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Mono Oxovanadium (V) Mixed Ligand Complexes Of Schiff Bases And Catecholates: Synthesis, Spectral And Electro Chemical Characterisation

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Abstract

The coordination chemistry of Vanadium has received considerable attention since the discovery of the presence of vanadium in enzymes like bromoperoxidase and azotobacter vinelandii(1) . its biological importance has been further exemptifield field by its incorporation in nature product (amavandin in Mushroom) in the blood of sessile marine organisms (A. Museariatunicates) and in the enzymes of potent inhibitor of phosphoryl transfer(2) . Recent investigation also support the fact that vanadium is involved in biological system in more than one way(3-5) Few oxo vanadium (lV) complexes of the type VOL_2 [LH =3-(2-hydroxy-1-naphthyl)- S = (4-X-phenyl)-2- isoxazoline X = H,Cl,OMe] have been prepared and characterized. IR-spectral studies indicate coordination of the ligand through phenolic oxygen and tertiary nitrogen to the metal. Electronic spectral and magnetic susceptibility studies indicate the presence of a single unpaired electron while EPR- studies confirm that unpaired electron is present in the d_{xy} orbital EPR- spectra recorded in pyridine show that the (V = O) bond is weakened leading to stronger in bonds due to the axial coordination of pyridine trans to the vanadyl oxygen .

Interest in vanadium chemistry has increased due to the role this element in both the inhibitory and promotory processes in various biological system like nitrogenases(6). Haloperoxidases(7) tunichromes(8) and several others(9) vanadium complexes of catechol and related molecules have exhibited varying oxidation state between +3 and +5 depending on the type of substituent experimental conditions(10-14) .
Here we described the synthesis ,spectral characterization and stability of mono oxovanadium(V), (VO^{3+}) mixed ligand complexes of mono basic tridentate Schiff bases and catechol, t-butyl catechol or pyrogallol . The extensive use of ^{51} V-NMR in identifying the species present in solution in understanding the suitability of the ligands to stailize the V (V) oxidation is also reported.

EXPERIMENTAL_: FTIR –Spectra were recorded in KBr-matrix on a Nicolet spectrometer, ^{51}V-NMR spectra were measured using a FT NMR- spectrometer working at 71.057 MHz equipped with a 10m tunable probe held at 30^0C for DMSO- d_6 or CD_2 Cl_2 solutions. ^{51}V NMR shifts are referred to the signal of an external $VOCl_3$ in a 1mm diameter capillary tube inserted coaxially in a 10mm NMR-tube.

MATERIALS AND METHODS :

catechol (cat) p-tert- butylcatechol (tbcat) vanadium pentoxide pyrogallol (pyr) 5-Bromo salicyaldehyde were B.D.H products. catechol and tertiary catechol were recrystallised from benzene and petroleum ether respectively. 3- methoxy- salicylaldehyde (Aldrich chemical Co, USA) 2-Hydroxy-1-naphthaldehyde (hnap) was prepared from p-naphthol by Duff' s method(15) VO(OEt)$_3$ was synthesized using a reported proceure(16) and morpholine-N-Thiohydrazone was prepared by literature method(17) **Synthesis of VO-morholine-N-Thiohydrazone Salicylidimine/ Morpholine-N- Thiohydrazone 5:6-Benzo Salicylidimine –Morpholine –N- Thiohydrazone –β-Methoxy salicylidimine/ Morpholine –N- Thiohydrazone 5-Bromo Salicylidimine/ catechol complexes 1 to 4, tertiary butyl catechol complexes 5 to 8 and pyrogallol complexes 9 to 12:**

All complexes are prepared by a similar strategy and hence a representative procedure for complex (1) is given as a general method for the synthesis.

To morpholine –N- Thiohydrazone (0.161 gm 1 mmol) in 15 cm^3 absolute ethanol was added salicylaldehyde (0.121g 1 mmol) in $15cm^2$ absolution etahol and heated at 50^0C for one hour. After cooling to room temperature catechol (0.110 g 1mmol) was added as solid . To the mixture was added VO $(OC_2H_5)_3$ (1 m mol) which resulted in a black precipitate almost immediately and this mixture was refluxed for one hour. The precipitate was filtered and stirred in hot absolute ethanol for 30-minute to give pure product. Addition of catechol to the prepared reaction mixture of VO $(OC_2H_5)_3$ and the Schiff base gives the same product.

For the synthesis of the complexes(5-8) tertiary catechol , and for complexes(9-12) pyrogallol was used. The abbreviations analytical result and yields of the complexes is given in table

TABLE (I) ELEMENTAL ANALYSIS OF COMPOUNDS

S.No.	Formula Catechol Complexes	% Chemical analysis: Found (Calculated)				% Yield
		C	H	N	V	
1	$[VO(C_{18}H_{18}N_3O_4S)]H_2O$	47.12(47.27)	4.25(4.37)	9.06(9.19)	11.01(11.14)	64
2	$[VO(C_{22}H_{20}N_3O_4S)]$	53.87(53.99)	3.94(4.09)	8.50(8.59)	10.32(10.42)	53
3	$[VO(C_{19}H_{20}N_3O_5S)]$	48.52(48.62)	4.15(4.26)	8.83(8.95)	10.76(10.86)	50
4	$[VO(C_{18}H_{17}N_3O_4SBr)]H_2O$	40.22(40.30)	3.46(3.54)	7.72(7.83)	9.39(9.50)	60
t-butyl Catechol Complexes						
5	$[VO(C_{22}H_{26}N_3O_4S)]H_2O$	51.36(51.46)	5.35(5.45)	8.11(8.18)	9.80(9.93)	56
6	$[VO(C_{26}H_{28}N_3O_4S)]$	57.13(57.25)	5.03(5.14)	7.55(7.70)	9.27(9.35)	54
7	$[VO(C_{23}H_{28}N_3O_5S)]H_2O$	50.71(50.83)	5.40(5.53)	7.62(7.74)	9.28(9.38)	50
8	$[VO(C_{22}H_{25}N_3O_4SBr)]$	45.88(46.00)	4.26(4.36)	7.23(7.32)	8.74(8.88)	60
Pyrogallol Complexes						
9	$[VO(C_{18}H_{18}N_3O_5S)]H_2O$	45.53(45.67)	4.10(4.23)	8.76(8.88)	10.50(10.57)	52
10	$[VO(C_{22}H_{20}N_3O_5S)]1.5H_2O$	49.59(49.63)	4.25(4.32)	7.78(7.90)	9.48(9.58)	50
11	$[VO(C_{19}H_{20}N_3O_6S)]H_2O$	45.23(45.33)	4.24(4.37)	8.23(8.35)	10.03(10.13)	46
12	$[VO(C_{18}H_{18}N_3O_5S)]1.5H_2O$	40.64(40.76)	3.85(3.96)	7.85(7.93)	9.49(9.61)	60

RESULTS AND DISCUSSION:

Formation of the title complexes:

Six coordinated complexes with $VNSO_4$ core were formed when $VO(OC_2H_5)_3$ was added to the mixture of the Schiff base and dibasic bidentate ligands, such as catechol, t-butyl catechol or pyrogallol in (1:1) ratio on the other hand the reactions carried out in the absence of these dibasic dibentate ligands .Yielded cis-dioxovanadium(V) complexes of trigonal bipyramidal geometry(18) .

However when the isolated product of such trigonal bipyramidal geometry cis dioxo vanadium(V) complexes are reacted with catechol or its derivative in 1:1 ratio in ethanol the reactions yielded the same 6-coordinate mixed ligand VO^{3+} complexes. All the complexes are highly soluble in Dichloromethane Dimethyl sulfoxide and Dimethyl formamide .

$$\mathrm{VO(OC_2H_5)_3 + HL} \xrightarrow{\text{Absolute,Ethanol}} \mathrm{VO_2} \xrightarrow[\text{R-Cat}]{\text{(5-coordinate)Absolute EtOH} \atop \text{5-hr/40}^0\text{C}} \underset{\text{(6-coordinate)}}{\mathrm{VO(L)\ (R\text{-}Cat)}}$$

$$\mathrm{R\text{-}Cat + HL} \xrightarrow[\mathrm{VO(OEt)_3}]{\text{Absolute EtOH}} \underset{\text{(6-coordinate)}}{\mathrm{VO(L)\ (R\text{-}Cat)}} \xrightarrow[\text{DMSO-water} \atop \text{(fast)}]{\text{DMSO (slow)}} \underset{\text{(5-coordinated)}}{\mathrm{LVO2 + R\text{-}\ Cat}}$$

(L)-Tridentate Schiff Base(Hydrazone ligand
(R-H,p-tert. Butyl, 3-OH)
(Scheme-1)

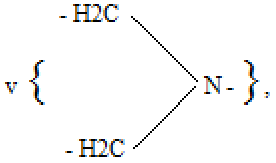
All the complexes reported are dark reddish violet in color. The molar conductance observed in the range 9.8-16.0 $ohm^{-1}\ cm^2\ mol^{-1}$, for these complexes indicates non-ionic nature of these complexes. The analytical data indicate that the complexes have the molecular formula VOLL. The complexes are diamagnetic in nature which is in agreement with the spin only value expected for d^0-system eith no orbital contribution(19-21) The electronic spectra of the complexes were recorded in chloroform and in pyridine. Though three transitions are expected for a square pyramidal vandyl complex(22) in the present study an intense charge transfer band makes the higher energy bands and so only a single band is observed .

IR- Spectral Studies: The IR-spectra of the octahedral complexes of $[VO\ (C_{22}H_{26}N_3O_4S)]\ H_2O$; $[VO(C_{26}H_{28}N_3O_4S)]$; $[VO\ (C_{23}H_{28}N_3O_5S)]H_2O$; $[VO(C_{22}H_{25}N_3O_4SBr)]\ H_2O$; showed clearly a distinct medium intensity band 2970 cm^{-1} that corresponds to the cm^{-1} (C-H) of t-butyl groups υ (C-H) corresponding to the aromatic moieties are also noted in all the complexes.

Presence of υ(OH) vibration was observed as an asymmetric band around 3445± $10cm^{-1}$ corresponding to free hydroxyl group as well as H_2O present in the compound. The υ(C=N) observed in the range 1600-1624 cm^{-1} for all these complexes is characteristic of N- complexes(23).The band observed in the range 1320-1340 cm^{-1} is assigned to υ (C-O) (phenolic) and that in the region 1150-1175 cm^{-1} to υ (N-N) mode(24). A negative shift of 10-12 cm^{-1} in υ (CH=N) and a positive shift of 10-35 cm^{-1} in υ(C-O) (phenolic) are observed upon coordination indicating that the treaty nitrogen of the azomethine group and phenolic oxygen are involved in coordination. A positive shift of 15-32 cm^{-1} is also observed in υ (N-N) due to relaxation in lone pair- lone pair electron repulsion(25) .The υ (N-H) stretching band registers a negative shift of 30-130 cm^{-1}. A strong band observed at 960 cm^{-1} is assigned to υ(V=O). Since monomeric venadyl complexes exhibit υ(V=O) in the range 950-1000 cm^{-1} and polymeric complexes in the 850-900 cm^{-1} range(26-28) the complexes under study are structurally monomers. All the complexes show a band for υ(OH) at 3450 cm^{-1} for lattice held water .

The IR-spectrum of the ligand display an absorption peak at 1630 cm^{-1} which is assigned to the (C=N) stretching frequency and a band observed at 1050 cm^{-1} is attributed to the υ(C=S) mode(29). A comparison of the spectra of the uncomplexed ligand and its metal complexes indicate that the υ(C=N) and (C=S) band are shifted to lower wave numbers by 10-50 cm^{-1} and 30-45 cm-^{1} respectively.

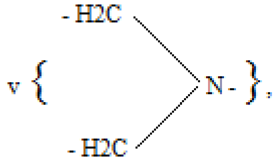
Such a negative shift in the υ(C=S) mode after complexation may be ascribed to the participation of nitrogen atom of the azomethine group and the thiono sulpher atom of the mercapto grpup(30) . These observation are in conformity with the tridentate coordination of the ligand. The ligand as well as the complexes show IR-absorptions near 2200,1400 and 950 cm^{-1} associated with



υ(C=C), and υ(C=S) modes respectively. The v $(-H_2C-N-)$

CH_2 and υ(C=C)

band observed at 2178 cm^{-1} (spilt band) and 1371 cm^{-1} respectively in the ligand show a positive shift on complexion (12-30 cm^{-1}) and (15-25) cm^{-1} respectively. A small positive shift in



and υ(C=C) simply indicates non involvement of tertiary nitrogen group in bonding(31) in complexes. There is lowering in υ(C=S) of thio group which occurs in the 925 cm^{-1} region in the complexes as compared to 950 cm^{-1} observed in the free ligand. The decrease in υ(C=S) is indicative of monoegative tridentate behavior of the ligand. This is consistent earth localization of charge on the sulpher atoms of the ligand in the complexes.

The characteristic(32-33) OH (stretching) band appears at 3150-3400 cm^{-1} but the band at 1620-1670cm^{-1} due to HOH (bending) frequency could not be identified precisely probably due to super imposition of this band with asymmetric stretching due to –(CH=N) group. Coordination through N-,S-and O-atoms is further supported by the appearance of υ(M-N), υ(M-S) and υ(M-O) absorption bands at 450-410 cm^{-1} 380-350 cm^{-1} and 450-500 cm^{-1} respectively in the IR-spectra of the complexes(34)

These complexes in CH_2Cl_2 and DSMO gave absorption band in the region 500-540 and 840-880 nm. For the catechol (1-4) complexes

$[VO(C_{18}H_{18}N_3O_4S)]\ H_2O$; $[VO(C_{22}H_{20}N_3O_4S)]$; $[VO(C_{19}H_{20}N_3O_5S)]$; $[VO(C_{18}H_{17}N_3O_4SBr)]\ H_2O$

and tertiary butyl catechol (5-8) complexes

$[VO(C_{22}H_{26}N_3O_4S)]$; $[VO(C_{26}H_{28}N_3O_4S)]$; $[(C_{23}H_{28}N_3O_5S)]H_2O$; $[VO(C_{22}H_{25}N_3O_4SBr)]$ complexes, substitution on the salicylaldehehyde part does not show any significant change in the spectra(35-36)

When catechol or tertiary catechol was replaced by pyrogallol(9-12) complexes $[VO(C_{18}H_{18}N_3O_5S)]H_2O$; $[VO(C_{22}H_{20}N_3O_5S)]$ 1. $5H_2O$; $[VO(C_{19}H_{20}N_3O_6S)]\ H_2O$; $[VO(C_{18}H_{18}N_3O_5SBr)]$ $.5H_2O$ the 450 nm transition found in (1-8) complexes shifted to lower energy 580 nm and that observed 850 nm for (1-8) complexes.

$[VO(C_{18}H_{18}N_3O_4S)]$ $[VO(C_{22}H_{20}N_3O_4S)]$ $[VO(C_{19}H_{20}N_3O_5S)]$; $[VO(C_{18}H_{17}N_3O_4SBr)]$ $[VO(C_{22}H_{26}N_3O_4S)]H_2O$ $[VO(C_{26}H_{28}N_3O_4S)]$ $[VO(C_{23}H_{28}N_3O_5S)]H_2O$; and $[VO(C_{22}H_{25}N_3O_4SBr)]$

was shifted to higher energy (770-800). The absorption data are given table (II) the high intensity of these bands suggest that these transition are ligand metal charge transfer in origin.

TABLE (II) ABSORPTION SPECTRA OF THE COMPLEXES

S.N.	**Formula**	**λ (mol^{-1} dm^3 cm^{-1})**
1	$[VO(C_{18}H_{18}N_3O_5S)H_2O]$	330, 350, 430, 530, 860
2	$[VO(C_{22}H_{20}N_3O_4S)]$	360, 462, 528, 850
3	$[VO(C_{19}H_{20}N_3O_5S)]$	350, 460, 510, 860
4	$[VO(C_{18}H_{17}N_3O_4SBr)H_2O]$	340, 350, 440, 520, 865
5	$[VO(C_{22}H_{26}N_3O_4S)]H_2O$	335, 350, 430, 520, 860
6	$[VO(C_{26}H_{28}N_3O_4S)]$	350, 460, 520, 850
7	$[VO(C_{23}H_{28}N_3O_5S)]H_2O$	350, 460, 510, 860
8	$[VO(C_{22}H_{25}N_3O_4SBr)]$	330, 350, 440, 520, 850
9	$[VO(C_{18}H_{18}N_3O_5S)]H_2O$	330, 350, 420, 550, 760
10	$[VO(C_{22}H_{20}N_3O_6S)]1.5H_2O$	350, 470, 560, 780
11	$[VO(C_{19}H_{20}N_3O_6S)]1.5H_2O$	360, 440, 560, 810
12	$[VO(C_{18}H_{18}N_3O_5SBr)]1.5H_2O$	330, 350, 430, 560, 800

These complexes are stable for more than a week in dichloride methane solution, in Dimethyl sulfoxide they convert into their dioxo penta coordinate counterparts in less than 48 hours due to the loss of the bidentate ligand. Addition of 0.5 cm^3 of water to 10cm^3 of DMSO solution facilitates the conversion of the VO^{3+} to VO^{2+} by replacing the bidentate ligand. A qualitative trend in the rate of this conversion was found to be Ome Sal << hnap < br sal < sal based on absorption studies among the catechol(38) and pyrogallol complexes (1-4) and (9-12) the t-butyl catechol complexes (5-8) were found to be least sensitive towards such conversions. A more quantitative support for this conversion was obtained based on ^{51}V-NMR studies . The formation and conversion of the VO^{3+} complexes info the VO_2 is depicted in scheme-1.

^{51}V-NMR-and Stability Studies:

^{51}V-NMR of the complex were measured in Dimethyl sulfoxide immediately folowing the dissolution. The chemical shifts are referred to $VOCl_{3.}$ All these complexes exhibited either one or two down filed signals in the range 310 to 530 ppm indicating a large deshielding of metal center in the presence of catechol and related ligands and are supported by low energy transitions in the absorption spectra. Highly deshielded chemical shifts are common among the catecholate complexes as reported in literature(37) complexes (1-12) showed an additional up filed signal in the rage -530 to -536 ppm. While this upfield peak is expected fro a decomposed product of dioxovanadium(V) (VO_2^+ species the other down filed signals are attributed to 6-coordinate mono oxovanadium(V) (VO^{3+}) species possessing catechol t-butyl catechol or pyrogallol as the second coordinating ligand.

VOL- cat-complexes

All the catechol complexes [$VO(C_{18}H_{18}N_3O_4)]H_2O$; [$VO(C_{22}H_{20}N_3O_4S)$]; [$VO(C_{19}H_{20}N_3O_5S)$] and [$VO(C_{18}H_{17}N_3O_4SBr)]H_2O$ exhibit only one downfield signal in the range 310- 380 ppm (peak-1). The filed shift of these complexes follow a trend 4>> 1> 2> 3.Bromo- salicylaldehyde [$VO(C_{18}H_{17}N_3O_4SBr)]H_2O$ showed maximum down filed shift owing to electron withdrawing nature. On decomposing the complex with water VO_2^+ species formed (peak-3).On ageing the solution the percent of peak(3) increases considerably. Based on ^{51}V-NMR it was consistently$^{(38-39)}$ noted that the addition of water to the solution enhances the formation of VO_2^+ species to result in higher intensities of the peak -3 at the cost of the peak-1

VOL-t-butyl catechol complexes (5-8)

Tertiary butyl catechol complexes showed consistently two downfield peaks as given in table (III) (peaks-1 and 2). One peak is present in larger percentage and the other present in smaller [$VO(C_{22}H_{26}N_3O_4S)]H_2O$; [$VO(C_{26}H_{28}N_3O_4S)$] [$VO(C_{23}H_{28}N_3O_5S)]H_2O$; [$VO(C_{22}H_{25}N_3O_4SBr)$]
Proportion. ^{51}V-NMR-has been used as a tool to identify isomers and different species are present in solution$^{(40)}$Two possible orientations of the p-t-butyl catechol unit with respect to (V=O) can give rise to the two isomers. The chemical shift difference between these two peaks (δ peak 2 – δ peak 1) is maintained constant in the complexes suggesting that the observed trend in the chemical shift [$VO(C_{22}H_{26}N_3O_4S)]H_2O$ [$VO(C_{26}H_{28}N_3O_4S)]H_2O$ [$VO(C_{23}H_{28}N_3O_5S)]H_2O$ [$VO(C_{22}H_{25}N_3O_4SBr)$] of these speak is due to substitution on salicyladhyde. Peaks-1 and 2 in the complexes(5-8) were shifted$^{(41-42)}$ to more down field and exhibited lowest percent of decomposed product among all the three categories of complexes reported here, suggesting that the bidentate catechol related.

TABLE (III) ^{51}V-NMR-CHEMICAL SHIFTS FOR COMPLEXES IN DMSO

S.No.	Complex	Chemical Shifts$^{(a)}$			% of product		
Catechol Complexes		**Peak-1**	**Peak-2**	**Peak-3**	**Peak-1**	**Peak-2**	**Peak-3**
1	[$VO(C_{18}H_{18}N_3O_4S)]H_2O$	315.4	-	-527.3	78	-	12
2	[$VO(C_{22}H_{20}N_3O_4S)$]	303.6	-	-527.5	72	-	18
3	[$VO(C_{19}H_{20}N_3O_5S)$]	310.0	-	-526.2	89	-	2
4	[$VO(C_{18}H_{17}N_3O_4SBr)]H_2O$	366.0	-	-526.0	84	-	6
t-butyl Catechol Complexes							
5	[$VO(C_{22}H_{26}N_3O_4S)]H_2O$	436.6	469.0	-527.3	62	14	11
6	[$VO(C_{26}H_{28}N_3O_4S)$]	420.0	453.0	-	62	27	-
7	[$VO(C_{23}H_{28}N_3O_5S)]H_2O$	425.5	457.4	-	62	27	-
8	[$VO(C_{22}H_{25}N_3O_4SBr)$]	478.6	512.2	-526.6	65	23	1
Pyrogallol Complexes							
9	[$VO(C_{18}H_{18}N_3O_5S)]H_2O$	371.5	-	-526.0	12	-	83
10	[$VO(C_{22}H_{20}N_3O_5S)]1.5H_2O$	358.4	472.7	-	82	12	-
11	[$VO(C_{19}H_{20}N_3O_6S)]H_2O$	361.0	478.8	-	82	12	-
12	[$VO(C_{18}H_{18}N_3O_5S)]1.5H_2O$	413.0	-	-523.2	27	-	68

(a)Peak 1&2 are down field with respect to VOCl3, Peak 3 corresponds to dioxovanadium(v) decomposed product.

(b) Based on the Peak integrations. Total integration in the spectrum is taken as 100%.

ligands (catechol) tertiary butyl catechol or pyrogallol are non-innocent in the formation and satbilisation of the six coordinated VO^{3+} complexes. Even in this series the bromo- salicyladhyde derivative $[VO(C_{22}H_{25}N_3O_4SBr)]$ shows more down field shift similar to that observed in case of catechol complexes(43). The characteristics of the spontaneous decomposition of the complexes(5-8) in DMSO solution over a period of time and their enhanced formation of VO_2^+ product upon addition of water are qualitatively similar to that explained for (1-4).

VOL-Pyrogallol Complexes

Pyrogallol complexes $[VO(C_{18}H_{18}N_3O_5S)]H_2O$ and $[VO(C_{18}H_{18}N_3O_5SBr)$ $1.5H_2O$ showed only one down filed peak (peak-1) and large upheld signal (peak-3) of the decomposed LOV_2^+ product to the extent of 85% and 70% respectively suggesting that these are least stable and there by not showing peak-2 at all, on the other hand $[VO(C_{22}H_{20}N_3O_5S)]1.5H_2O$ and $[VO(C_{19}H_{20}N_3O_6S)]H_2O$ showed no decomposition during the period of measurement and showed two down field peaks in a ratio of 80:20 attributable to the two isomers possible in solution(44) .Possible isomers of $[VO(C_{19}H_{20}N_3O_6S)]H_2O$ in solution are given in figure (a).The

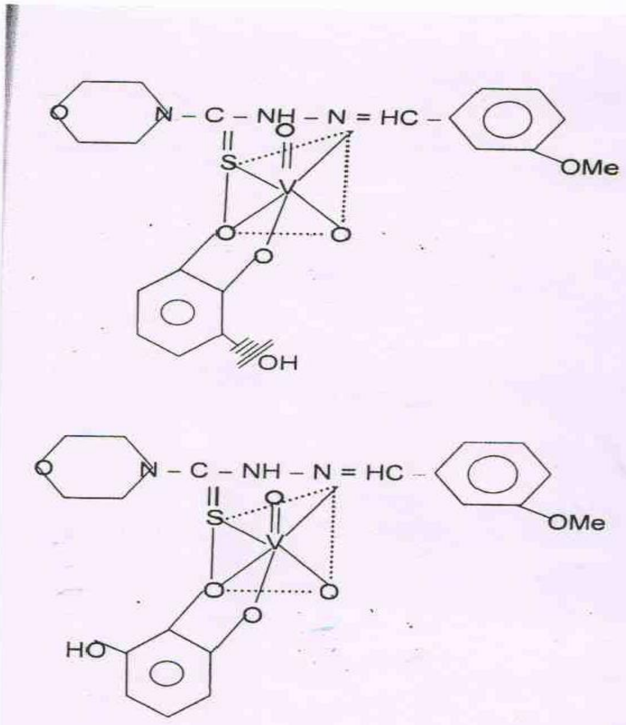


Fig (a) Possible isomers of complex $[VO(C_{19}H_{20}N_3O_6S)]H_2O$ in (DMSO) solution]

δ-difference (δ-peak-2-δ peak-1) for $[VO(C_{19}H_{20}N_3O_6S)]H_2O$ $[VO(C_{18}H_{18}N_3O_5SBr)]1.5H_2O$ are much larger and the intensity of peak-1 is smaller than the complexes Comparison of the $[VO(C_{22}H_{26}N_3O_4S)]H_2O$; $[VO(C_{26}H_{28}N_3O_4S)]H_2O$; $[VO(C_{23}H_{28}N_3O_5S)]H_2O$; $[VO(C_{22}H_{25}N_3O_4SBr)]H_2O$;.

^{51} V-NMR-data among the three categories of complexes suggest that it is the isomer corresponding to peak-2 that was shifted to more down field than the expected value. This may reflect on the position of the substitution in case of pyrogallol as compared to the tertiary butyl catechol(45-46)

Thus the ^{51}V-NMR spectral features of pyrogallol complexes Showed a behavior that is

$[VO(C_{18}H_{18}N_3O_5S)]H_2O$; $[VO(C_{18}H_{18}N_3O_5SBr]1.5H_2O$
$[VO(C_{19}H_{20}N_3O_6SBr]H_2O$ $[VO(C_{18}H_{18}N_3O_5SBr]1.5H_2O$
intermediate between the other two categories. The decomposition characteristics of these complexes in DMSO solution in DMSO+ water mixture were found to qualitatively similar to others.

Thus ^{51}V-NMR-and absorption studies are clearly indicative of the role of both the Schiff base (Hydrazone) ligand substitution on salicylaldehde and also the bidentate ligand. Such as catechol, tertiary butyl catechol or pyrogallol and their induced effect. Further the behavior is expected to be different with pyrogallol as thus possess$^{(47-50)}$ an additional active OH-group in the 3-position on the aromatic ring. The studies have also demonstrated the stability of these six coordinate VO^{3+} complexes in DMSO solution and its accelerated conversion in the presence of additional water$^{(51-54)}$ to the VO^{2+} counterpart.

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