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Synthesis and Comprehensive Spectroscopic Investigations of Novel Mixed-Ligand Oxovanadium Complexes

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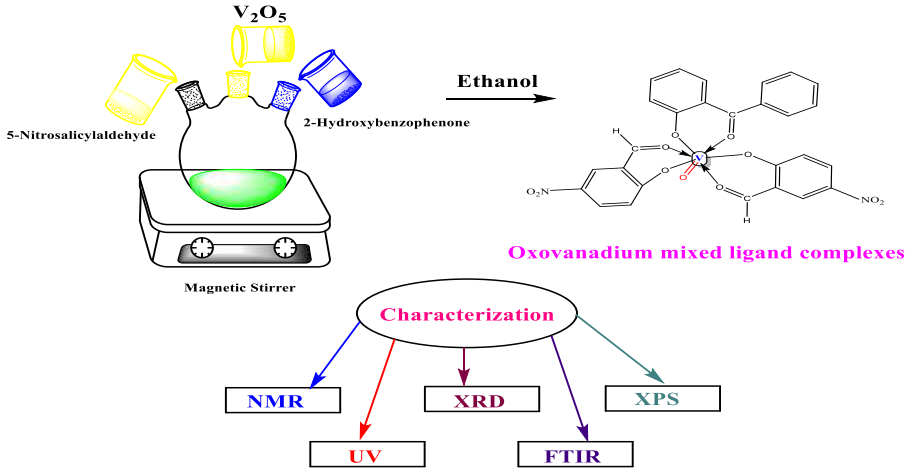
ABSTRACT

*Numerous kinds of Oxovanadium complexes of the type [VO(PL)$_2$(SL)] were produced using 5-nitrosalicylaldehyde as the major primary ligand **(PL)**and 2-hydroxybenzophenone, 1-phenyl-1,3-butanedione, and 5-chlorosalicylaldehyde as secondary ligands **(SL).**These compounds were produced using standard reflux techniques and confirmed through FT-IR, X-ray photoelectron spectroscopy (XPS), UV-visible, ^{1}H-NMR, and X-ray diffraction (XRD) micro elemental evaluation. As demonstrated by the appearance of characteristic ν(V=O) vibrations, modifications in ν(C=O) bands, and the removal of phenolic –OH signals, spectral investigations confirmed coordination between phenolic and carbonyl oxygen atoms. Electronic spectrum investigations revealed evidence of a distorted octahedral geometry surrounding the vanadium center, including low-intensity electronic transitions within the metal d-orbitals and ligand to metal charge transfer . procedures.XPS study identified the mixed oxidation states of vanadium (V^{5+}/V^{4+})and confirmed metal–oxygen coordination via V–O–C bonding.*

Keywords: *Oxovanadium complexes, mixed ligand, coordination chemistry, spectroscopy.*

GRAPHICAL ABSTRACT



1. INTRODUCTION

Researchers have long been captivated by transition metals because of their remarkable configurations toward various ligand fields that share structural liability, donor moiety, and molecular environment receptivity [1-3].In the last 10 years, coordination chemistry of vanadium with multidentate ligands has drawn particular attention due to its significance in catalysis[4-5], industry[6-7], medicine[8-9]and pharmacological properties. [10-11]
Vanadium may reach a variety of stable oxidation states due to its ground-state electron configuration [Ar] $3d^3$ $4s^2$.[12]Stable coordination complexes are formed by vanadium (IV) and (V), but vanadium (II) and (III) are less stable and only accessible in reducing circumstances.In general, however, the accessibility of low and high oxidation states depends on the nature of the ligands[13-19].Mixed ligand complexes of transition metals with β-diketone and its derivative have been synthesised with considerable effort [20-22].Due to their many biological actions, including antibacterial, Antidiabetes, antiviral, antioxidant, antifungal, and anticancer effects,

transition metal complexes ligated with β-diketone and its derivative have garnered a lot of attention [23-25].Maximum mixed ligand complexes are generated in 1:1:1 molar ratio [26-28]some other complexes are also created in 2:1:2 molar ratio of metal: main ligand: secondary ligand accordingly [29-30].

In this article, the synthesis of mixed ligand complexes in **1:2:1**molar ratio of metal: L_1:L_2 accordingly.The interaction between O,Odonar and O,N donar ligand groups with simple vanadium species (VO^{2+} and VO^{3+}). With an O,O donor atom, β-diketone and substituted salicylaldehydare great chelating group.The synthesis of new mixed ligand vanadium complexes with V_2O_5 as the metal precursor is the major focus of this investigation.The major ligand used is 5-nitrosalicylaldehyde **(PL)**, a substituted salicylaldehyde possessing both phenolic –OH and aldehydic functional groups, which allows chelation through oxygen donor atoms. In order to create stable chelated frameworks around the vanadium core, the main ligand is used in two molar equivalents in each compound. To create unique mixed ligand complexes, three different secondary ligands **(SL)** are added 2-hydroxybenzophenone, 1-phenyl-1,3-butanedione, and 5-chlorosalicylaldehyde.FT-IR, UV-Visible, ^{1}H NMR, XRD, XPS techniquesand Micro elemental analysis was used to examine the generated complexes.

2. MATERIALS

Recrystallisation with hot ethanol has been used to purify 5-nitrosalicylaldehyde (TCI), 2-hydroxybenzophenone (TCI), 1-phenyl-1,3-butanedione (TCI), and 5-chlorosalicylaldehyde (TCI). Before being used, n-butanol, 5-nitrosalicylaldehyde, and 5-chlorosalicylaldehyde were filtered using distillation.V_2O_5 of A.R. grade was utilised, as stated.

2.1 Physical Dimensions

KBr pellets were used to measure IR spectra using a PerkinElmer. The Agilent Cary 5000 UV-Visible-NIR spectrometer was used to identify UV-visible spectral data.1H spectra were obtained using an ECS 400MHz (JEOL) NMR spectrometer in DMSO-D6.1H chemical shifts are expressed in parts per million (ppm) with reference to Me4Si.Thermo Fisher Scientific's K-Alpha model was used to measure XPS spectra.XRD spectra were obtained using the Miniflex-600 X-ray Diffractometer (Table top).

2.2 Preparation

2.2.1 Synthesis of complexes A

Synthesis of novel ligand complex of V_2O_5 with 5-Nitrosalicylaldehyde and 2-hydroxybenzophenone

V2O5 (0.55 mmol, 0.10 g in 10 ml), 5-nitrosalicylaldehyde (1.197 mmol, 0.20 g in 10 ml), and 2-hydroxybenzophenone (0.555 mmol, 0.11 g in 10 ml) were added to an ethanolic solution while stirring continuously.To raise the mixture's pH to around 7.5, a 5% aqueous solution of sodium hydroxide was gradually added dropwise while continuing to mix. This treatment was carried out for six hours. The reaction mixture was then kept under reflux for five hours before being allowed to sit at room temperature for twelve.The settling solid was filtered, washed with ethyl alcohol and then ether, and dried properly under moderate pressure to get rid of stickiness.

2.2.2 Synthesis of complexes B

Synthesis of novel ligand complex of V_2O_5 with 5-Nitrosalicylaldehyde and1-phenyl-1,3-butanedione

Stirring constantly, ethanolic solutions of 2-hydroxybenzophenone (0.555 mmol, 0.11g in 10 ml), 5-nitrosalicylaldehyde (1.197 mmol, 0.20g in 10 ml), and V2O5 (0.55 mmol, 0.10g in 10 ml) were added.A 5% aqueous solution of sodium hydroxide was progressively added dropwise while the liquid was continually stirred in order to elevate the pH of the mixture to about 7.5. The duration of this process was six hours. After five hours of reflux, the reaction mixture was let to rest at room temperature for twelve hours.To get rid of stickiness, the settling solid was filtered, cleaned with ether and ethyl alcohol, and dried appropriately under moderate pressure.

2.2.3 Synthesis of complexes C

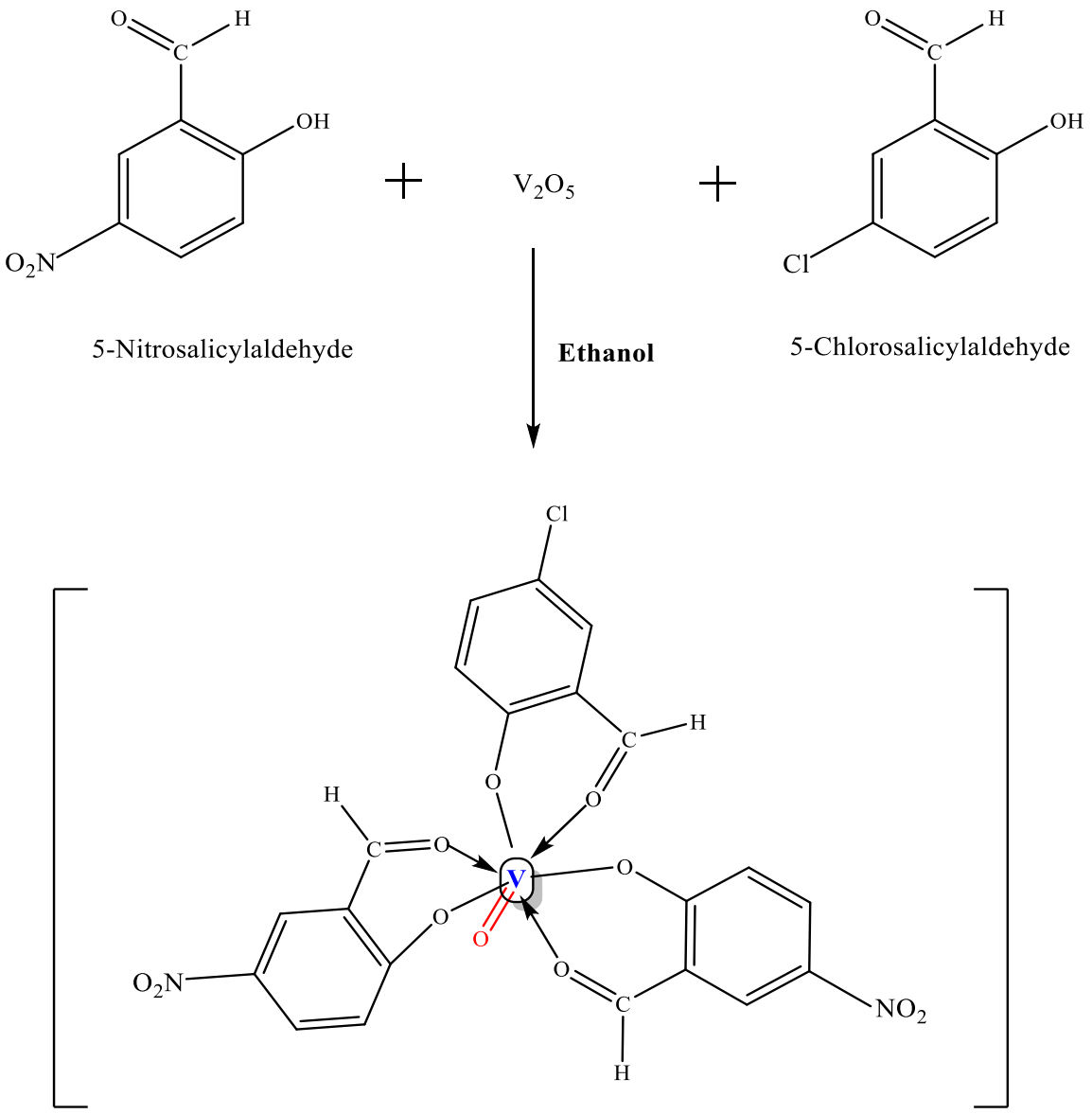
Synthesis of novel ligand complex of V_2O_5 with 5-Nitrosalicylaldehyde and 5-chlorosalicylaldehyde

An ethanolic solution was mixed with V2O5 (0.55 mmol, 0.10 g in 10 ml), 5-nitrosalicylaldehyde (1.197 mmol, 0.20 g in 10 ml), and 2-hydroxybenzophenone (0.555 mmol, 0.11 g in 10 ml) while being constantly stirred.A 5% aqueous solution of sodium hydroxide was progressively added dropwise while the mixture was

still being mixed in order to elevate the pH to about 7.5. For six hours, this therapy was administered. After five hours under reflux, the reaction mixture was let to remain at room temperature for twelve hours.To remove stickiness, the settling solid was filtered, cleaned with ether and ethyl alcohol, and dried appropriately under moderate pressure.

3. Results And Discussion

Vanadium mixed ligand complexes are formed when V_2O_5 reacts with 5-nitrosalicylaldehyde and β-diketones, such as 2-hydroxybenzophenone, 1-phenyl-1,3-butanedione, and salicylaldehyde derivative, 5-chlorosalicylaldehyde, in **1:2:1**molar ratios.**(Scheme-1)**



Scheme 1: Synthesis of novel mixed ligand complexes C of Vanadium with 5-Nitrosalicylaldehyde and 5-chlorosalicylaldehyde

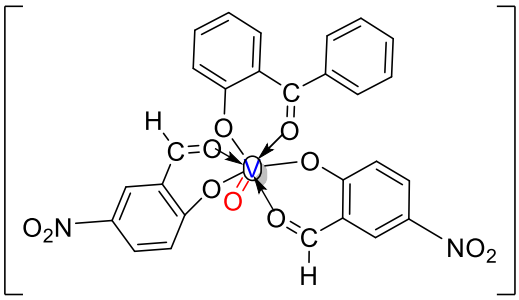


Figure 1: Structure of complex A "[VO(NO_2sal)$_2$(hbp)]"

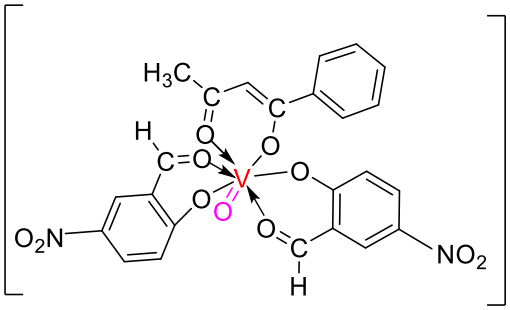


Figure 2: Structure of complex B "[VO(NO_2sal)$_2$(bzac)]"

For these mixed ligand complexes, deformed octahedral geometry has been suggested, which results in yellow-coloured solids. The determined values for the related complexes are in good accordance with proportion of C, H, and V. The complexes display a propensity to break down when heated to extreme temperatures. These are entirely soluble in DMF and DMSO, but very weakly soluble in nitrobenzene, chloroform, benzene,carbon tetrachloride and a wide range of organic solvents. **Table 1**shows the microanalytical data of the resultant complexes.

Table 1: Analytical and Spectroscopic Characterization of Mixed-Ligand Complexes

S.No.	Complex	Color Yield %	Molecular Formula Molecular Weight	Analysis%Found (calculated)			Melting point
				V	C	O	
A. 1.	[VO(NO_2sal)$_2$(hbp)]	Yellow 52.68	$C_{27}H_{17}O_{11}N_2$ V596.37 g/mol	8.47 (8.54)	54.27 (54.36)	29.30 (29.51)	310
B. 2.	[VO(NO_2sal)$_2$(bzac)]	Yellow 46.12	$C_{24}H_{17}O_{11}N_2$ V 560.34 g/mol	8.97 (9.09)	51.32 (51.46)	31.12 (31.41)	321
C.	[VO(NO_2sal)$_2$(5-Clsal)]	Yellow 59.56	$C_{21}H_{12}O_{11}N_2ClV$ 599.17 g/mol	8.61 (8.50)	41.93 (42.09)	29.67 (29.37)	318

3.1 UV–Visible Spectral Studies

Figure 3 represents the produced oxovanadium complexes's UV-visible spectra which showed distinctive absorption bands that corresponded to ligand-centred and charge transfer transitions. Aromatic ring $\pi \rightarrow \pi^*$ transitions are responsible for the intense bands seen in the 250–300 nm range.[31-32], while bands near 300–360 nm correspond to $n \rightarrow \pi^*$ transitions of carbonyl groups.[33]Prominent absorption in the visible range (420–450 nm) is assigned to ligand-to-metal charge transfer (LMCT), indicating strong relationship between ligand

donor atoms and the vanadium center.[34] Weak bands in the 550–650 nm region are attributed to d–d transitions, supporting the distorted octahedral geometry around the metal ion.[35] **(Table-2)**

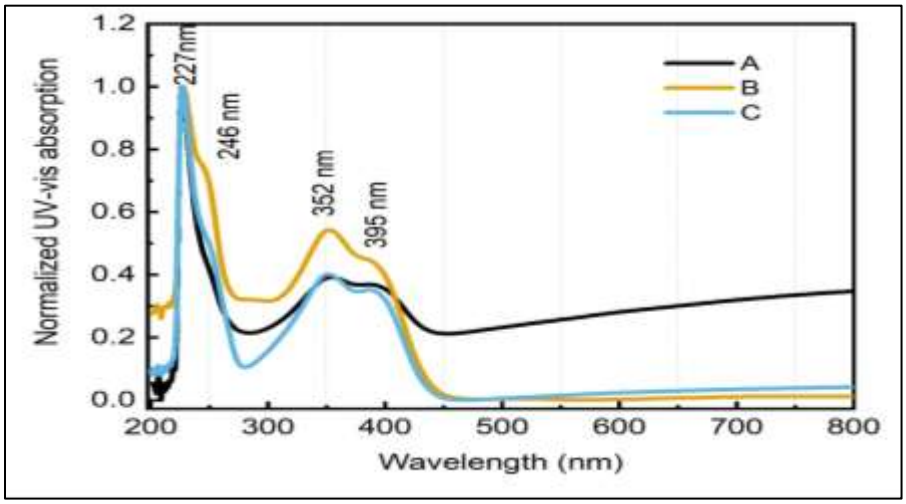


Figure 3: UV–Visible spectra of synthesized complexes

Table 2: Electronic Spectroscopic Data of Synthesized Mixed-Ligand Complexes

Complex	λmax (nm)	Assignment	Transition Type
[VO(NO$_2$sal)$_2$(hbp)]	275	Aromatic ring	π → π*
	340	Carbonyl group	n → π*
	430	LMCT	Ligand→ Metal
	580	Weak band	d–d transition
[VO(NO$_2$sal)$_2$(bzac)]	280	Aromatic ring	π → π*
	355	β-diketone	n → π*
	445	LMCT	Ligand→ Metal
	600	Weak band	d–d transition
[VO(NO$_2$sal)$_2$(Clsal)]	270	Aromatic ring	π → π*
	335	Carbonyl group	n → π*
	420	LMCT	Ligand→Metal
	570	Weak band	d–d transition

The observed spectral features collectively confirm successful complex formation and metal-ligand interaction.

3.2 FT-IR Spectra

IR spectra confirmed coordination of Vanadium complexes through carbonyl and phenolic atoms. The carbonyl stretching vibration ν(C=O), which generally appears near 1660–1680 cm^{1}in free ligands, shows a downward shift (~1618–1632 cm^{-1}) in the complexes. This shift is attributed to electron density transfer from the ligand to the vanadium center, weakening the C=O bond and confirming coordination [36]. A strong and sharp band observed around **965–975**cm^{-1} is assigned to the terminal oxo group (V=O) stretching vibration,

which is a distinct characteristic of oxovanadium(V) complexes. The existence of this band strongly supports the formation of oxovanadium species [37]. Furthermore, new bands emerging in the low-frequency range (~530–550 cm^{-1}) correspond to ν(V–O) vibrations, confirming the formation of metal–ligand bonds[38]**.** The nitro group (–NO_2) of 5-nitrosalicylaldehyde shows asymmetric and symmetric stretching vibrations at 1520–1540 cm^{-1} and 1340–1360 cm^{-1}, respectively. These bands undergo slight shifts in the complex, indicating the involvement of the nitro-substituted aromatic ring in coordination through adjacent oxygen atoms, though the nitro group itself remains non-coordinated [39-40]. Additionally, weak bands appearing around **430–470**cm^{-1} are assigned to V–O (phenolate) bending modes [41] these confirms formation of VO(IV) complexes. Higher V–O frequency in sample C indicates stronger V–O bond.**(figure-4)**

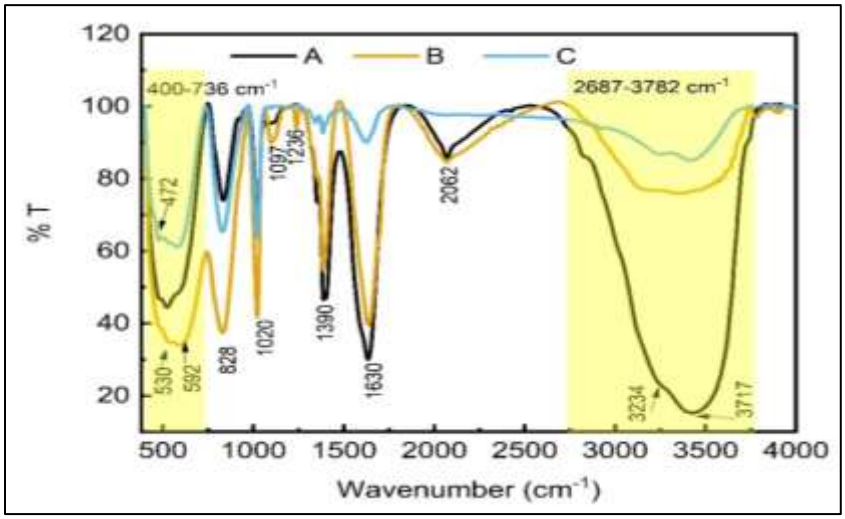


Figure 4: FT-IR Spectra of synthesized complexes

Additionally, C-O stretching vibration at 1200 cm^{-1} represent in free ligand, positively shifts towards the 1270cm^{-1}, 1265cm^{-1}, 1280cm^{-1} respectively for complex A, B, C presenting coordination through the deprotonated phenolic oxygen.Although these groups are not directly involved in metal coordination, noticeable shifts were observed in several bands in all complexes. These bands, assigned to aromatic C=C stretching, C–C, and C–H vibrations, were found to shift to either higher or lower frequencies. This variation is attributed to changes in the ligand environment upon coordination with the metal ion **(Table-3)**. The C-H stretching frequency peak at 2800 cm^{-1} - 3000cm^{-1} donates the aromatic C-H bond of the ligand. The C-H (aromatic) out-of-plane bending vibrations were observed between 900 and 700 cm^{-1}, while the in-plane bending vibrations were found between 1250 and 1000 cm^{-1}. The peak of the aldehydic C-H stretching frequency was detected between 2850 and 2720 cm-1.

Table 3: Important FT-IR Bands of resulting Complexes

Assignment	**Complex A(cm^{-1})**	**Complex B(cm^{-1})**	**Complex C(cm^{-1})**	**Interpretation**
C=O (aldehyde/ketone)	1625	1618	1632	Shift indicates coordination
C–O (phenolic)	1270	1265	1280	Metal–oxygen bonding
V=O	970	965	975	Oxovanadium formation
V–O	540	530	550	Metal–ligand bond

The observed spectral changes collectively indicate successful complex formation and coordination of ligands with vanadium central atom.

3.3 ^{1}H NMR Studies

The NMR data of all three complexes displays a complete disappearance of the phenolic –OH proton signal, which is typically observed in the region 10–13 ppm in free ligands. This confirms that the phenolic proton is lost during complex formation, resulting in coordination through the oxygen atom [42]. The aldehydic proton (–CHO) signal appears around 10.20ppm(Singlet), showing slight shifts compared to the free ligand. This indicates that while the aldehydic oxygen participates in coordination, the proton remains attached but experiences a different electronic environment due to metal–ligand interaction [43-44] .In Complex, which contains a β-diketone ligand, the enolic proton signal is absent, confirming enolate formation and strong chelation through oxygen atoms. Additionally, the presence of methyl proton(-CH_3) signals around 2.4 ppm further supports the incorporation of the diketone ligand. In β-diketone ligand enolic HC= bond peak at 7ppm [45-47].This overall spectral study supports the successful formation of mixed ligand oxovanadium complexes through oxygen atom coordination.

3.4 XRD Spectral studies

The major diffraction peaks of the complex [VO(5-Nitrosalicylaldehyde)$_2$(5-chlorosalicylaldehyde)] were observed at 2θ= 12°, 21°,25°, 27°, 30° and 33° and were subjected to crystallographic planes (101), (110), (112), (200), (202) and (220) respectively. This indicated the formation of highly ordered crystalline phase. Additionally, the purity of complex is confirmed by the lack of impurity peaks [48]. The Scherrer equation is utilized to estimate the crystallite size of synthesized complex and it was estimated to be between 40 and 45 nm (λ=0.15406 nm).For calculating density, crystallographic density equation was used and it was reported to be 1.85 g cm^{-3} [49]. The crystal system is found to be Monoclinic and its lattice parameters were calculated and were found as: a= 10.4Å , b=17.2Å , c= 12.1Å , α= 90° , β= 98.3° and γ= 90°.This study complements the successful formation of crystalline samples.

3.5 XPS Analysis

The XPS scanning spectra of thesample in the **figure 5** depicts that samples have mainly C, N, O and V elements. Further High-resolution core levels spectra of C 1s, N 1s,O 1s and V 2p, analyzed and charge correct in the binding energy carried out with respect to adventitious carbon and set it to 284.8 eV .[50-52]

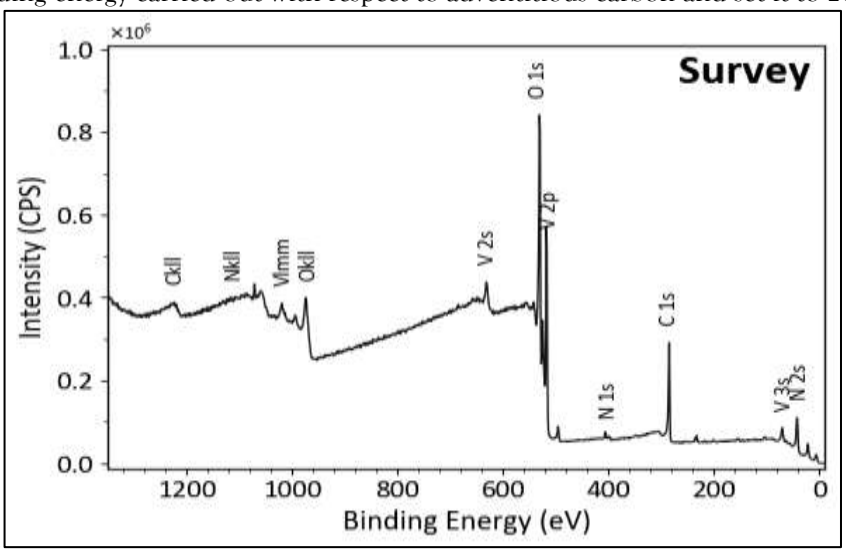


Figure-5: XPS survey spectrum of synthesized complexes

Figure 6 (a)indicates C 1s Core Level spectra and asymmetric peak deconvolutedint four peaks. The predominant peak of at 284.8 eV is assigned to C–C and C=C bonds, verifying the presence of an aromatic carbon.[51] A component at ~285.7 eV is attributed to C–O and/or C–N bonds, indicating functionalized carbon species.[52] A distinct peak at ~286.9 eV is assigned to C–O–V, which serves as strong evidence of

coordination between phenolic oxygen and vanadium.[47] The peak at ~288.9 eV relates to O–C=O groups, arising from oxidized carbon species.[52]

Figure 6 (b)describes the O 1s Core Level spectrum fitted with three components. The peak at binding energy at ~530.3 eV corresponds to lattice oxygen (V–O), indicating the presence of vanadium oxide .[53-54]A second component at ~532.0 eV is attributed to C–O and V–O–C bonds, which directly supports the formation of coordination between the ligand and the metal center .[53] Peak at ~533.5 eV is due to surface adsorption or contamination.

Figure 6 (c)signifies the N 1s spectrum shows a main peak at ~399.9 eV, corresponding to C–N bonds, indicating nitrogen present in the organic ligand framework.[55] A minimal contribution at ~398.3 eV is related to imine (C=N) or pyridinic nitrogen, suggesting the presence of conjugated nitrogen species. Another component at ~401.9 eV corresponds to protonated nitrogen, while a high binding energy peak at ~405.5 eV is assigned to oxidized nitrogen (N–O) species.[56] importantly, no peak corresponding to metal–nitrogen (V–N) bonding is observed,validating that nitrogen is not directly involved in coordination with vanadium.

V2p spectrum shows the spin-orbit splitting and presented in the **figure 6 (d)**. The spectrum is deconvolution for V^{5+} and V^{4+} oxidation states. The peak around ~517.5 eV is assigned to V^{5+} ($2p_{3/2}$), while the corresponding spin–orbit component appears at ~525.0 eV ($2p_{1/2}$).A lower binding energy peak at ~516.6 eV corresponds to V^{4+} ($2p_{3/2}$), with its counterpart at ~523.9 eV ($2p_{3/2}$). The observed spin–orbit splitting (~7.3 eV) is consistent with reported values.[54] The binding energy reveals the presence of mixed oxidation states of vanadium and majority is V^{5+} state. A weak satellite feature around ~522 eV is also observed of oxygen[57].

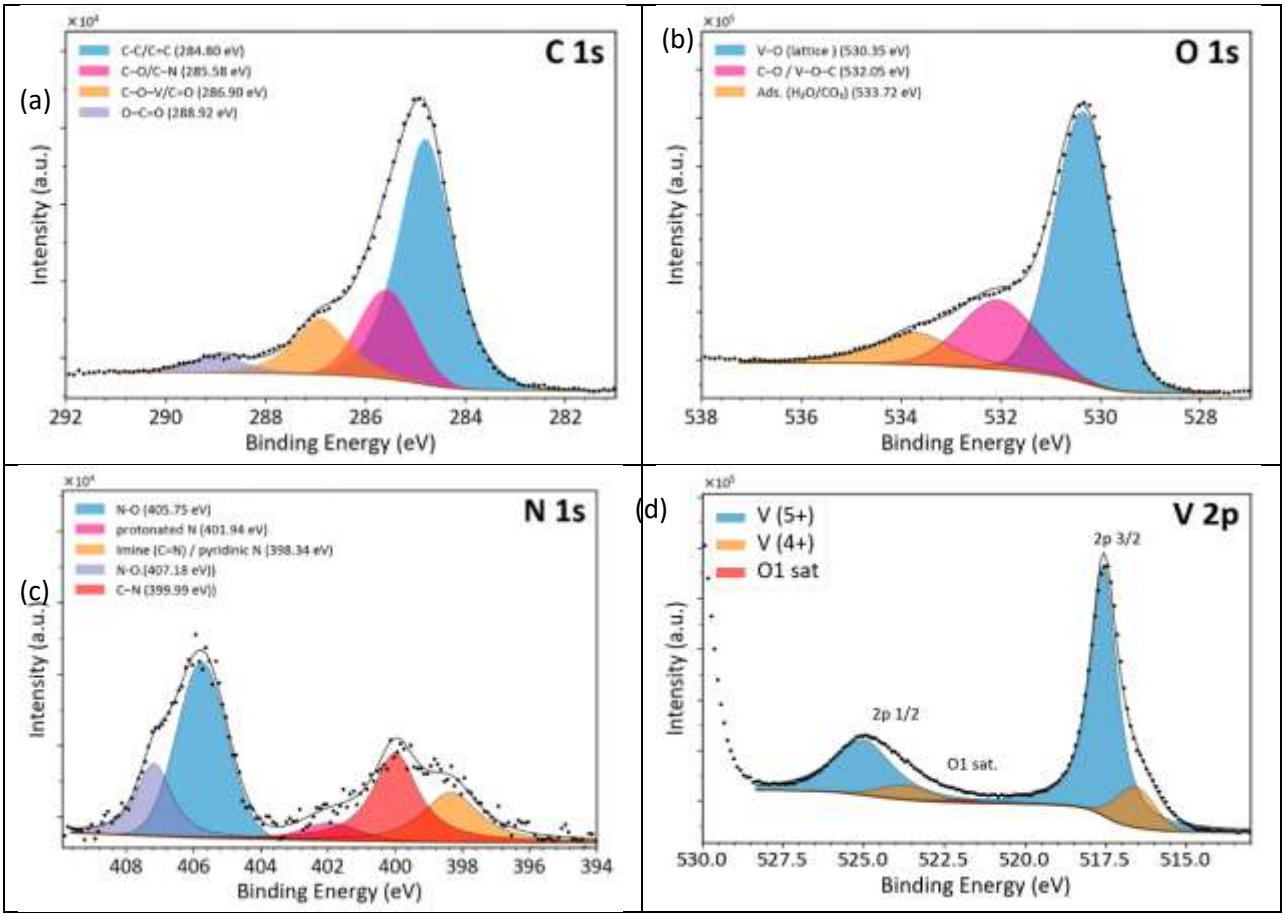


Figure 6: XPS Core Level spectra of (a) C 1s,(b) O 1s, (c) N 1s and (d) V 2p.

XPS results confirm formation of a vanadium–ligand coordination system mediated through phenolic oxygen (V–O–C bonding), accompanied by mixed valence states (V^{5+}/V^{4+}) and a well-defined aromatic framework, with nitrogen present but not directly involved in metal coordination.

4. CONCLUSION

Numerous novel mixed-ligand oxovanadium complexes of the kind $[VO(PL)_2(SL)]$ were successfully synthesized and confirmed by utilizing spectroscopic and analytical techniques including FT-IR,^{1}H NMR, UV–Visible, XRD studies confirmed the successful coordination of ligands through phenolic and carbonyl oxygen atoms, resulting in distorted octahedral oxovanadium(V) complexes. XPS analysis further supported metal-oxygen coordination and indicated the presence of mixed oxidation states of vanadium.Overall, the study demonstrates that mixed-ligand coordinationis a useful method for adjusting the structural and spectral characteristics of oxovanadium complexcompounds.

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