Synthesis, Characterization, X-ray Crystal Structure, DFT Calculations and Catalytic Properties of a Dioxidovanadium(V) Complex Derived from Oxamohydrazide and Pyridoxal - A Model Complex of Vanadate-Dependent Bromoperoxidase

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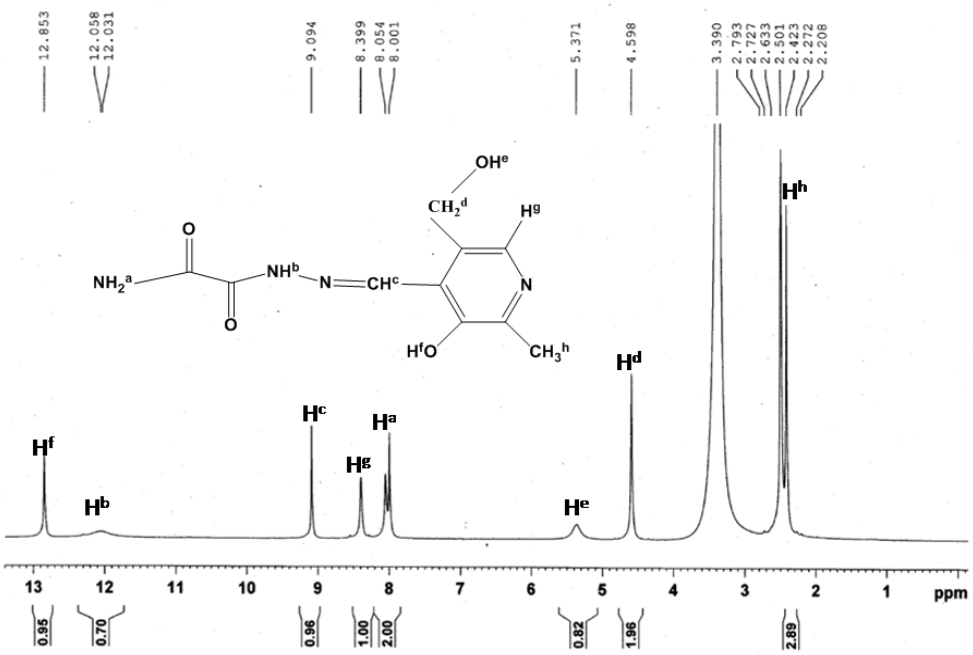


Figure S1. ^{1}H NMR spectrum of (soxH-pydxH) in DMSO-d_6.

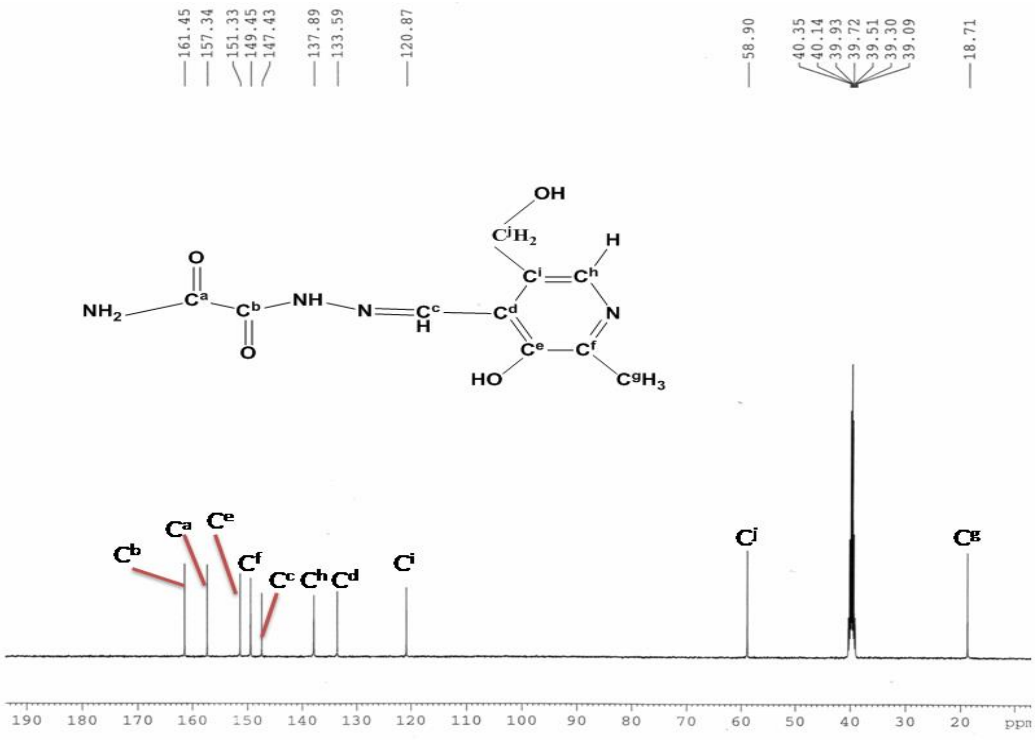


Figure S2: ^{13}C NMR spectrum of (soxH-pydxH) in DMSO-d_6

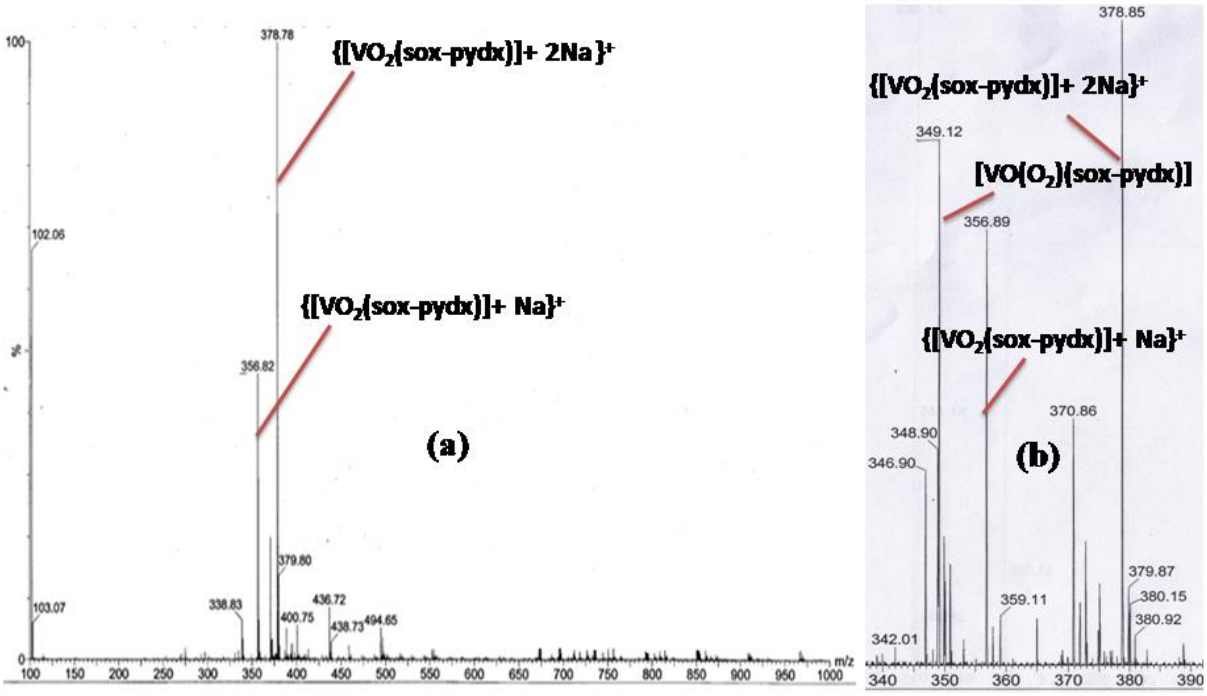


Figure S3. (a) Mass spectrum (in positive mode) of complex **1** in methanol solvent (b) Mass spectrum (in positive mode) of complex **1** with H_2O_2 in methanol solvent.

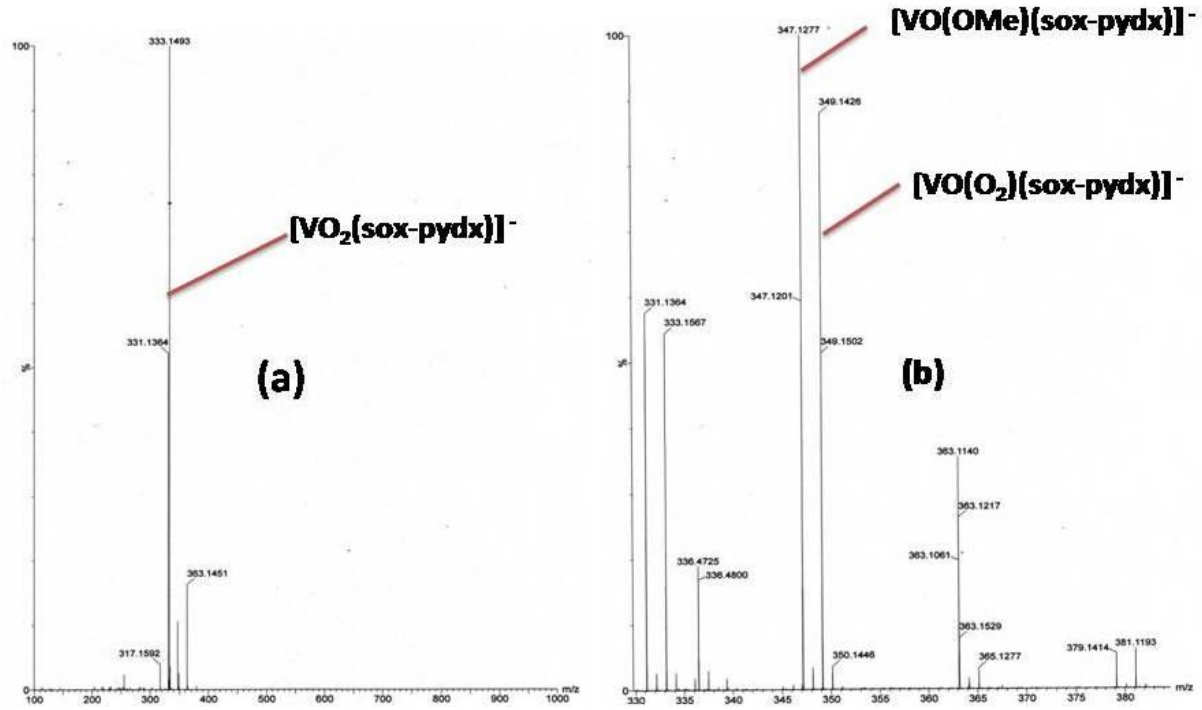


Figure S4. (a) Mass spectrum (in negative mode) of complex **1** in methanol solvent (b) Mass spectrum (in negative mode) of complex **1** with H_2O_2 in methanol solvent.

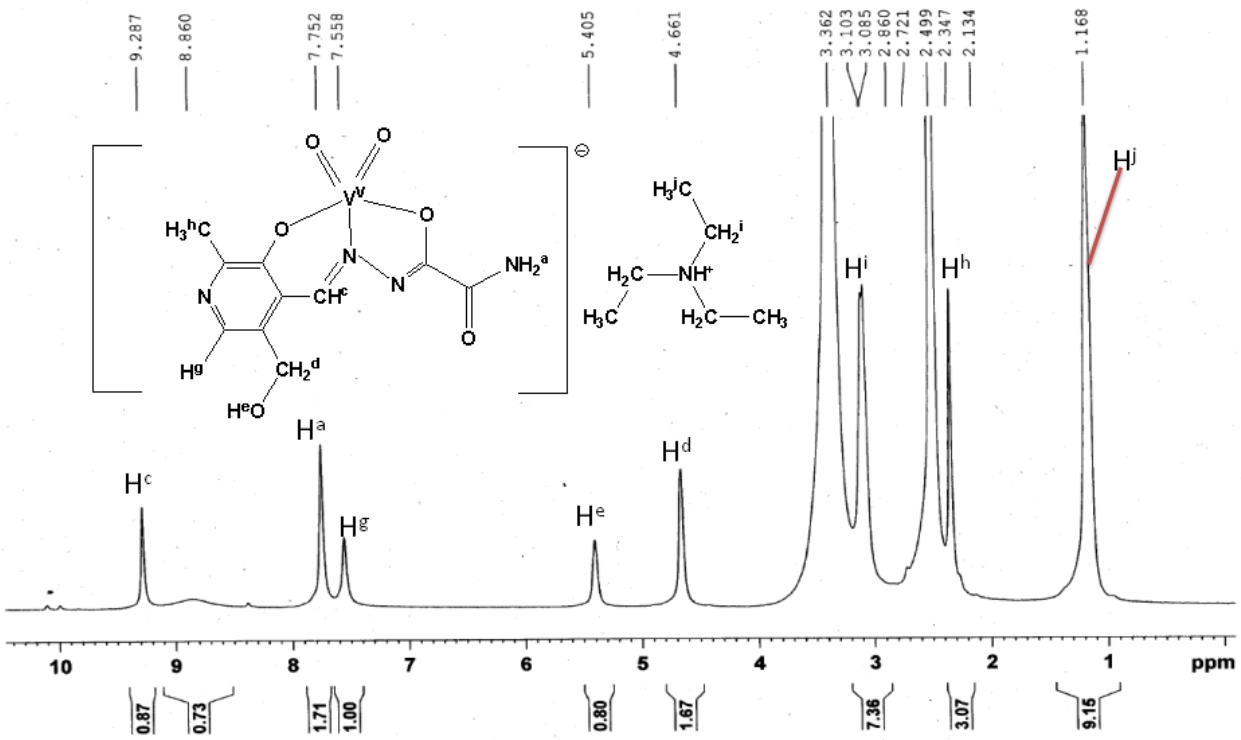


Figure S5. ^{1}H NMR spectrum of complex **1** in DMSO-d_6.

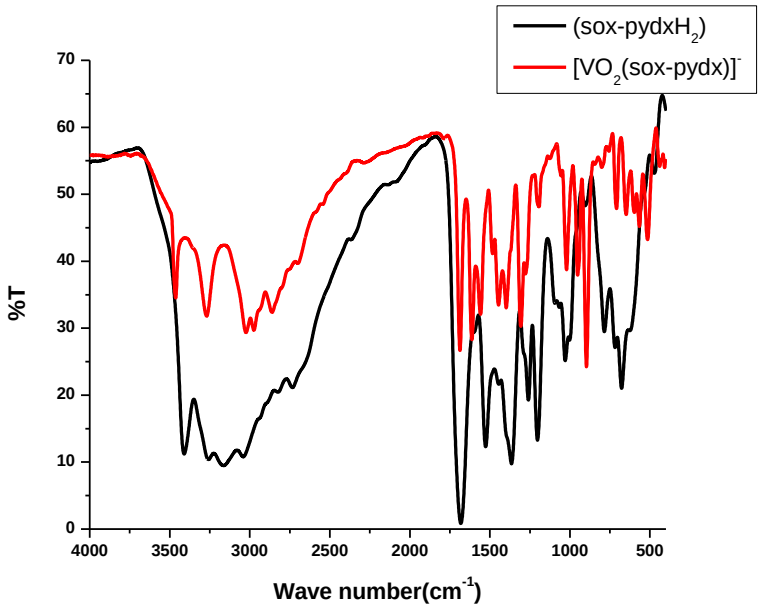


Figure S6. IR spectra of (soxH-pydxH) and complex **1**.

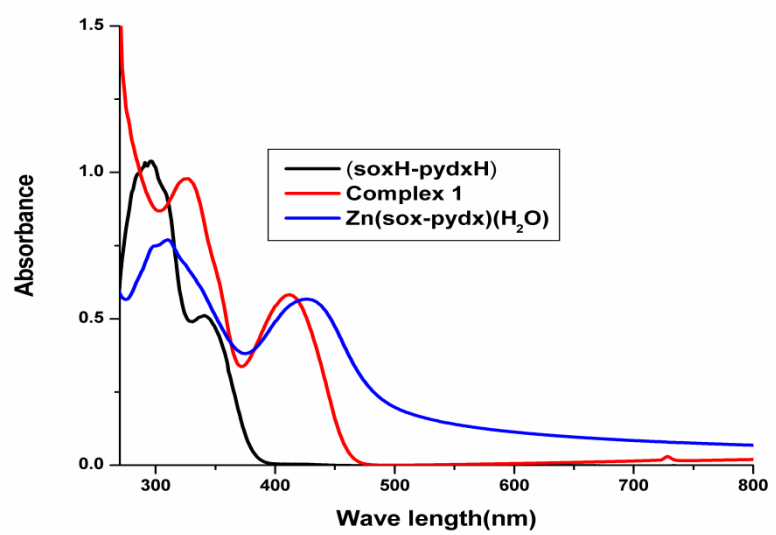


Figure S7. Electronic spectra of the ligand (soxH-pydxH), complex **1** and Zn(soxpydx)(H_2O).

Table S1. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1) #i	0.84	1.88	2.723(3)	177
N(4)-H(4A)...N(3) #ii	0.88	2.13	3.008(3)	174
N(4)-H(4B)...N(2)	0.88	2.43	2.769(3)	103
N(5)-H(5)...O(4)	0.93	2.23	2.918(3)	130
N(5)-H(5)...O(5)	0.93	1.93	2.771(3)	150

Symmetry transformations used to generate equivalent atoms: #i = x, −y, 1−z; #ii = −1+x,1+y, z

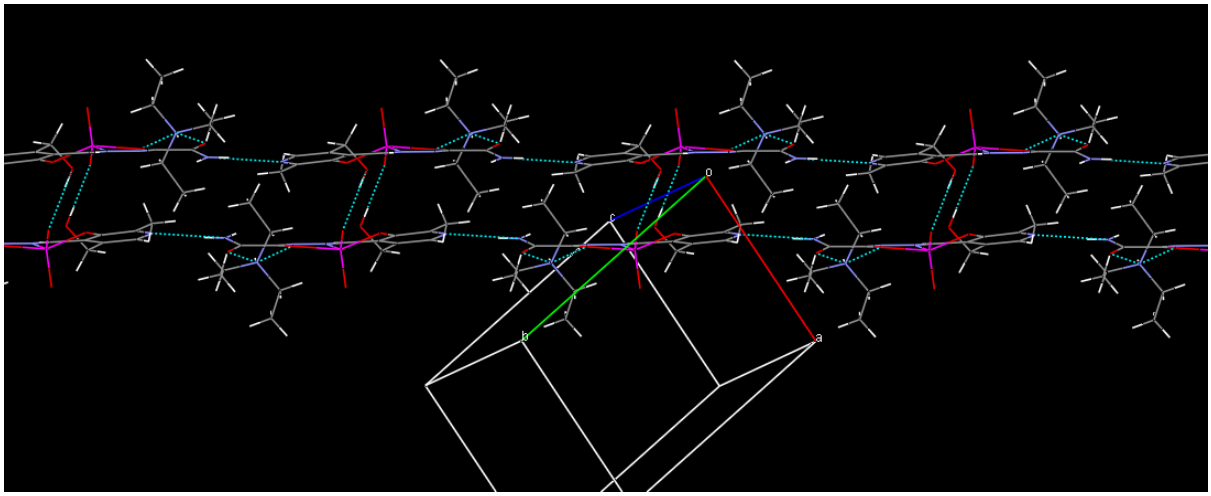
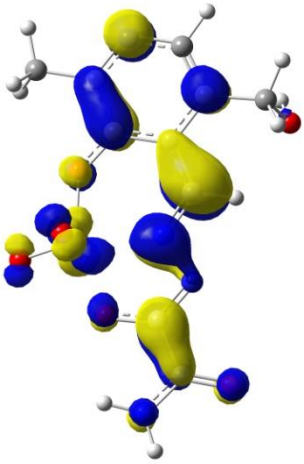
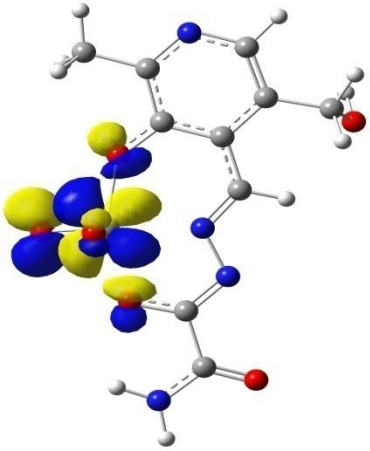
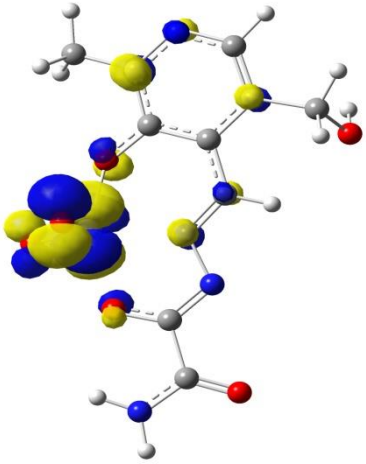


Figure S8. View of the one dimensional chain of **1** in the crystal.

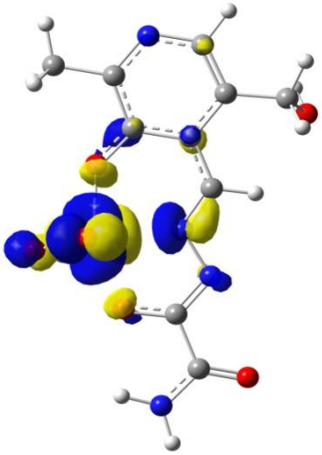


LUMO

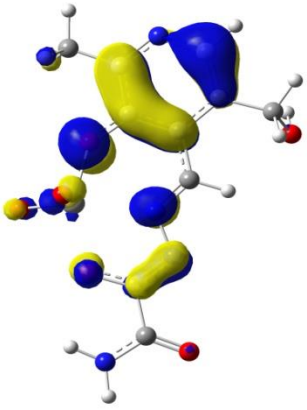




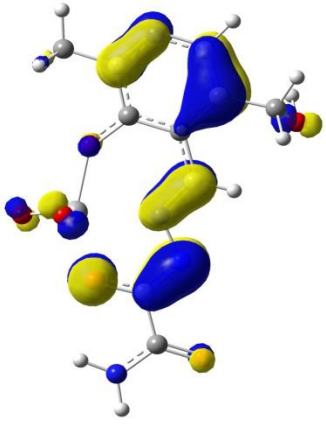
LUMO+2



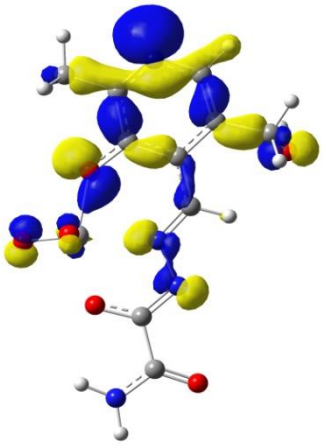
LUMO+3



HOMO



HOMO-1



HOMO-2

Figure S9. FMOs of complex **1**.

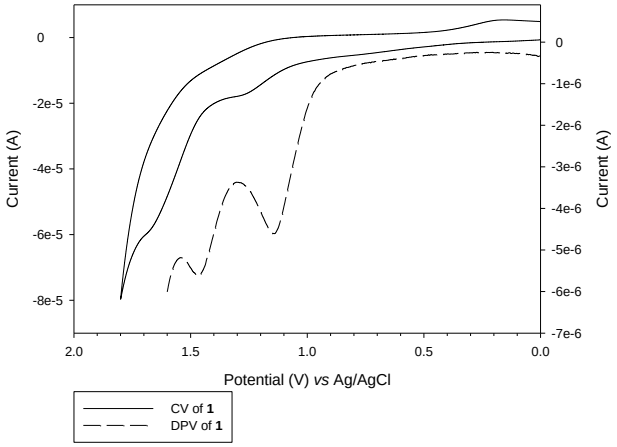


Figure S10. CV and DPV of complex **1** in DMF on the positive side of the reference electrode. For DPV the current axis is on the right hand side of the graphs.

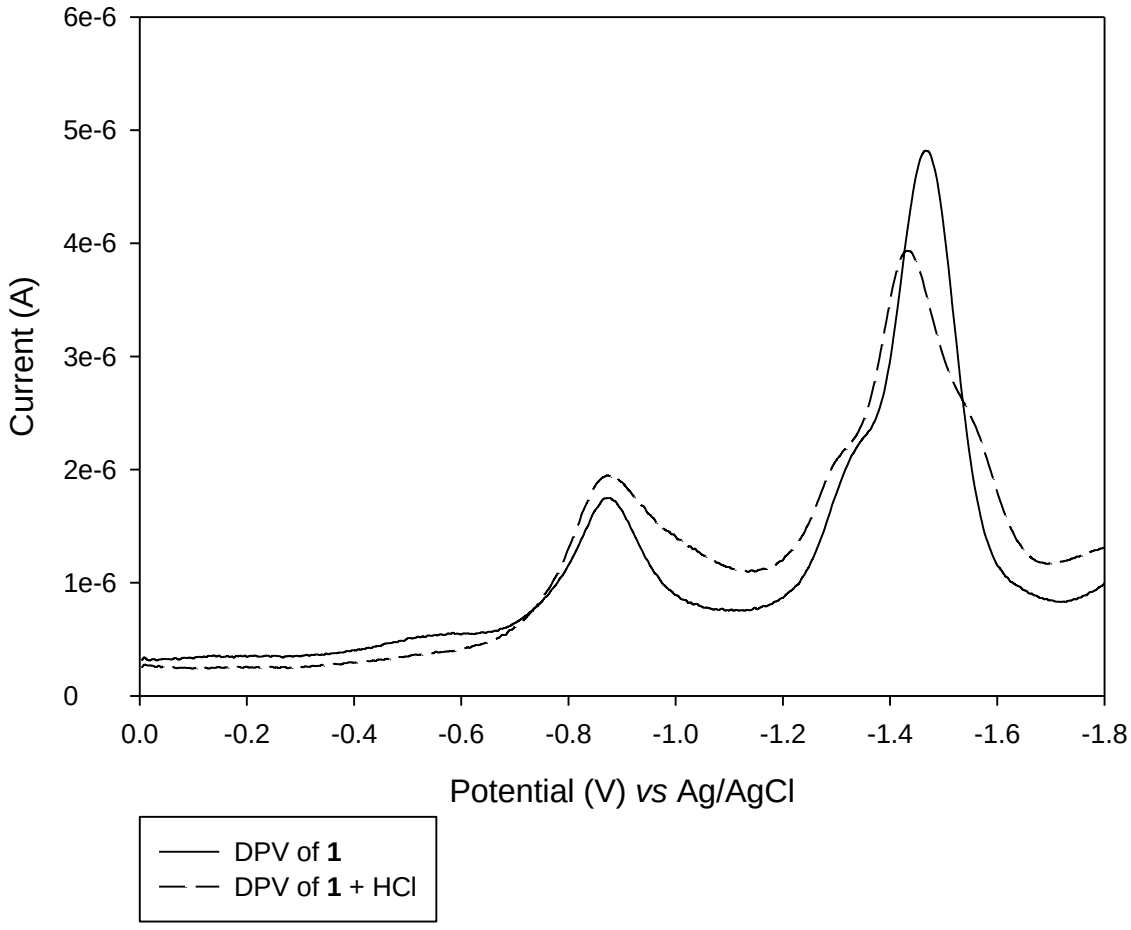


Figure S11. DPV of complex **1** before and after addition of HCl.

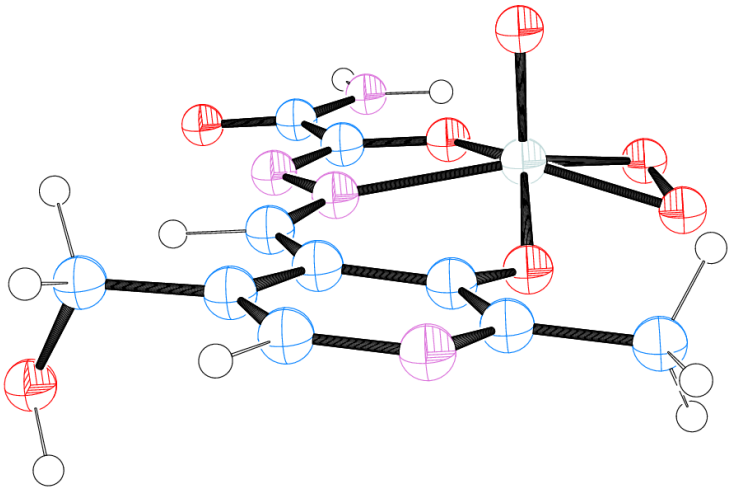


Figure S12. DFT optimized structure of $[VO(O_2)(sox\text{-}pydx)]^-$.

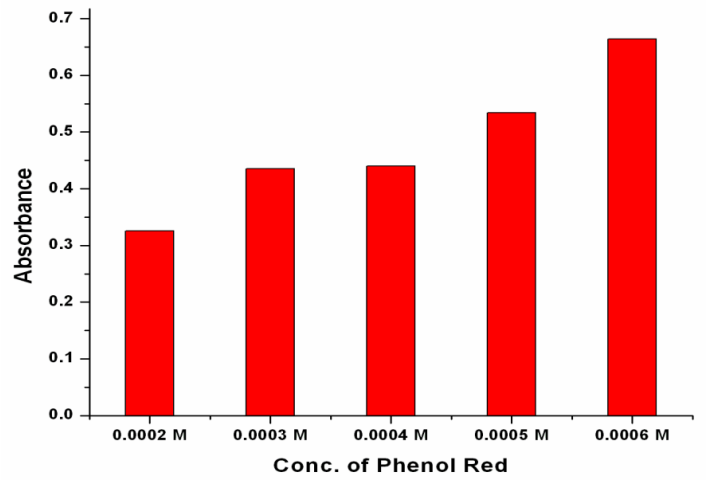


Figure S13. Relative increase of absorbance with change of concentration of Phenol red at 590 nm after 180 min (catalyst: 0.01 mmol).

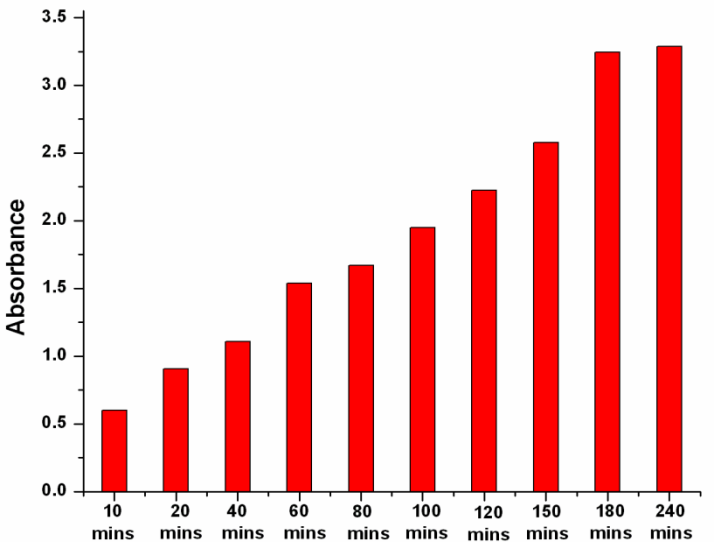


Figure S14. Relative change of absorbance with time monitored at 590 nm for the bromination of phenol red (conc. 0.25mmol, cat. 0.1 mmol)

Table S2. Comparison of kinetic parameters for bromination of Phenol red by Complex **1**

Nature of Plot	**V_{max}(M min^{-1})**	**K_m(M)**	**k_{cat}(min^{-1})**
Lineweaver-Burk Plot	4.39×10^{-3}	4.4×10^{-4}	439
Rate vs [Substrate] Plot	4.74×10^{-3}	5.1×10^{-4}	474

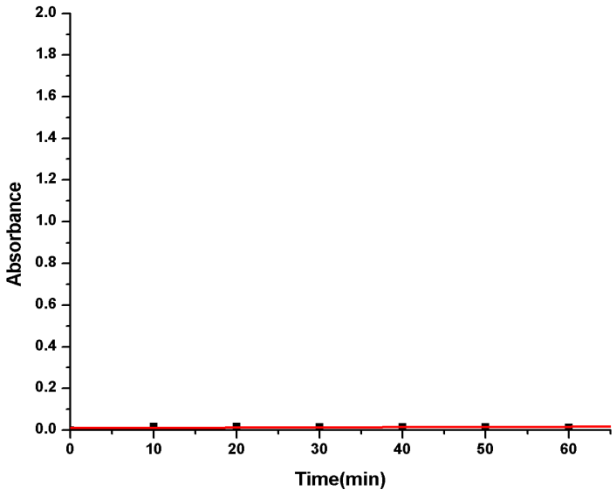


Figure S15. Absorbance vs. Time plot of a mixture of TBAB, H_2O_2, $HClO_4$ and Phenol Red in absence of Complex **1**. Spectral data taken of aliquots in pH=7.1 aqueous phosphate buffer.