

## Structural Investigation of Methanol {6-[(2-oxidopropyl)iminomethyl]phenolato} dioxidomolybdenum(VI) by X-Ray Crystallography and DFT Calculations

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### Abstract

This article presents the computational calculations of a *cis*-dioxomolybdenum(VI) complex by using density functional theory (DFT) with a DZP basis set (double zeta polarized basis set). The Schiff base 2-((E)-(2-hydroxypropylimino)methyl)-6-methoxyphenol was treated with MoO<sub>2</sub>(acac)<sub>2</sub> in dry methanol to produce the mononuclear complex methanol{2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato} dioxidomolybdenum(VI), whose structure has been solved and successfully refined in the monoclinic space group P2<sub>1</sub>/c, with  $a = 6.755 \text{ \AA}$ ,  $b = 15.835 \text{ \AA}$ ,  $c = 13.119 \text{ \AA}$ ,  $V = 1388.79 \text{ \AA}^3$ , and  $Z = 4$ .

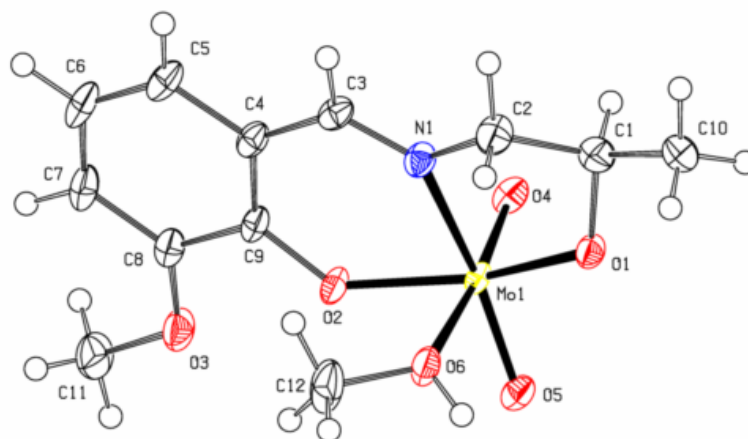
**Keywords:** DFT calculations, X-ray, *cis*-dioxomolybdenum (VI), Schiff base, Mo(VI) complexes

### Introduction

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals. In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metal containing sites in metallo-proteins and enzymes [1-5].

In previous work, we reported the synthesis, spectroscopic characterization, and semi-empirical Austin model 1(AM1) [6] calculations of arylazo substituted salen-type Schiff base ligands [7,8]. Here we present the *ab initio* [9] computational study of a molybdenum complex.

In this article, the structural properties of methanol {6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex calculated using the DFT method will be reported. All calculations had been performed using the ADF 2009.01 program package [10], with a B3LYP/DZP basis set [11-13]. In this study, we also report the comparison of theoretical calculations with X-ray crystallographic data for the more stable geometry of this molybdenum (VI) complex [14]. The stereoscopic plot of the unit cell of this complex (with atomic numbering) is illustrated in **Figure 1**.



**Figure 1** Stereoscopic ORTEP plot of methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex, showing with the atomic numbering scheme [12].

### Computational details

The density functional calculations have been performed to study the chemical environment of the Mo(VI) complex. The optimized geometrical parameters by DFT quantum chemical calculations are deposited in **Table 1**, in comparison with X-ray crystallographic data. The quantum chemical descriptors for the complex (highest occupied molecular orbital HOMO, lowest unoccupied molecular orbital LUMO, dipole moment and heat of formation) are calculated at the same level, and also the geometry and charge distribution of the conjugated base of the molecule have been investigated. All calculations have been carried out with the ADF 2009.01 software [10]. The percentage composition of the lowest-unoccupied and highest-occupied molecular orbitals (LUMO & HOMO), the molecular orbital (MO) diagrams, the important electronic excitation energies, and the Mulliken charge distribution analysis, for this structure, have been calculated by using B3LYP/DZP method.

### Results and discussion

The molecular structure of the dioxomolybdenum(VI) complex is illustrated in **Figure 1** and some theoretical with combined experimental parameters are shown in **Table 1**. The Mo1 atom has a distorted octahedral

coordination, being coordinated by the N and two O-atoms of the tridentate Schiff base ligand (N1, O1 and O2), two oxido atoms (O4 and O5), and by the O-atom (O6) of the coordinating methanol molecule. The Mo-O and Mo-N bond distances are similar to those reported for the molybdenum (VI) Schiff base complex [14-16]. The IR spectra of {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) in a KBr matrix confirm the presence of imine bond (C=N) mode at  $1630\text{ cm}^{-1}$  and the C=C vibration band of the aromatic ring at  $1587\text{ cm}^{-1}$  and the Mo-O vibration bands at  $903$  and  $928\text{ cm}^{-1}$ . **Table 1**, and the relevant bond distances and angles collected in **Figure 1**. The O=Mo=O angle is  $107.05^\circ$  and Mo=O distances are  $1.7038$  and  $1.7094\text{ \AA}$ .

The crystal structure analysis of a novel dioxomolybdenum complex by using X-ray crystallography confirmed the compound methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI). In this paper, we have shown the calculated bond lengths and angles at the B3LYP/DZP level are in good agreement with the crystallographic data as shown in **Table 2**, and **Table 1** shows some of the important calculated structural parameters while the computed structure is shown in **Figure 2**.

**Figure 3** shows some important calculated transition between occupied molecular orbital to unoccupied molecular orbital for methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenol-

lato}dioxidomolybdenum(VI) complex by using the B3LYP/DZP method.

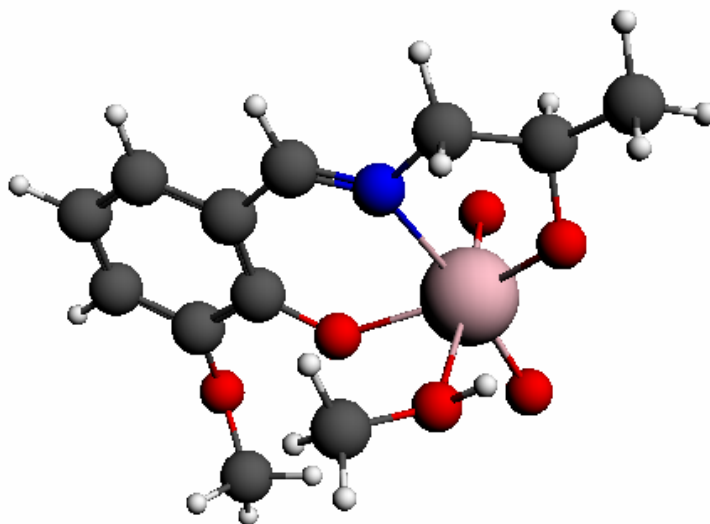
**Figure 4** shows the calculated molecular orbital HOMO energy is  $-6.571$  eV and the LUMO energy is  $-2.659$  eV. The calculated

energy (eV) for some of important molecular orbital levels for methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum (VI) complex is shown in **Table 4**.

**Table 1** Some of the important calculated structural parameters of methanol {2-methoxy-6-[(2-oxidopropyl) iminomethyl]phenolato} dioxidomolybdenum (VI) complex, using B3LYP/DZP method.

Empirical formula	E (HOMO) <sup>1</sup> (eV)	E (LUMO) <sup>2</sup> (eV)	( $\Delta E$ ) <sup>3</sup> (eV)	$\mu$ (Debye) <sup>4</sup>
[Mo(C <sub>11</sub> H <sub>13</sub> NO <sub>3</sub> )O <sub>2</sub> -(CH <sub>3</sub> OH)]	$-6.571$	$-2.659$	$3.912$	$3.191$

<sup>1</sup>Highest occupied molecular orbital, <sup>2</sup>lowest unoccupied molecular orbital, <sup>3</sup>band gap energy and <sup>4</sup>dipole moment.



**Figure 2** Theoretically predicted geometry for methanol {2-methoxy-6-[(2-oxidopropyl) iminomethyl]phenolato}dioxidemolybdenum(VI) complex, using B3LYP/DZP method.

**Table 2** Some important experimental (X-ray) data and calculated bond lengths (pm) and bond angles (°) for methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex, using B3LYP/DZP method.

	Experimental	Theoretical (B3LYP-DZP)*
Mo-O1	194.71	200.4
Mo-O2	194.31	205.0
Mo-O4	170.05	175.0
Mo-O5	170.22	175.1
Mo-O6	234.93	253.5
Mo-N1	225.1	239.5
O1-C1	143.3	142.4
O2-C9	133.7	132.1
O3-C8	135.4	136.7
O3-C11	142.7	143.9
O6-C12	140.3	143.5
O6-H6O	83.0	97.5
N1-C2	146.0	146.2
N1-C3	127.8	128.1
C1-C2	150.9	154.0
C1-C10	150.2	152.3
C3-C4	143.8	145.1
C4-C9	140.1	142.4
C4-C5	140.6	141.1
C5-C6	136.6	138.1
O1-Mo-O2	152.13	145.5
O1-Mo-O4	97.29	99.1
O1-Mo-O5	96.90	101.0
O1-Mo-O6	79.45	77.0
O1-Mo-N1	75.32	72.7
O2-Mo-O4	97.93	100.0
O2-Mo-O5	101.30	100.5
O2-Mo-O6	81.43	79.4
O2-Mo-N1	80.20	78.2
O4-Mo-O5	105.61	106.7
O4-Mo-O6	169.64	170.4
O4-Mo-N1	95.01	92.0
O5-Mo-O6	84.60	82.7
O5-Mo-N1	158.82	161.1
O6-Mo-N1	74.68	78.5
Mo-O1-C1	118.70	115.3
Mo-O2-C9	136.56	135.0
C8-O3-C11	117.57	118.2
Mo-O6-C12	128.21	127.4
C12-O6-H6O	107.7	111.0
Mo-O6-H6O	116.1	103.0
Mo-N1-C3	128.57	126.7
Mo-N1-C2	111.65	110.7
C6-C7	138.8	139.9
C7-C8	138.9	138.8
C8-C9	140.6	142.4

	Experimental	Theoretical (B3LYP-DZP)*
C1-H1	100.0	110.3
C2-H2A	99.00	109.8
C2-H2B	99.00	110.0
C3-H3	95.00	109.6
C6-H6	95.00	108.5
C7-H7	95.00	108.6
C10-H10A	98.00	109.6
C10-H10B	98.00	109.4
C10-H10C	98.00	109.6
C11-H11A	98.00	109.6
C11-H11B	98.00	109.1
C11-H11C	98.00	109.0
C12-H12A	98.00	109.5
C12-H12B	98.00	109.0
C12-H12C	98.00	109.5
C4-C9-C8	119.30	118.1
O2-C9-C4	123.2	123.9
O2-C9-C8	117.52	118.0
O1-C1-H1	109.00	108.8
C2-C1-H1	109.00	107.8
C10-C1-H1	109.00	109.4
N1-C2-H2A	110.00	111.8
N1-C2-H2B	110.00	108.9
C1-C2-H2A	110.00	111.7
C1-C2-H2B	110.00	108.7
H2A-C2-H2B	109.00	108.0
N1-C3-H3	118.00	119.4
C4-C3-H3	118.00	114.9
C4-C5-H5	120.00	118.8
C6-C5-H5	120.00	120.2
C5-C6-H6	120.00	120.6
C7-C6-H6	120.00	120.2
C8-C7-H7	119.00	120.9
C6-C7-H7	119.00	117.6
C1-C10-H10A	109.00	110.8
O6-C12-H12A	109.00	109.5
O6-C12-H12B	109.00	110.6
H12A-C12-H12B	109.00	109.0

\*All elements in compound optimized in DZP basis set except Mo which was optimized in the TZP basis set.

Some molecular orbital data of this complex are given in **Table 3**. In the case of this compound the lowest unoccupied molecular orbital (LUMO) has major contributions from the molybdenum d

orbital (29.82 %). The highest occupied molecular orbital (HOMO) is delocalized almost entirely on the ligand and is largely concentrated on the carbon atom fragment (45.65 %).

**Table 3** Some of calculated percentage composition of unoccupied and occupied molecular orbital for methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum (VI) complex, using the B3LYP/DZP method.

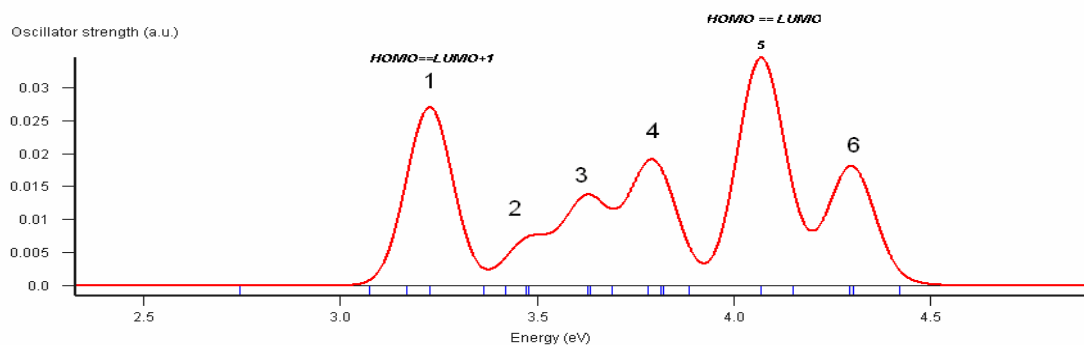
Orbital	E(ev)	% Mo	% O	% N	% C
54	-7.919		4.8(p <sub>x</sub> ) +53.2(p <sub>y</sub> ) +29(p <sub>z</sub> )	1.94(p <sub>y</sub> )	
55	-7.316		5.86(p <sub>x</sub> ) +5.93(p <sub>y</sub> ) +3.58(p <sub>z</sub> )	1.61(p <sub>y</sub> ) +10.10(p <sub>z</sub> )	12.45(p <sub>x</sub> ) +43.27(p <sub>z</sub> )
<b>56(HOMO)</b>	-6.571		5.33(p <sub>x</sub> ) +8.79(p <sub>y</sub> ) +13.97(p <sub>z</sub> )		12.12(p <sub>y</sub> ) +45.65(p <sub>z</sub> )
<b>57(LUMO)</b>	-2.659	29.82(d <sub>xz</sub> )	16.93(p <sub>x</sub> )	1.63(p <sub>y</sub> ) +9.17(p <sub>z</sub> )	5.85(p <sub>y</sub> ) +24.33(p <sub>z</sub> )
58	-2.357	25.87(d <sub>xz</sub> ) +14.48(d <sub>xy</sub> ) +1.06 (d <sub>z2</sub> )	5.2(p <sub>y</sub> ) +1.83(p <sub>y</sub> ) +1.91(p <sub>z</sub> )	1.42(p <sub>y</sub> ) +5.52(p <sub>z</sub> )	3.18(p <sub>x</sub> ) +18.56(p <sub>y</sub> ) +5.2(p <sub>z</sub> )
59	-2.207	45.12(d <sub>xy</sub> ) +5.2(d <sub>xz</sub> ) +3.23 (d <sub>x2-y2</sub> )	27.94(p <sub>x</sub> ) +1.22(p <sub>z</sub> )	2.07(p <sub>z</sub> )	4.11(p <sub>z</sub> )

**Table 4** Calculated energy (eV) for some important molecular orbital levels of methanol{2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex, using the B3LYP/DZP method.

Orbital	No. of electrons	E (a.u)	E(ev)
47	2	-0.34824508842182E+00	-9.476
48	2	-0.33350969807239E+00	-9.075
49	2	-0.32526241028850E+00	-8.851
50	2	-0.31459093326631E+00	-8.560
51	2	-0.30638868901801E+00	-8.337
52	2	-0.29661613503338E+00	-8.071
53	2	-0.29238647077826E+00	-7.956
54	2	-0.29100890046413E+00	-7.919
55	2	-0.26886253216103E+00	-7.316
56(HOMO)	2	-0.24149607852323E+00	-6.571
57(LUMO)	0	-0.97705525296172E-01	-2.659
58	0	-0.86630200716686E-01	-2.357
59	0	-0.81096963320104E-01	-2.207
60	0	-0.73827477619063E-01	-2.009
61	0	-0.25323177783978E-01	-0.689
62	0	-0.27956365728357E-02	-0.076
63	0	0.41333800456517E-02	0.112
64	0	0.12717738478392E-01	0.346
65	0	0.33005215217843E-01	0.898
66	0	0.37035344690910E-01	1.008

**Table 5** Electronic excitation energies, oscillator strengths *f*, and energy of the respective excited state calculated by using B3LYP/DZP method for methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex.

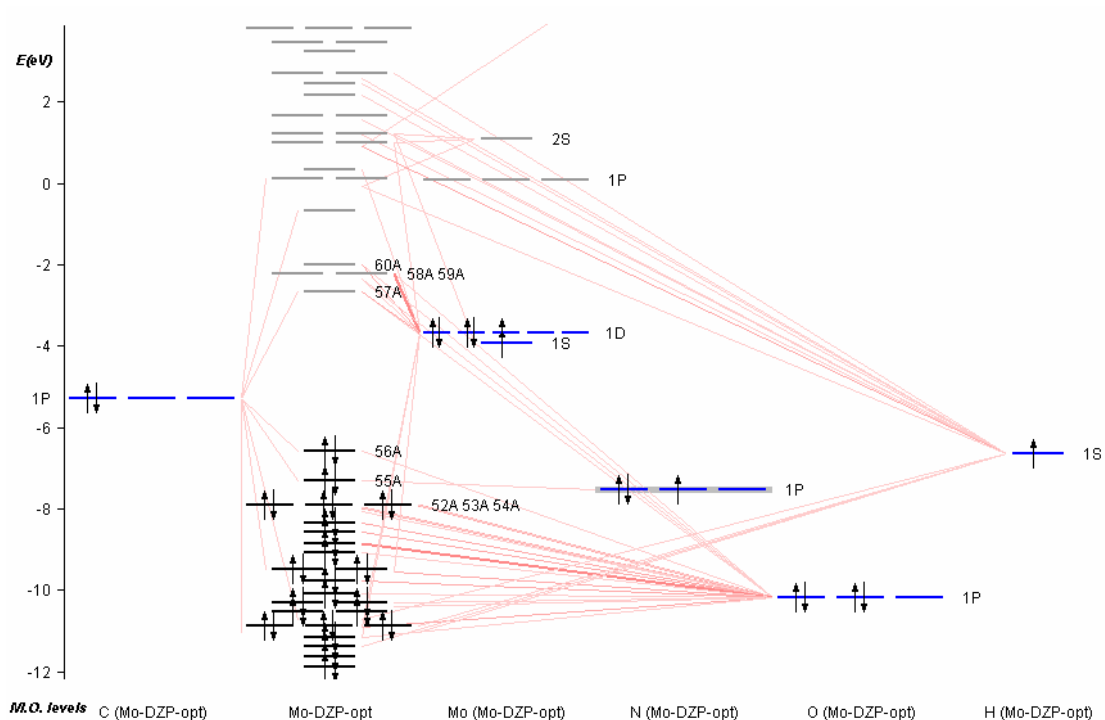
Transition No.	E/eV	Oscillator strengths, <i>f</i> (a.u)	Major MO → MO transitions	%
1	3.2270	0.27043E-01	56a → 57a	95
			56a → 58a	1
			55a → 57a	1
			56a → 59a	1
			56a → 58a	60
2	3.4783	0.69741E-02	56a → 59a	35
			55a → 59a	1
			55a → 58a	1
			56a → 59a	60
3	3.6272	0.13156E-01	56a → 58a	31
			55a → 57a	3
			56a → 57a	2
			54a → 57a	33
4	3.7810	0.12517E-01	56a → 60a	30
			54a → 58a	11
			55a → 57a	5
			56a → 60a	66
5	3.8149	0.71392E-02	54a → 57a	18
			55a → 57a	4
			54a → 58a	3
			55a → 57a	66
6	4.0670	0.33716E-01	53a → 57a	9
			54a → 57a	7
			55a → 58a	6

**Figure 3** Calculated spectrum\* for methanol{2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex with a B3LYP/DZP basis set.

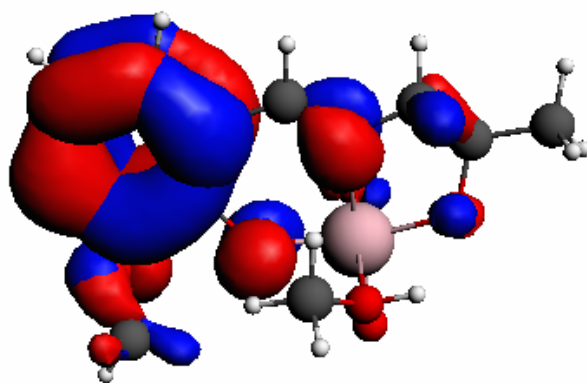
\*Main transitions 1: HOMO → LUMO, 2: HOMO → LUMO+1, 3: HOMO → LUMO+2, 4: HOMO-2 → LUMO, 5: HOMO → LUMO+3 and 6: HOMO-1 → LUMO.

Theoretically electronic spectra of this Mo(VI) complex is calculated and its data are shown in **Table 5**. This table shows the first electronic excitation energy with 3.2277 eV and the fifth electronic excitation energies with 3.8149

eV are attributed to HOMO→LUMO transition and HOMO→LUMO+3 transition. Also the important electronic spectra bands for this compound are shown in **Figure 5**.

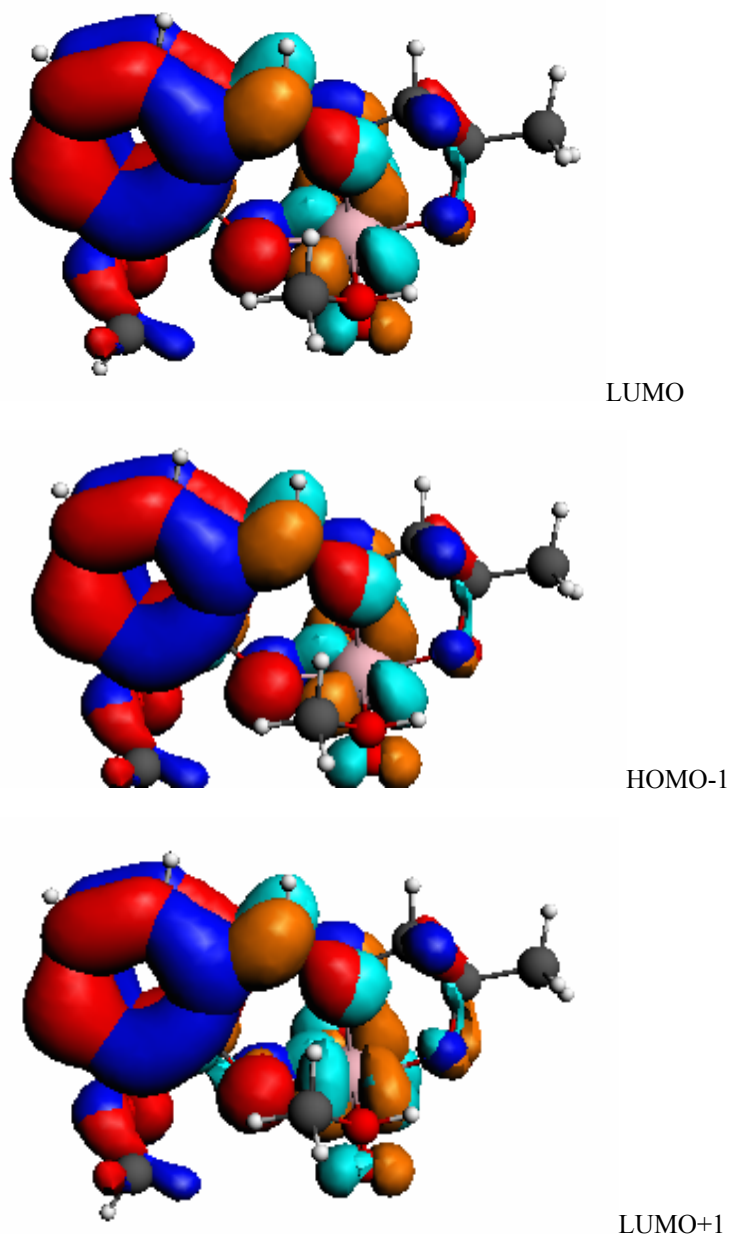


**Figure 4** Calculated molecular orbital (MO) diagram of methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex, using the B3LYP/DZP method.



HOMO





**Figure 5** Frontier molecular orbitals of methanol {2-methoxy-6-[(2-oxidopropyl)iminomethyl] phenolato}dioxidomolybdenum(VI) complex, using the B3LYP/DZP method.

### Conclusion

In the present study, we have carried out B3LYP DZP calculations using ADF 2009.01 program to determine the best molecular configuration of the title complex. In order to

optimize the geometry of the compound, the DFT method is used. This structure is a polar molecule according to the calculated structural parameters in **Table 1** ( $\mu = 3.91$  Debye). As a result of energy minimizing study on this metal complex, some selected bond distances and bond angles are given

in **Tables 2**. According to the geometry optimization in the gas phase, proposed molecular structure of this complex are shown in **Figure 2**. Also in **Table 2**, we compare the DFT calculated geometries data of the titled molybdenum complex with its X-ray data. We saw a good agreement between theoretical and experimental data in this study.

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