respectively) and is broadened (Figure 2). This behavior is consistent with two species in equilibrium, which are exchanging at a rate that is rapid compared to the chemical shift difference of the deuterium nuclei. At pHs well removed from the pK_a's, where the equilibrium is shifted predominantly to the right side of eq 2 and 3, the spectrum that is predicted is

$$[Cr(edta)]^- + OH^- \rightleftarrows [Cr(edta)(OH)]^{2-} \quad (2)$$

$$[Cr(edta)]^- + H_3O^+ \rightleftarrows [Cr(Hedta)(H_2O)] \quad (3)$$

essentially the same regardless of the exchange rate (i.e., there is no exchange). Although it is not possible to extract a rate constant directly, it is possible to estimate a lower limit if it is assumed that the resonance at 45 ppm in the spectrum of $[Cr(edta)]^-$ at pH 6.3 and the resonance at −15 ppm in the spectrum at pH 10.6 are the resonances associated with the exchanging G-ring.[31] The conditions for fast exchange dictate that the rate must be large (2×) compared to the chemical shift difference of the resonances of the two exchanging species.[32] Since the differences in chemical shifts are on the order of 60 ppm (1800 Hz), the exchange rates for the complex at pHs near the pK_a's must be on the order of several thousand per second. In an experiment in which $[Cr(edta)(OH)]^{2-}$ (in 0.1 M hydroxide) is added to a pH 4 buffer, Thorneley and Sykes found an apparent rate constant that is greater than 10^3 s^{-1}.[9]

Is it interesting to speculate why it is that the substitution by hydronium/water/hydroxide is so fast at pH 2.3 and 7.4 and not at other pHs. Considering that the concentration of water remains constant regardless of pH, the concentrations of H_3O^+ and OH^- are negligible (ca. 10^{-2} and 10^{-7} M in H_3O^+, respectively), and that small changes in pH are responsible for dramatic changes in both structure and reactivity, it becomes apparent that the phenomenon found here is a very subtle one. One possible explanation is that the sexidentate complex (with respect to edta) is really a seven-coordinate Cr(III) ion where water is bound as the seventh ligand. Although there is no precedent for this behavior in Cr(III) systems (nor is there any direct evidence presented here), Cr(III) compounds are known to undergo substitution via an associative mechanism[33] and seven-coordination has been observed in crystalline $[Fe(edta)(H_2O)]^-$ complexes.[34] The Fe(III) complex is also known to have acid–base properties similar to those of the Cr(III) complex in the neutral pH region.[7] The rapid equilibrium at pH 7.4 could then be viewed as the deprotonation of the bound water to form the dianionic complex, which converts to the six-coordinate quinquedentate $[Cr(edta)(OH)]^{2-}$ by losing one of the bound acetate arms of the edta. The process at pH 2.3 could be viewed as the protonation of the bound carboxylate arm followed by rearrangement to the quinquedentate complex.

Conclusions

It is found from ^2H NMR data that edta forms a sexidentate complex with Cr(III) in the pH range 3.5–6.5. Above and below these pHs there is a rapid equilibrium between the sexidentate and the quinquedentate species that favors the quinquedentate species at the more extreme pHs. At pHs near the pK_a's the equilibrium between these two species is fast on the time scale of the NMR experiment with an exchange rate greater than 10^3 s^{-1}. The Cr–medtra complex is quinquedentate at all pHs studied and provides a reference point for our structural assignments. We have reinterpreted the UV/visible spectra of these complexes as a function of pH and found that they are consistent with our NMR data.

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Registry No. $[Cr(edta)]^-$, 16091-77-3; $[Cr(edta)(H_2O)]^-$, 19610-17-4; $[Cr(edta)(OH)]^{2-}$, 21729-57-7; $[Cr(medtra)(H_2O)]$, 55622-36-1; $[Cr(medtra)(OH)]^-$, 92055-18-0.

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Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA 672, Université de Paris Sud, 91405 Orsay Cedex, France, Laboratoire de Chimie de Coordination du CNRS, 31400 Toulouse Cedex, France, and Laboratoire de Physique Quantique, ERA 821, Université Paul Sabatier, 31062 Toulouse Cedex, France

Ab Initio Direct Calculation of the Singlet–Triplet Splitting in a μ-Oxalato Copper(II) Binuclear Complex

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The singlet–triplet (S–T) splitting of (μ-oxalato)bis((*N,N,N′,N′*-tetramethyl-1,2-ethanediamine)aquacopper(II)) perchlorate has been calculated in an ab initio scheme. The method, based on a perturbation development of the configuration interaction problem, directly gives the S–T energy separation, after an ab initio SCF–MO calculation on the open-shell system, using pseudopotentials. The $2K_{ab}$ ferromagnetic potential-exchange contribution is important (720 cm^{-1}) and not balanced by the second-order kinetic-exchange mechanism (~−450 cm^{-1}). The other second-order contributions are the double-spin polarization (−38 cm^{-1}), the ligand–metal charge transfer (−146 cm^{-1}), and the kinetic-exchange + polarization (−177 cm^{-1}). The fourth-order terms allow one to reach a total value of −295 cm^{-1} not too far from the experimental one of −385 cm^{-1}. The magnitude of the different contributions is discussed and compared to that of a μ-dithiooxamido copper(II) binuclear complex.

There are only few works dealing with non-semiempirical calculations of the singlet–triplet splitting in exchange-coupled systems. Two of us performed an ab initio direct calculation of this kind on the cupric acetate hydrate dimer.[2] The same

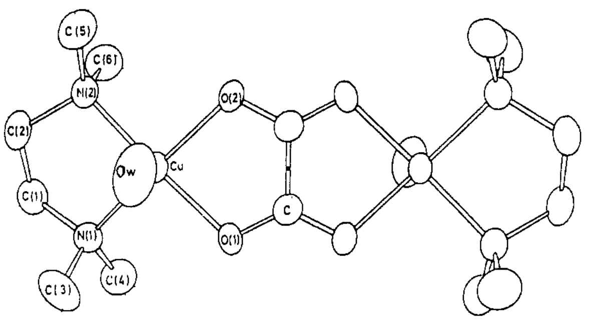

Figure 1. ORTEP drawing of [tmenCu(H_2O)oxCu(H_2O)tmen](ClO_4)$_2$.

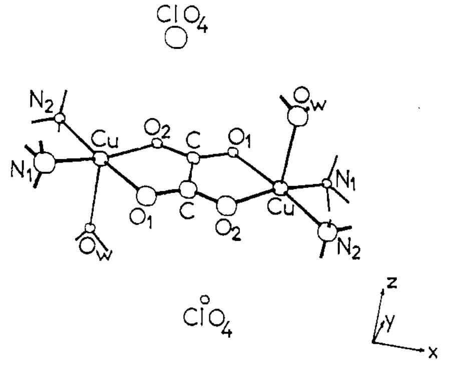

Figure 2. Schematic structure of the modelized binuclear μ-oxalato molecule.

approach has been used by the same authors for some other copper(II) dimers.[3] As experimental results have proved that extended bridges can transmit important magnetic interactions between ions far from each other,[4-6] a renewal of interest has appeared in theoretically understanding the factors that play a major part in the magnitude of the singlet–triplet (S–T) energy separation. The oxalate ion ($C_2O_4^{2-}$) is a bridging ligand that can lead to a large domain of values of the exchange-coupling constant J (from 0 to -384.5 cm^{-1} [7,8]) in copper(II) dimers, depending on the nature of the terminal ligands that constrain the geometry around the copper ion.

In this work we focus on the dimer [tmenCu(H_2O)oxCu(H_2O)tmen](ClO_4)$_2$·1.25H_2O, in which ox = oxalate and tmen = *N,N,N',N'*-tetramethyl-1,2-ethanediamine. The structure has been determined by X-ray diffraction[7,9] and we report the ORTEP plot of the binuclear unit in Figure 1. The S–T separation determined by magnetic measurements is $-J = 385.4$ cm^{-1}.[7]

We want to answer the following question: How is it possible to transmit an interaction as large as -384.5 cm^{-1} between two copper ions separated by a distance as large as 5.14 Å?

Table I. Coefficients of the Orthogonal Magnetic Orbitals for the μ-Oxalato and μ-Dithiooxamido Compounds[a]

oxalato dimer (A)				dithiooxamido dimer (B)			
		coefficients				coefficients	
atom	AO	a	b	atom	AO	a	b
Cu	d_{xy} ζ_1	0.618	−0.017	Cu	d_{xy} ζ_1	0.533	−0.017
	d_{xy} ζ_2	0.434	−0.016		d_{xy} ζ_2	0.369	−0.014
C	2s	0.011	−0.003	C	2s	0.040	−0.028
	$2p_x$	−0.029	−0.032		$2p_x$	−0.049	0.002
	$2p_y$	−0.088	0.091		$2p_y$	−0.093	0.065
	$2p_z$	−0.015	−0.003		$2p_z$	−0.006	−0.005
O1	2s	0.124	−0.035	N	2s	0.214	−0.055
	$2p_x$	0.204	0.077		$2p_x$	0.207	0.079
	$2p_y$	−0.205	−0.046		$2p_y$	−0.170	−0.014
	$2p_z$	−0.012	0.010		$2p_z$	−0.003	0.007
O2	2s	−0.124	0.034	S	3s	−0.098	0.017
	$2p_x$	−0.205	−0.077		$3p_x$	−0.399	−0.068
	$2p_y$	−0.209	−0.044		$3p_y$	−0.466	0.001
	$2p_z$	−0.001	−0.026		$3p_z$	0.013	−0.013
N1	2s	−0.182	−0.004	O	2s	−0.151	−0.016
	$2p_x$	0.174	−0.003		$2p_x$	0.054	0.010
	$2p_y$	0.181	−0.007		$2p_y$	0.148	−0.008
	$2p_z$	−0.079	0.003		$2p_z$	0	0
N2	2s	0.165	0.002	Ow	2s	0.139	0.006
	$2p_x$	−0.204	0.004		$2p_x$	−0.149	0
	$2p_y$	0.183	−0.007		$2p_y$	0.098	−0.007
	$2p_z$	0.003	0		$2p_z$	0.004	0
Ow	2s	−0.011	0.001				
	$2p_x$	−0.001	−0.001				
	$2p_y$	0	−0.006				
	$2p_z$	0.010	0				

[a] a and b refer to the two orthogonal magnetic orbitals. The coefficients are given for only one of the two equivalent atoms.

Method

The method is derived from that used for the calculation on the copper(II) acetate dimer.[2] Some modifications have been performed in order to decrease the computation time without significant loss in the validity and interpretation of the results.[3] The calculation proceeds in two steps: (i) An ab initio SCF–MO calculation is carried out on the open-shell system; it leads obviously to wrong energy values, but it allows us to define the "magnetic orbitals". (ii) A perturbative development of the configuration interaction problem directly gives the singlet–triplet splitting.

(A) SCF Calculation. For the calculation, a model complex of 30 atoms is derived from the X-ray structure of [tmenCu(H_2O)oxCu(H_2O)tmen](ClO_4)$_2$. It is represented in Figure 2. Each tetramethylethanediamine has been replaced by two NH_3 groups, the H atoms being located along each crystallographically determined N–C direction and the N–H distance being equal to 1.0 Å. In order to ensure the electroneutrality of the entity, we added two point charges located at the Cl nuclei instead of the two real perchlorate anions. The total symmetry C_i is taken into account in the whole program. The valence-electrons-only calculation is carried out by using atomic pseudopotentials

$$W_l = \exp(-\alpha r^2)\sum_{i=1}^{n} c_i r_i^{n_i} \qquad l = 0, 1, 2 \text{ for s, p, d subshells} \qquad (1)$$

as defined by Durand, Pelissier, and Barthelat.[10] The specific parameters used are taken from Pelissier[11] for copper and from standard calculations[12] for other atoms. A standard basis of Cartesian Gaussian type orbitals (GTO) has been optimized for the fundamental state of the H, C, N, and O neutral atoms and for the Cu^+ ion by using these pseudopotentials.[12] The choice of Cu^+ instead of Cu^0 is connected with the most relevant Cu configuration (d^9s^1)Cu^+ in the complex. The GTO's are then contracted in a single-ζ form for oxygen, nitrogen,

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carbon (4s4p to 1s1p contraction), hydrogen (3s to 1s), and for the 4pAO's of copper, and in a double-ζ form for the 3d AO's of copper. A polarization orbital is added to the single-ζ 4s orbital of copper in order to obtain a better description of the valence region. The final contraction is then 3s4p5d to s + s′1p2d. The SCF calculation is performed according to the PSHONDO program,[13] in which the open-shell calculation is carried out with a mean Fock operator after Nesbet[14]

$$\hat{F} = \hat{h} + \sum_{i}(2\hat{J}_i - \hat{K}_i) + (\hat{J}_u - \tfrac{1}{2}\hat{K}_u) + (\hat{J}_g - \tfrac{1}{2}\hat{K}_g) \qquad (2)$$

where, as usual, $\hat{h}$ is the monoelectronic part of the Hamiltonian, $\hat{J}$ and $\hat{K}$ are the Coulomb and exchange operators, respectively, i refers to the MO's of the closed shells, and u and g to the singly occupied MO's.

The open-shell SCF calculation gives two singly occupied MO's φ_u and φ_g, which are essentially built from the d_{xy} AO's of the Cu atoms: $d_{xy}(\mathrm{Cu}) \pm d_{xy}(\mathrm{Cu}^*)$. The asterisk indicates the atom transformed through the inversion center; the choice of the axes is reported in Figure 2. The two canonical MO's are then localized to give the so-called "orthogonal magnetic orbitals" (OMO)[15]

$$\mathbf{a} = (1/2^{1/2})(\varphi_g + \varphi_u) \qquad \mathbf{b} = (1/2^{1/2})(\varphi_g - \varphi_u) \qquad (3)$$

The coefficients of **a** and **b**, which we comment on in the discussion, are reported in Table I. Notice that **b** is the transform of **a** through the inversion center.

(B) Perturbative Treatment of the Configuration Interaction. The method leading to the S–T splitting has been extensively described.[2] We recall its principle and give the expression of the main contributions.

Formalism. We use a perturbation treatment of the CI problem[16]

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V} \qquad (4)$$

in which $\hat{\mathcal{H}}_0$ is the nonperturbed Hamiltonian and $\hat{V}$ the perturbative correlation potential. As discussed in ref 16–18, the choice of the partition of the exact Hamiltonian $\hat{\mathcal{H}}$ in (4) is not unique and leads to different convergence rates of the Rayleigh–Schrödinger perturbation expansion. In the Möller–Plesset (MP) partition[19]—often called "classical partition"—$\hat{\mathcal{H}}_0$ is the self-consistent Hamiltonian. In these scheme, the transition energies involved in the denominators are defined as differences between the eigenvalues ϵ of the SCF Hamiltonian

$$\Delta E_{p\to q} = \epsilon_p - \epsilon_q \qquad (5)$$

This choice enables us to use the same transition energies for all the configurations corresponding to a given space function and gives simplifications in the energy corrections.[16,20] With this definition, a degeneracy of the neutral $|a\bar{b}|$ or $|b\bar{a}|$ and ionic $|a\bar{a}|$ or $|b\bar{b}|$ determinants occurs and then the transition energy between magnetic orbitals $\Delta E_{a\to b}$ is zero. To overcome this difficulty, we define this transition energy as the difference between the mean values of the exact Hamiltonian

$$\Delta E_{a\to b} = \langle |a\bar{b}||\mathcal{H}||a\bar{b}|\rangle - \langle |a\bar{a}||\mathcal{H}||a\bar{a}|\rangle \qquad (6)$$

according to the Epstein–Nesbet (EN) definition.[14,21]

Zeroth Order. If we omit the closed shells, which play no part in the process, the zeroth-order eigenfunctions for the singlet and for the $S_z = 0$ component of the triplet state may be written

$$^1\psi_0 = (1/2^{1/2})\{|a\bar{b}| + |b\bar{a}|\} \qquad ^3\psi_0 = (1/2^{1/2})\{|a\bar{b}| - |b\bar{a}|\} \qquad (7)$$

With the choice of the MP partition, the zeroth-order energy splitting between these states is zero

$$\Delta E^0{}_{S\text{-}T} = E^0{}_S - E^0{}_T = \langle ^1\psi_0|\mathcal{H}_0|^1\psi_0\rangle - \langle ^3\psi_0|\mathcal{H}_0|^3\psi_0\rangle = 0 \qquad (8)$$

First Order. The first-order energy splitting is related to the exchange integral K_{ab} between the two degenerate OMO's

$$\Delta E^1{}_{S\text{-}T} = \langle ^1\psi_0|V|^1\psi_0\rangle - \langle ^3\psi_0|V|^3\psi_0\rangle = 2K_{ab} \qquad (9)$$

$$K_{ab} = \langle ab|r_{12}{}^{-1}|ba\rangle = (ab,ba) = \int\!\!\int \frac{a(1)b(1)\cdot a(2)b(2)}{r_{12}}\, d\tau_1\, d\tau_2 \qquad (10)$$

Second Order. The second-order CI corrections on the singlet and triplet states are

$$E^2{}_{S(T)} = \sum_{I\neq\psi_0} \frac{|\langle ^{1(3)}\psi_0|V|I\rangle|^2}{E^0{}_{S(T)} - E^0{}_1} \qquad (11)$$

where $E^0{}_1$ is the unperturbed energy of the excited configuration I represented by a single determinant. In the MP scheme

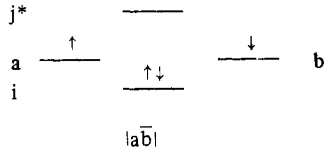
$$E^0{}_S - E^0{}_I = E^0{}_T - E^0{}_I \equiv E_0 - E_I \qquad (12)$$

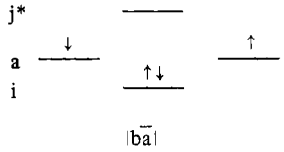
$$\langle ^{1(3)}\psi_0|\mathcal{H}_0|I\rangle = 0 \quad \text{for } I \neq \psi_0 \qquad (13)$$

so that $\hat{V}$ can be replaced by $\hat{\mathcal{H}}$ in (11). Hence, the second-order correction to the S–T splitting is

$$\Delta E^2{}_{S\text{-}T} = E^2{}_S - E^2{}_T = 2\sum_{I\neq\psi_0} \frac{\langle |a\bar{b}||\mathcal{H}||I\rangle\langle I|\mathcal{H}||b\bar{a}|\rangle}{E_0 - E_I} \qquad (14)$$

This equation shows that the configurations which play a part in the S–T energy difference are less numerous than those occurring in the energy of the singlet or triplet. The problem of finding all the determinants I that interact with both $|a\bar{b}|$ and $|b\bar{a}|$ can be solved by a diagrammatic method[2,22a] or by use of Slater's rules. The different second-order terms can be interpreted by using schemes that show the occupation of the OMO a and b as well as the eventual modifications in the occupied i and vacant j* MO's. The determinants $|a\bar{b}|$ and $|b\bar{a}|$





appear in all corrective terms. In Table II we report the scheme of the interacting contribution I and the expression of the correction for each type of contribution ((15)–(19)). We recall that all transition energies occurring in the denominators are negative and that they are calculated according to the MP definition except for $\Delta E_{a\to b}$, which is calculated according to the EN one. We name the corrections according to the definitions of the earlier work of Anderson.[22] The term $2K_{ab}$ is called "potential exchange"; it represents the energy gap between the homopolar singlet $^1\psi_0$ and triplet $^3\psi_0$ states due to the electronic repulsion. The second-order interaction between the homopolar and ionic singlets is named "kinetic exchange" to recall that it results from electron transfer from one site to the other.

Higher Order Terms. As previously shown,[2] corrections of order greater than 2 can play an important part owing to interaction of polyexcited states with the ionic configurations $a\bar{a}$ and $b\bar{b}$. As the role of these contributions is not still perfectly clear, we restricted the calculation to the fourth-order term referred to in ref 2 as "kinetic exchange, kinetic exchange + polarization"

$$\Delta E^4{}_{S\text{-}T} = \sum_{i}\sum_{j^*} \frac{4[(aa,ij^*) - (bb,ij^*)]^2\cdot F_{ab}{}^2}{(\Delta E_{a\to b})^2(\Delta E_{a\to b} + \Delta E_{i\to j^*})} \qquad (20)$$

Results

OMO. The orthogonal magnetic orbital of the model complex is presented in Figure 3 in the form of electronic isodensity curves, $|\mathbf{a}|^2$ = constant. The map is drawn in the mean mo-

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Table II. Second-Order Perturbation Contributions: Representation of $|I\rangle$ States and Expressions of the Corrections

contributions	$|I\rangle$		corrections	formula
kinetic exchange (KE)	**a,b** ↑↓ —	$|a\bar{a}|$	$\frac{4F_{ab}^2}{\Delta E_{a\to b}}$	15
double-spin polarization (DSP)	j* ↓ **a,b** ↑ ↑ i ↓	$|j^*\bar{i}ab|$	$-4\sum_{i}\sum_{j^*}\frac{(ia,j^*a)(ib,j^*b)}{\Delta E_{i\to j^*}}$	16
charge transfer (L → Cu)^2	**a,b** ↑↓ ↑↓ j ↑ i ↓	$|b\bar{i}j\bar{a}a\bar{b}|$	$2\sum_{i}\sum_{j}\frac{(ai,bj)(aj,bi)}{\Delta E_{i\to a}+\Delta E_{j\to b}}$	17
charge transfer (Cu → L)^2	j* ↓ i* ↑ **a,b** — —	$|i^*\bar{j}^*|$	$2\sum_{i^*}\sum_{j^*}\frac{(ai^*,bj^*)(aj^*,bi^*)}{\Delta E_{a\to i^*}+\Delta E_{b\to j^*}}$	18
kinetic exchange + polarization (KE + P)	j* ↑ a,b — ↑↓ i ↓	$|j^*\bar{i}b\bar{b}|$	$\sum_{i}\sum_{j^*}\frac{8(ab,ij^*)^2-4(ab,ij^*)[(ai,bj^*)+(aj^*,bi)]}{\Delta E_{a\to b}+\Delta E_{i\to j^*}}$	19

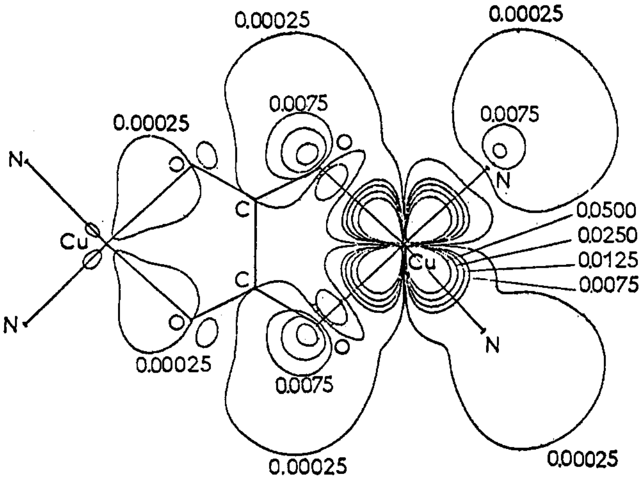

Figure 3. Electronic isodensity curves for the magnetic orbital: $|\mathbf{a}|^2$ = constant, in the mean molecular plane.

lecular plane $z = 0$, which contains the two copper and the two carbon atoms and almost the four oxygens of the bridging oxalato ligand and the four nitrogens of the NH_3 groups. This OMO **a** represents a set of in-plane antibonding bonds. Several not totally independent features can be noticed: (i) A high electronic density around the Cu atoms results from an important participation of the metallic d_{xy} orbitals. (ii) The delocalization from the metal toward the nearest oxygen atoms of the bridge is important and is greater than that toward the terminal nitrogen atoms. (iii) The electronic density is almost zero around the carbon atoms, because the AO's of carbon essentially contribute to low-lying MO's. (iv) As a consequence of the orthogonality of the OMO **a** and **b** constructed from the localization of the MO φ_g and φ_u, "delocalization tails" appear on the second copper atom and on its neighbor oxygen atoms. (v) The water molecules, which lead to a 4 + 1 coordination of each copper, play no part in **a** and **b**.

Potential Exchange. The K_{ab} exchange integral between magnetic orbitals defined in (10) is related to the overlap density between the two OMO **a** and **b** defined as

$$\rho_0 = a(1)b(1) \qquad (21)$$

The higher ρ_0 for points of space close to each other (i.e. small r_{12}), the larger K_{ab}. In this respect it is not surprising to obtain a very high exchange term ($\simeq$720 cm^{-1} as compared to 234 cm^{-1} in copper acetate[2]) owing to the concentration of **a** around the oxygen atoms and to the importance of the delocalization tails.

A semiquantitative interpretation of the S–T splitting based on the concept of overlap density between magnetic orbitals has been given in ref 23. In this last approach, however, **a** and **b** are not orthogonal and do not present delocalization tails on the other metallic center. In that case, the exchange integral between two nonorthogonal magnetic orbitals (NMO) is the only ferromagnetic (i.e. positive) contribution to the S–T energy gap, and it is smaller than K_{ab} between OMO. Relationships between bielectronic integrals defined in terms of NMO and OMO have been reported.[24]

Kinetic Exchange. Expression 15 leads to

$$\Delta E^2_{KE} = -\frac{(\epsilon_g - \epsilon_u)^2}{J_{aa} - J_{ab}} \qquad (22)$$

ϵ_g and ϵ_u being the SCF energies of φ_u and φ_g. Owing to the important metallic character of **a**, the "monocentric" Coulomb integral J_{aa} amounts to 152 000 cm^{-1} so that $J_{aa} - J_{ab}$ = 126 600 cm^{-1}. The delocalization of the copper electrons toward the oxygen atoms of the oxalato bridge results in $p(O_1)$–$p(O_2{}^*)$ and $p(O_1{}^*)$–$p(O_2)$ overlaps, which are bonding in φ_u and antibonding in φ_g; this gives rise to a large energy splitting, $\epsilon_g - \epsilon_u$ = 7572 cm^{-1}. Consequently, the kinetic-exchange term is important: ΔE^2_{KE} = −452.7 cm^{-1}.

Double-Spin Polarization. According to the terms (ia,j*a) and (ib,j*b) from (16), the only pairs of MO i and j* that significantly contribute to the DSP must have a nonnegligible participation in the regions where both **a** and **b** are relatively important. Table I points out that both **a** and **b** present noticeable values either on the oxygen and nitrogen atoms or on the copper atoms. Moreover, using symmetry properties, we readily see that if i and j* are both u or both g, the two bielectronic integrals (ia,j*a) and (ib,j*b) have the same sign; recalling that the transition energies are negative, we conclude that the triplet is stabilized (ferromagnetic contribution). If i and j* are of different symmetries, the contribution is antiferromagnetic.

The calculation shows that $\Delta E^2_{DSP} \simeq -38.3$ cm^{-1}. This term, rather small though not negligible, is the balance of both ferromagnetic and antiferromagnetic contributions, which can be as important as ±105.3 cm^{-1}. The only terms greater in absolute value than 22 cm^{-1} come from the highest two vacant MO's, j*, which are the g and u "oscillant MO's" built from the d_{xy} AO's of Cu and Cu*. These two excited j* MO's both interact with the same i orbitals giving contributions of opposite sign but of the same order of magnitude; all the i MO's involved contain a participation of the dxy AO's. The importance of such ij* pairs is related to the spatial form of the j*

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orbitals and to the delocalization tails of **a** and **b**, and we must not overestimate their physical meaning.

Charge Transfers $(L \rightarrow Cu)^2$ and $(Cu \rightarrow L)^2$. Looking at the expressions of these corrections ((17) and (18)), we conclude that both i and j (or i* and j*) must develop on the AO's that contribute to both **a** and **b**. But, in the case of charge transfer, we can have i ≡ j (or i* ≡ j*), giving rise to regions of high i(1)·i(2) (or i*(1)·i*(2)) values. Hence it is not surprising that such i ≡ j (i* ≡ j*) terms give the main part of the charge-transfer corrections, and it is worth noticing that these contributions are necessarily antiferromagnetic. On the other hand, terms with i $\not\equiv$ j (i* $\not\equiv$ j*) can lead to ferro- or antiferromagnetic corrections.

For the $(L \rightarrow Cu)^2$ transfer, the two principal contributions involve i = j MO's, which essentially consist of the p_x and p_y AO's of the oxygen atoms. Though their energies are nearly equal, the u MO gives a correction about 10 times as large as the g one. As for the $(Cu \rightarrow L)^2$ transfer, the corrections are very small because the i* ≡ j* MO's, which develop on the same AO's as **a** and **b** are very high in energy. Among them we can notice the two last vacant MO's, which, in our basis set, are the g and u oscillant combinations of the $d_{xy}(Cu)$ and $d_{xy}(Cu^*)$ AO's occurring in the DSP correction.

Kinetic Exchange plus Polarization (KE + P). It is striking to compare the value -177.0 cm^{-1} of this KE + P term to the very small value -2.3 cm^{-1} obtained in copper acetate. This correction (expression 19) may be written in the equivalent form

$$\Delta E^2{}_{\mathrm{KE+P}} = \sum_{\mathrm{i}}\sum_{\mathrm{j}^*} \frac{4(\mathrm{ab,ij}^*)[2(\mathrm{ab,ij}^*) - (\mathrm{ai,bj}^*) - (\mathrm{aj}^*\mathrm{,bi})]}{\Delta E_{\mathrm{a}\rightarrow\mathrm{b}} + \Delta E_{\mathrm{i}\rightarrow\mathrm{j}^*}} \tag{23}$$

which shows that the overlap density ρ_0 between OMO appears in all terms. Hence the overlap density i·j* must be as appreciable in the same region as ρ_0 to contribute to $\Delta E^2{}_{\mathrm{KE+P}}$. Moreover, in order to get a nonzero term, i and j* must be both g or both u and the correction is then positive or negative. Such a situation occurs with the oxalato bridge but not with the acetato one.

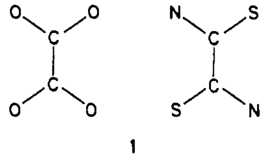
Fourth-Order Term. The expression (20) of the fourth-order correction is not easy to interpret. But, if we remark that

$$\Delta E^4{}_{\mathrm{S-T}} = \Delta E^2{}_{\mathrm{KE}} \cdot \sum_{\mathrm{i}}\sum_{\mathrm{j}^*} \frac{[(\mathrm{aa,ij}^*) - (\mathrm{bb,ij}^*)]^2}{\Delta E_{\mathrm{a}\rightarrow\mathrm{b}}(\Delta E_{\mathrm{a}\rightarrow\mathrm{b}} + \Delta E_{\mathrm{i}\rightarrow\mathrm{j}^*})} \tag{24}$$

we can conclude that the fourth-order correction may only be important in binuclear units that exhibit a large kinetic exchange and that the only pairs i,j* of MO's that can contribute must have different symmetry, leading in all cases to a negative contribution.

Discussion and Comparison with a Similar Binuclear Compound

In this section, we compare the results obtained in the μ-oxalato copper(II) compound—hereafter referred to as compound A—to those concerning another copper(II) entity, compound B, exhibiting a very similar bridging ligand, the dithiooxamido anion. The bridges are sketched in **1**. The structure of the centrosymmetric complex has been solved, and the magnetic susceptibility measurements give a very large singlet–triplet splitting, $-J$ = 594 cm^{-1} for a Cu–Cu distance as large as 5.61 Å.[4] The model compound used for calculation purposes is reported in Figure 4. The ab initio calculation of the S–T splitting has been carried out according to the method explained in this paper.[3] In this dimer the two monooccupied MO's of the open-shell system are also φ_g and φ_u, g and u combinations of $d_{xy}(Cu)$ and $d_{xy}(Cu^*)$. The two OMO's **a** and **b** result as above from the localization of φ_u and φ_g, and the main coefficients of **a** are reported in Table I. In Table III we give the contributions to the S–T energy gap.



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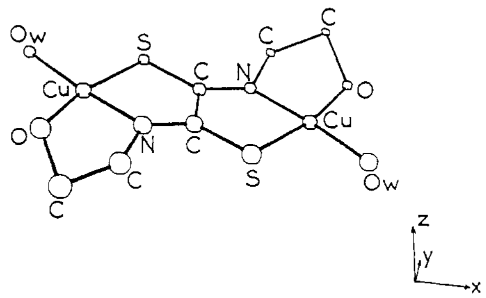


Figure 4. Schematic structure of the modelized binuclear μ-dithiooxamido molecule.

Table III. Numerical Values of the Different Contributions to the Singlet–Triplet Splitting for μ-Oxalato, μ-Dithiooxamido, and μ-Acetato Compounds

contributions	values of the corrections/cm^{-1} oxalato complex,[a] A	dithio-oxamido complex,[b] B	acetato complex[c]
zeroth order $K_{\mathbf{ab}}$	719.83	382.58	233.6
second order KE	−452.69	−507.04	−204.3
DSP	−38.29	−8.99	−52.0
$(L \rightarrow Cu)^2$	−145.86	−85.76	−5.9
$(Cu \rightarrow L)^2$	−9.08	−6.98	0.0
KE + P	−177.00	−120.60	−2.3
fourth order	−192.01	−242.77	−89.3[d]
total	−295.10	−589.56	−120.2[d]
exptl value	−385.4	−595	−286.0

[a] This work. [b] Reference 3. [c] Reference 2. [d] Another estimate of higher order terms gives −213.5 leading to a total of −244.2, close to the experimental value.

Comparison of the OMO's of A and B. Looking at Table I, we can notice that (i) the participation of $d_{xy}(Cu)$ is greater in A than in B, (ii) the electronic density around the oxygen in A is smaller than that around the sulfur in B, (iii) the delocalization toward the "external" ligands, N in A and O in B, is greater in A than in B, and (iv) the delocalization tails on the second copper atom and its first neighbors are smaller in B than in A.

This can be understood in the following way: The energy of the last "σ-type" occupied MO of the bridge lies closer to the energy of the d orbitals in B than in A. The copper–ligand interaction is then stronger in B than in A, and the Cu-bridge delocalization is larger in B. We must also take into account the fact that the less electronegative the coordinated atom is and the more diffuse its AO's are, the greater this delocalization is; that is S > O and N > O. The comparison of the OMO's of the two dimers may be summed up by the expression that the OMO is more "concentrated" (around copper and its *bridging* atoms) in the oxalate than in the dithiooxamide complex. However, we keep in mind that Nesbet's MO's are too delocalized; differences between calculations can then be overestimated.

Comparison of the Potential and Kinetic Exchange Terms in A and B. The more diffuse character of the OMO of B and the smaller extent of the delocalization tails in B as compared to those in A result in smaller values of the overlap density for B than for A. The exchange integral K_{ab} will then be smaller for the dithiooxamide than for the oxalate. This is corroborated by the calculation that specifies that the exchange term is about twice as small for the dithiooxamido as for the oxalato copper dimer.

The S–N* (or S*–N) distance in B is 2.674 Å[4] as compared to 2.226 Å for the O_1–O_2* distance in A. This can explain why the energy splitting $\epsilon_g - \epsilon_u$ is smaller for B than for A (6694 and 7572 cm^{-1}, respectively). On the other hand, the more "concentrated" character of the OMO in the oxalato compound as compared to that of the dithiooxamido one leads to a "monocentric" Coulomb integral J_{aa} greater for A than for B ($\simeq$ 152 000 cm^{-1} for A as compared to $\simeq$113 600 cm^{-1} for B) whereas the "bicentric" Coulomb integrals J_{ab} are nearly equal (25 400 and 25 200 cm^{-1} respectively); J_{aa}–J_{ab} is then greater for A than for B. Numerators and denominators vary in the same way, but the calculation shows that the kinetic-exchange contribution is greater for the dithiooxamido than for the oxalato binuclear unit. It is important to notice that the energy splitting $\epsilon_g - \epsilon_u$, which is often the only term invoked in the variation of the antiferromagnetic contribution (cf. ref 15), does not give the right conclusion.

At this stage, a statement in ref 2 needs some comment; it says that the delocalization on the ligands that increases the differential overlap between **a** and **b** should increase the magnitude of both the potential- and kinetic-exchange contributions, which are of opposite sign. A glance at Table III shows that the two points are not so readily correlated. First, in the case of polyatomic bridges **a** and **b** must delocalize on the same atoms in order to enhance the overlap density; this depends on the actual structure of the bridge. Second, as already noticed by Kahn and Charlot,[23] both ferro- and antiferromagnetic contributions are related to the overlap density $\rho = a' \cdot b'$ between nonorthogonal magnetic orbitals (NMO) **a**′ and **b**′. The ferromagnetic terms (here K_{ab}) essentially rely on regions of high ρ values, whereas the antiferromagnetic ones (here $\Delta E^2{}_{KE}$) are connected to the overlap integral between NMO's:

$$S = \int a'(1) b'(1) \, d\tau_1 = \int \rho(1) \, d\tau_1 \qquad (25)$$

They take into account, with their sign, not only the regions of great ρ values, which contribute the most to K_{ab}, but also the wide regions of weak ρ. It is in fact the diffuse character of the sulfur AO's, as well as the extension of the magnetic orbitals, that plays the most important part in enhancing the KE contribution in B as compared to that in A.

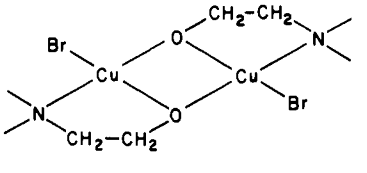
Comparison of Other Contributions. Results in Table I allow us to predict that in the dithiooxamide **a** and **b** will generally not be both as important as in the oxalate in the same point of space, because of the less important delocalization tails. Consequently, it is not surprising to obtain smaller DSP and charge-transfer contributions in B than in A.

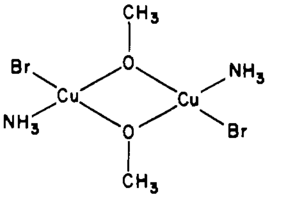
As for the fourth-order term, we must recall that it is proportional to the kinetic exchange term and hence may be more important in B than in A.

Comparison with the Acetato Binuclear Complex. It may be pointed out that in both the oxalato and dithiooxamido complexes all contributions to the S–T splitting—except the DSP—are larger than in the acetato complex, where only the potential and kinetic exchange terms are important (Table III). In this compound, the unpaired electron on each copper atom is delocalized toward four equivalent bridging ligands and only a few AO's contribute significantly to both **a** and **b**. But, on the other hand, both intra- and interligand excitations i → j* can occur in the DSP contribution, which is therefore larger in the acetato complex than in A or B. In copper acetate a near cancellation of potential and kinetic exchanges occurs. This result probably is fortuitous since the balance of these contributions is +267 cm^{-1} in the oxalato- and −124 cm^{-1} in the dithiooxamido-bridged compounds.

Conclusion

We present one of the first ab initio calculations performed on a binuclear copper(II) complex, with crystallographically determined geometry and only a slight modelization of the terminal ligands. The calculated value for the S–T splitting is −295 cm^{-1} whereas the experimental one is −385.4 cm^{-1}. We have therefore a good sign and a good order of magnitude, but we have a poorer agreement than in the dithiooxamido calculation (−589 cm^{-1} calculated for −594 cm^{-1} experimental). This discrepancy can arise from the real case studied. First, the crystal structure of A is made up of two binuclear entities by unit cell, each of them with a slightly different geometry. We performed the calculation on only one of these molecules, whereas the *J* experimental value is a mean. Second, we replaced in our calculation the *N*,*NN*′,*N*′-tetramethyl-1,2-ethanediamine terminal ligand by two ammonia molecules. The main phenomenon in the interaction between the two copper ions is likely due to the bridge between them. However, the part played by the terminal ligands remains to be thoroughly studied since it can modify the spin density on the bridge. A theoretical study in this direction has been performed recently[25] on the two compounds





Such a drastic modelization changed the S–T splitting by almost 30%. In the present case the replacement cannot infer such a large variation; it can nevertheless be noticeable.

The calculation method can also be invoked in several points: the basis set, the high order of perturbation, and essentially the choice of the partition of the exact Hamiltonian. At zeroth order we performed an open-shell SCF calculation using a mean Fock operator. On one hand, this use of a Nesbet operator is compulsory to obtain a cancellation of a great number of terms in the perturbative calculation of the S–T splitting because it ensures that both the singlet and triplet states have the same MO's. On the other hand, the magnetic orbitals that are solutions of this operator are too diffuse; this can lead to difficulties whenever there is a possible strong mixing of the magnetic orbitals with occupied orbitals. This is the case with end-on azido-bridged copper(II) dimers where another choice of the Fock operator must be made.[3] However, this situation does not occur in our complex.

More generally speaking, numerical agreement between experimental and theoretical values is not to be taken as the ultimate goal because until now imperfections are present in the calculation. It is evident from all the experiences gathered in quantum chemistry that an accurate determination of the S–T splitting requires more sophisticated means. Nevertheless, comparison of theoretical results obtained for slightly modelized compounds with low-cost ab initio calculations, such as the one presented in this paper, together with the use of other heuristic models[15,23] can lead to a better physical picture of the nature of the interaction between magnetic ions.

As a conclusion, we can answer the initial question. A large magnetic interaction between two copper(II) atoms separated by more than 5 Å occurs as a result of several effects of opposite sign that can be more important than the observed singlet–triplet splitting. The ferromagnetic potential-exchange

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contribution is the largest one. It decreases when the two unpaired electrons delocalize in wide or different regions of space. For "similar" bridges, the substitution of sulfur and nitrogen to oxygen shows that the less electronegative character of an atom and/or the more diffuse character of its AO's enhance the delocalization. The leading antiferromagnetic term is the kinetic exchange, which is greater the smaller the monocentric Coulomb integral is, that is the more important the delocalization is. Consequently, the large spatial extent of the magnetic orbitals favors the antiferromagnetic coupling.

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Design of μ-Oxalato Copper(II) Binuclear Complexes Exhibiting Expected Magnetic Properties

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The goal of this paper is to extract some basic concepts from the theory of the interaction between magnetic metal centers in coupled polymetallic systems and to show how they can be used to design μ-oxalato copper(II) binuclear complexes in which the magnitude of the antiferromagnetic coupling can be *tuned*. The two main concepts are those of *magnetic orbital*, defined as the singly occupied molecular orbital in a monomeric fragment, and of *overlap* between two magnetic orbitals in the binuclear unit. The magnitude of the antiferromagnetic interaction is expected to vary as the square of this overlap. In a $[LCu(C_2O_4)CuL']^{2+}$ binuclear cation, where L and L′ are terminal ligands, the two monomeric fragments $LCu(C_2O_4)$ and $L'Cu(C_2O_4)$ do actually exist. According to the nature of L and L′, the spatial orientation of the magnetic orbitals may be predicted, as well as the overlap between them. To test this approach, the synthesis, the crystal structures, and the magnetic properties of three new complexes are described: $[\text{tmen}(H_2O)Cu(C_2O_4)Cu(H_2O)\text{tmen}](ClO_4)_2\cdot1.25H_2O$ (**1**), $[\text{dien}Cu(C_2O_4)Cu(H_2O)_2\text{tmen}](ClO_4)_2$ (**2**), and $[\text{tmen}(2\text{-MeIm})Cu(C_2O_4)Cu(2\text{-MeIm})\text{tmen}](PF_6)_2$ (**3**), where tmen = *N,N,N′,N′*-tetramethylethylenediamine, dien = diethylenetriamine, and 2-MeIm = 2-methylimidazole. **1** crystallizes in the triclinic system, space group $P\bar{1}$ (a = 18.955 (3), b = 10.019 (3), c = 7.658 (3) Å; α = 98.30 (3), β = 98.37 (3), γ = 88.19 (2)°; Z = 2). Each copper atom is in a square-pyramidal environment with the two nitrogen atoms of tmen and two oxygen atoms of $C_2O_4^{2-}$ in the basal plane and a water molecule occupying the apical position. **2** crystallizes in the monoclinic system, space group $P2_1/c$ (a = 11.821 (4), b = 9.093 (3), c = 23.998 (6) Å; β = 96.50 (4)°; Z = 4). On the dien side, the four nearest neighbors of copper are the three nitrogen atoms of dien and only one oxygen atom of $C_2O_4^{2-}$; on the tmen side, the basal plane is again made of two oxygen atoms of $C_2O_4^{2-}$ and two nitrogen atoms of tmen. **3** crystallizes in the triclinic system, space group $P\bar{1}$ (a = 8.224 (2), b = 10.414 (3), c = 11.754 (3) Å; α = 94.63 (2), β = 108.57 (2), γ = 103.1 (2)°; Z = 2). The environment of each copper is intermediate between the square pyramid with only one oxygen atom of $C_2O_4^{2-}$ in the basal plane and the trigonal bipyramid. The magnetic properties of the three compounds were investigated in the 2–300 K temperature range and the singlet–triplet energy gaps deduced from the magnetic data were found as −385.4 cm^{-1} for **1**, −75.5 cm^{-1} for **2**, and −13.8 cm^{-1} for **3**. These values are compared to our previsions. Finally, the perspectives and the limits of such a molecular engineering of the coupled systems are discussed.

Introduction

The problem of the electronic structure of the coupled polymetallic systems has attracted the attention of a very large number of researchers. The main reason is probably that the phenomenon of interaction between metal centers lies at the meeting point of two apparently widely separated areas, namely the physics of the magnetic materials and the role of the polymetallic sites in the biological processes. Several orbital models have been proposed to describe the phenomenon of exchange interaction, and the controversies on the respective advantages and limits of each of them are still active.[2,3]

One of the goals of our group is to extract some basic ideas from these models and to show how they can be used to predict the nature of the transition ions and of the terminal and bridging ligands that must be utilized and the geometry that has to be achieved to obtain an interaction between the metal ions agreeing in sign and magnitude with the predicted values. In other words, we are attempting to lay the foundation of a molecular engineering of the coupled systems.[4]

In the last few years, several structural–magnetic correlations have been proposed.[5-11] In general, a dependence of the isotropic exchange parameter on some structural factors such as a bridging or a twist angle has been demonstrated. These correlations represent quite an important step in understanding the mechanism of the interaction. They cannot, however, be considered to be actual contributions to this molecular engineering. Indeed, except in very few cases, it seems extremely difficult to control the value of these structural parameters during the synthetic process. For instance, in dibridged copper(II) dimers like

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