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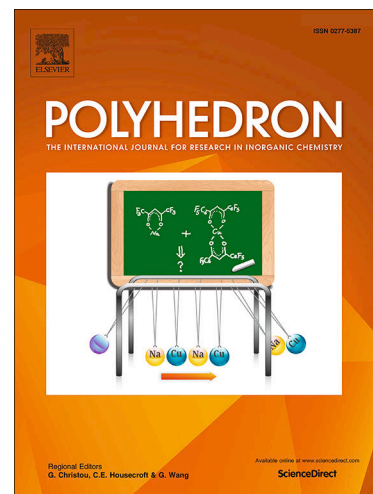
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Exploration of Br \cdots O halogen bonding interactions in dinuclear vanadium(V) complexes with Schiff base ligands

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Abstract

An oxo-bridged dinuclear vanadium(V) complex, $(\mu-O)_2[V(O)(L)]_2$, [where $HL = 2-((2-(\text{methylamino})\text{ethylimino})\text{methyl})-4\text{-bromo-6-methoxyphenol}$] has been synthesized and characterized by elemental and spectral analysis. Structure of the complex has been determined by single crystal X-ray diffraction study. The complex generates an infinite 1D chain governed by Br \cdots O halogen bond involving the oxygen atoms of the VO_2^+ unit as electron donor and the σ -hole at the halogen as electron acceptor. The molecular electrostatic potential (MEP) surface of the complex has been computed, which indicates that the most electron rich part corresponds to the oxygen atoms of the VO_2^+ unit and the existence of a σ -hole (+9.4 kcal/mol) around Br atom, and therefore justifies the formation of a directional halogen bonding interaction. The interaction in the complex has also been characterized energetically by using the Bader's quantum theory of "atoms in molecules" (QTAIM). The contribution of the halogen bond is found to be ~ -6.3

kcal/mol, which is in the range of typical halogen bonds. The results have been compared with the energies of $\text{Br}\cdots\text{O}$ halogen bond interactions in a structurally similar oxo-bridged dinuclear vanadium(V) complex.

Keywords: Vanadium(V) ; Schiff base; Dinuclear ; DFT calculation; Halogen bonding.

1. Introduction

Halogen bonding interaction has emerged as an important tool in the supramolecular aggregation of coordination entities and also has been prominent in the field of crystal engineering for quite long [1-7]. These interactions are usually widely different as far as their energetic and geometric features are concerned. Halogen molecules like bromine [8] and iodine [9], in some cases chlorine [10] and even fluorine [11], alkyl and aryl halides form complexes with atoms containing lone pairs [12-14]. The ability of halogen atoms to effectively interact with electron donors was recognized in dihalogens and halocarbons in the early 19th century [15,16]. After more than 50 years, Benesi and Hildebrand reported the first cases of intermolecular donor–acceptor complexes formed from iodine and aromatic hydrocarbons [17]. It is experimentally proved that the electron density is anisotropically distributed around halogen atoms in organic halides [18,19]. The effective atomic radius along the extended C-X bond axis in covalently bonded halogen atoms is smaller than in the direction perpendicular to this axis, hence generating a region of positive electrostatic potential along the covalent bond, which is referred to as the ' σ -hole' [20-22]. This σ -hole arranges the lone pair nearer the halogen atom and orients the halogen bonds. Halogen bonding is a highly directional interaction, more directional than hydrogen bonding ones [23,24].

The self assembly process of coordination entities can be driven by either hydrogen or halogen bonding, though the latter can dominate over the former under certain circumstances [2,25-27]. The σ -hole concept is useful in understanding the nature of halogen bonding. The idea of a σ -hole where a halogen atom exhibits both electrophilicity along the R-X axis and nucleophilicity perpendicular to the same axis. In other words, the halogen atom can act both as an electron acceptor (Lewis acid) owing to the positively charged region and an electron donor (Lewis base) in the ring region encompassing the halogen atom [28,29].

Over the past few years, vanadium(V) complexes reported in the literature were focused on their role in biological, catalytic and medicinal aspects. In one instance, they have been utilized in the dehydroperoxidation of alkyl hydroperoxides [30]. A thiosemicarbazone complex of vanadium(V) was found to show in vitro insulin mimicking activity against insulin responsive L6 myoblast cells [31]. Vanadium(V) complexes of catechol were found to exhibit significant anticancer activities against bone cancer cells [32], while a dinuclear vanadium(V) complex of tridentate ONS donor Schiff base ligand emerges as a potential anticancer molecule due to its ability to inhibit proliferation of breast and lung cancer cells and also in its influencing property in apoptosis and reproductive cell death [33]. Besides these, other reports involved catalytic efficiencies, specifically in oxidation of sulfide to sulfoxides [34] and some antimicrobial properties as well [35-38].

We have previously reported halogen bonding interactions in some vanadium(V) Schiff base complexes with a detailed theoretical approach [39]. Herein, we report a dinuclear vanadium(V) Schiff base complex, $(\mu-O)_2[V(O)(L)]_2$, synthesized from a N_2O donor ligand, $HL=$ 2-((2-(methylamino)ethylimino)methyl)-4-bromo-6-methoxyphenol. DFT calculations, combined with QTAIM computational tool, have been used to investigate the halogen bonding

interactions along with conventional hydrogen bonding interaction in this complex. The work will open up new research aspects concerning the halogen bonding interactions and its role in supramolecular assemblies in similar vanadium systems.

2. Experimental Section

$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ was bought from Loba Chemie Pvt. Ltd. and was of reagent grade. All other starting materials were commercially available, reagent grade, and used as bought from Sigma-Aldrich without further purification.

2.1 Preparation of $(\mu\text{-O})_2[\text{V}(\text{O})(\text{L})]_2$

The tridentate Schiff base ligand, *HL*, was synthesized by refluxing 5-bromo-2-hydroxy-3-methoxybenzaldehyde (231 mg, 1 mmol) with N-methylethylenediamine (~0.09 mL, 1 mmol) in CH_3CN (15 mL) for ca. 1 h 30 mins. The ligand was not isolated and was directly used for the preparation of the complex. Thereafter, a CH_3CN (10 mL) solution of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (253 mg, 1 mmol) was added to the CH_3CN solution (20 mL) of the ligand and the resulting solution was then kept under reflux. After 15 minutes of refluxing, few drops of DMSO were added to the reacting system and the refluxing was continued for another 3 h. Then it was cooled to room temperature, subsequently filtered and kept for crystallization. X-ray diffraction quality single crystals were collected after a week on slow evaporation of the filtrate in an open atmosphere.

Yield: 244 mg (66%), based on vanadium; Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{Br}_2\text{N}_4\text{O}_8\text{V}_2$ (F.W = 738.16): C, 35.80; H, 3.82; N, 7.59%; Found: C, 35.7; H, 3.7; N, 7.6%; FT-IR (KBr, cm^{-1}): 3222 ($\tilde{\nu}_{\text{N-H}}$), 1636 ($\tilde{\nu}_{\text{C=N}}$), 920, 843 ($\tilde{\nu}_{\text{V=O}}$), 463 ($\tilde{\nu}_{\text{V-O}}$), UV-Vis, λ_{max} (nm), [ϵ_{max} ($\text{L mol}^{-1} \text{cm}^{-1}$)] (CH_3CN): 393 (4.7×10^3). Magnetic moment = diamagnetic.

Crystal Data: formula = $C_{22}H_{28}Br_2N_4O_8V_2$, formula weight = 738.16, temperature(K) = 296, crystal system = orthorhombic, space group = *Pbca*, $a(\text{\AA}) = 9.971(3)$, $b(\text{\AA}) = 13.144(9)$, $c(\text{\AA}) = 20.842(10)$, $Z = 4$, $d_{\text{calc}}(\text{g cm}^{-3}) = 1.795$, $\mu(\text{mm}^{-1}) = 3.662$, $F(000) = 1472$, total reflections = 37338, unique reflections = 2431, observed data [$I > 2 \sigma(I)$] = 2163, no. of parameters = 176, $R(\text{int}) = 0.058$, $R1$, $wR2$ (all data) = 0.0476, 0.1224, $R1$, $wR2$ [$I > 2 \sigma(I)$] = 0.0420, 0.1188.

2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectrum in KBr ($4500\text{--}500 \text{ cm}^{-1}$) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectrum of the complex in DMF was recorded on a Shimadzu UV-1700 UV-Vis spectrophotometer. The magnetic susceptibility measurement was performed with an EG and PAR vibrating sample magnetometer, model 155 at room temperature (300 K) in a 5000 G magnetic field, and diamagnetic corrections were performed using Pascal's constants.

2.3 X-ray crystallography

A suitable single crystal of the complex was used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The molecular structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELX-2018/1 package [40,41]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to nitrogen atoms were located by difference Fourier maps. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [42].

2.4 Theoretical methods

The energetic and geometric features of the complexes included in this study were calculated at the B3LYP-D3/def2-TZVP level of theory using the crystallographic coordinates. For the calculations, the GAUSSIAN-16 program has been used [43]. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method [44]. Molecular electrostatic potential (MEP) surfaces have been computed at the same level of theory and represented using the 0.001 a.u. isosurface. The QTAIM analysis [45] has been performed using the AIMAll program at the same level of theory [46].

2.5 Hirshfeld surface Analysis

Hirshfeld surfaces [47] provide a three-dimensional representation of close contacts in a crystal, and these contacts can also be illustrated in a fingerprint plot [48]. Both these were calculated using Crystal Explorer [49,50] which accepted a structure input file in CIF format. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld isosurfaces, two distances are important; 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, are defined. The normalized contact distance (d_{norm}) based on d_e and d_i is given by

$$d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdw}})}{r_i^{\text{vdw}}} + \frac{(d_e - r_e^{\text{vdw}})}{r_e^{\text{vdw}}}$$

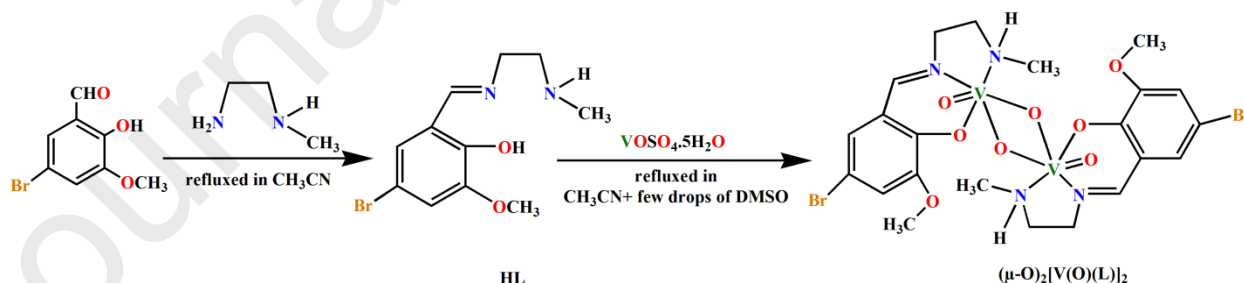
Where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms. The value of d_{norm} was negative or positive depending on intermolecular contacts, being shorter or longer than the van der Waals separations. The parameter d_{norm} displayed a surface with a red-white-blue color scheme, where bright red spots highlighted shorter contacts, white areas represented contacts around the van der

Waals separation, and blue regions were devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [51] and hence a significant means for analyzing intermolecular interactions, such as hydrogen bonds and the weaker $C\cdots H$ contacts ($C-H\cdots\pi$).

3. Results and discussions

3.1 Synthesis

The Schiff base ligand, *HL*, has been synthesized by the condensation reaction of 5-bromo-2-hydroxy-3-methoxybenzaldehyde with N-methylethylenediamine in CH_3CN , in accordance with a relevant literature method [52]. The ligand was not separated and was treated with $VOSO_4\cdot 5H_2O$ (dissolved in CH_3CN) in open atmosphere to synthesize a dinuclear vanadium(V) complex, $(\mu-O)_2[V(O)(L)]_2$. Preparation of this complex was attempted under N_2 environment, but that went unsuccessful. This is because the involvement of aerial oxygen, causing the oxidation of vanadium from +4 (in starting material) to +5 (in both complexes). Synthetic route to the complex is outlined in Scheme 1.



Scheme 1: Synthetic route to the ligand and the complex.

3.2 Description of structure of $(\mu\text{-O})_2[\text{V}(\text{O})(\text{L})]_2$

X ray crystallography reveals the complex to be crystallized in the orthorhombic space group *Pbca* and it is a μ_2 -oxo-bridged centrosymmetric dimer which contains a V_2O_2 core in its crystal structure. A perspective view of the complex is illustrated in Fig. 1. Vanadium(V) centers in the complex are six coordinate and they reside in a distorted octahedral environment. The asymmetric unit in the complex consists of one vanadium atom, V(1), two oxo groups, O(2) and O(3), and one tridentate (deprotonated) Schiff base ligand binding to the vanadium(V) center via imine nitrogen atom N(2), amine nitrogen atom N(1), and the phenolate oxygen atom O(1). The equatorial plane is composed of phenolic oxygen atom O(1), imine nitrogen atom N(2), and an amine nitrogen atom N(1), of the Schiff base ligand and one oxo oxygen atom O(3). Remaining two axial positions are occupied by two oxo oxygen atoms; O(2) and O(3^a) [^a = 1-x, 1-y, 1-z]. The two oxo groups in each vanadium(V) centers are cis to each other. Out of these two, the first one i.e. V(1)-O(2) is typical V=O, having a distance of 1.621(3) Å. The second oxo group, O(3), is engaged in bridging V(1) and V(1^a). It is strongly coordinated to V(1) [V(1)-O(3) = 1.668(3) Å] and is weakly associated with V(1^a) [V(1^a)-O(3) = 2.330(3) Å]. The V-O and V-N bond lengths in the complexes are comparable to the corresponding values observed in other similar oxovanadium(V) complexes with Schiff bases [53-56]. The intramolecular V...V separation is 3.092(1) Å, similar to the known V...V distances in double-bridged vanadium polynuclear systems [57].

The chelating angles, N(1)-V(1)-N(2) and N(2)-V(1)-O(1) have the values of 77.3(1)° and 83.3(1)° {Table S1, Supplementary Information (SI[†])}, indicating distortion of the octahedron around vanadium(V) centers. The $\{\text{V}_2\text{O}_4\}^{2+}$ core in any double oxo-bridged dinuclear cis- VO_2^+ complex is known to possess five different configurations (syn and anti-orthogonal,

syn- and anti-coplanar, twist) on the basis of the orientation of V=O groups with respect to the central V_2O_2 core [58]. The complex may be termed as anti-coplanar, as the two terminal V=O bonds in both complexes are oriented in an anti arrangement with respect to the $\{V_2O_2\}$ plane. The coordination environment may then be appropriately termed as significantly distorted two edge-shared vanadium octahedra. The +5 oxidation state for the vanadium center has been assigned by virtue of the bond valence sums calculations [59], which give 4.946 valence unit for vanadium atom in the complex.

A $C-H\cdots\pi$ interaction is observed involving a hydrogen atom, H(11C), attached with C(11), and a symmetry related $(1/2+x, y, 3/2-z)$ phenyl ring [C(5)–C(6)–C(7)–C(8)–C(9)–C(10)] of another adjacent moiety in the complex. Association of the individual units via this $C-H\cdots\pi$ interaction produces an infinite two dimensional supramolecular ladder like array, as demonstrated in Fig. 2. The detail of the said interaction is enlisted in Table 1. Moreover, the hydrogen atom, H(1), attached to amine nitrogen atom, N(1), is intra-molecularly hydrogen bonded to the phenoxo oxygen atom, O(1^a), predominantly holding the other half of the asymmetric part of the molecule. The said interaction is demonstrated in Fig. 1, having the details enlisted in Table 2.

3.3 Theoretical Studies on supramolecular interactions

The vanadium(V) complex, $(\mu-O)_2[V(O)(L)]_2$, has been synthesized using a tridentate N_2O donor Schiff base ligand. In the solid state, the complex forms an infinite 1D chain governed by $Br\cdots O$ halogen bond involving the oxygen atoms of the VO_2^+ unit as electron donor and the σ -hole at the halogen as electron acceptor, as shown in Fig. 3. The DFT study is devoted

to the analysis of the halogen bonding interaction in the complex and the interaction has been studied and characterized using the QTAIM computational tool.

At first, the molecular electrostatic potential (MEP) surface of the complex has been computed, which is shown in Fig. 4. The most electron rich part corresponds to the oxygen atoms of the VO_2^+ unit, as expected. In fact, one of these atoms participates in the formation of the halogen bonds highlighted in Fig. 3. The most positive MEP value is located at the hydrogen atom of the coordinated imidic group. The MEP surface around the bromine atom has also been represented, using a reduced energetic scale (± 10 kcal/mol). As a result, the anisotropy around the bromine atom can be clearly appreciated and it reveals the existence of the σ -hole (+9.4 kcal/mol) that is responsible of the formation of the directional halogen bonding interaction.

The interaction in the complex has been characterized energetically by using the Bader's quantum theory of "atoms in molecules" (QTAIM). The existence of a bond path connecting two atoms provides a universal indicator of bonding between them [60]. The distribution of critical points (CP) and bond paths is shown in Fig. 5 for the halogen bonded dimer of the complex. It shows the presence of a bond CP and bond path connecting the oxygen atom of the VO_2^+ unit to the bromine atom, thus confirming the halogen bonding interaction. Moreover, the dimer is also characterized by a bond CP and bond path connecting one hydrogen atom of the aromatic ring to the oxygen atom of the methoxy substituent. The total dimerization energy is moderately strong, $\Delta E_1 = -7.4$ kcal/mol. In order to estimate the contribution of the hydrogen bond, the QTAIM analysis has been used; in particular, the value of the kinetic $G(r_{\text{CP}})$ contribution to the local energy density of electrons at the critical point (CP). This method is adequate to compute the stabilization energy that accounts for each individual hydrogen bonding contact since it was specifically developed for HBs [61] [Energy = $0.429 * G(r)$ at the bond CP]. This methodology

has recently been used [62] in hydrogen bonded assemblies of hybrid adenine- β -alanine and adenine-GABA molecules. In Fig. 5 the value of $G(r)$ has been shown at the bond CP that characterizes the hydrogen bond and the concomitant interaction energy (in red), that is quite small (-1.1 kcal/mol). Therefore, the contribution of the halogen bond is approximately -6.3 kcal/mol, in the range of typical halogen bonds [63].

In order to assess whether the said halogen bonding interaction is a special feature in these type of vanadium(V) systems, another structurally similar vanadium(V) complex [57], $(\mu-O)_2[V(O)(L^1)]_2$, has been taken for study alongside the previous analysis. This complex is also an oxo-bridged dinuclear vanadium(V) complex containing a bromine atom in its structural unit. The complex also forms a 1D supramolecular chain via the halogen bonding (Fig. 6b). The main difference between the complexes is the hydroxyl group of the pendant arm of the ligand in this complex that significantly affects the crystal packing. This hydroxyl group also facilitates the generation of a 1D supramolecular chain that propagates in the a direction due to the formation of symmetrically equivalent $O-H\cdots O$ hydrogen bonds (Fig. 6c).

Again the DFT calculations have been employed to determine the energetics of the halogen bonds and the hydrogen bonds in this complex using complex $(\mu-O)_2[V(O)(L)]_2$ as a representative model of both. Moreover, the interactions have been studied and characterized using the QTAIM computational tools. As usual, the MEP surface of this complex (Fig. 7) illustrates the most electron rich part belonging to the oxygen atoms of the VO_2^+ unit, which accounts for their participation in both halogen and hydrogen bonding. Unlike in the complex $(\mu-O)_2[V(O)(L)]_2$, this complex has the highest MEP value located at the hydrogen atom of the hydroxyl group. Therefore, in this system, the most favorable interaction from an electrostatic

point of view should be a hydrogen bond between the OH and VO₂ groups, which is in good agreement with the experimental observation.

The Bader's quantum theory of "atoms in molecules" (QTAIM), gives the distribution of critical points (CP) and bond paths (Fig. 8), which further shows that each hydrogen bond is characterized by a bond CP and bond path interconnecting the hydrogen and oxygen atoms. Moreover, it also shows a bond CP and bond path connecting the close hydrogen atoms of the aliphatic chain. The dimerization energy is very large, $\Delta E_2 = -22.9$ kcal/mol, due to the formation of two strong hydrogen bonds, which is in agreement with the MEP surface analysis commented above.

From this entire study, it is observed that due to the presence of uncoordinated hydroxyl group in the complex $(\mu-O)_2[V(O)(L^1)]_2$, it has a prevalence of the intermolecular hydrogen bonding interaction over the halogen bonding one as a driving force for its supramolecular assembly in the solid state. Despite having the bromine atom, the halogen bonding interaction cannot become the major stabilizing factor in its supramolecular aggregation, making the point clear that both hydrogen and halogen bonding interactions are substrate specific, and if both interactions are possible in a system, one can largely prevail over the other. Theoretical studies on the supramolecular interactions in both these complexes have turned out to be a good comparative study which tells whether a subtle change in the ligand moiety affects the nature of the supramolecular interaction in what way.

3.4 IR, electronic spectra and magnetic moments

The presence of azomethine (C=N) group in the complex has been assured by the appearance of sharp band at 1636 cm^{-1} in infra-red spectrum of the complex (Fig. S1, Supplementary Information) [64]. Moderately strong bands at 920 cm^{-1} and 843 cm^{-1} in the complex may be assigned to asymmetric and symmetric $\tilde{\nu}_{(\text{O}=\text{V}=\text{O})}$ vibrations of cis-VO₂ groups present [65]. Sharp band at 463 cm^{-1} is indicative of $\tilde{\nu}_{(\text{V}-\text{O})}$ stretch [66]. The complex also has a sharp band at 3222 cm^{-1} , which may be assigned to $\tilde{\nu}_{(\text{N}-\text{H})}$ stretching vibration.

Electronic spectrum of the complex (Fig. S2, Supplementary Information) shows absorption band at 393 nm, which may be assigned to a ligand-to-metal charge transfer (LMCT) transition originating from the p_{π} orbital on the phenolate oxygen to the empty d orbitals of the vanadium(V) [67].

The complex is diamagnetic, with d^0 electronic configuration, as also observed for other similar oxo-bridged dinuclear vanadium(V) complexes [68].

3.5 Hirshfeld Surface analysis

Hirshfeld surfaces of the complex are illustrated in Fig. 9, while the 2D fingerprint plots are also shown in Fig. 10, where intermolecular interactions appear as distinct spikes. The fingerprint plots are also analyzed to emphasize particular atoms pair close contacts. The proportion of O \cdots H and H \cdots O interactions comprise 18.2% of the Hirshfeld surfaces for the complex. C \cdots H and H \cdots C interactions comprise of 20.3% of the Hirshfeld surfaces, while that of N \cdots H and H \cdots N interactions in the complex are very low, i.e. 0.7%. Br \cdots O and O \cdots Br have 4.4% interactions to that of the total surface.

4. Conclusions

A dinuclear vanadium(V) Schiff base complex has been synthesized and structurally characterized. Theoretical studies have been conducted on the supramolecular interactions in this complex. In the solid state, the complex exhibits Br \cdots O halogen bonding interactions along with conventional hydrogen bonding interaction. Analysis of energies associated with these interactions have been conducted using DFT calculations and further corroborated with the QTAIM computational tool. Halogen bonding interaction is found to be dominant in the investigated complex. Comparison of its supramolecular interaction with that of a structurally similar system determines that the said halogen bonding interaction may not be a special structural feature system, which further suggests that mere the possibility of halogen bonding in a complex does not make it a dominating factor in the supramolecular assembly of its molecules in the solid state.

Conflicts of interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

CCDC 1967803 contains the supplementary crystallographic data for the complex. These 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: Geometric features (distances in Å and angles in °) of the C–H··· π interactions obtained in the complex.

C–H···Cg(Ring)	H···Cg (Å)	C–H···Cg (°)	C···Cg (Å)
C(11)–H(11C)···Cg(4) ^b	2.69	158	3.598(6)

Symmetry transformation: ^b = 1/2+x, y, 3/2-z, Cg(4) = Center of gravity of the ring [C(5)–C(6)–C(7)–C(8)–C(9)–C(10)].

Table 2: Hydrogen bond distances (Å) and angles (°) of the complex.

D–H···A	D–H	H···A	D···A	\angle D–H···A
N(1)–H(1)–O(1) ^a	0.72(5)	2.38(5)	2.944(5)	137(5)

Symmetry transformations; ^a = 1-x, 1-y, 1-z.

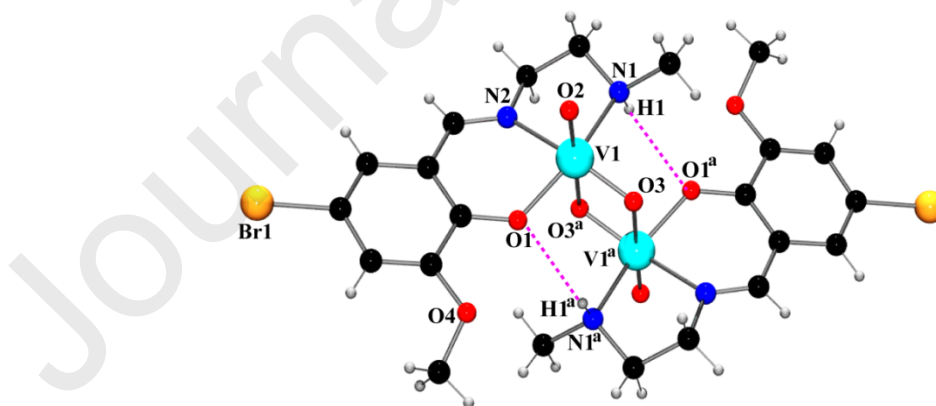


Fig. 1: Perspective view of the complex with selective atom numbering scheme. Intra-molecular hydrogen bonding interaction is also shown. Only the relevant atoms are labeled for clarity.

Symmetry transformation; ^a = 1-x, 1-y, 1-z. Selected bond lengths (Å): V(1)–O(1) = 1.913(3),

$V(1)-O(2) = 1.621(3)$, $V(1)-O(3) = 1.668(3)$, $V(1)-N(1) = 2.160(4)$, $V(1)-N(2) = 2.161(3)$, $V(1)-O(3^a) = 2.330(3)$

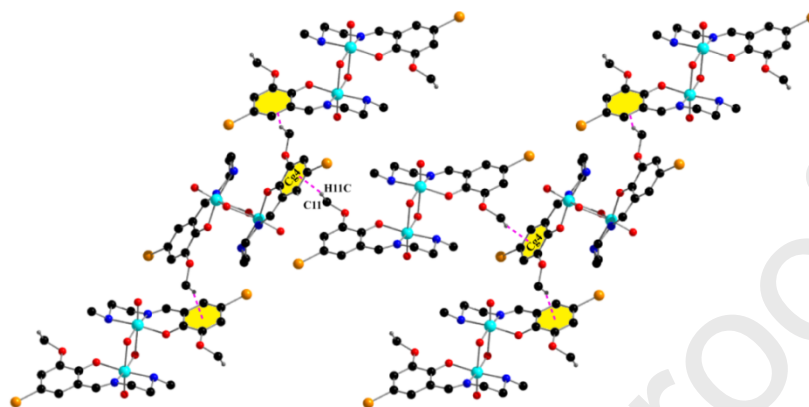


Fig. 2: Two dimensional supramolecular network of the complex, generated through C–H $\cdots\pi$ interactions. Only the relevant atoms and rings are labelled for clarity.

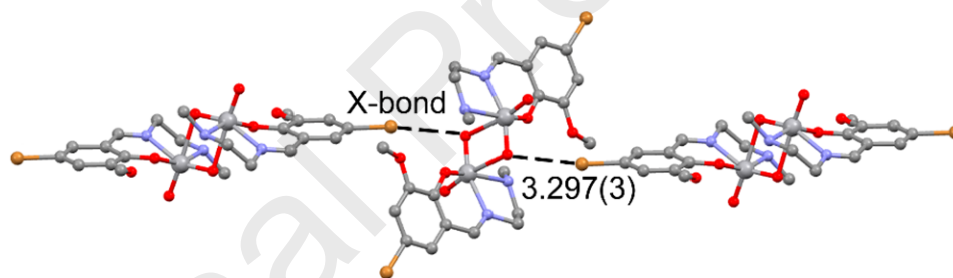


Fig. 3: Partial view of the X-ray structure of the complex. Distances in Å. Hydrogen atoms are omitted for clarity.

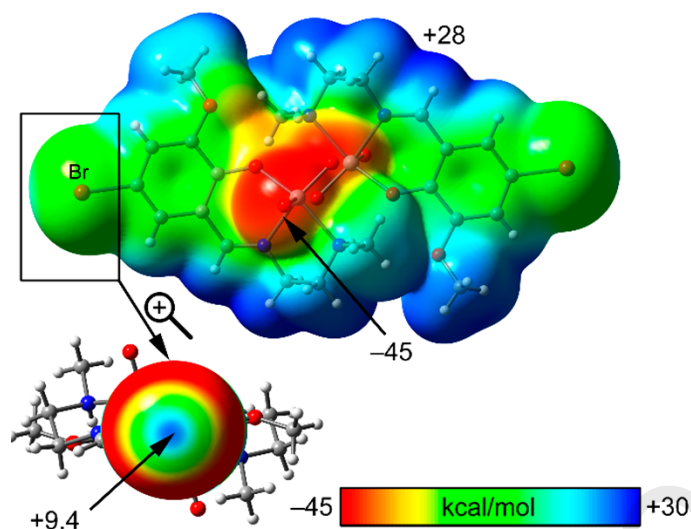


Fig. 4: MEP surface plotted onto the 0.001 a.u. isosurface of the complex. The values at selected points of the surface are given in kcal/mol. Bottom: MEP surface around the bromine atom using a ± 10 kcal/mol scale.

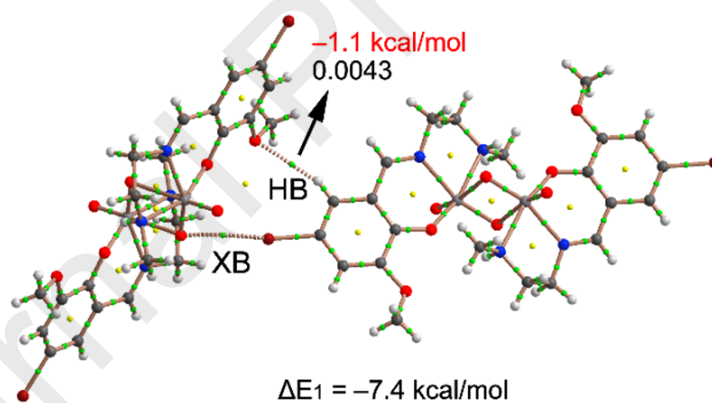


Fig. 5: AIM distribution of bond and ring critical points (green and yellow spheres, respectively) and bond paths for units the complex.

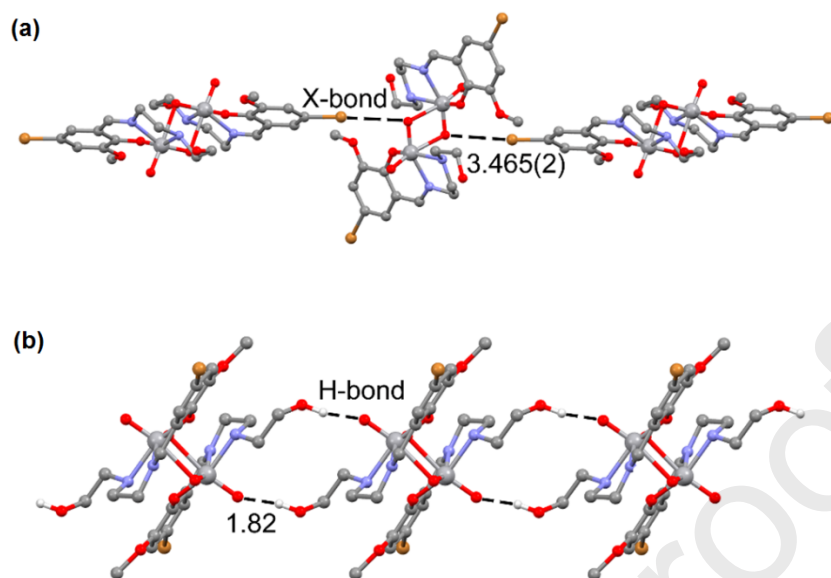


Fig. 6. Partial view of the X-ray structure of the complex $(\mu-O)_2[V(O)(L^1)]_2$ (a,b). Distances in Å. Hydrogen atoms are omitted apart from those involved in the hydrogen bonds in (b).

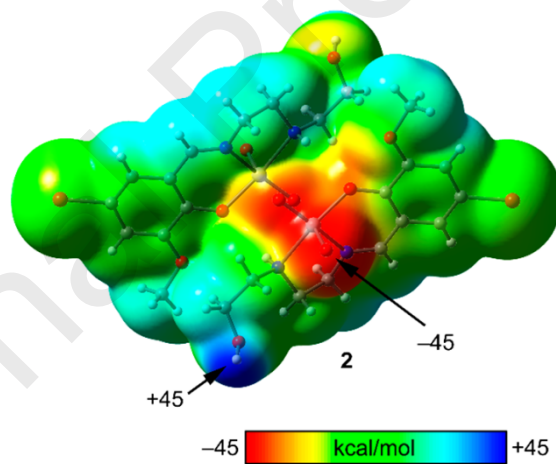


Fig. 7. MEP surfaces plotted onto the 0.001 a.u. isosurface of complex $(\mu-O)_2[V(O)(L^1)]_2$. The values at selected points of the surface are given in kcal/mol.

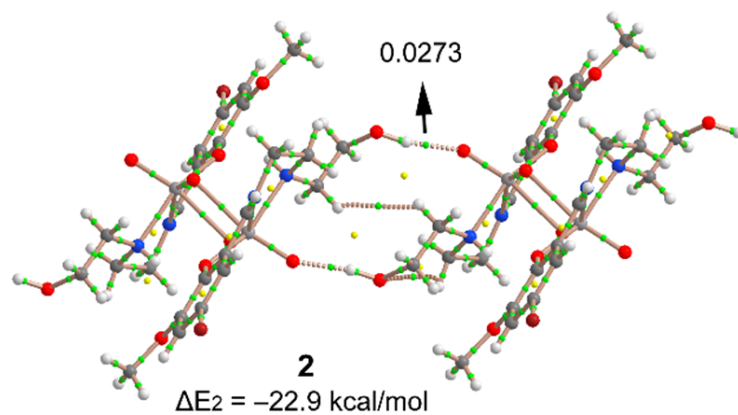


Fig. 8. AIM distribution of bond and ring critical points (green and yellow spheres, respectively) and bond paths for the complex $(\mu-O)_2[V(O)(L^1)]_2$.

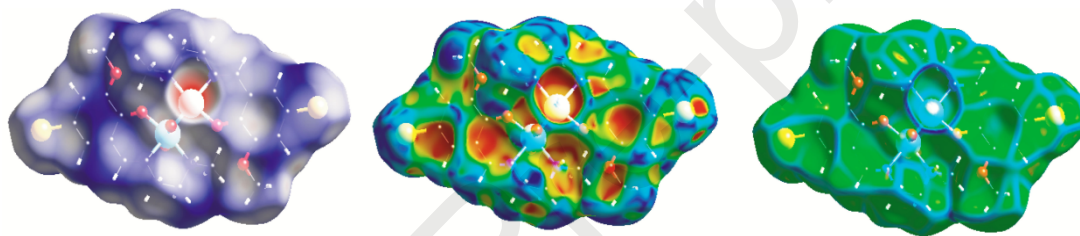


Fig. 9: Hirshfeld surfaces mapped with d_{norm} (extreme left), shape index (middle) and curvedness (extreme right) of the complex.

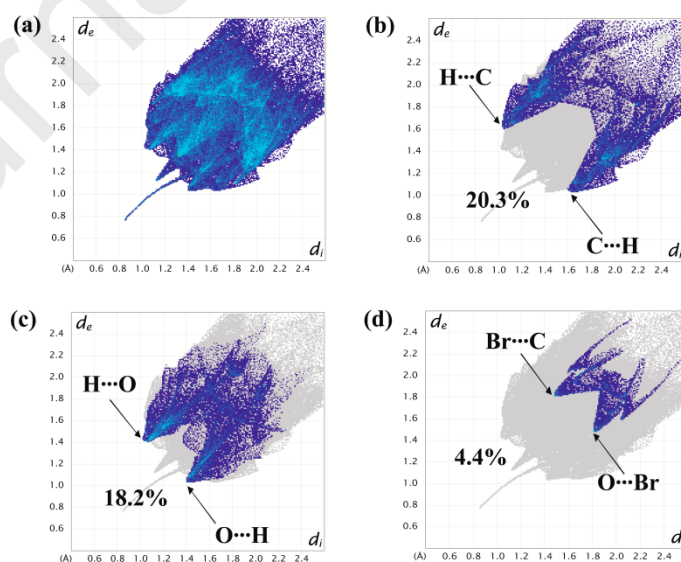


Fig. 10: 2D fingerprint plot of the complex showing (a) total surface area; proportions of (b) $C\cdots H/H\cdots C$, (c) $O\cdots H/H\cdots O$ and (d) $Br\cdots O/O\cdots Br$ interactions.

Author contribution section

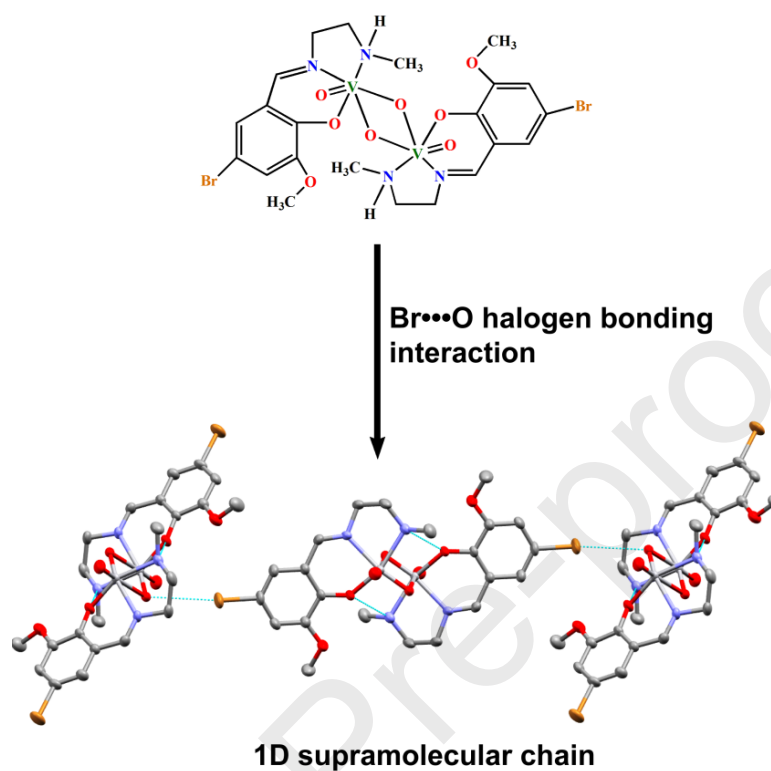
Snehasish Thakur synthesized the complex and characterized it by spectral and elemental analysis and performed all necessary works.

Antonio Frontera and Diego M. Gil performed the theoretical study on the supramolecular interactions in the complexes mentioned in this work.

Shouvik Chattopadhyay is the principal investigator of the project.

Exploration of $Br\cdots O$ halogen bonding interactions in dinuclear vanadium(V) complexes with Schiff base ligands

Snehasish Thakur, Diego M. Gil, Antonio Frontera and Shouvik Chattopadhyay



Exploration of $\text{Br} \cdots \text{O}$ halogen bonding interactions in dinuclear vanadium(V) complexes with Schiff base ligands

Snehasish Thakur, Diego M. Gil, Antonio Frontera and Shouvik Chattopadhyay

A novel μ_2 -oxo bridged dinuclear vanadium(V) complex, $(\mu\text{-O})_2[\text{V}(\text{O})(\text{L})]_2$, has been synthesized and characterized. Its structure has been confirmed by single crystal X-ray

diffraction study. An infinite 1D chain has been generated which is actually governed by the $\text{Br}\cdots\text{O}$ halogen bond involving the oxygen atoms of the VO_2^+ unit as electron donor and the σ -hole at the bromine atom as electron acceptor. The interaction energies have been characterized energetically by using the Bader's quantum theory of "atoms in molecules" (QTAIM). The results have been compared with the energies of identical halogen bonding interactions in a structurally similar oxo-bridged dinuclear vanadium(V) complex.

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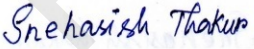
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