

Synthesis and characterization of mixed ligand catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes

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Abstract

Diamine-mono-dithiocarbamates are mono-basic bidentate ligand forming stable complexes with transition metals. Mixed ligand catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes were synthesized and characterized using FT-IR, UV-visible and ¹H-NMR spectroscopic techniques. The formation of vanadium complexes was confirmed by the disappearance of $\nu_{\text{S-H}}$ band in the complexes which was present in the ligands and incidence of $\nu_{\text{V-S}}$ and $\nu_{\text{V-O}}$ band in FT-IR spectra of the complexes. The mono-dithiocarbamate with one uncoordinated $\nu_{\text{NH/NH}_2}$ group was indicated by the presence of $\nu_{\text{N-H}}$ vibrational band in both the ligands and complexes. In the ¹H-NMR spectra, the peak for -SH proton of ligands disappeared in the complexes suggest the formation of [VL₂Cat] complex. Non-electrolytic nature of the synthesized complexes was established by their low molar conductance values. The +4 oxidation state of vanadium was confirmed by the electronic spectra of the complexes. On the basis of all physico-chemical data, a six-coordinated octahedral structure has been suggested for catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes.

Key words: Diamine-mono-dithiocarbamate-catechol mixed ligand; V(IV) complex; Molar conductance; FT-IR; Electronic and ¹H-NMR spectra

Introduction

Dithiocarbamate (DTC) is a group of organosulphur chelating ligand that form a wide variety of stable complexes with interesting and quite novel properties and structures. Research on these compounds has drawn special attention because of their potential applications as high pressure lubricants in industry, medicines, fungicides and pesticides. In DTC and their complexes, sulphur donor atoms and extensive delocalized π density act as a potential source of charge transfer intermolecular (weak) bonding. With o-donation and n-back-donation in the same order of magnitude through sulfur atoms of dithiocarbamate moiety, these ligands possess a special feature of additional n-electron flow from nitrogen to sulphur via a planar delocalized π -orbital system (Nabipour *et al.*, 2010). Krishnan *et al.* (2015) have synthesized cobalt (II) piperidine dithiocarbamate and diamines such as ethylene diamine, diethylene triamine and triethylene tetramine [Co(amine) (pmdtc)₂] and observed considerable activity of the complexes as anticancer agents. Uddin *et al.* (2012) have synthesized dioxo-uranium complexes of diamine-mono-dithiocarbamate ligands (UO₂L₂), where diamines are ethylenediamine, N, N- dimethyl ethylenediamine, N, N- diethyl ethylenediamine, 1,

3-propane diamine, N, N- dibutyl-tri-methylene diamine, 1, 6- hexanediamine and reported their antifungal and antibacterial activity. Phenylmercury (II) methyl ferrocenyl dithiocarbamate having light harvesting properties as a photosensitizer in dye sensitized solar cells (DSSCs) has been synthesized by Chauhan *et al.* (2015).

The synthesis of catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes is totally a new approach. Vanadium is a biologically active metal. The interest in vanadium complex is due to their potential therapeutic and catalytic applications. Therefore, catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) might become an effective catalyst as well as nontoxic metal antitumor, antifungal and antibacterial species.

Materials and methods

1, 3-propanediamine, N, N'-diethyl ethylenediamine, 1, 6-hexanediamine were obtained from SIGMA ALDRICH and carbon disulphide from E. Merck, Germany. Vanadium(IV) oxosulphate and catechol were purchased from Fisher Scientific Company, USA.

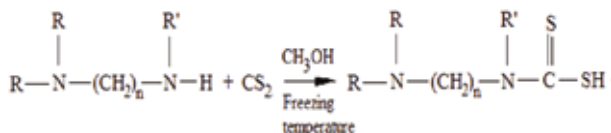
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Dimethyl sulphoxide (DMSO) and petroleum spirit were collected from E. Merck, Germany, DMF from DAEJUNG, KOREA and nujol mull from Merck, India. Ethylenediamine, methanol and ethanol were used as supplied (Scharlau, Spain). All of the chemicals and solvents were analytical grade and were used directly without further purification.

The diamine-mono-dithiocarbamate ligands were synthesized by the usual condensation of diamine or their substituted diamine (having at least one H-on amine group) with their same molar proportion of the carbon-disulphide (CS_2) (the type of $\text{R}_2\text{N}-(\text{CH}_2)_n-\text{NR}-\text{CS}_2$) by the published procedure (Chowdhury *et al.*, 2006).

Preparation of diamine-mono-dithiocarbamate ligands

The diamine-mono-dithiocarbamate ligands ($\text{R}_2\text{N}-(\text{CH}_2)_n-\text{NR}-\text{CS}_2$) were prepared by the condensation of equimolar proportion of diamine (having at least one H on amine group) with carbon-disulphide (CS_2). The solution of diamine viz. ethylenediamine, 1, 3- propanediamine, N, N'-diethyl ethylenediamine and 1, 6- hexanediamine (each of 150 mmol) in 50 mL methanol was allowed to cool in a freezing mixture of ice and salt. To this solution, CS_2 (140 mmol, a bit less to protect the dimerization) was added drop-wise over a period of about half an hour with constant stirring until white precipitate was formed. The precipitate was allowed to stand for about 5 hours in the ice-salt bath, filtered, washed with methanol and dried over silica gel. The prepared ligands were ethylenediamine-mono-dithiocarbamate (L^1), 1, 3-propanediamine-mono-dithiocarbamate (L^2), N, N'- diethyl ethylene diamine-mono-dithiocarbamate (L^3) and 1, 6-hexanediamine-mono-dithiocarbamate (L^4). The possible chemical reaction scheme is-

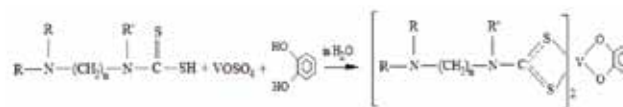


where R and R' = H, C_2H_5

Preparation of catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes

For the synthesis of vanadium complexes, 1 mmol each of vanadium(IV) oxosulphate, $\text{VO}(\text{SO}_4)$ and catechol were added to 2 mmol diamine-mono-dithiocarbamate ligand solubilized in 50 mL water. This solution was refluxed for about 2 hours to get the dark green precipitate of complex

which was then filtered off, washed with ethanol and finally dried over silica gel. Catecholato-bis (ethylenediamine-mono-dithiocarbamato) vanadium (IV) [VL^1Cat], Catecholato-bis (1, 3-Propanediamine-mono-dithiocarbamato) vanadium(IV) [VL^2Cat], Catecholato-bis (N,N'-diethyl- ethylenediamine-mono- dithiocarbamato) vanadium(IV) [VL^3Cat] and Catecholato-bis (1,6-hexanediamine- mono-dithiocarbamato) vanadium (IV) [VL^4Cat] were prepared following the above procedure. The proposed chemical reaction scheme is-



where R and R' = H, C_2H_5

Melting points of the ligands as well as of the complexes were obtained with Melting Point apparatus; model KRUSS, KSPINN. The elemental analysis of the prepared ligands and complexes were performed by Elementar (Vario-EL cube) and metal analysis by Shimadzu AA-7000 AAS using GFA-7000. Conductivity measurements of the samples were done by a conductometer model CTS-406K using N, N-dimethyl-formamide (DMF) as solvent. The FT-IR spectra were recorded with FT-IR 8400S Shimadzu spectrophotometer in the range $400-4000\text{ cm}^{-1}$ at 2 cm^{-1} resolution and 30 times scanning using KBr as reference. $^1\text{H-NMR}$ spectra were recorded on BRUKER 400 MHz NMR spectrometer. Electronic absorption spectra for ligands and their vanadium (IV) complexes were run on a Shimadzu UV-Visible spectrophotometer (model-UV 1800) using 1 cm cell and were recorded in the medium of water, DMSO and paraffin (Nujol mull). Physical data of the prepared ligands and complexes are shown in Table I.

Results and discussion

Elemental (C, H, N and S) Analysis

Elemental data of the prepared dithiocarbamate ligands and catecholato-bis (diamine-mono-dithiocarbamato) vanadium (IV) complexes are shown in Table I. From the elemental data, it is observed that there is a good agreement between experimental and calculated data which support the formation of vanadium complex.

Molar Conductance measurement

Molar Conductance was calculated by using the formula, $\Lambda_m = 1000/C \times \text{cell const.} \times \text{observed conductance}$. 10^{-3} M solution was used for conductivity measurement. The molar conductance (Λ_m) values of the prepared catecholato-bis

Table I. Physical, elemental and conductivity data for the diamine-mono-dithiocarbamate ligands and catecholato-bis (diamine-mono-dithiocarbamate) vanadium (IV) [VL₂Cat] complexes

Ligand /Complex	Physical data			Elemental analysis					Conductivity data	
	Colour	Yield %	m.p. (° C)	C% (Cal)	H% (Cal)	S% (Cal)	N% (Cal)	V% (Cal)	Molar conductance (Λ _m) ohm ⁻¹ cm ² mol ⁻¹ (Solvent: DMF)	
L ¹	White	87	184	(26.0) (26.5)	(5.1) (5.9)	47.0 (47.5)	20 (20.6)	--	--	
L ²	White	84	134	32.2 (32.0)	6.5 (6.7)	42.2 (42.7)	18 (18.7)	--	--	
L ³	White	85	139	44.1 (43.8)	7.9 (8.3)	32.7 (33.3)	14.7 (14.6)	--	--	
L ⁴	White	82	137	44.1 (43.8)	7.4 (8.3)	34.0 (33.3)	14.6 (14.6)	--	--	
VL ¹ ₂ Cat	Black	82	>230	32.8 (33.4)	3.8 (4.6)	28.0 (29.7)	--	10.2 (11.8)	6.7	
VL ² ₂ C	Black	80	>220	35.5 (36.7)	4.0 (4.8)	27.6 (28.0)	--	9.8 (10.9)	7.8	
VL ³ ₂ Cat	Black	81	>220	39.8 (41.7)	5.8 (6.5)	23.8 (24.7)	--	8.5 (9.8)	5.7	
VL ⁴ ₂ Cat	Black	80	>220	39.2 (40.1)	5.5 (6.1)	23.6 (24.2)	--	8.7 (9.4)	6.5	

(diamine-mono-dithiocarbamate) vanadium (IV) complexes were carefully determined as a function of their concentration in a very dilute solution of DMF at 30° C. Observed Λ_m values of the complexes are shown in Table I. The molar conductance of the complexes is in the range of 5.7-7.8 ohm⁻¹ cm² mol⁻¹ which is very low. The low molar conductivity values of all the prepared complexes revealed them to be essentially non-electrolyte (Geary, 1971). Thus, the observed low molar conductance is good evidence in support of the formation of catecholato-bis (diamine-mono-dithiocarbamate) vanadium (IV) complexes through V⁴⁺cation and mono basic nature of the coordinated diamine-mono-dithiocarbamate ligand.

FT-IR spectra

The bonding and structural properties of metal complexes were characterized by infrared studies. Dithiocarbamate possesses ν_{C-N} band at 1370-1410 cm⁻¹ (Percy *et al.*, 1976), ν_{C=S} (thio keto) band at 1104-1200cm⁻¹ and ν_{C-S} (thiolato) band at 760 cm⁻¹ reported by Onwudiwe *et al.* (2011) and Jayasree *et al.* (1993). The infrared spectra of the free ligands exhibit medium intense band at 2550cm⁻¹ for ν_{S-H} and 3150-3300 cm⁻¹ for ν_{N-H/NH₂} observed by Chowdhury *et al.* (2006). Strong bands at 1575-1600 cm⁻¹ and 1500 cm⁻¹ were recognized by Sharma (1989) for the δ_{N-H} vibrations in the amino salts. In the case of dithiocarbamate

ligand two bands at 960-1020 cm^{-1} were due to the asymmetric ν_{CSS} mode stated by Yin *et al.* (2008). It was anticipated that the presence of a single band at 1000 cm^{-1} region is the characteristic bidentate nature for the dithiocarbamate moiety in the complex, while the splitting of the same band within a difference of 20 cm^{-1} in the same region is due to the mono-dentate binding of dithiocarbamate ligand (Nami *et al.*, 2004). A strong band was observed in the region of 500-600 cm^{-1} for V-O absorption in the V(IV) complex (Mishra *et al.*, 2012). The band at 980- 990 cm^{-1} was attributed to the stretching vibration of the terminal V=O bond in the complex (Mishra *et al.*, 2005). The bands appeared in the region 617-670 cm^{-1} were assigned as $\nu_{\text{M-S}}$ (thiol) stretching modes and the bands in the region 408-555 cm^{-1} were assigned as $\nu_{\text{M-S}}$ (thioketo) vibrations (where, M indicate the central metal atom) (Chowdhury *et al.*, 2006; Sainorudin *et al.*, 2015; Sutriah *et al.*, 2014).

In the present study, the FT-IR data of all diamine-mono-dithiocarbamate ligands and their complexes are listed in Table II. The main stretching modes observed in the complexes are $\nu_{\text{NH/NH}_2}$, $\nu_{\text{C-N}}$, $\nu_{\text{C-S}}$, ν_{CSS} and $\nu_{\text{S-H}}$. The $\nu_{\text{S-H}}$ band for ligands disappeared in the IR spectra of the complexes while no significant change noticed for $\nu_{\text{N-H/NH}_2}$ modes. These indicate that the bonding taking place through the sulphur atom only and amino group in the ligand is not involved in the complexation. Ligands show FT-IR bands at 984 -1030 cm^{-1} due to ν_{CSS} mode (Yin *et al.*, 2008). But in the same region the presence of strong single band for all of the prepared complexes indicate that dithiocarbamate moiety is symmetrically coordinated to the metal ion (Johnson *et al.*, 1969) and show bi-dentate behavior.

Table II. Infrared spectral data of different diamine-mono-dithiocarbamate ligands and catecholato-bis (diamine-mono-dithiocarbamate) vanadium (IV) [VL₂Cat] complexes

Bands (cm^{-1})	Ligands				Complexes			
	L ¹	L ²	L ³	L ⁴	[VL ¹ ₂ Cat]	[VL ² ₂ Cat]	[VL ³ ₂ Cat]	[VL ⁴ ₂ Cat]
$\bar{\nu}$ NH/NH ₂	3240	3311	3200	3160	3183	3435	3431	3416
δ NH ₂	1517	1557	1520	1535	---	---	---	---
$\bar{\nu}$ C=S	1205	1205	1200	1208	1118	1112	1114	1126
$\bar{\nu}$ C-S	745	760	750	740	812	802	799	816
$\bar{\nu}$ CSS	1001	1032	1040	1030	1031	1045	1029	1031
$\bar{\nu}$ C-N	1351	1364	1350	1345	1323	1315	1391	1363
$\bar{\nu}$ S-H	2571	2570	2530	2570	---	---	---	---
$\bar{\nu}$ C-O	---	---	---	---	1269	1265	1254	1261
$\bar{\nu}$ V-S	---	---	---	---	399(keto) 653(ol)	418(keto) 618(ol)	420(keto) 610(ol)	432(keto) 630(ol)
$\bar{\nu}$ V-O	---	---	---	---	601	600	526	615

The band at $\sim 1200\text{ cm}^{-1}$ assigned for $\nu_{\text{C=S}}$ shifted by about $80\text{--}90\text{ cm}^{-1}$ to a lower wave number in the case of complexes indicate the involvement of the thioketo sulphur in coordination. The absence of any band around 2550 cm^{-1} in the prepared complexes (which was present in the ligand) indicates the de-protonation of the thiol group due to coordination. The band, $\nu_{\text{C-S}}$ at $\sim 760\text{ cm}^{-1}$ shifted by about $\sim 40\text{ cm}^{-1}$ to a higher energy due to coordination through sulphur atom. The $\nu_{\text{C-S}}$ (thiolato) shifted to higher energy due to the maintenance of a ring current arising for electron delocalization in a chelate ring. The presence of $\nu_{\text{v,S}}$ thiolato

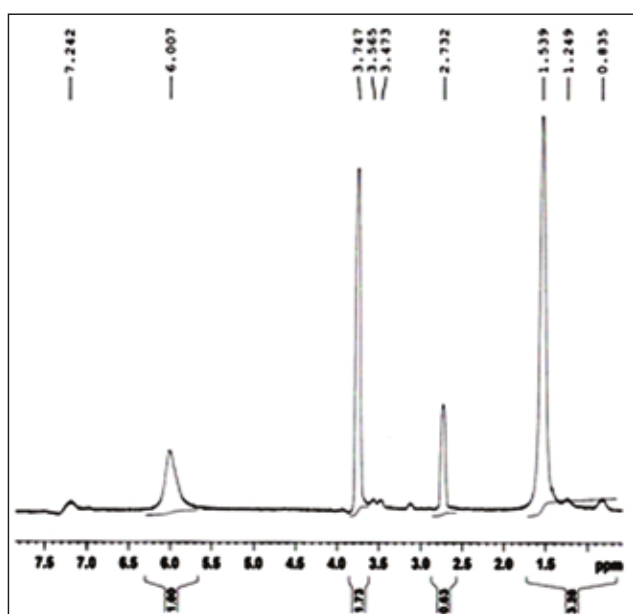


Fig. 1. ^1H NMR Spectrum of L^1 ligand

and $\nu_{\text{v,S}}$ thioketo and the disappearance of $\nu_{\text{S-H}}$ vibrations confirmed the coordination of S atoms to the metal ion and the monobasic nature of the ligands.

Chowdhury *et al.* (1998) observed the $\nu_{\text{C=O}}$ band at $\sim 1250\text{--}1260\text{ cm}^{-1}$ for the mono-dithiocarbamate and catechol mixed ligand complexes of Ti (IV). Thus the band appeared at $1254\text{--}1269\text{ cm}^{-1}$ in the present mixed ligand V(IV) complexes designate the $\nu_{\text{C=O}}$ vibration. The presence of $\nu_{\text{C=O}}$ mode at $\sim 1254\text{--}1269\text{ cm}^{-1}$ and $\nu_{\text{v=O}}$ mode at $526\text{--}601\text{ cm}^{-1}$ in the FT-IR spectra revealed the coordination of catechol with vanadium along with diamine-mono-dithiocarbamate ligands.

^1H NMR spectra

The ^1H NMR spectra of ligand L^1 and complex $[\text{VL}^1_2\text{Cat}]$ were taken dissolving in DMSO solvent and are

shown in Fig. 1 and 2, respectively. It was reported that the protons for $>\text{CH}_2$ group has chemical shift in the range $\delta = 1.43\text{--}1.54\text{ ppm}$ (Oliveira *et al.* 1999). The peak in the region $3.82\text{--}3.64\text{ ppm}$ for the protons of $-\text{NH}_2$ group was ascribed by Onwudiwe (2011). In both of the prepared ligand and V(IV) complex, $>\text{CH}_2$ protons observed at $\delta = 1.539$ and $\delta = 1.560\text{ ppm}$, respectively. The presence of $-\text{SH}$ proton at 2.732 ppm in the ligand (Nabipour, 2011) and absence of this peak in the spectra of the respective complex suggested the coordination between ligand and metal through the S moiety. Peak at 3.747 ppm and 3.750 ppm in both the spectra

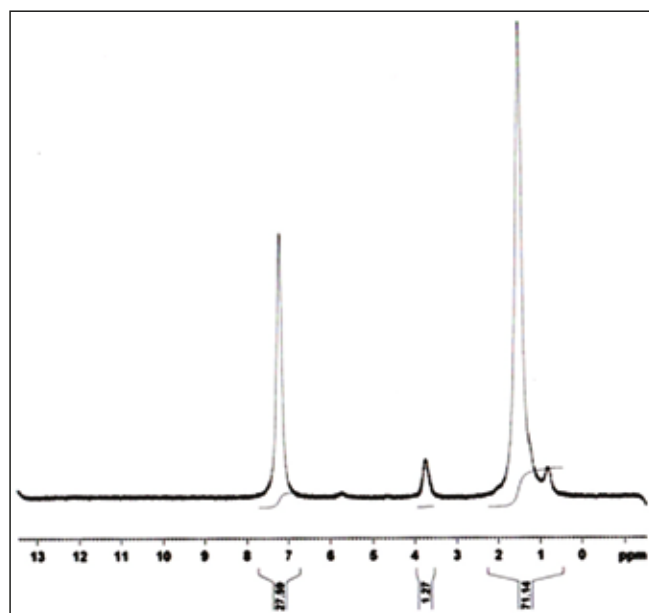


Fig. 2. ^1H NMR Spectrum of $[\text{VL}^1_2\text{Cat}]$ complex

of the prepared ligand and complex, respectively indicate the presence of $-\text{NH}_2$.

In the ^1H NMR spectrum of L^1 , the peak at 6.007 ppm corresponds to the proton of $>\text{NH}$ was hardly seen in the spectra of the complex. This could be explained as with the same order o-donation and n-back-donation characteristics in sulphur atom of dithiocarbamate. This type ligand has an additional n-electron flow from nitrogen to sulphur via a planar delocalized π -orbital system (Nabipour *et al.*, 2010).

The proton for the phenyl groups exhibit chemical shifts in the range $7.27\text{--}8.07\text{ ppm}$ due to deshielding on complexation reported by Yin *et al.* (2004). In the present V(IV) mixed ligand complex, peak is observed at $\delta = 7.250\text{ ppm}$, which indicate that catechol coordinate with vanadium. ^1H NMR data for ethylene

Table III. ^1H NMR data for ethylene diamine-mono-dithiocarbamate ligand, L_1 and its complex $[\text{VL}_1^1\text{Cat}]$

Compounds	$>\text{CH}_2$ protons δ ppm	$-\text{NH}_2$ protons δ ppm	$-\text{SH}$ protons δ ppm	phenyl protons δ ppm
L_1	1.539 (2H)	3.747(2H)	2.732(H)	---
$[\text{VL}_1^1\text{Cat}]$	1.560 (2H)	3.750(2H)	---	7.250(4H)

Table IV. Electronic spectral data for the diamine-mono-dithiocarbamate ligands and catecholato-bis (diamine-mono-dithiocarbamate) vanadium (IV) $[\text{VL}_2\text{Cat}]$ complexes

Ligands	Medium	Bands (nm)	Complexes	Medium	Bands (nm)
L^1	Water	269.9, 367.7	$[\text{VL}_1^1\text{Cat}]$	DMSO	252, 268
L^2	DMSO	250, 265, 300	$[\text{VL}_2^2\text{Cat}]$	DMSO	263
L^3	DMSO	250, 260, 305	$[\text{VL}_3^3\text{Cat}]$	NM	236
L^4	DMSO	260, 300, 367	$[\text{VL}_4^4\text{Cat}]$	NM	234

diamine-mono-dithiocarbamate ligand, L_1 and its complex $[\text{VL}_1^1\text{Cat}]$ are plotted in the Table III.

Electronic spectra

The region of the UV-visible bands of ligands and complexes are listed in Table IV. From the data of the complexes, it is observed that all the vanadium (IV) complexes have band at 234-268nm correspond to $\pi-\pi^*$ transition in the near ultraviolet region. Transition for $\pi-\pi^*$ observed at 250-367 nm in all the prepared ligands. In the case of 'd electron' system, absorption band for ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition might be expected at 500nm (Atkins *et al.*, 2006), but in the present complexes, there were no absorption band for ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition. This is because, according to selection rule if π -acceptor and π -donor ligands can mix with the d-orbital then d-d transitions are no longer purely d-d.

Conclusion

Diamine mono-dithiocarbamate ligands were synthesized and found monobasic bidentate in nature. The prepared catecholato-bis-diamine-mono-dithiocarbamate vanadium

(IV) complexes were found to be of the type $[\text{VL}_2\text{Cat}]$. Analytical data indicated that the complexes were 1:2:1 (metal:ligand:catechol) stoichiometry. Non-electrolytic nature of the prepared mixed ligand complexes was confirmed by conductance study. The presence of V-S thiolato and V-S thioketo and the disappearance of $\nu_{\text{S-H}}$ vibrations confirmed the coordination of S donor atoms of the ligands to the metal ion and the monobasic nature of the ligands. The shifts of $\nu_{\text{C=S}}$ bands to the lower wave number and shifts of $\nu_{\text{C-S}}$ bands to higher wave number in the IR spectra of the prepared mixed ligand complexes also suggested the bonding of ligands with V^{4+} ion through its thiocarbonyl and thioenolic sulphur atoms, thus enabling the ligands to act as bi-dentate one. The presence of $\nu_{\text{C=O}}$ and $\nu_{\text{V=O}}$ modes in the IR spectra of the present mixed ligand complexes revealed the coordination of catechol with vanadium(IV). In the NMR spectra, the presence of $-\text{SH}$ proton at 2.732 ppm in the ligand and absence in the spectra of complex suggested the formation of $[\text{VL}_2\text{Cat}]$ complex. The $[\text{VL}_2\text{Cat}]$ complexes are supposed to possess an octahedral structure. However, it is difficult to suggest the

exact geometry of $V(L_2)Cat$ complex without crystal structure determination. Therefore, further study is necessary to establish the exact structure of the prepared complexes and the reaction mechanism.

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