In the in vivo water-splitting process, oxygen evolution is apparently mediated by manganese ions[16] which presumably eliminate the deleterious oxygen inhibition effects. The photooxidation of the chlorophyll in vivo results in the reduction of water-soluble ferredoxin ($E_0 = -0.42$ V),[17] leading to the reduction of NADP at -0.32 V.[18] The matching of the reduction potential of ferredoxin with that of water in eq 2 may possibly be of significance. If we suppose that the in vivo light reaction directly connects water oxidation with ferredoxin reduction in a single two-quantum photoevent according to the energy upconversion postulate,[1,3c] we arrive at the overall stoichiometry[18a]

$$2H_2O + 4Fd_{ox} + 2ADP + 2P_i \xrightarrow[(Chl\ a\cdot 2H_2O)_2]{h\nu} 4Fd_{red} + 4H^+ + 2ATP + O_2 \quad (4)$$

In eq 4, the transfer of four electrons from H_2O to ferredoxin is accomplished by the expenditure of eight quanta. The reduction of ferredoxin is accompanied[18a] by a concomitant formation of ATP in photophosphorylation. The P700 light reaction is responsible for cyclic photophosphorylation,[19] leading to an additional four quanta/two electrons requirement.[20] The present scheme is consistent with the generally accepted view that oxygen evolution in plant photosynthesis is eight quanta/O_2, and that frequently observed higher-than-eight quanta requirements for the overall process may be attributed to cyclic photophosphorylation.[20] We note that our interpretation is in general agreement with the scheme proposed by Arnon,[20,21] except that Arnon had invoked two separate one-quantum photoevents in the activation of 4, and provides a viable alternate to the "zig-zag" scheme[10,11] of two sequential one-quantum light reactions, in which the NADP reduction occurs off the P700 light reaction and the water-splitting reaction is associated with a second photosystem (PSII) linked to the P700 (PSI) through a dark bridge of charge carriers.[22]

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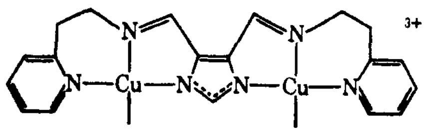
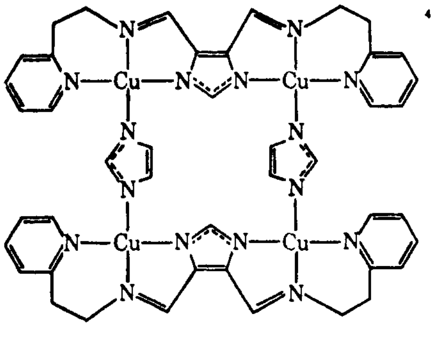
Magnetic Exchange Interactions in Imidazolate Bridged Copper(II) Complexes

Sir:

The properties of soluble binuclear imidazolate (im) bridged complexes are of current interest because the active site of the enzyme bovine erythrocyte superoxide dismutase (SOD) is known[1] to have a histidine bridged copper(II)-zinc(II) center in each of two identical subunits. An imidazolate (histidine) bridge has also been proposed[2] to exist between copper and iron in cytochrome *c* oxidase. Oligomeric and polymeric imidazolate bridged metal complexes are quite common in the solid state[3] and have occasionally been identified in solution.[4] Recently we reported[5] the synthesis and characterization of I and II, the first discrete imidazolate bridged transition metal complexes.[6] The existence in aqueous solution of the equilibrium reaction[5] shown in eq 1



Cu_2bpim^{3+}, I



$[Cu_2(bpim)(im)]_2^{4+}$, II

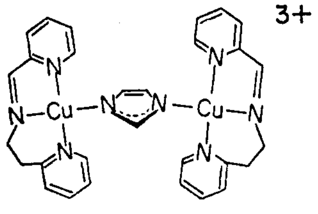
$$II + 4H^+ \rightleftharpoons 2I + 2imH_2^+ \quad (1)$$

suggested that it should be possible to prepare binuclear imidazolate bridged complexes with simpler ligands than bpim. Here we describe the synthesis of one such compound, III, as well as an investigation of the temperature dependence of the

Table I. Spin Exchange and Geometric Parameters in Imidazolate Bridged Copper(II) Systems

Complex	J, cm^{-1}	g_{av}	Cu–Cu, Å	α_1, α_2, deg[a]	Ref
I	−81.3 (1)	2.164 (3)	6.214 (estd)	4.7, 11.4 (estd)	*b, c*
II[k]	−87.4 (1)	2.227 (7)	6.214	4.7, 11.4	*b, c*
	−30 (1)		5.910	98.2, 80.5	
III	−26.74 (6)	2.097 (6)	5.93 (estd)	88, 88 (estd)	*b, d*
4Cu^{2+}-SOD	−26	2.31[e]	5.8[f]		*f, g*
Blue Cu(im)$_2$	−54 (estd)[h]	2.19	5.89[i]	31–75	*i, j*

[a] Defined as the angles between the best least-squares planes through the copper coordination planes and the bridging imidazolate ligand; estd, estimated. [b] This work; values in parentheses are standard deviations estimated from the least-squares fit. [c] Reference 5. [d] See ref 8. [e] Value reported for the $2Cu^+2Cu^{2+}$ derivative. [f] Calculated from the averaged metal coordinates of the $2Cu^{2+}2Zn^{2+}$ SOD: J. S. Richardson, K. A. Thomas, and D. C. Richardson, *Biochem. Biophys. Res. Commun.*, **63,** 986 (1975). [g] Reference 13. [h] Estimated from the approximation (ref 5b) $\theta = 2/3zS(S+1)(J/k)$ where θ is the Weiss constant, z denotes the number of nearest neighbors (four in this case). and k is the Boltzmann constant. [i] Computed from the coordinates in H. C. Freeman, *Adv. Protein Chem.*, 257 (1967). [j] Reference 3p. [k] Least-squares refinement of J_1, J_2, and g^2 always converged to the reported values irrespective of the trial starting parameters.



$[Cu(pip)]_2(im)^{3+}$, III

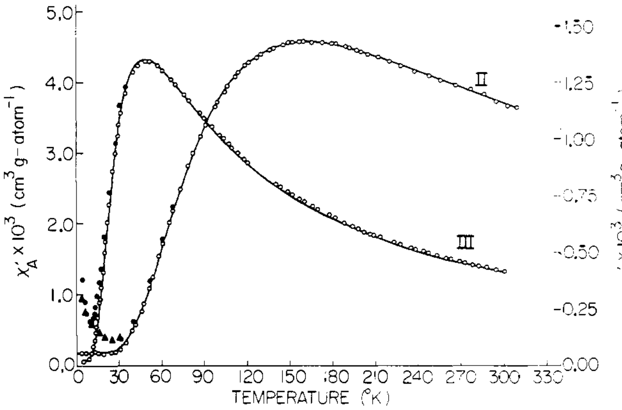


Figure 1. Susceptibility vs. temperature plots for imidazolate bridged copper(II) complexes II (right axis) and III (left axis). Experimental data corrected for the presence of paramagnetic impurity are shown as open circles; filled circles or triangles indicate the uncorrected values where the correction is significant. The solid lines show the best least-squares fit of the data to the spin exchange models discussed in the text.

magnetic susceptibilities of I, II, and III that fix the range of antiferromagnetic spin exchange interactions likely to occur in imidazolate bridged dicopper(II) complexes. The results of the latter study provide magnetic criteria to help identify histidine bridged dicopper(II) centers, should they exist, in metalloproteins of unknown structure.

Addition of 10 mmol of pyridine-2-carboxaldehyde to 10 mL of a methanolic solution containing 10 mmol each of cupric nitrate trihydrate and 2-(2-aminoethyl)pyridine caused immediate precipitation of ultramarine ($\lambda_{max}^{H_2O}$ 666 nm at pH 6.4) microcrystals. The product, obtained in 90% yield, analyzed[7a] as $Cu(pip)(NO_3)_2 \cdot H_2O$, the copper(II) complex (IV) of the tridentate Schiff's base ligand 2-[2-(2-pyridyl)ethyliminomethyl]pyridine (pip). This complex (10 mmol in 20 mL of boiling water) was converted into III by slow addition with rapid stirring of 5 mL of a 1.0 M aqueous sodium hydroxide solution containing 5 mmol of imidazole. Slow evaporation of the resulting deep blue solution (pH ~8.3) yielded fine blue needles of $[Cu(pip)]_2(im)(NO_3)_3 \cdot 2.5H_2O$.[7b,8] Spectroscopic studies of aqueous solutions of this complex showed the blue band to shift from λ_{max} 635 nm at pH 11 to 665 nm at pH 3.7, consistent with eq 2 (cf ref 5).

$$III + 2H^+ \rightleftharpoons 2IV + imH_2^+ \qquad (2)$$

The analytical, x-ray,[8] and spectroscopic data, together with the magnetic susceptibility results discussed below, are consistent with the imidazolate bridged structure shown in III.

The magnetic susceptibilities of solid samples of I, II, and III were determined by the Faraday method over the temperature range 4.2 K < T < 300 K.[9] All three compounds exhibit antiferromagnetic ($J < 0$) exchange coupling as evidenced by maxima in their susceptibility vs. T plots. Data for compounds I and III were analyzed by standard methods[10,11] assuming the Heisenberg-Dirac-van Vleck Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$. Two variable parameters, g^2 and J, were refined by least-squares methods in which the square of the difference between the observed and calculated χ_A' vs. T functions was minimized. Figure 1 shows the results for compound III. The possibility of two independent spin exchange pathways in compound II[6] required a slightly more complicated analysis.[12] The data were satisfactorily accounted for by two coupling constants and a single g value (Figure 1). Table I summarizes the results for these three compounds, an active derivative of bovine erythrocyte SOD in which copper(II) has been substituted for zinc(II),[13] and the blue modification of the $Cu(im)_2$ polymer.[3d,p]

The results in Table I reveal several interesting features. The two J values obtained for II are in reasonable agreement with those for I and III, respectively. The larger value is therefore assigned to a spin exchange pathway through the bridging imidazolate ring of the bpim ligand and the smaller exchange interaction is presumed to occur via imidazolate bridges connecting the two Cu_2bpim^{3+} halves of the dimer. The coupling constant ($J \sim -26$ to -30 cm^{-1}) for the latter type of exchange is identical with that reported[13] for the $4Cu^{II}$ derivative of bovine erythrocyte SOD. These findings suggest that histidine bridged dicopper(II) centers in metalloproteins will be characterized by antiferromagnetic exchange with coupling constants in the range -25 cm$^{-1} > J > -90$ cm^{-1}.

Although the J values in Table I are not correlated with metal-metal distance,[14] they do appear to be a function of the dihedral angles α_1 and α_2 between the bridging imidazolate and copper coordination planes. This result suggests a π contribution to the spin exchange mechanism analogous to that proposed recently for polymeric pyrazine bridged copper(II) complexes.[15,16] An analysis of orbital interactions[17] for the Cu(II)-im-Cu(II) fragment reveals the highest occupied molecular orbital of the bridging imidazolate ion to have appropriate symmetry to combine with the symmetric or antisymmetric metal combination $(2)^{-1/2}(d^a_{x^2-y^2} \pm d^b_{x^2-y^2})$, depending upon the relative signs of α_1 and α_2 and when their magnitudes are neither 0° nor 90 °. The stronger this interaction the more stable will be the singlet state (large negative J).[17] Further analysis of the spin exchange pathway will have to await the availability of additional experimental results for imidazolate bridged dicopper(II) complexes.

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(7) Analytical data. (a) Calcd for $C_{13}H_{15}N_5O_7Cu$: C, 37.46; H, 3.63; N, 16.80. Found: C, 37.35; H, 3.62; N, 16.51. (b) Calcd for $C_{29}H_{34}N_{11}O_{11.5}Cu_2$: C, 41.09; H, 4.04; N, 18.17; Cu, 14.99; O, 21.70. Found: C, 40.95; H, 3.92; N, 18.42; Cu, 15.4; O (by difference), 21.3. Heating the compound in vacuo at 90 °C for 16 h resulted in a 5.47% weight loss compared with the calculated value of 5.31%.

(8) X-ray data. The compound crystallizes in space group $P2_1/c$ with a = 17.531 (8) Å, b = 17.817 (10) Å, c = 23.582 (10) Å, and β = 105.80 (3)°. The density calculated for Z = 8, 1.589 (1) g cm^{-3}, agrees with the experimental value of 1.588 (1) g cm^{-3} determined by neutral buoyancy in CCl_4–$CHBr_3$ mixtures. Although single crystal x-ray diffraction data clearly reveal an imidazolate bridged dicopper(II) structure (Cu–Cu distance 5.93 Å), refinement has thus far been unsuccessful. Crystallographic work on this and other derivatives is continuing.

(9) The data were corrected for underlying diamagnetism using tabulated values of Pascal's constants. A value of 60×10^{-6} cm^3 g-atom^{-1} per copper was used for the temperature independent *paramagnetism* correction. Corrections for small amounts of paramagnetic impurities were made by fitting the low temperature data to a Curie–Weiss law and correcting all the data accordingly.[10]

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(12) The susceptibility may be calculated from the equation $\chi_A' = (g^2N\beta^2/kT)[(10W + 2X_1 + 2X_2 + 2Y)/(5W + 3X_1 + 3X_2 + 3Y + Z_1 + Z_2)] +$ TIP, where $W = \exp[(J_1 + J_2)/kT]$, $X_i = \exp\{[-(J_1 + J_2) + 2J_i]/kT\}$, $Y = \exp[-(J_1 + J_2)/kT]$, $Z_{1,2} = \exp\{[-(J_1 + J_2) \pm 2Q]/kT\}$, and $Q = (J_1^2 + J_2^2 - J_1J_2)^{1/2}$. The other symbols have their usual meaning.[11] Here it is assumed that copper atoms can spin exchange either through the bridging imidazolate ring of the bpim ligand or across the other im ring but not diagonally through space. An attempt to fit the data with the assumption that $J_1 = J_2$ gave statistically inferior results.

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(14) One might expect $|J|$ to increase with decreasing distance between the metal centers. *The data of Table I show the opposite correlation, if any.*

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(16) See also ref 3p, 5b, and references cited therein.

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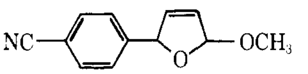
Photosensitized Electron-Transfer Reaction of Electron Donor–Acceptor Pairs by Aromatic Hydrocarbons[1]

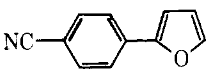
Sir:

Photosensitization is important in photochemistry, usually occurring in exothermic energy transfer.[2] Recently, photosensitized reactions which are endothermic in classical energy transfer have been discussed in terms of exciplexes.[3] In some photoreactions of electron donor–acceptor pairs, the final products arise only from the electron donor, showing a different type of "photosensitization" by the electron acceptor.[4-6] This reaction is shown to be initiated by photochemical electron transfer from the electron donor to the acceptor.[4-6] We wish to report here a novel type of photosensitization by aromatic hydrocarbons, in which excited singlet aromatic hydrocarbons catalyze electron transfer from an electron donor to an electron acceptor.

Irradiation of an acetonitrile–methanol solution containing furan (F), p-dicyanobenzene (p-DCNB), and phenanthrene (P) gave **1**, mp 50–51 °C, in 60–70% yield with 70% recovery of P.[7] Chromatography of **1** on silica gel or basic alumina gave **2**, mp 65–66 °C, in 20–40% yield with 30–50% recovery of **1**. Spectral properties of **1** and **2** accord with the structures assigned.



1



2

$(C_6H_5)_2CHCH_2OCH_3$

3

In control runs, it was confirmed that the recovery of P and yields of **1** were quantitative; irradiation at >300 nm in the absence of P did not give **1** at all. The quantum yield for the formation of **1** ([F] = 1.0 M) was 0.1 ± 0.01 at 313 nm.[8] Among aromatic hydrocarbons investigated, naphthalene can be effectively used in place of P.

Since physical excitation transfer from excited P to either F or p-DCNB is highly endothermic (Table I), the classical energy-transfer mechanism is very unlikely for the photosensitization by P. In fact, the formation of **1** was not quenched even by 1.0 M isoprene, a triplet mechanism being thus discarded. The fluorescence of P was quenched by p-DCNB. In benzene or ethyl acetate, the fluorescence quenching was accompanied by the appearance of an exciplex emission with each isoemissive point at 387 or 393 nm, while exciplex emission could not be observed in acetonitrile or acetonitrile–methanol.[9] However, an exciplex mechanism is unlikely, since the photoreaction in benzene or ethyl acetate containing 10% methanol did not occur or was very slow.

In a variety of exciplex-forming systems, fluorescence quenching in very polar solvents has been established to occur via electron transfer between the fluorophor and the quencher.[10] In Table II are listed the fluorescence quenching rate constants and the calculated values of the free energy change (ΔG) associated with the electron-transfer process, using eq 1.[11]

$$\Delta G\ (\text{kcal/mol}) = 23.06[E(\text{D}/\text{D}^+)_\text{v} - E(\text{A}/\text{A}^-)_\text{v} - e_0{}^2/\epsilon\alpha] - E_{\text{O-O}}\ (\text{kcal/mol}) \quad (1)$$

The diffusion-controlled fluorescence quenching and the negative values of ΔG suggest that electron transfer from excited singlet P (^{1}P*) to p-DCNB occurs to give P cation radical ($P^{+}\cdot$) and p-DCNB anion radical (p-DCNB$^{-}\cdot$).[12] From these results, therefore, a tentative mechanism for photosensitization by P is shown in Scheme I; a key mechanistic pathway is the hole transfer from $P^{+}\cdot$ to F, leading to the recovery of P and