

**Research Article****Stereochemical Features of Five-Coordinate Dimeric Square Pyramidal Oxovanadium (IV) Complexes**

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**Abstract:** Due to their hard nature, the oxovanadium (iv/v) ions have a good affinity towards O,N, donor ligands. The interaction of  $UO^{2+}$  with hydroxy carboxylic acid is also important because of their varied geometries. The vanadium atoms in the complexes are hex-coordinated and the coordination sphere is of the type  $[vo(oo)(NN)]$  where o-atoms are of oxo, carboxylic and phenolic type and N-atoms are of pyridine type. The sixth coordination position site is occupied by phenolic oxygen of neighbouring molecule forming a bridge, the  $(V=O)$  confirms, the hexa coordination. All the complexes have  $dxy'$  type axial EPR spectra and they exhibit two Ligand field transition at 740 and 440 nm.

**Keywords:** Five coordinate square pyramidal, Oxo vanadium complex, bridged oxygen atoms Magnetic and electronic spectral studies, Phenolic group vibration

**INTRODUCTION**

The oxovanadium (iv/v) ions have a good affinity towards o, N, donor ligands due to its hard nature. The interaction of  $UO^{2+}$  with hydroxycarboxylic acid is of importance because of their varied geometries and antimicrobial activity [1]. Solution study in the mixed ligand system containing these ligands have been done by Islam *et al.* [2] Bhattacharya and Ghosh [3] reported the results of the study with salicylic acid and bipy/phen ligands. The vanadium atoms in the complexes are hexacoordinated and the coordination sphere is of the type  $[vo(oo)(NN)]$ , where o-atoms are of oxo, carboxylic and phenolic type and N-atoms are of pyridine type. All the complexes have  $dxy'$  type axial EPR spectra and they exhibit two ligand field transition at 740 and 440 nm.

Biradaretal have studied several dimeric square planar  $cu(II)$  and monomeric octahedral uranyl (VI) complexes of hydrazones. A few complexes (4) of  $vo(II)$  with 2-3 dihydrazinoquinoxaline have been synthesized and characterized by analytical, conductance, thermal spectral and magnetic data. All the complexes are non electrolyte. The ESR spectrum of  $vo(II)$  complexes shows higher 'g' value (2.023G). The electronic configuration (Ar)  $d^1$  of  $v(IV)$  makes the oxovanadium (IV) complexes ideal models for magnetic investigations in different coordination environments, A square pyramidal geometry has been established for five coordinate oxovanadium (IV) complexes.

In the present paper, oxovanadium (iv) complexes of the composition  $[VO(L)_2]$  or  $[VO(L)]_2nH^2O$  ( $n=2,4,5$   $L=$   $(C^{24}H^{18}N^2O^2)$ ,  $(C^{19}H^{16}N^2O^3)$ ,  $(C^{20}H^{18}N^2O^3)$ ,  $(C^{21}H^{20}N^2O^3)$ ,  $(C^{23}H^{18}N^2O^2)$ ) have been synthesized. And their stereochemistry is ascertained by elemental analysis & by molecular weight, conductance, and magnetic, infrared & electronic spectral measurements. The complexes have a diametric structure involving bridging through phenolic oxygen & each unit appears to have a distorted square pyramidal structure.

**EXPERIMENTAL**

Preparation and isolation of the Complexes- A freshly prepared aqueous ethanol solution of vandyl chloride (0.001 mol) was added drop wise to ethanolic solution of ligand which produced a brown coloured precipitate. Drop wise addition of required dilute solution of sodium acetate with continuous stirring afforded brown coloured precipitate. Drop wise addition of required dilute solution of sodium acetate with continuous stirring afforded brown coloured solid after complete precipitation. It was refluxed on water bath for one hour. The complex so obtained was filtered, washed with ethanol and dried at  $120^\circ C$  under reduced pressure. All the metal complexes are coloured and stable to air and moisture. They are soluble in DMF and DMSO. Shows metal to ligand ratio as 1:1 vanadium metal in all the complexes was estimated using EDTA and Erichrome black-T as indicator and confirmed by igniting the complexes in air then estimating the metal as pantoaxide.

The conductance data show that the complexes are non electrolyte in nature. On heating the complexes above 130°C, loss in weight correspond to 7.4% weight loss equivalent to two mole of water per mol of the complex which accounts for one mole of water per metal ion.

## RESULTS AND DISCUSSION

The Complexes are not monomeric as revealed by the determination of their molecular weight in benzene (cryoscopic) which have been found to be ~ 1.8 times higher. This 1:18 ratio of molecular weight suggest dimeric nature of the complexes which has been confirmed by their spectral and magnetic studies.

### Infrared Spectral Studies

The infrared spectra of both type of complexes are similar. The broad band in the 3600-3200 cm<sup>-1</sup> region corresponds to UOH of the lattice held water molecules in the binuclear complexes of the type [VO(L)]nH<sub>2</sub>O

### Amide Group Vibrations

The free ligands show strong band in the region 1660-1675 cm<sup>-1</sup> which may be assigned to amide I of V(C=O) vibrations. The bands around 1510, 1250, 650-660 and 495-505 cm<sup>-1</sup> may be assigned to amide II (vCN+8NH), amide III (vCN), amide IV (C=O) out-of-plane deformation) and amide VI (C=O in plane deformation) vibrations, respectively indicating that the ligands are resent in keto form. The bands at 3000-3050 cm<sup>-1</sup> are assigned to v (NH). Qccurrence of V [C-N] of -C=O (amide III) band as well as azomethine stretching frequencies at higher by about 30 cm<sup>-1</sup> and 15 cm<sup>-1</sup> suggest the bonding of azomethine nitrogen. In the spectra of complexes at band occur around 1595-1598 cm<sup>-1</sup> due to >c=N-N=C< (azine group) suggest enolic

form of the ligand take part in chelation. A band around ~ 370 cm<sup>-1</sup> in the complexes have the origin of (O=V-O) Phenolic Vibration [5-6].

### Azomethine Group Vibrations

The sharp and strong band around 1615 cm<sup>-1</sup> in the spectra of ligand can be assigned to the stretching mode of >C=N group. The band get shifted to the lower frequency by 20-30 cm<sup>-1</sup> in the IR-spectra of all the vanadyl complexes along with its splitting due to the formation of >C=N-N-C< group in the complexes [7, 8].

### Phenolic Group Vibrations

The IR spectra of the ligands show strong bands in the regions 3200-3250 and 1320-1350 cm<sup>-1</sup>. The intra molecular H-bonding is also indicated by the presence of weak broad band around 2700-2775 cm<sup>-1</sup> in the free ligands<sup>(9)</sup>

The band at 540-550 cm<sup>-1</sup> is assigned to (v-o) aryl and those of 460-475 cm<sup>-1</sup> and 430-440 cm<sup>-1</sup> to the (V-N) and v(v-o) bands respectively [10]. The v(o-h) which appears on 3200-3250 cm<sup>-1</sup> in molecule is absent in the complexes white which is in the higher energy side by ~ 70 cm<sup>-1</sup> [11] such a large shift in higher energy direction indicates the involvement of phenoxide moiety in the lexidge in those complexes.

### Magnetic And Electronic Sectral Studies

The reported complexes are paramagnetic and magnetic moment values are lower than the expected value for a (d<sup>1</sup>) system (1.73 B.M). Such low value indicate that some amount of anti ferromagnetic interaction is taking place with the neighbouring moucule. Infrared spectra molecular weight of the complex suggests dimeric nature of the complexes.

**Table 1: Assignment of the Important Frequencies in the Infrared Spectra of Oxovanadium (iv) complexes (cm<sup>-1</sup>)**

[vo(C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )]	[vo(C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )]	[vo(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ]	[vo(C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ]	[vo(C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]	[vo(C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )]
1610 s	1605 s	1605 s	1600 s	1610 s	v(c=n) of Azomethine
1600 s	1610 s	1590 s	1595 s	1590 s	>c=N-N=c<
1530 s	1540 s	1535 m	1535 m	1545 s	phenolic Vco
1290 m	1300 m	1290 m	1295 m	1300m	phenolic co bending
960 s	970 s	985 s	990 s	980 s	v (v=o)
470 m	475 m	475 m	480 m	475 m	v (o-v-N)
460 m	465 m	460 m	460 w	464 m	v (o=v-o)
440 w	435 w	440 w	430 w	445	v (o=v-o) phenolic
430 w	425 w	435 w	442 w	435	
		420 w		425 m	
370 w	360 w	365 w	365 w	360 w	v (o=v-o) enolic

I.R. spectra of complexes

**Table 2: Magnetic Data and electronic Bands of Oxovanadium (iv) complexes (cm<sup>-1</sup>)**

Compound	lieff B.M. 300 <sup>0</sup> k	(v <sub>1</sub> ) XY → YZ (a <sub>2</sub> - b <sub>2</sub> )	(v <sub>2</sub> ) XY → XZ (a <sub>2</sub> b <sub>1</sub> )	(v <sub>3</sub> ) XY → Y <sup>2</sup> - Y <sup>2</sup> (a <sub>2</sub> - A <sub>1</sub> )	
[VO (C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub>	1.28	–	12760	16595	21670
[VO (C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.63	10225	12590	16813	22075
[VO (C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.57	10275	12215	16520	20280
[VO (C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.42	10530	12516	5710	20785
[VO (C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.40	–	13025	17218	22513
[VO (C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub>	1.30	–	12618	16780	21810
[VO (C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub> .2H <sub>2</sub> O	1.28	10310	12809	17125	22106
[VO (C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub> .4H <sub>2</sub> O	1.39	10400	12385	16716	21504
[VO (C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub> .4H <sub>2</sub> O	1.42	10218	12965	16972	20753
[VO (C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub> .2H <sub>2</sub> O	1.40	–	12238	16973	20301

The coordination around the vanadyl ion is distorted square pyramidal for square pyramidal oxovanadium (iv) complexes, the unpaired spin is expected to be in the 3dxy orbital. In the present complexes, two of the base atoms of the square pyramid are bridging oxygen atoms which are also bound to carbon atoms of the ligand molecule both the px and py orbitals of these oxygen atoms are involved in strong bonding and therefore π donate to vanadium 3dxy orbital. The 3dxy orbital is lowered in energy with respect to the 3dxz and 3dyz orbitals. This model predicts the energy level order as; dxy < dz<sub>2</sub> < dx<sup>2</sup>-y<sup>2</sup> < dz<sub>2</sub> and the bands in the regions 12200-13000 (v<sub>1</sub>) 16500-17200 (v<sub>2</sub>) and 20300-22500 (v<sub>3</sub>) cm<sup>-1</sup> may be assigned to xy-yz, xy → xz and xy → x<sup>2</sup>-y<sup>2</sup> transitions, respectively by assuming the effective symmetry of the complexes as c<sub>2v</sub>.

This model predicts another transition xy → z<sub>2</sub> and the energy of this band is too high as it falls in the u.v. region [12, 13]. (- 70000 cm<sup>-1</sup>)

On the basis of various physico-chemical studies, we have suggested square pyramidal diametric structure of vanadyl complexes.

#### Five- Coordinate square Pyramidal

- (i) Naphthoyl – 2; 5-Dihydroxyacetophenonehydrazone (C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>)
- (ii) Naphthoyl – 2; 5-Dihydroxy Propiophenonehydrazone (C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>)
- (iii) Naphthoyl 2; 5-Dihydroxy Butyrophenonehydrazone (C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>)
- (iv) Naphthoyl – 2-hydroxy Benzophenonehydrazone (C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>)
- (v) Naphthoyl – 2-hydroxy-acetyl Naphthalene hydrazone (C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>)

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