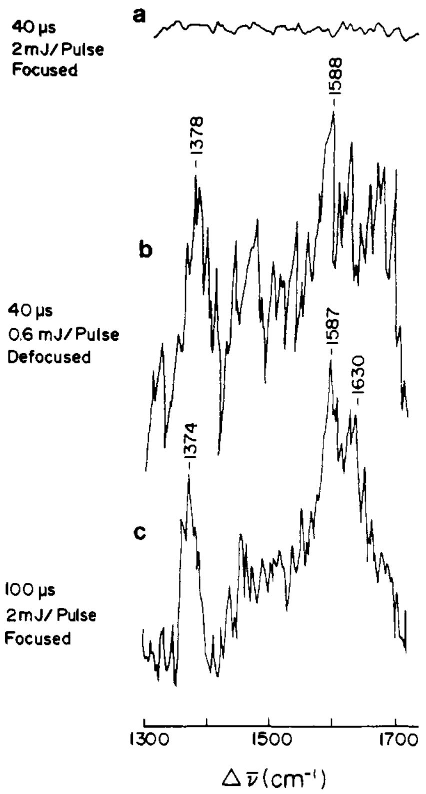

Figure 2. Estimates of the Raman properties of intermediate species formed during the reoxidation of cytochrome oxidase by O_2 at 40 (a,b) and 100 μs (c) after initiation. For spectra (a) and (c) data taken under the high power density conditions of Figure 1 were used. The scaled spectrum of the reduced photodissociated enzyme (the 10-ns spectrum in Figure 1) was subtracted from the experimental spectra so that cancellation of the reduced oxidation-state marker (1355 cm^{-1}) occurred. In the 40-μs spectrum of (b), the energy of the photolysis pulse was 2.5 mJ, but the probe energy was decreased to 0.6 mJ. A loose line focus at the sample plus a beam mask were used to decrease probe power density further. We estimate that the probe power density used to record spectrum (b) was 30-fold less than in (a), or 1-2 photons per molecule of enzyme in the illuminated volume. A total of 1320 experiments were averaged in (b); the other experimental conditions were the same as those in Figure 1.

intermediate(s) are, in fact, photolabile is supplied by the 40-μs difference spectrum (Figure 2b) obtained by using a low-intensity, defocused probe pulse.[11] Under these conditions, the principal intermediate at 40 μs is shown to have an oxidation-state marker ($\bar{\nu}_4$) at 1378 cm^{-1} and spin-state marker ($\bar{\nu}_2$)[3] at 1588 cm^{-1}. These frequencies are similar to those reported for oxymyoglobin and oxyhemoglobin. This observation, together with the photolability of the 40-μs transient, provides the best support to date for the suggestion that the reoxidation of cytochrome oxidase involves an oxycytochrome a_3 species at early times in the reaction.

The difference spectrum in Figure 2c (100-μs spectrum minus 10-ns photolysis product spectrum) was obtained under high light intensity conditions and frequencies characteristic of oxidized, low- or intermediate-spin heme a species ($\bar{\nu}_4$ 1374 cm^{-1}, $\bar{\nu}_2$ 1587 cm^{-1}) are apparent. Thus nonphotolabile intermediates are formed within 100 μs of initiation of reoxidation. Whether these species are actually ferric heme a intermediates or low-spin ferrous heme a complexes with strong π-acid ligand remains to be determined.

The results above establish a number of points regarding the oxidation of cytochrome oxidase by O_2. First, time-resolved resonance Raman, which offers greater molecular insight than optical spectroscopy and does not require paramagnetism in order to visualize intermediates, can be profitably applied to the study of the reaction. Second, the initial intermediate in the reaction mechanism is photolabile and indicates the formation of oxycytochrome a_3 as the precursor of dioxygen reduction. This conclusion may seem to be at odds with low-temperature work reported by Chance et al.[8] who described their compound A as "non photolabile", but their observation most likely results from the fact that oxyheme species have much lower photolysis quantum yields than carbon monoxy heme species. Whether a peroxy-type intermediate[8,12] will be photolabile remains to be established. Third, at reasonably early times in the reaction (~100 μs) heme iron oxidation apparently occurs and the photolysis quantum yield decreases significantly or goes to zero. Fourth, we note the apparent disappearance at longer times (>200 μs) of the 1666/1676-cm^{-1} cytochrome a_3 formyl C=O stretch. This mode is always observed in stable forms of the enzyme,[3] and its absence may suggest unusual reactivity of the formyl group in the turnover dynamics of the enzyme. The structures of these species, as well as those that occur in the mixed valence oxidase/O_2 reaction,[13] are under investigation.

Acknowledgment. We are most grateful to EG&G/Princeton Applied Research Corporation for the loan of the diode array detector OMA system and to R. T. Ingle for his efforts in supplying the beef heart oxidase used in these experiments. Research support from NIH (GM25480 to G.T.B., GM21337 to G.P., and AM33679 to W.H.W.), the Robert A. Welch Foundation (F733 to W.H.W.), and the University of Texas Research Institute for partial sabbatical support (G.T.B.) is acknowledged.

Registry No. O_2, 7782-44-7; cytochrome oxidase, 9001-16-5.

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[11] Control experiments in which the same illumination geometry as that used for Figure 2b was used to study oxymyoglobin showed that the oxy species, rather than the photodissociation product, predominated in the spectrum. The poor signal-to-noise ratio in Figure 2b results from the suboptimal illumination conditions necessary to record the spectrum.

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Copper(II), a Chemical Janus: Two Different (Oxalato)(bipyridyl)copper(II) Complexes in One Single Crystal. Structure and Magnetic Properties

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In our attempts to tune the exchange interaction between two copper(II) ions through multiatomic bridges[1-4] we obtained single crystals of $[Cu_2(bpy)_2(H_2O)_2(C_2O_4)][(Cu(bpy)(C_2O_4)](NO_3)_2$ (**1**) (bpy = 2,2'-bipyridyl) where both mononuclear and binuclear copper(II) complexes are present in the same cell. This is a rare case where two molecular complexes of copper(II) bound to the same ligands coexist in the same compound with different stoi-

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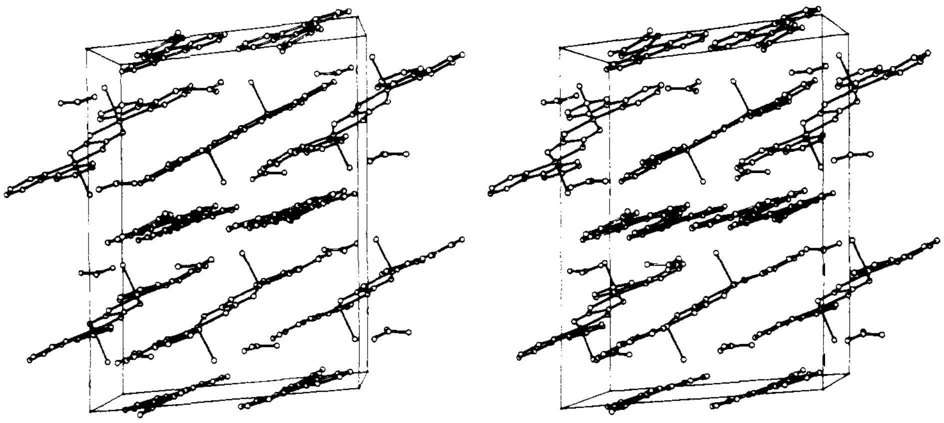

Figure 1. Stereoscopic view down the *b* axis (*a* axis vertical) of the molecular packing in $[Cu_2(H_2O)_2(bpy)_2(C_2O_4)][Cu(bpy)(C_2O_4)](NO_3)_2$. The binuclear cation is presented with black bounds. The nitrate anion is shown in its more frequent (60%) configuration.

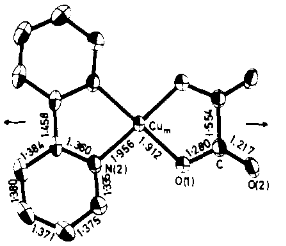

Figure 2. View of the neutral mononuclear complex $[Cu(bpy)(C_2O_4)]$ (50%) probability thermal ellipsoids).

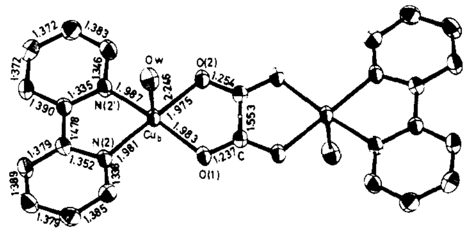

Figure 3. View of the binuclear cationic complex $[Cu_2(H_2O)_2(bpy)_2(C_2O_4)]^{2+}$ (50% probability thermal ellipsoids).

chiometries. For copper(II) only chloro complexes were reported with such a property.[5] A blue crystalline precipitate was obtained from reaction of a solution of 0.01 mol of $[Cu^{II}(bpy)](NO_3)_2$ with a solution of 0.005 mol of $Li_2C_2O_4$, in a minimum amount of water. Slow evaporation of hot aqueous solutions yielded dark-blue crystals of **1** as the main product.

The compound crystallizes in the monoclinic system, space group $C2/c$, $a = 21.739$ (2) Å, $b = 10.458$ (1) Å, $c = 16.023$ (2) Å, $\beta = 95.69$ (1)°. The crystal structure was determined from Patterson and Fourier analysis and was refined by full-matrix least-squares techniques: $R = 0.029$, $R_w = 0.051$, 3290 reflections with $I > 3\sigma(I)$, 295 variables. A stereoview of the cell is given in Figure 1. The mononuclear neutral entities (Figure 2) have the crystallographically imposed $C2$ symmetry; the copper atom Cu_m is bound to two oxalate oxygen atoms (Cu_m–O = 1.912 (2) Å) and two bipyridyl nitrogen atoms (Cu_m–N = 1.956 (2) Å) forming a 4-fold environment slightly deviating from planarity. The binuclear cationic entities are centrosymmetrical (Figure 3). The two $(bpy)Cu(H_2O)$ moieties are bridged by an oxalato group. The copper atoms Cu_b have a square-pyramidal environment, the equatorial sites being occupied by two oxalate oxygen atoms (Cu_b–O = 1.983 (2) Å) and two bipyridyl nitrogen atoms (Cu_b–N = 1.981 (2) and 1.987 (2) Å) and the summit by a water oxygen atom (Cu–O_w = 2.246 (2) Å).

The displacement of Cu_b above the mean plane of the base toward the water molecule is 0.1548 (2) Å. The intramolecular $Cu_b \cdots Cu_b$ distance is 5.154 (1) Å. The NO_3^- counterions were found to be slightly disordered with one oxygen atom spread over two positions (40–60%). The shortest intermolecular distance occurs between a Cu_b and a Cu_m atom (6.51 Å).

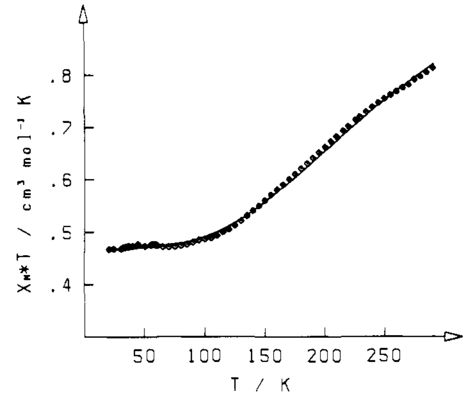

Figure 4. Thermal variation of the susceptibility under the form $\chi_M T$ (molar susceptibility times T) vs. T, in the range 20–300 K.

The thermal variation of the magnetic susceptibility χ_M is shown in Figure 4: $\chi_M T$ (T being the temperature) decreases upon cooling and exhibits a plateau when $T < 80$ K. The decrease of $\chi_M T$ can be associated with a strong antiferromagnetic interactions within the binuclear unit while the plateau corresponds to the Curie law expected for the mononuclear complex with no detectable interaction between the two kinds of entities in this temperature range. The experimental data closely follow the relation

$$\chi_M = \frac{2N_A\mu_B{}^2g_b{}^2}{kT}\,\frac{1}{3 + \exp(-J/(kT))} + \frac{N_A\mu_B{}^2g_m{}^2}{4kT} + N\alpha \qquad (1)$$

which is the sum of the Bleaney–Bowers equation for a coupled binuclear copper(II) species, the Curie law of an isolated copper(II) complex, and the temperature-independent paramagnetism, $N\alpha$. J is the singlet–triplet gap and g_b the mean g factor in the binuclear complex; g_m is the mean g factor in the mononuclear complex. The fit for $J = -385.9$ cm^{-1}, $g_b = 2.003$, and $g_m = 2.217$ is shown in Figure 4. The J value is large as in preceding planar μ-oxalato systems.[1-3]

The X-band EPR spectrum at 290 and 4 K looks like that of an axial doublet ($g_\parallel = 2.21$ (1), $g_\perp = 2.06$ (1)). At 290 K a very weak half-field forbidden transition, $\Delta M_S = 2$, clearly points out the presence of a populated triplet. We are now investigating the influence of counteranions on the structures and magnetic properties of the system copper (II)–oxalato–bipyridyl. Our preliminary results as well as recent ones[6] and the example presented here illustrate once more the rich coordination chemistry of

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copper(II), a modern chemical Janus.

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 reactions[1] 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 [Cu(TEEN)(C_2H_4)]ClO_4 (I) (TEEN = *N,N,N',N'*-tetraethylethylenediamine) was prepared from $Cu(ClO_4)_2 \cdot 6H_2O$ 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 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).

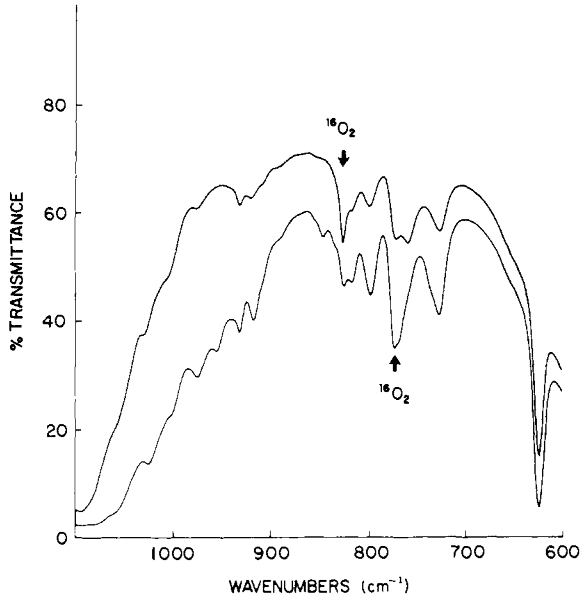

Figure 1. Infrared spectra of $[Cu_2(TEEN)_2(H_2O)(^{16}O_2)](ClO_4)_2$ (top) and $[Cu_2(TEEN)_2(H_2O)(^{18}O_2)](ClO_4)_2$ (bottom).

Analytical and spectroscopic data support the formulation $[Cu_2(TEEN)_2(H_2O)(O_2)](ClO_4)_2$, 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 $[Cu_2(TEEN)_2(OH)_2](ClO_4)_2$ (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 $^{18}O_2$. The spectra are otherwise identical in the 4000-600-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 $^{18}O_2$. 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 molecules[8] 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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