ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 6, pp. 457–466. © Pleiades Publishing, Ltd., 2019.

Synthesis, Crystal Structures, and Catalytic Oxidation of Olefins of Novel Oxomolybdenum(VI) Clusters

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Received May 30, 2018; revised December 20, 2018; accepted December 26, 2018

Abstract—Two Mo(VI) clusters, $(H_2L)_3[Mo_7O_{12}(\mu_2\text{-}O)_8(\mu_3\text{-}O)_4] \cdot 3H_2O$ (**I**) and $(H_2L)_2[Mo_8O_{14}(\mu_2\text{-}O)_6(\mu_3\text{-}O)_4(\mu_5\text{-}O)_2] \cdot 4DMF$ (**II**), derived from $MoO_2(Acac)_2$ and *N*-methylethane-1,2-diamine (L) in water and DMF, respectively, are reported. The complexes were characterized by single crystal structure analysis (CIF files CCDC nos. 1846032 (**I**) and 1443681 (**II**)). Compound **I** contains a seven nuclear molybdenum(VI) complex anion, three H_2L cations and three water molecules. Compound **II** contains an eight nuclear molybdenum(VI) complex anion, two H_2L cations and four DMF molecules. All Mo atoms are in octahedral coordination. Complex **I** crystallized as monoclinic space group $P2_1/n$ with unit cell dimensions $a = 12.3005(12)$, $b = 17.3944(17)$, $c = 15.9446(16)$ Å, $\beta = 93.862(2)°$, $V = 3403.8(6)$ Å^3, $Z = 4$, $R_1 = 0.0795$, $wR_2 = 0.1677$. Complex **II** crystallized as monoclinic space group $P2_1/n$ with unit cell dimensions $a = 11.1465(13)$, $b = 16.460(2)$, $c = 12.7942(16)$, $\beta = 97.368(2)°$, $V = 2328.0(5)$ Å^3, $Z = 2$, $R_1 = 0.0362$, $wR_2 = 0.0754$. The complexes were tested as catalyst for the oxidation of olefins and showed effective activity.

Keywods: oxomolybdenum(VI) cluster, *N*-methylethane-1,2-diamine, catalysis, oxidation, olefins

DOI: 10.1134/S1070328419060058

INTRODUCTION

Molybdenum is an essential metal that is capable of forming metal complexes with various ligands [1–5]. Molybdenum is not only much less toxic than many other metals of industrial importance but it is also an essential constituent of certain enzymes that catalyze reduction of molecular nitrogen and nitrate in plants and oxidation (hydroxylation) of xanthine and other purines and aldehydes in animals [6]. Epoxides are very important chemicals for manufacturing a range of important commercial products such as pharmaceuticals and polymers. Many transition metal compounds have been reported for oxidation of olefins [7–13]. Molybdenum compounds are known for considerable use in organic chemistry, in particular for the various oxidations of organic compounds [2, 4, 14]. Oxidoperoxido molybdenum compounds have been intensively investigated as oxidation catalysts for variety of organic substrates, particularly for sulfoxidation and epoxidation of olefins [15–18]. In order to further study the catalytic potentiality of the molybdenum compounds, in this paper, the synthesis, crystal structures and catalytic activity of Mo(VI) clusters, $(H_2L)_3[Mo_7O_{12}(\mu_2\text{-}O)_8(\mu_3\text{-}O)_4] \cdot 3H_2O$ (**I**) and $(H_2L)_2[Mo_8O_{14}(\mu_2\text{-}O)_6(\mu_3\text{-}O)_4(\mu_5\text{-}O)_2] \cdot 4DMF$ (**II**), derived from $MoO_2(Acac)_2$ and *N*-methylethane-1,2-diamine (L), are reported.

EXPERIMENTAL

Materials and methods. All the reagents and solvents used in the synthesis were procured commercially and used without subsequent purification. The starting material, bis(acetylacetonato) dioxomolybdenum(VI), $[MoO_2(Acac)_2]$ was prepared as described in the literature [19]. Microanalyses (C, H, and N) were performed using a Perkin-Elmer 2400 elemental analyzer. Single crystal X-ray data were collected on a Bruker SMART APEX II diffractometer.

Synthesis of I. *N*-Methylethane-1,2-diamine (0.074 g, 1.0 mmol) and $MoO_2(Acac)_2$ (0.328 g, 1.0 mmol) were dissolved in 20 mL water. The mixture was stirred at room temperature for 30 min, to give colorless solution. After leaving the solution for a few days at room temperature, colorless prism crystals were formed.

Table 1. Crystallographic data and refinement parameters for compounds **I**, **II**

Parameter	Value	
	I	**II**
Formula weight	1338.07	1628.20
Crystal size, mm	0.13 × 0.12 × 0.12	0.20 × 0.20 × 0.19
Temperature, K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	12.3005(12)	11.1465(13)
b, Å	17.3944(17)	16.460(2)
c, Å	15.9446(16)	12.7942(16)
β, deg	93.862(2)	97.368(2)
V, Å^3	3403.8(6)	2328.0(5)
Z	4	2
ρ_{calcd}, g cm^{-3}	2.611	2.323
$\mu(MoK_\alpha)$, mm^{-1}	2.600	2.180
$F(000)$	2592	1584
Number of measured reflections	19982	21579
Number observed reflections with $I > 2\sigma(I)$	6339	5301
Unique reflections	5134	4667
Refinement parameters	465	295
Number of restraints	27	0
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0795, 0.1677	0.0362, 0.0754
R_1, wR_2 (all data)*	0.0961, 0.1750	0.0435, 0.0795
Goodness of fit of F^2	1.236	1.342

* $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

The product was filtered and washed with methanol. The yield was 21%.

For $C_9H_{42}N_6O_{27}Mo_7$

Anal. calcd., %	C, 8.08	H, 3.16	N, 6.28
Found, %	C, 8.21	H, 3.25	N, 6.21

Synthesis of II. *N*-Methylethane-1,2-diamine (0.074 g, 1.0 mmol) and $MoO_2(Acac)_2$ (0.328 g, 1.0 mmol) were dissolved in 20 mL DMF. The mixture was stirred at room temperature for 30 min, to give slight yellow solution. After leaving the solution for a few days at room temperature, yellow block crystals were formed. The product was filtered and washed with methanol. The yield was 15%.

For $C_{18}H_{52}N_8O_{30}Mo_8$

Anal. calcd., %	C, 13.28	H, 3.22	N, 6.88
Found, %	C, 13.15	H, 3.31	N, 6.79

X-ray structure determination. X-ray data for the compounds were collected on a Bruker SMART APEXII diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). A preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s frame^{-1}. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS [20]. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-H atoms with the SHELXTL program [21]. The water H atoms were located from difference Fourier maps and refined isotropically, with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å. The remaining H atoms were calculated at idealized positions and refined with the riding models. Crystallographic data for the compounds is summa-

Table 2. Selected bond lengths (Å) for compounds **I**, **II***

Bond	d, Å	Bond	d, Å	Bond	d, Å	Bond	d, Å
				I			
Mo(1)–O(22)	1.685(10)	Mo(4)–O(13)	2.134(9)	Mo(1)–O(21)	1.734(11)	Mo(4)–O(9)	2.253(11)
Mo(1)–O(20)	1.951(10)	Mo(5)–O(14)	1.690(12)	Mo(1)–O(3)	1.988(11)	Mo(5)–O(15)	1.710(12)
Mo(1)–O(4)	2.161(10)	Mo(5)–O(16)	1.927(9)	Mo(1)–O(19)	2.252(9)	Mo(5)–O(12)	1.930(12)
Mo(2)–O(2)	1.719(11)	Mo(5)–O(13)	2.147(9)	Mo(2)–O(1)	1.727(12)	Mo(5)–O(26)	2.570(13)
Mo(2)–O(3)	1.907(11)	Mo(6)–O(17)	1.716(10)	Mo(2)–O(5)	1.934(13)	Mo(6)–O(18)	1.720(10)
Mo(2)–O(4)	2.162(9)	Mo(6)–O(20)	1.946(10)	Mo(2)–O(27)	2.428(11)	Mo(6)–O(16)	2.004(9)
Mo(3)–O(6)	1.708(11)	Mo(6)–O(13)	2.143(9)	Mo(3)–O(7)	1.718(12)	Mo(6)–O(19)	2.274(9)
Mo(3)–O(8)	1.901(10)	Mo(7)–O(27)	1.732(11)	Mo(3)–O(5)	1.973(11)	Mo(7)–O(26)	1.749(11)
Mo(3)–O(4)	2.109(10)	Mo(7)–O(19)	1.873(10)	Mo(3)–O(9)	2.268(10)	Mo(7)–O(9)	1.903(10)
Mo(4)–O(11)	1.710(12)	Mo(7)–O(13)	2.282(10)	Mo(4)–O(10)	1.716(12)	Mo(7)–O(4)	2.299(10)
Mo(4)–O(8)	1.941(11)			Mo(4)–O(12)	2.002(11)		
				II			
Mo(1)–O(1)	1.696(3)	Mo(3)–O(9)	1.697(3)	Mo(1)–O(3)	1.747(3)	Mo(3)–O(10)	1.698(3)
Mo(1)–O(4)	1.941(3)	Mo(3)–O(8)	1.896(3)	Mo(1)–O(2)	1.947(3)	Mo(3)–O(2*A*)	2.003(3)
Mo(1)–O(5)	2.158(3)	Mo(3)–O(4)	2.324(3)	Mo(1)–O(5*A*)	2.351(3)	Mo(3)–O(5*A*)	2.336(3)
Mo(2)–O(6)	1.701(3)	Mo(4)–O(12)	1.695(3)	Mo(2)–O(7)	1.709(3)	Mo(4)–O(11)	1.698(3)
Mo(2)–O(8)	1.911(3)	Mo(4)–O(13)	1.894(3)	Mo(2)–O(13*A*)	1.920(3)	Mo(4)–O(4)	1.996(3)
Mo(2)–O(3)	2.282(3)	Mo(4)–O(5)	2.318(3)	Mo(2)–O(5*A*)	2.460(3)	Mo(4)–O(2*A*)	2.333(3)

rized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1846032 (**I**) and 1443681 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic epoxidation of olefins. In a typical catalytic experiment, *tert*-butylhydroperoxide (TBHP) (1 mmol) was added to a solution of olefin (1 mmol), chlorobenzene (1 mmol) as an internal standard and the complexes (2×10^{-4} mmol) in 1,2-dichloroethane (0.5 mL). The mixture was stirred at 80°C under air and the course of the reaction was monitored using gas chromatography (Agilent Technologies Instruments 6890N, equipped with a capillary column (19019J-413 HP-5, 5% Phenyl Methyl Siloxane, Capillary 60.0 m × 250 μm × 1.00 μm) and a flame ionization detector). Assignments of products were made by comparison with authentic samples. All the reactions were run two times.

RESULTS AND DISCUSSION

Compounds **I**, **II** were prepared in a similar procedure with different solvents. Crystals of the compounds are stabilized in air at room temperature, and soluble in water, methanol, ethanol, and DMF.

Molecular structures of the compounds **I** and **II** are shown in Fig. 1. Compound **I** contains a seven nuclear molybdenum(VI) complex anion, three H_2L cations, and three water molecules. Compound **II** contains an eight nuclear molybdenum(VI) complex anion, two H_2L cations, and four DMF molecules. In the anionic moiety of compound **I**, there are eight μ_2-O bridging groups, four μ_3-O bridging groups, and twelve terminal oxido groups. In the anionic moiety of compound **II**, there are six μ_2-O bridging groups, four μ_3-O bridging groups, two μ_5-O bridging groups, and fourteen

Table 3. Selected bond angles (deg) for compounds **I**, **II***

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
I					
O(22)Mo(1)O(21)	104.4(6)	O(14)Mo(5)O(26)	177.1(5)	O(8)Mo(3)O(5)	155.6(4)
O(21)Mo(1)O(20)	100.7(5)	O(16)Mo(5)O(26)	80.2(4)	O(7)Mo(3)O(4)	156.3(5)
O(21)Mo(1)O(3)	92.2(5)	O(13)Mo(5)O(26)	70.2(3)	O(5)Mo(3)O(4)	74.2(4)
O(22)Mo(1)O(4)	96.0(5)	O(17)Mo(6)O(20)	100.0(5)	O(7)Mo(3)O(9)	87.3(5)
O(20)Mo(1)O(4)	87.7(4)	O(17)Mo(6)O(16)	92.6(4)	O(5)Mo(3)O(9)	85.2(4)
O(22)Mo(1)O(19)	166.2(5)	O(20)Mo(6)O(16)	155.9(4)	O(11)Mo(4)O(10)	104.3(6)
O(20)Mo(1)O(19)	74.5(4)	O(18)Mo(6)O(13)	95.9(5)	O(10)Mo(4)O(8)	101.1(6)
O(4)Mo(1)O(19)	72.5(4)	O(16)Mo(6)O(13)	73.2(4)	O(10)Mo(4)O(12)	90.3(5)
O(2)Mo(2)O(3)	101.6(5)	O(18)Mo(6)O(19)	165.8(5)	O(11)Mo(4)O(13)	94.5(5)
O(2)Mo(2)O(5)	102.7(6)	O(16)Mo(6)O(19)	85.9(4)	O(8)Mo(4)O(13)	89.3(4)
O(3)Mo(2)O(5)	147.2(4)	O(27)Mo(7)O(26)	104.9(5)	O(11)Mo(4)O(9)	164.5(5)
O(1)Mo(2)O(4)	105.9(5)	O(26)Mo(7)O(19)	101.6(5)	O(8)Mo(4)O(9)	73.5(4)
O(5)Mo(2)O(4)	73.7(4)	O(26)Mo(7)O(9)	102.3(5)	O(13)Mo(4)O(9)	72.8(4)
O(1)Mo(2)O(27)	176.3(5)	O(27)Mo(7)O(13)	170.8(4)	O(14)Mo(5)O(16)	99.3(5)
O(5)Mo(2)O(27)	81.4(4)	O(19)Mo(7)O(13)	76.9(4)	O(14)Mo(5)O(12)	99.0(6)
O(6)Mo(3)O(7)	103.4(6)	O(27)Mo(7)O(4)	82.0(4)	O(16)Mo(5)O(12)	146.7(4)
O(7)Mo(3)O(8)	99.7(5)	O(19)Mo(7)O(4)	76.7(4)	O(1)5Mo(5)O(13)	147.5(5)
O(7)Mo(3)O(5)	91.4(5)	O(13)Mo(7)O(4)	88.8(3)	O(1)2Mo(5)O(13)	73.5(4)
O(6)Mo(3)O(4)	97.6(5)	O(22)Mo(1)O(20)	98.0(5)	O(1)5Mo(5)O(26)	77.3(5)
O(8)Mo(3)O(4)	87.7(4)	O(22)Mo(1)O(3)	99.5(5)	O(1)2Mo(5)O(26)	80.1(4)
O(6)Mo(3)O(9)	167.9(5)	O(20)Mo(1)O(3)	154.9(4)	O(17)Mo(6)O(18)	104.7(5)
O(8)Mo(3)O(9)	73.8(4)	O(21)Mo(1)O(4)	156.4(5)	O(18)Mo(6)O(20)	98.4(5)
O(4)Mo(3)O(9)	73.1(4)	O(3)Mo(1)O(4)	72.7(4)	O(18)Mo(6)O(16)	98.2(5)
O(11)Mo(4)O(8)	98.2(5)	O(21)Mo(1)O(19)	88.5(4)	O(17)Mo(6)O(13)	156.6(4)
O(11)Mo(4)O(12)	101.6(5)	O(3)Mo(1)O(19)	84.5(4)	O(20)Mo(6)O(13)	87.8(4)
O(8)Mo(4)O(12)	154.0(4)	O(2)Mo(2)O(1)	104.3(6)	O(17)Mo(6)O(19)	88.6(4)
O(10)Mo(4)O(13)	156.8(5)	O(1)Mo(2)O(3)	99.1(6)	O(20)Mo(6)O(19)	74.1(4)
O(12)Mo(4)O(13)	72.5(4)	O(1)Mo(2)O(5)	95.8(6)	O(13)Mo(6)O(19)	72.1(4)
O(10)Mo(4)O(9)	90.2(5)	O(2)Mo(2)O(4)	149.7(5)	O(27)Mo(7)O(19)	101.5(5)

Table 3. (Contd.)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(12)Mo(4)O(9)	83.3(4)	O(3)Mo(2)O(4)	74.2(4)	O(27)Mo(7)O(9)	100.5(5)
O(14)Mo(5)O(15)	105.6(7)	O(2)Mo(2)O(27)	78.6(5)	O(19)Mo(7)O(9)	141.9(4)
O(15)Mo(5)O(16)	100.3(5)	O(3)Mo(2)O(27)	82.3(4)	O(26)Mo(7)O(13)	84.4(5)
O(15)Mo(5)O(12)	101.3(5)	O(4)Mo(2)O(27)	71.1(4)	O(9)Mo(7)O(13)	76.5(4)
O(14)Mo(5)O(13)	106.9(5)	O(6)Mo(3)O(8)	98.5(5)	O(26)Mo(7)O(4)	173.2(5)
O(16)Mo(5)O(13)	74.6(4)	O(6)Mo(3)O(5)	99.9(5)	O(9)Mo(7)O(4)	76.1(4)
II					
O(1)Mo(1)O(3)	104.31(15)	O(10)Mo(3)O(5*A*)	161.11(14)	O(6)Mo(2)O(3)	90.32(14)
O(3)Mo(1)O(4)	97.89(14)	O(4)Mo(3)O(5*A*)	71.03(10)	O(8)Mo(2)O(3)	78.51(13)
O(3)Mo(1)O(2)	96.33(14)	O(12)Mo(4)O(13)	101.18(15)	O(6)Mo(2)O(5*A*)	159.93(14)
O(1)Mo(1)O(5)	98.59(13)	O(12)Mo(4)O(4)	96.88(15)	O(8)Mo(2)O(5*A*)	74.04(11)
O(4)Mo(1)O(5)	78.10(11)	O(13)Mo(4)O(4)	146.63(12)	O(9)Mo(3)O(10)	104.83(17)
O(1)Mo(1)O(5*A*)	174.25(13)	O(11)Mo(4)O(5)	159.84(15)	O(10)Mo(3)O(8)	101.38(16)
O(4)Mo(1)O(5*A*)	77.56(11)	O(4)Mo(4)O(5)	73.30(11)	O(10)Mo(3)O(2*A*)	101.34(15)
O(5)Mo(1)O(5*A*)	75.70(12)	O(11)Mo(4)O(2*A*)	88.07(14)	O(9)Mo(3)O(4)	162.67(13)
O(6)Mo(2)O(8)	103.17(16)	O(4)Mo(4)O(2*A*)	71.42(11)	O(8)Mo(3)O(4)	83.99(12)
O(6)Mo(2)O(13*A*)	102.36(16)	O(1)Mo(1)O(4)	102.12(14)	O(9)Mo(3)O(5*A*)	93.82(14)
O(8)Mo(2)O(13*A*)	144.58(13)	O(1)Mo(1)O(2)	100.24(14)	O(8)Mo(3)O(5*A*)	77.40(12)
O(7)Mo(2)O(3)	164.34(13)	O(4)Mo(1)O(2)	149.54(12)	O(12)Mo(4)O(11)	105.57(17)
O(13)Mo(2)O(3*A*)	77.20(12)	O(3)Mo(1)O(5)	157.07(13)	O(11)Mo(4)O(13)	100.37(16)
O(7)Mo(2)O(5*A*)	94.76(13)	O(2)Mo(1)O(5)	78.33(11)	O(11)Mo(4)O(4)	101.48(15)
O(3)Mo(2)O(5*A*)	69.61(10)	O(3)Mo(1)O(5*A*)	81.38(12)	O(12)Mo(4)O(5)	94.46(14)
O(9)Mo(3)O(8)	101.27(15)	O(2)Mo(1)O(5*A*)	78.13(11)	O(13)Mo(4)O(5)	77.50(12)
O(9)Mo(3)O(2*A*)	96.48(14)	O(6)Mo(2)O(7)	105.29(16)	O(12)Mo(4)O(2*A*)	163.82(14)
O(8)Mo(3)O(2*A*)	146.37(12)	O(7)Mo(2)O(8)	98.58(15)	O(13)Mo(4)O(2*A*)	84.47(12)
O(10)Mo(3)O(4)	90.09(14)	O(7)Mo(2)O(13*A*)	97.90(15)	O(5)Mo(4)O(2*A*)	71.78(10)
O(2)Mo(3)O(4*A*)	71.52(11)				

* Symmetry code for *A*: $1 - x$, $1 - y$, $1 - z$.

terminal oxido groups. Each Mo center is coordinated by six O atoms, forming an octahedral geometry. The Mo–O bonds in both compounds are similar to each other and comparable to those observed in similar oxomolybdenum clusters [22, 23].

In the crystal structure of both compounds, the molybdenum clusters are linked by H_2L cations and water or DMF molecules through hydrogen bonds (Table 4), to form three-dimensional network (Fig. 2).

Considering the structures of two compounds are similar, the present work used compound **I** as catalyst to explore suitable experimental conditions. The catalytic property of compound **I** was first studied in the homogeneous epoxidation of cyclohexene, used as a model substrate, and TBHP as the oxygen donor. The influence of several solvents was evaluated (Table 5). It is clear that toluene and 1,2-dichloroethane produce the highest yields and the catalytic activity is the best when 1,2-dichloroethane was used as the solvent. At 80°C with 1,2-dichloroethane, a turnover number (TON) of 5530 with the compound can be achieved. So, 1,2-dichloroethane can be used as solvent in the catalyst experiment.

The catalytic epoxidation of some olefins using the compounds as catalysts is summarized in Table 6. In general, both compounds show similar catalytic properties. It is clear that the epoxide yields and selectivity are good for cyclohexene (entries 1 and 2). However, the catalytic property decreased for styrene, *p*-fluorostyrene, *p*-chlorostyrene, and *p*-bromostyrene. The electronic effects may play key roles in the catalytic processes. The catalytic property of *p*-fluorostyrene, *p*-chlorostyrene and *p*-bromostyrene is better than styrene (entries 3–10). The complexes were highly

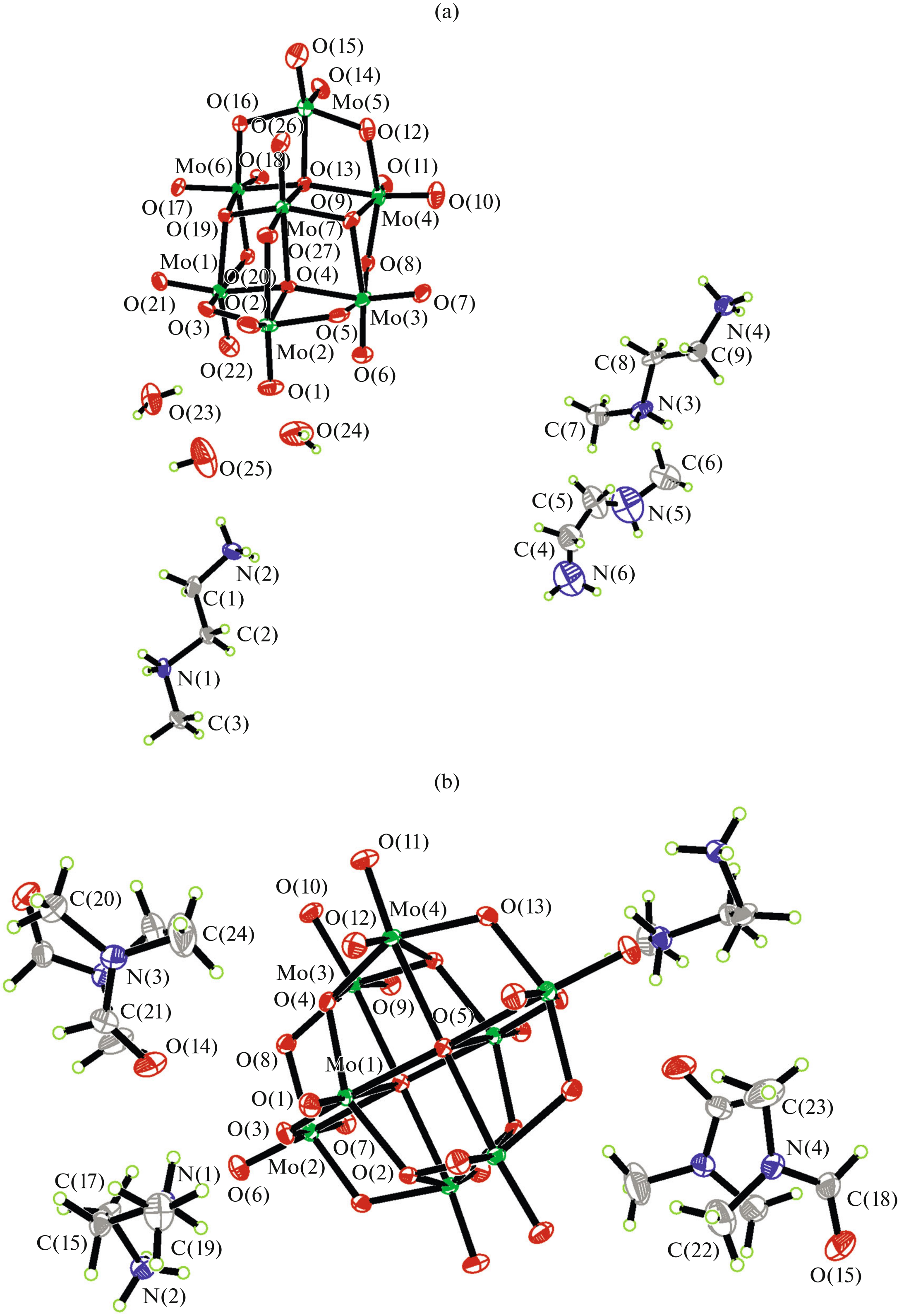


Fig. 1. Molecular structure of **I** (a) and **II** (b) with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms.

Table 4. Geometric parameters of hydrogen bond for compounds **I** and **II***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
N(1)–H(1*A*)···O(2)$^{\#1}$	0.90	2.21	3.050(18)	155(5)
N(1)–H(1*A*)···O(27)$^{\#1}$	0.90	2.31	2.992(16)	133(5)
N(1)–H(1*B*)···O(20)$^{\#2}$	0.90	1.94	2.826(15)	169(5)
N(2)–H(2*B*)···O(11)$^{\#2}$	0.89	2.02	2.857(18)	156(5)
N(2)–H(2*A*)···O(6)$^{\#3}$	0.89	2.23	2.937(19)	136(5)
N(2)–H(2*A*)···O(7)$^{\#3}$	0.89	2.52	3.26(2)	141(5)
N(2)–H(2*C*)···O(25)	0.89	1.95	2.74(3)	146(6)
N(3)–H(3*D*)···O(12)$^{\#4}$	0.90	2.04	2.771(18)	138(5)
N(3)–H(3*D*)···O(10)$^{\#4}$	0.90	2.50	3.32(2)	151(5)
N(3)–H(3*E*)···O(21)$^{\#5}$	0.90	2.28	3.004(17)	137(5)
N(3)–H(3*E*)···O(17)$^{\#5}$	0.90	2.32	2.852(18)	117(6)
N(3)–H(3*E*)···O(19)$^{\#5}$	0.90	2.55	3.355(17)	150(5)
N(4)–H(4*A*)···O(16)$^{\#5}$	0.89	2.02	2.898(18)	167(5)
N(4)–H(4*B*)···O(24)$^{\#6}$	0.89	1.87	2.75(2)	174(5)
N(4)–H(4*C*)···O(1)$^{\#7}$	0.89	2.22	3.00(2)	146(5)
N(4)–H(4*C*)···O(5)$^{\#7}$	0.89	2.40	3.127(18)	140(5)
N(5)–H(5*C*)···O(5)$^{\#8}$	0.90	2.31	2.81(4)	115(6)
N(5)–H(5*C*)···O(7)$^{\#8}$	0.90	2.56	3.14(4)	123(6)
N(5)–H(5*D*)···O(9)$^{\#8}$	0.90	2.60	3.42(4)	151(6)
N(6)–H(6*D*)···O(3)$^{\#3}$	0.89	2.03	2.81(3)	145(5)
N(6)–H(6*D*)···O(21)$^{\#3}$	0.89	2.61	3.32(3)	138(5)
N(6)–H(6*F*)···O(23)$^{\#5}$	0.89	2.22	3.05(4)	154(5)
N(6)–H(6*E*)···O(7)$^{\#8}$	0.89	2.14	2.97(3)	155(5)
O(24)–H(24*A*)···O(1)	0.85(1)	2.60(13)	3.22(2)	130(14)
O(23)–H(23*A*)···O(22)	0.85(1)	2.03(8)	2.84(2)	160(21)
		II		
N(1)–H(1*A*)···O(15)$^{\#9}$	0.90	1.95	2.788(6)	154(5)
N(1)–H(1*B*)···O(14)	0.90	1.84	2.681(6)	154(5)
N(1)–H(1*B*)···O(3)	0.90	2.51	3.015(5)	116(5)
N(2)–H(2*A*)···O(15)$^{\#9}$	0.89	2.07	2.859(6)	147(5)
N(2)–H(2*B*)···O(1)$^{\#7}$	0.89	2.04	2.893(5)	162(5)
N(2)–H(2*C*)···O(7)$^{\#6}$	0.89	2.07	2.943(5)	168(5)

* Symmetry codes: $^{\#1}$ $3/2 - x, -1/2 + y, 3/2 - z$; $^{\#2}$ $1 + x, y, z$; $^{\#3}$ $1 - x, 1 - y, 1 - z$; $^{\#4}$ $3/2 + x, 3/2 - y, -1/2 + z$; $^{\#5}$ $x, y, -1 + z$; $^{\#6}$ $1/2 - x, 1/2 + y, 1/2 - z$; $^{\#7}$ $-1/2 + x, 3/2 - y, -1/2 + z$; $^{\#8}$ $1/2 - x, -1/2 + y$, 1/2-z; $^{\#9}$ $1/2 - x, 1/2 + y, 3/2 - z$.

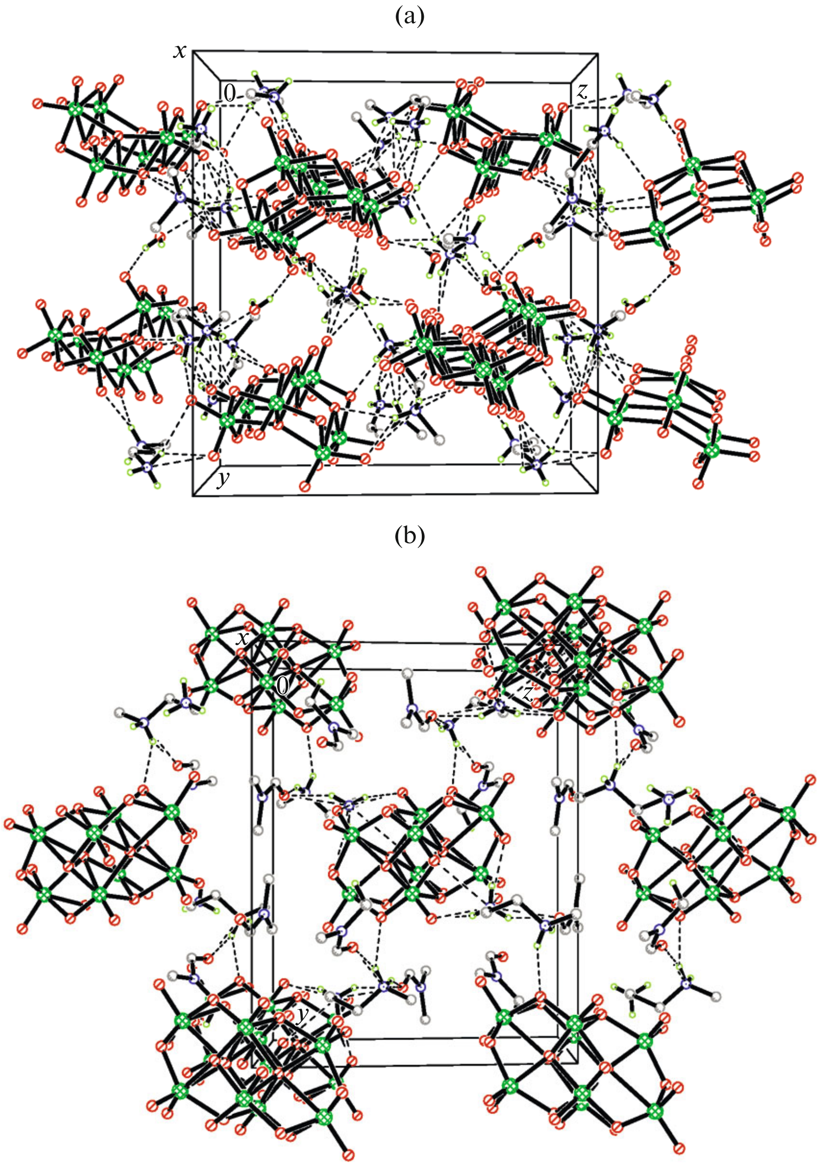


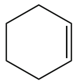
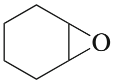
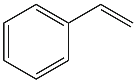
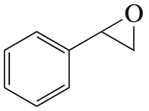
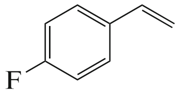
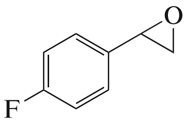
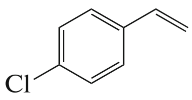
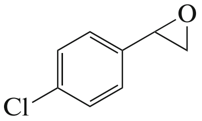
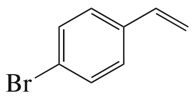
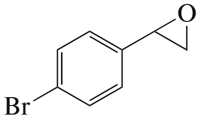
Fig. 2. Molacular packing diagrams of **I** viewed along the *x* axis (a) and **II** viewed along the *x* axis (b). Hydrogen bonds are shown as dashed lines.

Table 5. The solvent effects on the catalytic epoxidation of cyclohexene with TBHP using **I** as the catalyst*

Entry	Solvent	Conversion	Time, h	TON**
1	MeOH	78	1	3125
2	EtOH	82	1	3331
3	MeCN	90	1	3553
4	Cyclohexane	87	1	3446
5	Toluene	96	1	4572
6	1,2-Dichloroethane	100	30 min	5530

* The molar ratio for the compound : cyclohexene : TBHP is 1 : 5000 : 5000. The reactions were carried out at 80°C.
** TON = (mmol of product)/mmol of catalyst.

Table 6. Catalytic oxidation results*

Entry	Substrate	Product	Compound	Conversion, %	Selectivity, %	TON
1			**I**	100	100	5700
2			**II**	100	100	5560
3			**I**	64	59	1239
4			**II**	68	52	1356
5			**I**	82	69	1780
6			**II**	80	64	1655
7			**I**	77	58	1381
8			**II**	73	61	1527
9			**I**	72	65	2120
10			**II**	78	62	1897

* The molar ratio for the catalyst : olefin : TBHP is 1 : 5000 : 5000. The reactions were carried out at 80°C for 1 h.

selective for the epoxide for cyclohexene, but lower for various styrenes with benzaldehyde and acetophenone derivatives as side products.

Thus two novel Mo(VI) clusters have been synthesized and characterized by single crystal X-ray structure analysis. The Mo atoms are in octahedral coordination. The compounds were employed as catalyst for the epoxidation of various olefins with *tert*-butylhydroperoxide in dichloroethane. The compounds can catalyze cyclohexene to its epoxide with TBHP as the oxidant, with high yield and selectivity.

FUNDING

The author acknowledges the Zhengzhou University of Light Industry for supporting this work.

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