Electronic Supplementary Information

Electronic Versatility of Vanadium in Tris-chelates with Redox-Active Ligands

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Experimental Section

Synthesis of Complexes. All air-sensitive materials were manipulated using standard Schlenk techniques or a glovebox. The complexes [V(dbcat)$_3$] and Na[V(dbcat)$_3$] (dbcat^{2-} = 3,6-di-*tert*-butylcatecholate) were synthesised according to literature procedures.[1,2]

X-ray Absorption Spectroscopy. All data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 400 mA. Vanadium K-edge XAS data were measured using the focused 20-pole wiggler beam line 7-3. A Si(220) monochromator was utilised for energy selection and a harmonic rejection mirror was present to minimise higher harmonic components in the X-ray beam. Powder samples were prepared as a dilute matrix in boron nitride, pressed into a pellet and sealed between 38μm Kapton tape windows in a 1 mm aluminium spacer and maintained at 10 K during data collection by using an Oxford Instruments CF1208 continuous flow liquid helium cryostat. Data were measured in the transmission mode. A 30-element solid state Ge detector was utilised for the detection of fluorescence from solution samples. Internal energy calibrations were performed by simultaneous measurement of the reference foil places between a second and third ionisation chamber with the inflection point assigned at 5465 eV. Data represent four scan averages and were processed by fitting a second-order polynomial to the pre-edge region and subtracting this background from the entire spectrum. A three-region cubic spline was used to model the smooth background above the edge. The data were normalised by subtracting the spline and normalizing the post-edge to 1.0.

EPR Spectroscopy. Continuous wave X-band EPR spectra was recorded on a Bruker ELEXSYS E500 spectrometer. The spectra were simulated with the Bruker XSOPHE suite.[3] The fluid solution spectrum taken from ref. 2 was simulated using a spin Hamiltonian of the form $\hat{H} = g\cdot\mu_B\cdot B\cdot S + \sum a\cdot S\cdot I$; the other parameters have their usual meanings. A satisfactory fit was achieved using a Lorentzian lineshape with molecular tumbling accommodated by the isotropic liquids model given by $\sigma_v = a + bM_I + cM_I^2 + dM_I^3$ (Fig. S1).[4] The frozen solution spectrum was simulated following the spin Hamiltonian $\hat{H} = \mu_B\cdot\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$, where **g** and **A** are the 3 × 3

electron Zeeman and magnetic hyperfine interaction matrices, respectively. A Gaussian lineshape was employed to model the linewidth variation.

Calculations. The program package ORCA was used for density functional theory (DFT) calculations.[5] Geometry optimisation employed the BP86 generalised gradient approximation functional;[6] single-point calculations on optimised and crystallographic coordinates (with optimised hydrogen atoms) used the hybrid B3LYP functional.[7] The scalar relativistically recontracted ZORA-def2-TZVPP basis set as used for all atoms.[8] Auxiliary basis sets used to expand the electron density in the calculations were chosen to match the orbital basis. The RIJCOSX algorithm was used to speed the calculation of Hartree–Fock exchange.[9] Increased integration accuracy was applied to the vanadium (grid = 7) atom. Calculations included the zeroth-order regular approximation (ZORA) for relativistic effects[10] as implemented by van Wüllen.[11] The self-consistent field calculations were tightly converged (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the charge density, and 1×10^{-7} in the maximum element of the DIIS[12] error vector). The geometry was converged with the following convergence criteria: change in energy $<10^{-5}$ E_h, average force $<5 \times 10^{-4}$ E_h $Bohr^{-1}$, and the maximum force 10^{-4} E_h $Bohr^{-1}$. The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints.

The broken symmetry (BS) approach to describe computational results for all complexes.[13] The system divided into two fragments. The notation BS(m,n) refers then to a broken symmetry state with m unpaired α-spin electrons essentially on fragment 1 and n unpaired β-spin electrons localized on fragment 2. In each case, fragments 1 and 2 correspond to the two metal ions. In this notation the standard high spin, open-shell solution is written as BS(m+n,0). The BS(m,n) notation refers to the initial guess to the wavefunction. The variational process does, however, have the freedom to converge to a solution of the form BS(m−n,0) in which effectively the n β-spin electrons pair up with $n < m$ α-spin electrons on the partner fragment. Such a solution is then a standard $M_S \approx (m-n)/2$ spin-unrestricted Kohn-Sham solution. As explained elsewhere,[14] the nature of the solution is investigated from the corresponding orbital transformation (COT) which, from the corresponding orbital overlaps, displays whether the system should be described as a spin-coupled or a closed-shell solution. The exchange coupling constants J were obtained from broken symmetry solution using eq. S1,[15] and assuming the spin-Hamiltonian eq. S2 is valid,

$$J = \frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}} \quad \text{(S1)}$$

$$\hat{H} = -2J\hat{S}_A \cdot \hat{S}_B \quad \text{(S2)}$$

where E_{BS} is the energy of the broken symmetry solution, E_{HS} is the energy of the high spin state, $\langle \hat{S}^2 \rangle_{HS}$ is the expectation value of $\hat{S}^2$ operator for the high spin state, $\langle \hat{S}^2 \rangle_{BS}$ is the expectation value of $\hat{S}^2$ operator for the broken symmetry solution, and $\langle \hat{S}^2 \rangle_{HS}$ is the expectation value of $\hat{S}_A{}^2$ and $\hat{S}_B{}^2$ are local spin operators.

Time-dependent (TD-DFT) calculations of the vanadium K-pre-edges were conducted as previously described.[16,17,18] TD-DFT calculations[18,19] were performed allowing for only transitions from the vanadium 1s orbital. The absolute calculated transition energies are consistently underestimated because of shortcomings in the ability of DFT to model potentials near the nucleus. This results in the deep 1s orbitals being too high in energy relative to the valence, thus requiring a constant shift for a given absorber.[16] It was established that constant shift of +38.87 eV was required for this level of theory. Plots were obtained using "orca_mapspc" with a line broadening of 1.0 eV. Molecular orbitals and spin density maps were visualised via the programme Molekel.[20]

The multireference ground state composition of the complexes was examined using the state-averaged complete active space self-consistent field (SA-CASSCF) method[21] with the def2-TZVP basis set for all atoms. The ligand substitution was modified from *tert*-butyl to methyl (formulated $[V(dmcat)_3]$ and $[V(dmcat)_3]^{1-}$) to speed up the calculation. For charge-neutral complexes, the CASSCF(9,10) (nine electrons in ten active orbitals) calculation was averaged over 10 doublet states; for monoanionic $[V(dmcat)_3]^{1-}$, a CAS(10,10) was averaged over 10 singlet states. The NEVPT2 calculations were performed on each reference space.[22] In the case of the CASSCF/NEVPT2 method, the matrix elements are obtained with the CASSCF wavefunctions and only the diagonal energies contain the dynamic correlation brought in by the NEVPT2 procedure.

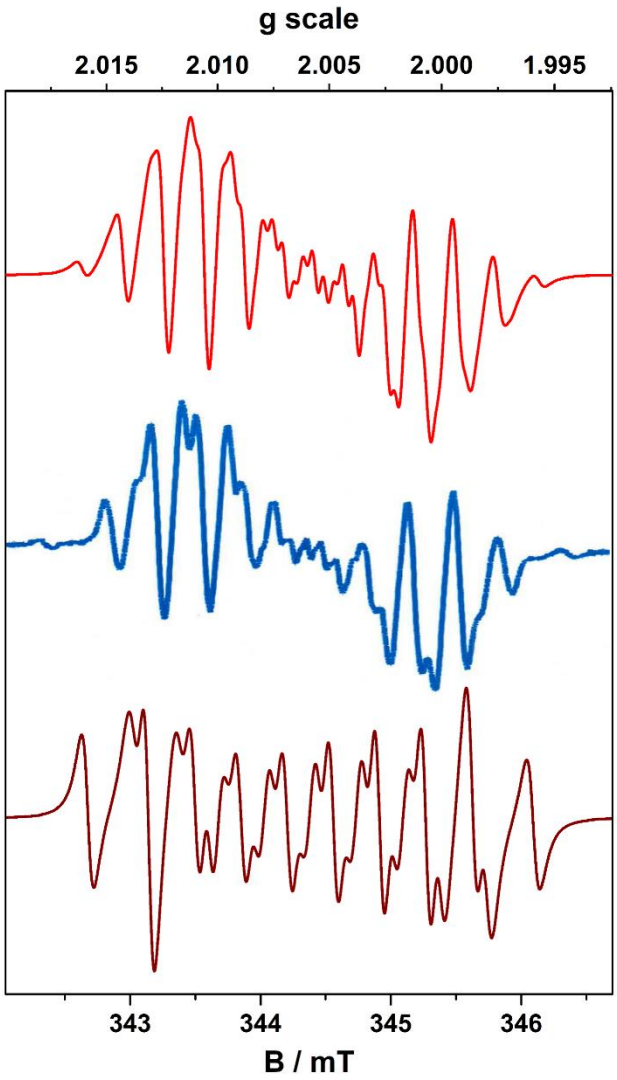

Fig. S1 Comparative simulations of the X-band EPR spectrum of [V(dbcat)$_3$] recorded at toluene solution at ambient temperature. The experimental data shown in the centre (blue) was taken from ref. 2. The top simulation for g_{iso} = 2.0058 gave isotropic hyperfine coupling constants for coupling to the ^{51}V nucleus of $–2.18 \times 10^{–4}$ cm$^{–1}$ and six protons of $2.92 \times 10^{–4}$ cm$^{–1}$ from three dbcat ligands (red). The spectral profile was reproduced using the Kivelson isotropic liquids model $\sigma_v = a + bM_I + cM_I^2 + dM_I^3$, with the best fit achieved for a = 0.85, b = 0.04, c = –0.004, d = –0.004. The bottom simulation for g_{iso} = 2.0058 uses the hyperfine coupling constants for coupling to the ^{51}V nucleus of 3.47 G and two protons at 4.53 G, assuming a localised unpaired spin on one dbcat ligand, as reported in ref. 2 (burgundy).

Table S1 Comparison of *g*- and *A*-values[a]

Complex	g_{iso}	g_x	g_y	g_z	$\langle g \rangle$ [b]	A_{iso}	A_{xx}	A_{yy}	A_{zz}	$\langle A \rangle$ [c]	**ref**
$[V(dbcat)_3]$	2.0058	2.014	2.017	2.009	2.013	–2.18	2.0	–13.9	2.0	–3.3	this work
$[V(Cl_4cat)_3]$	2.0058					~–2 [d]					1
$[V(35\text{-}dbcat)_3]$	2.004					~–2 [d]					23
$[V(bpy)_3]$	1.983	1.981	1.981	1.988	1.983	–73.5	–86.0	–86.0	–48.0	–73.3	24
$[V(^tbpy)_3]$ [e]	1.983	1.981	1.992	1.993	1.985	–77.9	–96.3	–96.3	–41.0	–77.9	24
$[V(edt)_3]$	1.990	1.988	1.989	1.990	1.989	–57.5	–84.0	–81.0	–8.0	–57.7	18
$[V(pdt)_3]$ [f]	1.991	1.989	1.991	1.993	1.991	–57.2	–83.0	–80.5	–5.0	–56.2	18

[a] Value in $\times 10^{-4}$ cm^{-1}; the sign is negative owing to the dominant Fermi-contact contribution. [b] $\langle g \rangle = (g_x + g_y + g_z)/3$. [c] $\langle A \rangle = (A_{xx} + A_{yy} + A_{zz})/3$. [d] Estimated from experimental value of 2.1 G in toluene. [e] ^{t}bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine. [f] pdt = 1,2-diphenyl-1,2-ethenedithiolate.

Table S2 Hydrogen-optimised coordinates of [V(dbcat)$_3$]

V	0.00222191039063	-0.00000002798449	0.00000031158779
O	-1.12965804268648	-1.10951438703271	0.98755324694831
O	-0.03412810922838	-1.50759434451131	-1.15325620411082
O	1.52121186897054	0.73992030482918	-1.01444166659049
C	-1.12856803813261	-2.39576558320075	0.64686631464325
C	-0.52954807882712	-2.61673231728852	-0.62223319615581
C	-0.44722808024390	-3.89410657615810	-1.20506837018665
C	-1.03569803898488	-4.88223896066231	-0.44852180873427
C	-1.62090798626812	-4.67288190530074	0.80556201222735
C	-1.67360799818067	-3.44088571066730	1.40913595875953
C	0.29101188228260	-4.12450441946237	-2.52518066658936
C	0.26193189126296	-5.61292768206964	-2.93113063414823
C	-0.37052816485230	-3.31630512378215	-3.64992048148381
C	1.75766187837701	-3.70688457493931	-2.37663672301556
C	-2.20247795773632	-3.18428367462297	2.83726373050430
C	-3.45103797568365	-2.31125379478904	2.75645241878581
C	-2.59685791628872	-4.52245961721492	3.50734761176552
H	6.02551164749723	0.74167741533076	-0.94747160382632
H	6.02551174512414	-0.74167732528294	0.94747181024601
H	-1.02444374138348	-5.90648721227522	-0.82266952857380
H	-2.02214126630029	-5.54357594676456	1.32262196914111
H	-1.02444165703695	5.90648600589470	0.82267413568850
H	-2.02214111413012	5.54358503262396	-1.32262202119038
C	-1.12293794226208	-2.54278629680401	3.68400058432092
C	2.70889188585364	0.43262931266879	-0.59172620714932
C	3.91710186435561	0.88471619694631	-1.17422639738861
C	5.05244188837624	0.43994936792324	-0.56211637242202
C	3.89438181247356	1.78376361532143	-2.41602368730954
C	3.23158178360613	1.02327644376471	-3.57407148716978
C	5.32523179240608	2.16180727906255	-2.84064371794181
C	3.13707180826927	3.08050635384397	-2.11351259820577
H	-1.73603061511163	-5.20192950842925	3.58793030897665
H	-3.39823067035245	-5.03570588518278	2.95737116859858
H	-2.96364366833366	-4.32349360591007	4.52445122764780
H	1.84816450254319	-2.64020929076105	-2.13335404232232
H	2.25047545553125	-4.28219405892676	-1.57944845867273
H	2.29958011892337	-3.89041736812424	-3.31662260194587
H	-0.35380049376472	-2.24115752536332	-3.42927854317249
H	0.16329590479922	-3.48138086791533	-4.59792170741545
H	-3.23056470128105	-1.33892268576808	2.29679466995221
H	-3.85324007006105	-2.12537587303113	3.76407525290690
H	-4.23388787117310	-2.80241003255030	2.16104245695882
H	5.85083495303866	2.71932701211703	-2.05104091607485
H	5.92295801835931	1.27600241390808	-3.10057335273142
H	5.28109118959782	2.80502508771738	-3.73131655085084
H	3.78833060371122	0.10400357346146	-3.80712300044938
H	2.19772350797393	0.74814096668428	-3.33419253752494
H	3.62372766196313	3.63268180567241	-1.29600761264523
H	3.12789542283994	3.72727848851640	-3.00377554417894
H	2.09736930439759	2.88565617386202	-1.82405563629533
H	3.21849133265671	1.65284055720583	-4.47664907000699
H	-1.41709772183239	-3.62430191355435	-3.78921440965839
H	0.79694555603480	-5.73821560022051	-3.88253182831098
H	0.75380249401200	-6.25056323520310	-2.18206048610624
H	-0.81119283572928	-1.57094091662479	3.28214325896695
H	-0.23332503175704	-3.18696637120224	3.73895557432065
H	-0.76624510359379	-5.97590799383115	-3.07392107875941
H	-1.48967352319474	-2.38355791671339	4.70928538094664
O	1.52121195291015	-0.73992032559503	1.01444218975477
C	2.70889193483739	-0.43262930591427	0.59172665212607
C	3.91710196216542	-0.88471616219290	1.17422676282176
C	5.05244193558037	-0.43994930686028	0.56211666310867
C	3.89438201287257	-1.78376358109389	2.41602405423893

C	3.23158204262323	-1.02327642489604	3.57407189773493
C	5.32523202952102	-2.16180721167687	2.84064399066987
C	3.13707201880233	-3.08050633716618	2.11351301499414
H	5.85083509686488	-2.71932709933943	2.05104124519396
H	5.92295822437601	-1.27600222240898	3.10057324241728
H	5.28109158331051	-2.80502478993799	3.73131699247186
H	3.78833054597496	-0.10400326687879	3.80712303229356
H	2.19772356183970	-0.74814146768689	3.33419325620373
H	3.62372783949350	-3.63268172719559	1.29600797946090
H	3.12789562754182	-3.72727857979003	3.00377591140796
H	2.09736951270484	-2.88565610358740	1.82405608399277
H	3.21849232016939	-1.65284037781845	4.47664958891514
O	-1.12965813362772	1.10951430483621	-0.98755254933741
O	-0.03412806817728	1.50759428771900	1.15325682968427
C	-1.12856813624145	2.39576550096357	-0.64686561700445
C	-0.52954809840891	2.61673224900537	0.62223385433453
C	-0.44722809107261	3.89410651005917	1.20506902301548
C	-1.03569812191582	4.88223888122212	0.44852249989181
C	-1.62090814715718	4.67289181307513	-0.80556126859260
C	-1.67360817066869	3.44088561638606	-1.40913522413692
C	0.29101195290934	4.12450437042397	2.52518127088869
C	0.26193195450060	5.61292763241741	2.93113124016888
C	-0.37052800183981	3.31630505974901	3.64992112934710
C	1.75766194880103	3.70688455944265	2.37663723101333
C	-2.20247821832806	3.18428356783359	-2.83726296100734
C	-3.45103821012509	2.31125365794012	-2.75645157000121
C	-2.59685825115246	4.52245951484118	-3.50735681186188
H	-1.73603002898322	5.20192778150467	-3.58794247564019
H	-3.39823097665304	5.03570917922759	-2.95738344188378
H	-2.96364311852836	4.32348608344539	-4.52445908914745
C	-1.12293824239522	2.54278621771131	-3.68399988622025
H	1.84816454019525	2.64020913223643	2.13335510023470
H	2.25047527952126	4.28219362131978	1.57944850643086
H	2.29958040364639	3.89041788680520	3.31662286658550
H	-0.35380041272495	2.24115749580893	3.42927904139363
H	0.16329620502631	3.48138070821092	4.59792228998505
H	-3.23056514517397	1.33892350513510	-2.29679163377947
H	-3.85323919975294	2.12537359088911	-3.76407444402392
H	-4.23388881539885	2.80241083212987	-2.16104333089968
H	-1.41709752465611	3.62430188453504	3.78921520613491
H	0.79694578466330	5.73821541137373	3.88253235556155
H	0.75380245597117	6.25056323457204	2.18206108503840
H	-0.81119217065098	1.57094114282068	-3.28214239212901
H	-0.23332576332911	3.18696681457300	-3.73895542057328
H	-0.76624499842712	5.97590793814307	3.07392190327340
H	-1.48967395265059	2.38355702645334	-4.70928452912904

Table S3 Geometry-optimised coordinates of [V(dbcat)$_3$]

V	0.55137301611858	-0.00001712875322	-0.00002451421505
O	-0.63851947216095	-1.04859257112504	1.04492458117752
O	0.32048530990392	-1.51265793123861	-1.14235050433043
O	2.02428772640995	0.60175312035971	-1.06078467726062
C	-0.97409548539966	-2.25115680283066	0.59719749601259
C	-0.45032600385378	-2.50261621087356	-0.71383261300078
C	-0.73177906325264	-3.69228689032873	-1.42110777038358
C	-1.52658202035346	-4.60588676670727	-0.72605979251814
C	-2.01700939903733	-4.37021044247341	0.57648840604662
C	-1.76213410517133	-3.19659147451680	1.28841618324704
C	-0.18607676782608	-3.92274201484725	-2.82920265204693
C	-0.62976618207153	-5.28082018571557	-3.39202401546529
C	-0.70822861180776	-2.80946140229857	-3.76465287844379
C	1.35811298545888	-3.88911389277139	-2.79300444694230
C	-2.27107311694432	-2.92052123269495	2.70226067369465
C	-3.17637074841693	-1.66875600685350	2.68535528369954
C	-3.08367127947344	-4.10150359192178	3.25242232780766
H	6.57676812727225	0.53906845769767	-1.08306041473998
H	6.57674936764795	-0.53896106298393	1.08318185456506
H	-1.78612690590196	-5.55213823707357	-1.19820758360025
H	-2.62208916157753	-5.15082388269394	1.03639327700730
H	-1.78604085098796	5.55212914341726	1.19822300363661
H	-2.62206544992926	5.15082542822632	-1.03635566059399
C	-1.06589084258016	-2.67852542487193	3.63793681919496
C	3.24818394365077	0.33246523472798	-0.63630095411390
C	4.44372796810721	0.65950223941894	-1.31504471538322
C	5.61121316374594	0.31568405621736	-0.63197030334500
C	4.41465175640394	1.33673824609066	-2.68448111944914
C	3.65085701320842	0.43423672393074	-3.68000333328438
C	5.83058691571881	1.57548757828745	-3.22953521194820
C	3.70032277551444	2.70318844841491	-2.56833588856325
H	-2.48145353675957	-5.02005861953260	3.30807108285275
H	-3.97356428955822	-4.30605916690105	2.63977742147920
H	-3.42622685289198	-3.86410282187944	4.26939408993097
H	1.72896308860624	-2.91853568909172	-2.44405214748297
H	1.74843221718189	-4.67106550925546	-2.12584740299120
H	1.75787478081348	-4.06966228815585	-3.80229718298493
H	-0.39889251071578	-1.81805534459696	-3.41380863358237
H	-0.31045544847577	-2.95568234957489	-4.77999245005436
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H	-3.54167611323532	-1.45789216105864	3.70129669544546
H	-4.04691421733711	-1.82928781138007	2.03328673381429
H	6.41251231059415	2.24204065435193	-2.57642970442567
H	6.38635543545469	0.63449206117607	-3.34963748982726
H	5.76320218741025	2.05278658138522	-4.21778845597140
H	4.15742314453823	-0.53518902466681	-3.79127550890253
H	2.62321951748174	0.25068804831005	-3.34326440240482
H	4.22850366834575	3.35653359540351	-1.85891208397490
H	3.68827568033323	3.19979527524943	-3.54993233898714
H	2.66467229914265	2.58621752237996	-2.22751480573369
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H	-1.80627115479894	-2.83198184092571	-3.81965196552958
H	-0.22605149426565	-5.40562958107489	-4.40674862590296
H	-0.25851036838002	-6.11646598230092	-2.78076756800074
H	-0.47116930723124	-1.81641869900932	3.31104272131180
H	-0.41067145780771	-3.56169113547935	3.66363530897442
H	-1.72502394804206	-5.35731011327255	-3.45686179466789
H	-1.41897026939520	-2.48518507163227	4.66188645194088
O	2.02426917545415	-0.60180292560876	1.06074661619080
C	3.24817293012651	-0.33249688057141	0.63629523921042
C	4.44370502231039	-0.65951065598582	1.31507230433832
C	5.61120190669982	-0.31562198331916	0.63205301062206
C	4.41460889928088	-1.33674493499412	2.68451029146659

C	3.65056750693725	-0.43436294529370	3.67994826833561
C	5.83053329461494	-1.57525000640723	3.22969646415343
C	3.70052297157497	-2.70332109815596	2.56831446085539
H	6.41262957372410	-2.24171785265654	2.57665590446140
H	6.38613291604582	-0.63415903255712	3.34983011775091
H	5.76313971853613	-2.05254063275233	4.21795315202834
H	4.15696171886062	0.53514715045065	3.79126737108183
H	2.62293342088177	-0.25098504805580	3.34310529782882
H	4.22887644547546	-3.35658158318286	1.85894099454039
H	3.68847475146477	-3.19992376348478	3.54991299912051
H	2.66488278867676	-2.58653000918286	2.22740352081917
H	3.61037053270268	-0.91607153057027	4.66819634507655
O	-0.63851341582245	1.04858729404892	-1.04495619887239
O	0.32053501639813	1.51263128577319	1.14230530218435
C	-0.97406241294016	2.25115457101057	-0.59722001599870
C	-0.45026609763829	2.50260233321944	0.71380212451779
C	-0.73168078933350	3.69227935609611	1.42108266890315
C	-1.52650898087194	4.60587961898979	0.72606412568593
C	-2.01697254775842	4.37020973400859	-0.57647180492709
C	-1.76210538677553	3.19660076485347	-1.28841836906964
C	-0.18594165656318	3.92272541837418	2.82916447903836
C	-0.62964672906113	5.28078430727269	3.39201984996110
C	-0.70804169320480	2.80941527340072	3.76460776282476
C	1.35824847680499	3.88913610788759	2.79292613475105
C	-2.27106811181483	2.92054384286646	-2.70225672984003
C	-3.17627249100884	1.66871158106493	-2.68535910412253
C	-3.08376823200275	4.10148698544936	-3.25235335940380
H	-2.48161849424999	5.02008771237515	-3.30798562534298
H	-3.97365927636270	4.30595659116173	-2.63967701942200
H	-3.42633452426455	3.86409779289938	-4.26932421550909
C	-1.06589887205588	2.67866677052543	-3.63798173747219
H	1.72911461535531	2.91857358926981	2.44394891422199
H	1.74853114171720	4.67110897606570	2.12577271898798
H	1.75803133415965	4.06967725056948	3.80221186564306
H	-0.39868718278651	1.81802371210911	3.41373777030146
H	-0.31024763209926	2.95562917302942	4.77994028620688
H	-2.63093550631916	0.78805054485420	-2.32594921418564
H	-3.54160372639620	1.45785436622424	-3.70129268749445
H	-4.04680146744087	1.82915511560392	-2.03324956020925
H	-1.80608351958827	2.83190516299224	3.81963380862676
H	-0.22590233742705	5.40558974416514	4.40673306364267
H	-0.25843170336806	6.11644762087333	2.78076254152116
H	-0.47110337263637	1.81659292691111	-3.31113655175982
H	-0.41074560596812	3.56188198578468	-3.66367164352534
H	-1.72490418457861	5.35724658502330	3.45689522296890
H	-1.41899884041004	2.48533586745726	-4.66192615669729

Table S4 Geometry-optimised coordinates of $[V(dbcat)_3]^{1-}$

V	0.03131064191852	0.00003872170933	0.00003822370997
O	-1.05547049278753	-1.11823573507341	1.05910152215028
O	-0.14756342120856	-1.50461350312040	-1.18128145045449
O	1.49911858299507	0.73464199348051	-0.98540824985550
C	-1.06399477155681	-2.41631558329020	0.72001572233119
C	-0.58955563734550	-2.62607724021718	-0.60575233270962
C	-0.57160978297255	-3.90838168471230	-1.18870099156336
C	-1.02677285497244	-4.95213956218799	-0.36862607672527
C	-1.46127889825912	-4.74740745275644	0.94874351731430
C	-1.48368463894708	-3.47713837461916	1.54373918576406
C	-0.02216743422581	-4.11034062302221	-2.60192262040190
C	-0.10959313826704	-5.57813607388277	-3.04507595943986
C	-0.82944612802622	-3.24956440815898	-3.59747480517831
C	1.46175419684300	-3.68035149493245	-2.63103297878960
C	-1.88397781590382	-3.22261469473138	2.99835897384005
C	-3.09811678408122	-2.26979698832715	3.04267085551031
C	-2.25649932310256	-4.52234659077731	3.72677812407413
H	6.07133897994619	0.73745972760581	-0.96500568319853
H	6.07136907558924	-0.73706785971790	0.96519101034580
H	-1.02607991279583	-5.97183491661275	-0.75400472734236
H	-1.77455489573003	-5.61609292209026	1.52713009404111
H	-1.02582753757074	5.97194831640913	0.75416028380631
H	-1.77437240518352	5.61625561522233	-1.52695898258734
C	-0.69137260766362	-2.57341705436683	3.73816317161490
C	2.73268176983316	0.42006128185752	-0.57141804876119
C	3.92524166690356	0.87475419367851	-1.16293695781851
C	5.11060344984000	0.42338567563764	-0.55795735952665
C	3.88506130059947	1.79525834134811	-2.38437906299105
C	3.18172462396179	1.06171126785651	-3.54806194526127
C	5.29426113786823	2.19726126747278	-2.84597937798760
C	3.09979513368817	3.08032662897794	-2.03653580976257
H	-1.41298465775823	-5.22863052316585	3.74956366101097
H	-3.11417851638967	-5.02318499755277	3.25316976673065
H	-2.53153606998262	-4.29278573681698	4.76740163425341
H	1.57415889963055	-2.62982554510672	-2.33688079684327
H	2.05331652812373	-4.29620284306649	-1.93805986999099
H	1.87508292476501	-3.80501943836384	-3.64507892872708
H	-0.78497204271568	-2.18954813462452	-3.31925814097430
H	-0.42273388653493	-3.36348958014820	-4.61530949130469
H	-2.86209103800743	-1.31659352334925	2.55475951408855
H	-3.38388134975165	-2.06694670279879	4.08702514716507
H	-3.96103202221007	-2.71902882586471	2.52862520482363
H	5.83778174367931	2.74494241816842	-2.06096971245731
H	5.89337205448041	1.32048401980115	-3.13454919466540
H	5.21626339338654	2.85533261313331	-3.72503479789127
H	3.74349561439198	0.15859987797811	-3.82999403859667
H	2.16742638561580	0.76262946061857	-3.26066267282740
H	3.59575638011314	3.62403680750749	-1.21861233238152
H	3.05058955102672	3.74469003547253	-2.91437688777668
H	2.07643272521958	2.84289795087330	-1.72299957655316
H	3.11636871922754	1.72016026423574	-4.42919855250629
H	-1.88428296862207	-3.56327698768089	-3.60943723366770
H	0.27925020712585	-5.67553565919629	-4.07012235698543
H	0.48676453893385	-6.23482192768560	-2.39500559547446
H	-0.38518384747528	-1.64301170679730	3.24597389652348
H	0.17176409449816	-3.25441883156340	3.74941429349699
H	-1.14826076283720	-5.94180052371143	-3.04362159864423
H	-0.96791871407543	-2.34799834945787	4.78020230826045
O	1.49913133045043	-0.73461471924869	0.98543194508859
C	2.73269278671724	-0.42008405107881	0.57139198919593
C	3.92527524916700	-0.87482673075112	1.16284332320895
C	5.11061927089056	-0.42307372957764	0.55811253303044
C	3.88517056039817	-1.79555899833493	2.38412014044357

C	3.18009238173195	-1.06295264609814	3.54733592430874
C	5.29446533318550	-2.19604334755911	2.84674083710898
C	3.10168679732298	-3.08151496200468	2.03552225129765
H	5.83920148686480	-2.74299291275111	2.06206350361047
H	5.89236900721923	-1.31863728830454	3.13590483653099
H	5.21653232618059	-2.85433571926866	3.72563634219270
H	3.74059708043098	-0.15922405475204	3.82981732115939
H	2.16566366413138	-0.76501486057668	3.25917520384538
H	3.59895919588014	-3.62455740856604	1.21795003529504
H	3.05256051380106	-3.74602831270454	2.91325651484164
H	2.07831623959331	-2.84528069191297	1.72116936145879
H	3.11480221905473	-1.72158196256935	4.42834203219980
O	-1.05546746334091	1.11835834850834	-1.05897996784966
O	-0.14745705154912	1.50469375438293	1.18136976015776
C	-1.06391628371310	2.41643987228664	-0.71989230643211
C	-0.58942768742243	2.62617575909347	0.60586311250944
C	-0.57140477414601	3.90847651670581	1.18881725831733
C	-1.02657268799274	4.95225606801617	0.36877346172430
C	-1.46112578274272	4.74755150514061	-0.94858405670589
C	-1.48356471201936	3.47729270452606	-1.54360033786004
C	-0.02188609530104	4.11040313610559	2.60201400065913
C	-0.10924061724794	5.57819630236337	3.04518877367353
C	-0.82914202538557	3.24964019629875	3.59759575309109
C	1.46202298780470	3.68036555037024	2.63104515580676
C	-1.88383407995281	3.22281440252700	-2.99823034933249
C	-3.09788943689453	2.26989188446608	-3.04259153856449
C	-2.25646290884963	4.52255708874555	-3.72657548693101
H	-1.41300856937942	5.22891480690942	-3.74931133804428
H	-3.11418917962351	5.02329294179355	-3.25294389246434
H	-2.53147181349055	4.29303525341563	-4.76721504149837
C	-0.69116601468761	2.57377048033397	-3.73806671704902
H	1.57437877300515	2.62984062302415	2.33687077528435
H	2.05357071960493	4.29620796838491	1.93805180002837
H	1.87540657258677	3.80500445119529	3.64507234641321
H	-0.78471450511819	2.18962582157338	3.31936350070542
H	-0.42237537281523	3.36354008872397	4.61541155021545
H	-2.86177757478871	1.31668486618442	-2.55472716018431
H	-3.38363399922413	2.06706780231971	-4.08695618759462
H	-3.96084579730502	2.71902047614758	-2.52852410792625
H	-1.88396843852176	3.56338538765011	3.60961455211227
H	0.27965771062191	5.67557109328652	4.07021676807560
H	0.48710646626662	6.23486957593687	2.39509597148218
H	-0.38490009659924	1.64336263128863	-3.24593692949652
H	0.17191371453235	3.25484719079324	-3.74926134696482
H	-1.14789601642217	5.94189562042231	3.04379079040430
H	-0.96768336615331	2.34839834764211	-4.78012357281215

Table S5 Geometry-optimised coordinates of [V(dmcat)$_3$]

V	0.58864681358355	-0.00196549790045	0.00000986888782
O	-0.64376915272781	-0.99959103769899	1.07340129217354
O	0.36504004029277	-1.55155140682585	-1.10575253884939
O	2.05617745136118	0.60636327309288	-1.07251413332138
C	-1.01522942650396	-2.18432459275926	0.61750867336019
C	-0.46049831624035	-2.48743450319173	-0.66648579138391
C	-0.77731982235601	-3.67892843489983	-1.34860819710604
C	-1.64253415323026	-4.54691552591648	-0.68053354986535
C	-2.17540669533563	-4.25639565303133	0.59382926059422
C	-1.88071619598959	-3.07709361755348	1.28017684716577
C	-0.19765923600432	-3.96185368714769	-2.70325098808639
C	-2.43643370168304	-2.74223701975540	2.63329265362938
C	3.27370620621494	0.33895888478636	-0.63212751178107
C	4.47142415921552	0.67533054601298	-1.29405798040628
C	5.64862294424088	0.33439720328985	-0.62562239152206
C	4.44216480769323	1.35842597221761	-2.63016773739380
O	2.05854209015176	-0.60387190865998	1.07304825845437
C	3.27491366072323	-0.32930369468035	0.63406316135335
C	4.47390435882368	-0.65895441047248	1.29710881966862
C	5.64982611456655	-0.31144525032759	0.62985266302774
C	4.44714540490073	-1.34224627017621	2.63319211569570
O	-0.64761167651681	0.99185947731322	-1.07268368191857
O	0.36114099053821	1.54741642942039	1.10567916025127
C	-1.02249101242064	2.17543235386303	-0.61663450050233
C	-0.46753531153953	2.48060798858552	0.66681611480706
C	-0.78772357904270	3.67112121427084	1.34910326959181
C	-1.65690702504453	4.53586203933433	0.68196116973505
C	-2.19042584238937	4.24312690726575	-0.59163246217369
C	-1.89228322875729	3.06481624647204	-1.27820470666940
C	-0.20770342873871	3.95620844978682	2.70312593485830
C	-2.44821809357196	2.72790096585469	-2.63073218520985
H	-1.91637217570580	-5.48690596399864	-1.16160169761471
H	-2.84410435720809	-4.98104845520535	1.06116352967497
H	-0.48575375742458	-3.18525905609074	-3.42678426820285
H	-0.53915826379745	-4.93308435071834	-3.08051685001084
H	0.90184848385775	-3.96565469776133	-2.67023919202759
H	-3.05249879774374	-1.83193047821777	2.59272312297445
H	-1.63038889466718	-2.54211148345864	3.35318658519260
H	-3.05389335373353	-3.56371630630945	3.01735125639234
H	6.60439475972117	0.57721324611152	-1.09215890747119
H	3.88802507484497	2.30641340918962	-2.57735494947002
H	3.92906857463102	0.73859103075170	-3.37969858937216
H	5.45807781951608	1.56624206609583	-2.98595921513445
H	6.60658570175188	-0.54885752868717	1.09715339470495
H	3.93004323023807	-0.72520260908650	3.38226511292610
H	5.46386647332630	-1.54458326565211	2.98984692617389
H	3.89818248138137	-2.29320751138163	2.57985382241790
H	-1.93350030791287	5.47492397555573	1.16326499016583
H	-2.86259053524414	4.96512286541774	-1.05809636493484
H	-0.54737660182627	4.92902350030319	3.07798040983305
H	0.89177138274098	3.95750243655122	2.67016929994609
H	-0.49753944065521	3.18222823849943	3.42878812320565
H	-3.07572635825427	3.54366357528054	-3.01065354864656
H	-3.05386376509994	1.81065763567339	-2.59109814682636
H	-1.64198038195030	2.53884003056854	-3.35347771196092

Table S6 Geometry-optimised coordinates of $[V(dmcat)_3]^{1-}$

V	-0.00045284758258	0.00011399627717	0.00011026837703
O	-1.23704559448729	-0.99086670160597	1.07608508044552
O	-0.21563961605490	-1.54806582976454	-1.11017162458963
O	1.46152026198587	0.61319392327854	-1.07708998865694
C	-1.60097177042665	-2.18784159026107	0.61200854133206
C	-1.05600881405353	-2.48439684588789	-0.66475045373233
C	-1.37885469359030	-3.67065683207616	-1.34180426544657
C	-2.24411841793514	-4.55755758626246	-0.68093710280955
C	-2.76674057615459	-4.27392663382154	0.58815365985917
C	-2.45744960921793	-3.08500973698583	1.26872314854239
C	-0.80019640349306	-3.94947853395327	-2.70067450059394
C	-3.00864682312659	-2.75146469694752	2.62696495315642
C	2.68671704518281	0.33340860546305	-0.62948464589717
C	3.88331510966285	0.65784071456185	-1.28758570549082
C	5.07667942393159	0.32792653725748	-0.62442054844101
C	3.85146235308748	1.33234858071460	-2.63098882367122
O	1.46393235661627	-0.60682485786312	1.07733489034743
C	2.68794898015255	-0.31979210000416	0.63107272917422
C	3.88569453331108	-0.63757430725854	1.29032966697025
C	5.07783967659642	-0.30099869625532	0.62834001734045
C	3.85630137914352	-1.31232307053829	2.63367012091375
O	-1.24107256535348	0.98698864838537	-1.07501163162426
O	-0.21973527704832	1.54793763506800	1.11040019174917
C	-1.60856271911720	2.18283158136917	-0.61079477209444
C	-1.06342309921367	2.48144599213613	0.66540006667656
C	-1.38962806958376	3.66676870608805	1.34250356319607
C	-2.25862474720536	4.55054228566745	0.68234468141395
C	-2.78165052772999	4.26479319787405	-0.58610555985317
C	-2.46897728793316	3.07679143263073	-1.26672955482265
C	-0.81077560079079	3.94772731708516	2.70085471563007
C	-3.02033564241548	2.74101572129507	-2.62436125425350
H	-2.51200141499163	-5.49483959780125	-1.17336602830263
H	-3.43477584945586	-4.99367805696407	1.06680120408224
H	-1.08605872636546	-3.16992862753980	-3.42321495359009
H	-1.14368877319201	-4.92060264678368	-3.08181574215972
H	0.30023202105324	-3.95363120162745	-2.67121972699992
H	-3.62806118322532	-1.84214102629897	2.59280061134287
H	-2.20006192822957	-2.54692411948633	3.34405427062405
H	-3.62193461268956	-3.57651552186722	3.01537431300999
H	6.02753947757699	0.57170696585474	-1.10325870558333
H	3.29772765626291	2.28189254924009	-2.58602126609660
H	3.33431873898291	0.70943943698074	-3.37651035641604
H	4.86828566970296	1.53633669084510	-2.99203898380049
H	6.02958035293313	-0.53947071232066	1.10811131596218
H	3.33518866855341	-0.69224313691492	3.37877937246180
H	4.87389894663647	-1.51089671537439	2.99557038528178
H	3.30769192994273	-2.26480941539635	2.58816313191158
H	-2.52918264609740	5.48702476482810	1.17482911482485
H	-3.45276586359080	4.98206478695176	-1.06416302223027
H	-1.15383147951733	4.91965749724198	3.08032467566501
H	0.28962619266765	3.95119765769652	2.67129563866804
H	-1.09702240277792	3.16964398424044	3.42485449081545
H	-3.64095356050546	3.56177223795205	-3.01021675275075
H	-3.63227338087717	1.82668888505164	-2.59027309750356
H	-2.21164824995361	2.54402846582572	-3.34350575236374

Table S7 Geometry-optimised coordinates of [V(Cl_4cat)$_3$]

V	0.01439122044908	0.00000474759502	-0.00000035349834
O	-1.24211087086621	-0.95324654415296	1.09008063085264
O	-0.20164269056507	-1.58609152838154	-1.05643263718322
O	1.48167470401217	0.57832567929867	-1.08910588480851
O	-1.24210959436432	0.95325594290135	-1.09008280372006
O	-0.20164513479937	1.58610040990590	1.05643228904554
O	1.48167320170464	-0.57831799125758	1.08910647999369
C	-1.62077809449301	-2.13362922447281	0.65930396901962
C	-1.04565306811064	-2.48481784025618	-0.60524533720662
C	-1.38172622512936	-3.69367694079515	-1.23598227345786
C	-2.27895845419729	-4.55748128113871	-0.58652829734598
C	-2.83816936831765	-4.21563648920080	0.67885557687900
C	-2.51055867451347	-3.00414297648049	1.30930515718266
C	2.68762296129881	0.31759440005688	-0.64225662865666
C	3.89477069254790	0.61942919331752	-1.29361829841067
C	5.09993394175059	0.30621969209363	-0.64347071733763
C	2.68762217534953	-0.31759262563687	0.64225576741358
C	3.89476921054826	-0.61943341450882	1.29361593751850
C	5.09993321708517	-0.30622998064873	0.64346683770922
C	-1.62078006729989	2.13363714966912	-0.65930501231131
C	-1.04565722652729	2.48482539632727	0.60524541401000
C	-1.38173420329363	3.69368275311463	1.23598373263842
C	-2.27896794386965	4.55748571810567	0.58653003131448
C	-2.83817669391721	4.21564133949275	-0.67885493823072
C	-2.51056223824614	3.00414955803594	-1.30930589031284
Cl	3.84815479968189	1.35722074323825	-2.84525727217349
Cl	3.84815151825691	-1.35722517168917	2.84525477011651
Cl	6.59313058120445	-0.66693962581601	1.41255747323126
Cl	6.59313213552534	0.66692149948927	-1.41256339757360
Cl	-0.68483467596290	-4.06585538260127	-2.76238831460612
Cl	-2.70670064795024	-6.04709385073157	-1.32782111278374
Cl	-3.16049697515894	-2.55079875791606	2.83445090409047
Cl	-3.92972491105909	-5.29712872508563	1.44729904143748
Cl	-0.68484559783710	4.06586059659853	2.76239128725250
Cl	-2.70671482000166	6.04709601287476	1.32782470558312
Cl	-3.92973426591334	5.29713187127852	-1.44729796024441
Cl	-3.16049791702127	2.55080564637665	-2.83445287642689

Table S8 Geometry-optimised coordinates of $[V(Cl_4cat)_3]^{1-}$

V	0.01412636282321	0.00000441303404	-0.00000045098653
O	-1.24132984422180	-0.94621625713389	1.09338906118838
O	-0.19547816837772	-1.58222596817598	-1.05933668170265
O	1.47509966238748	0.58173021910307	-1.09215138557312
O	-1.24132874350941	0.94622507911933	-1.09339126912799
O	-0.19548044295887	1.58223408665083	1.05933609878197
O	1.47509831192972	-0.58172328582378	1.09215170367900
C	-1.61530691217579	-2.13692835636697	0.65756894763411
C	-1.05198061180914	-2.48111347322411	-0.60378942204600
C	-1.39790123805657	-3.68403130527519	-1.22973157475472
C	-2.29213727703552	-4.56114170959601	-0.58218197796739
C	-2.83469157644821	-4.22930019194900	0.67475929007207
C	-2.49481881839656	-3.01363334390615	1.30288879871140
C	2.68734354602757	0.31088500962777	-0.64049094159216
C	3.89457574965834	0.60115799644914	-1.28672659788551
C	5.10954095514761	0.29676838892787	-0.63888401558641
C	2.68734284586765	-0.31088340250052	0.64048993976475
C	3.89457451778007	-0.60116174047155	1.28672424420180
C	5.10954033808730	-0.29677753558358	0.63888026996582
C	-1.61530877517183	2.13693581288871	-0.65757001879014
C	-1.05198447991519	2.48112041548485	0.60378941254480
C	-1.39790860744041	3.68403652389081	1.22973302143061
C	-2.29214596946705	4.56114582643803	0.58218376962740
C	-2.83469815820414	4.22930495983702	-0.67475859290860
C	-2.49482202936130	3.01363978030144	-1.30288949999134
Cl	3.85204527685659	1.33226314748141	-2.85296987624684
Cl	3.85204250116768	-1.33226666864854	2.85296758787866
Cl	6.60905677335119	-0.65929099689829	1.42623433666897
Cl	6.60905810560565	0.65927519333229	-1.42623978064408
Cl	-0.70826297890048	-4.05669071011284	-2.77087223772902
Cl	-2.72024469656447	-6.05791896265487	-1.34148849196245
Cl	-3.14082261272411	-2.56696587417597	2.84324864064401
Cl	-3.93062537018479	-5.31532167465469	1.46202961531700
Cl	-0.70827323625118	4.05669528607603	2.77087512002683
Cl	-2.72025764858757	6.05792097498175	1.34149210089342
Cl	-3.93063345608127	5.31532522362806	-1.46202848828419
Cl	-3.14082329484666	2.56697311889950	-2.84325065625183

Table S9 Geometry-optimised coordinates of [V(edt)$_3$]

V	-0.001298	-0.006948	-0.025720
S	1.772804	-0.017815	1.576998
S	1.796759	-0.015086	-1.601027
S	-0.927346	-1.531806	1.564740
S	-0.887001	-1.561188	-1.609254
S	-0.894456	1.557659	1.543602
S	-0.886599	1.527757	-1.630393
C	3.237053	-0.023359	0.691843
C	3.247457	-0.021346	-0.693706
C	-1.668071	-2.790274	0.672795
C	-1.649423	-2.803454	-0.712836
C	-1.626155	2.809936	0.635708
C	-1.623416	2.796300	-0.750137
H	4.180536	-0.028846	1.269069
H	4.199172	-0.022951	-1.257015
H	-2.163938	-3.596356	1.244782
H	-2.128019	-3.621372	-1.282850
H	-2.103450	3.634520	1.197696
H	-2.099731	3.609078	-1.329974

Table S10 Geometry-optimised coordinates of $[V(bpy)_3]$

V	0.005000	-0.003000	-0.008000
N	1.663000	-0.739000	1.063000
N	1.659000	0.741000	-1.081000
N	-0.181000	1.805000	1.060000
N	-1.470000	1.055000	-1.077000
N	-1.468000	-1.065000	1.059000
N	-0.173000	-1.812000	-1.075000
C	-2.121000	-0.600000	2.145000
C	-3.106000	-1.300000	2.800000
C	-1.814000	-2.306000	0.570000
C	-3.471000	-2.568000	2.307000
C	-2.825000	-3.059000	1.196000
C	-1.079000	-2.729000	-0.591000
C	-1.232000	-3.977000	-1.221000
C	1.587000	-1.529000	2.154000
C	2.910000	-0.418000	0.573000
C	0.545000	2.140000	2.147000
C	-1.088000	2.720000	0.574000
C	1.579000	1.531000	-2.172000
C	2.908000	0.423000	-0.594000
C	0.556000	-2.145000	-2.161000
C	-2.120000	0.589000	-2.165000
C	-1.819000	2.295000	-0.589000
C	-0.487000	-4.290000	-2.333000
C	2.686000	-2.026000	2.813000
C	4.067000	-0.911000	1.203000
C	0.421000	3.339000	2.807000
C	-1.245000	3.968000	1.204000
C	2.676000	2.030000	-2.833000
C	4.063000	0.918000	-1.226000
C	0.435000	-3.344000	-2.821000
C	-3.105000	1.287000	-2.822000
C	-2.830000	3.047000	-1.218000
C	3.966000	-1.709000	2.318000
C	-0.502000	4.283000	2.317000
C	3.958000	1.715000	-2.341000
C	-3.472000	2.555000	-2.330000
H	-1.819000	0.383000	2.479000
H	-3.588000	-0.871000	3.668000
H	-4.251000	-3.145000	2.788000
H	-3.100000	-4.025000	0.798000
H	-1.937000	-4.695000	-0.826000
H	0.584000	-1.759000	2.490000
H	1.252000	1.390000	2.480000
H	0.576000	1.759000	-2.506000
H	1.261000	-1.394000	-2.492000
H	-1.815000	-0.394000	-2.498000
H	-0.603000	-5.251000	-2.819000
H	2.556000	-2.650000	3.686000
H	5.041000	-0.666000	0.803000
H	1.028000	3.542000	3.678000
H	-1.950000	4.684000	0.807000
H	2.543000	2.654000	-3.706000
H	5.038000	0.675000	-0.828000
H	1.044000	-3.546000	-3.691000
H	-3.583000	0.858000	-3.691000
H	-3.107000	4.012000	-0.820000
H	4.856000	-2.089000	2.802000
H	-0.621000	5.243000	2.802000
H	4.846000	2.097000	-2.827000
H	-4.252000	3.131000	-2.813000

Table S11 Comparison of experimental and calculated bond distances (Å)

	$[V(dbcat)_3]$		$[V(dbcat)_3]^{1-}$
	exptl[a]	**calcd**	**calcd**
V–O1	1.868(2)	1.899	1.885
V–O2	1.898(2)	1.910	1.921
V–O3	1.971(2)	1.912	1.914
V–O4	1.971(2)	1.912	1.914
V–O5	1.868(2)	1.899	1.885
V–O6	1.898(2)	1.910	1.921
O1–C1	1.330(4)	1.326	1.342
O2–C2	1.326(4)	1.326	1.336
C1–C2	1.421(5)	1.434	1.424
C1–C6	1.404(5)	1.412	1.407
C2–C3	1.406(5)	1.412	1.409
C3–C4	1.376(5)	1.396	1.403
C4–C5	1.400(5)	1.412	1.402
C5–C6	1.373(6)	1.396	1.403
O3–C7	1.298(3)	1.323	1.339
O4–C8	1.298(3)	1.323	1.339
C7–C8	1.466(6)	1.436	1.418
C7–C12	1.415(4)	1.413	1.407
C8–C9	1.415(4)	1.413	1.407
C9–C10	1.364(4)	1.396	1.405
C10–C11	1.428(4)	1.413	1.401
C11–C12	1.364(4)	1.396	1.405
O5–C13	1.330(4)	1.326	1.342
O6–C14	1.326(4)	1.326	1.336
C13–C14	1.421(5)	1.434	1.424
C13–C18	1.404(5)	1.412	1.407
C14–C15	1.406(5)	1.412	1.409
C15–C16	1.376(5)	1.396	1.403
C16–C17	1.400(5)	1.412	1.402
C17–C18	1.373(6)	1.396	1.403

[a] Data taken from ref. 2.

Table S12 Total energies and exchange coupling constants from BS DFT calculations

	M_S	Rel. Total Energy / kcal mol^{-1}	J_{calcd} / cm^{-1}
[V(dbcat)$_3$]			
UKS	$^1/_2$	0.00	
BS(2,1)	$^3/_2$	+10.29	
	$^1/_2$	+7.55	–178
BS(3,2)	$^5/_2$	+39.57	
	$^1/_2$	0.00	–1919
[V(dbcat)$_3$]$^{1-}$			
UKS	0	0.00	
BS(1,1)	1	+8.94	
	0	+7.94	–371
[V(dmcat)$_3$]			
UKS	$^1/_2$	0.00	
BS(2,1)	$^3/_2$	+10.29	
	$^1/_2$	+7.55	–451
BS(3,2)	$^5/_2$	+38.85	
	$^1/_2$	0.00	–1818
[V(dmcat)$_3$]$^{1-}$			
UKS	0	0.00	
BS(1,1)	1	+6.78	
	0	+5.63	–431
[V(Cl$_4$cat)$_3$]			
UKS	$^1/_2$	0.00	
BS(2,1)	$^3/_2$	+9.31	
	$^1/_2$	+7.01	–351
BS(3,2)	$^5/_2$	+35.89	
	$^1/_2$	0.00	–1694
[V(Cl$_4$cat)$_3$]$^{1-}$			
UKS	0	0.00	
BS(1,1)	1	+5.74	
	0	+4.63	–412

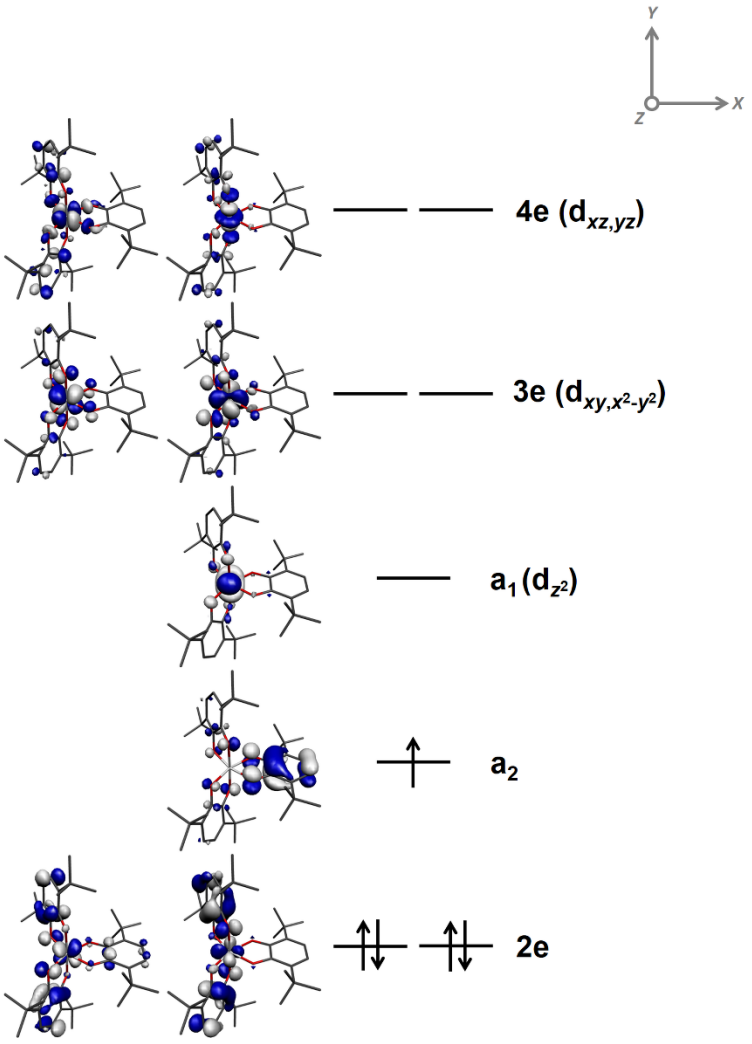

Fig. S2 MO energy level scheme of frontier Kohn-Sham orbitals for [V(dbcat)$_3$] with C_{3v} symmetry labels

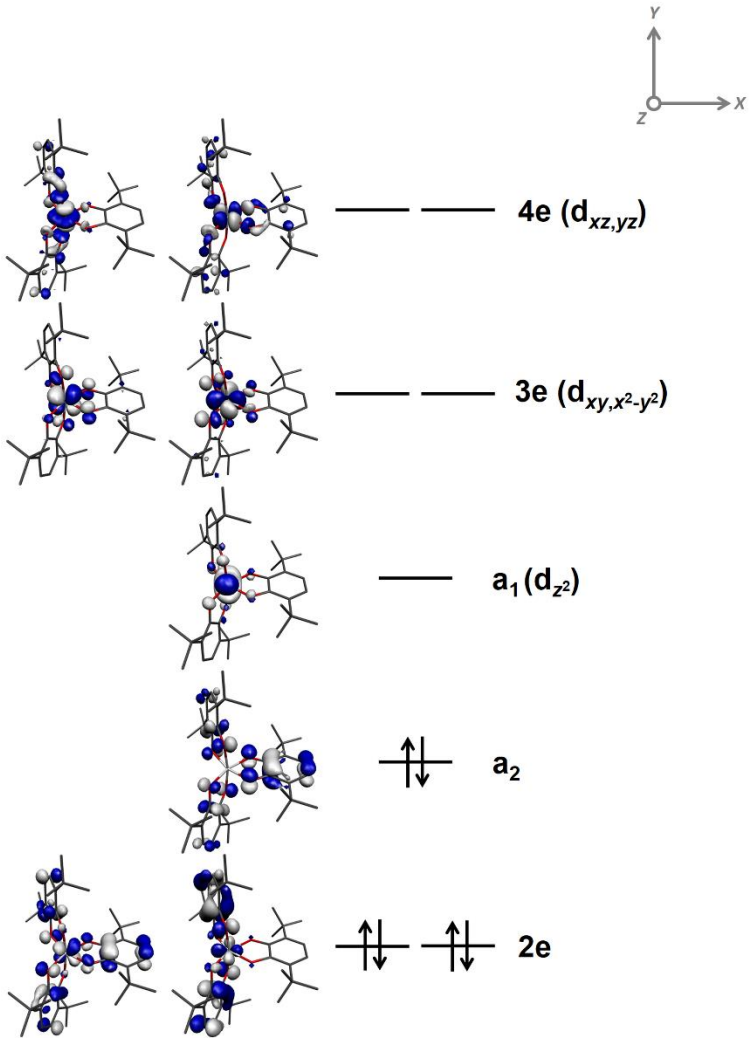

Fig. S3 MO energy level scheme of frontier Kohn-Sham orbitals for $[V(dbcat)_3]^{1-}$ with C_{3v} symmetry labels

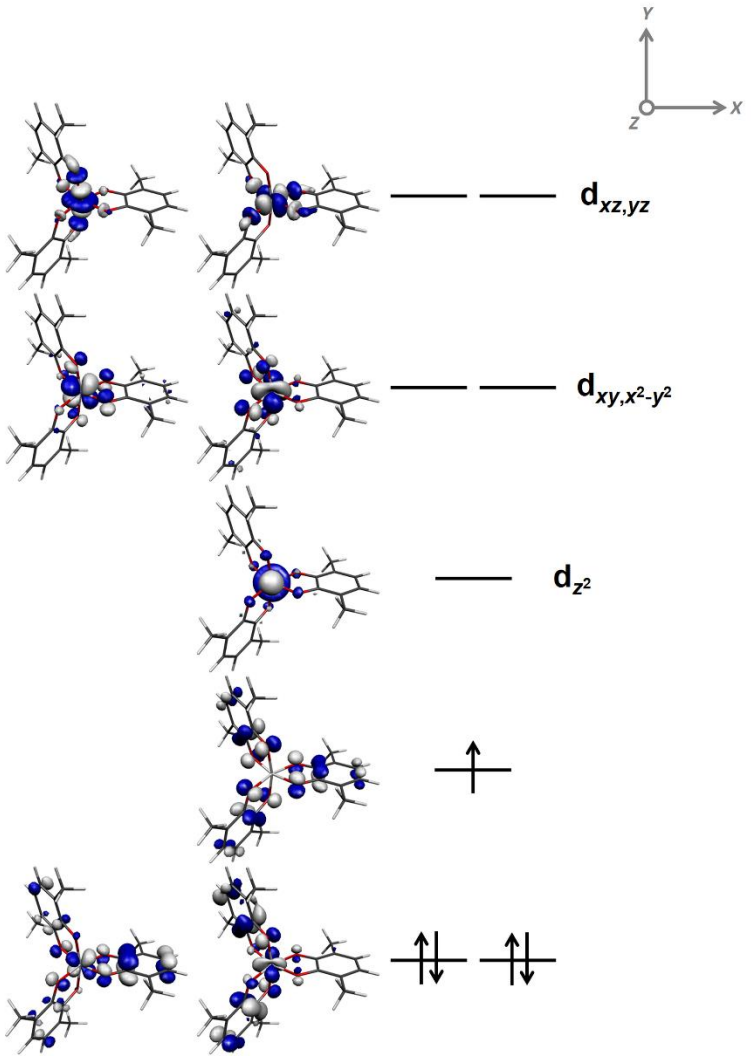

Fig. S4 MO energy level scheme of frontier Kohn-Sham orbitals for $[V(dmcat)_3]$

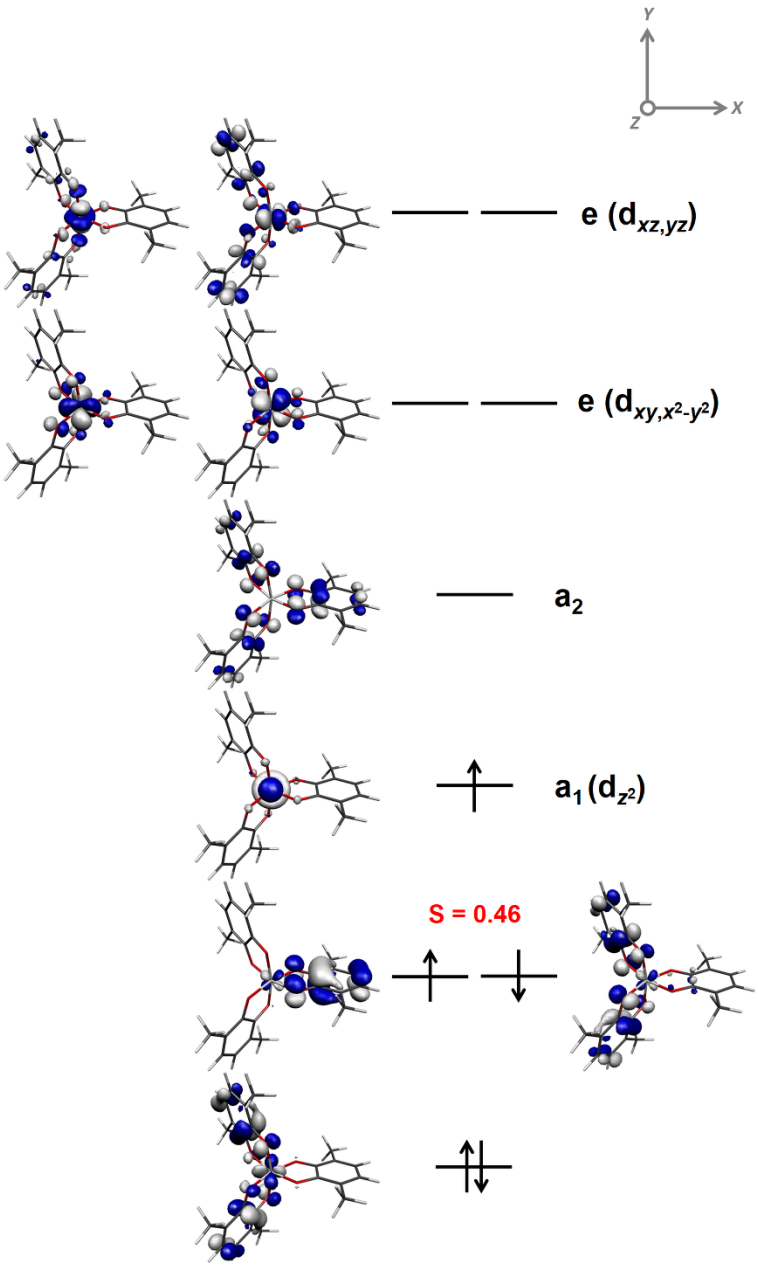

Fig. S5 MO energy level scheme of frontier Kohn-Sham orbitals for the BS(2,1) solution for [V(dmcat)$_3$]. The orbital overlap integral (S) for symmetry-matched α-spin and β-spin magnetic orbitals (SOMOs) is specified.

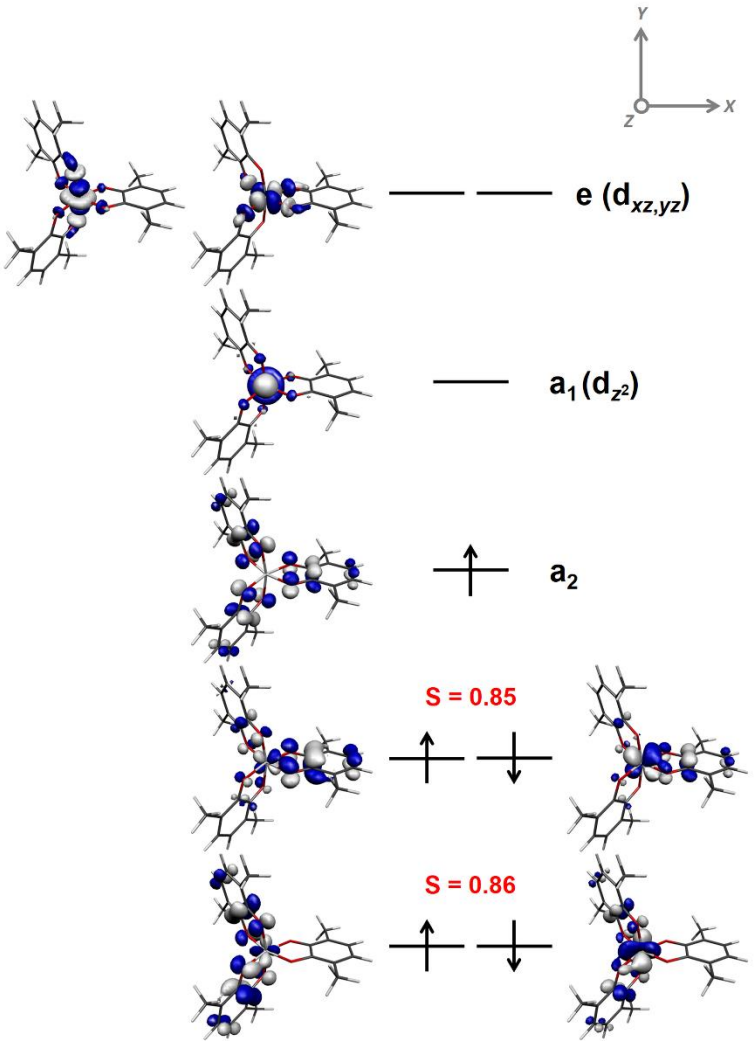

Fig. S6 MO energy level scheme of frontier Kohn-Sham orbitals for the BS(3,2) solution for [V(dmcat)$_3$]. The orbital overlap integrals (S) for symmetry-matched α-spin and β-spin magnetic orbitals (SOMOs) are specified.

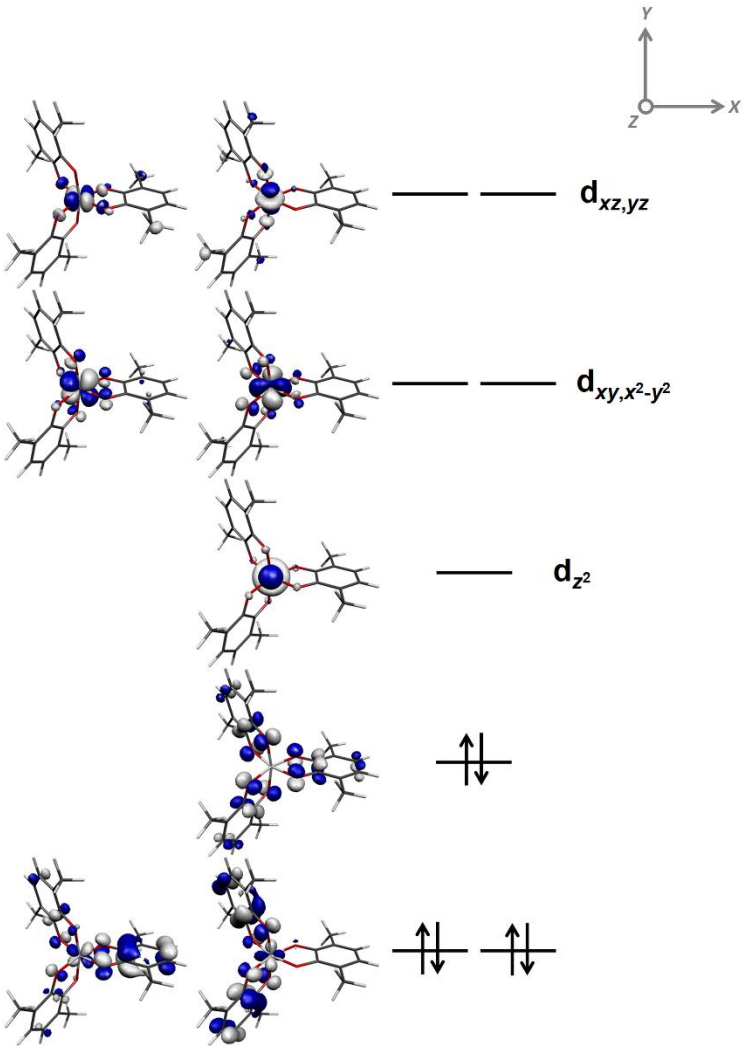

Fig. S7 MO energy level scheme of frontier Kohn-Sham orbitals for $[V(dmcat)_3]^{1-}$

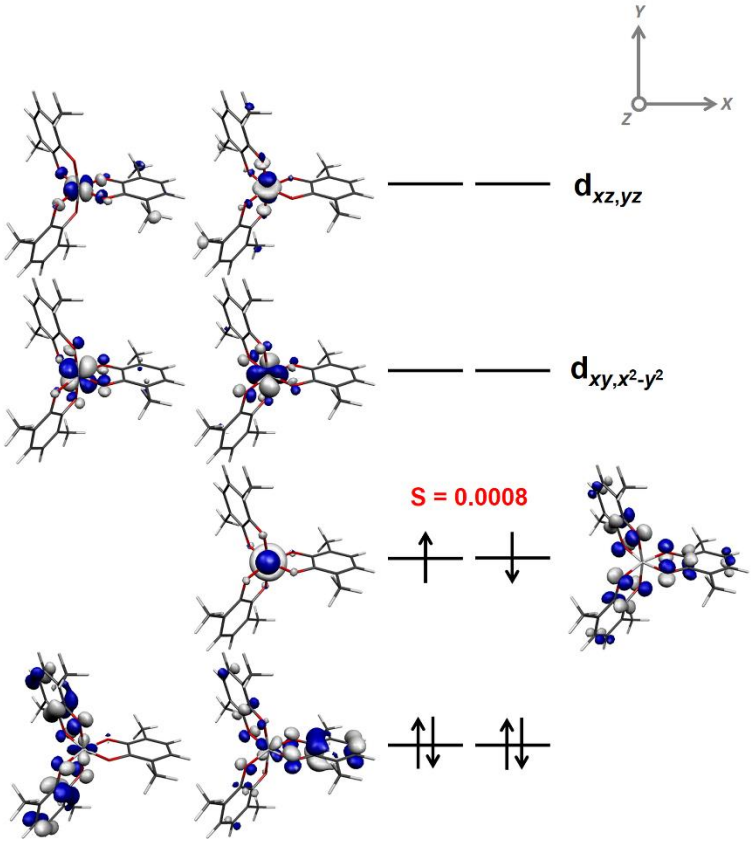

Fig. S8 MO energy level scheme of frontier Kohn-Sham orbitals for the BS(1,1) solution for $[V(dmcat)_3]^{1-}$. The orbital overlap integral (S) for symmetry-matched α-spin and β-spin magnetic orbitals (SOMOs) is specified.

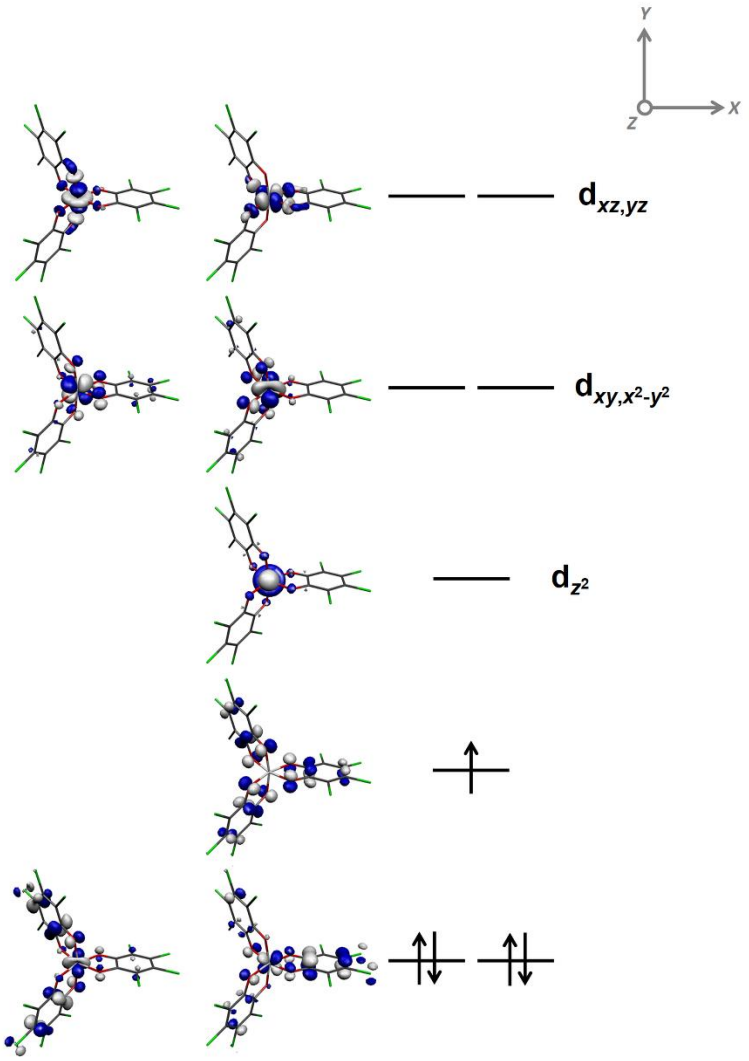

Fig. S4 MO energy level scheme of frontier Kohn-Sham orbitals for $[V(Cl_4cat)_3]$

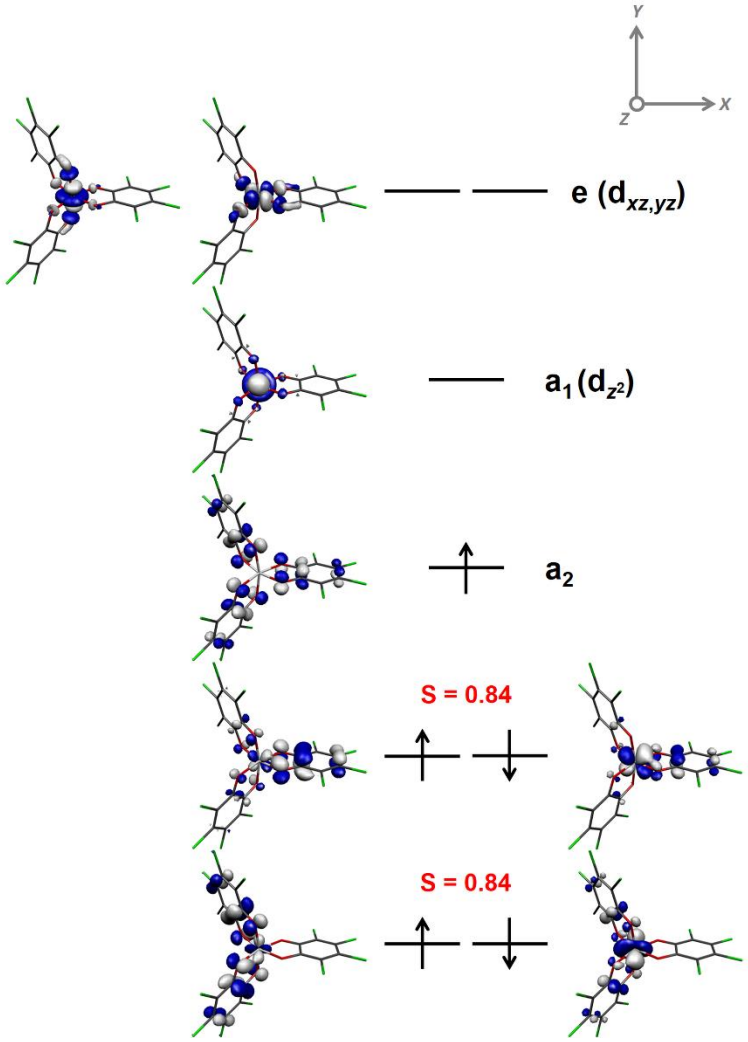

Fig. S10 MO energy level scheme of frontier Kohn-Sham orbitals for the BS(3,2) solution for $[V(Cl_4cat)_3]$. The orbital overlap integrals (S) for symmetry-matched α-spin and β-spin magnetic orbitals (SOMOs) are specified.

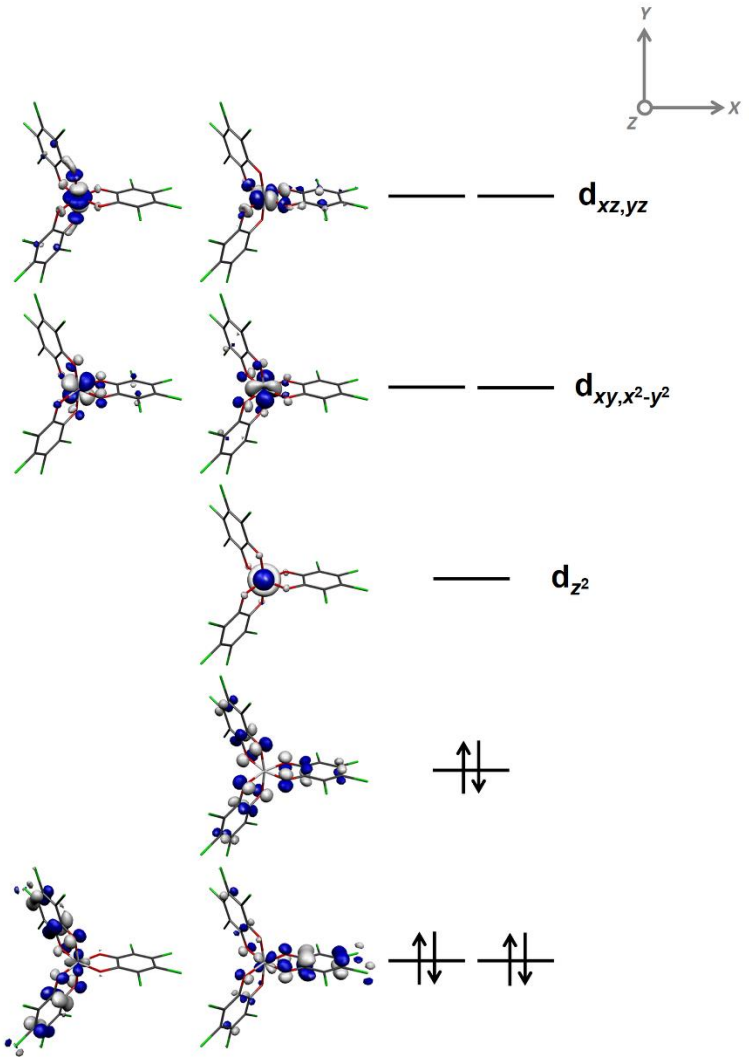

Fig. S11 MO energy level scheme of frontier Kohn-Sham orbitals for $[V(Cl_4cat)_3]^{1-}$

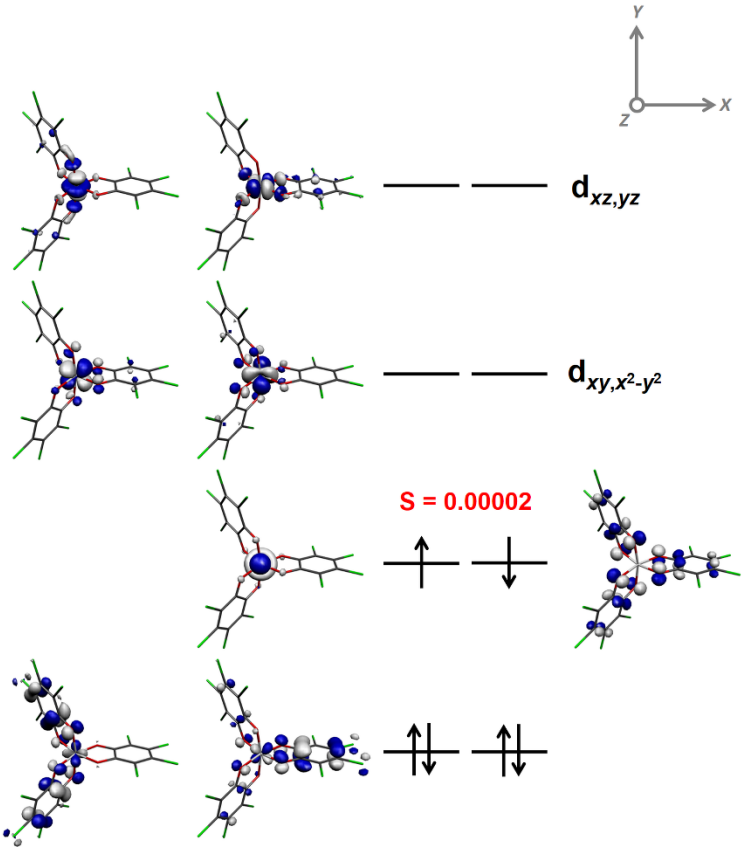

Fig. S12 MO energy level scheme of frontier Kohn-Sham orbitals for the BS(1,1) solution for $[V(Cl_4cat)_3]^{1-}$. The orbital overlap integral (S) for symmetry-matched α-spin and β-spin magnetic orbitals (SOMOs) is specified.

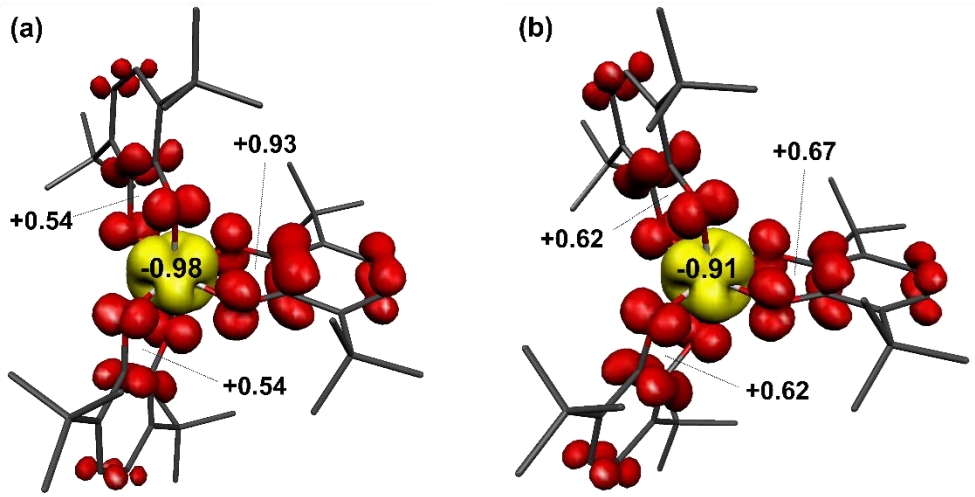

Fig. S13 Mulliken spin density population for $[V(dbcat)_3]$ with (a) crystallographic coordinates, and (b) geometry-optimised coordinates (red: α-spin; yellow: β-spin).

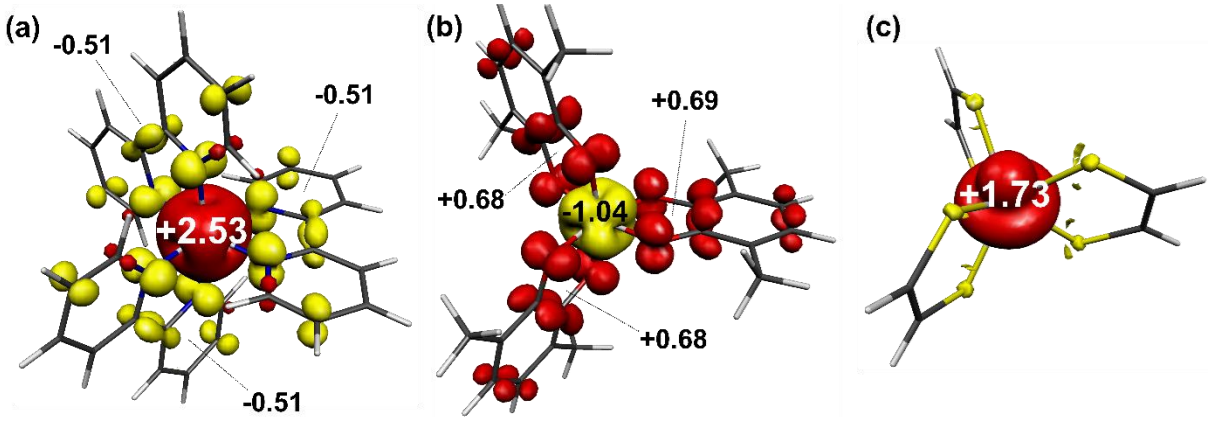

Fig. S14 Comparison of the Mulliken spin density distribution in (a) $[V(bpy)_3]$, (b) $[V(dmcat)_3]$, and (c) $[V(edt)_3]$ (red: α-spin; yellow: β-spin).

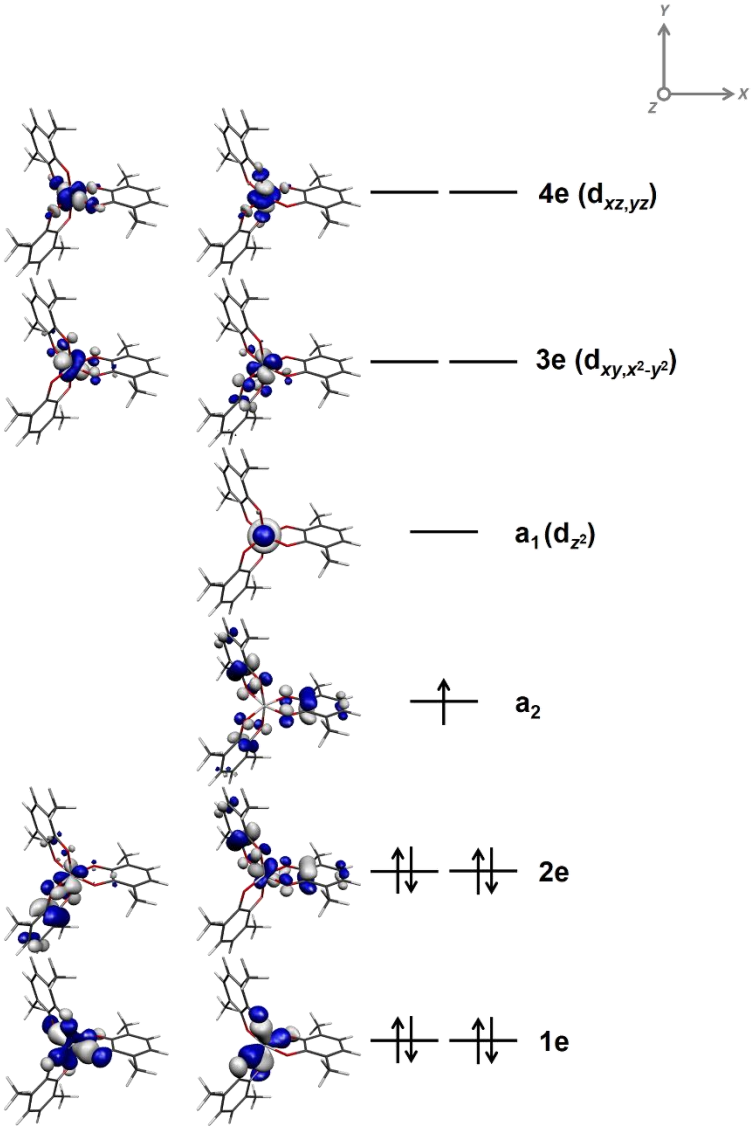

Fig. S15 Visualisation of the orbitals that comprise the active space of the SA-CASSCF/NEVPT2 CAS(9,10) calculation of [V(dmcat)$_3$] with C_{3v} symmetry labels.

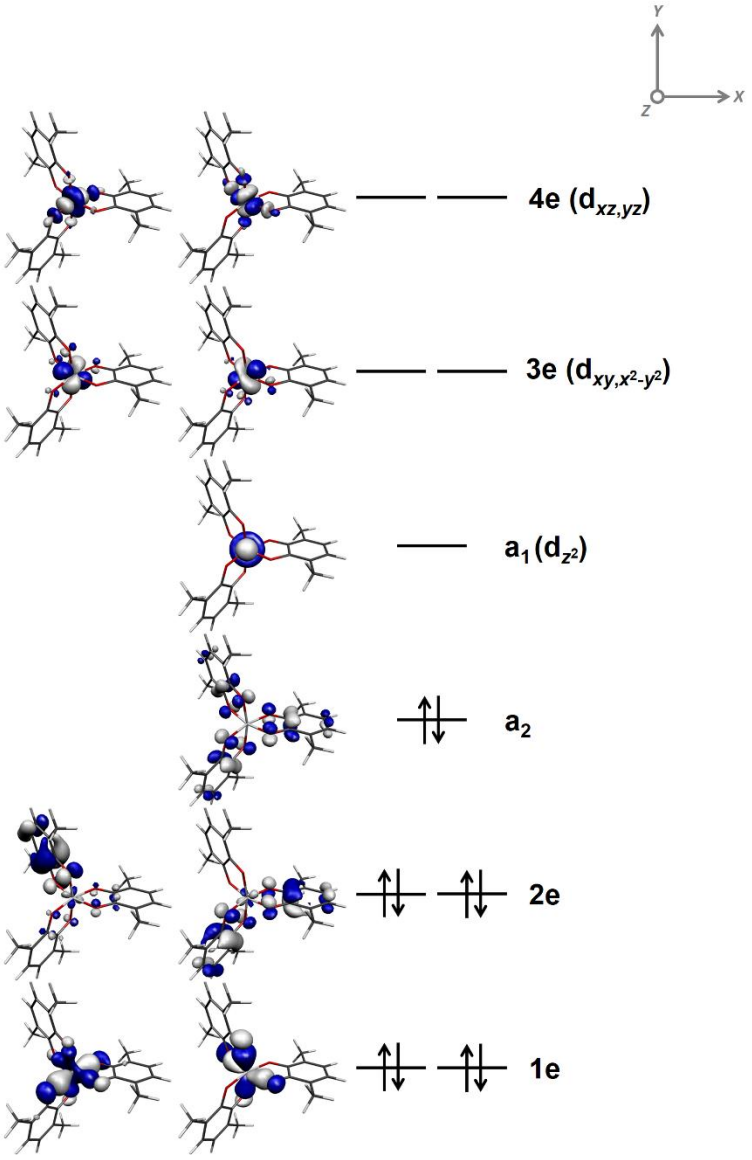

Fig. S16 Visualisation of the orbitals that comprise the active space of the SA-CASSCF/NEVPT2 CAS(10,10) calculation of $[V(dmcat)_3]^{1-}$ with C_{3v} symmetry labels.

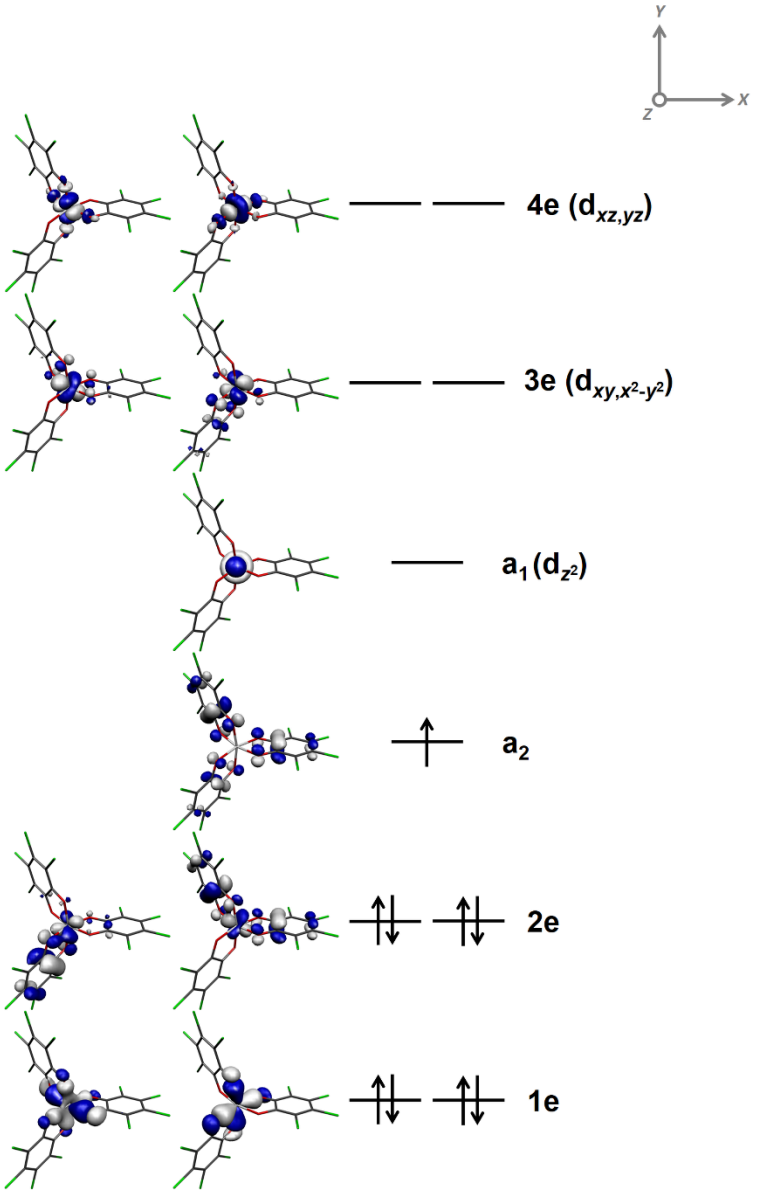

Fig. S17 Visualisation of the orbitals that comprise the active space of the SA-CASSCF/NEVPT2 CAS(9,10) calculation of $[V(Cl_4cat)_3]$ with C_{3v} symmetry labels.

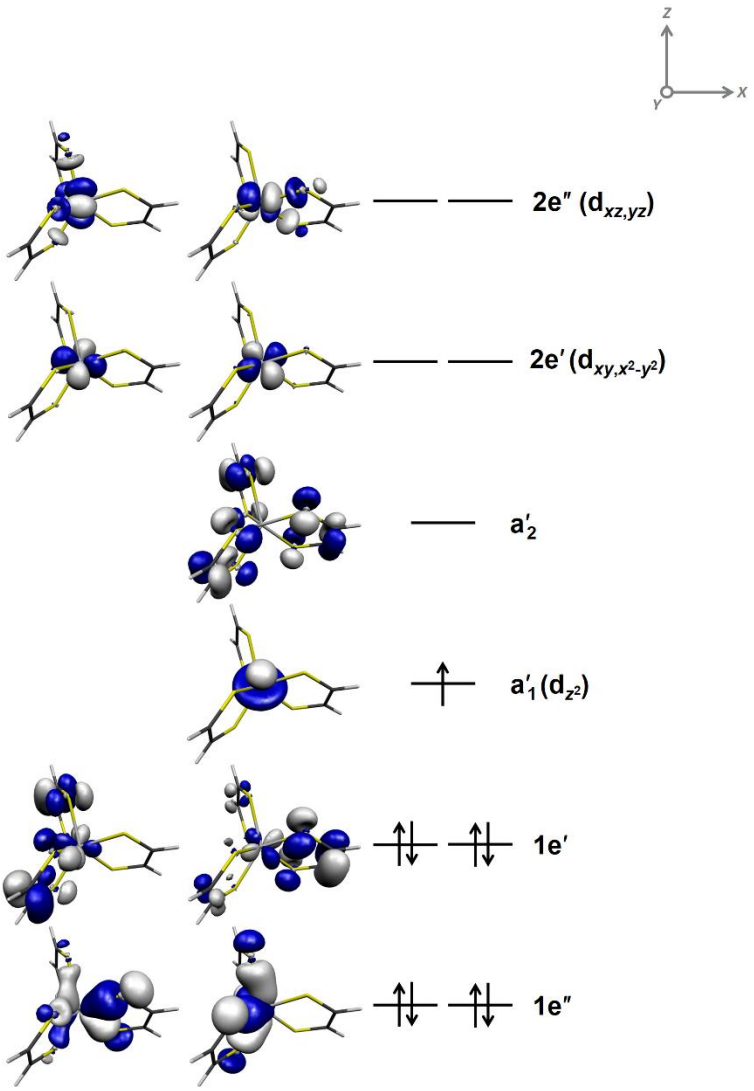

Fig. S18 Visualisation of the orbitals that comprise the active space of the SA-CASSCF/NEVPT2 CAS(9,10) calculation of [V(edt)$_3$] with D_{3h} symmetry labels.

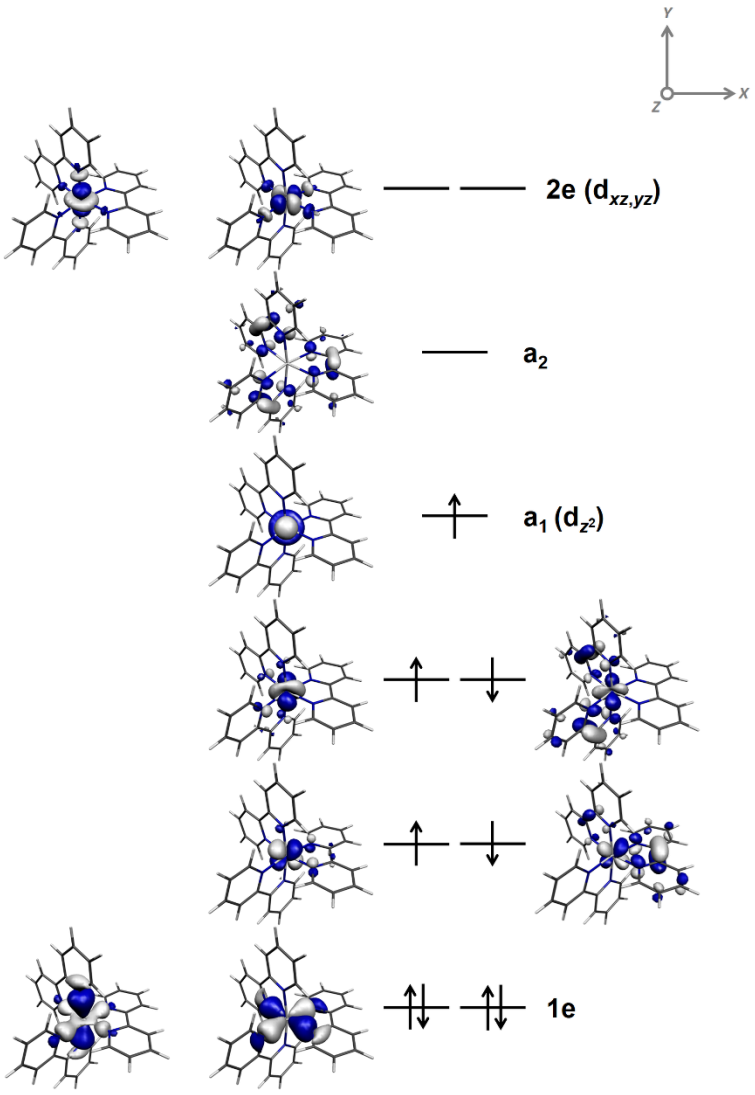

Fig. S19 Visualisation of the orbitals that comprise the active space of the SA-CASSCF/NEVPT2 CAS(9,10) calculation of [V(bpy)$_3$] with C_{3v} symmetry labels.

Table S13 Energies (eV) of frontier orbitals derived from SA-CASSCF/NEVPT2 calculations[a]

	4e / 2e″	3e / 2e′	a_1 / a_1'	a_2 / a_2'	2e / 1e′	1e / 1e″
$[V(dmcat)_3]$	0.28417	0.11111	**0.07260**	–0.15576	–0.17301	–0.54710
	0.28368	0.10768			–0.17463	–0.54917
$[V(dmcat)_3]^{1-}$	0.43072	0.23749	**0.20746**	–0.07885	–0.09534	–0.41585
	0.43062	0.23696			–0.09600	–0.41728
$[V(Cl_4cat)_3]$	0.23505	0.06048	**0.02347**	–0.20420	–0.22120	–0.59840
	0.23425	0.05649			–0.22274	–0.60022
$[V(edt)_3]$	0.14100	0.06617	–0.11432	**–0.00720**	–0.22905	–0.39549
	0.14075	0.06573			–0.22996	–0.39594
$[V(bpy)_3]$	0.26672	0.08102	–0.03197	**0.05562**	–0.07450	–0.50726
	0.26640	0.08033			–0.07453	–0.50740

[a] C_{3v} or D_{3h} symmetry labels applied; highest-occupied orbital indicated in red.

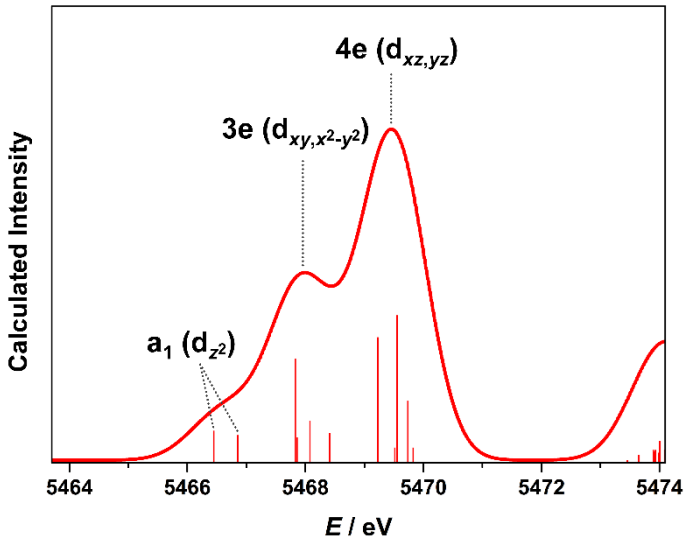

Fig. S20 TD-DFT calculated V K-pre-edge spectrum for [V(dbcat)$_3$]. Sticks denote individual transitions to acceptor orbitals presented in Fig. S2. Calculated intensity is in arbitrary units.

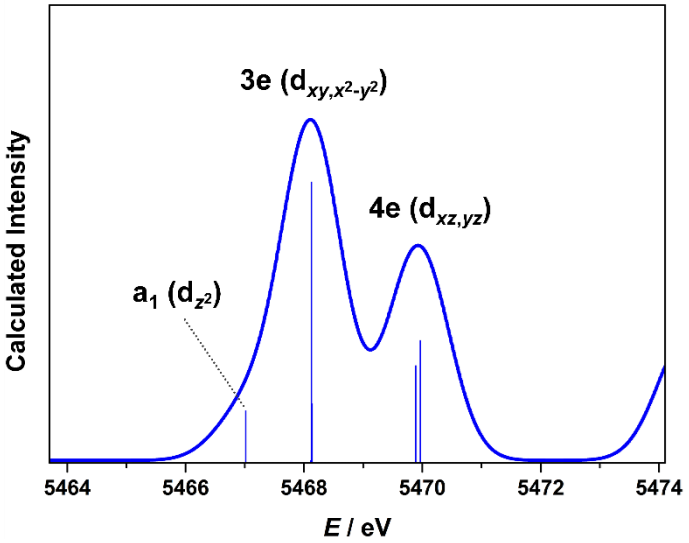

Fig. S21 TD-DFT calculated V K-pre-edge spectrum for [V(dbcat)$_3$]$^{1-}$. Sticks denote individual transitions to acceptor orbitals presented in Fig. S3. Calculated intensity is in arbitrary units.

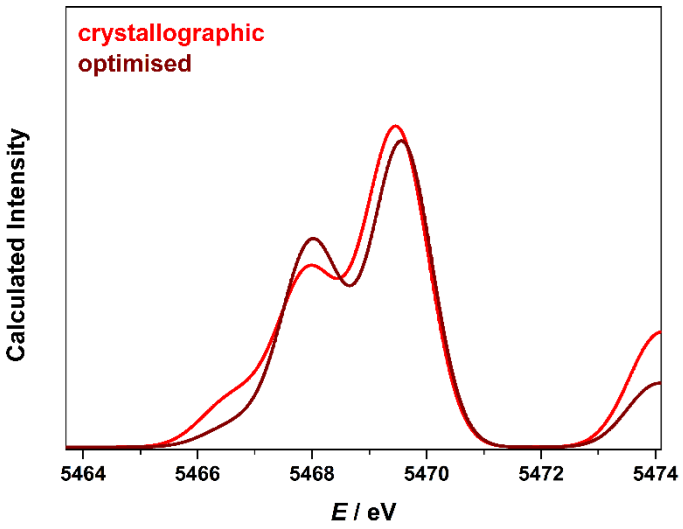

Fig. S22 Overlay of TD-DFT calculated V K-pre-edge spectrum for [V(dbcat)$_3$] based on crystallographic coordinates (red) and geometry-optimised coordinates (burgundy). Calculated intensity is in arbitrary units.

Table S14 Vanadium 3d and 4p contribution (%) to the lowest unoccupied MOs derived from B3LYP DFT calculations

		a_2	**a_1 (d_{z^2})**	**3e (d_{xy,x^2-y^2})**		**4e ($d_{xz,yz}$)**	
[V(dbcat)$_3$]	3d	0.1	78.3	56.1	59.1	47.2	34.2
	4p	0.5	0.0	0.0	0.3	0.4	0.0
[V(dbcat)$_3$]$^{1-}$	3d		78.7	61.9	62.9	53.5	48.5
	4p		0.0	0.1	0.5	0.3	0.1

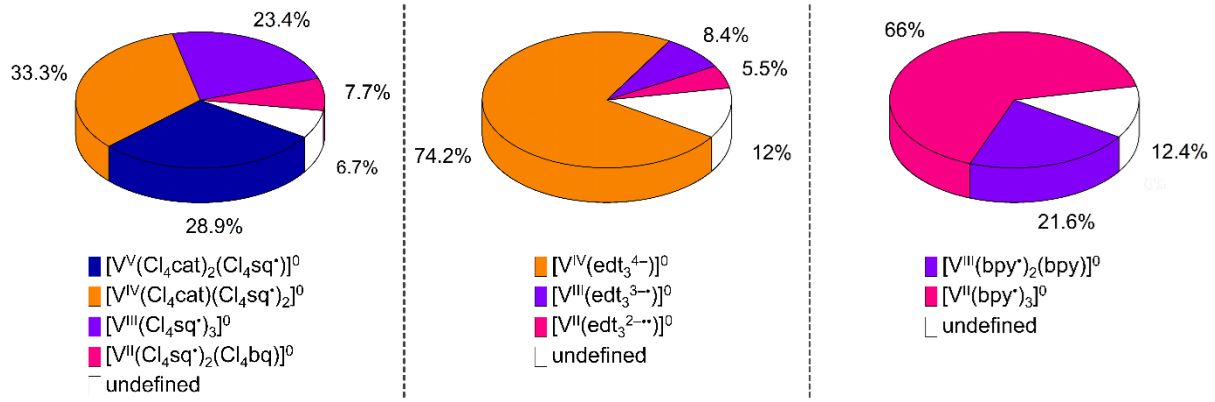

Fig. S23 Configurational ground state compositions from analysis of CAS wavefunctions for $[V(Cl_4cat)_3]$ (left), $[V(edt)_3]$ (centre), and $[V(bpy)_3]$ (right) in terms of vanadium d-electron counts, and representative configurations for the individual valence bond oxidation state assignments listed beneath.

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