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Role of the Electron Transfer and Magnetic Exchange Interactions in the Magnetic Properties of Mixed-Valence Polyoxovanadate Complexes

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Modeling the properties of high-nuclearity, high-electron-population, mixed-valence (MV) magnetic systems remains one of the open challenges in molecular magnetism. In this work, we analyze the magnetic properties of a series of polyoxovananadate clusters of formula $[V_{18}O_{42}]^{12-}$ and $[V_{18}O_{42}]^{4-}$. The first compound is a fully localized spin cluster that contains 18 unpaired electrons located at the metal sites, while the second one is a MV cluster with 10 unpaired electrons largely delocalized over the 18 metal sites. A theoretical model that takes into account the interplay between electron transfer and magnetic exchange interactions is developed to explain the unexpected enhancement of the antiferromagnetic coupling when the number of unpaired electrons is reduced from 18 to 10 in these clusters. In the MV area, these systems represent the most complex magnetic clusters studied theoretically so far. Because of the high complexity of the systems, the number of relevant parameters is too large for a conventional model Hamiltonian approach. We therefore perform a theoretical study that combines ab initio calculations with the model Hamiltonian. In this way, we use ab initio calculations performed on small fragments of the cluster to lower the degrees of freedom of the parameter set of the model Hamiltonian that operates in the whole MV cluster. This approach shows the usefulness of combining ab initio calculations with model Hamiltonians in order to explore the magnetic properties of large and complex molecular systems, emphasizing the key role played by the electron transfer in these model magnetic materials.

I. Introduction

The field of molecular magnetism has seen giant leaps since the 1980s, from the search for molecule-based magnets to the achievements of single-molecule magnets and multifunctional materials.[1–4] However, there are still several fundamental open problems, such as the interplay between electron delocalization and magnetic interactions in mixed-valence (MV) compounds. These kinds of systems are formally composed of localized magnetic moments and itinerant “extra” electrons that can undergo a rapid hopping over the magnetic sites. The main effect of this electron transfer is to ferromagnetically couple two localized magnetic moments through a kind of exchange interaction named double exchange.[5] Colossal magnetoresistance of manganites, among other relevant phenomena, can only be explained by taking into account this process.

Still, the study of the exchange interactions in MV systems with high nuclearity and high electron population remains a challenge. So far, only dinuclear, trinuclear, and tetranuclear systems have been deeply studied; general calculations have

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been performed, showing the influence of electron transfer on the magnetic properties.[6] Larger systems, like the MV oxide magnetic clusters (polyoxometalates), have only been studied for low electronic populations (two electrons).[7–10] Even then, the involved parameters were, until very recently, either guessed or fitted from experimental data.

Polyoxometalates constitute a rich and growing class of inorganic compounds with interest both for their possible applications[11–17] and for their ability to embody interesting physical models, such as magnetic exchange for various metals in growing nuclearities,[18,19] or electron transfer of unpaired electrons having a dramatic influence in magnetic coupling.[20,21] In this way, they are ideal systems for molecular magnetism studies.[22]

Among the polyoxometalates, polyoxovanadates represent a remarkable class of high-nuclearity MV clusters. These compounds have an appealing redox chemistry and can serve as redox pools, wherein the electron population can be chemically controlled.[19] This is the case of the family of compounds that includes the spin-localized cluster $[V_{18}O_{42}]^{12-}$ (V^{IV}_{18}), MV compounds oxidized by two electrons, $[V_{18}O_{42}]^{10-}$ ($V^{IV}_{16}V^{V}_{2}$), and MV compounds oxidized by eight electrons, $[V_{18}O_{42}]^{4-}$ ($V^{IV}_{10}V^{V}_{8}$).[23] This series of polyoxovanadates presents an unexpected magnetic behavior: as the electronic population is decreased, meaning a growing distance between unpaired electrons, an increasing antiferromagnetic (AF) coupling is measured, as seen in Figure 1. This is exactly the opposite behavior one could predict considering pure magnetic (super)exchange interactions. In fact, different explanations are possible, namely, (i) the oxidation could cause a shrinking of the molecule, changing bond angles and distances and thus resulting in a more intense AF exchange, (ii) the MV cluster suffers a lower degree of competition between AF interactions (less spin frustration) than the spin-localized cluster, or (iii) the enhancement of the AF spin coupling could be related to the larger electronic delocalization introduced by the presence of extra holes in the oxidized species.

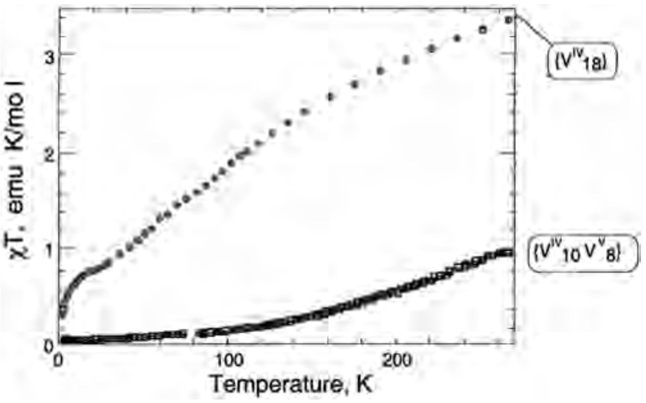

Figure 1. Temperature dependence of χT for the spin-localized V^{IV}_{18} and MV $V^{IV}_{10}V^{V}_{8}$ clusters (from ref23)

The aim of the present work is to find the origin of the surprising magnetic behavior in compounds V^{IV}_{18} and $V^{IV}_{10}V^{V}_{8}$. Thereby we will illustrate a novel theoretical approach for high-nuclearity MV clusters. From ab initio embedded cluster calculations, we have evaluated all of the nearest- (NN) and next-nearest-neighbor (nNN) interactions (magnetic coupling constants and electron-transfer integrals) in the V^{IV}_{18} and $V^{IV}_{10}V^{V}_{8}$ complexes. In a second step, the ab initio parameters have been introduced in a model Hamiltonian involving those electronic interactions to calculate the magnetic properties of these systems. Finally, this Hamiltonian is diagonalized to obtain the macroscopic properties of those compounds. Notice that a similar methodology was already successfully used to explain the strong AF spin coupling in the more simple MV polyoxometalate reduced by two electrons of formulas $[PW_{12}O_{40}]^{5-}$ [10,24,26] and $[W_{10}O_{32}]^{6-}$.[25] The present work not only extends this methodology but also aims at a much more challenging target. First, the experimental magnetic behavior is much more informative: rather than a flat diamagnetism, we have full χT curves for two different

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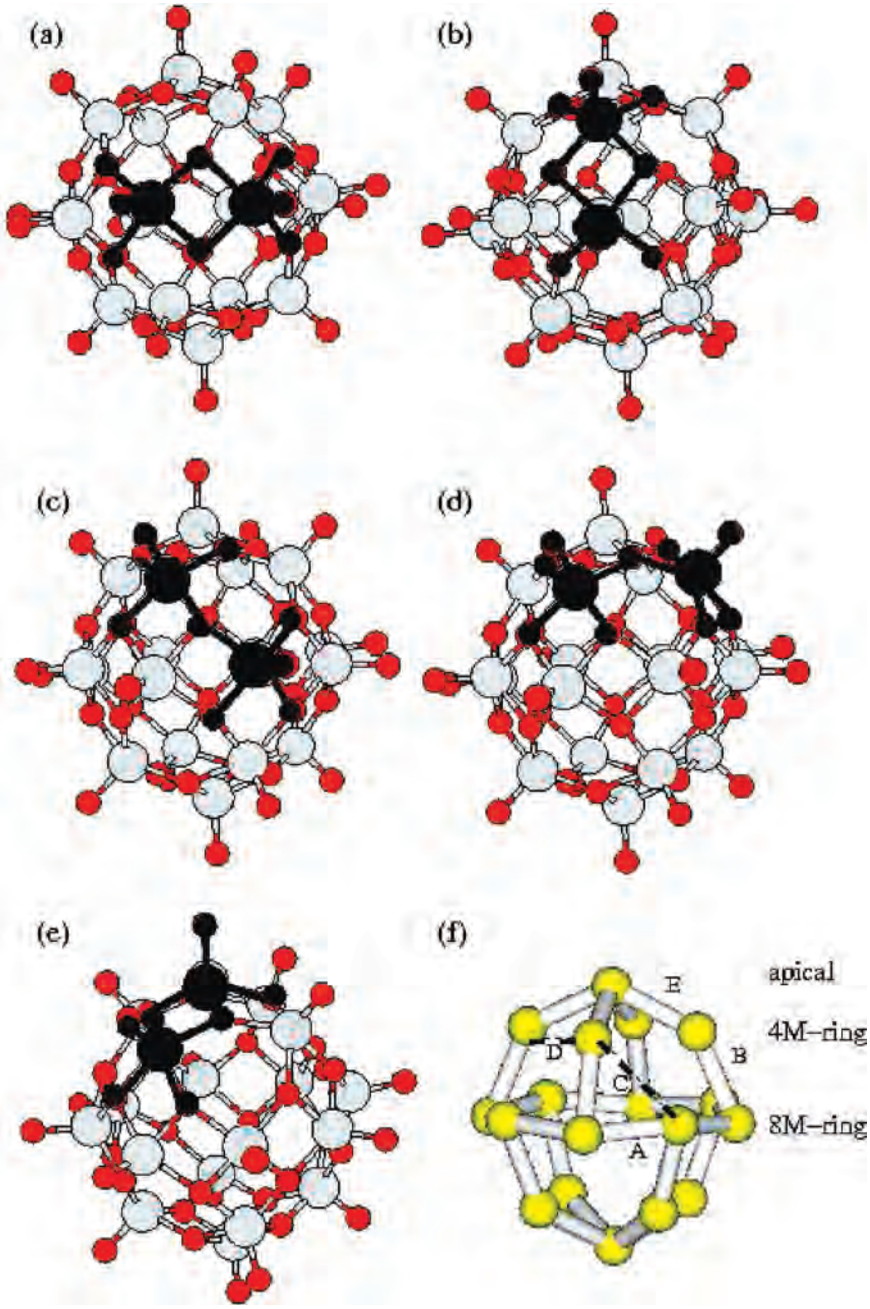

Figure 2. Binuclear fragments considered in the ab initio calculations. Parts a, b, and e correspond to the V_2O_8 fragments (interactions A, B, and E, respectively) and parts c and d to the V_2O_9 fragments (interactions C and D, respectively). In black are the atoms explicitly taken into account in the ab initio calculations (small and large black circles correspond to V and O atoms, respectively). The rest of the cluster is represented by gray and dark-gray circles (O and V atoms, respectively). (f) Schematic representation of $V_{18}O_{42}$ anion, showing only the V atoms. They are arranged in two 4M rings, one 8M ring, and two apical positions. NN (A, B, and E) and nNN (C and D) interactions in the $V_{18}O_{42}$ complex are also indicated.

electronic populations. In addition, the system is much more complex, with a larger nuclearity, a higher number of distinct exchange and transfer pathways, and a larger number of itinerant electrons. Moreover, the system has a much lower symmetry, showing up to 25 different pairs. From these considerations, one can assert that this system represents the most complex magnetic MV cluster studied theoretically so far.

This manuscript is organized as follows: Section II presents a description of the system under study. The methodology employed to analyze the properties of the system is shown in section III. Results and conclusions are presented in sections IV and V, respectively.

II. Description of the System

Polyoxovanadates of the general formula $[V_{18}O_{42}]^{n-}$ can exist in two different structural types: (i) the first one has an idealized T_d symmetry and presents a central VO_4 tetrahedron, which interacts strongly with the V atoms of the cluster, and (ii) the second one presents an idealized D_{4d} symmetry and encapsulates anionic or neutral guests, but the host−guest interactions are weak. The series of anions studied here is of the second type. Different compounds of this kind have been synthesized by Müller et al.[23] The structures of the spin-localized cluster anions are almost identical, and the slight differences in the bond distances and volumes of the cluster shells can be attributed to the kind of guest. The magnetic behaviors of these compounds are also similar: only small differences have been found at low temperature, probably more related to the structure of the anion shell induced by the guest than with its specific nature. In contrast, the magnetic properties show a dramatic dependence of the electronic population of the cluster, with an increasing AF behavior when the number of unpaired electrons decreases, as discussed above.

In our calculations, we have used the structure of the spin-localized cluster $Cs_{12}[V_{18}O_{42}(H_2O)] \cdot 14H_2O$ compound, characterized by Müller et al. (compound **1a** in ref 23). The results are expected to be helpful for other compounds of the same class, at least for those presenting a very close structure. The $Cs_{12}[V_{18}O_{42}(H_2O)] \cdot 14H_2O$ compound is formed by $[V^{IV}_{18}]$ anions separated by Cs counterions. A water molecule is encapsulated in each anion. V centers present a square-based pyramidal coordination (VO_5 units). They are connected by means of μ-O atoms and arranged in planes following the sequence: an apical V, a four-membered (4M) ring, an eight-membered (8M) ring, a 4M ring, and an apical V (Figure 2f). An S_4 axis relates the 4M rings. There are nine nonequivalent V atoms in the $[V^{IV}_{18}]$ cluster, with up to 25 different NN and nNN interaction pairs.

III. Methodology

The magnetic properties of the spin-localized cluster $[V^{IV}_{18}]$ and the MV-delocalized one $[V^{IV}_{10}V^{V}_{8}]$ have been modeled by using two complementary theoretical tools: (i) Ab initio calculations on embedded fragments are combined with effective Hamiltonians on the same systems to extract the value of the magnetic coupling constants J and hopping integrals t between NN and nNN V centers. (ii) The complete parameter set is introduced in a model Hamiltonian that mimics the whole anion and whose diagonalization allows the reproduction of the experimental data.[26] For the $[V^{IV}_{18}]$ cluster, a spin Hamiltonian is used, while for the $[V^{IV}_{10}V^{V}_{8}]$ cluster, a $t-J$ Hamiltonian is employed that simultaneously takes into account exchange interactions and transfer integrals.

A. Ab Initio Evaluation of Two-Body Interactions. Ab initio calculations have become a useful tool in estimating the values of J and t in different types of materials, ranging from molecular to extended systems. In most of the cases, the evaluations confirm the experimental values;[27–35] in others, they allow one to discern among different fittings.[36–38] They also provide access to quantities unavailable from experiments, such as the hopping integrals or the hole−hole repulsions.[26,34,39–42]

Different theoretical approaches have been proposed, depending on the way in which the electronic correlation is dealt with. In the present work, the estimates of J and t are obtained from truncated configuration interaction (CI) calculations on small fragments, embedded in a set of point charges that model the Madelung potential of the infinite lattice. Both J and t are essentially local parameters. Therefore, they do not correlate dynamically with their surroundings, and only a temporally averaged dependence on the Madelung field can be expected. For this reason, the use of reduced-size fragments to determine their values seems adequate.[10,28,32–35,42–46]

Our ab initio evaluations only concern the NN and nNN interactions. They are expected to be the largest ones, controlling the properties of the whole system. However, the possible role of other types of interactions, smaller in absolute value but crucial in the description of the magnetic properties of the system, must be noted. A popular case is the role played by the four-spin cyclic exchange terms in the two-dimensional and spin-ladder cuprates.[47]

Two types of fragments have been considered: V_2O_8 fragments, where two VO_5 units share an edge, with a double μ_3-O bridge (NN interactions), and V_2O_9 fragments, where two VO_5 units share a corner, that is, with a single μ_3-O bridge (nNN interactions). Depending on the position of the two V atoms on the $V_{18}O_{42}$ shell, we can distinguish five different interactions, as shown in Figure 2: (1) fragment A, where both V atoms belong to the 8M ring (Figure 2a), (2) fragment B, where a V atom is part of the 8M ring and the other of a 4M ring (Figure 2b), and (3) fragment C, with a

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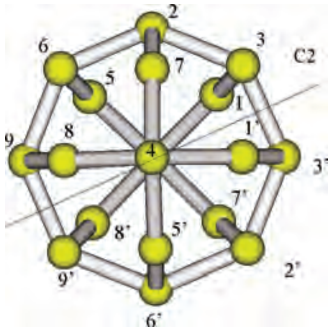
Table 1. Exchange Coupling Constant and Hopping Integral Values (in cm^{-1}) for Double μ-O-Bridged Fragments (A, B, and E-Type Interactions) with Model Env_{17}[a]



interaction	centers	V−V distance (Å)	V−O−V angle (deg)	$2J$	$2J_{\text{fit}}$	t
A1	V9−V9′	2.949	98.2, 98.2	−64	−64	−872
A2	V9−V6	2.899	97.9, 96.6	−194	−194	−1045
A3	V6−V2	2.938	99.1, 97.4	−114	−114	−787
A4	V2−V3	2.913	97.6, 98.2	−140	−140	−935
A5	V3−V3′	2.950	99.1, 99.1	−27	−27	−482
B1	V9−V8	3.009	101.7, 100.0	85	85	−2042
B2	V6−V5	3.011	100.5, 101.0	97	97	−772
B3	V3−V1	3.023	102.0, 102.6	114	114	−775
B4	V2−V7	3.008	101.6, 101.1	105	105	309
E1	V8−V4	2.929	98.2, 98.7	−82	−90	−636
E2	V5−V4′	2.901	97.4, 97.1	−210	−232	−1425
E3	V1−V4′	2.971	97.8, 100.4	−42	−46	−1181
E4	V7−V4	2.957	98.9, 97.1	−85	−94	−367

[a] Atoms in the $V_{18}O_{42}$ anion are related by a C_2 axis as shown in the chart. The same labels are used to distinguish the fragment centers. $2J_{\text{fit}}$ refers to the values used in the model $t-J$ Hamiltonian to explore the properties of the fully reduced V_{18} cluster (see the text).

Table 2. Exchange Coupling Constant and Hopping Integral Values (in cm^{-1}) for the C- and D-Type Interactions (One Bridging Oxygen Ligand) with Model Env_{17}[a]

interaction	centers	V−V distance (Å)	V−O−V angle (deg)	$2J$	$2J_{\text{fit}}$	t
C1	V9′−V8	3.689	146.4	−80	−88	−1571
C2	V9−V5	3.713	145.9	−50	−56	−928
C3	V2−V5	3.725	146.5	−21	−24	−441
C4	V2−V1	3.720	144.9	−80	−88	−2117
C5	V3−V1′	3.717	147.1	−3	−4	−905
C6	V3−V7	3.695	146.1	−47	−52	−1290
C7	V6−V7	3.704	146.2	−29	−32	−1004
C8	V6−V8	3.680	147.2	−49	−54	−1477
D1	V8′−V5	3.747	145.0	−157	−126	−2179
D2	V5−V1	3.739	144.9	−166	−132	−1889
D3	V1′−V7	3.719	145.2	−99	−80	−1867
D4	V7−V8	3.708	142.6	−133	−106	−2059

[a] See Table I for notation. $2J_{\text{fit}}$ refers to the values used in the model $t-J$ Hamiltonian to explore the properties of the fully reduced V_{18} cluster (see the text).

V atom belonging to the 8M ring and the other to the 4M ring, but now they are connected by only one bridging O atom (Figure 2c), (4) fragment D, with both V atoms placed at the same 4M ring (Figure 2d), (5) fragment E, where a V atom belongs to a 4M ring and the other is an apical V atom (Figure 2e).

Fragments A, B, and E contain a double μ_3-O bridge and will be used to extract NN interactions. According to the classification given by Plass[48] for dimeric oxovanadium(IV) complexes, fragments A, B, and E correspond to syn-orthogonal configurations of the vanadyl groups. Fragments C and D consist of V_2O_9 fragments and are employed to evaluate nNN interactions. Because of the asymmetry of the $V_{18}O_{42}$ shell, different fragments can be selected to study each interaction. All of the possibilities (up to 25 pairs) covering NN and nNN interactions have been explored. Their geometric parameters are presented in Tables 1 and 2, following the notation shown in the chart inside Table 1.

1. Evaluation of the Magnetic Coupling Constants. Magnetic systems are characterized by the presence of unpaired electrons, usually localized on the metal atoms. The properties of the system are governed by the interaction between these unpaired electrons on neighboring centers, which may be viewed as an effective interaction between site-centered spins and mapped onto a Heisenberg−Dirac−Van Vleck model Hamiltonian:[49]

$$\hat{H}_J = -2\sum_{i=1}^{N}\sum_{j>i}^{N} J_{ij}\hat{S}_i\hat{S}_j \cdot \delta_i \cdot \delta_j \tag{1}$$

Here J_{ij} is the amplitude of the coupling between centers i and j, $\hat{S}_i$ is the local spin operator, and δ_i (δ_j) equals 1 if there is an electron on site i (j) and 0 otherwise. In the polyoxovanadate spin-localized cluster, there is one unpaired electron per V center and the magnetic coupling constant for a binuclear fragment is then related to the energy difference between the lowest singlet and the triplet states:

$$2J = E(S) - E(T) \tag{2}$$

J has a negative value if the system is AF and positive when the triplet is the ground state (ferromagnetic, F). Then J can be evaluated from the energy of these two states. A method extensively used in the past to calculate these energies both in molecular systems and in solid-state magnetic materials[32,33,35,41,50–53] is the difference dedicated configuration interaction (DDCI) method.[54] This approach provides the energy and the eigenvectors of the desired states from a truncated CI expansion. The key point of the method is that the determinants in the CI expansion have been selected by means of a perturbative criterion, in such a way that they correspond to all of the single and double excitations on the top of a reduced number of determinants (the complete active space CAS) contributing to the energy difference between the states involved in the excitation. The method provides

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estimates of the exchange coupling constants in good agreement with the experimental values.[32,33,35,41,50–53]

2. Evaluation of the Electron-Transfer Integrals. In the MV complexes, the number of unpaired electrons is no longer equal to the number of metallic centers. In a completely localized situation, two types of V centers can be distinguished, depending on the number of unpaired electrons (d^1 V^{IV} or d^0 V^V). The hopping integral t is directly related to the rate of the hopping process[55] and can be evaluated from ab initio quantum chemistry calculations by means of the two-state model.[56]

Let us consider a system containing two sites A and B and one unpaired electron, which can be placed in site A or B. In a simplified picture, the electron transfer can be seen as the hopping between two orbitals, d_a and d_b, essentially localized, respectively, on sites A and B. The hopping integral t is equal to the coupling between the two resonant localized states:

$$t = \langle \text{core } d_a | H | \text{core } d_b \rangle \qquad (3)$$

where core corresponds to the inactive doubly occupied orbitals. There are two doublet states in competition, which correspond to the in-phase (g) and out-of-phase (u) combinations of the two localized states. The zeroth-order description of these two states is

$$|\varphi_g\rangle = \alpha|\text{core } d_a\rangle + \beta|\text{core } d_b\rangle \qquad (4)$$

$$|\varphi_u\rangle = \beta|\text{core } d_a\rangle - \alpha|\text{core } d_b\rangle \qquad (5)$$

where $\alpha^2 + \beta^2 = 1$. The energy of these doublet states depends on α (or β):

$$E_g = \alpha^2 E_a + \beta^2 E_b + 2\alpha\beta t \qquad (6)$$

$$E_u = \beta^2 E_a + \alpha^2 E_b - 2\alpha\beta t \qquad (7)$$

where E_a and E_b are the energies of the localized states. For symmetric binuclear fragments, $\alpha = \beta = 1/\sqrt{2}$, and then t is just half of the energy difference between the two lowest doublet states of symmetry g and u. However, when the hopping takes place between two nonequivalent centers, t cannot be extracted directly from an energy difference, but an analysis of the wave functions of the two involved states is necessary; i.e., we need the value of α (or β).

$$E_g - E_u = (\alpha^2 - \beta^2)(E_a - E_b) + 4\alpha\beta t \qquad (8)$$

This procedure implies the use of the effective Hamiltonian theory and the localization of the active orbitals on the two active sites participating in the electron-transfer process. This strategy has been extensively employed to determine t both in binuclear complexes and in polynuclear fragments.[26,29,39,41,42,57] Details concerning the use of effective Hamiltonians in this context can be found in refs 42 and 53.

3. Computational Details. As described above, J and t have been evaluated from the low-energy states of small fragments of the compound under consideration. These fragments must be embedded in a set of point charges and total ion potentials that model the effect of the rest of the crystal. This embedding is centered on the considered $V_{18}O_{42}$ anion, where the fragment is extracted. Three types of atoms can be distinguished in the model: (i) Atoms in the fragment. Their electrons are explicitly taken into account in the calculations. Extended basis functions are used for the most external electron, with the inner ones being replaced by effective pseudopotentials.[58] (ii) V atoms connected to the atoms of the fragment. They are substituted by total ion potentials, which model the Pauli exclusion and Coulombic effects. (iii) The rest of the ions of the $V_{18}O_{42}$ cluster and those of the neighboring shells, as well as the surrounding Cs ions, are replaced by point charges (3+ for V, 2− for O, 1− for apical O, and 1+ for Cs). A set of 1224 charges are used, emulating 17 $V_{18}O_{42}$ anions, and the surrounding Cs cations (306 V, 714 O, and 204 Cs; model Env_{17}). Two views of this embedding are included in the Supporting Information. An alternative embedding with 69 $V_{18}O_{42}$ anions (Env_{69}) has also been considered, with the results being in good agreement with those obtained when the Env_{17} model is used (see the Supporting Information).

In all of the calculations, the atomic coordinates correspond to the experimental structure of the stoichiometric $Cs_{12}[V_{18}O_{42}(H_2O)]\cdot 14H_2O$ compound,[23] and then the relaxation that the hole doping could induce in the MV $V_{18}O_{42}$ cluster is not explicitly taken into account. Even though this simplification could seem too crude, in our opinion, it is the most reasonable and least biased one in view of the complexity of the system. The reasons grounding this choice are the following ones. First of all, there are no available data for the oxidized $Cs_{12}[V_{18}O_{42}]$ compound. The synthesized oxidized species differ not only by the number of active electrons but also by the guests and counterions. Then, in this situation, it is difficult to distinguish between the geometrical effects coming from the hole doping and those resulting from the differences in their specific empirical formula. On the other hand, an evaluation of the extension of the nuclear relaxation on the MV system by means of a first-principles-based geometry optimization is ruled out. A meaningful optimization would require one to deal with the complete V_{18} anion on its different oxidation states. Even for the simplest case ($V^{IV}_{16}V^{V}_{2}$), the wave function of the lowest state can be composed of a large number of quasi-degenerate localized solutions, in such a way that the wave function presents a significant multireference character, which prevents the use of density functional theory based approaches, but the size and complexity of the system also eliminate the possibility of using any multireference approaches from our consideration. Moreover, inspection of the available crystallographic data shows that the average V−V distance decreases in only 0.03 Å when two V centers are oxidized in the cluster. The same effect is observed on the average

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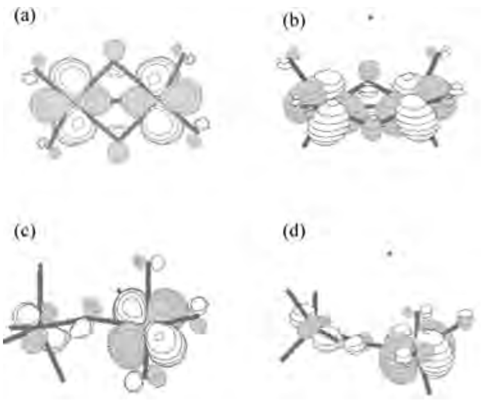

Figure 3. Two views of the active orbitals for A (a and b) and C (c and d) fragments. Views b and d show that V 3d orbitals are not placed on the same plane. The buckling of the VO_4 planes depends on the relative position of the V centers on the $V_{18}O_{42}$ cluster.

distance between V atoms and the center of the $V_{18}O_{42}$ shell. This relaxation is expected to have a non-negligible effect on *J*, as our magnetostructural correlations suggest. However, the macroscopic properties of the MV clusters are essentially controlled by the hopping integrals, which are always at least 1 order of magnitude larger than the corresponding magnetic coupling constants. Because the MV clusters are highly delocalized, classified as type III in the Robin and Day scheme,[23] it is reasonable to assume that the nuclear relaxation only produces a minor effect on the hopping integrals, and then the values obtained with the geometry of the spin-localized cluster anion constitute a good approximation to the correct ones.

On the other hand, water molecules are not included in the calculations. H-atom positions of water molecules are not reported because of disorder problems, which prevent an unambigous determination.[23] This reason, together with the weak character of the host−guest interaction in these kinds of systems, the large average distance $V-OH_2$, and the small effect of the guest on the magnetic behavior justify our choice.

Once the model has been fixed, a set of molecular orbitals for each fragment is obtained from a restricted open-shell Hartree−Fock calculation on the triplet state. Figure 3 shows the singly occupied magnetic orbitals for fragments A and C. Similar shapes have been found for fragments B and E (with a double O bridge) and D (with a single O bridge), respectively. These molecular orbitals correspond to the in-phase and out-of-phase combinations of the V $3d_{xy}$ orbitals, with tails on the bridging oxygen ligands as well as on the terminal O atoms. The ligands are placed along the *x* and *y* axes, and the O atom of the vanadyl group is placed along the *z* axis. In fragments with a double O bridge (Figure 3a), the V 3d orbitals point toward each other, with a direct σ overlap of the V $3d_{xy}$ orbitals for short V−V separations. In fragments with a single O bridge, the 3d−3d overlap is of π nature, mediated by the bridging ligand (Figure 3c). It must be pointed out that, because of the quasi-spherical symmetry of the $V_{18}O_{42}$ anion, the $[V(\mu\text{-}O)_2V]$ framework presents a distortion from planarity; the two active V $3d_{xy}$ orbitals are never placed in the same plane but in planes related with a certain torsion angle, in which the magnitude depends on the relative position of the fragment on the $V_{18}O_{42}$ anion (Figure 3b,d).

For evaluation of *J*, the active space is built on two electrons on two magnetic orbitals. To reduce the computational cost, the energy difference dedicated molecular orbital approach has been used.[59] In this approach, the inactive orbitals are selected in accordance with their participation on the singlet−triplet energy difference, in such a way that only those participating the most are included in the calculation, with the rest being neglected, without loss of accuracy in the estimates of *J*.

Regarding *t*, both the active and inactive orbitals used in the CI expansion are optimized to take into account the lack of an electron with respect to the stoichiometric situation. Starting with the triplet-state orbitals of the undoped fragment, a CI calculation involving all of the single excitations over the CAS (CAS+S) gives a set of average natural orbitals for the lowest two doublet states. These are used in the DDCI expansions. The dedicated molecular orbital approach has been used to reduce as much as possible the size of the CI matrices. The calculations involving the evaluation of the atomic integrals and the Hartree−Fock molecular orbitals have been performed with the *MOLCAS* package.[60] The CASDI code[61] has been used to diagonalize the CI matrices.

B. Model Hamiltonians. In the spin-localized cluster $[V^{IV}_{18}]$, a Heisenberg Hamiltonian that takes into account the different pairwise exchange interactions between the NN and nNN V^{IV} centers has been considered (see eq 1). The Hamiltonian has been solved using the *MAGPACK* program.[62] This program makes use of a general solution of the exchange problem in the high-nuclearity spin clusters (HNSCs) containing an arbitrary number of exchange-coupled centers and arbitary topology. All magnetic centers are supposed to possess well-isolated orbitally nondegenerate ground states so that the isotropic Heisenberg−Dirac−Van Vleck term is the leading part of the exchange spin Hamiltonian. The isotropic term of the Hamiltonian is expressed as irreducible tensor operators. This allows us to take full advantage of the spin symmetry of the system and an additional reduction of the matrices to diagonalize. The approach developed here is accompanied by an efficient computational procedure that allows us to calculate the bulk magnetic properties (magnetic susceptibility, magnetization, and magnetic specific heat) as well as the spectroscopic properties of HNSCs.

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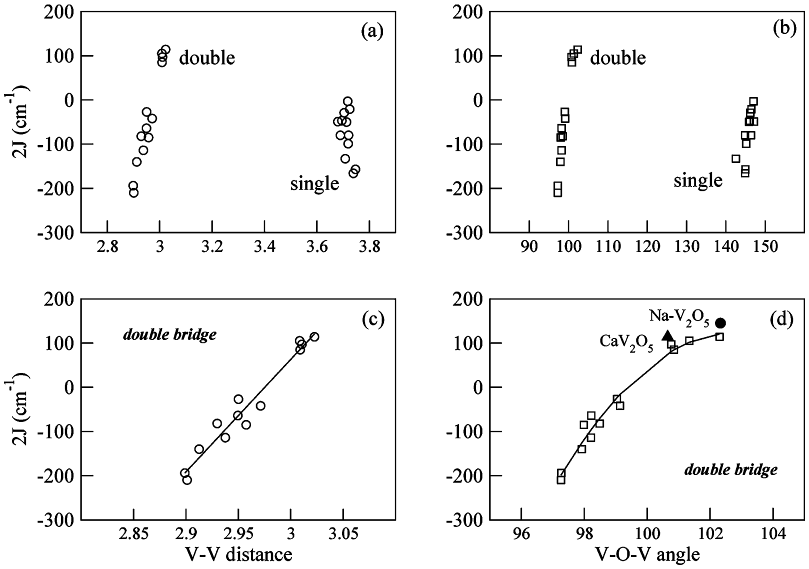

Figure 4. Relationship between the J values and the V−V distance (a) and V−O−V angle (b) in all of the interactions under study. Dependence of J value on the V−V distance (c) and the bridging angle (d) in interactions mediated by two bridging oxygen ligands. Closed circle and triangle correspond respectively to the interladder coupling in α NaV_2O_5[41] and CaV_2O_5 ladders.[38] In both cases, the coupling proceeds through two bridging ligands as in the interactions under consideration. All values are in cm $^{-1}$ (DDCI level, with Env_{17}).

In the MV spin-delocalized cluster $[V^{IV}_{10}V^{V}_{8}]$, an extended $t-J$-type model Hamiltonian has been used. This model Hamiltonian contains two types of interactions:

$$\hat{H}_{tJ} = \hat{H}_J + \hat{H}_t \tag{9}$$

where $\hat{H}_J$ takes into account the magnetic exchange coupling between unpaired electrons (eq 1) and $\hat{H}_t$ controls the electron transfer, assures the mobility of the holes, and takes the form

$$\hat{H}_t = \sum_{i=1}^{N} \sum_{j>i}^{N} t_{ij} \cdot \delta_i \cdot (1 - \delta_j) \tag{10}$$

The parameters J_{ij} and t_{ij} take different values depending on the relative positions of sites i and j and were obtained from ab initio estimates.

To solve this Hamiltonian, we developed a general computational approach based on the successive chainlike spin-coupling scheme and which takes full advantage of the quantum angular momentum theory.[63] This approach gives a general solution of the $t-J$ problem in the high-nuclearity MV systems containing an arbitrary number P of electrons delocalized over the network of N ($P < N$) localized spins. In the framework of the proposed computational scheme, electron transfer and magnetic exchange interactions are considered and an explicit analytical dependence of these interactions has been derived as a function of all relevant spin quantum numbers for an arbitrary MV system. Finally, from the calculated energy levels, the magnetic properties of the MV system can be derived.

IV. Results and Discussion

A. Ab Initio Calculations. 1. Estimates from Dinuclear Fragments. The values of J and t for the different fragments are reported in Tables 1 and 2. All of the calculations have been performed at the DDCI level, with the Env_{17} model, described in section III.A.3, once the adequacy of the embedding has been checked by complementary calculations described in the Supporting Information.

Regarding the magnetic exchange, all of the interactions are AF except those of type B, which are weakly F. The absolute values of J are strongly dependent on the structure of the fragment; small changes in the V−V distance and/or the bridging V−O−V angle result in large modifications in the magnetic coupling constants. Parts a and b of Figure 4 present the J values with respect to the V−V distance and the mean V−O−V angle, respectively. Two well-separated sets can be distinguished, which correspond to the two types of interactions between two V centers: those mediated by a single O bridge (on the right) and those with a double O bridge (on the left).

It must be noticed that both types of interactions present similar J values despite the larger V−V distances in single O-bridged fragments. This evidences an efficient superexchange pathway through the single bridging oxygen ligand and a different balance of the F ($J_F = 2K_{ab}$) and AF contributions ($J_{AF} = -4t^2/U$) to the magnetic coupling constant, $J = J_F + J_{AF}$. This point can be verified by representing J vs t^2 (Figure 5): a linear fitting is expected when the direct exchange ($2K_{2b}$) is negligible and the coupling is controlled by the superexchange mechanism through the bridging ligand. This is the case of the single O-bridged fragments, where neither the V−V distance nor the relative orientation of the V 3d orbitals allows an effective direct interaction between the magnetic orbitals (Figure 5b) and then the coupling is governed by the superexchange through the O atoms. All of the evaluated interactions of this type present a quite large negative value (Table 2), corresponding to AF interactions. However, in the case of double-bridged fragments, a substantial deviation is found, because of the non-negligible contribution of the direct

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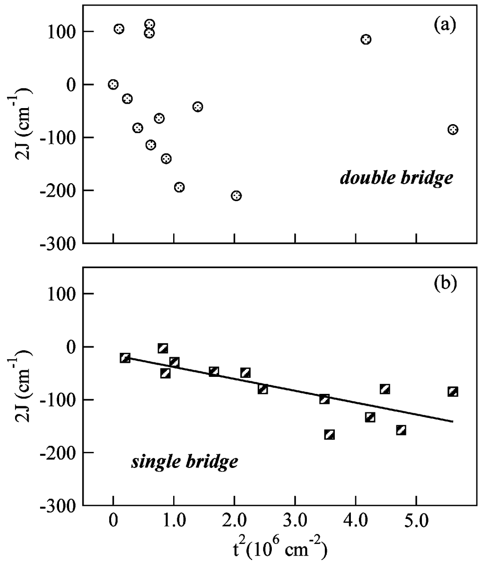

Figure 5. Plot of $2J$ vs t^2 values for all of the evaluated interactions. A linear fitting is expected for those magnetic interactions where the F contribution J_F is negligible with respect to the AF one J_{AF} (see the text).

exchange (Figure 5a). The F constants isolated in the cluster correspond to these types of interactions (Table 1; interactions B). Superexchange is most efficient in single-bridged fragments probably because of the relative orientation of the 3d V and 2p O orbitals, as shown in Figure 3.

Regarding the magnetostructural properties, for interactions with double bridges, A, B, and E, some general trends can be found with respect to the V−V distance and the V−O−V angle (Θ). In contrast, it has not been possible to establish any correlation between the dihedral angle defined by the two square-based VO_5 pyramids and the J values. Figure 4c shows the correlation of J with the V−V separation in these fragments. Notice that even the F values are also well correlated. When the distance increases, the coupling diminishes, as expected, following a linear law:

$$2J = -7569.8 + 2544.2d_{V-V} \quad (\mathrm{cm}^{-1}) \qquad (11)$$

With respect to the V−O−V angle Θ, a quadratic fit is observed, as shown in Figure 4d:

$$2J = -113390.0 + 2210.1\Theta - 10.7\Theta^2 \quad (\mathrm{cm}^{-1}) \quad (12)$$

This parabolic dependence with respect to the bridging angle has also been observed for hydroxo- and alkoxo-bridged dinuclear oxovanadium(IV) complexes,[64] hydroxo-bridged dinuclear copper(II) complexes,[30] double O-bridged copper(II) complexes,[31] as well as end-on azido-bridged transition-metal complexes.[65] Figure 4d also includes the interladder magnetic coupling values obtained for α-NaV_2O_5[41] and CaV_2O_5,[38] evaluated from DDCI calculations on small fragments. The coupling between the ladders is mediated by two bridging oxygen ligands, as in interactions A, B. and E. In spite of the antiorthogonal configuration of the oxovanadium centers involved in the interladder coupling, the J values correlate rather well with the quadratic law observed for the polyoxovanadates (with a syn-orthogonal configuration in all of the double O-bridged fragments).

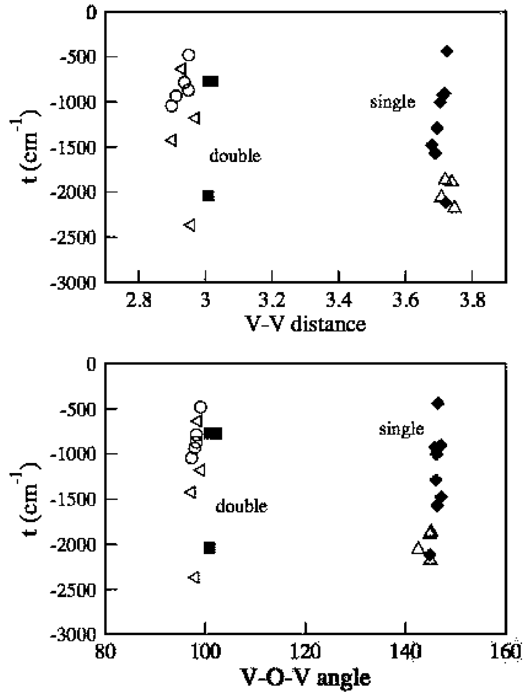

Figure 6. Relationship between the t values and the V−V distance (top) and the mean V−O−V angle (bottom) in all of the interactions under study. Open circles, closed squares, and left triangles correspond respectively to interactions A, B, and E . Closed diamonds and up triangles correspond to interactions C and D.

The decrease of the AF component of the exchange coupling when the bridging angle or the V−V distance increases can be rationalized within the framework of the qualitative model proposed by Kahn.[66] In this model, the coupling constant depends on the overlap between nonorthogonal localized magnetic orbitals, $J = 2K_{ab} + 4\beta S_{ab}$, where β and S_{ab} are respectively the transfer integral and overlap between the nonorthogonal magnetic orbitals a and b. When the V−V distance (or the V−O−V angle) increases, the overlap diminishes, and then the AF contribution to J ($4\beta S_{ab}$ in this model) decreases and the magnetic coupling takes a more positive value; that is, a large bridging angle or large V−V distance plays against the AF contribution coming from the direct 3d−3d overlap.

Regarding the hopping integrals, two sets of values can be distinguished as for J values, depending on the number of bridging ligands (Figure 6). Their amplitudes are larger than the corresponding J values, which favors a high delocalization of the holes in the cluster, as expected for a type III MV system. Hopping integrals are more sensitive to the particular structure of the fragment, but their values follow, in general, the same trends as the corresponding J values.

2. Effect of the Holes on the Magnetic Coupling Constants. In most of the studies where the $t-J$ model is used to analyze the collective properties of the doped

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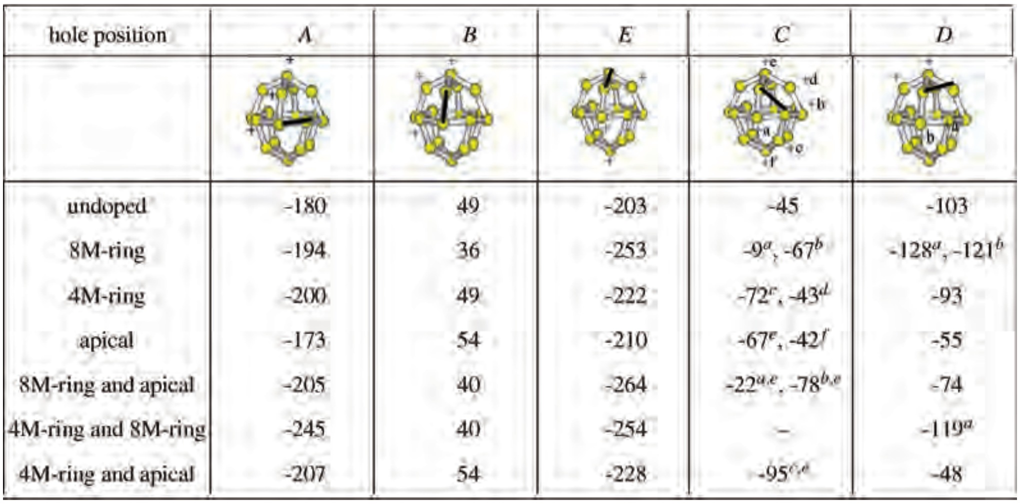
Table 3. Effect of the Hole Doping on the Magnetic Coupling Constant ($2J$) for Fragments A2, B2, C2, D1, and E2[a]



hole position	*A*	*B*	*E*	*C*	*D*
undoped	-180	49	-203	-45	-103
8M-ring	-194	36	-253	-9^{a}, -67^{b}	-128^{a}, -121^{b}
4M-ring	-200	49	-222	-72^{c}, -43^{d}	-93
apical	-173	54	-210	-67^{e}, -42^{f}	-55
8M-ring and apical	-205	40	-264	$-22^{a,e}$, $-78^{b,e}$	-74
4M-ring and 8M-ring	-245	40	-254	–	-119^{a}
4M-ring and apical	-207	54	-228	$-95^{c,e}$	-48

[a] All values are in cm^{-1}. All of the calculations were at the CAS+S level, with the Env_{17} model. In fragments C and D, labels refer to the relative position adopted by the hole(s).

systems, it is considered that J values in the doped systems take the same values as those in the undoped ones. Recent ab initio calculations in doped high-T_c superconductors[42] have shown that holes can affect the amplitude of the magnetic coupling, in different ways depending on the number and relative position of the hole with respect to the centers containing the unpaired electrons. A simple model based on the electrostatic effects induced by the holes has been used to rationalize this behavior.[42] The enhancement of the AF coupling observed in polyoxovanadates when the number of active electrons is decreased could be related to this phenomenon, and it has also been investigated by means of ab initio calculations on small fragments.

We have analyzed the effect of the position and number of holes on the J value for one fragment of each interaction type (A2, B2, C2, D1, and E2). Only low-cost calculations have been performed; the results are summarized in Table 3. The AF coupling between two V ions placed in the 8M ring (fragment A) is enhanced when a hole is introduced in the cluster. Only a small reduction of J is observed when the hole is placed in an apical position. A second hole favors the AF coupling. The same behavior is observed in fragment E; that is, the AF coupling between a 4M ring V and an apical V is enhanced by the holes. The effect on B interactions is smaller but follows the same trend. In most of the considered situations, the magnetic coupling between the 4M and 8M rings has a longer AF character when holes are present in the neighborhood. For the single O-bridged interactions (C and D), most of the considered hole distributions result in an increase of the AF nature of the coupling. Despite the qualitative character of these calculations, it seems possible to conclude that the enhancement of the AF nature of the coupling induced by the presence of the hole is an important contribution to the amazing magnetic behavior observed for MV polyoxovananadates.

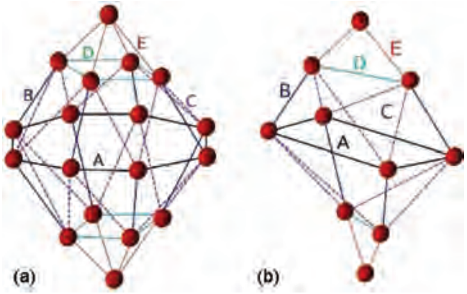


Figure 7. (a) Magnetic exchange and electron-transfer pathways on the 18-center model. (b) Construction of a simplified 10-center model, preserving the magnetic features of the complete 18-center model.

B. Model Hamiltonians. 1. Spin-Localized Cluster. All NN and nNN magnetic exchange interactions estimated by ab initio calculations were taken into account in the detailed model Hamiltonian. Figure 7a shows all considered paths. In a first step, a calculation was performed assuming the exact values for the parameters estimated by ab initio calculations. The general behavior is roughly correct: at room temperature the spins already show an AF coupling, but high-spin states contribute to the magnetic signal, and at low temperatures, only the lowest singlet and the lowest triplet states are populated. However, we found disagreements, both in the high-temperature regime as in the singlet−triplet energy gap. In particular, the calculated high-temperature χT value overestimates the experimental one, and the calculated singlet−triplet energy difference has a wrong sign.

The spin-localized cluster [V^{IV}_{18}] is a very complex network of frustrated spins. An analysis of the topology shows that the main source of frustration is the competition between the AF D-type interactions and A-, B-, C-, and E-type interactions. Indeed, both "indirect" interactions of types E−E and C−C and the route B−A−A−B would lead to an effective F coupling of the spins in the 4M rings. Nevertheless, the large inhomogeneity of the magnetic couplings of the same type (from 10% for B and D to an order of

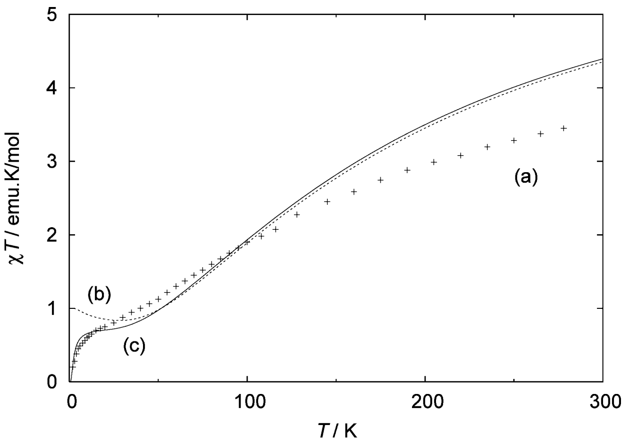


Figure 8. Magnetic susceptibility of the spin-localized cluster: (a) experimental; (b) ab initio estimates; (c) fit with the J_{fit} values reported in Tables 1 and 2, which differ up to 20% from ab initio J values.

magnitude for A and C) prevents such a simple description of the spin network. Therefore, the parameter space and its effects on the low-energy spectrum and the χT curve were explored. Model Hamiltonian calculations were performed with more than 100 sets of J interactions differing up to 20% from ab initio values. Our exploration showed that the high-temperature slope is quite robust, while both the height of the high-temperature signal and the singlet−triplet energy difference, in both magnitude and sign, are fairly tunable through small variations of the magnetic exchange parameters.

If the parameters are allowed to vary up to 50% apart from the ab initio values, the experimental curve can be exactly recreated. However, several parameter combinations yield similar results, and there is no physical reason to justify choosing one over the others. A similar problem was faced previously by Gatteschi et al.,[23] who based their guesses on the rather limited collection of previously described values.

We chose to restrict the fitting to a range of ±20% around our ab initio values. The fitting of χT shown in Figure 8 is in reasonable agreement with the experimental magnetic susceptibility and uses a set of parameters quite close to our ab initio estimates (values are included in Tables 1 and 2 as J_{fit}). Other sets of parameters, which are also inside a range of the ab initio values ±20%, gave rise to fits of similar quality.

2. MV System. To obtain the full energy level scheme of the eight-electron-oxidized MV cluster $[\mathrm{V}^{\mathrm{IV}}_{10}\mathrm{V}^{\mathrm{V}}_{8}]$, it would be necessary to diagonalize a matrix of dimension 4.4×10^7, which corresponds to the possible distributions of 10 electrons delocalized over 18 centers (43 748) times the possible spin microconfigurations from the exchange coupling of 10 centers with $S = 1/2$ (1024). Even considering the truncation of the matrix into spin-specific submatrices, one for each value of S_{tot}, we still would have to deal with the diagonalization of matrices of size larger than 10^6, something far from our computing capabilities. So, in order to make the system manageable, the dimension of the energy matrix had to be reduced.

Table 4. Magnetic Exchange and Electron-Transfer Parameters Used for the 10-Center Model (in cm^{-1})

interaction	$2J$	t
A	−140	280
B	−140	280
C	−70	−695
D	−70	−695
E	−35	−1040

We decided to use a simplified MV cluster, maintaining the electronic, magnetic, and structural features of the original $[\mathrm{V}^{\mathrm{IV}}_{10}\mathrm{V}^{\mathrm{V}}_{8}]$ system but of a reduced size. The model system is the 10-center cluster depicted in Figure 7b, which presents all A−E interaction types of the 18-center model, as well as all possible spin-frustration polygons (two triangles and a pentagon). Because this simplified 10-center model has much fewer electronic distributions and spin states, an exact evaluation of the full spectrum and of the derived magnetic properties can be accomplished for the fully reduced spin-localized cluster (10 electrons in 10 sites) and for the MV one (6 electrons in 10 sites, corresponding to an electron/site ratio close to 10/18 as in $[\mathrm{V}_{18}\mathrm{O}_{42}]^{4-}$). Up to three distinct models were considered: (a) a fully reduced spin-localized cluster where electron transfer t is not operative (localized electrons), (b) a MV system taking into account only the superexchange mechanisms (J), and (c) a MV system taking into account both superexchange (J) and electron-transfer (t) mechanisms.

A first step to explaining the experimental results used the ab initio parameters calculated in the first part of this work. Because it is impossible to consider all of the individual interactions in the simplified model, the parameters were averaged for each interaction type. The results of this simplified model provide an explanation to the experimental evolution of the magnetic signal at room temperature. In case a, the calculated χT value with 10 electrons on 10 sites is 2.80 emu·K·mol^{-1}, showing a partial AF coupling of the 10 localized spins. The scaling of this value for $\mathrm{V}^{\mathrm{IV}}_{18}$ would correspond to 2.80 (18/10) = 5.04 emu·K·mol^{-1} (experiment: 3.40 emu·K·mol^{-1}). One could expect that the change to six electrons in case b should on its own diminish the spin frustration and therefore promote the efficiency of the overall AF electron coupling. However, the calculated χT value, 1.91 emu·K·mol^{-1}, does not reflect that. On the contrary, scaling of the χT value in proportion to the number of electrons [1.91 (18/6) = 5.73 emu·K·mol^{-1}] shows that the effective AF coupling is even smaller in this case. Furthermore, variations of all J values by up to 20%, like those that could result from structural modifications as discussed above, have effects well below 10% on the χT value.

In sharp contrast, with the introduction of electron delocalization mechanisms in case c, the calculated magnetic signal is noticeably decreased down to 0.84 emu·K·mol^{-1}. For $\mathrm{V}^{\mathrm{IV}}_{10}\mathrm{V}^{\mathrm{V}}_{8}$, this would correspond to 0.84 (10/6) = 1.4 emu·K·mol^{-1} (experiment: 1.0 emu·K·mol^{-1}). Thus, this behavior is qualitatively in agreement with the experimental observation. Still, although this 10-center model is useful to extract the general trends of the real system, one cannot expect that the incorporation of the parameters derived from

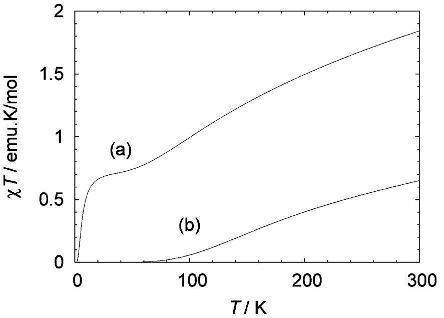


Figure 9. Magnetic susceptibility for the decanuclear model: (a) 10 electrons; (b) 6 electrons.

ab initio calculations to this simplified model allows us to quantitatively explain the magnetic behavior of the system in the whole temperature range. Therefore, in a second step, we performed a wide exploration of the parameter space, and we found that for some sets of parameters, it is possible to closely reproduce the distinct evolution of the two magnetic clusters. For example, the parameters in Table 4 give rise to Figure 9, which does indeed show analogies to the experimentally observed magnetic properties of V_{18}^{IV} and $V_{10}^{IV}V_8^V$ (Figure 1).

Again, variations of 20% in J result in changes of less than 10% in χT, while the participation of t results in a dramatic change of the curve.

Of course, this parameter set for the simplified system should not be considered as "more correct" than the sets in Tables 1 and 2 for the real system. Still, the theoretical reproduction of the experimentally observed magnetic evolution for the full temperature range, combined with the relative insensibility to changes in J, further strenghtens the point that the dramatic increase in the effective AF coupling can only be reproduced by considering electron transfer.

V. Conclusions

The magnetic properties of an extremely complex polyoxovanadate system formed by 10 spins delocalized over 18 metal sites have been analyzed by means of a combined strategy of ab initio quantum chemistry calculations and exact diagonalizations of a model $t-J$ Hamiltonian. The structural parameters of $Cs_{12}[V_{18}O_{42}(H_2O)]\cdot 14H_2O$ have been used, where each $V_{18}O_{42}$ anion contains nine nonequivalent V centers, with up to 25 different NN and nNN pair interactions. The amplitudes of the magnetic coupling and electron-transfer integrals for all of these pairs have been evaluated from ab initio quantum chemistry calculations on binuclear fragments appropriately embedded in a bath of point charges reproducing the crystal field. The high internal asymmetry of the $V_{18}O_{42}$ cluster prevents the use of larger fragments, as we have previously done for two-dimensional and ladder cuprates. Moreover, the extraction of effective parameters in these large clusters requires the use of the effective Hamiltonian theory, and so more economic approaches such as the perturbative ones are not adequate in this case. Two types of interactions have been considered: those mediated by a double O bridge and those with a single bridging oxygen ligand.

All analyzed pairs present an AF coupling, with J taking different values depending on the particular features of the fragment. Only the coupling between the 8 and 4 M rings is found to be weakly F. The AF contribution to the magnetic exchange decreases linearly with the V−V distance and parabolically with the V−O−V angle, as discussed in section IV. The coupling, which is essentially controlled by the direct σ overlap of the V $3d_{xy}$ orbitals is remarkably sensitive to small geometrical perturbations. It has been shown that small changes in the geometry of the $[V(O)_2V]$ frame can turn the weak F coupling into a weak AF coupling. With regard to the electron-transfer integrals, large t values have been estimated from the ab initio calculations for all considered interaction pairs, usually at least 1 order of magnitude larger than the corresponding J value. This result agrees with the delocalized nature of the MV systems.

A remarkable result of the present paper is the use of self-sufficient information (calculations from first principles) to explain the magnetic properties of the full system. Once the effective parameters have been determined, they are injected into a model $t-J$ Hamiltonian to analyze the collective properties of the system. A satisfactory reproduction of the properties of the spin-localized cluster V_{18}^{IV} is possible, with a parameter set in close agreement with the theoretical estimates. In the case of the MV system $V_{10}^{IV}V_8^V$, a simplified model is necessary. In spite of the qualitative nature of this model, it accounts for the general behavior of these polyoxovanadates, namely, a dramatic increase in the effective AF coupling in the system when part of the V^{IV} ions are oxidized (i.e., when part of the spins are removed), and the remaining spins can be delocalized over all of the metal sites. The electron-transfer integral, calculated from the ab initio calculations, plays the key role in the macroscopic properties of these MV polyoxovanadates, while both the structural effect of removing electrons from the initial spin-localized cluster on the amplitude of the magnetic coupling and the effect of alleviating the spin frustration only play a minor role.

As far as we know, this is the most complex problem addressed so far in MV magnetic polyoxometalates and maybe also in MV clusters. Previous studies on polyoxometalates were limited to two electrons delocalized over 12 centers (two-electron-reduced Keggin anion) or two electrons delocalized over 10 centers (decatungstate[25]), while general MV calculations were confined to low-nuclearity clusters (2, 3, and 4).

Besides, this work shows once again the usefulness of combining ab initio calculations with model Hamiltonians, in order to explore the macroscopic properties of large and complex systems, such as the polyoxovanadates considered here. The diagonalization of the model Hamiltonian provides the energy levels of the full system as a function of a few effective parameters, but it needs external information regarding the relative values of these parameters. Because the fittings are not univocal, it is crucial to have a reliable set of parameters, coming from as unbiased as possible ab initio calculations, which explains the physics of the system and helps in the rational design of compounds with amazing properties such as those studied in this work.

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Supporting Information Available: Effect of the embedding on the calculated hopping integral and magnetic coupling constant (Table S1 and Figure S1) as well as the validation of the F interactions by means of a computational experiment (Table S2 and Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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