orbitals overlaping with the Fe $d_{x^2-y^2}$ orbital in a σ-donation bonding fashion.

The coefficients of the iron atomic orbitals in the radical molecular orbital shown in Table II show the dominance of d_{xz} in our calculation. Contributions to spin density are these coefficients squared. The p_z contribution is significant, but EPR atomic parameters are unavailable for the p orbitals. Using s and d atomic parameters from the literature,[7] we have found a mixture of d_{xz}, d_{z^2}, and s spin density that reproduces the principal values of the ^{57}Fe hyperfine tensor from Fairhurst et al.[2] with signs as follows: $a_{zz} = 20.1$, $a_{yy} = -9.5$, and $a_{xx} = 13.6$. Other signs are inconsistent with d_{xz} dominance (the signs are not experimentally measurable). The spin density distribution is then $0.28d_{xz}$, $0.07d_{z^2}$, and 0.01s. These numbers must be ascribed some uncertainty because p-orbital contributions are not included. The spin density distributions from our molecular orbital calculations show, by using a Mulliken partitioning of the overlap regions, an unpaired electron density on Fe of only ~0.07, as may be seen in Table III. This underestimate results from our using an approximate non-self-consistent theory, which in this case appears to be overestimating the charge transfer to the apical CO. Fairhurst et al.[2] estimate a spin density of 0.24 on the apical carbon, about half of our calculated value. The orbital distribution on the Fe center based on the hyperfine tensor fitting and the molecular orbital calculation is $d_{xz} >> d_{z^2} > s$. The hyperfine splittings for the carbon atoms in the basal ligands run ~80 and 90% less than the apical splitting, in qualitative agreement with the calculated values in Table III.

It may be noted that the calculated oxygen atom spin densities are less (about half) than those of their neighboring carbon atoms. This is because the π* orbitals are polarized toward carbon.

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Registry No. $Fe(CO)_5^-$, 55472-73-6.

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Notes

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Self-Exchange Rate for the Cu(II)/Cu(I) Couple Complexed to TAAB, an N_4 Macrocycle

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A number of copper proteins that are believed to function as electron transferases have been isolated and subjected to detailed kinetic studies in vitro.[1-3] Electron-transfer rates have been measured for reactions between these proteins and a variety of small molecules[4-8] as well as other metalloproteins,[9] and more recently, some self-exchange rates have been reported.[10,11] The results are generally interpreted in terms of the Marcus theory for outer-sphere electron-transfer phenomena,[12] which, in its simplest form, relates the rate of an electron-transfer reaction to the equilibrium constant for the overall reaction and the self-exchange rate constant for each couple involved. Unfortunately, few self-exchange rates are available from relevant copper complexes so that the theory can be applied only in a restricted way. In fact, although self-exchange rates for several copper complexes have been estimated with use of Marcus theory,[13-17] the only directly measured value has been obtained in aqueous hydrochloric acid[18]—and there the reaction may occur via an inner-sphere mechanism.[5,13] In general the problem with these measurements is that the Cu(II) and Cu(I) oxidation states prefer different stereochemistries[19-22] and ligand types; hence, considerable structural reorganization is usually involved. Since both oxidation states are substitution labile, even defining species can be a problem. The proteins apparently avoid the reorganizational problems by dictating a coordination environment that is a compromise between ones that would be favored by copper(I) and copper(II).[23,24]

In an attempt to minimize the structural changes about copper attending electron transfer, we have studied the self-exchange reaction of the Cu(II)/Cu(I) couple when complexed to the relatively inflexible macrocyclic ligand tetrabenzo[*b*,*f*,*j*,*n*]-[1,5,9,13]tetraazacyclohexadecine (**1**), which is denoted TAAB. This system has been studied by Busch and coworkers, who have reported $E_{1/2} = 0.06$ V vs. SCE.[25] Although there has been some controversy regarding the proper formulation of the oxidation state of the reduced form,[25-29]

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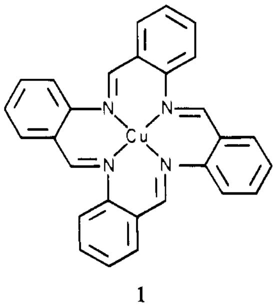

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as discussed below the evidence is that it is correctly formulated as a Cu(I) complex. Parenthetically we note that the closest protein analogue of the TAAB system is superoxide dismutase.[30]

Experimental Section

Materials. *o*-Aminobenzaldehyde was prepared from *o*-nitrobenzaldehyde according to the method of Smith and Opie.[31] All other reagents were procured from commercial sources. $Cu(TAAB)(BF_4)_2$ was prepared with use of the procedure developed by Melson and Busch,[32] substituting copper(II) tetrafluoroborate hexahydrate for copper(II) nitrate. (Anal. Calcd for $C_{28}H_{20}N_4CuB_2F_8$: C, 51.77; H, 3.10; N, 8.62. Found: C, 51.67; H, 3.26; N, 8.48.) $Pd(TAAB)Cl_2 \cdot 3H_2O$ was prepared with use of the method described by Brawner and Mertes[33] and was judged to be pure by its ^1H NMR spectrum. To prepare $Cu(TAAB)BF_4$, crystals of $Cu(TAAB)(BF_4)_2$ were dissolved in deoxygenated methanol inside an inert-atmosphere box. To this was added a fourfold excess of sodium ascorbate and ascorbic acid (1:1 mole ratio) dissolved in a minimal amount of methanol. The resultant deep blue solution and precipitate were stirred for 30 min before suction filtration of the solid. Submillimolar samples were dissolved in Aldrich 99.5% methanol-d_4 that had been deoxygenated by repeated freeze-pump-thaw cycles.

Instrumentation. All infrared characterization was performed on a Beckman Acculab 6 infrared spectrometer in Nujol mulls. ^1H NMR spectra were obtained on a Varian-XL 200 superconducting Fourier transform spectrometer at 22 °C. Typically, 2000 pulses (30° tilt angle, a 2-s acquisition time, and a 1-s delay) were used to obtain a spectrum.

Results and Discussion

Oxidation State of the Reduced Complex. On the basis of electrochemical results involving a series of metals, Busch and co-workers suggested that the reduced copper complex might better be formulated as a Cu(III) complex of the ligand dianion. The driving force envisioned for the electronic reorganization was that the "presumably planar" dianionic ligand would be aromatic and would be ideally suited for binding to a d^8 metal center.[26,27] As has been emphasized,[26,29] any oxidation-state formalism is an extreme view, the molecular orbitals being admixtures of ligand-centered and metal-centered orbitals; however, several lines of evidence argue that a Cu(I) formulation is more realistic.

Table I. Chemical Shift Data

system	δ (vs. Me_4Si)	system	δ (vs. Me_4Si)
[16]annulene	5.33[a]	$Cu(TAAB)^+$	9.33[c]
[16]annulene dianion	8.83[b]	$Pd(TAAB)^{2+}$	8.73[c,d]

[a] Center of a multiplet that reflects in part the resonance of the protons analogous to the iminoaldehyde protons of 1. Oth, J. F. M.; Gilles, J.-M. *Tetrahedron Lett.* 1968, 6259-6264. [b] Resonance of protons analogous to the iminoaldehyde protons of 1. Oth, J. F. M.; Anthoine, G.; Gilles, J.-M. *Tetrahedron Lett.* 1968, 6265-6270. [c] Resonance of iminoaldehyde protons of 1. [d] Reference is 3-(trimethylsilyl)propionic acid (sodium salt).

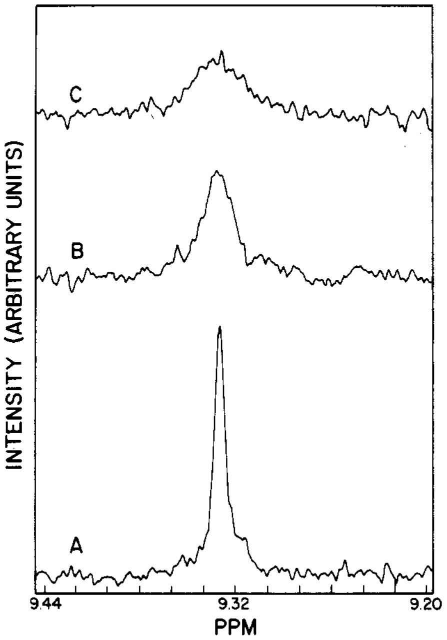

Figure 1. NMR signal of the iminoaldehyde protons of $Cu(TAAB)^+$ as a function of added $Cu(TAAB)^{2+}$: (A) $[Cu(TAAB)^{2+}] = 0$; (B) $[Cu(TAAB)^{2+}] = 1.8 \times 10^{-5}$ M; (C) $[Cu(TAAB)^{2+}] = 3.7 \times 10^{-5}$ M. The solvent is methanol-d_4; $T = 22$ °C.

In the first place the ligand dianion *cannot* be planar. There is already significant strain energy associated with [16]-annulene due to contacts between peripheral hydrogen atoms,[34] and the fused benzene rings of the TAAB moiety introduce even more severe steric barriers to achieving a planar structure.[35] Also telling is the fact that oxidation of the copper(II) complex of tetraphenylporphyrin occurs at the ligand rather than the metal[37] *despite* the fact that the porphyrin is aromatic. More directly, ionization of the 2p core electrons of the copper center of the reduced complex occurs at an energy that is consistent with a Cu(I) oxidation state.[28] Extended Hückel calculations are also consistent with this result.[29] Finally, the ^1H NMR results in Table I argue against the Cu(III) formulation. As can be seen from Table I, the protons of [16]annulene that are analogous to the iminoaldehyde protons of **1** undergo a pronounced downfield shift upon formation of the aromatic dianion, despite the increase in charge density. The annulene spectra cannot be compared directly to the spectrum of $Cu(TAAB)^+$ because of the nitrogen atoms and benzene rings present in the latter. However, it is significant that there is only a small shift in the resonance of the iminoaldehyde protons in going from $Cu(TAAB)^+$ to $Pd(TAAB)^{2+}$, which by all accounts contains the "neutral" TAAB ligand (Table I). Although there may be small differences in the orientations of the benzene rings and in the hydrogen atom/hydrogen atom interactions[38] between the two complexes, there is clearly no indication in the ^1H NMR results of a dramatic difference in the aromaticity of the ligands. Of course this does not rule out the possibility that d^8 and d^9

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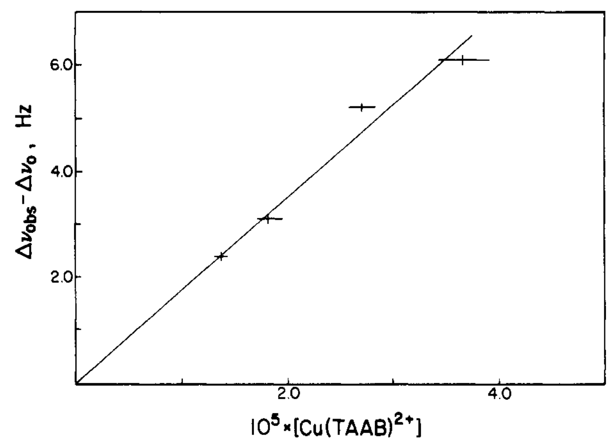

Figure 2. Exchange contribution to the NMR line width as a function of the concentration of $Cu(TAAB)^{2+}$. The solvent is methanol-d_4; $T = 22$ °C.

configurations of the metal center may make some contribution to the ground-state wave function.

Measurement of the Self-Exchange Rate. As shown in Figure 1, the resonance of the iminoaldehyde proton of the reduced TAAB complex is broadened in the presence of the Cu(II) complex, and the broadening is directly dependent upon the amount of the oxidized complex that is added (Figure 2). These results implicate some kind of exchange phenomenon,[39-41] presumably that involving the transfer of an electron between the oxidized and reduced forms of the couple (eq 1).

$$Cu(TAAB)^{2+} + Cu(TAAB)^{+} \xrightarrow{k} Cu(TAAB)^{+} + Cu(TAAB)^{2+} \quad (1)$$

This is of course the self-exchange reaction, which is characterized by a second-order rate constant k. The linear plot in Figure 2 suggests that the system can be analyzed in the slow-exchange limit, which requires[39]

$$T_1(II),\ T_2(II) << T_1(I),\ T_2(I) \quad (2)$$

$$T_1(II),\ T_2(II) << \tau(II) \quad (3)$$

where $T_1(II)$ denotes the longitudinal relaxation time of the iminoaldehyde proton of the Cu(II) complex, $T_2(II)$ represents the analogous transverse relaxation time, etc., and $\tau(II) = k^{-1}[Cu(I)]^{-1}$ is a measure of the mean lifetime of the Cu(II) form. In keeping with eq 2, Cu(II) complexes generally exhibit relatively long electron spin relaxation times; hence nuclear spins on a ligand are efficiently relaxed by the hyperfine field of the unpaired electron.[42] The conditions of eq 3 are consistent with the magnitude of k, vide infra, and the low Cu(I) concentrations that have been used. In the slow-exchange limit the resonance suffers Heisenberg broadening, and the line width is described by eq 4, where $\Delta\nu_{obsd}$ is the observed line

$$\pi(\Delta\nu_{obsd} - \Delta\nu_0) = k[Cu(II)] \quad (4)$$

width (full width at half-maximum) and $\Delta\nu_0$ is the line width measured in the absence of Cu(II). The least-squares fit of the data to eq 4 gives

$$k = 5.5\ (5) \times 10^5\ M^{-1}\ s^{-1} \quad (5)$$

where the error quoted is just the sample standard deviation. Due to experimental limitations only a small concentration range could be studied; hence, the actual precision of the measurement may be somewhat less than the data indicate.

Table II. Self-Exchange Rate Constants for Selected Copper Complexes

ligand complexed to $Cu^{2+/+}$	k, $M^{-1}\ s^{-1}$
H_2O	1×10^{-5}[a] 2.5×10^{-6}[b]
1,10-phenanthroline	4.3×10[c]
2,9-dimethyl-1,10-phenanthroline	1.7×10^4[c] 4×10^4[d]
1,4,8,12-tetrathiacyclopentadecine	4.1×10^2[b]
1,4,7,10,13-pentathiacyclopentadecine	3.2×10^4[b]
TAAB	5×10^5[e]
plastocyanin	$<<10^4$[f]
stellacyanin	1×10^5[g]
azurin	2×10^6[h]
Cl^-	5×10^7[i]

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In principle, the self-exchange reaction of the TAAB system could occur either by an inner-sphere or by an outer-sphere mechanism. Since methanol is expected to be a poor bridging ligand and since there are apt to be steric problems associated with the formation of the bridged transition state, the outer-sphere pathway seems more viable. As can be seen in Table II, the rate constant for this system falls in the upper end of the range of values that have been estimated for other Cu(II)/Cu(I) couples, suggesting that the inner- and outer-sphere reorganization energies associated with electron transfer from the TAAB complex are relatively modest. Except for the TAAB system, all of the data in Table II pertain to aqueous solution. As pointed out by a reviewer, comparisons with our results must be somewhat qualified because a smaller outer-sphere reorganization energy would be expected in methanol. A related effect may occur in the protein systems.[43]

The fact that the inner-sphere reorganization energy is not large is significant since it is likely that $Cu(TAAB)^{2+}$ and $Cu(TAAB)^{+}$ exhibit different coordination numbers. The Cu(II) complex of a methyl-substituted analogue of TAAB has recently been examined in the solid state, and the coordination geometry about the copper center has been described as a bicapped square pyramid that is defined by the N_4 donor set of the macrocycle and a bidentate nitrate counterion.[44] Of course, the coordination geometry could be different in solution; by analogy with the structure of the diiodo salt of $Ni(TAAB)^{2+}$ the structure might be expected to involve an essentially square-planar arrangement of the N_4 donor set with axially bound solvent molecules.[45] While the structure of $Cu(TAAB)^{+}$ has not been reported, our results reveal that it is a symmetrical structure, at least on the NMR time scale. On the basis of previous studies of the TAAB ligand[44,45] and the knowledge of the acceptor orbitals available on Cu(I), we would expect the complex to have approximate S_4 symmetry with a D_2-type distortion of the N_4 donor set. The Cu(II) structure demonstrates that some degree of D_2 distortion is possible.[44] Although detailed structural information is lacking, these results certainly suggest that electron transfer can be

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facile for a copper center in a tetragonal binding site, even if a change in coordination number attends reaction. This finding lends support for the mechanism that has been proposed for the blue copper oxidase laccase and that invokes rapid electron transfer from the type 2 copper site under some conditions.[46]

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Registry No. Cu(TAAB)$^+$, 47718-15-0; Cu(TAAB)$(BF_4)_2$, 68890-49-3; Pd(TAAB)$^{2+}$, 69799-64-0.

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Correlations between Core Size and Wavelength of the α Band for Nonhyper Metalloporphyrins[1a]

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A great deal of Raman data on metalloporphyrins[1b-10] and heme proteins[1b,11-21] has been reported in recent years. Molecular information is obtained from Raman spectra of these materials by two approaches: (a) Conventional normal-coordinate analyses[22-25] give information about porphyrin force constants and molecular structure. (b) Empirical correlations of Raman frequencies with structural or electronic properties give information about comparative differences in these properties.[2,4,5,11,13,26-30] The former method suffers from a lack of macrocycle normal modes consisting of pure group frequencies. The latter method has been highly successful for the pyrrole-substituted metalloporphyrins, because several Raman lines have been found to be markers of either porphyrin structure or electronic properties.

Empirical correlations between molecular parameters and the wavelength of absorption band maxima, especially the α-band maximum, have also enjoyed considerable success.[4,31-35] The ultimate goal of this work is to use these empirical correlations to predict chemical activity of metalloporphyrins in proteins and in other environments.

One of the most remarkable empirical structural correlations is that between the frequencies of a group of Raman lines and the center-to-nitrogen (pyrrole) distance or core size.[2,26] The frequencies of the ν_3, ν_{19}, and ν_{10} vibrations of pyrrole-substituted metalloporphyrins correlate well with the core size determined from X-ray crystal structures of pyrrole- and meso-substituted metalloporphyrins. The core-size marker lines are not sensitive to the nature of the pyrrole substituents,[24,25,36] since the correlation is good for a variety of substituent groups. The lines also must be insensitive to the out-of-plane distance of the metal.[2,3]

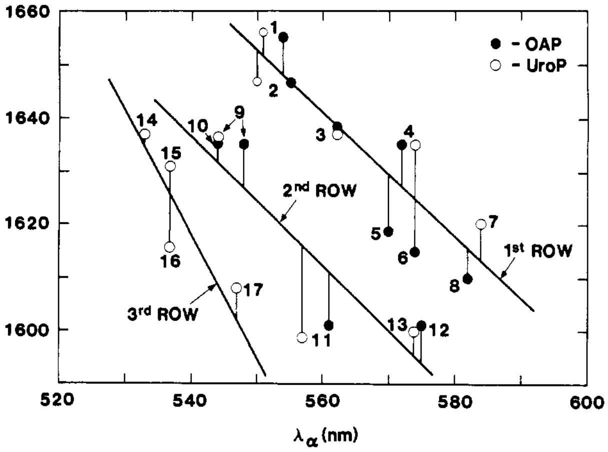

Figure 1. Correlations between frequency of ν_{10} and λ_α for first-, second-, and third-row transition metals: 1, Ni(II); 2, Co(II); 3, Cu(II); 4, $V^{IV}O$; 5, Zn(II); 6, H_2; 7, $V^{IV}(OH)_2$; 8, Mg(II); 9, Pd(II); 10, $Rh^{III}Cl$; 11, Ag(II); 12, $Sn^{IV}Cl_2$; 13, $Sn^{IV}(OH)_2$; 14, Pt(II); 15, Ir^{III}(CO)(OH); 16, Os^{II}(CO)(py); 17, Ir^{III}(CO)Cl. See Table I. The correlation coefficients are 0.89, 0.86, and 0.87 for periods 4, 5, and 6, respectively. Open circles represent metallouroporphyrins in aqueous solution; filled circles are octaalkylporphyrin metal derivatives in organic solvents.

Although the core-size lines are excellent structural markers, the correlation must result from electronic effects of the metal on the porphyrin ring.[37] One reason for this conclusion is that the correlation is not the typical one between frequency and

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