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ORIGINAL ARTICLE

Quantum chemical calculations and X-ray crystallographic studies of *cis*-dioxomolybdenum(VI) Schiff base complex

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KEYWORDS

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Abstract Treatment of the Schiff base 2-((E)-(2-hydroxy propylimino)methyl)phenol with $MoO_2(acac)_2$ in dry methanol gave the mononuclear complex (methanol{6-[(2-oxidopropyl)imino-meth-yl]phenolato}dioxidomolybdenum(VI), which was characterized by X-ray crystal analysis, and it has monoclinic space group $p2_1/c$, and a = 10.330(17) Å, b = 9.397(15) Å, c = 13.695(2) Å, V = 1252.1(3) Å^3, and Z = 4. B3LYP theoretical method with DZP basis sets calculations nicely reproduces the X-ray experimental geometry, molecular orbital levels and the other structural properties for this complex.

1. Introduction

Schiff base ligands is one of the oldest classes of ligands in the coordination chemistry, have been used extensively to complex transition metals (Goodwin and Bailar, 1961; Fenton, 2002; Piguet et al., 1997; Abu-Ragabah et al., 1992). The molybdenum Schiff base complexes have a good role in many catalytic reactions, and catalytic oxidation reactions are as an important area for many research groups during the past years. A large number of important chemical reactions are catalyzed by molybdenum(VI) compounds. The selective oxidation of organic sulfides to sulfoxides or sulfones has been thoroughly investigated for many years. Dioxomolybdenum(VI) compounds are commonly encountered in enzyme and metal surface models, oxidation catalysis and oxygen transfer reactions (Rajan and Chakravorty, 1981; Abu-Omar et al., 2005; Topich, 1981). Molybdenum complexes containing oxotransferases and hydroxylases belong to the class of molybdoenzymes with mono nuclear active sites (Eierhoss et al., 2008; Hille, 1996, 2002). Also molybdenum-oxo complexes have been studied in oxygen atom transfer processes, for instance the oxo transferase enzymes like nitrate reductase in which the active

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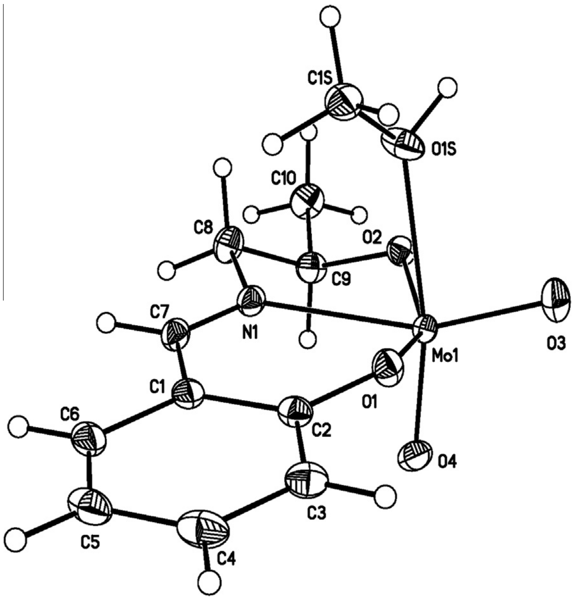


Figure 1 Stereoscopic ORTEP[20] plot of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex showing the atomic numbering scheme.

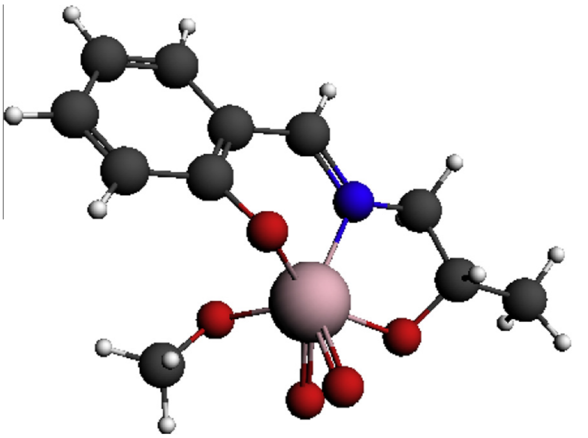


Figure 2 Theoretically predicted geometry for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

Table 1 Some of important calculated structural parameters methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxido-molybdenum(VI) complex by using .B3LYP/DZP method.

Empirical formula	E_{50}(HOMO)[a] (eV)	E_{51}(LUMO)[b] (eV)	μ[c] (D)	(ΔE)[d] (eV)	Volume (Å^3)
C11–H15–Mo–N–O5	−6.798	−2.641	0.058	4.157	1252.1

[a] Highestst occupied molecular orbital.
[b] Lowest unoccupied molecular orbital.
[c] Dipolmoment.
[d] Band gap energy. (*Hint:* for this compound 50 = number of HOMO and 51 = number of LUMO.)

Table 2 Some important experimental (X-ray) and theoretical (B3LYP/DZP basis set) bond angles (°) and bond lengths (Å) for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato} dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

	X-ray data for complex	Theoretical (B3LYP/DZP)[a] data for complex
Mo–O(1)	1.960	2.05
Mo–O(2)	1.952	2.00
Mo–O(3)	1.709	1.75
Mo–O(4)	1.703	1.75
Mo–O(1S)	2.355	2.52
Mo–N(1)	2.274	2.40
O(4)–Mo–O(3)	107.05	106.3
O(4)–Mo–O(2)	98.01	99.3
O(3)–Mo–O(2)	97.34	99.3
O(4)–Mo–O(1)	97.80	99.9
O(3)–Mo–O(1)	101.00	101.2
O(2)–Mo–O(1)	151.04	144.8
N(1)–Mo–O(4)	93.07	83.2
N(1)–Mo–O(3)	159.38	162.9
N(1)–Mo–O(2)	74.90	78.0
N(1)–Mo–O(1)	80.17	89.9
O(4)–Mo–O(1S)	168.84	170.5
O(3)–Mo–O(1S)	84.09	83.2
O(2)–Mo–O(1S)	79.45	77.6
O(1)–Mo–O(1S)	80.35	78.7
N(1)–Mo–O(1S)	75.77	79.9

[a] All elements in compound optimized in DZP basis set except Mo that optimized in TZP basis set.

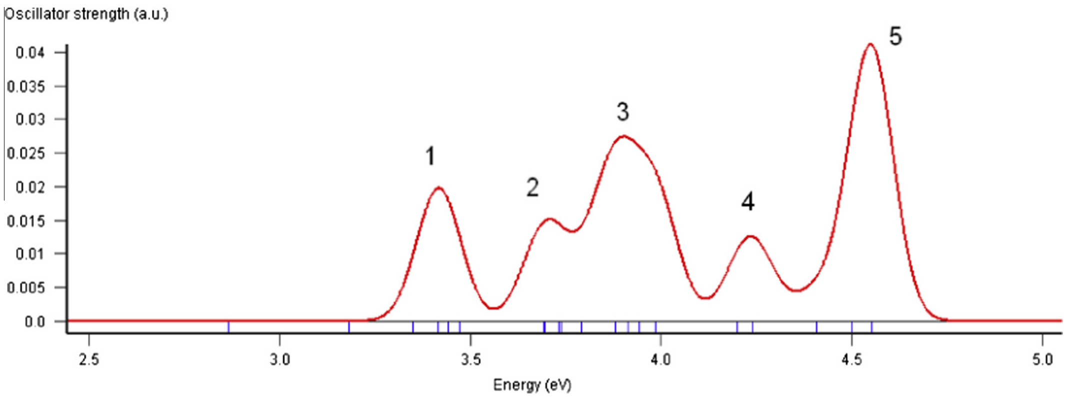


Figure 3 UV spectra calculated diagram for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method. *Main transitions (1) 50 → 51, (2) 50 → 52, (3) 50 → 54, (4) 47 → 51, (5) 49 → 51.

sites consist of a *cis* molybdenum dioxo moiety (Arzoumanian et al., 1995, 1997). Molybdenum(VI) dioxo-complexes have been extremely thoroughly investigated and there are many literature reports of their syntheses and reactivity, particularly in terms of oxo-transfer reactions (Holm, 1990; Spence, 1983).

In our previous works we reported a novel tridentate Schiff base dioxomolybdenum(VI) complex (Sheikhshoaie et al., 2009). In this work we will report the structural properties of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by DFT calculations. All calculations were performed by using ADF (te Velde et al., 2001; Guerra et al., 1998; ADF 2009.01) program package with B3LYP/DZP (Becke, 1993, 1988; Lee et al., 1988) basis sets. In this study we will report some comparisons to X-ray data and theoretical calculations data for the more stable geometry of this molybdenum(VI) complex. The stereo view or the stereoscopic ORTEP plot (Johnson, 1965) of the unit cell of this compound with atomic numbering of its structure is shown in Fig. 1.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 688077. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version.

2. Computational details

All final calculations, whose results are reported here, were performed using the ADF program (te Velde et al., 2001) by means of density functional theory (DFT). The hybrid B3LYP density functional was applied in all calculations and DZP basis sets were employed in this study (Becke, 1993, 1988; Lee et al., 1988). Fig. 2 shows the optimized structure of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex. Selected experimental and calculated structural parameters for are shown in Table 1.

Table 2 shows some selected important bond lengths and bond angles, and Fig. 3 shows the calculated UV spectrum for the optimized structure of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using ADF 2009.01 and B3LYP/DZP method.

Table 3 shows all important singlet–singlet (S–S) theoretical calculated transitions of this complex.

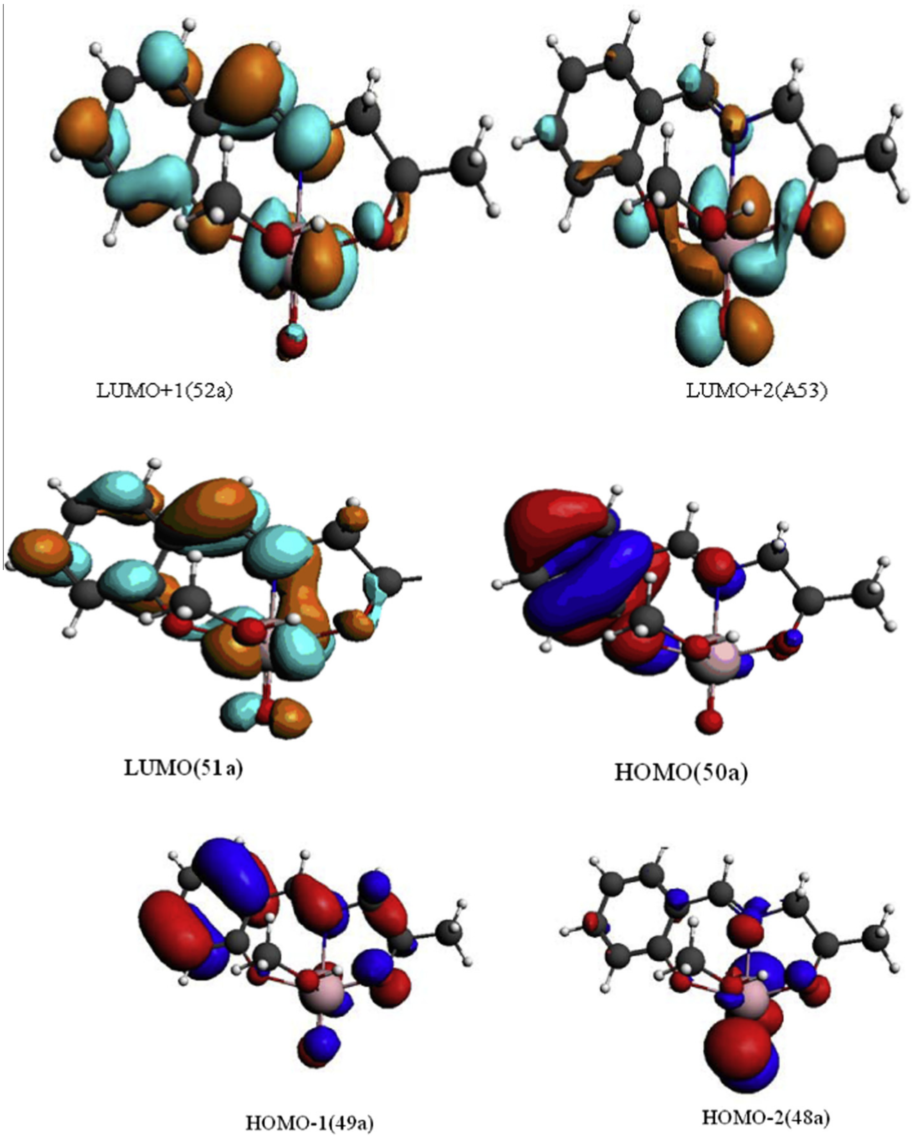
The contribution of atomic orbital in some of molecular orbital shows in Table 4, and some of frontier molecular-orbital diagram are shown in Fig. 4 (for methanol{6-[(2-oxidopropyl)-iminometh-yl]phenolato}dioxidomolybdenum(VI) complex).

Table 3 All singlet–singlet calculated excitations for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

Number of transition	*E* (eV)	Oscillator strength (a.u.)	Major MO → MO transitions	% Transitions
1	3.4173	0.19726E−01	50a → 51a	90
			50a → 52a	3
			48a → 51a	2
			50a → 54a	1
2	3.6958	0.13784E−01	50a → 52a	55
			50a → 53a	29
			48a → 51a	3
			49a → 51a	3
3	3.7903	0.38126E−02	48a → 51a	42
			48a → 52a	15
			50a → 53a	14
			49a → 51a	10
4	3.8796	0.22098E−01	50a → 53a	53
			50a → 52a	32
			48a → 51a	7
			48a → 52a	3
5	3.9862	0.18155E−01	50a → 54a	85
			48a → 51a	1
			50a → 52a	1
			49a → 51a	0.4
6	4.2003	0.18006E−02	48a → 53a	41
			48a → 52a	23
			49a → 53a	12
			47a → 51a	1
7	4.2382	0.11059E−01	47a → 51a	33
			49a → 51a	22
			48a → 53a	19
			48a → 51a	6
8	4.4058	0.39926E−02	46a → 51a	62
			48a → 49a	7
			45a → 51a	6
			48a → 51a	6
9	4.4992	0.30160E−02	45a → 51a	65
			45a → 52a	14
			48a → 54a	2
			46a → 52a	2
10	4.5513	0.38832E−01	49a → 51a	34
			47a → 51a	22
			46a → 51a	8
			49a → 52a	8

Table 4 Percentage composition of the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) levels of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

Orbital	*E* (eV)	%Mo	%O	%N	%C
48	−7.902	–	$41.67(p_y) + 25.64(p_z)$	$1.92(p_z)$	$1.11(p_z)$
49	−7.668	–	$2.06(p_x) + 11.46(p_y) + 4.06(p_z)$	$1.95(p_y) + 7.5(p_z)$	$18.61(p_y) + 39.88(p_z)$
50(HOMO)	−6.798	–	$2.24(p_x) + 6.52(p_y) + 13.04(p_z)$	$1.71(p_y) + 3.24(p_z)$	$18.6(p_y) + 43.41(p_z)$
51(LUMO)	−2.641	$30.52(d_{xz})$	$17.05(p_x)$	$2.22(p_y) + 8.46(p_z)$	$8.73(p_y) + 22.22(p_z)$
52	−2.351	$10.52(d_{xy}) + 26.31(d_{xz})$	$13(p_x) + 1.62(p_y) + 1.76(p_z)$	$2.05(p_y) + 5.90(p_z)$	$6.49(p_y) + 20.15(p_z)$
53	−2.132	$50.45(d_{xy}) + 4.2(d_{xz}) + 2.33(d_{x2-y2})$	$29.42(p_x)$	$1.25(p_z)$	$1.51(p_z)$



LUMO+1(52a) LUMO+2(A53)

LUMO(51a) HOMO(50a)

HOMO-1(49a) HOMO-2(48a)

Figure 4 Calculated (B3LYP/DZP) frontier molecular-orbital diagram for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex illustrating the HOMO−2, HOMO−1, HOMO, LUMO, LUMO + 1, LUMO + 2.

Fig. 5 shows a part of calculated molecular-orbital diagram of methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

3. Results and discussion

The geometry of this molybdenum complex optimized in the gas phase using tools from the density functional theory calculations. The agreement between theoretical and experimental data is for this metal complex as can be seen in Table 2. The most relevant differences are observed when the O2–Mo–O1, N1–Mo–O4, N1–Mo–O3 and N1–Mo–O1 bond angles are compared. The ideal gas phase values are O4–Mo–O3 (106.3), O4–Mo–O2 (99.3), O3–Mo–O2 (99.3), O4–Mo–O1 (99.9) and O3–Mo–O1 (101.2), respectively, whereas the experimental ones are 107, 98, 97, 97.8 and 101, respectively. These facts suggest that that this molybdenum complex becomes stabilized in the solid state. The electronic excitation energies and oscillator strengths f calculated by B3LYP/DZP method for this complex are summarized in Table 3. The longest wavelength transition is belonging to HOMO–LUMO with $n \rightarrow \pi^*$ character [the percentage composition of the lowest unoccupied and highest occupied molecular orbital levels for this compound are: *For HOMO level, %Mo = 0, %O = 2.24*(p_x) + 6.52(p_y) + 13.04(p_z), %N = 1.71(p_y) + 3.24(p_z) and %C = 18.6(p_y) + 43.41(p_z). *For LUMO level, %Mo = 30.52*(d_{xz}), %O = 17.05(p_x), %N = 2.22(p_y) + 8.46(p_z) and %C = 8.73(p_y) + 22.22(p_z)].

Fig. 5 shows the molecular-orbital diagram is in agreement with the calculated electronic spectra.

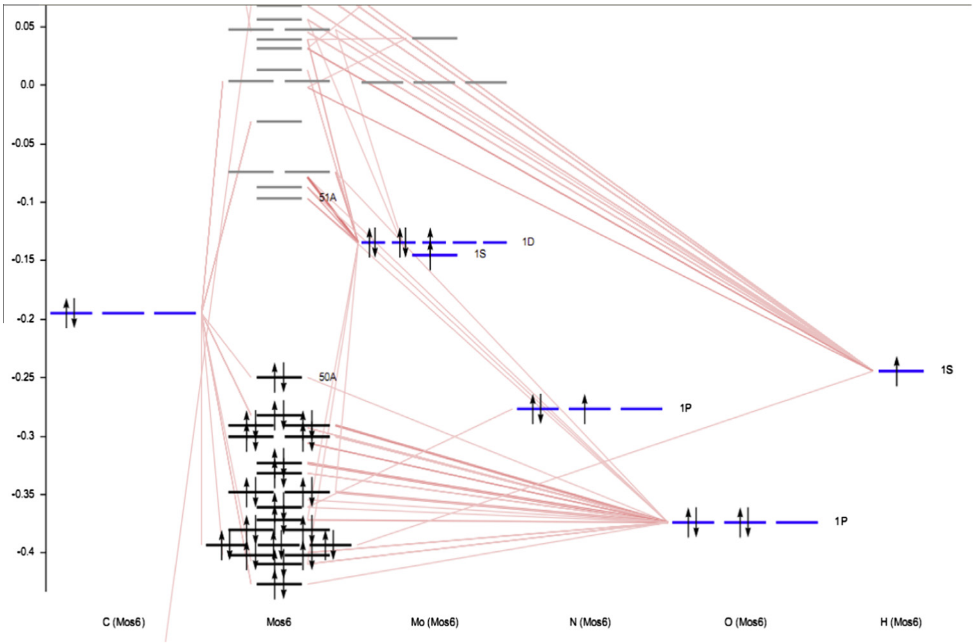


Figure 5 The calculated MO diagram for methanol{6-[(2-oxidopropyl)iminometh-yl]phenolato}dioxidomolybdenum(VI) complex by using B3LYP/DZP method.

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