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A novel tridentate Schiff base dioxo-molybdenum(VI) complex: Synthesis, experimental and theoretical studies on its crystal structure, FTIR, UV-visible, ¹H NMR and ¹³C NMR spectra

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HIGHLIGHTS

- A novel dioxo-molybdenum(VI) complex has been synthesized.
- It is used for single-crystal X-ray analysis and measuring FTIR, UVvisible, ¹H NMR and ¹³C NMR spectra.
- The chemical shifts predicted by DFT-B3LYP method are in accordance with the experimental data.
- ► The absorption maxima at 370– 380 nm is attributed to ligandto-metal $Mo(d\pi) \leftarrow O(\pi)$ charge transfer transition.

G R A P H I C A L A B S T R A C T

The novel dioxo-molybdenum(VI) complex $[MoO_2(L)(H_2O)]$ has been synthesized, using 5-methoxy 2-[(2-hydroxypropylimino)methyl]phenol as tridentate ONO donor Schiff base ligand and characterized by IR, ¹H NMR, ¹³C NMR spectroscopy and single-crystal X-ray analysis. Quantum chemical methods are used to reproduce the structure, UV-visible, FTIR, ¹H NMR and ¹³C NMR spectra of the compound.



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ABSTRACT

A new dioxo-molybdenum(VI) complex [MoO₂(L)(H₂O)] has been synthesized, using 5-methoxy 2-[(2-hydroxypropylimino)methyl]phenol as tridentate ONO donor Schiff base ligand (H₂L) and MoO₂(acac)₂. The yellow crystals of the compound are used for single-crystal X-ray analysis and measuring Fourier Transform Infrared (FTIR), UV-visible, ¹H NMR and ¹³C NMR spectra. Electronic structure calculations at the B3LYP and PW91PW91 levels of theory are performed to optimize the molecular geometry and to calculate the UV-visible, FTIR, ¹H NMR and ¹³C NMR spectra of the compound. Vibrational assignments and analysis of the fundamental modes of the compound are performed. Time-dependent density functional theory (TDDFT) method is used to calculate the electronic transitions of the complex. All theoretical methods can well reproduce the structure of the compound. The ¹H NMR spectra. However, the ¹³C NMR shielding tensors computed at the B3LYP/DGDZVP level of theory is in agreement with experimental ¹¹C NMR spectra. The electronic transitions calculated at the B3LYP/DGDZVP for Mo and 6 – 31 + G(2df,p) for other atoms, are in better agreement with experimental ¹³C NMR spectra. The electronic transitions calculated at the B3LYP/DGDZVP level by using TD-DFT method is in accordance with the observed UV-visible spectrum of the compound.

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Introduction

Dioxo-molvbdenum(VI) complexes have been extensively studied because of their important role in the oxo-transfer chemistry and oxidation catalysis. Imitating the enzymatic role of molybdenum complexes in biological systems [1,2] especially in the oxidation of aldehydes, purines and sulfides [3] vast variety of dioxomolybdenum complexes are synthesized and their oxygen atom transfer properties are investigated. Molybdenum complexes of dithiocarbamates [4,5]; bidentate Schiff bases such as cis-[MoO2 {(4,6-bis(tert-butyl)-2-{(benzyl)iminomethyl}-phenolate)2}], *cis*-[MoO2(L)2] where L = 4,6-bis(tert-butyl)-2-{(benzyl)iminomethyl}phenol [6]; tridentate Schiff bases such as sap (2-salicylideneamino phenolate(2-)), ssp (2-salicylideneamino benzenethiolate (2-)), salicylidene salicyloyl hydrazine and 2-[(2-hydroxypropylimino) methyl]phenol have been demonstrated to act as oxidation catalysts [7–12]. It is also established that the Mo^{VI} complexes of some selected ONO donor ligands may mimic the active sites of some oxotransfer molybdoenzymes [13].

In the present study, a novel dioxo-molybdenum(VI) complex (Fig. 1) has been synthesized and characterized by UV-visible, IR, ¹H NMR, ¹³C NMR spectroscopy and single-crystal X-ray analysis. This research is mainly aimed at spectral properties of the complex. In the past decade, by increasing development of computational chemistry, electronic structure calculations such as Density Functional Theory (DFT) and ab initio methods have been used extensively to calculate a wide variety of molecular properties such as equilibrium structure, charge distribution, UV-visible, FTIR and NMR spectra, and provided reliable results which are in accordance with experimental data [14]. Here, two DFT methods are used to perform theoretical calculations on the structure, UV-visible, FTIR, ¹H NMR and ¹³C NMR spectra of the title compound. The methods include Beck's three-parameter exchange functional [15] with Lee et al. [16] correlation functional (B3LYP); and Perdew and Wang's 1991 exchange with gradient-corrected correlation functional (PW91PW91) [17.18]. The theoretically predicted spectra of the compound enable us to assign each absorption band to the corresponding transition.



Fig. 1. A view of the molecular structure of the title compound, showing the atomic numbering scheme and the thermal displacement ellipsoids drawn at the 50% probability level.



Scheme 1. Schematic representation of the preparation of the dioxo-molybdenum(VI) complex using 5-methoxy 2-[(2-hydroxypropylimino)methyl]phenol and MoO₂(acac)₂.

Table 2 (continued)

Table 1Crystal and refinement data for the complex.

Empirical formula	C ₁₁ H ₁₅ MoNO ₆
Formula mass	353.18
Crystal symmetry	Triclinic
Space group	P-1
a (Å)	6.739(2)
b (Å)	9.915(3)
c (Å)	11.182(4)
α (°)	109.88(3)
β (°)	106.44(3)
γ (°)	92.50(3)
$V(Å^3)$	665.8(4)
Z	2
D_{calcd} . (g cm ⁻³)	1.762
F(000)	356
μ (MoK α) (mm ⁻¹)	1.007
Collected refl.	5537
Independent refl.	2354
R (int)	0.176
R	0.0736
wR2 (all data)	0.2085
S (goodness of fit)	1.15
Min./max. res. (e. Å ⁻³)	-1.73/1.06



Fig. 2. A view of the crystal packing illustrating the formation of the infinite onedimensional hydrogen bonded polymer. The H-atoms not involved in hydrogen bonding have been omitted for clarity.

Table 2

Selected bond lengths (Å), angles (°) and torsion angles in comparison with calculated values.

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	Parameters bond distances	X-ray analysis	B3LYP/BS1	PW91PW91/BS1
	Mo1-O1	1.898(9)	1.956	1.959
	Mo1-01 W	2.360(8)	2.565	2.553
	Mo 1-02	1.963(7)	2.020	2.031
	Mo1-05	1.673(9)	1.722	1.737
	Mo 1-06	1.718(8)	1.731	1.748
	Mo1-N1	2.268(9)	2.320	2.307
	01-C1	1.453(15)	1.423	1.427
	02-C5	1.364(13)	1.334	1.337
	03-C8	1.393(15)	1.372	1.376
	03-C11	1.432(16)	1.424	1.429
	01 W-H1A	0.860(12)	0.973	0.981
	N1-C2	1.452(15)	1.462	1.461
	N1-C3	1.287(15)	1.289	1.300
	C1-C10	1.476(19)	1.525	1.526
	C1-C2	1.494(17)	1.535	1.537
	C3-C4	1.423(17)	1.447	1.444
	C4–C9	1.427(17)	1.421	1.424
	C4–C5	1.392(15)	1.419	1.427
	C5–C6	1.370(17)	1.414	1.419
	C7–C8	1.390(16)	1.413	1.417
	C1-H1	0.990	1.101	1.109
	C3-H3	0.940	1.097	1.104
	C10-H10A	0.970	1.095	1.099

Parameters bond distances	X-ray analysis	B3LYP/BS1	PW91PW91/BS1
Bond angles			
01-Mo1-01 W	82.2(3)	80.6	81.8
01-Mo 1-02	151.1(3)	147.1	148.5
01-Mo 1-05	99.8(4)	101.4	101.1
01-Mo 1-06	97.8(4)	98.9	98.4
01-Mo1-N1	75.1(3)	74.1	74.5
01 W-Mo1-06	84.9(3)	79.5	78.9
01 W-Mo1-N1	76.5(3)	76.3	76.3
02-Mo1-05	94.9(4)	98.8	97.8
05-Mo1-06	106.7(4)	108.6	109.2
Mo1-O1-C1	119.0(7)	119.9	119.3
Mo1-02-C5	132.3(6)	133.7	133.4
C8-03-C11	117.0(10)	117.9	117.0
H1A-01 W-H1B	100.0(10)	105.5	104.6
Mo1-O1 W-H1A	108.0(8)	100.4	98.2
Mo1-N1-C3	1278(8)	127.6	127.6
C2-N1-C3	121.5(10)	121.0	120.8
01-C1-C2	105.0(9)	106.7	106.5
N1-C2-C1	106.2(10)	106.6	106.5
C3-C4-C5	123.4(10)	118.1	121.7
03-C8-C7	114.9(10)	115.6	115.4
C10-C1-H1	108.0	109.8	110.1
N1-C2-H2B	110.0	108.2	108.2
С8-С7-Н7	120.0	118.3	118.3
Torsion angles			
01 W-Mo1-01-C1	105.5(8)	106.7	105.9
02-Mo1-01-C1	57.1(11)	62.7	60.8
O5-Mo1-O1-C1	-62.3(8)	-64.4	-65.1
N1-Mo1-O1-C1	27.5(7)	28.4	27.9
01-Mo1-O2-C5	-66.0(12)	-69.1	-67.1
01 W -Mo1-02-C5	-115.1(9)	-114.2	-113.3
N1-Mo1-O2-C5	-37.0(9)	-35.6	-34.7
01-Mo1-N1-C2	3.5(7)	1.0	1.9
01 W-Mo1-N1-C2	-81.9(7)	-82.9	-83.2
O5-Mo1-N1-C2	103.0(7)	101.3	101.8
Mo1-O1-C1-C2	-52.9(11)	-51.4	-51.2
C11-O3-C8-C7	-179.3(10)	-179.5	-179.9
Mo1-N1-C2-C1	-30.2(10)	-25.2	-26.4
C3-N1-C2-C1	144.4(10)	151.0	148.7
Mo1-N1-C3-C4	-6.7(15)	-8.3	-9.6
01-C1-C2-N1	49.3(12)	45.4	46.4
N1-C3-C4-C5	-11.1(17)	-9.8	-9.3
C3-C4-C5-O2	0.2(16)	0.8	1.7
C3-C4-C5-C6	-175.9(10)	-176.7	-175.8
02-C5-C6-C7	-176.4(10)	-178.5	-178.9
C5-C6-C7-C8	0.2(0.17)	0.7	0.8
03-C8-C9-C4	179.8(10)	179.2	179.2

Table 3

Vibrational frequencies of the complex in comparison with the calculated values the B3LYP/DGDZVP level of theory.

Experiment	B3LYP/DGDZVP	Assignment
439	458	W(HCH)
490	524	W(HOH)
588	625	W(HCH)
781	831	BS(Mo-O)
866	875	OB(HCC)
910	952	BS(Mo=O)
922	963	BS(Mo=O)
971	1028	BS(C-O)
990	1051	BS(C-N)
1083	1110	R(HCH)
1133	1216	IB(HCC)
1174	1255	T(HCH)
1193	1268	BS(C=C)
1225	1283	BS(C-O)
1257	1309	IB(HCC)
1281	1361	SC(HCO)
1325	1409	ib(hcc)
1361	1437	W(HCH)

Table 3 (continued)

Experiment	B3LYP/DGDZVP	Assignment
1453	1509	SC(HCH)
1563	1597	SC(HOH)
1596	1656	BS(C=C)
1641	1678	BS(C=N)
2835	3024	BS(C-H)
2864	3047	BS(C-H)
2958	3107	BS(C-H)
3079	3188	BS(C-H)

BS: Bond stretching, SC: scissoring, R: rocking, W: wagging, T: twisting, IB: in-plane bending, OB: out-of-plane bending.



Fig. 3. A plot of experimental versus theoretical vibrational frequencies at the B3LYP/DGDZVP level.

Experimental section

Materials and measurements

All of the chemicals and reagents were purchased from Fluka and Merck chemical companies and were used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX-400 MHz ultrashield spectrometer using d6-DMSO as solvent. FT-IR (KBr pellet, 450–4400 cm⁻¹) spectrum was taken with Perkin-Elmer Model RX-I FT-IR spectrometer. The electronic spectra were recorded on a Beckman DU-7000 UV–Vis spectrophotometer. Microanalyses (C, H, and N) of the ligand and complex were carried out on a Heracuse CHN rapid analyzer. Melting points were determined on a Gallenkamp melting point apparatus.

Synthesis

The asymmetric Schiff base 5-methoxy 2-[(2-hydroxypropylimino)methyl]phenol (H₂L) was obtained by addition of a solution of 1-amino-2-propanol 0.01 mol (0.75 g) in 10 mL methanol to a solution of 5-methoxy salicylaldehide 0.01 mol (1.52 g) in 10 mL methanol and the reaction mixture heated for 1 h, giving a yellow precipitate. The crude product was recrystallized from an CHCl₃-hexane (1/4 v/v). Yellow powder, Yield: 81% (1.69 g) and m.p. 58°C, (Scheme 1).

IR (KBr) $3193 \text{ cm}^{-1}(v_{OH})$, $1645 \text{ cm}^{-1}(v_{C=N})$, $1521 \text{ cm}^{-1}(v_{C=C})$, 1153 cm⁻¹(v_{CO} phenolic); ¹H NMR (400 MHz, d6-DMSO, 25 °C) $\delta_{\text{ppm.}}$ 1.12 (d, *J* = 6.3, 3H, -CH₃), 3.47 (dd, ¹*J* = 11.8, ²*J* = 6.3, 1H, -CH₂), 3.57 (dd, ¹*J* = 11.85, ²*J* = 4.8, 1H, -CH₂), 3.41 (s, 3H, -OCH₃), 3.87–38.3 (m, 1H, –-CH), 6.8 (d, *J* = 8.9, 1H, aromatic proton), 6.94 (dd, ¹*J* = 8.9, ²*J* = 3.1, 1H, aromatic proton), 7.04 (d, *J* = 3.0, 1H, aromatic proton), 8.45 (s, 1H, C=N), 13.00 (s, 1H, –OH); ¹³C NMR (400 MHz, d6-DMSO, 25 °C) $\delta_{\text{ppm.}}$; 22.22, 56.42, 66.56, 67.26, 115.75, 118.02, 119.34, 120.01, 152.31, 155.59, 167.06; Elem. Anal. Calc: C, 63.16, H, 7.18, N, 6.70; C₁₁H₁₅NO₃ (209).

To 0.01 mol (2.09 g) of 5-methoxy-2-[(2-hydroxypropylimino)methyl]phenol ligand (H₂L), was added 0.01 mol (3.28 g) dioxo-molybdenum(VI) acetylacetonate in 10 mL methanol. The reaction mixture was stirred under reflux condition for 1 h. After washing with cold methanol, recrystallization from methanol and drying in vacuum, the yellow crystals were secured in 78% yield (2.62 g) and m.p. >250 °C, (Scheme 1).

IR (KBr) 1641 cm⁻¹($\nu_{C=N}$), 1596 cm⁻¹($\nu_{C=C}$), 910 and 932 cm⁻¹($\nu_{Mo=O}$); ¹H NMR (400 MHz, d6-DMSO, 25 °C) δ_{ppm} , 1.26 (d, J = 6.0, 3H, --CH₃), 3.59–3.52 (dd, 1H, --CH₂), 4.15 (dd, ¹J = 13.4, ²J = 3.7, 1H, --CH₂), 3.74 (s, 3H, --OCH₃), 4.45–4.41 (m, 1H, --CH), 6.82 (d, J = 8.9, 1H, aromatic proton), 7.13–7.08 (m, 2H, aromatic proton), 8.66 (s, 1H, C=N); ¹³C NMR (400 MHz, d6-DMSO, 25 °C) δ_{ppm} ; 20.30, 56.02, 67.05, 77.55, 116.40, 120.50, 121.01, 122.45, 152.27, 156.44, 162.79.

X-ray diffraction data of the dioxo-molybdenum(VI) complex

Crystal data for the complex, along with other experimental details, are summarized in Table 1. Single-crystal data collection was performed at 233 K on a Stoe Mark II-Image Plate Diffraction System [19] equipped with a two-circle goniometer and using graphite-monochromatized MoK_{α} radiation ($\lambda = 0.71073$ Å). The complex MoO₂(L)(H₂O) crystallizes in the Triclinic space group P-1. The structure was solved by Direct methods using the program SHELXS-97 [20]. The refinement and all further calculations were carried out using SHELXL-97 [20]. The water H-atoms were located in a difference electron density map and were refined with distance restraints: O-H = 0.84(2) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The Cbound H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.94, 0.97, 0.98 and 0.99 Å for H-aromatic, CH₃, CH₂, and CH H-atoms, with $U_{iso}(H) = k \times U_{eq}(C)$, where k = 1.2for H-aromatic and CH and CH₂ H-atoms, and 1.5 for H-methyl. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F². The molecular structure and crystallographic numbering scheme are illustrated in the PLATON [21] drawing, Fig. 1. Fig. 2 shows a view of the crystal packing illustrating the formation of the infinite one-dimensional hydrogen bonded polymer.

Theoretical section

The geometry of the complex was optimized at the B3LYP and PW91PW91 levels of theory with the basis set of DGDZVP [22]. The harmonic vibrational frequencies and their relative intensities were calculated by B3LYP/DGDZVP method and the results were compared with experimental FTIR spectra. The GIAO (Gauge Including Atomic Orbital) method [23,24] was employed to ¹H NMR and ¹³C NMR chemical shifts at the B3LYP and PW91PW91 levels. Two different basis sets were used: The standard DGDZVP basis set and a combined basis set in which DGDZVP was employed for Mo atom and 6 - 31 + G(2df,p) for other atom. The latter basis set is called BS2 in the present study. Solvent (DMSO) was considered as a uniform dielectric constant 46.7 and Polarizable Continuum Model (PCM) [25] was employed to calculate the NMR chemical shifts. Time-dependent density functional theory (TD-DFT) was used to compute excitation energies and oscillator strengths for electronic transitions from ground to excited states



Fig. 4. Experimental ¹H NMR spectrum of the complex.

 Table 4

 Experimental isotropic ¹H NMR chemical shifts of the complex in comparison with calculated theoretical values.

Experiment	B3LYP/BS1	B3LYP/BS2	PW91PW91/BS1	PW91PW91/BS2	Assignment
1.242	1.2011	1.3504	1.3736	1.352	H10
3.521	3.5062	3.5641	3.8196	3.6559	H2b
3.720	3.7746	4.025	3.9548	4.0416	H11
4.113	4.0951	4.319	4.354	4.4074	H2a
4.398	4.9364	5.0897	5.1714	5.1963	H1
6.802	7.0965	7.3601	7.1579	7.2706	H9
7.061	7.2501	7.3854	7.2818	7.3245	H6
7.106	7.6637	7.7408	7.7079	7.6389	H7
8.645	8.7475	9.0662	8.7376	8.9726	H3

[26–28]. All calculations were carried out with the GAUSSIAN03 software [29].

Results and discussion

A triclinic space group P-1 was determined by X-ray crystallography from single-crystal data of this complex. The details of experimental condition, data collection and refinement are summarized in Table 1. Some selected experimental bond lengths and bond angles are given in Table 2 in comparison with calculated values at the B3LYP/ DGDZVP and PW91PW91/ DGDZVP levels.

As shown in Table 2, the calculated bond lengths and bond angles at both levels of theory are in reasonable agreement with the values determined by crystallographic analysis. The molecule is optimized in gas phase and the deviations in molecular geometries are attributed to intramolecular interactions in the crystalline structure. The geometry around Mo ion is distorted octahedral. The Schiff base coordinates via O1, O2 and N1 atoms to the MoO_2 moiety. The sixth weaker coordinated water (the Mo–O bond length of 2.48 Å) makes a labile site for substitution and catalytic activity. The geometry and charge distribution (Mulliken population analysis) of the complex is given in Fig. 1S in the supplementary information. The high positive charge density (about 1.2) concentrated on molybdenum atom is indicative of the catalytic activity of this site of the molecule.

The experimentally observed Fourier transform infrared (FTIR) peaks of the complex are given in Table 3 and compared with the most intense harmonic vibrational frequencies calculated at



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Table 5

Experimental isotropic ¹³C NMR chemical shifts of the complex in comparison with calculated theoretical values.

Experiment	B3LYP/BS1	B3LYP/BS2	PW91PW91/BS1	PW91PW91/BS2	Assignment
20.30	23.7604	21.45	24.56075	21.1949	C10
56.02	61.5124	58.7128	64.63535	59.6554	C11
67.05	74.781	71.5764	78.57785	73.2378	C2
77.55	87.7117	87.305	90.81065	88.758	C1
116.40	120.89	115.8397	120.2081	113.412	C9
120.50	125.9176	119.7805	126.0441	117.7885	C6
121.01	126.7469	122.9233	126.1048	122.2917	C4
122.45	133.5713	127.7978	132.5068	125.305	C7
152.27	159.6168	156.7466	159.7327	155.4623	C8
156.44	166.4593	162.7386	164.7345	160.1335	C5
162.79	175.0918	165.8722	171.3957	160.799	C3

the B3LYP/DGDZVP level of theory. The vibrational frequencies are often overestimated by theoretical methods due to basis set truncation and neglect of electron correlation and mechanical anharmonicity [30,31]. To clarify the relation between the theoretical and experimental values of the frequencies, the observed FTIR peaks are plotted versus the most intense computed vibrational frequencies. As shown in Fig. 3, there is a good linear relationship between the experimental and theoretical values. Using the fitted linear equation, each absorption peak could be assigned to the corresponding normal mode. The results of the vibrational bands assignments are given in the third column of Table 3. The metal complex showed two prominent bands at 910 and 932 cm⁻¹ assigned to *cis*-dioxomolybdenum (MoO₂) which was consistent with similar previous studies [11]. In addition, the band found at 781 cm⁻¹ was assigned to symmetric stretching of O–Mo–O linkage formed through the coordination of the ligand. To the best of our knowledge, this is the first theoretical assignments of the latter vibrational modes.

Fig. 4 shows the ¹H NMR spectrum of the title compound. Experimentally, nine peaks are observed because the rotation of methyl groups causes their hydrogen atoms show unique NMR peaks. The computed ¹H NMR chemical shifts at the B3LYP/ DGDZVP, B3LYP/BS2, PW91PW91/DGDZVP and PW91PW91/BS2 levels of theory along with experimental data are given in Table 4. As can be seen, the results obtained by using all DFT methods are in reasonable agreement with experimental values. However, the computed ¹H NMR chemical shifts at the B3LYP/DGDZVP are in better agreement with the experimental data. The ¹³C NMR spectrum of the compound is demonstrated in Fig. 5. The isotropic chemical shifts calculated by all DFT methods are given in Table 5 and compared with the experimental data. As can be seen, the B3LYP and PW91PW91 methods, employing DGDZVP basis set, overestimate the ¹³C NMR chemical shifts. The predicted ¹³C NMR peaks by B3LYP/BS2 are in better agreement with the experimental data. These results clarify that the addition of diffuse and polarization functions to the basis set improves the predicted ¹³C

Fig. 6. A plot of experimental and theoretical ¹H NMR chemical shifts at the B3LYP/ DGDZVP level.

NMR peaks. To clarify the relation between theoretical and experimental values of NMR shielding tensors, the experimental data are plotted versus computed values. As shown in Fig. 6, there is a good linear relationship between experimental and theoretical chemical shifts. Similar plots, with the *R* values very near to 1.00, are obtained for other theoretical ¹H NMR and ¹³C NMR chemical shifts. The calculated ¹H NMR and ¹³C NMR magnetic shielding tensors are compared with the experimental values and assignments are performed and the results are given in Tables 4 and 5.

The electronic spectra of the complex recorded in CH₂Cl₂ displayed maxima in the range 280–290; 330–340 and 370–380 nm. The computed excitation energies and oscillator strengths by TD-DFT at the B3LYP/DGDZVP level represent three strong absorptions at 276, 341 and 364 nm. The absorption maxima at 370–380 nm could be assigned to ligand-to-metal Mo($d\pi$) \leftarrow O(π) charge transfer transition. This electronic transition is visualized by isosurfaces of the corresponding orbitals in Fig. 7. Other absorption maxima are attributed to $\pi^* \leftarrow \pi$ transitions in the ligand.

Conclusion

A novel dioxo-molybdenum(VI) complex has been synthesized and characterized by FTIR, ¹H NMR, ¹³C NMR spectroscopy and single-crystal X-ray analysis. The density functional methods B3LYP and PW91PW91 are used to obtain geometrical parameters and calculate the FTIR, ¹H NMR, ¹³C NMR spectra of the compound. The computed spectra are compared with the experimental observations.

The bond lengths, bond angles and dihedral angles computed by two theoretical methods are in agreement with the X-ray crystallographic data. The longest bond from the water coordination indicates a labile site which imparts catalytic property to the molecule. The normal mode vibrational frequencies calculated at the B3LYP/DGDZVP level of theory is compared with the recorded FTIR spectrum and vibrational bands assignments and analysis of the fundamental modes of the compound are performed. The chemical shifts of the ¹H NMR and ¹³C NMR spectra predicted respectively by B3LYP/DGDZVP and B3LYP/BS2 methods are in accordance with the experimental NMR spectra. The absorption maxima at 370–380 nm in the UV–visible spectrum of the compound is attributed to ligand-to-metal Mo($d\pi$) $\leftarrow O(\pi)$ charge transfer transition. Other absorption maxima are attributed to $\pi^* \leftarrow \pi$ transitions.

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Appendix A. Supplementary material

CCDC 785593 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012. 04.026.

Fig. 7. The electronic transition corresponding to the absorption maxima at 370-380 nm.

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