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Ferromagnetic Coupling in a Mixed-Valence Hexavanadate Core: Quantum-Chemical Forecast

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The electronic structure and magnetic properties of the recently synthesized V^{IV}/V^{V} mixed-valence alkoxo-polyoxovanadate comprising a hexanuclear vanadium core with four unpaired electrons have been studied within the DFT framework. The results of calculations suggest that the d electrons are completely trapped within the hexavanadate core, in agreement with the experimental observations. The exchange coupling constants computed using the broken symmetry formalism appeared to be of a ferromagnetic nature. Such interactions are very rare in oxovanadium complexes and are a consequence of a specific core geometry imposed by the polyoxometalate architecture. It has been shown that the earlier proposed intramolecular electron transfer cannot change the ground spin-state multiplicity irrespective of the sign of the exchange parameters.

Introduction

Polyoxometalates (POMs) constitute a large group of polynuclear metal–oxygen anionic species possessing interesting and potentially valuable physical, chemical, and electrochemical properties. The ability of some transition metals (e.g., V, Mo, W, etc.) in their high oxidation states (+5, +6) to form POMs in solution has inspired many studies on POMs, giving rise to a variety of POM derivatives with intriguing architectures. Because of their unique properties, these species have multiple applications in different disciplines, such as catalysis (both heterogeneous and homogeneous), medicine, and materials science.[1–4] It has been found that unstable POM architectures can be stabilized by the introduction of alkoxo ligands because of the charge compensation associated with formal substitution of peripheral oxo ligands.[5] Among many other alkoxo-polyoxometalates, the fully alkylated polyoxovanadate derivatives $[V^{IV}_{n}V^{V}_{6-n}O_7(OR)_{12}]^{(4-n)}$ (R = CH_3, C_2H_5) of the classical (Lindqvist) POM structure $[M_6O_{19}]^{n-}$, which as an entity is not known for vanadium, have been reported by Hartl et al.[6,7] In these complexes, the hexavanadate core contains an OV_6 unit in which the vanadium ions are arranged in an octahedral fashion; six oxo groups act as terminal ligands and twelve alkoxo groups act as bridging ligands. The chemical synthesis and crystal structures of such alkoxo-polyoxovanadium compounds differing in their V^{IV} content (n = 2, 3, 4, 5, 6) have been described (see Figure 1). Interestingly, the complexes with two, three, and four vanadium(IV) centers give rare examples of cationic and neutral POM species. With the exception of the isovalent systems comprising six unpaired electrons (n = 6), the reported complexes are mixed-valent and, as such, are of great interest for studying the interplay between exchange coupling and electron transfer in the hexanuclear framework. For the neutral and positively charged redox isomers of the methoxo and ethoxo series, experimental studies (X-ray structural, IR spectroscopic, cyclovoltammetric) of electron delocalization between vanadium centers have been performed.[7] The results obtained from these investigations suggest that the hexavanadate core can display either trapped metal valences or partly and fully delocalized d electrons, depending on the state of the compound (solid or solution), the V^{IV}/V^{V} ratio, the nature of the μ-bridging alkoxo ligands, and the temperature. The neutral methoxo and ethoxo species (n = 4) seem to contain trapped vanadium valences in the solid state, the four vanadium(IV) centers being located in a planar V_4O_4 ring. This result has been obtained from valence sum calculations conducted on the X-ray structural data collected at 173 K. The same conclusion has been drawn from the IR spectra (KBr pellet, room

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temperature), where the shape of the O_b–R absorption band is supposed to reflect the extent of trapped valence on the IR timescale. It should be mentioned, however, that the X-ray structure analysis conducted at room temperature yields, in the case of the ethoxo derivative, a structure displaying complete d-electron delocalization within the hexavanadate core. The phase transition[8] of the neutral ethoxo compound to the structure with completely detrapped vanadium valences is accompanied by disorder of the ethyl chains. It has been supposed that the latter is responsible for the delocalization of the unpaired electrons because it causes motion of the μ-bridging oxygen atoms. The event of valence detrapping at room temperature, which is revealed by valence sum calculations from crystallographic data, is not, however, manifested in the IR spectrum of the ethoxo derivative. As for the neutral methoxo species, the valence sums for its ambient-temperature X-ray structure still show the trapped vanadium valences, and differential scanning calorimetry measurements indicate no detectable phase transition in the temperature range 153–323 K. At the same time, the EPR-spectroscopic studies carried out for the $[V^{IV}_4V^{V}_2O_7(OCH_3)_{12}]$ single crystals[9] display the presence of an EPR signal, which has been attributed to a triplet ground state. As this observation does not agree with the expected antiferromagnetic interactions, active between four unpaired electrons, the results have been explained by introducing an internal dynamical process, namely, the intramolecular electron transfer. However, the attribution of the low-temperature signal to a triplet spin state is not unambiguous and, unfortunately, is not accompanied by thorough magnetic susceptibility measurements. Moreover, an abrupt transformation of the EPR spectrum discovered on cooling at about 190 K has been interpreted as a first-order phase transition. In the case of monocationic methoxo and ethoxo species containing three unpaired electrons ($n = 3$), the X-ray structures obtained from hexachloroantimonate salts at 173 K comprise a highly symmetrical hexavanadate core, for which the valence sums indicate that all three d electrons are equally delocalized over the vanadium centers. In the dicationic ethoxo species ($n = 2$), obtained again from its hexachloroantimonate salt, valence sum calculations conducted on the X-ray structure at 173 K indicate that the two unpaired electrons are located in a planar V_4O_4 ring, however it is not clear whether they are trapped or delocalized within the ring. The IR spectroscopic data (KBr pellet, room temperature) suggest that the monocationic derivatives exhibit a smaller degree of trapped valence than the neutral species, as well as the dicationic derivative in the ethoxo series, and are, therefore, in agreement with the solid-state results obtained by the X-ray structural analysis. We would also like to note that the earlier reported X-ray structural data for the methoxo compound series at 193 K[6] suggest that the monocationic derivative, if coupled with other counterions (e.g., polyhalide, $VOCl_4^-$), displays a distorted core and, apparently, a certain degree of trapped valence. Unfortunately, none of the mixed-valence alkoxo-polyoxovanadates have been studied using magnetic susceptibility measurements.

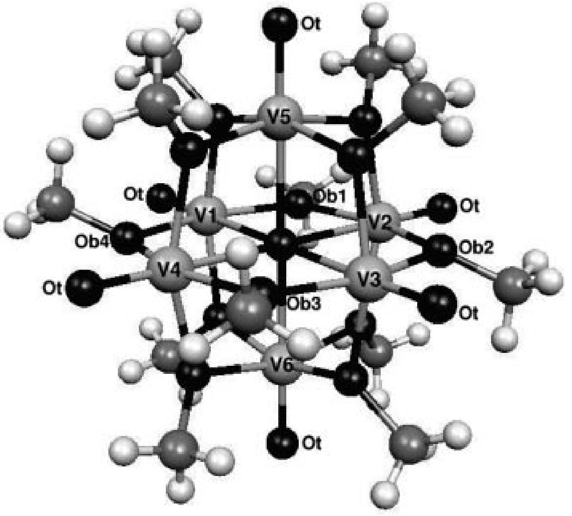


Figure 1. Crystal structure of the uncharged methoxo-bridged complex $[V^{IV}_4V^{V}_2O_7(OCH_3)_{12}]$ (ref.[6]).

The results of the cyclovoltammetric experiment carried out for the methoxo and ethoxo compound series are attributed to the solvated state of the redox isomers. Large potential separations $\Delta E^{\circ\prime}$ between successive one-electron redox processes have been observed in the cyclic voltammograms. Supposing that the stabilization energy imparted to the mixed-valence species by d-electron delocalization is the major factor influencing the splitting of the redox potentials, Hartl et al. have concluded that the unpaired electrons in redox isomers are significantly delocalized in the solvated state.[7] Interestingly, within any series of compounds (methoxo or ethoxo), the monocationic isomer displays a greater $\Delta E^{\circ\prime}$ value than the neutral complex (the $\Delta E^{\circ\prime}$ values for dicationic systems have not been determined yet).

On the basis of the obtained data, the given alkoxo-polyoxovanadium complexes have been classified as class II mixed-valence compounds. It has been assumed that the valence trapping found in the solid state is specifically linked to the cooperative effects encountered in the crystalline phase. However, the experimental results available to date are quite conflicting, especially for the $n = 4$ member of the series, and are not conclusive for the reported compounds. Hartl et al. have pointed out that investigations by UV/Vis and NIR spectroscopy are imperative to the further understanding of these series of compounds, as well as EPR-spectroscopic studies and magnetic measurements. Herein, we present the results of a density functional theory (DFT) investigation carried out for the neutral species $[V^{IV}_4V^{V}_2O_7(OR)_{12}]$. Such a study provides an insight into mixed valency in the individual molecule or allows assessment of the electronic properties of the compound in its solid state (if calculations are performed on the X-ray molecular structure). On the basis of the results obtained from the quantum-chemical investigation, strong dynamical vibronic coupling has been assumed to be effective in a given species. The DFT calculations allowed evaluation of the magnetic exchange constants which, contrary to widespread opinion, appeared to be of a ferromagnetic nature. Such interactions result in the magnetic ground state, whereas, as will be shown below, the intramolecular electron transfer, assumed in a previous publication,[9] cannot change the ground spin-state multiplicity and, consequently, cannot lead to a magnetic ground state in the presence of antiferromagnetic exchange.

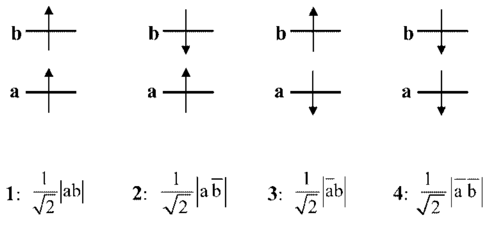
Computational Methodology

All DFT calculations reported in this paper were performed by means of the GAUSSIAN03 package[10] using the hybrid B3LYP exchange-correlation functional.[11–13] In some cases (see below), to simplify the calculations, we used hydroxo groups as μ-bridging ligands. In order to determine the extent of d-electron delocalization, we computed the electronic state with the highest total spin (S = 2) using the spin-unrestricted formalism. For both hydroxo- and methoxo-bridged complexes (**I** and **II** vide infra), the unrestricted high-spin (HS) solution obtained either on the optimized molecular structure or X-ray geometry (if available) is a good representation of the quintet state (the computed $<\mathbf{S}^2>$ values are close to 6.000, the expectation value for the pure S = 2 state, see Tables S1 and S2 in the electronic supporting information). The electronic states with lower spin multiplicity (three triplet and two singlet states) are not represented by a single-determinant wave function and can be described using sophisticated post-Hartree–Fock methods that take into account electron correlation effects (either only nondynamical correlation or both nondynamical and dynamical effects). However, such multideterminant approaches are very computationally demanding and have been applied so far only for small model systems.

As will be shown below, the unrestricted SCF calculations of the HS state resulted in the localization of four unpaired electrons on four vanadium centers. The magnetic properties of systems containing localized spins are generally interpreted using the Heisenberg–Dirac–van Vleck (HDVV) spin Hamiltonian

$$H = -\Sigma_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

which introduces an isotropic interaction between the paramagnetic centers i and j described through the exchange coupling constant J_{ij}. In the above notation, the J_{ij} value is positive if the spins S_i and S_j are coupled ferromagnetically; the negative J_{ij} value means antiferromagnetic coupling. The eigenfunctions of the HDVV spin Hamiltonian are simply spin functions of the system $|S,M>$, constructed as linear combinations of the products of single-center spin functions $|S_1,M_1>|S_2,M_2>...|S_n,M_n>$ ($|S_i,M_i>$ vide infra). The eigenvalues of the above Hamiltonian represent the energies of the total spin states expressed as functions of J_{ij}. In isotropic systems, the energies of the electronic states with different total spin are related to the eigenvalues of the HDVV spin Hamiltonian. For a simple system, the energies of electronic states can be accurately computed at a high level of theory (i.e., within a multiconfigurational approach) and they can be used to obtain the J_{ij} values. These values are directly comparable to those obtained by fitting the magnetic susceptibility data to the expression derived using the HDVV model Hamiltonian. For a system of chemical complexity, an accurate CI calculation becomes intractable. However, the exchange parameters can be estimated in the framework of a single-determinant method using the broken symmetry (BS) approach developed by Noodleman et al.,[14–17] as already described in the literature.[18–22] This method establishes the one-to-one matching between a diagonal element of the exact nonrelativistic Hamiltonian matrix computed in a basis set of single determinants (HS and so-called BS states) and the corresponding diagonal element of the HDVV spin Hamiltonian matrix computed in a basis set of products of single-center spin functions. It should be emphasized that the one-to-one matching is achieved provided that one deals with the orthogonal set of single determinants constructed from the same set of orthogonal space orbitals comprising doubly occupied closed-shell orbitals and singly occupied magnetic orbitals localized (not strictly) on the different spin centers. The set of n different J_{ij} values can be determined from the computed $n + 1$ single-determinant energies corresponding to different (nonequivalent) spin configurations. As these energies are related to the diagonal elements of the HDVV spin Hamiltonian matrix, the J_{ij} values are obtained from a system of n equations expressing the differences in energy between two single determinants as functions of J_{ij}. It is important to note that the HS and BS single determinants represent the wave functions related to one (ground) electronic configuration and, therefore, the BS approach neglects the dynamical correlation contribution to J_{ij} (see Figure 2 illustrating the simplest case of two unpaired electrons on two centers A and B, where a and b are magnetic orbitals mainly localized on A and B, respectively).



1: $\frac{1}{\sqrt{2}}|ab|$ **2**: $\frac{1}{\sqrt{2}}|a\bar{b}|$ **3**: $\frac{1}{\sqrt{2}}|\bar{a}b|$ **4**: $\frac{1}{\sqrt{2}}|\bar{a}\bar{b}|$

Figure 2. HS (**1** and **4**) and BS (**2** and **3**) single determinants for a dinuclear system with two unpaired electrons. **1** and **4** ($S = 1$, $M_S = \pm1$) represent the equivalent spin configurations (degenerate states) and are related to $|\alpha\alpha>$ and $|\beta\beta>$ products of single-center spin functions; **2** and **3** ($M_S = 0$) also represent the equivalent spin configurations and are related to $|\alpha\beta>$ and $|\beta\alpha>$ products of single-center spin functions.

All SCF calculations presented here were carried out within the spin-unrestricted formalism using the tight SCF convergence criteria[10] to ensure sufficiently well converged values for the HS- and BS-state energies. The stability of all unrestricted SCF solutions was confirmed by means of the stability analysis of Seeger and Pople.[23] Full geometry optimizations were carried out without imposing symmetry constraints; tight convergence criteria[10] were employed. The contracted Gaussian basis sets reported by Ahlrichs et al.[24,25] were used throughout the calculations. These all-electron basis sets are commonly applied[19,21,26–33] in the framework of the UB3LYP-BS computational procedure. 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 basis sets (SVP) that are of double-ζ quality in the valence region and contain one polarization function (d-function for C, p-function for H).

Results and Discussion

Exchange Interactions between Localized Electrons

In all systems studied, the spin-density distribution computed from the unrestricted HS solution clearly indicates that all four d electrons are completely trapped (see Tables S1 and S2) and our next task was the evaluation of exchange interactions between localized electrons. Before presenting the results of the DFT calculations of the exchange parameters in complexes **I** and **II**, we would like to mention the two problems arising when the BS approach is employed using a standard quantum-chemical program package. In this case, the HS and BS single determinants and their energies are obtained by performing unrestricted SCF calculations. One of the problems associated with this computational procedure is that the single determinants are constructed from the spatially nonorthogonal α and β orbitals. Another problem is that the spin-polarized orbitals are determined for each single determinant from a separate SCF calculation and, strictly speaking, the orbital sets obtained for different single determinants are not equivalent to each other. As a result, the computed single determinants have nonzero overlap integrals. In such a case, the energies of single determinants are not directly related to the diagonal elements of the HDVV spin Hamiltonian matrix and the effect of nonorthogonality should be taken into account to derive the relationships between the computed single-determinant energies and the J_{ij} values. Such a complex problem has been solved only for dinuclear systems, provided that all single determinants are built from the equivalent orbital sets, which causes the M_S components of the total spin state (constructed from these single determinants) to be degenerate.[18–20] For more complex systems, the effect of nonorthogonality of the computed single determinants can hardly be explicitly considered and it is simply ignored. Herein, we judge the performance of the UB3LYP-BS computational procedure to describe the magnetic structure of a given species by using the following two criteria. The first one establishes whether the nonorthogonality problem affects the single-determinant $<\mathbf{S}^2>$ values. Comparison of the computed $<\mathbf{S}^2>_{HS}$ and $<\mathbf{S}^2>_{BS}$ values with those derived using the Clebsch–Gordan algebra answers this question.[34] The second criterion is the compatibility of the equations for J_{ij} derived for the orthogonal single-determinant basis set with the computed HS- and BS-state energies. Apparently, this criterion can be employed if the number of J_{ij} is less than the number of the nonequivalent BS states that could be generated for a system. In these cases, any set of equations should have the same solution if the influence of the nonorthogonality on the J_{ij} values is negligible. The necessity of considering a complete set of BS single determinants has also been pointed out by Bencini et al.[22] However, in this work it was implicitly assumed that the computed J_{ij} values are not affected by the nonorthogonality problem and the consistency of equations for J_{ij} was tested to check the validity of the nearest-neighbors approximation.

For complex **I**, the UB3LYP-BS calculations were performed on the HS-state geometry. For complex **II**, besides its HS-state geometry, the X-ray molecular structure[6] was also used (see Figure 1). All three systems were found to possess C_i symmetry; the structural parameters are collected in Table 1. In each system, the hexavanadate core has a significantly distorted geometry: for the equatorial metal centers (V^{IV} sites, see the HS-state atomic spin densities in Tables S1 and S2), the $V–O_c$ bonds are significantly elongated, whereas the same bonds for the remaining axial metal ions (V^V sites) appear to be relatively short. In other words, the hexavanadate core has a "short" $O_t–V^V–O_c–V^V–O_t$ axis and two "long" $O_t–V^{IV}–O_c–V^{IV}–O_t$ axes. These results suggest that electron transfer is suppressed in the individual and solid-state molecules of **I** and **II** and their magnetic properties can be analyzed using the HDVV spin Hamiltonian. For the given systems, this Hamiltonian contains four exchange parameters (C_i symmetry) and reads

$$H(4) = -[J_{12}(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_3\cdot\mathbf{S}_4) + J_{14}(\mathbf{S}_1\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_3) + J_{13}\mathbf{S}_1\cdot\mathbf{S}_3 + J_{24}\mathbf{S}_2\cdot\mathbf{S}_4] \quad (1)$$

where $S_i = 1/2$. Spins are indexed according to the numbering shown in Figure 1.

Table 1. Structural parameters for complexes **I** and **II** (bond lengths in Å, bond angles in °).

Parameter	**I** (S = 2)[a]	**II** (S = 2)[a]	**II** (X-ray)[b]
$V_1–O_c$	2.37	2.33	2.280
$V_2–O_c$	2.38	2.33	2.296
$V_5–O_c$	2.32	2.31	2.266
$V_1–V_2$	3.36	3.30	3.247
$V_1–V_4$	3.36	3.30	3.224
$V_1–O_{b1}$	2.01	2.01	1.955
$V_1–O_{b4}$	2.01	2.00	1.965
$V_2–O_{b1}$	2.01	2.00	1.991
$V_2–O_{b2}$	2.01	2.01	1.979
$V_1–O_{b1}–V_2$	113.4	110.6	110.8
$V_1–O_{b4}–V_4$	113.0	110.5	109.7
$V_1–O_c–V_2$	90.0	90.0	90.4
$V_1–O_c–V_4$	90.0	90.0	89.6
$V–O_t$	<1.58>	<1.59>	<1.588>

[a] The geometry of a given complex optimized for the HS state. [b] The X-ray structural data collected at 193 K (ref.[6]).

The eight SCF single determinants computed for **I** and **II** are reported in Tables S1 and S2, respectively. The products of single-center spin functions associated with the computed single determinants representing different spin configurations are shown in Table 2. For any system, the remaining eight microstates are simply spin-reversed analogues of those listed in the table. In order to check whether the SCF convergence criteria were strong enough, such spin-reversed counterparts were computed for BS1, BS2, and BS3 states. In all cases, the degeneracy of the single determinants representing the equivalent spin configurations was found. As can be expected for C_i symmetry, BS4 and BS6 states, as well as BS5 and BS7 states, appear to be equivalent to each other (see Tables S1 and S2). From these tables it can also be seen that the single-determinant $<\mathbf{S}^2>$ values are not significantly affected by the nonorthogonality problem inherent in the computational procedure. The computed $<\mathbf{S}^2>_{BS}$ values are close to 2.000 and 3.000 expected for the pure BS states (which are eigenfunctions of $\mathbf{S}_z$) with $M_S = 0$ and $M_S = 1$, respectively; the computed $<\mathbf{S}^2>_{HS}$ values approach 6.000, the expectation value for the pure S = 2 state.

Table 2. Diagonal matrix elements of the model spin Hamiltonian H(4) [Equation (1)] associated with SCF energies corresponding to different spin configurations of the systems studied.

SD: $\lvert S_i,M_i>$	E_{SD}: $<S_i,M_i \lvert H(4) \rvert S_i,M_i>$
HS: $\lvert\alpha\alpha\alpha\alpha>$, $M_S = 2$	E_{HS}: $-\frac{J_{12}}{2}-\frac{J_{14}}{2}-\frac{J_{13}}{4}-\frac{J_{24}}{4}$
BS1: $\lvert\alpha\beta\alpha\beta>$, $M_S = 0$	E_{BS1}: $\frac{J_{12}}{2}+\frac{J_{14}}{2}-\frac{J_{13}}{4}-\frac{J_{24}}{4}$
BS2: $\lvert\alpha\alpha\beta\beta>$, $M_S = 0$	E_{BS2}: $-\frac{J_{12}}{2}+\frac{J_{14}}{2}+\frac{J_{13}}{4}+\frac{J_{24}}{4}$
BS3: $\lvert\alpha\beta\beta\alpha>$, $M_S = 0$	E_{BS3}: $\frac{J_{12}}{2}-\frac{J_{14}}{2}+\frac{J_{13}}{4}+\frac{J_{24}}{4}$
BS4 (BS6): $\lvert\alpha\alpha\alpha\beta>$ ($\lvert\alpha\beta\alpha\alpha>$), $M_S = 1$	$E_{BS4(BS6)}$: $-\frac{J_{13}}{4}+\frac{J_{24}}{4}$
BS5 (BS7): $\lvert\alpha\alpha\beta\alpha>$ ($\lvert\beta\alpha\alpha\alpha>$), $M_S = 1$	$E_{BS5(BS7)}$: $\frac{J_{13}}{4}-\frac{J_{24}}{4}$

Table 3. J_{ij} means and their standard deviations (in parentheses) obtained for complexes **I** and **II** using the model spin Hamiltonians H(4) and H(2) containing four and two exchange parameters, respectively (in cm^{-1}).

	J_{ij}	Sample size	**I** (S = 2)[a]	**II** (S = 2)[a]	**II** (X-ray)[b]
H(4)	J_{12}	$n = 5$	67.6 (0.3)	10.9 (1.8)	196.9 (1.6)
	J_{14}	$n = 5$	51.4 (0.3)	12.2 (1.8)	193.2 (1.6)
	J_{13}	$n = 7$	31.2 (0.7)	21.6 (4.7)	73.3 (4.1)
	J_{24}	$n = 7$	16.7 (0.7)	22.5 (4.7)	55.3 (4.1)
H(2)	J_{12}	$n = 5$	59.5 (0.3)	11.5 (1.8)	195.1 (1.6)
	J_{13}	$n = 4$	24.0 (0.3)	22.3 (2.0)	64.1 (1.7)

[a] The values computed on the HS-state geometry of a given complex. [b] The values computed for the X-ray structure (ref.[6]).

The diagonal matrix elements of the model spin Hamiltonian H(4) [Equation (1)] associated with the computed single-determinant energies are listed in the second column of Table 2. From Table 2, 15 equations for J_{ij} can be obtained (see Table S3 of supporting information). The consistency of these equations with the computed HS- and BS-state energies was tested by considering all possible sets of four equations. For any system, five noncoincident values were found for J_{12} and J_{14}, and seven for J_{13} and J_{24}. The average values and their standard deviations are reported in Table 3. According to these results, the influence of the single-determinant nonorthogonality on the J_{ij} values can be considered negligible for the given systems. The energies of the total spin states (one quintet, three triplet, and two singlet levels) computed using the obtained J_{ij} values are (in cm^{-1}):

I (HS-state geometry): –71.5 (S = 2); 1.1, 22.8, 47.5 (S = 1); 33.2, 109.7 (S = 0);
II (HS-state geometry): –22.6 (S = 2); 0.5, 10.2, 11.8 (S = 1); 12.0, 33.1 (S = 0);
II (X-ray geometry): –227.2 (S = 2); 23.0, 41.3, 162.9 (S = 1); 96.4, 358.0 (S = 0).

Interestingly, reasonable J_{ij} values can be obtained if the model spin Hamiltonian containing two J_{ij} parameters [Equation (1) with $J_{14} = J_{12}$ and $J_{24} = J_{13}$] is used:

$$H(2) = -[J_{12}(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_1\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_3\cdot\mathbf{S}_4) + J_{13}(\mathbf{S}_1\cdot\mathbf{S}_3 + \mathbf{S}_2\cdot\mathbf{S}_4)] \tag{2}$$

where $S_i = 1/2$. This Hamiltonian describes the total spin levels of a highly symmetrical system comprising the square $S_i = 1/2$ unit with the equivalent $\lvert\alpha\alpha\beta\beta>$ and $\lvert\alpha\beta\beta\alpha>$ states, as well as $\lvert\alpha\alpha\alpha\beta>$ and $\lvert\alpha\alpha\beta\alpha>$ ones. The diagonal matrix elements of such a Hamiltonian are equal to those listed in Table 2 provided that $J_{14} = J_{12}$ and $J_{24} = J_{13}$. From these expressions the following equations for J_{ij} can be obtained:

$$E_{HS} - E_{BS1} = -2J_{12}$$
$$E_{HS} - E_{BS2} = -J_{12} - J_{13}$$
$$E_{HS} - E_{BS4} = -J_{12} - \frac{J_{13}}{2}$$
$$E_{BS1} - E_{BS2} = J_{12} - J_{13}$$
$$E_{BS1} - E_{BS4} = J_{12} - \frac{J_{13}}{2}$$
$$E_{BS2} - E_{BS4} = \frac{J_{13}}{2}$$

The systems studied have only C_i symmetry and, thus, the computed BS2 and BS3 states, as well as BS4 and BS5 states, are not equivalent to each other (see Tables S1 and S2). From the above equations we obtained (for each system) the sets of noncoincident values for J_{12} and J_{13} using the average of BS2 and BS3 state energies for E_{BS2} and the average of BS4 and BS5 state energies for E_{BS4}. The J_{12} and J_{13} means and their standard deviations are reported in Table 3. For each system, the obtained J_{12} value coincides with the average of J_{12} and J_{14} values obtained using the model spin Hamiltonian H(4). Similarly, the J_{13} value [for H(2)] is equal to the average of J_{13} and J_{24} values [for H(4)].

We would like to stress that the one-to-one matching between the matrix elements of the electronic and spin Hamiltonians, being the basis of the BS approach, exists if all single-determinant states are constructed by assuming the same molecular geometry. Therefore, for the systems studied, we used the same structure (the HS-state or X-ray one) throughout the single-determinant calculations. We also did a series of test SCF calculations using the geometries optimized for all single-determinant states. As expected, the equations for J_{ij} became inconsistent. The J_{ij} values obtained from different sets of equations dramatically differ; the standard deviations were found to be twice as much as the mean values.

In the literature, the so-called nonprojected scheme[19] is often used for the estimation of the exchange coupling constant in dinuclear transition-metal complexes in the DFT framework.[19,26–29,32] Within this scheme, the single-determinant BS solution (associated with $|S_1,M_1 = S_1>|S_2,M_2 = -S_2>$ or $|S_1,M_1 = -S_1>|S_2,M_2 = S_2>$) is assumed to describe the electronic state with the lowest total spin $S = |S_1 - S_2|$, that is, the energy of the BS state is used as the energy of the pure $S = S_{min}$ state. Thus, the equation for J is obtained from the expressions for the eigenvalues of the HDVV spin Hamiltonian: $E(S_{max})$ and $E(S_{min})$. This scheme was found to give a better agreement between the computed and experimental exchange coupling constants in a number of dimers (especially when used with the B3LYP functional).[19,26,35] The success of the nonprojected approach was recently explained by a partial account of the nondynamical electron correlation in the DFT-BS solutions through the self-interaction error.[35] This statement was, however, questioned in the literature.[36] Such a technique may be adopted for a more complex system if its total spin states are described by the HDVV model Hamiltonian having the analytical solution. However, the use of this scheme in general cases of polynuclear systems is less straightforward. For example, in the case of the systems studied, the analytical expression for the energies of the total spin states is available only for the model spin Hamiltonian containing two J_{ij} parameters [Equation (2)]. The solution of this Hamiltonian reads

$$E(S,S_{13},S_{24}) = -\frac{J_{13}}{2}[S_{13}(S_{13}+1) + S_{24}(S_{24}+1) - 3] - \frac{J_{12}}{2}[S(S+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)], \text{ where}$$

$$S_{13} = S_1 + S_3, \ldots, |S_1 - S_3|$$
$$S_{24} = S_2 + S_4, \ldots, |S_2 - S_4|$$
$$S = S_{13} + S_{24}, \ldots, |S_{13} - S_{24}|.$$

The eigenvalues $E(S,S_{13},S_{24})$ and eigenfunctions $|S,S_{13},S_{24}>$ of the Hamiltonian (2) when $S_i = 1/2$ can be easily obtained and they are presented in Table S4 of the electronic supporting information. The given total spin levels are associated to a highly symmetrical system comprising the square $S_i = 1/2$ unit with the equivalent $|\alpha\alpha\beta\beta>$ (BS2) and $|\alpha\beta\beta\alpha>$ (BS3) states, as well as $|\alpha\alpha\alpha\beta>$ (BS4), $|\alpha\alpha\beta\alpha>$ (BS5), $|\alpha\beta\alpha\alpha>$ (BS6), and $|\beta\alpha\alpha\alpha>$ (BS7) ones. The systems studied were found to possess C_i symmetry and, therefore, the average of the computed BS-state energies may be used for the energy of the single-determinant states that should be degenerate in the idealized system having the square vanadium(IV) unit. Thus, there are three single-determinant energies, E_1 (for BS1), E_2 (for BS2 and BS3), and E_3 (for BS4, BS5, BS6, and BS7), to be associated with four pure-spin state energies, E(0,0,0), E(0,1,1), E(1,1,1), and E(1,1,0) = E(1,0,1). In the case of the singlet states, even if we suppose that E(0,0,0) can be approximated by E_2, the use of E_1 as E(0,1,1) is questionable (see the expressions for $|0,0,0>$ and $|0,1,1>$ in Table S4). As for the triplet states, it is not evident which of the two energies, E(1,1,1) or E(1,1,0) = E(1,0,1), can be approximated by E_3.

Table 3 shows that all J_{ij} values obtained for **I** and **II** are positive, that is, paramagnetic centers are coupled ferromagnetically. The HS state was found to be the ground state of the systems. This implies that complexes **I** and **II** considered as individual molecules should possess ferromagnetic properties, as well as complex **II** in the solid state. This result is very intriguing, as most of the oxovanadium(IV) compounds reported so far display antiferromagnetic coupling in the vanadium pairs.[32,37] From the results obtained for the individual molecules of **I** and **II**, it is seen that the introduction of the methyl groups weakens the ferromagnetic coupling within the dimeric units comprising the μ-OR bridges. The coupling between the diagonal vanadium(IV) ions bridged by the central oxygen atom is not significantly affected. In the case of the methoxo-bridged complex, the two geometries studied display a sizeable difference in the strength of exchange. In the solid-state structure, because of the crystalline effects, the hexavanadate core is compressed along the O_t–V–O_c–V–O_t axes. This results in smaller V–V distances (see Table 1). The decrease of the intermetal separations enhances the ferromagnetic interactions between the vanadium(IV) ions, especially within the dimeric units comprising the μ-methoxo bridges (the distance between the vanadium centers within the unit is reduced by 0.08 Å). In the diagonal vanadium(IV) pairs, where metal centers are separated by more than 4.5 Å, the coupling is not so sensitive to variations of the V–V distances.

The presence of ferromagnetic coupling in the alkoxo(hydroxo)-bridged dimeric units can be rationalized within the Kahn–Briat model, which 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.[38,39] In the systems studied, the V–O_t bonds are directed along the mutually orthogonal axes (the V–O_c–V angles are equal to 90°), that is, the d_{xy} orbitals[40] on the vanadium centers within an alkoxo(hydroxo)-bridged dimeric unit are orthogonal to each other (see Figure S1 in the supporting information presenting the HS-state spin density for the crystal structure of **II** as an example). Thus, the ferromagnetic coupling in the V_1–V_2 (V_3–V_4) and V_1–V_4 (V_2–V_3) pairs can be expected as the antiferromagnetic term in the expression for J_{ij} vanishes because of the orthogonality of the "magnetic orbitals" imposed by the POM architecture.

The given dimeric unit has syncoplanar configuration according to the classification proposed by Plass.[41] A DFT study of exchange coupling in alkoxo(hydroxo)-bridged dinuclear oxovanadium(IV) compounds with different core arrangements has been carried out by Ruiz et al.[32] In syncoplanar complexes, the antiferromagnetic interactions were found to be active between vanadium centers. It was shown that the coupling decreases from –94 to –43 cm^{-1} (for hydroxo-bridged model structures) when the V–O–V angle becomes smaller (angle values between 108 and 100° were considered). However, the situation when the V–O–V angle is 90°, encountered in the systems studied here, was not examined. Only a few examples of ferromagnetic coupling between the vanadium(IV) sites in oxovanadium complexes are known in the literature.[41–43] Among them, the octanuclear vanadium complex with the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) is the most exciting one.[43] The peculiar chelating properties of the ligand enforce a mutually orthogonal orientation of the $V–O_t$ bonds favoring ferromagnetic coupling between the vanadium(IV) centers.

Possible Effects of d-Electron Delocalization

Until now we have considered the energy spectrum of magnetic levels resulting from the exchange interactions between localized magnetic electrons. Let us now consider what effects can be expected on the energy spectrum from the electron hopping between vanadium centers. For the sake of simplicity, we consider an idealized system of six V centers forming an octahedron and four magnetic electrons, which can be transferred between orbitals localized on these centers. There are two types of distribution of four electrons between six octahedron vertices: in one type four paramagnetic centers form a square and in another type they are arranged in a rhombic butterfly structure. Three square distributions and twelve butterfly distributions can be formed. The magnetic interactions in the first case are described by the Hamiltonian (2). For the rhombic distribution, a very similar Hamiltonian can be written

$$H_b = -[J_{12}(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_1\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_4) + J_{13}\mathbf{S}_1\cdot\mathbf{S}_3]$$

with the following eigenvalues:

$$E(S,S_{13},S_{24}) = -\frac{J_{12}}{2}[S(S+1) - S_{13}(S_{13}+1) - \frac{3}{2}] - \frac{J_{13}}{2}[S_{13}(S_{13}+1) - \frac{3}{2}] \qquad (3)$$

The eigenvalues of both Hamiltonians are characterized by the values of the total spin S and the intermediate spin S_{13}, but for the Hamiltonian (2) the energies also depend on S_{24}, whereas the eigenenergies of (3) are degenerate over this quantum number.

The electron transfer between different vanadium sites can be taken into account by the same procedure that has been used before for two-electron mixed-valence polyoxometalates.[44,45] We consider that the eigenfunctions of the Hamiltonians (2) and (3) are linear combinations of the Slater four-electron determinants composed from orthogonal s-type orbitals localized on different centers. If we take into account only the possibility of the electron transfer between nearest neighbors and suppose that the matrix element of the transfer operator on a one-electron localized wave function is equal to t, the total matrix of the electron Hamiltonian can be built on the multielectron wave functions, characterized by spin quantum numbers and different positions of magnetic electrons, using the common Clebsch–Gordan algebra. The analysis of these matrices shows that only the states characterized by the same spin quantum numbers are mixed through the electron transfer. For each set of spin quantum numbers, the electron transfer Hamiltonian can be represented as a 15 × 15 matrix, where the diagonal elements are the energies resulting from the Hamiltonians (2) and (3) and the nondiagonal elements are obtained from the electron transfer operator. It can be seen that the nondiagonal parts of all matrices are similar. If we neglect the difference between the two exchange Hamiltonians (2) and (3) (i.e., supposing $J_{12} = J_{13}$), the electron transfer leads to 15 repeated energy spectra of the unique exchange Hamiltonian, with the center of gravity at 4t (1), 2t (6), 0 (3), –2t (2), and –4t (3), where the numbers in parentheses give the degeneracy of transfer levels. However, if the difference between the two exchange Hamiltonians is taken into account, the electron energy spectrum will consist of

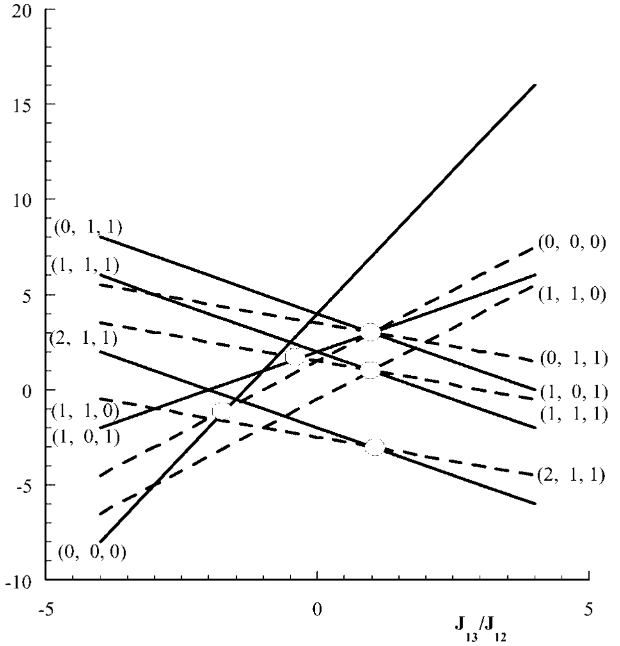


Figure 3. Spin levels of square (full lines) and rhombic four-nuclear complexes. The corresponding spin states (S, S_{13}, S_{24}) are indicated left and right for the square and rhombic configurations, respectively. The circles show the positions of avoided crossings resulting from the electron transfer.

15 similar groups presenting the superposition of the energy spectra of the two exchange Hamiltonians. Within each group, the electron transfer results in avoided crossings in the crossing points of energy levels belonging to different Hamiltonians but characterized by the same total and intermediate spins (see Figure 3). Although these effects will modify the energies in the vicinity of the crossing point, they are not able to change the multiplicity of the ground state imposed by the "static" exchange interaction.

Conclusions

The DFT results obtained for the neutral representative of the $[V^{IV}{}_nV^{V}{}_{6-n}O_7(OR)_{12}]^{(4-n)}$ series indicate that its individual molecule (because of internal vibronic interactions) does not possess octahedral symmetry within the hexavanadate core and comprises a slightly distorted square-bipyramidal OV_6 unit, which is characterized by localized spin-density distribution; the four vanadium(IV) centers are involved in ferromagnetic coupling. According to the available experimental data mentioned in the Introduction, the complex retains its structural features to a large extent in the crystal lattice and displays the trapped vanadium valences at least at low temperature. In solution, the experimental observations have been interpreted as arising from delocalization of the unpaired electrons, which has been associated with the intervalence electron transfer. However, it is improbable that interaction of the neutral species with the solvation sphere can result in significant changes in the core geometry enabling d-electron delocalization.

The results of the experimental studies could be explained without introducing the electron transfer process if the existence of strong dynamical vibronic coupling in a given species is proposed. Such coupling produces the three valence-trapped structures (states), which can be obtained from each other by changing the "short" axis, that is, the "short" and "long" axes in one structure change into the "long" and "short" axes in another structure, respectively. Apparently, one of these states is frozen (i.e., the transitions between the states are suppressed or their rates are very low) in the crystal lattice because of cooperative solid-state effects. Upon temperature increase, the rates of transitions increase and, on the timescale of the X-ray structural analysis, an averaged structure displaying a symmetrical octahedral vanadium framework and fully delocalized d electrons can be obtained. Such a structure has been obtained, for example, in the case of species with ethylated bridges, where the disorder of the ethyl groups apparently has a pronounced effect on the rates of transitions. Extensive d-electron delocalization detected by the cyclovoltammetric experiment implies the reduction of the barriers between the states in solution, that is, the electronic and molecular structure of the neutral complex in its solvated state can be assessed by taking a superposition of the three valence-trapped forms.

The most interesting feature of the systems studied is the ferromagnetic coupling in the vanadium(IV) pairs – a result obtained from the DFT calculations. Ferromagnetic interactions are very rare in oxovanadium complexes and are a consequence of a specific core geometry imposed by the POM architecture. The results described here present a step toward understanding the properties of a given alkoxo-polyoxovanadium compound series, however, magnetic susceptibility measurements and EPR-spectroscopic studies carried out on the freshly prepared samples are required to make final conclusions.

Supporting Information (see also the footnote on the first page of this article): Tables S1 and S2 deal with the SCF single determinants and present atomic spin densities, expectation values of $\mathbf{S}^2$, and energies (in a.u.) computed for complexes **I** and **II**. Table S3 shows the energy differences between the single-determinant states as functions of J_{ij} obtained with the model spin Hamiltonian H(4) [Equation (1)]. Table S4 contains the eigenvalues and eigenfunctions of the model spin Hamiltonian H(2) with $S_i = 1/2$. Figure S1 presents the plot of the HS-state spin density for the crystal structure of complex **II**.

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