Dioxomolybdenum (VI) and Oxomolybdenum (IV) Complexes With N, O, and S Bidentate Ligands, Spectral Characterization, and DFT Studies

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Research Article

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Abstract

Two dioxomolybdenum (VI) complexes with chemical formula [MoO_2(acac)(HPY)], and [MoO_2(DTO)(HPY)], with another two oxomolybdenum (IV) complexes [MoO(acac)(HPY)], and [MoO(DTO)(HPY)] have been prepared and characterized by different spectral techniques such as (FTIR, UV-Vis., Mass, ^{1}H-NMR) spectra, magnetic susceptibility, and theoretical studies. The bidetentate ligands used in this study were acetylacetone (acac), 2-hydrazinopyridine (HPY), and dithiooximid (DTO). All the spectroscopic data and the theoretical calculations support the suggestion that the dioxomolybdenum(VI) complexes are diamagnetic and have distorted octahedral structures wheras the oxomolybdenum(IV) complexes are paramagnetic and have distorted square pyramidal structures. Theoretical calculations of the free ligands and the prepared complexes have been done by using DFT calculations by using (GAUSSian 09W) software with basis sets (B3YLP/LanL2DZ). The complexes were very stable and their energies ranged from (-708.85 to -921.99 a.u.) and were very different from that of the free (HPY, DTO) ligands (-359.06 and -984.54 a.u.); respectivily. The prepared complexes are polar (8.11-10.80 Debye) for dioxocomplexes(VI), and (6.63-13.72 Debye) for oxocomplexes(IV), its more than the free (HPY and DTO) ligands (1.46-1.67 Debye); respectivly. The HOMO orbitals energies of the dioxocomplexes(VI) are (-0.229, and -0.377 a.u.), respectivily whereas oxocomplexes(IV) are (-0.192, -0.318 a.u.); respectivily while for the ligands are (-0.216, -0.262 a.u.), respectivily. The LUMO orbitals energies of the dioxocomplexes(VI) are (-0.124, and -0.247 a.u.) and for the oxocomplexes are (-0.093, -0.208 a.u.) its obvouse that they are more lower in their energies than that for the (HPY and DTO) ligands.

1. Introduction

Molybdenum is an essential trace element required in most biological systems [1]. It has many oxidation states (II-VI), the oxidation states (II, III, IV, and V) are air sensitive. The salts of molybdenum are more stable due to its being durability, toughness, and hardness, it was made them alloys and steel [2]. Water can contain another amount of different concentrations from molybdenum and on the other hand, humans, animals, and plants include a vital trace element from molybdenum [3]. The most important oxidation states of molybdenum are (IV) and (VI) states during the binding and reactions. A stable oxomolybdenum(IV) complexes are comparatively scarce than their dioxomolybdenum (VI) coordinate and structurally characterized oxomolybdenum (IV) complexes are excessively rare [4]. The importance of molybdenum complexes in the medicinal applications of dental caries, enhancement of immunological reaction, anticancer and antidiabetic agents, therapeutic, medicinal immense and its effect on different enzymes [5]. Molybdenum can be given oxidation state in oxo complex so determined by the number of oxo groups that to join in center atom [6]. Molybdenum play as a cofactor in three enzyme called molybdoenzymes. This molybdoenzymes has an oxo-group that to believe to responsible for the oxo transferase activity in this enzyme. The oxo-group includes a molybdenum center that can be coordinated by two or more S and N donor ligand [7]. Molybdenum(VI) complexes include a cis-MoO_2 unit that has worked the same as enzyme-like xanthine oxidase and nitrogenase, the complexes are contained a Mo = O unit used as catalysts in the industry because of oxygen atom transfer reactions [8]. The discovery of

the presence of NSO donor points around the Mo(VI) center of oxotransferase enzymes like xanthine oxidase and DMSO reductase led to the synthesis and exploration of the oxo transferability of model complexes that mimic the oxotransferase molybdoenzymes [9]. Dithiooximide (DTO) is an external active agent with varied coordination chemistry due to the intense color character, (DTO) can be used in photographic processes, coordination polymers, and histological agents. (DTO) complexes in transition metals have properties as semiconductor, spectroscopic and magnetic [10]. (DTO) has a long history of use as a reagent for the detection and determination of more transition metals due to the presence of two parts of the thioamide in this class of compounds, it plays an important role in chemotherapy because a large number of biologically active compounds contain this part (-N-C = S) [11]. Dioxomolybdenum(VI) complexes with bi-donor ligands and polydonor atoms such as O and N and ligands with donor sets O2N, O2N, SO2N, or S2N can catalyze oxo-atom transfer reactions. Mo(VI) complexes with 2-hydroxyarylidene thiosemicarbazones having N2O or ONS donor sets have important results in biological activity tests [11]. Other complexes of Mo(VI) with aroylhydrazone ligands containing a cis $[MoO_2]^{2+}$ core have been prepared and extensively studied due to their structural flexibility, facile preparation, and their stability. Mononuclear dioxomolybdenum(VI) complexes $[MoO_2LB]$ [H_2L = 2-aminobenzoylhydrazone of benzoyl acetone have been prepared and investigated [12]. Mo(VI) complexes are potential as an anti-diabetic agent but didn't have an understanding of Mo(VI) speciation in biological media. The complex speciation in aqueous solutions of molybdate is further underscored by the formation of several oligomeric species, conversion among oxidation states, and rapidly exchanging forms. This property gives the Mo(VI) complexes to be insulin-mimetic candidates and this can be explained as a result of reversible inhibition of phosphate-dependent enzymes by $[MoO_4]^{2-}$, similar to that of vanadate ion, or due to the irreversible oxidation of phosphatases by Mo(VI) peroxido complexes similar to V(V) peroxido complexes [13]. Mo(VI) complex of picolinic acid-based metallomicellar catalyst was used in the controlled and chemoselective oxidation of the activated alcohols in the aqueous medium. Interesting metathetic oxidation of 2-butene to acetaldehyde by O_2 gas catalyzed by the immobilized MoO_2-hydrazone complexes on SiO_2 afforded high yields. The heterogeneous molybdenum-salicylidene 2-picoloyl hydrazone complex, which supported on Fe_3O_4 nano-particles, showed high catalytic potential in the (ep)oxidation of various olefins. Molybdenum acetylacetonate complexes, which are supported on functionalized nano-particles, investigated as catalysts in the (ep)oxidation of unsaturated hydrocarbons presenting high potential. Dioxomolybdenum(VI) complexes as durable and highly efficient precatalysts for alkene epoxidation, were investigated recently by Mösch-Zanetti *et al*. [14]. Mo(VI) with unsaturated bidentate sulfur ligands complexes have been prepared and investigated. The Mo(VI) complexes such as tris-(benzene-1,2-dithiolate) molybdenum give stable species $[Mo(BDT)_3]$, which are neutral for [Mo(VI)], $[Mo(V)]^{-1}$ and $[Mo(IV)]^{-2}$ [15]. The present study is the destination to prepare and characterize Mo(IV), and Mo(VI) ternary complexes with dioxygen, ditholene, and dinitrogen donor atoms ligands. The reactions of the bidentate ligands with bis-(acetylacetonate) dioxomolybdenum(VI) gave the complexes. The structures and NBO charges of 2-hydrazinopyridne (HPY) and dithiooxamide (DTO) ligands are depicted in Fig. 1. Our research group is engage with the preparation and characterization of molybdenum and vanadium complexes in different oxidation states because of their biological activity, many industrial

uses, and important role in medicinal chemistry so this complexes will be inter in different applications in the future studies.

2. Experimental

2.1 Materials

The chemicals were in high purity, 2–hydrazinopyridine (HPY) (95%) was purchased from Fluka. Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) and dithiooxamide (DTO) were purchased from Aldrich. Solvents were of analytical grade. The starting complex $[MoO_2(acac)_2]$ was prepared as described in the literature [16-17].

2.2 Measurements

Infrared measurements of the 2–hydrazinopyridine (HPY), dithiooxamide (DTO) ligands, and the complexes, as KBr pellets, were carried out using a Bruker Tensor 27 FT-IR spectrophotometer in the range 4000-400 cm^{-1}. ^{1}H-NMR was recorded using ultra shield Bruker 500 MHNMR at (^{1}H at 500 MHz). Mass spectrometry measurements were carried out using GCMS-QP1000EX. The magnetic susceptibility of the complexes was carried out using a Balance Magnetic Susceptibility Model (MSB-MKI). UV-Vis. spectra were recorded in a 1.0 cm path length quartz cell by using a UV-Vis. spectrophotometer type Shimadzu UV-1800 UV–Vis. in DMSO. The structures of the 2–hydrazinopyridine (HPY), dithiooxamide (DTO) ligands, and the complexes were optimized by the use of [GAUSSIAN 09W] software program at the B3LYP/LanL2DZ basis sets for the complexes and B3LYP/6-31G (d, P) for the ligands.

2.3. Preparation of dioxomolybdenum(VI) complexes

2.3.1. $[MoO_2(acac)(HPY)]$ complex

The $[MoO_2(acac)_2]$ precursor salt has been prepared by the literature method [16-17]. The $[MoO_2(acac)_2]$ (0.30 g, 1 mmol), and (0.11 g, 1.0 mmol) of 2- hydrazinopyridine (HPY) ligand have been mixed dropwise with constant stirring and refluxed for two hours. The color of the solution changed from yellow to brown and obtained a precipitate. The precipitate was filtered and washed several times with ethanol and finally with diethyl ether and kept in dissector for 24 hrs. The complex have been subjected to elemental analysis: : *Anal. Calc. for; ($C_{10}H_{15}MoN_3O_4$), Calc.: C,* 35.62*; H, 4.48; N, 12.46, Found: C,* 35.43*; H,* 4.36*; N,* 12.19*%);* m.p >300 *C°*; Scheme 1.

2.3.2. $[MoO_2(DTO)(HPY)]$ complex

The $[MoO_2(acac)_2]$ (0.30 g, 1 mmol), and (0.12 g, 1.0 mmol) of dithiooxamide (DTO) ligand have been mixed dropwise with constant stirring and refluxed for two hours. The color of the solution changed from yellow to dark brown and obtained a precipitate. The precipitate was filtered and washed several times with ethanol and finally with diethyl ether and kept in dissector for 24 hrs. The complex have been

subjected to elemental analysis: *Anal. Calc. for; ($C_7H_{11}MoN_5O_2S_2$), Calc.: C,* 23.53*; H, 3.10; N, 19.60, Found: C,* 23.29*; H,* 2.89*; N,* 19.39*%);* m.p >300 *C°*; Scheme 2.

2.4. Preparation of oxomolybdenum(IV) complexes

2.4.1. [MoO(acac)(HPY)] complex

(0.3 g, 1 mmol) of [$MoO_2(acac)_2$] was dissolved in 20 ml of absolute ethanol, then (0.11 g, 1.0 mmol) of 2-hydrazinopyridine (HPY) had been added dropwise to a stirred solution, and (0.262 g, 1 mmol) of triphenylphosphine was added slowly with constant stirring. After two hours dark brown precipitate isolated washed several times with ethanol and finally with diethyl ether and kept in dissector for 24 hrs. The complex have been subjected to elemental analysis: *Anal. Calc. for; ($C_{10}H_{15}MoN_3O_3$), Calc.: C,* 37.40*; H, 4.71; N, 13.08, Found: C,* 37.19*; H,* 4.59*; N,* 12.89*%);* m.p >300 *C°*; Scheme 3.

2.4.2. [MoO(DTO)(HPY)] complex

(0.3 g, 1 mmol) of [$MoO_2(acac)_2$] was dissolved in 20 ml of absolute ethanol, and (0.12 g, 1.0 mmol) of dithiooxamide (DTO) dissolved in 20 ml of acetone had been added dropwise to a stirred solution, then (0.11 g, 1.0 mmol) of 2-hydrazinopyridine (HPY), and finally (0.262 g, 1 mmol) of triphenylphosphine was added slowly with constant stirring. After two hours light brown precipitate isolated washed several times with ethanol and finally with diethyl ether and kept in dissector for 24 hrs. The complex have been subjected to elemental analysis: *Anal. Calc. for; ($C_7H_{11}MoN_5OS_2$), Calc.: C,* 24.64*; H, 3.25; N, 20.52, Found: C,* 24.42*; H,* 3.09*; N,* 19.89*%);* m.p >300 *C°*; Scheme 4.

3. Results And Discussion

The physical and electronic transitions of the complexes are presented in **Table 1.**

3.1 FT-IR spectra.

The FT-IR spectral data of the complexes are illustrated in **Table 2**. The peaks of the complexes were compared with that of the free 2-hydrazinopyridine (HPY) and free dithiooxamide (DTO) ligands to monitor the variations in the frequencies of the coordination sites. The spectrum of the free 2-hydrazinopyridine (HPY) ligand showed bands at (3395, 3308 cm^{-1}) which are assigned to the stretching vibrations asymmetrical and symmetrical of the amine groups. The spectrum of the [MoO_2(acac)(HPY)] complex showed broad bands at (3089, 3016 cm^{-1}) attributed to asymmetrical and symmetrical (NH_2) stretching frequencies; respectively. This is an indication of the coordination between the 2-hydrazinopyridine (HPY) ligand and the Mo(VI) ion through the nitrogen atoms of the amine groups. The band at 1600 cm^{-1} vibration was assigned for the υ(C=O) stretching frequency in (acac). The spectrum exhibited new bands at (921, 1110 cm^{-1}) that can be attributed to symmetric and asymmetric stretching of υ(O=Mo=O) in cis-configuration [18-19]. The` spectrum of the [MoO_2(DTO)(HPY)] complex is illustrated

in **Fig. 2** showed broad bands at (3618, 3047 cm^{-1}) attributed to asymmetrical and symmetrical (NH_2) stretching; respectively [19]. This is confirmed the coordination between the 2-hydeazinopyridine (HPY) ligand and the Mo ion through the nitrogen atoms of the amine groups. The complex with (DTO) spectrum also exhibited a new band at (953, 1153 cm^{-1}) that can be attributed to symmetric and asymmetric stretching of υ(O=Mo=O) in cis-configuration [11, 19]. The thioamide group stretching three bands have appeared in this complex at (1527, 1423, and 1191 cm^{-1}), this confirms the coordination of the (DTO) ligand to the Mo ion [11]. The spectrum of the [MoO(acac)(HPY)] complex showed broad bands at (3606, 3101 cm^{-1}) attributed to asymmetrical and symmetrical (NH_2) stretching; respectively. The band at 1519 cm^{-1} assigned for the vibrations of υ(C=O) in (acac). The spectrum showed a band at (952 cm^{-1}) this band refers to the ν(Mo=O) stretching. The spectrum of the [MoO(DTO(HPY)] complex showed broad bands at (3738, 3603 cm^{-1}) attributed to asymmetrical and symmetrical (NH_2) stretching. The thioamide group stretching three bands have appeared in this complex at (1519, 1427, and 1172 cm^{-1}), this confirms the coordination of the (DTO) ligand to the Mo ion [11]. The spectrum showed a band at the range (952 cm^{-1}) which refers to the ν(Mo=O) stretching [18-19]. The M-N, M-O, and M-S bands appeared in the complexes at (450-467 cm^{-1}, 487-510 cm^{-1}, and 570-585cm^{-1}); respectively [12, 21-22]. The experimental FT-IR data of the dioxomolybdenum and oxomolybdenum complexes were compared with the calculated data of optimized complexes structure obtained from the DFT calculation by using (Gaussian 09W software) and it was without any negative value that and it's in good agreement with the experimental ones. The differences between the experimental and the calculated data due to the different methods used to obtain them.

3.2 Mass spectral analysis

The mass spectra of the complexes exhibited the main mass fragmentation peaks which are listed in **Table 3**. Mass spectrum of the complex [MoO_2(acac)(HPY)] (molecular weight 339.01) gave molecular ion peak (M) at m/z = 338.40, a peak at m/z = 238.23 assigned for (M-acac), a peak at m/z = 230.94 assigned for (M-HPY), a peak at m/z = 130.16 attributed to (MoO_2). The spectrum showed also peaks at m/z=95.08, 96.0, and 96.79 which are assigned to the stable molybdenum isotopes. Mass spectrum of the complex [MoO_2(DTO)(HPY)] (molecular weight equals 358.94) gave molecular ion peak (M) at m/z=(356.66), a peak at m/z=250.40 assigned for (M-HPY), a peak at m/z=235.59 assigned for (M-DTO), a peak at m/z=129.26 assigned for (MoO_2), a peak at m/z=119.89 assigned for (DTO), a peak at m/z=110.76 assigned for (HPY) ligand. The spectrum showed also peaks at m/z=97.41, 98.86, and 101.37 which are assigned to the stable molybdenum isotopes. Mass spectrum of the [MoO(acac)(HPY)] complex (molecular weight 323.02) gave molecular ion peak (M) at m/z=323.09, a peak at m/z=227.14 assigned for (M-acac), a peak at m/z = 215.01 assigned for (M-HPY), a peak at m/z=115.64 attributed to (MoO). The spectrum showed also peaks at m/z=95.08, 96.0, and 96.79 which are assigned to the stable molybdenum isotopes. Mass spectrum of the [MoO(DTO)(HPY)] complex (molecular weight equals 342.95) gave molecular ion peak (M) at m/z=(340.25), a peak at m/z=225.93 assigned for (M-DTO), a peak at m/z=235.15 assigned for (M-HPY), a peak at m/z=113.26 assigned for (MoO), a peak at

m/z=121.19 assigned for (DTO), a peak at m/z=111.96 assigned for (HPY) ligand. The spectrum of the complex showed also a peak at m/z=99.05, which is assigned to the stable molybdenum isotope [23]. The mass spectrum data of the [MoO_2(DTO)(HPY)] complex is presented in **Fig. 3** as a represented example. The data of mass spectra for the complexes are presented in (SI).

3.3 ^{1}H-NMR spectra

The ^{1}H-NMR spectral data for the free ligands and Mo(VI) complexes in DMSO-d^6 are presented in **Table 4**. The experimental data compared with the calculated spectra that obtained from the DFT calculations. The ^{1}H-NMR spectrum of the 2-hydrazinopyridine (HPY) ligand showed the signals at the range (δ=7.38-8.50 4H) ppm are assigned to the pyridine group protons as multiple peaks. The characteristic signal at (δ=4.36 H) ppm is assigned to the NH proton as a single peak. The signal at (δ=3.66 2H) ppm is assigned to the NH_2 proton as a single peak. The ^{1}H-NMR spectrum of the [MoO_2(acac)(HPY)] complex showed the signal at the range (7.8-8.7 4H,s) ppm assigned to pyridine group protons as multiple peaks. The signal at (δ=6.1 H) ppm is assigned to CH for the enol form of (acac), a peak at (δ= 3.34 2H) as a singlet peak which is assigned to NH_2 protons, and also peak at (δ=1.34 6H) ppm as a singlet peak which is assigned to CH_3 of (acac) ligand. The ^{1}H-NMR spectrum of the [MoO_2(DTO)(HPY)] complex showed signals at the range (δ=7.15-8.46 4H) ppm which are assigned to the pyridine group protons as multiple peaks. The signals at (δ=9.69-10.21) ppm are assigned to NH_2-DTO. The signal at (δ=2.23-3.37) ppm is assigned to NH_2 protons as a singlet peak, which is shifted to downfield from those of the free 2-hydrazinopyridine (HPY) ligand. The signal at (δ=4.21-4.30 H) ppm can be assigned for the NH. These data indicate that the 2-hydrazinopyridine (HPY) ligand coordinates with molybdenum(VI) atom by two nitrogen atoms of the NH_2 groups and with the dithiooxamide (DTO) ligand by the two sulfur atoms. The calculated ^{1}H-NMR data of the Mo(VI) complexes by use of DFT/LanL2DZ basis set were compared with the experimental data and it is in good agreement with the experimental data; **Fig. 4** shows the experimental and calculated ^{1}H-NMR spectra of [MoO_2(DTO)(HPY)] complexes [15, 24].

3.4 Electronic spectra

The electronic spectral data of the complexes in the DMSO solutions were recorded in the 200–1100 nm **Table 1** and compared with the calculated spectra obtained from the TD-DFT calculations in DMSO as solvent. The experimental UV-Vis. and calculated spectra of the [MoO_2(DTO)(HPY)] complexes are given in **Fig. 5**. The absorption spectrum showed peaks at (281, and 325 nm), which can be assigned to (π-π*) and (n- π*) of the intra-ligand electronic transitions. These peaks were shifted to lower wavenumbers when compared with the peak of free ligands. The spectrum also exhibited a peak at (438 nm) assigned to LMCT from L(pπ)→d_{Mo}. The spectrum of the [MoO_2(acac)(HPY)] complex showed peaks at (296, and 386 nm), which can be assigned to (π-π*) and (n- π*) of the intra-ligand electronic transitions. These peaks were shifted to lower wavenumbers when compared with the peak of free ligands. The spectrum also exhibited a peak at (407 nm) assigned to LMCT LMCT from L(pπ)→d_{Mo} (SI). UV-Vis. spectra of the [MoO(acac)(HPY)] and [MoO(DTO(HPY)] complexes are given in (SI). The absorption spectra showed

peaks at (270-268, and 318-369 nm); respectively which can be assigned to (π-π*) and (n- π*) of the intra-ligand electronic transitions. The spectra exhibited peaks at the range (440, and 447 nm) assigned to LMCT from L(pπ)→d_{Mo}. The d-d electronic transitions within the octahedral arrangement around Mo(VI) (d^0-configuration) have vanished whereas for Mo(IV) (d^2-configuration) observed as a weak band at the range (637 and 704 nm); respectively [12, 25]. The experimental UV-Vis. data of the prepared complexes have been compared with the calculated ones by using of TD-DFT/LanL2DZ basis set in DMSO as solevent. There were acceptable differences between the experimental and the calculated data due to the different ways used to determine each one; solid-state for the experimental data and gaseous state for the calculated data.

3.5 Magnetic measurements

The magnetic measurement of the prepared complexes showed that the Mo(VI) complexes were diamagnetic with d^0 configuration whereas the Mo(IV) complexes were paramagnetic with d^2 (t_{2g}^2,e_g^0) electronic configuration and the values of the μ_{eff} for the complexes are (2.9 and 3.1) [MoO_2(acac)(HPY)] and [MoO_2(DTO)(HPY)]; respectivily[26].

3.6 Theoretical studies

The optimized structures of the 2-hydrazinopyridine (HPY), dithiooxamide (DTO) ligands, dioxomolybdenum (VI), and oxomolybdenum(IV) complexes were carried out by using the B3LYP/LanL2DZ basis sets [27, 28]. The complexes structure with natural bond order (NBO) charges of the molybdenum and binding sites atoms are given in **Fig. 6**. Selected bond angles and bond lengths are given in Table 5. In Mo(VI) complexes the angles between Mo(VI) atoms and the surrounded atoms are ranged from 71.51 to 107.51 which suggests the distorted octahedral geometry for the complexes [15, 29]. The (N-Mo-N) bonds angle ranged from 71.51 to 72.58, it deviated from the perfect octahedral structure, which supports the suggestion of the distortion in the structure of the complexes. The bond lengths between the Mo(VI) atoms and the nitrogen atoms in the complexes are (2.18-2.44 Aº). The Mo=O bonds length are (1.72 Aº), angles with cis-configuration of (O=Mo=O) are in the range (106.74º-107.51º) and the angles contain the oxygen, and nitrogen atoms are in the range (81.33º-89.55º), whereas the angle between the two sulfur atoms and Mo(VI) is (81.49º). The Mo-S bonds length are (2.45-2.65 Aº) and the angle contains the sulfur and nitrogen atoms is (89.55º). These angles are compared with the reported Mo(VI) complexes havd been prepared prevously, the values are consistent with the values reported (2.43) [31]. Atomic charges are very important to conclude and expected the donor and acceptor atoms in the (HPY) and (DTO) ligands and molybdenum [25, 31]. The charge densities are on the nitrogen atoms in the 2-hydrazinopyridine (HPY) and on the sulfur atoms in the dithiooxamide ligands. Molybdenum with it hexavalent coordinate and positive charge in the complexes acts as the acceptor of the charge. This is a ligand to metal charge transfer (LMCT) from the π orbitals of the (HPY) and (DTO) ligands to the Mo_d orbital. The Mo(VI) complexes are more polarized than the (HPY) and (DTO) ligands, the dipole moments of the complexes are (8.11-10.80 Debye), whereas for (HPY) and (DTO) are (1.46 and 1.67 Debye); respectively [32-34]. In Mo(IV) complexes the

angles between Mo(IV) atoms and the surrounded atoms are (74.85º to 110.61º) which suggests the distorted square pyramidal geometry for the Mo(IV) complexes [35]. The (N-Mo-N) bond angles are (74.85º-77.18º) deviated from the perfect square pyramidal structure and the bond lengths between the Mo(IV) atom and the nitrogen atoms in the complexes are (2.12-2.24 Aº). The Mo=O bond lengths are in the range (1.70-1.71 Aº) for the two complexes, these data have been compared with the reported oxomolybdenum(IV) complexes, and the values are consistent with the value reported (1.68) [36]. The angles contain the oxygen, and nitrogen atoms are in the range (80.10º to 90.39º), whereas the angles between the two sulfur atoms and Mo(IV) is (85.30º). The Mo(IV) complexes are more polarized than the ligands as indicated from the values of the dipole moments values of the complexes (6.36-13.72 Debye) [33-34, 37]. The electronic energy, the atomic charges, and the dipole moments of the ligands, and the complexes are tabulated in Table 6. According to (NBO) analysis for Mo(VI) complexes the electronic configuration of Mo in the $[MoO_2(acac)(HPY)]$ complex are:[core] $5s^{0.21}$ $4d^{4.05}$ $5p^{0.47}$ $5d^{0.05}$, 35.968 core electrons, 4.732 valence electrons and 0.055 Rydberg electrons, which gives 40.755 total electrons and +0.556 e charge on Mo atom. The occupancies of 4d in orbitals are d_{xy} 0.824; d_{xz} 0.829; d_{yz} 0.867; $d_{x^2-y^2}$ 0.741 and d_{z^2} 0.785. The 4d-electron populations (4.046) are in agreement with the charge transfer from (HPY) and (acac) ligands to d_{Mo}. The electronic configuration of the complex $[MoO_2(DTO)(HPY)]$ are: [core] $5s^{0.27}$ $4d^{4.45}$ $5p^{0.68}$ $5d^{0.06}$, 35.974 core electrons, 5.460 valence electrons and 0.067 Rydberg electrons, which gives 41.501 total electrons and +0.556e charge on Mo atom. The occupancies of 4d orbitals are d_{xy} 0.857; d_{xz} 0.901; d_{yz} 0.824; $d_{x^2-y^2}$ 1.013 and d_{z^2} 0.857. The 4d-electron populations (4.453) are in agreement with the charge transfer from (DTO) and (HPY) ligands to d_{Mo}. The oxomolybdenum Mo(IV) complexes, the electronic configuration of [MoO(acac)(HPY)] complex are: [core] $5s^{0.17}$ $4d^{4.391}$ $5p^{0.24}$ $5d^{0.03}$ $6p^{0.11}$, 35.963 core electrons, 4.911 valence electrons and 0.032 Rydberg electrons, which gives 40.906 total electrons and +1.092e charge on Mo atom. The occupancies of 4d orbitals are d_{xy} 1.035; d_{xz} 0.677; d_{yz} 0.650; $d_{x^2-y^2}$ 1.355 and d_{z^2} 0.671. The 4d-electron populations of 4.388 are in agreement with (HPY) and (acac) ligands to d_{Mo} electron transfer [38]. The electronic configurations of [MoO(DTO)(HPY)] complex are: [core] $5s^{0.25}$ $4d^{4.91}$ $5p^{0.19}$ $5d^{0.04}$ $6p^{0.37}$, 35.968 core electrons, 5.713 valence electrons and 0.040 Rydberg electrons, which gives 41.721 total electrons and +0.276e charge on Mo atom. The occupancies of 4d orbitals are d_{xy} 1.166; d_{xz} 0.756; d_{yz} 0.760; $d_{x^2-y^2}$ 1.492 and d_{z^2} 0.729. The 4d-electron populations of 4.903 are in agreement with (HPY) and (DTO) ligands to d_{Mo} electron transfer. The electronic energies of the Mo(VI) complexes are (-784.07 and -921.99 a.u.); respectively and for the Mo(IV) complexes are (-708.85 and -846.76 a.u.); respectively these values indicate the stability of dioxomolybdenum complexes are more than the oxomolybdenum complexes [38]. HOMO and LUMO orbitals energies of the complexes are given in Table 6. The hardness ($\eta=(I-A)/2$) where $(I-A)=\Delta E$=HOMO-LUMO energy levels. The η values and ΔE are given in Table 6. The transitions of electrons are easier in the Mo(VI) complexes than the ligands which are indicated from ΔE of the Mo(VI) complexes (0.105-0.130) whereas for the (HPY) and (DTO) ligands are (0.124 and 0.191); respectively [39-43]. The Mo(VI) complexes are softer (η=(0.052-0.065) than the ligands also (0.062-0.095) [44]. The transitions are also easier in the Mo(IV) complexes than the ligands ΔE of the Mo(IV)

complexes are (0.099-0.110) [42]. The Mo(IV) complexes are softer (η=(0.045-0.055) than the ligands also [43]. The negative values of the energies for the HOMO orbitals and the LUMO orbitals in the Mo(VI) and Mo(IV) complexes support the suggestion of their stability [39]. The surface plots of the HOMO and LUMO orbitals for (HPY), (DTO) ligands, Mo(VI), and Mo(IV) complexes are presented in **Figs. 7 and 8**. The transition energies of the complexes have been calculated from (time-dependent density functional linear response theory) Table 7. The density of the electrons in the (HPY) ligand is localized on the pyridine part and on the nitrogen atoms which may point to a mixed π→π* and n→π* transitions, whereas for the (DTO) ligand the red regions are on the sulfur atoms and the blue regions are on the nitrogen atoms [39]. The HOMO energies (H to H-4), % of the contribution, and the main characters of (HPY), (DTO) ligands, and the molybdenum are calculated for the complexes and tabulated in Table 8. In the [MoO_2(acac)(HPY)] complex, % contribution of (HPY) to the HOMOs (H to H-4) in the range from 3% to 99% with the main character is HPY(π). The % contribution of (HPY) to LUMOs (L to L+4) is lower (6%-13%) (except L+4 90%). The % contribution of the (acac) ligand to the HOMOs is low and varies from 0% to 7% (except H-1 90% and H-2 86%) through acac(π) as the main character. The (acac) ligand % contribution to LUMOs is higher than its contribution to HOMOs and varied from 1% to 18% through acac(π*) (except L+3 69%). The Mo % contribution to the HOMOs varied from 0% to 4%, whereas, the % contribution of Mo to the LUMOs varied from 19% to 54% (L+4 7%) by Mo(e_g), which states the possibility of LMCT from O(π) and/or coordinated ligands to Mo(e_g) [12, 32-34]. In the [MoO(acac)(HPY)] complex, % contribution of (HPY) to the HOMOs (H to H-4), ranged from 4% to 83% with the main character is HPY(π). The % contribution of (HPY) to LUMOs (L to L+4) is higher (13%-87%). The % contribution of the (acac) ligand to the HOMOs is from 12% to 85% through acac(π) as the main character. The (acac) ligand % contribution to LUMOs is lower than its contribution to HOMOs and varied from 2% to 28% through acac(π*) (except L+1 32%). The Mo % contribution to the HOMOs varied from 1% to 6% (except H 74%) whereas, the % contribution of Mo to the LUMOs varied from 9% to 49% by Mo(e_g), which support the possibility of LMCT from O(π) and/or coordinated ligands to Mo(e_g). The Mo(VI) and Mo(IV) complexes with (DTO) ligand instead of (acac) ligand, the % of (DTO) ligand in HOMOs are much higher than Mo and (HPY). On the other hand, the LUMOs are mainly concentrated on the Mo atoms, which support the LMCT transitions. The % contribution and the main characters of Mo, (acac), (HPY), and (DTO) ligands to the different HOMO and LUMO orbitals in the Mo(VI) complexes are presented in Table 8. The molecular electrostatic potential (MEP) for the ligands and the complexes have been calculated and shown in **Fig. 9**, the red regions represent an electrophilic reactivity and the blue regions represent a nucleophilic reactivity. The nitrogen atoms of the (HPY) and the sulfur atoms in the (DTO) ligands; with their red regions (negative charge) are the reactive sites for the electrophilic attack, this constitutes the high electronegativity of the two atoms [32-34, 39]. The red regions in the complexes are mainly localized over the oxygen and sulfur atoms.

Conclusion

The synthesized Mo(VI) complexes have distorted octahedral and Mo(IV) have distorted square pyramidal geometries; the 2-hydrazinopyridine (HPY) and dithiooxamide (DTO) ligands behave as

bidentate N2 donor ligand and as bidentate S2 donor ligand; respectively by relying on spectroscopic data, and DFT theoretical calculations. The mass spectral data showed that the molybdenum(VI) complexes and molybdenum(IV) complexes are mononuclear. The magnetic susceptibility measurements indicate that the Mo(VI) complexes are diamagnetic with d^0 configuration and Mo(IV) are paramagnetic with d^2 configuration. UV-Vis. measurements showed the peaks of the charge transfer and the (d-d) metal transitions. The energies of the HOMO and LUMO orbitals of the ligands and the complexes are negative which indicates that the ligands stable and the complexes are more stable.

Abbreviations

LMCT	Ligand metal charge transfer
DMSO	Dimethyl sulphoxide
IR	Infrared spectroscopy
DFT	Density functional theory
B3LYP	Becke's three-parameter exchange with Lee, Yang, and Parr correlation functional
η	The hardness
TD-DFT	Time-dependent density functional theory
HOMO	High occupied a molecular orbital
LUMO	Low occupied a molecular orbital
MEP	Molecular electronic potential
PPh_3	Triphenylphosphine
acac	Acetylacetone
HPY	2-Hydrazinopyridine
DTO	Dithiooximide

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Tables

Table 1 Some physical and analytical properties of the Mo(VI) and the Mo(IV) complexes

Complex	Molar mass	Mass Spec. m/z (P^+)	m.p	color	Λ_m Ohm^{-1} cm^2 mol^{-1}	UV-Vis. absorption peaks (nm)	
$[MoO_2(acac)(HPY)]$	339.01	338.4	280	Brown	16.70 DMSO	281 325 407	Intra ligand(π→π*) Intra ligand(n→π*) LMCT
$[MoO_2(DTO)(HPY)]$	358.94	356.6	370	Yellow brown	13.20 DMSO	296 386 438	Intra ligand(π→π*) Intra ligand(n→π*) LMCT
$[MoO(acac)(HPY)]$	323.02	323.09	240	Dark brown	10.50 DMSO	270 318 440 637	Intra ligand(π→π*) Intra ligand(n→π*) LMCT d-d transitions
$[MoO(DTO)(HPY)]$	342.95	340.2	>300	Light brown	11.76 DMSO	268 369 447 704	Intra ligand(π→π*) Intra ligand(n→π*) LMCT d-d transitions

Table 2 The most diagnostic FT-IR bands experimental and calculated of the prepared complexes.

Compound	Exp.	Calc.	Assignment
2-hydrazinopyridine	3395,3308	3444, 3508	$\upsilon(NH_2)$
	1246	1299	ρtNH_2
	1086	1193	ρwNH_2
	804	866	ρrNH_2
	3577	3607	υ(N-H)
Dithiooximide	3291,3210	3482, 3691	υ(N-H)
	1196	1319	ρtNH_2
	1042	1232	ρwNH_2
	837	865	ρrNH_2
	1624	1632	υ(C=N)
$[MoO_2(acac)(HPY)]$	3089,3016	3443, 3553	$\upsilon(NH_2)$
	1519	1310	ρtNH_2
	1465	1179	ρwNH_2
	1265	861	ρrNH_2
	3734	3639	υ(NH)
	1600	1612	υ(C=O)
	883	979	O=Mo=O
$[[MoO_2(DTO)(HPY)]$	3618,3047	3445, 3577	$\upsilon(NH_2)$
	1527	1307	ρtNH_2
	1388	1165	ρwNH_2
	1107	888	ρrNH_2
	3618	3631	υ(NH)
	1697	1618	υ(C=N)
	921, 1110	960, 1190	O=Mo=O
[MoO(acac)(HPY)]	3606 , 3101	3409, 3508	$\upsilon(NH_2)$
	1415	1285	ρtNH_2

	1319	1189	ρwNH_2
	1269	769	ρrNH_2
	3838	3643	υ(N-H)
	1519	1585	υ(C=O)
	952	1017	Mo=O
[MoO(DTO)(HPY)]	3738,3603	3402, 3513	υ(NH_2)
	1523	1279	ρtNH_2
	1122	1171	ρwNH_2
	705	858	ρrNH_2
	3857	3649	υ(NH)
	1670	1599	υ(C=N)
	952	996	Mo=O

Table 3 Mass fragments data of the prepared complexes.

Complex	Molar mass	Mass spec. m/z (P^+)	(m/z) values
[MoO_2(acac)(HPY)]	339.01	338.4	338.4(M), 238.28(M-acac),230.94(M-HPY), 130.16(MoO_2), 95.08, 96.0 and 96.79 (Mo) isotopes
[MoO_2(DTO)(HPY)]	358.94	356.6	356.66 (M), 250.40(M-HPY), 235.59(M-DTO), 129.26 (MoO_2), 119.89 (DTO), 110.76 (HPY) ligand, 97.41, 98.86 101.37 (Mo) isotopes.
[MoO(acac)(HPY)]	323.02	323.09	323.09 (M), 215.01 (M-HPY), 227. 14 (M-acac), 115.64 (MoO), 108.24 (HPY) ligand, 97.41, 98.86 and 101.37 (Mo) isotopes
[MoO(DTO)(HPY)]	342.95	340.2	340.2(M), 225.93(M-DTO), 235.15(M-HPY), 113.26(HPY), 121.19 (DTO), 111.96 (HPY), 99.05 molybdenum isotope

Table 4: The experimental and calculated ^{1}H-NMR data of the 2-hydrazinopyridine (HPY), dithiooximide ligands and the molybdenum (VI) complexes measured in a DMSO-d^6 as a solvent and DFT/6-31G (d, P) and LanL2DZ basis sets.

Compound	Exp.	Calc.	Assignment
2-hydrazinopyridine (HPY)	4.36 (4H)	2.05-2.69	NH_2 protons
	6.382-6.50(4H)	6.20-6.45	pyridine group protons
Dithiooximide	1.89	-	SH proton
	6.51–9.6 (8H)	6.95-9.19	NH2
	10.16 (H)	-	NH proton
$[MoO_2(acac)(HPY)]$	3.36- 3.45	4.42-4.50(2H)	NH_2 protons
	1.07 – 2.22	1.32-1.96	CH_3 (acac)
	2.65	2.96 (1H)	NH
	6.84-8.08	6.24-8.02(4H)	pyridine group protons
	6.11	6.05 (1H)	CH-acac
$[MoO_2(DTO)(HPY)]$	4.21-4.30	4.16 (H)	NH-HPY
	2.23-3.37	3.91-4.41 (2H)	NH_2-HPY
	7.15-8.46	5.74-8.08 (4H)	pyridine group protons
	9.69-10.21	9.90-10.35 (2H)	NH-DTO

s= single, m= multiple

Table 5 The bond lengths and bond angles of the Mo(VI) and the Mo(IV) complexes using the DFT/B3LYP/Lan2DZ basis set.

$[MoO_2(acac)(HPY)]$	Bond Lengths ^oA		Bond Angles ^{o}
Mo(1)-N(17)	2.41	N(16)-Mo(1)-N(17)	72.58
Mo(1)-N(16) py	2.18	O(9)=Mo(1)=O(10)	106.74
Mo(1)=O(9)	1.72	O(4)-Mo(1)-O(7) acac	78.38
Mo(1)=O(10)	1.72	O(10)=Mo(1)-O(4)	98.95
Mo(1)-O(7)	2.19	N(16)-Mo(1)=O(10)	95.83
Mo(1)-O(16)	1.98	O(7)- Mo(1)-N(16)	81.33
$[MoO_2(DTO)(HPY)]$			
Mo(1)-N(8) py	2.20	N(8)-Mo(1)-N(9)	71.51
Mo(1)-N(9)	2.44	O(2)=Mo(1)=O(17)	107.51
Mo(1)=O(2)	1.73	S(15)-Mo(1)-S(16)	81.49
Mo(1)=O(17)	1.75	S(16)-Mo(1)-O(17)	92.41
Mo(1)-S(15)	2.65	O(17)-Mo(1)-N(8)	100.47
Mo(1)-S(16)	2.45	S(16)-Mo(1)-N(9)	89.55
[MoO(acac)(HPY)]			
Mo(1)-N(16)	2.21	N(15)-Mo(1)-N(16)	77.18
Mo(1)-N(15) py	2.12	O(4)-Mo(1)-O(7)	83.31
Mo(1)-O(4)	2.06	N(15)-Mo(1)-O(7)	90.39
Mo(1)-O(7)	2.07	N(16)-Mo(1)-O(4)	80.10
Mo(1)=O(9)	1.70	N(15)-Mo(1)=O(9)	110.42
		O(7)-Mo(1)=O(9)	106.20
[MoO(DTO)(HPY)]			
Mo(1)-N(8) py	2.18	N(8)-Mo(1)-N(9)	74.85
Mo(1)-N(9)	2.24	S(15)-Mo(1)-S(16)	85.30
Mo(1)-S(15)	2.42	S(16)-Mo(1)-N(9)	81.65
Mo(1)-S(16)	2.44	S(15)-Mo(1)-N(8)	87.79
Mo(1)=O(2)	1.71	S(15)-Mo(1)-O(2)	110.61
		N(8)-Mo(1)-O(2)	110.24

Table 6 The calculated quantum chemical parameters of the 2-hydrazinopyridine (HPY), dithiooxamide, acetylacetone ligands the Mo(VI) and the Mo(IV) complexes by DFT/B3LYP/6-31G(d, P) for the (HPY) ligand and LanL2DZ for the complexes basis sets.

Compound	HOMO a.u	LUMO a.u	η	ΔE a.u	Electronic Energy a.u	D.M Debye
2-hydrazinopyridine	-0.216	0.025	0.095	0.191	-359.06	1.46
Dithiooxiamaid	-0.262	-0.081	0.090	0.181	-984.54	1.67
$[MoO_2(acac)(HPY)]$	-0.229	-0.124	0.052	0.105	-784.07	10.80
$[MoO_2(DTO)(HPY)]$	-0.377	-0.247	0.065	0.130	-921.99	8.11
[MoO(acac)(HPY)]	-0.192	-0.093	0.045	0.099	-708.85	13.72
[MoO(DTO)(HPY)]	-0.318	-0.208	0.055	0.110	-846.76	6.63

Table 7 The excitation energies (eV), electronic transition configurations and oscillator strengths (*f*) of the Mo(VI) and Mo(IV) complexes.

Complex	Calc. nm(cm^{-1})	Exp. nm	*f*	Composition (>20%)
[MoO_2(acac)(HPY)]	260(38414)	281	0.063	HOMO→LUMO+4(42%), HOMO-6→LUMO+1(28%), HOMO-1→LUMO+1(24%)
	370(26961)	325	0.011	HOMO-1→LUMO+1(65%)
	400(24971)	407	0.013	HOMO-1→LUMO(65%), HOMO-1→LUMO+1(21%)
	446(22396)	430	0.002	HOMO→LUMO(70%)
[[MoO_2(DTO)(HPY)]	284 (35134)	296	0.94	HOMO-3→LUMO+3(30%), HOMO→LUMO+5(24%) HOMO-5→LUMO+1(23%), HOMO-3→LUMO+2(20%)
	371(26923)	368	0.013	HOMO-7→LUMO(45%), HOMO-4→LUMO(42%) HOMO-3→LUMO+1(22%)
	440(22692)	438	0.008	HOMO-1→LUMO+1(60%), HOMO-3→LUMO+1(24%)
	541(18472)	470	0.007	HOMO-1→LUMO(64%), HOMO-2→LUMO(22%)
[MoO(acac)(HPY)]	280(35689)	270	0.058	HOMO-2→LUMO+1(67%)
	315(31714)	318	0.043	HOMO-1→LUMO(66%)
	377(26511)	440	0.016	HOMO→LUMO+3(44%), HOMO→LUMO+5(40%)
	508(19669)	637	0.010	HOMO→LUMO+2(57%), HOMO→LUMO+1(27%)
[[MoO(DTO)(HPY)]	272(36668)	268	0.035	HOMO-7→LUMO(49%), HOMO-1→LUMO+5(28%)
	379(26353)	269	0.013	HOMO-2→LUMO(64%)
	460(21700)	447	0.009	HOMO→LUMO+4(46%), HOMO→LUMO+2(36%)
	661(15123)	704	0.023	HOMO→LUMO(61%)

Table 8 Excitation energies (a.u), % contribution from molybdenum, 2-hydrazinopyridine, acetylacetone, dithiooximide ligands and the main character of some frontier orbitals of the studied complexes.

Complex	Orbital	Energy (a.u.)	HPY	Mo	acac	Main character
[MoO_2(acac)(HPY)] (70)	HOMO	-0.377	99%	0%	0%	HPY(π)
(69)	HOMO-1	-0.393	3%	1%	91%	acac(π)
(68)	HOMO-2	-0.416	3%	3%	86%	acac(π)
(67)	HOMO-3	-0.431	10%	4%	3%	O_2(π)
(66)	HOMO-4	-0.441	76%	2%	7%	HPY(Py)
(71)	LUMO	-0.247	13%	52%	17%	Mo(dxz, dxy)
(72)	LUMO+1	-0.126	9%	51%	15%	Mo(dxy)
(73)	LUMO+2	-0.211	6%	54%	18%	Mo(dyz)
(74)	LUMO+3	-0.205	7%	19%	69%	acac(π*)
(75)	LUMO+4	-0.005	90%	7%	1%	HPY(π*)
			HPY	Mo	DTO	
[MoO_2(DTO)(HPY)] (64)	HOMO	-0.229	1%	1%	89%	DTO(π)
(63)	HOMO-1	-0.244	3%	7%	78%	DTO(π)
(62)	HOMO-2	-0.247	2%	1%	94%	DTO(π)
(61)	HOMO-3	-0.261	14%	12%	64%	DTO(π)
(60)	HOMO-4	-0.277	94%	1%	3%	HPY(π)
(65)	LUMO	-0.124	18%	50%	11%	Mo(dxy)
(66)	LUMO+1	-0.107	18%	54%	8%	Mo(dxz)
(67)	LUMO+2	-0.084	48%	28%	14%	HPY(π*), Mo(dxz, dyz)
(68)	LUMO+3	-0.081	48%	32%	10%	HPY(π*), Mo(dx^2-y^2, dyz)
(69)	LUMO+4	-0.055	26%	10%	60%	DTO(π*)
			HPY	Mo	acac	
[MoO(acac)(HPY)] (66)	HOMO	-0.138	14%	74%	12%	Mo(dx^2-y^2, dxy)
(65)	HOMO-1	-0.377	19%	1%	77%	acac(π)

(64)	HOMO-2	-0.380	83%	1%	15%	HPY(π)
(63)	HOMO-3	-0.411	4%	5%	85%	acac(π)
(62)	HOMO-4	-0.439	17%	6%	52%	acac(π)
(67)	LUMO	-0.439	31%	20%	42%	acac(π*), HPY(π*)
(68)	LUMO+1	-0.197	51%	12%	32%	HPY(π*), acac(π*)
(69)	LUMO+2	-0.171	13%	46%	28%	Mo(dyz, dxz)
(70)	LUMO+3	-0.155	87%	9%	2%	HPY(π*)
(71)	LUMO+4	-0.144	32%	49%	9%	HPY(π*)
			HPY	Mo	DTO	
[[MoO(DTO)(HPY)] (60)	HOMO	-0.192	12%	65%	24%	Mo(dx^2-y^2, dxy)
(59)	HOMO-1	-0.217	5%	4%	86%	DTO(π)
(58)	HOMO-2	-0.235	5%	6%	82%	DTO(π)
(57)	HOMO-3	-0.244	3%	11%	85%	DTO(π)
(56)	HOMO-4	-0.250	3%	18%	76%	DTO(π)
(61)	LUMO	-0.039	89%	6%	2%	HPY(π*)
(62)	LUMO+1	-0.056	95%	2%	2%	HPY(π*)
(63)	LUMO+2	-0.051	3%	12%	82%	DTO(π*)
(64)	LUMO+3	-0.041	21%	56%	8%	Mo(dyz, dxz)
(65)	LUMO+4	-0.033	33%	46%	9%	Mo(dxz, dyz)

Figures

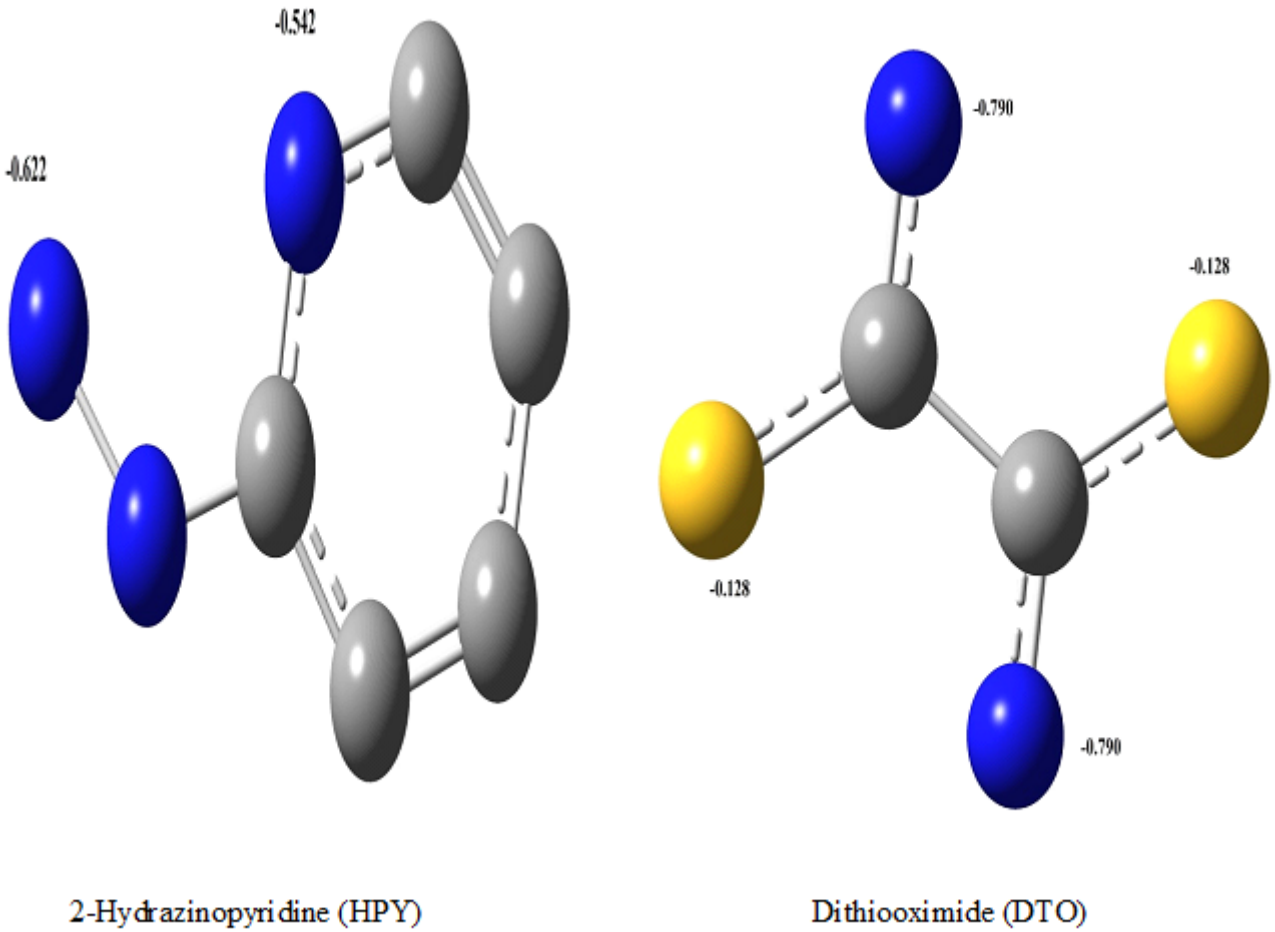


Figure 1

The structures and NBO charges of the ligands.

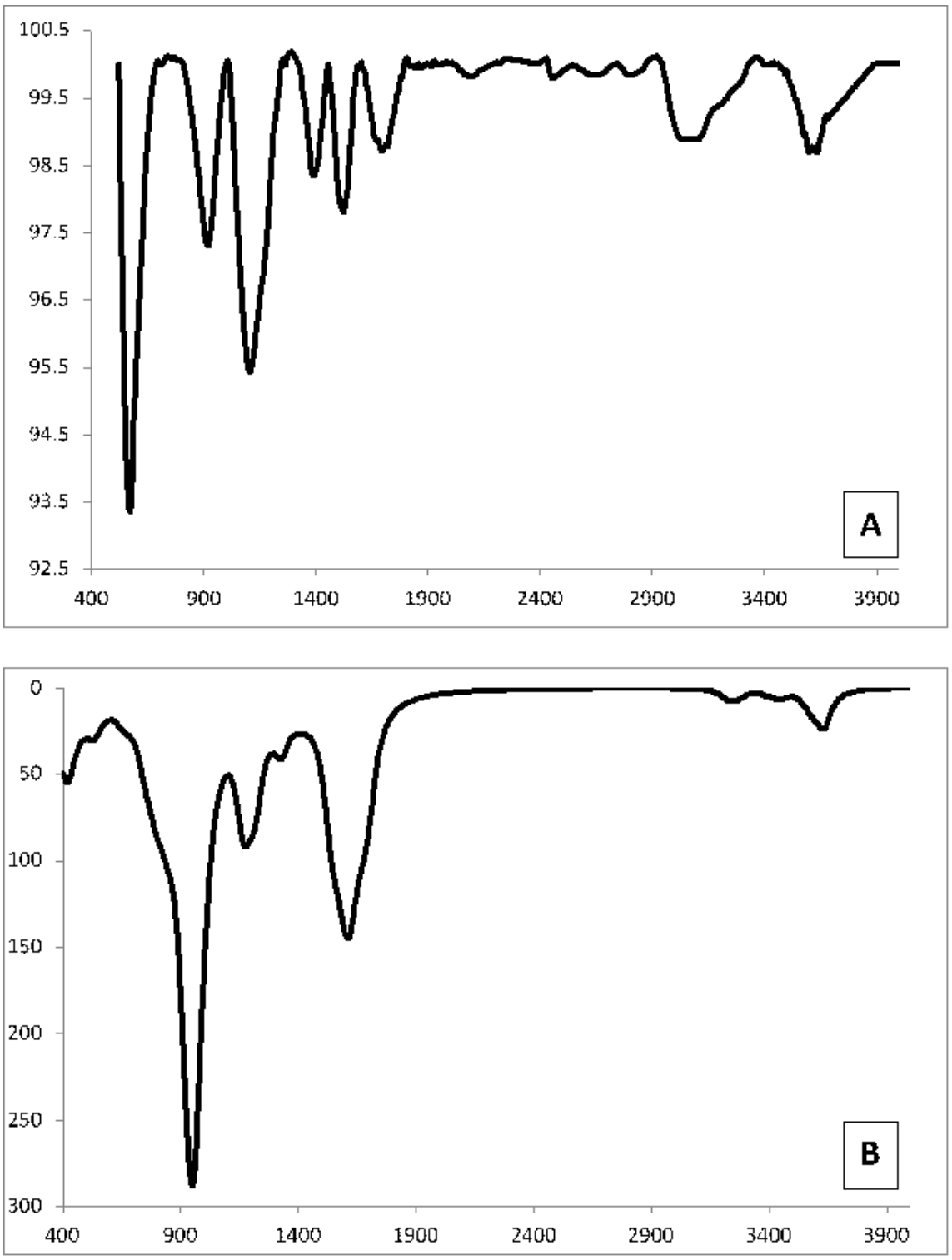


Figure 2

The experimental (a) and calculated (b) FT-IR spectrum of the [MoO2(DTO)(HPY)] complex.

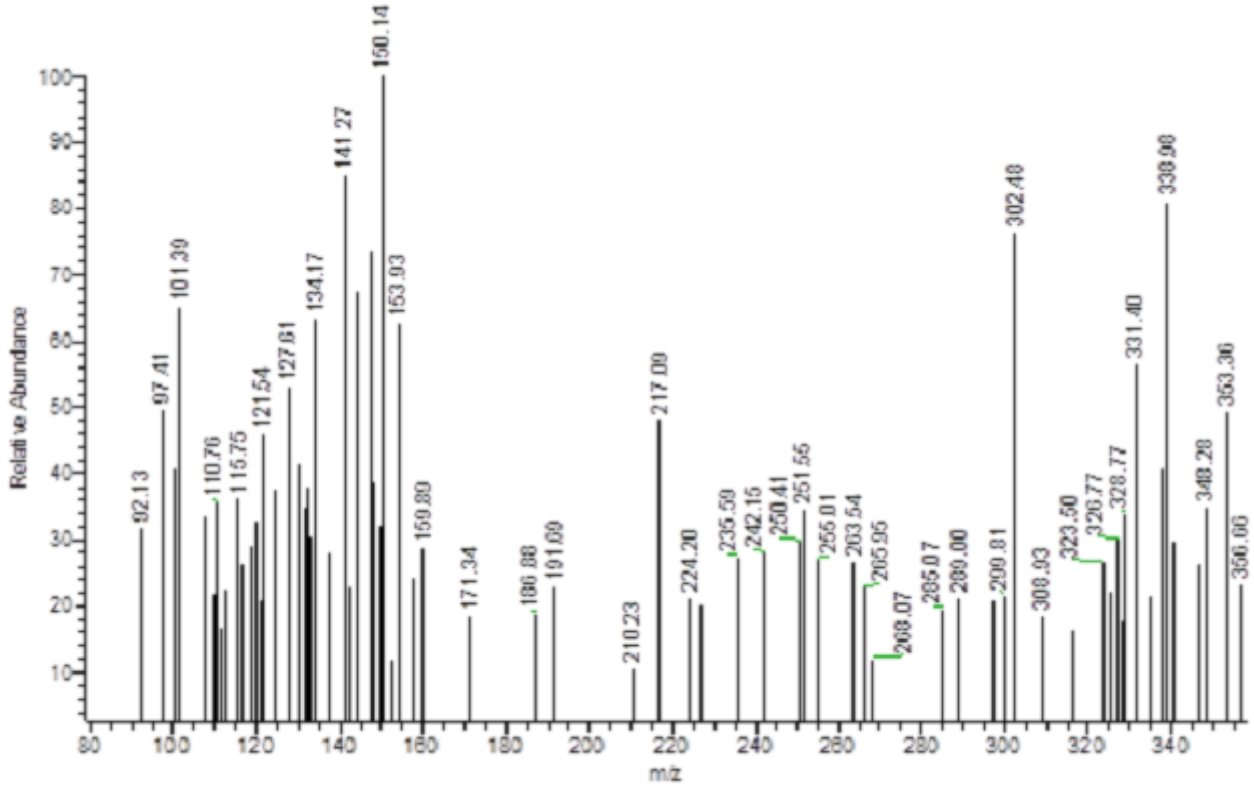


Figure 3

Mass spectrum of the [MoO2(DTO)(HPY)] complex.

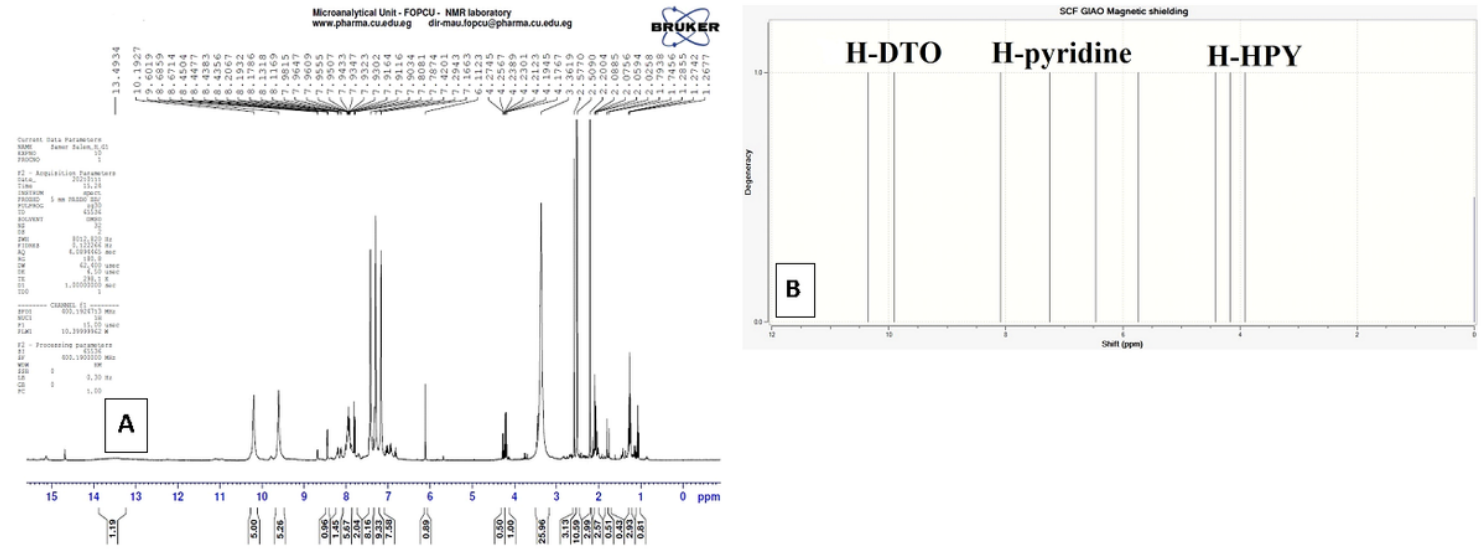
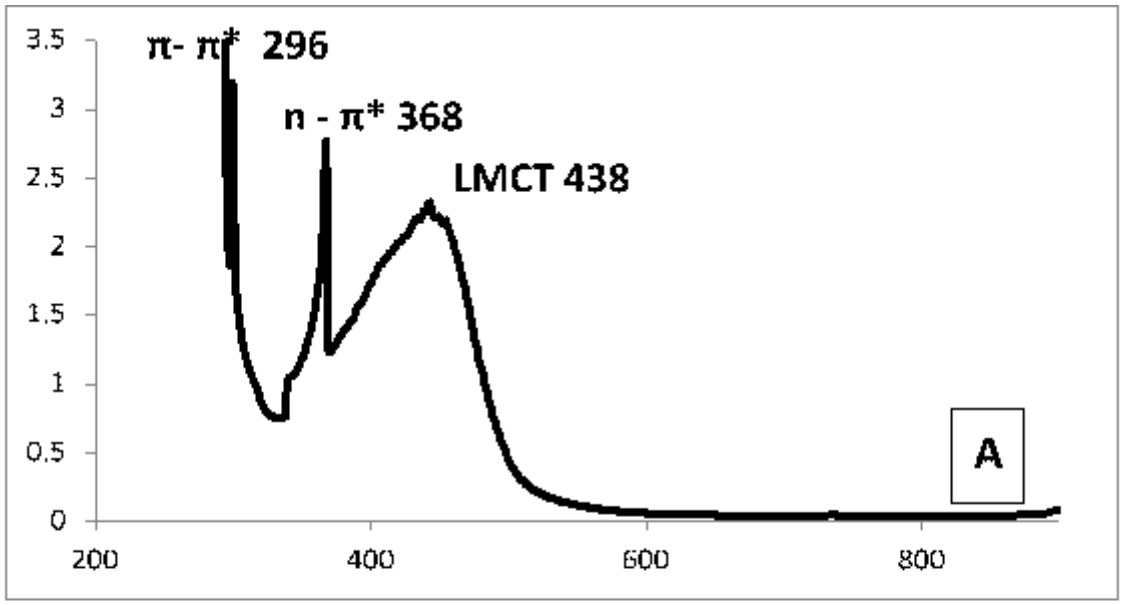


Figure 4

The experimental (a) and calculated (b) 1H-NMR spectra of the [MoO2(DTO)(HPY)] complex.



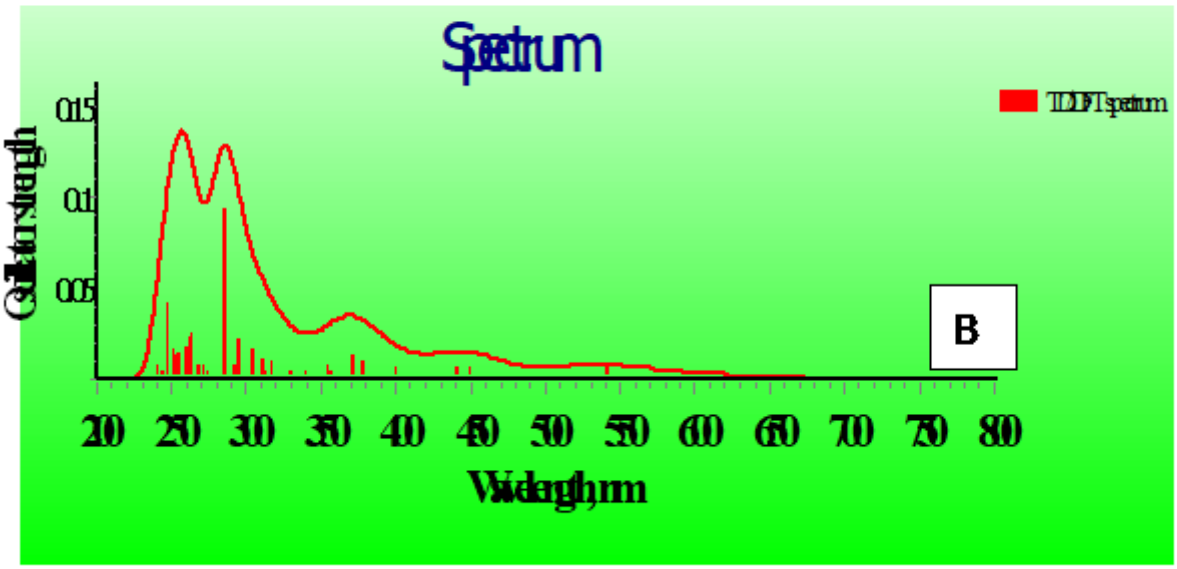


Figure 5

The experimental (a) and calculated (b) UV-Vis. spectra of the [MoO2(DTO)(HPY)] complex.

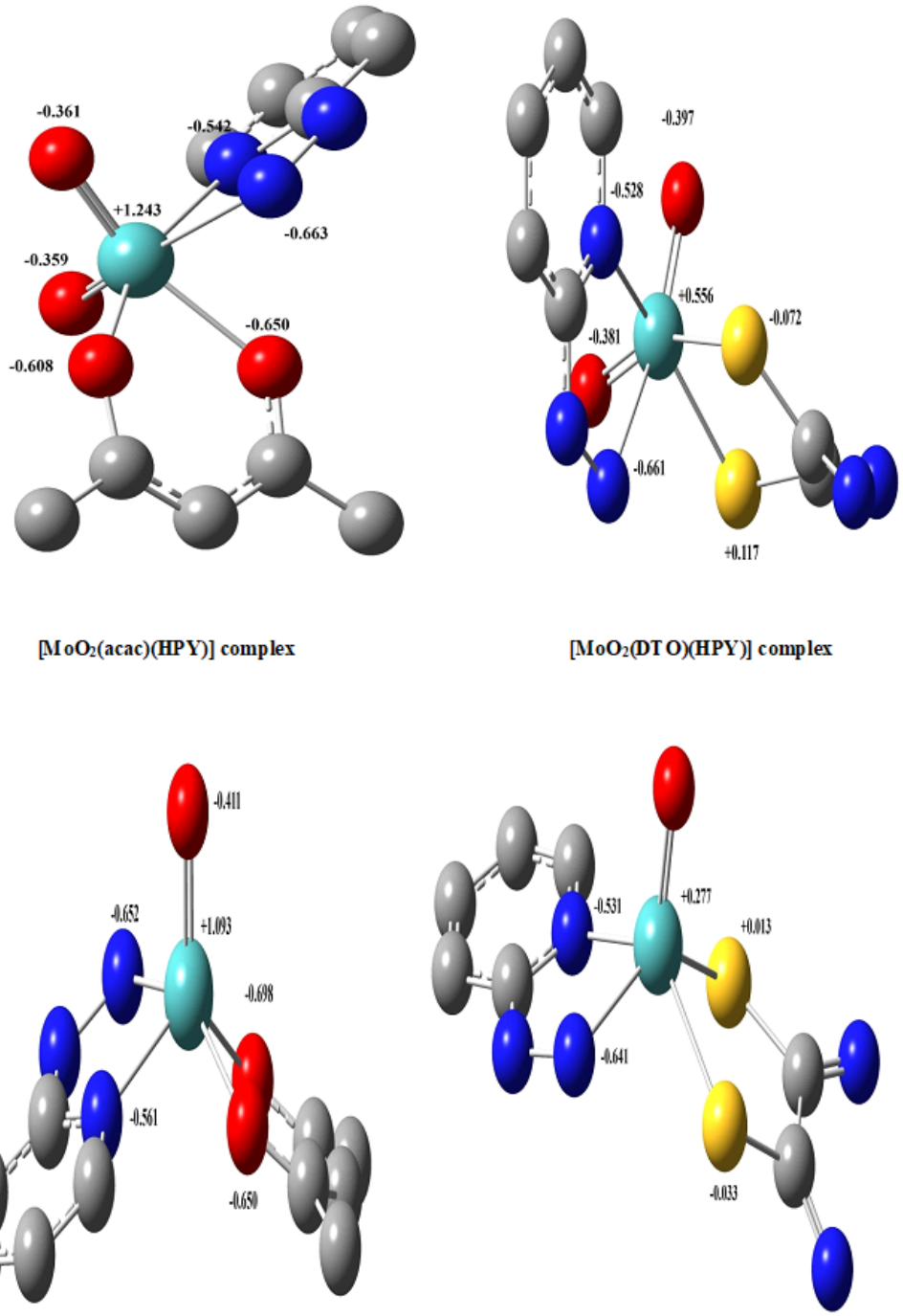


Figure 6

The proposed structures and NBO charges of the dioxomolybdenum(VI) and oxomolybdenum(IV) complexes.

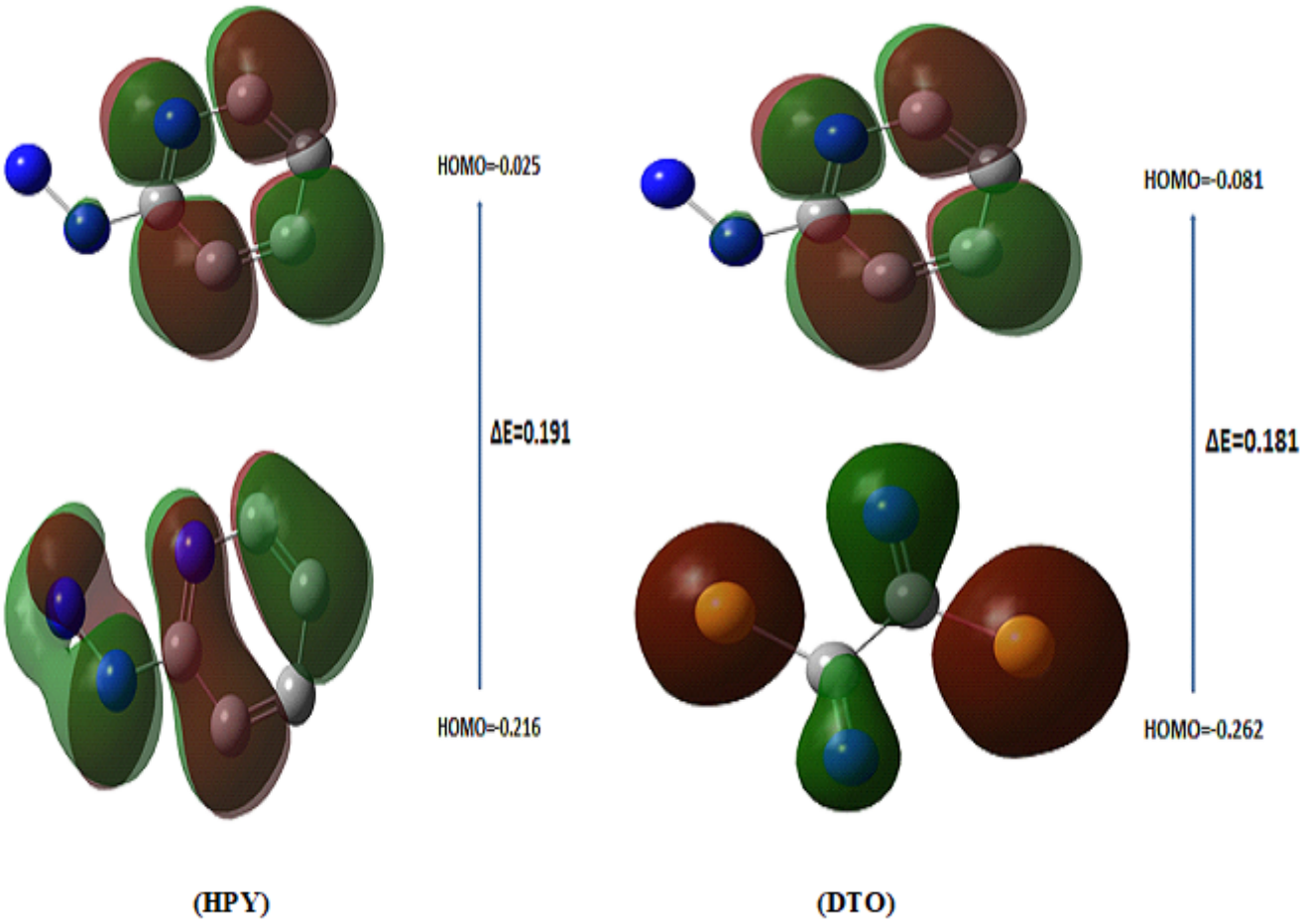


Figure 7

The HOMO and LUMO molecular orbitals and energy gap of the (HPY) and (DTO) ligands.

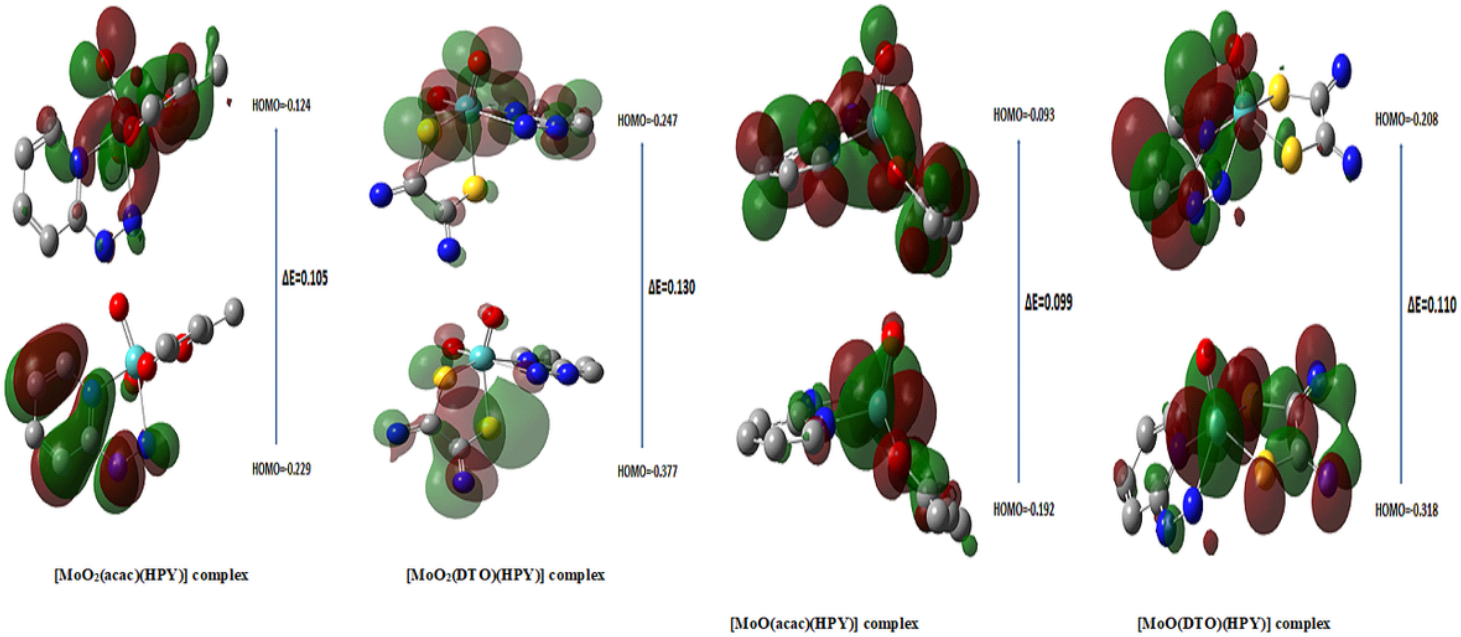


Figure 8

The HOMO and LUMO molecular orbitals and energy gap of the Mo(VI) and Mo(IV) complexes.

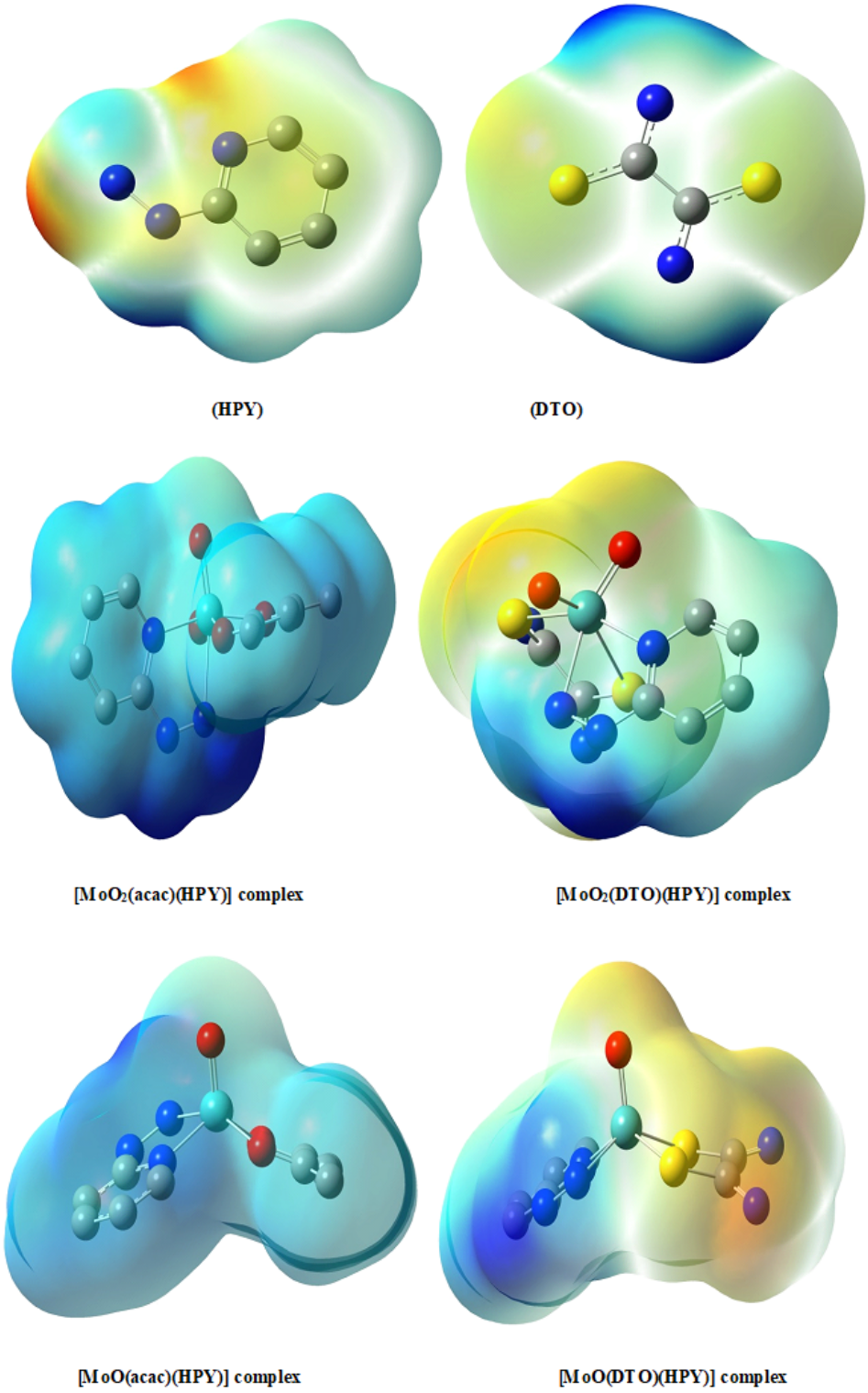


Figure 9

The MEP (Molecular Electrostatic Potential) of the ligands and Mo(VI) and Mo(IV) complexes.

Supplementary Files

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- SupplementaryData.docx