

## Stereochemical features of five-coordinate dimeric square pyramidal oxovanadium (iv) complexes

VIKAS MALIK, GEETA SOLANKI and VIJENDRA SINGH

Chemistry Department, J.V. College, Baraut, Baghpat - 250 611 (India).

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### ABSTRACT

A few complexes<sup>(1)</sup> of VO (II) with 2-3 dihydrazino quinoxaline have been synthesized and characterized by analytical, conductance, thermal, spectral and magnetic data. The ligand behaves as bis (NN) donor in all the complexes, coordinating through the ring azomethine nitrogen and nitrogen of terminal- NH<sub>2</sub>.

**Key words:** Stereochemical, Five-coordinate, Oxovanadium.

### INTRODUCTION

In the present paper, oxovanadium (IV) complexes of the composition [VO(L)]<sub>2</sub> or [VO(L)]<sub>2</sub> nH<sub>2</sub>O (n= 2, 4 and L = (C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>), (C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>), (C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>), (C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>), have been synthesised and their stereochemistry is ascertained by elemental analyses and by molecular weight, conductance, magnetic, infrared and electronic spectral measurements. The complexes have a dimeric structure involving bridging through phenolic oxygen and each unit appears to have a distorted a square pyramidal structure.

### EXPERIMENTAL

#### Preparation and Isolation of the Complexes

General methods for the preparation of oxovanadium (IV) complexes have been described.

#### Method (I)

The ligand (0.001 mole) was dissolved in ethanol (50 ml) and to this solution ethanolic solution of vanadyl chloride was added. The pH of the mixture was adjusted to 5-6 using 5% ammonia solution and the reaction mixture refluxed for 3 hrs. The coloured product thus obtained was filtered in not condition washed with methanol and petroleum ether and dried in vacuo.

#### Method (II)

A freshly prepared aqueous ethanolic solution of vanadyl 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 solid after complete precipitation. It was refluxed on water bath for one hour. The complex so obtained was filtered, washed with ethanol and dried ~ 120°C under reduced pressure to afford the desired product. Analyses of these complexes (Table 1) correspond to the general formula [VO(L)]<sub>2</sub>nH<sub>2</sub>O. All the metal complexes are coloured and stable to air and moisture. They are soluble in DMF and DMSO. They do not decompose below 300°C. The elemental analysis shows metal to ligand ratio as 1:1, Vanadium metal in all the complexes was estimated using EDTA and Eriochrome black-T as indicator and confirmed by igniting the complexes in air and then estimating the metal as pentaoxide.

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 moles of water per mol of the complex which accounts for one mole of water per metal ion. This low deaquation temperature suggests that water

molecules are outside the coordination sphere as crystal water.

## RESULTS AND DISCUSSION

The analytical data reveal that the complexes prepared by method-I have the general formula  $[VO(L)]$  whereas the complexes synthesized by method-II have one or two molecules of water of crystallization,  $[VO(L)]nH_2O$ . The complexes are not monomeric as revealed by the determination of their molecular weight in benzene (cryoscopic method) which have been found to be  $\sim 1.8$  times higher. This 1:1:8 ratio (calcd.Expt.) of the molecular weight suggest dimeric nature of the complexes which has been confirmed by their spectral and magnetic studies<sup>2,3</sup>.

### Infrared spectral studies

The infrared spectra of both type of complexes are similar. The broad band in the 3600-3200  $cm^{-1}$  region corresponds to  $\nu OH$  of the lattice held water molecules in the binuclear complexes of the type  $[VO(L)]nH_2O$ .

### Amide group vibrations

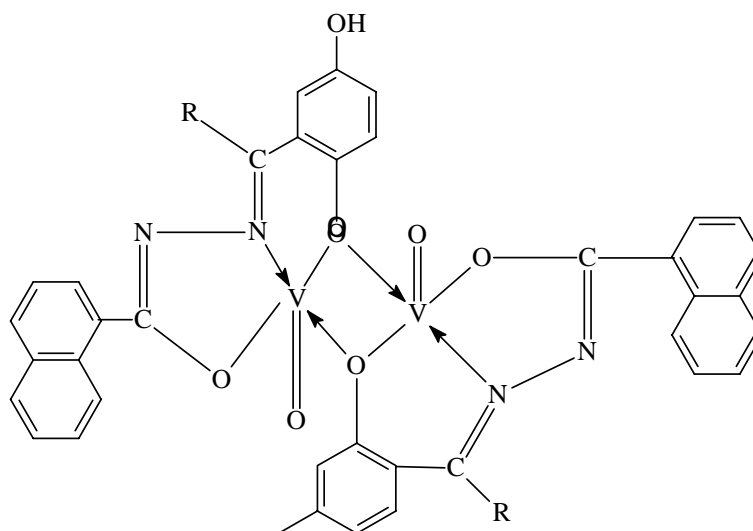
The free ligands show strong band in the region 1660-1675  $cm^{-1}$  which may be assigned to amide I of  $\nu(C=O)$  vibration<sup>4</sup>. The bands, around 1510, 1250, 650-660 and 495-505  $cm^{-1}$  may be assigned to amide II ( $\nu CN + \delta NH$ ), amide III ( $\nu CN$ ),

amide, IV ( $C=O$  out-of-plane deformation) and amide VI ( $C=O$  in-plane deformation) vibrations, respectively indicating that the ligands are present in keto-form, The bands at 3000-3050  $cm^{-1}$  are assigned to  $\nu(NH)$ <sup>5</sup>.

A decrease in the frequency of ( $C=O$ ) stretching vibration (1655  $cm^{-1}$  (amide-I band) by  $\sim 10$   $cm^{-1}$  as compared to the free ligand (1665  $cm^{-1}$ ) support this observation. This decrease is because of the drift in electron density from the carbonyl group of the amide function towards metal ions, Occurrence of  $\nu(C-N)$  of  $-C=O$  (amide-III) band as well as azomethine stretching frequencies at higher energies by about 30  $cm^{-1}$  and 15  $cm^{-1}$  suggest the bonding of azomethine nitrogen. In the spectra of complexes at band occur around 1595-1598  $cm^{-1}$  due to  $>C=N-N=C<$  (azine group) suggest enolic form of the ligand take part in chelation. A band around  $\sim 370$   $cm^{-1}$  in the complexes have the origin of ( $O=V-O$ ) phenolic vibration<sup>6,9</sup>.

### Azomethine group vibrations

The sharp and strong band around 1615  $cm^{-1}$  in the spectra of ligands can be assigned to the stretching mode of  $>C=N$  group. This band get shifted to the lower frequency by 20-30  $cm^{-1}$  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. This may be due to the



Five-coordinate square pyramidal

Table 1: Melting point, molecular weight and analytical data of Oxovanadium (IV) Complexes

S. No.	Compound	m.p. °C	Molecular weight		Analytical Data							
			Calcd.	Found	Found %			Calcd%				
			Calcd.	Found	V	C	H	N	V	C	H	N
1.	$[\text{VO}(\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	184	384	701	13.07	59.08	3.49	7.10	13.23	59.23	3.63	7.27
2.	$[\text{VO}(\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	175	398	705	12.60	60.02	3.85	6.90	12.76	60.16	4.01	7.01
3.	$[\text{VO}(\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	192	412	724	12.15	60.84	4.18	6.0	12.33	61.02	4.35	6.78
4.	$[\text{VO}(\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	216	418	759	15.82	65.73	3.71	6.55	15.97	65.88	3.81	6.68
5.	$[\text{VO}(\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	288	420	769	12.0	54.02	4.20	6.48	12.10	54.16	4.27	6.65
6.	$[\text{VO}(\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	286	434	764	11.54	55.01	4.40	6.22	11.71	55.18	4.59	6.43
7.	$[\text{VO}(\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	302	448	821	11.19	56.0	4.72	6.05	11.34	56.13	4.90	6.23
8.	$[\text{VO}(\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$	285	436	800	11.50	63.0	4.0	6.30	11.65	63.16	4.11	6.40

Table 2: Assignment of the Important Frequencies in the Infrared Spectra of Oxovanadium (IV) Complexes ( $\text{cm}^{-1}$ )

$[\text{VO}(\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3)]_2$	$[\text{VO}(\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3)]_2$	$[\text{VO}(\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3)]_2$	$[\text{VO}(\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3)]_2$	$[\text{VO}(\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3)]_2$	Assignment
1610s	1605s	1605	1600s	1610s	v (C=N) of azomethine
1600s	1610s	1590	1595s	1590s	>C=N-N=C<*
1530s	1540m	1535	1535m	1545m	Phenolic iCO
1290m	1300m	1290	1295m	1300m	Phenolic CO bending
960s	970s	985	990s	980s	v(V=O)
470m	475m	475	480m	475m	v(V=V-N)
460m	465m	460	460m	464m	v(O=V-O) phenolic
440w430w	435w425w	440435420wsh	430w442w	445w435m425m	Unassigned bands
370w	360w	365 w	365w	360w	v(O=V-O) enolic

Table 3: Magnetic Data and Electronic Spectral Bands of Oxovanadium (IV) Complexes (cm<sup>-1</sup>)

S. No.	Compound	$\mu_{\text{eff.}}$ 300°K	( $\nu_1$ ) XY→YZ ( $a_2 \rightarrow b_2$ )	( $\nu_2$ ) XY→XZ ( $a_2 \rightarrow b_1$ )	( $\nu_3$ ) XY X <sup>2</sup> Y <sup>2</sup> ( $a_2 \rightarrow a_1$ )
1.	[VO(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub>	1.28	—	16595	21670
2.	[VO(C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.63	10225	16813	22075
3.	[VO(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.57	10275	16520	20280
4.	[VO(C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub>	1.42	10530	5710	20785
5.	[VO(C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub>	1.40	—	17218	22513
6.	[VO(C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )] <sub>2</sub> , 2H <sub>2</sub> O	1.30	—	16780	21810
7.	[VO(C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )] <sub>2</sub> , 4H <sub>2</sub> O	1.28	10310	17125	22106
8.	[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	16716	21504
9.	[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	16972	20753
10.	[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	—	16973	20301

coordinate bond formation from one of the unsaturated nitrogen of the azomethine group to the vanadyl ion<sup>10,11</sup>.

### Phenolic group vibrations

The IR spectra of the ligands show strong bands in the regions 3200-3250 and 1320-1350 cm<sup>-1</sup> which may be assigned to stretching and deformation of phenolic OH vibrations involving hydrogen bonding. The intramolecular hydrogen bonding is also indicated by the presence of weak broad band around 2700-2775 cm<sup>-1</sup> in the free ligands<sup>12</sup>. A strong band at 1320-1350 cm<sup>-1</sup> may be due to phenolic (C-O) stretching vibration which shifts to higher frequency in the corresponding complexes showing thereby the bonding of the vanadyl ion through phenolic oxygen atom. The complexes display strong (V=O) stretching frequencies in the region 975-990 cm<sup>-1</sup> which is lower for penta coordination but compatible with hexa coordination<sup>13-15</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  $\nu$ (V-O) bands respectively. The  $\nu$ (O-H) which appears or 3200-3250 cm<sup>-1</sup> in molecule is absent in the complexes while  $\nu$ (C-O) bond in complexes is observed near 1380 cm<sup>-1</sup> which is in the higher energy side by ~70 cm<sup>-1</sup><sup>16</sup>. Such a large shift in higher energy direction indicates the involvement of the phenoxide moiety in the bridge in those complexes.

From the above discussion it is concluded that the ligands act in a terdentate manner and attacking the metal ion through phenolic and enolic oxygen (both deprotonated) and azomethine nitrogen<sup>17</sup>. The dimeric nature of the complexes is also supported by the appearance of a number of bands between 425-465 cm<sup>-1</sup>. Similar criterion for making distinction between dimeric and polymeric complexes has been advanced by Lever and Ramaswamy<sup>18</sup> on the basis of isotopic and variable temperature metal oxygen vibrations.

### Magnetic and electronic spectral studies

The reported complexes are paramagnetic and the 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

antiferromagnetic interaction is taking place with the neighbouring molecule. Infrared spectra molecular weight of the complexes suggests dimeric nature of the complexes.

A dimeric oxygen-bridged structure, which provides an appropriate symmetry for the  $3d_{xy}$  orbitals, of oxovanadium(IV) to overlap with each other and to form a strong  $\sigma$  – metal – metal bond, has been suggested for oxovanadium (IV) complexes of 5 – substituted N-(2 – hydroxyphenyl) salicylideneimine, which were also reported to have subnormal magnetic moments<sup>19-20</sup>. Poddar *et al.*<sup>21</sup> and Yamada *et al.*<sup>22</sup> also observed subnormal magnetic moment in case of oxovanadium (IV) complexes of tridentate Schiff bases and suggested in oxygen – bridged structure. A binuclear structure has been proposed<sup>23</sup> in a series of oxovanadium (IV) Schiff base complexes exhibiting subnormal magnetic moments, in which the  $\sigma$  – metal – metal interaction is the principal path for spin – spin coupling. It was argued that such an interaction leads to a singlet spin state and a higher triplet spin state with an energy separation equal to the exchange integral J. Therefore, it is presumed that the magnitude of J and the available thermal energy, both make some contribution to the population of the upper triplet state giving rise to subnormal magnetic moment of 1.28–1.67 B.M. at room temperature.

The coordination around the vanadyl ion is distorted square pyramid. For square pyramidal oxovanadium(IV) complexes, the unpaired spin is expected to be in the  $3d_{xy}$  orbital<sup>24</sup>. 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  $P_x$  and  $p_y$  orbitals of these oxygen atoms are involved in strong  $\sigma$  – bonding and therefore do not  $\pi$ -donate to the vanadium  $3d_{xy}$  orbitals ( $P_x$  has symmetry, with respect to  $d_{xy}$  of the second vanadium atom of the dimer). The  $3d_{xy}$  orbital is therefore lowered in energy with respect to the  $3d_{xz}$  and  $3d_{yz}$  orbitals. In the binuclear complexes the  $3d_{xy}$  orbitals have appropriate symmetry to  $\sigma$ -bond with each other and as such this  $\pi$ -metal-metal interaction should be the principal path for spin coupling.

The electronic spectra of complexes

recorded in ethanol exhibit bands in the regions 12200-13000, 16500-17200 and 20300-22500  $\text{cm}^{-1}$ .

The geometry is not ideal square pyramidal ( $C_{4v}$ ) due to in-equivalent chromophore donor atom  $\text{NO}_2$ . O of the ligands. Therefore lower symmetry ( $C_{2v}$ ) can be considered Kuska and Yang<sup>(25)</sup> have proposed the energy level scheme.  $a_2(xy) < b_1(xz) \sim b_2(yz) < a_1(x^2 - y^2) < a_1(z^2)$ , to interpret the spectra of oxovanadium (IV) complexes having  $C_{2v}$  symmetry. Wasson *et al.*<sup>(26)</sup> have advanced a crystal field model to account for electronic and electronic – spin resonance spectra of low symmetry oxovanadium (IV) complexes possessing effective  $C_{2v}$  symmetry. This model predicts the energy level order as;  $d_{xy} < d_{xz} < d_{yz} < d_x^2 - y^2 < d_z^2$ . Except for the splitting of  $d_{xz}$  and  $d_{yz}$  levels, this scheme is similar to the Ballhausen – Gray energy level scheme<sup>27</sup>.

Selbin *et al.*,<sup>28,29</sup> have also put forward an energy level order called 'clustered level scheme' of Ortolano, Selbin and McGlyn (OSM) which is somewhat different from that of Ballhausen and Gray, suggesting that the three basically d-d transition for  $C_{4v}$  symmetry occur in a narrow region of the spectrum below about 20000  $\text{cm}^{-1}$  and the total of four bands have been interpreted as d-d transitions in  $C_{2v}$  symmetry. This scheme does not apply to the present complexes because one band is observed above 20000  $\text{cm}^{-1}$ . Hence we have adopted the energy level schemes suggested by Wood *et al.* and Kuska and Yang. (*Loc. Cit.*) and modified by Wasson *et al.*<sup>30</sup> and accordingly, the bands in the regions 12000-13000 ( $\nu_1$ ), 16500-17200 ( $\nu_2$ ) and 20300-22500 ( $\nu_3$ )  $\text{cm}^{-1}$  may be assigned to  $XY \rightarrow YZ$ ,  $XY \rightarrow XZ$ , and  $XY \rightarrow X^2 - y^2$  transitions, respectively by assuming the effective symmetry of the symmetry of the complexes as  $C_{2v}$ . The splitting of  $d_{xz}$  and  $d_{yz}$  levels by 4000  $\text{cm}^{-1}$  is consistent with the prediction of the model proposed by Wasson *et al.* (*Loc. Cit.*) This model predicts another transition  $XY \rightarrow \nu Z^2$  and the energy of this band is too high as it falls in the ultraviolet region<sup>31-37</sup> ( $\sim 70000 \text{ cm}^{-1}$ ).

On the basis of various physico chemical studies, we have suggested square pyramidal dimeric structure to the vanadyl complexes

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