

## CHAPTER 7

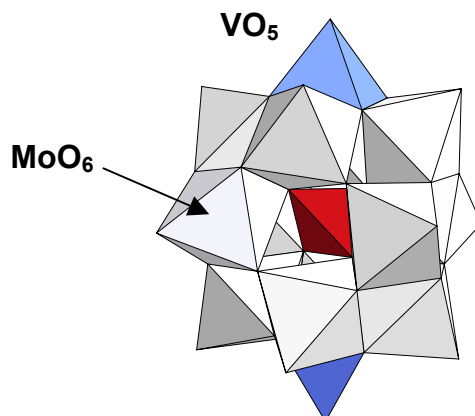
### Highly-reduced Polyoxometalates: Study of $[\text{PMo}_8\text{V}_4\text{O}_{40}(\text{VO})_4]^{5-}$

In the present chapter, a preliminary DFT/*ab initio* study to characterise the electronic structure of the  $10e^-$ -reduced  $[\text{PMo}_8\text{V}_4\text{O}_{40}(\text{VO})_4]^{5-}$  cluster (**1**) is reported. This molecule may be viewed as a Keggin-like  $[\text{PMo}_8\text{V}_4\text{O}_{40}]$  structure capped by four VO units. In mixed V/Mo clusters it is accepted that the first reductions occur at the  $\text{V}^{5+}$  ions. This behaviour was found in the  $8e^-$ -reduced bicapped cluster  $[\text{PMo}_{12}\text{O}_{40}(\text{VO})_2]^{5-}$  for which DFT calculations showed that each V has formally an oxidation state of +4, whereas the 12 Mo atoms share 6 electrons. Here we show that this principle is not fully accomplished when the number of  $\text{V}^{5+}$  centres increases. On the other hand, highly reduced clusters can present several configurations close in energy. In these circumstances, monoconfigurational methods like DFT or HF only give an approximate representation of the wave function and multi-reference SCF techniques are, in general, needed for an accurate treatment of the electron correlation. Part of this work was performed during a stay of three months at the Louis Pasteur University (Strasbourg) in the group of Dr. Marc Bénard.

## 7.1. Introduction

### *Mixed-addenda capped Keggin anions*

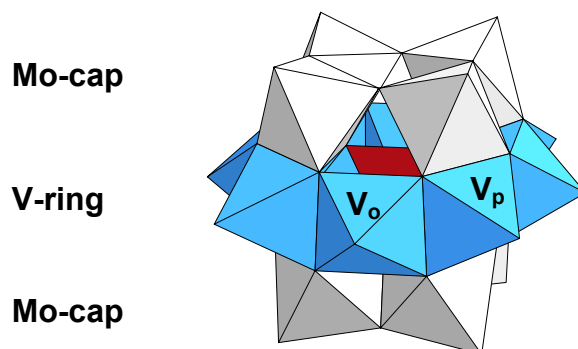
Modified cluster structures belonging to the family of POMs enrich and broaden the scope of this field. Several strategies are driven to alter the traditional characteristics of these inorganic systems. One of them incorporates capping units. It consists in the addition of  $M_xO_y$  units to the surface of a given POM cluster. Multiple capped clusters have been synthesised and characterised during the last ten years. Let us point out that these systems are restricted to compounds containing Mo, V and As atoms. A benchmark bicapped anion was characterised by Hill and co-workers in the middle 1990's,<sup>1</sup> composed of molybdenum and vanadium addenda atoms (Figure 7.1), with formula  $[PMo_{12}O_{40}(VO)_2]^{5-}$ . The special electronic features of this anion were analysed with the DFT methodology by Maestre *et al.*<sup>2</sup> Other derivatives were reported with similar molecular composition, with capping V or Mo units.<sup>3-12</sup> Some of them are not only capped structures but also substituted in the parent POM core. Novel capped clusters containing V and Ge centres were reported by Whitfield *et al.* in 2003.<sup>13</sup>  $[Ge_4V_{16}O_{42}(OH)_4]^{8-}$  constitutes the first example of  $Ge_2O_7$  capping units incorporated to vanadate derivatives based on the Keggin anion.



**Figure 7.1.** Bicapped phosphomolybdate Keggin anion obtained by Hill's group. The apical groups (blue pyramids) are, formally,  $VO_5$  units.

As a new V-capped molybdate Keggin anion, Xu *et al.* reported the synthesis of the first polyanion with a tetra-capped Keggin structure in 1999.<sup>14</sup> This species consists of a  $[\text{PMo}_8\text{V}_4\text{O}_{40}]^{7-}$  mixed-addenda cluster in which, formally, four additional  $\text{VO}^{3+}$  units are added to the external core. The four  $\text{VO}^{3+}$  capping units hold a charge of +12, which converts the parent oxidised  $\text{PMo}_8\text{V}_4\text{O}_{40}$  cluster into the  $[\text{PMo}_8\text{V}_8\text{O}_{44}]^{5+}$  cation. The resulting compound is indeed a  $10e^-$ -reduced molecule with a net charge of  $-5$ . More recently, the same group published a related compound with similar electronic structure<sup>8</sup> and, in 2003, Yuan *et al.* reported three novel V-capped Keggin derivatives with paramagnetic metal complexes attached to the surface of the cluster.<sup>15</sup> Perhaps, the most important feature of those clusters is that they are found in highly reduced forms.

The structure reported for **1** may be viewed as a  $\text{V}_8$  equatorial ring plus two polar units made of 4 Mo atoms each. Notice in Figure 7.2 that all Mo atoms are equivalent whereas there are two different vanadium types, four pseudo-octahedrally coordinated and four in a square-pyramidal environment, that are labelled as  $\text{V}_o$  and  $\text{V}_p$  from now on, respectively. These V centres are alternatively disposed in the  $\text{V}_8$ -ring, like  $\text{V}_o\text{-V}_p\text{-V}_o\text{-...}$ . Of course, all Mo centres have pseudo-octahedral environments.



**Figure 7.2.** Polyhedral representation of the  $[\text{PMo}_8\text{V}_4\text{O}_{40}(\text{VO})_4]^{5-}$  anion, **1**. This viewpoint permits to see the equatorial ring of 8 alternating  $\text{V}_o\text{-V}_p$  vanadiums (see text for details), as well as the two polar molybdenum caps. The overall symmetry of the cluster is  $D_{2h}$ .

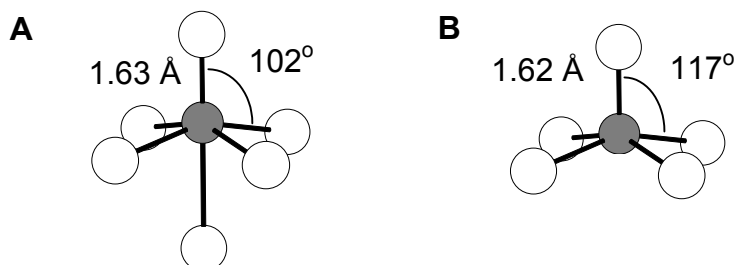
In general, it is difficult to unequivocally characterise the number and nature of the reduced centres in a partly reduced cluster and today this is still

a matter of debate.<sup>16</sup> Electrochemical reductions and EPR spectroscopy have usually been used to determine the localisation, or delocalisation, of the metal electrons in reduced HPAs. For example, Hervé and co-workers<sup>17</sup> found in electrochemical reductions on  $\text{XMo}_2\text{VW}_9$  and  $\text{XMoV}_2\text{W}_9$  anions ( $\text{X} = \text{P}, \text{Si}$ ) that the V centres are commonly reduced in first place. However, in  $\text{PMoV}_2\text{W}_9$ , the authors assigned the first reduction process to  $\text{Mo}^{\text{VI}} \rightarrow \text{Mo}^{\text{V}}$ . In this line of thought, Xu *et al.*,<sup>14</sup> from X-ray diffraction and EPR spectra analysis, claimed that the electronic structure for **1** corresponds to the 10 metal electrons delocalised over the whole system. In fact, after valence sum calculations they attributed oxidation states to Mo and V metal atoms of the structure, thus concluding that all vanadium atoms have an oxidation state of +4. This means that the 8 Mo ions should share two electrons. With the analysis of **1** we pursue two objectives: to rationalise reduced mixed-addenda Mo/V derivatives<sup>2,18</sup> and to progress in the understanding of capped clusters.<sup>1-2</sup>

## 7.2. Study of the Electronic Structure

### 7.2.1. Structure of $[\text{PMo}_8\text{V}_4\text{O}_{40}(\text{VO})_4]^{5-}$

The local geometry is, thus, slightly different between  $\text{V}_\text{o}$  and  $\text{V}_\text{p}$  centres. Apart of the coordination number, the degree of pyramidalisation is also different. Figure 7.3 shows geometrical parameters of both units computed as taking part in Xu's molecule at the DFT level. The rest of the parameters are similar to those of the uncapped Keggin partner.



**Figure 7.3.** Geometric parameters computed for the pseudo-octahedral  $\text{VO}_6$  (A) and pyramidal  $\text{VO}_5$  (B) units.

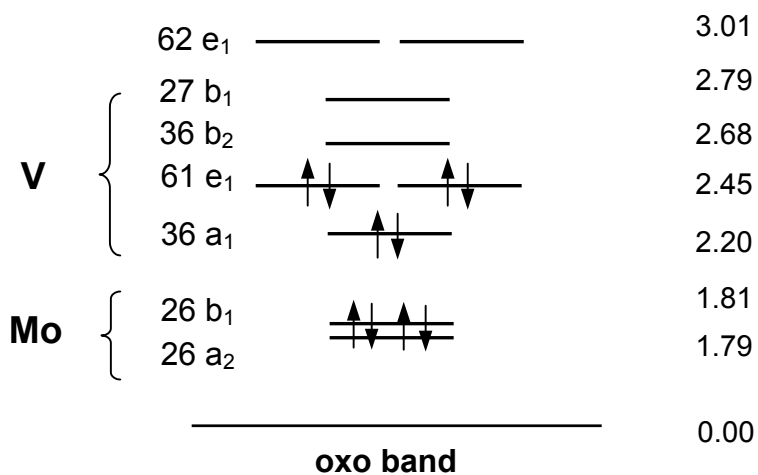
### 7.2.2. Computational details

DFT calculations were carried out with the same computational strategy described in chapter 2. We utilised triple- $\zeta$  + polarisation basis functions and the BP86 functional commonly employed in our work within the scope of the LDA formalism. In addition, HF calculations were conducted to complement the DFT analysis. The Gaussian 98 program<sup>19</sup> was used. Double- $\zeta$  basis functions of the type LANL2DZ<sup>20</sup> with effective core potentials describe vanadium and molybdenum atoms. For the purpose of *ab initio* calculations, DFT-optimised structures were utilised and single point runs performed. The main goal of the HF calculations presented here is to get a set of molecular orbitals, in which the exact exchange is included, although the electrons are described by a poorer wavefunction. HF results are a starting point for further improvement of the wavefunction by means of multi-reference calculations.

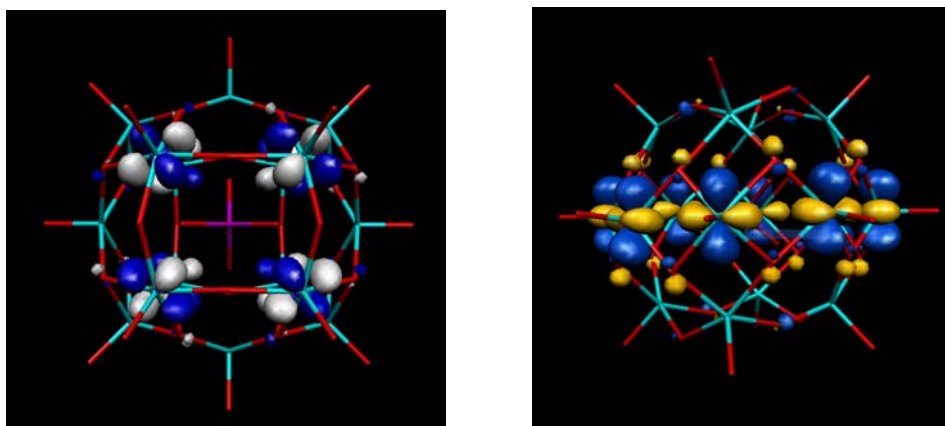
#### *Electronic configurations*

In the most stable closed-shell configuration for **1**, the two lowest metal orbitals are delocalised over Mo atoms. The next three doubly occupied MOs are  $d_{xy}$ -like combinations of V orbitals (Figure 7.4). This will be the reference configuration in the present discussion.

Figure 7.5-A shows orbital 26b<sub>1</sub>, which has a non-bonding character. The bridging Mo–O–Mo oxo sites have no contribution to this orbital because they lie in a node. Orbital 26 a<sub>2</sub> is almost degenerate to 26 b<sub>1</sub> and has the same nature. Orbital 36 a<sub>1</sub> (part B of the figure) shows slightly antibonding d(V)-p(O) interactions, and lies above in energy despite that all the  $d_{xy}$  orbitals of vanadiums are in phase. Orbitals of this nature accommodate six metal electrons. It is worth noting that V<sub>o</sub> and V<sub>p</sub> share the 6 upper electrons nearly in the same fashion. An analysis of the contributions to each of the 4 highest molecular orbitals occupied, leads to 71% Mo for 26 a<sub>2</sub>, 73% Mo for 26 b<sub>1</sub>, whereas for 36 a<sub>1</sub> we find 33% V<sub>p</sub> + 33% V<sub>o</sub>. The HOMO is formed by 27% V<sub>o</sub> + 29% V<sub>p</sub>. Despite their different coordination to O<sup>2-</sup>, they are chemically very similar, and metallic electrons are delocalised over vanadiums irrespective of their type. The first empty orbitals, the LUMO and LUMO+1, are formed by 75% of V<sub>o</sub> and 73% V<sub>p</sub>, respectively. The first relevant result in this study is that Mo atoms share 4 electrons, instead of 2 as the experimental data suggest.

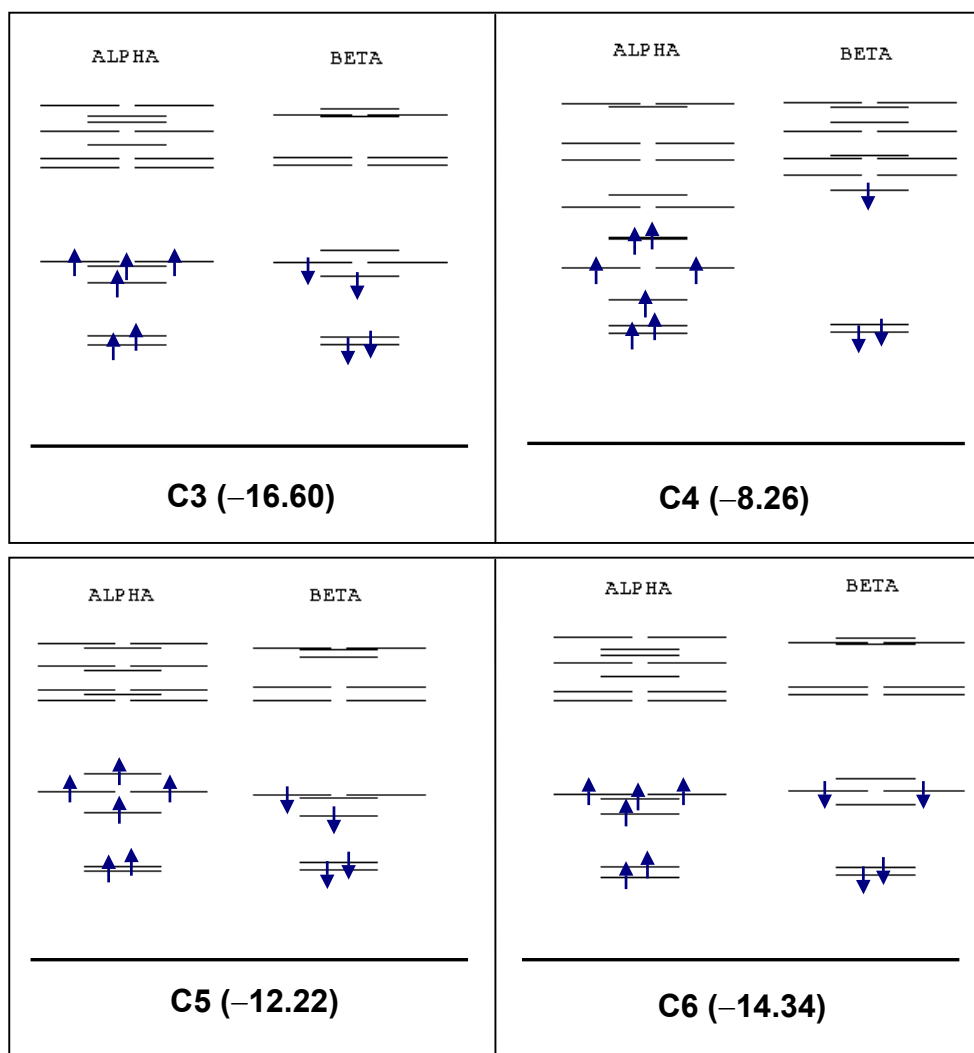


**Figure 7.4.** Closed-shell configuration (C1) for  $[PMo_8V_4O_{40}(VO)_4]^{5-}$ . Four electrons are localised on Mo atoms, whereas vanadium centres share the other six. Relative orbital energies are in eV.

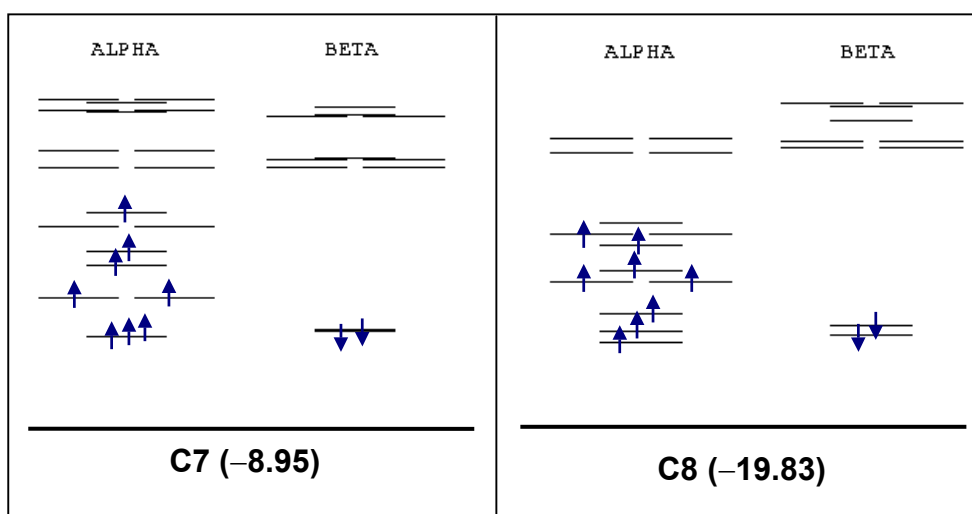


**Figure 7.5.** (A) Representation, perpendicular to the V-ring, of the doubly occupied 26 b<sub>1</sub> metal orbital, delocalised over the Mo atoms. (B) View of orbital 36 a<sub>1</sub> in the plane containing the vanadiums.

The promotion of two electrons from the 26  $b_1$  and 26  $a_2$  orbitals to 36  $b_2$  vanadium orbital requires 2.2 eV. This high energy clearly excludes the electron distribution ( $2e^-$  Mo/  $8e^-$  V) proposed by Xu *et al.*<sup>14</sup> The general assumption that in a mixed Mo/V anion the Mo ions are only reduced after all V ions have at least one electron<sup>17</sup> is not always accomplished as present DFT calculations strongly suggest.



**Figure 7.6.** DFT-computed electronic configurations **C3-C6** and relative energies (referred to that of **C1**), in kcal mol<sup>-1</sup>. Thick lines represent the O<sup>2-</sup> band.



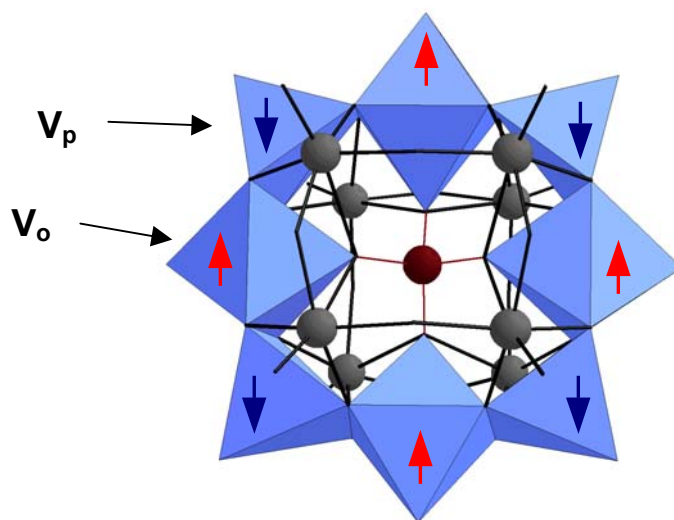
**Figure 7.6.** Continued. Configurations C7 and C8.

Another important question concerns the six vanadium electrons. Is the ground configuration actually a closed-shell? Or has the compound any kind of magnetic behaviour? Unfortunately, we are not able to give a definitive answer to this question, yet. When orbitals are nearly degenerate, the monoconfigurational treatment always favours the high-spin state. Consequently, the high-spin C8 configuration (Figure 7.6) was found to be the most stable at the DFT level, with relative energy of  $-19.8 \text{ kcal mol}^{-1}$  with respect to the closed-shell C1 configuration. The spin polarisation of the septuplet showed that the 6 unpaired electrons are fully localised on the  $V_g$ -ring (0.88 e and 0.79 e on each  $V_o$  and  $V_p$ , respectively). As the figure shows, the stability of the configurations increases with the number of unpaired electrons. Some of the cases calculated could present Jahn–Teller distortion. However, the reader can take for granted that it would be very small.<sup>21</sup> Calculations were also performed at HF level yielding similar results with the septuplet state (C8) as the most stable one.

Various singlet open-shell configurations were also studied. Within the framework of the DFT, a Broken-symmetry solution<sup>22</sup> might be calculated since it can evenly reproduce electron couplings of this type. Some authors made use of this approach in binuclear complexes and in polyoxometalates.<sup>23-24</sup> The most stable singlet open-shell calculation

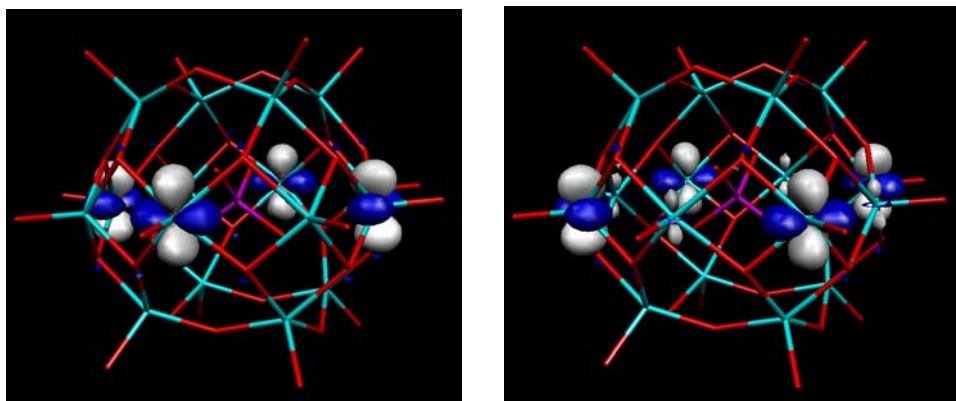


corresponds to a distribution of three alpha spin electrons localised on the four  $V_o$  centres, and the beta partners at  $V_p$  ions as shown in Figure 7.7. This solution was computed to be 0.32 eV above the septuplet. The Mulliken population analysis indicates a spin polarisation of 0.80 alpha and 0.77 beta electrons over  $V_o$  and  $V_p$ , respectively. It was shown that cluster **1** was EPR silent, and therefore it was assumed to be diamagnetic. Present Broken-symmetry calculations prove that an antiferromagnetic coupling of metal electrons would explain the lack of EPR signal mentioned by experimentalists.<sup>14</sup> Nevertheless, it would be desirable that the open-shell state be lower in energy than the septuplet state.



**Figure 7.7.** Schematic view showing the antiparallel coupling (coloured arrows) of the electrons in a singlet open-shell calculation. They are localised over the V-ring (blue polyhedra). Grey spheres represent molybdenum centres.

Figure 7.8 shows the nature of the V-centred metallic orbitals where the 6 electrons are located. Both  $V_o$  and  $V_p$  sites contribute to the same molecular orbital but the spatial parts describing the  $\alpha$  and  $\beta$  electrons are separated.



**Figure 7.8.** Doubly-occupied molecular orbital localised in the V-ring computed with Unrestricted DFT formalism. The left-hand picture corresponds to the spin- $\alpha$ , and the right-hand one to spin- $\beta$ . The pseudo-octahedral V-sites ( $V_o$ ) and the pyramidal positions ( $V_p$ ) do not share the spatial part of this MO.

To fully determine the ground state for this system, it is necessary to carry out a multi-reference calculation for including non-dynamical (or *static*) electron correlation to the wavefunction. With the collaboration of Dr. Coen de Graaf, a *Complete Active Space SCF* (CASSCF) calculation is under way. The active space will include the 8 lowest lying virtual orbitals and the 3 highest occupied orbitals of the closed-shell RHF run. This set of MOs contains the 6 metal electrons located on vanadiums. This calculation requires an enormous computational effort and represents a great challenge. For example, the storage of molecular orbital integrals needs more than 160 Gbytes. Nevertheless, if this test succeeds, new doors will be open to the study of magnetism in POMs, going further than the use of model fragments to represent the whole molecule.<sup>25</sup>

## References and Notes

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