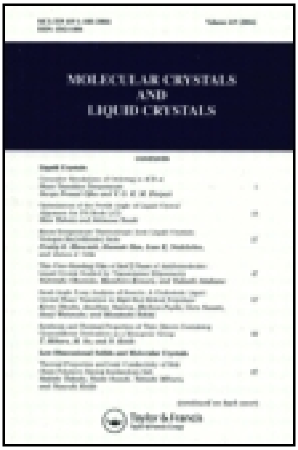

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ORTHOGONALITY OF THE MAGNETIC ORBITALS AND FERROMAGNETIC INTERACTION

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Abstract The strict orthogonality of the magnetic orbitals favors the ferromagnetic interaction. The basic idea of this strategy are recalled and three examples are presented. The first one concerns a copper(II)-orthosemiquinone entity, the second one a copper(II)-vanadyl(II) complex and the third one a Cr(III)Ni(II)3 tetranuclear species. In each case, the ground state has the highest spin mutiplicity. The status of the orthogonality concept is investigated through an ab-initio calculation dealing with the Cu(II)VO(II) compound.

INTRODUCTION

A strategy has been proposed to favor ferromagnetic interactions between nearest magnetic centers, based on the concept of orthogonality of the magnetic orbitals[1-3]. This strategy may be summarized as follows : we have an A-B pair with n_A unpaired electrons around A occupying the a_μ magnetic orbitals, and n_B unpaired electrons around B occupying the b_v magnetic orbitals. a_μ transforms as $\Gamma_\mu{}^a$ and b_v as $\Gamma_v{}^b$ irreducible representations of the point symmetry group adapted to the A-B pair. The magnetic orbitals are said to be strictly orthogonal if $\Gamma_\mu{}^a$ and $\Gamma_v{}^b$ are different for any couple μ and v. In such a case, the ground state has the highest spin multiplicity $S_g=(n_A+n_B)/2$. Indeed, owing to the orthogonality of the a_μ and b_v local functions, it is not possible to form low-energy molecular orbitals, delocalized on the whole A-B pair, on which the magnetic electrons would pair. Therefore, Hund's rule holds and the parallel spin state has the lowest energy.

In this paper, we present two A-B compounds in which the strict orthogonality of the magnetic orbitals is achieved. For the former one, no thorough theoretical study has been carried out yet; for the latter, on the other hand, an ab-initio calculation has been performed, of which the results will be reported. In addition, we describe a Cr(III)Ni(II)$_3$ tetranuclear species in which the S=9/2 ground state arises from the quasi orthogonality between the t_{2g} orbitals of Cr(III) and the e_g orbitals of Ni(II).

A COPPER(II)-ORTHOSEMIQUINONE COMPOUND

The [Cu(NHpy$_2$)(DTBSQ)]$^+$ cation with NHpy$_2$ = di - 2 - pyridylamine and DTBSQ = 3,5 - di - tert - butyl - o - semiquinone has a structure shown in Figure 1.

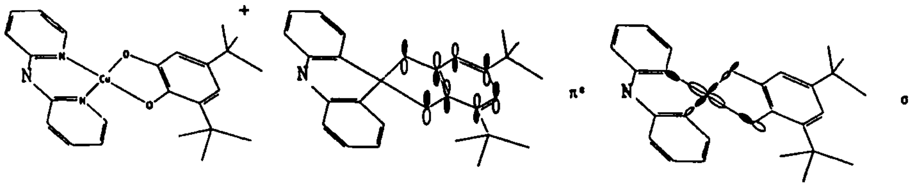


FIGURE 1 left : structure of the cation copper(II)-orthosemiquinone; center : magnetic orbital for orthosemiquinone; right : magnetic orbital for copper(II).

The copper(II) ion is in a 4 + 2 distorted octahedral environment with two nitrogen atoms of NHpy$_2$ and the two oxygen atoms of DTBSQ in the basal plane and two oxygen atoms of perchlorate groups in the apical positions with apical bond lengths above 2.4 Å. In addition, the copper(II) ion is slightly displaced from the basal plane towards one of the apical sites, so that the molecular skeleton is not rigorously planar. If one neglects this weak bending of the magnetic cation, the symmetry is C_{2v}. When considering this bending, the symmetry is C_s with a mirror-plane σ perpendicular to the pseudo-molecular plane[4].

The unpaired electron from the copper(II) ion is described by a magnetic orbital a_{Cu} pointing along the Cu-N and Cu-O bonds in the basal plane. a_{Cu} is antisymmetric with regard to the mirror-plane σ and transforms as b_1 in C_{2v} and a" in C_s. The unpaired electron of the orthosemiquinone radical is found from elementary molecular orbital theory to occupy the π^* orbital noted b_{sq}. This orbital transforms as b_2 in C_{2v} and a' in C_s and is symmetric with regard to the mirror-plane σ. Both a_{Cu} and b_{sq} are schematized in Figure 1. Even by taking into account the slight deviation of the $[Cu(NHpy_2)(DTBSQ)]^+$ unit from planarity, a_{Cu} and b_{sq} are strictly orthogonal and the interaction is expected to be purely ferromagnetic with a triplet ground state. Experimentally, the $\chi_M T$ versus T plot shown in Figure 2 agrees with this prediction[5].

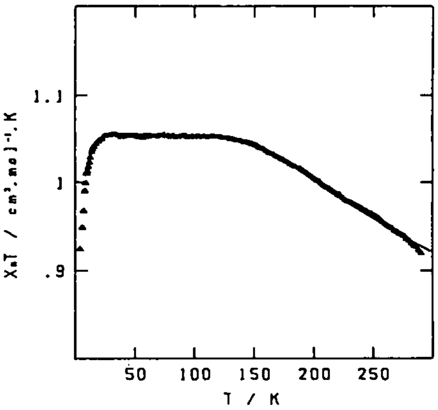


FIGURE 2 $\chi_M T$ versus T plot for the copper(II)-orthosemiquinone compound.

At room temperature, $\chi_M T$ is equal to 0.92 cm^3 K mol^{-1}, smoothly increases upon cooling, reaches an extended plateau between 150 and 20 K, and finally slightly decreases below 20 K. This behavior is quite characteristic of a strong intramolecular ferromagnetic interaction. The plateau corresponds to the temperature range where only the triplet ground state is thermally populated. The magnetic susceptibility then follows a Curie law $\chi_M T = 2N\beta^2 g^2/3k$. Below 20 K, intermolecular interactions are probably operative. Quantitative fitting of the experimental data leads to J larger than 200 cm^{-1}.

$CuVO(fsa)_2enCH_3OH$: QUALITATIVE APPROACH AND AB-INITIO CALCULATION

The compound noted $CuVO(fsa)_2en. CH_3OH$ has a structure represented in Figure 3.

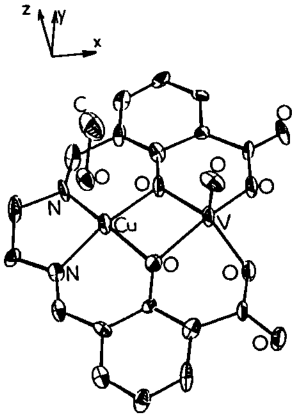


FIGURE 3 Structure of $CuVO(fsa)_2en.CH_3OH$.

The two metal ions, copper(II) and vandium(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[1]. 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 considerations, it is obvious to see that the unpaired electron around copper(II) is described by a xy-type magnetic orbital noted a_{Cu} and transforming as a", and that around vanadium(IV) by a x^2-y^2-type magnetic orbital noted b_{VO} and transforming as a'. Therefore, the strict orthogonality is achevied and actually the triplet state has been found to be the lowest with a ground triplet-excited singlet separation of 120 cm^{-1}.

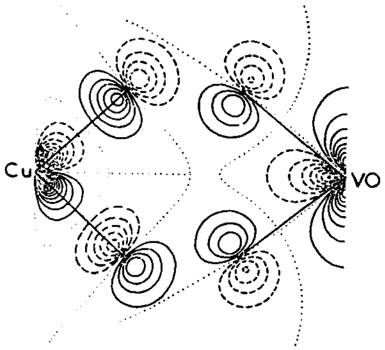


FIGURE 4 Schematic representation of the magnetic orbitals a_{Cu} and b_{VO} in $CuVO(fsa)_2en.CH_3OH$

This compound $CuVO(fsa)_2en.CH_3OH$ is particularly important because it allows to prove in a clearcut fashion that the nature of the interaction is related to the symmetry of the molecular species and of the interacting magnetic orbitals as a whole, and not to the local symmetry along each metal-bridge-metal linkage. As a matter of fact, the magnetic orbitals around copper(II) and vanadyl(II) are delocalized towards the bridges, in an antibonding σ fashion for the former one, and in an antibonding π fashion for the latter one, as schematized in Figure 4. Along each Cu-O-V linkage, the magnetic orbitals overlap, and ignoring the phase relations beween the two bridges, one could claim that the interaction is antiferromagnetic. In fact, the overlap density ρ defined as[1] :

$$\rho(1) = a_{Cu}(1)b_{VO}(1)$$

presents a positive zone around one of the bridges and a negative zone around the other bridge and the interaction is strongly ferromagnetic.

Implicitely, the concept of strict orthogonality lies on a qualitative model where the interaction parameter J can be decomposed into a ferromagnetic J_F and an antiferromagnetic J_{AF} contributions, this latter term vanishing when all the magnetic orbitals are orthogonal. However, in the ab-initio perturbational development of J proposed first by de Loth et al.[6], other terms may significantly contribute to the S - T energy gap . 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[7]. Moreover, in some cases, this negative balance prevails over the potential exchange term 2k, k being the two-electron exchange integral :

$$k = < a_{Cu}(1)b_{VO}(2) \mid r_{12}^{-1} \mid a_{Cu}(2)b_{VO}(1) >$$

Therefore, it was important to see what the contribution of these terms is with regard to the potential exchange term in the case of $CuVO(fsa)_2en.CH_3OH$.

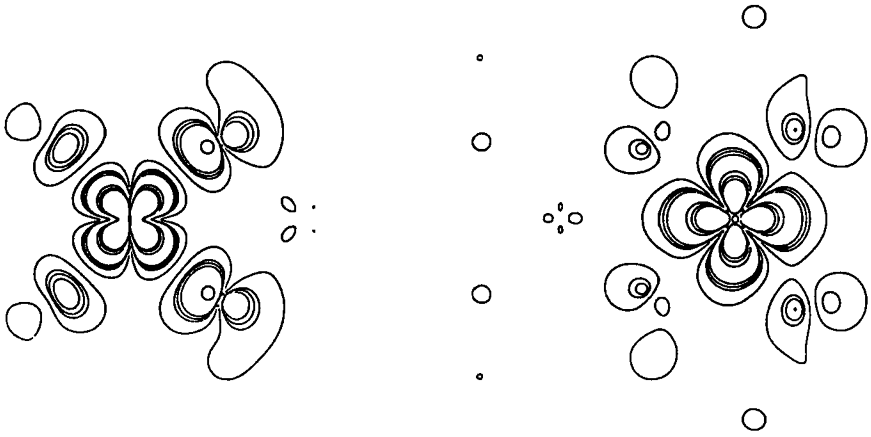


FIGURE 5 Electronic isodensity curves for the magnetic orbitals centered on Cu(II) and VO(II), respectively, in $CuVO(fsa)_2en.CH_3OH$, drawn in the mean molecular plane.

The calculation has been carried out by the method described by de Loth et al. as follows[8] : a model complex retaining the main characteristics of the actual complex, namely the CuO_2VO bridging network and the peripherical nitrogen and oxygen atoms bound to the metal centers has been built. This model complex has exactly the C_s symmetry, with the mirror-plane containing copper and vanadyl. The calculation is restricted to valence electrons by using pseudo-potential operators for replacing all core electrons. The open-shell SCF process with the Nesbet operator directly gives the magnetic orbitals. They are well localized on copper for the lowest one and on vanadium for the highest one, as shown in Figure 5. 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.

The magnetic orbitals are strictly orthogonal so that the kinetic energy term is exactly zero. As for the potential energy term 2k, it is found equal to 623 cm^{-1}. This rather large contribution is better understood when considering the overlap density $\rho(1)$ between the two magnetic orbitals, as defined above. A map of isooverlap density in the plane containing the copper and the bridging atoms is shown in Figure 6.

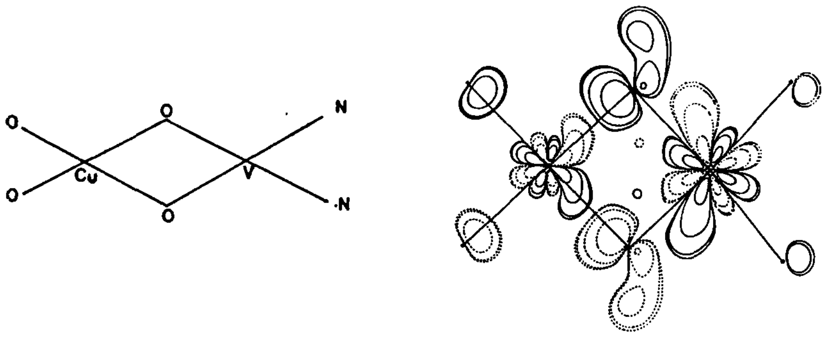


FIGURE 6 Isooverlap density curves in $CuVO(fsa)_2en.CH_3OH$ drawn in the mean molecular plane.

$\rho(1)$ 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 two-electron exchange integral k may be written as :

$$k = \int_{space} \rho(1)\rho(2) r_{12}^{-1} d\tau$$

which points out that the magnitude of k is governed by the extrema of the overlap density.

Another ferromagnetic contribution at the second-order is provided by the double-spin polarization process. All the other second-order contributions are negative. Globaly, the balance of the second-order terms is - 28O cm^{-1}, which does not compensate the strong potential energy term 2k. The results of the perturbational development of J are gathered in TableI.

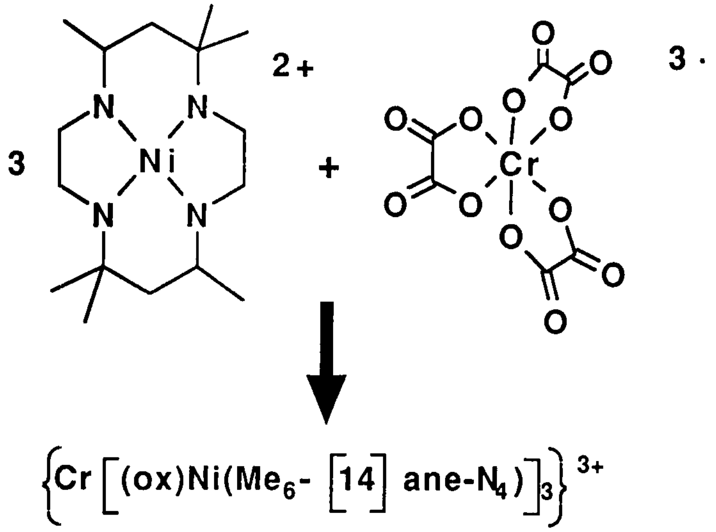
TABLE I Different types of contribution obtained at zeroth- and second-order and numerical values for the copper(II)-vanadyl(II) model complex .

type of contribution	value in cm^{-1}
potential exchange	623
kinetic exchange	0
double-spin polarization	79
ligand–metal charge transfer	-114
metal–ligand charge transfer	-38
kinetic exchange + polarization	-113
particule polarization	-33
hole polarization	-60
total value after second-order	**343**

The calculated J value (343 cm^{-1}) has the good sign but is more positive than the reported experimental one (12O cm^{-1}) . The important point arising from this calculation is that the terms appearing beyond the active-electron approximation do not modify the qualitative predictions made in the frame of this approximation as for the nature of the ground state.

A Cr(III)Ni(II)$_3$ TETRANUCLEAR CLUSTER WITH A S=9/2 SPIN.

The compound {Cr[(ox)Ni(Me$_6$-[14]ane-N$_4$)]$_3$}(ClO$_4$)$_3$, hereafter abbreviated as CrNi$_3$ was synthesized according to the scheme :



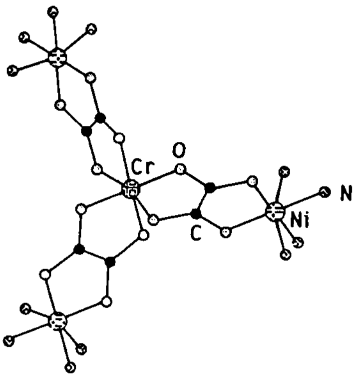


FIGURE 7 Schematic structure of the CrNi$_3$ tetranuclear cation.

A central Cr(III) ion in octahedral environment is linked to three Ni(II) ions through oxalato bridges. Each Ni(II) ion achieves an hexacoordination with the terminal macrocycle. Me_6-[14]ane-N_4 is known to give a folded tetracoordination in the presence of a bidentate anion (see Figure 7).

The molar magnetic susceptibility χ_M of $CrNi_3$ was investigated in the $1.3<T/K<270$ temperature range and the results are shown in Figure 8 in the form of the $\chi_M T$ versus T plot. At 270 K, $\chi_M T$ is equal to 5.52 cm^3 mol^{-1} K, which corresponds to what is expected for a Cr(III) and three Ni(III) ions magnetically isolated. Upon cooling, $\chi_M T$ increases in a continuous fashion down to ca. 6 K, then reaches a plateau or a broad maximum with $\chi_M T$=11.3(1) cm^3 mol^{-1} K.

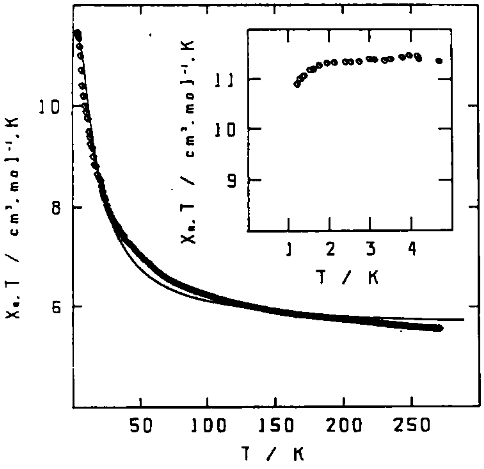


FIGURE 8 $\chi_M T$ versus T plot for $CrNi_3$.

This $\chi_M T$ versus T plot clearly shows that the Cr(III)-Ni(II) interactions are ferromagnetic so that the ground state has the spin S=9/2. The value of the maximum of $\chi_M T$ is close to what is expected for a S=9/2 ground state in the temperature range where only this state is thermally populated. Indeed, in this temperature range, we should have :

$$\chi_M T = 33N\beta^2 g^2_{9/2,3} / 4k$$

$g_{9/2,3}$ is the Zeeman factor associated with this ground state and the other symbols have their usual meaning. The magnetic data have been interpreted quantitatively. The interaction parameter J ($H = -JS_{Cr}.S_{Ni}$) has been found equal to 5.5 cm^{-1}.

In order to confirm that $CrNi_3$ has a S=9/2 ground state, we measured the molar magnetization M up to $6x10^4$ G at 4.2 K. The results shown in Figure 9 follow reasonably well the theoretical expression

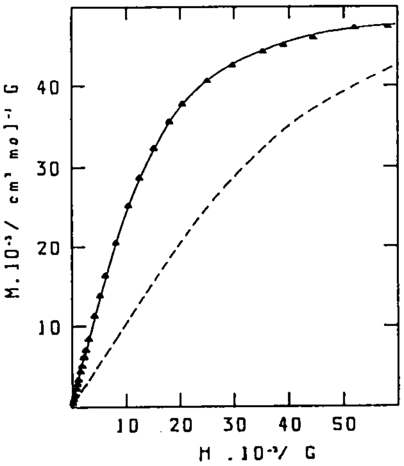


FIGURE 9 Magnetization M versus magnetic field plot H plot for $CrNi_3$. experimental data. – calculated curve for a S = 9/2 ground state and a g factor g = 1.97. --- calculated curve for a Cr(III) ion with S_{Cr} = 3/2 and three Ni(II) ions with S_{Ni} = 1 uncoupled plotted with $g_{Cr} = g_{Ni}$ = 1.97.

$$M = Ng_{9/2,3}\beta S B\,(y)$$

with :

$$y = g_{9/2,3}\beta SH/kT$$

in which *B* (y) is the Brillouin function. The best agreement is obtained for $g_{9/2,3} = 1.97$.

Let us analyse now the role of the symmetry in the nature of the interaction. A first approach consists of saying that Cr(III) in octahedral surroundings has three unpaired electrons occupying the three low-lying t_{2g} orbitals and each Ni(II), also in octahedral surroundings, has two unpaired electrons occupying the two high-lying e_g orbitals. A more rigourous approach requires to consider the actual symmetry of each Cr(ox)Ni bridging network, close to C_{2v}. In this symmetry, the unpaired electrons of Cr(III) occupy orbitals transforming as $a_1+a_2+b_2$ and those of Ni(II) orbitals transforming as a_1+b_1. These orbitals are schematized in Figure 10.

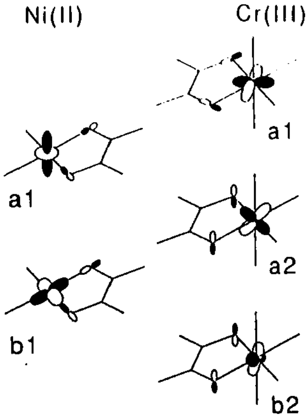


FIGURE 10 Schematic representation of the magnetic orbitals centered on Cr(III) and Ni(II) ions in $CrNi_3$

The Cr(III)-Ni(II) exchange parameter J may be written as a sum of J_{ij}'s contributions involving pairs of interacting orbitals as :

$$J=1/3(J_{a1a1}+J_{a1b1}+J_{a2a1}+J_{a2b1}+J_{b2a1}+J_{b2a2})$$

where all the J_{ij}'s are positive since involving orthogonal orbitals but J_{a1a1}. This contribution, however, may be expected to be rather small. Indeed, the $a_1(z^2)$ orbital centered on nickel is weakly delocalized in the plane of the oxalato bridge. Among the positive contributions, J_{a1b1} is certainly the most important since the a_1 orbital centered on chromium and the b_1 orbital centered on nickel are both situated in the plane of the bridging network and may efficiently interact[9].

CONCLUSION

Our main target is to design molecular-based ferromagnets[10-11]. Our strategy along this line consists of synthesizing high-spin molecules or chains, then of assembling them in a ferromagnetic fashion within the crystal lattice. To obtain high-spin molecules, we are exploring two different ways. The former is the achieving of ferromagnetic interactions thanks to the orthogonality of the magnetic orbitals. $CrNi_3$ provides a spectacular example of the possibilities of this approach. A S=9/2 ground state, if not unique anymore[10,11], is still quite unusual. The latter strategy, to which another paper in this issue is devoted[12], consists of polarizing high peripheral spins owing to antiferromagnetic interactions with a small central spin.

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