Magnetism in Clusters

Strong Ferromagnetic Interactions in $[V_8O_{14}(H_{-2}taci)_2]$: An Unprecedented Large Spin Ground State for a Vanadyl Cluster**

Kaspar Hegetschweiler, Bernd Morgenstern, Jon Zubieta,* Pamela J. Hagrman, Nicola Lima, Roberta Sessoli,* and Federico Totti*

The control of the spin of the ground state in molecular clusters behaving like single molecule magnets (SMM) has been an important challenge in coordination chemistry. The spin value is a critical parameter because the barrier for the orientation of the magnetization depends on the square of it.[1,2] The most common strategies exploit antiferromagnetic interactions both in hetero-spin clusters, such as the archetypal SMM, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$,[3–5] and in particular spin topologies, such as the propeller structure of Fe_4 clusters.[6,7] Ferromagnetic interactions are relatively rare in molecular clusters, and often encountered in very symmetric structures, where the orthogonality of the magnetic orbitals is more easily controlled.[8,9] In low-symmetry environments the sign of the magnetic interaction is, in general, easily predictable for paramagnetic centers with one unpaired electron.[10] Magneto-structural correlations are well established, for instance, for oxo-bridged $\{VO^{2+}\}$ fragments[11] and ferromagnetic interactions have been observed when the d_{xy} magnetic orbitals are orthogonal to each other, where a local reference system with the x and y axis pointing towards the oxo-bridging ligands is considered. The J values usually do not exceed $-10\ cm^{-1}$,[12] the Hamiltonian being defined as $\mathscr{H} =$

[*] N. Lima, Prof. R. Sessoli, Dr. F. Totti
Department of Chemistry & INSTM (UdR Firenze)
Università degli Studi di Firenze
Via della Lastruccia 5, 50019 Sesto Fiorentino (Italy)
Fax: (+39) 055-457-3372
E-mail: roberta.sessoli@unifi.it

Prof. J. Zubieta, Dr. P. J. Hagrman
Department of Chemistry
Syracuse University
Syracuse, NY 13244 (USA)
Fax: (+1) 315-443-4070
E-mail: jazubiet@mailbox.syr.edu

Prof. K. Hegetschweiler, Dr. B. Morgenstern
Universität des Saarlandes
Anorganische Chemie
Postfach 15 11 50, 66041 Saarbrücken (Germany)
Fax: (+49) 681-302-2663
E-mail: hegetschweiler@mx.uni-saarland.de

[**] 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a Ligand with a Remarkable Versatility for Metal Ions, Part 12. R.S. acknowledges the financial support of Italian MIUR and CNR, German DFG (SPP1137), and EC network MOLNANOMAG(contract Nos. HPRN-CT-1999–00012). K.H. thanks the Syracuse University and the Universität des Saarlandes for a visiting scholarship at Syracuse. taci = 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol. Part 11: ref. [21].

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$\sum_{i<j} J_{ij}\mathbf{S}_i\mathbf{S}_j$. In spite of the very rich chemistry of V^{IV} oxo clusters,[13,14] where the nuclearity can be as high as 20,[15] to date only singlet ground states, or $S = 1/2$ for odd nuclearity clusters, have been reported.

Herein we exploit the ability of the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) to multiple-bind metal ions[16,17] to obtain an octanuclear vanadyl cluster, $[V_8O_{14}(H_{-2}taci)_2]$ (**1**; Figure 1).[18–20] This complex is the first

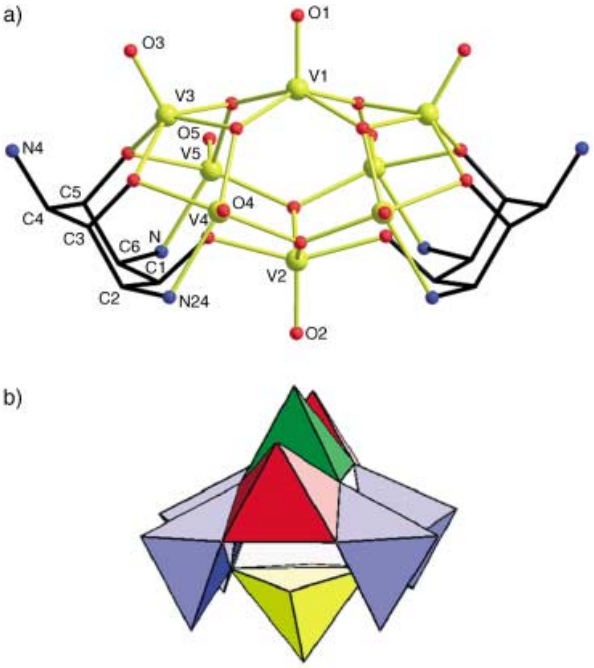

Figure 1. Molecular structure of $[V_8O_{14}(H_{-2}taci)_2]$.[19,20] a) Ball-and stick-representation. V yellow, O red, N blue. b) Polyhedral representation of the $\{V_8O_{20}N_4\}$ core rotated by 90°. The color scheme highlights the idealized C_{2v} symmetry of the cluster exploited in the analysis of the magnetic properties (the colors indicate symmetry related units). Averaged interatomic distances [Å] (215 K), values at 90 K are given in parentheses: V=O 1.621 (1.622), V-μ_3O 1.946 (1.939), V-μ_2O_{alkoxo} 2.019 (2.010), V2-O12 1.987 (1.981), V4/5-O12 2.433 (2.420) V-N 2.141 (2.130).

example where four metal cations are bonded simultaneously to one single taci molecule. The peculiar chelating properties of the ligand enforces a mutually orthogonal orientation of the $V–O_{terminal}$ vectors in the subsequent V5 V3 V4 array. This structural feature is unique in vanadium(IV)-oxo clusters and is a prerequisite for significant ferromagnetic interactions.

Of note is that the $[V_8O_{14}(H_{-2}taci)_2]$ aggregate was only obtained hydrothermally by using an excess of vanadium(V) as starting material.[18] If an excess of taci was allowed to react with $[VO]^{2+}_{(aq)}$, formation of a mononuclear bis(taci) complex $[V(taci)_2]^{4+}$ with exclusive binding of V^{IV} to six alkoxo groups was observed.[21]

Figure 2 illustrates the temperature dependence of the ratio of the magnetization and the applied field, labeled as χ_M, in the form $\chi_M T$ versus T.[22] The room temperature value is 2.62 emu K mol^{-1}, slightly smaller than the values of 2.94 emu K mol^{-1} expected for eight uncorrelated spins $S =$

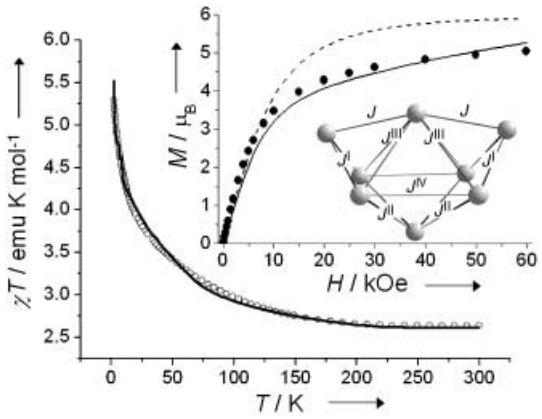

Figure 2. Temperature dependence of the $\chi_M T$ product of **1**.[23] —— calculated values with the best fit parameters (see text), ○ data points. Inset: the field dependence of the magnetization at 2.0 K, ----- simulation taking into account the spin-levels spectrum obtained from the best fit (see text), —— as above with $D(S=3) = 1.3$ cm^{-1}, ● data points. The labeling of the coupling constants is also shown.

1/2 with $g = 1.98$, thus suggesting the presence of antiferromagnetic (AF) interactions. The χT product decreases slightly on lowering the temperature with a broad minimum around 250 K and at lower temperature it steadily increases reaching the value of 5.52 emu K mol^{-1} at 2.1 K. This value is very close to that expected for an $S = 3$ ground state, $\chi_M T = 5.88$ emu K mol^{-1} for $g = 1.98$. This behavior is typical of a ferrimagnetic spin arrangement. The magnetization has been measured as a function of the field at three different temperatures: 2 K, 5 K, and 10 K. The highest measured value is 27930 emu mol^{-1}: this value is between the $S = 3$ (33175 emu mol^{-1}) and $S = 2$ (22117 emu mol^{-1}) saturation magnetization.

To rationalize the magnetic behavior an idealized C_{2v} symmetry, with five different coupling constants, is used in the HDVV spin Hamiltonian [Eq. (1)] where the labeling of the spin is the same as the vanadium atoms in Figure 1a and primes have been added for symmetry related atoms, and the exchange coupling scheme is shown in the inset of Figure 2.

$$\begin{aligned}\hat{\mathbf{H}} = {} & J(\mathbf{S}_1\mathbf{S}_3 + \mathbf{S}_1\mathbf{S}_{3'}) + J^{I}(\mathbf{S}_3\mathbf{S}_4 + \mathbf{S}_3\mathbf{S}_5 + \mathbf{S}_{3'}\mathbf{S}_{4'} + \mathbf{S}_{3'}\mathbf{S}_{5'}) \\ & + J^{II}(\mathbf{S}_2\mathbf{S}_4 + \mathbf{S}_2\mathbf{S}_5 + \mathbf{S}_2\mathbf{S}_{4'} + \mathbf{S}_2\mathbf{S}_{5'}) \\ & + J^{III}(\mathbf{S}_1\mathbf{S}_4 + \mathbf{S}_1\mathbf{S}_5 + \mathbf{S}_1\mathbf{S}_{4'} + \mathbf{S}_1\mathbf{S}_{5'}) + J^{IV}(\mathbf{S}_4\mathbf{S}_{5'} + \mathbf{S}_5\mathbf{S}_{4'})\end{aligned} \quad (1)$$

Even if five J values represent the smallest set of parameters able to take into account the different bridges in **1**, this choice leads inevitably to over-parameterization problems so that different fitting sets with very close agreement factors, R, are expected. Given that V1 and V3(V3′) are doubly μ_3-oxo bridged and arranged in a slightly bent *syn*-orthogonal[11] fashion, which gives rise to strong antiferromagnetic interactions, we can discard those sets for which the J is found to be ferromagnetic. J^I is associated to a μ_3-oxo and a μ-alkoxo bridge with an unprecedented quasi-orthogonality of the V=O bonds (80.26° (V3–V4) and 78.60° (V3–V5)) where the two bridging oxygen atoms occupy a basal position. The geometry can be described as that of two truncated octahedrons sharing one of the missing faces (see Figure 1b).

The V–V separation (2.95 Å (V3–V4), 2.97 Å (V3–V5)) is comparable to that observed for the strongly antiferromagnetic pairs V1–V3(V3′)(2.86 Å) but the orthogonality imposed by the taci ligand is expected to lead to a sizeable ferromagnetic J^{I} coupling. The quasi-orthogonality of the V=O bonds is also observed in the pairs described by J^{II} and J^{III}, which are both mediated by a single μ_3-oxo bridge. Ferromagnetic values for the two exchange constants are expected on the basis of the quasi-orthogonality of V=O directions. The last exchange constant, J^{IV}, is eventually related to a vertex-sharing bridge where the V=O groups are almost parallel (orthogonal–orthogonal interaction geometry with $\varphi = 2.1°$).[11] A moderate antiferromagnetic interaction is therefore expected. Negligible magnetic interactions have been assumed to be present between V4 and V5 since the V4–O12 and V5–O12 separations are 2.42 Å and 2.44 Å, respectively. With these assumptions the parameters range, for $R = 1.5\cdot10^{-5}$, in the following intervals: $390 < J < 440$, $-150 < J^{I} < -140$, $-60 < J^{II} < -44$, $-60 < J^{III} < -40$, $48 < J^{IV} < 50$.

To overcome the problem of over-parameterization and obtain reliable magnetochemical information on the unconventional bridging modes encountered in **1** we performed quantum mechanical calculations based on the density functional theory (DFT) in the B3LYP broken-symmetry[23] framework. The X-ray structure has been used throughout the calculations. Gaussian type LanL2DZ basis set with LanL2 effective potential was used for the vanadium atoms while D95(d) basis sets were used for the N, O, and H atoms. The NWChem 4.1 package[24] was employed. To date, few attempts have been made to compute the exchange coupling constants on magnetic clusters containing more than two transition-metal atoms without any approximation of the X-ray structure.[25] To calculate the five exchange coupling constants, we computed five broken-symmetry states BS1–BS5 (see Table 1). BS6 and BS7 have been computed to check the validity of the assumption of a C_{2v} symmetry and the consistency of the calculations. In a C_{2v} SH, BS6, and BS7 should be degenerate with BS1: the 3 BS states have been found to be degenerate on the order of few cm^{-1}. The average energy has then been used for BS1. The degeneracy with BS2 has to be considered fortuitous. In general, the number of possible BS states that can be computed (and the energy differences from which the J_{ij} values are obtained) exceed the number of SH parameters to be computed leading to a system of equations that contains more equations than parameters. One common solution of this problem is to choose only one subset of equations for computing the J_{ij} values.[25,26] Nevertheless, as shown by Bencini and Totti,[26] such an approach can give misleading values of the exchange coupling parameters J_{ij}, whenever a close agreement between the expected and the computed $\langle \hat{S}^2 \rangle$ value is not found. It is important to stress that in our case, the computed $\langle \hat{S}^2 \rangle$ values are in a good agreement with those expected. This result suggests that the choice of one subset of equations, in our case five of the possible 435 energy differences (Table S1 of the Supporting Information), can be fairly accurate, a feature which is also confirmed by the computed degeneracy between BS1, BS6, and BS7. It should be noted that BS4 with M_s (eigenvalue of **Z**) equal to 3, is the determinant with the lowest energy. The solution of the system of five equations and five parameters leads to the following values: $J = 723.6\ cm^{-1}$, $J^{I} = -113.4\ cm^{-1}$, $J^{II} = -74.8\ cm^{-1}$, $J^{III} = -74.9\ cm^{-1}$, $J^{IV} = 36.9\ cm^{-1}$. As expected, a very strong antiferromagnetic J and ferromagnetic J^{I}, J^{II}, and J^{III} couplings have been found. J^{IV} is also antiferromagnetic in character. To verify that the computed magnetic structure corresponds to the experimental data, we tried to fit the $\chi_M T$ curve imposing as starting values the computed J values. The fitting procedure has given the following values: $J = 430\ cm^{-1}$, $J^{I} = -153\ cm^{-1}$, $J^{II} = -72\ cm^{-1}$, $J^{III} = -75\ cm^{-1}$, $J^{IV} = 56\ cm^{-1}$, and $R = 1.7 \times 10^{-4}$, and the calculated curve is shown in Figure 2. The fitted J values are in a fairly good agreement with the computed ones, with the exception of J, which appears to be significantly overestimated as already observed for strong antiferromagnetic couplings.[26] Nevertheless, the picture of the magnetic structure given by the DFT calculations seems to be reliable and of significant assistance in the fitting procedure of the experimental data and, therefore, to be reasonably close to a meaningful magnetochemical solution.

If we look at the low-energy spectrum (not shown) of the spin states of the cluster, computed with the best fit J values, we see that the $S = 3$ ground state is separated only by $2.89\ cm^{-1}$ from the first $S = 2$ excited state. The first $S = 1$ and $S = 0$ are found at, respectively, $8.76\ cm^{-1}$ and $9.22\ cm^{-1}$. Of course the ferromagnetic $S = 4$ state is very high in energy, because it can only be attained by violating the strong antiferromagnetic interaction J. The existence of a group of levels close to the ground state is a direct consequence of the antiferromagnetic nature of J^{IV}, which is in competition with the parallel orientation of the spin of the two halves of the cluster.

We have taken into account these low-lying spin states to reproduce the magnetization curve of the inset of Figure 2. The calculated curve is, however, very different from the experimental one. The data can only give a reasonably fit assuming that the ground spin state is subject to zero-field splitting (ZFS). The ZFS has only been introduced in the ground $S = 3$ multiplet and the curve of Figure 2 has been obtained

Table 1: Determinants, computed expectation values of $\langle \hat{S}^2 \rangle$ (theoretical values in parenthesis and self-consistent-field energies (a.u.) for the high-spin (HS) and seven broken symmetry (BS) states. Only determinants with positive M_s values are reported.

BS state	M_s	$\langle \hat{S}^2 \rangle$[a]	SCF Energy
HS: $\lvert \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2} \rangle$	$M_s = \pm 4$	20.11 (20.00)	*−2878.378318*
BS1: $\lvert \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2} \rangle$	$M_s = \pm 0$	4.06 (4.00)	*−2878.380549*
BS2: $\lvert \frac{1}{2}\ \overline{\frac{1}{2}}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2} \rangle$	$M_s = \pm 1$	4.70 (5.00)	*−2878.379965*
BS3: $\lvert \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2} \rangle$	$M_s = \pm 2$	8.05 (8.00)	*−2878.380581*
BS4: $\lvert \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2} \rangle$	$M_s = \pm 3$	13.06 (13.00)	*−2878.381274*
BS5: $\lvert \overline{\frac{1}{2}}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2} \rangle$	$M_s = \pm 1$	5.11 (5.00)	*−2878.376602*
BS6: $\lvert \overline{\frac{1}{2}}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}\ \overline{\frac{1}{2}} \rangle$	$M_s = \pm 0$	4.05 (4.00)	*−2878.380570*
BS7: $\lvert \frac{1}{2}\ \overline{\frac{1}{2}}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \overline{\frac{1}{2}}\ \overline{\frac{1}{2}}\ \frac{1}{2}\ \overline{\frac{1}{2}} \rangle$	$M_s = \pm 1$	4.98 (5.00)	*−2878.380516*

with $D = 1.3\ cm^{-1}$ and $g = 1.98$. The positive value of D implies an easy-plane type anisotropy and therefore is consistent with the absence of out-of-phase ac susceptibility in zero field.[2]

Even if an SMM based on ferromagnetically coupled $S = 1/2$ spins is still lacking, a significant high-spin ground state has been achieved thanks to the use of a multidentate ligand that forces the V^{IV} coordination polyhedra into an unprecedented orthogonal closed packed motif. This situation is the result of a remarkable improvement in the control of the magnetic properties by the use of tailored ligands. A method that combines ab initio calculations with simulations based on the spin Hamiltonian approach has been shown to be crucial for the proper description of complex magnetic structures.

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Keywords: cluster compounds · density functional calculations · magnetic properties · N,O ligands · vanadium

[1] J. Villain, F. Hartman-Boutron, R. Sessoli, A. Rettori, *Europhys. Lett.* **1994**, *27*, 159.
[2] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268.
[3] R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804.
[4] N. Regnault, T. Jolicoeur, R. Sessoli, D. Gatteschi, M. Verdaguer, *Phys. Rev. B* **2002**, *66*, 054409.
[5] C. Raghu, I. Rudra, D. Sen, S. Ramasesha, *Phys. Rev. B* **2001**, *64*, 4419.
[6] A. L. Barra, A. Caneschi, A. Cornia, F. F. De Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, *121*, 5302.
[7] R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel, G. B. M. Vaughan, *Chem. Eur. J.* **2001**, *7*, 2765.
[8] J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem.* **2000**, *112*, 1667; *Angew. Chem. Int. Ed.* **2000**, *39*, 1605.
[9] V. Marvaud, C. Decroix, A. Scuiller, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* **2003**, *9*, 1677.
[10] W. A. Hatfield, *Inorg. Chem.* **1983**, *22*, 833.
[11] W. Plass, *Inorg. Chem.* **1997**, *36*, 2200.
[12] W. Plass, *Angew. Chem.* **1996**, *108*, 699; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 627.
[13] a) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239. b) R. E. P. Winpenny, *Adv. Inorg. Chem.* **2001**, *52*, 1; c) L. Cronin, *Comprehensiv Coordation Chemistry II*, *Vol. 7*, (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, p. 1.
[14] a) C. J. Warren, J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter, J. Zubieta, *Polyhedron* **1998**, *17*, 2599. b) R. P. Bontchev, J. Do, A. J. Jacobson, *Angew. Chem.* **1999**, *111*, 2063; *Angew. Chem. Int. Ed.* **1999**, *38*, 1937.
[15] A. Müller, M. Koop, H. Bögge, M. Schmidtmann, F. Peters, P. Kögerler, *Chem. Commun.* **1999**, 1885.
[16] a) K. Hegetschweiler, M. Ghisletta, T. F. Fässler, R. Nesper, *Angew. Chem.* **1993**, *105*, 1514; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1426; b) N. Ouali, J.-P. Rivera, D. Chapon, P. Delangle, C. Piguet, *Inorg. Chem.* **2004**, *43*, 1517.
[17] K. Hegetschweiler, *Chem. Soc. Rev.* **1999**, *28*, 239.
[18] K. Hegetschweiler, R. C. Finn, R. S. Rarig Junior, J. Sander, S. Steinhauser, M. Wörle, J. Zubieta, *Inorg. Chim. Acta* **2002**, *337*, 39.
[19] Crystal data for **1**·7 $H_2$0: $C_{12}H_{40}N_6O_{27}V_8$ ($M_r = 1108.02$), tetragonal, space group $I4_1/a$; $a = 16.160(2)$, $c = 24.179(5)$ Å, $V = 6314.2(17)$ Å^3, $Z = 8$, $T = 215(2)$ K, $\rho_{calcd} = 2.331\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 2.377\ mm^{-1}$, refl. 19634 collected, 2488 unique ($R_{int} = 0.0616$), 1952 observed [$I > 2\sigma(I)$]. 255 parameters refined with $R = 0.0363$ [$I > 2\sigma(I)$], $wR_2 = 0.979$ [all data], $GOF = 1.055$; residual electron density: $+0.573$, $-0.444\ e\,Å^{-3}$. SHELX-97 program set for structure solution (direct methods) and refinement (full-matrix least-squares on F^2). The positions of hydrogen atoms were calculated (riding model). An additional data set was recorded at 90(2) K (see supporting information). CCDC-232009 (90 K) and CCDC-232010 (215 K) contains 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).
[20] Bond-valence calculations confirmed the exclusive presence of V^{IV}: The valences are 4.05 (V1), 4.03 (V2), 4.03 (V3), 3.99 (V4), 3.97 (V5); see N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192.
[21] B. Morgenstern, S. Steinhauser, K. Hegetschweiler, E. Garribba, G. Micera, D. Sanna, L. Nagy, *Inorg. Chem.* **2004**, *43*, 3116.
[22] The dc magnetization and ac susceptibility (not shown) on microcrystalline powder samples have been recorded using a Cryogenic S600 SQUID magnetometer, with applied fields of 10000, 1000, and 100 Oe upon decreasing temperature to avoid saturation effects. The diamagnetic contributions of the sample were estimated from Pascal's constants and subtracted from the data.
[23] a) L. Noodleman, J. G. J. Norman, *J. Chem. Phys.* **1979**, *70*,4903; b) L. Noodleman, *J. Chem. Phys.* **1981**, *74*, 5737.
[24] T. P. Straatsma, E. Apra', T. L. Windus, M. Dupuis, E. J. Bylaska, W. de Jong, S. Hirata, D. M. A. Smith, M. Hackler, L. Pollack, R. Harrison, J. Nieplocha, V. M. Tipparaju Krishnan, E. Brown, G. Cisneros, G. Fann, H. Fruchtl, J. Garza, K. Hirao, R. Kendall, J. Nichols, K. Tsemekhman, M. Valiev, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M.,Deegan, K. Dyall, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G., Thomas, J. van Lenthe, A. Wong, Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, v. 4.5, Pacific Northwest National Laboratory, Richland, Washington, USA, **2003**; R. A. Kendall, E. Apra, D. E. Bernholdt, E. J. Bylaska, M. Dupuis, G. I. Fann, R. J. Harrison, J. L. Ju, J. A. Nichols, J. Nieplocha, T. P. Straatsma, T. L. Windus, A. T. Wong, *Comput. Phys. Commun.* **2000**, *128*, 260. See references therein for the effective core potentials LanL2DZ and D95(d) basis sets, and for the B3LYP functional.
[25] a) D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Bashkin, S. Wang, H.-L. Tsai, J. B. vincent, P. D. W. Boyd, J. C. Huffman, K. Folting, Q. Li, W. E. Streib, *J. Am. Chem. Soc.* **1992**, *114*, 2455; b) R. A. Torres, T. Lovell, L. Noodleman, D. A. Case, *J. Am. Chem. Soc.* **2003**, *125*, 1923; c) T. A. O'Brien, E. R. Davidson, *Int. J. Quantum Chem.* **2003**, *92*, 294.
[26] A. Bencini, F. Totti, *Int. J. Quantum Chem.* accepted for publication.

