A Theoretical Study of the Exchange Coupling in Hydroxo- and Alkoxo-Bridged Dinuclear Oxovanadium(IV) Compounds

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A density functional study of exchange coupling in hydroxo- and alkoxo-bridged dinuclear oxovanadium(IV) compounds is presented. Coupling constants calculated for full unmodeled structures are in good agreement with experimentally reported values, confirming the ability of the computational strategy used in this work to predict the exchange coupling in dinuclear V^{IV} compounds. The influence of the configuration of the $[VO(\mu\text{-}OR)_2VO]^{2+}$ core in compounds with two edge-sharing octahedrally coordinated oxovanadium(IV) centers, of the nature of the terminal ligands and of structural distortions on the coupling constant have been analyzed through model calculations. The results indicate that the coupling constant is less affected by these factors than for hydroxo- and alkoxo-bridged Cu^{II} compounds. The calculations support the orbital models usually employed in qualitative interpretations of magneto-structural correlations, showing good correlations between the calculated coupling constants and the overlap between the two magnetic orbitals or the square of the orbital gap.

Introduction

The phenomenon of exchange coupling between the spins of unpaired electrons located at different metal atoms in polynuclear complexes leads to magnetic behaviors that differ completely from the one predicted for independent paramagnetic entities. Antiferromagnetic coupling results when the ground state presents an antiparallel alignment of the spins, whereas ferromagnetic coupling is a consequence of the alignment of the electron spins in a parallel manner. Since the discovery of intramolecular antiferromagnetic coupling in copper(II) acetate monohydrate in 1951,[1] much experimental and theoretical work has been carried out to elucidate the mechanism of exchange coupling in polynuclear complexes. This work has led to the now well-established field of molecular magnetism, that is, the synthesis and the study of the magnetic properties of materials based on molecular entities.[2−7]

Dinuclear systems have been the most studied compounds because of their relative simplicity, especially the family of Cu^{II} compounds. This ion, with a d^9 electronic configuration, presents only one unpaired electron per metal atom, and is therefore the simplest case for the analysis of magnetic properties. A large number of compounds with different bridges have been studied and interesting relationships between the magnetic properties and the structural parameters of the bridge have been established, especially for dihydroxo-bridged compounds.[8−12] Such magneto-structural correlations are very useful for predicting magnetic properties of new compounds.

Vanadium(IV) dinuclear complexes constitute another interesting family of compounds for the study of intramolecular exchange coupling since the electronic configuration of V^{IV} is d^1, thus having one unpaired electron per metal center as in Cu^{II} compounds. A considerable number of oxovanadium(IV) dimers have been characterized, since they play an important role in biological processes[13−21] and are also relevant in solid-state chemistry,[22−28] but the established magneto-structural correlations are much fewer than for dinuclear Cu^{II} complexes.

The main difference between the Cu^{II} and V^{IV} cations is in the orbitals in which the unpaired electron is placed. In octahedral or square-planar Cu^{II} systems the unpaired electron is occupying an orbital of the e_g set, with a large contribution of the $d_{x^2-y^2}$ metal orbital, whereas for V^{IV} the only occupied orbital is of t_{2g} symmetry, mainly a d_{xy} metal orbital, if the ligands are placed along the x and y axis and the oxygen atom of the vanadyl group along the z axis. As a consequence, the exchange mechanism in dinuclear Cu^{II} and in dinuclear V^{IV} compounds is expected to be different,

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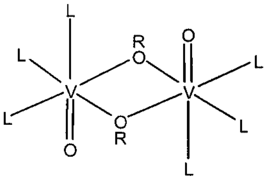
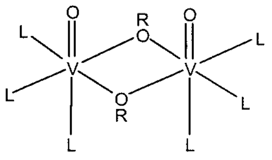
since the $d_{x^2-y^2}$ metal orbital is pointing directly towards the orbitals of the bridging ligands, thus favoring a superexchange mechanism, whereas the d_{xy} metal orbital does not point to orbital ligands, but to the other d_{xy} metal orbital, leading to direct σ overlap between them and resulting in a direct through-space exchange mechanism, as suggested by Ginsberg[29] and other authors.[16,30−33]

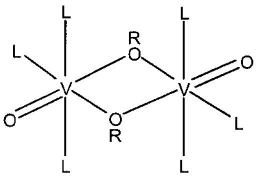
The aforementioned direct exchange mechanism is, however, not effective in all dinuclear V^{IV} compounds, since specific geometric arrangements exist in which a direct overlap between the orbitals that bear the unpaired electron (the so called magnetic orbitals) is not possible. A useful classification of the geometries of the $[VO(\mu\text{-}OR)_2VO]^{2+}$ cores in compounds built from two edge-sharing octahedrally coordinated oxovanadium(IV) centers has been given by Plass.[34] The arrangements are classified (i) according to the orientation of the V=O groups with respect to the bridging plane, that is the plane formed by the two vanadium centers and the two oxo bridging atoms (orthogonal, coplanar or twisted), and (ii) the relative orientation of the two V=O groups (*syn* or *anti*), as shown in **1**−**5**.



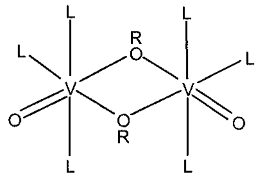
anti-orthogonal (**1**)



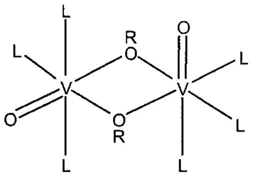
syn-orthogonal (**2**)



anti-coplanar (**3**)



syn-coplanar (**4**)



twisted (**5**)

Many dinuclear V^{IV} complexes have been reported in the two orthogonal[17,32,33,35−38] and the *anti*-coplanar configurations,[34,39−44] but the *syn*-coplanar[44,45] and the twisted arrangements[34,44] are not so frequent. There are also dinuclear V^{IV} complexes in which the metallic centers are five-coordinate in a square-pyramidal environment with the apical position occupied by the oxo group. In such a family of compounds, the classification of Plass can also be applied, the orthogonal geometries being the only possible ones.[16,20,36]

As far as the nature of the exchange coupling is concerned, it has been found that compounds with *anti*-orthogonal, *syn*-orthogonal or *syn*-coplanar configurations (**1**, **2** and **4**) present strong to moderate antiferromagnetic coupling, whereas compounds with *anti*-coplanar and twisted arrangements (**3** and **5**) show weak ferromagnetic coupling (Table 1). These experimental results have been interpreted in a qualitative way regarding the interaction between the magnetic orbitals of each center:[34] for the orthogonal configurations the direct (through-space) exchange mechanism is more effective than the superexchange pathway, and is the predominant mechanism of the exchange interaction. For *syn*-coplanar compounds, the direct exchange mechanism is not as effective as in orthogonal configurations and antiferromagnetic coupling can be qualitatively justified by considering the superexchange mechanism to be operative. For *anti*-coplanar and twisted configurations the situation is, however, different since neither mechanism seems to be effective in mediating the exchange interaction, resulting in a weak ferromagnetic coupling.[34]

Despite the large amount of experimental data for hydroxo- and alkoxo-bridged oxovanadium(IV) dinuclear complexes reported so far, theoretical studies of their magnetic properties are still rare.[34,46−49] Computation of exchange coupling constants for some structures within the density functional theory (DFT) framework has been reported by Plass, reproducing the nature of the coupling for *anti*-orthogonal (antiferromagnetic), *anti*-coplanar and twisted configurations (both ferromagnetic). Other DFT studies of the exchange interaction for hydroxo- and alkoxo-bridged oxovanadium(IV) dinuclear systems exist: (i) an analysis of the effects of the bridging V−O distance, the bridging V−O−V angle and the protonation of the bridging ligands on the coupling constant for a *syn*-coplanar core configuration,[47] and (ii) a study of the exchange interaction in the three phases of vanadyl pyrophosphate, by means of modelization with dinuclear molecular fragments.[48,49]

The aim of this contribution is to examine the exchange coupling phenomenon for hydroxo- and alkoxo-bridged oxovanadium(IV) dinuclear systems by applying a recently developed computational strategy that is able to quantitatively reproduce the coupling constants for a large variety of compounds with different bridging ligands and/or paramagnetic centers.[50−60] We will report first calculations of the exchange coupling constant for a variety of full non-modeled structures to compare them directly with the experimental data. We will then extensively study the exchange coupling in hydroxo-bridged compounds by analyzing the influence of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core geometry on the coupling constant and studying magneto-structural correlations for distortions found in these systems. We will also study the effect of the nature of the terminal ligands on the coupling constant. Finally, we will analyze the effect that some of the aforementioned factors have on the coupling constant in the related alkoxo-bridged compounds.

Table 1. Experimental exchange coupling constants for hydroxo- and alkoxo-bridged dinuclear V^{IV} complexes along with some of their most characteristic structural parameters: the bridging angle, V−O−V; the distance between the V atoms, V···V; the angle that measures the out-of-plane displacement of the H (or R) group from the bridging plane, τ (**7**); and the angle between the bridging plane and the plane formed by the V atom and the other two equatorially coordinated atoms, σ, defined in **6**

Compound	Bridge	Conf.	V−O−V (°)	V···V (Å)	τ (°)	σ (°)	J (cm^{-1})	Refcode	Ref.
A	OH	**1**	101.2	3.03	7.5	25.6	−354	CINKUF	[32]
B	OR	**1**	98.6	3.12	30.0	19.2	−336	DOTQAE	[37]
C	OR	**1**[a]	103.9	3.08	5.0	49.0	−214	PUTBAH	[20]
D	OH	**1**	103.2	3.12	39.2	19.4	−78	RELMAW	[35]
E	OR	**2**[b]	96.0[c]	2.95	37.7[c]	37.6[c]	−424	REPPOR	[36]
F	OH	**2**	98.1[c]	2.97	[d]	25.7[c]	−300	VAFZAD	[33]
G	OR	**2**	99.4[c]	3.08	5.1[c]	20.8[c]	−256	WARBIA	[38]
H	OH	**4**[e]	122.8	3.45	1.3	[f]	−334	YEYGAK	[45]
I	OR	**1**[b]	104.8[c]	3.11	3.1[c]	49.9[c]	−60	YIKZAT	[17]
J	OR	**3**	107.0	3.31	36.6	[f]	+3	ZUFXIH	[34]
K	OR	**5**	104.1[g]	3.22	29.0[g]	29.5	+10.6	ZUFXUT	[34]

[a] One metal ion is six-coordinate and the other one is five-coordinate. [b] The metal ions are five-coordinate. [c] The V−O−V, τ and σ angles are averages of the two different values found in each of these compounds. [d] The position of the H atoms has not been determined in the crystal structure. [e] The values for the structural parameters correspond to the bridge that is not in *trans* position with respect to the oxo ligand. [f] The σ angle is not defined for coplanar configurations. [g] Average of the two significantly different V−O−V (100.1 and 108.0°) and τ (44.1 and 13.8°) angles.

Computational Methodology

Since a detailed description of the computational strategy adopted in this work can be found elsewhere,[51,53,55,59] we will only briefly sketch its most relevant aspects here. Using a phenomenological Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$ to describe the exchange coupling in a dinuclear compound, where J is the coupling constant, and S_1 and S_2 the local spins on centers 1 and 2, respectively, the coupling constant J can be related to the energy difference between states with different spin multiplicity. For the case in which $S_1 = S_2$, the coupling constant may be obtained by using Equation (1), where E_{HS} is the energy of the state with the highest total spin, E_{LS} that of the lowest total spin state ($S = 0$ when $S_1 = S_2$), and S_i are the local spins on each metal atom.

$$E_{HS} - E_{LS} = -2JS_i(S_i + 1/2) \quad (1)$$

It has been found that, when using DFT-based wavefunctions, a reasonable estimate of the energy corresponding to the low spin state, E_{LS}, can be obtained directly from the energy of a broken-symmetry solution, E_{BS}.[53,61] In this case, introducing $S_i = 1/2$ in Equation (1), we arrive at the following expression for J:

$$J \approx E_{BS} - E_{HS} \quad (2)$$

Experience has shown that the use of this equation leads to a good agreement with experimental data for a large variety of compounds with exchange-coupled electrons.[50−60] The inclusion of an unspecified amount of non-dynamic correlation energy in the broken symmetry solution by means of the commonly used functionals is probably responsible for such a good agreement, as pointed out recently by Polo et al.[62]

The hybrid, DFT-based B3LYP method[63] has been used in all calculations as implemented in Gaussian-98,[64] mixing the exact Hartree−Fock exchange with Becke's expression for the exchange functional[65] and using the Lee−Yang−Parr correlation functional.[66] Double-ζ quality basis sets[67] have been employed for all atoms except for the metal ones, for which a triple-ζ basis set[68] with two extra *p* orbitals (polarization functions) has been used. Due to the small magnitude of the exchange coupling constants all energy calculations must be performed including the *SCF=Tight* option of Gaussian to ensure sufficiently well converged values for the state energies.

Results and Discussion

1. Calculations for Full Structures: In order to check the accuracy of the computational procedure employed in this work for the family of hydroxo- and alkoxo-bridged dinuclear V^{IV} complexes, we have performed calculations for several full non-modeled structures with hydroxo and alkoxo bridging ligands in which the metal atom presents distorted square-pyramidal or octahedral coordination environments (Figure 1). We note that the experimental magnetic susceptibility used to obtain the coupling constant is measured from solid samples in which packing forces can induce small deviations from the minimum energy geometry of the individual molecules. In order to be able to compare our computed coupling constants for full structures, we have used in our calculations the molecular structure as determined experimentally by X-ray diffraction rather than an optimized one, in which small changes with respect to the experimental structure could result in significant deviations of the calculated coupling constant.

The results (Table 2) show that there is a fair agreement between calculated and experimental coupling constants, reproducing the sign of the coupling constant in all cases, but obtaining rougher estimations than for other systems studied previously.[55] However, considering that the coupling constants are obtained as energy differences that are

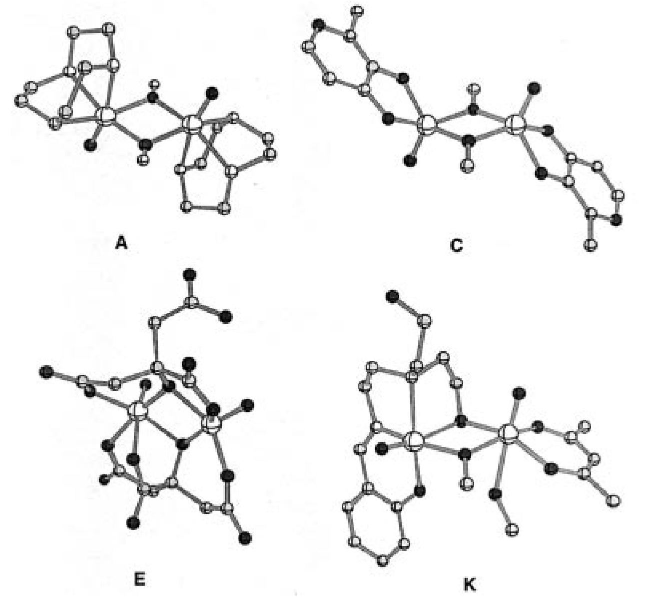


Figure 1. Crystal structures of hydroxo- and alkoxo-bridged dinuclear V^{IV} compounds whose coupling constants have been computed; large white spheres represent V atoms, medium white spheres N atoms, small white spheres H atoms, grey spheres C atoms, and dark spheres O atoms; H atoms of terminal ligands have been omitted for clarity; the labels **A**, **C**, **E** and **K** refer to Entries in Tables 1 and 2

calculated from total energy values eight or nine orders of magnitude larger, these deviations can be considered as acceptable.

2. Exchange Coupling in μ-Hydroxo Compounds: After verifying the agreement between calculated and experimental values of J for full non-modeled structures, we study now the effects of different factors on the coupling constant by performing calculations on a model system. In this model system, the terminal ligands present in experimental structures have been replaced by ammonia molecules (L = NH_3) and idealized structures have been considered. The bond lengths and angles used in the model system are averages of experimental values (see the Appendix). First of all, we analyze the dependence of the exchange coupling on the configuration of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core (**1**−**5**), studying then some magneto-structural correlations for distortions found in this family of compounds. Finally, we have looked at the influence of the terminal ligands on the coupling constant as well.

(a) Influence of the Configurations of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ Core on the Exchange Coupling: Five different configurations of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core in complexes consisting of two edge-sharing octahedrally coordinated V^{IV} centers have been experimentally characterized (**1**−**5**). All the structural parameters are kept the same in the five models in order to study which is the effect of the core

Table 2. Experimental and calculated coupling constants for complete structures of some hydroxo- and alkoxo-bridged dinuclear V^{IV} complexes

Compound	Formula[a]	Conf.	$J_{calcd.}$ (cm^{-1})	$J_{exp.}$ (cm^{-1})	Ref.
A	$[(VO)_2(OH)_2([9]aneN_3)_2]^{2+}$	**1**	−259	−354	[32]
C	$[VO(OCH_3)(ma)]_2$	**1**[b]	−84	−214	[20]
E	$[(VO)_2(cit)(Hcit)]^{3-}$	**2**[c]	−293	−424	[36]
K	$[(VO)_2(Hsabhea)(OCH_3)(HOCH_3)(acac)]$	**5**	+15.4	+10.6	[34]

[a] Abbreviations: $[9]aneN_3$ = 1,4,7-triazacyclononane; H_4cit = citric acid; $H_3sabhea$ = *N*-salicyclidene-2-[bis(2-hydroxyethyl)amino]ethylamine; Hacac = 2,4-pentanedione; ma = maltolato anion. [b] The metal ions are five-coordinate. [c] One metal ion is six-coordinate and the other one is five-coordinate.

Table 3. Computed coupling constants, together with the overlap integrals between BS-OMSOs for hydroxo-bridged model structures **1**−**5** (R = H) presenting different V−O−V angles (and the related V···V distances); the energy of the antiferromagnetic state relative to the minimum of each configuration is also included

Configuration	V−O−V (°)	V···V (Å)	J (cm^{-1})	S_{ab} x 100	$E_{rel.}$ (kcal/mol)
anti-Orthogonal (**1**)	100	3.03	−204	9.86	0.0
	104	3.12	−23.8	4.73	0.5
	108	3.20	+31.0	0.51	3.0
syn-Orthogonal (**2**)	100	3.03	−215	10.7	0.9
	104	3.12	−27.2	5.50	0.0
	108	3.20	+30.9	1.21	1.3
anti-Coplanar (**3**)	100	3.24	+3.7	1.92	6.3
	104	3.33	+7.4	1.18	1.9
	108	3.42	+8.8	0.48	0.0
syn-Coplanar (**4**)	100	3.03	−43.4	2.83	12.1
	104	3.12	−71.0	3.92	5.1
	108	3.20	−93.8	4.64	0.0
Twisted (**5**)	100	3.03	−26.7	0.52	5.9
	104	3.12	−11.7	0.37	2.1
	108	3.20	−3.3	0.25	0.0

configuration on the coupling constant. For each core configuration the V−O−V bridging angle has been varied between 100 and 108°. The calculated coupling constant J, together with the overlap between the broken-symmetry occupied magnetic spin orbitals (BS-OMSOs)[69] S_{ab} and the relative energy of each configuration, are shown in Table 3.

In the orthogonal configurations (**1** and **2**), the calculated coupling constant experiences a significant variation with the V−O−V angle (more than 200 cm^{-1}), becoming more negative — enhanced antiferromagnetic coupling — for smaller values of the V−O−V bridging angle and correspondingly shorter V···V distances. The calculated values for configurations **1** and **2** are very similar, showing the small influence on the coupling constant of the orientation of the V=O groups in orthogonal configurations. These effects can be understood considering that the orbital that bears the unpaired electron is on the basal plane of the axially distorted octahedron, and its mixing with the orbitals of the ligands in the apical positions is very small for symmetry reasons. It is worth noting that the coupling constant for a model compound consisting of two edge-sharing square-pyramidally coordinated $\mathrm{V^{IV}}$ centers in an *anti*-orthogonal configuration with a V−O−V angle of 104° is $-19.7\ \mathrm{cm}^{-1}$, a value that is also in agreement with such an orbital explanation.

On the other hand, there is a much smaller variation of the coupling constant (about 50 cm^{-1}) in the model with *syn*-coplanar configuration (**4**) when the V−O−V angle is varied. Moreover, the angular dependence is opposite to that presented by orthogonal configurations, **1** and **2**, since in **4** the antiferromagnetic coupling decreases when the V−O−V angle becomes smaller. These results are consistent with the existence of different exchange mechanisms between the unpaired electrons located at the metal centers in the orthogonal and the *syn*-coplanar configurations, as suggested previously by other authors.[16,29,31−34,46] The predominant mechanism in orthogonal configurations (**1** and **2**) is direct through-space exchange, because of the important σ overlap between the d_{xy} metal orbitals (Figure 2, a) that becomes larger when the V−O−V angle and the V···V distance decrease. On the other hand, in the *syn*-coplanar configuration (**4**), the direct exchange is not so effective because the overlap between the metal orbitals that bear the unpaired electron is poor due to their relative orientation. In this case, the superexchange mechanism becomes more important since the orbitals of the bridging ligand overlap with the metal orbitals (Figure 2, b). Finally, in the *anti*-coplanar (**3**) and twisted configurations (**5**) the coupling constant is relatively small regardless of the V−O−V angle considered, showing that neither a direct exchange nor a superexchange pathway are important. It is interesting to note, though, that a weak ferromagnetic coupling is predicted for the *anti*-coplanar configuration **3**, whereas for the twisted configuration **5** weak antiferromagnetic coupling is calculated. The expectation of antiferromagnetic coupling contrasts with the experimental finding of ferromagnetic behavior for the twisted configuration **5**.[34,46] In our results we see that although the overlap between BS-OMSOs is small in the twisted configuration, it is non-zero (i.e. the orbitals are not strictly orthogonal), and the antiferromagnetic contribution to the coupling constant is larger than the ferromagnetic one, obtaining as a result a weak antiferromagnetic coupling. This result is, however, consistent with the experimental data because we use an undistorted model structure in our calculations. Distortions of the structure or the effect of terminal ligands can be at the origin of the ferromagnetic behavior shown by compound **K**,[34] whose experimental coupling constant is also well reproduced by our computational method, as shown above (Table 2).

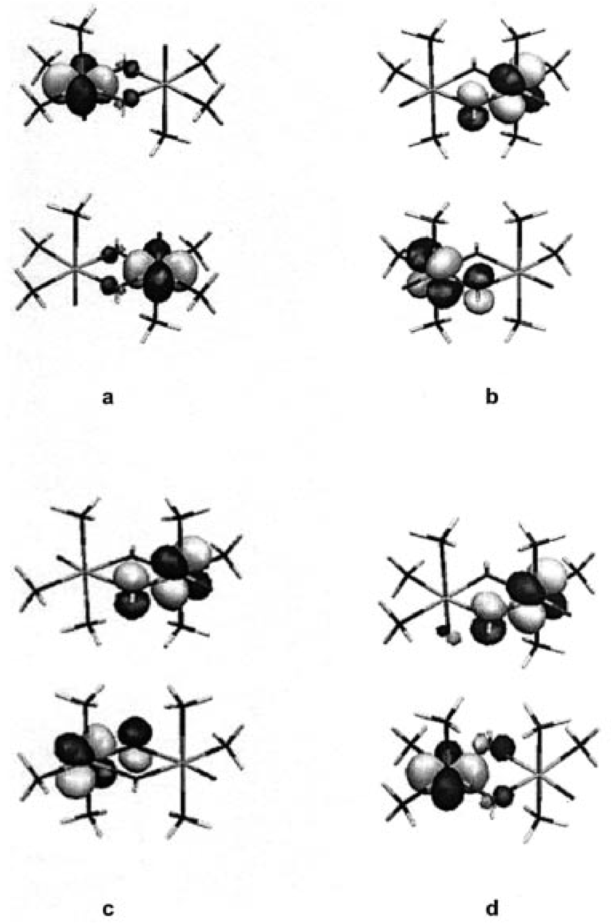


Figure 2. Computed magnetic orbitals (BS-OMSOs) for the *anti*-orthogonal (a), *syn*-coplanar (b), *anti*-coplanar (c) and twisted (d) $[\mathrm{VO(\mu\text{-}OH)_2VO}]^{2+}$ core configurations

Together with the topology of the BS-OMSOs, two additional results support the prevalence of a direct exchange mechanism in orthogonal configurations and of a superexchange mechanism in the coplanar ones. First, a correlation between the type of core arrangement and the V···V distance exists in experimental hydroxo- and alkoxo-bridged oxovanadium(IV) dinuclear compounds: orthogonal configurations present V···V distances up to 3.20 Å, whereas in coplanar and twisted configurations the distance is larger (up to 3.45 Å), hinting to the existence of a through-space interaction in orthogonal configurations that keeps the two metal atoms closer than in the coplanar ones. The other result is related to the sign of the spin population in the high-spin state: in the *syn*-coplanar configuration the spin density at the oxygen atom of the only effective bridge presents the same sign as in the vanadium atoms, showing that the delocalization of the spin density is more important than the spin polarization mechanism and confirming the primacy of superexchange over the direct exchange mechanism in that core configuration. On the other hand, spin polarization predominates at the oxygen atoms of the bridge in orthogonal configurations showing that delocalization through the bridging atoms (i.e. superexchange) is not so effective in this case.

From Table 3 (last column, $E_{\mathrm{rel.}}$), it can also be seen that the type of distortion considered here is possible from the energetic point of view for each of the five configurations studied, since only a few kcal/mol are needed to produce such a distortion. This result is in good agreement with the fact that the experimental structures of hydroxo- and alkoxo-bridged six-coordinate oxovanadium(IV) dinuclear compounds present values for the V−O−V angle over a wide range (Table 1). It is also important to note that the minimum energy for each of the configurations corresponds to a V−O−V angle of 108°, except for the orthogonal configurations in which the minimum energy corresponds to smaller angles.

The dependence of the coupling constant on the core configuration can be rationalized within the framework of the qualitative model proposed by Kahn and coworkers[3,70−76] that results in an expression for the coupling constant dependent on the overlap between non-orthogonal localized magnetic orbitals [Equation (3)].

$$J \approx 2K_{ab} + 4\beta S_{ab} \qquad (3)$$

Here K_{ab} is the exchange integral involving non-orthogonal magnetic orbitals a and b, β the transfer integral and S_{ab} the overlap between the magnetic orbitals as well. The first term in Equation (3) ($2K_{ab}$) is positive and can be interpreted as a ferromagnetic contribution (J_{F}) to the exchange coupling constant, responsible for the stability of the triplet state, whereas the second one ($4\beta S_{ab}$) is negative and represents an antiferromagnetic term (J_{AF}) favoring the singlet state. Since within the Wolfsberg−Helmholtz approximation the transfer integral is proportional to the overlap, $\beta \propto S_{ab}$, then the antiferromagnetic contribution to the coupling constant should be proportional to the square of the overlap between magnetic orbitals, $J_{\mathrm{AF}} \propto S^2_{\mathrm{ab}}$.

Although Equation (3) has been obtained within the framework of the wave function based theory, it has been shown that Kohn−Shan orbitals obtained from density functional calculations are physically sound and suitable for qualitative molecular orbital theory.[77,78] In Figure 3, the values of the coupling constant corresponding to the five core configurations and three different V···V distances (Table 2) are plotted as a function of the square of the overlap between the broken-symmetry occupied magnetic spin-orbitals (BS-OMSOs).[69] We have used BS-OMSOs because they are the most suitable orbitals to represent the so-called *magnetic orbitals* for d^1 centers, since they form a non-orthogonal basis set (a must in Kahn and Briat's model) and are very similar to the localized natural orbitals as well.[79,80] From the linear fittings in Figure 3 we can find estimates for the value of the exchange integral K_{ab} by comparison with Equation (3). The estimated K_{ab} values for the five core configurations are +18.1, +15.1, +4.7, −6.9 and +1.8 cm^{-1} for the *anti*-orthogonal, *syn*-orthogonal, *anti*-coplanar, *syn*-coplanar and twisted configurations (**1**−**5**), respectively. These values are rather small compared to that found for hydroxo-bridged dinuclear $\mathrm{Cu^{II}}$ compounds (+412 cm^{-1}),[51] showing the low ability of hydroxo-bridged dinuclear oxovanadium(IV) compounds to propagate ferromagnetic interactions. It should be noted that although the predicted K_{ab} sign for the *syn*-coplanar configuration is wrong (−6.9 cm^{-1}, whereas K_{ab} must be positive), its value is very small, thus indicating that it must also be a small positive value as has been found for the other configurations.

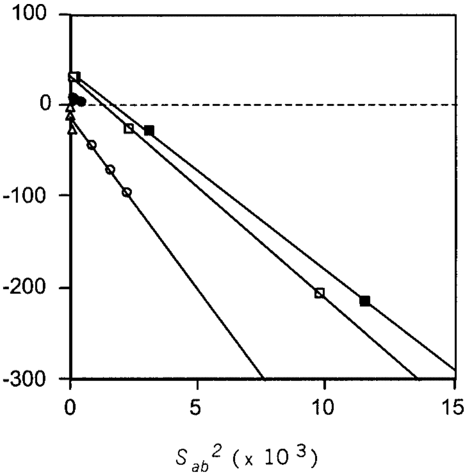
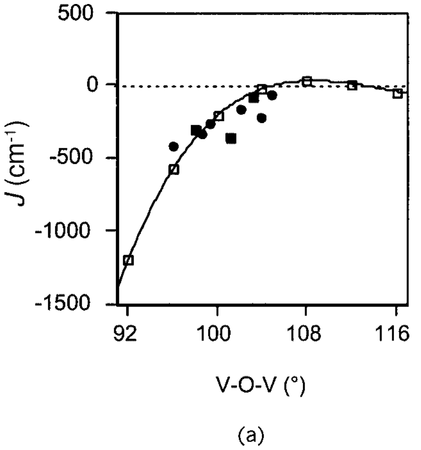


Figure 3. Dependence of the coupling constant J on the square of the overlap integral S^2_{ab} (×1000) between BS-OMSOs for the different $[\mathrm{VO}(\mu\text{-OH})_2\mathrm{VO}]^{2+}$ core configurations (three different V···V distances have been considered for each configuration): *anti*-orthogonal (**1**, solid squares), *syn*-orthogonal (**2**, squares), *anti*-coplanar (**3**, solid circles), *syn*-coplanar (**4**, circles) and twisted (**5**, triangles); linear fittings for the *anti*-coplanar and twisted configurations have been omitted for clarity

(b) Magnetostructural Correlations: The experimental structures for hydroxo- and alkoxo-bridged dinuclear oxovanadium(IV) compounds often deviate from the idealized geometries adopted in our model compounds. In this section we analyze the effect of the most common distortions on the coupling constant.

Effect of the V−O−V Bridging Angle (or the V···V Distance): We have studied exhaustively the dependence of the coupling constant on the V−O−V angle (or what is the same, on the V···V distance, since the V−O distance has been kept frozen), but in this section we consider only the orthogonal configurations **1** and **2**. We have checked that the variation of J with the V−O−V angle for each of the orthogonal configurations is almost identical, in good



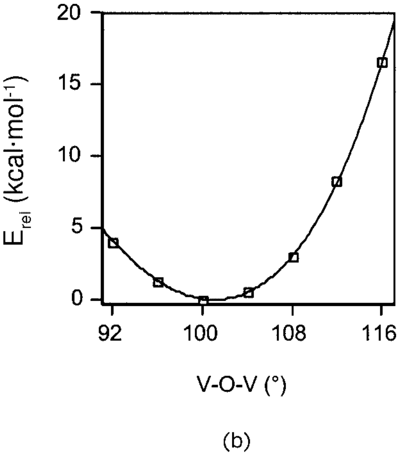


Figure 4. (a) Dependence of the calculated coupling constant J (solid line) on the bridging V−O−V angle for the model compound with an *anti*-orthogonal core configuration (**1**); black squares and circles correspond to experimental values for hydroxo- and alkoxo-bridged compounds, respectively; (b) relative energy of the ground state as a function of the V−O−V bridging angle

agreement with the simple two electrons—two orbitals approximation. In Figure 4 the results corresponding to the *anti*-orthogonal configuration are presented. From Figure 4 (a) it can be seen that strong antiferromagnetic coupling appears at small V−O−V angles (i.e. short V···V distances), as a consequence of the increased through-space overlap between the metal orbitals. This strong antiferromagnetic coupling drops sharply and becomes weakly ferromagnetic at V−O−V angles between 104° and 110° (i.e. V···V distances between 3.12 and 3.20 Å) reaching a maximum at about 108° (3.20 Å). The ferromagnetic coupling appears at much larger V−O−V angles than in the case of hydroxo-bridged dinuclear copper(II) compounds (at about 98°).[9,51] The experimental values of the coupling constant for hydroxo- and alkoxo-bridged compounds fit very well with our theoretical prediction (Figure 4a). As can be seen in Figure 4 (b), the minimum energy corresponds to the structure with a V−O−V angle of 100°. Structures with V−O−V angles ranging from 92° to 110° (V···V distances from 2.85 to 3.24 Å) are however possible (less than 5 kcal/mol), in good agreement with the fact that experimental structures present V···V distances within this range of values, as can be seen in Table 1 (configuration **1** and **2**).

The dependence of the coupling constant on the V−O−V angle for orthogonal configurations has also been analyzed by means of the qualitative model proposed by Hay, Thibeault and Hoffmann (HTH).[81] These authors obtained an approximate expression for the coupling constant of a homodinuclear complex with two unpaired electrons that predicts that the antiferromagnetic contribution to the coupling constant depends on the square of the orbital gap according to Equation (4), where K_{ab}, J_{aa}, and J_{ab} are the exchange and Coulomb integrals involving orthogonal localized orbitals a and b, and ε_1 and ε_2 are the energies of the two SOMOs of the complex.

$$E_S - E_T = J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}} \tag{4}$$

A plot of J versus the square of the orbital gap for the *anti*-orthogonal configuration **1** is shown in Figure 5. It can be seen that the linear relation predicted by HTH holds for the hydroxo-bridged oxovanadium(IV) models studied here if the occupied magnetic spin orbitals (OMSOs)[69] are considered. An almost identical behavior is found when the *syn*-orthogonal configuration **2** is considered (not shown in Figure 5). The estimated values for K_{ab} are +13.9 and +14.7 cm^{-1} for **1** and **2**, respectively. These values are very similar to the ones predicted in Kahn and Briat's model for these core configurations (+18.1 and +15.1 cm^{-1} for **1** and **2**, respectively). Within the HTH model, it is also possible to estimate the value of ($J_{aa} - J_{ab}$) — 6.5 × 10^4 and 6.3 × 10^4 cm^{-1} for **1** and **2**, respectively — which are similar to that found for hydroxo-bridged dinuclear Cu^{II} compounds (7.2 × 10^4 cm^{-1}).[51,58]

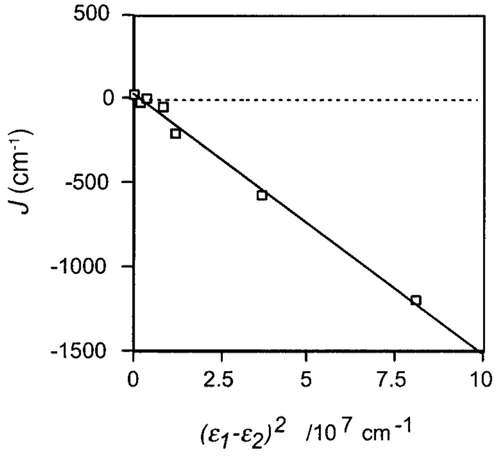
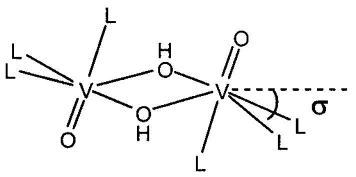


Figure 5. Dependence of the coupling constant J on the square of the energy gap between the two OMSOs for model compounds with an *anti*-orthogonal core configuration (**1**) at different values of the V−O−V bridging angle

Effect of Bending of the Terminal Ligands: The experimental structures of some compounds with orthogonal core configurations are distorted with respect to the idealized model in the way shown in **6**.



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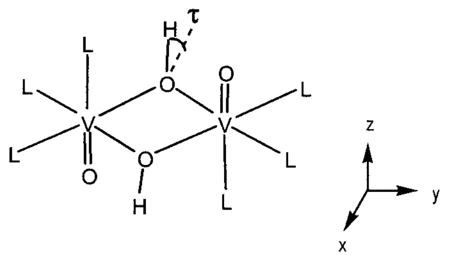
To study the effect of the angle σ on the coupling constant, we have performed calculations using model compounds that present an *anti*-orthogonal core configuration (**1**), keeping other structural parameters constant (a value of 104° has been taken for the V−O−V bridging angle). An increase of the antiferromagnetic coupling constant is found when σ changes from 0° (-23.8 cm^{-1}) to 30° (-86.4 cm^{-1}). This result can be rationalized by means of the HTH model since an increase in the orbital gap between OMSOs appears when the structure is distorted in this way. It is also seen that the most stable structure corresponds to that with a σ angle between 10° and 20°, in good agreement with most of the experimental structures, which present values for the σ angle of approximately 20° (Table 1). It is, however, very difficult to check the accuracy of the theoretically predicted dependence of the coupling constant on σ because J also depends on other structural parameters (especially on the V−O−V angle or the equivalent V···V distance) that change significantly from one structure to another.

Effect of the Orientation of the Bridge: We have also studied the dependence of the coupling constant on the displacement of hydrogen atoms out of the V_2O_2 plane for structures with an *anti*-orthogonal configuration (**1**). This type of distortion, commonly found for this family of compounds, can be represented by the structural parameter τ (**7**). The other structural parameters have been kept constant (V−O−V = 104°). A change in the nature of the magnetic coupling is found at an angle of about 20° (Figure 6), reaching a maximum of $J \approx +60$ cm^{-1}, a small value in good agreement with the predictions of qualitative models. This type of distortion is energetically possible since less than 5 kcal/mol are required to reach a τ angle of 50°, in good agreement with experimental data, where it is possible to find τ angles ranging from about 0° to 40° (Table 1).



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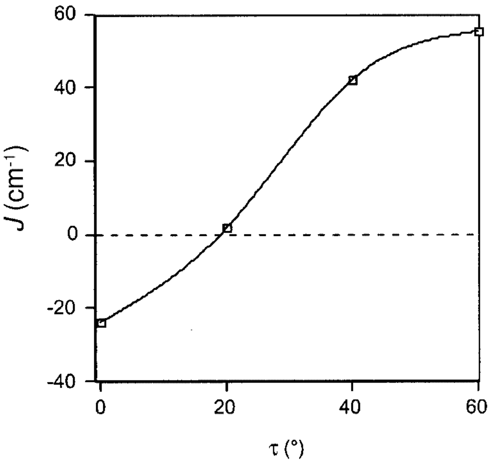

Figure 6. Dependence of the coupling constant J on the τ angle for the model compound with an *anti*-orthogonal core configuration (**7**)

(c) Influence of the Terminal Ligands on the Exchange Coupling Constant: The effect of changing the terminal ligands has been previously studied for several families of dinuclear Cu^{II} compounds.[50,57,59] To explain the observed shifts in the coupling constant, a detailed analysis of the magnetic orbitals for each particular case is needed and no general rules can be established.

We have studied this effect on the coupling constant of dinuclear oxovanadium(IV) compounds for two different core configurations, *anti*-orthogonal (**1**) and *syn*-coplanar (**4**). Ammonia (NH_3) and aqua (H_2O) terminal ligands have been used for the present analysis since most of the known experimental structures present N-donor and/or O-donor ligands. A value of 104° for the V−O−V angle has been employed in the model compounds. A rather small influence on the coupling constant is observed, the antiferromagnetic coupling decreasing in the *anti*-orthogonal configuration (from -23.8 to -10.0 cm^{-1}) and increasing in the *syn*-coplanar one (from -71.0 to -80.1 cm^{-1}) when ammonia is replaced by aqua ligands. This minute effect of the terminal ligands can be rationalized by the small contribution of the donor (N or O) atomic orbitals to the OMSOs: both ammonia and aqua ligands are σ-donor ligands whereas the metal orbitals that contribute to the OMSOs are of a π nature.

3. Exchange Coupling in μ-Alkoxo Compounds: Finally, we have also studied how the exchange coupling is affected by the replacement of the hydroxo bridges by alkoxo groups. We have modeled the alkoxo bridging ligands by methoxy groups (see Appendix), maintaining for the rest of the structural parameters the same values as those used in hydroxo-bridged models.

The results (Table 4) show that no significant differences appear when the hydroxo bridging ligands are replaced by methoxy groups, in contrast to the behavior found for dinuclear Cu^{II} compounds, in which an important enhancement of the antiferromagnetic coupling occurs.[51] The most

Table 4. Computed coupling constants, together with the relative energy of the antiferromagnetic state for methoxo-bridged model structures **1−5** (R = Me) presenting different V−O−V angles (and the related V···V distances)

Configuration	V−O−V (°)	V···V (Å)	J (cm^{-1})	$E_{\text{rel.}}$ (kcal/mol)
anti-Orthogonal (**1**)	100	3.03	−196	0.0
	104	3.12	−13.9	0.7
	108	3.20	+34.4	3.3
syn-Orthogonal (**2**)	100	3.03	−208	0.8
	104	3.12	−17.6	0.0
	108	3.20	+34.9	1.4
anti-Coplanar (**3**)	100	3.24	+8.8	4.9
	104	3.33	+11.4	1.2
	108	3.42	+12.0	0.0
syn-Coplanar (**4**)	100	3.03	−72.9	10.7
	104	3.12	−109	4.2
	108	3.20	−137	0.0
Twisted (**5**)	100	3.03	−24.0	5.1
	104	3.12	−11.3	1.6
	108	3.20	−4.1	0.0

notable changes, even though not very significant, correspond to structures with *syn*-coplanar configurations, which show a moderate increase in the antiferromagnetic coupling constant, and the *anti*-coplanar ones, in which a slight increase of the ferromagnetic coupling is found. In orthogonal configurations, the results are almost identical to those found for hydroxo-bridged systems (the experimental alkoxo-bridged compounds fit well in the predicted dependence of J on the V−O−V angle for hydroxo-bridged model compounds, Figure 4a). The coupling constant for a model compound consisting of two edge-sharing square-pyramidally coordinated V^{IV} centers in an *anti*-orthogonal configuration, with a V−O−V angle of 104°, has been predicted to be -7.5 cm^{-1}, a value that is also similar to that in hydroxo-bridged compounds (-19.7 cm^{-1}), if somewhat smaller. Consistently, no significant differences in the experimental coupling constants are found when replacing the bridging hydroxo by alkoxo groups, and the structural parameters that play an important role in the magnetic coupling of the complexes are not very different (Table 1).

The different behavior of dinuclear V^{IV} complexes compared to that of the Cu^{II} ones is related to the predominant mechanism of exchange interaction for each family of compounds. In Cu^{II} complexes superexchange is the main mechanism and, as a consequence, the larger the orbital delocalization through the bridging ligands, the stronger the antiferromagnetic coupling. This explains the considerable enhancement of antiferromagnetic coupling when hydroxo bridging ligands are replaced by methoxo ones.[51] For V^{IV} complexes with orthogonal core configurations, the direct through-space interaction between metal orbitals is the prevalent mechanism, thus making the nature of the bridging ligands much less important. For V^{IV} complexes with *syn*-coplanar configurations, superexchange is more important than in orthogonal configurations, but still much less than in Cu^{II} complexes, thus having an intermediate behavior: a moderate enhancement of the antiferromagnetic coupling when the hydroxo bridging ligands are replaced by alkoxo ligands.

As far as the energetic cost of the V−O−V angle distortion is concerned, we obtain similar results to those found for hydroxo-bridged compounds (Table 4): (i) a few kcal/mol are needed to perform such a distortion, and (ii) the minimum energy structures present smaller V−O−V angles for orthogonal configurations **1** and **2**.

The magneto-structural correlation for the distortion corresponding to a displacement of the R group of the alkoxo bridges out of the bridging plane (**7**) has also been studied for a model structure with an *anti*-orthogonal core configuration (with an V−O−V angle of 104°). An almost identical behavior as for hydroxo-bridged compounds has been found: a change in the nature of the coupling, becoming ferromagnetic at a τ angle of about 10° and reaching a maximum of $+56$ cm^{-1} at $\tau = 40°$. It has been seen that this type of distortion is energetically possible as well: the most stable structures are the ones with τ angles about 20°, and less than 7 kcal/mol are needed to reach τ values of 40°.

Conclusions

The present contribution confirms that the computational strategy — based on density functional theory — employed to investigate the exchange coupling in hydroxo- and alkoxo-bridged dinuclear oxovanadium(IV) compounds provides fair estimates of their experimental coupling constants. With its moderate demand for computer time, it also permits us to investigate separately the effect on the coupling constant of the different types of core arrangements that exist in $[VO(\mu\text{-}OH)_2VO]^{2+}$ compounds, as well as the influence of the nature of terminal and bridging ligands and the magneto-structural correlations corresponding to the most common distortions for this family of compounds. The results confirm that different exchange mechanisms predominate in orthogonal (through-space mechanism) and coplanar configurations (superexchange mechanism). This is a consequence of the dissimilar topology of the OMSOs in each geometrical configuration. Qualitative orbital models (Kahn−Briat and Hay−Thibeault−Hoffmann) are seen to be useful in analyzing the results, giving estimates for the ferromagnetic contribution to the exchange coupling in this family of compounds. A minute influence of the nature of the terminal ligand on the coupling constant has been found, a consequence of the σ-donor character of N- and O-donor ligands considered, opposed to the π nature of the interacting electrons.

Regarding the magneto-structural correlations, a very strong antiferromagnetic coupling is found for structures that present short V···V distances when orthogonal configurations are considered, a result related to the important overlap between BS-OMSOs in such configurations. Another interesting finding is the small effect of the displacement of the hydrogen atom of the bridge out of the plane on the coupling constant, that induces a change in the nature of the coupling (from antiferromagnetic to ferromagnetic), but that is not as important as in the case of hydroxo-bridged dinuclear Cu^{II} compounds. Finally, it is worth mentioning that important changes in the coupling are not found when the hydroxo bridging ligands are replaced by alkoxo groups, a result that differs from the behavior shown by dinuclear Cu^{II} compounds, in which an important increase in the antiferromagnetic coupling occurs.

Appendix

The bond lengths and angles used for model compounds are: 1.59 Å for the V=O bond; 1.98 Å for V−O (2.24 Å when the O bridging atom is in the *trans* position with respect to the oxo O-atom); 2.11 Å for V−N (2.34 Å when the N atom is *trans* with respect to the oxo O-atom); 0.85 Å for O−H; a value of 104° for the V−O−V bridging angle; and 91.5° for N−V−N. The N−H distance within the ammonia ligands is 1.02 Å and the H−N−H angle is 109°. For alkoxo-bridged compounds: 1.43 and 0.98 Å for O−C and C−H distances, respectively and 109° for the H−C−O angle.

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[1] B. Guha, *Proc. Roy. Soc.* **1951**, *206*, 353.
[2] O. Kahn, Y. Pei, Y. Journaux, *Inorganic Materials*, John Wiley & Sons, Chichester, **1992**.
[3] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**.
[4] O. Kahn, *Magnetism: A Supramolecular Function NATO ASI Series, Vol. 484*, Kluwer, Dordrecht, **1996**.
[5] D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio, *Magnetic Molecular Materials*, Kluwer Academic, Dordrecht, **1991**.
[6] J. S. Miller, M. Drillon, *Magnetism: Molecules to Materials, Vol. 1 and 2*, Wiley-VCH, Weinheim, **2001**.
[7] E. Coronado, P. Delhaes, D. Gatteschi, J. S. Miller, *Magnetic Molecular Materials: From Molecular Assemblies to the Devices NATO ASI Series, Vol. 321*, Kluwer, Dordrecht, **1996**.
[8] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, W. E. Hatfield, *Inorg. Chem.* **1976**, *15*, 2107.
[9] D. J. Hodgson, *Prog. Inorg. Chem.* **1975**, *19*, 173.
[10] E. D. Estes, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1974**, *13*, 1654.
[11] D. L. Lewis, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1972**, *11*, 2216.
[12] T. P. Mitchell, W. H. Bernard, J. R. Wasson, *Acta Crystallogr., Sect. B* **1970**, *26*, 2096.
[13] A. Butler, C. J. Carrano, *Coord. Chem. Rev.* **1991**, *109*, 61.
[14] N. D. Chasteen, *Vanadium in Biological Systems*, Kluwer Academic Publishers, Dordrecht, **1990**.
[15] D. Rehder, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 148.
[16] C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies, V. L. Pecoraro, *Inorg. Chem.* **1990**, *29*, 944.
[17] S. L. Castro, M. E. Cass, F. J. Hollander, S. L. Bartley, *Inorg. Chem.* **1995**, *34*, 466.
[18] W. R. Harris, C. J. Carrano, *J. Inorg. Biochem.* **1984**, *22*, 201.
[19] Y. Sun, B. R. James, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1996**, *35*, 1667.
[20] Y. Sun, M. Melchior, D. A. Summers, R. C. Thompson, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1998**, *37*, 3119.
[21] M. R. Bond, L. M. Mokry, T. Otieno, J. Thompson, C. J. Carrano, *Inorg. Chem.* **1995**, *34*, 1894.
[22] G. Villeneuve, P. Amorós, D. Beltrán, M. Drillon, *Organic and Inorganic Low-Dimensional Crystalline Materials*, Plenum, New York, **1987**, Vol. B168.
[23] G. Villeneuve, K. H. Suh, P. Amorós, N. Casañ-Pastor, D. Beltrán-Porter, *Chem. Mater.* **1992**, *4*, 108.
[24] O. Centi, F. Trifiro, J. R. Ebner, V. M. Franchetti, *Chem. Rev.* **1988**, *88*, 55.
[25] D. Beltrán, P. Amorós, R. Ibañez, E. Martinez, A. Beltrán, A. LeBail, G. Ferey, G. Villeneuve, *Solid State Ionics* **1989**, *32−33*, 57.
[26] D. Beltrán-Porter, A. Beltrán-Porter, P. Amorós, R. Ibañez, E. Martinez, A. LeBail, G. Ferey, G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 131.
[27] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, **1983**.
[28] V. M. Day, W. G. Klemperer, *Science* **1985**, *228*, 533.
[29] A. P. Ginsberg, E. Koubek, H. J. Williams, *Inorg. Chem.* **1966**, *5*, 1657.
[30] E. F. Hasty, T. J. Colburn, D. N. Hendrickson, *Inorg. Chem.* **1973**, *12*, 2414.
[31] A. Syamal, *Coord. Chem. Rev.* **1975**, *16*, 309.
[32] K. Wieghardt, U. Bossek, K. Volckmar, W. Swiridoff, J. Weiss, *Inorg. Chem.* **1984**, *23*, 1387.
[33] A. Neves, K. Wieghardt, B. Nuber, J. Weiss, *Inorg. Chim. Acta* **1988**, *150*, 183.
[34] W. Plass, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 627.
[35] N. S. Dean, M. R. Bond, C. J. O′Connor, C. J. Carrano, *Inorg. Chem.* **1996**, *35*, 7643.
[36] S. Burojevic, I. Shweky, A. Bino, D. A. Summers, R. C. Thompson, *Inorg. Chim. Acta* **1996**, *251*, 75.
[37] A. S. Ceccato, A. Neves, M. A. de Brito, S. M. Drechsel, A. S. Mangrich, R. Werner, W. Haase, A. Bortoluzzi, *J. Chem. Soc., Dalton Trans.* **2000**, 1567.
[38] R. Das, K. K. Nanda, A. K. Mukherjee, M. Mukherjee, M. Helliwell, K. Nag, *J. Chem. Soc., Dalton Trans.* **1993**, 2241.
[39] F. Jiang, O. P. Anderson, S. M. Miller, J. Chen, M. Mahroof-Tahir, D. C. Crans, *Inorg. Chem.* **1998**, *37*, 5439.
[40] X. Li, M. S. Lah, V. Pecoraro, *Inorg. Chem.* **1988**, *27*, 4657.
[41] M. E. Cass, D. L. Greene, R. M. Buchanan, C. G. Pierpont, *J. Am. Chem. Soc.* **1983**, *105*, 2680.
[42] M. Velayutham, B. Varghese, S. Subramanian, *Inorg. Chem.* **1998**, *37*, 1336.
[43] Z.-H. Zhou, H.-L. Wan, S.-Z. Hu, K.-R. Tsai, *Inorg. Chim. Acta* **1995**, *237*, 193.
[44] W. Plass, *Inorg. Chem.* **1997**, *36*, 2200.
[45] M. I. Khan, Y.-D. Chang, Q. Chen, J. Salta, Y.-S. Lee, C. J. O′Connor, J. Zubieta, *Inorg. Chem.* **1994**, *33*, 6340.
[46] W. Plass, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1290.
[47] L. Zhang, Z. Chen, *Chem. Phys. Lett.* **2001**, *345*, 353.
[48] L. M. Lawson Daku, S. Borshch, V. Robert, B. Bigot, *Phys. Rev. B* **2001**, *63*, 174439.
[49] S. Petit, S. A. Borshch, V. Robert, *J. Am. Chem. Soc.* **2002**, *124*, 1744.
[50] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *Inorg. Chem.* **1997**, *36*, 3683.
[51] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297.
[52] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122.
[53] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* **1999**, *20*, 1391.

[54] E. Ruiz, S. Alvarez, P. Alemany, *Chem. Commun.* **1998**, 2767.
[55] E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, in *Magnetism: Molecules to Materials, Vol. 2* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 227−279.
[56] A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem. Eur. J.* **2001**, *7*, 627.
[57] J. Cano, P. Alemany, S. Alvarez, M. Verdaguer, E. Ruiz, *Chem. Eur. J.* **1998**, *4*, 476.
[58] J. Cano, E. Ruiz, P. Alemany, F. Lloret, S. Alvarez, *J. Chem. Soc., Dalton Trans.* **1999**, 1669.
[59] J. Cano, A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem. Eur. J.* **2000**, *6*, 327.
[60] A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, A. Scuiller, C. Decroix, V. Marvaud, J. Vaissermann, M. Verdaguer, I. Rosenman, M. Julve, *Inorg. Chem.* **2001**, *40*, 5868.
[61] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.
[62] V. Polo, E. Kraka, D. Cremer, *Theor. Chem. Acc.* **2002**, *107*, 291.
[63] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[64] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Ciolowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. A. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Gaussian, Inc., Pittsburgh, PA, **1998**.
[65] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[66] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[67] A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.
[68] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.
[69] C. Desplanches, E. Ruiz, A. Rodríguez-Fortea, S. Alvarez, *J. Am. Chem. Soc.* **2002**, *124*, 5197.
[70] O. Kahn, B. Briat, *J. Chem. Soc., Faraday Trans. 2* 1976, *72*, 1441.
[71] O. Kahn, B. Briat, *J. Chem. Soc., Faraday Trans. 2* 1976, *72*, 268.
[72] O. Kahn, B. Briat, J. Galy, *J. Chem. Soc., Dalton Trans.* **1977**, 1453.
[73] O. Kahn, M. F. Charlot, *Nouv. J. Chim.* **1980**, *4*, 567.
[74] O. Kahn, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 834.
[75] C. Kollman, O. Kahn, *Acc. Chem. Res.* **1993**, *26*, 259.
[76] J. J. Girerd, Y. Journaux, O. Kahn, *Chem. Phys. Lett.* **1981**, *82*, 534.
[77] E. J. Baerends, O. V. Gritsenko, *J. Phys. Chem. A* **1997**, *101*, 5383.
[78] R. Stowasser, R. Hoffmann, *J. Am. Chem. Soc.* **1999**, *121*, 3414.
[79] A. Rodríguez-Fortea, E. Ruiz, P. Alemany, S. Alvarez, manuscript to be submitted.
[80] J. Cabrero, C. J. Calzado, D. Maynau, R. Caballol, J. P. Malrieu, *J. Phys. Chem. A* **2002**, *106*, 8146.
[81] P. J. Hay, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1975**, *97*, 4884.

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