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Figure 1. Perspective view of the $[Cu_2(tren)_2(BZD)]^{4+}$ cation for one of the two independent dimers. The bond distances about the copper(II) ions and in the BZD bridge are quite similar for the two units.

Magnetic Exchange Interactions in Copper(II) Dimers Bridged by Aromatic Diamines. Crystal and Molecular Structure of μ-Benzidine-bis(2,2′,2″-triaminotriethylamine)-dicopper(II) Nitrate

Sir:

The determination of the spatial and time-dependent delocalization of electrons in molecules or more complex systems is an important problem.[1,2] For example, it is relevant to electron transfer in redox reaction precursors[3] and electron transport chains.[4] Mixed-valence compounds provide the opportunity to monitor the propagation time of an electron from one region of the molecule to another.[5-7] It is also possible to study electron dynamics in biradical systems that are involved in magnetic exchange interactions. The frequency of *electron exchange* between the two radical centers parallels the magnitude of the magnetic exchange interaction (as gauged by the exchange parameter J in the spin Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$).[8] In a series of nitroxyl biradicals, then, the biradical which is *not* involved in a magnetic exchange interaction will *not* have electrons exchanging between the two radical centers. This noninteracting biradical has an electronic structure consisting of two *localized* nitroxyl radical moieties. Recent work on nitroxyl biradicals has shown that electrons can exchange *intra*molecularly via a through-bond mechanism.[9]

Determining the presence and magnitude of a magnetic exchange interaction between the copper(II) centers in a copper(II) dimer with an extended organic bridge is one means of learning whether the extended organic moiety does support electron exchange between two paramagnetic centers. It was with this in mind that we prepared a series of copper(II) dimers with extended aromatic amine bridges having the composition of $[Cu_2(tren)_2(DA)]X_4$, where DA is various aromatic diamines such as benzidine (BZD), *o*-tolidine (OT), or *p*-phenylenediamine (PPD); tren is 2,2′,2″-triaminotriethylamine; and X is ClO_4^-, NO_3^-, or PF_6^-. In this paper we communicate the structural and magnetic properties of these complexes.[10]

The single-crystal x-ray structure of $[Cu_2(tren)_2(BZD)]$-$(NO_3)_4$ was solved using 8154 ($I > 2\sigma(I)$) unique reflections collected on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator, λ (Cu $K\alpha_1$) = 1.54178 Å. The crystal data are as follows: $C_{24}H_{48}N_{14}O_{12}Cu_2$, mol wt 851.83; monoclinic, space group $P2_1/c$; a = 29.799 (4), b = 13.960 (2), c = 18.732 (3) Å; β = 106.49 (1)°; V = 7471.9 Å³; Z = 8; ρ_{calcd} = 1.51, ρ_{obsd} = 1.52 g/cm³. The asymmetric unit consists of 104 nonhydrogen atoms (2 formula weights, 937 variables) and, as such, only Gauss–Seidel block refinements were used to refine the structure to final discrepancy indices[11] of R = 0.11 and R_w = 0.16. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of the 96 hydrogen atoms were calculated with fixed bond lengths of 1.05 Å and assigned isotropic thermal parameters of 9.5 Å². The
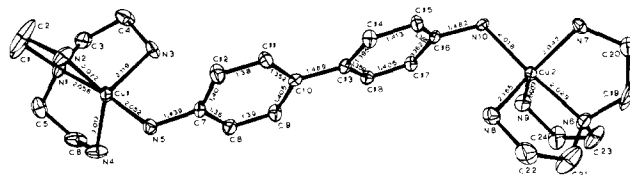
two crystallographically independent dimers are related by a translation of *almost* ($\frac{1}{2}$,0,0).

The geometry of one of the dimeric cations is illustrated in Figure 1 which shows the trigonal–bipyramidal coordination about each copper(II) ion. The bond distances and angles are quite similar for the two dimers which give copper–copper distances within each dimer of 12.270 (2) and 12.074 (2) Å. The phenyl rings of the BZD bridge are planar with dihedral angles of 13.8 and 22.5° about the C–C bond connecting them for each dimer. The nitrate anions exhibit weak (O–N distance >2.9 Å) hydrogen-bonding interactions with the tren nitrogens. There are copper–copper *inter*dimer separations as short as 7.499 (2) Å.

Variable-temperature (4.2–286 K) magnetic susceptibility data for $[Cu_2(tren)_2(BZD)](NO_3)_4$ show an antiferromagnetic exchange interaction with a maximum in the susceptibility data at 6 K. The data were least-squares fit to equations for an isotropic magnetic exchange interaction (exchange parameter J in a spin Hamiltonian of $-2J\hat{S}_1 \cdot \hat{S}_2$) to give J = -3.2 cm^{-1} and a Curie–Weiss constant of θ = 0.75°. The g values used in the fitting were taken from the Q-band EPR spectrum, which shows signals at g = 2.030, 2.124, and 2.191. Replacement of the NO_3^- counterion with ClO_4^- or PF_6^- leads to very similar magnetic susceptibility results with J values fit to -3.0 and -2.6 cm^{-1}, respectively. The lack of a counterion dependence for the exchange parameter J is clear indication that the magnetic exchange interaction is propagated by the benzidine bridge. A similar complex, $[Cu_2$-$(tren)_2(OT)](PF_6)_4$, shows a slightly weaker exchange interaction with J fit to -2.3 cm^{-1}.

Further substantiation for the fact that the benzidine bridge is propagating the interaction is found in the susceptibility data for the $[Cu_2(tren)_2(PPD)]X_4$ compounds. All three of these *p*-phenylenediamine compounds exhibit a stronger antiferromagnetic interaction than found for the BZD compounds. For example, the data for the NO_3^- compound were fit to give J = -26 cm^{-1} with the average g value fixed at 2.115 (EPR).

The copper(II)–BZD compounds demonstrate that electrons can exchange between two metal ions separated by >12 Å via a biphenyl moiety. This is relevant to previous work which suggests that, in certain redox reactions between transition metal ions, the electron transfer occurs through extended ligands such as the *p*-dicarboxylic acid of biphenyl.[12,13] These same compounds are the first stable nonpolymeric copper(II) complexes of BZD and PPD, two reagents which are used to monitor the enzymatic activity of various cuproproteins such as ceruloplasmin[14,15] and laccase.[14b]

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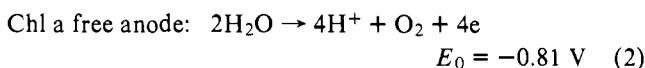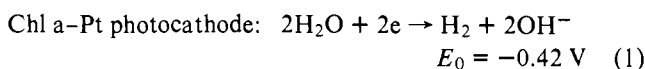
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Electron Spin Resonance Observation of the Photooxidation of Hydrated Chlorophyll a Dimers by Water. In Vitro Photochemical Characterization of Reaction Centers in Photosynthesis

Sir:

In 1953, Levitt proposed that the light reaction in photosynthesis results from the photooxidation of the chlorophyll.[1] In the succeeding years, photoinduced electron spin resonance (ESR) signals were observed in photosynthetic whole cells and chloroplast preparations.[2] A reversible ESR signal, known as signal I, was found to have the free electron *g* value 2.0025 and a peak-to-peak width of about 7.5 G.[2] In 1971, Norris et al. proposed that the in vivo unpaired electron in signal I was delocalized over two Chl a molecules.[3] These authors postulated that the width of the ESR signal is narrowed by a factor of $\sim 1/\sqrt{n}$ when an unpaired electron is spread over *n* Chl a molecules. A comparison of the ESR signal width for the monomeric Chl a radical[4] in vitro with that of the P700 in vivo radical shows that the latter is reduced relative to the former by a factor of $\sim 1/\sqrt{2}$.[3] The P700 photoreaction in plant photosynthesis is generally considered[5] to be not directly associated with the water splitting reaction.[5,6] In 1974, Van Gorkum et al. reported[7] a photoinduced ESR signal associated with the water-splitting photoreaction in vivo. In the present communication we describe the first ESR observation of in vitro radical cations of Chl a dimers that are light induced without the introduction of extraneous electron acceptors. We show that these radical cations most probably arise from the photoreactions between water and the dimers of the monohydrate and the dihydrate of Chl a, $(Chl\ a\cdot H_2O)_2$ and $(Chl\ a\cdot 2H_2O)_2$, which have, respectively, been proposed to be the P700 and the water-splitting reaction centers in plant photosynthesis.[8]

The observed photogalvanic response in Chl a–H₂O cells has been attributed[8] to the photochemical splitting of water by the chlorophyll according to the half-cell reactions (at pH 7)

Chl a–Pt photocathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$
$$E_0 = -0.42\ V \quad (1)$$

Chl a free anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e$
$$E_0 = -0.81\ V \quad (2)$$

Evidence for reactions 1 and 2 has been derived from the observation of a greatly enhanced P740 $(Chl\ a\cdot 2H_2O)_n$ photo-
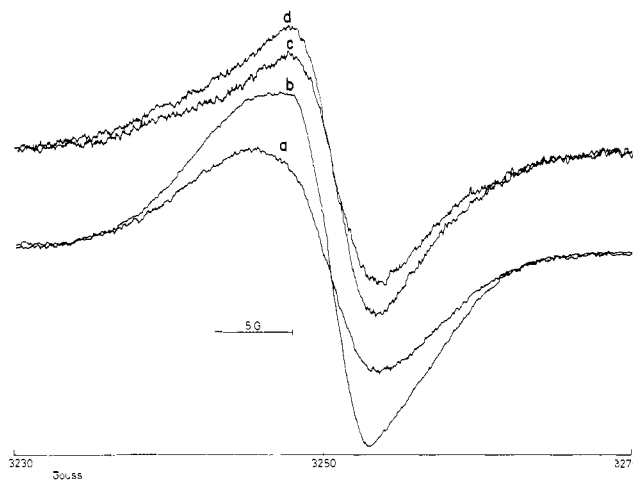

Figure 1. Light-induced ESR spectrum of hydrated Chl a radical cation in dry 1:1 *n*-pentane and cyclohexane: (a) 10 °C dark spectrum after several cycles of illumination; (b) 10 °C spectrum of sample in a under subsequent illumination by white light; (c) dark spectrum at −140 °C after several cycles of illumination; (d) spectrum of sample in c during illumination at −140 °C. The experimental conditions are given as follows: microwave power, 10 mV; modulation, 6.3 G; gain (a) 3.2×10^3, (b) 4×10^3, (c and d) 6.3×10^3.

galvanic response on introduction of appropriate pH buffers (low pH values at the Chl a half cell and high pH values at the Chl a free half cell). The enhancement effects have been attributed to product disposal of H⁺ and OH⁻ in reactions 1 and 2, respectively. Similar enhancement effects, observed when Fe^{2+}, Ba^{2+}, and Zn^{2+} ions are introduced in the Chl a half cell, are accompanied by the precipitation of the corresponding insoluble hydroxides,[8] providing further positive evidence for the occurrence of reaction 1.

The reduction of the water in reaction presumably results from the photooxidation of the chlorophyll. The oxidation of water in reaction 2 is probably caused by the reduction of the photooxidized chlorophyll to its neutral state. Experimental observations related to the Chl a–H₂O photogalvanic conversion[8] have been made in other laboratories.[9,10] It occurred to us that it would be desirable to attempt a direct detection of the photooxidation of Chl a–H₂O complexes by an ESR determination of the corresponding Chl a radical cations. In particular we hope to delineate further the recently noted[8] differences between the photochemical activities of the monohydrate dimer $(Chl\ a\cdot H_2O)_2$ and the dihydrate aggregate $(Chl\ a\cdot 2H_2O)_n$.

Chlorophyll monohydrate $(Chl\ a\cdot H_2O)$ prepared as a solid in the usual manner[11] was dissolved in a 1:1 mixture of *n*-pentane and cyclohexane that was dried over solid Na and degassed by freeze-thawing under vacuum. The resulting solution ($\sim 10^{-4}$ M in concentration) was encapsulated in a 4-mm-o.d. quartz Spectrosil sample tube under vacuum (5×10^{-6} Torr). The ESR experiments were carried out with a Varian E9 spectrometer equipped with a variable-temperature attachment. The sample was illuminated with white light from a 1000-W tungsten–iodide source. The optical properties of the sample preparation were monitored using a Cary 14 spectrophotometer in the usual manner.[11,12]

The experimental observations are described as follows. (i) The light-induced ESR signal is shown in Figure 1. The *g* value of this signal is 2.003 ± 0.001. From the decay kinetics observed after the light is turned off (see Figure 2), we note that the ESR signal consists of two components, one transient and the other long lived. (ii) The relative importance of these two components varies with the temperature. At 10 °C the signal decays within 1 s by ~20%. At −140 °C the observed ESR signal is mostly irreversible. (iii) The line shape of the 10 °C