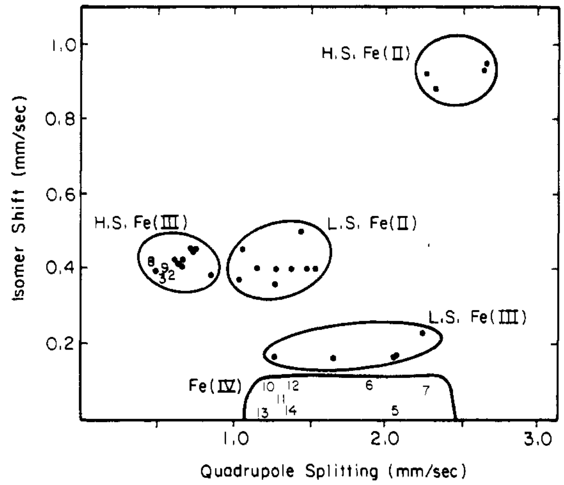

Figure 1. Plot of Mössbauer parameters for tetraarylporphyrins. Numbered points are taken from Table I. Unnumbered data are given in ref 11. All isomer shifts are relative to iron metal.

the nature of the electron density at the iron nucleus, so care must be used to avoid oversimplification of the descriptions of electronic structure. Qualitative comparisons, however, between related complexes can be made.

In addition, we have examined the infrared spectra of **4**–**7** as Nujol mulls. There are no major bands in the 1290–1270-cm^{-1} region. A strong absorption in this region has been associated with π-radical-cation character in a variety of tetraarylporphyrin complexes.[7] The absence of this band supports the proposal that the oxidation of μ-nitrido and the μ-carbido dimers is metal rather than porphyrin based. Furthermore, the electron paramagnetic resonance spectrum of the μ-nitrido dimer, **4**, argues against a π-radical-cation formulation. The small nitrogen hyperfine splitting in the EPR spectrum[18,19] of **4** argues that the unpaired electron density interacts with the bridging nitrogen atom mostly through spin polarization. Thus, the combination of Mössbauer, infrared, and EPR spectra argues that the μ-nitrido dimer, **4**, is best represented formally as Fe(3.5+)/Fe(3.5+), in accord with theoretical calculations.[20]

The nature of the electronic structure of the μ-carbido dimer, **6**, may be represented in its extremes as two iron(II) porphyrins bridged by a carbenic carbon atom, as a dimer of iron(III) porphyrin π radical cations, or as a dimer of iron(IV) porphyrins. The Mössbauer parameters of **6**, however, clearly eliminate the first two descriptions as being major contributors to the overall electron density. From Table I, the isomer shift and the quadrupole splitting of the μ-carbido dimer are typical of those associated in other systems with oxidation of the iron. In addition, the lack of the infrared marker band for porphyrin π radical cations and the chemical stability of this dimer to oxygen and water are consistent with this description. The dichlorocarbene complex, **7**, has a rather small isomer shift, indicative of reduced electron density at the iron nucleus compared to common Fe(II) or Fe(III) complexes.

We have presented in Figure 1 a useful plot of isomer shift vs. quadrupole splitting for a representative number of (porphyrinato)iron complexes in various electronic configurations. It is clear from this figure that there are discrete and well-separated regions associated with each of these configurations, as has been noted before for ferrous and ferric porphyrin complexes.[11] This figure should be taken as only a general guide.

Thus, as the ligated atom becomes more electronegative, the site of oxidation in these complexes shifts from being metal based to residing in the porphyrin π system, as one might have expected on an intuitive basis. In keeping with this trend, comparison of the Mössbauer parameters of FeTPP(Cl) with those of its monomeric cation in [FeTPP(Cl)]$SbCl_6$ indicates that oxidation has occurred from porphyrin-based orbitals rather than from those of iron.[9] This is in keeping with the high electronegativity of Cl, which would not be expected to stabilize a charge removal from the iron rather than from the porphyrin π system.

In summary, the nature of highly oxidized iron porphyrin complexes is extremely sensitive to the nature of axial coordination. In the series of single-atom-bridged dimers of (tetraarylporphyrin)iron complexes, as the bridge atom changes from carbon or nitrogen to oxygen, the Mössbauer spectra clearly show a change in the site of oxidation from the metal-based orbitals to those of the porphyrin. For the dichlorocarbene complex, the Mössbauer parameters are similar to those of the μ-carbido dimer, indicating similar electron densities at the iron. In the heme proteins which support high-oxidation-state intermediates, the axial ligation varies from N (from a histidine imidazole in peroxidase[3]) to O (from a tyrosine phenolate in catalase[2]) to S (from a cysteine thiolate in cytochrome P-450[4]). In light of the vastly differing modes of reactivity that these enzymes show, the importance of a detailed understanding of the electronic structure of highly oxidized porphyrins is clear.

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Registry No. **1**, 12582-61-5; **2**, 80766-28-5; **3**, 79633-64-0; **4**, 59114-43-1; **5**, 83967-78-6; **6**, 75249-87-5; **7**, 65979-89-7; **8**, 16456-81-8; **9**, 78023-40-2; **10**, 82512-02-5; peroxidase, 9003-99-0.

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Tunable Exchange Interaction in μ-Oxalato Copper(II) Dinuclear Complexes

Sir:

Several structural–magnetic correlations have been proposed in the last few years, which have led to a better understanding of the mechanism of the interaction between magnetic centers in polymetallic complexes.[1-4] Generally, a dependence of the exchange parameter J on a structural parameter such as a bond length or a bond angle has been demonstrated. Such an approach, whatever its importance may be, does not allow the construction of a molecular engineering of the polymetallic systems. Indeed, it does not seem that the value of this structural parameter can be controlled during the synthesis process. On the other hand, our group is engaged in the design

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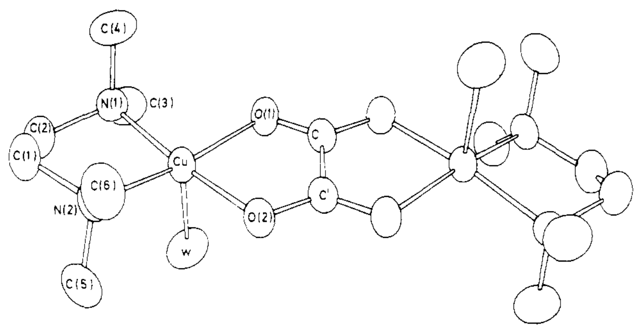

Figure 1. Perspective view of one of the [tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen]$^{2+}$ cations in **1**. Thermal ellipsoids are drawn at the 50% level.

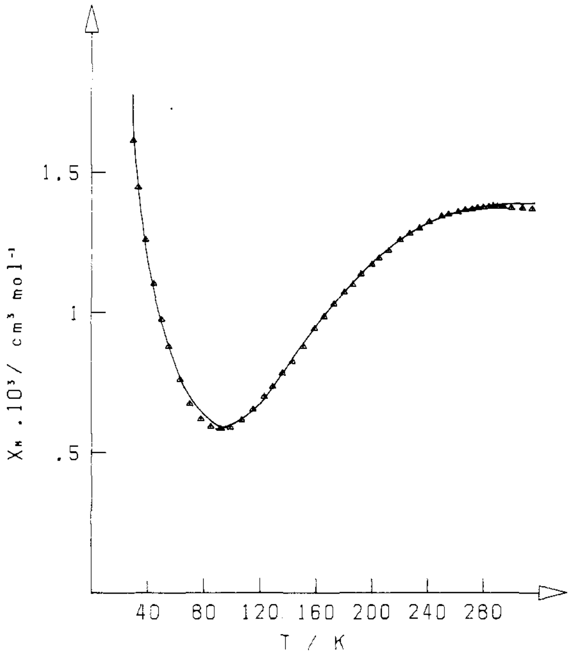

Figure 2. Calculated (—) and experimental (▲) magnetic data for **1**. The equation of the calculated curve is $\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + (N\beta^2g^2/2kT)\rho + 2N\alpha$, with $J = -385.4$ cm^{-1}, $g = 2.16$ (7), $\rho = 0.0509$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}.

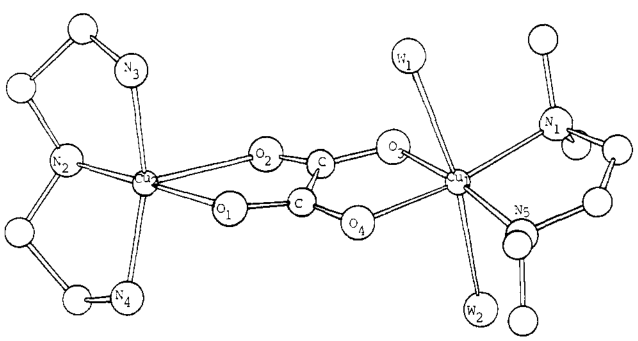

Figure 3. Perspective view of the [dienCu(C_2O_4)Cu(H_2O)$_2$tmen]$^{2+}$ cation in **2**.

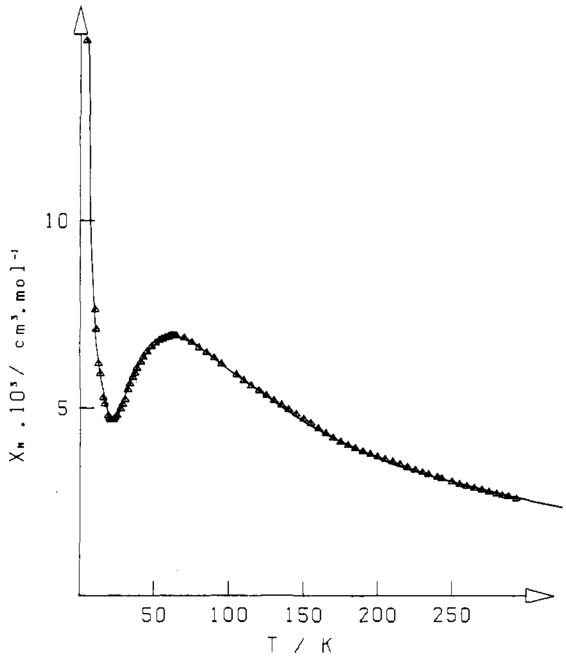

Figure 4. Calculated (—) and experimental (▲) magnetic data for **2**. The calculated curve is obtained with $J = -75.5$ cm^{-1}, $g = 2.12$ (4), $\rho = 0.0914$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}.

of polymetallic systems exhibiting expected magnetic properties.[5] Up to now, the most striking results deal with the design of ferromagnetically coupled dinuclear complexes.[6,7] In this communication, we purpose showing that it is potentially possible to control the J singlet–triplet energy gap in μ-oxalato copper(II) dinuclear complexes. With the same bridging network Cu(C_2O_4)Cu, J may vary from zero to about -400 cm^{-1}. Such a variation can be induced by a modification in the nature of the L and L′ terminal ligands bound to each of the Cu(II) ions. We propose a method of synthesis leading eventually to the asymmetric complexes [LCu(C_2O_4)CuL′]$^{2+}$, so that we dispose of two parameters to tune the magnitude of the interaction through the oxalato bridge. Hendrickson and co-workers had already shown that, with L = L′ = diethylenetriamine, J was close to zero and, with L = L′ = 1,1,4,7,7-pentaethyldiethylenetriamine (Et_5dien), J was in the range–20 to -70 cm^{-1} depending on the nature of the counteranion.[8] The magnitude of the antiferromagnetic interaction, related to the square of the overlap between the magnetic orbitals centered on each copper(II), is essentially governed by the delocalization of these magnetic orbitals on the oxygen atoms of the oxalato bridge.[9] It is found that the distorted trigonal bipyramid surrounding around each Cu(II) in [Et_5dienCu(C_2O_4)CuEt_5dien]$^{2+}$ is far from being the most favorable geometry to achieve a strong interaction through the oxalato bridge. A coordination of 4 or 4 + 1 for each Cu(II) with the oxygen atoms of the C_2O_4 group as nearest neighbors should lead to a much stronger antiferromagnetic coupling. This is realized with L = L′ = 1,1,4,4-tetramethylethylenediamine (tmen). [tmen(H_2O)Cu(C_2O_4)Cu(H_2O)tmen](ClO_4)$_2$·1.25H_2O (**1**), first reported by Nonoyama and coworkers,[10] crystallizes in the triclinic system: $a = 18.955$ (5), $b = 10.019$ (3), $c = 7.658$ (3) Å; $\alpha = 98.30$ (3), $\beta = 98.37$ (3), $\gamma = 88.19$ (2)°; $Z = 2$. The structure is made of centrosymmetric, crystallographically independent but almost identical, dinuclear cations, isolated by ClO_4^- anions and intercalated water molecules. The Cu(C_2O_4)Cu network is planar with almost equal Cu–O bond lengths (1.98 Å). A water molecule is weakly bound to each of the Cu(II) atoms with Cu–O(H_2) distances of 2.363 (5) and 2.312 (5) Å, respectively, the displacement of Cu(II) toward the apical water

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molecules being 0.148 and 0.182 Å. Each magnetic orbital is delocalized toward the nitrogen and oxygen nearest neighbors.[9] From the magnetic properties represented in Figure 2, J, determined by least-squares fitting, was found to equal -385.4 cm^{-1}.

An intermediate situation may be obtained with L = dien and L′ = tmen. The complex [dienCu(C_2O_4)Cu(H_2O)$_2$tmen](ClO_4)$_2$ (**2**) was obtained by adding a methanolic solution of Cu(ClO_4)$_2$·6H_2O–dien to a methanolic solution of tmen(H_2O)Cu(C_2O_4)·3H_2O and by dissolving the precipitate in water. **2** recrystallizes 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. The dimeric cation may be described as two Cu(II) ions in 4 + 2 coordination bridged by a nonplanar oxalato ligand. On the tmen side, the four nearest neighbors are the nitrogen atoms of tmen and two oxygen atoms of C_2O_4, with two water molecules in apical positions [Cu–O(H_2) = 2.61 (7) and 2.68 (6) Å]. On the dien side, the four nearest neighbors are the nitrogen atoms of dien and an oxygen atom of C_2O_4, with apical positions for a second oxygen atom of C_2O_4 (Cu–O = 2.45 (2) Å) and an oxygen atom belonging to the oxalato bridge of another cationic unit (Cu–O = 2.74 (2) Å). The Cu–Cu distance is 5.400 (8) Å. The two magnetic orbitals, each of them pointing toward the four nearest neighbors of the Cu(II) on which they are centered, overlap on only one side of the Cu(C_2O_4)Cu network. From the magnetic properties of **2** shown in Figure 4, J was found to equal -75.5 cm^{-1}.

Starting from tmen(H_2O)CuC_2O_4, we can reverse the orientation of the magnetic orbital[11,12] by fixing a nitrogen-containing ligand on Cu(II) and achieve a very weakly coupled new binuclear complex. This is realized in [tmen(2-MeIm)Cu(C_2O_4)Cu(2-MeIm)tmen](ClO_4)$_2$ (**3**) with 2-MeIm = 2-methylimidazole. J was then found around -15 cm^{-1}.

These three examples clearly illustrate, we believe, the concept of tunable exchange through a given bridging network and the large possibilities in this field. In other respects, the complexes [LCu(C_2O_4)CuL′]$^{2+}$ (**4**) seem to us also important for the following reasons: (i) In any case, the mononuclear complexes LCu(C_2O_4) and L′Cu(C_2O_4) (**5** and **6**) do exist. This allows us to substantiate the concept of the semilocalized magnetic orbital, which is the cornerstone of the orbital model of the exchange developped in our group.[9] The magnetic orbitals in **4** may be defined as the singly occupied molecular orbitals in **5** and **6**. (ii) The comparative investigation of the EPR spectra of **4**–**6** should allow us to specify to what extent it is possible to derive the spin-Hamiltonian parameters for the dinuclear species **4** from those of the mononuclear species **5** and **6**.[13] (iii) Finally, the comparison of the EPR spectra with L = L′ and L ≠ L′ may eventually provide unique information on the role of the antisymmetric exchange.[14]

Registry No. **1**, 83928-09-0; **2**, 83928-11-4; tmen(H_2O)Cu(C_2O_4), 83928-12-5.

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