Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Electronic Structure Study of Divanadium Complexes with Rigid Covalent Coordination: Potential Molecular Qubits with Slow Spin Relaxation

Stephen Sproules

WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

Experimental Section

Synthesis of Complexes. All air-sensitive materials were manipulated using standard Schlenk techniques or a glovebox. The complexes $[V_2(\mu\text{-}S_2)_2(Et_2dtc)_4]$ (**1-Et**),[1] $[V_2(\mu\text{-}S_2)_2(^iBu_2dtc)_4]$ (**1-Bu**),[2] $[V_2(\mu\text{-}S_2)_2(Et_2dtc)_4]BF_4$ (**2-Et**),[3] and $[V_2(\mu\text{-}S_2)_2(^iBu_2dtc)_4]BF_4$ (**2-Bu**),[3] have been synthesised according to literature procedures.

Sulfur K-edge 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. S K-edge data were measured using the 54-pole wiggler beam line 4-3 in a high-magnetic field mode of 10 kG with a Ni-coated harmonic rejection mirror and a fully tuned Si(111) double-crystal monochromators. Details of the optimisation of this setup for low-energy have been previously described.[4] All samples were measured at room temperature as fluorescence spectra using a Lytle detector. Samples were ground finely and dispersed as thinly as possible on Mylar tape to minimise the possibility of fluorescence saturation effects. Data represent 2–3 scan averages. All samples were monitored for photoreduction throughout the course of data collection. The energy was calibrated using the S K-edge spectrum of $Na_2S_2O_3{\cdot}5H_2O$, run at intervals between sample scans. The maximum of the first pre-edge feature in the spectrum was fixed at 2472.02 eV. A step size of 0.08 eV was used over the edge region. Data were averaged, and a smooth background was removed from all spectra by fitting a polynomial to the pre-edge region and subtracting this polynomial from the entire spectrum. Normalisation of the data was accomplished by fitting a flattened polynomial or straight line to the post-edge region and normalising the post-edge to 1.0.

Other Physical Methods. Electronic absorption spectra were recorded on a Shimadzu UVA 3600 spectrophotometer (range 200–1600 nm). Continuous wave X-band EPR spectra was recorded on a Bruker ELEXSYS E500 spectrometer. The spectra were simulated with the Bruker XSOPHE suite.[5] Fluid solution spectra were simulated using a spin Hamiltonian of the form $\hat{H} = g{\cdot}\mu_B{\cdot}B{\cdot}S + \sum a{\cdot}S{\cdot}I$, where the weighted summation is over all naturally occurring vanadium isotopes; 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 $\sigma_v = a + bM_I + cM_I^2 + dM_I^3$.[6] Randomly orientated EPR spectra were simulated following the spin Hamiltonian $\hat{H} = \mu_B \cdot \mathbf{g} \cdot \mathbf{B} \cdot \mathbf{S} + \sum \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$, where **g** and **A** are the 3 × 3 electron Zeeman and magnetic hyperfine interaction matrices, respectively. A Gaussian lineshape and distribution of *g*- and *A*-values (strain) were employed to account for the linewidth variation.

For the unpaired electron located in an antibonding molecular orbital (ψ) is defined in eq S1,

$$\psi = \beta|3d\rangle - \beta'|\varphi_L\rangle \quad \text{(S1)}$$

where φ_L is an MO comprising the symmetry-adapted linear combination of S 3s and 3p orbitals, and β, β' are mixing coefficients that represent covalency.[7,8] The mixing coefficient β, is calculated by evaluating the vanadium hyperfine structure tensor *A*, by means of eq. S2 and S3,

$$A_{\parallel} = -K - (4/7)\beta^2 P + (g_{\parallel} - g_e)P + (3/7)(g_{\perp} - g_e)P \quad \text{(S2)}$$

$$A_{\perp} = -K + (2/7)\beta^2 P + (11/14)(g_{\perp} - g_e)P \quad \text{(S3)}$$

where *K* is the isotropic hyperfine contact term arising from the polarisation of inner s electrons by the unpaired spin in the d orbital; $P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle_{3d}$, where g_e is the *g*-value of the free electron ($g_e = 2.0023$), g_n is the nuclear *g*-value, and β_e and β_n are the Bohr and nuclear magnetons, respectively. It has been found that the sign of *K* is the same as g_n, and $P = 128 \times 10^{-4}$ cm^{-1} is used here.[8]

Calculations. The program package ORCA was used for density functional theory (DFT) calculations.[9] Geometry optimisation employed the TPSS meta-generalised gradient approximation functional;[10] single-point calculations on optimised and crystallographic coordinates used the one-parameter hybrid variant TPSSh.[11] The scalar relativistically recontracted ZORA-def2-TZVP basis set as used for all atoms.[12] 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.[13] Increased integration accuracy was applied to the vanadium and sulfur (grid = 7) atoms. Calculations included the zeroth-order regular approximation (ZORA) for relativistic effects[14] as implemented by van Wüllen.[15] 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[16] 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 **1-Et** and **1-Bu**.[17] 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,[18] 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. S4,[19] and assuming the spin-Hamiltonian eq. S5 is valid,

$$J = \frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}} \quad \text{(S4)}$$

$$\hat{H} = -2J\hat{S}_A \cdot \hat{S}_B \quad \text{(S5)}$$

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.

The property calculations at the optimized geometries were done using dichloromethane as solvent.[20] In this case the same basis sets were used but with enhanced integration accuracy (SPECIALGRIDINTACC 10) for the vanadium and sulfur atoms. Calculation of the **g**-matrix included a larger the integration grid (Grid7) and fully decontracted basis sets.[21] Vanadium hyperfine coupling values (**A**-matrix) were computed using Sauer's aug-cc-pVTZ-J basis set.[22] Electronic spectra were reproduced using the time-dependent (TD)-DFT protocol. The first 80 states were calculated, and the maximum dimension of the expansion space in the Davidson procedure (MAXDIM)

was set to 800. The full width at half maximum (FWHM) was set to 3000 cm^{-1}. Molecular orbitals and spin density maps were visualised via the programme Molekel.[23]

The multireference ground state composition of **1-Et** and **2-Et** was examined using the state-averaged complete active space self-consistent field (SA-CASSCF) method[24] with the def2-TZVP basis set for all atoms. A CASSCF(2,10) (two electrons in the ten active metal d-based orbitals) and CASSCF(1,10) was performed for **1-Et** and **2-Et**, respectively. For **2-Et**, the calculation was averaged over 10 doublet states; for **1-Et**, the calculation was averaged over 10 triplet and 10 singlet states. The NEVPT2 calculations were performed on each reference space.[25] 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.

Table S1 Continuous shape measures for eight-coordinate geometry of VS_8 unit

Geometry	**CShM**[a]
octagon	36.2
heptagonal pyramid	21.5
hexagonal bipyramid	16.1
cube	12.1
square antiprism	5.5
triangular dodecahedron	**3.7**
Johnson gyrobifastigium (J26)	13.1
Johnson elongated triangular bipyramid (J14)	27.6
biaugmented triangular prism (J50)	4.6
biaugmented trigonal prism	**4.4**
snub diphenoid (J84)	6.3
triakis tetrahedron	12.6
elongated trigonal bipyramid	24.3

[a] Ref. 26

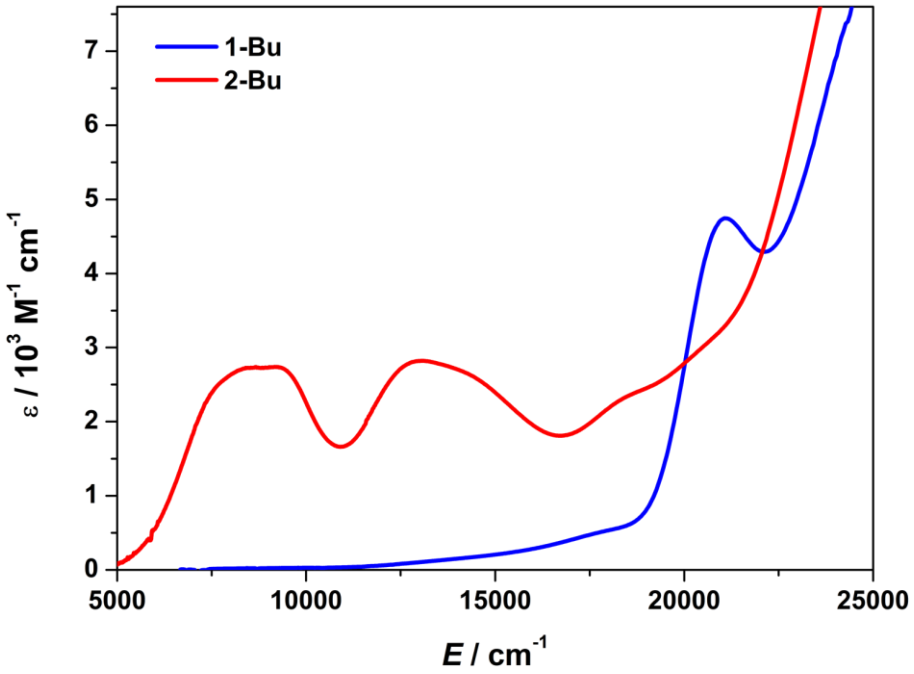


Fig. S1 Overlay of the electronic spectra of **1-Bu** and **2-Bu** recorded in dichloromethane solution at ambient temperature.

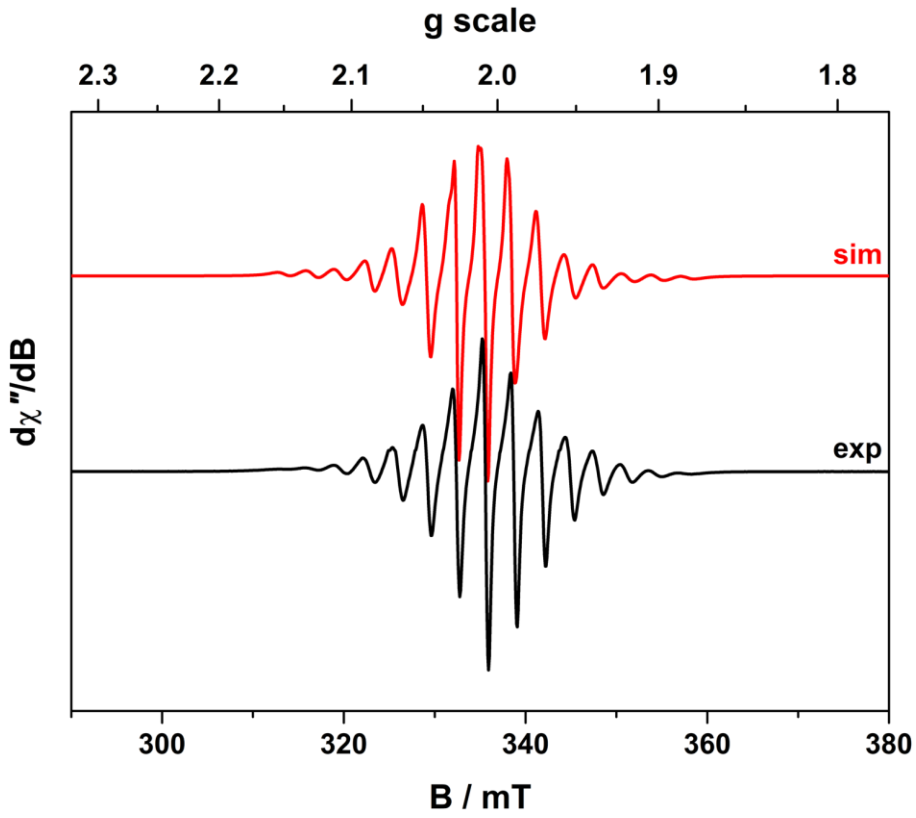


Fig. S2 X-band EPR spectrum of **2-Et** in CH_2Cl_2 at 293 K (experimental conditions: frequency, 9.4039 GHz; modulation, 0.8 mT; power, 0.063 mW). Experimental data are shown by the black line; simulation depicted by the red trace: g_{iso} = 2.0066; A_{iso} = 29.6 × 10^{-4} cm^{-1}.

Table S2 Comparison of *g*- and *A*-values[a] for related compounds

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**
2-Et	2.0066	2.0021	2.0069	2.0152	2.0081	–29.6	–18.0	–18.0	–52.9	–29.6	this work
$[V_2(\mu\text{-}S_2)_2(^n Bu_2dtc)_4]^+$	2.004	2.004	2.001	2.011	2.005	–29.1	–10.3	–24.3	–53.1	–29.2	27
$[VO(Et_2dtc)_2]$	1.9794	1.9871	1.9871	1.9640	1.9794	–83.5	–51.2	–51.2	–147.6	–83.3	28
$[V(Et_2dtc)_4]$	1.9746	1.9831	1.9831	1.9576	1.9746	–66.6	–37.8	–37.8	–123.5	–66.4	28
$[V(S_2CNR)_4]$											
R = pyrrole	1.976	1.986	1.986	1.961	1.978	–62.7	–36.9	–36.9	–118.3	–64.0	29
R = carbazole	1.976	1.986	1.986	1.964	1.979	–63.5	–36.4	–36.4	–116.0	–62.9	29
R = indole	1.979	1.986	1.986	1.966	1.979	–63.8	–37.1	–37.1	–118.6	–64.3	29
R = indoline	1.980	1.989	1.989	1.963	1.980	–63.3	–36.9	–36.9	–118.1	–64.0	29
$[V(S_2CMe)_4]$	1.9735	1.9817	1.9778	1.9610	1.9735	–61.2	–31.3	–43.0	–107.3	–60.5	30
$[V(S_2CPh)_4]$	1.976	1.9816	1.9814	1.9632	1.9754	–59.0	–34.45	–34.50	–104.9	–57.95	30
$[V(S_2CC_5H_3(NHR)_4]$											
R = H	1.971	1.985	1.985	1.931	1.967	–101.0	–74.1	–74.1	–174.9	–107.7	31
R = Et	1.969	1.983	1.983	1.932	1.966	–102.8	–70.6	–70.6	–169.6	–103.6	31
R = ^{n}Pr	1.968	1.984	1.984	1.929	1.966	–104.9	–71.8	–71.8	–173.8	–105.8	31
R = ^{n}Bu	1.969	1.986	1.986	1.933	1.968	–105.0	–73.0	–73.0	–176.0	–107.3	31

[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] $\langle A \rangle = (A_{xx} + A_{yy} + A_{zz})/3$.

Table S3 Comparison of β^2 and *K*-values[a] for related compounds

	CN[b]	Geometry	Symmetry	Ground State	d-orbital	β^2	K / 10^{-4} cm^{-1}	A_{iso} / 10^{-4} cm^{-1}
2-Et	8	bicapped trigonal prism	C_{2h}	a_g	$x^2–y^2$ [c]	0.66	30.4	–29.6
$[V(Et_2dtc)_4]$	8	dodecahedral	D_{2d}	b_1	$x^2–y^2$	0.74	62.8	–66.6
$[VO(Et_2dtc)_2]$	5	square pyramidal	C_{2v}	a_1	$x^2–y^2$	0.84	80.4	–83.5
$[V(S_2C_2(CN)_2)_3]^{2-}$ [d]	6	octahedral	D_3	a_1	z^2	0.65	55.2	–57.7

[a] Calculated using eqs S2 and S3. [b] CN = coordination number. [c] Non-standard axis alignment with *x*-axis along V···V vector. [d] Values taken from ref. 32.

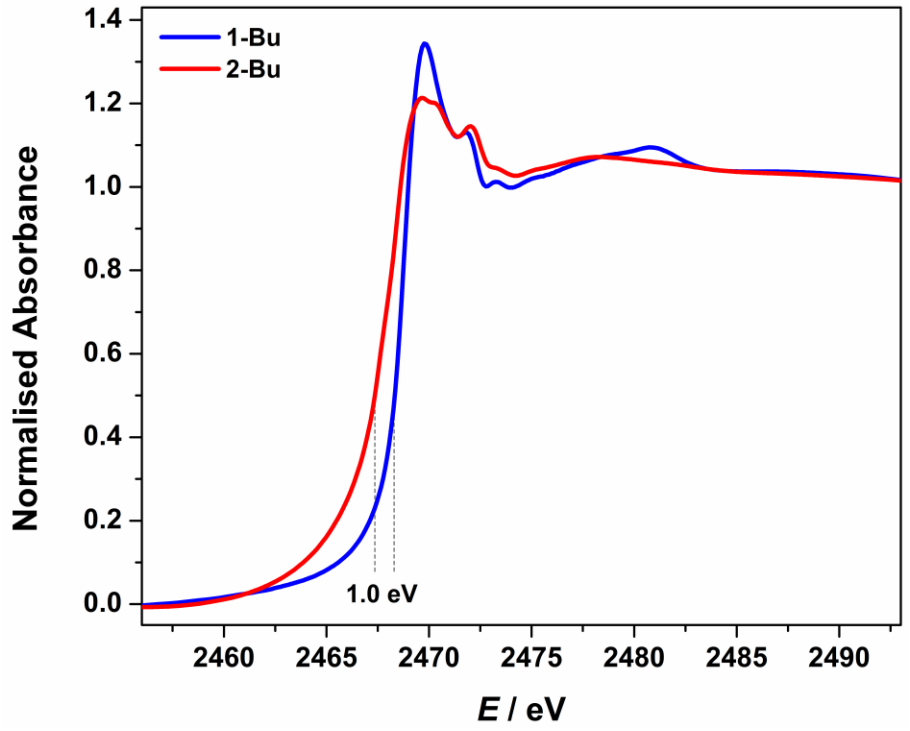


Fig. S3 Overlay of the normalised sulfur K-edge spectra of **1-Bu** and **2-Bu**

Table S4 Geometry-optimised coordinates of **1-Et**

V	1.08549101696758	10.76263712427527	-0.63527047216000
V	-1.08548098045553	9.72936539367769	0.63528079240439
S	1.10401653717003	8.73490121131349	0.65816126801282
S	0.90135572078665	10.44682341799428	1.70236427993384
S	1.61625007618664	13.08320128130520	0.15754577535688
S	3.53130841789361	10.99634238101503	-0.21333471014536
S	1.56229983538613	11.93212363082761	-2.78328556226583
S	2.07072998773385	9.16485298909911	-2.29331924370009
S	-1.10400638727720	11.75710191997463	-0.65815001226405
S	-0.90134592300606	10.04518011507447	-1.70235374741192
S	-1.61623858896166	7.40880162915587	-0.15753733465222
S	-3.53129829932384	9.49565919250676	0.21334394903234
S	-1.56229068449811	8.55987787833236	2.78329526421870
S	-2.07072239092037	11.32714822018429	2.29332892941278
N	4.24049082110737	13.44585259020327	0.66986387951042
N	2.65033659085337	10.32488956516683	-4.65893557062272
C	3.26218872319715	12.61330256504408	0.26407860000138
C	5.63234166845869	12.99649812381533	0.72347459889451
C	6.36644230959847	13.22667820782974	-0.59811118440917
C	3.94575904598671	14.82451705711189	1.06209535516064
C	3.64529584848974	14.95126625612815	2.55520147278616
C	2.15131907280462	10.46045667130097	-3.41456691108632
C	2.68271846288569	11.45923640721417	-5.58247516650369
C	1.41006033944643	11.55721646912871	-6.42358231888937
C	3.19561827020224	9.04644880636680	-5.11696109972369
C	4.68989681806690	8.91664406119643	-4.82108434970441
H	6.12229943992572	13.53476095630728	1.54858416943585
H	5.62893427607103	11.92669873810012	0.97801761174463
H	7.40661567905639	12.87944657101047	-0.52238872679002
H	6.37898961303855	14.29281430440508	-0.86639694651643
H	5.87075350211857	12.66945889392521	-1.40386887667519
H	4.81309527903677	15.44070320584197	0.78053438039345
H	3.08778478533734	15.16827437084485	0.46620606183491
H	3.44146298108511	15.99952864035125	2.81561907708480
H	4.49426827715865	14.60702297535213	3.16370688643029
H	2.76317142024099	14.35122424843014	2.81552254702066
H	3.57166235893854	11.34140699375133	-6.22023272556894
H	2.81908180450116	12.37355332021327	-4.98653851616568
H	1.47177708256052	12.41306872546005	-7.11098646490171
H	0.53793160851007	11.69823197840666	-5.77117561669417
H	1.25536687931372	10.64781602575538	-7.02276920679471
H	2.63437635656338	8.24352941624239	-4.61762729347150
H	2.99695000918755	8.96788923752876	-6.19658813681728
H	5.06734870883704	7.94693727767654	-5.17613604053956
H	4.86553297434332	8.98371900063136	-3.73886450740571
H	5.26621177153997	9.70933504264607	-5.31948123625157
C	-3.26217711066031	7.87870025157560	-0.26407286618359
C	-2.15131668289363	10.03154300147631	3.41457442155574
N	-4.24047795924849	7.04615106155872	-0.66986283956509
N	-2.65034499210323	10.16710741450536	4.65893899364143
C	-5.63232866022725	7.49550547021587	-0.72347667365324
C	-3.94574428523042	5.66748829848474	-1.06209893553532
C	-2.68273484848187	9.03275891116868	5.58247621770159
C	-3.19563615900845	11.44554580975830	5.11695992273467
C	-6.36643417495428	7.26532037556962	0.59810554494780
H	-6.12228343127999	6.95724560661114	-1.54858995496942
H	-5.62892048972576	8.56530578380130	-0.97801577844468
C	-3.64527678383599	5.54074550190491	-2.55520471754729
H	-4.81308088964859	5.05130039409766	-0.78054301663718
H	-3.08777148810216	5.32372913057270	-0.46620861150365
C	-1.41008579116635	8.93477934703396	6.42359709101491
H	-3.57168583263014	9.15058584765435	6.22022441493981
H	-2.81909051566878	8.11844282110568	4.98653651823354

C	-4.68991133127121	11.57534623424978	4.82106389773230
H	-2.63439036644291	12.24846784358472	4.61763473387932
H	-2.99698209096678	11.52410414129296	6.19658965631920
H	-7.40660743369839	7.61255171401205	0.52238032780594
H	-6.37898192197544	6.19918334380030	0.86638751506216
H	-5.87074886496825	7.82253708471556	1.40386718235663
H	-3.44144143098572	4.49248451705618	-2.81562595459633
H	-4.49424810290638	5.88498979942080	-3.16371110677394
H	-2.76315264066170	6.14079007532873	-2.81552078250331
H	-1.47180863031381	8.07892549031038	7.11099867036090
H	-0.53794953268509	8.79376681865539	5.77119982137428
H	-1.25540051862924	9.84417874347561	7.02278763379606
H	-5.06737098375037	12.54505133502997	5.17611193665210
H	-4.86553299129397	11.50827205319807	3.73884161001496
H	-5.26623018072849	10.78265269065187	5.31945220725152

Table S5 Geometry-optimised coordinates of **1-Bu**

V	-3.51822499523900	6.00573936451236	2.60978607069722
V	-3.51760322645555	8.72715529195405	2.61007856710278
S	-5.12227993684712	7.37518533453788	3.73989780792049
S	-3.27976347819861	7.35184928196260	4.55564625559773
S	-3.98550920796735	4.16868145843839	4.22499727779247
S	-1.37505941203927	5.06661506999167	3.49543736358090
S	-5.61086828158417	9.65340863838636	1.62111536178980
S	-4.40752438599809	10.56492745471863	4.03121799628531
N	-1.75277118548002	3.06433069149951	5.26550853597827
N	-6.79401486911663	11.51998218263594	3.17999829877140
C	-2.30353120653598	3.98073950329457	4.44517626461251
C	-2.60941018470502	2.22202620781831	6.10314220318743
C	-3.13242990431223	2.93354710120558	7.36256703101689
C	-1.99250399559524	3.44039869556763	8.24767253903861
C	-4.06599683865694	1.98761495116839	8.12169132610784
C	-0.29981078339501	2.88640072607231	5.30118771365698
C	0.24913720176229	2.06611565997309	4.12162326907786
C	-0.37971598581942	0.67323048049537	4.04982544063449
C	1.77438559935955	1.99913656764488	4.22071768969636
C	-5.74365819546940	10.69642637667582	2.97713967250172
C	-7.96134188454593	11.49384285927259	2.30175590679836
C	-9.16649838314780	10.75150911681338	2.90924470543237
C	-8.82835873422082	9.30156153962774	3.26543908556412
C	-10.34645957093761	10.83478224233314	1.93564655188162
C	-6.83126160776212	12.43482906919746	4.31874761387174
C	-6.52453704772576	13.89408698786054	3.94159212219916
C	-5.12726015797966	14.04068058768344	3.33534150371597
C	-6.69894314244388	14.78049859935904	5.17844923545015
H	-3.46194528742640	1.88407548010266	5.49203323100751
H	-2.02492295854513	1.33359850988638	6.38409403547933
H	-3.71856678428849	3.80066066371959	7.01722703387156
H	-1.34553770875840	4.14495372086500	7.70637737031644
H	-1.36929343461447	2.60642434331945	8.61015753457689
H	-2.38880549713422	3.96520143466551	9.12850242230154
H	-4.48586185926496	2.47969914234154	9.01005371232481
H	-3.52604436484762	1.08944598835995	8.46272437445964
H	-4.90435513341135	1.65875986157269	7.49045064359988
H	0.16805096647201	3.88344895513119	5.30528215666026
H	-0.04990693467980	2.39634927687081	6.25367399906154
H	-0.01808233529520	2.61297823080273	3.20254579430902
H	0.01457105637740	0.11576142224829	3.18793024159867
H	-1.47130146500051	0.73233146923136	3.93627356505858
H	-0.15716622826406	0.08553935391321	4.95588101769389
H	2.19882528322735	1.44656594577208	3.37048049058828
H	2.08936929088605	1.48286550820231	5.14256975782231
H	2.22230678852540	3.00349736852225	4.22610145402138
H	-8.24126067518602	12.53257646304415	2.06725733402643
H	-7.66348141697374	11.01176286473429	1.35916430711423
H	-9.45319661551702	11.27815116729175	3.83724784641135
H	-9.68230266671094	8.81673296652671	3.76045728174739
H	-7.96371601144514	9.23683119054842	3.94060404354316
H	-8.58218492780119	8.72421368206043	2.36289395717600
H	-11.24085055443843	10.35890084544500	2.36123508445041
H	-10.11010851055617	10.31643479607595	0.99337819758803
H	-10.60109975198529	11.87706858545379	1.69334531482005
H	-7.82992771338905	12.37094813961247	4.77919106165007
H	-6.10264608382797	12.07473047854453	5.05961786101796
H	-7.26674078888509	14.21070246417663	3.18713961879879
H	-4.99123283976893	13.38771393148762	2.46292918389911
H	-4.35523059962776	13.76775855792092	4.06917329555924
H	-4.94807969347130	15.07778686163025	3.01682353943451
H	-6.52056766767668	15.83688634083972	4.93183533287527
H	-5.98233329202016	14.49456426179304	5.96404258796679

H	-7.71250300661921	14.69791501665275	5.59985066463833
S	-1.91576954784131	7.37471066672050	1.47784138522933
S	-3.75917581856772	7.35233488642169	0.66403093864521
S	-3.04865189099358	4.16887151968088	0.99507507987025
S	-5.66018703824390	5.06283262595805	1.72569624013882
S	-1.42196758907774	9.64766390888344	3.59967962847992
S	-2.62402892047520	10.56487971308994	1.19098224540312
C	-4.73046371757311	3.97709316106066	0.77702988605330
C	-1.28844588134367	10.69378186288417	2.24608762909748
N	-5.28023264684968	3.05798135296995	-0.04095346617559
N	-0.23730077885869	11.51679675053802	2.04507991876640
C	-4.42292617099651	2.21622421545935	-0.87842872457752
C	-6.73282477373380	2.87646767227975	-0.07400226680358
C	0.92978585695070	11.48796784917364	2.92354557918458
C	-0.19959242053143	12.43464417913101	0.90876917869392
C	-3.90399344489978	2.92660356413263	-2.14018736781531
H	-3.56844125187789	1.88161555820620	-0.26821463159155
H	-5.00567323159960	1.32576266762522	-1.15654282602150
C	-7.27777910746735	2.05675376035010	1.10783471226688
H	-7.20305793931311	3.87237540804173	-0.07883010161168
H	-6.98314511197850	2.38436458341280	-1.02531739979160
C	2.13453184810731	10.74601647908865	2.31476890840776
H	1.21045496789383	12.52597366656420	3.16036146889910
H	0.63132327235065	11.00406364877602	3.86500528455057
C	-0.50430439665541	13.89329891149642	1.28989253472353
H	0.79870399035473	12.37078866072971	0.44749862125147
H	-0.92912272168327	12.07736075960141	0.16745593726930
C	-5.04674652276349	3.42977543138475	-3.02376528620175
C	-2.97015687005521	1.98123041858031	-2.89971090462121
H	-3.31885753101536	3.79548004584127	-1.79756436937609
C	-6.64575328306874	0.66536164737554	1.18065719030632
C	-8.80305993171864	1.98625173378089	1.01167602609656
H	-7.01005530337953	2.60565322212102	2.02555267630737
C	1.79528558135461	9.29711853266664	1.95535058166594
C	3.31430612365073	10.82622937877251	3.28883847263333
H	2.42189860220748	11.27440515954934	1.38796380049885
C	-1.90038041295685	14.03994793595935	1.89891161729076
C	-0.33112922189050	14.78234372526734	0.05475918895549
H	0.23948137402063	14.20750320552732	2.04377188751934
H	-5.69366111308900	4.13434105875980	-2.48242017529889
H	-5.66939801551808	2.59411080824346	-3.38330171487845
H	-4.65317491664920	3.95351664393258	-3.90643968232582
H	-2.55299455185119	2.47274114559423	-3.78965575329800
H	-3.50911918227537	1.08154587918496	-3.23829401863127
H	-2.12992824601965	1.65491025465117	-2.26965337411863
H	-7.03696702794973	0.10855501899958	2.04440063599890
H	-5.55404970850233	0.72695683630299	1.29173361857270
H	-6.86905957406347	0.07561567231380	0.27613512666139
H	-9.22470424170969	1.43408445103456	1.86357546959203
H	-9.11860451203053	1.46781894294261	0.09122771223928
H	-9.25322422243734	2.98959429762279	1.00554834305618
H	2.64927043817264	8.81237911565914	1.46031098079174
H	0.93135979898462	9.23470400921015	1.27903812681651
H	1.54743182859984	8.71822152087512	2.85643976627565
H	4.20850982993873	10.35083642251473	2.86230768864843
H	3.07743873691040	10.30575438728170	4.22980493553130
H	3.56953073874644	11.86776719356838	3.53371398136262
H	-2.03518463716064	13.38602494073251	2.77079496681245
H	-2.67395760887256	13.76840894528392	1.16621701440106
H	-2.07825769400858	15.07676267973820	2.21907961175973
H	-0.50777353989099	15.83837959193080	0.30412491297998
H	-1.04951711933563	14.49905515205266	-0.73017218745670
H	0.68155862352951	14.69954423240166	-0.36871301653898

Table S6 Geometry-optimised coordinates of **2-Et**

V	1.18514747096641	10.80813750914009	-0.68317182784047
V	-1.18513864509603	9.68386987356756	0.68315389905701
S	1.07573539613467	8.75684862205080	0.64385084806128
S	0.85077806020747	10.48710163980184	1.67124405718764
S	1.67805051410439	13.13884737467093	0.10768230487717
S	3.57845993560283	11.03601820027379	-0.18921041516314
S	1.63091280569717	11.92956569599717	-2.81896262417455
S	2.16904204635024	9.17779295457160	-2.31395611597042
S	-1.07572657450185	11.73515869061171	-0.64386875732844
S	-0.85076922012782	10.00490570511153	-1.67126202149885
S	-1.67804163494445	7.35315996995806	-0.10769997987177
S	-3.57845111657034	9.45598977099419	0.18919244405084
S	-1.63090382361834	8.56244170106661	2.81894460519425
S	-2.16903321281488	11.31421438129195	2.31393809275293
N	4.29459274788943	13.49131407433796	0.70951716025006
N	2.67210519805991	10.30662161688893	-4.72368926673985
C	3.32618719472864	12.67321120961524	0.28400944993752
C	5.69098631330474	13.03421668268869	0.82273223870180
C	6.52476002076441	13.35708180009249	-0.41767508894075
C	4.01101733101751	14.89001914544967	1.07593498829119
C	3.75873897374860	15.07276838842261	2.57247352367424
C	2.21459615776171	10.44834745482573	-3.47501256866401
C	2.68033755160299	11.43639839229789	-5.66920386364533
C	1.42909972653176	11.48654191759959	-6.54608714847074
C	3.18882562792251	9.01450098036593	-5.20804016878894
C	4.70678148137608	8.89309920859091	-5.07675886198642
H	6.11537581013601	13.51553904826583	1.71590081998558
H	5.67570058183136	11.95143081900398	1.01041676697799
H	7.55814586171029	13.01549808439114	-0.26688999097379
H	6.55347804337361	14.43740700846455	-0.61670730425208
H	6.12032567694949	12.84948424912089	-1.30302346628562
H	4.87245797086625	15.49003551939542	0.74725219799174
H	3.14111645106947	15.22150757025593	0.49112849193891
H	3.57982895462593	16.13490386019983	2.78907804638217
H	4.62103425806010	14.74914268095059	3.17252326761873
H	2.87593225316981	14.50380489284755	2.89332031487055
H	3.58643359070605	11.33480163077260	-6.28389584190742
H	2.78259149453628	12.36261770850037	-5.08618916070170
H	1.50018533658586	12.33382949170642	-7.24234349098425
H	0.52707686407493	11.62054205971156	-5.93437682658920
H	1.31365315421849	10.57107877722976	-7.14388044493825
H	2.68518097513202	8.21889933285932	-4.64079868713762
H	2.87578884051061	8.91479568517433	-6.25808952352785
H	5.03426724825540	7.91933267285016	-5.46675052491587
H	5.01491497817765	8.96227628350531	-4.02518490360724
H	5.22828780724293	9.67368874773727	-5.64772764726345
C	-3.32618106562359	7.81879218140665	-0.28401354455385
C	-2.21459150641410	10.04365881401161	3.47499322644693
N	-4.29459041021860	7.00068309217643	-0.70950069468099
N	-2.67210577822259	10.18538314851444	4.72366820225688
C	-5.69098613519370	7.45777683354541	-0.82270368643170
C	-4.01101722088631	5.60197437768089	-1.07590632499762
C	-2.68034052192558	9.05560561531844	5.66918183791843
C	-3.18882928143332	11.47750283555168	5.20801835183461
C	-6.52474428522299	7.13492320763366	0.41771706260487
H	-6.11538557281170	6.97644452358259	-1.71586217641356
H	-5.67570443536856	8.54056079047158	-1.01039959399171
C	-3.75875649382589	5.41920878349039	-2.57244580626964
H	-4.87245306280835	5.00196035578236	-0.74720666901542
H	-3.14110891657602	5.27049364015635	-0.49110648031028
C	-1.42910576304111	9.00546273970981	6.54606951985709
H	-3.58643887548071	9.15720098144412	6.28387063509424
H	-2.78259146186780	8.12938661279005	5.08616610337642

C	-4.70678466160164	11.59890361627909	5.07673073852352
H	-2.68518279382121	12.27310547576601	4.64077989190996
H	-2.87579700541447	11.57720718156256	6.25806914725762
H	-7.55813239648264	7.47650404181180	0.26694103477098
H	-6.55345854201779	6.05459999058469	0.61676071818692
H	-6.12029980903112	7.64253034029566	1.30305533138277
H	-3.57984813609496	4.35707105908572	-2.78904061370630
H	-4.62105919308281	5.74282705304657	-3.17248891198789
H	-2.87595405749717	5.98816945808815	-2.89330942894929
H	-1.50019299294415	8.15817466784636	7.24232509605996
H	-0.52708062324546	8.87146384352946	5.93436227569273
H	-1.31366217653795	9.92092563327558	7.14386377295741
H	-5.03427280454562	12.57266945584024	5.46672214753349
H	-5.01491367255702	11.52972752079252	4.02515541001609
H	-5.22829282553540	10.81831304570286	5.64769643199372

Table S7 Geometry-optimised coordinates of **2-Bu**

V	3.02436105824923	11.52297866966432	9.22043121336215
V	2.55366594920449	12.16455595212476	6.44738153250917
S	3.80400241993504	13.41186857051739	8.01211111903825
S	4.71843577099080	11.69059536623118	7.47162083178282
S	1.86565675616987	10.17227861977311	7.59809235780896
S	0.88658479649433	11.84875907574053	8.15765473038059
S	3.43397234917964	10.50652738036932	4.84287285784249
S	0.86780664158340	11.73209086112448	4.76181592938796
S	3.58882858237747	13.62143723485027	4.77953326598467
S	1.37135318249121	14.36007292334432	6.41507550701638
S	2.05600807327321	13.37525885689735	10.56348218098642
S	4.63150465268325	12.22592171469294	10.91542730363929
S	1.91592021469219	10.25910615206887	10.96986875835595
S	4.25195607104633	9.41057613727900	9.58368520416669
N	1.69931023375843	10.03900825228606	2.82265466509257
N	2.55081799691336	16.11745332503531	4.74569394519801
N	3.88079241743442	14.48195867474911	12.22026597980839
N	3.09843458507100	7.87431471516799	11.47631241370983
C	1.95355711566875	10.65180854327535	3.98256687066738
C	2.63679974366074	9.06547836191982	2.25441263295212
C	2.21060495588220	7.60518977195172	2.48319315077791
C	3.21595865616405	6.68325169078291	1.78611791776558
C	0.49314902813369	10.34479820790933	2.04610354419134
C	0.75625097144993	11.31238954956181	0.87740786049902
C	-0.54740592511672	11.51260281320182	0.09738207525777
C	1.34217567488325	12.64647751098841	1.34781418533637
C	2.51486753907229	14.87799498346680	5.24150998348460
C	3.47852655305754	16.45000386363028	3.65512135863254
C	2.99719115623323	15.95755739303214	2.28056161296573
C	4.05869213626136	16.29394199439494	1.23019644096873
C	1.62742058908977	16.53257320079949	1.91491170802635
C	1.67631861024630	17.15777606158835	5.30605193771804
C	2.19537042093454	17.72217642390819	6.63969597828393
C	3.58417263864834	18.34873062863973	6.49627847085902
C	1.17328228450210	18.71632713026332	7.19636604780672
C	3.57148833503365	13.50192316190138	11.36573664842005
C	2.94744480439970	15.58296741851335	12.48157420800067
C	3.30310047866851	16.87936365553272	11.73315574786183
C	3.36101717322189	16.68490254639200	10.21523463490572
C	2.29227776049798	17.96356732533274	12.11980452214337
C	5.17405261391202	14.51436070373626	12.91120523111141
C	5.09570142930230	14.09415000770441	14.38912166078516
C	6.50111186929386	14.16741811620648	14.99423966637361
C	4.47875547250140	12.70363391821920	14.55257806552931
C	3.07864059069632	9.00897236841200	10.77364838605755
C	2.16424716712500	7.64613648946865	12.58473243298136
C	2.80576942410406	7.85752062198817	13.96659289621124
C	3.38028552750335	9.26707897642383	14.12628964562917
C	1.76318475011638	7.54477530067803	15.04502474034130
C	4.11836449910861	6.85043828273675	11.20854727718074
C	3.82926492366555	5.99803739638062	9.96093416268551
C	4.97365671518684	4.99798513543787	9.77463912576501
C	2.47109564733054	5.29823458721610	10.04223361227470
C	2.07475289218810	7.27196308850313	3.97092700305405
H	2.72087003294209	9.27088699771413	1.17725857316868
H	3.62606702314296	9.24646951204453	2.70040218007192
H	1.22541975195832	7.46183237467335	2.00382615903908
H	3.29761555033214	6.90734792571528	0.71245728169954
H	2.91442693704314	5.63182544263919	1.88855179639695
H	4.21695593323395	6.78884444991900	2.23231740935125
H	-0.25476743359941	10.77005830500357	2.73078587432648
H	0.08918524288183	9.39540686214749	1.66548521428001
H	1.48667004042740	10.83304824954293	0.20093034923733

H	-0.38246752647251	12.16159613030962	-0.77319888388602
H	-1.31157235622058	11.98985723041174	0.73012976886389
H	-0.95559530136111	10.55900444469900	-0.26740387350865
H	2.27052502903788	12.51013546011866	1.92091456110150
H	0.62920948132891	13.18275043770547	1.99122611377568
H	1.57128823086350	13.28675529858333	0.48482803395536
H	4.45827362576925	16.00500833543476	3.89042961074830
H	3.59861817326346	17.54197078925389	3.65117135769122
H	2.90797307734721	14.86078558693849	2.34764115017421
H	4.19604203175736	17.38306504543266	1.13997822119090
H	3.76228858981214	15.91454317710795	0.24269790793080
H	5.03206367489668	15.84878062115842	1.48259415233141
H	1.66099538888759	17.63238172116939	1.85863194003936
H	0.85810572323281	16.24910341298019	2.64736587431619
H	1.30183199206755	16.16096813092444	0.93398116904223
H	0.67268471791607	16.72751331421878	5.44562467898822
H	1.59326888291289	17.95555135230665	4.55554757189649
H	2.26980938188683	16.87246925755505	7.33889051279188
H	4.32974708897788	17.61512091755821	6.15862664934238
H	3.92925963975370	18.74635327059058	7.46050999428054
H	3.57291144773182	19.18561389951671	5.77985705429082
H	1.04547899189079	19.57503097824957	6.51913650918092
H	1.50333875391503	19.10611974265498	8.16851403696494
H	0.18926622643370	18.24639589602342	7.33784974560678
H	2.93854615737304	15.76375526778370	13.56662354943951
H	1.93963611314379	15.24762761441901	12.19708425118418
H	4.30069355814518	17.20451929424619	12.07668297160544
H	3.67651663072862	17.61787452839286	9.72744917117062
H	2.37562846344021	16.40548292113692	9.81505575117599
H	4.07537223382370	15.90091303436805	9.92521755487595
H	2.54355071906337	18.91845425644378	11.63856702110399
H	2.26851241595989	18.13119009485699	13.20628698264233
H	1.27774521442275	17.68317128593753	11.79703679111204
H	5.57347087497307	15.53673562447105	12.82913081128698
H	5.85871808057470	13.84865917659678	12.36615699795085
H	4.45752468642949	14.82396635440094	14.91736204123318
H	6.47641354830869	13.91422184564918	16.06255408242592
H	6.93723763650633	15.17287975639452	14.89733060855950
H	7.17674134438376	13.45537949108755	14.49583478280332
H	3.46676862899074	12.65283174318884	14.12908290484738
H	4.41148618651413	12.43418046486740	15.61554832762650
H	5.09054239228442	11.94198881492565	14.04684176684755
H	1.78385460230932	6.61822475604153	12.49604017780904
H	1.31251072691681	8.32905976146564	12.45383926706132
H	3.63344475281803	7.13304008609165	14.06831588964517
H	4.11351039953411	9.50740855917760	13.34403134208889
H	3.88250747867098	9.36526932594021	15.09865395843380
H	2.58466814975319	10.02485030704519	14.07762880350855
H	0.91270432764703	8.24097001864383	14.97863299728248
H	2.19962307725526	7.64434599689375	16.04823247937632
H	1.37135814743689	6.52159925365516	14.94892645303816
H	4.16994261351130	6.20892611468280	12.10024341580024
H	5.09345002410887	7.35124479896118	11.10392271890282
H	3.81710157712499	6.68115784038212	9.09514186017460
H	4.82615570742332	4.40461714584757	8.86200991548163
H	5.02626933671201	4.29682403263858	10.62290287251617
H	5.94593841347673	5.50512960604332	9.69325695230030
H	1.64487860188848	6.01859712216272	10.12512659997478
H	2.42501267140125	4.61847820390221	10.90816029912273
H	2.29417679166754	4.69587124713998	9.14028108537520
H	1.36121344532285	7.93665520086254	4.47780469662577
H	3.04348594589860	7.36824315954181	4.48284169580204
H	1.72172836189019	6.23948451439773	4.10091695353259

Table S8 Comparison of experimental and calculated bond distances (Å)

	1-Et		1-Bu		2-Et	2-Bu	
	exptl[a]	calcd	exptl[b]	calcd	calcd	exptl[c]	calcd
V1–S1	2.446(5)	2.405	2.402(2)	2.395	2.400	2.373(1)	2.374
V1–S2	2.393(5)	2.366	2.402(1)	2.383	2.446	2.447(2)	2.441
V1–S3	2.426(6)	2.405	2.402(2)	2.395	2.401	2.424(2)	2.410
V1–S4	2.386(6)	2.367	2.402(1)	2.383	2.444	2.401(2)	2.408
V1–S5	2.518(6)	2.505	2.492(1)	2.494	2.507	2.479(2)	2.470
V1–S6	2.491(6)	2.492	2.501(2)	2.488	2.453	2.413(1)	2.426
V1–S7	2.495(5)	2.493	2.492(1)	2.494	2.510	2.435(2)	2.439
V1–S8	2.496(6)	2.509	2.501(2)	2.488	2.454	2.505(2)	2.484
V2–S1	2.426(6)	2.405	2.413(1)	2.379	2.401	2.384(2)	2.360
V2–S2	2.386(6)	2.367	2.403(2)	2.392	2.444	2.449(2)	2.441
V2–S3	2.446(5)	2.405	2.413(1)	2.378	2.400	2.422(1)	2.409
V2–S4	2.393(5)	2.366	2.403(2)	2.392	2.446	2.403(2)	2.401
V2–S9	2.518(6)	2.509	2.500(2)	2.502	2.507	2.473(2)	2.494
V2–S10	2.491(6)	2.493	2.487(1)	2.490	2.453	2.443(1)	2.445
V2–S11	2.495(5)	2.492	2.500(2)	2.502	2.510	2.436(2)	2.423
V2–S12	2.496(6)	2.505	2.487(1)	2.490	2.454	2.467(2)	2.470
V1⋯V2	2.900(6)	2.719	2.851(1)	2.721	2.958	2.935(1)	2.885
S1–S2	2.00(1)	2.015	1.997(4)	2.015	2.025	2.007(2)	2.023
S3–S4	2.00(1)	2.015	1.997(4)	2.015	2.025	2.003(2)	2.020
S5–C1	1.737(2)	1.715	1.703(8)	1.716	1.722	1.715(6)	1.719
S6–C1	1.716(2)	1.706	1.705(6)	1.707	1.722	1.718(7)	1.719
C1–N1	1.326(2)	1.348	1.343(5)	1.350	1.337	1.321(5)	1.335
S7–C2	1.701(2)	1.715	1.703(8)	1.716	1.722	1.723(6)	1.719
S8–C2	1.717(2)	1.707	1.705(6)	1.707	1.723	1.713(7)	1.719
C2–N2	1.304(2)	1.347	1.343(5)	1.350	1.337	1.310(9)	1.337
S9–C3	1.737(2)	1.715	1.721(5)	1.716	1.722	1.718(5)	1.718
S10–C3	1.716(2)	1.706	1.699(5)	1.707	1.722	1.712(7)	1.716
C3–N3	1.326(2)	1.348	1.325(9)	1.348	1.337	1.338(6)	1.335
S11–C4	1.701(2)	1.715	1.721(5)	1.716	1.722	1.726(7)	1.718
S12–C4	1.717(2)	1.707	1.699(5)	1.707	1.723	1.718(6)	1.718
C4–N4	1.304(2)	1.347	1.325(9)	1.348	1.337	1.303(9)	1.336

[a] Data taken from ref. 1; [b] Data taken from ref. 2; [c] Data taken from ref. 3.

Table S9 Comparison of experimental and calculated bond angles(°)

	1-Et		1-Bu		2-Et	2-Bu	
	exptl[a]	calcd	exptl[b]	calcd	calcd	exptl[c]	calcd
S1–V1–S2	49.2(2)	49.97	49.14(8)	49.90	49.39	49.18(5)	49.66
S3–V1–S4	48.9(2)	49.96	49.14(8)	49.90	49.39	49.05(5)	49.59
S5–V1–S6	69.3(2)	69.72	69.27(7)	69.63	70.10	71.04(5)	71.07
S7–V1–S8	69.2(2)	69.65	69.27(7)	69.63	70.10	70.00(5)	70.51
S1–V2–S2	48.9(2)	49.96	49.00(9)	49.97	49.39	49.05(5)	49.80
S3–V2–S4	49.2(2)	49.97	49.00(9)	49.97	49.39	49.06(5)	49.67
S9–V2–S10	69.3(2)	69.72	69.26(7)	69.78	70.10	70.24(5)	70.56
S11–V2–S12	69.2(2)	69.65	69.26(7)	69.77	70.10	70.72(5)	71.11
V1–S1–V2	73.1(2)	70.14	72.61(6)	69.52	76.06	76.20(5)	75.10
V1–S2–V2	74.8(2)	68.65	72.79(6)	69.49	74.45	73.67(5)	72.45
V1–S3–V2	73.1(2)	68.65	72.61(6)	69.53	74.45	74.55(4)	73.55
V1–S4–V2	74.8(2)	70.14	72.79(6)	69.47	76.06	75.30(4)	73.72
V1–S5–C1	88.4(2)	88.24	88.70(7)	88.70	88.23	87.50(5)	87.84
V1–S6–C1	89.7(2)	88.86	89.05(8)	89.10	90.04	89.58(5)	89.28
S5–C1–S6	111.1(2)	113.17	112.74(8)	112.38	111.65	111.81(5)	111.77
V1–S7–C2	89.5(2)	88.24	88.70(7)	88.70	88.23	90.52(5)	89.41
V1–S8–C2	89.1(2)	88.94	89.05(8)	89.09	90.04	87.97(5)	87.91
S7–C2–S8	112.1(2)	113.17	112.74(8)	112.37	111.66	111.11(5)	111.51
V2–S9–C3	88.4(2)	88.86	88.96(7)	88.28	88.26	88.58(5)	87.63
V2–S10–C3	89.7(2)	88.24	89.89(8)	88.85	90.00	89.72(5)	89.30
S9–C3–S10	111.1(2)	113.17	111.89(9)	113.10	111.65	111.08(5)	112.31
V2–S11–C4	89.5(2)	88.24	88.96(7)	88.28	88.23	89.58(5)	89.32
V2–S12–C4	89.1(2)	88.94	89.89(8)	88.85	90.04	88.73(5)	87.79
S11–C4–S12	112.1(2)	113.17	111.89(9)	113.09	111.66	110.98(5)	111.74

[a] Data taken from ref. 1; [b] Data taken from ref. 2; [c] Data taken from ref. 3.

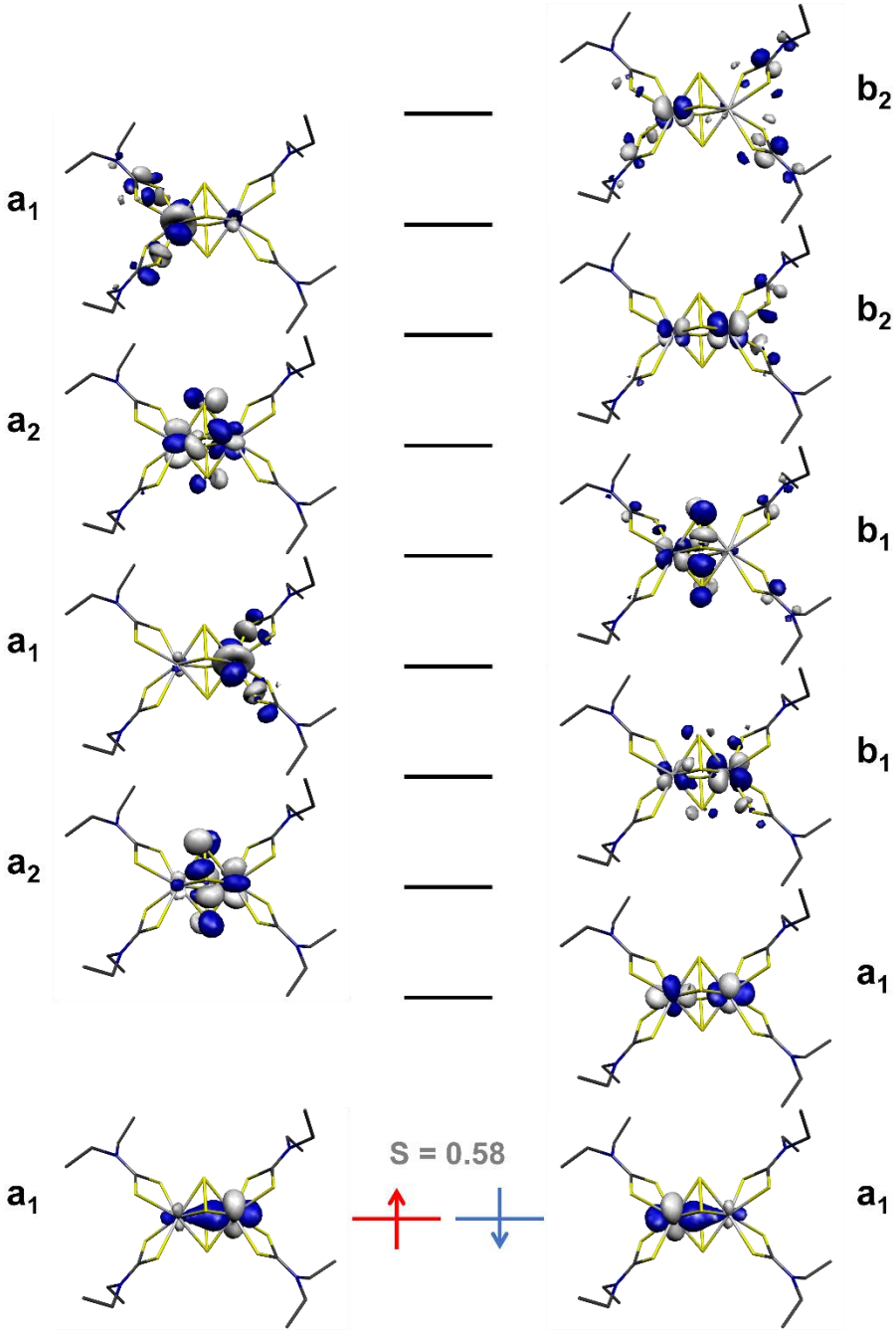


Fig. S4 MO energy level scheme of frontier Kohn-Sham orbitals for **1-Et** with C_{2v} symmetry labels. α-spin and β-spin magnetic orbitals (SOMOs) are highlighted red and blue, respectively, with overlap integral (S) specified.

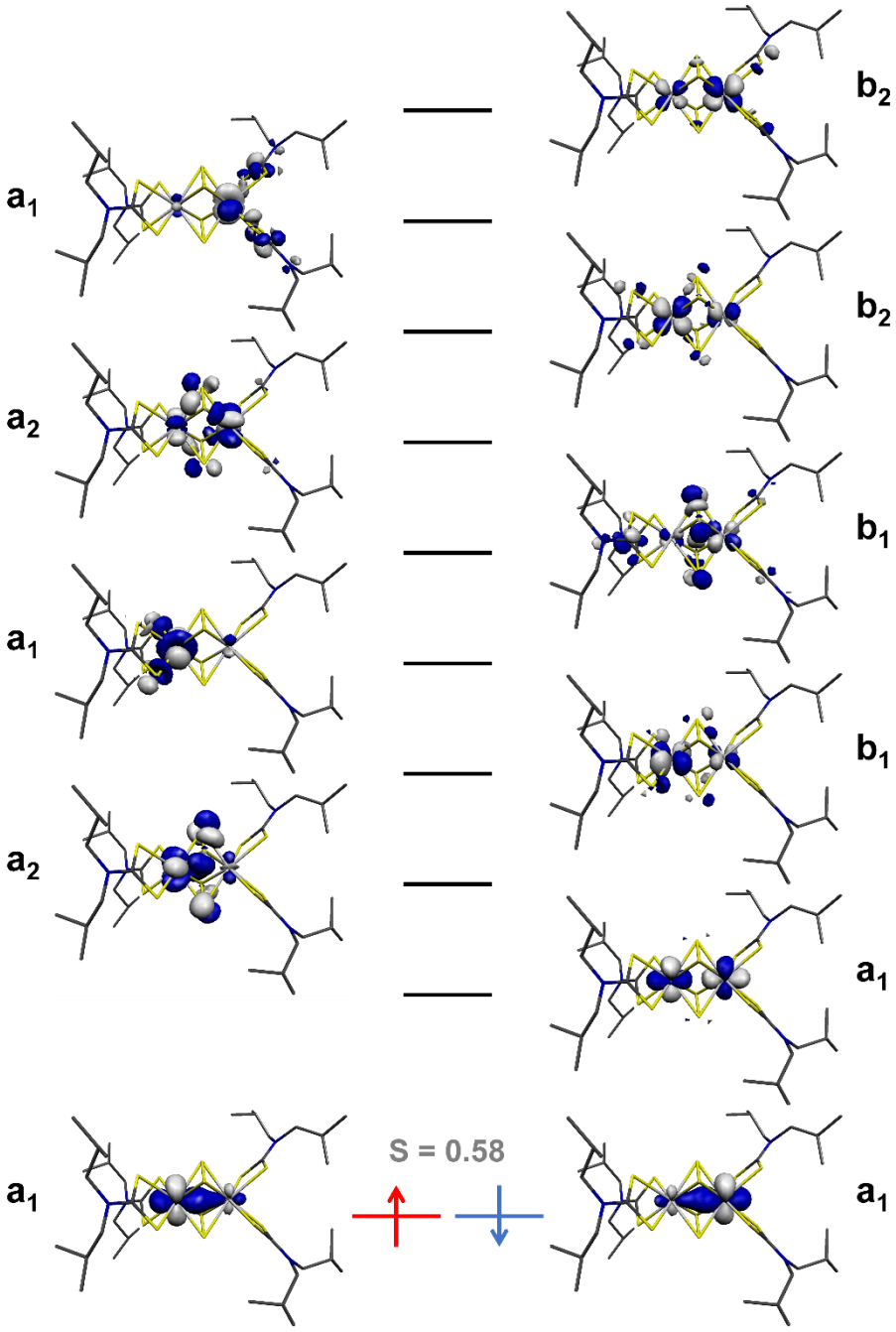


Fig. S5 MO energy level scheme of frontier Kohn-Sham orbitals for **1-Bu** with C_{2v} symmetry labels. α-spin and β-spin magnetic orbitals (SOMOs) are highlighted red and blue, respectively, with overlap integral (S) specified.

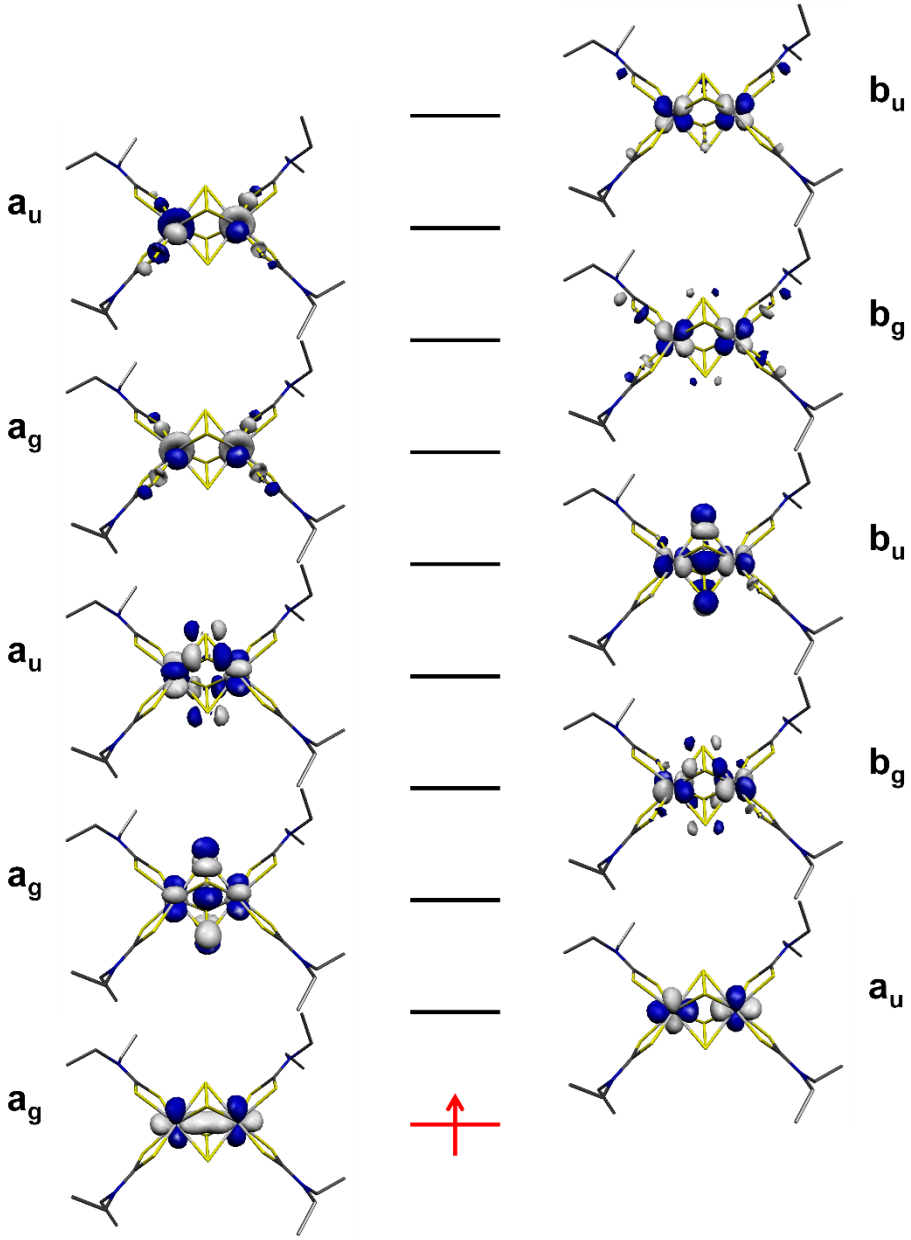


Fig. S6 MO energy level scheme of frontier Kohn-Sham orbitals for **2-Et** with C_{2h} symmetry labels. The magnetic orbital (SOMO) is highlighted red.

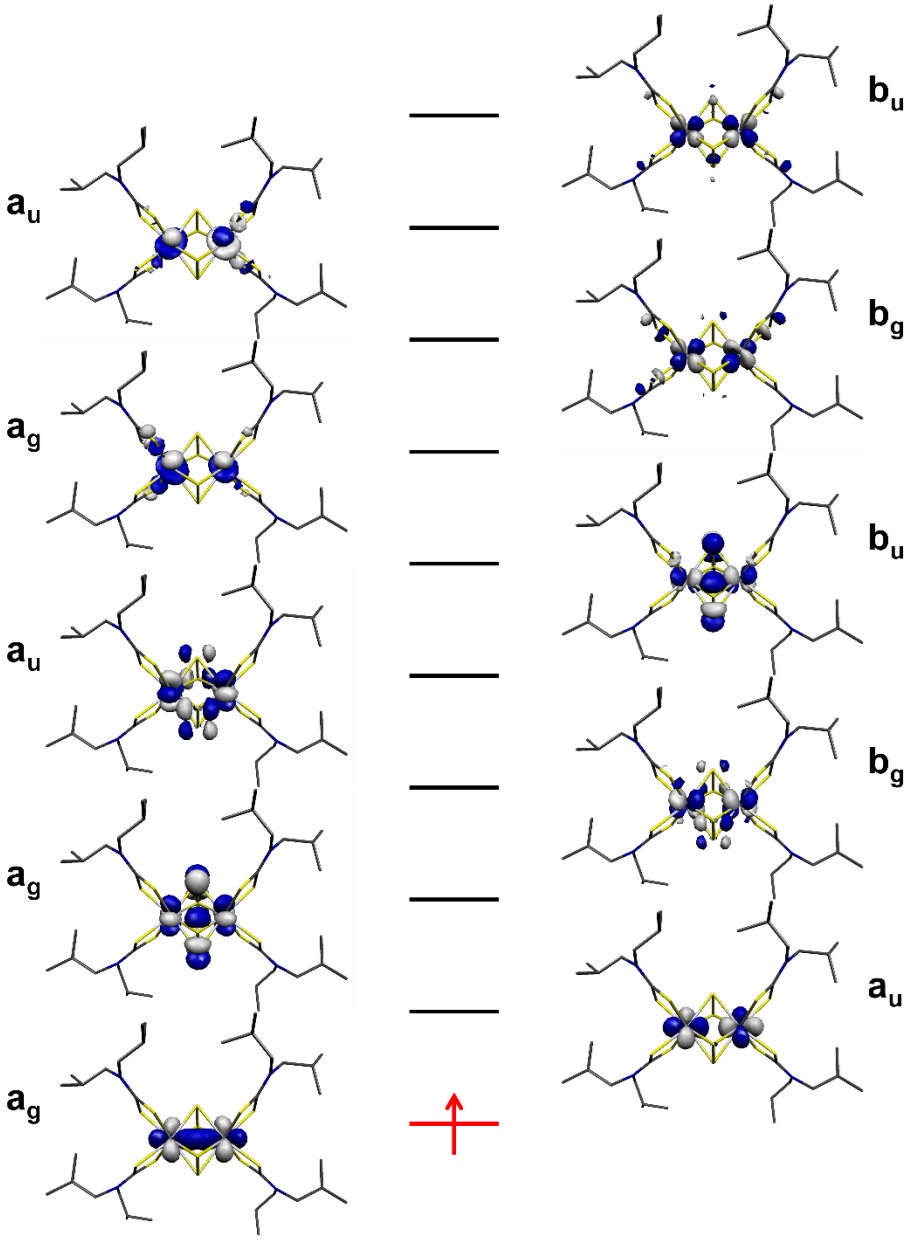


Fig. S7 MO energy level scheme of frontier Kohn-Sham orbitals for **2-Bu** with C_{2h} symmetry labels. The magnetic orbital (SOMO) is highlighted red.

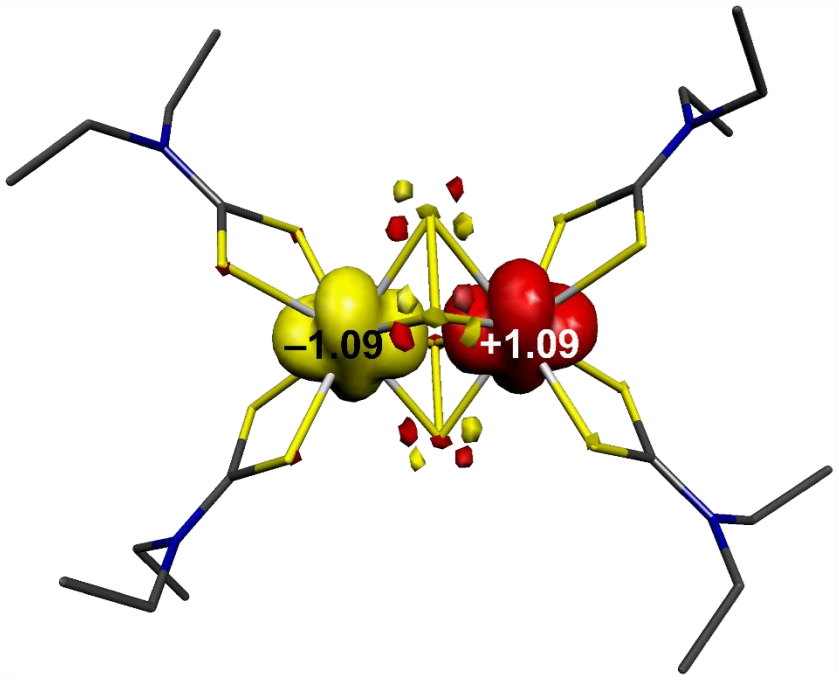


Fig. S8 Mulliken spin density map for **1-Et** (red: α-spin; yellow: β-spin)

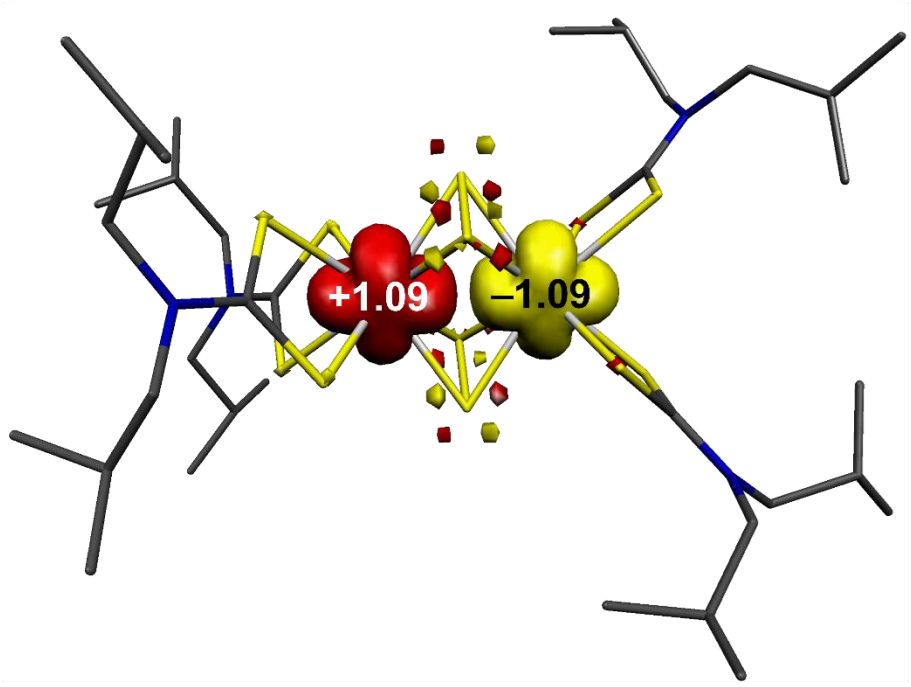


Fig. S9 Mulliken spin density map for **1-Bu** (red: α-spin; yellow: β-spin)

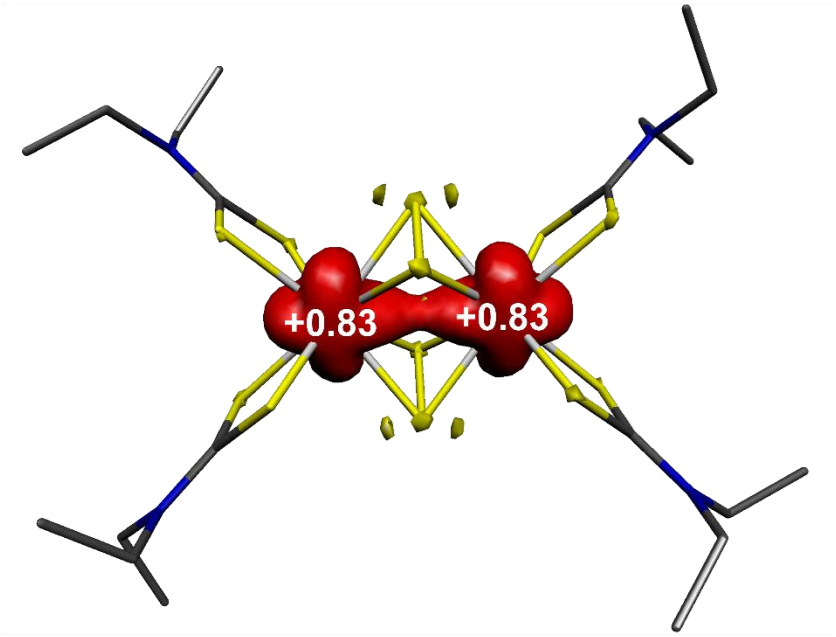


Fig. S10 Mulliken spin density map for **2-Et** (red: α-spin; yellow: β-spin)

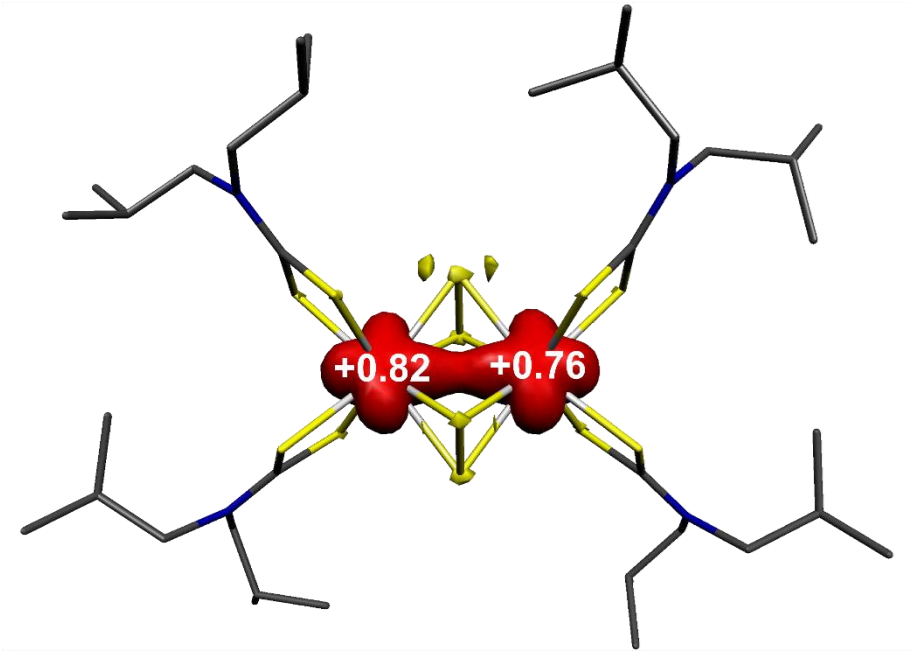


Fig. S11 Mulliken spin density map for **2-Bu** (red: α-spin; yellow: β-spin)

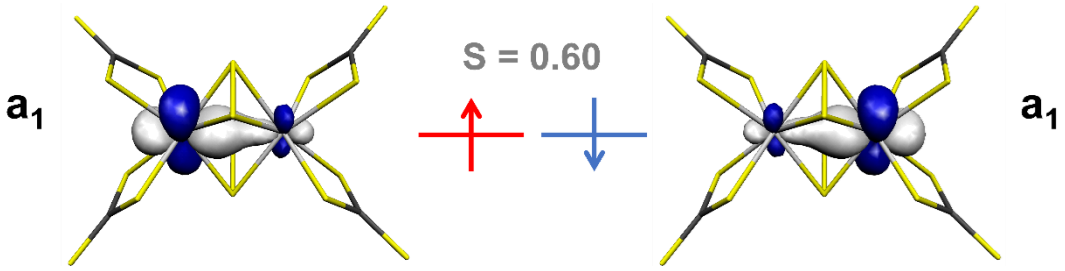
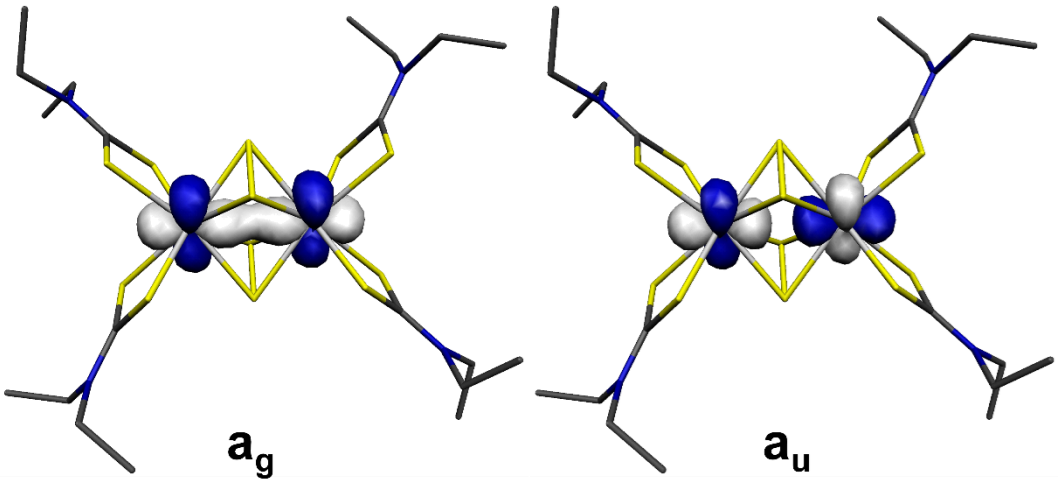
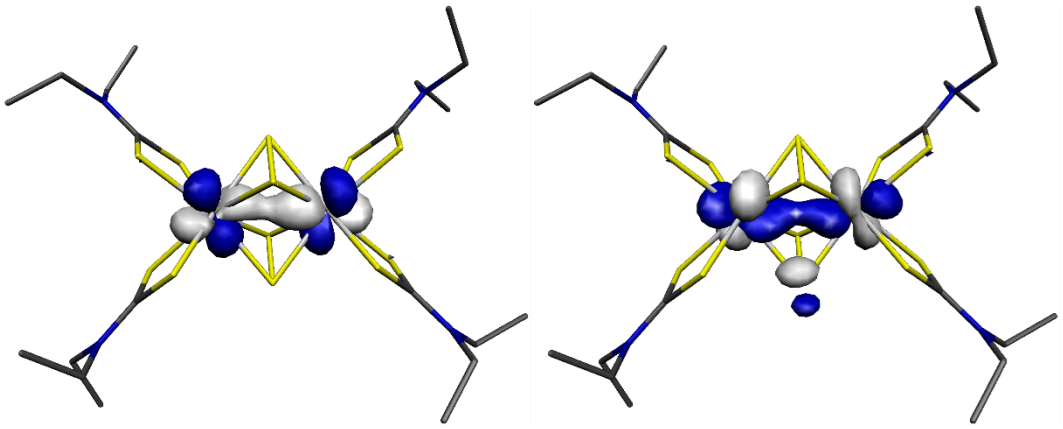


Fig. S12 Corresponding orbitals of $[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$ determined from BS(1,1) DFT calculations on the crystallographic coordinates of the complex, with C_{2v} symmetry labels. The orbital overlap integral (S) is specified.



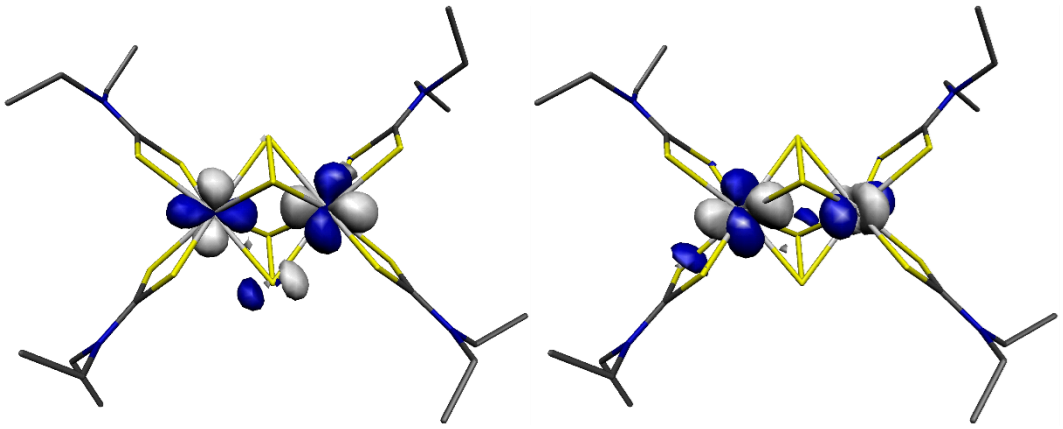
Ground state M_S = 1	0.607	0.393

Fig. S13 Visualisation of the occupied MOs of **1-Et** from the SA-CASSCF/NEVPT2 CAS(2,10) calculation. The singlet ground state is comprised of an admixture 60.6% of a_g and 39.3% a_u. This configurational interaction estimates a 20% V–V σ-bond contribution to the ground state of the $\{V^{IV}_2(\mu\text{-}S_2)_2\}$ core unit. The triplet excited state, which comprises 1:1 admixture of these singly-occupied orbitals, $(a_g)^1(a_u)^1$, resides 1204.5 cm^{-1} above the ground state.



Ground state $M_S = 2$ 0.478 0.419

Fig. S14 Visualisation of the singly-occupied MOs of that comprise the ground state of **2-Et** from the SA-CASSCF/NEVPT2 CAS(1,10) calculation. The remaining 10% comes from an admixture of other d orbitals which results in the slightly deviation of these MOs from true C_{2h} symmetry.



Excited state $M_S = 2$ 0.632 0.243

Fig. S15 Visualisation of the unoccupied MOs of that comprise the first excited state of **2-Et** from the SA-CASSCF/NEVPT2 CAS(1,10) calculation, which define the IVCT transition.

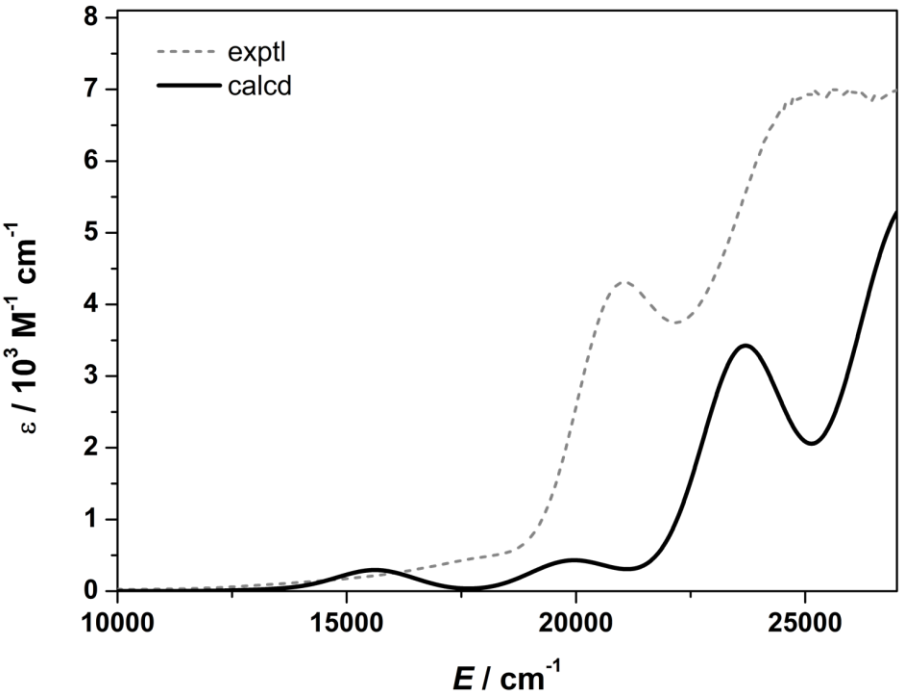


Fig. S16 Overlay of the experimental and TD-DFT calculated electronic spectrum for **1-Et**. Transition assignment is detailed in Table S10.

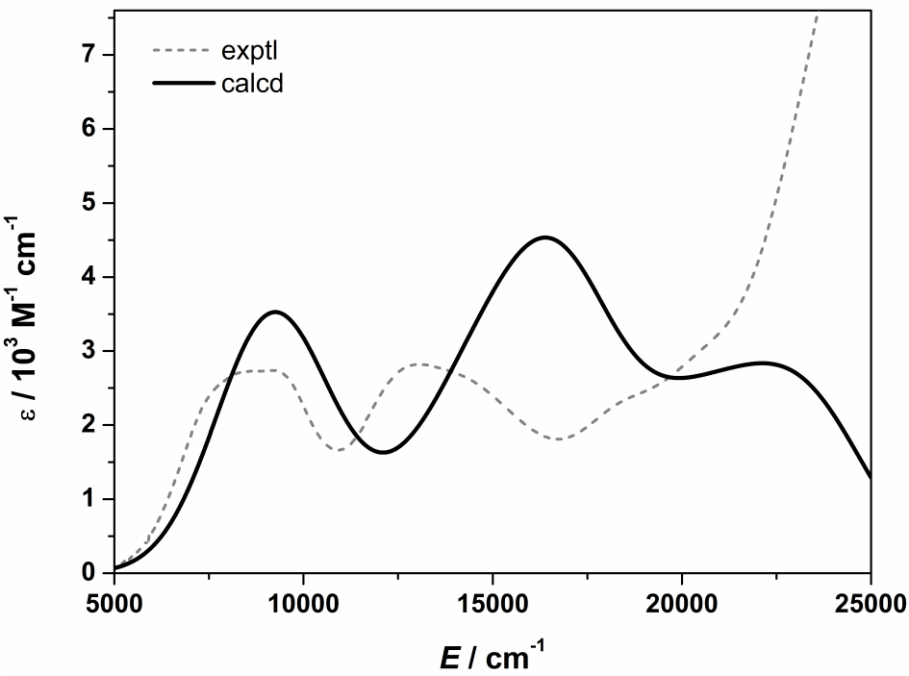
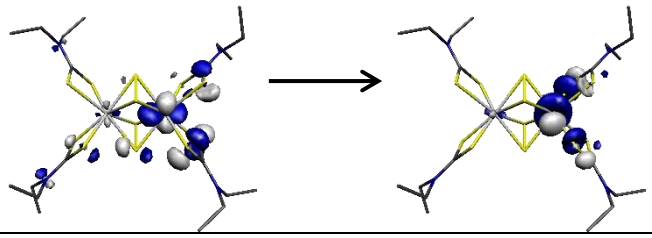
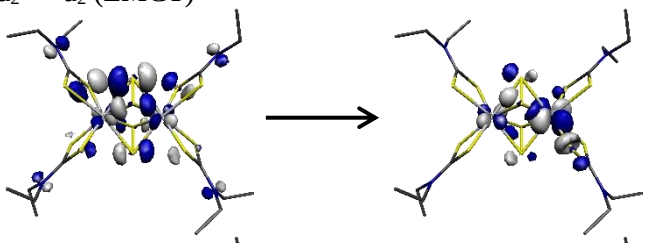
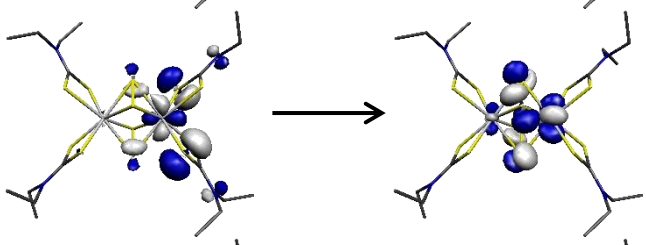
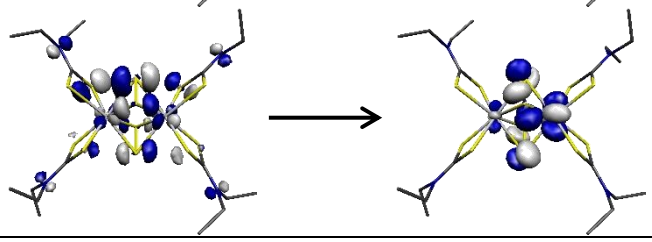
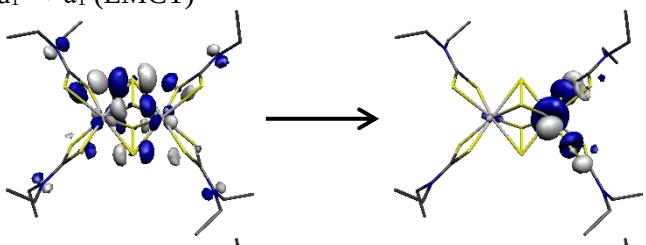
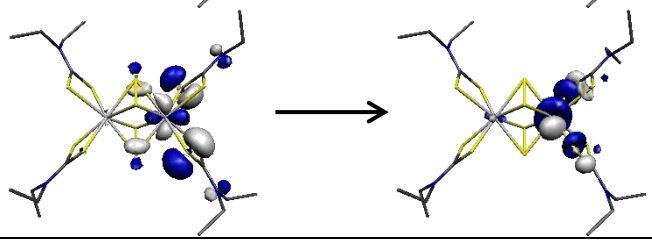


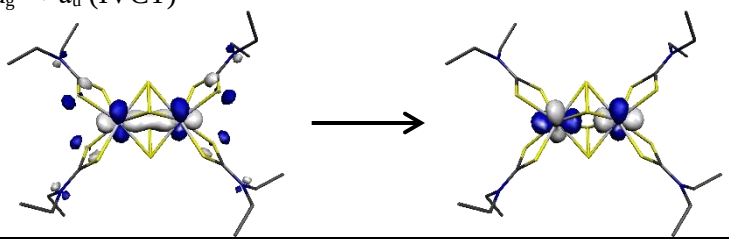
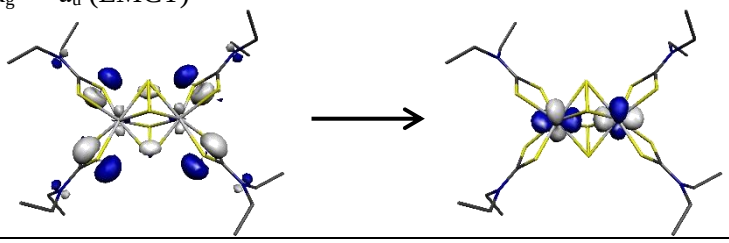
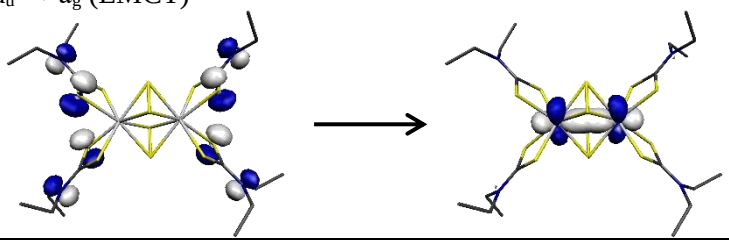
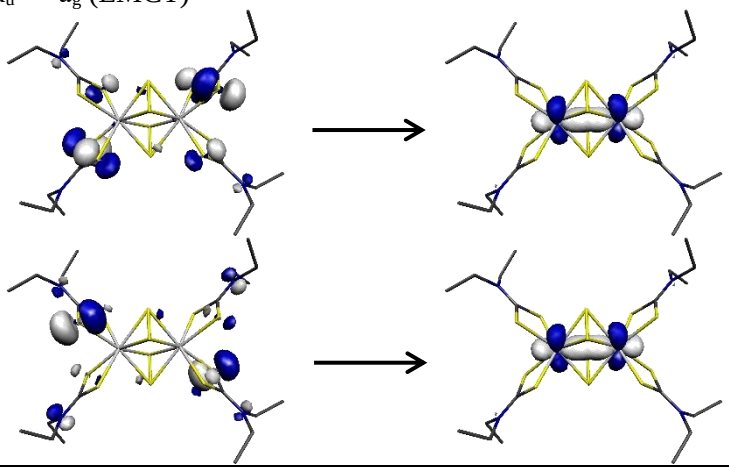
Fig. S17 Overlay of the experimental and TD-DFT calculated electronic spectrum for **2-Et**. Transition assignment is detailed in Table S11.

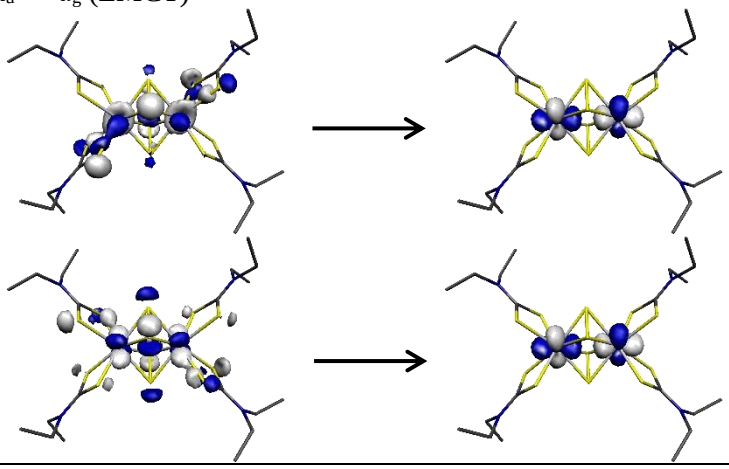
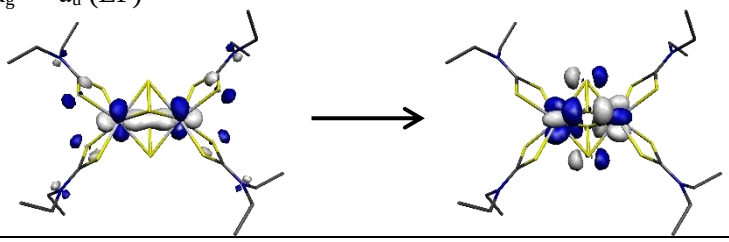
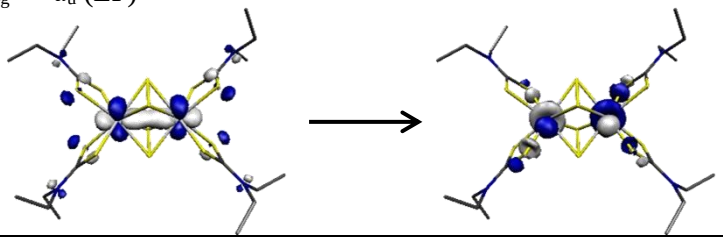
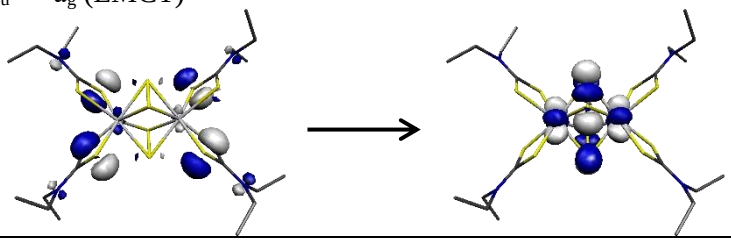
Table S10 Assignment of electronic transitions in **1-Et**

Exptl[a]	**Calcd**[b]	**Transition**
15100	15597	$a_1 \rightarrow a_1$ (LF) 
18400	19703	$a_2 \rightarrow a_2$ (LMCT) 
		
	20287	
21050	23620	$a_1 \rightarrow a_1$ (LMCT) 
	23652	

[a] Recorded in CH_2Cl_2 solution at ambient temperature, energy in cm^{-1}; sh = shoulder. [b] From TPSSh/ZORA-def2-TZVP+CPCM(CH_2Cl_2) TD-DFT calculations.

Table S11 Assignment of electronic transitions in **2-Et**

Exptl[a]	**Calcd**[b]	**Transition**
9120	9157	$a_g \rightarrow a_u$ (IVCT) 
	11779	$a_g \rightarrow a_u$ (LMCT) 
13400	14295	$a_u \rightarrow a_g$ (LMCT) 
14250	15836	$a_u \rightarrow a_g$ (LMCT) 

Exptl[a]	**Calcd**[b]	**Transition**
19100	17014 17433	$a_u \rightarrow a_g$ (LMCT) 
	17433	$a_g \rightarrow a_u$ (LF) 
21100	20086	$a_g \rightarrow a_u$ (LF) 
	20685	$a_u \rightarrow a_g$ (LMCT) 

[a] Recorded in CH_2Cl_2 solution at ambient temperature, energy in cm^{-1}; sh = shoulder. [b] From TPSSh/ZORA-def2-TZVP+CPCM(CH_2Cl_2) TD-DFT calculations.

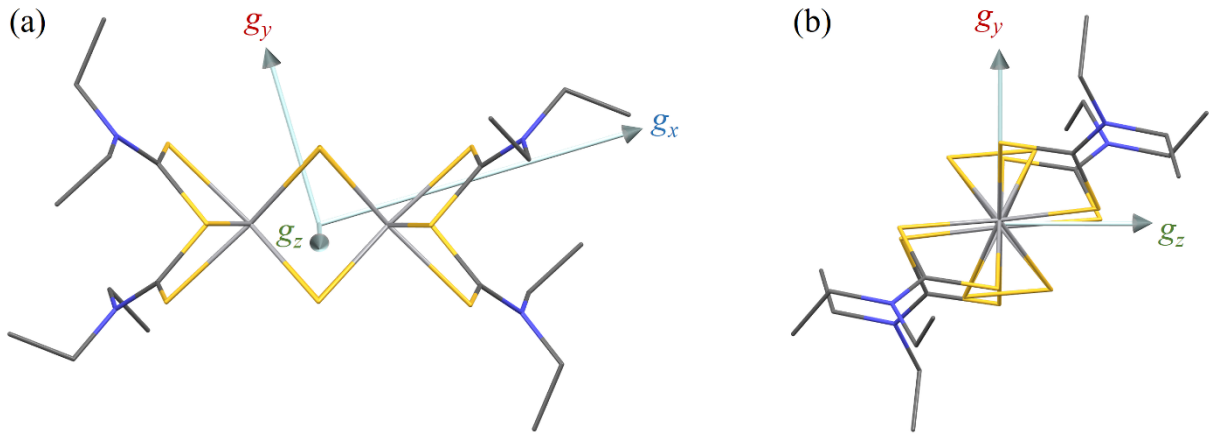


Fig. S18 Orientation of the principal *g*-values superimposed on the optimized structure of **2-Et**: (a) the view along g_z which is orthogonal to the V···V (defined as the *x*-axis in this non-standard alignment of the molecular axes in C_{2h} symmetry) but parallel to the S–S bonds on the bridging disulfide ligands; and (b) the view along the V···V bond showing g_z parallel and g_y orthogonal to the S–S bonds of the bridging disulfide ligands.

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