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An amino acid coordinated vanadium (IV) complex: Synthesis, structure, DFT calculations and VHPO mimicking catalytic bromoperoxidation of organic substrates

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ABSTRACT

A new VHPO mimicking oxovanadium(IV) complex [VO(sal-L-val)(phen)] (sal-L-val = Schiff base derived from salicylaldehyde and L-valine; phen = 1,10-phenanthroline) has been synthesized and characterized by elemental analysis, UV–vis, IR spectroscopy, ESI-MS, EPR and single crystal XRD studies. The structural and spectral parameters were further supported using DFT calculations. The complex was found to exhibit vanadium dependent haloperoxidase (VPHO) activity.

The discovery of vanadium-dependent haloperoxidase enzymes (VHPO) [1,2], the antiproliferative as well as the cytotoxic effects [3] and insulin mimetism by some vanadium complexes [4,5] laid special attention in the field of the coordination chemistry of vanadium. Among these, vanadium haloperoxidases (VHPOs) have received increasing interest due to their unique characteristics and potential use in oxidation and epoxidation reactions [6]. Vanadium haloperoxidase (VHPO) catalyses the oxidative halogenation of organic compounds [7–9] (hydrocarbons and alcohols, organic sulfide etc.) in the presence of halide ions [10,11] and hydrogen peroxide under physiological conditions. Irrespective of their origin they all show a high degree of amino acid homology with oxovanadium moiety in their active centers. The synthesis of oxovanadium(IV/V) complex with Schiff bases derived from different types of amino acids and peptides has been an area of interest in order to get a better understanding on the mechanism of interaction of vanadium with biogenic molecules [1–3]. But the first report of synthesis of metal complexes with Schiff bases derived from amino acid was made by Rây and Mukherjee in 1950 [12]. Although, the synthesis of some oxovanadium complexes with various amino acid Schiff bases has been reported [13–20] but the detail investigation on the VHPO mimicking activity as well as the mechanism of action of such complexes containing aminoacid–salicylaldehyde ligands are very scanty [21,22]. The peroxidative bromination is an important route for the biosynthesis of many natural brominated organic compounds [6]. So, investigation on the vanadium complex catalyzed conversion of organic substrates to corresponding brominated products has been a field of active research. As a result of which, we have accomplished the synthesis of the compound [V^{IV}O(sal-L-val)(phen)] with a view to employ for the first time, any valine based Schiff base complex of oxovanadium moiety, as a catalyst for the peroxidative bromination of organic substrates.

A solution of potassium hydroxide in 10 mL absolute alcohol and L-valine (1 mmol, 0.117 g) was stirred until dissolved in the methanol–KOH solution, thereafter a methanolic solution (2 mL) of salicylaldehyde (1 mmol) was added to it dropwise and stirred for 2 h. The resultant solution was added to a methanolic solution of vanadyl sulfate pentahydrate (1 mmol, 0.253 g) with continuous stirring, followed by the dropwise addition of a methanolic solution (5 mL) of 1,10-phenanthroline monohydrate (1 mmol, 0.198 g) and stirred for another 2 h, which on standing produced brown yellow solid. The slow diffusion of dichloromethane solution of the complex in n-hexane medium left at room temperature yielded diffractable grade brown single crystals after 15 days. Yield: 76%. IR [KBr, cm^{-1}]: 1618.08 [υ_{as}(COO)], 1538.19 [υ(C=N)], and 960.91 [υ(V=O)]. ESI-MS(+) in MeOH: m/z (relative intensity) 489 [M^+ + Na, 100], 467 [m^+ + 1, 23], and 466 [M^+, 11]. UV–vis in methanol [λ_{max}nm (ε M^{-1} cm^{-1})]: 383 (3290), 264 (29,900), 229 (47,500). Elemental analysis: Calc.C 53.77%, H 5.41%, and N 7.52%; found: C 53.81%, H 5.35%, and N 7.43%.

The single crystal X-ray diffraction analysis [23] shows that the complex [VO(sal-L-val)(phen)]·CH_2Cl_2 is hexa coordinated with octahedral geometry (Fig. 1) and the unit cell contains five complexes and five

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[1] Contributed by solving crystal structure only.

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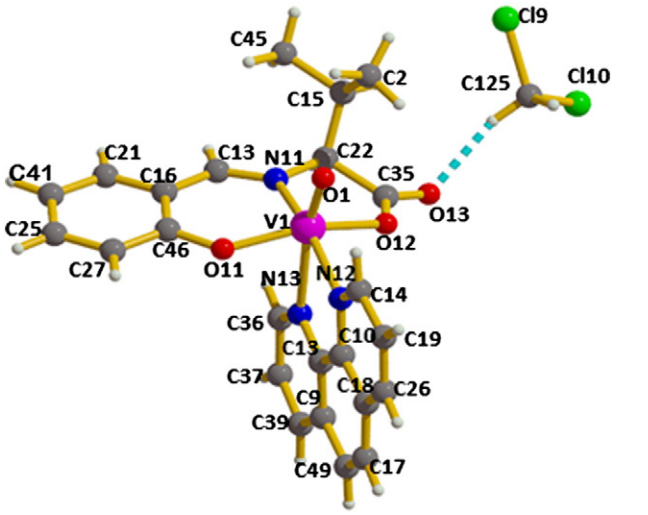

Fig. 1. The structural representation of [VO (sal-L-val)(phen)]·CH_2Cl_2.

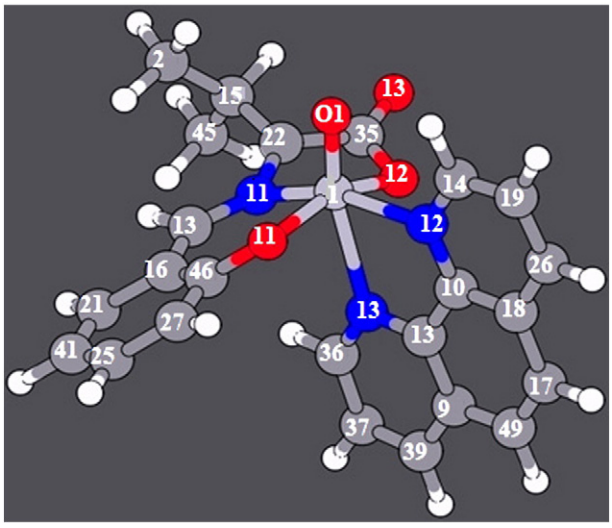

Fig. 2. B97D/6-31G** optimized structure of [V^{IV}O(sal-L-val)(phen)] in methanol.

solvent molecules (Fig. S1) (all crystallographic data are given in Supplementary file Table S1, S2). The two oxygen atoms O11 and O12, one nitrogen atom N11 (from deprotonated Schiff base) and another nitrogen N12 (from phenanthroline) constitute the equatorial plane. The axial positions of vanadium(IV) are occupied by a double bonded oxygen O1 and one nitrogen atom N13 from phen finishing its octahedral coordination sphere.

The solvent dichloromethane (CH_2Cl_2) is present outside the coordination sphere through weak hydrogen bonding interaction (C125-H12c···O13 = 3.132 Å) between the H atom (H12c) of CH_2Cl_2 and carboxylate oxygen O13 of the Schiff base. The bond lengths in basal plane V1–O11, V1–O12, V1–N11 and V1–N12 are 1.926(8), 1.991(9), 2.067(11) and 2.067(11) Å respectively, while the vanadium-oxo bond (V1–O1) distance 1.603(9) Å, is slightly longer than the normal range [24] but close to other reported values [25,26]. Another V1–N13 axial bond length 2.396(10) Å, is also longer [27] than the respective equatorial bond length. The basal bond angles are all close to 90 [O12–V1–N12, O11–V1–N11 and O11–V1–N12 are 93.6(4), 89.7(4), 89.4(4) respectively] except O12–V1–N11 [79.9(4)] which is smaller than expected [28].

The DFT has been proved to be an important tool either to support the conclusions reached from experiments or to explore the properties that have not been explained by experiments. In the present work DFT calculations have been done both to support quantitatively the experimental findings and to ascertain the electron population in the complex in the form of HOMO and LUMO to assign electronic transitions, which could not be established experimentally. The experimental structural parameters (Fig. 2, Table-S3) of the vanadium complex [V^{IV}O(sal-L-val)(phen)] are substantiated by DFT calculations [29–34]. The calculated IR stretching frequencies of the complex are compared with experimental findings (Table-S4). The experimental value (1618 cm^{-1}) of $\upsilon_{(CO)}$ reasonably agrees with the B97D calculated value (1639 cm^{-1}) at lower basis set, however, B3LYP value (1693 cm^{-1}), differs rather within wide margin. The experimental value of $\upsilon_{(C=N)}$ (1538 cm^{-1}) shows excellent agreement with the result calculated by the B97D/6-31G** (1539 cm^{-1}). The calculated C–H stretching frequencies (in cm^{-1}) also remain within reasonable limits (2958–3177 and 3043–3240 respectively). The calculated λ_{max} values are also consistent with the experimental observations. The orbital plots (Fig. S2a–d) indicate that lobes of HOMO is mostly concentrated on the adjacent carbon atoms of N(11) atom while that of LUMO+7 is concentrated over the phenanthroline ring. Therefore, the dominant transition of the complex is accompanied by a charge transfer from carbon atoms 13 and 22 to the phenanthroline ring. The electronic transition (Table S5) in the ultraviolet region of the spectrum, however, involves charge transfer from the carboxylate group (–COO) (Fig. S2c) to the lower part (with respect to V=O) of the phenanthroline ring (Fig. S2d). Therefore, the theoretical calculations also support the experimental findings, including the molecular structure of the complex.

The X-band EPR spectra of the complex (Fig. 3) in dichloromethane–toluene (1:1) glass at 77 K gives rise to well resolved ^{51}V (I = 7/2) hyperfine eight lines [g (A/G) = 1.943 (71.81), g (A/G) = 1.985 (58.7) and gav (A_{av}/G) = 1.971 (63.07)]. The spectrum has axial symmetry with $g_{\parallel} < g_{\perp}$. The characteristic relationships $g_{\parallel} < g_{\perp}$ and $a_{\parallel} \gg a_{\perp}$ corresponding to an axially compressed d1xy configuration [10,17,35] were observed. The EPR study confirms the presence of mononuclear vanadium(IV) moiety in the complex.

The peroxidative bromination by the vanadium complex has been accomplished by treating olefinic alcohols (e.g. 1-buten-3-ol, 1-octene-3-ol and 9-decene-1-ol), KBr, H_2O_2 (terminal oxidant) and catalytic amount of vanadium complex at pH ~ 3.0. The substrate to catalyst ratio is 200:1 in all the experiments.

The catalyst [V^{IV}O(sal-L-val)(phen)] in the presence of H_2O_2 is assumed to be converted to a bound peroxide intermediate (III) [9,36,37], which is nearly equivalent to the active site of VHPO enzyme and this step is crucial for the biomimicking role in the catalytic processes (Fig. 4). This intermediate in turn oxidizes the bromide (Br^-) ion in the medium to bromonium ion (Br^+) which exists in the reaction medium as Br_3^-, Br_2 or HOBr [6]. The in situ generated bromonium ion reacts with olefinic alcohols to form corresponding brominated derivatives. After 8 h of reaction (Table 1) two major isomeric brominated products are characterized from each of olefinic alcohols by GC-Mass analysis. 3-Bromobutan-2-ol (25%) and 4-bromobutan-2-ol (15%) (m/z 151, 153) are obtained from 1-buten-3-ol; 2-bromooctan-3-ol (38%) and 1-bromooctan-3-ol (19%) (m/z 207, 209) are produced from 1-octen-3-ol; and 10-bromodecan-1-ol (41%) and 9-bromodecan-1-ol (2%) (m/z

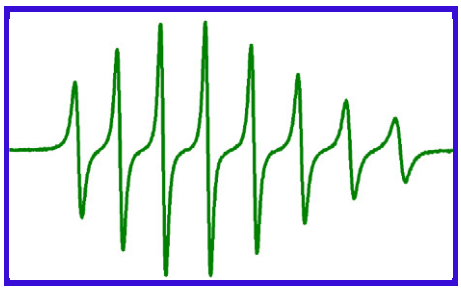

Fig. 3. EPR spectrum of complex in solution (dichloromethane/toluene) at 77 K.

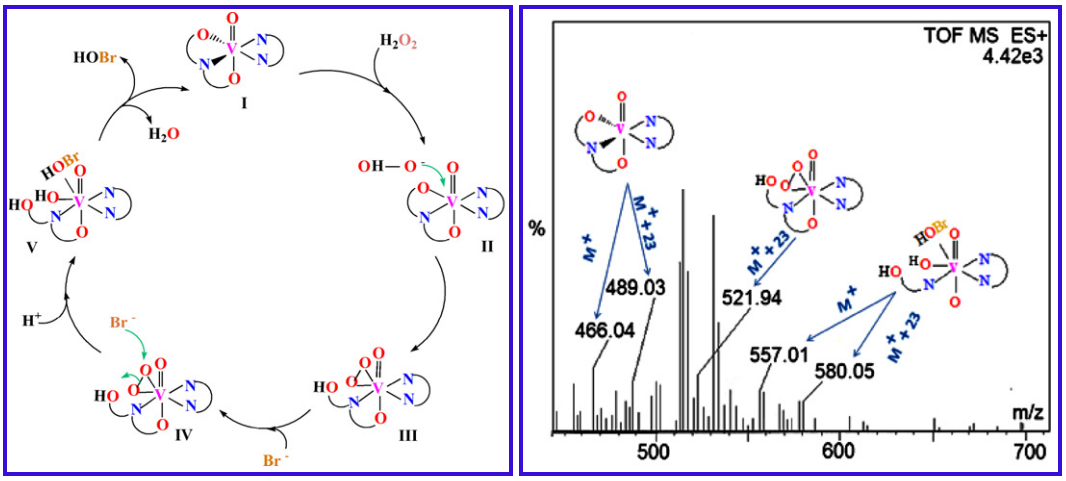

Fig. 4. Schematic representation of the proposed mechanism of the catalytic bromination (left); ESI-MS of the catalytic intermediates of the bromination reaction of olefinic alcohols (right).

238, 240) are obtained from 9-decen-1-ol. Small amount of epoxides is detected in the case of 1-octen-3-ol (3%) and 9-decen-1-ol (7%) by GC-Mass analysis. The stability of one isomeric brominated product is higher than the other in each case, due to the stability of intermediate carbocations during the electrophilic (Br^+) addition reaction in the unsymmetrical double bond of olefinic alcohols. Control experiments, maintaining all other additives and parameters fixed without the catalyst, show that the yields of the brominated products are negligibly small. The proposed catalytic cycle i.e. the mechanism of catalytic activity has been established and confirmed by ESI-MS in CH_3CN (Fig. 4), which is in conformity with the proposed mechanism of catalytic activity of other VHPO model studies [9,36–40]. During the catalytic process, the catalyst (I) (MS m/z: 466.04 [M^+], 489.03 [$M^+ + 23$]) was converted to a bound peroxide intermediate (III) (MS m/z: 521.94 [$M^+ + 23$]) in the presence of peroxide. Subsequent attack of a bromide ion at one of the oxo atoms of the peroxo group (IV) and the uptake of a proton from a surrounding water molecule lead to the generation of hypobromous acid (HOBr) (V) (MS m/z: 557.01 [M+], 580.05 [$M^+ + 23$]) followed by the restoration of the native state (I). The figures of GC-Mass analysis, % yields of products of different olefinic alcohols with respect to time and plot of turnover number against time for the conversion of products for different substrates are included as supplementary informations (Fig. S3–S10).

Hence, it can be concluded that a new oxovanadium complex [$V^{IV}O$(sal-L-val)(phen)] has been designed and synthesized with the aim of developing active biocatalyst. The compound mimics the VHPO activity by effecting in vitro bromination of olefinic alcohols to the corresponding brominated products with good efficiency.

Acknowledgments

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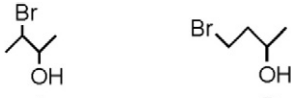
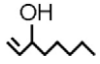
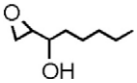
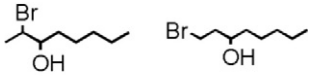
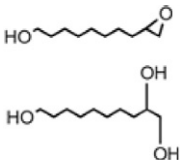
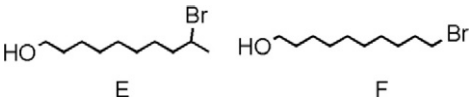
Appendix A. Supporting data

The X-ray crystallographic data (CIF file) for the structure reported in this paper have been deposited in the Cambridge

Table 1
Details of the catalytic bromination[a] of olefinic alcohols using the [$V^{IV}O$(sal-L-val)(phen)] complex as catalyst[b] in the presence of H_2O_2[c] and KBr in an acidic medium at room temperature.

Sl. No.	Substrate	Products		Yields of epoxidic products (%)	Yields of brominated products (%)	Turnover number (TON)[d]
		Epoxides/diols	Brominated			
I			 A B		40 A(25) + B (15)	80
II			 C D	3	57 C (38) + D (19)	120
III			 E F	7	43 E (2) + F (41)	100

[a] Time of reaction: 8 h.
[b] Concentration of catalyst 0.025 mmol.
[c] Concentration of H_2O_2: 25 mmol.
[d] Turnover number is defined here as the ratio of the moles of product obtained to the moles of catalyst used. The mole ratio of substrate: catalyst = 200:1.

Crystallographic Data Centre and the deposition number is CCDC 877860. Additional structural figures, tables, and the GC–MS are available in the supplementary materials. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.09.057.

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