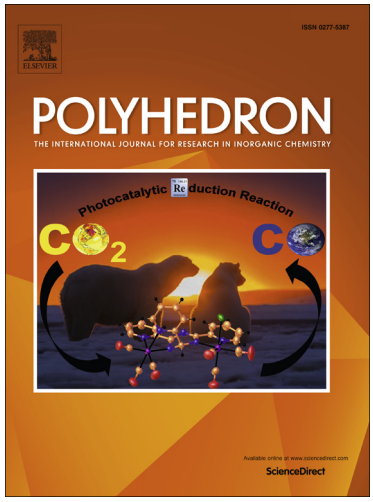

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Synthesis, crystal structure and catecholase activity of a vanadium(V) Schiff base complex

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Abstract

An X-ray structurally characterized vanadium(V) complex, $[VO_2(L\text{-}H)]$ [L-H = H_2L derived ligand (H_2L = N-(salicyaldimine)-1,3-diaminopropan-2-ol)], was found to behave as an effective catalyst towards the oxidation of 3,5-di-tert-butylcatechol in methanol to its corresponding quinone derivative in aerial oxygen. The reaction follows Michaelis–Menten enzymatic reaction kinetics with a turnover number (K_{cat}) of 2.063×10^3 h^{-1}.

Keyword: Vanadium, Schiff base, catecholase activity

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1. Introduction

The ubiquitous plant enzyme catechol oxidase catalyzes exclusively the oxidation of catechols to the corresponding *o*-quinones in the presence of molecular oxygen. The resulting highly reactive *o*-quinones auto-polymerize to form brown polyphenolic catechol melanins, a process thought to protect the damaged tissues of plants from pathogens or insects. The active site of catechol oxidase contains an antiferromagnetically coupled (EPR silent) dicopper(II) centre [1]. It is well documented that the active site of catechol oxidase consists of a hydroxo-bridged dicopper(II) centre in which each copper(II) centre is coordinated to three histidine nitrogen atoms and adopts a trigonal pyramidal environment with one nitrogen atom in the apical site [1]. Since the publication of the crystal structure of the active site of catechol oxidase [2] several model complexes have been reported [3-6] to elucidate the structure-function relationship of this biocatalytic catechol-quinone conversion. Moreover, some monometallic complexes of copper(II) [7] and some other metal ions, such as Mn(II/III/IV) [7e,8], Fe(III) [9], Co(III) [10], Ni(II) [11] and Zn(II) [12], are also found to show catecholase activity. The catecholase activity of vanadium(V) was first reported by Chakravarty *et al* [13] about a decade ago. Some other groups also reported vanadium(V) complexes showing catecholase activity [14]. Here in this present work, we report the synthesis and X-ray structural characterization of a mononuclear vanadium(V) complex with an (N,O) donor Schiff base ligand, $[VO_2(L\text{-}H)]$ (**1**) [L-H = H_2L derived ligand (H_2L = N-(salicyaldimine)-1,3-diaminopropan-2-ol); alcoholic and phenolic protons are removed from H_2L, and the primary amine is protonated as $-NH_3^+$ to derive L-H)] [15] which show catecholase activity in methanol. The behaviour of the complex as a catecholase mimic is described in this present report.

2. Experimental

2.1.Materials

High purity salicyaldehyde (Sisco Research Laboratories Pvt Ltd, India), 1,3-diamino-2-propanol (Aldrich, UK), ammonium vanadate (Aldrich, UK), 3,5-di-*tert*-butylcatechol (Aldrich, UK) and all other solvents were purchased from the respective concerns and used as received. Solvents were dried according to standard procedures and distilled prior to use.

The ligand H_2L was prepared using a reported method [16]. For the catecholase activity study, 1×10^{-4} mol dm^{-3} solutions of **1** (0.0003 g) were treated with 1×10^{-2} mol dm^{-3} (100 equivalents) of 3,5-DTBC (0.0222 g) under aerobic conditions.

2.2. X-ray diffraction

Single crystals of **1** for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data for **1** at 293 K for **1** were collected on a Bruker SMART APEX II CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The crystal data and refinement details are listed in Table 1. **1** was identified having the *P*na2_1 space group. The structure was solved by direct methods, and the structure solution and refinement were based on $|F|^2$. The final differences Fourier map showed the maximum and minimum peak heights at 0.267 and -0.289 e $Å^{-3}$ with no chemical significance. All calculations were carried out using SHELXL-97 [17] and were refined using SHELSL-97 [17], which are available within the Olex-2 [18] suite. All the figures have been generated using ORTEP-32 [19].

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. UV-Vis and IR spectra (KBr discs, 4000-300 cm^{-1}) were recorded using a Shimadzu UV-Vis 2450 spectrophotometer and Perkin-Elmer FT-IR model

RX1 spectrometer, respectively. The ^{1}HNMR spectral data of the quinine were collected in $CDCl_3$ on a Bruker 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectra of compound **1** were recorded in DMSO-d_6 using a Bruker 300 MHz spectrometer. ^{51}V NMR data of **1** were also recorded in DMSO-d_6 with a Bruker 131 MHz spectrometer. The mass spectrometry was recorded using a wQtof Micro instrument.

*2.4. Preparation of **1***

A warm methanolic solution of NH_4VO_3 (0.0116 g, 0.1 mmol) was added over half an hour to a stirring solution of the ligand (0.0298 g, 0.1 mmol) in methanol. The yellow solution was filtered and the supernatant liquid was kept in air for slow evaporation. The product was obtained as yellow crystals.

Yield: (based on metal salt) 0.0073 g (23.62 %). *Anal*. calc. for $C_{10}H_{16}N_2O_6V$ (**1**): C, 38.59; H, 5.18; N, 8.99; Found: C, 39.69; H, 5.43; N, 8.94% (Table S1, Supplementary file). Selected IR bands (KBr pellet, cm^{-1}): 3329 (s), 1633 (s), 898 (s). UV-Vis (λ, nm, MeOH): 318, 250, 217. ^{1}H NMR (300 MHz, DMSO-d_6) δ, ppm: 2.94 (t, J = 9.6 Hz, 1H), 3.07 (d, J = 9.6 Hz, 1H), 3.22-3.61 (m, 2H), 3.68-3.75 (m, 1H), 4.09 (dd, J = 13.8, 4.5 Hz, 1H), 4.50 (brs, 1H), 6.77 (t, J = 8.1 Hz, 2H), 7.40 (t, J = 8.1 Hz, 1H), 4.41 (d, J = 7.8 Hz, 1H), 8.80 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ, ppm: 42.72, 63.83, 71.31, 115.55, 120.08, 120.65, 132.98, 133.86, 165.58, 166.30. ^{51}V NMR (131 MHz, DMSO-d_6) δ, ppm: -531.14

3. Results and discussion

3.1. Synthesis and formulation

The reaction between NH_4VO_3 and the ligand H_3L in methanol afforded the pentacoordinated mononuclear complex **1**. The complex was characterized by microanalytical (C, H and N), spectroscopic and other physicochemical results. The

microanalytical data are in good conformity with the formulation of **1**. The moisture insensitive complex is stable over long periods of time in powdery and crystalline states, and is soluble in methanol, ethanol etc, but is insoluble in water. In the IR spectrum, relatively intense peaks around 1630 cm^{-1} due to the C=N stretching frequency appear in the complex. The ^{51}V NMR signal of **1** at -531.14 ppm (Fig. S1, Supplementary file) is characteristic of a V(V) complex with a coordination sphere that is dominated by O functionalities [20].

3.2. X-ray structure

The molecular view of the complex is shown in Fig. 1. Single crystal X-ray diffraction analysis (Table 1) reveals that **1** crystallized in the orthorhombic space group *P*na2_1. The coordination geometry around the vanadium(V) centre in **1** is best described as a distorted square pyramid with a VNO_4 chromophore (the τ value for the metal centre is calculated as 0.07) [21]. Among the coordinating atoms, O3 and O4 are phenoxy and alkoxy oxygen atoms, O1 and O2 are oxo groups, and N1 is the imine nitrogen atom. Considering the bond angle and bond distance data (Table 2), O1, O3, O4 and N1 form the base of the square pyramid. The V1 and O2 are positioned on the vertical axis of the geometry. The V-O bond distances span the range 1.909(3)-1.614(4) Å and the difference Δ between the longest and shortest bonds amounts to 0.295 Å. The shorter V1-O1 (1.649(4) Å) and V1-O2 (1.614(4) Å) bonds than the other bonds are indicative of double bond character [22].

3.3. Thermal behaviour

The thermal behavior of the vanadium complex was followed up to 800 °C in a static nitrogen atmosphere with a heating rate of 10 °C per minute. The complex decomposes in three steps (Fig. S2, Supplementary file). The first two steps, from

32.11 to 112.88 and 112.88 to 216.98 °C, correspond to the loss of two lattice water molecules and an ammonia molecule, respectively with mass losses of 11.51% (calcd. 11.56%) and 6.19% (calcd. 6.18%), respectively. The release of the organic moiety takes place in the third step (216.98-461.58 °C). The experimental mass loss of 53.21% agrees with the calculated mass loss of 56.55%, with the formation of vanadium(IV)oxide (VO_2). However, more than 3% mass loss difference between the theoretical and experimental data may suggest some other species, like vanadium(V) oxide.

*3.4. Catecholase activity of **1**: Spectrophotometric study*

In order to study the catecholase activity of complex **1**, 3,5-DTBC, with two bulky *t*-butyl substituents on the ring and low quinone-catechol reduction potential, was chosen as the substrate. This makes it easily oxidized to the corresponding *o*-quinone, 3,5-DTBQ, which is highly stable and shows a maximum absorption at 401 nm in methanol. A solution of **1** was treated with 100 equivalents of 3,5-DTBC under aerobic conditions. The repetitive UV-Vis spectral scan was recorded in pure MeOH (Fig. 2). Spectral bands at 318, 250 and 217 nm appear in the electronic spectrum of complex **1**, whereas 3,5-DTBC shows a single band at 282 nm.

After addition of 3,5-DTBC, the time dependent spectral scan shows a very smooth growth of the quinone band at 400 nm, as reported by Krebs et al [23], concomitant with a decrease in the characteristic 282 nm band for 3,5-DTBC, which indicates the formation of the respective quinone derivative, 3,5-DTBQ; this latter compound was purified by column chromatography. The product was isolated in high yield (67 %) by slow evaporation of the eluant and was identified by ^{1}H NMR spectroscopy (Fig. S3, Supplementary file). ^{1}H NMR

(CDCl3, 400 MHz) δ, ppm: 1.16 (s, 9H), 1.20 (s, 9H), 6.15 (d, J = 2.4 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H).

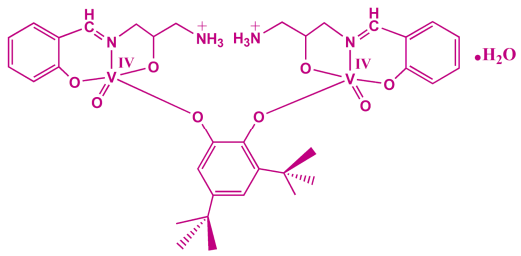
To find out the comparative reaction velocity between 3,5-DTBC and **1**, the reaction kinetics between **1** and 3,5-DTBC were studied by observing the time dependent change in absorbance at a wavelength of 400 nm, which is characteristic of 3,5-DTBQ in methanol. The colour of the solution gradually turned deep brown, indicative of a gradual conversion of 3,5-DTBC to 3,5-DTBQ. The difference in absorbance ΔA at 400 nm was plotted against time to obtain the velocity for that particular catalyst to substrate concentration ratio (Fig. 3). A first-order catalytic reaction was observed, with a velocity of 1.72×10^{-3} min^{-1}.

3.5. Enzyme kinetics study

Enzymatic kinetic experiments were performed UV-Vis spectrophotometrically, thermostated at 25 °C for complex **1** and the substrate 3,5-DTBC in MeOH. 0.04 ml of the complex solution, with a constant concentration of 1×10^{-4} M, was added to 2 ml of 3,5-DTBC of a particular concentration (varying its concentration from 1×10^{-3} to 1×10^{-2} M) to achieve the ultimate concentration of the complex as 1×10^{-4} M. The conversion of 3,5-DTBC to 3,5-DTBQ was monitored with time at a wavelength of 400 nm for a MeOH solution. The rate for each concentration of the substrate was determined by the initial rate method. The rate versus concentration of substrate data were analyzed on the basis of the Michaelis-Menten approach of enzymatic kinetics to get a Lineweaver-Burk (double reciprocal) plot as well as the values of various kinetic parameters, V_{max}, K_M and K_{cat}. The observed rate vs. [substrate] plot in methanol solution as well as the Lineweaver-Burk plot are given in Fig. 4. The kinetic parameters are listed in Table S2 (Supplementary file). The turnover number (K_{cat}) was found to be 2.063×10^{3} h^{-1} in MeOH.

3.6. Mechanism of catecholase activity

To obtain a mechanistic inference of the catecholase activity and to get an idea about the complex substrate intermediate, we recorded an ESI-MS spectrum (Figs. S4a and S4b, Supplementary file) of a 1:100 mixture of complex **1** and 3,5-DTBC. The signal at m/z = 195 is due to the formation of the protonated ligand $[(H_2L)H]^+$. The peak at m/z = 243 can be assigned to a sodium aggregate of quinone $[3,5\text{-DTBQ-Na}]^+$. The complexes $[VO_2(L\text{-}H)(Na)]^+$ and $[VO_2(L\text{-}H)\text{-}(H_2O)_2H]^+$ exhibit peaks at m/z = 299 and 313, respectively. The formation of a VO^{2+} species, **1a** (Scheme 1), is identified by the peak at m/z = 758. The V(V) complex **1** is reduced to the VO^{2+} species **1a** by 3,5-DTBC, and 3,5-DTBC itself gets oxidised to quinone in the presence of aerial oxygen. The formation of **1a** can also be identified from the appearance of a blue colour (Fig S5, Supplementary file) in the reaction mixture after mixing **1** and 3,5-DTBC. In a repetitive UV-Vis scan (Fig. S6, Supplementary file) of the mixture, this blue coloration is supported by the appearance of a peak at 613 nm. The molecular oxygen that takes part in the oxidation of 3,5-DTBC to 3,5-DTBQ in the presence of **1** is converted to H_2O_2. The H_2O_2 thus liberated was identified and characterized spectrophotometrically (S1; Supplementary file) [6b,24].



Scheme 1. Intermediate species **1a**.

4. Conclusions

In conclusion, we have synthesized and characterized one mononuclear vanadium(V) Schiff base complex **1** which mimics the enzyme catecholase. The synthetic methodology of the complex in this present work is simpler than described elsewhere [15]. Simple one-pot mixing of the metal salt, organic ligand at room temperature in methanol generates the title complex, avoiding pH control, an hour-long reflux etc, as described in the existing report [15]. In methanol the catalytic reaction follows a first order reaction rate. The turnover number of the reaction in MeOH is found to be 2.063×10^3 h^{-1}, which is much higher than the few recently reported complexes [5b,5e,6b,10a,25] showing catecholase activity. To the best of our knowledge, our reported complex is one of the few monometallic vanadium compounds which is found to show this activity [26].

5. Supplementary data

CCDC 1052877 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. Crystallographic data for **1**.

Emperical formula	$C_{10}H_{13}N_2O_4V.2(H_2O)$
Formula weight	312.20
Temperature, K	293
Wavelength, Å	0.71073
Crystal system	orthorhombic
Space group	*P*na2_1
a, Å	6.9427(8)
b, Å	26.568(3)
c, Å	7.3384(9)
Volume, Å^3	1353.6(3)
Z	2
ρ, Mg m^{-3}	1.527
μ, mm^{-1}	0.756
F (000)	644
Crystal size, mm^3	0.2 × 0.2 × 0.2
Theta range for data collection	1.533 to 25.023 deg
Limiting indices	$8 \leq h \leq 8$, $-31 \leq k \leq 31$, $-8 \leq l \leq 8$
Reflections collected / unique	6867 / 3197 [R(int) = 0.0375]
Completeness to theta	26.000 (100.0 %)
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2347/5/195
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR_2 = 0.0973
R indices (all data)	R1 = 0.0456, wR_2 = 0.1044
Absolute structure parameter	0.42(2)
Largest difference peak and hole, e Å^{-3}	0.267 and -0.289

Table 2. Bond distances [Å] and angles [°] for **1**.

Bond distances			
V(1)-N(1)	2.149(4)	V(1)-O(3)	1.892(4)
V(1)-O(1)	1.649(4)	V(1)-O(4)	1.909(4)
V(1)-O(2)	1.614(4)		
Bond angles			
O(1)-V(1)-O(2)	109.4(2)	O(2)-V(1)-O(4)	102.3(2)
O(1)-V(1)-O(3)	94.9(2)	O(2)-V(1)-N(1)	105.4(2)
O(1)-V(1)-O(4)	92.0(2)	O(3)-V(1)-O(4)	149.51(19)
O(1)-V(1)-N(1)	144.8(2)	O(3)-V(1)-N(1)	81.48(15)
O(2)-V(1)-O(3)	103.3(2)	O(4)-V(1)-N(1)	75.89(14)

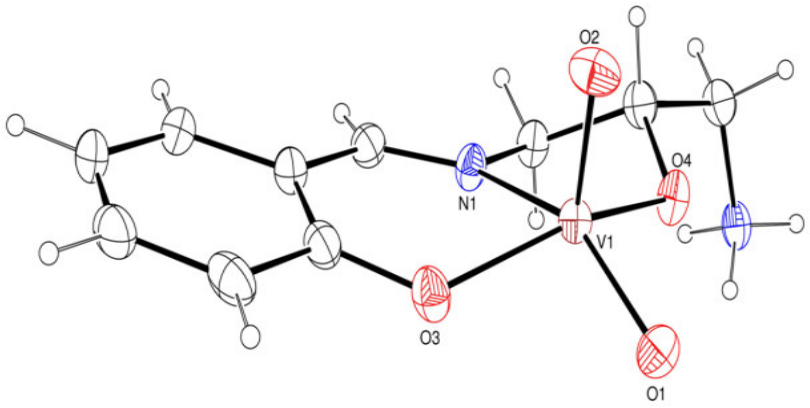

Fig. 1 Molecular view of **1** with 20% ellipsoid probability

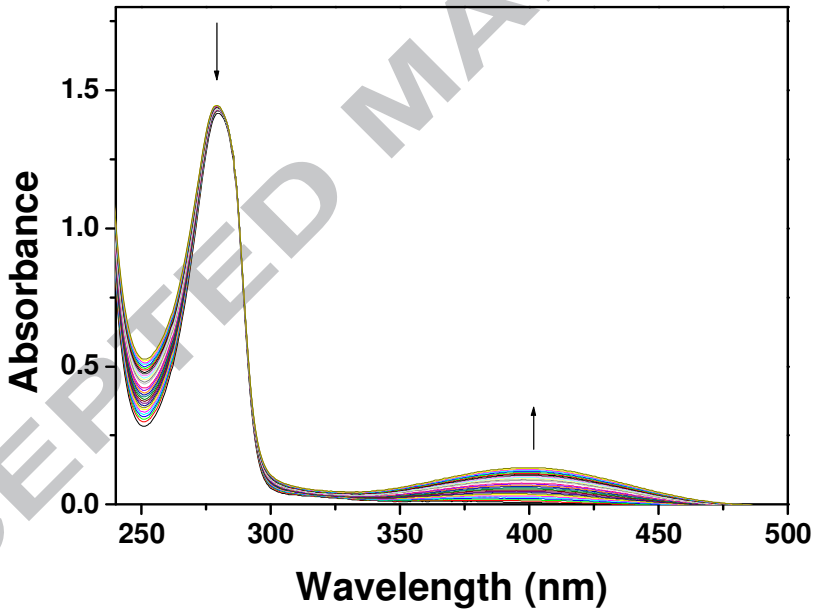

Fig. 2 Change in spectral pattern for the reaction of **1** with 3,5-DTBC in MeOH after observing the reaction for 6 h

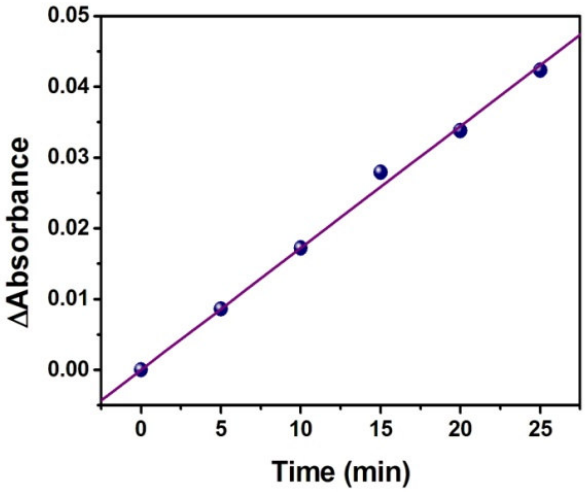

Fig. 3 A plot of the difference in absorbance (ΔA) vs time to evaluate the initial velocity of the catalytic oxidation of 3,5-DTBC by **1** in MeOH

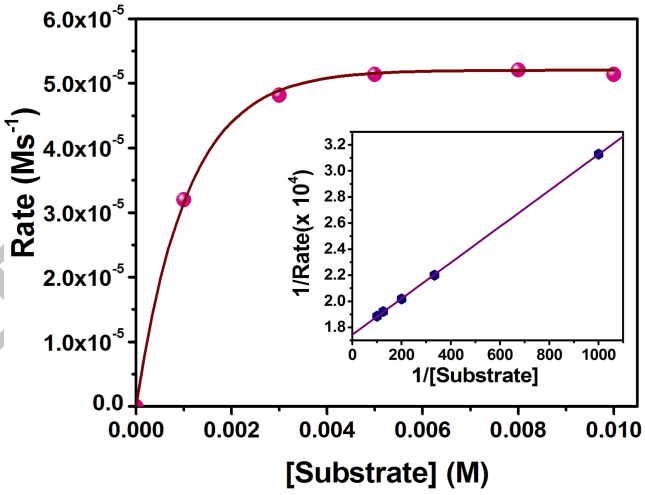

Fig. 4 Plot of rate vs. [substrate] in the presence of **1** in MeOH; inset: Lineweaver-Burk plot

Synthesis, crystal structure and catecholase activity of a vanadium(V) Schiff base complex

Sunit Kumar Mal, Merry Mitra, Hareram Yadav, Chandra Shekhar Purohit, Angshuman Roy Choudhury, and Rajarshi Ghosh

A structurally characterized vanadium(V) complex, [VO_2(L-H)] [L-H = H_2L derived ligand (H_2L = N-(salicyaldimine)-1,3-diaminopropan-2-ol], was found to behave as an effective catalyst towards the oxidation of 3,5-di-tert-butylcatechol in methanol to its corresponding quinone derivative in aerial oxygen. The reaction follows Michaelis–Menten enzymatic reaction kinetics with a turnover number (K_{cat}) of 2.063×10^3 h^{-1}.

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