Solvothermal Syntheses of High-Nuclearity Vanadium(III) Clusters

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Abstract: Superheating alcohol solutions of simple trimetallic vanadium(III) precursors gives the octa- and decametallic vanadium(III) clusters $[V_8(OEt)_8(OH)_4(O_2CPh)_{12}]$ (**1**) and $[V_{10}(OMe)_{20}(O_2CMe)_{10}]$ (**2**). Cluster **2** is the largest vanadium(III) cluster synthesised to date. Thus solvothermal synthetic techniques are an excellent route to high-nuclearity vanadium(III) clusters. Both **1** and **2** consist of a planar or near-planar array of V^{III} ions. The metal ions in **1** are bridged by either a μ_2-hydroxide and two μ_2-benzoate groups or two μ_2-ethoxides and a μ_2-benzoate groups, the two bridging arrangements alternating around the ring. In **2** each pair of neighbouring metal ions is bridged by two μ_2-methoxides and a μ_2-acetate, and this molecule is the V^{III} analogue of Lippard's famous "ferric wheel". Preliminary magnetic susceptibility studies show the exchange coupling in both complexes to be antiferromagnetic in nature, with the coupling stronger in **1** than in **2**.

Keywords: cage compounds · cluster compounds · metal–metal interactions · solvothermal synthesis · vanadium

Introduction

The vanadium(III) ion can give rise to very strong ferromagnetic interactions in dimeric species[1] and often exhibits very large zero-field splitting in monomers.[2] This makes it a very promising building block for single-molecule magnets (SMMs), which rely on a large ground state spin with a large, negative zero-field splitting.[3] Despite this there is very little literature on V^{III} clusters,[4,5] presumably due to the easily oxidisable nature of this ion. In contrast there is a very extensive literature on high-oxidation state vanadium cluster chemistry mainly due to the work of Zubieta and co-workers[6] and Müller and co-workers[7]. In this work we show that solvothermal methods are an excellent route to high-nuclearity V^{III} clusters and report the synthesis and preliminary magnetic studies of octa- and decametallic molecules, the latter of which is the highest nuclearity example reported to date.

Ferromagnetic coupling in transition-metal clusters can generate the high-spin ground states required to exhibit SMM behaviour. However, the ground state not only needs to have a large S value, it also needs to be well separated from the excited spin states. Thus it is desirable for the coupling to be ferromagnetic and large in magnitude. Wieghardt and co-workers have shown the exchange coupling J in the dimers $[L_2V_2O(O_2CR)_2]^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclonane; R = Ph, CH_3, CF_3, CH_2F, CH_2Br) to be $> +200\,cm^{-1}$ with the remarkable result that the $S = 2$ ground states of these complexes are exclusively populated at room temperature.[1] If this strong coupling could be built into larger clusters then higher blocking temperature SMMs could result. Beyond dimers and oxo-centred trimers, the most significant V^{III} clusters reported to date are the $[V_4O_2(O_2CEt)_7(bipy)_2]ClO_4$ tetramers of Christou and co-workers which have $S = 3$ ground states.[4] There is one report of a larger species—the octametallic $[V_8(OH)_4(OEt)_8(O_2CMe)_{12}]$ (no magnetic studies were reported).[5] Christou's tetramers exhibit SMM behaviour—this emphasises the potential of V^{III} in this field and the need to develop new synthetic strategies.

We recently reported the solvothermal synthesis of high-nuclearity Cr^{III}[8] and Fe^{III}[9] species via simple trimetallic "basic metal carboxylates"—$[M_3O(O_2CR)_6L_3]X$ (R = alkyl, aryl; L = for example, pyridine (py), H_2O; X = anion)—in superheated alcoholic solutions. We reasoned that this route should also be amenable to V^{III} clusters because the vanadium trimers are known[10] and the reducing nature of alcohols under solvothermal conditions should prevent oxidation of

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the V^{III} ion. Solvothermal techniques have been used previously to prepare V^{III} polymers[11] but not discrete clusters. In this work we report the synthesis and preliminary magnetic measurements of octa- and decametallic V^{III} clusters.

Experimental Section

Synthesis

Synthesis of $[V_3O(O_2CMe)_6(py)_3]ReO_4$ and $[V_3O(O_2CPh)_6(H_2O)_3]Cl$: Most literature preparations for $[V_3O(O_2CR)_6L_3]X$ have X = perchlorate.[4] Given the potentially explosive nature of perchlorates, and the high-temperature/pressure nature of our synthetic route, we have used alternative anions, for example, halides and perhenate, by making trivial modifications of the literature preparations.

*Synthesis of $[V_8(OEt)_8(OH)_4(O_2CPh)_{12}]$ (**1**)*: A solution of $[V_3O(O_2CPh)_6(H_2O)_3]Cl$ (0.3 g) in EtOH (9 mL) was heated at 150 °C in a Teflon-lined autoclave for 12 h followed by slow cooling to room temperature to yield green-brown crystals of **1** (30 %). These were separated by filtration and dried in vacuo. IR (KBr): $\tilde{\nu}=3608$ (w), 3066 (w), 2976 (w), 2921 (w), 1611 (m), 1593 (m), 1572 (m), 1540 (s), 1494 (s), 1422 (s), 1044 (m), 717 (m), 497 cm^{-1} (m); elemental analysis calcd (%) for $V_8C_{100}H_{104}O_{36}$: C 52.46, H 4.58; found: C 52.47, H 4.34. $[V_8(OEt)_8(O\text{-}D)_4(O_2CPh)_{12}]$ was prepared by using EtOD in place of EtOH, under anaerobic conditions (glove box and Schlenk line).

*Synthesis of $[V_{10}(OMe)_{20}(O_2CMe)_{10}]$ (**2**)*: A solution of $[V_3O(O_2CMe)_6(py)_3][ReO_4]$ (0.3 g) in MeOH (9 mL) was treated similarly to that of $[V_3O(O_2CPh)_6(H_2O)_3]Cl$ in the synthesis of **1**, to yield dark green crystals of **2** (13 %). MALDI-MS (dithranol matrix, in CH_2Cl_2 solution), *m/z*: 1722 (molecular ion); IR (KBr): $\tilde{\nu}=2927$ (m), 2823 (m), 1542 (s), 1454 (s), 1350 (m), 1042 (s), 676 (m), 622 (m), 549 (m), 506 cm^{-1} (s); elemental analysis calcd (%) for $V_{10}C_{40}H_{90}O_{40}$: C 27.9, H 5.23, V 29.65; found: C 27.16, H 5.09, V 28.72.

X-ray crystallography: Crystal structure data for **1:** $C_{100}H_{104}O_{36}V_8$, $M_r=2289.35$, crystal size $0.20\times0.04\times0.02$ mm^3, orthorhombic, space group *Ibam*, $a=33.5857(18)$, $b=17.9509(10)$, $c=18.2181(10)$ Å, $V=10\,983.6(10)$ $Å^3$, $T=200(2)$ K, $Z=4$, $\rho_{calcd}=1.384$ $g\,cm^{-3}$, λ (synchroton) = 0.6879 Å, 15 002 reflections collected, 5585 unique ($R_{int}=0.0354$), $R(F)=0.0748$ and $wR2=0.2279$ using 4162 reflections with $I>2\sigma(I)$.

Crystal structure data for **2:** $C_{40}H_{90}O_{40}V_{10}$, $M_r=1720.52$, crystal size $0.25\times0.15\times0.05$ mm^3, monoclinic, space group, *P2(1)/c*, $a=25.277(2)$, $b=15.8544(14)$, $c=29.310(3)$ Å, $\beta=114.808(2)°$, $V=10\,662.1(16)$ $Å^3$, $T=100(2)$ K, $Z=6$, $\rho_{calcd}=1.608$ $g\,cm^{-3}$, $\lambda=0.71073$ Å, 60 157 reflections collected, 21 755 unique ($R_{int}=0.1071$), $R(F)=0.0592$ and $wR2=0.1196$ using 10 981 reflections with $I>2\sigma(I)$. The methyl groups from some of the methoxide groups are disordered over two sites (C50, C54, C57).

Data were measured on a Bruker SMARTAPEX CCD (**2**) or on a Bruker SMART 1 K CCD diffractometer (**1**). Structure solution and refinement were performed with SHELXTL.[12] Structures were solved by direct methods. Refinement of F^2 was against all reflections. All non-hydrogen atoms were refined anisotropically except those that had to be split due to disorder. There are several carbon atoms in the benzoate ligands of **1** that have a maximum to minimum displacement parameter ratio of around 6:1; however, as splitting these would not add any new chemical information it was decided to leave them as they were. Hydrogen atoms were added geometrically to carbon atoms; however, this was not possible with the OH groups in **1** and therefore these hydrogen atoms were omitted. It was necessary to use geometrical and displacement restrains in the refinement of **1** to model the disorder in the ethoxide groups. Only the major occupancy sites of the disordered atoms are shown in Figure 1 and Figure 2. No solvent is found in the lattice in the crystal structures of either **1** or **2**.

CCDC-214672 (**1**) and CCDC-214673 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic measurements: Variable-temperature magnetic data were measured on polycrystalline samples in a 1 kG magnetic field using a SQUID magnetometer, and corrected for diamagnetic contributions from the sample and capsule. Samples used for magnetic measurements were synthesised and handled under strict anaerobic conditions and in each case the IR and powder X-ray diffraction data were consistent before and after measurements. All *J* values quoted in this paper are based on the 2 *J* formalism ($H=-2J\Sigma S_i.S_j$), with a positive *J* implying a ferromagnetic interaction, and where necessary values from the literature have been converted to this formalism for consistency.

Results and Discussion

Synthesis: Heating an ethanol solution of $[V_3O(O_2CPh)_6(H_2O)_3]Cl$ at 150 °C for 12 h, followed by slow cooling to room temperature, yields fibrous green-brown crystals of the cyclic octametallic cluster $[V_8(\mu_2\text{-}OEt)_8(\mu_2\text{-}OH)_4(\mu_2\text{-}O_2CPh)_{12}]$ (**1**; Figure 1) in reasonable yield. A similar reaction of $[V_3O(O_2CMe)_6(py)_3][ReO_4]$ in methanol yields dark green crystals of the cyclic, decametallic cluster $[V_{10}(\mu_2\text{-}OMe)_{20}(\mu_2\text{-}O_2CMe)_{10}]$ (**2**; Figure 2). Thus **1** and **2** add to the growing family of metallic "wheels".[13] In both **1** and **2** all the vanadium ions are in the +3 oxidation state, as determined from structural, spectroscopic and magnetic data (see below). Indeed, the syntheses of **1** and **2** are remarkably insensitive to the presence of air - preparations under aerobic and anaerobic conditions give identical products. This is in contrast to the majority of preparations for V^{III} dimers where strict anaerobic conditions are necessary to prevent oxidation of the V^{III} ion to V^{IV} (often forming vanadyl species).[14]

Analogous reactions of the trimeric starting materials under non-solvothermal conditions—in refluxing alcohols under an inert atmosphere—give pale yellow powders which are similar in colour to, and have similar IR spectra as, the trimeric starting materials—we have yet to identify the species in these powders. Thus, the solvothermal conditions have lead to new products and their direct crystallization from the reaction mixtures.

Crystalline samples of **1** and **2** are relatively air stable although they do oxidize on exposure to air over a period of weeks, as witnessed by the growth of peaks at about 985 cm^{-1} in IR spectra (characteristic of vanadyl) over this timescale. Furthermore, the observation of a molecular ion peak in the mass spectrum of **2** from CH_2Cl_2 solution indicates the integrity of this cluster in solution.

Crystal structures: The octametallic, cyclic structure of **1** (Figure 1, Table 1) is analogous to the acetate wheel made by Kumagai and Kitagawa.[5] The molecule lies on a centre of symmetry, and the eight vanadium ions (and the four O(H) ions) lie on a mirror plane (C_{2h} point symmetry, see Table 1 for important bond distances and angles). All the metal ions are pseudo-octahedral six-coordinate with neighbouring ions bridged by either one benzoate and two ethoxides (V···V distances of 3.012 and 3.010 Å, close to those seen for **2** which has a similar bridging motif, see below), or by two benzoates and a hydroxide (V···V of 3.377 and 3.382 Å), and the two bridging modes alternate around the

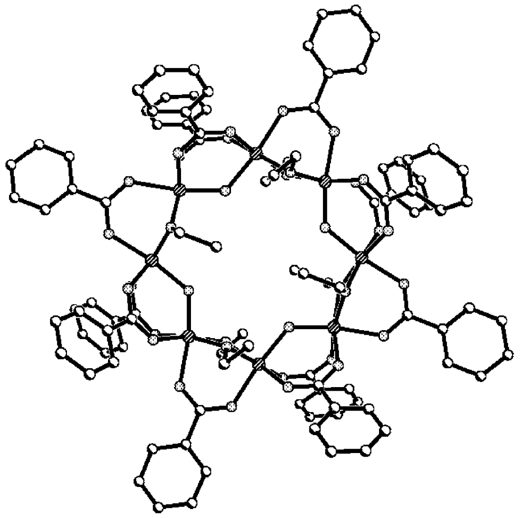

Figure 1. The molecular structure of **1** viewed perpendicular to the V_8 plane. Bond length ranges [Å]: V–O(benzoate) 1.892(12)–2.300(10), V–O(H) 1.822(4)–1.963(3), V–O(Et) 1.963(3) and 1.971(3) Å. Inter-bond angle ranges [°]: V-O(H)-V both 129.1(3), V-O(Et)-V 99.85(16) and 100.09(15). Shading: cross-hatched (V), dotted (O), white (C). H atoms omitted for clarity.

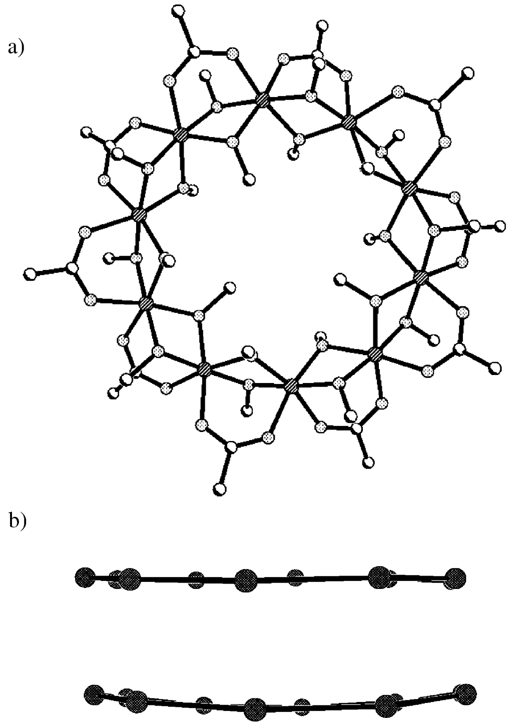

Figure 2. a) The molecular structure of a molecule of **2** viewed perpendicular to the V_{10} ring. b) Side-on view of the V_{10} ring: molecule B (top) and molecule A (bottom). Bond length ranges [Å]: V–O(acetate) 2.014(4)–2.051(4), V–O(Me, "inner") 1.917(4)–2.047(4), V–O(Me, "outer") 1.943(4)–2.038(4). V-O(Me)-V inter-bond angle range [°]: 95.40(16)–99.06(18) ("inner"), 98.53(18)–100.74(17) ("outer"). V···V distances [Å]: 2.9884(15)–3.0331(14) Å.

Table 1. Selected structural parameters for **1**. Interatomic distances [Å] and inter-bond angles [°].[a]

V1–V4	3.0127(16)	V1–O61	1.963(3)	V3–O2	1.830(5)	V4–O2	1.910(4)
V2–V3	3.0101(14)	V2–O1	1.924(4)	V3–O22	2.032(5)	V4–O32	2.006(4)
V1–O1	1.822(4)	V2–O12	2.300(10)	V3–O31	2.025(4)	V4–O41	2.024(5)
V1–O11	1.993(4)	V2–O21	2.023(5)	V3–O51	1.963(3)	V4–O61	1.967(3)
V1–O42	2.057(4)	V2–O51	1.971(3)				
V1-O1-V2	129.1(3)	V3-O2-V4	129.1(3)	V2-O51-V3	99.85(16)	V1-O61-V4	100.09(15)

[a] O1 and O2 are the O atoms of the hydroxide groups, O51 and O61 are the O atoms of the ethoxide groups.

ring. Kumagai and Kitagawa formulated their wheel as all V^{III} based on crystallographic arguments regarding the V–O distances and V-O-V angles, and pointed out that this was only consistent if all the non-alkoxide/carboxylate bridges are protonated and are in fact hydroxide.[5] As with that study, the hydrogen atoms of the hydroxide bridges in **1** are not found crystallographically, but the metric parameters are only consistent with all V^{III}—there are no short V–O distances to support formulation as V^{IV}. In support of this, an O–H stretch is observed in the IR spectrum of **1** (KBr disk) at 3608 cm^{-1} (in addition, characteristic bands are observed for bridging alkoxides and carboxylates). The assignment as OH is supported by the IR spectrum of the selectively deuterated compound $[V_8(OEt)_8(OD)_4(O_2CPh)_{12}]$, in which this band is absent and is replaced by a new band at 2655 cm^{-1} (the spectra are otherwise identical). Thus the vanadium ions in **1** are all V^{III}.

Complex **2** contains a cyclic array of ten vanadium ions (Figure 2, Table 2). The asymmetric unit contains 1.5 molecules such that one molecule (A) has ten unique V^{III} ions whilst the second molecule (B) contains five and has twofold symmetry. As with **1**, all the metal ions are pseudo-octahedral and six-coordinate, though now all neighbouring ions are bridged by one acetate and two methoxide groups. The methoxide groups alternate between pointing towards and away from the V_{10} ring. The mean deviations from the best planes of the 10 V^{III} ions are significantly different in the two independent molecules: 0.0265 Å in molecule B and 0.1267 Å in molecule A, making the latter noticeably non-planar (Figure 2b). This may be related to the presence of three V-O(Me)-V angles in molecule A that are significantly smaller (95–96°) than the others and than those in molecule B. Indeed, the lower symmetry of molecule A is apparent in the greater range of interatomic distances and inter-bond angles compared to B (Table 2). The formula of **2** dictates that all the vanadium ions are in the +3 oxidation state and this is consistent with the metric parameters.

Complex **2** is the V^{III} analogue of Lippard's famous "ferric wheel" $[Fe_{10}(OMe)_{20}(O_2CCH_2Cl)_{10}]$ (**3**),[15] (the direct analogue—with acetate rather than chloroacetate—was reported later by Winpenny and co-workers)[16]. The Cr^{III} "chromic wheel" $[Cr_{10}(OMe)_{20}(O_2CCH_3)_{10}]$ (**4**; also prepared by a solvothermal route) has also been reported by us.[8] Table 3 lists some of the important mean structural parameters for **2** to **4**, although the relatively wide ranges of some

Table 2. Selected structural parameters for **2**. Interatomic distances [Å] and inter-bond angles [°].[a]

V1–V2	2.9991(14)	O23–V2	1.958(4)	O32–V7	2.028(4)	O52–V12	1.940(4)
V1–V10	3.0217(14)	O23–V3	2.029(4)	O33–V8	2.009(4)	O52–V11	1.990(4)
V2–V3	3.0331(14)	O24–V3	1.942(4)	O33–V7	2.029(4)	O53–V13	1.985(4)
V3–V4	3.0117(15)	O24–V2	2.027(4)	O34–V7	1.967(4)	O53–V12	1.993(4)
V4–V5	2.9884(15)	O25–V4	1.951(4)	O34–V8	1.971(4)	O54–V12	1.974(4)
V5–V6	3.0124(15)	O25–V3	2.033(4)	O35–V8	1.956(4)	O54–V13	1.986(4)
V6–V7	3.0208(14)	O26–V3	1.927(4)	O35–V9	2.038(4)	O55–V14	1.997(4)
V7–V8	3.0013(14)	O26–V4	2.047(4)	O36–V9	1.940(4)	O55–V13	2.014(4)
V8–V9	3.0245(15)	O27–V4	2.016(4)	O36–V8	2.036(4)	O56–V13	1.954(4)
V9–V10	3.0282(15)	O27–V5	2.024(4)	O37–V9	1.996(4)	O56–V14	1.979(4)
V11–V12	3.0005(15)	O28–V5	1.951(4)	O37–V10	2.016(4)	O57–V14	1.986(4)
V11–V15	3.0088(15)	O28–V4	1.961(4)	O38–V10	1.963(4)	O57–V15	1.994(4)
V12–V13	3.0185(15)	O29–V5	1.943(4)	O38–V9	1.969(4)	O58–V14	1.976(4)
V13–V14	3.0125(15)	O29–V6	2.019(4)	O39–V1	1.962(4)	O58–V15	1.979(4)
V14–V15	3.0039(16)	O30–V6	1.927(4)	O39–V10	2.034(4)	O59–V15	1.964(4)
O21–V1	2.016(4)	O30–V5	2.040(4)	O40–V10	1.917(4)	O59–V11	1.980(4)
O21–V2	2.021(4)	O31–V7	1.954(4)	O40–V1	2.024(4)	O60–V11	1.979(4)
O22–V1	1.962(4)	O31–V6	2.030(4)	O51–V11	1.976(4)	O60–V15	2.014(4)
O22–V2	1.969(4)	O32–V6	1.931(4)	O51–V12	2.021(4)		
V1-O21-V2	95.95(17)	V7-O31-V6	98.62(18)	V11-O51-V12	97.32(18)	V1-O22-V2	99.46(18)
V6-O32-V7	99.43(18)	V12-O52-V11	99.56(18)	V2-O23-V3	99.06(18)	V8-O33-V7	96.04(17)
V13-O53-V12	98.71(18)	V3-O24-V2	99.67(17)	V7-O34-V8	99.32(17)	V12-O54-V13	99.30(18)
V4-O25-V3	98.19(17)	V8-O35-V9	98.42(17)	V14-O55-V13	97.37(17)	V3-O26-V4	98.53(18)
V9-O36-V8	99.02(18)	V13-O56-V14	99.96(17)	V4-O27-V5	95.40(16)	V9-O37-V10	98.03(17)
V14-O57-V15	98.00(18)	V5-O28-V4	99.61(17)	V10-O38-V9	100.74(17)	V14-O58-V15	98.85(18)
V5-O29-V6	98.96(17)	V1-O39-V10	98.22(18)	V15-O59-V11	99.42(17)	V6-O30-V5	98.76(18)
V10-O40-V1	100.10(19)	V11-O60-V15	97.81(18)				

[a] V1 to V10 are in molecule A, V11 to V15 in molecule B. O22, 24, 26, 28, 30, 32, 34, 36, 40 (molecule A) and O52, 54, 56, 58, 59 (molecule B) are the O atoms of the methoxide groups pointing inside the wheel. O21, 23, 25, 27, 29, 31, 33, 35, 37, 39 (A) and O51, 53, 55, 57 and 60 (B) are from the "outer" methoxide groups.

of the bond lengths and angles in these systems (the molecules have at most twofold or inversion symmetry) makes meaningful comparison of average parameters difficult. It is however noticeable that the average M···M distance is significantly shorter for Cr^{III} than for Fe^{III} or V^{III}. This effect has been observed in some polynuclear systems previously, and has been ascribed to the smaller ionic radius of Cr^{III}.[4]

Magnetic studies: The magnetic behaviour of **1** and **2** are similar (Figure 3). The room-temperature values of χT ($\chi =$ molar magnetic susceptibility) of 4.43 and 7.45 $cm^3 K mol^{-1}$ for **1** and **2**, respectively, are below those you would expect for eight and ten uncoupled V^{III} ions, respectively, (much more so in the case of **1**) and decrease as the temperature is decreased. This is indicative of significant antiferromagnetic coupling between the V^{III} ions in both compounds. The larger deviation of **1** from the expected value for uncoupled spins implies that the exchange is overall more antiferromagnetic than in **2**. This can be easily rationalised from the structures of **1** and **2**. We would expect two distinct J values in **1** (although the crystallographic C_{2h} symmetry means that there are in principle 4 distinct values): those in the $\{V(OEt)_2(O_2CPh)V\}$ and $\{V(OH)(O_2CPh)_2V\}$ moieties. We might expect the former to be similar to the exchange coupling in **2** which has a similar $\{V(OMe)_2(O_2CMe)V\}$ bridging arrangement (V-O(R)-V angles in the range 95–101°). However, we would expect the coupling in the $\{V(OH)(O_2CPh)_2V\}$ groups of **1** to be much more antiferromagnetic due to the much more obtuse V-O(H)-V angles found (ca. 130°). Thus, χT would be expected to fall quicker for **1** than for **2**. Similar behaviour has been observed by Christou and co-workers for structurally related Fe_8^{III} and Fe_{10}^{III} clusters.[17] Attempts to model the magnetic data have been hampered by what appears to be an intrinsic impurity in **1** (as witnessed by a weak signal in its EPR spectra at low temperature). We believe that this corresponds to oxidation of a V^{III} ion in some of the molecules in the lattice with retention of the gross

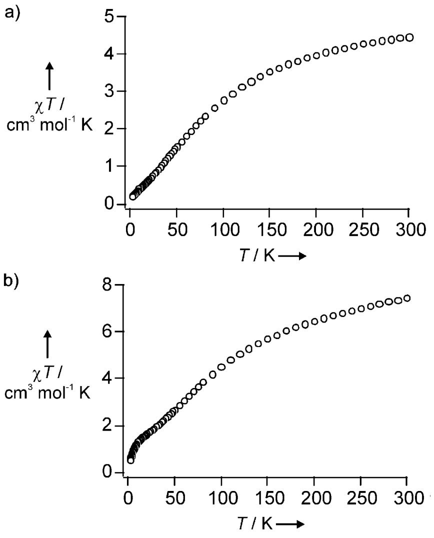

Figure 3. The magnetic susceptibility of **1** (a) and **2** (b) plotted as χT versus T.

Table 3. Comparison of mean structural parameters in $[M_{10}(OMe)_{20}(O_2CMe)_{10}]$ wheels.

M	V	Cr[a]	Fe[b]
M···M	3.012(2)	2.989(3)	3.028(4)
M···O(Me)	1.974(4)[c], 2.000(4)[d]	1.963(8), 1.963(8)	1.975(4), 1.987(6)
M···O(acetate)	2.034(4)	1.99(1)	2.07(1)
M-O(Me)-M	97.7(2),[c] 99.5(2)[d]	99.2(4), 99.2(4)	99.3(4), 100.0(4)
deviation from best M_{10} plane	0.0265, 0.1267[e]	0.0151, 0.0194[e]	0.009

[a] Reference [8]. [b] Reference [15]. [c]"Inner" OMe groups. [d] "Outer" OMe groups. [e] Two crystallographically independent molecules.

structure, but at a concentration that is not apparent in IR spectra, and is only manifest in the X-ray data as disorder. This could result in the magnitude of χT data for **1** being slightly underestimated in Figure 3. Because of this we have restricted ourselves to the qualitative description above. No such impurity is present in **2**, but its analysis is complicated by the two structurally unique molecules in the crystal structure and the wide ranges of the structural parameters. For example, because we expect J to be strongly dependent on the V-O(Me)-V angles it seems likely that a single J value model would be inadequate given that there are three angles in molecule A that are significantly smaller than the rest (see above). Indeed, attempts to fit the magnetic data of **1** with a single J value do not give satisfactory fits, although they suggest that the dominant exchange coupling is in the region of ca. $-25\,cm^{-1}$—this number should be treated with some caution. We are now attempting to recrystallise **2**, and prepare analogues with different carboxylates, in the hope of isolating a higher symmetry crystal form. These results will be reported at a later date.

A survey of the V^{III} dimers in the literature reveals that all the strongly ferromagnetically coupled examples are bridged by a single oxide or by $\{(O)(O_2CR)_2\}$, whilst those examples bridged by $\{(OR)_2\}$ or $\{(OH)(O_2CR)_2\}$ tend to be antiferromagnetically coupled.[18] The latter two examples are more akin to the bridging observed in **1** and **2** and therefore the observed antiferromagnetic exchange is not unexpected. It is not possible at present to provide a detailed comparison of the magnetic exchange in the $[M_{10}(OMe)_{20}(O_2CMe)_{10}]$ complexes. The Fe^{III} wheel is antiferromagnetically coupled with $J=-5\,cm^{-1}$,[15] while the Cr^{III} analogue appears to be ferromagnetically coupled with $J=+2.25\,cm^{-1}$.[8] There is not a complete series of simple $\{M(OR)_2(O_2CR')M\}^{n+}$ dimers for us to compare these compounds to. However, the dimers $[LM(OH)(O_2CR')_2ML]^{n+}$ ($M=V^{III}$, Mn^{III}, Cr^{III}, Fe^{III}; L=1,4,7-trimethyl-1,4,7-triazacyclonane, $n=3$ or hydrotris(1-pyrazolyl)borate(1−), $n=1$) have been studied and show the coupling in the vanadium compound to be antiferromagnetic and larger in magnitude than the coupling in the chromium and iron compounds.[19] Qualitatively, we seem to be seeing the same pattern in **2**–**4**. In addition to our on-going studies on **2**, **4** and analogues, we are attempting to synthesise dinuclear model compounds with $\{(OR)_2(O_2CR')\}$ bridging arrangements to probe this further.

Conclusion

This work shows that solvothermal chemistry is an excellent route to V_n^{III} clusters, providing only the second and third examples with $n>4$, and **2** is the largest reported to date. We previously reported the use of solvothermal conditions to overcome the kinetic inertness of the Cr^{III} ion in the preparation of complex **4**, structurally analogous to **2**. In this work the use of solvothermal techniques under reducing conditions has helped prevent the oxidation of V^{III}—even under aerobic conditions. It is at present unclear whether it is the difference in carboxylate, anion or alcohol that leads to the different structural motifs in **1** and **2** and we are currently exploring this systematically. Furthermore, these structures will allow important comparison with clusters of other 3d metal ions: related M_8[17,20] wheels to **1** are also known for Cr^{III} and Fe^{III}. These families will provide rare examples of systems which allow the study of the magnetic properties of a range of metal ions (d^2, d^3, d^5) in the same high-nuclearity cluster environment.

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