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Tetranuclear Vanadium(III) Carboxylate Chemistry, and a New Example of a Metal Butterfly Complex exhibiting Spin Frustration: Structure and Properties of $[V_4O_2(O_2CEt)_7(bpy)_2](ClO_4)$

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Treatment of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with bpy (bpy = 2,2′-bipyridine) and NaO_2CEt in a 1:1:3 molar ratio in Me_2CO followed by addition of ClO_4^- allows isolation of $[V_4O_2(O_2CEt)_7(bpy)_2](ClO_4)$ [**4**(ClO_4)], which contains a butterfly-like V_4 unit; variable-temperature magnetic susceptibility studies show **1** to possess both ferro- and antiferro-magnetic exchange interactions leading to spin-frustration effects and an $S = 3$ ground state.

Our interest in spin-frustration effects within molecular metal carboxylate clusters began with the tetranuclear butterfly species $[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$ **1** (bpy = 2,2′-bipyridine),[1] $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$ **2**[2] and $[Mn_4O_2(O_2CMe)_7(pic)_2]^-$ **3** (Hpic = picolinic acid).[3] Since then, we have analysed these effects within complexes of various metal nuclearities, including Fe_6,[4] Mn_7,[5] Mn_8,[6] Mn_9[6] and Mn_{18}[7] species, to mention but a few. Spin frustration within appropriate topologies represents the inability of certain spins to adopt their preferred alignments *vis-à-vis* their exchange coupling with neighbouring spins, owing to competing exchange interactions in the rest of the molecule. As a result, such clusters often possess large ground-state spin values and not the small values that might logically be expected for these (usually) predominantly antiferromagnetically-coupled systems. In fact, spin frustration is very likely a major contributing factor to the large ground-state spins in a majority of the molecular clusters determined to possess this property.[1–10]

We have recently sought to extend our studies of this phenomenon at the tetranuclear level by obtaining the analogues of cations **1** and **2** with other paramagnetic M^{III} ions, and have been particularly attracted by V^{III}. We herein report successful attainment of the new butterfly cation $[V_4O_2(O_2CEt)_7(bpy)_2]^+$ **4**, and show that spin-frustration effects are operative and are responsible for the observed $S = 3$ ground state of **4**.

A reaction slurry comprising $[VCl_3(thf)_3]$, bpy and NaO_2CEt (3:3:9 mmol) in acetone (50 ml; degassed but not distilled) was stirred under argon overnight, and the resulting red–brown solution was filtered, $NBu^n{}_4ClO_4$ (0.75 mmol) added to the filtrate, and the solvent removed *in vacuo*. The residue was washed with Et_2O, and recrystallized from $Me_2CO–Et_2O$ to give brown microcrystals of **4**(ClO_4).† The same procedure can be employed for the $PhCO_2^-$ and substituted-bpy analogues of **4**. The structure of **4**‡ contains a $[V_4(\mu_3\text{-}O)_2]^{8+}$ butterfly core with the oxides slightly out of each V_3 ‘wing’ plane (Fig. 1). Peripheral ligation by seven $EtCO_2^-$ and two bpy groups completes six-coordination at all V^{III} centres and gives C_2 idealized symmetry to the cation. The V···V distances indicate the absence of metal–metal bonds, with the shortest distance [V(1)···V(2) 2.909(2) Å] being significantly longer than the 2.6 Å expected for $V^{III}–V^{III}$ single bonds.[11] The structure of **4** is thus very similar to those of **1**–**3**. Cation **4** becomes the fourth member of the $[M_4O_2(O_2CR)_7(bpy)_2]^+$ (M = Mn^{III}, Fe^{III}, Cr^{III}, V^{III}) family for tripositive 3d metals, the Cr^{III} analogue having been reported by others.[12] In a wider context, **4** is the first structurally characterized example of a tetranuclear vanadium(III) carboxylate complex; there is, however, a mixed-metal $V^{III}–Zn^{II}$ species known, namely $[Zn_4V_4O_4(O_2CPh)_{12}(thf)_4]$, which contains a cubane-like $[V_4O_4]^{4+}$ core.[13]

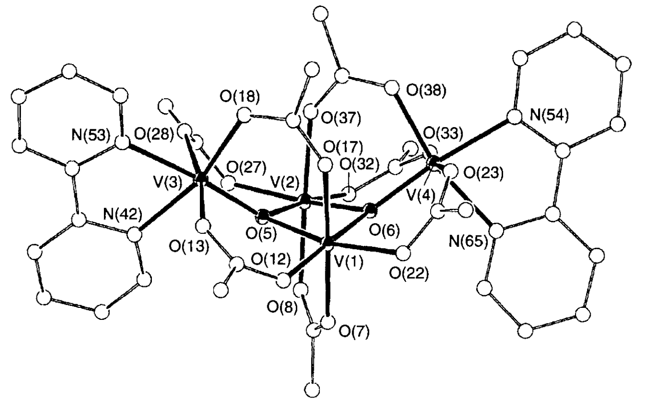


Fig. 1 ORTEP representation of $[V_4O_2(O_2CEt)_7(bpy)_2]^+$ **4**. Selected interatomic distances (Å) and angles (°) are: V(1)···V(2) 2.909(2), V(1)···V(3) 3.315(2), V(1)···V(4) 3.480(2), V(2)···V(3) 3.465(2), V(2)···V(4) 3.321(2), V(1)–O(5) 1.928(4), V(1)–O(6) 1.972(5), V(2)–O(5) 1.981(5), V(2)–O(6) 1.931(4), V(3)–O(5) 1.830(4), V(4)–O(6) 1.841(4), V(1)–O(5)–V(3) 123.8(2), V(2)–O(5)–V(3), 130.8(2), V(1)–O(5)–V(2) 96.2(2), V(1)–O(6)–V(2) 96.4(2), V(1)–O(6)–V(4) 131.6(2), V(2)–O(6)–V(4) 123.4(2). Carboxylate Me groups and all H atoms are omitted for clarity.

Variable-temperature magnetic susceptibility studies have been performed on powdered samples of **4**(ClO_4) (restrained in Vaseline™ to prevent torquing) in a 10 kG field and 2.00–300 K temperature range. The effective magnetic moment (μ_{eff}/V_4) gradually increases from 5.79 μ_B at 300 K to a maximum of 6.80 μ_B at 25 K and then decreases to 4.72 μ_B at 2.00 K (Fig. 2). The 300 K value is slightly higher than the spin-only value for four

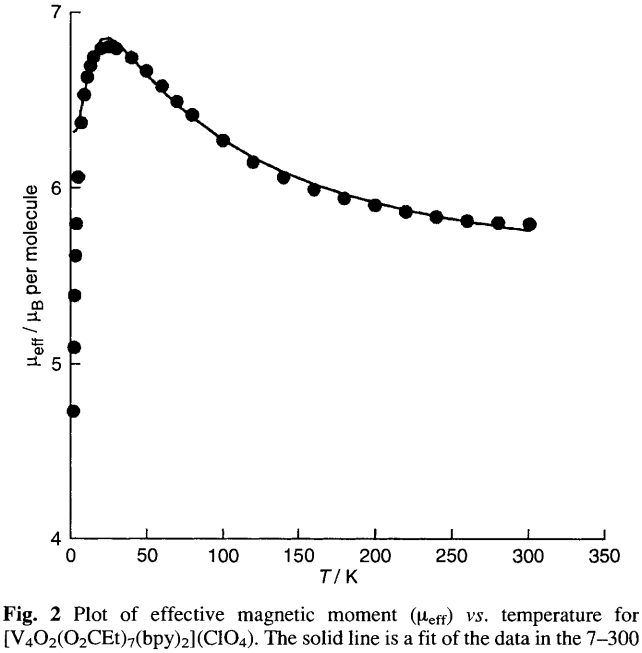
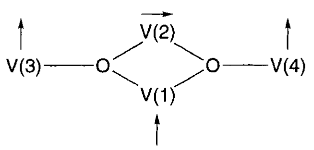


Fig. 2 Plot of effective magnetic moment (μ_{eff}) *vs.* temperature for $[V_4O_2(O_2CEt)_7(bpy)_2](ClO_4)$. The solid line is a fit of the data in the 7–300 K range to the appropriate theoretical expression (data delow 7 K were omitted owing to zero-field splitting effects that cause the decrease in μ_{eff}); see text for fitting parameters.

non-interacting V^{III} ions (5.66 μ_B/V_4). The experimental data were fit to the equation derived previously for a $[M_4O_2]$ butterfly complex of idealized C_{2v} core symmetry,[1–3] adjusted for the present 4 V^{III} system. The fitting parameters (using the $H = -2JS_i{\cdot}S_j$ convention) are $J_{bb} = -31.2$ cm^{-1}, $J_{wb} = 27.5$ cm^{-1} and $g = 1.82$, with no paramagnetic impurity term, and a temperature-independent paramagnetism term held constant at 400×10^{-6} cm^3 mol^{-1}; J_{bb} and J_{wb} refer to the inner 'body–body' and outer 'wingtip–body' interactions, respectively, of the V_4 butterfly. The fit is shown as a solid line in Fig. 2. The corresponding values for **1** and **2** are (in the format **1**/**2**) $J_{bb} = -8.9/-23.5$ cm^{-1}, $J_{wb} = -45.5/-7.8$ cm^{-1} and $g = 2.00/2.00$.[1,2] In addition to the changes in relative J_{bb}/J_{wb} ratios in this triad, the main difference between **4** and **1**/**2** is the occurrence of ferromagnetic exchange interactions in the former. The ground states for the three complexes are $S = 0$, 3 and 3 for **1**, **2** and **4**, respectively.

The J_{bb} (negative) and J_{wb} (positive) parameters for **4** indicate that (*i*) the spins on the two 'body' V atoms, V(1) and V(2), should prefer to align antiparallel in the ground state, and (*ii*) the spins on all four V atoms should prefer to align parallel. Both conditions are clearly impossible to fulfill at the same time, and the preferred spin alignments are therefore frustrated. As a result, the ground state becomes sensitive to the J_{bb}/J_{wb} ratio: an analysis of the data in Fig. 2 indicates the actual ground state to be, in the format (S, S_A, S_B), the (3, 1, 2) state, where $\hat{S}_A = \hat{S}_1 + \hat{S}_2$ and $\hat{S}_B = \hat{S}_3 + \hat{S}_4$. These spin alignments in the ground state can be depicted as shown below.



The $S = 3$ ground state was confirmed by magnetization *vs.* field studies in the 0.500–50.0 kG and 2–300 K magnetic field and temperature ranges, respectively. A fit of the data to a model that assumes only the ground state is occupied and includes Zeeman and axial zero-field splitting effects gave the following fitting parameters: $S = 3$, $g = 1.96$, and $D = 3.71$ cm^{-1}, where D is the axial zero-field splitting parameter.

In summary, the successful development of tetranuclear vanadium(III) carboxylate chemistry not only presages a potentially large new area of $V^{III}_x/O/RCO_2^-$ ($x \geqslant 4$) chemistry, but demonstrates that the pervasive occurrence of spin-frustration effects in polynuclear transition-metal clusters extends also to vanadium(III). Further studies on the magnetic properties of $V^{III}_x/O/RCO_2^-$ clusters are in progress.

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Footnotes

† The complex analysed satisfactorily (C, H, N) as $\mathbf{4}(ClO_4){\cdot}Et_2O{\cdot}H_2O$.

‡ Suitable single crystals of $\mathbf{4}(ClO_4){\cdot}2CH_2Cl_2$ were grown from CH_2Cl_2–hexane. *Crystal data*: $C_{43}H_{55}Cl_5N_4O_{20}V_4$, $M_r = 1328.95$, triclinic, space group $P\bar{1}$, $a = 13.302(3)$, $b = 13.265(3)$, $c = 15.905(4)$ Å, $\alpha = 87.51(1)$, $\beta = 96.70(1)$, $\gamma = 86.66(1)°$, $U = 2778.8$ Å^3 and $Z = 2$. The structure was solved by direct methods (SHELXTL) and standard Fourier techniques, and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in a difference Fourier map and refined isotropically. Final residuals were $R(F) = 0.0716$ using 5730 unique reflections with $F > 4\sigma(F)$, and $R(F^2) = 0.1649$ using all 7256 unique intensities. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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