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Orbital Reversal in (Oxalato)copper(II) Linear Chains

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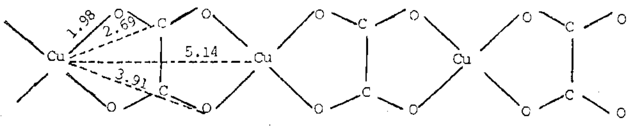
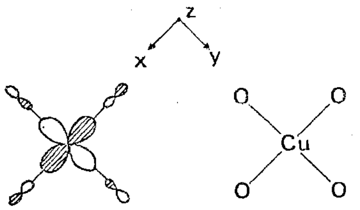
It is well established that the magnetic behavior of the copper oxalate $Cu(C_2O_4)\cdot{}^1/_3H_2O$ is that of a linear chain of strongly antiferromagnetically coupled spin doublets.[1-4] However, up to very recently, no orbital interpretation of this coupling had been proposed, owing to the lack of structural information. Indeed, all attempts to grow single crystals of $Cu(C_2O_4)\cdot{}^1/_3H_2O$, suitable for X-ray study, have been unsuccessful. An EXAFS study carried out in the Laboratoire d'Utilisation du Rayonnement Electromagnetique (LURE) in Orsay revealed that the structure was of the ribbon type as shown in **1**, with a 5.14-Å distance between nearest-neighbor copper(II) ions.[5]



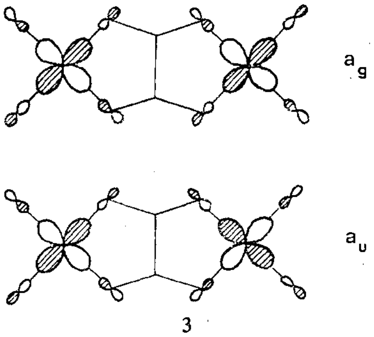
1

Knowing this structure, we may interpret the antiferromagnetic coupling as follows: the unpaired electron around each Cu(II) ion is described by a magnetic orbital from the $d_{x^2-y^2}$ metallic orbital pointing toward the oxygen atoms surrounding the metallic center as schematized in **2**. Here a magnetic orbital is defined as a singly occupied orbital centered on a transition-metal ion and partially delocalized toward the ligands surrounding this ion.[6]



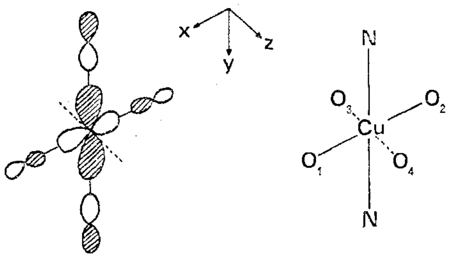
2

In a hypothetical centrosymmetric dimeric entity, the interaction of two magnetic orbitals centered on nearest-neighbor Cu(II) ions leads to two molecular orbitals, one symmetric (a_g) and the other antisymmetric (a_u) with regards to inversion (see **3**). The distance between two oxygen atoms linked to the same carbon atom of an oxalato bridge is relatively short, so that the oxygen–oxygen overlaps are far from being negligible and the a_u MO in which the oxygen–oxygen overlaps are positive is much lower in energy than the a_g MO in which the oxygen–oxygen overlaps are negative. This large energy gap between the two MO's, which is responsible for the antiferromagnetic coupling, will be quantitatively specified below. This interpretation is qualitatively identical with that given to explain the very strong antiferromagnetic coupling between Cu(II) ions separated by 5.61 Å in a (dithiooxamidato)copper(II) binuclear complex.[7]



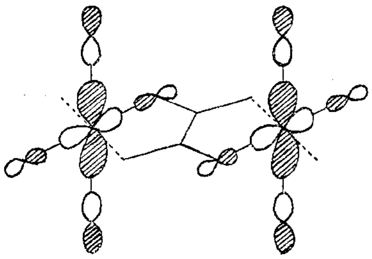
3

By fixing two nitrogen containing ligands per Cu(II) ion on both sides of the oxalato ribbon plane, we can expect that the surrounding of each Cu(II) will adopt an elongated rhombic geometry with two short Cu–N distances, two short Cu–O distances (CuO(1) and CuO(2)), and two long Cu–O distances (CuO(3) and CuO(4)). This drastic modification of the surrounding of each metallic center must induce a reversal of 90° around the O(1)CuO(2) axis of the magnetic orbital in such a way that the new magnetic orbital points toward the nearest-neighbor nitrogen and oxygen atoms (see **4**).



4

As shown in **5**, such a direction for the magnetic orbitals is particularly unfavorable for the interaction along the chain and should lead to a vanishing of the coupling. In fact the actual site symmetry of the Cu(II) ions is close to D_{2h}. Consequently there could be a small admixture of d_{z^2} orbital in the magnetic orbital, which could allow a weak "residual" coupling.



5

The situation we have pointed out above is encountered in $Cu(C_2O_4)(NH_3)_2\cdot 2H_2O$, the structure of which was determined.[9] The Cu–N bond length and short and long Cu–O bond lengths are 1.96, 2.16, and 2.33 Å, respectively. It can be noticed here that the final R agreement factor of this structure is only 0.14. The temperature dependence of the magnetic susceptibility of $Cu(C_2O_4)(NH_3)_2\cdot 2H_2O$, studied only in the range 80–300 K, was interpreted by the Ising Hamiltonian with $J = -11.9$ cm^{-1}. We reinvestigated the magnetic behavior of $Cu(C_2O_4)(NH_3)_2\cdot 2H_2O$ down to 3.6 K and interpreted the experimental data with the Heisenberg

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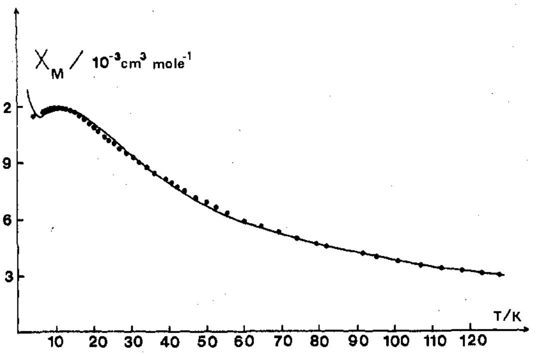


Figure 1. Temperature dependence of the molar magnetic susceptibility of $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$. The experimental points are noted • and the best fitting calculated curve is a continuous line.

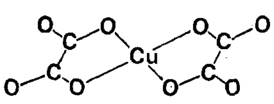
Hamiltonian $\mathcal{H} = -J\sum_{i=0}^{N-1}\hat{S}_i{\cdot}\hat{S}_{i+1}$ ($N \to \infty$). Indeed, we pointed out that only this phenomenological Hamiltonian has an orbital justification in the case of the interaction in a chain of ions, the ground term of which is an orbital singlet.[12]

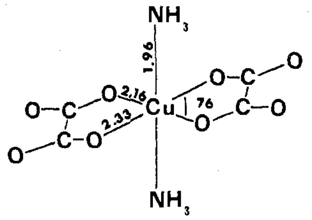
The χ_M measured susceptibility was expressed according to

$$\chi_M = \chi_C(1 - \rho) + \chi_I\rho$$

by taking into account the presence of a proportion ρ of noncoupled Cu(II), including impurities and ends of chain. For the χ_C susceptibility of the chain, we used the analytical expression proposed by Estes et al.[10] and we assumed that the monomeric impurity had the same molecular weight as the basis unit of the chain and that its magnetic susceptibility followed Curie law $\chi_I = N\beta^2g^2/4kT$. Least-squares fitting of the experimental data led to $J = -15.4$ cm^{-1}, $g = 2.13$, and $\rho = 0.0276$. The R factor defined as $\sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi_{obsd}^2$ is then equal to 3.43×10^{-4}. Experimental data and the theoretical curve are shown in Figure 1. In order to obtain a J value for $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ as accurate as that determined for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$, we reinvestigated the magnetic behavior of the former compound in the range 3.6–300 K and we fitted the experimental data by taking into account the monomeric impurity. The obtained J value was then -291 cm^{-1} with an R factor of 0.55×10^{-4}. As expected, the J value previously determined without correcting the experimental data of the monomeric impurity, -275 cm^{-1},[1-3] was too weak in absolute value.[11] So, the orbital reversal when one goes from $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ to $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$ induces a drastic weakening of antiferromagnetic coupling.

We now wish to specify more quantitatively this phenomenon of orbital reversal and its influence on the magnitude of the exchange interaction. We have proposed[12] an orbital model to describe the exchange interaction in linear chains where the J parameter is expressed as a sum of a J_{AF} antiferromagnetic contribution and a J_F ferromagnetic contribution. For spin-doublet interacting ions J_{AF} is given by $4\beta S$ where S is the overlap integral $\langle\phi_i|\phi_{i+1}\rangle$ between two magnetic orbitals centered on nearest-neighbor metallic ions and β the one-electron-exchange integral $\langle\phi_i|\mathcal{H}_1|\phi_{i+1}\rangle$, $\mathcal{H}_1$ being the one-electron part of the electrostatic (nonphenomenological) exchange Hamiltonian. 2β is the Δ energy gap between the two molecular orbitals in a dimeric entity arising from the interaction between these two nearest-neighbor magnetic orbitals; thus J_{AF} may be reexpressed as $-2S\Delta$. At the approximation level of the extended Hückel method, S and Δ are proportional, so that J_{AF} varies as Δ^2.[13,14] In Figure 2 are sketched the magnetic orbitals for both compounds, as obtained by extended Hückel calculations with the parametrization of the Appendix on the monomeric units. Calculation on hypothetic dimers gives $\Delta = 0.106$ eV for $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ and $\Delta = 0.0279$ for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$. The nonzero value of Δ for the latter compound essentially arises from the $d_{x^2-y^2}$–d_{z^2} mixing in the magnetic orbital. This admixture of d_{z^2} makes the unpaired electron density on the O_3 and O_4 oxygen atoms (see **4**), although weak, nonnegligible. This allows a small oxygen–oxygen interaction in the oxalato bridges. The Δ energy gap is 3.8 times larger for $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ than for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$. If we assume that in antiferromagnetically coupled systems, the variation of the experimentally observed J parameter is a good indication of the variation of J_{AF}, then we should expect a J value for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$, close to $-291/3.8^2 \approx -20$ cm^{-1}. The agreement between this prediction and the actual value, -15.43 cm^{-1}, appears fairly good. Perhaps even, it goes beyond the possibilities of the extended Hückel method.





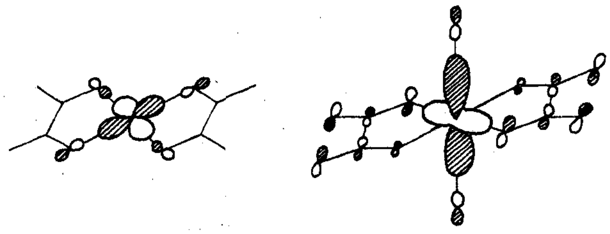


Figure 2. Magnetic orbitals in $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ and in $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$, as calculated by the extended Hückel method.

Experimental Section

$Cu(C_2O_4){\cdot}{}^1/_3H_2O$ was prepared according to previously described procedures.[1-3] To obtain $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$, we heated 10 g of $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ at reflux during 0.5 h in 150 mL of a 1/1 mixture of an ammonia solution (density 0.90 g/mL) and of water. The solution was then filtered, and crystals of $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$ appeared overnight in the filtrate.[8]

The magnetic measurements were carried out on polycrystalline samples of about 10 mg with a Faraday type magnetometer, equipped with a continuous-flow cryostat designed by Oxford Instruments. Magnetic inductions of about 10 kG for $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ and 2 kG for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$ were used. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. The absolute accuracy on temperature is estimated at ±0.1 K, and the relative accuracy on the apparent increase of the weight of the sample when the magnetic field is applied is better than 1%. The corrections for diamagnetism are estimated at -46×10^{-6} cm^3 mol^{-1} for $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ and -103×10^{-6} cm^3 mol^{-1} for $Cu(C_2O_4)(NH_3)_2{\cdot}2H_2O$. For the latter compound the TIP was taken as 60×10^{-6} cm^3 mol^{-1}; it was considered as an adjustable parameter for the former. The best R factor was obtained for a negligible value of the TIP. If the TIP is no longer considered as an adjustable parameter, the R factor varies from 0.55×10^{-4} to 1.65×10^{-4} when the TIP varies

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Table I. Parameters Used in the Extended Hückel Calculations

		orbital exponent	A_μ	B_μ	C_μ	$g_{\mu\mu}$
Cu	4s	2.05	0.942	8.84	7.72	6.5
	4p	1.325	1.05	6.639	3.98	4.4
	3d	5.95 (0.59332) 2.30 (0.57442)	3.449	6.198	10.646	10.9
C	2s	1.55		11.9	20.4	11.9
	2p	1.325		11.9	10.6	11.9
O	2s	2.2		15.2	33.0	15.2
	2p	1.975		15.2	16.4	15.2
N	2s	1.875		13.7	26.4	13.7
	2p	1.650		13.7	13.4	13.7

from zero to 60×10^{-6} cm^3 mol^{-1}. In the same time, the least-squares fitting value of J only varies from -291 to -289 cm^{-1}.

Appendix

For the calculations performed in this note, we use the version Forticon 8 of the extended Hückel method,[15] with the weighted H_{ij} formula. The atomic orbitals are simple Slater-type orbitals but for metallic 3d orbitals for which we choose two-component orbitals. The exponents and the relative weights for metallic 3d orbitals are given in Table I. The calculations on the monomeric fragments shown in Figure 2 to obtain the magnetic orbitals are performed with charge iteration on all atoms and Madelung correction. The A_μ, B_μ, C_μ, and $g_{\mu\mu}$ parameters of the method are given in Table I. The energies of the molecular orbitals in the dimeric entities are calculated from the noniterative extended Hückel method using as diagonal matrix elements the previously obtained H_{ii} values corrected for the energy shift due to the 2− charge of the monomeric fragments. The K parameter of the Wolfsberg-Helmholz approximation is taken equal to 1.75.

Registry No. $Cu(C_2O_4)$, 814-91-5; $Cu(C_2O_4)(NH_3)_2$, 52582-05-5.

Supplementary Material Available: A listing of the experimental magnetic data (2 pages). Ordering information is given on any current masthead page.

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(15) Forticon 8, Quantum Chemistry Program Exchange, No. 344, Indiana University, Bloomington, Ind.

Additions and Corrections

1979, Volume 18

S. S. Krishnamurthy,* K. Ramachandran, Arjun C. Sau, Robert A. Shaw, A. R. Vasudeva Murthy, and Michael Woods: Studies of Phosphazenes. 9. Reactions of (Primary amino)chlorocyclotetraphosphazenes with Dimethylamine: Formation of "Bicyclic" Phosphazenes.

Page 2010. In the first paragraph of the text, line 2, $N_4P_4Cl_6(NHEt)_5$ should read $N_4P_4Cl_6(NHEt)_2$. In the Experimental Section, second paragraph, line 11 should read, "which on recrystallization from *petroleum ether gave* 2,4,4,8,8-pentakis(dimethylamino)-6-(methylamino)-9-methyl-2,6-epiminocyclotetraphosphazatetraene...."—S. S. Krishnamurthy.