## Tetranuclear Vanadium(III) Carboxylate Chemistry, and a New Example of a Metal Butterfly Complex exhibiting Spin Frustration: Structure and Properties of $[V_4O_2(O_2CEt)_7(bpy)_2](CIO_4)$

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Treatment of  $[VCl_3(thf)_3]$  (thf = tetrahydrofuran) with bpy (bpy = 2,2'-bipyridine) and NaO<sub>2</sub>CEt in a 1:1:3 molar ratio in Me<sub>2</sub>CO followed by addition of  $ClO_4^-$  allows isolation of  $[V_4O_2(O_2CEt)_7(bpy)_2](ClO_4)$  [4(ClO<sub>4</sub>)], which contains a butterfly-like V<sub>4</sub> 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),<sup>1</sup>  $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+ 2^2$  and  $[Mn_4O_2(O_2CMe)_7(pic)_2]^- 3$ (Hpic = picolinic acid).<sup>3</sup> Since then, we have analysed these effects within complexes of various metal nuclearities, including  $Fe_{6,4}$  Mn<sub>7,5</sub> Mn<sub>8,6</sub> Mn<sub>96</sub> and Mn<sub>187</sub> 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 groundstate 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<sup>III</sup> ions, and have been particularly attracted by V<sup>III</sup>. 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<sub>2</sub>CEt (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<sup>n</sup><sub>4</sub>ClO<sub>4</sub> (0.75 mmol) added to the filtrate, and the solvent removed *in vacuo*. The residue was



Fig. 1 ORTEP representation of  $[V_4O_2(O_2CEt)_7(bpy)_2]^+$  4. Selected interatomic distances (Å) and angles (°) are:  $V(1)\cdots V(2)$  2.909(2),  $V(1)\cdots V(3)$  3.315(2),  $V(1)\cdots V(4)$  3.480(2),  $V(2)\cdots V(3)$  3.465(2),  $V(2)\cdots V(4)$  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.

washed with Et<sub>2</sub>O, and recrystallized from Me<sub>2</sub>CO-Et<sub>2</sub>O to give brown microcrystals of  $4(ClO_4)$ .<sup>†</sup> The same procedure can be employed for the  $PhCO_2^-$  and substituted-bpy analogues of 4. The structure of 4<sup>±</sup> contains a  $[V_4(\mu_3-O)_2]^{8+}$  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<sup>III</sup> 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  $[V(1)\cdots V(2) 2.909(2) \text{ Å}]$  being significantly longer than the 2.6 Å expected for  $V^{III} - V^{III}$  single bonds.<sup>11</sup> 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<sup>III</sup>, Fe<sup>III</sup>, Cr<sup>III</sup>, V<sup>III</sup>) family for tripositive 3d metals, the Cr<sup>III</sup> analogue having been reported by others.<sup>12</sup> In a wider context, 4 is the first structurally characterized example of a tetranuclear vanadium(III) carboxylate complex; there is, however, a mixedmetal V<sup>III</sup>–Zn<sup>II</sup> species known, namely  $[Zn_4V_4O_4(O_2CPh)_{12}(thf)_4],$ which contains a cubane-like [V<sub>4</sub>O<sub>4</sub>]<sup>4+</sup> core.<sup>13</sup>

Variable-temperature magnetic susceptibility studies have been performed on powdered samples of  $4(\text{ClO}_4)$  (restrained in Vaseline<sup>TM</sup> to prevent torquing) in a 10 kG field and 2.00–300 K temperature range. The effective magnetic moment ( $\mu_{eff}/V_4$ ) gradually increases from 5.79  $\mu_B$  at 300 K to a maximum of 6.80  $\mu_B$  at 25 K and then decreases to 4.72  $\mu_B$  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 ( $\mu_{eff}$ ) vs. temperature for  $[V_4O_2(O_2CEt)_7(bpy)_2](CIO_4)$ . 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  $\mu_{eff}$ ); see text for fitting parameters.

non-interacting V<sup>III</sup> ions (5.66  $\mu_B/V_4$ ). The experimental data were fit to the equation derived previously for a  $[M_4O_2]$ butterfly complex of idealized  $C_{2\nu}$  core symmetry,<sup>1-3</sup> adjusted for the present 4 V<sup>III</sup> system. The fitting parameters (using the  $H = -2JS_i \cdot S_j$  convention) are  $J_{bb} = -31.2 \text{ cm}^{-1}$ ,  $J_{wb} = 27.5 \text{ cm}^{-1}$  and g = 1.82, with no paramagnetic impurity term, and a temperature-independent paramagnetism term held constant at  $400 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ;  $J_{bb}$  and  $J_{wb}$  refer to the inner 'bodybody' and outer 'wingtip-body' interactions, respectively, of the V<sub>4</sub> 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)  $J_{bb} =$  $-8.9/-23.5 \text{ cm}^{-1}$ ,  $J_{wb} = -45.5/-7.8 \text{ cm}^{-1}$  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, 3and 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<sup>-1</sup>, 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  $V^{III}_x/O/RCO_2^-$  ( $x \ge 4$ ) 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 4(ClO<sub>4</sub>)·Et<sub>2</sub>O·H<sub>2</sub>O. ‡ Suitable single crystals of 4(ClO<sub>4</sub>)·2CH<sub>2</sub>Cl<sub>2</sub> were grown from CH<sub>2</sub>Cl<sub>2</sub>hexane. *Crystal data*: C<sub>43</sub>H<sub>55</sub>Cl<sub>5</sub>N<sub>4</sub>O<sub>20</sub>V<sub>4</sub>, *M*<sub>r</sub> = 1328.95, triclinic, space group *P*Ī, *a* = 13.302(3), *b* = 13.265(3), *c* = 15.905(4) Å, *α* = 87.51(1), β = 96.70(1), γ = 86.66(1)°, *U* = 2778.8 Å<sup>3</sup> 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* > 4σ(*F*), and *R*(*F*<sup>2</sup>) = 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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