Solid state synthesis of $[V_5O_2(Me_3CCO_2)_9Cl_2]$†

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The synthesis of a new pentanuclear V(III) complex $[V_5O_2(Me_3CCO_2)_9Cl_2]$ (1) by solid state methods is described.

Interest in transition metal complexes spans areas as different as bioinorganic chemistry[1] and quantum computing.[2] In 1992, the property of single-molecule magnetism was discovered in a Mn_{12} complex.[3] This opened up many possible applications of single-molecule magnets (SMMs) if blocking temperatures could be raised to a more practical level. It is now known that an SMM requires a large spin ground state and large and negative anisotropy. Therefore V(III) complexes could be of interest in this area given V(III)'s large single-ion anisotropy.[4] Unfortunately, there are not many V(III) high nuclearity complexes,[5] and only one V(III) SMM has been reported in the literature.[6]

Given the interest in new high nuclearity complexes it is valuable to search for new synthetic methodologies. Sometimes control can be achieved over a particular reaction method by variation of parameters such as reaction times, solvent or temperature. One system that has been exploited is the reaction of a trinuclear basic carboxylate[7] with a ligand[8] under ambient pressure and in solvothermal[9] reactions. Our group has also developed the solid state decomposition of these M_3 species as a means of obtaining new coordination complexes. This has resulted in a variety of new species for chromium, iron, vanadium and manganese.[10–12] In this technique, the solid is heated under a flow of N_2 gas in a tube furnace. In general the product is then isolated by extraction of a soluble species and crystallization of the new complex. This has been very effective for chromium and iron. In targeting new V(III) complexes the N_2 atmosphere within the tube furnace should be useful in that it reduces the possibility of oxidation.

The synthesis of $[V_3O(PhCO_2)_6(H_2O)_3]Cl$ is a well known procedure.[13] Vanadium trichloride is treated with benzoic acid and NaOH in a mixture of ethanol and water under anaerobic conditions. Upon stirring, the product precipitates after a few hours and can be easily isolated by filtration. As we previously reported, the solid state decomposition of this species lead to the isolation of a family of hexanuclear V(IV) complexes due to oxidation of the V(III) during the alcoholysis of the solid obtained from the thermal decomposition of the starting material.[12] We decided to use pivalic acid instead of benzoic acid in the same synthetic procedure in order to obtain the pivalate analog to $[V_3O(PhCO_2)_6(H_2O)_3]Cl$. and study its thermal decomposition in a tube furnace. Vanadium trichloride was treated with pivalic acid and NaOH in a toluene–THF mixture under N_2. After overnight stirring under inert atmosphere, a green precipitate was collected by filtration under N_2. Thermogravimetric analysis of a sample of this solid up to 500 °C showed that approximately 65% of the weight is lost between 200 and 350 °C, which indicates the loss of the terminal ligands and some of the carboxylates. The six pivalates would amount to 67% of the weight of the trinuclear complex. Therefore 300 °C was chosen as the working temperature due to the fact that only some carboxylates had been lost at that temperature in the TGA analysis, leaving a product that is still rich in carboxylate ligands. 1.0 g of the solid was heated to 300 °C under a constant flow of N_2 in a Carbolite tube furnace equipped with an open pyrex container for the solid that was sitting on a pyrex tube. The sample was heated at a constant temperature of 300 °C for one hour and allowed to cool over ten days. After cooling, brown crystals of $[V_5O_2(Me_3CCO_2)_9Cl_2]$ **1** (Fig. 1) were found on the surface of the pyrex tube. By the use of pivalate, the extraction and crystallization steps that had previously resulted in the oxidation of V(III) compounds to V(IV)[12] were avoided. It appears that in addition to being able to use thermal decomposition to make a new cage complex, the great volatility common in pivalate complexes has resulted in the formation of a compound that can be easily sublimed in the tube furnace, hence aiding separation and isolation of a pure material. This appears to be the first time a V(III) coordination complex has been isolated by thermal decomposition in a tube furnace.

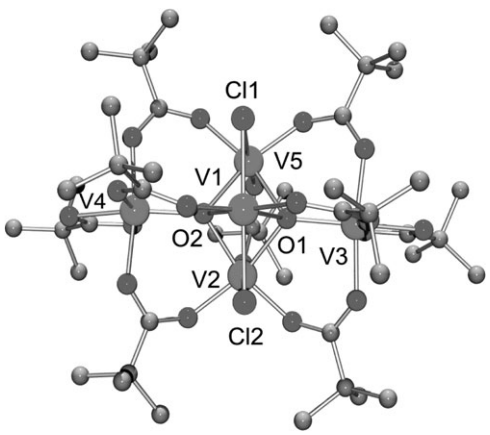

Fig. 1 Crystal structure of $[V_5O_2(Me_3CCO_2)_9Cl_2]$ **1**.

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† The HTML version of this article has been enhanced with colour images.

The brown crystals were air sensitive and were collected and kept under N_2.‡ The crystal structure revealed a pentanuclear vanadium cluster, with the five V ions at the vertices of a trigonal bipyramid. All of the metal centres were hexacoordinated in a distorted octahedral fashion. The central V_3 unit (V1, V2 and V5) is linked to the other two V(III) ions by two 4.4-oxides[14] (O1 and O2). Two of the sides of the central V_3 unit (V1–V2 and V1–V5) are capped by two 2.2-chlorides; the two V(III) ions of the third side (V2 and V5) are bridged by a 2.11-pivalate group. The two axial V(III) centres (V3 and V4) complete their coordination sphere by a chelating pivalate group and three 2.11-pivalates, which bridge V(end) to V(triangle). The V–O distances are in the range of 1.928 to 2.057 Å, indicating the oxidation state V(III), as required for charge balance. The oxidation state V(III) was also confirmed by bond valence sum calculations.[15]

DC magnetic susceptibility of a crushed crystalline sample of complex **1** was studied at an applied field of 1.0 T. Due to the air sensitivity of the sample the specimen for magnetism was prepared under N_2. $\chi_M T$ at 300 K has a value of 4.3 cm^3 K mol^{-1}, slightly lower than the spin-only value of 5.0 cm^3 K mol^{-1} expected for five non-interacting V(III) ions, and it decreases with temperature, indicating antiferromagnetic coupling between the metal centres leading to a spin ground state of $S = 1$. At 25 K $\chi_M T$ has a value of 2.2 cm^3 K mol^{-1} and it then sharply decreases to a value of 1.1 cm^3 K mol^{-1} at 2 K. The magnetization *vs.* field plots at 2 and 4 K reach a value of 2.4 at 7 T but do not completely saturate, which indicates a $S = 1$ spin ground state with low lying excited states. The variable temperature magnetic data were modelled with the Hamiltonian:

$$H = -2J_1(S_3 + S_4)(S_1 + S_2 + S_5) - 2J_2S_2S_5 - 2J_3(S_1S_2 + S_1S_5)$$

where S_i refers to the spin on the V centre as labelled in Fig. 1.

The experimental data were fitted using the full-matrix diagonalization program MAGPACK.[16] The data down to 25 K were fitted with three exchange interactions: $J_1 = -28$ cm^{-1}, $J_2 = -21$ cm^{-1}, $J_3 = +5$ cm^{-1}. The g value was fixed at 1.80. It was not possible to model the variable temperature data using fewer exchange interactions. The best fit is shown in Fig. 2 as a solid line. The rapid fall below 20 K can be fitted with an axial zero-field splitting parameter, $D = -11$ cm^{-1}, but other possible explanations include intermolecular exchange and this D-value should not be regarded as accurate. Both J_1 and J_2 correspond to the exchange coupling through a pivalate group, and are expected to be antiferromagnetic and of the same order.[17] J_3, on the other hand, is the measure of the exchange through the oxide and the chloride. The V–O–V angles have an average value of 85.8°, while the V–Cl–V angles have an average value of 71°, which makes the magnetic orbitals nearly orthogonal. Thus, J_3 is found to be small and ferromagnetic. The J values obtained lead to a low spin ground state of $S = 1$.

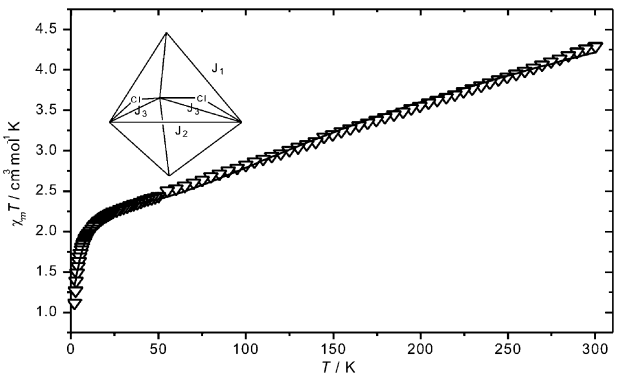

Fig. 2 $\chi_M T$ *vs.* T plot for complex **1** at 1.0 T applied field.

In conclusion, the conditions of the tube-furnace have been successfully used to obtain a new pentanuclear V(III) complex with large anisotropy. This is a powerful new synthetic route that could be easily extended to other starting materials containing volatile ligands such as pivalate.

Experimental

Synthesis

VCl_3 (2.0 g, 0.012 mol) was treated with pivalic acid (2.5 g, 0.025 mol) and NaOH (1.0 g, 0.025 mol) in a toluene–THF mixture under N_2. After overnight stirring, a green precipitate was collected. 1.0 g of this solid was heated to 300 °C for 1 h under a constant flow of N_2 in a tube furnace. The sample was allowed to cool over ten days, after which brown crystals of **1** were found on the surface of the pyrex tube. Typical yields were between 5 and 15%; elemental analyses calcd. (found): C 42.64 (42.03), H 6.44 (6.22), Cl 5.52 (5.18)%.

Crystal structure data for 1‡

$C_{45}H_{81}O_{20}Cl_2V_5$, $M_w = 1267.70$, crystal size 0.39 × 0.23 × 0.03 mm, triclinic, space group $P\bar{1}$, $a = 14.294(3)$, $b = 14.484(3)$, $c = 16.671(2)$Å, $\alpha = 64.42(7)$, $\beta = 86.24(7)$, $\gamma = 84.80(9)$°, $V = 3202.8(5)$ Å^3, $T = 150(2)$ K, $Z = 2$, $\lambda = 0.6933$ Å, 19 153 reflections collected, 8131 independent ($R_{int} = 0.0330$), $R(F) = 0.0478$ and $wR2 = 0.1195$ for $I > 2\sigma(I)$ [$R(F) = 0.0750$, $wR2 = 0.1349$ for all data].

References

‡ CCDC reference number 638407. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704191h

1 (*a*) J. McMaster, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 2004, **100**, 611; (*b*) S. Mukhopadhyay, S. K. Mandal, S. Bhaduri and W. H. Armstrong, *Chem. Rev.*, 2004, **104**, 3981.
2 F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. A. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.*, 2005, **94**, 207208.
3 (*a*) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; (*b*) H. J. Eppley, H. L. Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 301.
4 J. Krzystek, A. T. Fiedler, J. J. Sokol, A. Ozarowski, S. A. Zvyagin, T. C. Brunold, J. R. Long, L.-C. Brunel and J. Telser, *Inorg. Chem.*, 2004, **43**, 5645.
5 (*a*) R. H. Laye, Q. Wei, P. V. Mason, M. Shanmugam, S. J. Teat, E. K. Brechin, D. Collison and E. J. L. McInnes, *J. Am. Chem. Soc.*, 2006, **128**, 9020; (*b*) I. S. Tidmarsh, R. H. Laye, P. R. Brearley, M. Shanmugam, E. C. Sañudo, L. Sorace, A. Caneschi and E. J. L. McInnes, *Chem. Commun.*, 2006, 2560; (*c*) R. H. Laye, M. Murrie, S. Ochsenbein, A. R. Bell, S. J. Teat, J. Raftery, H. U. Guedel and E. J. L. McInnes, *Chem.–Eur. J.*, 2003, **9**, 6215.

6 S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1998, **120**, 2365.
7 (*a*) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195–298; (*b*) R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983.
8 G. Aromi and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1.
9 R. H. Laye and E. J. L. McInnes, *Eur. J. Inorg. Chem.*, 2004, **14**, 2811.
10 (*a*) A. Parsons, A. A. Smith and R. E. P. Winpenny, *Chem. Commun.*, 2000, 579; (*b*) I. M. Atkinson, C. Benelli, M. Murrie, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 1999, 285; (*c*) F. E. Mabbs, E. J. L. McInnes, M. Murrie, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 1999, 643.
11 R. A. Coxall, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *J. Solid State Chem.*, 2001, **159**, 321.
12 E. C. Sañudo, A. A. Smith, P. V. Mason, M. Helliwell, G. Aromí and R. E. P. Winpenny, *Dalton Trans.*, 2006, 1981.
13 S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1998, **120**, 2365.
14 Harris notation describes the binding mode as $[X.Y_1Y_2Y_3\cdots Y_n]$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules. See R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2000, 23.
15 (*a*) W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102; (*b*) I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1973, **29**, 266.
16 J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985.
17 M. R. Bond, R. S. Czernuszewicz, B. C. Dave, Q. Yan, M. Mohan, R. Verastegue and C. J. Carrano, *Inorg. Chem.*, 2001, **34**, 5857.