**Synthesis, Crystal Structures and Catalytic Property of Dioxomolybdenum(VI) Complexes Derived from Tridentate Schiff Bases**

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**Abstract**

A pair of structurally similar new dioxomolybdenum(VI) complexes, [MoO2L1(EtOH)]·EtOH (1) and [MoO2L2(MeOH)] (2), where L1 and L2 are the dianionic form of 2-[(2-hydroxyphenylimino)methyl]-6-methoxyphenol (H2L1) and 2-ethoxy-6-[(2-hydroxyphenylimino)methyl]phenol (H2L2), respectively, were prepared and characterized by IR and UV-Vis spectra, as well as single crystal X-ray diffraction. X-ray analyses indicate that the complexes are dioxomolybdenum(VI) species. Complex 1 contains ethanol as co-ligand, and complex 2 contains methanol as co-ligand. The coordination geometry around the Mo atoms can be described as distorted octahedron, with one imino-N and two phenolate-O of the Schiff base ligand, and one oxo group defining the equatorial plane, and with the other oxo group and one solvent-O occupying the axial positions. The catalytic oxidation property of the complexes with *tert*-butylhydroperoxide in CH2Cl2 was studied. Both complexes have excellent catalytic properties on cyclooctene and cyclohexene, and good properties on 1-hexene and 1-octene.

**Keywords:** Schiff base; Dioxomolybdenum complex; Crystal structure; Catalytic property

**1. Introduction**

Schiff base complexes have various catalytic properties, such as ring opening polymerization of cycloalkenes,1 oxidation of hydrocarbons,2 ring opening of large cycloalkanes,3 reduction of ketones to alcohols,4 alkylation of allylic substrates,5 improve enantioselectivity in the cyclopropanation reactions.6 The capability of molybdenum to formation of complexes with oxygen-, nitrogen-, and sulfur-containing ligands led to development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions.7 The properties of the complexes vary obviously with the different types of ligands and coordination sites. Recently, we have reported a molybdenum complex with hydrazone ligand and its catalytic property.8 In the present work, two new dioxomolybdenum(VI) complexes with Schiff base ligands 2-[(2-hydroxyphenylimino)methyl]-6-methoxyphenol (H2L1) and 2-ethoxy-6-[(2-hydroxyphenylimino)methyl]phenol (H2L2; Scheme 1), [MoO2L1(EtOH)]·EtOH (1) and [MoO2L2(MeOH)] (2), are presented.



Scheme 1. H2L1: X = OMe; H2L2: X = OEt

**2. Experimental**

**2.1. Materials and methods**

3-Methoxysalicylaldehyde, 3-ethoxysalicylaldehyde, 2-aminophenol and MoO2(acac)2 were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. The ligands H2L1 and H2L2 were synthesized according to the literature method with modification.9 Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 900 spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer. 1H and 13C NMR spectra were recorded on a Bruker 300 MHz instrument.

**2.2. Synthesis of 2-[(2-hydroxyphenylimino)methyl]-6-methoxyphenol (H2L1)**

3-Methoxysalicylaldehyde (0.010 mol, 1.52 g) and 2-aminophenol (0.010 mol, 1.10 g) were dissolved in ethanol (50 mL). The mixture was stirred for 30 min to give red solution. Then, the solvent was removed by distillation. The red solid was recrystallized from ethanol to give the Schiff base H2L1. Yield: 2.12 g (87%). IR data (cm–1): 3432 (O–H), 1628 (C=N), 1277 (Ar–O). UV-Vis data (CH3OH, λmax, nm): 267, 346, 451. 1H NMR (500 MHz, DMSO) δ 14.02 (s, 1H, OH), 9.74 (s, 1H, OH), 8.95 (s, 1H, CH=N), 7.37 (d, 1H, ArH), 7.20–7.07 (m, 3H, ArH), 6.98-6.84 (m, 3H, ArH), 3.81 (s, 3H, CH3). 13C NMR (126 MHz, DMSO) δ 161.54, 151.80, 150.95, 148.15, 134.47, 127.98, 123.78, 119.57, 119.48, 119.22, 117.89, 116.49, 115.22, 55.85. Anal. calcd. for C14H13NO3 (%): C, 69.12; H, 5.39; N, 5.76. Found (%): C, 68.95; H, 5.50; N, 5.83.

**2.3. Synthesis of 2-ethoxy-6-[(2-hydroxyphenylimino)methyl]phenol (H2L2)**

3-Ethoxysalicylaldehyde (0.010 mol, 1.66 g) and 2-aminophenol (0.010 mol, 1.10 g) were dissolved in ethanol (50 mL). The mixture was stirred for 30 min to give red solution. Then, the solvent was removed by distillation. The red solid was recrystallized from ethanol to give the Schiff base H2L2. Yield: 2.33 g (91%). IR data (cm–1): 3435 (O–H), 1628 (C=N), 1275 (Ar–O). UV-Vis data (CH3OH, λmax, nm): 270, 345, 450. 1H NMR (500 MHz, DMSO) δ 13.89 (s, 1H, OH), 9.76 (s, 1H, OH), 8.95 (s, 1H, CH=N), 7.37 (d, 1H, ArH), 7.20–7.03 (m, 3H, ArH), 6.98-6.84 (m, 3H, ArH), 4.07 (q, 2H, CH2), 1.33 (t, 3H, CH3). 13C NMR (126 MHz, DMSO) δ 161.53, 151.80, 151.02, 147.50, 134.47, 127.96, 123.81, 118.86, 119.48, 118.83, 117.45, 116.49, 118.16, 64.87, 14.75. Anal. calcd. for C15H15NO3 (%): C, 70.02; H, 5.88; N, 5.44. Found (%): C, 70.15; H, 5.96; N, 5.37.

**2.4. Synthesis of complex 1**

H2L1 (0.010 mol, 2.43 g) and MoO2(acac)2 (0.010 mol, 2.65 g) were mixed and dissolved in ethanol (50 mL). The mixture was stirred for 1 h to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a few days. Yield: 1.87 g (41%). IR data (cm–1): 3357 (O–H), 1612 (C=N), 1263 (Ar–O), 929 and 910 (Mo=O). UV-Vis data (CH3OH, λmax, nm): 273, 330. Anal. calcd. for C18H23MoNO7 (%): C, 46.86; H, 5.03; N, 3.04. Found (%): C, 46.67; H, 4.89; N, 3.13.

**2.5. Synthesis of complex 2**

H2L2 (0.01 mol, 2.57 g) and MoO2(acac)2 (0.01 mol, 2.65 g) were mixed and dissolved in methanol (50 mL). The mixture was stirred for 1 h to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a few days. Yield: 2.12 g (51%). IR data (cm–1): 3382 (O–H), 1611 (C=N), 1267 (Ar–O), 930 and 912 (Mo=O). UV-Vis data (CH3OH, λmax, nm): 275, 330. Anal. calcd. for C16H17MoNO6 (%): C, 46.28; H, 4.13; N, 3.37. Found (%): C, 46.10; H, 4.07; N, 3.51.

**2.6. X-ray crystallography**

X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoKα radiation (λ = 0.71073 Å). The collected data were reduced with SAINT,10 and multi-scan absorption correction was performed using SADABS.11 The structures of the complexes were solved by direct method, and refined against *F*2 by full-matrix least-squares method using SHELXTL.12 All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complexes are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

**Table 1.** Crystallographic and refinement data for the complexes

|  |  |  |
| --- | --- | --- |
|  | 1 | 2 |
| Formula | C18H23MoNO7 | C16H17MoNO6 |
| Formula weight | 461.31 | 415.25 |
| Crystal shape/color | Block/yellow | Block/yellow |
| *T* (K) | 298(2) | 298(2) |
| Crystal dimensions (mm3) | 0.23 × 0.22 × 0.18 | 0.27 × 0.27 × 0.22 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P*21/*c* | *P*21/*c* |
| *a* (Å) | 8.3857(11) | 10.0718(10) |
| *b* (Å) | 6.9208(12) | 18.1333(12) |
| *c* (Å) | 34.0235(15) | 19.234(2) |
| *β* (º) | 91.317(2) | 97.354(2) |
| *V* (Å3) | 1967.7(4) | 3483.9(6) |
| *Z* | 4 | 8 |
| *D*calc (g cm–3) | 1.557 | 1.583 |
| *μ* (Mo Kα) (mm–1) | 0.705 | 0.783 |
| *F*(000) | 944 | 1680 |
| Measured reflections | 9054 | 20401 |
| Unique reflections | 3611 | 6469 |
| Observed reflections (*I* ≥ 2*σ*(*I*)) | 2385 | 5125 |
| Parameters | 251 | 443 |
| Restraints | 1 | 5 |
| Goodness of fit on *F*2 | 1.135 | 1.093 |
| *R*1, *wR*2 [*I* ≥ 2*σ*(*I*)]*a* | 0.0896, 0.1551 | 0.0395, 0.1001 |
| *R*1, *wR*2 (all data)*a* | 0.1393, 0.1742 | 0.0549, 0.1096 |

*a R*1= *Fo* – *Fc*/*Fo*, *wR*2 = [∑ *w*(*Fo*2 – *Fc*2)/∑ *w*(*Fo*2)2]1/2

**Table 2.** Selected bond distances (Å) and angles (º) for the complexes.

|  |  |  |  |
| --- | --- | --- | --- |
| 1 | | | |
| Mo(1)-O(1) | 1.919(6) | Mo(1)-O(2) | 1.950(6) |
| Mo(1)-O(4) | 2.315(7) | Mo(1)-O(5) | 1.683(6) |
| Mo(1)-O(6) | 1.708(6) | Mo(1)-N(1) | 2.255(7) |
| O(5)-Mo(1)-O(6) | 103.8(3) | O(5)-Mo(1)-O(1) | 98.6(3) |
| O(6)-Mo(1)-O(1) | 100.7(3) | O(5)-Mo(1)-O(2) | 97.8(3) |
| O(6)-Mo(1)-O(2) | 97.6(3) | O(1)-Mo(1)-O(2) | 151.7(3) |
| O(5)-Mo(1)-N(1) | 92.7(3) | O(6)-Mo(1)-N(1) | 162.7(3) |
| O(1)-Mo(1)-N(1) | 81.6(3) | O(2)-Mo(1)-N(1) | 74.7(3) |
| O(5)-Mo(1)-O(4) | 170.1(3) | O(6)-Mo(1)-O(4) | 86.0(3) |
| O(1)-Mo(1)-O(4) | 80.8(3) | O(2)-Mo(1)-O(4) | 79.1(3) |
| N(1)-Mo(1)-O(4) | 77.4(2) |  |  |
| 2 | | | |
| Mo(1)-O(1) | 1.975(3) | Mo(1)-O(2) | 1.951(3) |
| Mo(1)-O(4) | 1.685(3) | Mo(1)-O(5) | 1.690(3) |
| Mo(1)-O(6) | 2.301(3) | Mo(1)-N(1) | 2.286(3) |
| Mo(2)-O(10) | 1.684(3) | Mo(2)-O(11) | 1.691(3) |
| Mo(2)-O(8) | 1.958(3) | Mo(2)-O(7) | 1.968(3) |
| Mo(2)-N(2) | 2.273(3) | Mo(2)-O(12) | 2.329(3) |
| O(4)-Mo(1)-O(5) | 104.70(16) | O(4)-Mo(1)-O(2) | 102.31(14) |
| O(5)-Mo(1)-O(2) | 95.90(14) | O(4)-Mo(1)-O(1) | 95.52(14) |
| O(5)-Mo(1)-O(1) | 104.44(14) | O(2)-Mo(1)-O(1) | 148.54(12) |
| O(4)-Mo(1)-N(1) | 90.80(14) | O(5)-Mo(1)-N(1) | 163.45(14) |
| O(2)-Mo(1)-N(1) | 74.77(12) | O(1)-Mo(1)-N(1) | 79.32(12) |
| O(4)-Mo(1)-O(6) | 169.69(13) | O(5)-Mo(1)-O(6) | 84.85(14) |
| O(2)-Mo(1)-O(6) | 80.18(12) | O(1)-Mo(1)-O(6) | 78.07(11) |
| N(1)-Mo(1)-O(6) | 80.14(12) | O(10)-Mo(2)-O(11) | 105.69(18) |
| O(10)-Mo(2)-O(8) | 96.57(15) | O(11)-Mo(2)-O(8) | 100.16(15) |
| O(10)-Mo(2)-O(7) | 102.51(15) | O(11)-Mo(2)-O(7) | 98.82(14) |
| O(8)-Mo(2)-O(7) | 148.24(12) | O(10)-Mo(2)-N(2) | 163.87(15) |
| O(11)-Mo(2)-N(2) | 89.44(14) | O(8)-Mo(2)-N(2) | 74.83(12) |
| O(7)-Mo(2)-N(2) | 80.14(11) | O(10)-Mo(2)-O(12) | 84.58(15) |
| O(11)-Mo(2)-O(12) | 169.73(14) | O(8)-Mo(2)-O(12) | 78.56(13) |
| O(7)-Mo(2)-O(12) | 78.24(11) | N(2)-Mo(2)-O(12) | 80.38(12) |

**2.7. Catalytic epoxidation of olefins**

Epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene catalyzed by the complexes with *tert*-butylhydroperoxide (TBHP) in CH2Cl2 was carried out according to the following general procedure. To a 25 mL round bottomed flask equipped with a magnetic stirring bar and immersed into water thermo-stated bath, was added 10 mL CH2Cl2, 1.0 mmol TBHP, 0.01 mmol catalyst and 1.0 mmol olefin. The mixture was refluxed with vigorous stirring for 2 h at an appropriately chosen temperature. The progress of the reaction was monitored by carefully withdrawing aliquots of the sample at different time intervals to determine concentrations of the products by GC analysis, using *n*-hexane as an internal standard and was left to proceed until near complete conversion of TBHP. The concentration of the TBHP was determined by iodometric titration method.13 The yield of epoxide (%) was calculated according to the starting amount of olefin. Assignments of the products were made by comparison with authentic samples. All the reactions were run in triplicates. Control experiments showed that no epoxide was formed in a measurable extent in the absence of catalyst.

**3. Results and discussion**

**3.1. General**

The Schiff base ligands H2L1 and H2L2 were readily prepared by the condensation reaction of 2-aminophenol with 3-methoxysalicylaldehyde and 3-ethoxysalicylaldehyde, respectively. The molybdenum(VI) complexes 1 and 2 were synthesized by stirring equimolar quantities of the Schiff bases with MoO2(acac)2 in ethanol or methanol at room temperature. Single crystals of the complexes are stable in air at ambient condition. The complexes are soluble in methanol, ethanol, acetonitrile, DMSO, DMF, but insoluble in water. The chemical formulae of the complexes have been confirmed by elemental analyses, IR spectra, and single crystal X-ray diffraction.

**3.2. Spectral characterization**

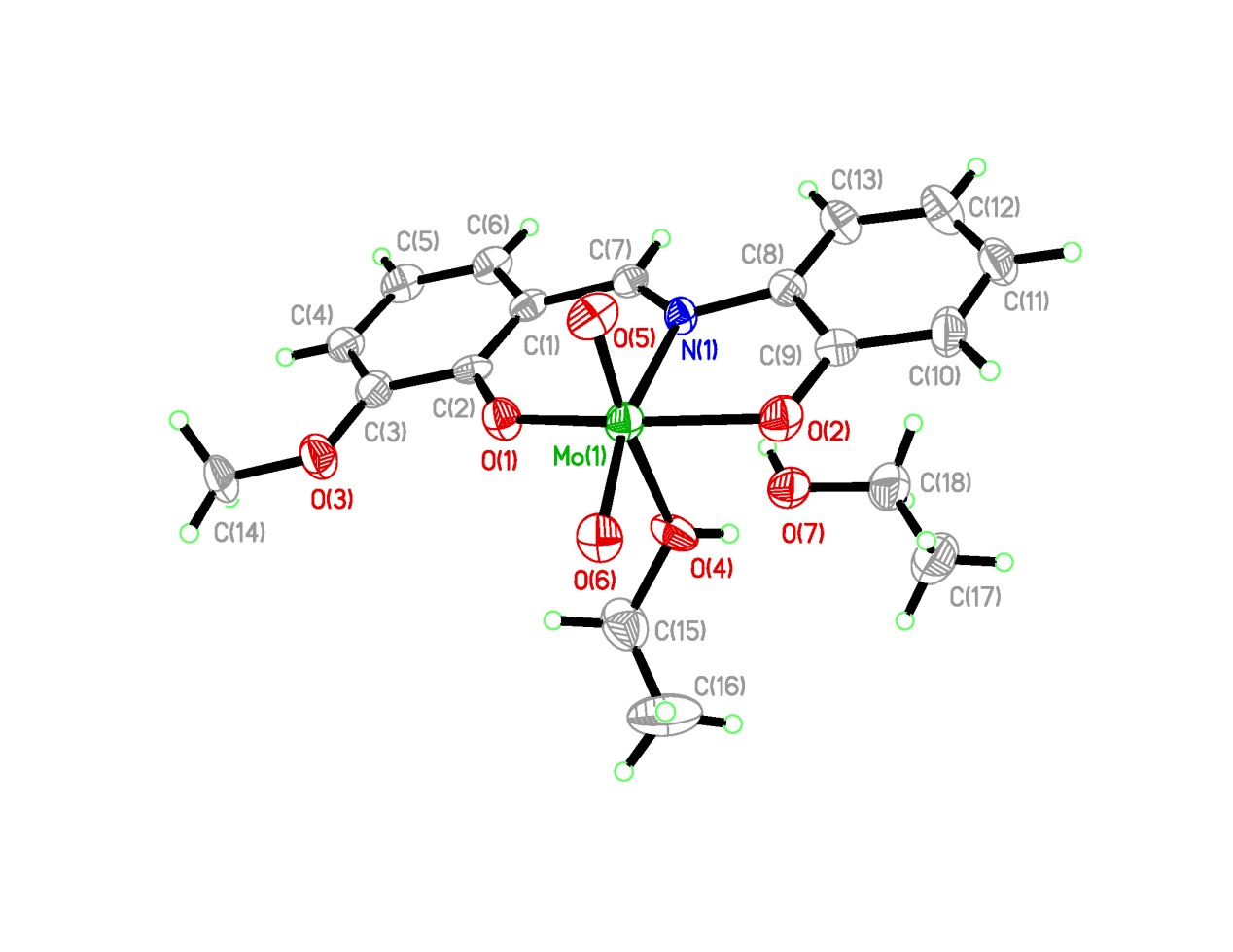
The bands at 1628 cm–1 characteristic of the azomethine groups present in the free Schiff bases, were shifted to lower wave numbers at 1612 cm–1 for 1 and 1611 cm–1 for 2, indicating that the involvement the azomethine nitrogen atoms in coordination. The bands at 1275–1277 cm–1 in the spectra of the Schiff bases are ascribed to the phenolic C–O stretching vibration. These bands are found at 1263 and 1267 cm–1 in the spectra of the complexes. These changes suggest that the hydroxyl groups of the Schiff bases took part in the complex formation. The Schiff bases and the complexes exhibit broad bands at 3300–3400 cm–1, which may be assigned to the ν(O-H). Further evidence of the bonding is also shown by the observation that new bands in the IR spectra of the metal complexes appear at 450–650 cm–1 assigned to Mo–N and Mo–O stretching vibrations. The Mo=O stretching mode occur as double bands at 930 and 910 cm–1, assigned to the symmetric and asymmetric stretching modes of the MoO2 moieties.14

Electronic absorption spectra of the Schiff base and the complexes were obtained in methanol solutions. The electronic absorption spectra of the free Schiff bases displayed three bands at 270, 345 and 450 nm, which are assigned for the *π*→*π*\* and *n*→*π*\* transitions, respectively. In the electronic spectra of the complexes, the strong bands centered at 273 nm are attributed to the intra-ligand *π*→*π*\* absorption peak of the Schiff base ligand. The LMCT and to some extent *π*→*π*\* bands appear at about 330 nm.

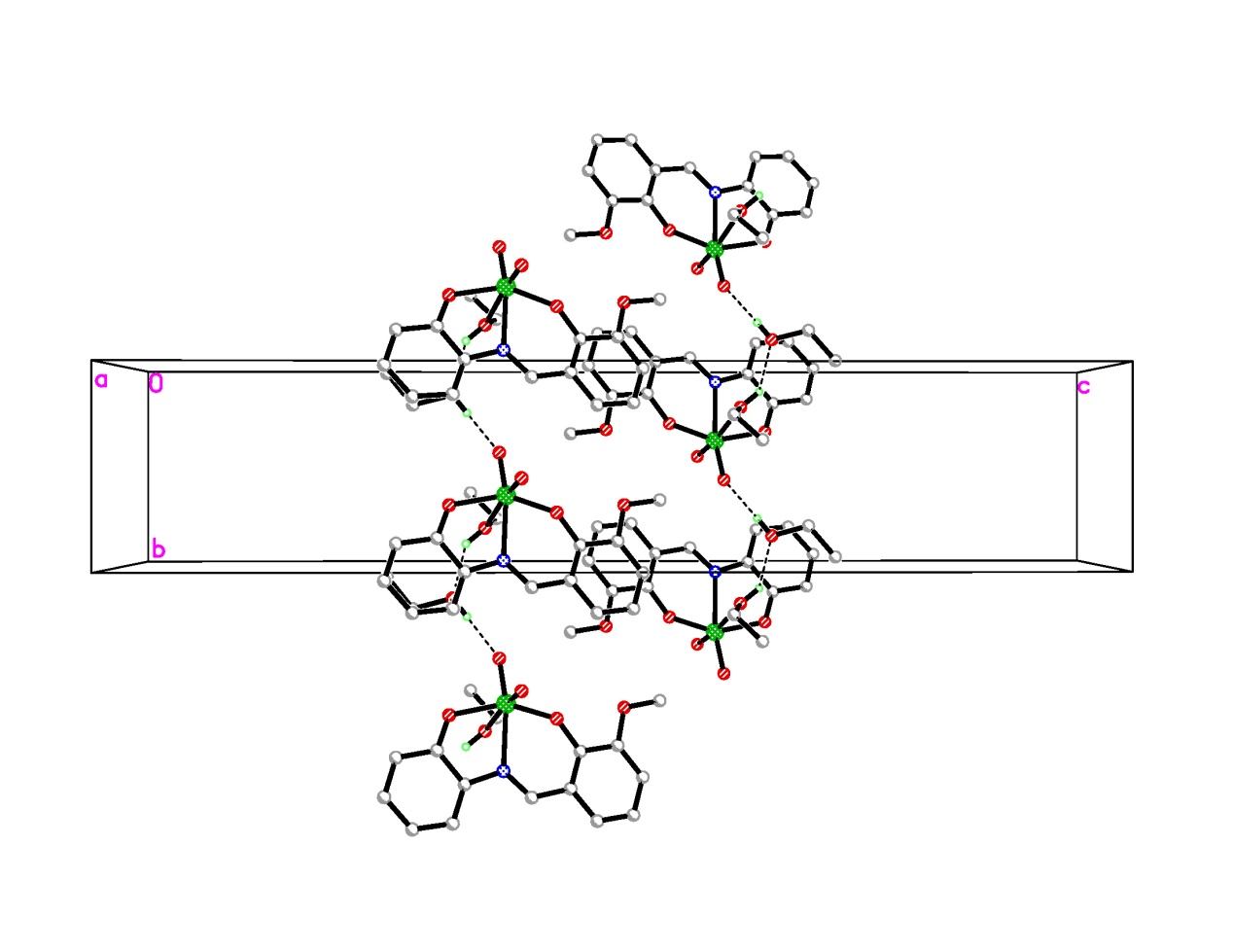
**3.3. Structural description of complex 1**

The molecular structure of complex 1 is shown in Figure 1. It contains a dioxomolybdenum complex molecule and an ethanol molecule of crystallization. The coordination geometry around the Mo atom can be described as distorted octahedron, with one imino-N and two phenolate-O of the Schiff base ligand, and one oxo group defining the equatorial plane, and with the other oxo group and one ethanol-O occupying the axial positions. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.7(3) and 81.6(3)°. The dihedral angle between the two benzene rings of the Schiff base ligand is 6.5(3)°. The O=Mo=O angle (103.8(3)º) and the Mo=O distances (1.683(3)–1.708(3) Å) are typical for *cis*-dioxomolybdenum(VI) complexes.7 The imino nitrogen and ethanol oxygen atoms, which are *trans* to the terminal oxo groups, bond to the Mo(VI) atom with distances of 2.255(7) Å for nitrogen and 2.315(7) Å for oxygen, respectively. The Mo–O distances vary from 1.919(6) to 1.950(6) Å for the phenolate oxygen, which are in accord with these types of bonds in hexa-coordinated dioxomolybdenum(VI) complexes.7

In the crystal structure of the complex, the [MoO2L1(EtOH)] complex molecules are linked by ethanol molecules through two intermolecular O–H···O hydrogen bonds [O(7)–H(7A) = 0.82 Å, H(7A)···O(6)i = 1.91 Å, O(7)···O(6)i = 2.725(9) Å, O(7)–H(7A)···O(6)i = 174(5)º; symmetry code for i: *x*, 1 + *y*, *z*], to form one dimensional chains along the *b* axis (Figure 2).



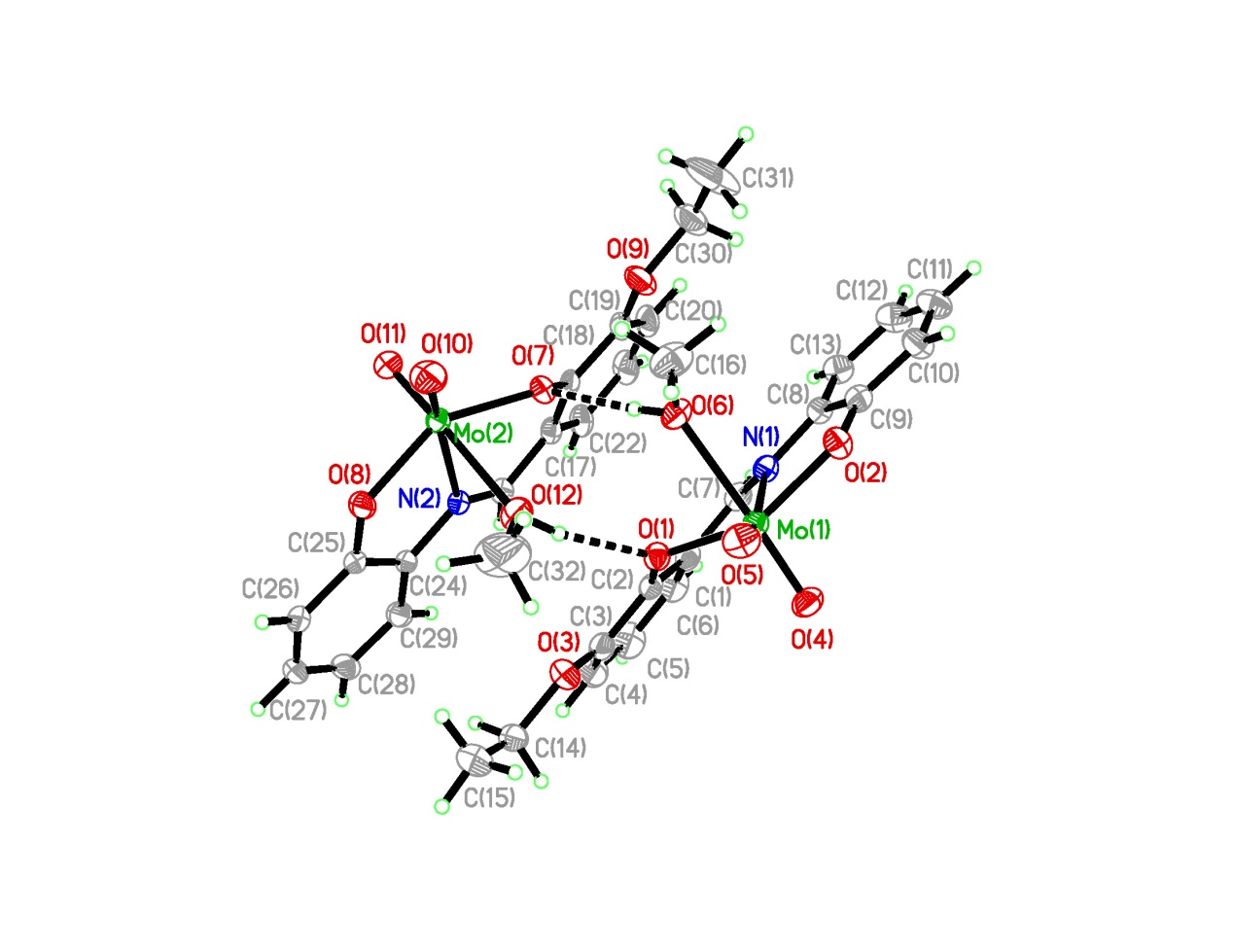
**Figure 1.** A perspective view of complex 1 with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.



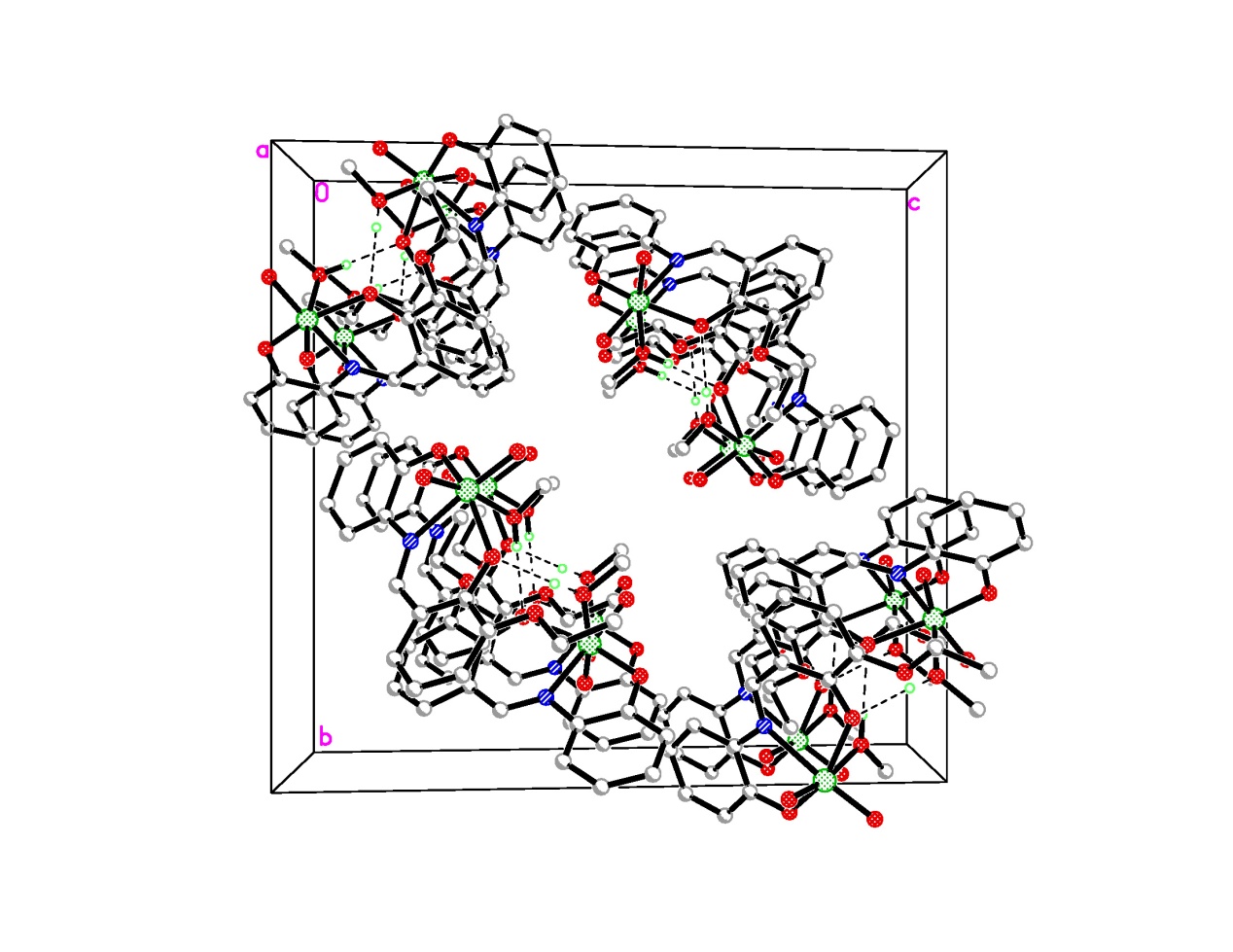
**Figure 2.** The hydrogen bonds (dashed lines) linked molecules into one dimensional chains of complex 1, viewed along the *a* axis.

**3.4. Structural description of complex 2**

The molecular structure of complex 2 is shown in Figure 3. It contains two dioxomolybdenum complex molecules in the asymmetric unit. The two complex molecules are linked through O–H···O hydrogen bonds [O(12)–H(12A) = 0.85(1) Å, H(12A)···O(1) = 1.96(2) Å, O(12)···O(1) = 2.792(4) Å, O(12)–H(12A)···O(1) = 169(4)º; O(6)–H(6) = 0.85(1) Å, H(6)···O(7) = 1.92(1) Å, O(6)···O(7) = 2.776(4) Å, O(6)–H(6)···O(7) = 175(2)º]. The coordination geometry around the Mo atom can be described as distorted octahedron, with one imino-N and two phenolate-O of the Schiff base ligand, and one oxo group defining the equatorial plane, and with the other oxo group and one methanol-O occupying the axial positions. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.68(12) and 81.67(12)° for Mo(1) moiety, and 74.83(12) and 80.14(11)° for Mo(2) moiety. The dihedral angles between the two benzene rings of the Schiff base ligands are 10.8(5)° and 6.7(5)°. The O=Mo=O angles (104.70(16) and 105.69(18)º) and the Mo=O distances (1.684(3)–1.691(3) Å) are typical for *cis*-dioxomolybdenum(VI) complexes.7 The imino nitrogen and ethanol oxygen atoms, which are *trans* to the terminal oxo groups, bond to the Mo(VI) atom with distances of 2.273(3)–2.286(7) Å for nitrogen and 2.301(3)–2.329(3) Å for oxygen, respectively. The Mo–O distances vary from 1.951(3) to 1.975(3) Å for the phenolate oxygen, which are in accord with these types of bonds in hexa-coordinated dioxomolybdenum(VI) complexes.7 In the crystal structure of the complex, molecules are stack along the *a* axis (Figure 4).



**Figure 3.** A perspective view of complex 2 with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.



**Figure 4.** The hydrogen bonds (dashed lines) linked dimeric structure of complex 2, viewed along the *a* axis.

**3.5. Catalytic property of the complexes**

Catalytic property of the complexes was investigated in the epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene with TBHP and CH2Cl2 as a solvent at different temperatures 25, 45 and 65 °C. The catalytic reactions were initially performed in order to test the performance of the system under the easiest possible reaction conditions. A substrate, oxidant, and catalyst ratio of 100:100:1 was used. In general, the epoxide yields are higher for cyclic olefins than those for terminal olefins. As seen in Table 3, the order of increasing reactivity based on yield% are as cyclooctene > cyclohexene > 1-hexene > 1-octene. In addition, the epoxide yields increase with the rise in temperature. Both complexes have similar catalytic properties, because of their similar structures. As a comparison, the catalytic property of the complexes on cyclohexene is similar to the molybdenum complex with tris(hydroxymethyl)amino methane as ligand.15 The complexes have in general higher catalytic property on the substrates than the molybdenum complex derived from the Schiff base ligand *N,N’*-bis(salicylidene)4,5-dichloro-1,2-phenylenediamine.7d

**Table 3.** Epoxide yields (%) for the catalytic processes at different temperatures

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Substrate | 25 °C | | 45 °C | | 65 °C | |
| 1 | 2 | 1 | 2 | 1 | 2 |
| Cyclooctene | 87 | 85 | 93 | 93 | 98 | 97 |
| Cyclohexene | 81 | 81 | 89 | 90 | 94 | 94 |
| 1-Hexene | 70 | 73 | 78 | 80 | 85 | 84 |
| 1-Octene | 62 | 61 | 70 | 70 | 77 | 75 |

**4. Conclusion**

Two new dioxomolybdenum(VI) complexes derived from the Schiff base ligands 2-[(2-hydroxyphenylimino)methyl]-6-methoxyphenol and 2-ethoxy-6-[(2-hydroxyphenylimino)methyl]phenol have been prepared and structurally characterized. The Mo atoms in the complexes are in octahedral coordination. Both complexes have effective catalytic properties on cyclooctene and cyclohexene.

**5. Supplementary material**

CCDC–1849701 and 1849702 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

**6. References**

1. D. Huang, C. Wang, Y. Song, *Russ. J. Gene. Chem.* **2013**, *83*, 2361–2369.
2. (a) S. Biswas, A. Dutta, M. Dolai, M. Debnath, A. D. Jana, M. Ali, *RSC Advances* **2014**, *4*, 34248–34256; (b) B. Bahramian, F. D. Ardejani, V. Mirkhani, K. Badii, *Appl. Catal. A General* **2008**, *345*, 97–103.
3. (a) A. Schriescheim, R. J. Muller, C. A. Rowe, *J. Am. Chem. Soc.* **1962**, *84*, 3164–3172; (b) F. Farzaneh, M. Ghiasi, M. Ghandi, M. Ghandi, V. Daadmehr, *Porous Mater.* **2013**, *20*, 267–275; (c)Ｋ. Pamin, G. Pozzi, E. Tabor, W. Bukowski, J. Poltowicz, *Catal. Commun.* **2013**, *39*, 102–105.
4. G. Ventakachalam, R. Ramesh, *Inorg. Chem. Commun.* **2005**, *8*, 1009–1013.
5. D. Pou, A. E. Platero-Prats, S. Perez, C. Lopez, X. Solans, M. Font-Bardia, P. W. N. M. van Leeuwen, G. P. F. van Strijdonck, Z. Freixa, *J. Organomet. Chem.* **2007**, *692*, 5017–5025.
6. (a) G. Koz, D. Astley, S. T. Astley, *Turk. J. Chem.* **2011**, *35*, 553–560; (b) D. S. Masterson, T. L. Hobbs, D. T. Glatzhofer, *J. Mol. Catal. A Chemical* **1999**, *145*, 75–81.
7. (a) M. Bagherzadeh, R. Latifi, L. Tahsini, V. Amani, A. Ellern, L. K. Woo, *Polyhedron* **2009**, *28*, 2517–2521; (b) Z. Moradi-Shoeili, M. Zare, M. Bagherzadeh, M. Kubicki, D. M. Boghaei, *J. Coord. Chem.* **2015**, *68*, 548–559; (c) M. Bagherzadeh, M. Amini, H. Parastar, *Inorg. Chem. Commun.* **2012**, *20*, 86–89; (d) A. A. A. Aziz, *J. Mol. Struct.* **2010**, *979*, 77–85; (e) R. D. Chakravarthy, K. Suresh, V. Ramkumar, D. K. Chand, *Inorg. Chim. Acta* **2011**, *376*, 57–63; (f) S. Rayati, N. Rafiee, A. Wojtczak, *Inorg. Chim. Acta* **2012**, *386*, 27–35.
8. X. W. Zhu, *Russ. J. Coord. Chem.* **2018**, *44*, 421–424.
9. (a) H. Petek, C. Albayrak, M. Odabasoglu, I. Senel, O. Buyukgungor, *Struct. Chem.* **2010**, *21*, 681–690; (b) B. Chattopadhyay, S. Basu, P. Chakraborty, S. K. Choudhuri, A. K. Mukherjee, M. Mukherjee. *J. Mol. Struct.* **2009**, *932*, 90–96.
10. Bruker, SMART (Version 5.625) and SAINT (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
11. G. M. Sheldrick, SADABS. Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany, 1996.
12. G. M. Sheldrick, SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, 1997.
13. W. F. Brill, *J. Am. Chem. Soc.* **1963**, *85*, 141–145.
14. (a) S. N. Rao, K. N. Munshi, N. N. Rao, M. M. Bhadbhade, E. Suresh, *Polyhedron* **1999**, *18*, 2491–2497; (b) S. M. El-Medani, M. M. Aboaly, H. H. Abdalla, R. M. Ramadan, *Spectrosc. Lett.* **2004**, *37*, 619–632.
15. (a) Q. Liu, J. Lin, J. Liu, W. Chen, Y. Cui, *Acta Chim. Slov.* **2016**, *63*, 279–286; (b) M. Liang, D.-H. Zou, *Acta Chim. Slov.* **2016**, *63*, 180–185; (c) Y. Sui, X. Zeng, X. Fang, X. Fu, Y. Xiao, L. Chen, M. Li, S. Cheng, *J. Mol. Struct. A* **2007**, *270*, 61–67.