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A Reinvestigation of the Reaction of Dioxygen with (Phthalocyaninetetrasulfonate)iron(II)[1a]

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Received August 30, 1976 AIC60638T

Recent investigations of oxygen complexation by transition metals have generated considerable interest.[2] Iron–dioxygen complexes are of particular interest as biological models. Recent investigations have suggested that iron–dioxygen adducts are stabilized by, first, providing a hydrophobic environment for the iron and, second, inhibiting dimerization, which appears to offer a pathway for irreversible oxidation. One apparent curious exception to these generalizations is provided by the report of Fallab[3] that (tetrasulfophthalocyanine)iron(II), referred to below as Fe^{II}PTS, reversibly complexes dioxygen in aqueous solution, presumably forming a μ-peroxo complex. At about the same time, Weber and Busch[4] described the formation and reactions of some metal phthalocyanines which indicated that irreversible oxidation of Fe^{II}PTS to Fe^{III}PTS occurs in aqueous solution.

In the present note, we have reexamined the reaction of Fe^{II}PTS with dioxygen in an attempt to resolve these conflicting conclusions.

Experimental Section

Phthalocyaninetetrasulfonate (PTS) was prepared in low yield by the method of Fallab,[5] with purity characterized by visible spectroscopy (ϵ_{630} 9.3×10^4). Fe^{II}PTS was then prepared by reacting ferrous ammonium sulfate with PTS under strictly anaerobic conditions to give a dark green solution (λ_{max} 670 nm). On exposure to air or on running the synthesis in the presence of air (after the method of Fallab), a blue solution (λ_{max} 634 nm) with a small shoulder at 670 nm is obtained. The product was also prepared by the template synthesis of Weber and Busch.[4] Ferrous ammonium sulfate was slowly added to a refluxing nitrobenzene solution of 4-sulfophthalic acid, urea, and ammonia sulfate. (Slow addition of iron(II) is necessary for maximum yield.) The dark mass so obtained was washed with methanol–water. A number of purification techniques were attempted, the most successful being size separation on a gel permeation (Saphadex G10) column, which eliminates contaminating inorganic salts and results in elution of several distinct fractions. The isolated fractions were characterized by absorption spectroscopy and magnetic susceptibility. Absorbance spectra were obtained on a Cary 14 spectrophotometer using matched quartz cells. Magnetic susceptibility measurements on solid samples were obtained on a Gouy balance and were confirmed in solution by the Evans method, on a Varian A-60A NMR instrument.

Results and Discussion

The complexes prepared herein were made in two ways, with somewhat differing results. Free PTS, prepared in low yield by the method of Fallab[5] and found to be spectrally pure, was reacted with ferrous ammonium sulfate in the presence of air to give a product with a major band at 634 nm with a shoulder at ca. 670 nm. When preparation was by a template condensation however (using ferrous ammonium sulfate as the metal template), a dark green solid resulted with a major peak at 670 nm and a small shoulder at 634 nm. As this was felt to be a possible mixture of products, a number of purification techniques were attempted with the crude material, with little success (using the 632-nm band as a measure of purity).

Finally, size separation on a gel permeation column (Sephadex G10) resulted in the elution of several distinct fractions. The first, dark green, component showed minimal absorption at ca. 630 nm, with a strong peak at 670 nm. This green component was insensitive to oxygen under a pressure of 1 atm at 25 °C. The second major band was dark blue with strong absorption at 632 nm and minimal absorption at 670 nm. The third band showed no 670-nm absorption but was affected by some residual salt contamination. The yellow-green column tailings, which contained most of the inorganic salts and low molecular weight contaminants, were discarded.

The second band could be refractionated into a major blue component and a small green band, with the resulting blue component having a spectrum essentially identical to that obtained by Weber and Busch.[4] A magnetic moment, determined by the Evans method (NMR shift), was ca. 1.90 μ_B, in good agreement with 1.80 μ_B expected for low-spin ferric iron.

Template condensation with ferric sulfate, fractioned in the same manner, also gave a mixture of 670- and 630-nm bands. On separation, the blue component showed a spectrum identical on the Cary 14 with the blue band obtained from the ferrous preparation. This blue complex thus represents a simple low-spin ferric chelate with no complexed dioxygen.

The product of the Fallab preparation after similar fractionation also gave a blue band that on crystallization gave the same magnetic moment (1.92 μ_B) as the Busch preparation, with an identical spectrum.

A referee has pointed out that the solution composition of Fe^{II}PTS is pH sensitive. This sensitivity as we observed is consistent with μ-oxodimerization (i.e., slight shift in λ_{max} 630 nm to give a component which travels more rapidly on Sephadex G10). We have observed no case where changing the pH leads to a net change in uptake of oxygen, as measured by an oxygen-sensitive electrode.

As a secondary characterization, complexes prepared by all three methods (ferric condensation, ferrous condensation, and free ligand reaction) were reacted with imidazole. All three complexes gave identical results, forming a complex with λ_{max} 628 and 664 nm, ϵ_{664} 5.6×10^5, in excellent agreement with the results of Weber and Busch.[4] Reaction of the complexes with dithionite resulted in an immediate loss of the 634-nm band and an increase in absorbance at 670 nm. On subsequent exposure to oxygen, the 634-nm band was recovered, but recovery was not quantitative. It appears that excess dithionite may result in some reduction of the ligand, in qualitative agreement with the work of Fallab.

In a final experiment the blue component was heated to 70 °C, under an inert atmosphere. On subsequent cooling, only a small increase in the 670-nm band was observed, unlike Fallab's results. On oxygenation, the 670-nm band disappeared, but quantitative recovery of the 630-nm band was not observed. These results may be due to simple reduction of Fe(III) (with ligand oxidation). Alternative exposure to high vacuum, over two freeze–thaw cycles, did *not* result in spectral changes. We believe these results are more consistent with high-temperature reduction than an oxygenation–deoxygenation cycle.

In summary, the available data support the contention of Weber and Busch[4,7] that $\mathrm{Fe^{II}PTS}$ is irreversibly oxidized by air in aqueous solution and that a dioxygen complex is not formed. This conclusion is consistent with all other known examples of model iron–dioxygen complexes which are stabilized in nonaqueous solvents at low temperatures; for these complexes dimerization must be excluded for reversibility.[2]

Registry No. $\mathrm{Fe^{II}PTS}$, 59784-64-4; dioxygen, 7782-44-7; $\mathrm{Fe^{III}PTS}$, 62521-18-0.

References and Notes

(1) (a) Supported by Grant No. A-259 from the Robert A. Welch Foundation. (b) Texas A&M University Health Fellow, 1974–1976.

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(7) Weber and Busch[4] also noted possible dioxygen adduct formation in the solid state. The present results deal only with aqueous solution and do not preclude interaction in the crystal (or in any other medium).

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Magnetic Exchange Interaction in the Chloro-Bridged Copper(II) Complex *N,N,N′,N′*-Tetramethylethylenediammonium Hexachlorodicuprate(II)

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Received October 23, 1976 AIC60775Q

Within recent years, extensive studies of the structural and magnetic properties of dimeric and polymeric copper(II) complexes have provided insight into the features responsible for magnetic exchange interactions. For the most thoroughly studied case, that of hydroxy-bridged copper(II) dimers, it is now possible to accurately predict both the sign and magnitude of the exchange integral from knowledge of the structural parameters of the bridge.[2]

Unfortunately, similar correlations have not proven possible for the analogous case of chloride-bridged copper(II) dimers. This arises largely from the paucity of structural and magnetic data on such species but also because of the variety of structural types adopted by those materials which have been characterized. We have engaged in a program designed to synthesize and characterize chloride-bridged copper(II) dimers in order to determine if correlations between structural and magnetic properties are possible. We report here on the synthesis and characterization of tetramethylethylenediammonium hexachlorodicuprate(II) and compare the properties of this material with the structurally characterized compound potassium trichlorocuprate, $\mathrm{KCuCl_3}$.[3]

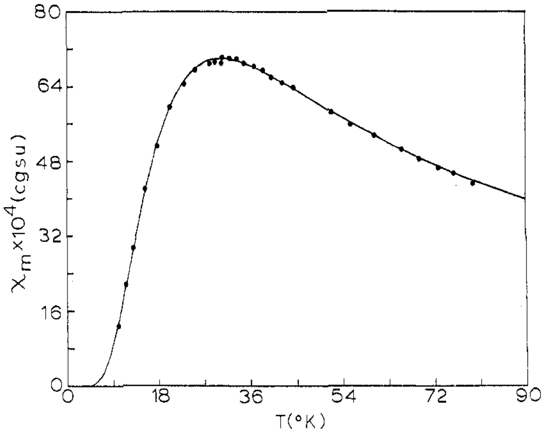

Figure 1. Magnetic susceptibility as a function of temperature in the range 8–80 K. The solid line was generated by the Van Vleck equation for exchange-coupled $S = {}^1/_2$ ions with $2J = -33.7\ \mathrm{cm^{-1}}$ and $g = 2.12$.

Experimental Section

Preparation of Tetramethylethylenediammonium Hexachlorodicuprate. Tetramethylethylenediamine dihydrochloride (3.05 g, 0.016 mol) (prepared by the reaction of tetramethylethylenediamine and concentrated hydrochloric acid) and 6.9 g (0.040 mol) of cupric chloride dihydrate were dissolved in 30 mL of 3 M HCl. The solution was heated to boiling and evaporated at the boiling point until the volume was approximately 15 mL. The solution was cooled, and the bronze-colored needle-shaped crystals which formed were filtered, washed briefly with cold 3 M HCl, and vacuum-dried; yield 0.65 g (9%). Anal. Calcd for $\mathrm{[(CH_3)_2NHCH_2CH_2NH(CH_3)_2]Cu_2Cl_6}$: C, 15.73; H, 3.96; Cu, 27.75. Found: C, 15.77; H, 3.96; Cu, 27.80. Further crops of product could be obtained by reduction in the solution volume. Attempted precipitation of the product by addition of acetone led exclusively to the monomeric complex $\mathrm{[(CH_3)_2NHCH_2CH_2NH(CH_3)_2]CuCl_4}$.[4]

Physical Measurements. Magnetic susceptibility measurements were made on powdered samples using a Foner-type vibrating-sample magnetometer[5] operating at 10 kG. Nickel metal was used as a susceptibility standard. Measurements were made in the temperature range 8–80 K. Temperatures were measured using a calibrated Ga–As diode.[6] Susceptibilities were corrected for the diamagnetism of the substitutent atoms using Pascal's constants[7] and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/copper atom).

EPR spectra were obtained at room temperature using a Varian E-3 spectrometer. Electronic spectra were obtained at room temperature in the region 4000–30 000 $\mathrm{cm^{-1}}$ using the mull transmittance technique on a Cary 17 spectrometer.

Analyses were by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Results

The magnetic susceptibility data for $\mathrm{[tmenH_2]Cu_2Cl_6}$ in the temperature range 8–80 K are shown in Figure 1. By assuming the exchange Hamiltonian $H = -2J\hat{S}_1 \cdot \hat{S}_2$, for the pair of interacting spins, the familiar singlet–triplet susceptibility equation

$$\chi_m = \frac{Ng^2\beta^2}{3kT}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} + N\alpha$$

results. This equation, which is written per copper ion, may be fitted to the experimental data yielding a value for the exchange energy $2J$ of $-33.7\ \mathrm{cm^{-1}}$ with $g = 2.12$.

The electronic absorption spectrum of a sample of the compound mulled in mineral oil exhibited bands at 11 400