Low-valent vanadium catecholate clusters: Supplementary Information

E. Scales, L. Sorace, A. Dei, A. Caneschi, C. A. Muryn, D. Collison and E. J. L. McInnes

Table S1. Bond valence sum analyses for Complexes **1-5**.

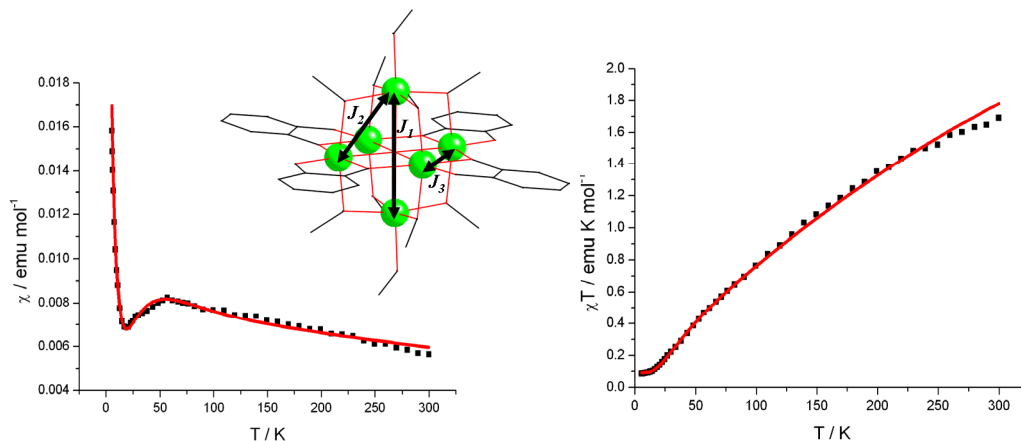| Complex		Bond Valence Sums		
		V(1)	V(2)	V(3)
$[V_6O(dbcat)_4(MeO)_8(MeOH)_2]$ **(1)**	V^{III}	**2.95**	**2.93**	**2.94**
	V^{IV}	3.24	3.22	3.23
	V^V	3.47	3.44	3.46
$[V_6O_2(dbcat)_4(acac)_2(PhCO_2)_4(EtO)_2]$ **(2)**	V^{III}	**3.01**	3.37	**3.05**
	V^{IV}	3.30	**3.71**	3.35
	V^V	3.54	3.96	3.59
$[V_2(dbcat)_4(EtOH)_2]$ **(3)**	V^{III}	3.47	3.41	
	V^{IV}	**3.82**	**3.75**	
	V^V	4.09	4.01	
$[V_6O_3(\text{"dbcat"})_4(MeO)_8]$ **(4)**	V^{III}	3.73 (3.72)	**3.22 (3.25)**	**3.07 (3.10)**
	V^{IV}	**4.10 (4.08)**	3.54 (3.57)	3.38 (3.41)
	V^V	4.39 (4.37)	3.79 (3.82)	3.62 (3.65)
$[V_2O_2(\text{"dbcat"})_4]$ **(5)**	V^{III}	4.27		
	V^{IV}	4.69		
	V^V	**5.02**		

Figure S1. $\chi(T)$ (*left*) and $\chi T(T)$ (*right*) for polycrystalline sample of **1** measured in a 1 T applied field; experimental (black squares) and fitted (red lines) to the spin Hamiltonian:

$$H = -J_1(\hat{s}_1.\hat{s}_{1A} + \hat{s}_2.\hat{s}_{2A} + \hat{s}_3.\hat{s}_{3A}) - J_2(\hat{s}_1.\hat{s}_2 + \hat{s}_1.\hat{s}_{2A} + \hat{s}_1.\hat{s}_3 + \hat{s}_1.\hat{s}_{3A} + \hat{s}_{1A}.\hat{s}_2 + \hat{s}_{1A}.\hat{s}_{2A} + \hat{s}_{1A}.\hat{s}_3 + \hat{s}_{1A}.\hat{s}_{3A})$$
$$- J_3(\hat{s}_2.\hat{s}_3 + \hat{s}_2.\hat{s}_{3A} + \hat{s}_{2A}.\hat{s}_3 + \hat{s}_{2A}.\hat{s}_{3A})$$

representing the three chemically unique $V^{III}…V^{III}$ interactions [*trans* across the linear μ_6-O1; *cis* via μ_2-O(Me); *cis* via μ_2-O(dbcat), respectively; see inset Scheme]. Fitting gives J_1 = -136, J_2 = -128 and J_3 = -54 cm^{-1} with g = 1.85. These antiferromagnetic interactions result in a total spin S = 0 ground state for the molecule. Strong AF coupling has been observed in a V(III) trimer bridged

by a "T-shaped" μ_3-oxide, i.e. with ca. 180° "*trans*" (*ca.* -130 cm^{-1}) and 90° "*cis*" (*ca.* -26 cm^{-1}) couplings; see I.S. Tidmarsh, L.J. Batchelor, E. Scales, R.H. Laye, L. Sorace, A. Caneshi, J. Schnack and E.J.L. McInnes, *Dalton Trans.* 2009, 9402.
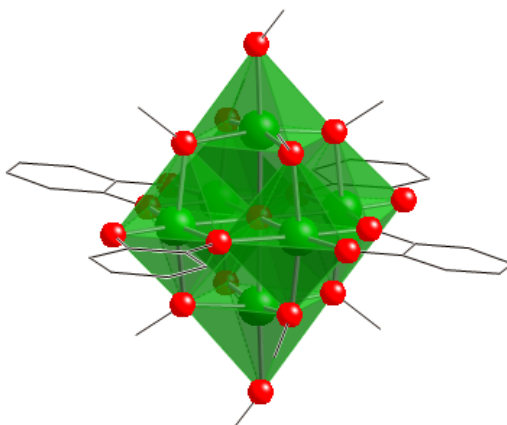

Figure S2. {VO$_6$} polyhedral representation of the crystal structure of **1**, highlighting the Lindqvist-type structure.
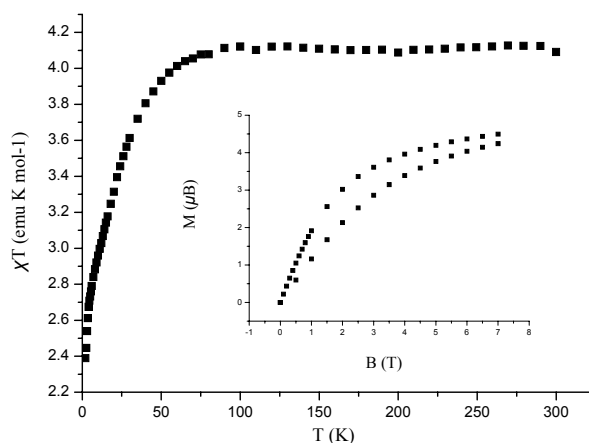

Figure S3. $\chi T(T)$ for a polycrystalline sample of **2** measured in 0.1 T applied field. The room temperature value of χT is 4.13 emu K mol^{-1}. Inset: Magnetisation (*M*) vs. applied magnetic field (*B*) measured at 2 (*top*) and 4 K (*bottom*). *M(B)* is tending towards saturation at ca. 5 μ_B, suggesting a total spin ground state for the molecule of *S* = 3 at most. This is consistent with antiferromagentic coupling between four V(III) (*s* = 1) ions with two *s* = ½ centres but does not discriminate between the latter being from two V(IV) ions or from two strongly AF coupled V^{III}(dbsq) fragments.
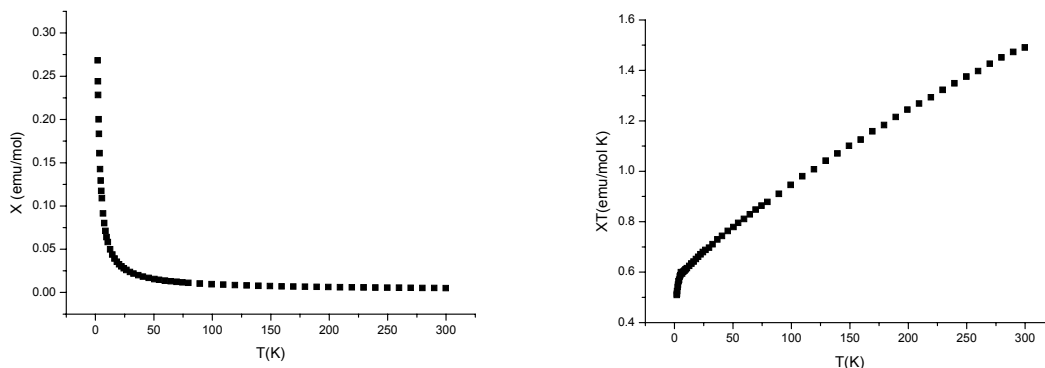
2

Figure S4. $\chi(T)$ (*left*) and $\chi T(T)$ (*right*) for a polycrystalline sample of **4** measured in a 1 T applied field. If V1,1A (with terminal oxides) were V^{V} then the formula of **4** must be $[(V^{V}O)_2V^{III}_4O(dbcat)_4(OMe)_8]$. This would give a straightforward spin-Hamiltonian of a square of $s = 1$ ions. We have been unable to fit the data to this model. This is consistent with V1,1A being V^{IV} as supported by BVS. Any physically meaningful model for $[(V^{IV}O)_2V^{III}_4O(dbcat)_2(dbsq)_2(OMe)_8]$ or $[(V^{IV}O)_2V^{III}_2V^{IV}_2O(dbcat)_4(OMe)_8]$ would involve at least six different *J*-values and would be hopelessly overparameterised, hence we have not attempted this.
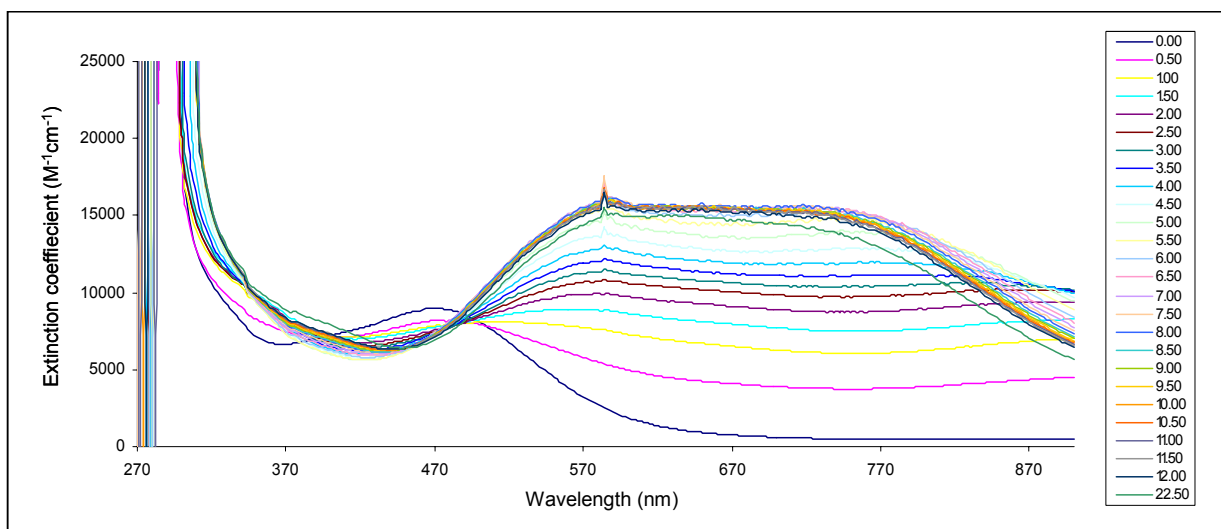

Figure S5. UV-Vis spectra following the aerial oxidation of complex **1** $\rightarrow$ **4** in 0.145 mM CH_2Cl_2 solution; spectra measured every 0.5 h for 24 h.
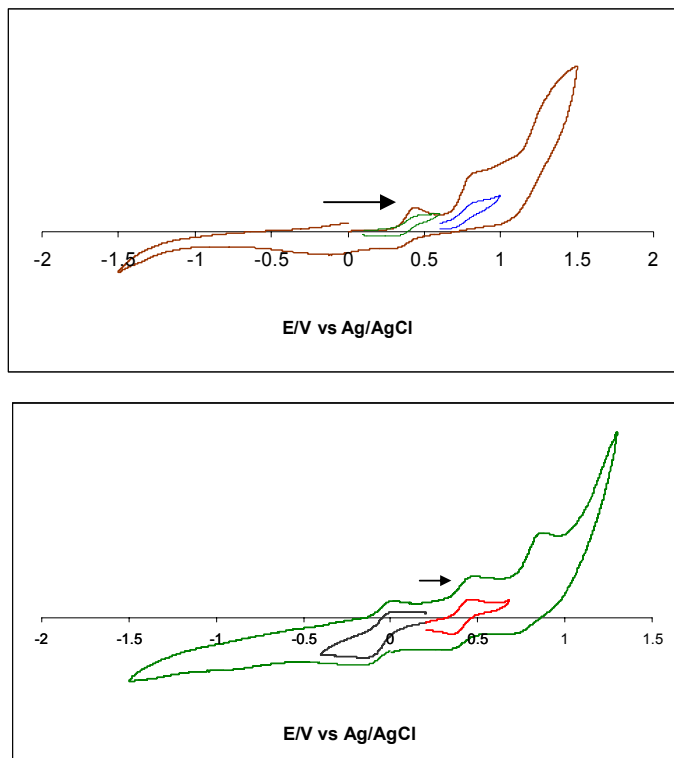
3

Figure S6. Top: Cyclic voltammograms (CVs) of complex **1** in (^{n}Bu$_4$N)BF$_4$ CH$_2$Cl$_2$ solution at room temperature. Full potential sweep and isolated sweeps about redox processes shown. The quasi-reversible processes (green and blue curves) are at +0.47 and +0.85 V *vs*. Ag/AgCl. Bottom: CVs of the same solution after standing for 30 mins, after which it was turning to blue/black colour. A third redox process has appeared at -0.05 V vs. AgAgCl.