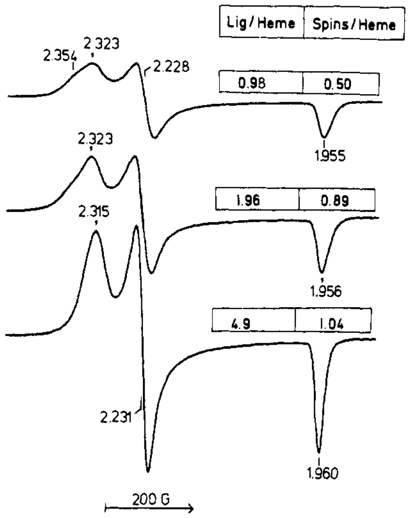

Figure 2. ESR spectra of hemin–mercaptide complexes at 100 K. The same samples of Figure 1 were used. The ESR spectrometer (Varian E-9) was connected to a computer (Data General NOVA 820) for the double integration of the spectra. ESR was recorded at a microwave frequency of 9.35 GHz, at a microwave power of 20 mW, and with a modulation amplitude of 10 G; 1 mM copper(II)-EDTA was used as standard for the determination of the spin concentration by double integration.

thiol complexes by our dimercaptide-heme complexes (Table I) increases the evidence for mercaptide sulfur as one native ligand of ferric cytochroms P450. Also the data for the corresponding phosphine complexes[11] contribute to this evidence.

For the formation of a ferrous hyperporphyrin spectrum, obviously only one mercaptide ligand was necessary, while the sixth ligand was CO (or pyridine, isocyanide, or presumably carbene[12] according to ligand spectra with ferrous cytochrome P450). In the ferric state, however, two mercaptides or one mercaptide and one phosphine were necessary ligands for the hyperporphyrin spectrum. Mercaptide-hemin complexes with isocyanide, thioether, or nitrogeneous bases[10] exhibited normal porphyrin spectra with one Soret band, although red shifted to ~430 nm. Hemin with two negative mercaptide ligands is remarkably stable: the irreversible electron transfer from sulfur to iron is quenched below −50 °C even with alkyl mercaptides.[13]

It is interesting to note the only slight shift of the ESR spectra when the second mercaptide ligand was bound, while the electronic spectra changed rather drastically to the hyperporphyrin type. This finding supports the interpretation[6] of the hyperporphyrin spectrum by a charge-transfer interaction between mercaptide and porphyrin which does not directly involve the iron d orbitals responsible for the g values.

Recently Chang and Dolphin[14] described a spectral species, with peaks at 378, 476, and ~563 nm which was formed after the addition of O_2 to a ferrous protoheme-mercaptide complex at −45 °C, and interpreted it as a mercaptide-heme (II)-oxygen complex. This species would differ from the described oxy complex of cytochrome P450.[15] In view of the striking spectral similarity with our dimercaptide-hemin complex, one should consider the possibility that dioxygen may cause the oxidation to a ferric protoheme-dimercaptide complex which can be reduced by mercaptide in the presence of CO.

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(8) The structures of the intermediate spectral species at mercaptide/heme ratio of 1 and 2 were not examined in detail; possible ligands were DMF, chloride, and mercaptide.
(9) We obtained identical data for the hyperporphyrin spectra when we prepared the mercaptides either from mercaptans with equimolar base ($(CH_3)_4NOH$) or from sodium mercaptides with dibenzo-18-crown-6.
(10) The comparison of the data from the mercaptide/imidazole/heme system with the data for a diimidazole–heme complex[2b] show that imidazole, even at 10-fold excess, exchanges only *one* mercaptide. By this ligand exchange method, we were able to obtain spectroscopic data for the complexes $[RS^-Fe^{III}L]$ where L was imidazole, primary amine, and thioether. Since their Soret bands were found between 426 and 434 nm, compared to 418 nm for low spin ferric cytochrome P450, none of these ligands appear to be the native sixth ligand in cytochrome P450.
(11) When 10 equiv of diethylphenylphosphine was added to a dimercaptide–hemin complex, a new spectral species was observed (Table I) showing also a hyperporphyrin spectrum, although the bands were blue shifted. The ESR spectrum indicated also low spin ferric heme. The relative shifts of the g values compare favorably with those of the thiol and phosphine complexes of cytochrome P450.[7]
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(13) Measuring the concentration of ferric heme by double integration of the ESR spectrum, we found in the system hemin/n-BuS$^-$ in DMF that the reduction of the heme proceeds above −40 °C. With CO the reduction was facilitated: it began at −45 °C.
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H. H. Ruf,* P. Wende
Department of Physiological Chemistry
University of the Saarland, D-6650 Homburg/Saar, G.F.R.

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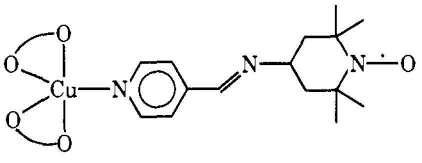
Metal–Nitroxyl Interactions. 2. A Resolved Weak Exchange Electron Paramagnetic Resonance Spectrum in Solution[1]

Sir:

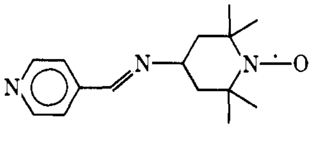
Interaction of paramagnetic transition metals with nitroxyl radicals is being used to provide structural information about biological systems.[2] Transition metal-nitroxyl radical species also provide an entree to the study of interactions between nonequivalent unpaired electrons, i.e., electrons with different g values, coupling constants, and/or relaxation times.[3]

Following a theory put forth by Leigh,[4] the analysis of EPR spectra of spin-labeled biomolecules to ascertain the distance between the metal and the nitroxyl spin label assuming dipolar interaction is quite common.[2] In some cases in which a nitroxyl radical containing moiety functions as a ligand to a paramagnetic metal or encounters the metal in collisions in solution, the EPR spectra of the nitroxyl radical differs from the spectrum of the nitroxyl in the absence of the metal. In some of the papers the investigators assumed that the spectral changes were due to exchange interactions.[3b,5] In other papers it was assumed that the effects were dipolar in origin.[6] Molin and coworkers have explored collisions of nitroxyl radicals with paramagnetic metal complexes and found evidence for both exchange and dipolar interaction.[7] Wilbur and Kreilick observed differences in the broadening in the EPR spectra of nitroxyl radicals upon collision with metal acetylacetonates and concluded that the variations may be due to differences in either the dipolar or exchange terms.[8]

In order to develop a means to evaluate quantitatively the effect of the presence of paramagnetic metal ions on the nitroxyl EPR line shape, we are investigating a large variety of transition metal complexes containing nitroxyl radicals. In this paper we present unambiguous evidence for exchange interaction in the adduct I, of bis(hexafluoroacetylacetonato)copper(II), Cu(hfac)$_2$, with the Schiff base, II, formed from pyridine-4-aldehyde and 4-amino-2,2,6,6-tetramethylpiperidinooxy (the copper coordination geometry is not known).



I



II

The Schiff base, II, was prepared by stoichiometric combination of the commercially available precursors in absolute ethanol. The analytically pure ligand was combined with anhydrous Cu(hfac)$_2$[9] in CCl$_4$ and the complex I was obtained analytically pure by recrystallization from CCl$_4$.[10] The X-band EPR spectrum of a sample of I in degassed CCl$_4$ at $\sim$21 °C is presented in Figure 1. The nitroxyl EPR spectrum consists of six broad lines $\sim$15 G apart. Superimposed on these are three sharp lines typical[2a] of free nitroxyl radicals. The copper spectrum appears to have five poorly resolved peaks instead of the usual four ($I = \frac{3}{2}$). For comparison, the analogous compound, III, with the nitroxyl replaced by the reduced (secondary amine) form of the ligand was also prepared. The EPR spectrum of III, also shown in Figure 1, exhibits the expected partially resolved four-line pattern. The splitting pattern observed for I, analyzed by a first-order computer-simulation of the spectrum, results from an electron-electron interaction, J, of 45 G (0.0042 cm^{-1}). The nitroxyl spectrum is thus a doublet of triplets in which couplings of 45 and 15 G yield six approximately equally spaced lines. Similarly, the additional coupling of 45 G gives a copper spectrum which is an overlapping doublet of quartets ($\langle a \rangle_{^{63}\mathrm{Cu}} = 50$ G) yielding five apparent lines as shown in the figure. The intensity of the sharp three-line pattern is dependent on solvent and is assumed to be due to a small amount of dissociation of the complex. Thus the EPR spectrum of I is attributed to an "ABMX"-type coupling pattern in which the electron-electron interaction is only about three times as large as the electron-nitrogen interaction in the nitroxyl, and about the same magnitude as the electron-copper interaction in the Cu(hfac)$_2$. The spectra were simulated using the "X approximation" for coupled spins. The two-electron spins, the copper nuclear spin, and the nitrogen nuclear spin were taken as an ABMX spin set by analogy with NMR hyperfine splitting calculations.[11] A similar "AB" analysis was applied to the interpretation of the EPR spectrum observed during catalysis by enzymes using coenzyme B$_{12}$.[12]

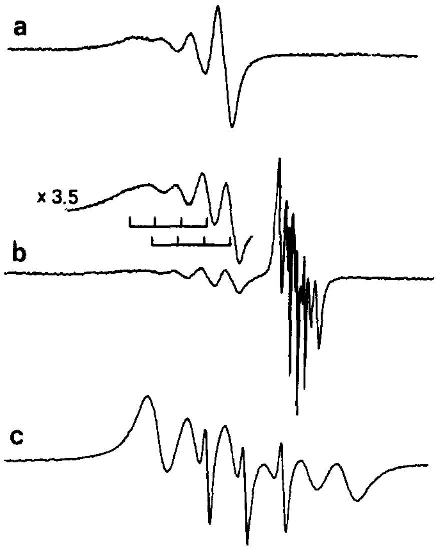


Figure 1. X-band spectra of $\sim$21 °C CCl$_4$ solutions: (a) 1000-G scan of III, the amine ligand analogue of the nitroxyl complex I; (b) 1000-G scan of copper-nitroxyl complex I; (c) expanded presentation of the nitroxyl region of spectrum.

Prior observations of resolved electron-electron exchange splitting in EPR spectra have involved pairs or clusters of ions in crystals[13] and in vanadium and copper dimers in solution[14] and in bi- and polynitroxides.[2] This is the first observation of resolved electron-electron splitting involving nonequivalent electrons. It is to be emphasized that this observation was made on a complex dissolved in a low-viscosity solvent at room temperature.

Preliminary results on related compounds indicate that the observations reported here are not an isolated phenomenon.

Based on CPK molecular models, the copper-nitroxyl distance in I is roughly 10 Å. This distance is in the range claimed to be measured in spin-labeled biomolecules assuming pure dipolar interactions.[2a] Since there is so far no evident correlation between distance or intervening bond pathways and the magnitude of electron-electron exchange splitting,[15] attempts to derive distance information from nitroxyl EPR line shapes must keep in mind the potential uncertainties.

It is to be emphasized that, although the exchange interaction is clearly established by the multiplicity of the peaks in the spectrum, the contribution of dipolar interactions, if any, is not proven. It is generally assumed that dipolar interactions average to zero in cases of rapid isotropic tumbling. However theoretical expressions are not yet available for defining the relative values of spin relaxation times and molecular correlation times which, considering phase memory, etc., could lead to observable dipolar effects for "rapid tumbling" in room temperature low viscosity systems.

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(16) Visiting Professor, University of Denver, 1975-1976. Permanent address: University of Essex, England.

P. M. Boymel, J. R. Chang, D. L. DuBois
D. J. Greenslade,[16] G. R. Eaton*
Department of Chemistry, University of Denver
Denver, Colorado 80208

S. S. Eaton
Department of Chemistry
University of Colorado at Denver
Denver, Colorado 80202

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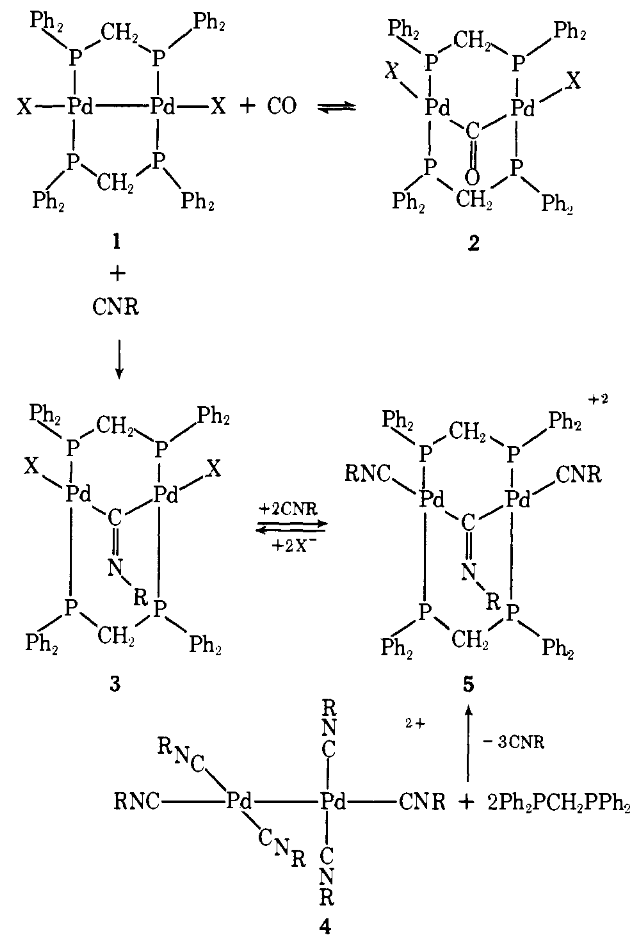
Insertion of Isocyanides and Carbon Monoxide into Metal-Metal Bonds. Preparation and Structure of $[Pd_2(CNCH_3)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2][PF_6]_2$

Sir:

Recent suggestions[1] that polynuclear metal complexes may exhibit heretofore unobserved modes of catalytic activity have stimulated interest in the behavior of such complexes and particularily those complexes (e.g., $Os_3H_2(CO)_{10}$[2] and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$[3]) containing unsaturated metal-metal bonds. Here we report some addition reactions of two coordinatively unsaturated palladium(I) dimers. The most conspicuous feature of these reactions is the expansion of the palladium-palladium distance which occurs upon formation of an isocyanide or carbon monoxide bridge. In contrast, with most other complexes containing monohapto, doubly bridging carbon monoxide or isocyanide ligands, these ligands span two metal centers which are generally thought to be connected by a direct metal-metal bond.[4]

Scheme I



When a dichloromethane solution of the phosphine bridged palladium(I) dimer $Pd_2(dpm)_2X_2$[5] (**1**, X = Cl, Br) (dpm, $Ph_2PCH_2PPh_2$) is exposed to 1 atm of carbon monoxide, 1 equiv of carbon monoxide is absorbed and the dark red crystalline complex $Pd_2(dpm)_2(CO)X_2$ (**2**) may be isolated. This product contains only a bridging carbonyl (ν_{CO} 1704 cm^{-1}, X = Cl). Carbon monoxide addition to **1** is readily reversed. Refluxing a dichloromethane solution of **2** or heating solid **2** at 56 °C under vacuum causes it to revert to **1**. Although numerous examples of reversible carbon monoxide bonding to terminal sites in metal complexes are known, to our knowledge this is the first case in which reversible carbon monoxide bonding to a bridging position occurs.

Addition of isocyanides to **1** proceeds similarly to produce $Pd_2(dpm)_2(CNR)X_2$ (**3**, R = CH_3, C_6H_{11}, C_6H_5, $p\text{-}CH_3C_6H_4$; X = Cl, Br) (Scheme I). However, the addition of isocyanide has not yet been reversed. The infrared spectra of the crystalline yellow orange products indicate that only bridging isocyanide ligands are present in the products (ν_{CN} 1624-1677 cm^{-1}). Related isocyanide complexes are obtained when $Pd_2(CNR)_6(PF_6)_2$ (**4**, R = CH_3 or $p\text{-}CH_3C_6H_4$)[6] is treated with dpm. Crystalline 1:2 electrolytes of the stoichiometry $[Pd_2(dpm)_2(CNR)_3][PF_6]_2$ (**5**) are obtained. Solution infrared spectra of these cations reveal the presence of both terminal (ν_{CN} 2183-2231 cm^{-1}) and bridging (ν_{CN} 1640-1680 cm^{-1}) isocyanide ligands. Complexes of the types **3** and **5** are interconverted by exchange of terminal ligands. Addition of halide ion to solutions of **5** causes **3** to precipitate. Although **3** has extremely limited solubility, it readily dissolves in acetone or acetonitrile in the presence of an excess of isocyanide to form **5**.

Because of the low CN or CO stretching frequencies observed in the infrared spectra of these bridged complexes **2**, **3**, and **5**, an x-ray structural determination of **5** was undertaken to obtain precise structural data on one member of this group. Crystals of $[Pd_2(dpm)_2(CNCH_3)_3](PF_6)_2$ were obtained as an acetone solvate by slow diffusion of diethyl ether into an