

A Mixed-Valence Polyoxovanadate(III,IV) Cluster with a Calixarene Cap Exhibiting Ferromagnetic V(III)–V(IV) Interactions

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Abstract: A series of compounds (cat)[V₆O₆(OCH₃)₈(calix)(CH₃OH)] was obtained under anaerobic conditions and solvothermal reaction of VOSO₄ with *p*-*tert*-butylcalix[4]arene (calix) in methanol using different types of bases (Et₄NOH, NH₄OH, pyridine, Et₃N). All compounds contain the same polyoxo(alkoxo)-hexavanadate anion [V₆O₆(OCH₃)₈(calix)(CH₃OH)][−] (**1**) exhibiting a mixed valence {V^{III}V^{IV}₅O₁₉} core with the so-called Lindqvist structure coordinated to a calix[4]arene macrocycle and cocrystallizing with the conjugated acid of the base (cat = Et₄N⁺, NH₄⁺, pyridinium, Et₃NH⁺) involved in the synthesis process. The structures have been fully established from X-ray diffraction on single crystals and the mixed valence state has been confirmed by bond valence sum calculations. The magnetic behavior of all compounds are the same because of the polyalkoxohexavanadate anion [V₆O₆(OCH₃)₈(calix)(CH₃OH)][−] (**1**) and have been interpreted by DFT calculations. Thus the V(III)⋯V(IV) interactions are found to be weakly ferromagnetic (<5.5 cm^{−1}) while the V(IV)⋯V(IV) are antiferromagnetic (−17.6; −67.6 cm^{−1}). The set of the coupling exchange parameters allows a good agreement with the magnetic experimental data.

Introduction

In the frame of the emerging nanosciences there is a general concern for preparing nanoscale polymetallic species¹ with a narrow size distribution.² In that regard, coordination chemistry offers a smart approach as it can produce tailored and functionalized one-sized nanoscale polynuclear complexes of high nuclearity. The synthetic approach generally uses multidentate and bulky ligands that favor the metal aggregation then keep the resulting clusters aside from each other by lying at their periphery.^{3,4} Among the wide number of multidentate ligands, calixarenes macrocycles look particularly attractive. Indeed they are bulky while the phenol oxygen platform is available for coordination of 3d,^{5–7} 4d,^{8,9} 5d,^{10,11} 4f,^{12,13} and 5f^{14–16} metal

ions for example. Another interest is that they are available with different ring size and modifications which may be useful for shaping the cluster size^{17–19} or for further functionalization.^{20,21}

With this in mind and as part of our interest in magnetism of polynuclear metal complexes,^{22,23} we investigated the coordination chemistry of calixarene²⁴ and thiocalixarene macrocycles.^{25,26} Because of the low solubility of most calixarenes in proper solvents for complexation and crystallization in standard conditions we adopted the solvothermal method which has proved with the hydrothermal method to be efficient for the synthesis of numerous metal clusters^{27–32} and polyoxometalates.^{33–36} This method has already allowed us to synthesize

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successfully a series of Mn(II) and Fe(II) polynuclear complexes with thiacalixarene macrocycles.^{25,26} We also recently reported on a dinuclear cobalt(II) complex with calix[8]arenes exhibiting strong magnetic anisotropy of the cobalt(II) ions.²⁴ In this paper we present a part of the extension of this investigation to vanadium.

Our interest for vanadium holds in its well-known ability to form many oxo-clusters^{37–40} among which are a great number of hexavanadate^{33,38,41,42} clusters but also some larger clusters^{43–52} up to [V₃₄].⁵¹ Some of these systems exhibit interesting magnetic properties.^{52–54} Let us note that some calixarene-based oxova-

nadium are known as catalytic systems but are mainly mono- and binuclear complexes.⁵⁵

We report hereafter a series of compounds (cat)[V₆O₆(OCH₃)₈(calix)(CH₃OH)] which were obtained under anaerobic conditions and a solvothermal method when reacting VOSO₄ with *p*-tert-butylcalix[4]arene (calix) in methanol with different bases (Et₄NOH, NH₄OH, pyridine, Et₃N). All compounds contain the same polyoxo(alkoxo)hexavanadate anion [V₆O₆(OCH₃)₈(calix)(CH₃OH)][–] (**1**), exhibiting a mixed valence {V^{III}V^{IV}₅O₁₉} hexavanadate core with the so-called Lindqvist structure, coordinated to a calix[4]arene macrocycle. The different compounds that come from **1** cocrystallize with cations (cat = Et₄N⁺, NH₄⁺, PyH⁺, Et₃NH⁺) that are the conjugated acids of the base involved in the synthesis process. Whereas V(III, IV) mixed valences are known in three-dimensional open-framework^{56–58} such polynuclear species are very rare and of quite recent discovery. Indeed, the first polynuclear system with V(III, IV) mixed valence states was reported in the early 1990s by Mikuriya et al.,⁵⁹ but it is only in the last 2 years that novel examples have been reported by McInnes et al.^{34–36,60} However, to the best of our knowledge, the compounds reported here are the first examples showing a hexavanadate with the Lindqvist type structure and V(III, IV) mixed valence states. Owing to their common polyoxo(alkoxo)hexavanadate anion [V₆O₆(OCH₃)₈(calix)(CH₃OH)][–] (**1**), all compounds of the series show the same magnetic behavior which has been interpreted by DFT calculations. Whereas the previous examples of mixed valence V(III, IV) systems reported antiferromagnetic exchange couplings, we evidenced the presence of ferromagnetic interaction between V(III) and V(IV).

Experimental Section

Syntheses. All chemicals and solvents were used as received. *p*-tert-Butylcalix[4]arene was synthesized as previously reported.⁶¹ All solvothermal preparations of the complexes were performed under anaerobic conditions.

Preparation of (cat)[V^{III}V^{IV}₅O₆(OCH₃)₈(calix)(CH₃OH)] (1**(cat) (cat = Et₄N, NH₄, PyH, Et₃NH). Green single crystals were obtained from the reaction mixture of *p*-tert-butylcalix[4]arene (calix, 0.1 g, 0.15 mmol), VOSO₄ (0.21 g, 0.9 mmol), tetraethyl ammonium hydroxide (0.3 mL, aqueous solution 40%) (**1**.Et₄N), or triethylamine (1.5 mL) (**1**.Et₃NH) or pyridine (1 mL) (**1**.PyH) or ammonia (1 mL) (**1**.NH₄) and methanol (23 mL) in a 43 mL Teflon-lined autoclave under anaerobic conditions at 170 °C for 3 days: yield, 0.13 g, 58%. The crystals were isolated upon filtration then washed with methanol and dichloromethane. The compounds were kept in a N₂ atmosphere. (**1**.Et₄N) Yield: 65%. Anal. Calcd for C₆₁H₁₀₀N₁O₁₉V₆: C, 50.3; H, 6.92; N, 0.96; V, 21.0. Found: C, 49.7; H, 6.87; N, 0.98; V, 21.2. IR (cm^{–1}): 3460 (w), 2954 (w), 2915 (vw), 2812 (w), 1463 (m), 1204 (w), 1057 (vw), 966 (vw), 793 (vw), 577 (w). (**1**.Et₃NH) Yield: 61%. Anal. Calcd for C₅₉H₉₆N₁O₁₉V₆: C, 49.6; H, 6.77; N, 0.98; V, 21.4. Found: C, 49.8; H, 6.89; N, 0.97; V, 20.9. IR (cm^{–1}): 3460 (w), 2954**

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Table 1. Crystal Data and Structure Refinement Parameters for Compounds **1.cat**

	1.Et₄N	1.NH₄	1.Et₃NH	1.pyH
formula	C ₆₁ H ₁₀₀ NO ₁₉ V ₆	C ₅₃ H ₈₅ NO ₁₉ V ₆	C ₅₉ H ₉₆ NO ₁₉ V ₆	C ₅₈ H ₈₆ NO ₁₉ V ₆
fw (g·mol ⁻¹)	1457.09	1345.89	1429.04	1406.95
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/m (No. 12)	C2/m (No. 12)	C2/m (No. 12)	P2 ₁ /c (No. 14)
<i>a</i> (Å)	28.815 (5)	28.885 (5)	28.805 (5)	15.798 (5)
<i>b</i> (Å)	15.726 (5)	15.613 (5)	15.638 (5)	15.555 (5)
<i>c</i> (Å)	15.904 (5)	15.789 (5)	15.833 (5)	28.662 (5)
α (deg)	90	90	90	90
β (deg)	104.809 (5)	104.356 (5)	104.546 (5)	104.676 (5)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	6967 (3)	6898 (3)	6903 (3)	6814 (3)
<i>Z</i>	4	4	4	4
<i>T</i> (K)	293	293	293	293
λ (Mo K α) (Å)	0.71069	0.71069	0.71069	0.71069
<i>D</i> (g·cm ⁻³)	1.387	1.280	1.372	1.370
μ (mm ⁻¹)	0.84	0.84	0.84	0.86
<i>R</i> (<i>F</i> ²) ^a , <i>I</i> > 2 σ (<i>F</i> _o)	0.0518	0.0738	0.050	0.058
<i>R</i> _w (<i>F</i> ²) ^b , <i>I</i> > 2 σ (<i>F</i> _o)	0.0602	0.0803	0.059	0.066
<i>S</i>	1.16	1.10	1.11	1.14

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F) = \sum [w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

(w), 2915 (vw), 2812 (w), 1467 (m), 1200 (w), 1057 (vw), 962 (vw), 798 (vw), 573 (w). (**1.PyH**) Yield: 57%. Anal. Calcd for C₅₈H₈₆N₁O₁₉V₆: C, 49.5; H, 6.16; N, 1.00; V, 21.7. Found: C, 49.0; H, 6.12; N, 0.99; V, 21.2. IR (cm⁻¹): 3429 (w), 3058 (w), 2954 (vw), 2920 (vw), 2807 (w), 1627 (w), 1467 (m), 1182 (w), 1053 (vw), 970 (vw), 793 (vw), 642 (m), 582 (w). (**1.NH₄**) Yield: 65%. Anal. Calcd for C₅₃H₈₅NO₁₉V₆: C, 49.2; H, 6.01; N, 1.01; V, 22.0. Found: C, 49.0; H, 5.92; N, 0.99; V, 21.8. IR (cm⁻¹): 3429 (w), 3058 (w), 2954 (vw), 2920 (vw), 2807 (w), 1627 (w), 1467 (m), 1182 (w), 1053 (vw), 970 (vw), 793 (vw), 642 (m), 582 (w).

X-ray Crystallography. Data Collection. Processing of the data was performed by the KappaCCD analysis softwares.⁶² The lattice constants were refined by least-square refinement using 3883 reflections (0° < θ < 27.9°), 4100 reflections (0° < θ < 27.9°) and 4938 reflections (0° < θ < 25.7°) for compounds (cat)[V^{III}V^{IV}₅O₆(OCH₃)₈(calix)(CH₃OH)] (**1.cat**), respectively, with cat = Et₄N⁺, NH₄⁺, PyH⁺, Et₃NH⁺. No absorption correction was applied to the data sets.

Structure Solution and Refinement. (cat) [V^{III}V^{IV}₅O₆(OCH₃)₈(calix)-(CH₃OH)] (cat = Et₄N⁺, NH₄⁺, Et₃NH⁺) crystallize in the monoclinic system and according to the observed systematic extinctions, the structures have been solved in the C2/m space group (No. 12). (PyH)-[V^{III}V^{IV}₅O₆(OCH₃)₈(calix)(CH₃OH)] (**1.PyH**) crystallizes also in the monoclinic system with close crystal cell parameters but according to the observed systematic extinction, the structure was solved in the P2₁/c space group (No. 14). All structures were solved by direct methods using the SIR97 program⁶³ combined to Fourier difference syntheses and refined against *F* using reflections with [*I*/ σ (*I*) > 3] with the CRYSTALS program.⁶⁴ All atomic displacements parameters for non-hydrogen atoms have been refined with anisotropic terms. The hydrogen atoms were theoretically located on the basis of the conformation of the supporting atom. Table 1 summarizes the crystallographic data and refinement details for **1.cat** (cat = Et₄N⁺, NH₄⁺, PyH⁺, Et₃NH⁺). Selected bond lengths and angles are given in Table 2 for **1.Et₄N** and in Supporting Information Tables S1–S2 for **1.Et₃NH**, **1.NH₄**, and **1.PyH**.

Magnetic Measurements. The magnetic studies were carried out using a Quantum Design SQUID magnetometer on freshly made samples kept under a N₂ atmosphere in a PTFE capsule. The magnetic

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1.Et₄N**^a

V1–O1	2.032(4)	V2–O2	1.608(5)
V1–O3	2.186(5)	V3–O4	1.598(5)
V1–O7	1.944(4)	V4–O5	1.600(5)
V1–O8	1.953(4)	V5(V5i)–O6	1.605(4)
V1–O9	1.955(3)		
V1...V2	4.426(1)	V2...V4	3.294(1)
V1...V3	3.182(1)	V2...V5(V5i)	3.294(1)
V1...V4	3.162(1)	V3...V4	4.715(1)
V1...V5(V5i)	3.172(1)	V3...V5(V5i)	3.335(1)
V2...V3	3.299(1)	V4...V5(V5i)	3.332(1)
V1–O7–V3	105.4(2)	V2–O1–V3	87.6(1)
V1–O8–V4	103.7(2)	V2–O1–V4	88.1(1)
V1–O9–V5	104.2(1)	V2–O1–V5	87.8(1)
V1–O1–V2	179.8 (2)	V3–O13–V5	112.3(2)
V1–O1–V3	92.2(2)	V4–O14–V5	112.7(2)
V1–O1–V5	92.2(1)	V3–O1–V4	175.7(2)
V1–O1–V4	92.2(2)	V3–O1–V5	89.6(1)
V2–O10–V3	111.9(2)	V4–O1–V5	90.2(1)
V2–O12–V4	110.6(2)	V5–O1–V5i	175.5(2)
V2–O11–V5	110.7(2)		

^a Symmetry code: (i) *x*, $-y$, *z*.

susceptibilities were measured from 2 to 300 K in an applied field of 5 kOe. The magnetization was measured at 2 and 5 K in the 0–55 kOe range. The data were corrected for diamagnetism of the sample holder and of the constituent atoms using Pascal's constants.

Computational Details. The exchange parameters were estimated using the DFT-broken symmetry approach developed by Noodleman et al.^{65–68} as already described in the literature.^{69–74} All single-determinant calculations were performed by means of the Gaussian 03 package⁷⁵ within the spin-unrestricted formalism using the tight SCF convergence criteria to ensure sufficiently well converged values for the high spin (HS) and broken symmetry (BS) state energies. The hybrid

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B3LYP exchange-correlation functional^{76–78} was used, in conjunction with the contracted all-electron Gaussian basis sets reported by Ahlrichs et al.^{79,80} On the vanadium and oxygen atoms, the triple- ζ valence basis sets extended by one polarization function (p-function for V, d-function for O) were used (TZVP). The carbon and hydrogen atoms were described by slightly smaller polarized split-valence SVP basis sets that are of double- ζ quality in the valence region and contain one polarization function (d-function for C, p-function for H). The X-ray geometry was used throughout the calculations. The influence of the nonorthogonality of the computed single determinants on $\langle S^2 \rangle$ values and on J values was estimated by using the following criteria: (i) deviation of the computed $\langle S^2 \rangle_{\text{HS}}$ and $\langle S^2 \rangle_{\text{BS}}$ values from those derived using the Clebsch–Gordan algebra and (ii) compatibility of all possible equations for J values derived for the orthogonal set of single determinants with the computed HS and BS state energies. Some details about the origin of the nonorthogonality problem are given in ref 74.

Results and Discussion

Synthesis. The (cat) $[\text{V}^{\text{III}}\text{V}^{\text{IV}}_5\text{O}_6(\text{OMe})_8(\text{calix})(\text{MeOH})]$ (cat = Et_4N , NH_4 , Et_3NH , pyH) compounds were synthesized by solvothermal synthesis under anaerobic conditions (N_2 atmosphere) in methanol by reacting VOSO_4 with *p*-tert-butylcalix[4]arene (calix) in presence of a base (Et_4NOH , NH_4OH , Et_3N , pyridine). Whatever the base used in the reaction, we obtained the same $[\text{V}_6]^-$ anionic complex

$[\text{V}^{\text{III}}\text{V}^{\text{IV}}_5\text{O}_6(\text{OMe})_8(\text{calix})(\text{MeOH})]^-$ (**1**) is charge balanced by a cation (cat) issued from the base (cat = Et_4N , NH_4 , Et_3NH , pyH). As reported elsewhere the V^{III} valence state obtained here has to be ascribed to the solvothermal method that tends to stabilize the low valence state.^{26,35,81,82}

Description of the Structure. All compounds are made of $[\text{V}_6\text{O}_6(\text{OCH}_3)_8(\text{calix})(\text{CH}_3\text{OH})]^-$ anion (**1**) plus cations (cat = Et_4N^+ , NH_4^+ , Et_3NH^+ , pyH^+). The crystal structures established from single-crystal X-ray diffraction show that the $\{\text{V}_6\text{O}_{19}\}$ vanadium framework of the cluster exhibits the so-called Lindqvist structure with a capping macrocycle (Figure 1).

The $\{\text{V}_6\}$ octahedron comprises eight μ_2 -oxygen ions from the methoxo groups and four from the phenoxo groups of the capping calix[4]arene. The six vanadium ions are linked together by a central $\mu_6\text{-O}^{2-}$ ion (O1). In contrast with other hexavanadates^{40,42} there are only five vanadyl groups in a syn-coplanar conformation⁸³ (V2, V3, V4, V5, V5i), easily identified by the characteristic short $\text{V}=\text{O}$ distances of ~ 1.60 Å as reported in Table 2 and Table S1 (V2–O2, V3–O4, V4–O5, V5–O6, V6–O19). The $\{\text{V}^{\text{IV}}\text{O}_6\}$ octahedron are distorted because of the short $\text{V}=\text{O}$ and the long $\text{V}-\text{O1}$ bond lengths. Concerning the sixth vanadium ion (V1) which is coordinated to the lower rim of the calixarene macrocycle there is no vanadyl group. Instead there is a coordinated methanol group ($\text{V}-\text{O}(\text{H})\text{Me}$) with a longer bond length [V1–O3: 1.946(7)–2.227(5) Å]. It follows that to balance the charge of the compound (**1**.cat) one vanadium should be in the +III valence state. To further identify the valence states of each vanadium center, bond valence sum

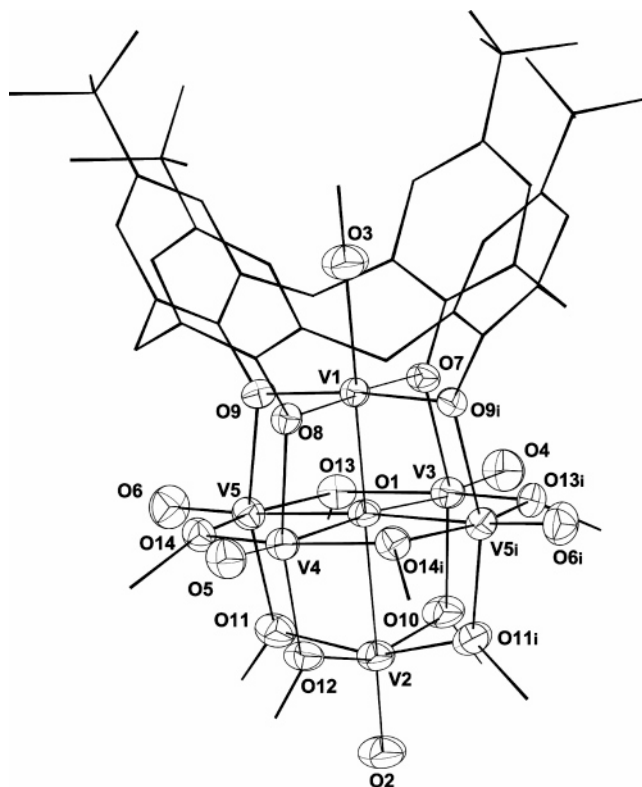


Figure 1. Molecular structure of **1**. For clarity, H atoms have been omitted, and thermal ellipsoids (30% probability) are only drawn for the V and O atoms.

Table 3. Bond Valence Sum (BVS) Calculations for **1**. $\text{Et}_4\text{N}^{84–86}$

V1	3.03
V2	3.89
V3	4.01
V4	4.03
V5	4.02

(BVS) calculations^{84–86} were performed. For five of the vanadium ions, V2, V3, V4, V5, and V5i (or V6 for **1**.PyH) the BVS calculations (Tables 3 and S3) agree with +IV oxidation states, whereas for the vanadium (V1) capped by the calixarene macrocycle the BVS calculations (Tables 3 and S3) indicate a +III oxidation state which is in good agreement with the charge balance of the compounds **1**.cat. Some polynuclear systems with V(III)/V(IV) have been already reported,^{34–36,59,60} but to the best of our knowledge these compounds (**1**.cat) are the first example of polyoxo(alkoxo)hexavanadate with the Lindqvist-type structure.

Magnetic Studies. As may be expected all compounds of the series (**1**.cat) have the same magnetic behavior as exemplified for **1**. Et_4N in Figure 2. At 300 K, the product of the magnetic susceptibility with temperature (χT) is $2.60 \text{ cm}^3 \text{ K mol}^{-1}$ which is lower than the value expected for five V(IV) ($S = 1/2$) plus one V(III) ($S = 1$) magnetically independent ($2.875 \text{ cm}^3 \text{ K mol}^{-1}$). Upon cooling χT continuously decreases to reach a minimum at 90 K ($2.17 \text{ cm}^3 \text{ K mol}^{-1}$) then increases to the maximum value of $2.74 \text{ cm}^3 \text{ K mol}^{-1}$ at 6 K and decreases again. The field dependence of the magnetization at 2 K (inset

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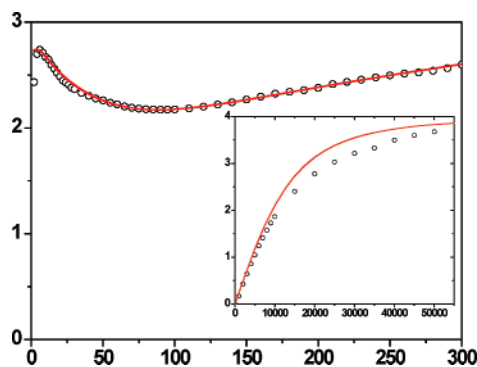
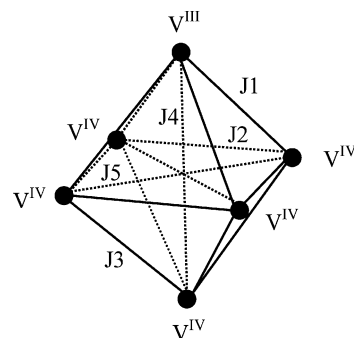


Figure 2. Temperature dependence of the χT product and field dependence of the magnetization at 2 K (inset) for **1**.Et₄N. The solid lines hold for the fitting with values discussed in the text.

Scheme 1. Magnetic Exchange Pathways in **1**



of Figure 2) reaches the maximum value of $3.7 \mu_B$ at 5 T corresponding to a spin ground state $S = 3/2$ or $S = 2$.

According to the structural parameters of (**1**.cat) (Figure 1) we can consider that from the magnetic point of view there are only three different vanadium (C_4 symmetry): (a) the terminal V(III) (V1 with spin S_1), (b) the four equatorial V(IV) [V3, V4, V5, V5i, (or V6) with spin S_3 , S_4 , S_5 , and S_{5i} (or S_6), respectively], and (c) the terminal V(IV) (V2 with S_2). Considering the V···V distances (Table 2), this leads to five possible magnetic exchange couplings (Scheme 1): J_1 between the V(III) (V1) and the equatorial V(IV) (V3, V4, V5, V5i, or V6 mean V···V distance = 3.17 Å); J_2 between next neighbor of the equatorial V(IV) (mean V···V distance = 3.3 Å); J_3 between the terminal V(IV) and the equatorial V(IV) (mean V···V distance = 3.29 Å); J_4 between the V(III) (V1) and the terminal vanadium V(IV) through the central oxygen μ_6 -O1 (V1···V2 distance = 4.43 Å); and J_5 between next next neighbor of the equatorial V(IV) through the central oxygen μ_6 -O1 (mean V···V distance = 4.71 Å). The corresponding spin Hamiltonian may thus be written as follow:

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5 + \hat{S}_1\hat{S}_{5i}) - 2J_2(\hat{S}_3\hat{S}_5 + \hat{S}_5\hat{S}_4 + \hat{S}_4\hat{S}_{5i} + \hat{S}_{5i}\hat{S}_3) - 2J_3(\hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_2\hat{S}_5 + \hat{S}_2\hat{S}_{5i}) - 2J_4(\hat{S}_1\hat{S}_2) - 2J_5(\hat{S}_3\hat{S}_4 + \hat{S}_5\hat{S}_{5i})$$

Straightforward running of the MAGPACK fitting procedure^{87,88} to describe the magnetic data with this Hamiltonian led to several mathematically satisfactory but contradicting sets of exchange parameters. To find a reasonable set of coupling

constants we thus investigated the magnetic interactions through DFT calculations.

DFT Calculations: DFT study of the exchange coupling was carried out on cluster **1** with structural parameters found in compound **1**.Et₄N. The goal was to assess the relative importance of the exchange pathways and to figure out the dominant exchange interactions. To simplify calculations, the *tert*-butyl groups of the calixarene macrocycle were replaced by hydrogen atoms. As usual in the DFT-broken symmetry approach the single-determinant states representing different spin configurations were computed, namely the high-spin (HS) state with the total spin $S = 7/2$ and the broken-symmetry (BS) states. The spin density distribution computed from the unrestricted HS solution (see Figure S1 of Supporting Information) clearly indicates that all seven d-electrons are completely trapped, in agreement with the experimental observation. The spin density is concentrated on the metal ions; the contributions from the V(IV) centers are d_{xy} in character, while the two magnetic electrons on the V(III) center occupy its d_{xz} and d_{yz} orbitals.⁸⁹ Apparently, the formation of the relatively short bond between V(III) site and central oxygen atom results in the destabilization of the d_{xy} orbital on the corresponding metal ion. The unrestricted HS solution is a good representation of the octet state, the computed $\langle S^2 \rangle$ value (15.82) is close to the expectation value for the pure $S = 7/2$ state (15.75).

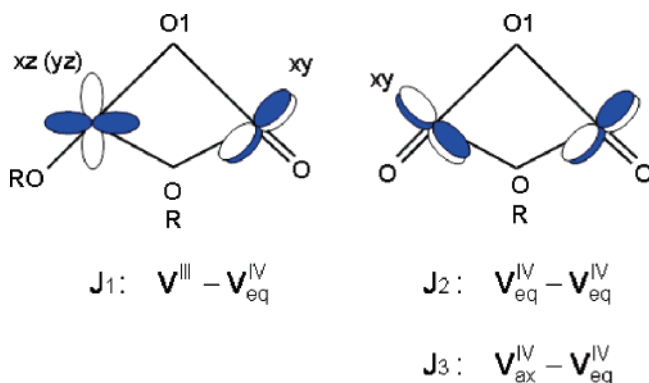
The HS and 31 BS single determinants computed for **1** are reported in Table S4. The remaining 32 microstates are simply spin-reversed counterparts of those listed in the table and we do not consider them. From Table S4 one can see that the single-determinant $\langle S^2 \rangle$ values are not significantly affected by the nonorthogonality problem inherent in the computational procedure, the computed values are close to the expected ones. The diagonal matrix elements of the model spin Hamiltonian associated with the computed single-determinant energies are listed in Table S5. As one can see, the diagonal matrix elements are given by the same expression for the states that are equivalent under the symmetry imposed by the Hamiltonian. From Table S5 one can obtain different equations expressing the differences in energy between two single determinants as functions of J values. Six different sets of five equations were considered to test the consistency of these equations with the computed HS and BS state energies. Since the crystal structure of **1** was found to possess a lower symmetry, the average of the computed BS state energies was used for the energy of the single-determinant states that should be degenerate in the idealized system having the square equatorial unit. The average J values and their standard deviations are $J_1 = 2.0(1) \text{ cm}^{-1}$, $J_2 = -17.6(2) \text{ cm}^{-1}$, $J_3 = -67.6(2) \text{ cm}^{-1}$, $J_4 = 5.5(3) \text{ cm}^{-1}$, $J_5 = 0.5(6) \text{ cm}^{-1}$. Apparently, the influence of the single-determinant nonorthogonality on J values can be considered negligible for **1**.

Let us consider in detail the calculated values of exchange coupling constants. As expected, the exchange couplings are weak in the diagonal pairs, where the metal centers are well separated by 4.43 and 4.71 Å for J_4 and J_5 exchange pathways, respectively, and appeared to be of ferromagnetic nature. The dimeric units comprising the μ -OMe bridges display a difference

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Scheme 2. Magnetic Orbital Orientations for Different Vanadium Pairs

in the strength and sign of exchange. In V(IV)–V(IV) units, the metal centers are coupled antiferromagnetically; the coupling is stronger in the case of smaller intermetal separation (3.33 Å for J_2 and 3.29 Å for J_3) in agreement with previous results on syn-coplanar conformation.⁸³ In V(III)–V(IV) units, the coupling is ferromagnetic but weak despite the short V...V distance (3.17 Å). One can try to rationalize these results by considering the mixed oxo- and alkoxo-bridged dimeric units within the Kahn–Briat model.^{90,91} This model relates the antiferromagnetic contribution of the exchange coupling constant between two paramagnetic centers (A and B) with the overlap between “magnetic orbitals”, that is, the orbitals of the two localized A–X and X–B fragments (if a simple A–X–B system is considered) bearing the unpaired electrons. Scheme 2 shows the metal components of the two magnetic orbitals for both V(III)–V(IV) and V(IV)–V(IV) dimeric units. In V(III)–V(IV) pairs, the bridging angle (V–O1–V) is close to 90° (Table 2), and these orbitals are composed of pure 3d vanadium orbitals— $d_{xz}(d_{yz})$ on V(III) and d_{xy} on V(IV). One can see that the d-orbitals on the vanadium centers are orthogonal to each other. Thus, one can expect that the antiferromagnetic term in the expression for J vanishes because of the orthogonality of the “magnetic orbitals” imposed by the polyoxometalate architecture. Apparently, the coupling is weak because the orbital orientation is not optimal for the ferroexchange. In V(IV)–V(IV) units, the d_{xy} orbitals on the vanadium centers are also orthogonal to each other. However the magnetic electrons were found to be coupled antiferromagnetically. This has to be compared with our recent study of V^{IV}/V^V mixed-valence alkoxo-polyoxovanadate⁷⁴ comprising the same type of hexanuclear vanadium core but having only four unpaired electrons (four V(IV) and two V(V)). In that case the coupling within the V(IV)–V(IV) dimeric units is ferromagnetic, whereas both systems were studied applying exactly the same computational procedure. Then, it follows that the exchange coupling within a dimeric unit depends on the overall number of magnetic electrons of the system. The dimeric fragments within a polynuclear framework cannot be treated as independent units. Our calculations show that the addition of the three extra electrons changes even the sign of exchange within the same dimeric unit. It also means that the magnetostructural correlations encountered in vanadium oxo-dimers⁸³ cannot be directly applied to polynuclear architectures. Of course, the differences can also be partly

attributed to the presence, in our case, of mixed oxo-alkoxo bridges.

Interestingly, in contrast with all our previous attempts when we input these computed exchange parameters in the MAGPACK package^{87,88} we obtained a very good agreement with the experimental magnetic susceptibility data without any fitting procedure if we consider $g = 2$ and a $\chi_{\text{TIP}} = 0.74 \cdot 10^{-3} \text{ emu mol}^{-1}$ (Figure 2). A $g = 2$ may seem surprising considering the anisotropic contribution generally accounted for from the V(III).^{92,93} However, such a value was also found for other V(III,IV) mixed-valence polynuclear systems.^{36,59} The relatively high χ_{TIP} value used in the simulations is in the range of those encountered in mixed-valence V(III,IV) open-framework structures ($\sim 0.8 \cdot 10^{-3} \text{ emu mol}^{-1}$),⁹⁴ $[\text{V}_{14}\text{Ge}_8\text{O}_{42}\text{S}_8]^{12-}$ clusters ($5.5 \cdot 10^{-3} \text{ emu mol}^{-1}$),⁹⁵ in vanadium oxide V_2O_5 xerogels (0.1 – $8.5 \cdot 10^{-3} \text{ emu mol}^{-1}$),⁹⁶ and in $\text{TIV}_{5-y}\text{Cr}_y\text{S}_8$ materials (0.3 – $10.5 \cdot 10^{-3} \text{ emu mol}^{-1}$).⁹⁷

Thus, we can suppose that our DFT-based estimations of exchange parameters, as well as the earlier predictions of the ferromagnetic coupling in the system with four magnetic electrons,⁷³ are reliable. Although, the description of the magnetization data is less satisfactory (Figure 2), we must note that this dependence is very sensitive to the energy gap between the ground and first excited states, which is found with calculated parameters at just about 2 cm^{-1} , and the presence of intermolecular interactions. In previously reported V(III,IV) mixed-valence clusters, the V(III)–V(IV) couplings were found antiferromagnetic and generally strong.^{36,59,60} For example in $[(\text{V}^{\text{IV}}\text{O})_8\text{V}^{\text{III}}_2]^{60}$ all magnetic interactions were found antiferromagnetic, with a V(IV)···V(III) exchange constant of -39 cm^{-1} [$\hat{H} = -2J(\hat{S}_1\hat{S}_2)$] related to a V(IV)···V(III) distance of 3.68 Å and a V(IV)–O–V(III) angle of 128°. In **1**, this exchange is found ferromagnetic (2.0 and 5.5 cm^{-1}) with a V(IV)···V(III) distance of 3.17 Å and V(III)–O–V(IV) angles of $\sim 104^\circ$ through the phenoxo-groups of the calixarene and $\sim 92^\circ$ through the $\mu_6\text{-O1}$ central ion (Table 2). Therefore, the ferromagnetic character of the V(IV)···V(III) found in **1** may be due to the shortest distance between the vanadium ions and the smallest V–O–V angle values with one almost orthogonal.

Conclusions

We have reported in this paper a series of compounds (cat)- $[\text{V}_6\text{O}_6(\text{OCH}_3)_8(\text{calix})(\text{CH}_3\text{OH})]$ which were obtained under anaerobic conditions and a solvothermal method when reacting VOSO_4 with *p*-tert-butylcalix[4]arene (calix) in methanol. Cluster **1** may be obtained starting from other oxovanadium(IV) salts and the final compound (**1.cat**) always incorporate cations (cat) that are the conjugated acid of the base used in the reaction. Whereas some V(III)/V(IV) compounds have already been reported, cluster **1** is the first polyoxovanadate(III, IV) with a Lindqvist-type structure. The study of the

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magnetic behavior shows that the V(IV)···V(III) magnetic interactions are ferromagnetic (2.0 and 5.5 cm^{-1}). Moreover it is the only example of polyoxovanadate coordinated to a calixarene macrocycle. Thus this novel family of polyoxovanadates is interesting both from the magnetic point of view but also for other fields such as catalysis. The synthesis of similar clusters with larger calixarene macrocycles is under progress.

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09385-C03). The Laboratoire des Multimatériaux et Interfaces (UMR 5615) at Université Claude Bernard Lyon1 and the Laboratoire de Chimie (UMR 5182) at Ecole Normale Supérieure de Lyon are members of the Institut de Chimie de Lyon.

Supporting Information Available: Complete ref 75. Selected interatomic distances (Å), selected interatomic angles (deg), and BVS calculation for all compounds are given in Table S1, Table S2, and Table S3, respectively. The SCF single determinants: atomic spin densities (Table S4) and diagonal matrix elements of the model spin Hamiltonian associated with the SCF energies (Table S5). Figure S1 presents the plot of the HS-state spin density for **1**. X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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