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Supplementary Material Available: A listing of atomic positional and thermal parameters, Table I (1 page). Ordering information is given on any current masthead page.

Copper-Dioxygen Chemistry. Synthesis and Properties of a Dicopper(II)-Peroxide Complex

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In this communication I present initial results on the synthesis and properties of a peroxodicopper(II) complex prepared from the reaction of dioxygen with a copper(I) complex. Small molecules such as ethylene and carbon monoxide displace dioxygen to yield the corresponding Cu(I) complex. Dioxygen adducts of this type have been proposed in copper autoxidation reactions¹ and in the reactions of copper oxidases and dioxygen-binding proteins.² However, there are few stable, well-characterized examples of copper complexes that bind dioxygen reversibly.³⁻⁶ Our approach involves reaction of dioxygen with a monomeric cuprous complex having a ligand that is easily displaced without oxidation. This approach has been used previously to prepare a Cu(II)-superoxide complex.⁷

The synthesis of the dioxygen adduct requires several steps. The Cu(I)-ethylene complex $[\text{Cu}(\text{TEEN})(\text{C}_2\text{H}_4)]\text{ClO}_4$ (I) (TEEN = *N,N,N',N'*-tetraethylethylenediamine) was prepared from $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and copper dust in methanol, as described elsewhere.^{8,9} The methanol solution of I was stirred open in a drybox under a nitrogen flush for approximately 10 min and then cooled in dry ice for 1 h. Dioxygen was then flushed vigorously through the flask for approximately 30 s. The flask was maintained at -78°C for 1 h and then at -40°C overnight. A deep blue color developed. The reaction mixture was filtered under nitrogen pressure at -78°C , to remove unreacted I. Vapor

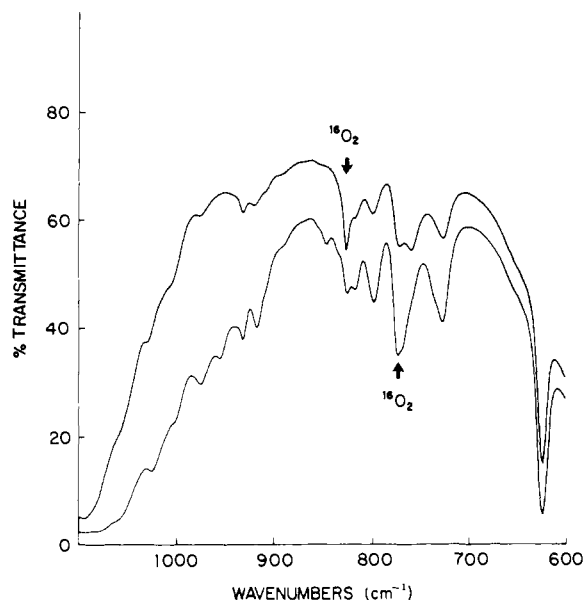


Figure 1. Infrared spectra of $[\text{Cu}_2(\text{TEEN})_2(\text{H}_2\text{O})(^{16}\text{O}_2)](\text{ClO}_4)_2$ (top) and $[\text{Cu}_2(\text{TEEN})_2(\text{H}_2\text{O})(^{18}\text{O}_2)](\text{ClO}_4)_2$ (bottom).

diffusion with dioxygen-saturated diethyl ether at -40°C yielded a blue powder, which can be handled at room temperature without any apparent decomposition. Methanol solutions decompose at room temperature to a variety of products (vide infra).

Analytical and spectroscopic data support the formulation $[\text{Cu}_2(\text{TEEN})_2(\text{H}_2\text{O})(\text{O}_2)](\text{ClO}_4)_2$, a Cu(II) dimer with bridging oxygen and water molecules. Elemental analyses are consistent with this formulation.¹⁰ The material is EPR silent at -160°C , a result that is consistent with the formation of a copper dimer. The visible absorption spectrum consists of a broad band centered at 630 nm, which can be assigned as a d-d band on the basis of its intensity and position. This portion of the spectrum is similar to that of $[\text{Cu}_2(\text{TEEN})_2(\text{OH})_2](\text{ClO}_4)_2$ (III) a Cu(II) dimer with bridging hydroxyl groups.¹¹ Infrared data are particularly useful in the characterization of II. A medium-intensity band occurs at 825 cm^{-1} in the spectrum of II (Figure 1); this band shifts to 770 cm^{-1} when the complex is prepared with $^{18}\text{O}_2$. The spectra are otherwise identical in the $4000\text{--}600\text{ cm}^{-1}$ range. A dioxygen stretch at 825 cm^{-1} is characteristic of peroxide complexes.^{3,12} In particular, (μ -peroxo)dicobalt(III) complexes have oxygen stretching frequencies in this region;¹³ a similar shift is observed with use of $^{18}\text{O}_2$. Karlin et al. recently reported an O-O stretching frequency of 803 cm^{-1} for a dicopper(II)-peroxide complex.^{3a} Finally, bands attributable to a water molecule are observed at 3570 , 1670 , and 1620 cm^{-1} . These bands shift to lower energy when II is prepared in methanol- d_4 in the presence of D_2O . Water molecules, but not hydroxide ions, have stretches in the 1600 cm^{-1} region, which correspond to HOH deformation modes.¹⁴ The starting ethylene complex, the Cu(II) dimer III, and other TEEN complexes without coordinated water molecules⁸ do not have bands in this region. The infrared data establish the presence of a peroxide moiety and a water molecule in II. All of the analytical and spectroscopic data support the formulation of II as a Cu(II) dimer with a bridging water molecule and peroxide group; how-

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(9) (a) The preparation of the starting Cu(I)-ethylene complex is identical with that for ethylene(2,2'-dipyridylamine)copper(I) perchlorate.^{9b} (b) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813-2819.

(10) Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{11}$: C, 33.33; H, 6.99; N, 7.77. Found: C, 33.69; H, 6.86; N, 7.57.

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ever, assignment of overall geometry requires further characterization. Dimeric structures are characteristic of Cu(II)-TEEN complexes reported here and elsewhere.¹⁵

The reaction chemistry of II is consistent with the formation of a dioxygen complex. Addition and removal of dioxygen cause the metal ion to shuttle between the +1 and +2 oxidation states. Adding dioxygen to methanol solutions of I produces II; this reaction is reversed by bubbling ethylene through the solution to produce I in nearly quantitative yield. Similarly, bubbling carbon monoxide through solutions of II yields the Cu(I)-carbonyl complex [Cu(TEEN)(CO)ClO₄].⁸

The decomposition reactions of II are characteristic of a peroxide complex. Stirring solutions of II under nitrogen at room temperature or low temperature yields the hydroxy-bridged copper(II) dimer III. The complex produced in this reaction has been identified by analytical, spectroscopic, and X-ray diffraction techniques.¹⁶ This complex also precipitates from methanol solutions of II when a dioxygen atmosphere is not maintained over the solution and when dioxygen is added to I in the presence of excess ethylene. III may result from formation and disproportionation of hydrogen peroxide, a reaction characteristic of copper-dioxygen chemistry.¹³

The reaction chemistry of II under an atmosphere of dioxygen at room temperature is different from that under nitrogen. We have isolated and characterized by analytical, spectroscopic, and X-ray diffraction techniques a second bis(μ -hydroxy)dioxygen(II) complex in which one of the eight ethyl groups of the two TEEN ligands has been hydroxylated, [Cu₂(TEEN)(TEEN+OH)(OH)₂]₂X₂ (IV) (X = ClO₄, BF₄).¹⁷ The copper coordination spheres in this dimeric product are very similar to those in III with the addition of a weakly coordinated hydroxyl group of the TEEN+OH ligand to one copper ion in the dimer. The complex with X = ClO₄ shows OH stretches at 3595 and 3565 cm⁻¹ corresponding to the ethylhydroxyl and bridging hydroxyl groups. Hydroxylation of alkyl groups is not usually observed in the reactions of Cu(I) complexes with molecular oxygen, although hydroxylation of aromatic substrates is well-established.^{13,18} The complex IV is obtained at least in part because the copper ions hold both the reduced oxygen moiety and the alkyl group in the proper orientation for reaction. Also, the oxygen atmosphere is critical. Experiments are in progress to determine the source of the incorporated oxygen atom. Oxidation of the ethyl groups of this ligand has been suggested in reactions of other Cu(I)-TEEN complexes with dioxygen.¹⁵

Three important properties of copper-dioxygen coordination chemistry emerge from this initial study. First, stable copper(II) peroxide complexes can be prepared with the proper choice of ligands and reaction conditions. Choice of the other ligands in the copper coordination sphere is critical. Use of less sterically hindered ligands does not yield stable dioxygen complexes; rather, only Cu(II) products and fully reduced oxygen species (water, hydroxide, oxide) are obtained.¹³ Second, bound oxygen can be displaced. All copper proteins for which a μ -peroxodicopper(II) active-site structure has been proposed show reversible dioxygen binding.² Finally, the isolation of IV demonstrates that Cu(II)-peroxide species are potent oxidizing agents, provided the reduced oxygen species and substrate are held in the proper orientation. However, the chemistry of these dioxygen complexes is dominated by the disproportionation reaction.

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(16) (a) Anal. Calcd for C₂₀H₃₀Cl₂Cu₂N₄O₁₀: C, 34.09; H, 7.15; N, 7.95. Found: C, 34.13; H, 7.34; N, 7.87. (b) Crystallization from dichloromethane/petroleum ether yielded the β -form of the complex.^{11a}

(17) (a) Thompson, J. S.; Tulip, T. H., manuscript in preparation. (b) The blue BF₄ salt crystallizes in the monoclinic space group P2₁/c with a unit cell of dimensions $a = 7.613$ (2) Å, $b = 15.416$ (3) Å, $c = 14.129$ (2) Å, and $\beta = 103.05$ (1)°. Least-squares refinement of 198 variables led to $R = 0.039$ and $R_w = 0.038$ for 2267 reflections having $F_o^2 > 3\sigma(F_o^2)$.

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Phosphorus-Oxygen Bond Order in Adenosine 5'-O-Phosphorothioate Dianion

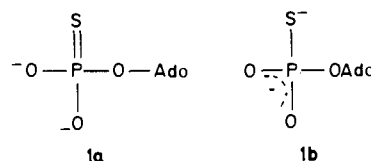
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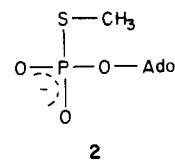
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Structural formulas for nucleoside phosphorothioate anions are generally written with P=S double bonds, P-O single bonds, and negative charges localized on oxygens.^{1a-c} These assignments originated with the analysis of the crystal and molecular structure of the triethylammonium salt of *endo*-uridine-2',3'-phosphorothioate.² In this paper we report new data bearing on charge distribution and P-O bond order of adenosine 5'-phosphorothioate (AMPS) dianion in water.

The structure of AMPS may be represented as **1a**, with P-O



bond orders of 1 and charges localized on oxygen, or **1b**, with P-O bond orders of 1.5, one charge localized on S and the second delocalized between two oxygens. Both structural formulas imply little or no involvement of S in charge delocalization. The data in Table I support **1b** as the more accurate representation of charge distribution and bonding for AMPS dianion in water. An effect of ¹⁸O substituted for ¹⁶O in phosphates is to shift the ³¹P NMR signal upfield by an amount directly proportional to the P-O bond order.^{3a-c} This upfield shift is the ¹⁸O-isotope shift, $\Delta\delta_p$. The values of $\Delta\delta_p$ given in Table I for [α -¹⁸O]AMPS, [α -¹⁸O₂]AMPS, S-methyl-[\alpha-¹⁸O]AMPS, and S-methyl-[\alpha-¹⁸O₂]AMPS are the same for all species.⁴ Since the P-O bond orders in S-methyl-AMPS (**2**) are 1.5 and the ¹⁸O-isotope shifts for S-methyl-[\alpha-



] α -¹⁸O]AMPS are the same as those for [α -¹⁸O]AMPS, the P-O bond orders in AMPS must also be 1.5. The $\Delta\delta_p$ values in Table

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