Electronic Supplementary Information

Reconciling valence state with magnetism in mixed-valent polyoxometalates: The case of {VO₂F₂@V₂₂O₅₄} cluster

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1. Details of density functional theory calculations

DFT calculations were carried out using the ADF2016 program.^[1–3] Structural minima were obtained with the BP86 functional^[4] and a Slater-type basis set of triple- ζ + polarisation (TZP)^[5] quality with internal electron shells treated by the frozen (medium) core approximation.^[6] With the BP86-optimized geometries, molecular properties were obtained from B3LYP single points with all-electron TZ2P basis sets and the conductor-like screening model (COSMO)^[7,8] to mimic aqueous solutions (ε = 78.4). Scalar relativistic effects at the Zeroth Order Regular Approximation (ZORA)^[9] level were taken into account throughout this study. The spin-unrestricted formalism for open-shell electronic configurations, taking all unpaired spins parallel in each case, and Grimme's dispersion corrections of D3 generation were employed in all the calculations.^[10–16] Atomic spin densities (ASDs) were obtained with the Bader's electron density partition.^[17]

1.1. Electron distribution

Table S1. ASDs of vanadium atoms for **1a**, **1b** and, **1c** in the $C_{2\nu}$ and C_1 forms. A distinction between the two hemispheres is made. Shaded cells correspond to formally V^V centres.

		$C_{2\nu}$			_	<i>C</i> ₁			
	V atom/ Structure	1a	1b	1c		1a	1b	1c	Number of
	Nr. of electrons	8	7	9		8	7	9	vanadium atom
	Apical	0.95	0.96	0.97	_	0.50	0.45	0.89	1
		0.59	0.33	0.60		0.51	0.46	0.56	2
		0.05	0.05	0.05		0.04	0.04	0.04	3
	Outer	0.59	0.33	0.60		0.63	0.62	0.62	4
F-hemisphere	ring	0.05	0.05	0.05		0.60	0.64	0.15	5
		0.59	0.33	0.60		0.53	0.53	0.53	6
		0.59	0.33	0.60		0.63	0.62	0.59	7
		0.27	0.57	0.59	_	0.63	0.57	0.42	8
		0.27	0.57	0.59		0.06	0.06	0.55	9
		0.27	0.57	0.59		0.55	0.56	0.53	10
	Inner	0.27	0.57	0.59		80.0	0.07	0.64	11
	ring	0.59	0.57	0.60		0.06	0.07	0.54	12
		0.59	0.57	0.60		0.64	0.54	0.34	13
		0.59	0.57	0.60		0.07	0.08	0.64	14
		0.59	0.57	0.60		0.53	0.62	0.48	15
O-hemisphere		0.39	0.06	0.34	_	0.63	0.62	0.62	16
		0.04	0.04	0.05		0.69	0.60	0.17	17
	Outer	0.39	0.06	0.34		0.50	0.45	0.55	18
	ring'	0.04	0.04	0.05		0.04	0.03	0.04	19
		0.39	0.06	0.34		0.63	0.07	0.49	20
		0.39	0.06	0.34		0.52	0.07	0.45	21
	Apical'	0.96	0.94	0.97	_	0.40	0.48	0.87	22



Figure S1. Numbering used in Table S1 to show the distribution of the Bader atomic spin densities (ASDs) in the POV. In the external cage, only vanadium atoms are depicted for clarity. Internal ion: green balls for fluorine, red balls for oxygen.



Figure S2. SOMO 1 and SOMO 2 for species 1a and 1c.

1.2. Basicity studies

1b (7 electrons)



Figure S3. Different viewpoints of the MEP for **1b** (top) and **1a** (bottom). The electrostatic potential values range from -0.33 (blue) to -0.51 (red) for **1b** and -0.42 (blue) to -0.59 (red) for **1a**, thus more negative for the more charged species, as expected.

In addition to the calculation of the MEPs, we further explored protonation in the $\{VO_2F_2@V_{22}O_{54}\}$ structure with one proton. It was found that single-bridge oxygens (A-type), when protonated, allow for two different H orientations that, in principle, may be close in energy. Namely, the H atom can be positioned (*i*) towards the solvent bulk or, (*ii*) towards another bridging oxygen in proximity forming a weak O···H interaction, as indicated in Figure S4a. In order to have rigorous data on this topic, we explored computationally the energetics of the mentioned options. Depending on the model adopted for these calculations, results may seem contradictory. We clarify these aspects below.

Model 1: In the model shown in Figure S4a, with no explicit water molecules included, orientation (ii) is 5 kcal mol⁻¹ more stable than (*i*) thanks to the intramolecular hydrogen bond formed between two A-type oxygens. The process that switches (*i*) and (*ii*) was studied doing a relaxed scan by changing

the dihedral angle shown in Figure S4a (right). A marginal energy barrier of approximately 0.02 eV (0.46 kcal mol⁻¹) was found connecting both orientations.

Model 2: Using a second, more realistic model with one explicit water molecule (Figure S4b), orientations (*i*) and (*ii*) were re-evaluated performing geometry optimisation calculations. It comes out that, at variance with the model 1, orientation (*i*) (in this case, the H is solvated by the explicit water molecule) is 0.1 eV (2.36 kcal mol⁻¹) more stable than orientation (*ii*). Moreover, when a water molecule is situated in sufficient proximity of the H with orientation (*ii*), as in Figure S4c, this H atom leaves its original position and freely adopts orientation (*i*). These results show, therefore, that (*i*) is probably the preferred and only orientation in this POM.



Figure S4. Protonated forms of the POV. a) Protonation Model 1, with no explicit solvent water molecule. Schematic view of the two main orientations, (*i*) and (*ii*), adopted by the H in single-bridge (A-type) oxygens. Shown in the right, the dihedral angle that is varied in the relaxed scan study. b) Protonation Model 2, with one explicit molecule. In form (*ii*) the water molecule tends not to form a hydrogen bond with H if the latter is forced to adopt this orientation. If c) is adopted as starting point for optimisation, it leads spontaneously to form (*i*). d) Conformation of highest energy found in the study of an itinerant proton hopping between nearby bridging oxygens. The structure in the right shows the starting point of this scan, with d_1 and the black arrow showing the distance and the direction, respectively, that are tracked. The concerted deprotonation-protonation process is completed as indicated by d_2 and the blue arrow. In the final step, a new covalent O–H bond is formed (d_2). Red colour is used for oxygen atoms, white for hydrogen and orange for vanadium atoms.

Another process tackled in this analysis is protonation-deprotonation (see Figure S4d). We computed an equilibrium structure in which a monoprotonated POV molecule is solvated (at the H position) by an explicit water molecule. From this initial conformation, a scan of the distance d_1 was done, decreasing it while leaving the rest of the system free for optimisation. The scan tracks the O–H lengthening movement, associated to deprotonation, in the course of which we found an energy barrier of approximately 0.15 eV (~3.5 kcal mol⁻¹) leading to protonation at a nearby oxygen site, indicated with the blue arrow. In this process, distance d_2 decreases freely and concertedly with increasing d_1 . These results suggest that the proton is itinerant across the molecule in aqueous solution, by virtue of the relatively low barriers computed.

2. Details of magnetochemical modelling

2.1. Hamiltonian and coupling schemes

$$H = \sum_{\langle i,j \rangle} J_{ij} \delta_i \delta_j S_i \cdot S_j + \sum_{i,j=1}^N t_{ij} \delta_i (1 - \delta_j) - g \mu_B B \sum_{i=1}^N \delta_i S_i^z \qquad \delta_i = 0, 1 \qquad \sum_{i=1}^N \delta_i = n \quad (1)$$

Since the local coordination of vanadium ions has strongly distorted octahedral symmetry (square pyramid) it is assumed that orbital effects are quenched due to large energy gap between lowest t_{2g} orbitals and thus enforcing at most single occupancy ($\delta_i = 0,1$)^[18] of vanadium sites. The use of a classical electron transfer term in equation (1) is motivated by computational complexity of the fully quantum *t-J* model. It is also possible to use a term accounting for inter-site electron repulsion which seems to be important in smaller compounds,^[19] but since the electron transfer term used by us has a classical form the introduction of a repulsion term which has a similar form would not improve the modelling. Thus the transfer term can be considered as accounting for inter-site repulsion as well. The numbering of sites in (1) depends on the considered species and is different than the numbering in Figure S1.

Three different coupling schemes can be proposed for **1**. The simplest one (I) assumes only three different exchange couplings (and three electron transfer ones) determined by the type of an oxygen bridge: single, single-shared, and double (see the left panel in Figure 3 in the main text). However single and single-shared bridges can be further differentiated on the basis of different angle and distance distribution (Figure S5) giving rise to five J_i (and only four t_i due to the forbidden transfer to the V^{IV} vanadium sites) – coupling scheme II.



Figure S5. Distance between V ions versus V–O–V angles for different kinds of oxide bridges in **1**. For double bridges an average of two V–O–V angles is shown.

Finally, one could also use even further differentiation of the couplings corresponding to the double and single-shared oxygen bridges implied by the oxidation states of the third vanadium ion (besides the two coupled ones) connecting to the bridging oxide^[20,21] (see the left panel in Figure 3 in the main text). This would lead to consideration of eight different exchange and seven electron transfer couplings – coupling scheme III. It should be noted that in scheme III contrary to schemes I and II the values of the couplings are assigned dynamically depending on the distribution of the delocalized electrons. All the coupling schemes are summarized in Table S2.

bond	dist. [Å]	V–O–V angle [°]	I	II	111
single	3.47 – 3.48	153	$J_1 t_1$	$J_1 t_1$	$J_1 t_1$
	3.33 - 3.36	136 - 139	$J_1 t_1$	$J_2 t_2$	$J_2 t_2$
single-shared	3.62 - 3.67	141 - 143	J ₂	J ₃	J ₃ (∀ [∨])
	3.67 – 3.69	155 - 160	$J_2 t_2$	$J_4 t_4$	<i>J</i> ₄ <i>t</i> ₄ (V [∨])
					J₅ t₅ (V ^{IV})
double	2.9 - 3.05	97 -105	$J_3 t_3$	$J_5 t_5$	$J_6 t_6 (V^{\vee})$
					$J_7 t_7 (V^{\vee}/V^{\vee})$
					<i>J</i> ₈ <i>t</i> ₈ (∨ ^{ı∨})
Total number of para	parameters 6 9				15

Table S2. Coupling schemes I - III. In scheme III for single-shared and double bonds in the bracket the oxidation state of a third connecting V ion is given.

2.2. Fits to the magnetic data

Theoretical curves have been obtained by simultaneous fitting of susceptibility and magnetisation curves using the least-squares method coupled to the evolutionary algorithm. The search for optimal Hamiltonian parameters has been conducted in the range [-600 K, 1000 K] for exchange couplings and [-4000 K, 4000 K] for electron transfer couplings. Despite the large size of Hamiltonian matrix (up to almost 6 million x 6 million) susceptibility and magnetisation have been calculated by means of exact diagonalisation. Such calculations were possible because due to the classical transfer term the Hamiltonian matrix could be block-diagonalised with respect to electron distributions. Besides, we exploited the symmetry of the Hamiltonian and of the molecule and used large parallel supercomputers to facilitate the calculations.



Figure S6. The best least squares fits to molar susceptibility (B = 0.1 T) and magnetisation (T = 2 K) for **1a** ($C_{2\nu}$) in coupling schemes I-III. Experimental results are marked by circles.



Figure S7. The best least squares fits to molar susceptibility (B = 0.1 T) and magnetisation (T = 2 K) for **1b** in coupling scheme I and for two symmetries C_{2v} and C_1 . Experimental results are marked by circles.

In order to better estimate the quality of the fits one can use a following measure of a goodness of fit:

$$\Delta = \sqrt{\frac{1}{N_e} \sum_{i=1}^{N_e} \left(\frac{x_i^e - x_i^t}{x_i^e}\right)^2}$$

where $x_i^e(x_i^t)$ stand for experimental (theoretical) results and N_e signifies a number of experimental data points (susceptibility and magnetisation). Typical values of Δ in % for various best fits are presented in Table S3.

Table S3. Relative average distance Δ (in %) between experimental data points and theoretical predictions for various compounds in different coupling schemes and symmetries.

	1a – I, <i>C</i> _{2v}	1a – II, <i>C</i> _{2v}	1a – III, $C_{2\nu}$	1b – I, C _{2v}	1b – I, <i>C</i> ₁	1c – I, <i>C</i> _{2v} , asym. <i>J</i> ₁
Δ [%]	11.21	10.41	8.83	9.37	3.11	2.07
Δ for <u></u> <i>χ</i> [%]	2.51	3.38	4.35	9.45	1.63	0.80
∆ for <i>M</i> [%]	21.86	19.87	15.90	9.13	5.51	3.87

2.3. Distribution of itinerant electrons



Figure S8. Probability of finding an electron at V^{IV}/V^V site in the cage versus temperature for parameters from Table 2. The lower blue curve corresponds to sites 8, 9, 10, 11 in Figure S1.

3. Literature

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