Electronic Supplementary Information for Dalton Transactions

Interpretation of the multiple vanadium-oxygen bonds in the central $VO(\eta^2\text{-}O_2)^+$ group. Synthesis, structure, supramolecular interactions and DFT studies for complexes with 2,2'-bipyridine, 1,10-phenanthroline, pyrazinato(1–) and pyrazinamide ligands

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ELECTRONIC SUPPLEMENTARY INFORMATION

Tables 1S & 2S. The first six calculated UV-Vis transitions (Table 1S) and selected frontier orbital energies for $VO(O_2)^+$ (Table 2S). Only the largest contribution to individual UV-Vis transitions is listed. (Gaussian-03 Revision B.05, time-dependant DFT, Becke/Perdew-Wang 91 functional, 6-311+G(3d,p) basis set, Douglas-Kroll-Hess 2nd order scalar relativistic calculation, ultrafine integration grid.)

Table 1S

State	Orbital nos.	λ (nm)	Oscillator strength
1	$23 \rightarrow 24$	1488.63	0.0000
2	$23 \rightarrow 26$	517.45	0.0041
3	$23 \rightarrow 25$	510.32	0.0067
4	$22 \rightarrow 24$	395.52	0.0036
5	$21 \rightarrow 24$	370.11	0.0003
6	$23 \rightarrow 28$	321.15	0.0005

Table 2S

Orbital nos.	ε [a.u.]	Symm.	Contributions [%]		
			V	Peroxo	Oxo
16	–0.70114	A’	3.11	96.41	0.48
17	–0.67894	A’	27.30	70.36	2.34
18	–0.67247	A’	28.88	55.21	15.90
19	–0.61128	A’’	34.48	12.28	53.23
20	–0.60547	A’	30.78	7.43	61.78
21	–0.58285	A’	17.48	24.10	58.42
22	–0.57649	A’’	31.61	59.97	8.42
23 (HOMO)	–0.49167	A’’	7.59	80.78	11.63
24 (LUMO)	–0.46260	A’	90.35	8.24	1.41
25	–0.42339	A’’	59.27	32.89	7.83
26	–0.40717	A’	83.05	3.09	13.86
27	–0.35676	A’’	50.95	35.23	13.82
28	–0.35145	A’	65.92	9.54	24.55
29	–0.28308	A’’	3.59	96.37	0.04

Tables 3S & 4S. The first ten calculated UV-Vis transitions (Table 3S) and selected frontier orbital energies for **1** (Table 4S). Only the largest contribution to individual UV-Vis transitions is listed. (Gaussian-03 Revision B.05, time-dependant DFT, Becke/Perdew-Wang 91 functional, 6-311+G(3d,p) basis set, Douglas-Kroll-Hess 2nd order scalar relativistic calculation, ultrafine integration grid.)

Table 3S

State	Orbital nos.	λ (nm)	Oscillator strength
1	$96 \rightarrow 98$	512.15	0.0003
2	$96 \rightarrow 97$	502.23	0.0049
3	$96 \rightarrow 99$	428.59	0.0024
4	$96 \rightarrow 103$	388.92	0.0013
5	$96 \rightarrow 99$	373.91	0.0018
6	$96 \rightarrow 100$	372.37	0.0060
7	$95 \rightarrow 97$	362.57	0.0003
8	$96 \rightarrow 104$	359.19	0.0001
9	$96 \rightarrow 102$	344.99	0.0046
10	$96 \rightarrow 105$	334.39	0.0006

Table 4S

Orbital nos.	ε [a.u.]
90	–0.30188
91	–0.29443
92	–0.28447
93	–0.27880
94	–0.27596
95	–0.26240
96 (HOMO)	–0.21588
97 (LUMO)	–0.09907
98	–0.09840
99	–0.07248
100	–0.06630

Tables 5S & 6S. The first ten calculated UV-Vis transitions (Table 5S) and selected frontier orbital energies for **2** (Table 6S). (Gaussian-03 Revision B.05, time-dependant DFT, Becke/Perdew-Wang 91 functional, 6-311+G(3d,p) basis set, Douglas-Kroll-Hess 2nd order scalar relativistic calculation, ultrafine integration grid).

Table 5S

State	Orbital nos.	Coeff.	λ (nm)	Oscilator strength
1	102 → 103	–0.23721	506.19	0.0003
	102 → 104	0.63914		
2	102 → 103	0.64894	502.84	0.0049
	102 → 104	0.22666		
3	102 → 104	0.12510	463.69	0.0014
	102 → 105	0.69099		
4	102 → 104	–0.13318	425.06	0.0027
	102 → 106	0.46518		
	102 → 107	0.41823		
	102 → 108	0.13283		
	102 → 109	0.14295		
5	102 → 107	–0.25827	385.59	0.0011
	102 → 108	0.46867		
	102 → 109	0.42829		
6	102 → 106	0.46031	371.80	0.0016
	102 → 107	–0.36110		
	102 → 108	–0.17392		
	102 → 110	0.25333		
	102 → 112	0.19333		
7	101 → 103	0.66831	361.17	0.0003
8	102 → 106	–0.16136	358.80	0.0007
	102 → 110	0.62042		
	102 → 111	–0.23157		
	102 → 112	–0.11136		
9	102 → 106	–0.14948	340.51	0.0007
	102 → 107	0.27041		
	102 → 109	0.17205		
	102 → 110	0.13225		
	102 → 111	0.35751		
	102 → 112	0.44009		
10	100 → 104	–0.12256	320.42	0.0029
	102 → 108	–0.44521		
	102 → 109	0.48511		
	102 → 112	–0.12477		

Table 6S

Orbital nos.	ε [a.u.]
92	–0.32991
93	–0.31417
94	–0.30348
95	–0.30150
96	–0.29471
97	–0.28581
98	–0.28303
99	–0.27711
100	–0.26840
101	–0.26231
102 (HOMO)	–0.21523
103 (LUMO)	–0.09842

104	–0.09760
105	–0.09273
106	–0.06853

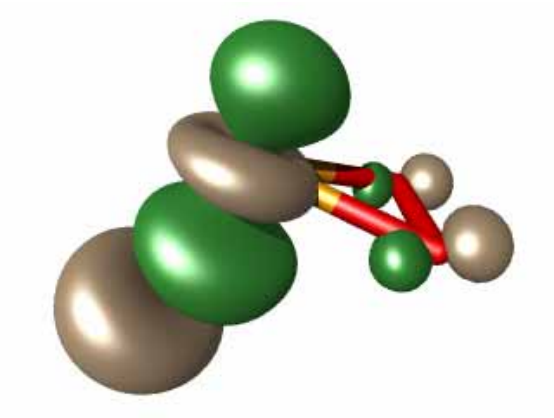

Fig. 1S Orbital 19 of the$VO(O_2)^+$ group.

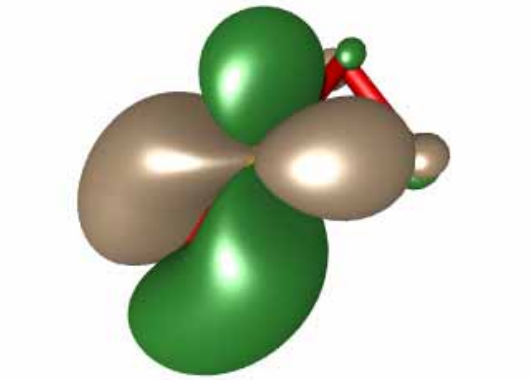

Fig. 2S Orbital 20 of the $VO(O_2)^+$ group.