

## Chemistry of oxovanadium(IV) bound to tetradentate ONNO donors: Influence of axial coordination on the V–O<sub>(1)</sub> bond

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**Abstract.** Chelating behaviour of some tetradentate ONNO donors derived from *o*-aminobenzoylhydrazide and some diketones toward oxo-vanadium(IV) ion is reported. The donors react with oxometal cation depending on the pH of the reaction medium. The product containing the neutral keto and the binegative enol form of the donors have the formulae [VO(H<sub>2</sub>L)(SO<sub>4</sub>)] (at pH 3.0) (1) and [VO(L)(H<sub>2</sub>O)] (at pH 6.0) (2) respectively [H<sub>2</sub>L = (2-NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CONH: C(R)-(CH<sub>2</sub>)<sub>m</sub>C(R): NNH CO-C<sub>6</sub>H<sub>4</sub>(2-NH<sub>2</sub>); H<sub>2</sub>L = H<sub>2</sub>DA (R = CH<sub>3</sub>, m = 0), H<sub>2</sub>BA (R = C<sub>6</sub>H<sub>5</sub>, m = 0), H<sub>2</sub>AA (R = CH<sub>3</sub>, m = 2)]. Both (1) and (2) react with a neutral monodentate donor B (B = pyridine, aniline etc.) yielding mixed-ligand complexes [VO(L)(B)]. Influence of the axial coordination on the V–O<sub>(1)</sub> bond is discussed and a monomeric distorted octahedral donor environment for the oxovanadium(IV) ion has been suggested.

**Keywords.** Oxovanadium(IV) chemistry; tetradentate donors; axial coordination; V–O<sub>(1)</sub> bond.

### 1. Introduction

As part of our programme of exploring the coordination behaviour of some multidentate mixed N–O donors towards oxometal cations (Ghosh and Maiti 1987), we present here the syntheses, characterisation and chemical reactivities of the oxovanadium(IV) complexes of diacetyl *bis*(2-aminobenzoylhydrazone) (H<sub>2</sub>DA), benzil *bis*(2-aminobenzoylhydrazone) (H<sub>2</sub>BA) and hexan-2,5-dione *bis*(2-aminobenzoylhydrazone) (H<sub>2</sub>AA). These tetradentate ligands act in the keto form as neutral donors or in dinegative enolate form depending on the experimental conditions. The tetradentate ONNO donors of our choice, because of their structural constraints, offer exclusive planar coordination and are capable of occupying four positions on the equatorial plane of the coordination polyhedron of a metal ion. Since one of the two axial positions of a mono oxocation like VO<sup>2+</sup> is permanently occupied by the oxo oxygen, such a ligand is expected to provide a general pathway of preparing complexes of mono oxometal acceptor centres in general and VO<sup>2+</sup> in particular with a highly stable penta-coordinate core, the sixth coordination position being occupied by

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a comparatively weak and easily interchangeable monodentate donor. This situation can be utilised for varying the electron density in the vanadium orbital by placing different monodentate donors in a position *trans* to the V–O<sub>(1)</sub> bond. Such a change should be reflected in the change of the  $\nu(\text{V–O}_{(1)})$  mode and the change in the stretching force constant of the same bond. It is with this objective that the present work is undertaken.

## 2. Experimental

### 2.1 Preparation of the Schiff bases

The ligands were prepared by standard methods (Ghosh and Maiti 1987). Melting points of H<sub>2</sub>DA, H<sub>2</sub>AA and H<sub>2</sub>BA are 276, 143 and 227°C respectively.

### 2.2 Syntheses of the complexes

The compounds [VO(H<sub>2</sub>DA/H<sub>2</sub>BA)(SO<sub>4</sub>)] were prepared by adding 10 ml methanolic solution of VOSO<sub>4</sub>·5H<sub>2</sub>O (2 mmol) to 20 ml ethanolic suspension of the ligand (1 mmol) and stirring the mixture for 3 h (pH 3.0). The precipitated brown solid was filtered, washed with ethanol and dried over fused CaCl<sub>2</sub>. The greyish compound [VO(H<sub>2</sub>AA)(SO<sub>4</sub>)] was prepared by refluxing a mixture of the ligand (3 mmol) and VOSO<sub>4</sub>·5H<sub>2</sub>O (2 mmol) in 25 ml ethanol for 3 h (pH 3.5).

The compounds [VO(DA/BA)(H<sub>2</sub>O)] were prepared by adding 10 ml methanolic solution of vanadyl acetate (1 mmol) to 20 ml ethanolic suspension of the ligand (1 mmol) and stirring the mixture for 3 h (pH 6.0). The precipitated brownish solid was filtered, washed with ethanol and dried over fused CaCl<sub>2</sub>.

The light yellow compound [VO(AA)(H<sub>2</sub>O)] was prepared by stirring a mixture of vanadyl chloride (2 mmol in 5 ml ethanol) and the ligand (1 mmol suspended in 20 ml ethanol) for 3 h followed by filtration, washing of the precipitate with ethanol and subsequent drying over fused CaCl<sub>2</sub>.

Compounds of the general formula [VO(L)(B)] (B = pyridine, picoline, aniline, methylamine etc.) were prepared by keeping an alcoholic solution of [VO(H<sub>2</sub>L)(SO<sub>4</sub>)] or [VO(L)(H<sub>2</sub>O)] in contact with the liquid base (B) in 1:3 molar ratio at a pH of 6–7 for 1 day in a stoppered vessel and evaporating the resultant brown solution at room temperature to a pasty mass. It was then taken up with a little ethanol, filtered, washed with ether and stored in a fused CaCl<sub>2</sub> desiccator.

### 2.3 Physical measurements

The methods utilised for the characterisation of the compounds are the same as reported earlier (Maiti *et al* 1988). Analytical data together with the magnetic moment and molar conductance values, the more important IR and electronic spectral bands and the metal–oxygen multiple bond stretching force constants are presented in table 1.

## 3. Results and discussion

The compound [VO(H<sub>2</sub>L)(SO<sub>4</sub>)] behaves as a nonelectrolyte in DMSO indicating the presence of coordinated sulphate. All other complexes are also nonelectrolytes in the same solvent.

Table 1. Analytical and other physical data of the compounds.

Compound	Found (Calc.%)				$\mu_{\text{eff}}$ (BM)	$\Lambda_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\nu(\text{V}-\text{O}_{(i)})$ (cm <sup>-1</sup> )	$F_{\text{V}-\text{O}_{(i)}}$ (mdynes/Å)	Electronic spectral band (cm <sup>-1</sup> )
	M	N	C	H					
H <sub>2</sub> DA		23.4 (23.8)	61.9 (61.3)	5.2 (5.6)					
[VO(H <sub>2</sub> DA)(SO <sub>4</sub> )]	9.5 (9.9)	15.8 (16.3)	41.7 (41.9)	4.2 (3.9)	1.77	20	970	6.706	11760, 17540, 21740
[VO(DA)(H <sub>2</sub> O)]	11.2 (11.7)	18.9 (19.3)	49.9 (49.6)	4.3 (4.1)	1.72	5	975	6.775	22220
[VO(DA)(py)]	10.7 (10.3)	19.2 (19.7)	55.9 (55.6)	4.8 (4.6)	1.75	6	960	6.568	17860, 22220
[VO(DA)(3-pic)]	9.7 (10.0)	19.0 (19.2)	56.8 (56.4)	4.7 (4.9)	1.73	8	960	6.568	18350, 23260
[VO(DA)(4-pic)]	10.2 (10.0)	19.1 (19.2)	56.1 (56.4)	4.7 (4.9)	1.7	6	950	6.432	18180, 23810
[VO(DA)(aniline)]	9.0 (10.0)	19.5 (19.2)	56.2 (56.4)	4.7 (4.9)	1.73	7	965	6.637	17860
[VO(DA)MeNH <sub>2</sub> ]	11.5 (11.3)	21.3 (21.8)	50.2 (50.8)	5.2 (5.1)	1.7	10	940	6.297	17850, 23200
H <sub>2</sub> BA		17.8 (17.6)	70.9 (70.6)	5.1 (5.0)					
[VO(H <sub>2</sub> BA)(SO <sub>4</sub> )]	7.7 (8.0)	12.9 (13.2)	52.4 (52.7)	3.5 (3.8)	1.78	15	975	6.775	16670, 20200
[VO(BA)(H <sub>2</sub> O)]	9.2 (9.1)	15.4 (15.0)	59.8 (60.1)	4.4 (4.2)	1.7	7	965	6.637	18690, 21050
[VO(BA)(py)]	8.1 (8.2)	15.9 (15.8)	63.5 (63.8)	4.2 (4.3)	1.69	6	950	6.432	17540, 20620
H <sub>2</sub> AA		22.2 (22.1)	63.6 (63.2)	6.5 (6.3)					
[VO(H <sub>2</sub> AA)(SO <sub>4</sub> )]	9.6 (9.3)	15.8 (15.4)	44.6 (44.2)	3.9 (3.7)	1.7	17	975	6.775	12990, 18180, 23255

(Continued)

Table I. (Continued)

Compound	Found (Calc.%)				$\mu_{\text{eff}}$ (BM)	$\Lambda_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\nu(\text{V}-\text{O}_{(1)})$ (cm <sup>-1</sup> )	$F_{\text{V}-\text{O}_{(1)}}$ (mdynes/Å)	Electronic spectral band (cm <sup>-1</sup> )
	M	N	C	H					
[VO(AA)(H <sub>2</sub> O)]	10.9 (11.0)	17.8 (18.1)	52.2 (51.8)	5.2 <sup>a</sup> (5.1)	1.75	6	995	7.056	14280, 19800
[VO(AA)(py)]	9.6 (9.7)	18.2 (18.7)	57.7 (57.2)	5.2 (5.1)	1.76	2	958	6.541	14080, 23255
[VO(AA)(3-pic)]	9.6 (9.5)	18.6 (18.2)	57.8 (57.9)	5.1 (5.4)	1.71	3	955	6.500	18020, 23150
[VO(AA)(4-pic)]	9.7 (9.5)	18.0 (18.2)	57.4 (57.9)	5.6 (5.4)	1.74	7	955	6.500	18250, 23530
[VO(AA)(Aniline)]	9.2 (9.5)	17.7 (18.2)	57.5 (57.9)	5.2 (5.4)	1.74	4	960	6.568	13850, 18020, 22730
[VO(AA)(MeNH <sub>2</sub> )]	10.7 (10.7)	17.8 (17.6)	53.2 (52.9)	5.5 (5.6)	1.72	8	940	6.297	18180, 23260

### 3.1 Electronic spectra

Electronic spectra of the present oxovanadium(IV) compounds in methanol or DMSO exhibit two/three rather broad bands in the 11760–23810  $\text{cm}^{-1}$  region. Of these three, the high energy band is assigned to the  $b_2 \rightarrow a_1^*$  transition (20200–23810  $\text{cm}^{-1}$ ) while the lower energy bands are attributed to the  $b_2 \rightarrow e^*$  (11760–14280  $\text{cm}^{-1}$ ) and  $b_2 \rightarrow b_1^*$  transitions (16670–19800  $\text{cm}^{-1}$ ) respectively (Ballhausen and Gray 1962; Ballhausen *et al* 1968; Ghosh and Maiti 1987). Most of these bands have high extinction coefficients (ranging from  $\approx 100$  to 2900  $\text{cm}^{-1} \text{mol}^{-1}$ ) indicating that the  $d-d$  transitions are not pure as a result of their mixing with ligand  $\pi-\pi^*$  systems (Lever 1984).

### 3.2 Infrared spectra

From our earlier work it is evident that in the present ligands, Schiff base formation has taken place exclusively from the hydrazinic  $-\text{NH}_2$  part of the 2-aminobenzoylhydrazide leaving the aromatic ring  $-\text{NH}_2$  group free (Ghosh and Maiti 1987). The two  $\nu_{\text{as}}(\text{N-H})$  and  $\nu_{\text{s}}(\text{N-H})$  modes of the ring  $-\text{NH}_2$  group for the ligands  $\text{H}_2\text{DA}$  (3480 and 3380  $\text{cm}^{-1}$ ),  $\text{H}_2\text{BA}$  (3465 and 3350  $\text{cm}^{-1}$ ) and  $\text{H}_2\text{AA}$  (3450 and 3350  $\text{cm}^{-1}$ ) remain more or less unaltered in all their complexes pointing to the nonparticipation of the ring  $-\text{NH}_2$  group in complexation to the  $\text{VO}^{2+}$  acceptor centre (Bellamy 1975; Ghosh and Maiti 1987). The strong amide I or  $\nu(\text{C=O})$  band located at 1640, 1635 and 1672  $\text{cm}^{-1}$  for the ligands  $\text{H}_2\text{DA}$ ,  $\text{H}_2\text{AA}$  and  $\text{H}_2\text{BA}$ , respectively, undergoes 10–17  $\text{cm}^{-1}$  negative shift in the complexes of the formula  $[\text{VO}(\text{H}_2\text{L})(\text{SO}_4)]$  containing the keto form of the ligands. This points to the coordination of the amide carbonyl oxygen to the  $\text{VO}^{2+}$  moiety. Coordination from the azomethine nitrogen to the oxometal moiety in all the complexes is manifested through the lowering of the  $\nu(\text{C=O})$  mode from 1608  $\text{cm}^{-1}$  (for both  $\text{H}_2\text{DA}$  and  $\text{H}_2\text{AA}$ ) and 1615  $\text{cm}^{-1}$  (for  $\text{H}_2\text{BA}$ ) to the 1580–1590  $\text{cm}^{-1}$  region. In the complexes prepared at higher pH (6–7), the amide I band disappears completely indicating the enolisation of the amide carbonyl group. In these complexes, each tetradentate ligand coordinates to the oxometal acceptor centre through two deprotonated enolate oxygens and two azomethine nitrogens.

All the oxovanadium(IV) complexes exhibit the fairly strong  $\text{V}-\text{O}_{(1)}$  stretching frequency in the 940–995  $\text{cm}^{-1}$  region (table 1). Based on the extent of perturbation of the  $\nu(\text{V}-\text{O}_{(1)})$  mode in all the oxovanadium(IV) complexes of the general formulae  $[\text{VO}(\text{L})(\text{B})]$  containing the Lewis base B occupying the sixth coordination position *trans* to the  $\text{V}-\text{O}_{(1)}$  bond, the following ligand series can be established in which the Lewis bases are arranged in the increasing order of their  $\sigma$ -donor capacity:  $\text{H}_2\text{O} < \text{aniline} < \text{py} < 3\text{-pic} < 4\text{-pic} < \text{CH}_3\text{NH}_2$ .

From the IR spectra of the compounds  $[\text{VO}(\text{H}_2\text{L})(\text{SO}_4)]$ , the sulphate is found to be coordinated in a monodentate fashion ( $\nu_3(\text{SO}_4)$ : 1140–1110  $\text{cm}^{-1}$  and 1040–1020  $\text{cm}^{-1}$ ,  $\nu_1$ : 980–970  $\text{cm}^{-1}$ ,  $\nu_4$ : 610–600  $\text{cm}^{-1}$ ). The specific bands of the coordinated Lewis bases and water molecules are also observed in the IR spectra of the corresponding complexes.

### 3.3 Evaluation of the $\text{V}-\text{O}_{(1)}$ stretching force constant

The vanadium to apical oxygen bond is regarded as the primary  $\text{V}-\text{O}_{(1)}$  bond which is a multiple covalent bond consisting of the  $p\pi-d\pi$  donation of electrons from the oxygen to the vanadium atom (Selbin 1965). The  $\text{V}-\text{O}_{(1)}$  stretching force constant was

computed by using a simple harmonic relation (Ferguson 1973) and the values are included in table 1. The  $\nu(\text{V}-\text{O}_{(1)})$  mode for the  $\text{VO}^{2+}$  complexes is known to be most sensitive to the nature of its *trans* ligand. Donors that increase the electron density on vanadium, effect a reduction in the degree of  $p\pi-d\pi$  donation from the multiple-bonded oxygen atom. The lowering of the  $\text{V}-\text{O}_{(1)}$  bond order is reflected in the reduction of both  $\nu(\text{V}-\text{O}_{(1)})$  and  $F_{\text{V}-\text{O}_{(1)}}$  values observed at  $975\text{ cm}^{-1}$  and  $6.775\text{ mdynes/\AA}$  for the complex  $[\text{VO}(\text{DA})(\text{H}_2\text{O})]$  which are shifted towards lower values when the coordinated water molecule is replaced by the stronger monodentate donor B. This is also true for the complexes of the other two ligands (Maiti *et al* 1988, Selbin *et al* 1963).

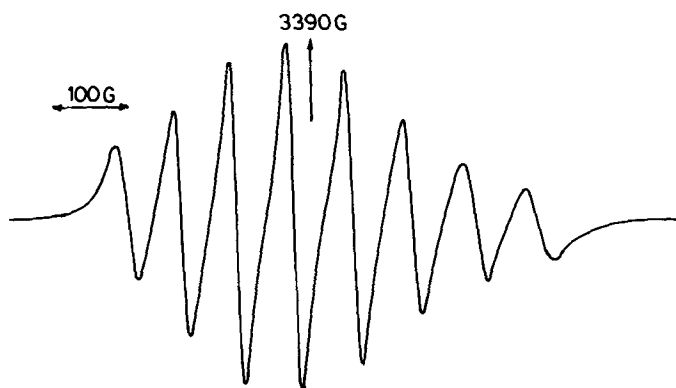
### 3.4 Magnetic moment and ESR spectra

The room temperature magnetic moment values of the reported oxovanadium(IV) complexes (table 1) correspond to the spin-only value expected for a  $d^1$  system and are consistent with the monomeric distorted octahedral structure of the complexes (Ballhausen and Gray 1962).

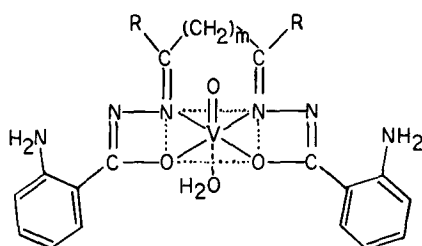
The X-band ESR spectra of some of the oxovanadium-(IV) complexes were studied and the results presented in table 2. The powder and the solution (DMF) spectra of the compound  $\text{VO}(\text{L})(\text{H}_2\text{O})$  exhibit a set of eight hyperfine lines arising due to the interaction of the unpaired  $d$ -electron with the vanadium nucleus (figure 1) (Maiti *et al* 1988). However, in the powder spectrum, the ESR signals are a little broadened due to

**Table 2.** ESR parameters of some of the oxovanadium (IV) complexes at  $25^\circ\text{C}$ .

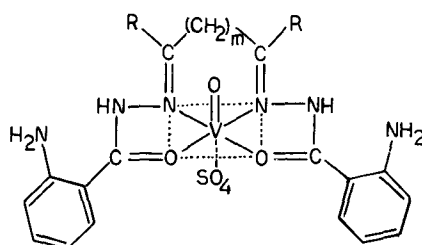
Compound	$A_{av}(\text{G})$	$g_{av}$
$[\text{VO}(\text{H}_2\text{DA})(\text{SO}_4)]$	76	1.97
$[\text{VO}(\text{DA})(\text{H}_2\text{O})]$	75	1.99
$[\text{VO}(\text{H}_2\text{BA})(\text{SO}_4)]$	112	2.00
$[\text{VO}(\text{BA})(\text{H}_2\text{O})]$	120	1.94
$[\text{VO}(\text{H}_2\text{AA})(\text{SO}_4)]$	110	1.96
$[\text{VO}(\text{AA})(\text{H}_2\text{O})]$	79	1.97



**Figure 1.** ESR spectrum of  $[\text{VO}(\text{AA})(\text{H}_2\text{O})]$  in DMF solution.



**Figure 2.** Donor environment around  $\text{VO}^{2+}$  in  $[\text{VO}(\text{L})(\text{H}_2\text{O})]$  type complexes where  $\text{H}_2\text{L} = \text{H}_2\text{DA}$  ( $\text{R} = \text{CH}_3$ ,  $m = 0$ ),  $\text{H}_2\text{BA}$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $m = 0$ ),  $\text{H}_2\text{AA}$  ( $\text{R} = \text{CH}_3$ ,  $m = 2$ ).



**Figure 3.** Donor environment around  $\text{VO}^{2+}$  in  $[\text{VO}(\text{H}_2\text{L})(\text{SO}_4)]$  type complexes.

some contribution of spin-spin relaxation in the solid state. The observation is common to most of the compounds reported in this paper.

Considered together with the electronic spectral data and magnetic moment values, the ESR characteristics of  $\text{VO}(\text{L})(\text{H}_2\text{O})$  indicate the presence of the oxovanadium(IV) acceptor centre in a distorted octahedral coordination environment with the unpaired electron of oxovanadium(IV) located in the  $d_{xy}$  level in the ground state. Presence of metal hyperfine lines in the powder spectrum indicates that the separation between the nearest  $\text{VO}(\text{II})$  acceptor centres is quite large and as a result the hyperfine interaction is greater than the exchange interaction. Absence of any nitrogen hyperfine splitting signifies that the unpaired electron is predominantly localised on vanadium and that the in-plane  $\pi$ -bonding is very slight (Kivelson and Lee 1964; Selbin 1966).

From the above considerations, the probable structure of the complexes of formula  $[\text{VO}(\text{L})(\text{H}_2\text{O})]$  may be as presented in figure 2. The structure of  $[\text{VO}(\text{L})(\text{B})]$  can be visualised from that of  $[\text{VO}(\text{L})(\text{H}_2\text{O})]$  by replacing the coordinated water molecule by B. The structure of  $[\text{VO}(\text{H}_2\text{L})(\text{SO}_4)]$  follows from that of the enolic compound by the appropriate modification of the ligand skeleton and replacing the axially bound water molecule by a monodentate sulphate as shown in figure 3.

The present work describes a general strategy for fabricating a penta-coordinated complex core around a monooxocation like  $\text{VO}^{2+}$  with the sixth position of the coordination octahedron, *trans* to the  $\text{V}-\text{O}_{(1)}$  multiple bond, capable of harbouring a monodentate donor. Influence of this sixth donor on the  $(\text{V}-\text{O}_{(1)})$  mode is clearly reflected in the observed shift of the relevant frequency.

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