Chemistry of molecular and supramolecular structures of vanadium(IV) and dioxygen-bridged V(V) complexes incorporating tridentate hydrazone ligands

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Four hydrazone ligands: 2-benzoylpyridine benzoyl hydrazone (HBPB), di-2-pyridyl ketone nicotinoyl hydrazone (HDKN), quinoline-2-carbaldehyde benzoyl hydrazone (HQCB), and quinoline-2-carbaldehyde nicotinoyl hydrazone (HQCN) and four of their complexes with vanadyl salts have been synthesized and characterized. Single crystals of HBPB and complexes [VO(BPB)(l2-O)]2 (1) and [VO(DKN)(l2-O)]2 1/2H2O (2) were isolated and characterized by X-ray crystallography. Each of the complexes exhibits a binuclear structure where two vanadium(V) atoms are bridged by two oxygen atoms to form distorted octahedral structures within cis-N2O4 donor sets. In most complexes, the uninegative anions function as tridentate ligands, coordinating through the pyridyl- and azomethine-nitrogen atoms and enolic oxygen whereas in complex [VO(HQCN)(SO4)]SO4 4H2O (4) the ligand is coordinated in the keto form. Complexes [VO(QCB)(OMe)] 1/2H2O (3) and 4 are found to be EPR active and showed well-resolved axial anisotropy with two sets of eight line pattern.

1. Introduction

Interest in coordination chemistry of aroylhydrazones has been a subject of enthusiastic research since they show a wide range of catalytic properties, especially those examples derived from heterocyclic aldehydes or ketones [1]. The heightened interest in vanadium coordination complexes stems from its importance in biological systems, which is only now beginning to be fully appreciated [2]. Vanadium may or may not play an essential role in normal mammalian metabolism [2]. However, at pharmacological concentrations, some species are potential therapeutic agents [3,4]. Thus, the insulin-enhancing, insulin mimetic properties of oxovanadium(V) complexes, their use as model complexes for the active site of vanadoenzymes, and their use as catalysts in biological and industrial processes have been reported [5–9]. Furthermore, these compounds exhibit potential as anti-tumour agents by inhibiting growth of malignant cell lines by induction of cell-cycle arrest and/or cytotoxic effects [10]. Although most known insulin-like complexes contain vanadium in oxidation state +IV, vanadium(V) compounds have also been found to have insulin-like properties [11]. Depending on the number and type of donor atoms, and the nature of substitution in these oligodentate ligands, a variety of mononuclear and polynuclear oxo-, dioxo-vanadium(V) complexes and complex clusters have been reported [12–14]. The metal centres in oxovanadium(V) monomers with a N2O5 chromophore usually exhibit square pyramidal or trigonal bipyramidal geometries. The two coordinate vanadium(V) centres often dimerise into octahedral bis(μ-oxo)-bridged complexes via (L)V=O–V=O(L) intermolecular interactions with highly asymmetric metal-(μ-O) distances.

In view of importance of vanadium complexes, we present here the synthesis, spectroscopic characterization of VO2+ and VO2+ complexes of some aroyl hydrazones and crystal structure determinations of two representative binuclear (μ-oxo)-bridged vanadium species.

2. Experimental

2.1. Materials

Di-2-pyridylketone (Aldrich), 2-benzoylpyridine (Aldrich), quinoline-2-carbaldehyde (Aldrich), Benzhydrazide (Aldrich), and nicotinic hydrazide (Aldrich), vanadyl sulfate (Aldrich) and VO(acac)2 (E-Merck) were used as received. Solvents were purified by standard procedures before use.

2.2. Syntheses of ligands

All the hydrazone ligands were synthesized by adapting the earlier reported procedure, namely via condensation between...
appropriate aldehyde/ketone with the respective acid hydrazide as described below [15]. The chemical structures and abbreviations for the ligands are given in Fig. 1.

2.2.1. Synthesis of 2-benzoylpyridine benzoyl hydrazone (HBPB)
A methanol solution of benzoic hydrazide (0.136 g, 1 mmol) was refluxed with 2-benzoylpyridine (0.183 g, 1 mmol) continuously for 4 h after adding a few drops of glacial acetic acid. There was no immediate formation of the product. Then the reaction mixture was kept aside for slow evaporation at room temperature. After 3–4 days, colourless block-shaped crystals suitable for single crystal analyses were formed which were carefully separated (Scheme 1). Yield: 79%, m.p.: 128–130°C. Elemental Anal. Calc.: C, 75.73; H, 5.02; N, 13.94. Found: C, 75.46; H, 5.23; N, 13.98%.

Selected IR (cm⁻¹) bands: ν(N–H) 3063; ν(C=O) 1678; ν(C=N) 1571.

Electronic absorption bands (MeCN) λ_max (nm): 241, 271, 315.

2.2.2. Synthesis of di-2-pyridyl ketone nicotinoyl hydrazone hemihydrate (HDKN_{0.5H_2O})
Colourless HDKN_{0.5H_2O} was synthesized from di-2-pyridyl ketone and nicotinoyl hydrazone by a procedure similar to that described for HBPB. Yield: 84%, m.p.: 158–160°C. Elemental Anal. Calc.: C, 65.37; H, 4.52; N, 13.98. Found: C, 65.94; H, 4.26; N, 13.98%.

Selected IR (cm⁻¹) bands: ν(N–H) 3063; ν(C=O) 1678; ν(C=N) 1571.

Electronic absorption bands (MeCN) λ_max (nm): 233, 271, 322.

2.2.3 Synthesis of quinoline-2-carbaldehyde benzoyl hydrazone sesquihydrate (HQC\(_{2}\)O)_{1.5H_2O}
Pale-yellow HQC\(_{2}\)O_{1.5H_2O} was synthesized from quinoline-2-carbaldehyde and benzoic hydrazide. Yield: 89%, m.p.: 143–145°C. Elemental Anal. Calc. for HQC\(_{2}\)O_{1.5H_2O}: C, 67.54; H, 5.33; N, 13.90. Found: C, 67.81; H, 4.86; N, 14.40%.

Selected IR (cm⁻¹) bands: ν(N–H) 3191; ν(C=O) 1655; ν(C=N) 1593.

Electronic absorption bands (MeCN) λ_max (nm): 223, 269, 318.

2.2.4. Synthesis of quinoline-2-carbaldehyde nicotinoyl hydrazone sesquihydrate (HQC\(_{1}\)O_{1.5H_2O})
Colourless HQC\(_{1}\)O_{1.5H_2O} was prepared in the same way as for HDKN except quinoline-2-carbaldehyde was used instead of di-2-pyridyl ketone. Yield: 84%, m.p.: 140–142°C. Elemental Anal. Calc. for HQC\(_{1}\)O_{1.5H_2O}: C, 63.36; H, 4.98; N, 18.47. Found: C, 63.16; H, 4.59; N, 18.58%.

Selected IR (cm⁻¹) bands: ν(N–H) 3173; ν(C=O) 1656; ν(C=N) 1591.

Electronic absorption bands (MeCN) λ_max (nm): 241, 271, 315.

2.3 Syntheses of complexes

2.3.1. Syntheses of [VO(BPB)(\mu_2-O)]_2 (1)
Complex 1 was prepared by refluxing a methanolic solution of HBPB (1 mmol, 0.301 g) and vanadyl sulfate (1 mmol, 0.163 g) for 5 h. The resulting solution was allowed to stand at room temperature and after slow evaporation, yellow crystals of complex 1 were separated, filtered and washed with ether and dried over P_2O_5 in vacuo.

[VO(BPB)(\mu_2-O)]_2: Yield: 63%, m.p.: 225–227°C. λ_m (DMF): 8 ohm⁻¹ cm² mol⁻¹. Elemental Anal. Calc.: C, 60.01; H, 3.87; N, 10.77. Found: C, 59.86; H, 4.28; N, 11.31%.

2.3.2. Synthesis of [VO(DKN)(\mu_2-O)]_2·2H_2O (2)
To a solution of HDKN (1 mmol, 0.312 g) in methanol, a DMF–methanol mixture of VO(acac)_2 (1 mmol, 0.265 g) was added. The resulting solution was refluxed for 5 h. and then kept at room temperature. The pale-yellow crystals of 2 that separated out were filtered, washed with ether and dried over P_2O_5 in vacuo.

[VO(DKN)(\mu_2-O)]_2·2H_2O: Yield: 83%, m.p.: 182–184°C. λ_m (DMF): 8 ohm⁻¹ cm² mol⁻¹. Elemental Anal. Calc. for [VO(DKN)(\mu_2-O)]_2·2H_2O: C, 51.23; H, 3.69; N, 17.07. Found: C, 51.65; H, 3.23; N, 17.71%.

2.3.3. Synthesis of [VO(QCB)(OMe)]_2·1.5H_2O (3)
Complex 3 was prepared in similar manner as complex 2 by refluxing methanol solutions of HQCB (1 mmol, 0.303 g) and VO(acac)_2 (1 mmol, 0.265 g) for 5 h. A green crystalline precipitate was filtered, washed with ether and dried over P_2O_5 in vacuo.

[VO(QCB)(OMe)]_2·1.5H_2O: Yield: 89%, m.p.: >300°C. λ_m (DMF): 20 ohm⁻¹ cm² mol⁻¹. Elemental Anal. Calc. for [VO(QCB)(OMe)]_2·1.5H_2O: C, 54.14; H, 4.54; N, 10.52. Found: C, 53.73; H, 4.41; N, 10.63%.

2.3.4. Synthesis of [VO(HQCN)(SO_4)]SO_4·4H_2O (4)
Complex 4 was prepared in similar manner as complex 1 refluxing methanol solutions of HQCN (1 mmol, 0.303 g) and vanadyl

Fig. 1. Chemical structures of hydrazone ligands and their abbreviations.

sulfate (1 mmol, 0.163 g) for 5 h. A green crystalline precipitate was filtered off, washed with ether and dried over P₂O₅ in vacuo.

[VO(HQCN)(SO₄)²⁻·4H₂O]: Yield: 63%, m.p.: 225–227 °C. ρₘ (DMF): 62 ohm⁻¹ cm² mol⁻¹. Elemental Anal. Calc. for [VO(HQCN)(SO₄)²⁻·4H₂O]: C, 37.58; H, 3.94; N, 10.96. Found: C, 37.44; H, 3.81; N, 10.72%.

2.4. Physical measurements

Elemental analyses of the ligands and the complexes were conducted on a Varian E-112 spectrometer using direct-reading conductivity bridge. The EPR spectra of the complexes were recorded on a Varian E-112 spectrometer using TCNE as the standard at the SAIF, IIT, Bombay, India.

2.5. X-ray crystallography

Single crystal X-ray diffraction experiments for colourless HBPB and yellow 1 were performed on an Oxford CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) [16]. The CrystAlis RED software was used for cell refinement and data reduction [16]. The structures were solved by direct-methods using SHELXS-97 [17] and each refinement was carried out by full-matrix least-squares on F² (SHELXL-97) [17] with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form w = 1/[σ²(Fo)² + (aP)² + bP], where P = (Fo² + 2Fc²)/3. For HBPB, the nitrogen-bound hydrogen atom was located from a difference Fourier map and refined. The remaining hydrogen atoms in each model were placed in their calculated positions in the riding model approximation. As evident

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>HBPB</th>
<th>[VO(BPB)₂·2O]Cl₂ (1)</th>
<th>[VO(DKN)₂·2O]Cl₂·H₂O (2)</th>
</tr>
</thead>
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<tr>
<td>Formula</td>
<td>C₃₀H₂₇N₂O₂</td>
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<td>C₃₄H₄₆N₂O₆V₂</td>
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<tr>
<td>Formula weight</td>
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<td>766.54</td>
<td>779.52</td>
</tr>
<tr>
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<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
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<td>P2₁/n</td>
<td>P1</td>
</tr>
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<td>9.9435(1)</td>
<td>8.0494(12)</td>
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<td>b (Å)</td>
<td>8.6486(5)</td>
<td>9.9285(2)</td>
<td>9.750(2)</td>
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<tr>
<td>c (Å)</td>
<td>11.3168(8)</td>
<td>17.1187(2)</td>
<td>10.7678(19)</td>
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<td>α (°)</td>
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<td>89.291(9)</td>
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<td>β (°)</td>
<td>84.85(5)</td>
<td>90.46(1)</td>
<td>77.852(5)</td>
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<tr>
<td>γ (°)</td>
<td>72.32(3)</td>
<td>90</td>
<td>81.034(9)</td>
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<tr>
<td>V (Å³)</td>
<td>746.03(8)</td>
<td>1689.97(4)</td>
<td>815.8(3)</td>
</tr>
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<td>Z</td>
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<tr>
<td>T(K)</td>
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<tr>
<td>Dₐ (g cm⁻³)</td>
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<td>1.587</td>
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<tr>
<td>F(000)</td>
<td>316</td>
<td>784</td>
<td>397</td>
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<tr>
<td>μ(Mo Kα) (mm⁻¹)</td>
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<td>0.611</td>
<td>0.639</td>
</tr>
<tr>
<td>Measured data</td>
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<td>13 940</td>
<td>12 219</td>
</tr>
<tr>
<td>Δ(%)</td>
<td>3.0–25.0</td>
<td>3.1–25.0</td>
<td>2.8–26.5</td>
</tr>
<tr>
<td>Unique data</td>
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<td>2992</td>
<td>3325</td>
</tr>
<tr>
<td>Observed data (I &gt; 2σ(I))</td>
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<td>2476</td>
<td>3180</td>
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<tr>
<td>R₁ observed data; observed data</td>
<td>0.035; 0.079; 0.036; 0.091</td>
<td>0.043; 0.103</td>
<td></td>
</tr>
<tr>
<td>α; β in weighting scheme</td>
<td>0.048; 0</td>
<td>0.045; 1.357</td>
<td>0.047; 0.923</td>
</tr>
<tr>
<td>Rw, observed data; all data</td>
<td>0.052; 0.084</td>
<td>0.047; 0.095</td>
<td>0.045; 0.104</td>
</tr>
</tbody>
</table>

Fig. 3. The molecular structure of centrosymmetric [VO(BPB)₂·2O]Cl₂ (1) along with the atom numbering scheme. Symmetry operation i: –x, –y, 2 – z. Geometric details describing the closest intermolecular interactions operating in the crystal structure of 1: C16–H16 . . . O2 = 2.55 Å and C16 – O2 = 3.28(3) Å with angle at H16 = 135° for symmetry operation i: –x, –y, –z + ½; C17–H17 . . . N3 = 2.56 Å and C17 – N3 = 3.44(4) Å with angle at H2 = 155° for symmetry operation ii: ½ – x, ½ + y, ½ – z; π · π: Cg(N1,C1–C5) · · · Cg(N1,C1–C5) = 3.6940(14) Å for iii: –1 – x, –y, 2 – z.
from Fig. 3, there is high thermal motion associated with the pendant C7–C12 aromatic ring. However, multiple sites were not discerned for this residue.

Intensity data for a pale-yellow prism of 2 were collected at 93 K on a Rigaku AFC12/Saturn724 CCD fitted with Mo Kα radiation. The data set was corrected for absorption based on multiple scans [18] and reduced using standard methods [19]. The structure was solved and refined using SHELXL-97 [17], as described above. A residual electron density peak, consistent with the presence of a disordered solvent water molecule was evident towards the end of the refinement. This was modelled as 0.25 of a water molecule

3. Results and discussion

All the hydrazones discussed here are NNO donors and they can coordinate either in the keto form or in enolic form. All newly synthesized complexes are soluble in polar organic solvents such as chloroform, CH₂CN, DMF, DMSO, etc. Infrared spectral evidence supports the presence of coordination of the respective hydrazones through the enolate form in complexes 1, 2 and 3, while in complex 4, the ligand coordinates in the keto form. The molar conductivity measurements in 10⁻³ M DMF solutions show non-electrolytic nature for complexes 1, 2 and 3 but complex 4 behaves as a 1:1 electrolyte [22]. Complexes 3 and 4 are EPR active due to the presence of an unpaired electron, while complexes 1 and 2 are EPR silent. The structures of complexes 1 and 2 have been confirmed by single crystal X-ray crystallography as has the structure of HBPB.

3.1. Crystal and molecular structure of HBPB

The colourless block-shaped crystals suitable for analysis were grown by slow evaporation from a methanolic solution of the HBPB. A perspective view of the compound showing the crystallographic numbering scheme is shown in Fig. 2a; selected geometric parameters are collected in Table 2. The central part of the molecule is essentially planar due to the presence of an intramolecular N–H···Npyridine hydrogen bond. The maximum deviation from the least-squares plane calculated for the hydrazine moiety, i.e. C6–N3–C13–O1, is 0.0189(12) Å for the N2 atom. The terminal aromatic rings are twisted out of this plane as seen in the values of the N2–C6–C7–C8 and N3–C13–C14–C15 torsion angles of 66.67(7)° and 159.25(12)°, respectively. The dihedral angle formed between the terminal rings is 66.67(7)°. The C13–O1 bond distance of 1.2213(14) Å indicates the molecule exists in the keto form in the solid-state. The N2–C6 bond length is 1.2955(16) Å, with significant double-bond character, is comparable to those previously reported in analogous of hydrazone structures [23]. The above notwithstanding, the values of the N2–N3 and N3–C13 bond dis-
tances of 1.3682(15) and 1.3610(16) Å, respectively, indicate significant delocalization of π-electron density over the hydrazone portion of the molecule. The conformation about the N2–C6 bond is Z.

The principal feature of the crystal packing is the formation of a supramolecular chain mediated by cooperative C–H···N and C–H···O contacts; the formation of a chain mediated by amide ···O=C–N···H hydrogen bonds is precluded owing to the presence of the intramolecular N···Npyridine contact. The supramolecular [HQCN1.5H2O] 3173 1656 1591 (HQCN)0.5H2O(2) resembles that just described, Fig. 4a and Table 3. In this case, the pyridine-N1 atom forms a significantly longer V–N1 bond, i.e. 2.3013(16) Å, compared with the V–N3 bond, i.e. 2.110(2) Å, formed by the azomethine-nitrogen atom. Significant differences in the V–O bond distances are also evident between 1 and 2. Thus, in 2, each of V–O1, V–O2 and V–O3 are longer but the bridging V–O3’ distance is shorter. It is noted that with the exception of the elongation of the C5–C6 bond distance in 2 to 1.485(3) Å, compared with 1.460(3) Å in 1, the bond distances defining the N1–C2–N2–C12–O1 backbones of the tetradeinate ligands in each of 1 and 2 are indistinguishable. In the absence of any obvious electronic influence exerted by the pendant pyridine residue in 2, compared to phenyl in 1, this reorganisation of electron density giving rise to disparate bond distances in the structures is ascribed to participation of solvent water in the (supramolecular) structure of 2, see above.

The crystal structure of 1 is consolidated into a three-dimensional network by a C–H···O, C–H···N and π···π contacts. The intervention of solvent water in the crystal structure of 2, Fig. 4b, leads to the formation of a supramolecular chain along the c-direction. While the solvent water molecule is only partially occupied and disordered across a centre of inversion, see Section 2, it forms significant alternating O···O interactions of 2.834(9) and 3.2923(9) Å with the vanadyl–O2 atom, Fig. 4b. Chains are consolidated into the crystal structure by a large number of C–H···O, C–H···N and π···π contacts.

3.3. Infrared spectra

The comparison of the main vibrational bands of the ligands with those of the complexes helps to establish their ligating behaviour to the metal centre. Select IR bands of the complexes are represented in Table 4. The IR spectra of the ligands exhibit two bands at ca. 3089 and 1672 cm⁻¹ due to the v(NH) and v(C=O) stretch.

Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>v(N–H) (cm⁻¹)</th>
<th>v(C=O) (cm⁻¹)</th>
<th>v(C=N) (cm⁻¹)</th>
<th>v(C=N)</th>
<th>v(C=O) (cm⁻¹)</th>
<th>v(V–O–V) (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>HBPP</td>
<td>3182 2928</td>
<td>1659 1689</td>
<td>1588</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(HDKN 0.5H2O)</td>
<td>3063 3193</td>
<td>1591 1655</td>
<td>1593</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HQQB 1.5H2O)</td>
<td>3173 3173</td>
<td>1591 1656</td>
<td>1593</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[VO(BPB)[µ-O]2]2 (1)</td>
<td>1509 1509</td>
<td>1368 1359</td>
<td>946 939</td>
<td>853</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[VO(DKN)[µ-O]2]2H2O (2)</td>
<td>1509 1509</td>
<td>1373 1373</td>
<td>945 945</td>
<td>853</td>
<td></td>
<td></td>
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<tr>
<td>[VO(QCB)[µ-O]2]2H2O (3)</td>
<td>1582 1582</td>
<td>1384 1384</td>
<td>940 940</td>
<td>853</td>
<td></td>
<td></td>
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<tr>
<td>[VO(HQCN)[µ-O]2]SO3 4H2O (4)</td>
<td>3186 3186</td>
<td>1560 1560</td>
<td>980 980</td>
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<td></td>
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</table>

* Newly formed C=N.
struckes, respectively, and are indicative of their ketonic nature in the solid-state [27,28]. The existence of the ligand in the keto tautomeric form was confirmed from the crystal structure determination (see above). These bands disappear on complexation in 1–3. A new band appearing in the region 1360–1385 cm\(^{-1}\) is assigned to \(\nu(C=O)\) indicating the involvement of the original carbonyl-oxygen in bonding as an enolate. However, in complex 4 no considerable shift is observed for the \(\nu(C=O)\) and \(\nu(NH)\) bands which implies that the ligand is coordinating in the keto form. Each of the aroylhydrazones under discussion display a strong and sharp band in the region 945–980 cm\(^{-1}\) ascribed to \(\nu(C=N)\) of the azomethine group [29]. These bands undergo shifts to the lower wave-numbers upon complexation which suggest the coordination of the azomethine-nitrogen to vanadium. The presence of new bands in the region at ca. 853 cm\(^{-1}\) which may be due to the newly formed \(\nu(C=N)\) bond except in complex 4, confirms the coordination via azomethine-nitrogen. The out-of-plane bending modes of vibrations of the free ligands at 622 cm\(^{-1}\) are found to be shifted to higher energies in the spectra of complexes indicating the coordination via pyridine nitrogen [30]. Further, the intense band observed in the region 945–980 cm\(^{-1}\) in all the complexes corresponds to the terminal V=O stretching. In addition to this, the dimeric complexes 1 and 2 exhibit bands at ca. 853 cm\(^{-1}\) due to the V–O–V bridging vibrations [31]. In complex 4, two sulfate ligands are present and accordingly in the IR spectrum, strong bands are observed at 1044 and 1170 cm\(^{-1}\), due to \(\nu_{s}\), and 469 cm\(^{-1}\), due to \(\nu_{v}\), which can be assigned to a bidentate bridging sulfato group; bands at 1126 and 606 cm\(^{-1}\) can be assigned to the presence of an ionic sulfato group [32].

3.4. Electronic spectra

The electronic absorption bands of the ligands and complexes are recorded in acetonitrile solution and all data are summarised in Table 5. The bands at ca. 320, 275 and 235 nm, attributed to the \(n-\pi^*\)- and \(\pi-\pi^*\) transitions shifted upon complexation. For complexes 1 and 2, high energy bands in the range 405 nm are assigned to the ligand to metal charge transfer (LMCT) transitions arising from phenolate oxygen of the ligand to an empty d orbital of the vanadium ion. These dioxo-vanadium(V) complexes have a d\(^6\) configuration, and d–d bands are therefore not expected. For the oxovanadium complexes the bands at 415 nm are assigned to the charge transfer transitions arising due to the O(phenolate) → V\(^{IV}\) LMCT transitions. The two bands at 856 and 541 nm for 3 are due to the \(d_{xy} → d_{z^2}\) and \(d_{xy} → d_{x^2-y^2}\) transitions, while in 4 only one d–d band at 852 nm is observed [33].

3.5. EPR spectra

The oxidation state of the central vanadium atom in the complexes was confirmed by the measurements of EPR spectroscopy. Complexes 3 and 4 are paramagnetic samples and EPR spectra were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K. In polycrystalline state at 298 K, compound 3 is axial with \(g_1 = 1.941\) and \(g_2 = 1.947\). In frozen DMF the complex 4 displayed well-resolved axial anisotropy characterized by two sets of eight lines which result from coupling of the electron spin to the spin of the \(^{51}\)V nucleus (\(I = \frac{1}{2}\)). The EPR spectrum of complexes 3 in DMF at 77 K and 4 in polycrystalline state were not of good quality, probably due to poor glass formation in the case of 3. Spectral parameters are collected in Table 6 and representative spectrum is displayed in Fig 5. The \(g_1 < g_2\) and \(A_{g} > A_{k}\) relationship are characteristic of an axially compressed \(d_{xy}\) configuration [31]. The lower values for \(\xi^2\) compared to \(\beta^2\) indicate that in-plane \(\sigma\)-bonding is more covariant than in-plane \(\pi\)-bonding. For the dimeric vanadium complexes with VO\(^{2+}\) motif, vanadium is in +5 oxidation state and therefore EPR silent.

Table 6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Polycrystalline state (298 K)</th>
<th>DMF (77 K)</th>
<th>(A_{g})*</th>
<th>(A_{k})*</th>
<th>(\beta)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.941/1.947 (g(<em>{1}/g</em>{2}))</td>
<td>176.42</td>
<td>73.51</td>
<td>1.0335</td>
<td>0.756</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.928/1.978 (g(<em>{1}/g</em>{2}))</td>
<td>195.71</td>
<td>77.14</td>
<td>1.0335</td>
<td>0.756</td>
<td></td>
</tr>
</tbody>
</table>

* Expressed in units of cm\(^{-1}\) multiplied by a factor of \(10^{-4}\).
Kerala, India for elemental and IR analyses. We are thankful to IIT, Bombay, India for EPR analysis and National Single Crystal X-ray Diffraction Facility, IIT, Bombay, India for providing single crystal intensity data for HBPB and 1.

Appendix A. Supplementary material

CCDC 686871, 686872 and 723096 contain the supplementary crystallographic data for HBPB, 1 and 2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.06.029.

References