# Ab Initio Calculation of the Ferromagnetic Interaction in a $Cu^{II}V^{II}O$ Heterodinuclear System

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**Abstract:** The heterodinuclear compound $CuVO(fsa)_2en{\cdot}CH_3OH$, where $(fsa)_2en^{4-}$ is the dinucleating ligand derived from the Schiff base *N,N'*-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane, is a classical example of an exchange-coupled system in which the experimentally observed ferromagnetic interaction (singlet-triplet splitting $J = 120$ cm$^{-1}$) has been attributed to the strict orthogonality of the magnetic orbitals. In order to specify the mechanism of the phenomenon, $J$ has been calculated in an ab initio scheme on a slightly idealized molecular structure with a $C_s$ symmetry. The two magnetic orbitals have been obtained through an ab initio SCF-MO calculation on the open-shell system, using pseudopotentials. As expected, the magnetic orbital centered on copper(II) is antisymmetric and that centered on vanadium(IV) is symmetric with regard to the mirror plane. $J$ has been directly obtained by a perturbation expansion of the configuration interaction problem. The first-order potential exchange term $2K_{ab}$ has been found as 623 cm$^{-1}$. The second-order kinetic exchange term is exactly zero due to the fact that the magnetic orbitals do not transform in the same way as the irreducible representation of $C_s$. Globally, the second-order terms have been found equal to $-279$ cm$^{-1}$, which does not compensate the zeroth-order ferromagnetic contribution. The calculated $J$ value has been found as $+344$ cm$^{-1}$. Finally, the strategy of strict orthogonality of the magnetic orbitals to design molecular systems in which the ground state has the highest spin multiplicity has been discussed in the light of results of our calculation.

One of the main challenges in the field of molecular materials is the design of molecule-based systems ordering ferromagnetically below a critical temperature $T_c$.[1-7] Such a situation may occur when the balance of the interactions between the magnetic centers within the crystal lattice leads to a noncompensation of the local spins. The first idea that came to mind to obtain such a situation is to favor the parallel alignment of the spins between nearest neighbors. A strategy has been proposed for this, based on the concept of orthogonality of the magnetic orbitals.[7-11] Let us recall the broad outlines of this strategy. For that we consider a pair A-B of nearest neighbor magnetic centers. We assume that the local ground states of A and B are characterized by the local spins $S_A$ and $S_B$, respectively, and have no first-order angular momentum. It follows that we have $n_A = 2S_A$ unpaired electrons around A occupying $n_A$ magnetic orbitals $a_\mu$ and $n_B = 2S_B$ unpaired electrons around B occupying $n_B$ magnetic orbitals $b_\nu$. $a_\mu$ transforms as $\Gamma^a_\mu$ and $b_\nu$ as $\Gamma^b_\nu$ irreducible representations of the point symmetry group adapted to the A-B pair. The magnetic orbitals are said to be strictly orthogonal if $\Gamma^a_\mu$ and $\Gamma^b_\nu$ are different for any couple $\mu$ and $\nu$. In such a case, it has been stated that the interaction between A and B was purely ferromagnetic with a $S = S_A + S_B$ ground state. Qualitatively, this stabilization of the pair state of highest spin multiplicity has been explained as follows:[7] owing to the orthogonality of the local functions $a_\mu$ and $b_\nu$, it is not possible to form low-energy molecular orbitals, delocalized on the whole pair A-B, on which the magnetic electrons would pair. Therefore, Hund's rule holds and the parallel spin state has the lowest energy.

In the last few years, several dinuclear systems have been reported, in which this strict orthogonality has been carried out and, in any case, as expected, the ground state was the state of highest spin multiplicity.[8-11] The classical example of this is provided by the $CuVO(fsa)_2en{\cdot}CH_3OH$ compound, of which the structure is recalled in Figure 1. The two metal ions copper(II) and vanadium(IV) as well as the oxygen atoms of the vanadyl group and of the methanol molecule weakly bound to copper are located in a pseudo mirror plane perpendicular to the plane of the macrocycle. Pseudo, here means that this plane is not a crystallographic plane; however, the molecular symmetry is very close to $C_s$. From elementary ligand field consideration, it is obvious to see that the unpaired electron around copper(II) is described by a $xy$-type magnetic orbital transforming as a″ and that around vanadium(IV) by a $x^2-y^2$-type magnetic orbital transforming as a′. Therefore, the strict orthogonality is achieved and actually the triplet state has been found to be the lowest with a ground triplet-excited singlet separation of 120 cm$^{-1}$. Moreover, the magnitude of the ferromagnetic interaction has been related to the presence of strong extrema of the overlap density between the magnetic around the bridging oxygen atoms.[8]

Implicitly, this strategy of strict orthogonality lies on a model where the interaction parameter $J$ can be decomposed into ferromagnetic $J_F$ and an antiferromagnetic $J_{AF}$ contributions, with $J = J_F + J_{AF}$. In this model, $J_F$ is governed by the two-electron exchange integrals involving the magnetic orbitals and $J_{AF}$ by the overlap and transfer integrals.[12] If we refer to Anderson's formalism, $J_F$ is the potential exchange term and $J_{AF}$ the kinetic exchange term.[13] This latter term actually vanishes when all the magnetic orbitals are orthogonal. However, since the recent ab

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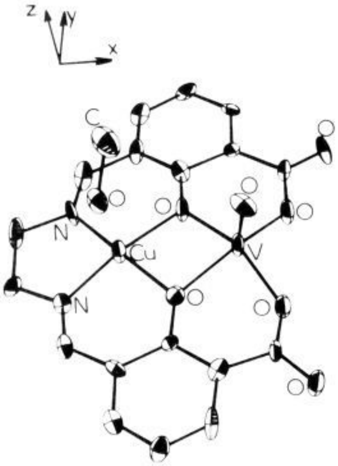

**Figure 1.** Perspective view of the structure of $CuVO(fsa)_2en{\cdot}CH_3OH$.

initio calculations on exchange coupled copper(II) dinuclear compounds, it is now well established that other terms may significantly contribute to the energy gaps between low-lying states.[14-20] In the perturbational formalism used in this paper (vide infra), these terms are defined as the double spin polarization, the metal → ligand and ligand → metal charge transfers, the kinetic exchange + polarization, etc.... In all the copper(II) dinuclear compounds studied so far, the balance of these additional terms is negative, i.e., in favor of the antiferromagnetic interaction, even if some of them may be positive.[14-19] Moreover, in some cases, this negative balance takes over on the potential exchange term. Therefore, it seemed important to us to see the contribution of these terms with regard to the potential exchange term in the case of $CuVO(fsa)_2en{\cdot}CH_3OH$.

The main goal of this paper is, from an ab initio calculation, to test the strategy of orthogonality of the magnetic orbitals, of which the theoretical background has not yet been fully explored. Another goal is to extend our perturbation approach of the singlet–triplet (S–T) splitting to nonsymmetrical exchange-coupled dinuclear systems. The paper is organized as follows: The next section deals with the calculation methods of the S–T splitting in dinuclear compounds involving two interacting local doublet states. The following section presents the computational aspects, the SCF results, and the S–T splitting analysis. Finally, the last section is devoted to the discussion of the results.

## Calculation Methods

The ab initio calculation of the singlet–triplet splitting $J$ in exchange coupled copper(II) dinuclear compounds recently has been the subject of several investigations.[14-23] Direct applications of standard quantum chemistry methods face the difficult problem of evaluating a small quantity ($|J| < 500$ cm$^{-1}$) as the difference between very large numbers. Especially cumbersome is the correlation energy calculation, which requires large molecular basis sets and very long configuration interaction (CI) expansions. To the author's knowledge such a direct approach has only been applied to the model system $[Cu_2Cl_2X_4]^{2-}$ where X is a pure negative charge which is supposed to represent the out of the bridge ligands.[21] Other methods are based on broken symmetry single configuration UHF calculations and relate $J$ to the difference between the UHF energy of this broken symmetry single configuration solution and the UHF energy of the highest multiplet.[23] The necessary UHF calculations are generally made within the $X_\alpha$ approximation scheme. A related approach using the projected UHF method[24] has been proposed by Yamaguchi et al., and ab initio and semiempirical tests have been made on magnetically interacting organic compounds.[25-27] They mention[25] that dynamical correlation effects could have a non-negligeable impact on the $J$ value.

De Loth and co-workers[14] have proposed a different approach which is simply related to a remark by Malrieu.[28] He showed that by using ordinary Rayleigh–Schrödinger perturbation theory it was not necessary to calculate the total correlation energy of both the singlet and triplet states but rather it was possible to get a direct expression for the energy differences between those states. Another very interesting aspect of this method is the clear physical meaning that can be given to the many processes appearing in the perturbation development.[15]

Since the first reported calculation on copper(II) acetate,[14] the influence of the calculation ingredients on the final $J$ value (namely the molecular basis set choice, the modelization of the ligands) has been studied and series of compounds have been investigated.[16-20] Although the limitation of the perturbation development to second order (which is a sine qua non condition for the study of real complexes) may cause some problems, a reasonable overall agreement between calculated and experimental values of $J$ has been consistently reported. Another positive point is the fact that the variation of $J$ in chemically related series of compounds is well reproduced (see for instance the work by Nepveu et al.[18]); this strongly indicates that the method takes into account the main effects produced by varying the chemical environment of the metal atoms. In a forthcoming paper[29] a more detailed analysis of the convergence of the perturbation series will be reported, along with comparisons with other methods. The procedure has been applied so far to centrosymmetrical copper(II) dinuclear complexes. Its extension to compounds in which the two copper(II) chromophores are related through another symmetry element, a mirror plane or a 2-fold axis, is straightforward. On the other hand, in $CuVO(fsa)_2en{\cdot}CH_3OH$, the $Cu^{II}$ and $V^{II}O$ chromophores are obviously independent, which leads to some differences with regard to the preceding calculations.

The starting point of the method is to consider the singlet and triplet state ($S_z = 0$) which can be built from the two magnetic (singly occupied) orbitals $a$ and $b$ localized on the metal centers A and B.

$$^1\psi_0 = \mathcal{A}[(\prod_{i=1}^{n} i\bar{i})(a\bar{b} + b\bar{a})/\sqrt{2}] = (\Phi_1 + \Phi_2)/\sqrt{2}$$

$$^3\psi_0 = \mathcal{A}[(\prod_{i=1}^{n} i\bar{i})(a\bar{b} - b\bar{a})/\sqrt{2}] = (\Phi_1 - \Phi_2)/\sqrt{2}$$

In these expressions i represents one of the doubly occupied molecular orbitals corresponding to ligands and doubly occupied metal d orbitals. $\mathcal{A}$ is the antisymmetrizer operator for the set of $2n + 2$ electrons. The molecular orbitals that are used to define the zeroth approximations $^1\psi_0$ and $^3\psi_0$ are determined by an open-shell SCF calculation. In the case of centrosymmetric species, such a procedure provides two nearly degenerate symmetry-adapted MOs $\sigma_g$ and $\sigma_u$, and the localized magnetic orbitals are obtained by a simple rotation:

$$a = (\sigma_g + \sigma_u)/\sqrt{2}$$

$$b = (\sigma_g - \sigma_u)/\sqrt{2}$$

In the case of the $Cu^{II}V^{II}O$ complex, the SCF process directly gives localized magnetic orbitals. The localization degree as determined by the SCF calculation only reflects the amplitude of the interaction. If the interaction is very weak, the magnetic orbitals will be almost pure atomic d orbitals. The important point to notice here is that even if a and b are not equivalent, which is the case for non-symmetry-related dinuclear species, the determinants $\Phi_1$ and $\Phi_2$ corresponding to different spin occupations of $a$ and $b$ are exactly degenerate.

From this point, the development of $J$ is straightforward. At zeroth order we have

$$\Delta E_0 = \langle ^1\psi_0|H|^1\psi_0\rangle - \langle ^3\psi_0|H|^3\psi_0\rangle = 2K_{ab}$$

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**Table I.** Different Types of Contribution Obtained at Zeroth- and Second-Order and Numerical Values Obtained for the Model Complex of Figure 2

| type of contribution | | value (cm$^{-1}$) |
|---|---|---|
| potential exchange | $(ab,ab)$ | 623 |
| kinetic exchange | $\dfrac{4F^2ab}{\Delta E(a\rightarrow b)}$ | 0 |
| double-spin polarization | $-4\sum_i\sum_{j^*}\dfrac{(ia,j^*a)(ib,j^*b)}{\Delta E(i\rightarrow j^*)}$ | 79 |
| charge-transfer ligand → transition metal | $2\sum_i\sum_j\dfrac{(ia,j^*b)(ja,ib)}{\Delta E(i\rightarrow a^*)+\Delta E(j\rightarrow b^*)}$ | −114 |
| charge-transfer transition metal → ligand | $2\sum_{i^*}\sum_{j^*}\dfrac{(i^*a,j^*b)(j^*a,i^*b)}{\Delta E(a\rightarrow i^*)+\Delta E(b\rightarrow j^*)}$ | −38 |
| kinetic exchange polarization | $\sum_i\sum_{j^*}\dfrac{8(ab,j^*i)-4(ab,j^*i)[(ai,j^*b)+(j^*a,ib)]}{\Delta E(a\rightarrow b)+\Delta E(i\rightarrow j^*)}$ | −113 |
| particle polarization | $2\sum_{j^*}\left[\dfrac{Faj^*(ab,j^*b)}{\Delta E(a\rightarrow j^*)}+\dfrac{Fbj^*(ba,j^*a)}{\Delta E(b\rightarrow j^*)}\right]$ | −33 |
| hole polarization | $2\sum_i\left[\dfrac{Fai(ab,ib)}{\Delta E(i\rightarrow a)}+\dfrac{Fbi(ba,ia)}{\Delta E(i\rightarrow b)}\right]$ | −60 |
| total value after second order | | +344 |

where $K_{ab}$ is the exchange integral between orbitals a and b. This contribution called potential exchange is always positive (ferromagnetic). At second order, the correlation energies for $^1\psi_0$ and $^3\psi_0$ are

$$^1\epsilon_2=\sum_I\frac{\langle ^1\psi_0|H|\Phi_I\rangle^2}{\Delta E_{0I}}$$

$$^3\epsilon_2=\sum_I\frac{\langle ^3\psi_0|H|\Phi_I\rangle^2}{\Delta E_{0I}}$$

where $\Phi_I$ are the excited configurations generated from the zeroth order approximation and $\Delta E_{0I}$ is the corresponding transition energy.

By expanding $^1\psi_0$ and $^3\psi_0$ in terms of $\Phi_1$ and $\Phi_2$ we get

$$^1\epsilon_2=\frac{\sum_I\langle\Phi_1|H|\Phi_I\rangle^2+\langle\Phi_2|H|\Phi_I\rangle^2+2\langle\Phi_1|H|\Phi_I\rangle\langle\Phi_I|H|\Phi_2\rangle}{2\Delta E_{0I}}$$

$$^3\epsilon_2=\sum_I\frac{\langle\Phi_1|H|\Phi_I\rangle^2+\langle\Phi_2|H|\Phi_I\rangle^2-2\langle\Phi_1|H|\Phi_I\rangle\langle\Phi_I|H|\Phi_2\rangle}{2\Delta E_{0I}}$$

and the second-order contribution to $J$ is

$$\Delta E_2={}^1\epsilon_2-{}^3\epsilon_2=2\sum_I\frac{\langle\Phi_1|H|\Phi_I\rangle\langle\Phi_I|H|\Phi_2\rangle}{\Delta E_{0I}}$$

In this expression it is clear that at second order, the excited configurations $\Phi_I$ which do contribute to the splitting must interact simultaneously with $\Phi_1$ and $\Phi_2$. Their number is much smaller than the usual number of configurations involved at second order. A more detailed analysis of the different terms can be found elsewhere[14,15] along with a diagramatic representation of the processes involved. It is also shown that the matrix elements $\langle\Phi_1|H|\Phi_I\rangle$ and $\langle\Phi_2|H|\Phi_I\rangle$ only imply molecular integrals $\langle ij||kl\rangle$ where at least two of the indices are equal to *a* or *b*. The computational effort is therefore considerably reduced with respect to ordinary correlation energy calculations. The definition and physical meaning of the different terms appearing in $\Delta E_2$ are given in Table I, which also presents the numerical results. Let us mention here that some of these terms have been previously analyzed,[13,30,31] but not in a systematic way.

## Computational Aspects, SCF Result, and S-T Splitting Analysis

To determine the molecular orbitals used in the construction of $\Phi_1$ and $\Phi_2$ we applied standard LCAO-MO-SCF theory. The open-shell SCF operator used is of the type proposed by Nesbet[32]

$$F=h+\sum_{i=1}^{n}(2J_i-K_i)+(J_a-\tfrac{1}{2}K_a)+(J_b-\tfrac{1}{2}K_b)$$

where $J_i$ and $K_i$ are the Coulomb and exchange operators associated with orbital *i*. The calculation is restricted to valence electrons by using pseudopotential operators for replacing all core electrons. The specific form of pseudopotential used was described by Pelissier and Durand[33] and the parameters are given in ref 34. For the vanadium atom, we used the pseudopotential derived by Hay and Wadt.[35] The atomic basis set used to form molecular orbitals by linear combination is of the contracted Cartesian Gaussian type. For the metal atoms, the basis set [21/1/32] was optimized through atomic calculations of the atomic neutral ground state. In the molecular environment, the metal atoms have a net charge that is around +1.5, and it would have been conceivable to optimize the basis sets for the positive ions. Many molecular tests have shown that the resulting effect is quite small. For the bridging oxygen atoms a split valence [31/31] basis set was used, since the quality of the basis set in the bridge region has a non-negligible impact on the final $J$ value.[16] For the ligands, minimal [3/3] sets were used in order to keep the calculation at a reasonable computing cost. Even with such a restricted basis set, it was not possible to study CuVO(fsa)$_2$en·CH$_3$OH with the whole organic surroundings. Then, we decided to build the model complex shown in Figure 2, retaining the main characteristics of the actual complex, namely the CuO$_2$VO bridging network and the peripherical nitrogen and oxygen atoms bound to the metal centers. Our model complex has exactly the $C_s$ symmetry, with

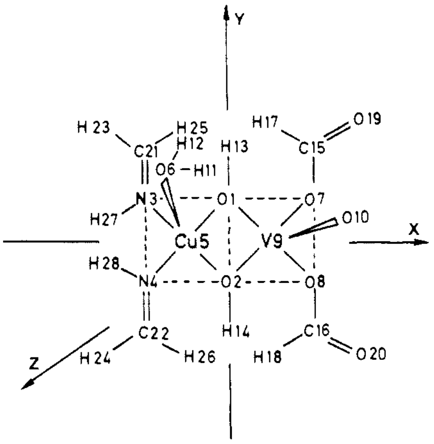

**Figure 2.** Modelization of the structure of CuVO(fsa)$_2$en·CH$_3$OH.

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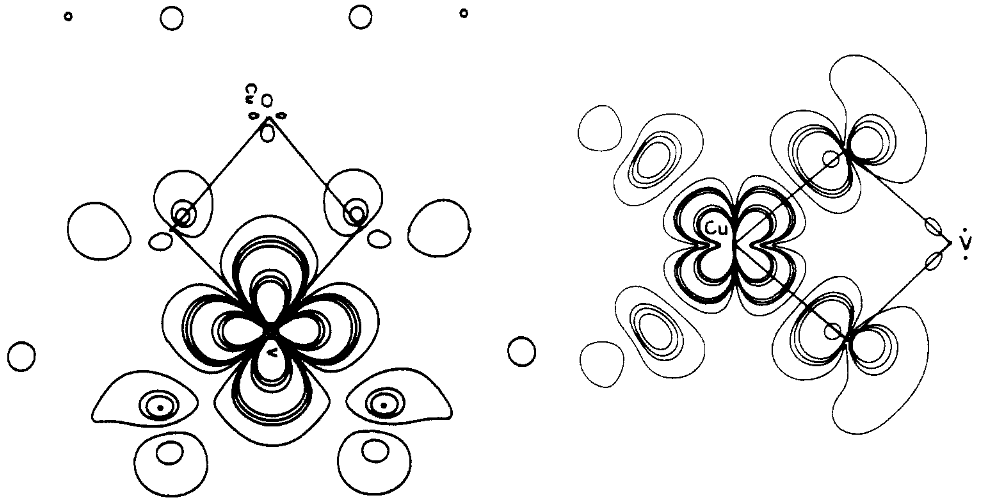


**Figure 3.** Electronic isodensity curves for the two magnetic orbitals localized respectively around Cu$^{II}$ (a) and V$^{II}$O (b) in the plane bisecting the dihedral formed by Cu(5)V(9)O(1) and Cu(5)V(9)O(2) planes.

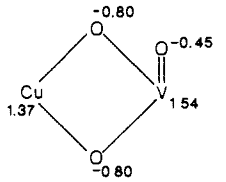
**Table II.** Geometrical Parameters (in au) Used in the Modelization of the Complex[a]

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu(5) | -2.781 | 0.0 | 0.554 |
| V(9) | 2.563 | 0.0 | 0.569 |
| O(1) | 0. | 2.371 | 0.463 |
| O(6) | -3.263 | 0.0 | 4.881 |
| O(7) | 4.901 | 2.666 | 0.034 |
| O(10) | 3.388 | 0.0 | 3.431 |
| N(3) | -5.293 | 2.468 | 0.0 |
| C(15) | 4.901 | 5.140 | 0.034 |
| C(21) | -5.293 | 4.894 | 0.0 |
| O(19) | 6.804 | 6.352 | -0.132 |
| H(11) | -3.386 | -1.431 | 5.893 |
| H(13) | 0.0 | 4.183 | 0.463 |
| H(17) | 3.119 | 6.123 | 0.190 |
| H(23) | -7.054 | 5.920 | -0.154 |
| H(25) | -3.532 | 5.915 | 0.154 |
| H(27) | -6.946 | 1.510 | -0.145 |

[a] Numbers in parentheses refer to Figure 2. The mirror plane is the XZ plane.

the mirror plane containing copper and vanadyl. The number of atoms is 28 and the dimension of the basis set is 106. Geometrical parameters and details for the basis set are given in Tables II and III.

The SCF result reflects the symmetry of the problem. The highest two molecular orbitals are the magnetic orbitals. They are well localized on copper for the lowest one and on vanadium for the highest one, as shown in Figure 3, a and b. The former has essentially an $xy$ character and is antisymmetric with regard to the mirror plane; the latter has essentially an $x^2$–$y^2$ character with some admixture of $z^2$ and is symmetric with regard to the mirror plane. Mulliken's analysis of charges (see Table IV) gives the following picture for the bridging network.



Results of the perturbational development for $J$ are given in Table I. At zeroth order, we get a large potential exchange term $2K_{ab}$, namely 623 cm$^{-1}$. The kinetic exchange term which is generally the leading term at second order is strictly zero, due to the orthogonality of the two magnetic orbitals. Another ferromagnetic contribution at the second order is provided by the double spin polarization processes. All the other second-order contributions are negative contributions, but final $J$ is found positive and equal to 344 cm$^{-1}$.

**Table III.** Exponents and Contraction Coefficients of the Gaussian Basis Set[a]

| | s | | p | | d | |
|---|---|---|---|---|---|---|
| Cu | 0.5710 | -0.6363 | 0.1060 | 1.0 | 31.0293 | 0.0898 |
| | 0.1794 | 1.4213 | | | 8.3121 | 0.3980 |
| | | | | | 2.5343 | 0.6915 |
| | 0.0729 | 1 | | | 0.6922 | 0.9191 |
| | | | | | 0.1765 | 0.1533 |
| V | 0.4591 | -0.3390 | 0.08 | 1.0 | 31.2066 | 0.0211 |
| | 0.1014 | 0.8904 | | | 8.3960 | 0.1187 |
| | | | | | 2.8238 | 0.3313 |
| | 0.0428 | 1 | | | 0.9703 | 0.4841 |
| | | | | | 0.3003 | 0.3620 |
| O | 5.7991 | -0.1377 | 12.6551 | 0.0682 | | |
| | 1.2983 | 0.2929 | 2.9536 | 0.2744 | | |
| | 0.5473$^b$ | 0.5312 | 0.8862 | 0.4823 | | |
| | 0.2261 | 0.3028 | 0.2599 | 0.4160 | | |
| N | 3.6941 | -0.1715 | 9.7494 | 0.0626 | | |
| | 1.2710 | 0.2217 | 2.2697 | 0.2594 | | |
| | 0.4677 | 0.5880 | 0.6781 | 0.4968 | | |
| | 0.1731 | 0.3527 | 0.2022 | 0.4126 | | |
| C | 2.3820 | -0.2421 | 0.9176 | 0.0436 | | |
| | 1.4431 | 0.1853 | 0.6852 | 0.2095 | | |
| | 0.4058 | 0.5913 | 0.3339 | 0.5028 | | |
| | 0.1384 | 0.4546 | 0.0638 | 0.4695 | | |
| H | 13.2478 | 0.0965 | | | | |
| | 2.0031 | 0.1619 | | | | |
| | 0.4558 | 0.1893 | | | | |
| | 0.1246 | 0.0752 | | | | |

[a] For the nonbridging oxygen atoms the basis set was completely contracted. [b] Bridging.

**Table IV.** Mulliken Net Charges Resulting from SCF Calculation

| | | | |
|---|---|---|---|
| Cu(5) | 1.37 | C(21) | -0.23 |
| V(9) | 1.54 | O(19) | -0.46 |
| O(1) | -0.80 | H(11) | 0.39 |
| O(6) | -0.71 | H(13) | 0.19 |
| O(7) | -0.59 | H(17) | 0.07 |
| O(10) | -0.45 | H(23) | 0.26 |
| N(3) | -0.54 | H(25) | 0.28 |
| C(15) | 0.27 | H(27) | 0.28 |

## Discussion

In this last section, we would like to discuss the results of our calculation and to see to what extent they confirm or modify the previous semiempirical approach concerning the same compound.[7,8,12]

As expected, the two magnetic orbitals around copper(II) and vanadium(IV) are antisymmetric and symmetric, respectively, with

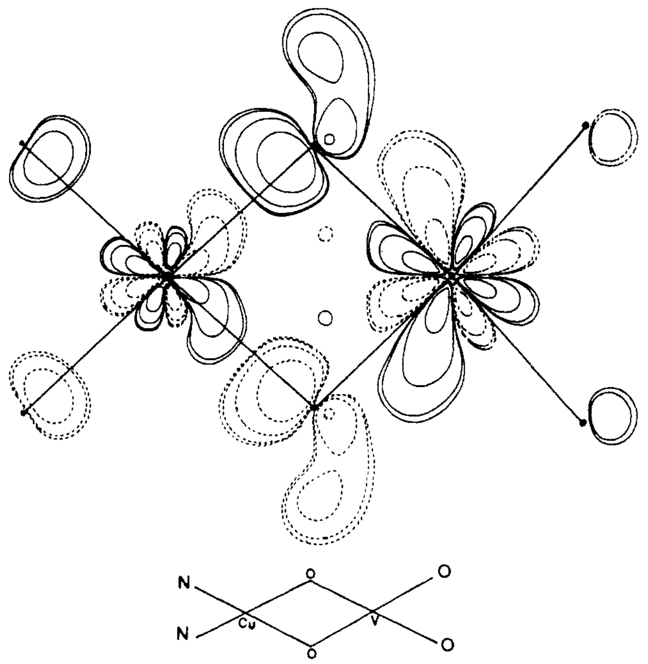


**Figure 4.** Isooverlap density curves in the same plane as Figure 3.

regard to the mirror-plane. They are less delocalized toward the bridging atoms than the magnetic orbitals deduced from extended-Hückel calculation. This confirms, if it was still necessary, that the Extended Hückel method overestimates the delocalization of the metal orbitals toward the ligands. These magnetic orbitals are strictly orthogonal so that the kinetic exchange (superexchange) term is exactly zero. As for the potential exchange term $2K_{ab}$, it is found equal to 623 $cm^{-1}$. This rather large contribution is better understood when considering the overlap density $f(i) = a(i)b(i)$ between the two magnetic orbitals. A map of isooverlap density in the plane containing the copper and the bridging atoms is shown in Figure 4. $f(i)$ is of course antisymmetric with regard to the mirror plane with non-negligible contributions around the bridging oxygen atoms as well as the metal atoms and the peripherical nitrogen and oxygen atoms. The $K_{ab}$ integral may be written as

$$K_{ab} = \int_{\text{space}} \frac{f(i)f(j)}{r_{ij}} \mathrm{d}V(i)\, \mathrm{d}V(j)$$

which points out that the magnitude of $K_{ab}$ is governed by the extrema of the overlap density.[36] $f(i)$ as obtained from this ab initio calculation significantly differs from the overlap density deduced from the semiempirical approach.[8] Indeed, this latter showed non-negligible contributions only around the bridging atoms. The basic reason for the discrepancy lies in the definition itself of the magnetic orbitals. In the semiempirical approach, those were determined as the highest singly occupied molecular orbitals for the hypothetical monomeric fragments consisting of the metal ions surrounded by its terminal bridging nearest neighbors.[7,8] Only the bridging atoms are common to the two fragments. Consequently, by definition, the magnetic orbital around copper had a zero contribution on the vanadyl and vice versa.

In the calculation presented here, each magnetic orbital is obviously a molecular orbital for the dinuclear complex as a whole and may be delocalized on all the atoms of the system including the metal ion on which it is not centered and the peripherical ligands bound to this ion.

The other positive contribution to $J$ is the double spin polarization term. If it is not easy to justify this sign in a simple way, one can notice that in most of the ab initio calculations on copper(II) dinuclear compounds, this term appears negative. There is, however, an exception concerning a $\mu$-hydroxo, $\mu$-azido complex in which both the double spin polarization term and $J$ as a whole have been found positive. Experimentally, this compound has been found to be ferromagnetically coupled.[15] All the other second-order contributions are negative, as in the already reported calculation of the same kind. Globally, the balance of the second-order terms is $-280$ $cm^{-1}$, which does not compensate the strong potential exchange term $2K_{ab}$.

The calculated $J$ value (343 $cm^{-1}$) is more positive than the reported experimental one (120 $cm^{-1}$). We do not attach too much importance to this discrepancy. As a matter of fact, it has been conclusively shown that the modelization of the actual structure may lead to a significative change of the S–T splitting, even when this modelization does not involve the atoms directly bound to the metals.[16] In the present case, we idealized the structure by imposing a $C_s$ symmetry. Otherwise, the kinetic exchange term would not be exactly zero, but would have a small negative value, which would diminish the calculated $J$ value. The choice of the basis set as well as the limitation of the expansion of $J$ at the second order may also been invoked. Moreover, the experimental value itself may not be very accurate. It is indeed well established that the accuracy in the determination of the S–T splitting is much weaker for $J > 0$ than for $J < 0$.[7,36]

To sum up the main information arising from this work, we can say that the ferromagnetic interaction in $CuVO(fsa)_2en{\cdot}CH_3OH$ is actually driven by the orthogonality of the two magnetic orbitals transforming as two different irreducible representations of the $C_s$ symmetry group. The magnitude of the interaction is related to the extrema of the overlap density map. There is, however, a question to which this work does not answer, namely, can a dinuclear compound exhibit an antiferromagnetic interaction in spite of the orthogonality of the magnetic orbitals, owing to the second and higher order terms in the expansion of $J$? Since no compound of this kind has been reported so far, we shall conclude this work by pointing out that, even if some accident cannot be excluded, this strategy of orthogonality remains one of the most efficient tools for the experimentalists looking for design molecular systems in which the ground state has the highest spin multiplicity.

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[36] Kahn, O. *Comments Inorg. Chem.* **1984**, *3*, 105.