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Synthesis, characterization and density function theory (DFT) calculations of two oxovanadium (IV) complexes derived from 1.10phenathroline and amino acids

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Abstract
Three oxovanadium complexes with three amino acids and 1.10Phenanthrolinum chloride monohydrate, 1.10 phenanthoroline (L1), glycine (L2), tyrosine (L3), and homoserine (L4) are synthesized. The complexes C1, [VO(Cl) (gly)(phen)] C2, [VO (Cl) (tyro)(phen)] were characterized by conductivity measurements, magnetic susceptibility, UV-Vis, IR, thermal gravimetric analysis TGA, ^{1}H and ^{13}C NMR. The molecular structure of the complexes C1, and C2 were confirmed using the DFT calculation to obtain the optimized geometries using the Gaussian09 program at the B3LYP/LANL2DZ level of theory. The vanadium atoms in the three complexes were coordinated in distorted octahedral geometries with L1, L2, L3, L4 acting as a bidentate and tridentate ligands through the amino nitrogen atoms and carboxylate oxygen atom.

Keywords: oxovanadium, glycine, tyrosine, homoserine, 1.10 phenanthroline

1. Introduction
Vanadium is the only natural metal found in trace amounts in all tissues of the human body. According to calculations, the human body contains about 100–200 μg of vanadium [1]. In brain, muscles, liver, testes, and lungs vanadium concentrations are 0.59 ±0.16, 1.18 ± 0.06, 0.78 ± 0,.2, 3.92 ± 1.58, and 1.96 ±0.39 μg/kg, respectively [2]; blood vanadium concentration is less than 0.9 μmol/L [3]. Importance of vanadium for living organisms was originally determined in 1911, when Heinze found large amounts of this element in blood of the tunicate ascidia (marine invertebrate chordate) [4], in which it was detected as a low molecular weight complex of green blood cells, vanadocytes. Tunicate vanadocytes can concentrate vanadium up to 106–107 as compared with the vanadium concentration in marine water. Active studies of the physiological role of vanadium started in 1977, when it was discovered that vanadium compounds inhibited activity of Na+, K+-ATPase [5]. Numerous studies have shown that vanadium is involved in regulation of carbohydrate and lipid metabolism, in processes of bone and teeth formation; it also stimulates growth and reproduction of cells. First experiments demonstrating vitally important role of vanadium for biological organisms were carried out on rats [6] and chickens [7]. Vanadium coordination chemistry has attracted increasing interest during the last few years, due to the model character of many vanadium complexes for the biological function of vanadium[8-12] the use of (oxo)vanadium complexes in oxidation and oxo transfer catalysis [13,14].

2. Materials and methods
2.1 Materials
vanadium sulfate hydrate, purchased from Sigma-Aldrich, L-Tyroseine purchased from - Cambrain chemicals, 1.10 phenanthroline and Glycine were purchased from MERCK, Sodium bicarbonate purchased from Elgomhouria, Diethylether purchased from LaboratoryRasyan, Ethanol purchased from ADWIC.(all of chemicals were Analytical grade) .
The melting points of were determined by Fisher-Johns melting point apparatus in °C Fisher Scientific Company - USA model 6200, Molar conductivities of freshly prepared DMF complexes solutions c =1.0×10^{-3}Mol\dm^{-3} were measured on conductivity meter model-JENCO-3173R-USA, The magnetic susceptibilities were measured on Sherwood scientific-England, Carbon, hydrogen, and nitrogen contents were determined on a elemental analyzer. UV/Vis spectra in complexes solutions (c =1.0×10^{-3}mol dm^{-3}) were recorded on UV.3101PC-Schimadzu Japan, Infrared spectra were recorded on a 8001-PC FT-IR- Schimadzu spectrophotometer using KBr pellets in the mid-infrared region 4000-400 Cm^{-1}, NMR spectra were recorded on a Varian Mercury VX-300 and VX-500 MH_Z NMR Spectrometer,^{1}H spectra were run at 75.46 MH_Z and ^{13}C spectra were run at 300 MH_Z in DMSO-d_6 as a solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm. Splitting patterns are designed as follows: s- singlet, d- doublet, t- triplet, q- quartet and m- multiplet, and TGA were carried on a TGA-Q500 Thermo Gravimetric Analyzer.

2.2 Methods
2.2.1 Synthesis of the complexes
[VO(Cl) (gly)(phen)].H_2O (0.163g, 1mmol) of vanadyl

sulfate was dissolved in 20 ml water and added to (0.075g, 1mmol) of glycine dissolved in 20ml ethanol and mixed with (0.234g, 1mmol) of 1.10phenanthroline chloride monohydrate dissolved in 20 ml ethanol , after added (0.168g, 1mmol) of sodium hydrogen carbonate mixture was stirred and refluxed for 6h at 72°C dark green ppt was formed, solid was filterd and washed with ethanol. For (C1) $[C_{14}H_{12}Cl\ N_3O_3V].H_2O$ (M_f = 356.7); yield 56.2%; Anal. Calcd: C, 47.15; H, 3.39; N, 11.78 %. Found: C, 47.0; H, 3.2; N, 11.5%.

2.2.2 [VO(Cl) (tyro)(phen)].H_2O (0.163g, 1mmol) of vanadyl sulfate was dissolved in 20 ml water and added to (0.181g, 1mmol) of tyrosine dissolved in 20 ml ethanol and mixed with (0.234g, 1mmol) of 1.10phenanthrolin chloride monohydrate dissolved in 20 ml ethanol, after added (0.168g, 1mmol) of sodium bicarbonate mixture was stirred and refluxed for 6h at 72°C dark green ppt was formed, solid was filterd and washed with ethanol. For (C2) $[C_{21}H_{18}\ Cl\ N_3O_4V].H_2O$ (M_f = 462.8); Yield 43.5%; Anal. Calcd: C, 54.50; H, 3.92, N, 9.08 %. Found: C, 53.6; H, 3.8; N, 8.9%.

3. Results and discussion

3.1 Physiochemical data

The melting points of complexes C1, C2 were found to be >240°C.

The magnetic moment is calculated from the magnetic susceptibility *d*-configuration C1 d^1-C2 d^1 and number of unpaired electrons μs C1= 1.87 - μs C2= 1.83 for Vanadium V^{+4} ions with an octahedral geometry. Molar conductivities of freshly prepared DMF complexes C1 and C2 solutions, c=1.0×10^{-3}Mol/dm^{-3} were C1= 25.9 mScm^{2}mol^{-1} – C2 =29.3 mScm^{2}mol^{-1} which indicates its non-electrolytic nature, Table1.

3.2 Infrared Spectra of C1 and C2 complexes (IR)

The IR spectra of complexes (C1 and C2) and their free ligands (L1, L2 and L3) were determined, Figures 2 and 3. Complexes C1, C2;

- **[VO(Cl) (gly)(phen)].H_2O** IR (KBr) ν_{max}/ cm^{-1} (C1) 1604 (C=N) 972 (V=O) 682 (V─O) 548 (V─N) 3338 (N─H_2), (L1) (phen) 1537 (C=N), (L2) (gly) 3381 (O─H), 3035 (N─H_2).
- **[VO(Cl) (tyro)(phen)].H_2O** IR (KBr) ν_{max}/ cm^{-1} (C2) 1588 (C=N) 851(V=O) 686 (V─O) 541 (V─N) 3398 (N─H_2), (L1) (phen) 1537 (C=N), (L3) (tyro) 3425 (O─H), 3206 (N─H_2).

For the free ligands L1, L2, and L3, characteristic stretching vibration bands appear at 1537cm^{-1} corresponding to the C=N vibration L1. A strong band is observed in 3381cm^{-1}, and 3425cm^{-1} Characteristic of the (O─H) vibration, 3035cm^{-1}, and 3206 cm^{-1} Characteristic of the stretching (N─H2) of the free ligands L2 and L3 respectively. In the spectra of new complexes C1- C2, the band due to ν(C=N) showed a positive shift to, 1604cm^{-1}, and 1588cm^{-1}, indicating coordination of the nitrogen to vanadium. ν(O–H) (carboxylic) vibration was absent in the complexes indicating deprotonation to coordination .and the band due to ν(N–H_2) showed a positive shift to 3338cm^{-1}, and 3328cm^{-1}, indicating coordination of the nitrogen to vanadium too .In addition, the complexes exhibit the characteristic ν(V=O) bands at 972 cm^{-1}, 851 cm^{-1} , and ν(V–O) bands at 682 cm^{-1} , 686 cm^{-1} , and ν(V–N) bands at 548 cm^{-1}, 541 cm^{-1} for complexes C 1and C2, respectively.

3.3 Nuclear Magnetic Resonance Spectrophotometer (NMR)

The ^{1}H and ^{13}C NMR data confirms the complex formation and the coordination mode of the ligands. For complex (C1) ^{1}H NMR (300 MHz, DMSO-d_6,ppm): δ 4.50 (d, 2H- CH_2), 7.77 - 8.49 (m, 8H- arom), 9.06 (s, 2H- NH_2), ^{13}CNMR (500 MHz, DMSO-d_6, ppm): δ = 40.80 (1C, CH_2), 123.7 - 136.6 (10C, phen, CH and C), 146.1 (2C, phen, C=N), 150.3 (1C, C─O─V).

For complex (C2) ^{1}HNMR (300 MHz, DMSO-d_6, ppm): δ = 3.45 (m, 2H- CH_2), 4.10 (m, 1H- CH), 6.50 – 6.96 (m, 4H, arom (tyro)), 7.76 - 8.48 (m, 8H, phen), 9.10 (s, 2H- NH_2), 9.80 (s, 1H- OH), ^{13}CNMR (300 MHz, DMSO-d_6, ppm): δ = 40.04 (1C, CH_2), 60.60 (1C, CH), 115.3 – 128.4 (5C, arom (tyro), 129.5 – 149.8 (10C, phen, CH and C) 155.9 (2C, phen, C=N), 164.4 (1C, C─O─V), 174.7 (1C, C=O).

3.4 Thermo gravimetric studies (TGA)

Thermo gravimetric studies TGA for the complexes C1 and C2 were carried out within the temperature range from room temperature up to 1000 ºC with a heating rate of 10 degree/min. The remaining residue is in both complexes is VO_2. As shown in the curves there is mass loss in 95 – 100 C^0 which confirm the analysis data that water of crystallization in the complex C1 and C2 The total weight losses is 77.1 for C1 and 82.5 for C2. The remaining residue of VO_2 is 22.9 (calculated 23.25) for C1 and is 17.55 (calculated 17.92) for C2, Figure 6.

4. Theoretical DFT calculations

The density functional theory was applied to calculate the optimized geometries using the Gaussian09 program. The DFT/B3LYP method was used for the geometry optimization. Full geometry optimization was performed using B3LYP/LANL2DZ as a basis set to generate the optimized structure for ligands and complexes

4.1 The Molecular modeling of ligand L1, L2 and complex C1

Figure 7, shows the optimized structures of ligand (L1) and its complex (C1) as the most stable configurations. The vanadium atom is six-coordinate in a distorted octahedral geometry, the bond angles ranging from 77.57 to 162.3°, (Table 2).

The distance between donor atoms involved in coordination N1- - - - -N2 is decreased upon complex formation from 2.735Å (in free ligand) to 2.695 Å (in the complex). But the distance between N1- - - - -O1, is slightly increased from 2.588 (in free ligand) to 2.625Å (in the complex) this is probably due to the formation of hydrogen bonding between N1---HO1 in L2. The bond length of V-O1 is 1.925Å longer than V=O3 1.610. The atoms N1, N2, N3 and O1 are almost in one plane deviated by 3.98°. The axial bond angles of N1-V-O1 and N1-V-N3, 162.3° and 160.0° is deviated from linearity due to coordination to vanadium. The bite angle N1-V-N2 , O1-V-N2 and N3-V-O1 are 77.57°, 87.25°, and 79.84 lower than 90° due to coordination, and The bite angles and

N3-V-N1 are 112.0° more than 90° due to coordination also.

4.2 The Molecular modeling of ligand L1, L3 and complex C2

Figure 8 shows the optimized structures of ligand (L1), (L3) and its complex (C2) as the most stable configurations. The vanadium atom is six-coordinate in a distorted octahedral geometry, the bond angles ranging from 78.27 to 162.5°, (Table 3).

The distance between donor atoms involved in coordination N1- - - - -N2 is decrease upon complex formation from 2.735Å (in free ligand) to 2.695 Å (in the complex). The distance between N3- - - - -O1, is also decreased from 3.535Å (in free ligand) to 2.611 Å (in the complex).The bond length of V-O1 is 1.920Å longer than V=O3 1.611 Å. The atoms N1, N2, N3 and O1 are almost in one plane deviated by 6.28°. The axial bond angles of N1-V-O1 and N2-V-N3, 162.5° and 159.1° is deviated from linearity due to coordination to vanadium. The bite angle N1-V-N2 , O1-V-N2 and N3-V-O1 are 77.54°, 87.39°, and 79.39°, lower than 90° due to coordination, and The bite angles and N3-V-N1 are 112.2° more than 90° due to coordination also.

The computed total energy, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies and the dipole moment for the ligands L1, L2 and L3 and their complexes C1 and C2 were calculated, Table 4. The more negative values of total energy of the complexes than those of free ligands indicate the extra stability of the complexes than the free ligands. The polarities of the complexes are much larger than those of the free ligands, Table 4. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies of C1 and C2 are represented in Figures 9 and 10, respectively.

5. Tables and figures

Table 1: Molar conductance values, magnetic measurement, and UV/Vis-bands of C1 and C2

Codes Name of the complex	Molar conductance (Ω^{-1} cm^{-1} mol^{-1})	Magnetic values (298 K)	Bands observed λ_{max} (nm)
C1	25.9	μs 1.87 paramagnetic	222 and 270
C2	29.3	μs 1.83 paramagnetic	222 and 270

Table 2: Optimized Bond Lengths and angles of ligand L1 and complex C1

Type of bond	Bond length (Å)		Type of Angle	Angle (°)	
	L1-L2	C1		L1-L2	C1
V-O1	-	1.925	O1-V-N1	-	160.0
V=O3	-	1.610	O1-V-N2	-	87.25
V-N1	-	2.198	O1-V-N3	-	79.84
V-N2	-	2.101	O1-V-O3	-	104.7
V-N3	-	2.156	O3-V-N1	-	87.95
V- Cl	-	2.588	O3-V-N2	-	103.7
N1 - -N2	2.753	2.695	O3-V-N3	-	94.40
N3- -O1	2.588	2.625	N1-V-N2	-	77.57
			N1-V-N3	-	112.0
			N2-V-N3	-	162.3
			O1-V-Cl	-	93.31
			O3-V-Cl	-	159.2
			N2-V-Cl	-	87.21
			N3-V-Cl	-	78.45

Table 3: Optimized Bond Lengths and angles of ligand L1 and complex C2

Type of bond	Bond length (Å)		Type of Angle	Angle (°)	
	L1-L3	C1		L1-L3	C1
V-O1	-	1.920	O1-V-N3	-	79.39
V=O3	-	1.611	O1-V-O3	-	104.8
V-N1	-	2.101	O1-V-N1	-	162.5
V-N2	-	2.101	O1-V-N2	-	87.39
V-N3	-	2.157	N1-V-O3	-	87.61
V- Cl	-	2.594	N1-V-N2		77.55
N1- - -N2	2.753	2.695	N1-V-N3		112.2
N3- - -O1	3.535	2.611	N2-V-N3	-	159.1
			N2-V-O3	-	106.7
			O3-V-N3	-	103.4
			O1-V-Cl	-	93.49
			O3-V-Cl	-	159.5
			N2-V-Cl	-	86.39
			N3-V-Cl	-	78.27

Table 4: Calculated energies of Ligands, L1, L2, L3, and complexes, C1and C2.

	E[a]	HOMO[b]	LUMO[c]	ΔE[d]	Dipole moment[d]
L1	-571.488	-0.2310	-0.0654	0.1656	4.096
L2	-284.382	-0.2405	-0.0206	0.2199	1.803
C1	-1017.053	-0.2274	-0.1043	0.1231	10.873
L3	-629.904	-0.2233	-0.0188	0.2045	2.206
C2	-1362.585	-0.2152	-0.1035	0.1117	10.297

[a]E: the total energy (a.u.). [b]HOMO: highest occupied molecular orbital (eV).
[c]LUMO: lowest unoccupied molecular orbital (eV).
[d]ΔE:E_{LUMO}- E_{HOMO} (eV). [e] dipole moment (Debye).

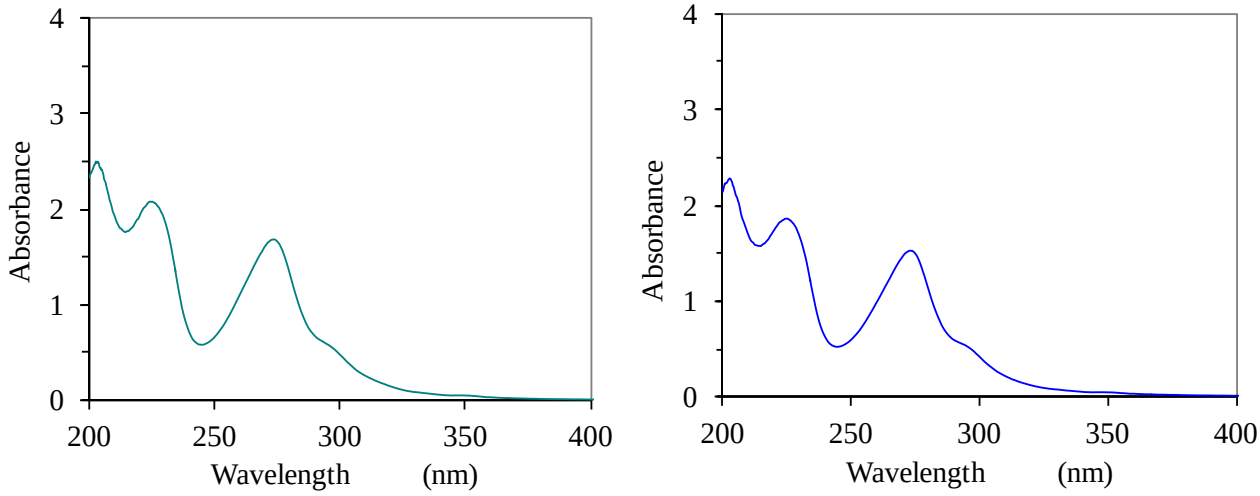


Fig 1: Ultra violet spectrum bands (λ) nm of C 1, C2

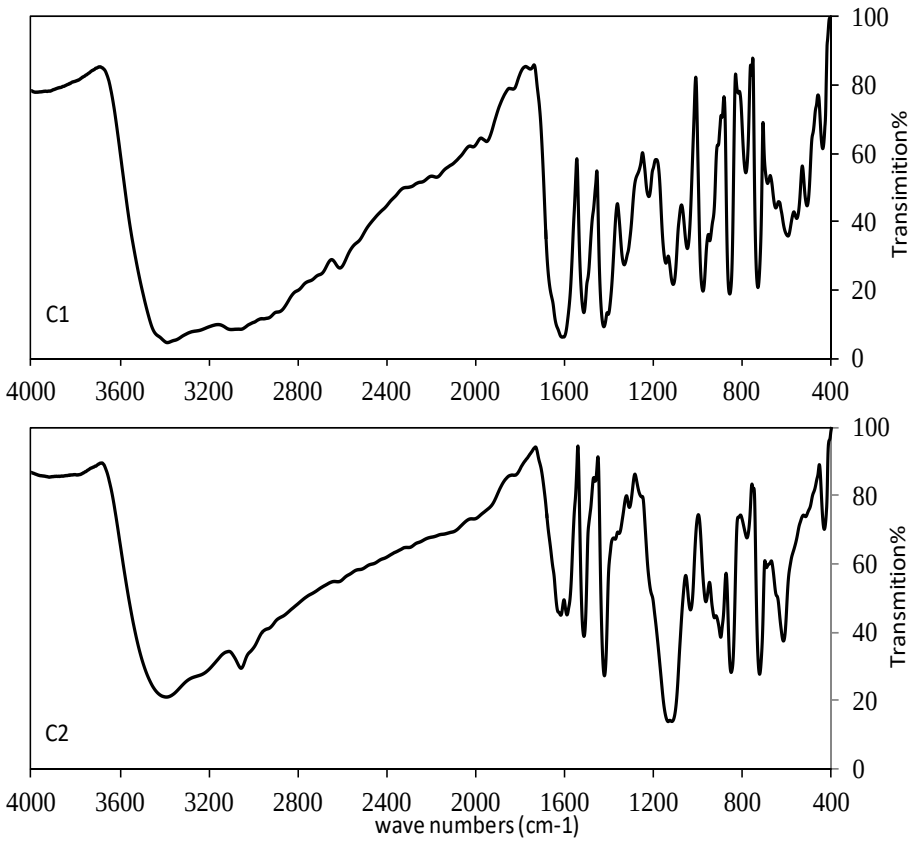


Fig 2: Infra red spectrum bands (KBr) cm^{-1} of C1, and C2

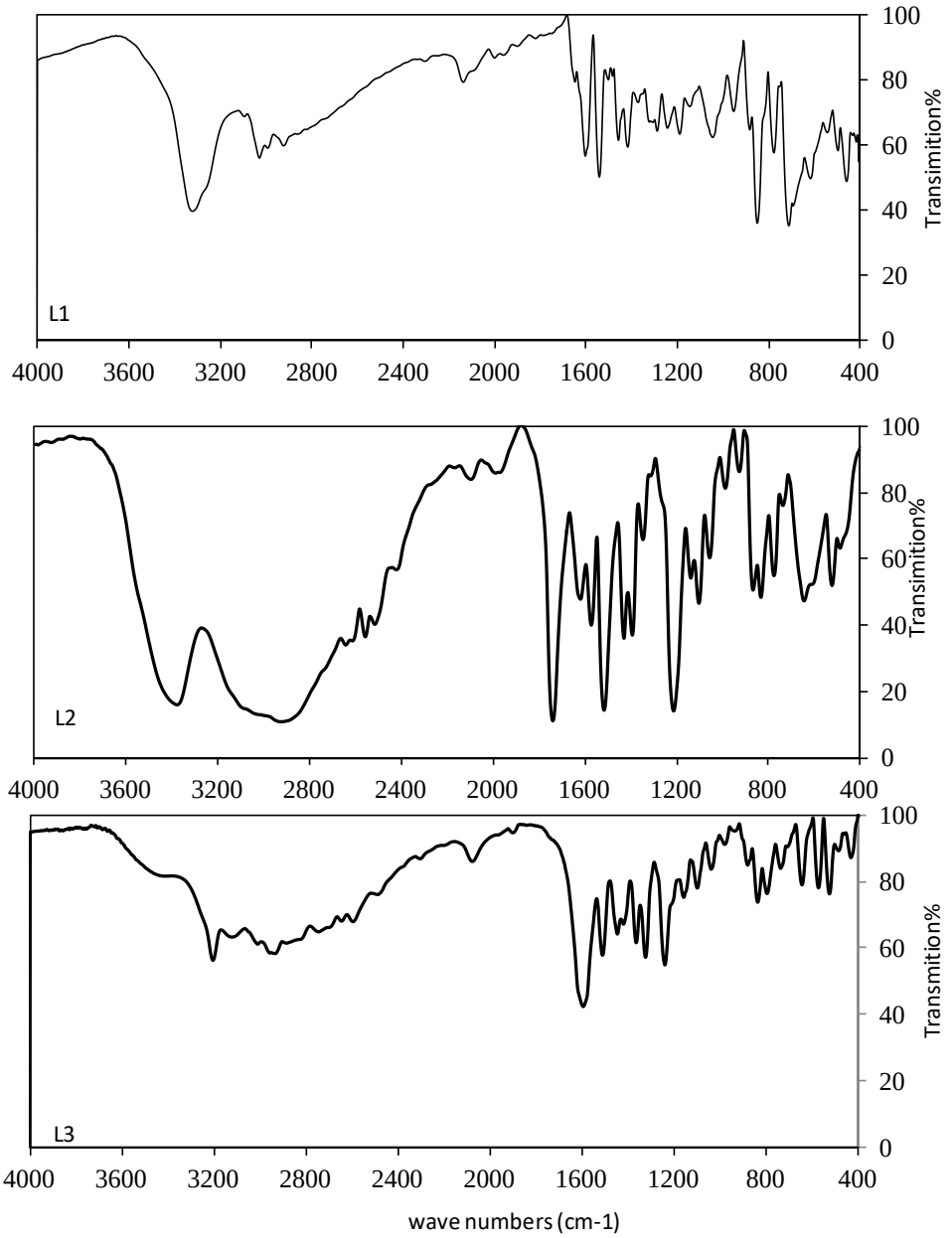


Fig 3: Infra red spectrum bands (KBr) cm^{-1} of L1, L2, and L3

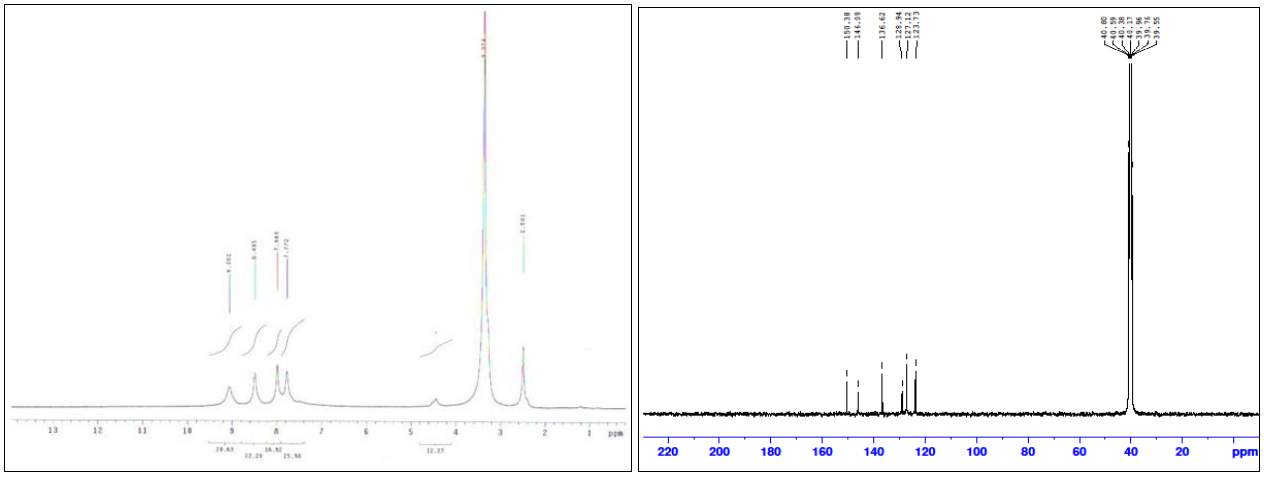


Fig 4: ^{1}H- and ^{13}C- NMR for complex C1

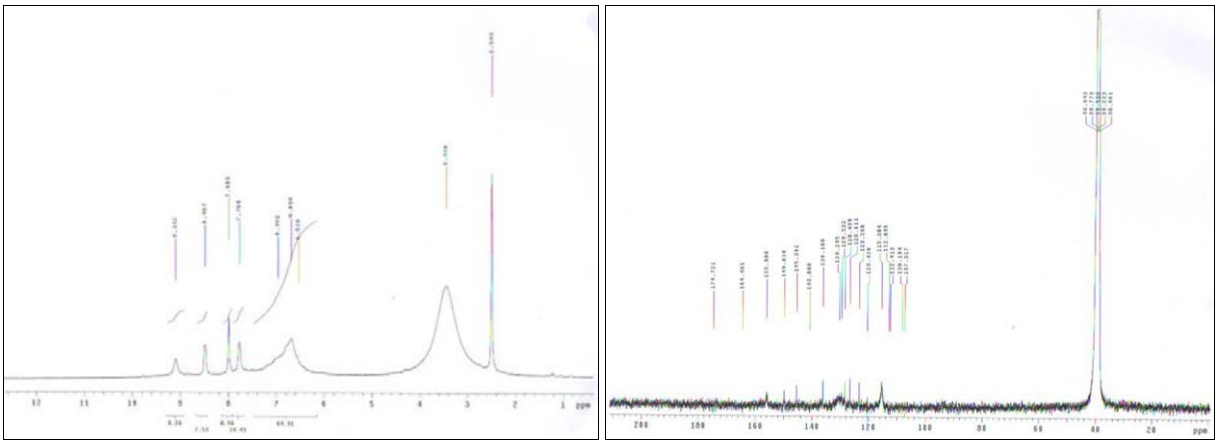


Fig 5: ^{1}H- and ^{13}C- NMR for complex C2

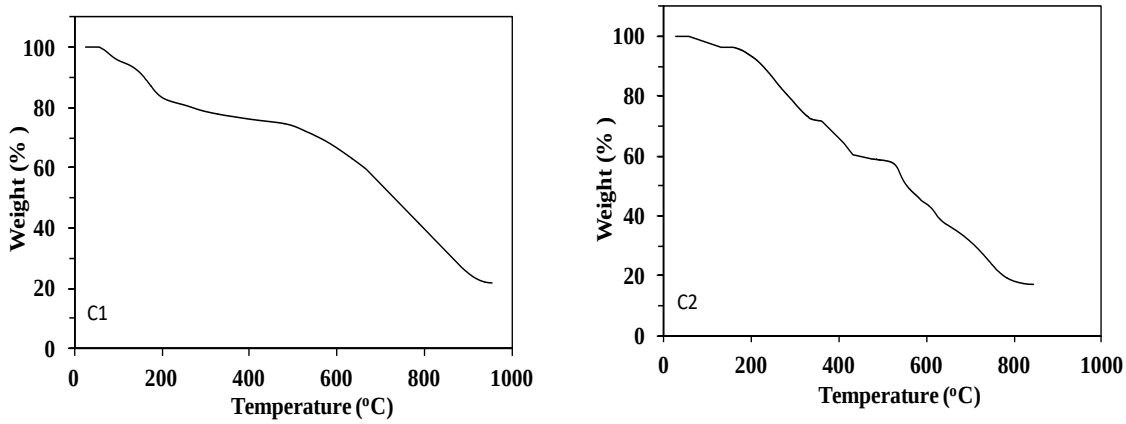
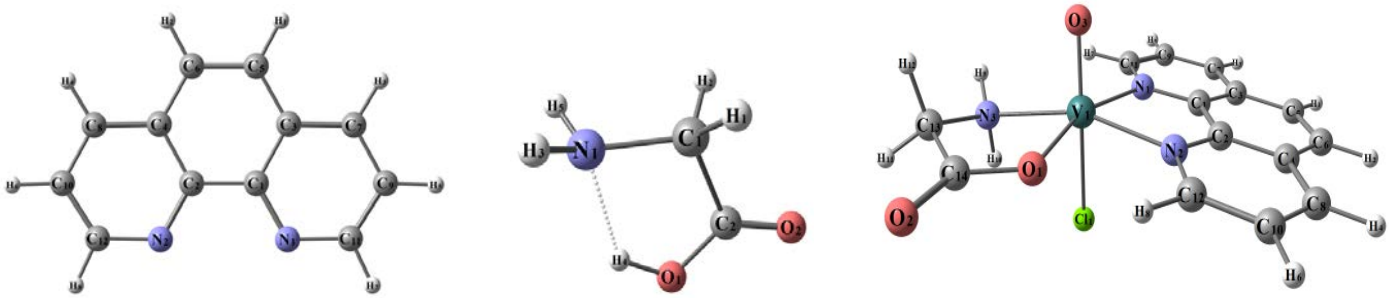
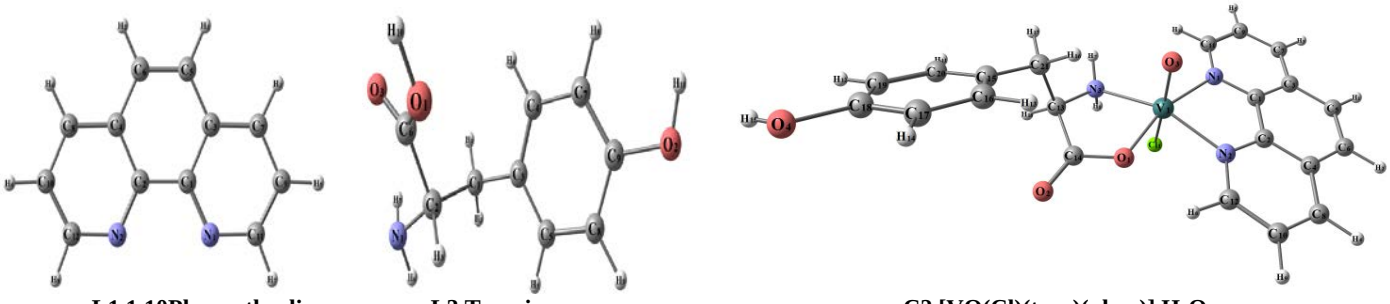


Fig 6: TGA curve of complexes C1 and C2.



L1 1.10Phenanthorline **L2 Glycine** **C1 [VO (Cl)(gly)(phen)].H_2O**

Fig 7: Optimized structure of **C1** by DFT B3LYP/LANL2DZ, ligands in upper and complex in lower.



L1 1.10Phenanthorlin **L3 Tyrosine** **C2 [VO(Cl)(tyro)(phen)].H_2O**

Fig 8: Optimized structure of **C2** by DFT B3LYP/LANL2DZ, ligands in upper and complex in lower.

6. References

1. Nozdryukhina LR. (Biological Role of Microelements in Animal and Human Organism) Moscow: Nauka, 1977.
2. Henze M, Hoppe-Seyer's Z. Physiol. Chem, 1911; 72:494-501.
3. Ueki T, Shintaku K, Yonekawa Y, Takatsu N, Yamada H, Hamada Y, *et al*. Biochim. Biophys. Acta, 2007; 1770:951-957.
4. Stacey JE, Driedzic WR. J. Exper. Marine Biol. Ecol, 2010; 386:11-18.
5. Ueki T, Michibata H. Coordination Chem. Rev. 2011; 255:2249-2257.
6. Bayer E. Metal Ions in Biological Systems, 1995; 31:407-421.
7. Almeida M, Humanes M, Melo R, Silva A, Silva JJRFD, Vilter H, *et al*. Phytochemistry, 1998; 48:229-239.
8. Tracey AS. DC Crans Vanadium Compounds, Chemistry, Biochemistry and Therapeuti Applications, 1998 ACS Symp, Ser, 711.
9. Rehder D, Conte V. Special Issue on Biological Aspects of Vanadium. J. Inorg, Biochem. 2000; 80.
10. Sigel H, Sigel A. Vanadium and Its Role in Life, Metal Ions in Biological Systems, Marcel Dekker, New York, 1995; vol. 31.
11. Rehder D. Coord. Chem. Rev, 1999; 182:297.
12. Nriagu JO. *Vanadium in the Environment*, Wiley, New, York, 1998.
13. Hirao T. *Chem. Rev*. 1997; 97:2707.
14. Arends JWCE, Pellizon M, Sheldon RA. *Stud. Surf. Sci. Catal.*, 1997; 110:1031.