Supporting Information For:

Synthesis, Structure, and Magnetic Properties of $[(CH_3CN)_5V\text{-}O\text{-}V(CH_3CN)_5][BF_4]_4$

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Table S1. Eigenvalues of effective Hamiltonian $\boldsymbol{H_{eff}}$ given in eq (S1), collected as van Vleck coefficients $E_n^{(0)}$, $E_n^{(1)}$ and $E_n^{(2)}$.

H ∥ z			H ∥ x*		
$E_n^{(0)}$	$E_n^{(1)}$	$E_n^{(2)}$	$E_n^{(0)}$	$E_n^{(1)}$	$E_n^{(2)}$
$2D_2$	$-2g_{2,\parallel}\beta$	0	$2D_2$	0	$g_{2,\perp}^2\beta^2/3D_2$
$-D_2$	$-g_{2,\parallel}\beta$	0	$-D_2$	0	$7g_{2,\perp}^2\beta^2/6D_2$
$-2D_2$	0	0	$-2D_2$	0	$-3g_{2,\perp}^2\beta^2/D_2$
$-D_2$	$g_{2,\parallel}\beta$	0	$-D_2$	0	$7g_{2,\perp}^2\beta^2/6D_2$
$2D_2$	$2g_{2,\parallel}\beta$	0	$2D_2$	0	$g_{2,\perp}^2\beta^2/3D_2$

* $|D_2|$ is assumed to be larger than $g_{2,x}\beta H$

Derivation of the magnetization of a S = 2 system.

The partition function for the parallel orientation is given by

$$Z = \sum_n \exp(-E_n / k_B T).$$

Insertion of the individual energy levels provide $Z_{\parallel}$ given in equation S1.

$$Z_{\parallel} = \exp\left(\frac{-2g_{\parallel}\beta H - 2D_2}{k_B T}\right) + \exp\left(\frac{2g_{\parallel}\beta H - 2D_2}{k_B T}\right) + \exp\left(\frac{-g_{\parallel}\beta H + D_2}{k_B T}\right) + \exp\left(\frac{g_{\parallel}\beta H + D_2}{k_B T}\right) + \exp\left(\frac{-2D_2}{k_B T}\right)$$

(S1)

The magnetization is related to the partition function by Equation S2

$$M = NkT\left(\frac{\partial \ln Z}{\partial H}\right) \qquad \text{(S2)}$$

Evaluating the differential of $Z_{\parallel}$ and substituting it in eq (S2) provides the orientation-dependent magnetization ($M_{\parallel}$) as:

$$\frac{M_{\parallel}}{N\beta} = \frac{4g_{\parallel}e^{(-2D_2/k_BT)}\sinh(2g_{\parallel}\beta H/k_BT) + 2g_{\parallel}e^{(-2D_2/k_BT)}\sinh(g_{\parallel}\beta H/k_BT)}{2e^{(-2D_2/k_BT)}\cosh(2g_{\parallel}\beta H/k_BT) + 2e^{(D_2/k_BT)}\cosh(g_{\parallel}\beta H/k_BT) + e^{(2D_2/k_BT)}} \quad \text{(S3)}$$

The single crystal data shown in Figure S1 were fit to $M_{\parallel}$ given in eq (S3) with $|D_2| = 0.60 \pm 0.04$ K and $g_{\parallel} = 2.01 \pm 0.01$.

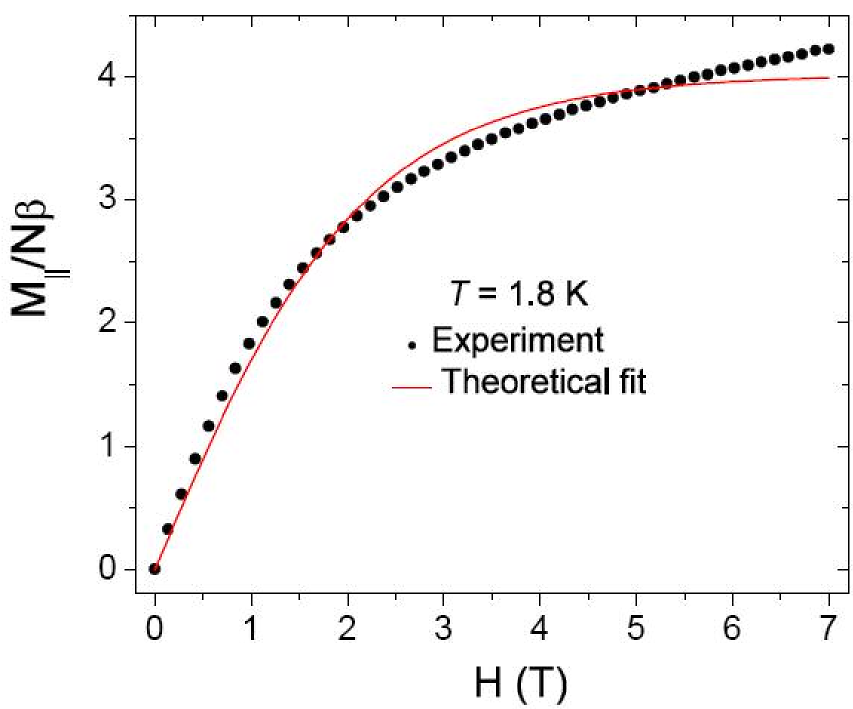

Figure S1. Reduced magnetization of a single crystal of $[(CH_3CN)_5VOV(CH_3CN)_5][BF_4]_4$ with (H ‖ 001 axis). The saturated magnetic moment of 4 μ_B, corresponds to $S_{total} = 2$.

Table S2. Crystal data and refinement details for $[(CH_3CN)_5VOV(CH_3CN)_5][BF_4]_4•2CH_3CN$

Formula	$C_{24}H_{36}N_{12}OB_4F_{16}V_2$
Formula weight	957.77
Temperature (K)	223(2)
Crystal System	Monoclinic
Space Group	*P2(1)/n*
a (Å)	10.0610(5)
b (Å)	22.2252(10)
c (Å)	10.7939(5)
α (˚)	90.00
β (˚)	109.6(1)
γ (˚)	90.00
Volume ($Å^{3)}$	2273.75(19)
Z	2
Density ($g\cdot cm^{-3}$)	1.399
Crystal Size (mm)	0.45 x 0.25 x 0.15
Goodness of Fit	1.065
Final *R* indices [I>2σ(I)]	$R1 = 0.0496$, $wR2 = 0.1324$
Final *R* indices (all data)	$R1 = 0.0584$, $wR2 = 0.1431$

Quantity minimized = $wR2 = R(wF^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^2\}^{1/2}$: $R1 = R(F) = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$: $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$: $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$