Alajrawy O.I et al., Mong. J. Chem., 26(53), 2025, 29-39
https://doi.org/10.5564/mjc.v26i53.3732

Mongolian Journal of Chemistry
www.mongoliajol.info/index.php/MJC

Cytotoxic evaluations, spectral characterizations and DFT theoretical calculations of new dioxidovanadium(V) complexes

Othman I. Alajrawy[1], Huda A. Hadi[2], Roaa S. Awad Al-Luhaibi[2], Sarah S. Sabar[3]

[1]Department of Biology, College of Education, University of Fallujah, Fallujah, Iraq
[2]Ministry of Education, The General Directorate of Education, Ramadi, Anbar, Iraq
[3]Ministry of Health, The General Directorate, Tarmia Hospital, Baghdad, Iraq

Corresponding author: othman_ibraheem2000@yahoo.com; ORCID: https://orcid.org/0000-0002-3509-6060

Received: 11 November 2024; revised: 10 May 2025; accepted: 12 May 2025

ABSTRACT

Two dioxidovanadium(V) complexes have been prepared with dinitrogen atoms donor (*o*-phenylenediamine (OPD) and dithiooxamide (DTO)) ligands. The cytotoxicity studies of the prepared complexes against the L20B cell line displays that they have moderate activity against the L20B cell line. Then, the complexes were characterized by different spectral techniques such as FT-IR, UV-Vis, mass, ^{1}H-NMR spectroscopy, magnetic susceptibility, and molar conductivity. Finally, the spectral data were compared with the data obtained by the DFT theoretical calculations. The obtained spectroscopic data confirmed that the two ligands are coordinated from the two amine groups and in *cis*-conformation with the two oxygen atoms. The experimental and theoretical calculations show that the two complexes are mononuclear with proposed distorted octahedral structures. The complexes are very stable, the electronic energies are (-773.10 and -907.56 a.u.), the HOMO orbitals energies are (-0.386 and -0.504 a.u.), and the LUMO orbitals energies are (-0.213 and -0.421 a.u.) for the complexes, respectively. The bond angles around the vanadium(V) atoms are in the range (69.44-91.36 Å), and the dihedral angles are in the range (111.22-161.94°). Calculations explained that the complexes are polarized (3.39-5.28) more than free ligands (0.002-3.00). The electronic transition in the complex (**2**) (0.083) is less than for the complex (**1**) (0.173). After that, the findings showed that the two complexes have the feature of solubility in water rather than other anticancer compounds that lack such a property; even though using different metal complexes like Platine complexes, *etc*. Thus, this feature will help researchers use such complexes in future studies.

Keywords: dioxidovanadium (V) complexes, *o*-phenylenediamine, dithiooxamide, L20B cell line, theoretical calculations, cytotoxicity

INTRODUCTION

Metal ions have a tendency to bind to biomolecules, as a result of this feature; metal ions perform wide tasks and play crucial roles in organisms. Vanadium metal is widely distributed and has many oxidation states [1]. The vanadium advantages are less moisture sensitive, its compounds are cheap and used particularly in catalytic oxidations due to its properties such as easily inter-convertible vanadium oxidation states, and the high affinity of the vanadium(V) centers of oxygen-donor atom. The oxidations may be easily achieved by green oxidants such as H_2O_2, O_2 (oxidovanadium(V) and dioxidovanadium(V) complexes which can be easily transformed to oxidoperoxidovnadium(V) complexes and considered as intermediates in many of the catalytic reactions [2].

Accordingly, one of the important oxidation states of the vanadium ion in biological systems is (V). This oxidation state is regarded as a stable state and can be changed to the oxidation state (IV) easily. The complexes of vanadium(V) are very significant in many applications such as anticancer drugs, insulin-enhancing, and catalysts in many reactions [3]. The use of oxidovanadium complexes in many fields encourages researchers to prepare more and more of these complexes. The most important applications of oxidovanadium complexes are oxidation and reactions with oxo transfer, and potential medicinal chemistry [4]. The limiting of further clinical applications of inorganic vanadium compounds is important because of the low oral bioavailability when vanadium binds to organic ligands [5].

Vanadium(V) has a very well-defined geometry (octahedral structures) for its inner coordination with different mono and multi-dentate ligands [6-10]. The significance of the medicinal applications of vanadium complexes has attracted attention in material and organic syntheses, therapeutic, medicinal immense, anticancer, and anti-diabetes [11-16]. Nitrogen-containing compounds are critical in the preparation of complexes containing various ions that are used in a variety of fields. Diamines are organic compounds with functional groups in their structure of two nitrogen groups attached on the edges of the alkyl or aryl group. Diamine ligands have been used as primary steric ligands for many types of metal complexes and their complexes are most stable kinetically and thermodynamically. Dithiooxamide ligand and its analogs are used in many syntheses of complexes especially with that complexes have been used in the industry of chemotherapeutic therapy. This importance came from the containing of two different donor atoms one soft (sulfur) and the other hard (nitrogen) with thioamide moiety; this property gives dithiooxamide biological importance [16].

Dithiooxamide has been used as a reagent to detect and determine many metals, such as Pd(II) and Pt(II). It has a planar structure in an S-trans conformation. In solution, the molecule is assumed to convert to a cis-configuration and have properties as a complexing agent. The rotation around the C-C bond in the dithiooxamide allows the preparation of the complexes [17]. The main aim of this work is the study of new dioxidovanadium(V) complexes, preparing, and characterizing, the cytotoxicity and the DFT calculations with two dinitrogen donor ligands the *o*-phenylenediamine (OPD) and the dithiooxamide (DTO). These complexes have a vanadium ion that binding the organic ligands with low molecular weight to be water-soluble compounds [9]. The structures and charge distribution of the (OPD) and the (DTO) ligands are depicted in Fig. 1.

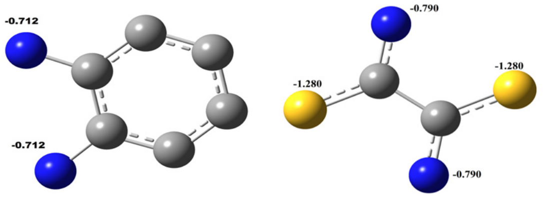


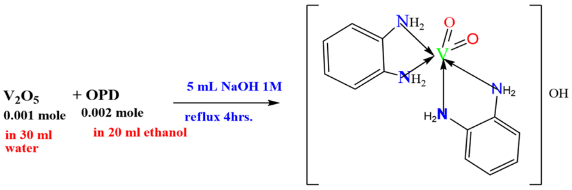
Fig. 1. Optimized structures and atomic charges (NBO) of the (OPD) and the (DTO) ligands by DFT/B3LYP/6-31G (d, P) basis set

EXPERIMENTAL

Materials and Methods: Chemicals used in this study were in very high purity, *o*-phenylenediamine (OPD) (97%), and dithiooxamide (DTO) (98%) were purchased from Sigma-Aldrich (Amman, Jordan). Vanadium pentoxide (V_2O_5) was purchased from Fluka (Cairo, Egypt). All solvents were of analytical grade.

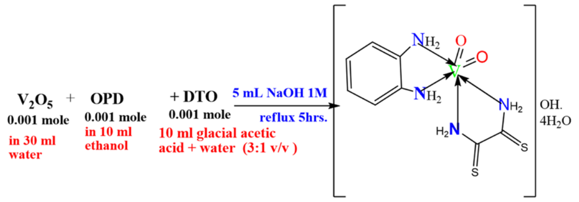
Methods: Infrared measurements of the ligands, and the dioxidovanadium complexes, as KBr pellets, were carried out using a Shimadzu (FT-IR)-8400S spectrophotometer in the range (400-4000 cm^{-1}), mass spectrometry measurements were carried out using GCMS-QP1000EX Shimadzu and the ^{1}H-NMR spectrometry was recorded using ultra shield 300 MHz Bruker. The UV-Vis. Spectra were recorded in a 1.0 cm path length quartz cell by using UV-Vis. Spectrophotometer type Shimadzu UV-1800 at 10^{-3} M concentration in DMSO as solvent. Conductivity measurements were carried out by the use of Philips PW digital meters conductivity in DMSO at 10^{-3} M. The optimized structures of the ligands and the complexes were carried out by the use of the [Gaussian 09 W] software program in the B3LYP/6-31G(d, P) for (C, H, N and O) atoms and LanL2DZ for the vanadium atom basis set.

Preparation of the [$VO_2(OPD)_2$]OH complex (1): The (0.182 g, 1.0 mmol) of V_2O_5 was dissolved in 30 mL of distilled water and then 5 mL of NH_4OH solution (1M) concentration was added slightly until the color of the solution turned yellow. The solution was filtered off and mixed with (0.216 g, 2.0 mmol) of the (OPD) ligand dissolved in (20 mL of ethanol), then refluxed for 4 hrs. The deep red precipitate was filtered off, washed with warm water, ethanol, and diethyl ether, and dried in a vacuum dissector for 24 hrs. [10]. The obtained deep red precipitate complex (1) (yield: 88%), Scheme 1. m.p >300 C°. *(C.H.N. Analysis. Exp.(Cal.))*= Chemical Formula: $C_{12}H_{16}N_4O_2V$: C, 48.17 (47.87); H, 5.39 (5.28); N, 18.72 (18.59).



Scheme 1. The preparation of the [$VO_2(OPD)_2$]OH complex (**1**)

Preparation of the [VO_2(OPD)(DTO)]OH × $4H_2O$ complex (2): An amount of (0.182 g, 1.0 mmol) of V_2O_5 was dissolved in (30 mL of distilled water) and then 5 mL of NH_4OH solution (1 M) concentration was added slightly until the color of the solution turned yellow. The liquid was filtered off and mixed with (0.108 g, 1.0 mmol) of the (OPD) ligand dissolved in (10 mL of ethanol) after refluxing for one hr., then (0.120 g, 1.0 mmol) of the (DTO) ligand dissolved in (10 mL of a mixture of glacial acetic acid and water) (3:1 v/v ratio) added to the solution and refluxed for 4 hrs. The deep red precipitate was filtered off, washed with warm water, ethanol, and diethyl ether, and dried in a vacuum dissector for 24 hrs [10]. The obtained deep red precipitate for complex (**2**) (yield: 54%), Scheme 2. m.p >300 C°. *(C.H.N. Analysis (Exp. (Cal.))*= Chemical Formula: $C_8H_{12}N_4O_2S_2V$: C, 30.87(30.77); H, 3.89(3.78); N, 18.00(17.79).



Scheme 2. The preparation of the $[VO_2(OPD)(DTO)]OH\times4H_2O$ complex (2)

In vitro cytotoxic activity: The anticancer efficacy of the complexes (1-2) against the L20B cell line was calculated. The colorimetric cell viability MTT assay was used as described by [18]. Firstly, an amount of 100 μL/ well of L20B cells (106 cells/ mL) were refined in a 96-well tissue culture plate. Then, different concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 μg/mL) of the complex solutions were prepared by dissolving in DMSO. After that a proportion of, 100 μL of various concentrations was added to each well and incubated at 37 ºC for 24 hrs. After the incubation, 10 μL of MTT solution (5 mg/ mL) was added to each well and incubated at 37 ºC for 4 hrs. Finally, 50 μL of DMSO (dimethyl sulfoxide) was added to each well and incubated for 10 min. L20B cells were cultured in a complete medium without a complex solution as a control. The absorbance was measured for each well at 620 nm using an ELISA reader. The live cells, percentage of viability, and inhibition ratio were calculated according to the formula.

The experiment was done with three trails, and the mean of these trails gave the finding are shown.

$$GI\% = ((OD_{\text{of control wells}} - OD_{\text{of test wells}}))/(OD_{\text{of control wells}}) \times 100$$

Where, GI - Growth inhibition, and OD - Optical density

RESULTS AND DISCUSSION

The physical and analytical data of the complexes were given in Table 1. The complexes are air-stable and exhibit very good solubility in water, 1,4-dioxane, and acetone. The molar conductance in DMSO as solvent was found to be (52.00 and 53.50 Ohm^{-1} cm^2 mol^{-1}) for the complexes (1-2); respectively, indicating that the complexes are electrolytes. This is the fact that conductivity values for electrolytes are more than 50 ohm^{-1} cm^2 mol^{-1} in DMSO solution [19]. The experimental and calculated FT-IR peaks of the dioxidovanadium complexes are depicted in Table 2. The mass spectral data of the dioxidovanadium(V) complexes are listed in Table 3. The ^{1}H-NMR spectral data for the (OPD), (DTO) ligands, and dioxidovanadium(V) complexes in DMSO-d^6 are tabulated in Table 4. The (OPD) ligand showed signals appearing at the range (δ= 6.504-6.382, 4H) and (δ =4.36, 4H) ppm are attributed to a phenyl ring and NH_2 groups proton; respectively. The (DTO) ligand exhibited signals at δ = 9.5 and 10.5 ppm are attributed to NH_2 and NH protons; respectively. The electronic spectral data of the DMSO solutions for the dioxidovanadium(V) complexes were recorded in the 200-1100 nm range and are given in Table 1.

Table 1. Some physical and analytical properties of the dioxidovanadium (V) complexes.

Complex	Molar mass	Color	m.p	Mass spec. m/z(P$^+$)	Λ_m Ohm^{-1} cm^2 mol^{-1}	UV-Vis absorption peaks (nm)	
$[VO_2(OPD)_2]OH$ (**1**)	317.07	Deep red	>300	316.92	52.00	274 431 501-572	Intra ligand ($\pi\rightarrow\pi^*$) Intra ligand ($n\rightarrow\pi^*$) LMCT
$[VO_2(OPD)(DTO)]OH \times 4H_2O$ (**2**)	401.27	Deep red	>300	401.57	53.50	290 340 405-477	Intra ligand ($\pi\rightarrow\pi^*$) Intra ligand ($n\rightarrow\pi^*$) LMCT

FT-IR spectra: The peaks of the complexes were compared with that of the free ligands, to monitor the changes in the vibration frequencies of the coordination sites Table 2. The spectrum of the free (OPD) ligand Fig. **S1** (a, b) showed bands at (3383, and 3364 cm^{-1}) which are assigned to the stretching asymmetric and symmetric vibrations of the NH_2 groups; respectively. The deformation bands of the amine groups appeared at (1115 cm^{-1}) assigned for the (ρtNH$_2$), at (1057 cm^{-1}) assigned for the (ρwNH$_2$), and at (925 cm^{-1}) assigned for the (ρrNH$_2$). In the spectrum of the (DTO) ligand Fig. **S2** (a, b) the bands at (3294, and 3206 cm^{-1}), which are assigned to the asymmetric and the symmetric vibration of the NH_2 groups, respectively.

The N-H of secondary amine appear at 3138 cm^{-1}, the presence of three N-H bands of the (DTO) suggest that thione-thiol tautomerism may be taken place [20]. The first thioamide band appeared at (1589 cm^{-1}) in the free (DTO) ligand, the second band was found at (1431 cm^{-1}), and the third band was found at (1197 cm^{-1}), which has a contribution from N-C-S stretching vibration. The fourth thioamide band is due to C=S found at (837 cm^{-1}). In the spectra of the complexes, the stretching assigned to the asymmetric and the symmetric vibrations of the NH_2 bands are shifted to lower frequencies at (3183, and 3043 cm^{-1}) for the complex (**1**) and at (3418, and 3260 cm^{-1}) for the complex (**2**); respectively. The deformation vibrations of the NH_2 groups also are shifted and found at (1231-1134 cm^{-1}), (1134-1022 cm^{-1}), and (833-829 cm^{-1}) for (ρtNH$_2$), (ρwNH$_2$) and (ρrNH$_2$); respectively for the complexes (1-2) [21]. In the spectrum of the complex (**2**), the first thioamide band appeared in the (DTO) ligand at (1331 cm^{-1}), the second band was split into two bands of higher and lower frequencies at (1260 cm^{-1}), and the third band at (1090 cm^{-1}), was also split into two bands at higher and lower frequencies.

Table 2. The experimental and calculated FT-IR peaks in cm^{-1} for the ligands, and the dioxovanadium(V) complexes.

Compound	Exp.	Calc.	Assignment
o-phenylenediamine (OPD)	3453, 3364	3780, 3667	ν(NH_2)
	1153	1166	ρtNH_2
	1057	1089	ρwNH_2
	925	1005	ρrNH_2
dithiooxamide (DTO)	3291, 3210	3690, 3480	ν(NH_2)
	1196	1232	ρtNH_2
	1042	943	ρwNH_2
	837	865	ρrNH_2
	3341	3477	ν(N-H)sec
	1385	1319	1 thioamide
	1431	1415	2 thioamide
	1510	1598	3 thioamide
$[VO_2(OPD)_2]OH$ (**1**)	3341, 3183	3539, 3444	ν(NH_2)
	1231	1208	ρtNH_2
	1134	1154	ρwNH_2
	829	862	ρrNH_2
	914	102	ν(O=V=O)
	501	601	ν(M-N)
$[VO_2(OPD)(DTO)]OH \times 4H_2O$ (**2**)	3418, 3379	3561,3509	ν(NH_2)
	1134	1135	ρtNH_2
	1115	1106	ρwNH_2
	822	894	ρrNH_2
	972	1056	ν(O=V=O)
	501	532	ν(M-N)
	1331	1325	1 thioamide
	1260	1279	2 thioamide
	1090	1104	3 thioamide
	837	918	4 thioamide

The fourth thioamide band is due to C=S didn't shift in the complex (**2**). This can be attributed to the (DTO) ligand being coordinated from the two amine groups and the C=S doesn't take part in the complexation, this type of coordination is because the hardness property of the nitrogen and vanadium metal depended on the Pearson basis (Hard and soft theory), also the spectrum of the complex (**2**) showed a broad band at (3510 cm^{-1}) assigned to the uncoordinated water. Finally, the spectra of the complexes also showed new additional bands at (914-945 cm^{-1}) assigned to the stretching of ν(O=V=O) in *cis*-geometry [21-22]. The bands at (474-563 cm^{-1}) are assigned to the stretching of the V–N [23]. The experimental FT-IR data of the prepared dioxidovanadium complexes are compared and agree perfectly with the calculated data obtained from the DFT calculation. There were no negative wavenumbers in the calculated data, this is evidence for the correct optimized proposed structures for the complexes. The experimental and calculated spectra of the complexes are explained in Figs. 2 and 3.

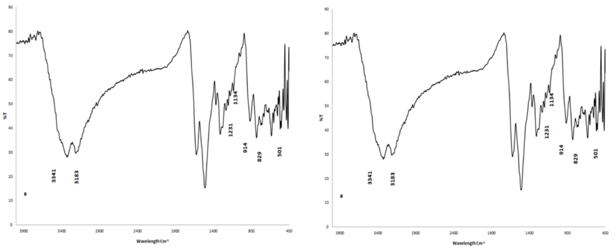


Fig. 2. Experimental (a) and calculated (b) FT-IR spectra of the $[VO_2(OPD)_2]OH$ complex (**1**)

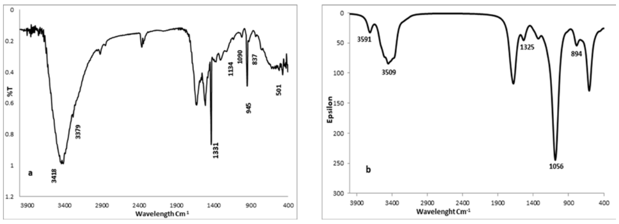
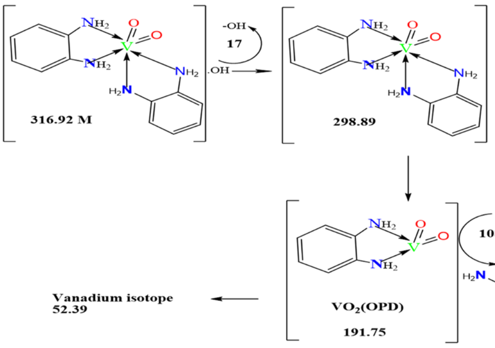


Fig. 3. Experimental (a) and calculated (b) FT-IR spectra of the $[VO_2(OPD)(DTO)]OH \times 4H_2O$ complex (**2**)

Mass spectral analysis:

The spectrum of the $[VO_2(OPD)_2]OH$ complex (**1**) (molecular weight 316.20) showed molecular ion peaks at *m/z*=(316.92) assigned for M, a peak at *m/z*=298.89 assigned for ($VO_2(OPD)_2$), a peak at *m/z*= 282.08 assigned for ($VO_2(OPD)_2$-O), a peak at *m/z*= 235.92 assigned for (($VO_2(OPD)_2$ - (O+2NH_2)), a peak at *m/z*=210.90 assigned for (VO_2OPD), a peak at *m/z*=108.89 assigned for (OPD) ligand, and a peak at 52.39 for the vanadium isotope. The spectrum of the $[VO_2(OPD)(DTO)]OH \times 4H_2O$ complex (**2**) (molecular weight 401.27) showed molecular ion peaks at *m/z*=401.57 assigned for M, a peak at *m/z*=384.99 assigned for $[VO_2(OPD)(DTO)]OH \times 3H_2O$, a peak at *m/z*-366.76 assigned for $[VO_2(OPD)(DTO)]OH \times 2H_2O$, a peak at *m/z*=348.07 assigned for $[VO_2(OPD)(DTO)]OH \times H_2O$, a peak at *m/z*=329.04 $[VO_2(OPD)(DTO)]OH$, a peak at *m/z*=312.08 assigned for $[VO_2(OPD)(DTO)]$, a peak at *m/z*=252.93 assigned for $[VO_2(OPD)(CHSNH_2)]$, a peak at *m/z*= 206.86 assigned for $[VO_2(OPD)]$, a peak at *m/z*=121.92 assigned for the (DTO) ligand, and a peak at 52.39 for the vanadium isotope [24], Scheme 3. The mass spectra analyses of the complexes is presented in Figs. 6 and 7 and Table 3.



Scheme 3. The proposed mass of the spectral analysis of the fragmentation of the $[VO_2(OPD)_2]OH$ complex (**1**)

Table 3. The mass fragments data of the dioxidovanadium (V) complexes

Complex	Molar mass	Important mass fragmentations (m/z) values
$[VO_2(OPD)_2]OH$ (1)	316.92	316.92 (M), 298.89 ($VO_2(OPD)_2$), 282.08 (($VO_2(OPD)_2$-O)), 235.92 (($VO_2(OPD)_2$-O)+($2NH_2$)), 210.90 (VO_2OPD), 108.89, (OPD), 52.39 for vanadium isotope
$[VO_2(OPD)(DTO)]OH\times4H_2O$(2)	401.27	401.57 (M), 384.99 $[VO_2(OPD)(DTO)]OH\times3H_2O$, 366.76 $[VO_2(OPD)(DTO)]OH\times2H_2O$, 348.07 $[VO_2(OPD)(DTO)]OH\times H_2O$, 329.04 $[VO_2(OPD)(DTO)]OH$, 312.08 $[VO_2(OPD)(DTO)]$, 252.93 $[VO_2(OPD)(CHSNH_2)]$, 206.86 $[VO_2(OPD)]$, 121.92 (DTO), 52.39 vanadium isotope

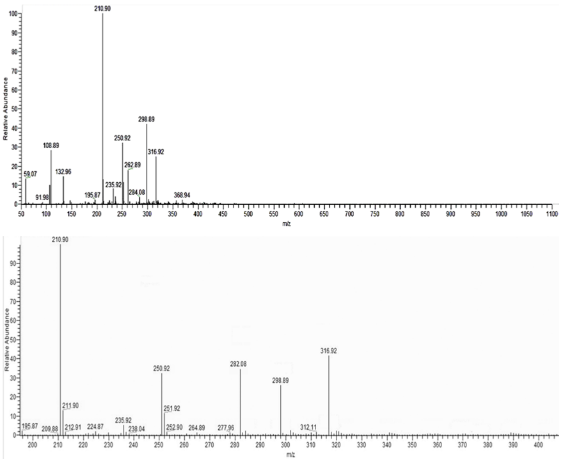


Fig. 4. The mass spectrum of the $[VO_2(OPD)_2]OH$ complex (**1**)

^{1}H-NMR spectra: The ^{1}H-NMR spectra of the dioxidovanadium(V) complexes are compared with that of the free ligands and with the calculated spectra obtained from the DFT calculations Table 4. The ^{1}H-NMR spectrum of the complex (**1**) showed the signals in the range (δ=6.77-7.539, 4H) ppm are assigned to phenyl ring protons. The characteristic signal at (3.34, 4H) ppm is assigned to NH_2 protons, which are shifted downfield from those of the free (OPD) ligand. This indicates the (OPD) ligand coordinates with the vanadium(V) ion by the nitrogen atoms of the NH_2 groups.

Table 4. The ^{1}H-NMR data for the ligands and the dioxido-vanadium(V) complexes.

Compound	Found.	Calc.	Assignment
o-phenylenediamine (OPD)	4.36 (4H)	2.05-2.69	NH_2 protons
	6.50-6.382 (4H)	6.20-6.45	phenyl ring protons
dithiooxamide (DTO)	10.21 (2H)	6.93	NH_2 protons
	9.73 (H)	9.13	NH proton
$[VO_2(OPD)_2]OH$ (**1**)	3.34 (8H)	3.55-3.83	NH_2 protons
	5.77- 7.89 (8H)	6.50-7.32	phenyl ring protons
$[VO_2(OPD)(DTO)]OH\times4H_2O$ (**2**)	2.50 (4H)	3.68-3.94	NH_2 protons (OPD)
	3.50 (4H)	4.50-5.13	NH_2 protons (DTO)
	6.60-8.48 (4H)	6.78-7.48	phenyl ring protons

The ^{1}H-NMR spectrum of the complex (**2**) showed the signals at (δ =2.50) and (δ =3.50) ppm are assigned to NH_2 protons, which are shifted downfield. This indicates the (DTO) ligand coordinates with the vanadium(V) ion by the nitrogen atoms of the NH_2 groups. The spectrum also showed a chemical shift of phenyl ring protons at the range (δ =6.60-8.49, 4H) ppm and there is no signal to the SH group which confirmed that the sulfur atoms are not the binding sites with the vanadium(V) ion [25]. The calculated ^{1}H-NMR data by use of the DFT/B3LYP/6-31G(d, p) for the free ligands and the DFT/B3LYP/Lan2DZ for the dioxidovanadium complexes basis set are compared with the experimental data and it was in a good agreement; Figs. 5 and 6 show the experimental and the calculated ^{1}H-NMR spectra of the dioxidovanadium complexes.

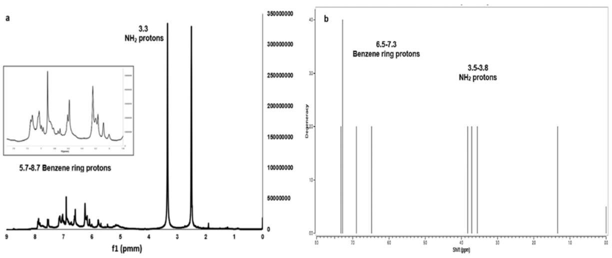


Fig. 5. The experimental (a) and calculated (b) ^{1}H-NMR spectra of the $[VO_2(OPD)_2]OH$ complex (**1**)

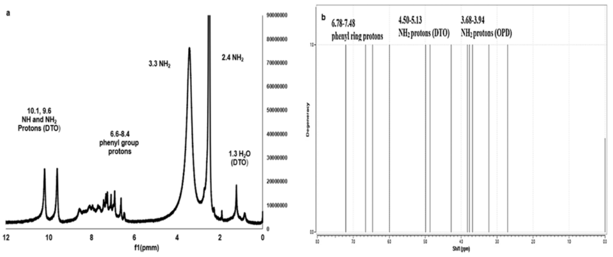


Fig. 6. The experimental (a) and calculated (b) ^{1}H-NMR spectra of the

Electronic spectra: The spectra of the two complexes showed absorption bands at the range (274-290 nm) and (340-431 nm) assigned to the (π→π*) and (n→π*) transitions, respectively. These bands are assigned to the phenyl ring and diamine groups in the (OPD), and the π bond in the (DTO) ligands, respectively. The spectra of the complexes showed shoulders at (405-572 nm), which are assigned to LMCT (ligand-to-metal charge transfer) from the ligands to the empty (*d*) orbital of vanadium(V). Vanadium(V) complexes with (d^0) electronic configuration don't have the (*d-d*) electronic transition which can be explained by the fact that vanadium(V) has an empty (*d*) orbital [26]. The experimental UV-Vis. spectra of the complexes have been compared with the calculated ones obtained by use of the TD-DFT method. The main excitation electronic transition and the oscillator strength (f) of the complexes are given in Table 5.

Table 5. Main excitation energies (eV), electronic transition configurations and oscillator strengths (f) of the dioxidovanadium(V) complexes.

Complex	Calculated nm (cm^{-1})	Exp. nm	*f*	Composition (>10%)
$[VO_2(OPD)_2]OH$ (**1**)	217(46022)	274	0.016	HOMO-6→LUMO+2 (40%) HOMO-7→LUMO+2 (38%)
	242(41207)	431	0.023	HOMO-3→LUMO+3 (56%), HOMO-7→LUMO+2 (19%)
	294(33933)	501-572	0.012	HOMO-4→LUMO (60%), HOMO-5→LUMO (32%)
$[VO_2(OPD)(DTO)]OH \times 4H_2O$ (**2**)	298 (33520)	290	0.023	HOMO→LUMO+7 (46%), HOMO-8→LUMO+1 (33%), HOMO-1→LUMO+4 (25%)
	339 (29442)	340	0.075	HOMO→LUMO+4 (39%), HOMO-6→LUMO+1 (37%), HOMO-7→LUMO+1 (33%)
	459 (21746)	405-477	0.011	HOMO→LUMO+3 (70%)

The calculated transitions agree perfectly with the experimental values. The experimental and calculated UV-Vis spectra of the complexes and the electronic transitions are presented in Figs. 7 and 8.

Magnetic susceptibility: Measurements of the magnetic susceptibility of the dioxidovanadium complexes have been done to ensure the V(V) oxidation state. The complexes are diamagnetic which can be described as the V(V) ion is (d^0) electronic configuration. These data support the suggested octahedral structures for the complexes with electronic distribution ($t2g^0$, eg^0) [27].

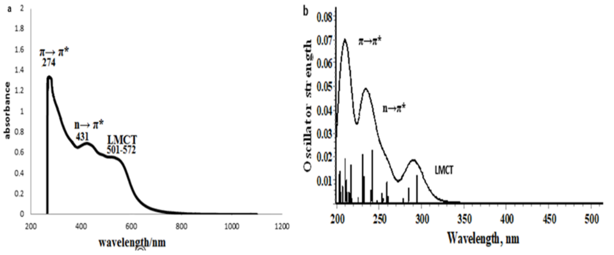


Fig. 7. Experimental (a) and calculated (b) UV-Vis spectra of the $[VO_2(OPD)_2]OH$ complex (**1**)

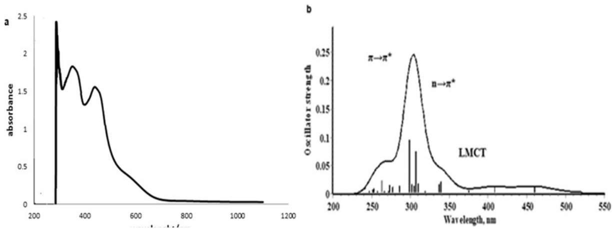
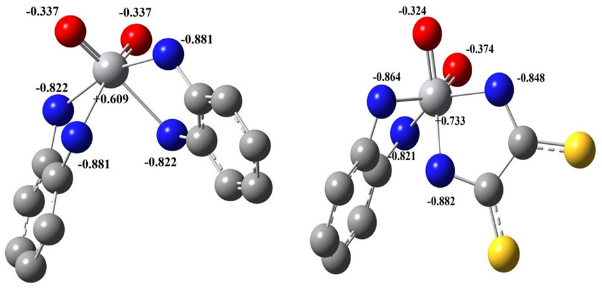


Fig. 8. Experimental (a) and calculated (b) UV-Vis spectra of the $[VO_2(OPD)(DTO)]OH \times 4H2O$ complex (2)

Theoretical studies

The optimized structures are carried out by using the B3LYP/6-31G(d, p) for the ligands and LanL2DZ for the dioxidovanadium(V) complexes basis set; respectively [28, 29]. The complexes' structures are given in Fig. 9 with natural bond order (NBO) charges of atoms.



$[VO_2(OPD)_2]OH$ complex (**1**) $[VO_2(OPD)(DTO)]OH \times 4H_2O$ complex (**2**)

Fig. 9. The proposed structures of the dioxidovanadium(V) complexes and atoms natural bond order (NBO) charges. Vanadium (pale gray), carbon (deep gray), nitrogen (blue), oxygen (red), sulfur (yellow). The hydrogen atoms were omitted foe simplicity.

Selected bond angles and bond lengths are given in Table 6. The angles between vanadium(V) atoms and the surrounded nitrogen atoms of the ligands varied from (69.44° to 91.36°) and the dihedral angles ranged from (111.22° to 161.94°), which suggests the distorted octahedral geometry for the two complexes [30]. The (N-V-N) bond angles (74.55°-74.56°) in complex (**1**) and (76.34°-78.92°) in complex (**2**) are deviated from the ideal angle (90°) for the perfect octahedral structure, this is an evidence for the suggested distortion structure of the complexes. The bond lengths between the vanadium(V) atom and the oxygen atoms are in the range (1.61 Å) in complex (**1**) and in the range (1.59-1.76 Å) in complex (**2**), this is because the high affinity of the vanadium(V) atom to bind to the oxygen atom. The vanadium atoms in the complexes are out of the plan geometries (vanadium atoms are closer to the oxygen atoms). The V-O and V-N bond lengths are compared with the reported dioxidovanadium(V) complexes, and the values found are consistent with the values reported [31].

Table 6. The geometric parameters (bonds lengths and bond angles) of the dioxidovanadium complexes using DFT/B3LYP/Lan2DZ basis set.

$[VO_2(OPD)_2]OH$ (1)	**Bond Lengths Å**	**Bond Angles °**	
V(17)-N(15)	2.34	N(15)-V(17)- N(16)	74.56
V(17)-N(16)	2.15	N(7)-V(17)-N(8)	74.55
V(17)-N(7)	2.34	N(15)-V(17)-N(7)	78.70
V(17)-N(8)	2.15	N(15)-V(17)-N(8)	91.36
V(17)=O(18)	1.61	N(8)-V(17)-N(16)	161.94
V(17)=O(19)	1.61	N(15)-V(17)=O(18)	160.72
		N(7)-V(17)=O(19)	160.73
		O(18)=V(17)=O(19)	108.52
$[VO_2(OPD)(DTO)]OH \times 4H_2O$ (2)			
V(9)-N(15)	2.19	N(14)-V(9)- N(15)	76.34
V(9)-N(14)	2.12	N(13)-V(9)-N(12)	69.44
V(9)-N(13)	2.19	O(11)=V(9)=O(10)	138.17
V(9)-N(12)	2.24	N(14)-V(9)-N(13)	78.92
V(9)=O(10)	1.59	N(13)-V(9)=O(10)	96.46
V(9)=O(11)	1.76	N(13)-V(9)-N(15)	152.81
N(12)-C(1) (DTO)	1.47	N(14)-V(9)=O(10)	111.22
N(13)-C(2) (DTO)	1.50	N(15)-V(9)-N(12)	136.66
		N(12)-V(9)-N(14)	146.66

The calculated V-N bond length values in the range (2.15-2.34 Å) are consistent with the range of vanadate complexes [31].

Atomic charges explain the donor and the acceptor atoms in the molecules [32]. Higher charge densities are on nitrogen and sulfur atoms of the ligands, this explains the expected donor properties of nitrogen atoms in the two ligands. In the (DTO) ligand despite the sulfur atoms having the higher charges, the nitrogen atoms were the binding sites with the vanadium(V) ion, this is a result of the hard soft theory. Vanadium atoms with their +5 charge in the complexes act as the acceptors of the charge from the ligands. The dioxidovanadium complexes are more polarized than the ligands as indicated by the values of the dipole moments for the complexes (1-2) (5.28 and 3.39 Debye); respectively [8-10]. The electronic energies and the dipole moments of the complexes are tabulated in Table 7. Natural bond orbital calculations for the complexes [32] were performed at the LanL2DZ basis set. (NBO) analysis for the complex (**1**) the electronic configuration of V is: [core] $4s^{0.25}$ $3d^{3.66}$ $4p^{0.34}$ $4d^{0.05}$, 17.978 core electrons, 4.30 valence electrons and 0.050 Rydberg electrons, which gives 22.33 total electrons and +0.609e charge on V atom. The occupancies of V 3d orbitals are d_{xy} 0.737; d_{xz} 0.726; d_{yz} 0.731; $d_{x^2-y^2}$ 0.719 and d_{z^2} 0.754. The 3d-electron populations of 3.667 correspond with the ligand to d_v electron transfer. A similar trend is shown by the complex (**2**) with V 3d populations the electronic configuration of V is [core] $4s^{0.23}$ $3d^{3.68}$ $4p^{0.33}$ $4d^{0.05}$, 17.973 core electrons, 4.06 valence electrons and 0.056 Rydberg electrons, which gives 22.089 total electrons and +0.733e charge on V atom. The occupancies of V 3d orbitals are d_{xy} 0.648; d_{xz} 0.715; d_{yz} 0.788; $d_{x^2-y^2}$ 0.740 and d_{z^2} 0.786. The 3d-electron populations of 3.667 correspond with ligand to d_v electron transfer confirming the ligand-to-metal electron transfer [32]. The electronic energies of the complexes are (-907.56 and -773.10 a.u.); respectively [8-10]. The HOMO and the LUMO orbitals energies of the complexes are given in Table 7. The hardness ($\eta=(I-A)/2$) where *I* - the ionization energy, *A* - the electron affinity, and *(I-A)* - the gap between the HOMO and LUMO energy levels. The η values and ΔE (HOMO-LUMO) are given in Table 7. The transitions are easier in the complexes than the free ligands which are indicated by the ΔE values of the complexes (0.173 and 0.083); respectively compared with the ligands and are easier in complex (**2**) than the complex (**1**) [33]. The complexes are softer (η=(0.086 and 0.041) than the ligands [34]. The negative values of the energies of the HOMO, and the LUMO orbitals in the complexes indicate their stability [33-34].

Table 7. The calculated quantum chemical parameters of the ligands and the dioxidovanadium(V) complexes by DFT/B3LYP/6-31G(d,P) for ligands and LanL2DZ for complexes basis set.

Complex	HOMO a.u	LUMO a.u	η	ΔE a.u	Electronic energy a.u	D.M Debye
o-phenylenediamine (OPD)	-0.164	0.029	0.067	0.135	-342.96	3.00
Dithiooxamide (DTO)	-0.232	-0.108	0.054	0.108	-984.53	0.002
$[VO_2(OPD)_2]OH$ (**1**)	-0.386	-0.213	0.086	0.173	-907.56	5.28
$[VO_2(OPD)(DTO)]OH \times 4H_2O$ (**2**)	-0.504	-0.421	0.041	0.083	-773.10	3.39

The isodensity surface plots of the HOMO and LUMO molecular orbitals for the ligands and the complexes are presented in Figs. 10 and 11. The transition energies of the dioxidovanadium(V) complexes have been calculated from TD-DFT. The density of the electrons in the (OPD), and the (DTO) ligands is localized on the phenyl part and the (N, S) atoms; respectively which may point to a mixed π→π* and n→π* transition [26].

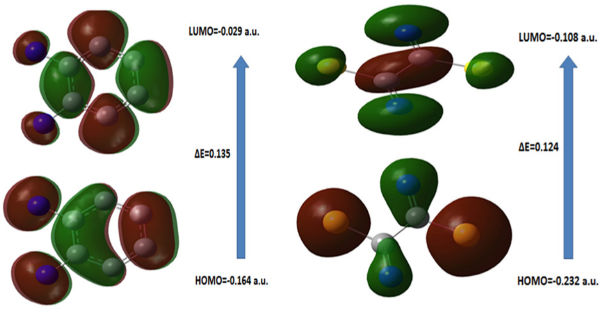


Fig. 10. The isodensity plots for the HOMO and LUMO molecular orbitals for the (OPD) and the (DTO) ligands. The red regions on the nitrogen and sulfur atoms. Carbon (deep gray), nitrogen (blue), and sulfur (yellow). The hydrogen atoms were omitted foe simplicity.

The HOMO state energies (H to H-4), the main characters, the % of contribution of the ligand, the (O), and the V(V) atoms are calculated for the dioxidovanadium(V) complexes and tabulated in Table 8. In the complex (**1**), the % contribution of oxygen to the HOMO states (H to H-4) varies in a wide range from 1% to 44% with the main character being the O(π). The % contribution of oxygen to LUMO states (L to L+4) is much lower (0%-16%). The % contribution of the (OPD) ligand to the HOMO states has been found to vary from 54% to 98% through the OPD(π) as the main character.

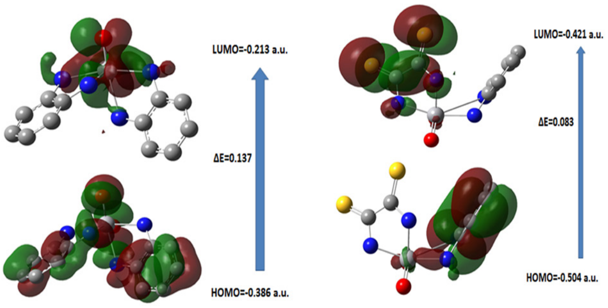


Fig. 11. The isodensity plot of the HOMO and the LUMO molecular orbitals for the dioxidovanadium complexes. Vanadium (pale gray), Carbon (deep gray), Nitrogen (blue), Oxygen (red), and Sulfur (yellow). The hydrogen atoms were omitted foe simplicity.

The (OPD) ligand % of contribution to LUMO states is much higher than its contribution to HOMO states and varies from 14% to 99% through OPD(π^*) as the main character. The electronic transition of the type π-π^* may arise from the HOMO states of high O(π) character to LUMO states with high OPD(π^*) character, Table 8. The V(V) % contribution to the HOMO states varies from 1% to 2%, while the % of contribution of V(V) to the LUMO states varies from 61% to 76% (except L+3 and L+4 in which the contribution of V are 1% and 8%) which points to the possibility of LMCT from the O(π^*) and/or the OPD(π^*) to the V(*d*) empty orbital [8-10]. The % of contribution and the main characters of the V(V), the (O), and the (DTO) ligand to the different HOMO and LUMO states in complex (**2**) are presented in Table 8.

Table 8. Excitation energies (a.u), % contribution from the vanadium ion, the oxygen, the OPD, the DTO, and the main character of some frontier orbitals of the dioxidovanadium(V) complexes.

Complex		Orbital	Energy (a.u.)	DTO (%)	OPD (%)	V (%)	$(O)_2$ (%)	Main character
[VO$_2$(OPD)$_2$]OH (**1**)	(72)	HOMO	-0.386		54	1	44	L(π), O(π)
	(71)	HOMO-1	-0.500		98	1	1	L(π)
	(70)	HOMO-2	-0.503		69	2	29	L(π), O(π)
	(69)	HOMO-3	-0.506		82	1	16	L(π)
	(68)	HOMO-4	-0.562		96	2	1	L(π)
	(73)	LUMO	-11.043		17	76	16	V(dxy)
	(74)	LUMO+1	-10.446		14	62	14	V(dxz), V(dx^2-y^2)
	(75)	LUMO+2	-10.204		25	61	15	V(dx^2-y^2),V(dxz)
	(76)	LUMO+3	-9.489		99	1	0	L(π^*)
	(77)	LUMO+4	-8.139		91	8	2	L(π^*)
[VO$_2$(OPD)(DTO)]OH×4H$_2$O(**2**)	(64)	HOMO	-0.504	50	1	3	1	DTO(π)
	(63)	HOMO-1	-0.507	3	95	1	0	L(π)
	(62)	HOMO-2	-0.510	0	99	1	0	L(π)
	(61)	HOMO-3	-0.521	87	1	1	0	DTO(π)
	(60)	HOMO-4	-0.552	64	1	3	1	DTO(π)
	(65)	LUMO	-0.421	15	8	66	11	V(dx^2-y^2),V(dxy)
	(66)	LUMO+1	-0.414	64	3	4	1	DTO(π^*)
	(67)	LUMO+2	-0.395	7	10	65	16	V(dxy), V(dxz)
	(68)	LUMO+3	-0.386	9	11	64	15	V(dxy), V(dxz)
	(69)	LUMO+4	-0.386	5	8	61	25	V(dxy), V(dxz)

The % of contribution of the (O) to the HOMO states (H to H-4) is in the range (0-1%). The % of contribution of the (O) to LUMO states (L to L+4) is much lower (15% to 25%) except for (L+1 was 1%). The % contribution of the (DTO) ligand to the HOMO states varies from 50% to 84% (except H-1 3% and H-2 0%). The (DTO) ligand % contribution to LUMO states is much lower than its contribution to HOMO states and varies from 5% to 15% (except L+1 64%) through the DTO(π^*) as the main character. The % contribution of the (OPD) ligand to the HOMO states is low and varies from 95% to 99% through the (OPD)(π) as the main character. The (OPD) ligand % contribution to LUMO states is much lower than its contribution to HOMO states and varies from 8% to 11% through the (OPD) (π^*) as the main character. The electronic transition of the type π-π^* may arise from the HOMO states of high O(π) character to LUMO states with high DTO(π^*) or/and OPD(π^*) character, Table 8. The vanadium % contribution to the HOMO states varies from (1% to 3%) V(*d*) as the main character, while the % contribution of the vanadium to the LUMO states varies from 61% to 66% which points to the possibility of LMCT from O(π^*), DTO(π^*) and/or OPD(π^*) to V(*d*) [8-10]. Molecular recognition involves the interaction between the molecules. This is a guide to the formation of thermodynamically stable, and relatively long-lived complexes. These include induced polarization of delocalized electrons by nearby charges and dipoles and the charge transfer between electron-rich and electron-poor molecules. Molecular surfaces of interacting moieties can be close to each other. The coulombic attraction between unlike charges is rather long-range. The electron density falls off roughly exponentially with the distance from the nucleus. The electrostatic potential surfaces can be displayed as mapped onto the molecular electron density. The molecular electrostatic potential (MEP) has been calculated and shown in Fig. **S4**, the red regions indicate the electron-rich regions with electrophilic reactivity and the blue regions indicate electron-poor regions with nucleophilic reactivity. The nitrogen atoms of the (OPD) and sulfur atoms of the (DTO) ligands; with their negative regions (red) are the reactive sites for the electrophilic attack [8-10]. On the contrary, the negative regions (red) in the complexes are mainly localized over the oxygen atoms. This supports the suggestion that these complexes will bind to the biomolecules from the oxygen atoms. The novel prepared complexes are low molecular weight and have good water solubility. This type of complex encourages us to continue the preparation and investigation of more and more complexes with another metal in different oxidation states for the ligands used in this study.

On the other hand, we can explore the vanadium metal with the same oxidation state (+5) with other ligands same as the ligands used in the study. This study opens the door for our teamwork and the researchers to understand the behavior of the bidentate ligands with different donor atoms such as (N, O), (N, S), (S, O), and tridentate (N, O, S).

The cytotoxic activity: The cytotoxic activities of the dioxidovanadium complexes were determined in DMSO solutions against the L20B cell line. The IC_{50} values of the tested complexes were deduced in Table 9.

Table 7. IC_{50} values of prepared dioxidovanadiumV(V) complexes against L20B cell line.

Complexes	IC_{50} μg mL⁻¹ for complexes	IC_{50} μg mL⁻¹ for DMSO (as a negative control)
$[VO_2(OPD)_2]OH$	145.2	204.5
$[VO_2(OPD)(DTO)OH×4H_2O$	175.5	190.0

The complexes gave different cytotoxic activity against the L20B cell line. The $[VO_2(OPD)_2]OH×H_2O$ complex (**1**) has a better cytotoxicity (145.2)±1.89 than the $[VO_2(OPD)(DTO)OH×H_2O$ complex (**2**) (175.5) ± 2.09.

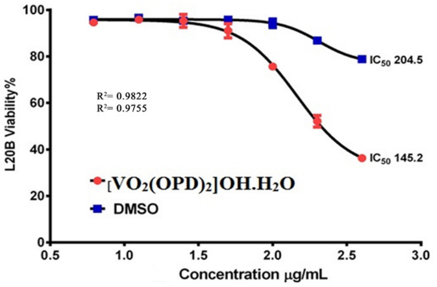


Fig. 12. IC_{50} curve of the $[VO_2(OPD)_2]OH×H_2O$ complex (1) against L20B cell line.

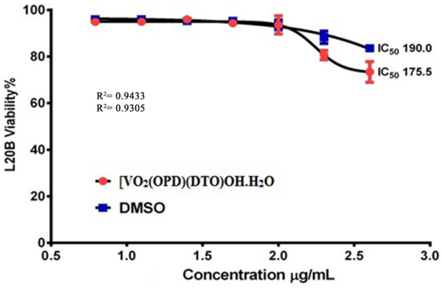


Fig. 13. IC_{50} curve of the $[VO_2(OPD)(DTO)OH×H_2O$ complex (2) against L20B cell line.

The moderate activity of the complexes can be explained depending on the behavior of the diamine ligand, which means the ligands didn't hydrolyze just like the *cis*-platin and its analogous complexes to bind the DNA nitrogen bases. The complexes' cytotoxicity with IC_{50} (μg/mL) against the L20B cell line depicted in Figs. 12 and 13, respectively. The study suggestions for future studies is to prepare more and more antitumor complexes that have high solubility in water.

CONCLUSIONS

From what has been said above, the study concludes that the complexes have distorted octahedral geometries, and the (OPD) and the (DTO) ligands behave as bidentate N_2 donor ligands, by relying on the spectroscopic, and the DFT theoretical data. The energies of the HOMO and LUMO molecular orbitals of the ligands and the complexes were negative which indicates that the state of ligands and the complexes are stable. The complexes have moderated cytotoxicity against the used carcinogenic cell line. The complexes are promising antitumor candidates because of their high solubility in water which may ease their injection and/or enhance the chance of oral administration trial.

ACKNOWLEDGMENT

This project was supported by the deanship of the College of Education at the University of Fallujah, Iraq.

REFERENCES

1. Costa Pessoa J., Etcheverry S., Gambino D. (2015) Vanadium compounds in medicine. *Coord. Chem. Rev*., **301-302**, 49-86. https://doi.org/10.1016/j.ccr.2014.12.002
2. Pessoa J.C., Maurya M.R. (2017) Vanadium complexes supported on organic polymers as sustainable systems for catalytic oxidations. *Inorg. Chim. Acta*, **455**, 415-428. https://doi.org/10.1016/j.ica.2016.04.012
3. Del Carpio E., Hernández L., Ciangherotti C., Villalobos Coa V., Jiménez L., *et al.* (2018) *Coord. Chem. Rev.,* **372** ,117-140. https://doi.org/10.1016/j.ccr.2018.06.002
4. Bhakat S., Adão P., Majumder S., Dash S.P., Roy S., *et al*. (2018) Synthesis, structure, solution behavior, reactivity and biological evaluation of oxidovanadium (IV/V) thiosemicarbazone complexes. *Dalton Trans*., **47**, 11358-11374. https://doi.org/10.1039/C8DT01668B
5. Fedorova E.V., Buryakina A.V., Zakharov A.V., Filimonov D.A., Lagunin A.A., *et al.* (2014) Design, synthesis and pharmacological evaluation of novel vanadium-containing complexes as antidiabetic agents. *PLoS ONE* 24, **9**(7), e100386. https://doi.org/10.1371/journal.pone.0100386
6. Alajrawy O.I., Ibraheem K.R., Hadi H.A. (2019) Vanadyl VO(II) with o-phenylenediamine complexes: Preparation and spectral characterization. *Res. J. Chem. Environ*., **23**(I), 43-49.
7. Sabar S.S., Alajrawy O.I., Elbohy S.A.H., Sharaby C.M. (2022) New molybdenum(VI) and vanadium(IV) complexes with 3-aminopyridine and dithiooxamide ligands spectroscopic

characterization, DFT calculations, and in vitro cytotoxic activity. *Materials Today*: *Proceedings*, **65**, 2537-2550. https://doi.org/10.1016/j.matpr.2022.04.725

8. Ahmed T.Th., Alajrawy O.I. (2023) Oxovanadinum(IV) complexes with bidentate ligands synthesis, characterization, and comparison between experimental and theoretical. *Materials Today: Proceedings*, **80**, 3823-3836. https://doi.org/10.1016/j.matpr.2021.07.396
9. Alajrawy O.I., Hadi H.A., Awad Al-Luhaibi R.S., Sabbar B.A. (2023) *In-vitro* cytotoxic activity and theoretical investigations for new mononuclear Pt(IV) and dinuclear Ru(III) with o-phenylenediamine ligand complexes against L20B cell line. *Results in Chemistry* 5, **100712**. https://doi.org/10.1016/j.rechem.2022.100712
10. Alajrawy O.I., Tuleab S.F., Alshammary E.T. (2022) Vanadium(IV) and vanadium(V) complexes: Syntheses, structural characterization, DFT studies and impact of oral uptake on enhancing insulin activity of diabetic albino rats. *J. Mol. Struct.*, **1269**, 133821. https://doi.org/10.1016/j.molstruc.2022.133821
11. Refat M.S., and El-Shazly S.A. (2010) Identification of a new anti-diabetic agent by combining VOSO4 and vitamin E in a single molecule: Studies on its spectral, thermal and pharmacological properties. *Eur. J. Med. Chem.*, **45**(7), 3070-3079. https://doi.org/10.1016/j.ejmech.2010.03.040
12. Dabrowiak J.C. (2017) Metals in Medicine. John Wiley&Sons. e-ISBN: 9781119191377, https://doi.org/10.1002/9781119191377
13. Bioinorganic Medicinal Chemistry (2011) Ed. AlessioEnzo, John Wiley & Sons; 440. https://doi.org/10.1002/9783527633104
14. Kioseoglou E., Petanidis S., Gabriel C., Salifoglou A. (2015) The chemistry and biology of vanadium compounds in cancer therapeutics. *Coord. Chem. Rev.*, **301**, 87-105. https://doi.org/10.1016/j.ccr.2015.03.010
15. Deepika T., Mani V., and Pal R.P. (2018) Vanadium in biosphere and its role in biological processes. *Biol. Trace Elem. Res.*, **186**(1), 52-67. https://doi.org/10.1007/s12011-018-1289-y
16. Kamp H.V. (1975) Sulfur atoms as ligands in metal complexes. *Angew. Chem. Int. Ed. Engl.*, 14,322. https://doi.org/10.1002/anie.197503221
17. Green M.H., Jubran M., Bursten B.E., Busch D.H. (1987) Transition-metal complexes of dithiooxamide ligands. Vibrational fine structure in the electronic spectra of symmetrically N,N'-disubstituted dithiooxamides and their divalent nickel ion complexes. *Inorg. Chem.*, **26**(14), 2326-2332. https://doi.org/10.1021/IC00261A032
18. Freshney R.I. (2012) Culture of animal cells: A manual of basic technique and specialized applications. 6th Edition, Wily-Liss, New York. https://doi.org/10.1002/9780470649367
19. Geary W.J. (1971) The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.*, **7**, 81-122. https://doi.org/10.1016/S0010-8545(00)80009-0
20. Muhyedeen B.R.J. and A-Ali Drea A. (2014) Synthesis and identification of Pd(II) and Ni(II) dithiooxamide complexes-Part I: Experimental. *Journal of Multifunctional Materials and Photoscience*, **5**(1), 1-19
21. Nakamoto, Kazuo. (2009) Infrared and raman spectra of inorganic and coordination compounds. Part B: Applications in coordination, organometallic, and bioinorganic chemistry. John Wiley & Sons; https://doi.org/10.1002/9780470405840
22. Maurya M.R., Chaudhary N., Avecilla F., Adão P., and Costa Pessoa J. (2015) Oxidovanadium(IV) and dioxidovanadium(V) complexes of hydrazones of 2-benzoylpyridine and their catalytic applications. *Dalton Transactions*, **44**(3), 1211-1232. https://doi.org/10.1039/c4dt02474e
23. Soliman A.A., Attaby F.A., Alajrawy O.I. Majeed S.R. (2019) Soluble ruthenium(II) with 3,4-diaminobenzoic acid complexes. *J. Therm. Anal. Calorim.*, **135**, 2457-2473. https://doi.org/10.1007/s10973-018-7405-6
24. Wua F., Zeng Z. (2023) Vanadium isotope geochemistry: Recent advancements, and developments in vanadium isotopic analysis by MC-ICP-MS. *Atom. Spectrosc.*, **44**(5), 298-310. https://doi.org/10.46770/AS.2023.222
25. Mohan Jag. (2004) Organic spectroscopy: Principles and applications. 2nd ed., CRC Press;
26. Lever ABP. (1984) *Inorganic electronic spectroscopy*. 2nd ed., Amsterdam,Elsevier;.
27. Housecroft C.E., Sharpe A.G. (2005) Inorganic Chemistry, 2nd ed., England, Pearson, 579
28. Lee C., Yan, W. and Parr R.G. (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.*, **37**, 785-789. https://doi.org/10.1103/PhysRevB.37.785
29. Robinson R., Abbasi K.K., Ariafard A., Stranger R., and Yates B.F. (2015) Sulfur dioxide activation: A theoretical investigation into dual S=O bond cleavage by three-coordinate molybdenum(III) complexes. *Inorg. Chem.*, **54**(2), 534-543. https://doi.org/10.1021/ic502298j
30. Vahid M., Bahram B., K.Aliakbar D., Morgane P., Michal D., *et al*. (2021) A new vanadium complex having [OVV(μ-O)2VVO] core with anti-coplanar configuration: Synthesis, crystal structure, DFT calculation, antibacterial and a homogeneous catalyst for epoxidation of alkenes. *Polyhedron*, **194**, 114939. https://doi.org/10.1016/j.poly.2020.114939
31. Mannar R.M., Shilpa K., Carola S., and Rehder

D. (2001) Dioxo- and oxovanadium(V) complexes of biomimetic hydrazone ONO donor ligands: Synthesis, characterisation, and reactivity. *Eur. J. Inorg. Chem*., 779-788. https://doi.org/10.1002/1099-0682(200103)2001:3<779::AID-EJIC779>3.0.CO;2-%23

32. Mansour A.M. (2013) Coordination behavior of sulfamethazine drug towards Ru(III) and Pt(II) ions: Synthesis, spectral, DFT, magnetic, electrochemical and biological activity studies. *Inorg. Chim. Acta*, **394**, 436-445, https://doi.org/10.1016/j.ica. 2012.08.025
33. Assfeld X., Rivail J.L. (1996) Quantum chemical computations on parts of large molecules: The ab initio local self-consistent field method. *Chem. Phys. Lett*., **263**(1-2),100-106, https://doi.org/10.1016/S0009-2614(96)01165-7
34. Małecki J.G., Zwolinski P. (2012) Synthesis, characterization and molecular structure of Pd(II) complex containing the methyl-hemiacetal form of isonicotinaldehyde. *Polyhedron*, **39**(1), 85-90, https://doi.org/10.1016/j.poly.2012.03.025