

Supplementary Information

DFT study on the redox behavior of two dioxovanadium(V) complexes with N₂O donor Schiff base ligands and their use in catalytic oxidation of *ortho*- aminophenol

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AIM study

The AIM theory has been successfully used to characterize and understand a great variety of interactions as shown in Fig. 9, where the $\text{CH}\cdots\pi$ interaction is characterized by the presence of one bond critical point (orange) that connects the hydrogen atom to one carbon atom of the ring (3,-1). As a consequence, two ring critical points (yellow) are also generated upon complexation due to the formation of the supramolecular rings (3,+1).

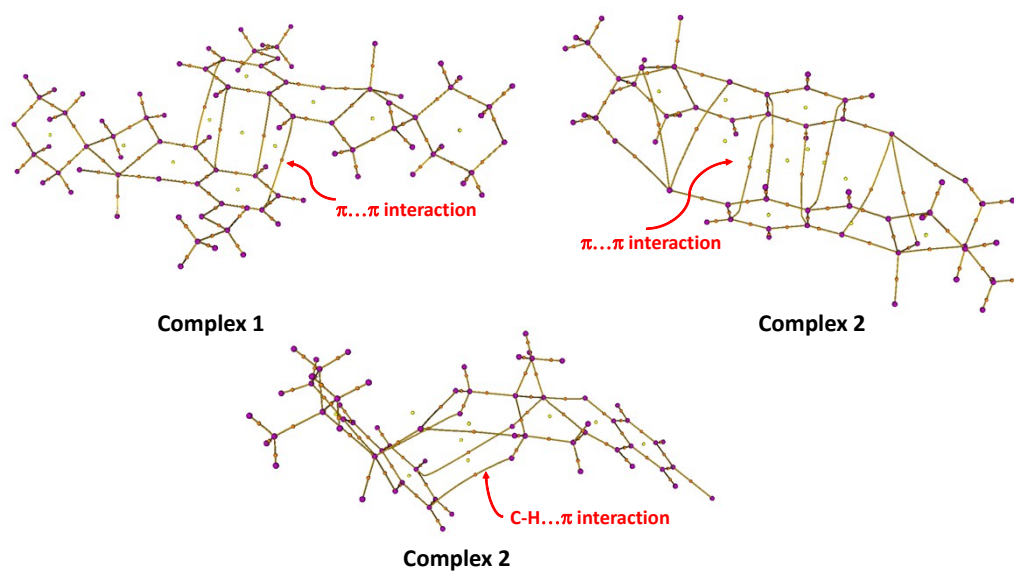


Fig. S1: Theoretical models used to evaluate $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions in complexes **1** and **2**.

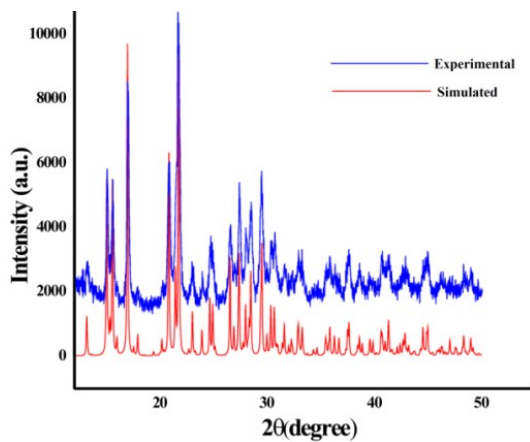


Fig. S2: Experimental and simulated powder XRD patterns of complex **2**, confirming the purity of the bulk material.

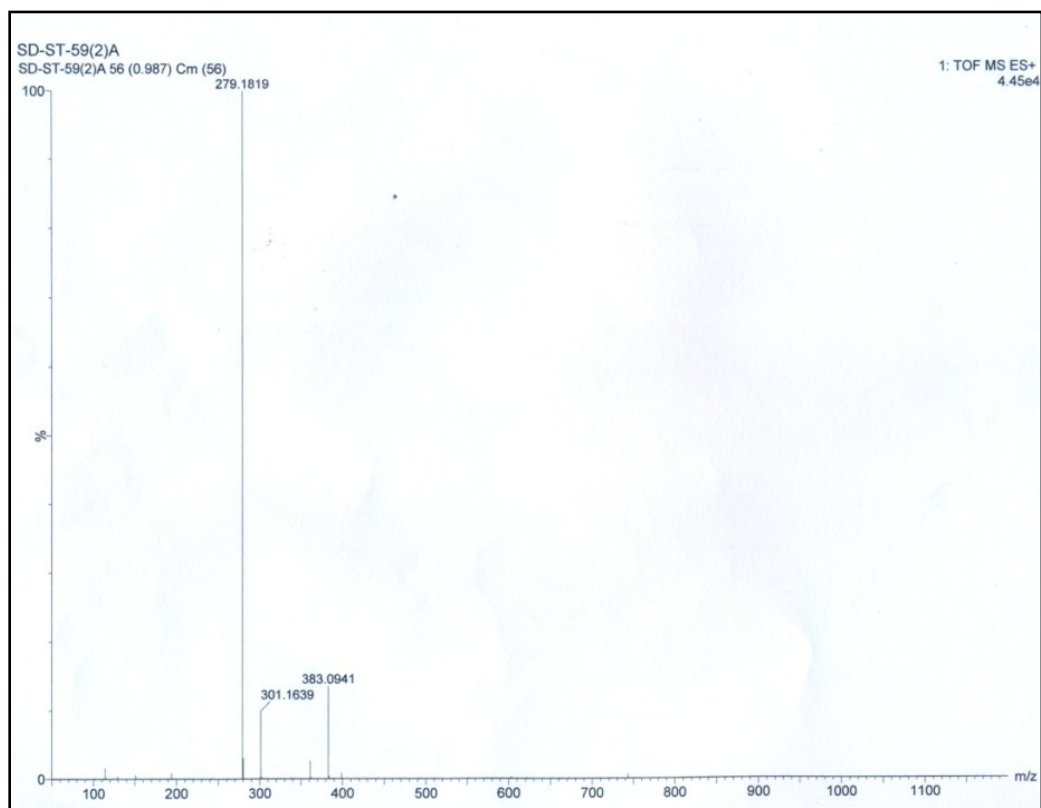


Fig. S3: The ESI-MS spectrum of complex **1**.

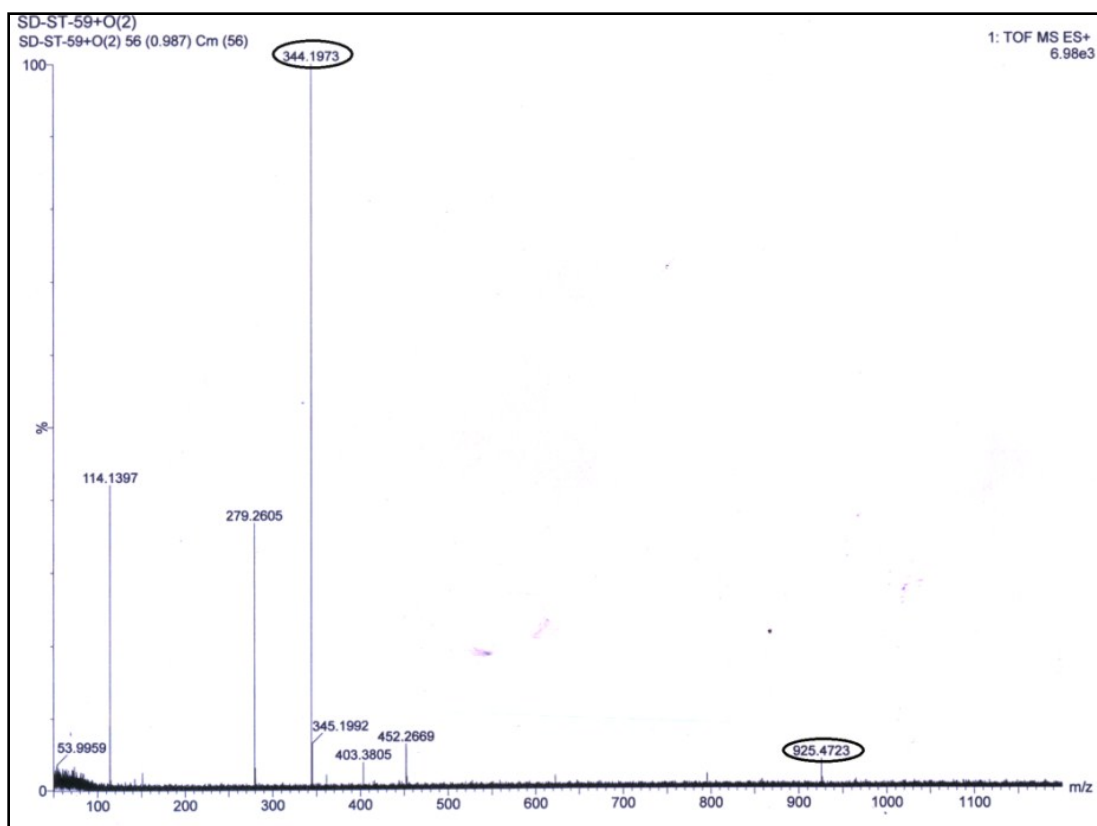


Fig. S4: The ESI-MS spectrum of 1:50 molar proportion mixture of complex **1** and *o*-aminophenol in acetonitrile-methanol medium. The peaks due to the formation of the product ($m/z = 344.1973$) and that of complex-substrate adduct ($m/z = 925.4723$) are circled.

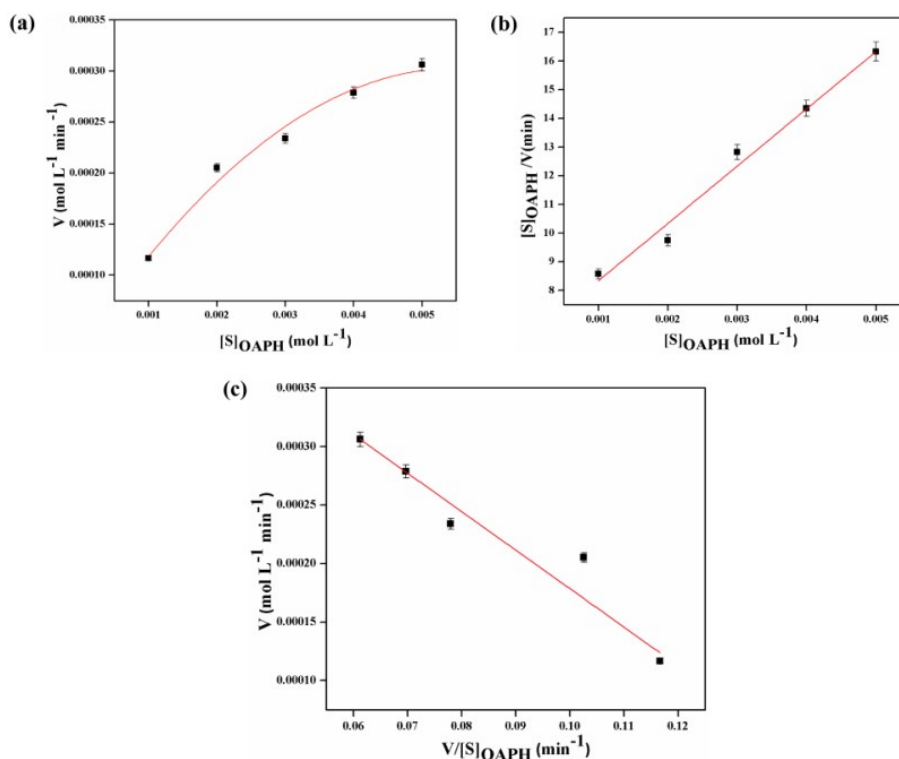


Fig. S5: (a) Michaelis-Menten plot; (b) Hanes-Woolf plot and (c) Eadie-Hofstee plot of complex 2 in acetonitrile medium for oxidation of *o*-aminophenol.

Hirshfeld surface Analysis

Hirshfeld surfaces¹ mapped with d_{norm} , shape index and curvedness and 2D fingerprint² plots were calculated with the help of Crystal Explorer³ software using cifs of both complexes. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld isosurfaces, two distances, d_e and d_i , were defined. The normalized contact distances (d_{norm}) were calculated using d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest nucleus internal to the surface).

Hirshfeld surfaces of two complexes are illustrated in Fig. S6. In Fig. S7, the 2D fingerprint plots are shown, where intermolecular interactions appear as distinct spikes. The fingerprint plots are also decomposed to highlight particular atoms pair close contacts. The

proportion of $\text{O}\cdots\text{H}$ and $\text{H}\cdots\text{O}$ interactions comprise 35.8% and 26.6% of the Hirshfeld surfaces for each molecule of **1** and **2**, respectively. The $\text{C}\cdots\text{H}$ and $\text{H}\cdots\text{C}$ interactions comprise 10.4% and 11.4% of the Hirshfeld surfaces for complexes **1** and **2** respectively.

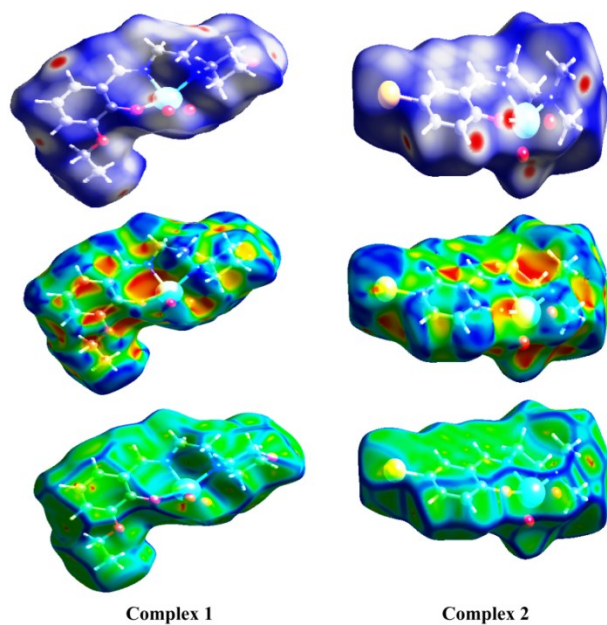


Fig. S6: Hirshfeld surfaces mapped with d_{norm} (top), shape index (middle) and curvedness (bottom) of complexes **1** and **2**.

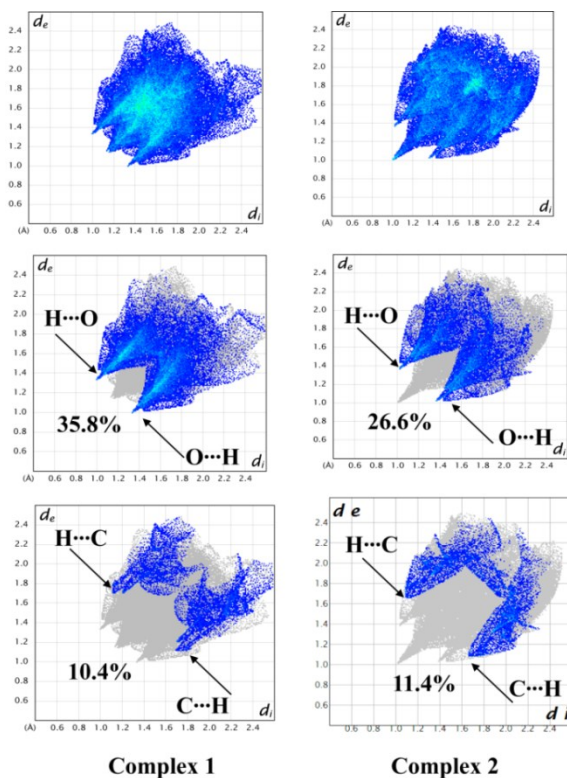


Fig. S7: Fingerprint plot: Full (Upper) and resolved into O \cdots H/H \cdots O (middle) and C \cdots H/H \cdots C (bottom) contacts contributed to the total Hirshfeld Surface area of complexes **1** and **2**. The lower spike ($d_i = 1.37$, $d_e = 1.00$ Å in **1**, $d_i = 1.29$, $d_e = 1.20$ Å in **2**) indicates O–H interaction and the upper spike ($d_i = 1.00$, $d_e = 1.37$ Å in **1**, $d_i = 1.20$, $d_e = 1.29$ Å in **2**) indicates H \cdots O interaction. C \cdots H interaction is also represented by lower spike ($d_i = 1.71$, $d_e = 1.13$ Å in **1**, $d_i = 1.64$, $d_e = 1.10$ Å in **2**) and H \cdots C interaction is represented by upper spike ($d_i = 1.13$, $d_e = 1.71$ Å in **1**, $d_i = 1.10$, $d_e = 1.64$ Å in **2**).

References

- 1 M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19-32.
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