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1. Introduction

The chemistry of metals plays a central role in developing functional materials. Bulk metals and their stable compounds, such as metal salts and common oxides/sulfides, are currently well known; however, atomically precise intermediates in the formation or cleavage of metal-metal and metal-oxygen bonds are insufficiently explored.¹⁻³ In recent years, a variety of ligand-protected metal nanoclusters (NCs) have been synthesized, providing new insights into metals at reduced sizes, and opening a new window of wet synthesis and modern inorganic chemistry.^{4,5} Metal NCs containing metal-metal bonds and metal-ligand coordination interactions could exhibit altered atomic stacking comparing with that of bulk metals. It is important to explore how such metal clusters are integrated into a whole and what the relation is between NCs *via* wet synthesis and isolated clusters in the gas phase.^{6,7}



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An oxygen-passivated vanadium cluster $[V@V_{10}O_{15}]^-$ with metal-metal coordination produced by reacting V_n^- with O_2^+

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Vanadium cluster anions are highly reactive making the preparation of pure V_n^- and the observation of their reactivity extremely challenging. Herein, well-resolved anionic V_n^- clusters are prepared enabling an in-depth study on their reactions with O_2 in the gas phase. While pure metal clusters of a magic number are not identified due to the strong V–O bonding, interestingly an unexpected oxide $V_{11}O_{15}^-$ was experimentally observed in surviving O_2 etching reactions. First-principles theory calculations indicate that $V_{11}O_{15}^-$ possesses a body-centered pentagonal prism structure (D_{5h} , ${}^{5}A_1$), with the V@V₁₀ core fully protected by 15 oxygen bridges. Such an oxygen-protected metal cluster [V@V₁₀O₁₅]⁻ exhibits typical superatom orbital features pertaining to the V@V₁₀ core which shows effective metal–metal coordination bonding. Meanwhile, the high stability of [V@V₁₀O₁₅]⁻ is reinforced by the V–O–V conjugation interactions which help to maintain the structural integrity, resulting in 3D inorganic aromaticity. This finding of such an oxygen-passivated superatom cluster sheds light on the bonding nature in ligand-protected metal clusters *via* wet synthesis.

Because the oxidation of metals is essentially associated with the electronic activity and bonding nature,⁸ as one of the most fundamental redox processes, the reactivity of metal clusters towards oxygen is often studied to explore the stability of these materials in the gas phase.9-11 Nevertheless, the doping of heteroatoms (such as halogens) enables to tune the surface charges and even alter the core structures, thus to passivate the metallic cluster or induce reactive Lewis acid/base sites (*i.e.*, activating the cluster reactivity).^{12,13} This provides new insights into the role of ligands in the stability of metal clusters irrespective of nascent shell closure. Among others, there are abundant investigations of vanadium oxide clusters in the gas phase,¹⁴⁻³⁰ and a class of stable polyoxometalates sheds light on the multicentre bonding nature and conjugation effects31-35 that lead to reasonable stability and inorganic aromaticity.36-41

However, subject to difficulties in preparing pure metal clusters, the seemingly simple reaction processes of metal clusters, such as " $V_n^- + O_2$ ", have not been fully elucidated to the best of our knowledge, and the as-prepared superatom species with prominent stability are open to being explored. It is worth mentioning that the oxidation of transition metals occurs in a variety of minerals and surfaces, and their functionalized compounds with different compositions and oxidation states bear fascinating properties, with applications in catalysts for industry,⁴² materials for battery cathodes,⁴³ magnetic bodies, and devices.⁴⁴ The oxygen passivation and protection are important for some

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active metals (such as Al and Mg) which are generally coated with a "dead" layer of oxides that protects the metals from full corrosion, as well as in the studies of perovskite solar cells,⁴⁵ and magnetic cobalt nanoparticles.⁴⁶

Here we have prepared anionic V_n^- clusters *via* homemade laser evaporation (LaVa) source, and observe the reactions of $V_n^$ clusters with oxygen *via* a customized reflection time-of-flight mass spectrometry (Re-TOFMS) instrument.⁴⁷ It was found that $V_{11}O_{15}^-$ shows up in the mass distribution especially in the presence of a large amount of oxygen. Density functional theory (DFT) calculations based on the evolutionary algorithm method and basin-hopping global minimum search reveal that the ground-state $V_{11}O_{15}^-$ has a D_{5h} body-centered pentagonal prism structure (*i.e.*, $[V@V_{10}O_{15}]^-$), with a wide HOMO–LUMO gap, large atomic dissociation energy and electronic vertical detachment energy (VDE). In particular, the dramatic V–O–V conjugation interactions and multi-centre V–V metal–metal bonding nature result in superatomic characteristics and 3D aromaticity which, in turn, reinforce the stability of this cluster.

2. Results and discussion

2.1 Mass spectrometry observation

Vanadium is a polyvalent element and the V–O bond energy is about three times as that of V–V bond,^{48,49} which challenges the preparation of pure vanadium clusters. By extensive efforts to optimize experimental parameters of the homemade laser vaporization (LaVa) source, size-controllable anionic V_n^- clusters have been prepared as shown in Fig. 1A where a near-Gaussian distribution is seen but with inevitable small peaks attributed to O* and O₂ attachments due to trace amounts of background air contamination. Fig. 1B shows the mass distribution of the as-prepared clusters V_n^- (n = 5-60) in the absence and presence of different amounts of oxygen in helium as the reaction gas. As is shown, massive oxide products emerge in the mass spectrum, with rare nascent vanadium clusters surviving.⁵⁰

Compared to the inconspicuous relative stability of the naked vanadium clusters, we find an interesting oxide product, $V_{11}O_{15}^{-}$, which becomes dominant in the mass spectra upon introducing a large flow rate of oxygen, as shown in Fig. 1B(c). At the same time, a few small vanadium oxides (VO_3^{-} , $V_2O_5^{-}$, $V_2O_7^{-}$) emerge in the low mass range, suggesting likely fragmentation pathways with a removal of a high-oxidation-state moiety, such as,

$$V_n^- + yO_2 \rightarrow [V_{n-1}O_{2y-2}]^{0,-} + [VO_2]^{-,0} \rightarrow (1)$$

$$V_n^{-} + yO_2 \rightarrow [V_{n-1}O_{2y-3}]^{0,-} + [VO_3]^{-,0} \rightarrow (2)$$

$$V_n^{-} + yO_2 \rightarrow [V_{n-2}O_{2y-5}]^{0,-} + [V_2O_5]^{-,0} \rightarrow (3)$$

On this basis, the observation of $V_{11}O_{15}^-$ as a magic number cluster could be due to a mixture of these channels, summarized as " $V_n^- + yO_2 \rightarrow V_{11}O_{15}^- + xVO_2 + zVO_3$ ". In this equation, a typical reaction could be " $V_{13}^- + yO_2 \rightarrow V_{11}O_{15}^- +$ V_2O_5 ", which is strongly exothermic according to the DFT calculation results (ESI,† Table S2). It is worth noting that the repeated experiments of reactions based on different size distributions of the nascent V_n^- clusters all arrive at the same end with $V_{11}O_{15}^-$ showing up (Fig. S1 and S2, ESI†) indicative of its prominent stability.



Fig. 1 (A) The mass spectra of the anionic vanadium clusters V_n^- in different mass range. The V_n^- clusters are rather reactive and the small peaks are assigned to O^{*} and O₂ attachments due to trace amounts of background air contamination. (B) The mass spectra of V_n^- , n = 5-60 (a) and V_n^- reacting with different amounts of O₂ by 10% and 20% O₂/He, respectively (b and c). Insets are the side view, top view, and the van der Waals (VDW) cluster radius (given in Å) of the global minima of $V_{11}O_{15}^-$ (D_{5n} , ${}^{5}A_1$).

2.2 Structural determination

Inspired by the experimental observation, we aim to determine the structure and bonding of the superatom $V_{11}O_{15}^{-}$ cluster next. Based on an evolutionary algorithm, we conducted an extensive global search on V11O15 by USPEX combined with the Vienna ab initio Simulation Package (VASP).⁵¹ Low-lying isomers were further optimized at the DFT level of BP86,^{52,53} with the def2-TZVP basis set.⁵⁴ An independent basin-hopping search was also performed using TGMin code55 which reproduces the global minimum structure of $V_{11}O_{15}^{-}$ (details in ESI,† Fig. S3, S4 and Table S1). As the well-defined global minimum of the quintet D_{5h} [V@V₁₀O₁₅]⁻ (⁵A₁') possesses a two-way open-nest structure, in which the body-centred core, a V@V₁₀ pentagonal prism, has a structure similar to flattened ferrocene in which every two adjacent vanadium atoms (except the central V atom) are bridged by an oxygen atom (insets in Fig. 1B). What's more, DFT calculations find that the D_{5h} V₁₁O₁₅⁻ bears high electrondetachment energy (VDE = 3.66 eV), and there are large fragmentation energies to remove an O atom (8.3 eV), a V atom (10.4 eV), or a VO group (6.0-6.3 eV) from this stable cluster (ESI,† Table S3 and Fig. S5). Also, the van der Waals (VDW) radius of the V₁₁O₁₅⁻ cluster is calculated (with VDW radius of atoms involved) and the lengths of three sides are 9.64 Å, 9.47 Å, and 7.53 Å respectively showing a cluster system of ~ 1 nm.

To compare the relative stability of $V_{11}O_{15}^{-}$ with those of other vanadium oxides, Fig. 2a depicts a thermodynamic phase diagram involving the observed $V_n O_m^-$ clusters (VO₃⁻, V₂O_{5,7}⁻, $V_{10}O_{14}^{-}$, $V_{11}O_{14}^{-}$, $V_{13}O_{17}^{-}$) in the mass spectra within a convex hull of a point set-based 2D Euclidean space. By connecting the bottom points, as shown by the dashed lines, $V_{11}O_{15}^{-}$ is located at the minimum, unambiguously divulging its prominent thermodynamic stability. A few other vanadium oxides, such as $V_{13}O_{17}^{-}$, $V_2O_5^-$, and $V_2O_7^-$, also exhibit reasonably high stability in the phase diagram. Such a phase diagram is consistent with the observation of prominent peaks in the mass spectra (Fig. 1B(c)). It is worth mentioning that the enhanced stabilities of these stable vanadium oxides are largely ascribed to the V-O-V bridge bonds. Without the protection of oxygen bridges, the ferrocenestructured V₁₁ core will be severely distorted (ESI,† Fig. S7). Born–Oppenheimer molecular dynamics (BOMD)⁵⁶ simulations indicate that the $D_{5h} V_{11} O_{15}^{-}$ is dynamically stable at 300 K and 1200 K, as shown in Fig. 2b, with the small root-mean-squaredeviation values RMSD = 0.07 Å and 0.12 Å. The severely deformed isomer at 1200 K can be optimized to the global minima D_{5h} structure.

2.3 Bonding analysis

We have conducted a detailed analysis of its frontier molecular orbitals (MOs) to better understand the structural stability and bonding nature of the anionic $V_{11}O_{15}^{-}$ cluster, as shown in Fig. 3a. First, it is noteworthy that the gap between the highest occupied α -molecular orbital (α -HOMO) and the lowest unoccupied α -molecular orbital (α -LUMO) is 0.99 eV. The relatively large gap is consistent with the high stability of the cluster. More interestingly, the frontier orbitals of the complex which



Fig. 2 (a) Relative ground state formation enthalpies per atom of all the studied $V_n O_m^-$ clusters within a convex hull (with respect to $V_{13}^$ and O₂). The points of the set (x, y) are given by $y = \left[\frac{E_{V_n O_m^-}}{E_{V_n O_m^-}} - n \cdot \frac{E_{V_1 3^-}}{13} - m \cdot \frac{E_{O_2}}{2} \right] / (n+m), \text{ corresponding}$ т m+nto the total energy of a $V_n O_m^-$ cluster. The x-axis refers to the atomic number ratio of O relative to the total, while the y-axis shows the relative formation enthalpies per atom above the hull. Insets are the structures of the clusters labelled with green and orange words, while the clusters labelled with blue and black words are given in Fig. S6, ESI.† (b) Born-Oppenheimer molecular dynamics (BOMD) simulations of D_{5h} V₁₁O₁₅⁻ at 300 K and 1200 K for 30 ps, with the average rootmean-square-deviation (RMSD, given in Å) of the V-V and V-O bond lengths for the structure in each step. The time interval for each step was set to be 1 fs (BOMD simulations at 600 K, 800 K, and 1000 K are given in Fig. S8, ESI†).

are all bonding orbitals exhibit obvious superatomic orbital characteristics.^{7,57,58}

In specific, the doubly occupied orbital 173 shows an S-type superatomic orbital feature, while orbitals 176–180 correspond to five D-orbital profiles, and the three orbitals 181–183 can be recognized as superatomic P orbitals. Besides, the orbitals no. 184–189 exhibit superatomic F-orbital characteristics, with two of them being doubly occupied and four of them singly occupied. Although an open-shell electronic configuration, the well-delocalized superatomic orbitals and unique geometric structure of this oxygen-passivated cluster $[V@V_{10}O_{15}]^-$ account for its reasonably high stability.

It is also notable in Fig. 3a that, there is another obvious energy gap up to 1.28 eV between MO-176 and MO-175. This gap could be associated with the densities of states (DOS) of the $[V@V_{10}O_{15}]^-$ cluster. In view of this, Fig. 3b depicts the partial densities of states (PDOS) of V₁₀ (blue curve) and O₁₅ (green curve).



Fig. 3 (a) Selected Frontier canonical molecular orbitals (CMOs) of $V_{11}O_{15}^{-}$, with their superatomic features (S, P, D, and F) indicated. (b) Total and partial density of states (DOS) of the $V_{11}O_{15}^{-}$ cluster.

Considering the electronic configuration of V ($[Ar]3d^34s^2$) and O ([He] $2s^22p^4$), there are 146 (*i.e.*, $11 \times 5 + 15 \times 6 + 1$) valence electrons involved in this system (ESI,† Fig. S13). Except for the 30 lone-pair electrons distributed on the 15 oxygen atoms, the other 116 electrons contribute to the V-V and V-O interactions. As shown in Fig. 3b, the 92 electrons lying below MO-176 could exhibit main contributions to the V-O interaction. In comparison, the PDOS of V1 (red curve) and V10 (blue curve) show that all the 24 electrons $(\alpha + \beta)$ lying above MO-175 are primarily V-based and are involved in direct metal-metal bonding. Utilizing the natural atomic orbital (NAO)59,60 methods, we performed further molecular orbital composition analysis to provide more detailed information on specific orbitals. It is clear that the contributions to MOs 173, 176/177, 178, 179/180, 181/182, and 184 mainly arise from the V(3d)-V(3d) overlaps, while MO-143 is composed of both O(2p)and V(3d) atomic orbitals pertaining to V-O interactions (more details in ESI,† Fig. S13, S14 and Tables S5-S8). In addition, we also compared the difference of V–V interactions within $V_{11}O_{15}^{-1}$ and $V_2O_5^-$ by plotting the PDOS for the V–O–V unit (ESI,† Fig. S15). As a result, in the high energy level orbitals (-2 to -4 eV), the positive value of the overlap population density of states (OPDOS) in V₁₁O₁₅⁻ indicates V-V bonding features (especially for orb. 183 and orb. 173), while the negative value of OPDOS in $V_2O_5^$ reflects the antibonding feature, related to V-V bond dissociation by the insertion of oxygen atoms. The lower overlap between vanadium and oxygen atoms in V11O15 indicates a weaker V-O interaction than that in $V_2O_5^-$. Therefore, the oxygen atoms in



Fig. 4 AdNDP bonding patterns of the D_{5h} V₁₁O₁₅⁻, with the occupation numbers (ON) and superatomic orbital features S, P, D, and F indicated.

 $V_{11}O_{15}^{-}$ clusters contribute to protecting the V–V bonds (*i.e.*, metallic V_{11} core) without breaking the metal–metal bonds.

To further reveal the chemical bonding nature of such an oxide cluster, we conducted a detailed adaptive natural density partitioning $(AdNDP)^{61}$ analysis on $D_{5h} V_{11}O_{15}^{-}$, as shown in Fig. 4. The fifteen 1c-2e lone pairs on 15 oxygen atoms with the occupation number of ON = 1.94 |e| in the first row correspond to the 15 CMOs (orb. 115–129). The thirty 2c-2e σ -bonds (V–O) with ON = 1.96 |e| and fifteen 3c-2e π -bonds (V–O–V) with ON = 1.94–1.96 |e| in the second row originate from the 45 CMOs related to V–O interactions, in which the 15 V–O–V π -bonds represent the oxygen bridges. There exist two types of V–O–V π -bonds in this cluster, one with two vanadium atoms in the V₅ plane and the other with V–V perpendicular to the pentagonal plane. These (d–p) π conjugation interactions between the metal and the oxygen bridge help to maintain the stability and integrity of the V@V₁₀ framework.

More intriguingly, there exist 15 totally delocalized 11c-2e bonds mainly originating from V(3d)–V(3d) overlaps over the V@V₁₀ core which well exhibits the superatomic orbital characteristics of the cluster shown in Fig. 4. Among these novel metal-metal coordination interactions, the nine doubly-occupied 11c-2e bonds $(1\sigma + 3\pi + 5\delta)$ (in the third, fourth, and fifth rows) with ON = 1.88–1.96 |*e*| represent superatomic S, P, and D orbitals which follow the 18-electron rule and match the 3D aromatic requirement $2(n + 1)^2$ (n = 2). The remaining 8 valence electrons are distributed in six 11c-2e ψ -bonds in the sixth row which exhibit obvious F orbital features of a superatom, including 2 doubly-occupied 11c-2e ψ -bonds with ON = 1.92 |*e*| and 4 singly-occupied 11c-1e ψ -bonds with ON = 0.93 |*e*| that form an open-shell 3D aromatic ψ -system matching the electron count of $2(n + 1)^2$ (n = 1).

Natural bond orbital (NBO) analysis indicates that the V center in the V@V₁₀ core possesses the net atomic charge of $q_V = -0.13 |e|$, total Wiberg bond order of WBI_v = 5.93, and V_1-V_{2-11} coordination bond order of $WBI_{V-V} = 0.51$ (more details in Table S4, ESI[†]), indicating the formation of effective metal-metal coordination bonding in the open-shell superatom cluster $[V(a)V_{10}O_{15}]^{-}$. A comparison study shows that similar bonding patterns also exist in septet $D_{5h} V_{11} O_{15}^{+} (^7 A_1)$ and sextet $C_s V_{11} O_{15} (^6 A')$ which possess six and five singly occupied α -orbitals, respectively (ESI,† Fig. S16). Both the mono-cation and neutral with reduced stabilities possess higher spin multiplicities than the highly stable quintet $V_{11}O_{15}$ $({}^{5}A_{1})$, with the neutral being slightly distorted from a perfect D_{5h} geometry due to the Jahn-Teller effect. The core-shell interaction between the interior mono-vanadium and the outer V10O15 cage can be also revealed by the Kohn-Sham orbital energy-level correlation diagram between fragments based on the method of natural bond for chemical valence (NOCV).^{62,63} As indicated by the energy-level correlation diagram in Fig. S17 (ESI[†]), the superatomic S orbital of $D_{5h} V_{11} O_{15}^{-}$ is contributed by both the 4s² orbital of V⁻ and the correlated orbital of V10O15 moiety. Similarly, the superatomic D orbital of D_{5h} $V_{11}O_{15}^{-}$ is also contributed by both fragments. In comparison, the superatomic P and F orbitals are mainly contributed by the outer $V_{10}O_{15}$ fragment (mainly by V_{10} as revealed in Fig. 3) which functions as a shield for metal-metal coordination allowing the related electrons to occupy the lower energy levels, hence enhanced stability of the D_{5h} V₁₁O₁₅⁻.

2.4 Aromaticity characterization

Fig. 5a and b depicts three-dimensional and two-dimensional electron localization function (ELF)⁶⁴ analyses of the cluster,



Fig. 5 (a) Calculated three-dimension electron localization function (3D-ELF) with an iso-surface value at 0.15. (b) A projection of ELF on the XY-plane. (c and d) Top and side views of the iso-chemical shielding surfaces (ICSSs) of $D_{5h} V_{11}O_{15}^{-}$, an iso-surface value at 15.

which provide further insights into its bonding nature by displaying the locality of electrons at a certain region. As is shown, there exists a complete electron delocalization over the whole D_{5h} V@V₁₀ core in V₁₁O₁₅⁻, well demonstrating the formation of totally delocalized metal-metal coordination bonds in the complex which are reinforced by the conjugated V-O-V π bonds surrounding the V@V₁₀ pentagonal prism core in both horizontal and vertical directions.

To evaluate the aromaticity of $D_{5h} V_{11}O_{15}^-$, Fig. 5c and d plots the top and side views of the iso-chemical-shielding surfaces (ICSSs)⁶⁵ which is derived from the nucleus independent chemical shift (NICS). As shown in Fig. 5d, there exist clearly three chemical shielding regions with positive ICSS values (*i.e.*, negative NICS values) symmetrically distributed in the vertical direction along the molecular C_5 axis, including two equivalent quasi-planar areas over two V_5O_5 zig-zag rings on the top and bottom with five 3c-2e V–O–V π bonds on each and one oblate spheroidal region around the central V atom surrounded by fifteen 11c-2e V–V metal–metal coordination bonds. The three chemical shielding regions indicate the existence of local 2D planar aromaticity over the V_5O_5 rings and 3D spherical aromaticity in the V@V₁₀ pentagonal prism. Overall, D_{5h} [V@V₁₀O₁₅]⁻ exhibits unique 3D inorganic aromaticity in transition-metal complexes.

3. Conclusions

In summary, we have prepared well-resolved anionic V_n^- clusters (n = 5-60) in gas-phase for the first time and identified a highly stable magic cluster D_{5h} [V@V₁₀O₁₅]⁻ by reacting with oxygen. The high stability of such an oxygen-passivated superatom cluster originates from its unique electronic structure and bonding pattern, with 15 conjugated V–O–V π -bonds evenly distributed over the D_{5h} V@V₁₀ core which is effectively stabilized by 15 delocalized 11c-2e V–V metal-metal coordination bonds. We illustrate the superatomic characteristics of [V@V₁₀O₁₅]⁻ and unveil its unique bonding nature. The discovery of such a superatom cluster may arouse more interest in 3D inorganic aromaticity. In view of the wide uses of vanadium oxides, such a highly stable cluster could be beneficial to design new catalysts for correlative reactions and genetic materials for spin-electronics.

4. Methods

4.1 Experimental methods

A customized reflection time-of-flight mass spectrometer (Re-TOFMS),⁴⁷ coupled with a pulsed laser vaporization cluster source and an after-grow reaction tube, was utilized to study the formation and stability of anionic vanadium oxides. The apparatus has been successfully applied in the research of the reactivity of other metal clusters,^{66,67} and also the discovery of stable metal-benzene clusters.⁶⁸ A brief description is given here. The anionic vanadium clusters V_n^- were generated *via* the formation nozzle by laser ablation of a vanadium disk (99.9%) with an Nd:YAG (532 nm) laser. The buffer gas He (99.999%) was controlled by a pulsed general valve (Parker, Series 9) with a

backing pressure of 1.0 MPa. The different distributions of the vanadium clusters (Fig. 1A) are controlled by adjusting the length and inner diameter of the formation nozzle. After cluster generation, the V_n^- clusters reacted with diluted oxygen in the reaction tube to produce anionic vanadium oxides, and then the molecular beam was skimmed into the vacuum system of Re-TOFMS for mass abundance analysis. The molecular number density of oxygen in the reaction tube for each concentration of reaction gas is estimated to be $\sim 3.7 \times 10^{19} (10\% \text{ O}_2/\text{He})$ and $\sim 7.4 \times 10^{19} (20\% \text{ O}_2/\text{He})$ molecules m⁻³, respectively.

4.2 Theoretical methods

Unbiased global-minimum searches of the $V_{11}O_{15}^{-}$ cluster was performed using both ab initio evolutionary algorithm USPEX,^{51,69} and the basin-hopping based TGMin code55 at PBE (Perdew, Burke, and Ernzerhof) level.⁷⁰ More than 2200 structures were probed until the global minimum (GM) was found. Low-lying structures were then fully optimized at the density functional theory (DFT) level of BP86,^{52,53} with the basis set of def2-TZVP,⁵⁴ implemented in the Gaussian 09 program.⁷¹ All the DFT calculations were performed using tight convergence criteria and ultrafine level of integral lattice. Born-Oppenheimer molecular dynamics (BOMD) simulations were performed for the global minima of $V_{11}O_{15}^{-}$ (D_{5h}) at 300 K, 600 K, 800 K, 1000 K, and 1200 K for 30 ps using the software suite of CP2K.⁵⁶ Bonding analyses were performed using the adaptive natural density partitioning (AdNDP)^{61,72} method which recovers both the localized and delocalized bonding elements of the concerned systems. The through space NMR shielding which was visualized as iso-chemical-shielding surfaces (ICSSs)^{65,73} is calculated on the basis of gauge-invariant atomic orbitals (GIAO)^{74,75} methods. All the electronic wavefunction analyses were conducted by Multiwfn 3.7 software package⁷⁶ and VMD⁷⁷ was the visualization program for the structures and orbitals. More details of the experimental and theoretical methods are given in ESI.†

Conflicts of interest

There are no conflicts to declare.

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