Table I. Positive Ion FAB MS of the Complex in Glycerol[a]

m/z	rel intensity	assignment[b]	m/z	rel intensity	assignment[b]
69	100	$(I + H)^+$	195	17.60	$(IP + H)^+$
109	1.01	$(P - OH)^+$	263	2.40	$(IP + I + H)^+$
127	6.24	$(P + H)^+$	321	2.43	$(IP + P + H)$
137	3.21	$(I_2 + H)^+$	390	0.55	$(IP + H_2)^+$

[a] The sample was inserted on a stainless steel probe tip into the mass spectrometer (a kratos MS-30 with a DS-55 data system) and sputtered into the gas phase as ions by bombardment with 6 keV neutral xenon atoms. [b] I = imidazole; P = $(MeO)_2PO_2H$; IP = complex.

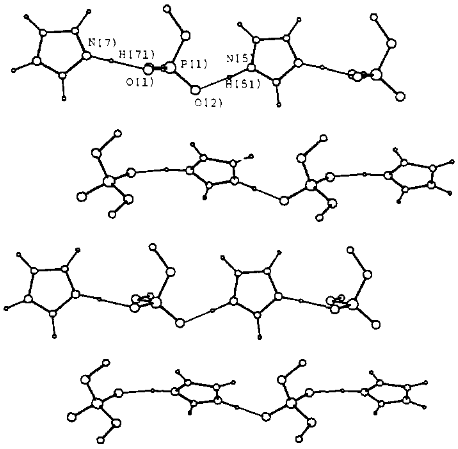

Figure 1. Diagram of the packing and chain-type structure of the imidazole-$(MeO)_2PO_2H$ complex. The positions of the hydrogen atoms have been geometrically calculated.

of the complex formed. We now wish to report the first use of fast-atom-bombardment mass spectrometry (FAB MS) as a means of characterizing a complex containing a strong hydrogen bond. The structure of the complex has been independently confirmed by conventional X-ray crystallography.

Ordinary electron-impact mass spectrometry (EI MS) of the crystals isolated from an equimolar mixture of imidazole and trimethyl phosphate gave the highest mass peak at m/z 126 followed by peaks characteristic of the fragmentation of imidazole and the phosphate. Such an experiment requires thermal volatilization of the complex and subjects it to bombardment with electrons, the combination of which effectively precludes the use of EI MS for the analysis of hydrogen bonding. In an attempt to overcome this problem we have used FAB MS, which as a soft ionization technique that does not require sample heating may allow the direct observation of hydrogen-bonded species.

The FAB MS of the crystalline complex dissolved in glycerol shows the three most intense peaks occurring at m/z 69, 127, and 195. Significant higher mass peaks at m/z 263, 321, and 390 were also observed in a remarkably clear spectrum. It is interesting to note that the complex is obviously strong enough to survive the hydrogen-bonding competition provided by the hydroxylic solvent and that it does not significantly dissociate in solution as this would be expected to produce intense fragments containing glycerol. We believe that the observed spectrum is only consistent with a polymeric complex of imidazole with $(MeO)_2PO_2H$ (Table I).

In order to disprove the possibility that the observed imidazole-phosphate species were produced by reactions between fragment species in the desorption-ionization process, systems containing imidazole and weaker hydrogen-bond electron donors were investigated. The FAB MS of imidazole-Ph_2O, imidazole-Ph_2CO, and imidazole-dioxane systems in glycerol gave spectra very similar to that of imidazole itself with no evidence of any peaks due to the hydrogen-bonded complexes. The more powerful hydrogen-bond electron donor Ph_2SO does, however, appear to form strong hydrogen bonds to imidazole. The FAB MS of this system in glycerol shows a peak at m/z 271, which can be assigned to a protonated imidazole-Ph_2SO hydrogen-bonded complex ion. The relative intensity of this peak is approximately one-half of the intensity of the corresponding (imidazole-phosphate + H^+) ion peak.

The observed crystal structure of the imidazole-phosphate complex is in excellent agreement with the structure deduced from the FAB MS data and is shown in Figure 1. The complex contains infinite chains of imidazole-$(MeO)_2PO_2H$ units. The two N-O distances are 2.68 (1) and 2.67 (1) Å, i.e., equal within experimental error, and the bond angles are 171.0 (4)° and 176.5 (4)°, which are consistent with the presence of strong NHO hydrogen bonds.

The successful application of FAB MS to the analysis of a hydrogen-bonded complex suggests that this technique may well become a routine analytical method for the study of strong hydrogen bonding.[4] The information obtained is complementary to that obtained from other "fast" analytical technqiues such as infrared and NMR spectroscopy. While FAB MS cannot provide the same detailed information as X-ray crystallography, it is a much simpler technique and it can be used to study liquids or solutions thus removing the need for a crystalline sample.

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Registry No. Ph_2O, 101-84-8; Ph_2CO, 119-61-9; Ph_2SO, 945-51-7; imidazole, 288-32-4; trimethyl phosphate, 512-56-1; dioxane, 123-91-1.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Copper-Dioxygen Chemistry. Synthesis, Spectroscopy, and Properties of a Copper(II) Superoxide Complex

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In this contribution, I present initial results on a copper-dioxygen adduct prepared by reaction of molecular oxygen with a Cu(I) complex having an easily displaced ligand. Analytical and spectroscopic data and physical properties suggest formation of a Cu(II)-superoxide complex. Bound dioxygen is displaced by small molecules such as carbon monoxide, acetonitrile, and ethylene. Copper-dioxygen adducts are often proposed as intermediates in Cu(I) autoxidation reactions but have not been previously isolated and characterized.[1,2] These adducts are generally unstable and rapidly decompose to hydrogen peroxide or other reduced oxygen species.[2] This study presents the first well-characterized example of reversible dioxygen binding by a copper complex.

The Cu(I)-ethylene complex $Cu(HB(3,5\text{-}Me_2(pz))_3)(C_2H_4)$ (I) $(HB(3,5\text{-}Me_2(pz))_3$ = hydrotris(3,5-dimethyl-1-pyrazolyl)-

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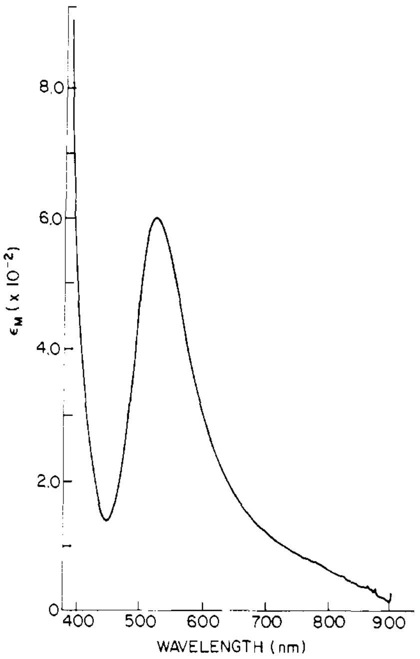

Figure 1. Visible spectrum of $Cu(HB(3,5\text{-}Me_2(pz))_3)(O_2)$ in dichloromethane at −14 °C.

borate) recently reported[3,4] reacts rapidly at room temperature with molecular oxygen in acetone to yield an intensely reddish-purple precipitate. A microcrystalline solid II with the same color is obtained on recrystallization at −40 °C by slow diffusion of oxygen-saturated diethyl ether into an oxygen-saturated dichloromethane solution of the acetone precipitate. This solid is indefinitely stable under oxygen or nitrogen at −40 °C but turns green on standing for several days at room temperature.

Analytical[5] and spectroscopic data suggest formulation of II as $Cu(HB(3,5\text{-}Me_2(pz))_3)(O_2)\cdot{}^1/_8Et_2O$, a tetrahedral Cu(II)–superoxide complex. The material does not have an EPR spectrum at liquid nitrogen temperature. The ^1H NMR spectrum in CD_2Cl_2 is consistent with this formulation.[5c] These results support the assignments of the copper and oxygen oxidation states. Both Cu(II) and superoxide ions have an unpaired electron; coordination of these ions should lead to strong coupling of spins and formation of an EPR-silent complex. This coupling of spins is observed for a Cu(II)–superoxide complex prepared directly by adding KO_2 to a Cu(II) complex at low temperature.[6] The visible spectrum of II (Figure 1) obtained at approximately −14 °C in dichloromethane consists of a relatively intense band at 524 nm ($\epsilon = 600$ M^{-1} cm^{-1}) with a broad shoulder on the low-energy side that tails into the near-infrared region. This spectrum closely resembles that of another Cu(II) complex with this polypyrazolylborate ligand $Cu(HB(3,5\text{-}Me_2(pz))_3)(SR)$, SR = *p*-nitrobenzenethiolate,[7] which is dominated by a low-energy charge-transfer transition. We tentatively assign the 524-nm band to a ligand-to-metal charge-transfer band because of its intensity and position, and the broad shoulder on the low energy side to d–d transitions; this region of the spectrum is similar to that of the previously reported Cu(II) complex $Cu(HB(3,5\text{-}Me_2(pz))_3)(OR)$, OR = *p*-nitrophenolate, which has a weak absorption at 660 nm.[7a] Hence, the visible absorption data are consistent with the formation of a tetrahedral Cu(II) ion with a N_3O inner coordination sphere.[7,8] The best evidence for a bound superoxide ion in II comes from an infrared study of the $^{16}O_2$ and $^{18}O_2$ derivatives IIa and IIb (Figure 2). The infrared spectrum of IIa is essentially the same as those of the starting ethylene complex I and the analogous carbonyl[9] and acetonitrile[10] complexes (without the bands attributable to these small molecules). No band appears that can be assigned to a coordinated dioxygen stretching vibration. The spectrum of IIb has a new, relatively weak band at 1015 cm^{-1} but is otherwise identical with that of IIa. An oxygen stretching vibration should appear at higher energy in the spectrum of IIa, but a strong band from the polypyrazolylborate ligand occurs at 1060 cm^{-1}. A dioxygen stretching vibration in this region is characteristic of an unsymmetrically bound superoxide ion.[11,12]

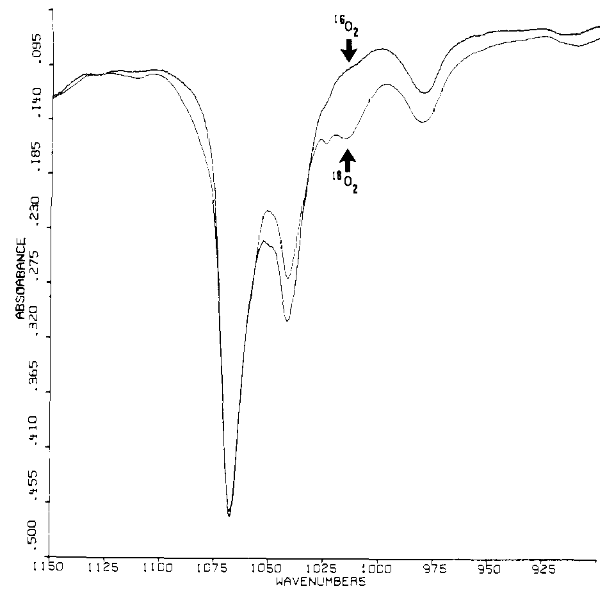

Figure 2. Infrared spectra of $Cu(HB(3,5\text{-}Me_2(pz))_3)(^{16}O_2)$ (top) and $Cu(HB(3,5\text{-}Me_2(pz))_3)(^{18}O_2)$ (bottom).

The reaction chemistry of II is consistent with the indicated formulation. Addition and removal of molecular oxygen cause the metal ion to shuttle between the +1 and +2 oxidation states. Adding molecular oxygen to I produced II. This reaction is reversed by bubbling ethylene through the mixture to yield I and a green material, III. The origin and identity of III are not yet known, but it may result from the irreversible oxygenation of the Cu(I) dimer $Cu_2(HB(3,5\text{-}Me_2(pz))_3)_2$, described previously.[9] We have shown that substitution reactions with I yield significant amounts of this dimer,[3] which reacts rapidly with oxygen in solution.[9] Reacting acetonitrile with II gives a similar result: production of $Cu(HB(3,5\text{-}Me_2(pz))_3)(CH_3CN)$[10] and a green material. Less than stoichiometric amounts of molecular oxygen (50–60%) are obtained from this reaction;[13] the mixture turns

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(4) Better yields of I can be obtained by dissolving $KHB(3,5\text{-}Me_2(pz))_3$ in approximately 10 mL of tetrahydrofuran before addition to the Cu(I) solution and by washing the solids obtained from the first filtration with small amounts of this solvent. Recrystallization of the ethylene complex before oxygen addition may be necessary.

(5) (a) Anal. Calcd for $C_{15.5}H_{23.25}BCuN_6O_{2.125}$: C, 46.31; H, 5.83; N, 20.90. Found: C, 46.18; H, 6.20; N, 20.78. This analysis corresponds to $Cu(HB(3,5\text{-}Me_2(pz))_3)(O_2)\cdot{}^1/_8Et_2O$. Samples isolated from acetone or petroleum ether contain significant amounts of these solvents. (b) Molecular weight determinations by vapor-phase osmometry are consistent with monomer formation. (c) NMR (ppm, relative to external tetramethylsilane) 5.74 (s, 3 H, pyrazole ring protons), 3.40 (q, diethyl ether methylene protons), 2.40 (s, 9 H, pyrazole methyl protons), 2.31 (s, 9 H, pyrazole methyl protons), 1.68 (t, diethyl ether methyl protons).

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reddish-purple again on exposure to molecular oxygen. Removing solvent under high vacuum produces a green solid, from which the Cu(I) dimer is obtained on recrystallization. Carbon monoxide displaces the bound oxygen cleanly to yield the Cu(I)–carbonyl complex $Cu(HB(3,5\text{-}Me_2(pz))_3)(CO)$.[9,14] Finally, evaporation of dichloromethane solutions of II with molecular oxygen at room temperature yields the Cu(II) complex $Cu(HB(3,5\text{-}Me_2(pz))_3)Cl$.[15] The chloride ion must come from the solvent; the oxygen-containing products have not yet been identified.

Two important conclusions on copper–oxygen coordination chemistry emerge from this initial study. First, relatively stable dioxygen adducts can be prepared by adding molecular oxygen to a Cu(I) complex. The stability of II is indeed remarkable in light of the overwhelming tendency of Cu(I) complexes to fully reduce molecular oxygen[1,2] and may result at least in part from use of the ligand $HB(3,5\text{-}Me_2(pz))_3^-$, which imposes a geometry suitable for both the Cu(I) starting material and the Cu(II) product.[3,7] Second, reacting molecular oxygen with a cuprous complex can produce a superoxide complex. This species has been proposed as an initial reduction product in Cu(I) autoxidations but has not been observed chemically or spectrophotometrically in these reactions.[1] Use of the polypyrazolylborate ligand enables us, at least in part, to isolate this superoxide complex. The methyl substituents minimize molecular aggregation, especially with other Cu(I) species that could lead to further reduction of the bound dioxygen species.[1]

Acknowledgment. The excellent technical assistance of R. M. Swiatek is gratefully acknowledged. Helpful discussions with Drs. P. L. Watson and J. Valentine are greatly appreciated.

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(13) Standard high-vacuum techniques were used to collect and measure gas evolved during these reactions. Mass spectral analysis confirms the presence of molecular oxygen. Both $^{16}O_2$ and $^{18}O_2$ samples were analyzed in this way.

(14) Infrared and ^1H NMR data agree with published values. Anal. $(C_{16}H_{22}BCuN_6O)$ C, H, N.

(15) This formulation is based on infrared, visible absorption, and EPR data. Anal. $(C_{15}H_{22}BClCuN_6)$ C, H, N.

Proton-Transfer Kinetics in Solids: Tautomerism in Free Base Porphines by ^{15}N CPMAS NMR

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There is considerable interest in studying proton-transfer reactions in the solid state by dynamic NMR spectroscopy, since rate constants may be obtained at low temperatures that are not accessible in solution.[2,3] The fact that the transfer rate constants in solution and in the solid state may be completely different at a given temperature (kinetic solid state effect—KSSE) does present a complication. Little is known about such effects because it has not been possible so far to obtain rate constants for both phases at the same temperature. KSSE's are inherently very interesting phenomena and may become so large that proton transfer is not observable in the solid state within the NMR time scale, as in the cases of naphthazarin at low temperature[3,4] and of tropolone.[5] We present here results of a dynamic ^{15}N CPMAS NMR study of ^{15}N-enriched free-base *meso*-tetraarylporphines which show that a tautomerism known to occur in solution according to Scheme I[6-10] also takes place in the solid state. We have measured rate constants and kinetic isotope effects in the solid state that are identical with or different from solution data depending on substitution in the aryl groups. These results suggest the resolution of a long-standing paradox involving the problem of proton localization in solid-state porphines.[11-14] Finally, our findings suggest how proton-transfer systems may have to be designed to minimize kinetic solid-state effects.

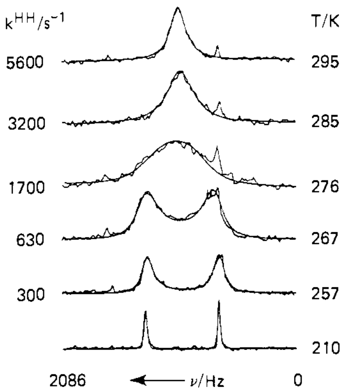
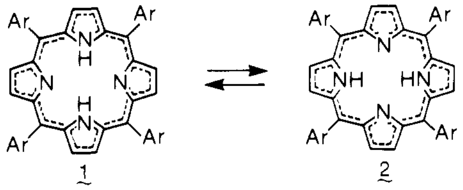


Figure 1. Superposed experimental (6.082 MHz) and calculated ^{15}N CPMAS NMR spectra of 95% ^{15}N-enriched TTP, 10-Hz line broadening, 8000-Hz sweep width, 1.2-s repetition time, 9-μs ^1H-π/2 pulses, quadrature detection, 25 000 scans on the average; reference, external $^{15}NH_4NO_3$. The line width in the absence of exchange was taken from the spectrum at 210 K. The equilibrium constant of the tautomerism was assumed to be unity. k^{HH} is the HH migration rate constant. We attribute the sharp small high-field line to the NH signal of a low-level impurity of nonexchanging tetratolylchlorin, a byproduct of the synthesis.[16]

Scheme I



TPP: Ar ≡ phenyl
TTP Ar ≡ p-tolyl

Figure 1 shows the ^{15}N CPMAS NMR spectra of 95% enriched *meso*-tetra-*p*-tolylporphine (TTP) at 6.082 MHz in the solid state at different temperatures.[15] As expected from the solution

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(1) (a) On leave from the Institute für Physikalische Chemie der Universität Freiburg, i.Br. (b) Institut für Physikalische Chemie der Universität Freiburg, i.Br. (c) IBM Research Laboratory.

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