The sixth site of distorted octahedral geometry of the complex is occupied by methanol. $[MoO_2(L)(CH_3OH)]$ is employed as a catalyst for the homogeneous epoxidation of olefins using TBHP. The complex catalyzed epoxidation of olefins to afford the corresponding epoxides in high yield and selectivity for aliphatic terminal alkenes and cyclic alkenes.

Supplementary material

CCDC 932253 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK.

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