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ORIGINAL ARTICLE

Crystal structure and DFT calculations of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido} dioxidomolybdenum (VI) complex

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Abstract The crystal and molecular structure of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) was determined by single crystal X-ray diffraction. B3LYP/DZP basis set theoretical calculations nicely reproduce the X-ray experimental geometry. The obtained results are discussed in connection with the electronic and structural properties of the compound.

1. Introduction

Molybdenum (VI) dioxo compounds are commonly encountered in enzyme and metal surface models, oxidation catalysis and oxygen atom transfer reactions (Cervilla et al., 1991). We and others have reported on the epoxidation of sulfides and olefins catalyzed by a large of molybdenum (VI) dioxo complexes (Sheikhshoaie et al., 2009; Rezaeifard et al., 2010; Bagherzadeh et al., 2008; Hroch et al., 2000; Herrmann et al., 1997; Gómez et al., 2001; Kuhn et al., 2000a,b, 2001a,b). We report here the single crystal X-ray structure for the methanol {E-N′-(2- hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) complex, this compound has been studied theoretically and experimentally by NMR, IR and UV-vis spectroscopy.

2. Synthesis

The titled (Scheme 1) complex was prepared by this common method. A dry methanol solution (15 ml) of MoO_2 $(acac)_2$ (0.327 g) was added to another solution (15 ml) of (E)-N′-(2-hydroxybenzlidene)benzohydrazid (0.240 g). The mixture was refluxed for 6 h. The clear solution was cooled to room temperature. A yellow powder separated was collected by filtration

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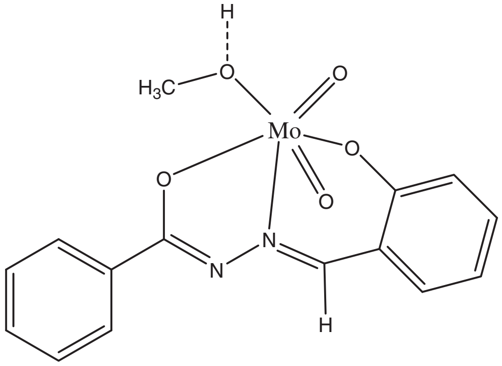

Scheme 1 The structure of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

and dried in air. Crystals of the title Mo^{VI} complex, suitable for X-ray analysis, were obtained as yellow blocks by slow evaporation at room temperature in a solution of ethanol.

2.1. X-ray structure determination

Suitable crystals of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) were obtained as yellow rods. The intensity data were collected at 233 K (−40 °C) on a Stoe Mark II-Image Plate Diffraction System (Stoe, 2009) equipped with a two-circle goniometry and using MoKα graphite monochromatic radiation (λ = 0.71073 Å). Image plate distance 130 mm, ω rotation scans 0–180° at φ 0°, and 0–92.0° at φ 90°, step $\Delta\omega$ = 1.0°, exposures of 6 mines per image, 2θ range 1.76–52.59°, $d_{\min}$–$d_{\max}$ = 23.107–0.802 Å. The structure was solved by direct methods using the program SHELXS-97 (Sheldrick, 2008). The refinement and all further calculations were carried out using SHELXL-97 (Spek, 2009). The OH H-atom was located from a difference electron-density map and refined with a distance restraint of 0.84(2) Å. The remaining H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. An empirical absorption correction was applied using the MUL scan ABS routine in PLATON. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing, Fig. 1, and the crystal packing viewed along the b-axis is illustrated in Fig. 2 (the O–H···N hydrogen bonds are shown as dashed lines). Some of X-ray's data for the titled compound were shown in Tables 1–3.

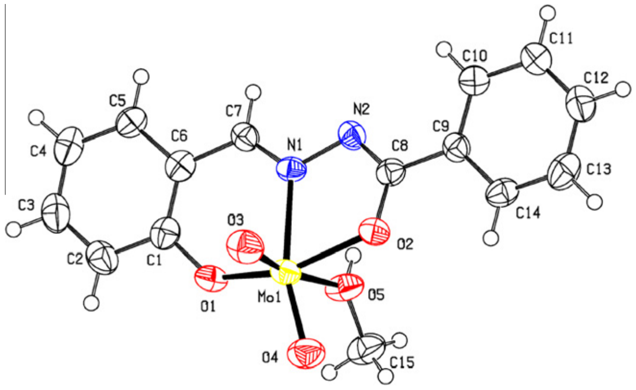

Figure 1 The X-ray structure for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

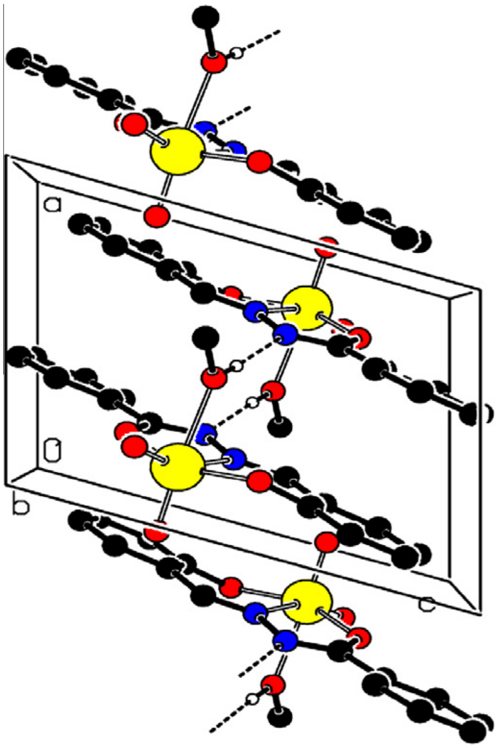

Figure 2 The molecular arrangement of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

CCDC 785592 contains the supplementary crystallographic data for this paper, this data can be obtained free of charge at www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic

Table 1 Crystal data and details of the structure determination for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

Formula	C_{15} H_{14} Mo N_2 O_5
Formula weight	398.22
Crystal system	Triclinic
Space group	P-1
a, b, c [Å]	7.8478 (13), 9.7989 (16), 10.3766(17)
Alpha, beta, gamma (deg)	94.315 (13), 107.834 (13), 90.565(13)
V (Å^3)	757.0 (2)
Z	2
D(calc) (g/cm**^{3})	1.747
Mu(MoKα) (/mm)	0.894
F (0 0 0)	400
Crystal size (mm)	0.15 × 0.15 × 0.40
Temperature (K)	233
Radiation (Angstrom)	MoKα 0.71073
Theta Min–Max (deg)	2.1, 25.1
Dataset	−9: 9; −11: 11; −12: 12
Tot., Uniq. data, R (int)	7483, 2696, 0.123
Observed data (I > 2.0 sigma (I))	2195
Nref, Npar	2696, 213
R, wR2, S	0.0632, 0.1511, 1.00

Table 2 Fractional atomic coordinators and equivalent isotropic displacement parameters (Å^2) of the nonhydrogen atoms for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

Atom	*x*	*y*	*z*	U (eq) (Angˆ2)
Mo1	0.18299(7)	0.74501(5)	0.35415(5)	0.0349(2)
O1	0.2149(6)	0.8351(4)	0.5321(5)	0.0426(16)
O2	0.2402(6)	0.5888(4)	0.2376(4)	0.0406(12)
O3	−0.0407(6)	0.7151(5)	0.3074(5)	0.0510(17)
O4	0.2168(6)	0.8739(5)	0.2642(5)	0.0510(17)
O5	0.4978(6)	0.7478(5)	0.4335(5)	0.0455(16)
N1	0.2485(6)	0.5613(5)	0.4755(5)	0.0305(16)
N2	0.2980(6)	0.4449(5)	0.4082(5)	0.0324(16)
C1	0.1760(8)	0.7958(7)	0.6427(6)	0.0379(19)
C2	0.1307(8)	0.8984(7)	0.7266(7)	0.047(2)
C3	0.1037(9)	0.8622(8)	0.8460(8)	0.051(3)

Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

2.2. Theoretical calculations

All calculations in the present study were performed by using the ADF 2009.01 program (Spek, 2003; te Velde et al., 2001; Fonseca Guerra et al., 1998; ADF, 2009.01). The stationary points on potential energy surfaces were located by using B3LYP density functional calculations (Becke, 1993,1988; Lee et al., 1988; Canal Neto et al., 2005), with the DZP basis sets (all-electron double zeta plus polarization function) (Lee et al., 1988; Camiletti et al., 2008). The geometrical parameters of the titled complex have been optimized with B3LYP DZP basis sets.

The final positional parameters for some important atoms are given in Table 2, and some experimental and theoretical bond lengths are summarized in Table 3 and some experimental and theoretical bond angles are listed in Table 3.

Some of electronic properties of this molybdenum (VI) complex were shown in Table 5.

The contributions of atomic orbital in each molecular orbital (HOMO and LUMO) are shown in Table 6. Each percentage contribution in the table below corresponds to the indicated SFO. In general, a SFO may be a linear combination of several fragment orbital on the same, or on symmetry-related fragments. Plots of frontier molecular orbitals of HOMO and LUMO are shown in Figs. 5 and 6; also the orbital energies are given in Table 5.

DFT calculations predict two close lying transitions (440 nm (HOMO/LUMO with oscillator strength 0.0669726) and 340 nm (HOMO/LUMO+4 with oscillator strength 0.265256) (see Fig. 4).

Table 3 Some important experimental (X-ray) and theoretical (B3LYP DZP basis set) bond distances (Å) for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

Bond	Experimental (X-ray)	Theoretical (B3LYP/DZP)	Bond	Experimental (X-ray)	Theoretical (B3LYP/DZP)
Mo1–O1	1.928	2.025	N1–N2	1.412	1.376
Mo1–O2	2.019	2.069	N1–C7	1.281	1.291
Mo1–O3	1.688	1.743	N2–C8	1.303	1.305
Mo1–O4	1.691	1.756	C1–C2	1.40	1.402
Mo1–O5	2.352	2.539	C1–C6	1.39	1.421
Mo1–N1	2.248	2.326	C2–C3	1.39	1.387
O1–C1	1.356	1.340	C5–C6	1.42	1.411
O2–C8	1.301	1.318	C6–C7	1.458	1.448
O5–C15	1.415	1.444	C7–H7	0.940	1.090
O5–H5O	0.84	0.976	C8–C9	1.470	1.479

Table 4 Some important experimental (X-ray) and theoretical (B3LYP DZP basis set) bond angles (°) for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

Angle	Experimental (X-ray)	Theoretical (B3LYP/DZP)	Angle	Experimental (X-ray)	Theoretical (B3LYP/DZP)
O1–Mo1–O2	149.1	142.4	Mo1–O1–C1	132.6	126.8
O1–Mo1–O3	98.4	101.0	Mo1–O2–C8	121.6	120.1
O1–Mo1–O4	103.1	103.3	Mo1–O5–C15	126.7	117.9
O1–Mo1–O5	82.1	74.8	Mo1–O5–H5O	122	102.9
O1–Mo1–N1	81.5	79.0	C15–O5–H5O	111	109.9
O2–Mo1–O3	97.5	102.7	Mo1–N1–N2	115.4	115.5
O2–Mo1–O4	97.6	97.4	Mo1–N1–C7	127.4	125.8
O2–Mo1–O5	77.7	77.5	N2–N1–C7	117.1	118.3
O2–Mo1–N1	71.0	69.9	N1–N2–C8	109.3	110.2
O3–Mo1–O4	106.2	106.6	O1–C1–C2	117.2	118.0
O3–Mo1–O5	169.8	171.5	O1–C1–C6	121.8	122.7
O3–Mo1–N1	94.5	95.7	C1–C6–C7	124.1	123.1
O4–Mo1–O5	83.4	81.8	N1–C7–C6	122.9	123.7
O4–Mo1–N1	157.7	156.6	N1–C7–H7	118.6	118.0
O5–Mo1–N1	75.5	76.3	O2–C8–N2	122.8	124.1

Table 5 Some of the calculated electronic properties of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) complex by B3LYP DZP basis sets with using ADF 2009.01 program.

Formula	ΔH[a] (kcal/mol)	$E_{60(\mathrm{HOMO})}$[b] (Hartree)	$E_{61(\mathrm{LUMO})}$[c] (Hartree)	μ[d] (debye)	Δ(*E*)[e] (Hartree)
$C_{15}\ H_{14}\ Mo\ N_2\ O_5$	–	−0.248985	−0.118643	1.615	0.130342

[a] Heat of formation.

[b] Highest occupied molecular orbital.

[c] Lowest unoccupied molecular orbital.

[d] Dipolmoment.

[e] Band gap energy (Hint: for this compound 60 = number of HOMO and 61 = number of LUMO).

Table 6 The calculated contributions of atomic orbitals in each of HOMO & LUMO molecular orbitals for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) complex by B3LYP DZP basis set by using ADF 2009.01 program.

	% (contribution of atomic orbital)	SFO	*E* (eV)	Number of MO	Fragment
HOMO with 2 electrons (60A)	14.42%	1 P:*x*	−7.531	1.00	N2
	6.42%	1 P:*x*	−7.531	1.00	N1
	5.90%	1 P:*x*	−5.298	0.67	C6
	4.99%	1 P:*x*	−5.298	0.67	C1
	4.36%	1 P:*x*	−5.298	0.67	C12
	4.24%	1 P:*x*	−5.298	0.67	C8
	3.85%	1 P:*x*	−5.298	0.67	C7
	3.80%	1 P:*x*	−5.298	0.67	C4
	3.63%	1 P:*x*	−10.182	1.33	O1
	3.58%	1 P:*x*	−5.298	0.67	C3
	3.41%	1 P:*z*	−5.298	0.67	C6
	3.32%	1 P:*z*	−5.298	0.67	C1
	3.13%	1 P:*x*	−5.298	0.67	C9
	2.81%	1 P:*x*	−10.182	1.33	O2
	2.74%	1 P:*z*	−5.298	0.67	C4
	2.66%	1 P:*x*	−5.298	0.67	C10
	2.57%	1 P:*z*	−5.298	0.67	C3
	1.95%	1 P:*z*	−7.531	1.00	N2
	1.72%	1 P:*x*	−5.298	0.67	C14
	1.48%	1 P:*z*	−7.531	1.00	N1
	1.29%	1 P:*z*	−10.182	1.33	O1
	1.12%	1 P:*z*	−10.182	1.33	O2
	1.11%	1 P:*y*	−10.182	1.33	O3
	1.08%	1 P:*x*	−5.298	0.67	C13
LUMO (61 A)	9.39%	1 D:*x*2–*y*2	−3.661	1.00	Mo1
	8.52%	1 D:*xz*	−3.661	1.00	Mo1
	8.44%	1 P:*x*	−5.298	0.67	C7
	7.65%	1 D:*xy*	−3.661	1.00	Mo1
	7.57%	1 P:*y*	−10.182	1.33	O3
	6.72%	1 P:*z*	−10.182	1.33	O4
	6.51%	1 D:*yz*	−3.661	1.00	Mo1
	5.09%	1 P:*z*	−10.182	1.33	O3
	4.70%	1 P:*x*	−5.298	0.67	C8
	2.99%	1 P:*x*	−7.531	1.00	N1
	2.70%	1 P:*x*	−5.298	0.67	C3
	2.38%	1 P:*y*	−10.182	1.33	O4
	1.99%	1 P:*z*	−5.298	0.67	C1
	1.98%	1 P:*z*	−5.298	0.67	C7
	1.62%	1 P:*x*	−5.298	0.67	C5
	1.61%	1 P:*z*	−5.298	0.67	C3
	1.54%	1 P:*x*	−5.298	0.67	C12
	1.50%	1 P:*z*	−5.298	0.67	C5
	1.30%	2 D:*xz*	4.940	0.00	Mo1
	1.29%	1 P:*x*	−5.298	0.67	C1
	1.17%	1 P:*x*	−5.298	0.67	C10
	1.13%	1 P:*x*	−5.298	0.67	C14
	1.04%	2 D:*x*2–*y*2	4.940	0.00	Mo1

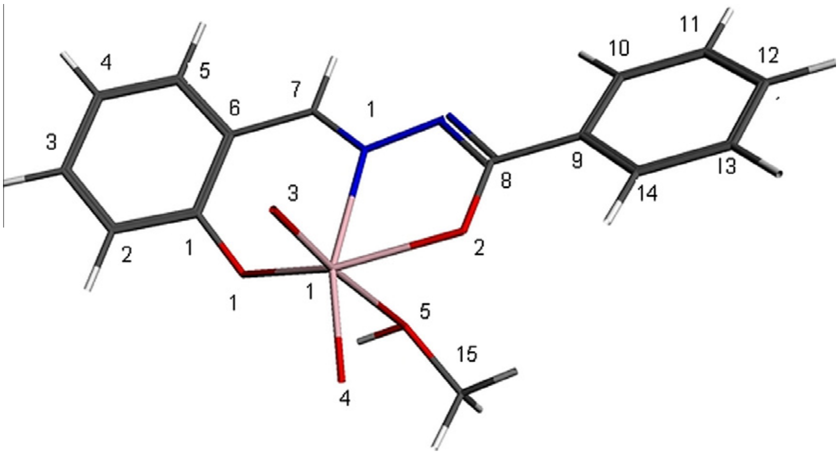

Figure 3 The optimized structure of methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) by B3LYP DZP basis set by using ADF 2009.01 program.

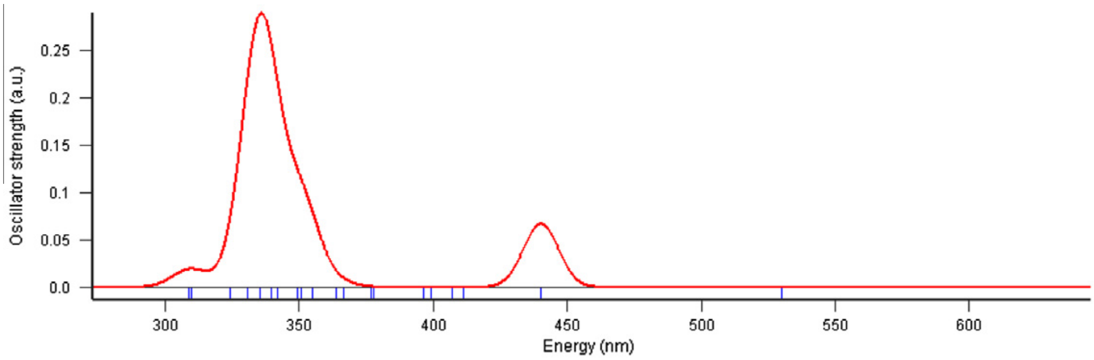

Figure 4 The DFT calculated of UV spectra for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI).

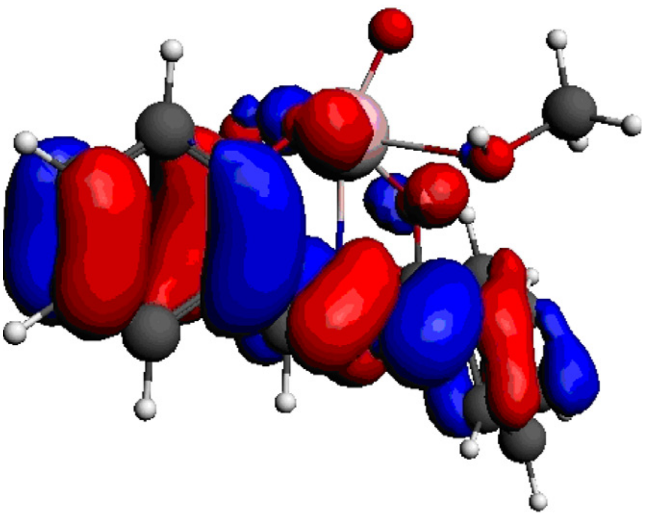

Figure 5 Plots of frontier molecular orbital of HOMO level for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) molecule calculated by using B3LYP DZP method.

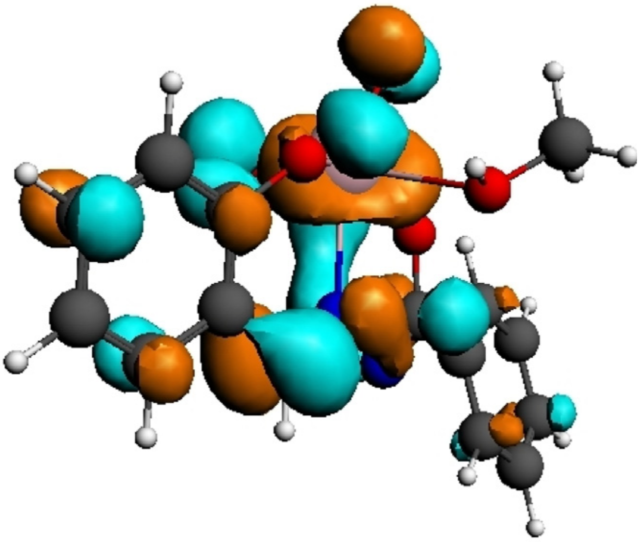

Figure 6 Plots of frontier molecular orbital of LUMO level for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) molecule calculated by using B3LYP DZP method.

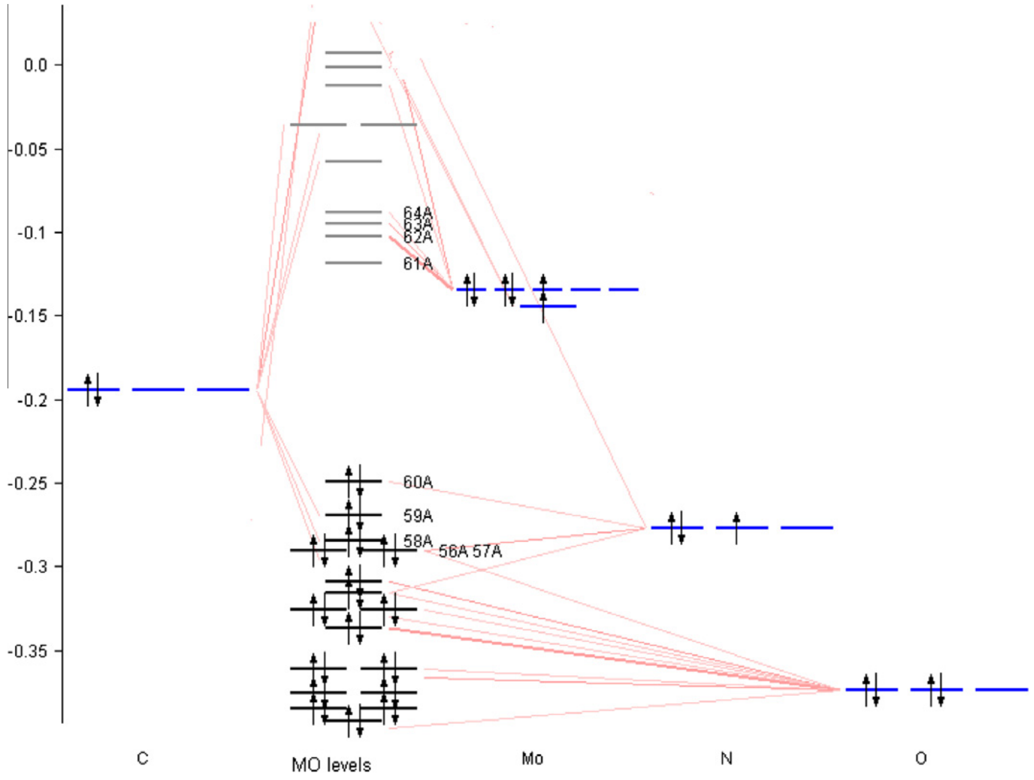

Figure 7 The calculated MO diagram for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) molecule.

Fig. 7 shows the calculated molecular orbitals diagram for methanol {E-N′-(2-hydroxybenzlidene)benzohydrazido}dioxidomolybdenum (VI) molecule calculated by using B3LYP DZP method.

3. Results and discussion

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. The initial geometry for input to the DFT calculation was obtained by means of the MM+ molecular mechanic program for gas phase. In order to optimize the geometry of the compound, the DFT method is used. As a result of energy minimizing study on this metal complex, some selected bond distances and bond angles are given in Tables 3 and 4. According to the geometry optimization in the gas phase, proposed molecular structure of this complex are shown in Fig.3. In this paper, 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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