Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Decoding the role of encapsulated ions in electronic and magnetic properties of mixed-valent polyoxovanadate capsules {X@$V_{22}O_{54}$} (X = ClO_4^-, SCN^-, $VO_2F_2^-$): A combined theoretical approach

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XPS analysis of compound 3

X-ray Photoelectron Spectroscopy (XPS) measurements were conducted with a PHI 5000 Versa Probe (Physical Electronics Inc., USA) under ultra-high vacuum conditions. The XPS investigation of compound **3** was performed via fixation of finely powdered **3** on silver conductive paste which was cured without additional heating. Due to potential charging effects caused by the insulating character of **3**, the lowest C 1s binding energy was used as the reference (284.5 eV). In the region between 512.0 eV and 538.0 eV after background subtraction (Shirley fit), three different O 1s species and various V^{IV}/V^{V} (V $2p_{3/2}$ and V $2p_{1/2}$) species were identified. Following previous results[1,2], the V^{IV}/V^{V} ratios were fixed to 8:15 and 9:14 corresponding to $[V^{V}O_2F_2@HV^{IV}_8V^{V}_{14}O_{54}]^{6-}$ and $[V^{V}O_2F_2@H_2V^{IV}_9V^{V}_{13}O_{54}]^{6-}$, respectively. For all signals Gaussian fits were used and the FWHM was limited to 4.0 eV. Furthermore, the distance between the V $2p_{1/2}$ signals was set to the values obtained for the difference of the V $2p_{3/2}$ signals (1.4 eV).

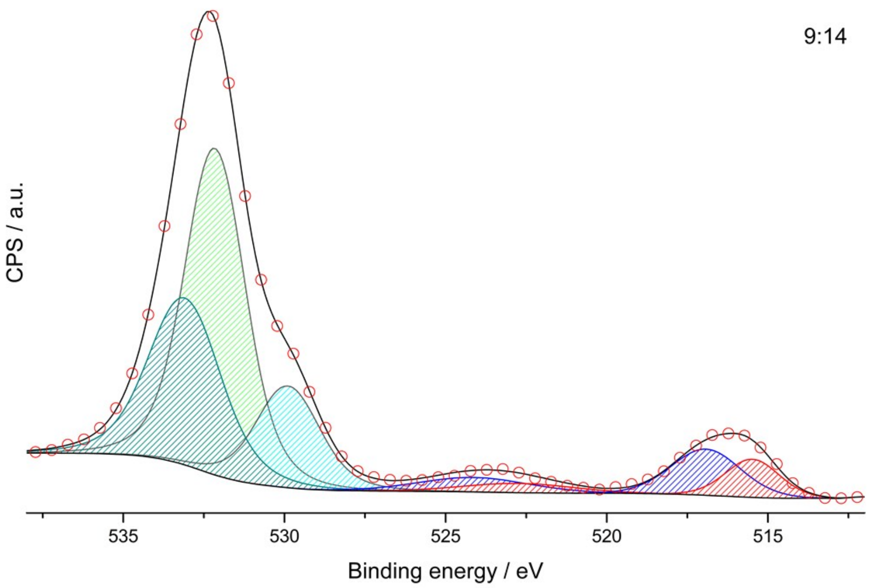
For both fitted V^{IV}/V^{V} ratios the O 1s signals are maintained at 533.1 eV, 532.2 eV and 529.9 eV and can be attributed to $R\text{-}ONO_2$ (ingredient of the Ag conductive paste), alcohols or water and vanadium oxides (V–O–V, V=O, etc.).[3–6] The vanadium signals are detected with the fitted $2p_{1/2}$ peaks at 524.1 eV and 522.7 eV and the $2p_{3/2}$ peaks at 516.9–516.8 eV and 515.5–515.4 eV for V^{V} and V^{IV}, respectively (see Figure S1). The positions of the V 2p signals are in good agreement with the reported values.[5–7]

Due to the fact that the standard deviation (STD) for both fits does not differ significantly (see Table S1), it is impossible to differentiate between the two analysed $V^{IV}:V^{V}$ electron populations 8:15 and 9:14 of compound **3**.

Table S1 Obtained fit parameters for the two fixed $V^{IV}:V^{V}$ ratios 9:14 and 8:15 in compound **3**.

	9:14 fix	**STD[a] = 1.34651**		**8:15 fix**	**STD[a] = 1.37664**	
	Position / eV	FWHM[b] / eV	Area / %	Position / eV	FWHM[b] / eV	Area / %
O 1s	533.1	2.65	26.33	533.1	2.65	26.84
O 1s	532.2	2.22	43.11	532.2	2.22	42.73
O 1s	529.9	2.35	14.22	529.9	2.31	13.88
V $2p_{1/2}$ (5+)	524.1	4.00	3.32	524.1	4.00	3.51
V $2p_{1/2}$ (4+)	522.7	4.00	2.13	522.7	4.00	2.26
V $2p_{3/2}$ (5+)	516.9	2.54	6.63	516.8	2.50	7.03
V $2p_{3/2}$ (4+)	515.5	1.97	4.26	515.4	1.85	3.75

[a] Averaged standard deviation. [b] Full-width at half maximum.



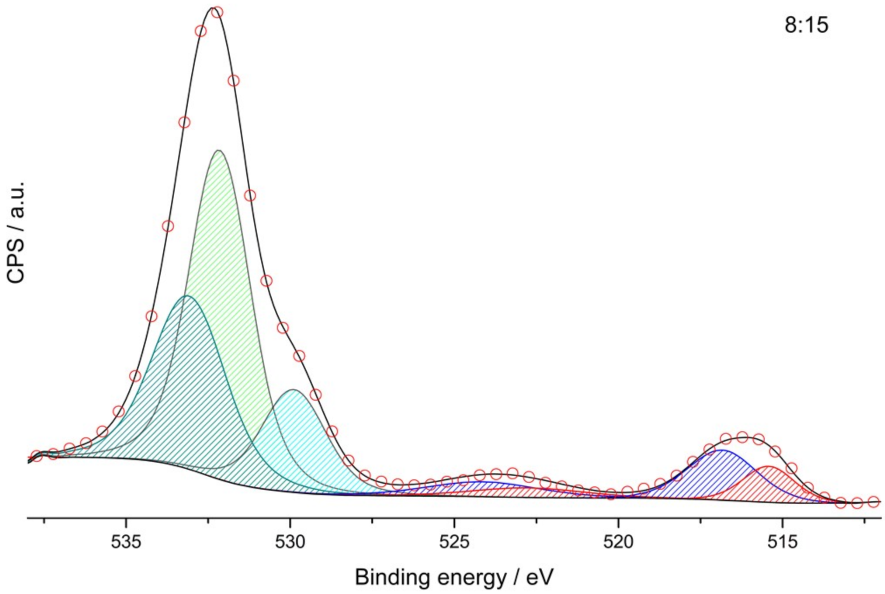


Fig. S1 XPS spectra of compound **3** with fitted O 1s, V $2p_{1/2}$ and V $2p_{3/2}$ signals for the fixed V^{IV}:V^{V} ratios of 9:14 (top) and 8:15 (bottom). Red spheres: exp. data, dark cyan/green/cyan curves: O 1s, blue curves: V^{V}, red curves: V^{IV}, brown line: background, black line: fitted data.

DFT data

Table S2 Vanadium ASDs and region spin densities (RSD, in bold) computed for high symmetry structures (D_{2d} or C_{2v}, see main text) for different numbers of unpaired electrons (**a**-**c**). In the case of structure **2**, we denote the N- or the S-hemisphere, respectively. Shaded cells correspond to formally V^{V} centres (ASD < 0.10).

	Empty cage						X = ClO_4^- **(1)**						X = SCN^- **(2)**						
	b		**a**		**c**		**b**		**a**		**c**		**b**		**a**		**c**		
Region	7 e^-		8 e^-		9 e^-		7 e^-		8 e^-		9 e^-		7 e^-		8 e^-		9 e^-		
Apical	**0.92**		**0.92**		**0.93**		**0.94**		**0.94**		**0.95**		**0.91**		**0.92**		**0.92**		**N**
Outer ring	0.27		0.38		0.57		0.25		0.47		0.56		0.10		0.55		0.57		
	0.06		0.06		0.06		0.05		0.05		0.05		0.06		0.07		0.07		
	0.27	**1.18**	0.38	**1.65**	0.57	**2.40**	0.25	**1.11**	0.47	**1.99**	0.56	**2.36**	0.10	**0.52**	0.55	**2.33**	0.57	**2.42**	
	0.06		0.06		0.06		0.05		0.05		0.05		0.06		0.07		0.07		
	0.27		0.38		0.57		0.25		0.47		0.56		0.10		0.55		0.57		
	0.27		0.38		0.57		0.25		0.47		0.56		0.10		0.55		0.57		
Inner ring	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.58		0.47		
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.58		0.47		
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.58		0.47		
	0.51	**4.09**	0.54	**4.32**	0.50	**3.99**	0.53	**4.22**	0.46	**3.68**	0.51	**4.08**	0.55	**4.37**	0.58	**2.70**	0.47	**3.95**	
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.09		0.51		**S**
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.09		0.51		
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.09		0.51		
	0.51		0.54		0.50		0.53		0.46		0.51		0.55		0.09		0.51		
Outer ring	0.27		0.38		0.57		0.25		0.47		0.56		0.35		0.60		0.57		
	0.06		0.06		0.06		0.05		0.05		0.05		0.06		0.06		0.06		
	0.27	**1.18**	0.38	**1.65**	0.57	**2.40**	0.25	**1.11**	0.47	**1.99**	0.56	**2.36**	0.35	**1.50**	0.60	**2.52**	0.57	**2.42**	
	0.06		0.06		0.06		0.05		0.05		0.05		0.06		0.06		0.06		
	0.27		0.38		0.57		0.25		0.47		0.56		0.35		0.60		0.57		
	0.27		0.38		0.57		0.25		0.47		0.56		0.35		0.60		0.57		
Apical	**0.92**		**0.92**		**0.93**		**0.94**		**0.94**		**0.95**		**0.93**		**0.90**		**0.93**		

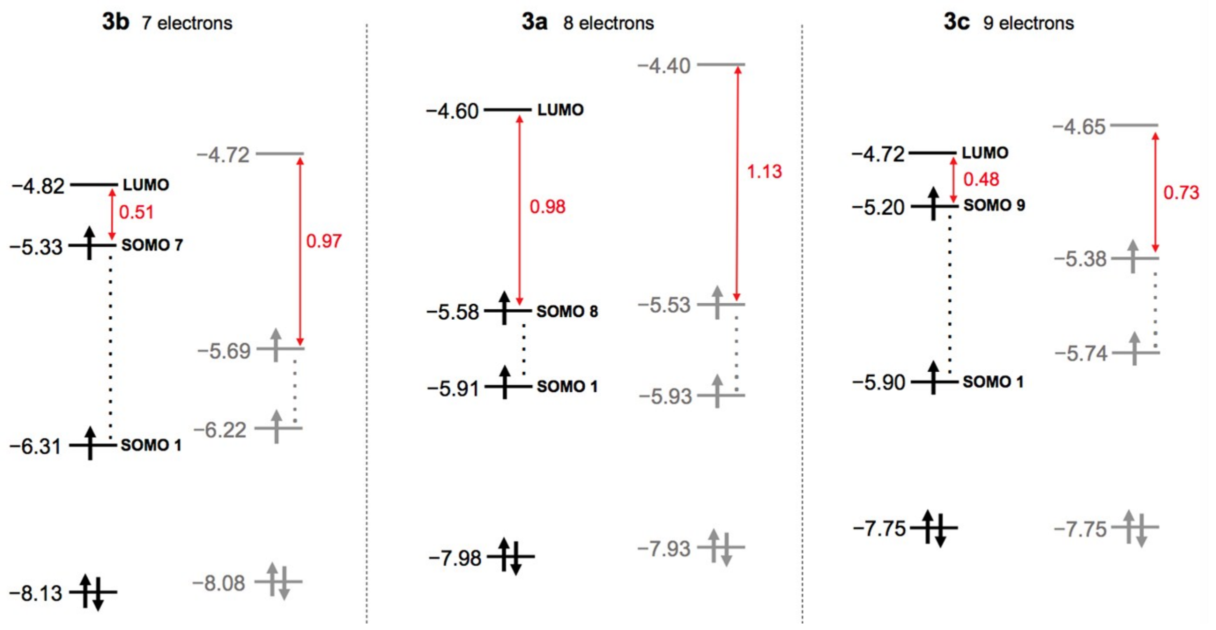


Fig. S2 Electronic structure of compound **3** (X = $VO_2F_2^-$). Computed SOMO-LUMO energy gaps (red) and orbital energies in high (black) and low (grey) symmetries are shown. Values are given in eV.

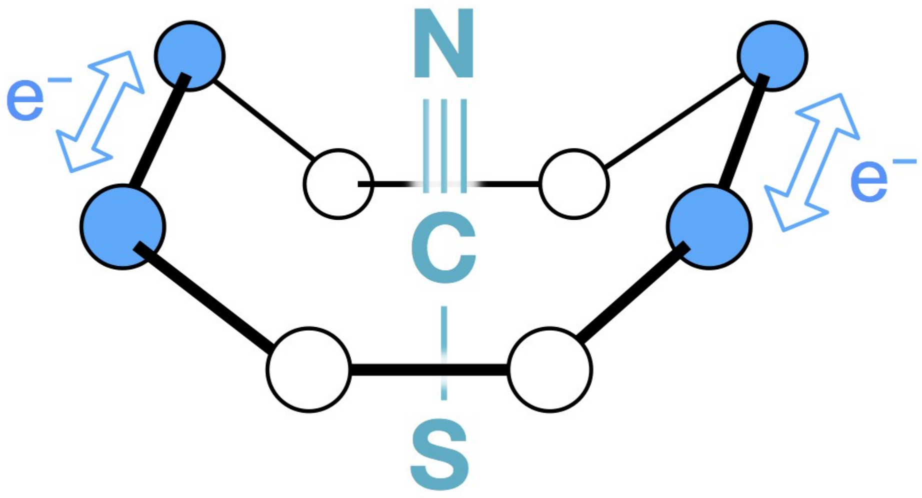


Fig. S3 Schematic view of the inner V_8 ring of the $[SCN@V_{22}O_{54}]^{8-}$ structure, **2a**. Each couple of neighbouring blue V atoms share one unpaired electron, whereas the white V atoms possess only a residual fraction of an electron. The orientation of the SCN guest is shown.

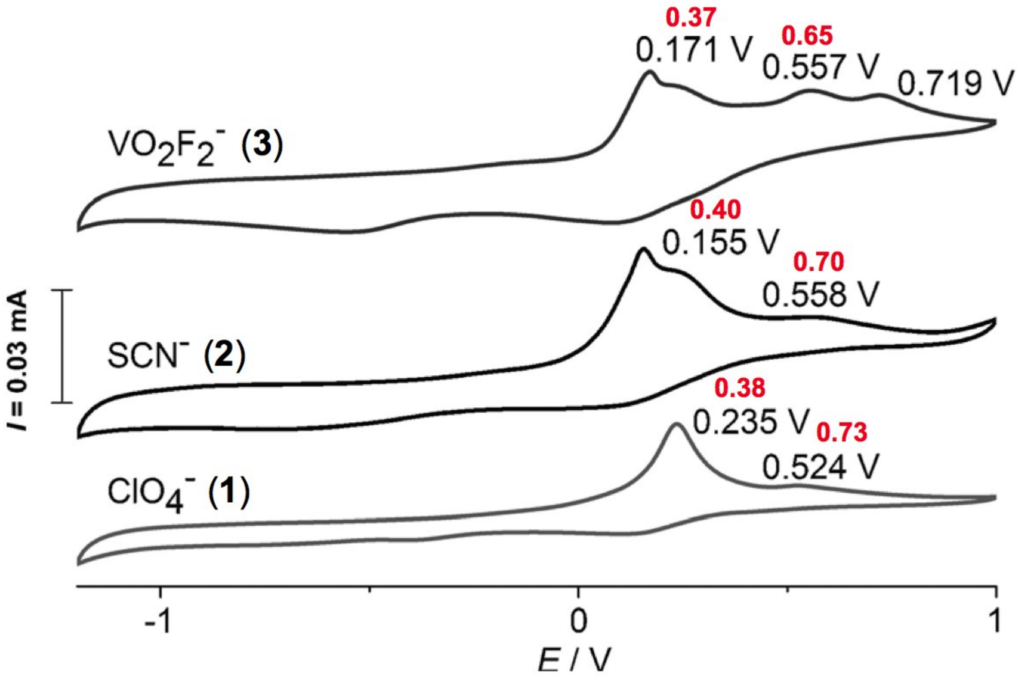


Fig. S4 Cyclic voltammograms of **1**–**3** with a scan rate of 25 mV s^{-1} versus a Ag/AgCl reference electrode. The theoretical values are indicated in red.

Magnetochemical data

Theoretical values of susceptibility and magnetisation have been obtained by exact diagonalisation of Hamiltonian (1) (in the main text). Due to a large size of the molecules considered the maximal size of the Hamiltonian matrix can reach even 16 mln x 16 mln (for **1c** in C_2 symmetry). Direct exact diagonalisation of such large matrices is practically impossible. However a classical transfer term does not mix different electron distributions and therefore it is possible to block-diagonalise a Hamiltonian matrix with respect to the electron distribution. Thus, instead of diagonalizing one very large matrix it is enough do diagonalise many smaller matrices of a maximal size not larger than 512 x 512 (for **c** compounds – with 9 valence electrons). Exploiting the symmetry of the molecules equivalent electron distributions were determined to avoid superfluous calculations. For each non-equivalent electron distribution the speed of diagonalisation was additionally improved by treating separately non-interacting electron clusters. Finally each cluster Hamiltonian was block-diagonalised with respect to a total magnetisation (possibility arising from the symmetry of the Hamiltonian). Thus, the largest matrix directly diagonalised (using lapack package) had a dimension of 126 x 126. Such a computational scheme is ideal for implementation at large parallel computers since their power can be effectively used. Therefore the calculations were parallelised at about 300 computing cores.

The fitting procedure requires many diagonalisations to be performed for different values of parameters. To optimise this process, which is especially demanding due to a large number of fitting parameters, an evolutionary algorithm has been employed.[8,9] In each run 20000 steps have been made with population of 20 individuals. To improve the speed and precision of the algorithm a “roulette” selection function, a decreasing mutation rate, an arithmetic cross over and scaling of the cost function have been implemented.

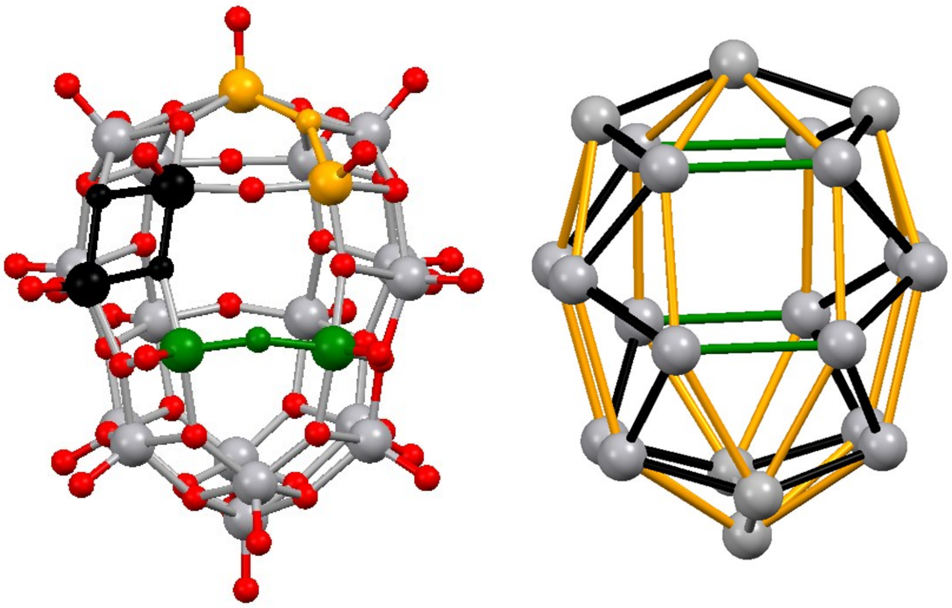


Fig. S5 Left: Examples of vanadium ions connected by three types of oxygen bridges: double (black), single (green), single-shared (orange). Remaining atoms: V (grey), O (red). Guest anions are omitted. Right: All possible exchange paths for **1**, **2** and **3**: J_1 (green), J_2 (orange), J_3 (black). Grey spheres stand for V centres. Oxygens and guest anions are omitted.

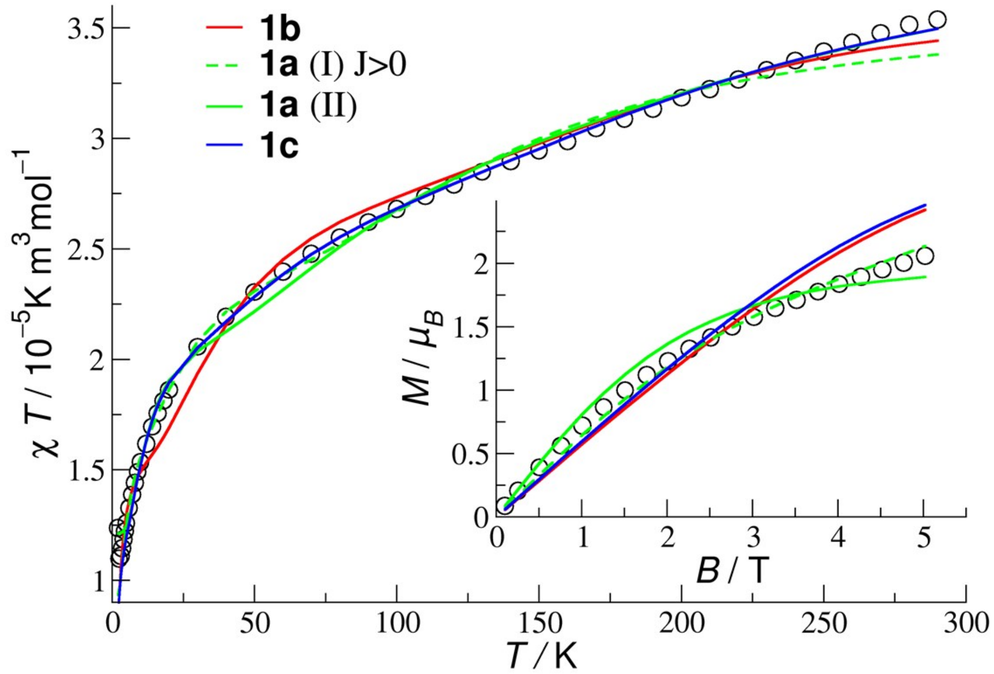


Fig. S6 Fits for **1** in symmetry C_2 with different number of valence electrons. Circles stand for the experiment. T = 2 K for M and B = 0.1 T for χ.

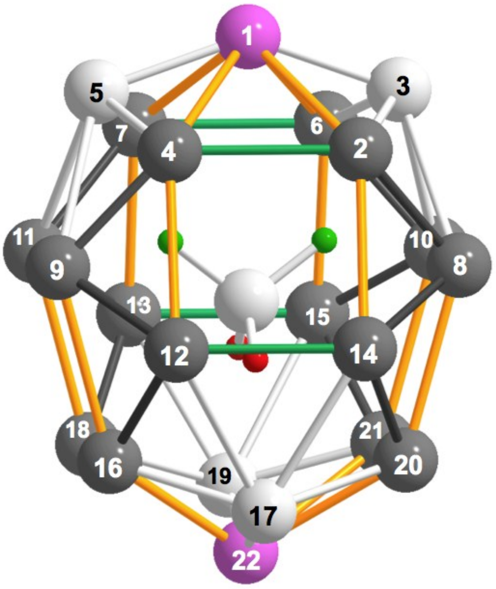


Fig. S7 Numbering of vanadium sites in the cage used in some figures in the main text. In the external cage only vanadium atoms are depicted for clarity. Internal ion ($VO_2F_2^-$): green balls for fluorine, red balls for oxygen.

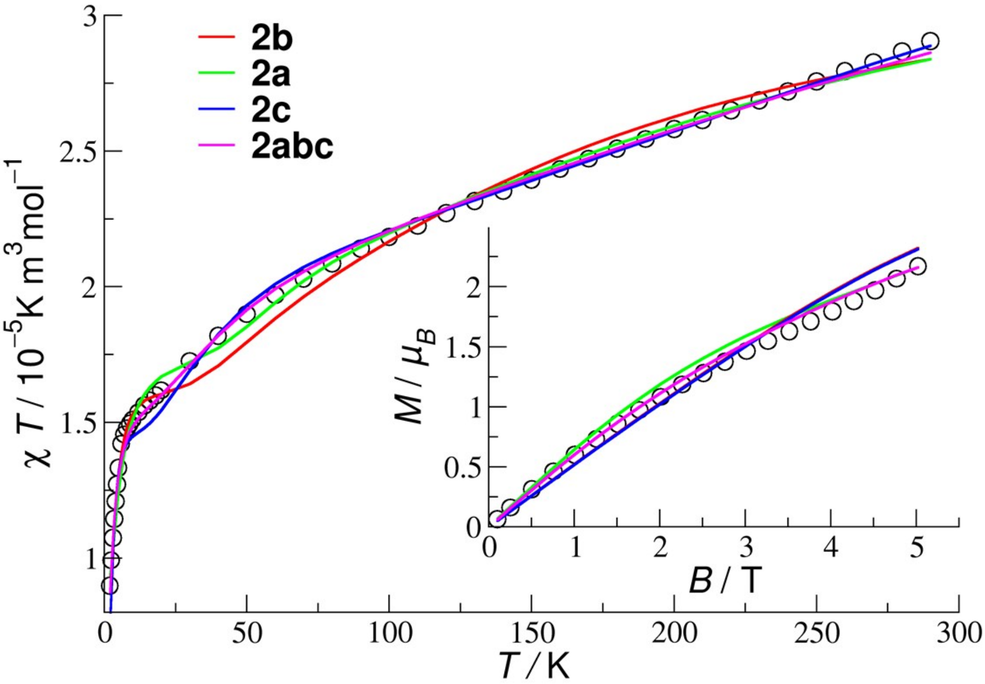


Fig. S8 Fits for **2** in symmetry C_2 with different number of valence electrons. Circles stand for the experiment. T = 2 K for M and B = 0.1 T for χ.

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 and symmetries. The best fits used for analysis are marked in orange.

	1a (I), C_2	**1a** (II), C_2	**1b**, C_2	**1c**, C_2	**2a**, C_{2v}	**2b**, C_{2v}	**2c**, C_{2v}	**2abc**, C_{2v}
Δ [%]	6.24	5.36	10.89	10.34	4.81	6.33	6.42	2.19
Δ for χ [%]	4.58	2.90	6.45	5.72	2.67	3.82	3.87	1.32
Δ for M [%]	8.74	8.45	16.73	16.20	7.52	9.68	9.81	3.34

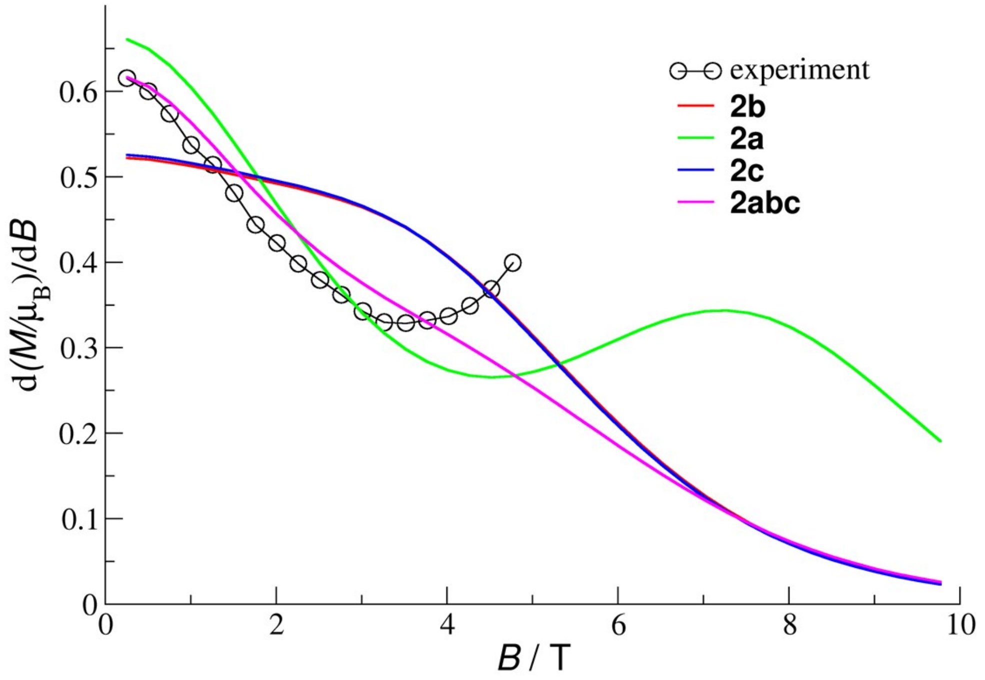


Fig. S9 Derivative of magnetisation with respect to magnetic field for **2**. Minima correspond to inflection points in magnetisation profiles. The curves for **2b** and **2c** almost coincide. T = 2 K.

References

1 K. Y. Monakhov, O. Linnenberg, P. Kozłowski, J. van Leusen, C. Besson, T. Secker, A. Ellern, X. López, J. M. Poblet and P. Kögerler, Supramolecular Recognition Influences Magnetism in $[X@HV^{IV}_8V^{V}_{14}O_{54}]^{6-}$ Self-Assemblies with Symmetry-Breaking Guest Anions, *Chem. - A Eur. J.*, 2015, **21**, 2387–2397.

2 P. Kozłowski, A. Notario-Estévez, C. de Graaf, X. López and K. Y. Monakhov, Reconciling the valence state with magnetism in mixed-valent polyoxometalates: the case of a $\{VO_2F_2@V_{22}O_{54}\}$ cluster, *Phys. Chem. Chem. Phys.*, 2017, **19**, 29767–29771.

3 C. D. Wagner, D. A. Zatko and R. H. Raymond, Use of the Oxygen KLL Auger Lines in indentification of Surface Chemical States by Electron Spectroscopy for Chamical Analysis, *Anal. Chem.*, 1980, **52**, 1445–1451.

4 A. Swift, A. J. Paul and J. C. Vickerman, Investigation of the surface activity of corrosion inhibitors by XPS and time-of-flight SIMS, *Surf. Interface Anal.*, 1993, **20**, 27–35.

5 G. Silversmit, D. Depla, H. Poelman, G. B. Marin and R. De Gryse, Determination of the V2p XPS binding energies for different vanadium oxidation states (V^{5+} to V^{0+}), *J. Electron Spectros. Relat. Phenomena*, 2004, **135**, 167–175.

6 O. Linnenberg, M. Moors, A. Solé-Daura, X. López, C. Bäumer, E. Kentzinger, W. Pyckhout-Hintzen and K. Y. Monakhov, Molecular Characteristics of a Mixed-Valence Polyoxovanadate $\{V^{IV/V}_{18}O_{42}\}$ in Solution and at the Liquid−Surface Interface, *J. Phys. Chem. C*, 2017, **121**, 10419–10429.

7 J. Mendialdua, R. Casanova and Y. Barbaux, XPS studies of V_2O_5, V_6O_{13}, VO_2 and V_2O_3, *J. Electron Spectros. Relat. Phenomena*, 1995, **71**, 249–261.

8 Z. Michalewicz, *Genetic Algorithms + Data Structures = Evolution Programs*, Springer-Verlag, Berlin Heidelberg, 1996.

9 D. A. Coley, *An Introduction to Genetic Algorithms for Scientists and Engineers*, World Scientific, 1999.