Supporting Information

Photoelectron Spectroscopy and Electronic Structure Calculations of d^1 Vanadocene Compounds with Chelated Dithiolate Ligands: Implications for Pyranopterin Mo/W Enzymes.

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Table S1. DFT optimized geometry for $Cp_2V(S_2C_2H_2)$.

V	0.001552	0.018091	0.000000
S	1.793378	0.045752	-1.582184
S	1.793378	0.045752	1.582184
C	3.047668	0.793674	-0.678502
C	3.047668	0.793674	0.678502
H	3.890781	1.203876	-1.238051
H	3.890781	1.203876	1.238051
C	0.324174	2.223067	0.000000
C	-0.447026	1.914045	-1.149459
C	-0.447026	1.914045	1.149459
C	-1.667722	1.384345	-0.711858
C	-1.667722	1.384345	0.711858
H	1.327977	2.627614	0.000000
H	-0.144238	2.051282	-2.179701
H	-0.144238	2.051282	2.179701
H	-2.470391	1.035808	-1.352300
H	-2.470391	1.035808	1.352300
C	-1.772860	-1.312949	0.000000
C	-1.002616	-1.613528	-1.151149
C	-1.002616	-1.613528	1.151149
C	0.220292	-2.161568	-0.703073
C	0.220292	-2.161568	0.703073
H	-2.790381	-0.943030	0.000000
H	-1.306968	-1.493197	-2.185201
H	-1.306968	-1.493197	2.185201
H	1.031579	-2.513727	-1.326908
H	1.031579	-2.513727	1.326908

Table S2. DFT optimized geometry for $Cp_2V(bdt)$.

V	-0.021157	0.013544	0.000000
S	1.779173	0.060346	-1.556333
S	1.779173	0.060346	1.556333
C	2.969454	0.992600	-0.706007
C	2.969454	0.992600	0.706007
C	3.971279	1.687663	-1.389245
C	3.971279	1.687663	1.389245
C	4.961877	2.359570	-0.695474
C	4.961877	2.359570	0.695474
H	3.965519	1.688861	-2.476092
H	3.965519	1.688861	2.476092
H	5.736571	2.890932	-1.243013
H	5.736571	2.890932	1.243013
C	0.243961	2.250342	0.000000
C	-0.513743	1.914241	-1.147568
C	-0.513743	1.914241	1.147568
C	-1.716581	1.342212	-0.712527
C	-1.716581	1.342212	0.712527
H	1.228970	2.700883	0.000000
H	-0.205830	2.051335	-2.176414
H	-0.205830	2.051335	2.176414
H	-2.508708	0.972627	-1.354261
H	-2.508708	0.972627	1.354261
C	-1.771159	-1.368111	0.000000
C	-0.993266	-1.646703	-1.149301
C	-0.993266	-1.646703	1.149301
C	0.247440	-2.155213	-0.703552
C	0.247440	-2.155213	0.703552
H	-2.795968	-1.018902	0.000000
H	-1.298677	-1.525469	-2.183100
H	-1.298677	-1.525469	2.183100
H	1.066258	-2.488063	-1.327606
H	1.066258	-2.488063	1.327606

Table S3. DFT optimized geometry for $Cp_2Mo(bdt)$.

Mo	0.009454	0.031379	0.000000
S	1.795749	0.148274	-1.588752
S	1.795749	0.148274	1.588752
C	3.297905	0.110252	-0.698528
C	3.297905	0.110252	0.698528
C	4.514639	0.095114	-1.384424
C	4.514639	0.095114	1.384424
C	5.714692	0.080105	-0.694284
C	5.714692	0.080105	0.694284
H	4.511493	0.094871	-2.471884
H	4.511493	0.094871	2.471884
H	6.652628	0.066575	-1.243958
H	6.652628	0.066575	1.243958
C	0.226041	2.282184	0.000000
C	-0.539714	1.951614	-1.154124
C	-0.539714	1.951614	1.154124
C	-1.761284	1.416232	-0.709444
C	-1.761284	1.416232	0.709444
H	1.229331	2.690327	0.000000
H	-0.238851	2.100521	-2.183990
H	-0.238851	2.100521	2.183990
H	-2.556271	1.045806	-1.347617
H	-2.556271	1.045806	1.347617
C	-1.704368	-1.419949	0.000000
C	-0.920196	-1.697092	-1.160262
C	-0.920196	-1.697092	1.160262
C	0.309780	-2.231775	-0.699211
C	0.309780	-2.231775	0.699211
H	-2.736243	-1.093445	0.000000
H	-1.233894	-1.622398	-2.195065
H	-1.233894	-1.622398	2.195065
H	1.146963	-2.528733	-1.319638
H	1.146963	-2.528733	1.319638

Table S4. Comparison of unrestricted, C_s symmetry geometry optimized molecular structures of $Cp_2V(S_2C_2H_2)$ and $Cp_2V(bdt)$ with crystallographic structures.[a]

$Cp_2V(S_2C_2H_2)$		
	Calculated	Experimental
Cp_{C-C}	1.401-1.424 (1.413)[b]	1.394-1.407 (1.399)
M-Cp_c	2.220-2.300 (2.259)	2.282-2.338 (2.302)
M-S	2.391	2.437, 2.412
S-C	1.718	1.757, 1.742
C-C	1.357	1.330
S-M-S	82.9°	81.1°
$Cp_2V(bdt)$[c]		
	Calculated	Experimental
Cp_{C-C}	1.401-1.425 (1.412)	1.322-1.422 (1.371) 1.293-1.445 (1.367)
M-Cp_c	2.242-2.298 (2.265)	2.273-2.308 (2.300) 2.287-2.343 (2.310)
M-S	2.379	2.428, 2.435 2.432, 2.427
S-C	1.735	1.699, 1.776 1.727, 1.782
C-C[d]	1.412	1.406, 1.401
S-M-S	81.7º	79.7º, 79.9º

a: All distances are given in Å, *b*: average distance, *c*: crystallographic data taken from Stephan *et al.*[24] *d*: C-C distances are for M-S-C-C-S metallocycle.

Table S5. Orbital character (%) for the valence orbitals calculated for $Cp_2V(S_2C_2H_2)$ and $Cp_2V(bdt)$.

		$Cp_2V(S_2C_2H_2)$		$Cp_2V(bdt)$	
Orbital	Character	Alpha	beta	alpha	beta
SOMO[a]	V $3d_{z2}$	23.67	45.33	27.78	53.57
	S 3p	47.24	26.36	43.63	16.61
	C_α 2p[b]	16.7	9.14	6.67	1.97
	C_{Cp} 2p[c]	6.61	11.21	5.18	11.83
	C_{other}[d]	n/a	n/a	12.3	4.59
HOMO	V $3d_{z2}$	55.45	25.6	<1	16.68
	S 3p	16.66	38.6	64.94	44.89
	C_α 2p	7.65	15.46	<1	9.67
	C_{Cp} 2p	8.82	10.17	4.65	9.62
	C_{other}	n/a	n/a	21.84	8.84
HOMO-1	V $3d_{z2}$	4.46	3.66	52.25	<1
	S 3p	70.81	71.52	18.42	65.89
	C_α 2p	9.71	10.29	5.51	<1
	C_{Cp} 2p	11.03	9.69	7.95	6.8
	C_{other}	n/a	n/a	3.87	22.25

a: The beta spin in the SOMO is a vacant orbital. *b*: C_α are the carbon atoms in the M-S-C-C-S metallocycle. *c*: C_{Cp} includes all Cp carbon atoms. *d*: C_{other} includes all remaining carbon atoms.

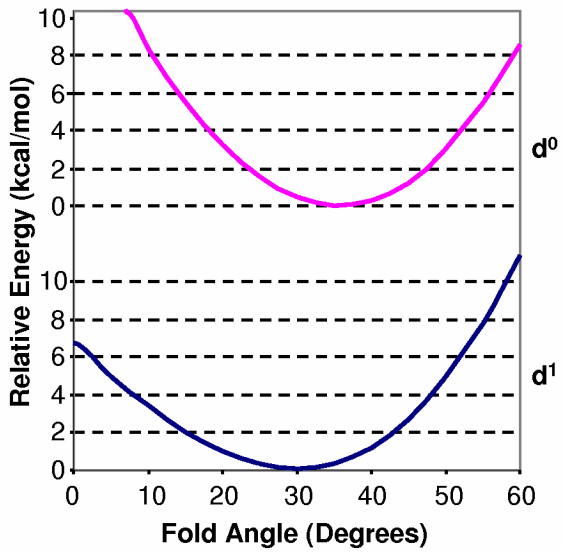

Figure S1. Potential energy curves showing the calculated total energy with change in fold angle for the neutral and cation of $Cp_2V(edt)$.

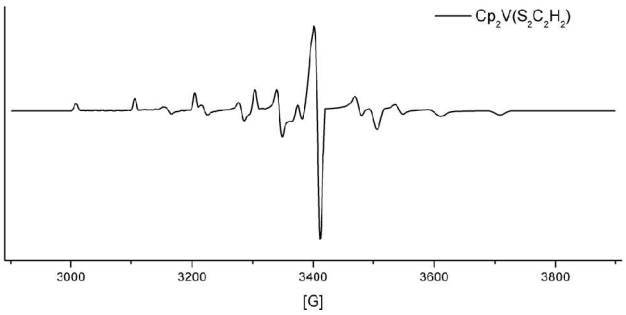

Figure S2. Frozen solution EPR spectrum of $Cp_2V(S_2C_2H_2)$ showing single electron localized on vanadium.

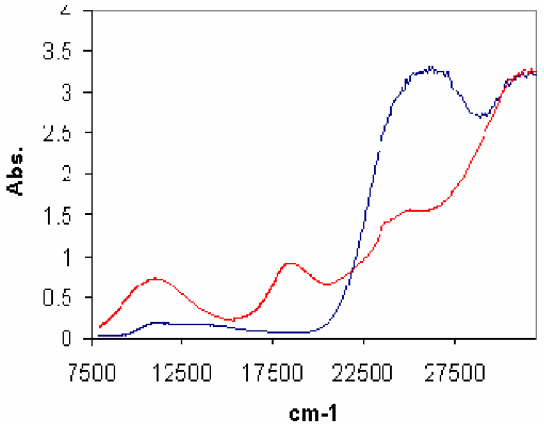

Figure S3. UV-Vis/NIR of Cp_2VCl_2 (blue) and $Cp_2V(S_2C_2H_2)$ (red).