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Interactions in Cu(II)Cu(II), VO(II)VO(II) and Cu(II)VO(II) Pairs Through Oxalato Bridging Ligand

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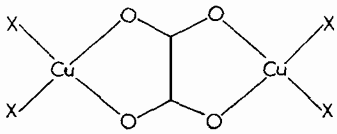
The goal of this paper was to compare the interaction in Cu(II)Cu(II), VO(II)VO(II) and Cu(II)-VO(II) pairs through the same oxalato bridging ligand. For this, two new bimetallic complexes were synthesized, namely acacVO(C_2O_4)VOacac·4H_2O noted [VOVO] and tmenCu(C_2O_4)VO(C_2O_4)·3H_2O noted [CuVO], with acac = acetylacetonato and tmen = N,N,N′,N′-tetramethylethylenediamine. The [CuCu] compound of formula [tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen](ClO_4)$_2$·1.25H_2O has already been described and its crystal structure solved by X-ray diffraction. The singlet–triplet energy gaps arising from the intramolecular interaction, determined from the magnetic data, are -385.4 cm^{-1} in [CuCu], -5.75 cm^{-1} in [VOVO] and $|J| < 1$ cm^{-1} in [CuVO]. The EPR spectrum of this last compound, however, shows a transition in a triplet state with a singlet–triplet energy gap larger, in absolute value, than the incident quantum (~0.3 cm^{-1} in X-band). To obtain this result, the spectrum was compared to those of the monomeric species tmenCu(C_2O_4)·4H_2O and (NH_4)$_2$VO(C_2O_4)$_2$·2H_2O. The magnitude of the singlet–triplet gaps J was rationalized within the framework of an orbital model developed in our group. [CuVO] is a new heterobimetallic compound in which the interaction is expected to be purely ferromagnetic owing to the strict orthogonality of the magnetic orbitals. Finally, an explanation of the absence of zero field splitting in the triplet state of [CuCu] was proposed. It was shown that the anisotropic exchange interaction in [CuCu] might be considered as being proportional to the isotropic exchange interaction in [CuVO].

Introduction

For about half a decade our group has been engaged in the design of polymetallic systems exhibiting expected magnetic properties. Our goal is to establish a molecular engineering of these systems allowing to predict the nature of the metallic ions and of the bridging and terminal ligands we have to choose, the whole geometry we have to realize, in order to obtain an interaction between the metal centers predictable in sign and magnitude [1]. In this way, two results may be pointed out: (i) ferromagnetically-coupled heterobimetallic complexes have been obtained by realizing the strict orthogonality of the magnetic orbitals [2]; CuVO(fsa)$_2$en·CH_3OH is one of them, where (fsa)$_2$en^{4-} is the binucleating ligand derived from the Schiff base N,N′-(2-hydroxy, 3-carboxybenzilidene)ethylenediamine; (ii) strong antiferromagnetic interactions between metal ions separated by more than 5 Å through extended bridging ligands have been achieved. Such a situation is realized in planar or nearly planar μ-oxalato copper(II) complexes like *1*, with eventually a fifth ligand occupying an apical position around each copper [3].



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In this paper, we attempt to answer two questions emerging from the two results mentioned above. These questions are: (i) If the two Cu(II) ions of d^9 configuration are replaced in *1* by two VO(II) ions of

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d^1 configuration, what will be the magnitude of the interaction through the oxalato bridge? (II) If one of the Cu(II) ions in *1* is replaced by a VO(II) ion in order to obtain an heterobimetallic complex, will the interaction be ferromagnetic as in CuVO-$(fsa)_2en{\cdot}CH_3OH$, and what will be the magnitude of the phenomenon?

To answer these questions, we describe two new compounds, namely $acacVO(C_2O_4)VOacac{\cdot}4H_2O$ with acac = acetylacetonato, noted [VOVO], and $tmenCu(C_2O_4)VO(C_2O_4){\cdot}3H_2O$ with tmen = N,N,N′,N′-tetramethylethylenediamine, noted [CuVO]. We investigate their magnetic properties and their EPR spectra. These results will be compared to those obtained with $[tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen](ClO_4)_2{\cdot}1.25H_2O$, noted [CuCu]. Finally, we propose a rationalization of the results concerning the interaction between the metal centers within the framework of the orbital model developed in our group [4]. The key concept of this model is that of magnetic orbitals defined as the singly-occupied molecular orbitals for each monomeric fragment made up by the metal center surrounded by the nearest neighbour ligands. For [CuCu] and [CuVO], these monomeric fragments do actually exist. Their formula are $tmenCu(C_2O_4){\cdot}4H_2O$ and $(NH_4)_2VO(C_2O_4)_2{\cdot}2H_2O$ respectively, denoted as [Cu–] and [–VO]. The comparison of the EPR spectrum of [CuVO] with those of [Cu–] and [–VO] will be important to estimate the magnitude of the interaction in the heterobimetallic complex.

Experimental

Syntheses

$[tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen](ClO_4)_2{\cdot}1.25H_2O$ [CuCu], with tmen = N,N,N′,N′-tetramethylethylenediamine was prepared as recently described [3].

$tmenCu(C_2O_4){\cdot}4H_2O$ was synthetized by following a similar procedure as for $dmenCu(C_2O_4){\cdot}H_2O$, with dmen = N,N′-dimethylethylenediamine [5].

$acacVO(C_2O_4)VOacac{\cdot}4H_2O$ [VOVO] was prepared from $VO(C_2O_4){\cdot}4H_2O$ [6] and $VO(acac)_2$ [7], as follows: stoichiometric amounts of $VO(acac)_2$ and $VO(C_2O_4){\cdot}4H_2O$ dissolved in methanol were mixed together under nitrogen. The resulting green solution was then concentrated over P_2O_5 under vacuum and [VOVO] slowly precipitated. It was filtered off, washed with ethanol and ether and dried under vacuum.

Anal. (%) Calcd for $C_{12}H_{22}O_{14}V_2$: C, 29.29; H, 4.47; V, 20.70. Found: C, 29.42; H, 4.56; V, 19.80.

$tmenCu(C_2O_4)VO(C_2O_4){\cdot}3H_2O$ [CuVO] was obtained by mixing, under nitrogen, stoichiometric amounts of $tmenCu(C_2O_4){\cdot}4H_2O$ and $VO(C_2O_4){\cdot}4H_2O$ dissolved in methanol. [CuVO] precipitated as a blue powder. After centrifuging, [CuVO] was washed with methanol and dried over silica gel under vacuum. [CuVO] slowly decomposes when exposed to air. *Anal.* (%). Calcd for $C_{10}H_{22}N_2O_{12}CuV$: C, 25.15; H, 4.62; N, 5.88; Cu, 13.33; V, 10.69. Found: C, 25.26; H, 4.71; N, 5.91; Cu, 13.85; V, 10.64.

$(NH_4)_2VO(C_2O_4)_2{\cdot}2H_2O$ was prepared as reported [8].

Magnetic Measurements

These were carried out with a Faraday type magnetometer equipped with a helium continuous flow cryostat working in the 2–300 K temperature range. Mercuritetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetism corrections were estimated at -215×10^{-6} cm^3 $mole^{-1}$ for [VOVO] and -205×10^{-6} cm^3 $mole^{-1}$ for [CuVO].

E.P.R.

The spectra were recorded at X-band frequency with a Bruker ER 200 D spectrometer equipped with

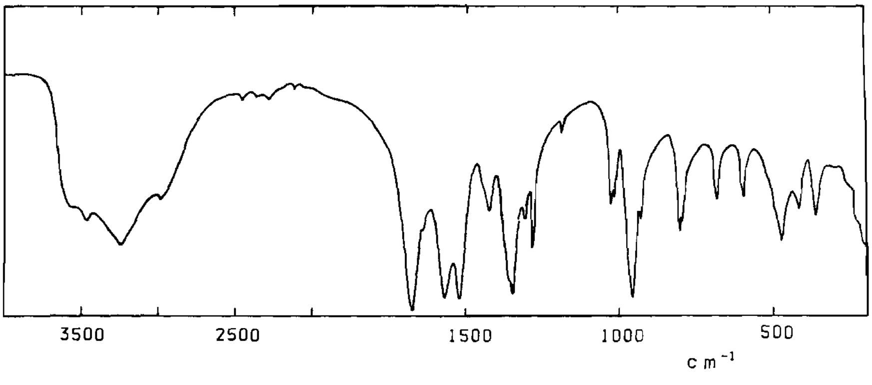

Fig. 1. Infra-red spectrum of acac $VO(C_2O_4)VOacac{\cdot}4H_2O$ in KBr pellet.

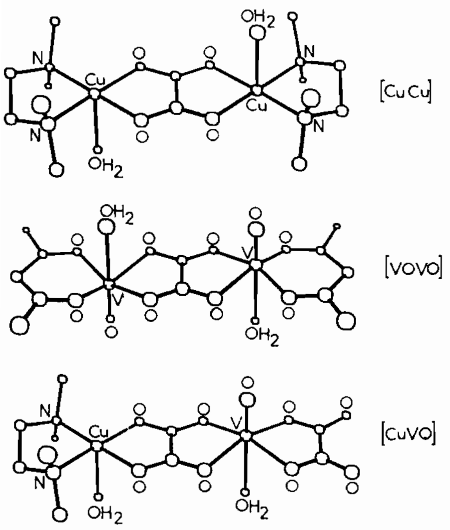

Fig. 2. Schematic structures of [CuCu] = tmen(H_2O)Cu(C_2O_4)(Cu(H_2O)tmen^{2+}; [VOVO] = acacVO(C_2O_4)VO acac; [CuVO] = tmen(H_2O)Cu(C_2O_4)VO(C_2O_4). Only the structure of [CuCu] was determined by X-ray diffraction.

a helium continuous flow cryostat. The magnetic field was determined with a Hall probe and the klystron frequency with a Hewlett-Packard frequency-meter.

Structure of the Complexes

The structure of [CuCu] has been previously described [3]. It is made of centrosymmetric [tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen]$^{2+}$ cations isolated by ClO_4^- anions and intercalated water molecules. The Cu(C_2O_4)Cu network is nearly planar with quasi equal Cu–O bond lengths. A water molecule is weakly bound to each of the Cu(II) ions. The Cu··· Cu distance is 5.14 Å and the whole symmetry very close to C_{2h}.

The structure of [VOVO] can be deduced from the IR spectrum shown in Fig.1. This spectrum exhibits the bands of the acetylacetonato ligands, the bands characteristic of the bridging oxalato ligand (ν_{C-O} = 1675 cm^{-1} and 1315 cm^{-1}, ν_{O-C-O} = 805 cm^{-1}), the ν_{V-O} at 965 cm^{-1} characteristic of the vanadyl ion and a broad feature from 3600 cm^{-1} to 3100 cm^{-1} showing the presence of both coordinated and lattice water molecules. By analogy with the previously reported structures of VO(II) bimetallic complexes [9–11]*, we assumed in Fig. 2 that the two VO(II) ions were up-down with a molecular symmetry center, so that the whole symmetry is C_{2h}.

TABLE I. Singlet–triplet Energy Gap J for [CuCu], [VOVO] and [CuVO].

	J/cm^{-1}
[CuCu]	−385.4
[VOVO]	−5.75
[CuVO]	$0.3 < \lvert J \rvert < 1$

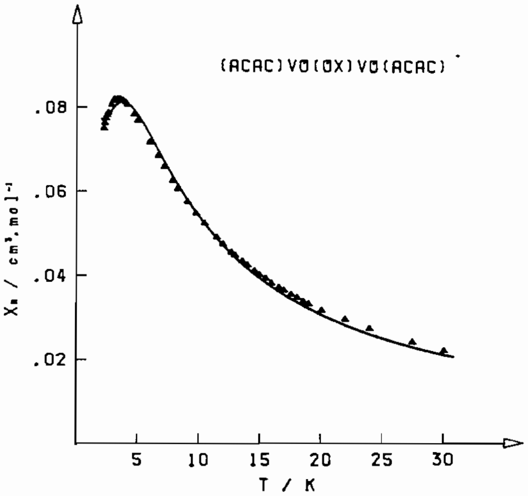

Fig. 3. Experimental (▲) and calculated (–) magnetic data for [VOVO].

The IR spectrum of [CuVO] also exhibits the features expected for the structure shown in Fig. 2, with the C_s symmetry.

Magnetic Properties

The magnetic behaviour of [CuCu] has already been reported [3]. The molar magnetic susceptibility χ_M *versus* temperature T plot exhibits a maximum around room temperature characteristic of a large antiferromagnetic interaction. By least-squares fitting of the experimental data, the singlet–triplet energy gap was found equal to −385.4 cm^{-1}.

The magnetic behaviour of [VOVO] is shown in Fig. 3 in the form of χ_M *versus* T plot. χ_M exhibits a maximum at 3.6 K, characteristic of a very weak antiferromagnetic interaction. We expressed the magnetic susceptibility according to:

$$\chi_M = \frac{2N\beta^2g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}(1-\rho) + \frac{C}{T}\rho \qquad (1)$$

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*The structure of a VO(II) bimetallic complex with an up-up configuration has been recently described [26].

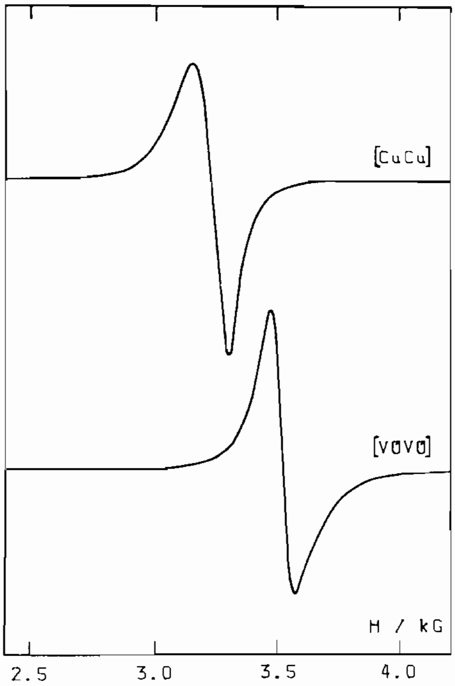


Fig. 4. X-band powder E.P.R. spectra of [CuCu] and [VOVO].

where the symbols have their usual meaning. ρ is the massic proportion of non-coupled metallic impurity, assumed to follow a Curie law. The singlet–triplet energy gap J was determined by least-squares fitting of the experimental data. g, ρ and C are correlated, so that several sets of parameters lead to the same minimum value of the R factor defined by $\Sigma\ (\chi_M^{obs} - \chi_M^{calc})^2/\Sigma(\chi_M^{obs})^2$. In all the cases, J is equal to -5.75 ± 0.05 cm^{-1}; R is then equal to 2.75×10^{-4}. The calculated curve is compared to the experimental data in Fig. 3.

The magnetic behaviour of [CuVO] was also investigated in the 2–300 K temperature range. Down to 20 K, the magnetic susceptibility follows perfectly the Curie law $\chi_M \times T = 0.80 \pm 0.01$ cm^3 mol^{-1} K. Below 20 K, $\chi_M \times T$ very slowly decreases down to a value of 0.68 cm^3 mol^{-1} K at pumped liquid helium temperature. This behaviour means either that the two metal ions do not interact through the oxalato bridge, or that the singlet and triplet states arising from the intramolecular interaction are almost accidentally degenerate with a $|J|$ gap smaller than 1 cm^{-1}. In the latter case, the average value of the g-factor for the triplet state can be deduced from the Curie constant according to $\chi_M T = N\beta^2 g^2/2k$. This leads to g = 2.06(5). The weak decrease of $\chi_M T$ at low temperature could be due to small intermolecular interactions.

The values of the singlet–triplet energy gap for the three compounds are given in Table I.

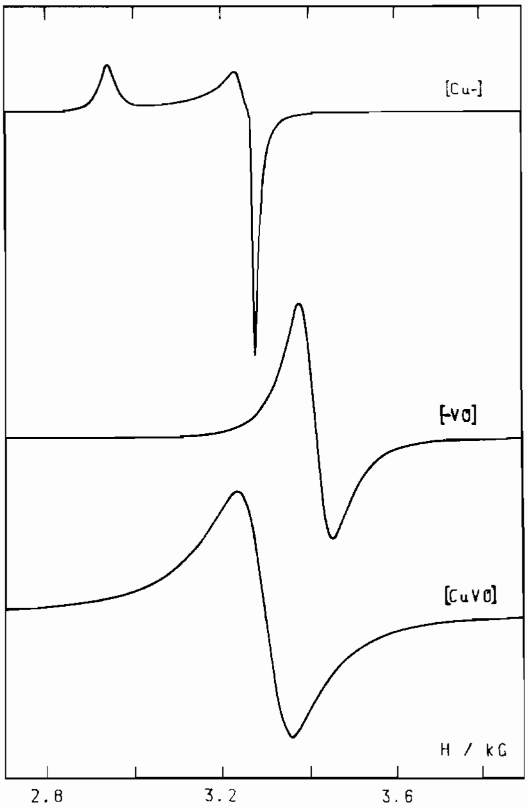


Fig. 5. X-band powder E.P.R. spectra of [Cu–], [–VO] and [CuVO].

E.P.R. Spectra

The powder E.P.R. spectra of [CuCu] and [VOVO] at 300 K are shown in Fig. 4. Both are associated to very weakly anisotropic triplet states without detectable zero field splitting, nor half field signals. They can be interpreted with the following principal values of the *g* tensors.

$g_\parallel = 2.12(5)$
$g_\perp = 2.08(6)$ for [CuCu]

$g_\parallel = 1.97(3)$
$g_\perp = 1.99(2)$ for [VOVO]

The powder E.P.R. spectrum of [CuVO] is shown in Fig. 5 as well as the E.P.R. spectra of the actual monomeric fragments [Cu–] and [–VO]. All these spectra are recorded at 4.2 K. The spectrum of [Cu–] is typical of a non-coupled copper(II) ion in an elongated tetragonal environment to which is superimposed a weak rhombic distortion. The principal values of *g* are $g_x = 2.06(4)$, $g_y = 2.08(8)$ and $g_z = 2.29(5)$. At room temperature, the rhombic distortion is no longer detectable. The spectrum of [–VO] is typical of a non-coupled vanadyl ion in a tetragonal environment with $g_\parallel = 1.96(7)$ and $g_\perp = 1.97(6)$. The spectrum of [CuVO] exhibits a quasi isotropic feature with $g = 2.04(6)$. It is clear that this spectrum is not the superposition of those of [Cu–] and [–VO]. Therefore, the metal ions cannot be considered as non-interacting and the observed resonance occurs in the triplet pair state. Furthermore, the shape of the spectrum enables us to give a lower limit for |J| in [CuVO]. The spin Hamiltonian for the pair may be written as [2, 12–14]:

$$\mathcal{H} = \beta[g_{Cu}\cdot\hat{S}_{Cu} + g_{VO}\cdot\hat{S}_{VO}]\cdot$$
$$\cdot\vec{H} - J\hat{S}_{Cu}\cdot\hat{S}_{VO} + \hat{S}_{Cu}\cdot D\cdot\hat{S}_{VO} \qquad (2)$$

where g_{Cu} and g_{VO} are local tensors. D is the tensor of dipolar interaction and anisotropic exchange. Since we have not detected any sign of zero field splitting in [CuVO] as well as in [CuCu] and [VOVO], we assume that the elements of D are zero [12–13]. In fact the zero field splitting could be very small and detectable only on a single-crystal. The matrix associated to $\mathcal{H}$ defined in (2) on the $|S, M_S>$ basis set is:

$$\begin{array}{cccc}
|1,1> & |1,0> & |1,-1> & |0,0> \\
\hline
g_u\beta H_u & 0 & 0 & 0 \\
 & 0 & 0 & \delta_u\beta H_u \\
 & & -g_u\beta H_u & 0 \\
 & & & J
\end{array} \qquad (3)$$

where the index u notes the direction of the applied magnetic field taken as quantization axis. The tensors g and δ are defined as:

$$g = \frac{1}{2}(g_{Cu} + g_{VO})$$
$$\delta = \frac{1}{2}(g_{Cu} - g_{VO}) \qquad (4)$$

and the axes of g_{Cu} and g_{VO} are assumed to be coincident. The eigenvalues of (3) are $\pm g_u H_u$ and $\frac{1}{2}(J \pm \sqrt{J^2 + 4\delta_u^2\beta^2 H_u^2})$. For J = 0, the spectrum for the u direction exhibits two signals at:

$$H_{1(2)} = \frac{h\nu}{\beta(g_u \pm \delta_u)} \qquad (5)$$

where hν is the frequency of the incident quantum (~0.3 cm^{-1} in X-band). From (4), (5) is equivalent to:

$$H_1 = \frac{h\nu}{\beta g_{Cu}}\ ; H_2 = \frac{h\nu}{\beta g_{VO}} \qquad (6)$$

Therefore, although the spectrum is formally associated to a singlet and triplet pair states accidentally degenerate, it is identical to what is expected for two non-interacting local doublet sates.

For $0 < |J| < h\nu$, each signal is split into two components, so that four signals are expected. The two signals at lowest and highest fields respectively correspond to the singlet–triplet transitions experimentally observed by Hendrickson *et al.* [15]. Their intensity decreases when |J| increases [16]. When |J| reaches the value of hν, the lowest field signal disappears and the highest field signal may occur with an extremely weak intensity beyond the range covered in the X-band. The two median transitions occur in the triplet state. They merge in a single transition at $H = h\nu/\beta g_u$ when |J| increases.

From the discussion above, it follows that the E.P.R. spectrum of [CuVO] is exactly what it is expected for $|J| > h\nu$ with a g value intermediate between g_{Cu} and g_{VO}. Since the magnetic data gave an higher limit for |J|, it is possible to conclude that |J| in [CuVO] is between 0.3 and 1 cm^{-1}. However, the sign of J cannot be specified.

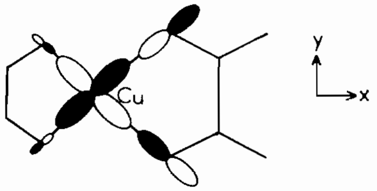
Discussion

In this section, our purpose is to rationalize the magnitude of the interaction in the [CuCu], [VOVO] and [CuVO] pairs through the same oxalato bridge. To begin with, we briefly recall the key expression of the orbital model of the exchange interaction developed in our group [4]. The singlet–triplet energy gap J in a pair of interacting single-ion doublet states is given by:

$$J = J_{AF} + J_F$$
$$J_{AF} = -2S(\Delta^2 - \delta^2)^{1/2} \qquad (7)$$
$$J_F = 2j$$

S is the overlap integral and j the two-electron exchange integral between the magnetic orbitals. δ is the energy gap between the magnetic orbitals centered on the one and the other interacting metal ions, so that δ is zero in the [CuCu] and [VOVO] symmetrical complexes, and Δ is the energy gap between the two molecular orbitals constructed from the magnetic orbitals. At the first order, $(\Delta^2 - \delta^2)^{1/2}$ and S are proportional, so that the antiferromagnetic contribution J_{AF} varies as S^2 or $(\Delta^2 - \delta^2)$.

The magnetic orbital ϕ_{Cu} around Cu^{II} in the square pyramidal CuN_2O_3 chromophore with the metal very close to the CuN_2O_2 basal plane is schematized in *2*.

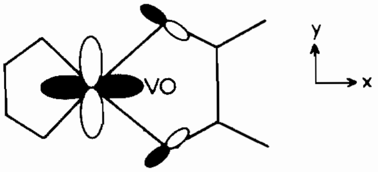


$a''(xy)$

2

Assuming a C_s site symmetry, this magnetic orbital transforms as a'' and is delocalized in an antibonding fashion towards the oxygen atoms of the bridge with σ metal–oxygen overlaps.

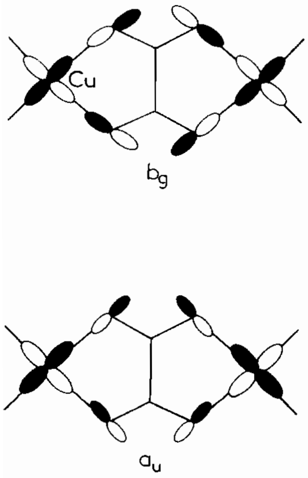
The magnetic orbital ϕ_{VO} around VO(II) in the VOO_5 chromophore, schematized in *3*, transforms as a' (referring to C_s site symmetry) and is delocalized towards the oxygen atoms of the bridge with π metal–oxygen overlaps. Since the π overlaps are weaker than the σ ones, the delocalization towards the bridge is less pronounced in ϕ_{VO} than in ϕ_{Cu}.



$a'(x^2-y^2)$

3

In [CuCu] the two magnetic orbitals interact of each side of the oxalato bridge owing to the out-of-bond oxygen–oxygen overlaps. This interaction leads to the two molecular orbitals (m.o.) schematized in *4*, transforming as b_g and a_u in the C_{2h} group.



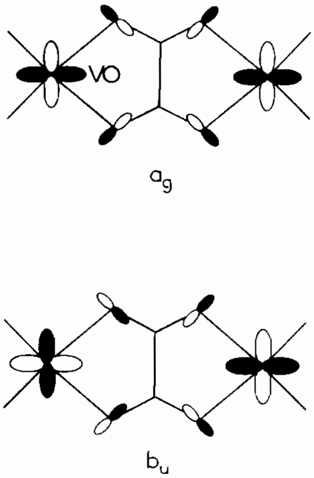
b_g

a_u

4

The overlaps between oxygen atoms linked to the same carbon atom are negative in b_g and positive in a_u. This destabilizes the former m.o. and stabilizes the latter, so that the Δ gap may be important and the interaction strongly antiferromagnetic in spite of the large Cu$\cdots$Cu separation [17–18].

In [VOVO], the interaction between the two magnetic orbitals gives rise to the a_g and b_u m.o.'s (referring to C_{2h} symmetry) shown in *5*. Owing to the oxygen–oxygen overlaps, a_g is stabilized with regard to b_u. However the Δ gap is weaker than in the [CuCu] case since the delocalization of ϕ_{VO} towards the nearest-neighbour oxygen atoms is less pronounced.

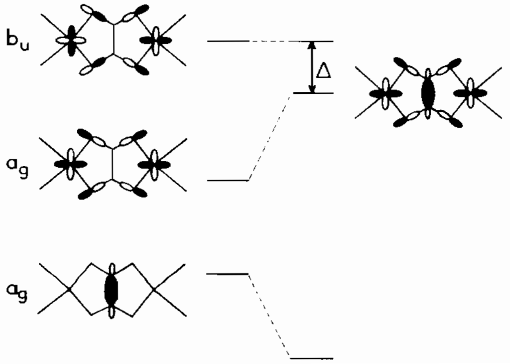


a_g

b_u

5

Another factor could significantly contribute to the weak interaction in [VOVO]. Until now, we did not consider the role of the C–C single bond of the oxalato bridge. The σ bonding m.o. describing this bond has the a_g symmetry, hence it may interact with the a_g m.o. constructed from the magnetic orbitals and push it away towards the higher energies, as schematized in *6*. This $a_g - a_g$ interaction tends to diminish Δ. To the best of our knowledge, only one comparison of Cu(II)Cu(II) and VO(II)VO(II) pairs already appeared, concerning complexes with 1,3,5-triketones [19]. The metal ions are then bridged by



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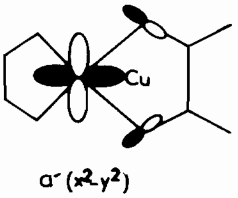
the two oxygen atoms of the central ketone group. From limited magnetic data, the singlet–triplet gaps were found as -825 cm^{-1} in the dicopper(II) complex and -160 cm^{-1} in the divanadyl complex. The relatively large interaction in this latter compound could be due, in part, to the direct interaction between $a'(x^2 - y^2)$ type magnetic orbitals (see *3*) centered on metal ions separated by less than 3 Å.

In [CuVO], the two magnetic orbitals are strictly orthogonal [2]. they transform as different irreducible representations of the C_s site group. Thus, J_{AF} in (7) is identically zero. The interaction is expected to be ferromagnetic with a triplet ground state stabilized by $J_F = 2j$, regarding the low lying singlet state. In contrast to what happens in $CuVO(fsa)_2en \cdot CH_3OH$ [2], ϕ_{Cu} and ϕ_{VO} do not give any region of strong overlap density $\rho(i) = \phi_{Cu}(i)\phi_{VO}(i)$. This explains why the triplet and singlet states are found to be almost degenerate.

The last problem we would like to approach is the following: why, in spite of the large intramolecular interaction ($J = -385.4$ cm^{-1}), no zero field splitting is detected in the triplet state of [CuCu]? The zero field splitting in a symmetrical pair arises from the combined effect of the dipolar interaction and the anisotropic exchange. The former term which varies as d^{-3}, is negligible for two metal ions separated by 5.14 Å. Therefore, we have to focus on the anisotropic exchange which involves the interaction between the ground state of an ion and the excited states of the other. The single-ion excited state for the CuN_2O_3 chromophore which potentially could interact with the single-ion ground state a'' (xy) (see 2) is a' $(x^2 - y^2)$ (see *7*).



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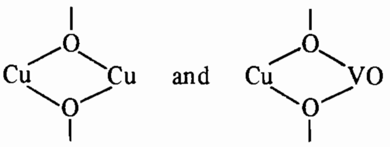
Indeed, the a'' (xy) and a' $(x^2 - y^2)$ orbitals are localized in the same basal plane containing the oxalato bridge. In a quite simplified form, the axial zero field splitting parameter D arising from the anisotropic exchange may then be written as [22–24]:

$$D = \frac{1}{16}(\Delta g_z)^2 \times j_{a'',a'} \tag{8}$$

with $\Delta g_z = (g_z - 2)$ referring to the monomeric fragment [Cu–]·$j_{a'',a'}$ is the bicentric two-electron exchange integral between the a''(xy) and a' $(x^2 - y^2)$ localized orbitals. If we assimilate the a' orbital (*7*) in CuN_2O_3 to the a' orbital (*3*) in VOO_5, then we may write:

$$\underset{\text{in [CuCu]}}{D} \cong \frac{1}{32}\underset{\text{in [Cu–]}}{(\Delta g_z)^2} \cdot \underset{\text{in [CuVO]}}{J} \tag{9}$$

In other words, the anisotropic exchange in [CuCu] is proportional to the isotropic exchange in [CuVO], hence is extremely weak. A relation similar to (9) was recently proposed by Bencini *et al.*, but in the case of the networks



where both D in [CuCu] and J in [CuVO] were important [25].

Conclusion

In the Introduction to this paper, we put two questions which the results of this work allow us to answer:

(i) The interaction between two VO(II) ions through the oxalato bridge is drastically reduced with regard to the situation in the [CuCu] species. More generally, the oxalato group is an excellent bridging ligand to achieve a strong antiferromagnetic interaction between metal ions far away from each other in homobimetallic complexes when the xy exchange pathway is operative [3, 18, 20, 21]. This pathway does not exist in [VOVO].

(ii) Even when the strict orthogonality of the magnetic orbitals is realized, as in [CuVO], the oxalato bridge is apparently not appropriate to achieve a strong ferromagnetic interaction. This is due to the fact that the overlap density ρ_{xy,x^2-y^2} does not present any zone of strong magnitude.

In addition to these two answers, we attempted to explain why the anisotropic exchange in [CuCu] was negligible whereas the isotropic exchange was as large as -385.4 cm^{-1}. This explanation is based on an analogic relationship between anisotropic exchange in [CuCu] and isotropic exchange in [CuVO].

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