Biomimetic oxo-, dioxo- and oxo-peroxo-hydrazonato-vanadium(IV/V) complexes†

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[VO(acac)₂] reacts with HL (HL is the hydrazone Hacpy-inh, or Hacpy-bhz; acpy = acetylpyridine, 
inh = isonicotinic acid hydrazide, bhz = benzoylhydrazide) in dry methanol to yield the oxovanadium(IV) complexes 
[VOL(acac)] (HL = I: 1, HL = II: 3). The dioxovanadium(IV) complexes [VO₂L] (HL = I: 2, HL = II: 4) are obtained by 
aerial oxidation of 1 and 3 in methanol. Treatment of 1 and 3, or 2 and 4, with H₂O₂ yields the 
oxoperoxovanadium(IV) complexes [VO₅O₂L] (HL = I: 5, HL = II: 6). In the presence of catechol or benzohydroxamic 
acid, 1 and 3 give the mixed chelate complexes [VOL(cat)] (HL = I: 7, HL = II: 8) or [VOL(bha)] (HL = I: 9, HL = II: 
10). The peroxo complexes 5 and 6 undergo oxygen transfer reaction with PPh₃ in DMF. In DMF and DMSO, 7, 8, 9 
and 10 slowly convert to the corresponding dioxo species 2 and 4. Acidification of 2 and 4 with HCl dissolved in 
methanol affords oxo-hydroxo complexes. Reaction of 7 with L-ascorbic acid yields 2. The crystal and molecular 
structures of 2 and 4 have been determined, confirming the ONN binding mode of I and II from their enolate form.

Introduction

Schiff base and related complexes of vanadium, known in a 
large variety, have received renewed attention in the context of 
the role of vanadium in living organisms. This resurgence of 
interest in vanadium chemistry stems from the discovery of 
two classes of vanadium enzymes, viz. vanadium-nitrogenases, 
containing vanadium in medium oxidation states, and 
vanadate-dependent haloperoxidases. The latter catalyse the 
oxidation by peroxide of halides to hypohalous acid. Under 
local conditions, thioethers are oxidized to sulfoxides. 
The enzymes lose their activity upon reduction or removal of 
vanadate. Re-oxidation, or reconstitution of the apo-enzyme 
with vanadate, fully restores their activity, demonstrating that 
vanadium(IV) is essential for the catalytic activity. Intermediate 
species having [VO₂], [VO(OH)], [VO₃(H₂O)] and [VO₂O₂] 
cores have been proposed during catalytic turnover, in 
which vanadium is in a trigonal-bipyramidal (native form) or 
tetragonal-pyramidal (peroxo form) environment, covalently 
linked to the N⁺ of a histidine. The stability of V⁵ complexes 
under aerobic conditions has allowed the design of structural 
and/or functional models for the haloperoxidases. Vanadium-
(IV) has also been shown to act as an electron acceptor and thus 
initiator in the photo-cleavage of DNA. Further, many 
vанадий(IV) complexes show haloperoxidase activity and 
activity in other oxidation and oxo transfer reactions, including 
the enantioselective oxidation of prochiral thioethers to 
sulfoxides. The insulin like effect of vanadium coordination 
compounds is another intriguing and promising feature that has 
further stimulated vanadium coordination chemistry. 

The objective of the present work is to introduce bio-mimetic 
dioxovanadium(IV) complexes of the hydrazone ligands I and II 
(Scheme 1) having pyridine-N, enamine-N and amide-O donor 
functions, and to study their reactivity with various substrates to characterise species with [VO(H₂O)], [VO₃], [VO₂O₂] and 
[VO(OH)] cores, similar to those observed for the enzyme. We also report on mixed ligand complexes containing, in 
addition to I and II, catecholate or benzohydroxamate. 
Catecholates and hydroxamates are able to bind vanadium 
rather strongly in both the + IV and + V oxidation states. 
The relevance of catecholato-vanadium complexes in terms of 
their biological significance arises from the role of 
turnchymes in reduction, stabilisation and accumulation of vanadium by certain ascidians (sea squirts); the iron binding siderophore 
desferroxamine, which contains hydroxamates functions, also 
strongly binds to VO²⁺. 

Experimental

Materials and methods

V₅O₁₀[HN₄][VO₃], isonicotinic acid hydrazide (H₂inh), benzoyl 
chloride, hydrazine hydrate, catechol (H₂cat) and benzo-

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hydroxamic acid (H₂bha) were purchased from Loba Chemie, India, acetylacetone (Hacac) and 2-acetylpyridine (acpy) were obtained from Aldrich. [VO(acpy)] was prepared as described. Benzoylhydrazide (H₂bhz) was prepared by the reaction of a two-fold excess of hydrazine hydrate with ethyl benzoate, which in turn was prepared by refluxing benzoyl chloride in an excess of absolute ethanol. All chemicals and solvents were of analytical grade and used as obtained.

Microanalyses of the ligands and complexes were performed by Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow, India. Magnetic susceptibilities of the oxovanadium(iv) complexes were recorded at the Institute’s Instrumentation Centre III, Roorkee. Thermograms of the complexes were recorded on a single manually operated thermo balance constructed in our laboratory. Crystallised CuSO₄·5H₂O was used to calibrate the instrument, and thermograms were recorded under dynamic air atmosphere with a heating rate of 3 to 5 °C min⁻¹. IR spectra were recorded as KBr pellets with a Perkin-Elmer model 1600 FT-IR, and UV–Vis spectra (in DMF) on a UV-1601 PC spectrophotometer. H NMR spectra were run on a Bruker 200 MHz spectrometer. ¹³C and ¹⁷O NMR spectra on a Bruker AM 360 with the common parameters settings. All δ (¹³C) values are referenced relative to VOCl₃ as external standard. EPR spectra (in DMSO and MeCN) were run in the X-band mode (9.75 MHz) on a Bruker ESP 300E spectrometer.

**Crystal structure determinations**

Data were collected on a Bruker SMART CCD Apex diffractometer using a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å) at 153(2) K. Hydrogen atoms were placed in calculated positions and included in the last cycles of refinement. A disorder of C12 and C13 in Hacpy-inh I. See http://www.rsc.org/suppdata/dt/b2/b202852m/ for crystallographic data in CIF or other electronic format.

**Preparations**

**Hacpy-inh I.** A mixture of 2-acetylpyridine (1.22 g, 10 mmol) and isonicotinic acid hydrazide (1.37 g, 10 mmol) in 50 ml of methanol was refluxed on a water bath for 6 h. After reducing the solvent to ca. 15 ml and cooling to room temp. for 2 h, the precipitated white solid was filtered off, washed with methanol and dried. Recrystallisation from methanol yielded pure I as a white solid. Yield 1.92 g (80%). M.p: 160 °C. (Found: C, 64.83, H, 5.10; N, 23.11. Calc. for C₁₅H₁₄N₆O₇: C, 65.0; H, 5.0; N, 23.33). IR (KBr, ν_max/cm⁻¹): 3200 (NH), 1661(C=C), 1608, 1573(C=N, C=C).

**Hacpy-bhz II.** This ligand was prepared by following the same procedure outlined for Hacpy-inh. The pure product was obtained as a white solid. Yield 1.55 g (65 %) on crystallisation from methanol. M.p: 141 °C. (Found: C, 70.35; H, 5.80; N, 17.48. Calc. for C₁₅H₁₄N₆O₇: C, 70.29; H, 5.86; N, 17.57). IR (KBr, ν_max/cm⁻¹): 3230 (NH), 1653(C=C), 1622, 1581(C=N, C=C).

**[VO(acpy-inh)]** 1 A stirred solution of Hacpy-inh (0.480 g, 2 mmol) in dry methanol (20 ml) was treated with [VO(acac)₂] (0.530 g, 2 mmol), and the resulting reaction mixture was refluxed on a water bath for 4 h. After cooling to room temp., dark green I was filtered off, washed with methanol and dried in vacuo. Yield 0.73 g (90%). (Found: C, 53.04; H, 4.48; N, 12.81. Calc. for C₁₅H₁₄N₆O₇: C, 53.33; H, 4.44; N, 13.82). IR (KBr, ν_max/cm⁻¹): 1591 (C≡N, C=C), 1273 (C-O, enolic), 1022 (N–N), 954 (V=O), 469, 442, 411 (V–O, V–N).

**[VO(acpy-bhz)]** 2. Method 1. I (0.405 g, 1 mmol) was dissolved in hot methanol (75 ml) and air was passed through the solution with occasional shaking and heating at ca. 50 °C. Residual solid material slowly dissolved, and the green solution gradually changed to yellow; yellow crystalline 2 precipitated within 2 d. This was filtered off, washed with methanol and dried in vacuo. Yield 0.229 g (71%). (Found: C, 48.58; H, 3.47; N, 17.19. Calc. for C₁₅H₁₄N₆O₇: C, 48.45; H, 3.42; N, 17.39). IR (KBr, ν_max/cm⁻¹): 1598, 1565 (C≡N, C=C), 1256 (C-O, enolic), 1022 (N–N), 946, 899 (sym and antisym O=V=O), 507, 441, 421 (V–O, V–N).

**Method 2.** VO₂(O)₅ (0.500 g, 5 mmol) was suspended in 10 ml of aqueous KOH (containing 0.336 g, 6 mmol) and stirred. The vanadate solution thus generated was filtered after 2 h, and to this was added, under continuous stirring, a filtered solution of Hacpy-inh (1.20 g, 5 mmol) dissolved in 20 ml of aqueous KOH (containing 0.280 g, 5 mmol). The pH of the reaction mixture was slowly adjusted to 7.5 with 4 M HCl, and stirring was continued. After 2 h, the precipitated yellow 2 was filtered off, washed with water and dried. Recrystallisation from DMF–MeOH 1:3 gave 0.810 g (50%) yield of 2.

**[VO(acpy-bhz)acac]** 3. Complex 3 was prepared as described for I by replacing Hacpy-inh for Hacpy-bhz. Yield 0.69 g (50%). (Found: C, 56.31; H, 4.90; N, 10.25. Calc. for C₁₅H₁₄N₆O₇V₂C: 56.44; H, 4.70; N, 10.3). IR (KBr, ν_max/cm⁻¹): 1596 (C≡N, C=C), 1267 (C-O, enolic), 1018 (N–N), 957 (V=O), 494, 442, 415 (V–O, V–N).
[VO(acpy-bhz)] 4. This complex was prepared from [VO(acpy-bhz)(acac)] as well as from KVO₃ and Hacpy-bhz by the methods 1 and 2, respectively, as outlined for 2, in ~5% yield. (Found: C, 52.54; H, 3.96; N, 13.12. Calc. for C₁₅H₁₉O₅N₂V: C, 52.34; H, 3.74; N, 13.08). IR (KBr, ν/cm⁻¹): 1598, 1565 (C=O, C=N), 1260 (C-O, enolic), 1028 (N–N), 946, 909 (sym and antisym O–V–O), 509, 472, 441, 410 (V–O, V–N).

[VO(O₂)(acpy-bhz)] 5. Method 1. A 30% H₂O₂ (2 ml, 17.6 mmol) was added to an aqeous solution of KVO₃ (5 mmol), prepared as outlined in method 2 for 2, and the resulting solution was stirred at ~10 °C for 1/2 h. Separately, the potassium salt of Hacpy-inh was prepared by reacting 1 (1.2 g, 5 mmol) and KOH (0.280 g, 5 mmol) in 20 ml of water, followed by filtration. This solution was added dropwise to the above solution with constant stirring. After 2 h of stirring, the orange–yellow solid which had separated was filtered off, washed with water and dried. The crude mass was dissolved in a minimum amount of DMF while heating to ~50 °C and filtered. After treatment with DMF by heating on a water bath, this was treated with 30% H₂O₂ (3 ml, 26.5 mmol) while stirred at room temperature, which caused an immediate change of color to orange–yellow. After 2 h of stirring, the volume of the solvent to ca. 5 ml. In the case of 2 as the precursor, 20 ml of MeOH was added. These solutions were kept at 10 °C overnight. The orange–red crystals were filtered off and dried in vacuo. Yield 0.085 g (40%). Analytical and spectral data of the isolated complexes match well with those of compound 5 prepared according to method 1.

[VO(acpy-bhz)] 6. This complex was prepared by analogy to 5 (method 1) replacing Hacpy-inh by Hacpy-bhz. Crystallisation from DMF–MeOH as outlined above afforded 6. Yield 0.925 g (55%). (Found: C, 50.0; H, 4.48; N, 12.37. Calc. for C₁₅H₁₉O₅N₂V: C, 49.85; H, 3.56; N, 12.47). IR (KBr, ν/cm⁻¹): 1598, 1570 (C=O, C=N), 1260 (C-O, enolic), 1022 (N–N), 968 (V–O), 921 (V=O), 714 (VO₂ antisym), 562 (VO₃ sym), 472, 440, 414 (V–O, V–N).

[VO(acpy-inh)] 7. 1 mmol of 1 was dissolved in hot methanol (40 ml) and cooled to ambient temp. To this was added catechol (0.110 g, 1 mmol) and the reaction mixture was stirred for 5 h. After reducing the solvent to ca. 10 ml and keeping overnight at 10 °C, dark brown complex 7 was filtered off and dried in vacuo. Yield 0.21 g (50%). (Found: C, 57.35; H, 4.16; N, 12.57. Calc. for C₁₅H₁₉O₅N₂V: C, 57.14; H, 4.08; N, 12.70). IR (KBr, ν/cm⁻¹): 1600, 1564 (C=N, C=C), 1261 (C-O, enolic), 1026 (N–N), 959 (V–O), 509, 452, 422 (V–O, V–N).

[VO(acpy-bhz)cat] 8. Complex 8 was prepared analogously to 7, replacing 1 by 3. Yield 0.226 g (55%). (Found: C, 58.24; H, 3.76; N, 9.93. Calc. for C₁₅H₁₉O₅N₂V: C, 58.11; H, 3.87; N, 10.17). IR (KBr, ν/cm⁻¹): 1598, 1578 (C=N, C=C), 1272 (C-O, enolic), 1022 (N–N), 951 (V–O), 468, 452, 417 (V–O, V–N).

[VO(acpy-inh)acac] 9. 1 mmol of 1 was dissolved in 40 ml of hot methanol and this, after cooling to ambient temp., was added benzoehydroxamic acid (0.137 g, 1 mmol). The obtained reaction mixture was stirred for 4 h and then kept overnight at 10 °C after reducing the volume to ca. 10 ml. Complex 9 was filtered off, washed with methanol and dried in vacuo. Yield 0.24 g (55%). (Found: C, 54.21; H, 3.96; N, 15.68. Calc. for C₁₅H₁₉O₅N₂V: C, 54.30; H, 3.85; N, 15.84). IR (KBr, ν/cm⁻¹): 1597, 1573 (C=N, C=C), 1235 (C-O, enolic), 1029 (N–N), 965 (V–O), 552, 462, 432 (V–O, V–N).

[VO(acpy-bhz)bh]a 10. This was prepared following the procedure outlined for 9. Yield 0.21 g (48%). (Found: C, 57.35; H, 4.16; N, 12.57. Calc. for C₁₅H₁₉O₅N₂V: C, 57.14; H, 4.08; N, 12.70). IR (KBr, ν/cm⁻¹): 1600, 1564 (C=N, C=C), 1261 (C-O, enolic), 1026 (N–N), 959 (V–O), 509, 452, 422 (V–O, V–N).

Synthesis. Reaction between equimolar amounts of [VO(acac)] and Hacpy-inh (I in Scheme 1) in dry, refluxing methanol yields [VO(acpy-inh)acac]. 1. Here, as in all of the complexes formed with I and II, the ligand reacts out of its enolic tautomeric form, i.e. in the NVO(1–) mode. On aerial oxidation in methanol, the dioxoanavanadium(V) complex
[VO(acpy-inh)]2, is obtained, a reaction which requires water. The intermediate green complex 1 can be isolated from the methanolic solution prior to aeration. Eqsns. (1) and (2) represent the synthetic procedures:

\[ \text{[VO(acpy-inh)]}_2 + \text{Hacpy-inh} \rightarrow \text{[VO(O(acpy-inh)acac)] + Hacac} \]  

(1)

\[ 2\text{[VO(acpy-inh)acac]} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{[VO}_2\text{(acpy-inh)]} + 2\text{Hacac} \]  

(2)

Similarly, the complex [VO(acpy-bhz)acac], 3, can be oxidised in methanol to [VO(acpy-bhz)]. Further, 2 and 4 were obtained from the reaction of vanadate, prepared in situ by dissolving V2O5 in an aqueous solution of KOH, by addition of solutions of the potassium salt of I or II, and after adjustment to pH ~ 7.5. Aqueous vanadate solutions actually contain a mixture of mono-, di-, tetra- and pentavanadates. Addition of H2O2 to 1 and 3 yields the peroxo complexes 5 and 6, eqn. (3). The complexes [VO(O2L)] (HL = I or II, 5 or 6) can also be prepared from aqueous solutions of potassium metavanadate, hydrogen peroxide and the potassium salts of the ligands, as symbolically depicted in eqn. (4). The actual vanadium precursor probably is in situ generated [VO(O2L)(OH/H2O3)],.  

\[ 2\text{[VO(acac)L]} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{[VO}_2\text{L]} + 2\text{Hacac} + 2\text{H}_2\text{O} \]  

(3)

\[ \text{KL + KVO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{[VO}_2\text{L]} + 2\text{KOH} \]  

(4)

\[ \text{KL = I: 5; HL = II: 6} \]

Oxo-monoperoxo complexes may further be generated by treating cis-dioxo-vanadium(v) complexes with H2O2 at ice temperature. This reaction was studied by electronic absorption spectrophotometry. The spectral changes obtained during the reaction (Fig. 1) include a shift of the 370 nm band of I to 385 nm in 5, and the appearance of a weak shoulder at ~410 nm. The rate at which peroxo complex formation occurs depends upon the amount of H2O2 added. The band at 243 nm becomes relatively sharp while the band at 282 nm slowly shifts to 273.5 nm. The feature of the final spectrum is similar to that of authentic 5 (see below).

The peroxo complexes undergo oxygen transfer reactions with PPh3 in DMF to give the corresponding dioxovanadium(v) complexes [VO2L]2 and 4; Scheme 3.

\[ \text{[LV)] + PPh}_3 \rightarrow \text{[VO}_2\text{L] + PPh}_3 \]  

Scheme 3

Treatment of 1 and 3 with catechol or benzohydroxamic acid in methanol under aerobic conditions leads to the formation of the mixed-ligand complexes 7, 8, 9 and 10 as represented by eqns. (5) and (6). During this reaction, oxidative replacement of the remaining acetylacetonato group by catecholate or benzodioximate takes place.

\[ 2\text{[VO}_2\text{L] + 2\text{Hacac} + 2\text{H}_2\text{O}_2 \rightarrow 2\text{[VO}_2\text{L]} + 2\text{Hacac + H}_2\text{O}} \]  

(5)

\[ 2\text{[VO}_2\text{L] + 2\text{Hacac + H}_2\text{O}_2 \rightarrow 2\text{[VO}_2\text{L]} + 2\text{Hacac + H}_2\text{O}} \]  

(6)

Complexes 1 and 3 are paramagnetic with a magnetic moment of 1.89 and 1.96 BM, respectively, while the other complexes are diamagnetic as expected for 3d8 systems. The dioxo complexes 2 and 4, and the peroxo complexes 5 and 6 are soluble in DMF and DMSO only, while the other complexes also dissolve in methanol and ethanol. Complexes 7 to 10 are also soluble in CH2Cl2.

Thermal studies. The TGA profiles of the VO2+ complexes 1 and 3 show that these complexes lose acetylactone, one oxygen remaining attached to vanadium, between 200 and 275 °C, with concomitant formation of [VO2L]2 as shown by eqn. (7).

\[ \text{[VO}_2\text{L]} \rightarrow \text{[VO}_2\text{L] + [acac – O}} \]  

(7)

On further heating, [VO2L]2 decomposes in the presence of air to yield V2O5. The peroxo complexes 5 and 6 degrade in the temperature range 120–220 °C, the decrease of weight by ~9.5% corresponding to the loss of the peroxo group (calcd. 9.5%). Thermograms of the other complexes indicate continuous degradation to V2O5 in the 250–700 °C temperature range.

Structure description. The crystal structure of [VO2(acpy-inh)](2) and [VO2(acpy-bhz)](4) with atom numbering schemes are shown in Fig. 2, selected bond lengths and angles in Table 2. In 2, a mirror plane bisecting the angle O1–V1–O1′ contains all of the other atoms except of the pyrinine carbons C13 and C12, which are disordered so as to satisfy the symmetry conditions (O1′ in 2 corresponds to O3 in 4). The N1–O2 coordination sphere around the vanadium atom is defined by the pyridine-N, imine-N and the amide-O of the monobasic tridentate ligand acpy-inh/bhz(1–), and by two cisoid exo-groups. The three ligand functions occupy meridional positions. The bond distances N2–N3 [1.384(5), 1.381(3)], N3–C8 [1.311(6), 1.314(3)] and O3–C8 [1.296(6), 1.300(3) Å] are consistent with the enolate form of the amide functionality. The V–O distances of 1.615 and 1.618 Å are typical of non-hydrogen bonded V=O groups. Other bond lengths, e.g. d(V–N1), d(V–N2) and d(V–O3), are in accord with reported values for comparable complexes.22,24 The ligand forms two five-membered rings with bite angles of 72.96° (N1–V–N2) and 73.56° (O2–V–N2). With an N1–V–O2 angle of 146.51°, N1 and O2 are inclined towards N2.

The coordination geometry around vanadium can best be described as distorted square-pyramidal with one of the doubly bonded oxo groups (O3), the enolate oxygen (O2) and the two

![Fig. 1](image-url)
Table 2  Selected bonding parameters for [VO\(_2\)(acpy-inh)] (2) and [VO\(_2\)(acpy-bhz)] (4)

<table>
<thead>
<tr>
<th>Bond lengths/Å</th>
<th>2</th>
<th>4</th>
<th>Bond angles/°</th>
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<tr>
<td>V–O(1)</td>
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<td>1.615(2)</td>
<td>O1–V–O2 102.95(10) 102.97(10)</td>
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<td></td>
<td>O1–V–O1/O3 110.22(19) 110.35(10)</td>
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<tr>
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<td></td>
<td>O3–V–O2 102.29(8)</td>
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<tr>
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<tr>
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<td></td>
<td>O3–V–N2 125.17(9)</td>
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<tr>
<td>O(3)–C(8)</td>
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<tr>
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<td>O2–C(8)–N3</td>
<td>124.9(5)</td>
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<td>O2–C(8)–N3 117.7(4) 118.4(2)</td>
</tr>
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</table>

Due to symmetry restrictions, there is no O3 in compound 2. O3 in 4 corresponds to O1′ in 2.

Fig. 2 ORTEP plots (35% probability level) and numbering schemes for 2 and 4.

N functions (N1, N2) forming the tetragonal plane. There are substantial distortions towards a trigonal bipyramid, quantified by a \(\tau\) parameter of 0.37 (\(\tau = 0\) for an ideal tetragonal pyramid; \(\tau = 1\) for an ideal trigonal bipyramid). The distortion thus compares to that in [VO\(_2\)LL], where HL is a Schiff base derived from 2-hydroxy-1-naphthaldehyde and 8-aminoquinoline,\(^ {21}\) or another type of penta-coordinated hydrazonate.\(^ {22}\) In [VO\(_2\)LL] complexes with an ideally square-pyramidal geometry, there is a distinct tendency towards dimerisation to [VOL(µ-O)], with octahedral arrangement.\(^ {22,26}\) Examples of trigonal-bipyramidal vanadium complexes are also known.\(^ {26,28}\)

IR spectra. The complexes display a sharp band in the 946–968 cm\(^{-1}\) region due to the ν(V=O) mode. In the case of 2 and 4, there are two such bands between 899 and 946 cm\(^{-1}\) due to cis-[VO\(_2\)] structure, as noted previously by other workers for similar complexes.\(^ {29}\) The peroxo complexes 5 and 6 show three IR active vibrational modes associated with the [V(O\(_2\))\(^{2-}\)] moiety at 562–574, 701–714 and 921–926 cm\(^{-1}\), which are assigned to the symmetric V=O stretch (\(v_1\)), the antisymmetric VO\(_2\) stretch (\(v_3\)) and the O–O intra-stretching (\(v_6\)) mode, respectively.\(^ {9}\) The presence of these bands confirms the \(\varphi\)-coordination of the peroxo group.

The IR spectra of the ligands exhibit two bands in the regions 3200–3230 and 1653–1661 cm\(^{-1}\) due to ν(NH) and ν(C=O) stretches. The absence of these bands in the spectra of all complexes is consistent with the enolisation of the amide functionality and subsequent proton replacement by the metal ion. A new band appearing in the 1235–1274 cm\(^{-1}\) range is assigned to the ν(C=O)(enolic) mode. Unequivocal assignment of the ν(C–N) (azomethine) as well as ν(C–C) (ring) stretches of the ligands could not be carried out due to the complexity of the spectra. In the 1600 cm\(^{-1}\) region, however, the appearance of a sharp band between 1593 and 1608 cm\(^{-1}\) should indicate the coordination of both nitrogen atoms. The band due to ν(N–N) mode appears at 991 cm\(^{-1}\) in Hacpy-inh, and at 976 cm\(^{-1}\) in Hacpy-bhz. This band, which, on coordination of the ligands, shifts up to 50 cm\(^{-1}\) to higher wave numbers with respect to the free ligand, falls within the range commonly observed for the monodentate coordination of the >N–N< residue.\(^ {11}\) The high frequency shift is expected because of diminished repulsion between the lone pairs of adjacent nitrogen atom.\(^ {11}\) The absence of the band corresponding to the ν(NH) and ν(OH) stretches in the complexes 9 and 10 of benzohydroxamic acid (Hbha) is indicative of the enolisation of the –C=O group of Hbha and subsequent replacement of H by the metal ion. In addition, these complexes exhibit a weak but broad band covering the region 2500–2800 cm\(^{-1}\), which suggests intermolecular hydrogen bonding. Catechol complexes do not show any band due to ν(OH) and thus confirm the coordination of catecholate to the metal ion.

Solution studies

Electronic absorption spectra. Table 3 lists electronic spectral data for the ligands and various complexes. The visible absorption spectra of all complexes are dominated by an intense absorption at 378–392.5 nm and are assigned to a ligand-to-metal charge transfer (LMCT) band. The intra-ligand band at ca. 370 nm merges with this band. Benzohydroxamate and catecholate usually induce strong charge transfer to a high valent metal centre. The new band at ca. 550 nm in 9 and 10, and two intense bands at ca. 778 and 516 nm in 7 and 8 are thus con-
transitions appear along with other aromatic protons, thus making the benzohydroxamate complexes give rise to two multiplets in the 6.58 ppm region, while in the catecholate complexes give rise to two multiplets in the 6.73 ppm region, and aromatic protons of the coordinated catecholate (in DMF) 269.5(13783), 386.5(5221.6) ppm, and aromatic protons of the ligands as well as aromatic protons of dioxo species, again showing that partial decomposition of these complexes occurs to give dioxo species.

1H NMR spectra. The coordinating modes of the ligands were also confirmed by recording 1H NMR spectra of the ligands as well as complexes. As presented in Table 4, the sharp signal appearing at 11.19 (in Hacpy-inh) and 10.90 ppm (in Hacpy-bhz) due to the hydrazine NH proton, disappears in the spectra of the complexes, which suggests the conversion of the keto to the tautomeric enol group and subsequent coordination of the enolate oxygen. Aromatic protons of the ligands as well as the complexes appear well within the expected range. The aromatic protons of the coordinated catecholate (in DMF) 269.5(13783), 386.5(5221.6) ppm, while in the benzohydroxamate complexes and aromatic protons of dioxo species, again showing that partial decomposition of these complexes occurs to give dioxo species.

13C NMR spectra. Assignments of the relevant peaks recorded for the ligands and complexes are presented in Table 5. A large coordination-induced shift \( \Delta \delta = \delta(\text{complex}) - \delta(\text{free ligand}) \) of the signals for the carbon atoms in the vicinity of the coordinating atoms (e.g. the azomethine carbon C1 and the enolate carbon C7) demonstrates their coordination. Even the methyl carbons associated with the azomethine group give rise to some downfield shift. The coordination of catecholate is reflected by the appearance of a new peak at 145.3 in \( g = 2 \) and at 148.6 in \( g = 3 \), while coordination of benzohydroxamate is confirmed by the appearance of at least two new peaks in the 165–180 ppm region. Several additional peaks of low intensity in the 120–130 ppm region for the complexes 7 to 10 correspond to the respective dioxo complexes formed by partial decomposition (see also above and below).

15V NMR spectra. Table S1 (ESI) presents 15V NMR spectral data of the complexes. The resonances have line widths at half-height of approximately 200 Hz, which is still considered as narrow in 15V NMR spectroscopy. The dioxovanadium(IV) complexes 2 and 4 exhibit one strong resonance at \( g = 3 \), an expected value for the dioxovanadium(IV) complexes having a mixed O/N donor set. The catecholato complexes 7 and 8 display two bands: one in the 319–362 ppm region characteristic of catecholate coordination, and a second peak in the range of dioxo species, again showing that partial decomposition occurs in solution. Similarly, complexes 9 and 10 display two bands in the 51 to 71 and at \( g = 1 \) to \( g = 3 \) ppm region. The former resonance belongs to the complexes 9 and 10 while the latter is due to decomposition to 2 and 4. In some of the solutions, there is an additional minor resonance around \( g = 9 \), which coincides with the chemical shift of the authentic oxo–peroxo complexes 5 and 6. These resonances do not appear under strict exclusion of air, suggesting that some reox chemistry takes place between the vanadium complexes and oxygen in solution.

EPR studies. DMSO solutions of the complexes [VOL(acac)] (1 and 3) provide EPR patterns with a g value of 1.957 and the following hyperfine coupling constants: 1: \( A_1 = 98.7, A_2 = 175.3 \), \( A_{SD} = 60.2 \times 10^{-4} \) cm\(^{-1} \); 3: \( A_1 = 99.7, A_2 = 180.3 \), \( A_{SD} = 58.9 \times 10^{-4} \) cm\(^{-1} \). Practically the same values have been obtained in MeCN. If compared with EPR parameters of other VO\(^{2+} \) complexes.

Table 3  Electronic absorption spectra

<table>
<thead>
<tr>
<th>Compound (solvent)</th>
<th>( \lambda_{\text{max}}/\text{nm} (\varepsilon /\text{M}^{-1} \cdot \text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hacpy-inh (DMF)</td>
<td>211.5(21387), 240(11140), 293(14895), 369(3038)</td>
</tr>
<tr>
<td>[VO(acpy-inh)acac], 1 (DMF)</td>
<td>275(13783), 385(10661)</td>
</tr>
<tr>
<td>(MeOH)</td>
<td>205(11200), 243(7100), 282(7238), 370(4450)</td>
</tr>
<tr>
<td>[VO(acpy-inh)], 2 (DMF)</td>
<td>269.5(13783), 386.5(5221.6)</td>
</tr>
<tr>
<td>[VO(O2)2(acpy-inh)], 3 (DMF)</td>
<td>242(12030), 273.5(12270), 385(7053), 410(sh)4890</td>
</tr>
<tr>
<td>[VO(acpy-inh)kat], 7 (MeOH)</td>
<td>214.5(35922), 379(17010), 516.5(6460), 778(6608)</td>
</tr>
<tr>
<td>[VO(acpy-inh)bha], 9 (MeOH)</td>
<td>214(28414), 378(12052), 551(2958)</td>
</tr>
<tr>
<td>Hacpy-bhz (DMF)</td>
<td>205.5(18060), 229.5(11835), 295.5(21660), 367(2007)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)acac], 3 (DMF)</td>
<td>275.5(15162), 389(11527)</td>
</tr>
<tr>
<td>(MeOH)</td>
<td>379(6515), 292(16110), 205(23320)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)], 4 (DMF)</td>
<td>392.5(22041), 274(18999), 236(4703), 202.5(6683)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)bha], 6 (DMF)</td>
<td>392(520310), 268(57538), 255.5(6613)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)kat]bha, 8 (MeOH)</td>
<td>777(4800), 516(4087), 385(522830), 219.5(38040)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)bha]hba, 10 (MeOH)</td>
<td>550(4325), 388.5(14551), 249.5(23160), 211.5(32632)</td>
</tr>
</tbody>
</table>

Table 4  \(^1\)H NMR spectra (6 ppm in ppm) of ligands and complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH</th>
<th>CH(_3)</th>
<th>Aromatic protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hacpy-inh</td>
<td>11.19(s, 1H)</td>
<td>2.51s(3H)</td>
<td>7.45–8.76(m, 8H)</td>
</tr>
<tr>
<td>[VO(acpy-inh)], 2</td>
<td>2.30(s, 3H)</td>
<td>7.76(m, 5H), 8.76–8.83(m, 3H)</td>
<td></td>
</tr>
<tr>
<td>[VO(O2)2(acpy-inh)], 5</td>
<td>2.71(s, 3H)</td>
<td>7.94–8.81(m, 7H), 9.60–9.63(d, 1H)</td>
<td></td>
</tr>
<tr>
<td>[VO(acpy-inh)kat], 7</td>
<td>2.71, 2.82(s each, 3H)</td>
<td>6.58–6.73(m, 4H), 7.79–8.82(m, 8H)</td>
<td></td>
</tr>
<tr>
<td>[VO(acpy-inh)bha], 9</td>
<td>2.74, 2.82(s each, 3H)</td>
<td>7.40–8.76(m, 13H)</td>
<td></td>
</tr>
<tr>
<td>Hacpy-bhz</td>
<td>10.90(s, 1H)</td>
<td>2.51(s, 3H)</td>
<td>7.43–8.61(m, 9H)</td>
</tr>
<tr>
<td>[VO(acpy-bhz)], 4</td>
<td>2.78(s, 3H)</td>
<td>7.48–8.40(m, 9H)</td>
<td></td>
</tr>
<tr>
<td>[VO(O2)2(acpy-bhz)], 6</td>
<td>2.77(s, 3H)</td>
<td>7.48–8.84(m, 9H)</td>
<td></td>
</tr>
<tr>
<td>[VO(acpy-bhz)kat]bha, 8</td>
<td>2.77, 2.78(s each, 3H)</td>
<td>6.58–6.73(m, 4H), 7.48–8.83(m, 9H)</td>
<td></td>
</tr>
<tr>
<td>[VO(acpy-bhz)bha]hba, 10</td>
<td>2.71, 2.81(s each, 3H)</td>
<td>7.40–8.47(m, 14H)</td>
<td></td>
</tr>
</tbody>
</table>

* Letters given in parentheses indicate the signal structure: s = singlet, d = doublet, m = multiplet.

sidered LMCT transitions originating from oximate oxygens or phenolate oxygen. As vanadium(V) complexes have a 3d\(^{0} \) configuration, d-d transitions are not expected. However, such d-d transitions appear at ca. 600 nm in complexes 1 and 3 as a very weak band.

Even the catecholate complexes having a 507 ppm region. The EPR studies. Table S1 (ESI) presents 507 ppm region. The EPR spectra of the complexes \([\text{VOL(acac)}] \) provides EPR patterns with a g value of 1.957 and the following hyperfine coupling constants: 1: \( A_1 = 98.7, A_2 = 175.3 \), \( A_{SD} = 60.2 \times 10^{-4} \) cm\(^{-1} \); 3: \( A_1 = 99.7, A_2 = 180.3 \), \( A_{SD} = 58.9 \times 10^{-4} \) cm\(^{-1} \). Practically the same values have been obtained in MeCN. If compared with EPR parameters of other VO\(^{2+} \) complexes.
Stability studies. The stability of complexes 7, 8, 9 and 10 in various solvents were studied. Solutions of these complexes are stable for about a week in dry CH₂Cl₂ and for about two days in methanol, but as already evidenced by the spectral studies – they slowly decompose in DMF and DMSO. The conversion of the [VO²⁺] complexes 7 and 8 into the [VO₃⁻] species with the loss of the bidentate ligand catecholate(2⁻) was established by electronic absorption studies of DMSO solutions, Fig. 3. In dry DMSO conversion is rather slow and takes about 24 h. During this period, a gradual loss in intensity of the LMCT bands due to coordinated catecholate and their final disappearance is observed. Addition of water facilitates this conversion. In a typical experiment, addition of 1 drop of H₂O in 5 ml of ∼10⁻⁴ M solution of 7 gives rise to complete conversion into 2 within 8 h, as illustrated in Fig. 3. Similar observations have also been noted in oxovanadium(V) complexes containing catecholates along with Schiff bases derived from salicylaldehyde and 8-aminoquinoline.²⁵ Eqn. (8) represents the decomposition reaction.

\[
[\text{VO(acpy-inh)}] + \text{H}_2\text{O} \rightarrow \text{[VO(acpy-inh)]} + \text{H}_3\text{O}^+ \quad (8)
\]

Reactivity of 7 towards L-ascorbic acid. The reactivity of complex 7 towards L-ascorbic acid was monitored by electronic absorption spectroscopy. In a typical reaction, 7 (10⁻⁴ M solution in CH₃Cl₂) was treated with L-ascorbic acid dissolved in the minimum amount of MeCN in an approximately 1:2 molar ratio. The two LMCT bands at 790 and 518 nm slowly disappeared. The 274 nm band sharpened. The spectra recorded at different intervals of time are shown in Fig. 4. Since catecholate and benzohydroxamato complexes are stable in CH₃Cl₂ and CH₂Cl₂-MeCN for several days, any change in the absorption spectra should come about by the reaction between L-ascorbic acid and the complex. As L-ascorbic acid has reducing properties, intermediate reduction of 7 with concomitant removal of coordinated catecholate may occur. The matching of the final spectrum with the dioxovanadium(V) complex 2 indicates that VO⁺ is reoxidised to form [VO₂L₂]. The net reaction is thus an oxidation of ascorbic acid by atmospheric oxygen, catalysed by VO⁺.

![Absorption spectra of [VO(acpy-inh)cat] (7) in DMSO (ca. 10⁻⁴ M solution) plus one drop of H₂O as a function of time over a period of 8 h.](image-url)
peroxidases, for which a hydroxo group in an apical position of an oxo–hydroxo complex, viz. [VO(OH)HL]−, generated with HCl from the respective dioxovanadium(v) dimer,8 and based on established hydroxo–oxovanadium complexes,19 the formation of [VO(OH)(acpy-inh)]− is also proposed here. On allowing the solution to stand overnight, or on addition of KOH dissolved in methanol, the reaction is reversed, i.e. the solution acquires the original spectral pattern of 2. The formation of a hydroxo species is an important observation in the context of the vanadate-dependent haloperoxidases, for which a hydroxo group in an apical position has been confirmed.41

Conclusion
Monomeric, distorted square-pyramidal dioxovanadium(v) complexes have been obtained by using bulky monobasic tridentate ONH ligands based on hydrazones. These can be looked at as structural models for the active site in vanadate-dependent haloperoxidases. Intermediate species containing the [VO(OH)2]3− core can be obtained by protonation of dioxo complexes. One of the oxo-groups can also be replaced by peroxide to form oxoperoxo complexes, another feature which is pertinent to the peroxidases. Electron transfer processes are modeled with the complex [VO(acpy-inh)cat]− in the presence of ascorbic acid and air, yielding [VO4L2]− possibly via a [V4OL]− intermediate.

Acknowledgements
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References