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Synthesis, characterization of schiff bases derived from salicylaldehyde with some amino acids and its oxovanadium(IV) complexes via a new developed method

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Abstract

The study was aimed to synthesized and characterization of two new amino acid Schiff base and the synthesized ligands was reacted with oxovanadium(IV) ion, and to evaluate the catalytic activity of the obtained complexes against the cyclooctene epoxidation, namely, 5-Chlorosalycialdehyde-alanine and 5-Nitrosalycialdehyde-alanine, Derived from condensation reaction of substituted salicylaldehyde with some amino acids; α-alanine, with a new alternative method, The development includes the use of 10-2 mole sodium hydroxide as a new catalyst, which is considered a new method of Schiff bases synthesis. For characterization purpose, Elemental analysis (EA),

Spectroscopic analysis; IR, ^1H and ^{13}C NMR studies were carried out on the prepared ligands its complexes. The results showed that the Schiff base ligands act as chelating ligands and coordinated via one nitrogen from azomethine group and one oxygen from hydroxyl attached to benzene ring and one oxygen from hydroxyl of carboxyl group to a vanadium center, and the catalytic activity of the two complexes against cyclooctene epoxidation revealed that both were highly effective and selective in optimized conditions when used as catalysts for the epoxidation of cyclooctene into cyclooctene oxide in acetonitrile. The conversion of cyclooctene varied from 86.71% to 88.42% at 78°C within ten hours.

Keywords; ***Oxo vanadium Complexes, Epoxidation catalysis, Schiff-Base, Characterization. Synthesis. IR spectra***

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I. Introduction

Schiff bases play vital role in inorganic chemistry because they readily form stable complexes ions with most transition metals. The progress of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically useful species [1-3].

Complexes of the transition metal synthesized from Schiff bases have exhibited high potential to be versatile catalysts in organic synthesis and have remarkable developments in recent decades, and share in some kinds of chemical transformations such as hydrogenation [4].hydration [4], decarbonylation [5], olefin metathesis [6], Diels-Alder reaction [7], nitro aldol reaction [8], isomerization [2], cyclopropanation [4], enol-ester synthesis [9], oxidation of hydrocarbon [10,11], epoxidation [12,13]

Metal complexes prepared from Schiff bases have also revealed high activities in asymmetric catalysis [14], The complexes derived from aromatic carbonyl compounds have found to be very active in metalloprotein modeling as well as asymmetric catalysis [15,16]. Epoxidation reaction catalysis as special field have received great attention in last few years and many reports have advanced on several methods of prepare of catalyst complexes from many Schiff bases along with their catalytic activity assessment [17,18].

Schiff bases are classified according to the number of electrons that the molecule has or to the type of atoms or donor atom group that the molecule contains. The donor atom such as (N_2, O_2, P or S). These donor atoms that stabilize the structure of Schiff bases and that locate the bioactivity. In compounds of nitrogen the presence of a -C=N- group in Schiff bases boost bioactivity [13, 14]

The complexes of Vanadium have usually used in widely utilized in epoxidation catalysis, oxovanadium complexes synthesized from Schiff-base ligands are the most useful, for example oxovanadium(IV) complexes when combined with oxygen or other peroxide were found to be very effective in sulfide and olefin epoxidation [19-21]. Mukaiyama aldol additions have been unraveled by catalytic activity of vanadyl complexes based on 2,2'-biphenol-core ligand [22], as such up to 90/10 (anti/syn) diastereoselectivity was achieved, other worthy mentioned finding is that revealed by Uang on the use of V(O)(acac)2 in the aerobic oxidative coupling of 2-naphthols [23]. In this paper we focused on developing a new type of active vanadyl complexes specifically for the epoxidation process.

The objectives of this study are to synthesize two new Schiff bases by condensation reactions of α-alanine with 5-chlorosalicylaldehydeand 5-nitrosalicylaldehyde and its complexes, {[(E) - (5 – chloro - 2-hydroxyphenyl) methylidene] amino} propanoic acid and {[(E)-(2-hydroxy-5-nitrophenyl) methylidene] amino}propanoic acid. Followed by analyze and identify the structures of the synthesized Schiff bases using elemental Analysis (EA) in addition to spectroscopic methods; IR, (^{1}H and ^{13}C) NMR.

II. Material and Methods

2.1 Material

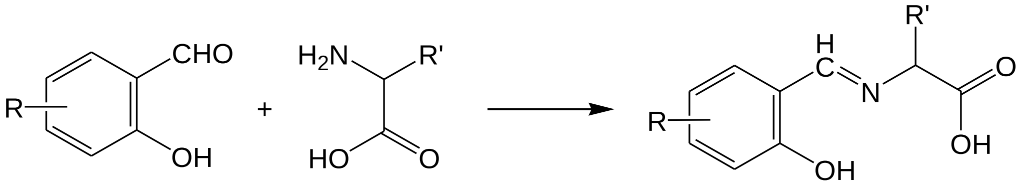
All chemicals, reagents and solvents were purchased from Merck and were used as received without further purification. Deuterium oxide, 99.9%, from Aldrich chemical company USA. Cis-cyclooctene, 95%, Substituted salicylaldehyde (5-chloro, 5-nitro), amino acids (α-alanine), sodium hydroxide, tris(acetylacetonato)vanadium(IV) and VO(acac)$_2$ were purchased from (Sigma Aldrich). Ethanol, acetonitrile, hexane, methanol, p-xylene, acetophenone and iso propanol were used as solvents for purification, recrystallization, epoxidation, and solution making.

2.2 Instrumentation:

Infrared spectral of the ligands and their corresponding catalysts were recorded on FTIR spectrometer 10.5.1, frontier (MIR)-Perkin Elmer-ZnSe/Diamond-ATR. NMR spectra of the ligands and catalysts were recorded on Bruker AVIII 40, 126, 500 US. The elemental analysis of the ligands and complexes were recorded on HEKA tech EURO EA (CHSN). An Agilent GC Model 7890B was used for determining the epoxidation of cyclooctene to cyclooctene epoxide. The Colum used is Agilent HP-5 with dimensions 0.25µm, the oven temperature was set at 70°C.

2.3 Synthesis of Schiff Bases (H_2L_1 and H_2L_2):

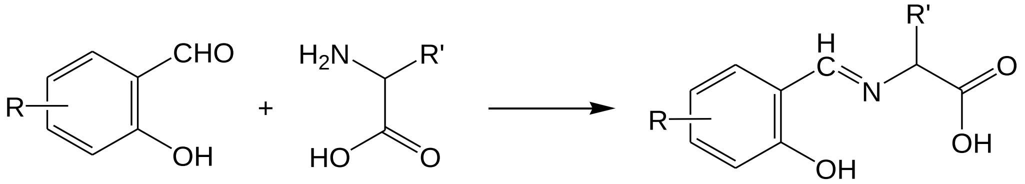
To a 250 ml round bottom flask containing 150 ml absolute ethanol 10mmol (5-nitrosalicyaldehyde (1.671g)), 10mmol of α- alanine (0.85g)) and 10mmol of NaOH were added and the content was refluxed with stirring for 5h. After cooling to room temperature the content was added to 100ml of water in 0°C in a baker and kept in an ice bath for 2h. The yellow crystals were filtered off and washed with slightly cold water and dried in an oven [24].



H_2L_1;R= Cl / R′= CH_3

Scheme (1): 2-{[(E)-(5-chloro-2-hydroxyphenyl) methylidene] amino} propionic acid (H_2L_1)

Color: Bright Yellow
Yield: 96.08 %, 2.187g
Mol. Formula: C10H10CLNO3
Mol. Wt.: 227.644 g /mole
Anal. Calcd for $C_{10}H_{10}CLNO_3$ (227.644g/ mole), C, 52.76; H, 4.43; N, 6.15. Found: C, 52.46; H, 4.42; N, 11.46
FT-IR (KBr, ν, cm^{-1}): 3059.56, 3000.17 ν (OH) , 2111.68 ν(C=O) (acid), 1737.06 ν(C=N).
^{1}H NMR (400 MHz, D2O, δ/ppm): 7.37-6.57 (C-H ring), 9.90 (s, COOH), 8.22 (CH=N) 1.49 (CH_3CH), 1.08 (CH_3CH), 4.70 (D2o).
^{13}CNMR (100 MHz, CDCl3, δ, ppm): 193.28 (C9=O), 177.59 (C7azomethine), 165.47 (C_2OH), 124.27 (C5ring), 123.33 (C3ring), 125.27 (C6ring), 121.57 (C1ring), 118.31 (C4rig), 50.68 (C8H2), 18.87 (C10).



H_2L_2;R= NO_2, R′= CH_3

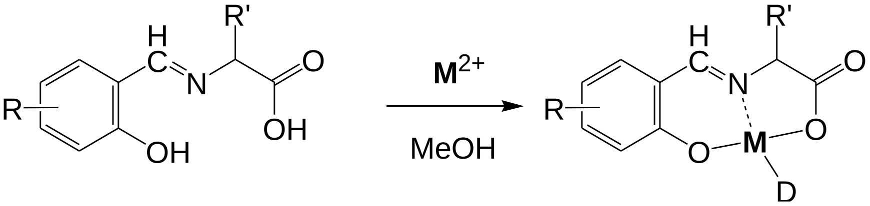
Scheme (2): 2-{[(E)-(2-hydroxy-5-nitrophenyl) methylidene] amino} propanoic acid (H_2L_2)

Color: faint Yellow
Yield: 92 %, 2.194g
Mol. Formula: $C_{10}H_{10}N_2O_5$
Mol. Wt.: 238.19 g/mole
Anal. Calcd for $C_{10}H_{10}N_2O_5$: (238.197g/ mole), C, 50.42.; H, 4.23; N, 11.76. Found: C, 50.32; H, 4.03; N, 11.46.
FT-IR (KBr, n, cm-1): 3067.38, 2987.53 (OH) (br, alcohol and acid), 1735.89 ν(C=O), 1612.30 ν(C=N).
^{1}H NMR (400 MHz, D2O, δ/ppm): 8.00-6.52 (C-H ring), 9.92 (COOH), 8.4 (CH=N), 3.67 (CH_3CH), 1.38 (CH_3CH), 4.70 (D2o).
^{13}C NMR (100 MHz, CDC13, δ, ppm): 193.57 (C9=O), 179.70 (C7azomethine), 175.98 (C_2OH), 131.18 (C5ring), 124.00 (C3ring), 133.99 (C6ring), 128.5 (C1ring), 123.26 (C4rig), 50.47 (C_8H_2), 16.18 (C10).

2.4 Synthesis of VOL_1 and VOL_2 complexes:

A 100 mL round bottom flask, 5 mmol each of (H_2L_1 and H_2L_1) 1.138 g and 1.190g respectively were dissolved in 40 mL of MeOH and to this solution added 5 mmol of VO(acac)$_2$ (1.280g) (in 10 mL of MeOH) and the content was refluxed with stirring for 4h. After evaporating of the solvent to 1/5 volume, the solution was kept in refrigerator for one week. Then the greenish crystals were filtered off and washed with n-hexane and dried in an oven [25].

2.5 Synthesis of complex VOL_1

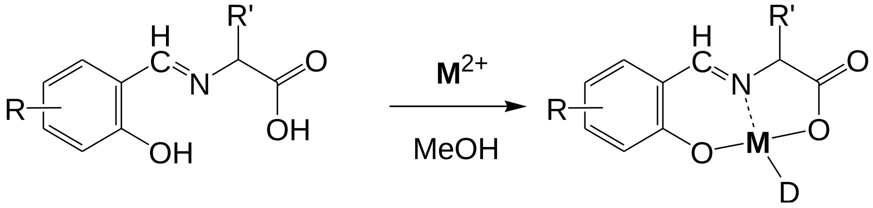


H_2L_1;R= Cl / R′= CH_3

Scheme (3): Complex 1

Color: Faint green
Yield: 70%, 1.02g
Mol. Formula: $C_{10}H_8CLNO_4V$
Mol. Wt.: 292.568 g/mole
Anal. Calcd for $C_{10}H_8CLNO_4V$: C, 41.01.; H, 2.73; N, 4.78. Found: C, 4.38; H, 2.83; N, 4.38.
FT-IR (KBr, n, cm-1): 936.29 ν(V=O), 1737.25 ν(C=O), 1633.63 ν(C=N).
^{13}C NMR (100 MHz, CDC13, δ, ppm): 125.4 (C1ring), 165.8 (C2ring), 132.6 (C3ring), 122.4 (C4ring), 134.9 (C5ring), 145.0 (C6ring), 179.1 (C7=N), 31.1 (C8), 207.0 (C9), 31.1 ((C10)).

2.6 Synthesis of complex VOL_2



H_2L_2;R= NO_2, R′= CH3

Scheme (4): Complex 2

Color: Faint green blue

Yield: 62%, 0.93g

Mol. Formula: $C_{10}H_8N_2O6V$

Mol. Wt.: 303.121g/mole

Anal. Calcd for C10H8N2O6V: C, 39.58.; H, 2.63; N, 9.23. Found: C, 39.55; H, 2.82; N, 9.03.

FT-IR (KBr, n, cm-1): 994.80 ν(V=O), 1644.57 ν(C=O), 1598.78 ν(C=N).

13C NMR (100 MHz, CDCl3, δ, ppm): 129.9 (C1ring), 121.7 (C2ring), 119.8 (C3ring), 67.7 (C4ring), 124.6 (C5ring), 126.1 (C6ring), 131.7 (C7=N), 33.5 (C8), 136.9 (C9), 19.0 (C10).

2.7 Epoxidation of cyclooctene

Batch reactions were conducted in 4mL solvent. Unless otherwise noted, the solvent for epoxidation reactions was GC-grade acetonitrile. A stock solution of the catalyst (1:1.mgmL-1, 2: 1.2 mgmL-1, in acetonitrile) was prepared and added according to the stoichiometry to a preformed solution of cis-cyclooctene (0.2687 mmol, 35.25 mg, 100mol %) and H_2O_2 (0.403 mmol, 22.91 mL, 50% in H2O,150mol%) in acetonitrile to give a total reaction volume of 4mL. Variations of oxidation agents were used according to stoichiometry using 0.403 mmol of oxidant. For all reactions, control experiments without the use of a catalyst were performed as a reference. The reactions were aborted by the addition of electrolytically precipitated and activated MnO2as a H2O2 decomposition agent. After filtration over activated neutral alumina oxide, two GC samples were prepared for each experiment using 200mL filtrate, 500 mL external standard solution (p-xylene and aceatopheone 4mg/mL in iPrOH) and 800 mL n-hexane. Time-dependent yield experiments were conducted in a total volume of 12 mL using the same stoichiometry and concentrations. The reactions were started by the addition of the catalyst solution, and samples were taken and immediately added to MnO_2 [26].

III. Results and Discussion

Scheme (1,2,3, and 4) shows the preparation procedures for the tridentate ligands H_2L_1 and H_2L_2 and their corresponding VOL_1 and VOL_2 complexes. The Schiff base ligands H_2L_3 and H2L4 were prepared by the reaction of nitro salicyaldehyde or chloro-salicyaldehyde with an equimolar amount of α-alanine in presence of NaOH in methanol as a solvent under reflux conditions. In the subsequent reaction the prepared ligands H_2L_1 or H_2L_2 and VO(acac)2 in a molar ratio of 1:1 in methanol were refluxed for10 Hours, then vanadyl Schiff base complexes were separated.The ligands and complexes were characterized using ^{1}H and ^{13}C NMR, IR spectroscopy and Elemental analysis methods, The details given below:

Table-1: ^{1}H NMR of Prepared Schiff Bases H_2L_1 and H_2L_2

Ligands	C-H ring	COOH	CH_2COOH	CH=N	CH_3CH	CH_3CH	D2o
H2L1	7.37-6.57	9.90	-	8.22	1.49	1.08	4.70
H2L2	8.00-6.52	9.92	-	8.4	3.67	1.38	4.70

Table-2: ^{13}C NMR of the Prepared Schiff Bases H_2L_1 and H_2L_2 and its complexes

Ligands	C_9=O	$C_{7azomethine}$	C_{2OH}	C_2ring	C_{5ring}	C_{3ring}	C_{6ring}	C_{1ring}	C_{4rig}	C_8H_2	C_9	C10
H_2L_1	193.28	177.59	165.47	--	124.27	123.33	125.27	121.57	118.31	50.68		18.87
H_2L_2	193.57	179.70	175.98	--	131.18	124.00	133.99	128.5	123.26	50.47		16.18
VOL_1	--	179.1	--	165.8	134.9	132.6	145.0	125.4	122.4	31.1	207.0	31.1
VOL_2	--	131.7	--	121.7	124.6	119.8	126.1	129.9	67.7	33.5	136.9	19.0

Table3. IR frequencies of the ligands and its complexes

Comp.	v(OH)	v(C=O)	v(C=N)
$H2L_1$	**3059.56, 3000.17**	**2111.68**	**1737.06**
$H2L_2$	**3067.38, 2987.53**	**1735.89**	**1612.30**
VOL_1	**3059.56, 3000.17**	**2111.68**	**1737.06**
VOL_2	**3067.38, 2987.53**	**1735.89**	**1612.30**

Table-4: Elemental analysis of the ligands and its complexes

Compounds	H%(calculated)	C%(calculated)	N%(calculated)
H2L1	**4.42(4.43)**	**52.46(52.76)**	**6.05(6.15)**
H2L2	**4.03(4.23)**	**50.32(50.42)**	**11.46(11.76)**
VOL1	**2.83(2.73)**	**41.09(41.01)**	**4.38(4.78)**
VOL2	**2.82(2.63)**	**39.55(39.58)**	**9.03(9.23)**

Table-5: The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) s complex 1 in presence of H_2O_2 in refluxed condition at RT (20°C)

Run	Solvent	Time(h)	Conversion%
1	**CH_3CN**	**2**	**9.30**
2	**CH_3CN**	**4**	**13.50**
3	**CH_3CN**	**10**	**32.26**

Reaction(4 mL CH3CN), (cyclooctene (0.268 mmol, 35.25 mg) 1:2 ratio, oxidant(0.403 mmol, 22.91 μmL, 50% in H_2O) and (0.268mmol, 78.40 mg).

Table-6:The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) complex 1 in presence of H_2O_2 in refluxed condition at (60 °C)

Run	Solvent	Time(h)	Conversion%
1	CH_3CN	2	34.16
2	CH_3CN	4	37.68
3	CH_3CN	10	39.50

Reaction (4 mL CH3CN), (cyclooctene (0.268 mmol, 35.25 mg) 1:2 ratio, oxidant (0.403 mmol, 22.91 μmL, 50% in H2O) and (0.268mmol, 78.40 mg)

Table-7: The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) complex 1 in presence of H2O2 in refluxed condition at (78 °C)

Run	Solvent	Time(h)	Conversion%
1	CH_3CN	2	83.63
2	CH_3CN	4	86.83
3	CH_3CN	10	88.42

Reaction (4 mL CH3CN), (cyclooctene (0.268 mmol, 35.25 mg) 1:2 ratio, oxidant (0.403 mmol, 22.91 μmL, 50% in H2O) and (0.268mmol, 78.40 mg).

Table -8: The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) complex 2 in presence of H_2O_2 in refluxed condition at RT (20°C)

Run	Solvent	Time(h)	Conversion %
1	CH_3CN	2	09.19
2	CH_3CN	4	18.27
3	CH_3CN	10	26.90

Reaction (4 mL CH3CN), (cyclooctene (0.268 mmol, 35.25 mg) 1:2 ratio, oxidant (0.403 mmol, 22.91µmL, 50% in H_2O) and (0.268mmol, 81.12 mg).

Table-9: The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) complex 2 in presence of H_2O_2 in refluxed condition at (60°C)

Run	Solvent	Time(h)	Conversion %
1	CH_3CN	2	46.65
2	CH_3CN	4	55.79
3	CH_3CN	10	79.11

Reaction(4 mL CH3CN), (cyclooctene (0.268 mmol, 35.25 mg) 1:2 ratio, oxidant(0.403 mmol, 22.91 µmL , 50% in H_2O) and (0.268mmol, 81.12.mg).

Table-10: The epoxidation of cyclooctene in acetonitrile as the solvent by the oxovanadium (IV) complex 2 in presence of H_2O_2 in refluxed condition at (78°C).

Run	Solvent	Time(h)	Conversion %
1	CH_3CN	2	58.45
2	CH_3CN	4	74.12
3	CH_3CN	10	86.71

Reaction(4 mL CH3CN), (cyclooctene (0.268 mmol ,35.25 mg) 1:2 ratio, oxidant (0.403 mmol , 22.91 µmL , 50% in H_2O) and (0.268mmol, 81.12 mg)

Characterization of the prepared Schiff bases and its complexes by (^{1}H ,^{13}C and IR) NMR spectroscopy

Table (1) show the ^{1}H NMR and ^{13}C NMR data are reported below. All the protons were found at their expected region. The ^{1}HNMR spectra of ligands (H_2L_1 and H_2L_2) using D_2O as the solvent in (400 MHz exhibit singlet signals at expected region of protons calculated from the integration curves and those obtained also from the values of the expected (CHN)analyses agree with each other.

The ^{1}H NMR spectral data of H_2L_1 the (OH) proton showed a chemical shift value at to 9.92 ppm due to the amino acid hydroxyl group and the OH group proton in the aromatic ring shielded by the (NO_2) group [27]. The azomethine proton is observed at 8.30 ppm is attributed to the CH=N [26]. The peak at 3.45 ppm is due to two protons (CH_2COOH) in glycine amino acid, whereas the peak at 9.92 ppm is assigned to one proton in (COOH) group [28]. The protons in aromatic ring have shown a chemical shift at (6.52-8.05) ppm due to (C=H). All these protons confirmed by elemental analysis protons [26].

The ^{1}H NMR spectral data of H_2L_2. The proton has shown chemical shift value at 8.4 ppm due to azomethine group (CH=N).The OH proton showed a chemical shift value at 9.92 ppm due to the carbonyl amino acid group. The proton of the OH group of the aromatic ring was not observed due to the presence and orientation of the electronegative group (NO_2). This proton is further confirmed by the OH group in the IR spectra of the ligands. The protons agree with each other by elemental analysis). The(C-H) protons in the aromatic ring appeared in the (6.52-8.00) ppm range [26]. The peak at 3.67 ppm is due to three protons (CH_3CH) in amino α-alanine acid [26]. The peak at 1.38ppm is assigned to one proton in CH_3CH in the amino acid.

The ^{1}H NMR of oxovanadium (IV) complexes was recorded in DMSOd$_6$ (500, 400 and 126) MHz. In two complexes no signal was observed. This is due to the nature of vanadium (IV) center (paramagnetic) [29].

^{13}C NMR analysis of H_2L_2 in table 2. The carbon atom in azomethine (C7=N) has shown peak at 177.59 ppm. The aromatic ring carbon atoms are shown at (C1) 121.57 ppm, (C2) 165.47 ppm, (C3) 123.33ppm, (C4) 118.31 ppm, (C5) 124.27 ppm and (C6) 125.27 ppm. The carbonyl carbon atom (C9=O) was found at 193.30 ppm [26]. The (C8H2) observed peak at 50.68 ppm. The (C10) shown peak at 18.87 ppm. All these carbon atoms confirmed by elemental analysis and all carbon atoms agree with each other

Table 2 show ^{13}CNMR analysis of $H_2L_1$the azomethine carbon (C7) was found at δ179.68 ppm. The aromatic carbon atoms in the ring appeared at δ 128.53 ppm (C1), δ172.49m, ppm (C2), δ124.00 ppm (C3), δ123.25 ppm (C4) δ131.18 ppm (C5), δ135.10 ppm (C6). Signal at δ193.57ppm due to carbonyl group (C9=O). Methyl group carbon atom is shown at δ41.4 ppm (C8H2) [26].

The ^{13}C NMR analysis of the VOL1 and VOL2 showed signals at 125.41 ppm and 129.94 ppm respectively, which are assigned to C1 in benzene ring, the signals at165.84 ppm and 121.77 ppm are assigned to C2 in benzene ring of 4 complexes, signals at 132.61 ppm and 119.87ppm are assigned to C3 in benzene ring, 122.42 ppm and 67.79ppm are assigned to C4 in benzene ring, 134.99 ppm and 124.66 ppm are assigned to C5 in benzene ring, 145.09 ppm and 126.19 ppm respectively due to C6 in benzene ring. The carbonyl (C9=O) carbon atom are found at 207.09 ppm and 136.96 respectively, signals at 31.13 ppm and 33.50 respectively for complexes are assigned to C8 in amino acid, signals at 179.15ppm and 131.70 assigned to azomethine group.

Table 2 shows The IR spectral data Schiff base $H_2L_1$are [24]. The band at 1737.06 cm-1 is due to azomethine (C=N), that condensation between the aldehyde and amino acid [27]. The two broad bands at 3059.56 and 3000.17 are assigned to (OH) group [30].

The IR spectral of the ligand H_2L_2 reported sharp band at 1612.30 is assigned to (C=N)[24]. The peak at 1735.89 indicating a (C=O) vibrations. Two broad bands 3067.38 and 2987.53 are assigned to (OH) vibrations [30]. These bands in which frequencies of two complexes indicating the involvement of the (–C=N) metal ion coordination.

The IR spectral of the oxovanadium(IV) complexes, are shown in Table 1, These complexes showed bands to lower wave numbers indicating that the nitrogen of the (C=N) is coordinated to the vanadium (IV) center[31]. Showed a major shift to lower wave number by 14 – 104cm^{-1} azomethine (C=N) with the metal ion [29], 936.29, and 994.80 cm^{-1} respectively, corresponding to the (V=O) stretching vibrations, and to the(V=O) frequency in chloro dreviteves late to weakness of bond among vanadium and oxygen [32]. The absorption peaks at1737.25 and 1644.57 are assigned to v(C=O) vibrations, in two complexes there were showed the highest shift to lower frequencies, vibration to be reduced by (171.71 - 374.43) of chloro dreviteves and (81.85- 91.32) cm-1of 5-nitro salicyaldehyde derivatives late to weakness of the bond between vanadium center and oxygen [29]. Unlike most of the known oxovanadium(IV) complexes that are five-coordinate the complexes reported here are four-coordinate as is shown by the elemental analysis in solid state. These complexes having different configuration in the solid state might be (4-cordinate) tetrahedral or (5-coordinate) square pyramidal or trigonal bipyrmidal configuration confirmed by the IR of these complexes suggest that in solid state to give polymeric state showed in oxovanadium(iv) complexes before [33]. In the solvent here used MeOH might be gave also 5-coordinating (square pyramidal or trigonal bipyramidal) configuration. Oxovanadium(IV) complexes are known to assume a square pyramidal or a trigonal bipyramidal. A consideration of the IR spectra of the ligands have shown a large change in the frequency of the carbonyl groups of the ligands on coordination to oxovandium(IV). This is consistent with the coordination of the carbonyl group of a ligand being coordinated to another to an adjacent oxovanadium(IV). It is very likely that the complexes in the solid state are polymeric.

Spectral data and elemental analysis in Table 4 shows all the synthesized ligands and their oxo vanadium (IV) complexes were in good agreement with their structure indicating the high purity of all the compounds. All result found % agree with the result (calculated %). Most of known vanadium(IV) complexes have a square pyramidal structure.

Application in epoxidation catalysis

The proposed mechanism, the first step is the oxidation of oxovanadium (IV) species to oxovanadium(V) species with H2O2, and the next step involves transferring one of its oxygen atoms to the substrates. The oxovanadium(IV) complexes can react further, ultimately forming oxodiametric specie. It seems that the approach of cyclooctene to the metal center take place fast. Blank reactions showed that no significant amounts of epoxide are formed in the absence of catalyst. At 20°C temperature the complexes show lowest conversion monitored in Tables 5, 8, are compared at different temperature this meaning before the olefin in partial conversion .The temperature was increase to 60°C the conversion show that the conversion of olefin started show Tables 6,9. The reaction observed high conversion at 78°C indicating complete conversion of olefin is reached with catalyst decomposes, see Tables 7 and 10, Complex VOL_1 gave also high conversion (88.42%) after 10 h at 78°C, compared with the complex VOL_2The 5- nitro derivative complexe at all temperatures (20,60 and 78) °C and time,2 and 10 h found results 86.71 % with reactions which shown slower conversion than complexe VOL_3 at 78°C, Generally, the values are higher conversion for 5-chloro salicylaldehyde amino acids derivative first complex than 5-nitro salicyaldehyde amino acids derivative in second complex under optimized conditions, these in agreement with that reported by reference [34] complexes . In general the complex VOL_1 was gave the best rate (1.1×10-10) mole mg-1 s-1 at 78°C after 2h coppeared to the complex VOL_2 was gave the (8.00×10-11) mole mg-1 s-1 at78°C after 2hr.

The pattern of reactivity showed that the oxovandium(IV) complexes bonded to the chloro substituent are more reactive than those bonded to the nitro group. The IR spectra have shown a considerable decrease in the V=O frequency bond in the former complexes compared to the latter ones.

IV. Conclusion

In conclusion the four new ligands namely, 5chlorosalycialdehyde– alanine (H_2L_1), 5-nitrosalycialdehyde–alanine (H_2L_2) and oxovanadium(IV) complexes VOL_1, and VOL_2 have been synthesized. A consideration of the IR spectra of the ligands have shown a large change in the frequency of the carbonyl groups of the ligands on coordination to oxovandium(IV). This is consistent with the coordination of the carbonyl group of a ligand being coordinated to another to an adjacent oxovanadium(IV). It is very likely that the complexes in the solid state are polymeric. The catalytic activity of the two complexes was tested using the epoxidation of cyclooctene. The results showed that the oxovanadium (IV) complexes were found to be very active in the epoxidation of cyclooctene under optimized conditions. We recommend that to do more about polymeric oxovanadium complexes in solid and liquid state and which one is active as catalyst.

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Disclosure statement

Conflict of interest: we declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from us.

Conclusion

In conclusion the four new Schiff base ligands namely, 5chlorosalycialdehyde– alanine (H_2L_1), 5-nitrosalycialdehyde–alanine (H_2L_2) and oxovanadium(IV) Schiff base complexes VOL_1, and VOL_2 have been synthesized. A consideration of the IR spectra of the ligands have shown a large change in the frequency of the carbonyl groups of the ligands on coordination to oxovandium(IV). This is consistent with the coordination of the carbonyl group of a ligand being coordinated to another to an adjacent oxovanadium(IV). It is very likely that the complexes in the solid state are polymeric. The catalytic activity of the four complexes was tested using the epoxidation of cyclooctene. The results showed that the oxovanadium (IV) Schiff base complexes were found to be very active in the epoxidation of cyclooctene under optimized conditions. We recommend that to do more about polymeric oxovanadium complexes in solid and liquid state and which one active as catalyst.

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References

[1]. Chohan, Z.H.; Sheazi, S.K.A. Synthesis and characterization of some Co(II), Cu(II) and Ni(II) complexes with nicolinylhydrazine derivatives and their biological role of metals and anions (SO4 2− , NO3 − , C2O4 2− and CH3CO2−) on the antibacterial properties. Synth. React. Inorg. Met.-Org. Chem. 1999, 29, 105-118.

[2]. Jayabalakrishnan, C.; Natarajan, K. Synthesis, characterization and biological activities of ruthenium(II) carhonyl complexes containing bifunctional tridentate Schiff bases. Synth. React. Inorg. Met.-Org. Chem. 2001, 31, 983-995.

[3]. Jeeworth, T.; Wah, H.L.; Bhowon, K.; Ghoorhoo, M.G.; Babooram, D. Synthesis and antibacterial/catalytic properties of schiff bases and Schiff base metal complexes derived from 2,3-diaminopyridine. Synth. Read. Inorg. Met.-Org. Chem. 2000, 30, 1023-1038

[4]. Drozdzak, R., Allaert, B., Ledoux, N., Dragutan, I., Dragutan, V., Verpoort, F., “Ruthenium complexes bearing bidentate Schiff-base ligands as efficient catalysts for organic and polymer synthesis”, Coordination Chemistry Reviews, 249, 15, December 2005, pp. 3055- 3067.

[5]. Pariya, C., Jayaprakash, K.N., Sarkar, A., “Alkene metathesis: new developments in catalyst design and application”, Coordination Chemistry Reviews, 168, January 1998, pp. 1-48.

[6]. Gan, C., Lai, G., Zhang, Z., Wang, Z., Zhou, M., “Efficient and enantioselective nitroaldol reaction catalyzed by copper Schiff-base complexes”, Tetrahedron: Asymmetry, 17, 5, March 2006, 725-728.

[7]. Liu, D.F., Lu, X.Q., Lu, R., “Homogeneous and heterogeneous styrene epoxidation catalyzed by copper(II) and nickel(II) Schiff base complexes”, Transition Metal Chemistry, 39, 6, September 2014, pp. 705-712.

[8]. Ray, A., Rosair, G.M., Pilet, G., Dede, B., Gomez- Garcia, C.J., Signorella, S., Bellu, S., Mitra, S., “Preferential azido bridging regulating the structural aspects in cobalt(III) and copper(II)–Schiff base complexes: Synthesis, magnetostructural correlations and catalytic studies”, Inorganica Chimica Acta, 375, 1, September 2011, pp. 20-30.

[9]. Kardanpour, R., Tangestaninejad, S., Mirkhani, V., Moghadam, M., Mohammadpoor-Baltork, I., Zadehahmadi, F., “Efficient alkene epoxidation catalyzed by molybdenyl acetylacetonate supported on aminated UiO-66 metal−organic framework”, Journal of Solid State Chemistry, 226, March 2015, pp. 262-272.

[10]. Shrikanth, A., Nagendrappa, G., Chandrasekaran, S., “Catalytic epoxidation of cyclic vinyl silanes by ruthenium(II) complexes under aerobic conditions”, Tetrahedron, 59, 39, September 2003, pp. 7761-7765.

[11]. Sabater, M.J., Corma, A., Domenech, A., Fornes, V., Gancia, H., “Chiral salen manganese complex encapsulated within zeolite Y: a heterogeneous enantioselective catalyst for the epoxidation of alkenes”, Chemical Communications, 14, January 1997, pp. 1285-1286.

[12]. De Clercq, B., Verpoort, F., “Assessing the scope of the introduction of Schiff bases as co-ligands for monometallic and homobimetallic ruthenium ring-opening metathesis polymerisation and ring-closing metathesis initiators”, Advanced Synthesis and Catalysis, 344, 6-7, August 2002, pp. 639-648.

[13]. Xi, Z., Wang, H., Sun, Y., Zhou, N., Cao, G., Li, M., “Direct epoxidation of olefins catalyzed by heteropolyoxometalates with molecular oxygen and recyclable reductant”, Journal of Molecular Catalysis A: Chemical, 168, 1-2, March 2001, 299-301.

[14]. Canali, L., Sherrington, D.C., “Utilisation of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis”, Chemical Society Reviews, 28, 2, January 1999, pp. 85-93.

[15]. Maurya, M. R. A. Kumar, J. Mol. Cata. Chem, 2006., 250, 190

[16]. Solomon, E.I., Sundaram, U.M., Machonkin, T.E., “Multicopper oxidases and oxygenases”, Chemical Reviews, 96, 7, November 1996, pp. 2563-2606.

[17]. Ho C. W., Cheng W. C., Cheng M. C., Peng S. M., Cheng K. F., Che, C.M., “Preparation and reactivities of chiral manganese(III) and copper(II) complexes of binaphthyl Schiff bases”, Journal of the Chemical Society, Dalton Transaction, 4, January 1996, pp. 405-414.

[18]. Wei, F.Y., “A mononuclear nickel(II) complex and a dinuclear manganese(III) complex derived from N,N'- bis(5-methoxysalicylidene)-1,2-ethanediamine: Synthesis, crystal structures and catalytic epoxidation property”, Russian Journal of Coordination Chemistry, 42, 1, January 2016, pp. 44-49.

[19]. Ramos, M.L. M.M. Calderia, V.M.S. Gil, J. Chem. Soc., 2000, Dalton Trans., 2099

[20]. G. Du, S. Lim, M. Pinault, C. Wang, F. Fang, L. Pfefferle, G.L. Haller, J. Catal., 2008, 253, 74.

[21]. Maurya, M. R. A. Kumar, J. Mol. Cata. Chem., 2006, 250, 190.

[22]. Maurya, M. R. S. Sikarwar, J. Mol. Cata. Chem., 2007, 263, 175.

[23]. Kirillova, M. V. M. L. Kuznetsov, V. B. Romakh, L. S. Shul’pina, J. J. R. Frasto da Silva, A. J. L. Pombeiro, G. B. Shul’pin, J. Catal., 2009, 267, 140.

[24]. Judmaier, M.E., Holzer, C., Volpe, M., Mosch- Zanetti, N.C., “Molybdenum(VI) dioxo complexes employing Schiff base ligands with an intramolecular donor for highly selective olefin epoxidation”, Inorganic Chemistry, 51, 8, August 2012, pp. 9956-9966.

[25]. Alsalim, T. A., Hadi, J. S., Ali, O. N., Abbo, H. S., & J Titinchi, S. (2013). J. Cen. Chem, 15.

[26]. EI- Hendawy, A. M., EI-Kourashy, E. G., Shanab, M. M. (1992). Polyhedron, 11: pp. 523-530.

[27]. J. W. Kick, M. Anneser, B. Hofmann, A. Pcthig, M. Cokoja, F. Kuhen, ChemPubSoc Eurepe, 2015 , 8, pp, 4056

[28]. Dickman, M. H. M. T. Pope, Chem. Rev,1994., 94, pp.569

[29]. Butler, A. M. J. Clague, G. E. Meister, Chem. Rev. ,1994, 94, pp.625.

[30]. Rehman, M. Imran, M. Arif, A. J. App. Chem. (2013), pp,59

[31]. Grivani, G. Bruno, H.A. Rudbari, A.D. Khalaji, P. Pourteimouri, Inorg. Chem. Commun, 2012., 18,pp, 15

[32]. Alsalim T. A., J. S. Hadi, O. N. Ali, H. S. Abbo and S. J Titinchi, J. Cen. Chem. 2013 ,pp,15

[33]. Hon S. W., C. Hsin Li, J.H. Kuo, N. B. Barhate, Y.H. Liu,Y. Wang, C.T. Chen, J. Am. Chem. Soc. 2001., 3, pp, 869

[34]. Nazarov, A.M.S.L.Khursan, G.A.Yamilova, V.D.Komissarov, Russ. Chem. Bull,1999, 48, 1079.

Supplementary (1)

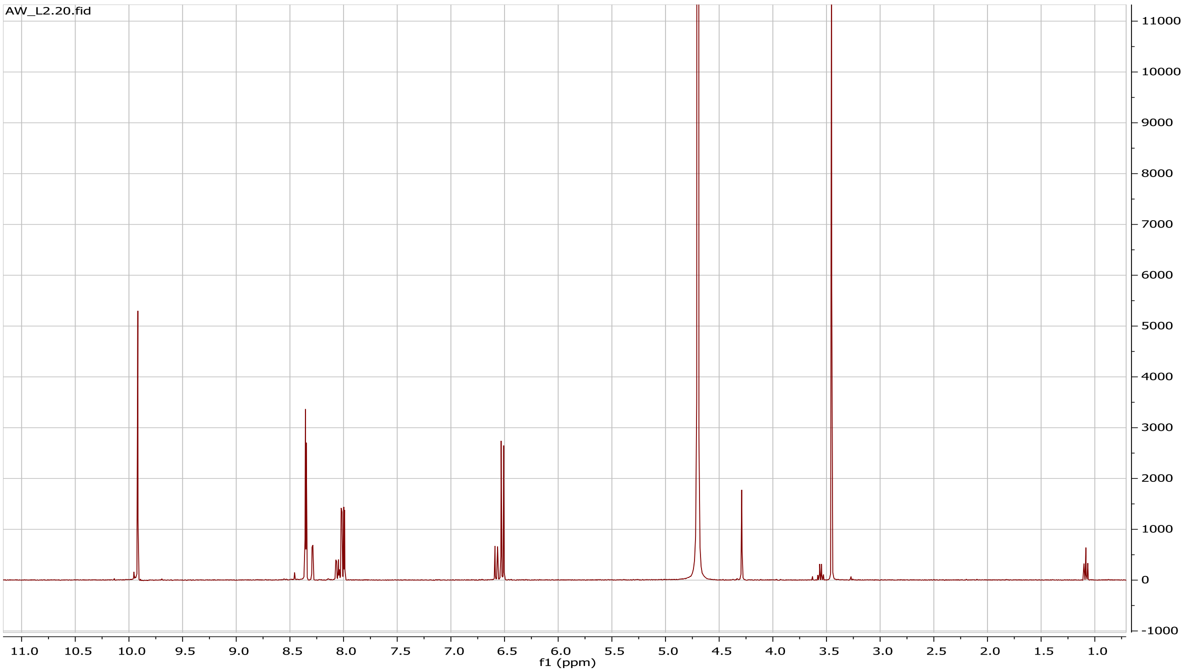

Fig-1: ^{1}HNMR for the H_2L_1

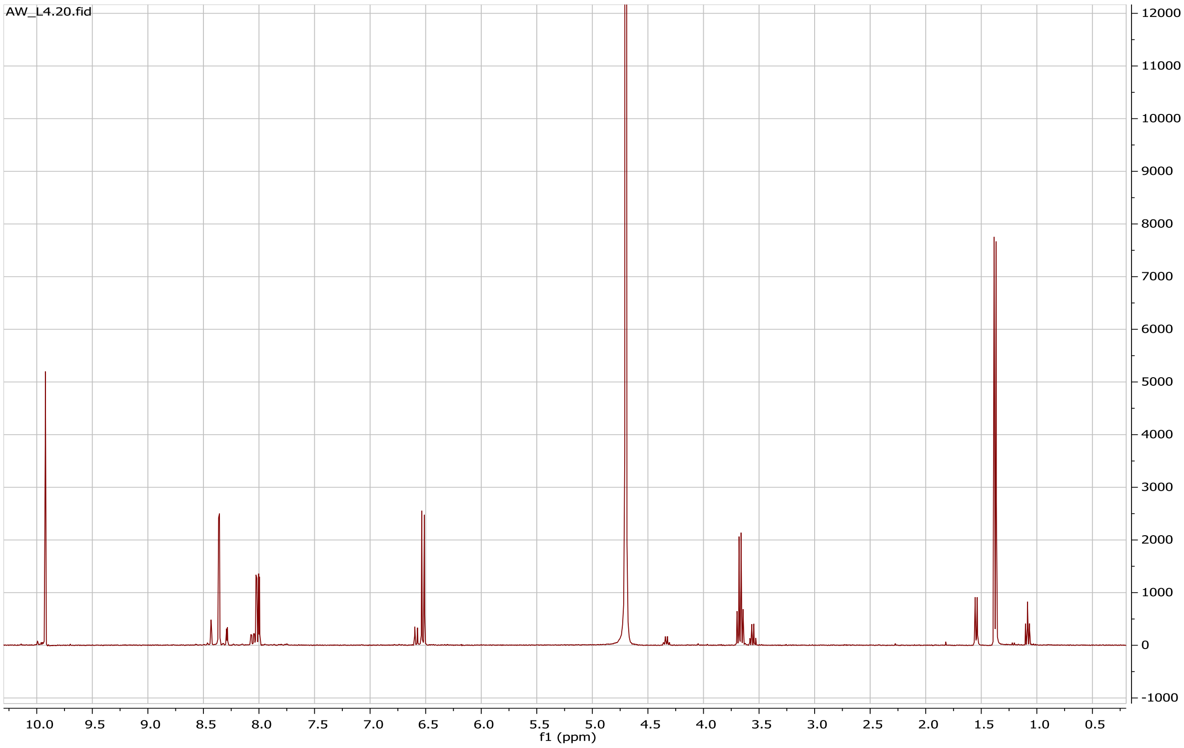

Fig-2: ^{1}HNMR for the H_2L_2

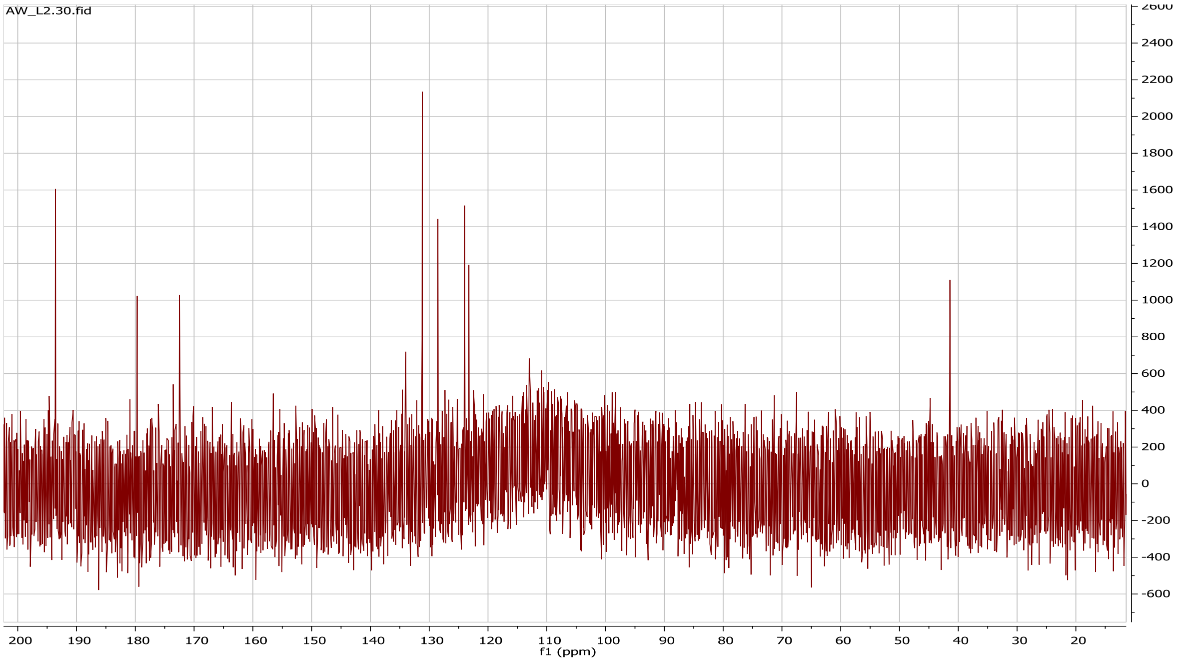

Fig-3: ^{13}C NMR for the H_2L_1

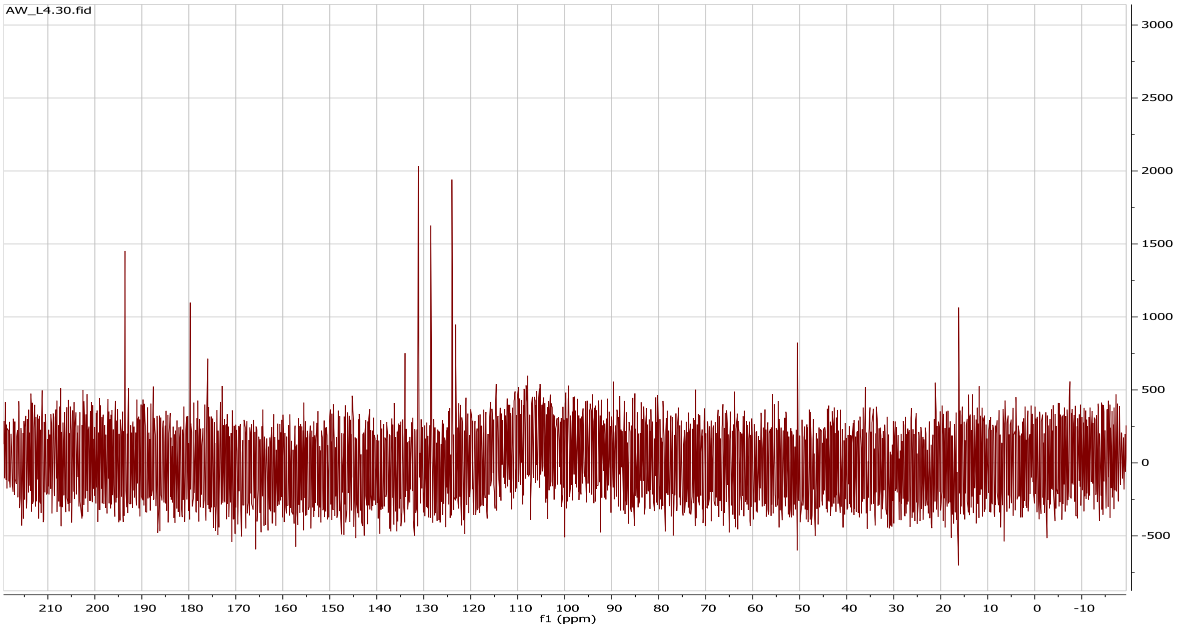

Fig-4: ^{13}C NMR for the H_2L_2

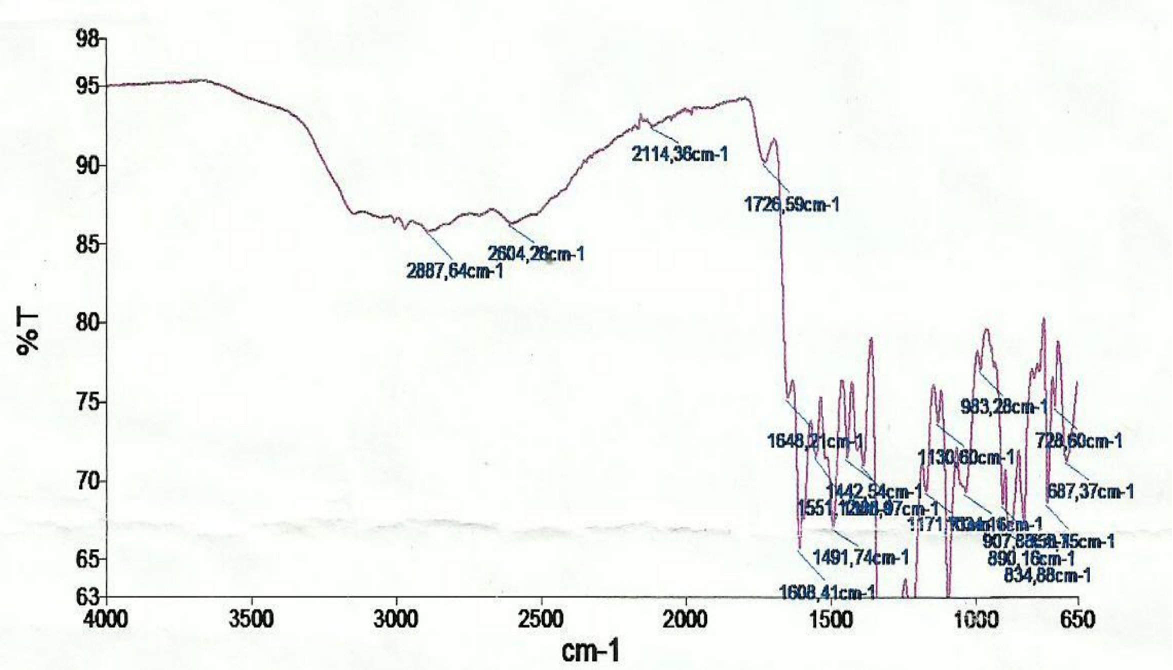

Fig-5: IR Spectral of the H_2L_1

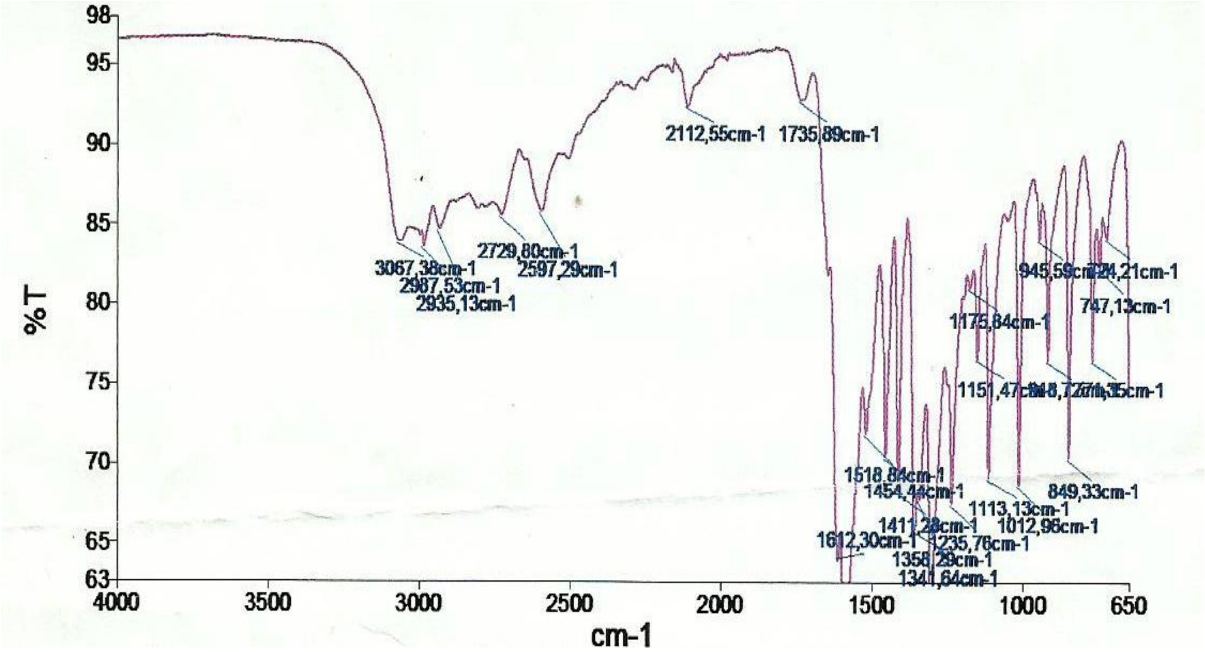

Fig-6: IR Spectral of the H_2L_2

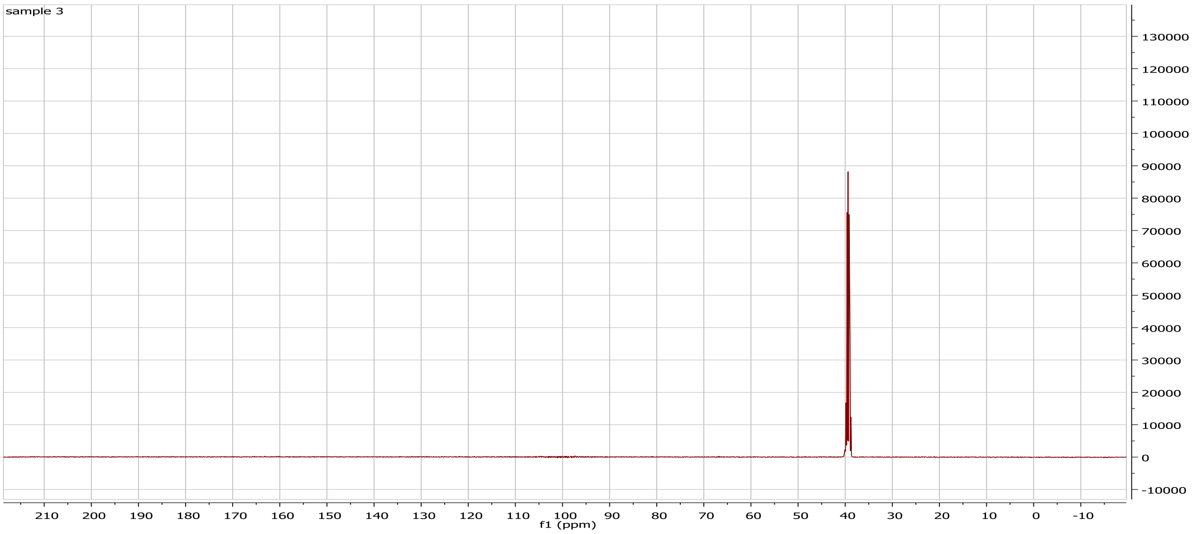

Fig-7: ^{1}H NMR for the VOL_1

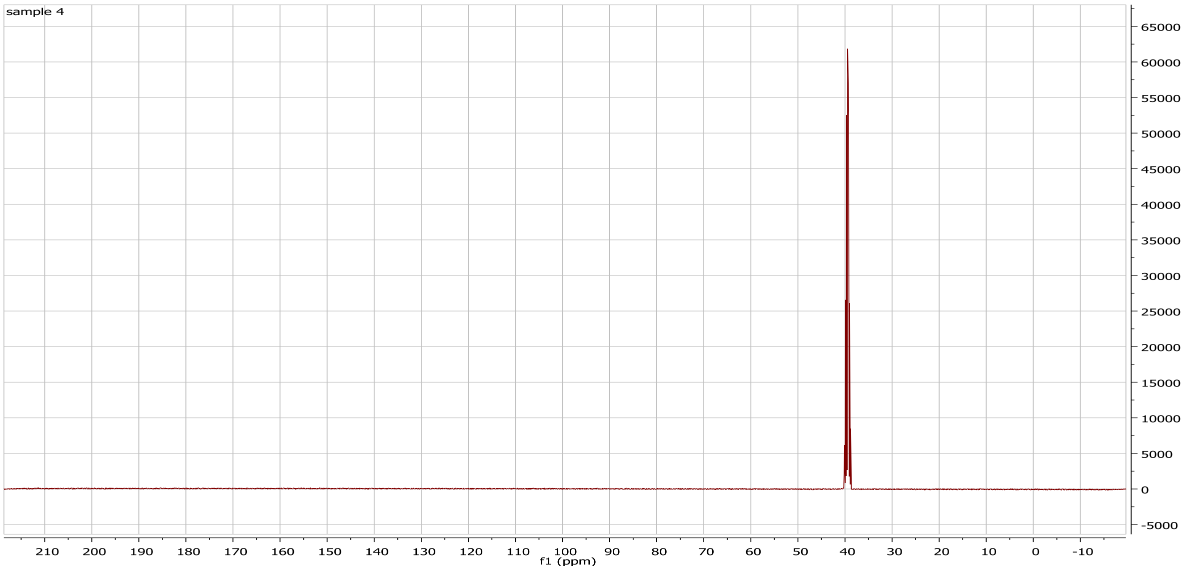

Fig-8: ^{1}H NMR for the VOL$_2$

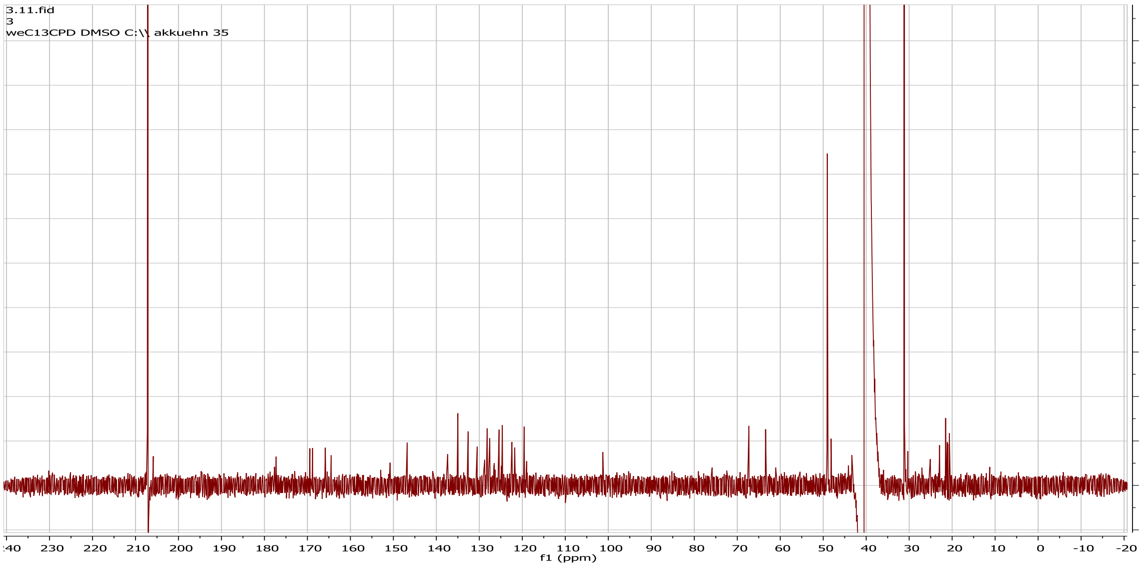

Fig-9: ^{13}C NMR for the VOL$_1$

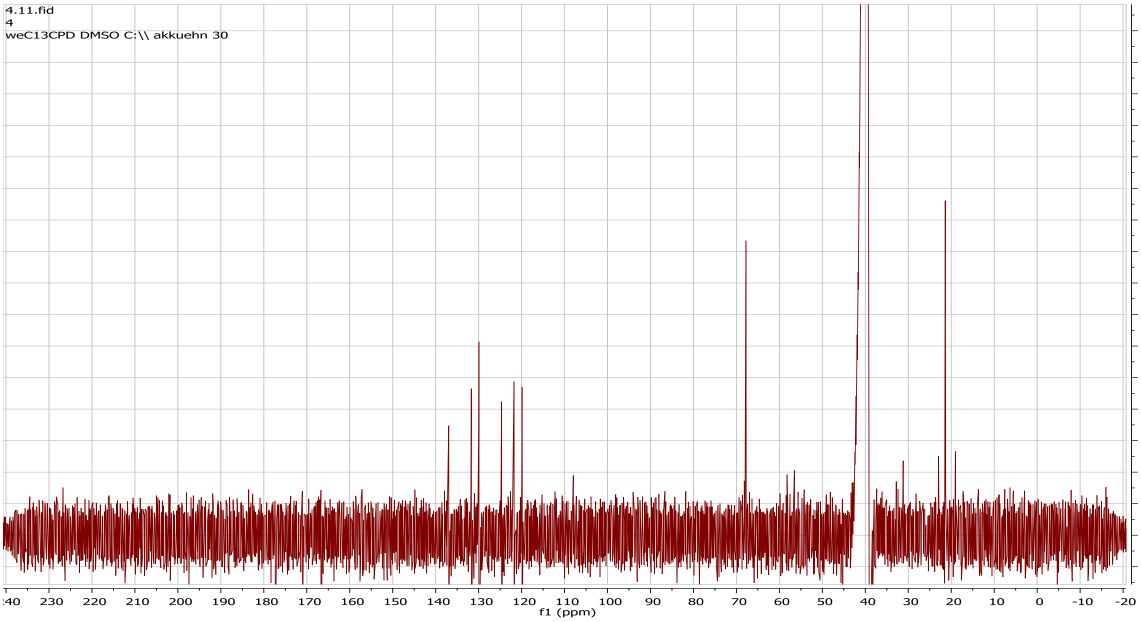

Fig-10: ^{13}C NMR for the VOL$_2$

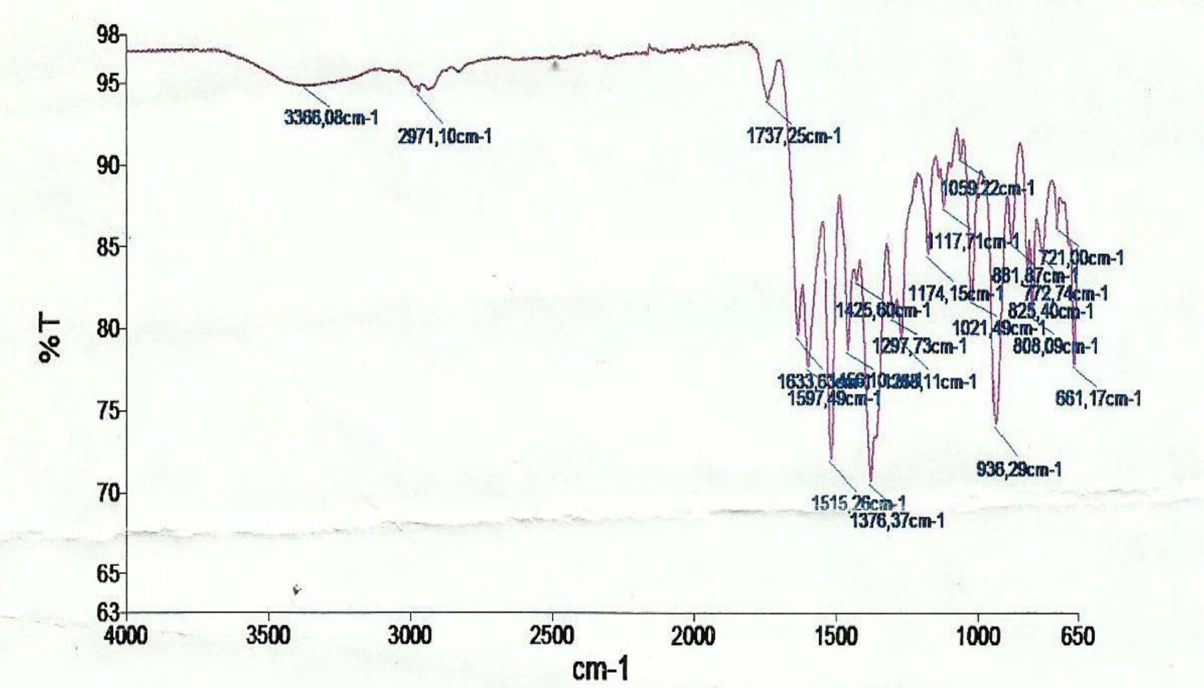

Fig-11: IR Spectral for the VOL$_1$

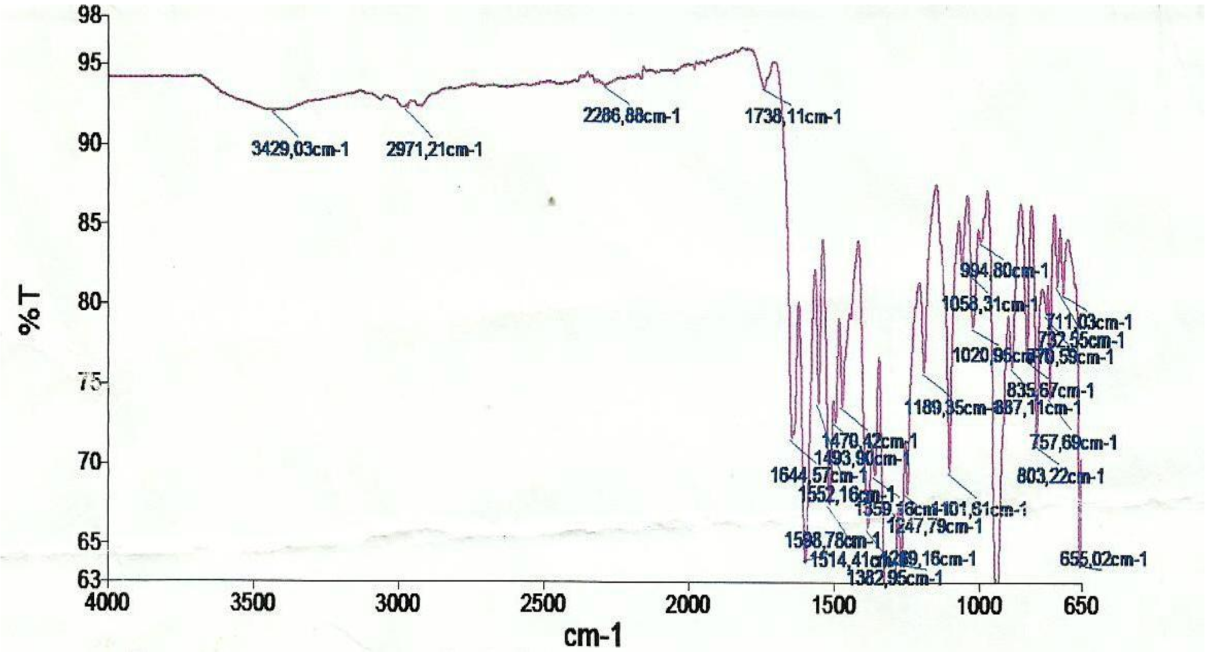

Fig-12: IR Spectral for the VOL$_2$

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