Oxovanadium(IV) Salicylidene Glycine Complex with Phenanthroline as Co-ligand: Synthesis, Crystal Structure and Catalytic Degradation of Methyl Orange with H₂O₂

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Index Abstract

Oxovanadium(IV) Salicylidene Glycine Complex with Phenanthroline as Co-ligand: Synthesis, Crystal Structure and Catalytic Degradation of Methyl Orange with $\text{H}_2\text{O}_2$

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A glycine derived Schiff base vanadium complex with phenanthroline as co ligand has been synthesized under ambient conditions. The complex showed good catalytic activity for the degradation of methyl orange in presence of hydrogen peroxide.
Abstract

A Schiff base oxido vanadium complex derived from glycine and salicylaldehyde with phenanthroline as co-ligand viz. \([\text{VO(salgly)(phen)}]_24\) (where salgly = Schiff base derived from salicylaldehyde and glycine, phen = 1,10-phenanthroline) was synthesized under ambient conditions. The complex was characterized by elemental analysis and spectroscopic techniques such as FT-IR, UV-vis and electron paramagnetic resonance (EPR). The structure of the complex was determined by single crystal X-ray diffraction. The asymmetric unit of complex \(1\) consists of two crystallographically unique V(IV) centers along with four water molecules of crystallization. The crystal packing of \(1\) is stabilized by \(\pi-\pi\) stacking and C-H-\(O\) hydrogen bonding interactions. Thermogravimetric analysis (TGA) of the complex was carried to determine its thermal stability. Moreover, complex \(1\) showed good catalytic activity for the degradation of methyl orange (MO) in presence of hydrogen peroxide.

Key words: Schiff base, oxidovanadium complex, catalyst, methyl orange, hydrogen peroxide

Introduction

Vanadium(IV) complexes are frequently found as vanadyl derivatives containing the VO\(^{2+}\) core with 4 (tetrahedral and square planar), 5 (square pyramidal or trigonal bipyramidal), and 6 (octahedral) as the most prevalent coordination numbers [1]. The stable oxovanadium (VO\(^{2+}\)) cation dominates the chemistry of vanadium(IV), which remains intact during many processes [2]. The Schiff bases have been shown to form a variety of stable complexes with the oxovanadium(IV) ion. The Schiff bases derived from salicylaldehyde and amino acids reveals that the ligands mainly act as tridentate ligands, coordinating through the phenolato oxygen, imine nitrogen and carboxylate oxygen [3]. In order to fill the vanadium coordination sphere, additional ligands are utilized. Furthermore, in order to stabilize the +4 oxidation state of vanadium, chelating bidentate ligands such 1,10-phenanthroline or 2,2′-bipyridine are often employed resulting in octahedral vanadium complexes [4-7]. Schiff bases ligands have attracted significant attention due to their simple synthesis, variable coordination behavior toward metal ions and numerous applications in various fields such as catalysis [8], adsorption [9], chemosensors [10], bactericidal agents [11] and anticancer agents [12].
Environmental concerns are raised worldwide by the discharge of wastewaters from the textile industry that contain organic contaminants. Every year, over 280,000 tons of textile dyes are released into industrial effluents worldwide [13, 14]. Azo dyes, the largest group of synthetic pigments makes up more than 50% of all commercial dyes are extensively employed by the textile industry [15]. Azo bonds, which are the most active bonds in azo dye molecules, can be reduced by an electron in the conduction band or oxidized by a positive hole or hydroxyl radical [16]. Dye decolorization is caused by the breaking of -N=N- bonds [16]. These dyes possess potential carcinogenic properties, so their effect on the environment is a major concern [17]. Even at modest quantities (1 ppm L\(^{-1}\)), these dyes are poisonous and non-biodegradable [18], and they also reduce water transparency [19], which in turn reduces the amount of sunlight that can reach aquatic plants for photosynthesis [20]. Numerous studies have been conducted on advanced oxidation processes (AOPs), which use highly reactive oxidative species (such as HO\(^{•}\), O\(_2^{•-}\), O\(_2\), HOO\(^{•}\), and HO\(_2^{•}\) [21] as an alternate method of treating organic contaminants [22]. The azo dye molecules are subsequently broken down by HO\(^{•}\) through a series of processes into smaller, less toxic compounds. In many instances, the dye molecules are totally converted into carbon dioxide and water [16]. AOP’s frequently employ oxidation systems based on the conventional Fenton reagent (hydrogen peroxide and an iron catalyst) to eliminate persistent organic contaminants during wastewater treatment. Systems comprising metal compounds with varying valence, such as vanadium, manganese, nickel, and cobalt, can be employed as an alternative to iron-based catalysts [23]. The VO\(^{2+}\) ion interacts with H\(_2\)O\(_2\) in Fenton-type reactions to form hydroxyl radicals (•OH), just like Fe(II) does. As a result, numerous vanadium compounds can catalyze Fenton-like pathways for the peroxide oxidation of a variety of organic and inorganic substances [24-26]. In recent years, vanadium complexes were found to show good catalytic activity towards the degradation of harmful azo dyes. Vanadium amino acid complexes such as [VO(Hpro)(SO\(_4\))(H\(_2\)O)\(_3\)] (Hpro = proline), [VO(H\(_2\)lys)\(_2\)(H\(_2\)O)\(_3\)]Cl\(_2\)H\(_2\)O (Hlys = lysine) and [VO(H\(_2\)his)(2,2’-bipy)(H\(_2\)O)\(_2\)]Cl\(_2\)H\(_2\)O (Hhis = histidine) have been reported to show catalytic activity towards methyl orange degradation [27]. Some mixed ligand oxidovanadium(IV) complexes VO(ox)(im)\(_2\)H\(_2\)O, VO(ox)(4-mim)\(_3\), K\(_2\)[VO(ox)(2-mim)]\(_2\)H\(_2\)O and [V\(_2\)O\(_3\)(edta)(phen)]\(_2\)11H\(_2\)O (H\(_2\)ox = oxalic acid, H\(_4\)edta = ethylenediaminetetraacetic acid, im = imidazole, 2-mim = 2-methylimidazole, 4-mim = 4-methylimidazole, and phen = 1,10-phenanthroline) showed potential catalytic degradation of methyl orange [28].

In this work, we report the synthesis and crystal structure of a glycine derived oxovanadium(IV) Schiff base complex with phenanthroline as co-ligand viz. [V\(_{IV}\)O(salgly)(phen)].4H\(_2\)O (1). The complex crystallizes in P-1 space group with the asymmetric unit containing two crystallographically unique vanadium(IV) centers along with four water molecules of crystallization. Complex 1 was further characterized by FT-IR, UV-vis and EPR spectroscopic techniques. The crystal packing of 1 is stabilized by π–π stacking and hydrogen bonding interactions. The harmful azo dye, methyl orange, which is used extensively in the paper and textile industries, has been selected as a model contaminant [29]. Concentrations of methyl orange in industrial textile effluent are typically in the range of 2.5–10 mg/L [30]. The degradation of methyl orange dye by the title complex in presence and in absence of hydrogen peroxide was investigated. The result shows that the complex has good catalytic activity towards degradation of methyl orange in presence of hydrogen peroxide.
Results and discussion

Crystal structure of VO(salgly)(phen).4H₂O (1)

The asymmetric unit of complex 1 consists of two crystallographically independent vanadium(IV) complexes with four water molecules of crystallization (Fig. 1). The vanadium centers are six-coordinated with a N₃O₃ donor set. The bond lengths and bond angles for the two VO²⁺ complex units are listed in Table 2. The comparison of main bond lengths and angles shows a close similarity between the two crystallographically independent V(IV) centers. As can be seen from the bond parameters listed in Table 2, both vanadium centers have a distorted octahedral geometry. The V=O bond distances for V1 and V2 units are in the range from 1.593(8) Å to 1.603(8) Å which is in agreement with those reported in the literature [31-33]. The V–N bond distances range from 2.052(9) Å to 2.343(9) Å for the V1 unit and from 2.038(8) Å to 2.375(9) Å for the V2 unit. It is observed that the V–Nimine is shorter than the V–Nphen in the V1 and V2 centers which implies that the coordinated ability of salicylidineglycine is stronger than phenanthroline. The V–N bond distance trans to the V=O bond is longer than the V–N bond in the equatorial plane, which may due to the strong trans influence of the terminal oxo group. This trend was also observed in a similar complex previously reported by Zhao et al [33].
The crystal packing of 1 consists of π···π stacking and C-H···O hydrogen bonding interactions. Two types of π···π interactions were observed in the crystal structure of 1 involving the crystallographically unique VO\(^{2+}\) centers. In one type, a π···π interaction occurs between phenolate ring of salicylaldehyde of V1 center and phenanthroline ring of V2 center with centroid-centroid separation of 3.684 Å. The second type of π···π interactions takes place between the aromatic rings of phenanthroline ligands of V1 centers with centroid-centroid distance of 3.638 Å as shown in Fig. 2. The two crystallographically unique vanadium centers are connected by C-H···O hydrogen bonds as shown in

<table>
<thead>
<tr>
<th>Parameters</th>
<th>VO(salgly)(phen).4H(_2)O (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C(<em>{21})H(</em>{35})N(<em>{3})O(</em>{6})V</td>
</tr>
<tr>
<td>Formula weight</td>
<td>456.30</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>296(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P - 1</td>
</tr>
<tr>
<td>(a/Å)</td>
<td>10.4250(3)</td>
</tr>
<tr>
<td>(b/Å)</td>
<td>14.3372(5)</td>
</tr>
<tr>
<td>(c/Å)</td>
<td>16.9186(6)</td>
</tr>
<tr>
<td>(\alpha^\circ)</td>
<td>70.2390(10)</td>
</tr>
<tr>
<td>(\beta^\circ)</td>
<td>88.9690(10)</td>
</tr>
<tr>
<td>(\gamma^\circ)</td>
<td>81.4790(10)</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>2352.16(14)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (Mgm(^{-3}))</td>
<td>1.289</td>
</tr>
<tr>
<td>F (000)</td>
<td>932</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.13 x 0.12 x 0.12</td>
</tr>
<tr>
<td>Theta range for data collection ((\circ))</td>
<td>1.976 to 28.584</td>
</tr>
<tr>
<td>Limiting indices, (h,k,l)</td>
<td>-13 ≤ h ≤ 13, -16 ≤ k ≤ 19, -22 ≤ l ≤ 22</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>34764</td>
</tr>
<tr>
<td>Unique data ((R_{int}))</td>
<td>10830 [(R(int) = 0.1183)]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data/restraints/ parameters</td>
<td>10830 / 0 / 559</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.098</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2(\sigma) (I)]</td>
<td>R1 = 0.0958, wR2 = 0.2545</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1895, wR2 = 0.3000</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å(^{-3}))</td>
<td>0.933 and -0.588</td>
</tr>
</tbody>
</table>
Fig. 3. The uncoordinated oxygen atom (O8) of the carboxylate group of salgly ligand participates in C-H···O hydrogen bonding interaction with the carbon atom (C20) of salgly of V1 center with a C-H···O bond distance of 2.537 Å. Furthermore the coordinated oxygen atom (O7) of salgly ligand involving the V2 center participates in C-H···O hydrogen bonding interaction with the carbon atom (C2) of phenanthroline of V1 center. The C-H···O hydrogen distances and angles are listed in Table 3.

Table 2 Selected bond lengths (Å) and angles (deg.) in coordination metal core in 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>d, Å</th>
<th>Angle</th>
<th>Degree(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1–O1</td>
<td>1.955(2)</td>
<td>O2–V1–O3</td>
<td>99.0</td>
</tr>
<tr>
<td>V1–O2</td>
<td>1.602(2)</td>
<td>N2–V1–N3</td>
<td>159.3</td>
</tr>
<tr>
<td>V1–O3</td>
<td>2.013(2)</td>
<td>O1–V1–N1</td>
<td>81.1</td>
</tr>
<tr>
<td>V1–N1</td>
<td>2.345(2)</td>
<td>N1–V1–N3</td>
<td>86.5</td>
</tr>
<tr>
<td>V1–N2</td>
<td>2.129(2)</td>
<td>O1–V1–N2</td>
<td>91.9</td>
</tr>
<tr>
<td>V1–N3</td>
<td>2.052(2)</td>
<td>O1–V1–N3</td>
<td>88.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N1–V1–N2</td>
<td>73.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O3–V1–N2</td>
<td>93.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1–V1–O3</td>
<td>159.0</td>
</tr>
<tr>
<td>V2–O5</td>
<td>1.946(2)</td>
<td>O5–V2–O7</td>
<td>160.1</td>
</tr>
<tr>
<td>V2–O6</td>
<td>1.596(2)</td>
<td>N5–V2–N6</td>
<td>87.3</td>
</tr>
<tr>
<td>V2–O7</td>
<td>2.006(2)</td>
<td>O5–V2–N4</td>
<td>94.2</td>
</tr>
<tr>
<td>V2–N4</td>
<td>2.131(2)</td>
<td>O5–V2–N6</td>
<td>89.0</td>
</tr>
<tr>
<td>V2–N5</td>
<td>2.347(2)</td>
<td>O7–V2–N5</td>
<td>80.8</td>
</tr>
<tr>
<td>V2–N6</td>
<td>2.044(3)</td>
<td>N6–V2–O7</td>
<td>79.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O5–V2–N5</td>
<td>82.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O6–V2–N5</td>
<td>167.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7–V2–O6</td>
<td>98.5</td>
</tr>
</tbody>
</table>
Fig. 2 Perspective view of π–π stacking interactions between the phen and phenolate rings along \(ab\) plane.

Fig. 3 C-H–O hydrogen bonding interactions involving the two crystallographically unique vanadium centers in 1.
Table 3 Hydrogen bond distances (Å) and angles (deg.) for 1

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>d(D–H)</th>
<th>d(D···A)</th>
<th>d(H···A)</th>
<th>&lt; (DHA)</th>
<th>Symmetry Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2–H2···O7</td>
<td>0.930  (6)</td>
<td>3.326 (8)</td>
<td>2.580 (4)</td>
<td>138.7</td>
<td>x,y,z</td>
</tr>
<tr>
<td>C20–H20B···O8</td>
<td>0.970  (6)</td>
<td>3.510 (8)</td>
<td>2.537 (5)</td>
<td>169.5</td>
<td>x,y,z</td>
</tr>
</tbody>
</table>

FT-IR spectrum of 1

The FT-IR spectrum of the 1 (Fig. 4) shows a broad band at 3454 cm\(^{-1}\) attributed to O-H stretching vibrations of the lattice water molecules in agreement with the X-ray structure result [34]. The sharp peaks at 1626 cm\(^{-1}\) and 1417 cm\(^{-1}\) are assignable to asymmetric and symmetric stretching frequency of carboxylate group (COO\(^-\)) of salgly ligand respectively [35, 36]. The difference in asymmetric and symmetric vibration of carboxylate group are greater than 200 cm\(^{-1}\) \([\Delta \nu = \nu_{as}(OCO) - \nu_{s}(OCO) = 209 \text{ cm}^{-1}\]\) suggests monodentate coordination of carboxylate group of glycine derived Schiff base which is agreement with the crystal structure result [37]. A weak band observed at 1536 cm\(^{-1}\), may arise from the vibration of imine (-C=N) bond of the condensed salicylaldehyde and glycine [38]. The peaks at 1529 and 1445 cm\(^{-1}\) are assigned to ring stretching vibrations of pyridine rings of phenanthroline co-ligand. The sharp absorption peak observed at 727 cm\(^{-1}\) is attributed to ring breathing vibration of phenanthroline ring. The sharp peak observed at 951 cm\(^{-1}\) attributed to stretching vibration of V=O bond. Furthermore, bands in the region of 532-559 cm\(^{-1}\) are caused by the V-O\(_{phenoxy}\) stretching vibration and therefore these bands support the coordination of the salgly to the metal center [31].
Fig. 4 FT-IR spectra of [VO(salgly)(phen)]4H2O (1)

UV-vis spectrum of 1

UV-vis spectrum of 1 was recorded in DMF and shown in Fig. 5(a). The sharp peak observed at 300 nm is due to π-π* transition of the aromatic ring of the Schiff base or phenanthroline co-ligand. The absorption peak at 386 nm is attributed to n → π* transition. Moreover, in the visible region, a broad band is observed at 479 nm which is attributed to the ligand to metal charge transfer transition (LMCT) [39]. In the UV-vis spectrum of 1, d-d transition is not observed which may be attributed to very low intensity. The UV-vis reflectance spectrum of 1 is presented in Fig. 5(b). The spectrum resemblance those of the solution one, but due to the low intensity of d-d band in the solution phase, this band can be clearly seen at 754 nm in the solid state.
Fig. 5 (a) UV-vis spectrum of [VO(salgly)(phen)].4H_2O (1) in DMF (1 x 10^{-4} M)
Fig. 5(b) Solid state UV-vis reflectance spectrum of [VO(salgly)(phen)].4H$_2$O (1)

The X-band EPR spectrum of a powdered sample of 1 was recorded at room temperature. As shown in Fig. 6, the EPR spectrum of 1 exhibit $S = \frac{1}{2}$ signal centered on $g = 1.997$ which is consistent with a 3d$^1$ V(IV) metal center [7]. The spectrum of 1 display isotropic EPR spectrum without any resolved hyperfine structure, which indicates strong spin–spin and spin–orbit coupling interactions between the vanadium centers.
The TGA experiment was performed between 25 to 700 °C under N₂ atmosphere in order to determine the thermal stability of complex 1. As shown in Fig. 7, the complex starts to decompose at 25 °C and the first decomposition step is finished at ca. 138 °C. This weight loss is due to the elimination of four water molecules of crystallization (observed weight loss = 14.0%, calculated 14.2%). Then a continuous weight loss in the temperature range 140 to 700 °C from the dehydrated complex occurs which is connected to the loss of Schiff base and phenanthroline ligands. The final residue cannot be determined as the thermal decay is not finished at 700 °C.
Catalytic degradation of Methyl orange (MO) by 1

The catalytic degradation characteristics of the complex was analyzed by using 50 ml aqueous solution of methyl orange (6.8 mg/L), 650 μL H₂O₂ and 10 ml of complex (141 mg/L in MeOH). The degradation activity was carried out for 180 minutes under visible light with constant stirring, and the activity was monitored by recording UV-visible spectra of the reaction mixture at a definite time interval of 30 minutes. As shown in Fig. 8, the absorption bands of MO (λ̴max = 465 nm) gradually decreases with prolong reaction time in presence of complex 1 (catalyst) and H₂O₂. However no significant decrease in the absorption peak of MO was observed with time when the reaction mixture contains only the complex or H₂O₂ (see supplementary figures Fig. S1 and Fig. S2). It was observed that the complex shows good catalytic activity towards degradation of methyl orange in presence of H₂O₂, and the catalytic efficiency of MO was found to be 74.7 % after reacting for 180 minutes (Fig. 9). The catalytic efficiency of 1 towards MO degradation is only 18.81 % after reacting for 180 minutes in absence of H₂O₂, whereas the catalytic efficiency of H₂O₂ is only 14.31 % in absence of 1 (Fig. 9). Therefore, this indicates that extent of MO degradation is minimal when only complex or only H₂O₂ is present. The addition of very small amount of H₂O₂ (650 μL) to the complex enhances the catalytic degradation of MO to a significant extent. This shows that the combination of the complex with the H₂O₂ oxidant has a potent synergetic impact.
H$_2$O$_2$ is a good oxidizing agent and a precursor of hydroxyl radical (•OH). Organic dyes can be broken down into non-polluting simple molecules, such as CO$_2$ and H$_2$O, by the action of highly effective and active hydroxyl radical (•OH). This led us to determine that during the degradation reaction, the vanadium ion may oxidize and coordinate with oxygen atoms from H$_2$O$_2$ to form a transition state, producing hydroxyl radicals (•OH) [40]. It is possible to transform the oxovanadium(IV) complex into vanadium(V) species and •OH, which can efficiently break down methyl orange [41].

![Time dependent UV-visible absorption spectra of methyl orange solution in presence of [VO(salgly)(phen)].4H$_2$O (1) and H$_2$O$_2$](image_url)

**Fig. 8** Time dependent UV-visible absorption spectra of methyl orange solution in presence of [VO(salgly)(phen)].4H$_2$O (1) and H$_2$O$_2$
Kinetics study of catalytic degradation of methyl orange (MO) by 1

To study the reaction kinetics of catalytic degradation of MO by 1, ln(C/C₀) versus reaction time(t) was plotted and it was observed that the catalytic degradation of MO by 1 in presence of H₂O₂ follows a pseudo-first order kinetics. The catalytic degradation of MO can be expressed as-

\[ \ln(C/C_0) = -kt \]

where, \( C_0 \) and \( C \) are the concentration of MO at reaction time \( t_0 \) and \( t \) respectively. ‘\( k \)’ is the pseudo-first order rate constant, and \( k = -\text{slope} \).

As shown in Fig. 10, the plot of \( \ln(C/C_0) \) versus time(t) was found to be linear which reveals that the catalytic degradation of methyl orange by 1, follows pseudo-first order kinetics. From Fig. 10, the rate constant of this pseudo-first order reaction was found to be 0.00752 min⁻¹ or \( 7.52 \times 10^{-3} \) min⁻¹ and the correlation coefficient \( (R^2) \) was calculated to be 0.97453.
Fig. 10 Pseudo-first order reaction kinetics of methyl orange degradation in presence of 
[VO(salgly)(phen)].4H₂O (1)

Conclusions

An oxido vanadium salicylidene glycine complex containing phenanthroline as co-ligand have been synthesized and 
characterized by elemental analysis, spectroscopic techniques such as UV-vis, FT-IR and EPR. The structure of the 
complex was determined by single crystal X-ray diffraction. The complex molecules of 1 self assembles via π··π 
stacking and C-H··O hydrogen bonding interactions. Furthermore, the catalytic efficiency of the complex towards 
degradation of methyl orange was investigated. The result showed good catalytic activity towards degradation of 
methyl orange in presence of hydrogen peroxide.

Experimental

Materials and physical measurements

All the chemicals used in this work, viz. vanadyl sulphate hydrate, salicyaldehyde, glycine, 1,10-
phenanthroline and methyl orange were purchased from Sigma Aldrich and Merk (India) Ltd. and used without 
further purification. Methanol, dimethyl formamide (DMF) and hydrogen peroxide were of analytic grade and used 
as supplied. UV-visible spectra was recorded using a Shimadzu UV-2600 spectrophotometer (model no. UV-
18000). For solid state UV-Vis reflectance spectra, BaSO₄ powder was used as a reference (100% reflectance). The 
KBr phase FT-IR spectrum was recorded in a Bruker APEX II spectrophotometer in the frequency range 500-4000
cm\(^{-1}\). Thermogravimetric studies were carried out under a flow of N\(_2\) gas using a Mettler Toledo TGA/DSC1 STARe system at a heating rate of 10 °C min\(^{-1}\). The X-band EPR spectrum was recorded using a JEOL JES-FA 200 instrument.

Crystallographic data collection and refinement

Intensity data were collected on Bruker SMART APEX II CCD equipped with a graphite monochromator and a MoK\(_\alpha\) fine-focus sealed tube (\(\lambda = 0.71073\) Å) at 296 K. The structure was solved by a direct method in the triclinic space group \(P-1\) with SHELXS-97 and refined by full-matrix least squares techniques with SHELXL-97 [42] via WinGX [43]. All the non-hydrogen atoms were refined in the anisotropic approximation against F\(^2\) of all reflections. The hydrogen atoms were refined isotropically and refined with isotropic displacement coefficients. Moreover, the hydrogen atoms attached to oxygen atoms of water molecules could not be located in the difference Fourier maps. The structural diagrams were drawn with DIAMOND 3.0 [44].

Catalytic degradation of methyl orange (MO) solution

In a typical experiment, \(3.11 \times 10^{-4}\) M (1.41 mg in 10 ml DMF) of complex 1 was added to \(2.1 \times 10^{-5}\) M (0.68 mg in 100 ml de-ionized water) methyl orange solution. To it 650 \(\mu\)L of \(2.1 \times 10^{-2}\) M H\(_2\)O\(_2\) was added and the reaction mixture was constantly stirred at room temperature for 180 minutes. The reaction mixture was analyzed by recording UV-visible spectra at regular time intervals of 30 minutes. The catalytic activity of the complex was observed by measuring its absorbance at \(\lambda_{\text{max}} = 465\) nm. The degradation rate of methyl orange solution was calculated using the formula: \([ (A_0 - A)/ A_0 ] \times 100\%\), where \(A_0\) is the absorbance value of sample solution before methyl orange degradation and \(A\) is the absorbance value of the sample solution after methyl orange degradation. To study the effect of the complex and H\(_2\)O\(_2\) on the degradation of MO, blank experiments were carried out without the complex and H\(_2\)O\(_2\). For comparison, methyl orange degradation rates were also measured in presence and in absence of H\(_2\)O\(_2\). Furthermore, degradation was also studied only in presence of H\(_2\)O\(_2\) without the catalyst.

Synthesis of [VO(Salgly)(phen)].4H\(_2\)O (1)

Salicylaldehyde (2 mmol, 0.24 ml) was dissolved in methanol (10 ml) and added slowly to an aqueous solution of glycine (2 mmol, 0. 150 g). The resulting mixture was stirred for 1 h to obtain a yellow color solution. To this mixture was added vanadyl sulfate hydrate (2 mmol, 0.326 g) followed by methanolic solution of 1,10-phenanthroline monohydrate (2 mmol, 0.366 g) and stirred for 4 h to obtain a reddish brown product. The precipitate was filtered off, washed with methanol and dried over fused CaCl\(_2\). The product was recrystallized from methanol to afford brown crystals suitable for single crystal X-ray diffraction. Yield: 0.802 g (88.2%)

Anal. Calcd for C\(_{22}\)H\(_{15}\)N\(_3\)O\(_8\)V: C, 51.77; H, 4.94; N, 8.23%. Found: C, 51.88; H, 4.97; N, 8.56%. FT-IR (KBr, cm\(^{-1}\)): 3454(br), 1626(s), 1536(w), 1445(w), 1417(w), 1369(m), 1306(w,sh), 1146(m), 951(s), 853 (s), 802 (m), 769(m), 727(s), 615 (w), 559(w), 532 (w).
Appendix A. Supplementary data

CCDC2235852 contains the supplementary crystallographic data for 1. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk 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. CIF and Check files of 1 are included in supporting information. Figures S1-2 includes time dependent UV-visible absorption spectra of methyl orange solution in presence of 1 and H$_2$O$_2$ respectively.

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Declarations

Conflict of interest The authors declare no conflicts of interest regarding this article.

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