8.3 Hz, CH_2O), 131.63 (d, J_{CP} = 3.2 Hz, *p* C), 133.78 (d, J_{CP} = 163.8 Hz, ipso C), 128.00 (d, J_{CP} = 15.1 Hz, *o* or *m* C) 129.90 (d, J_{CP} = 11.0 Hz, *o* or *m* C); MS, *m/e* (rel intensity) 243.0, M^+ (3.8), 156.9 (6.6), 69.0 (100.0), 56.1 (26.9).

Reaction of 15 with PhSSPh. Bis(dimethylamino)phenylphosphine (1.08 g, 5.51 mmol) and 2-(methylamino)ethanol (0.48 g, 6.4 mmol) were dissolved in dry *p*-xylene (30 mL) under argon. The solution was heated to 120-130 °C for 3 h and then allowed to cool. The *p*-xylene was removed, and the residue was Kugelrohr distilled under high vacuum. The desired 2-phenyl-1,3,2-oxazaphospholidine (**15**) was found in two fractions along with its polymer (110-120 °C, 120-140 °C, 0.2 mmHg, lit. 64-66, 0.03 mmHg[29]): yield 0.530 g, 2.93 mmol (53% determined by ^{31}P NMR, 32.2 MHz, $CDCl_3$) resonance of monomer at 143.1 ppm.[30]

Phenyl disulfide (0.20 g, 0.92 mmol) was then added to one of the fractions (0.256 g, 1.41 mmol) and dissolved in ~0.5 mL of $CDCl_3$. The ^{31}P NMR spectrum of this solution, taken within 15 min, showed that the peaks for the monomer *and* polymer had greatly diminished, and a new peak at +43.59 ppm had appeared.

Acknowledgment. The mass spectrometer used in these studies was purchased by funds contained in N.S.F. Grants CHE-8100424 and CHE-8310031. Support of this research by Grant CHE 8311090 and previous grants from the National Science Foundation and Grant CA11045 from the National Cancer Institute of the Public Health Service are gratefully acknowledged.

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Communications to the Editor

Dioxygen-Copper Reactivity: EXAFS Studies of a Peroxo-Dicopper(II) Complex

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As part of our efforts in establishing the relevant coordination chemistry of copper proteins[2,3] which bind and/or activate dioxygen,[4] we previously reported the preparation and preliminary characterization of a dioxygen-copper complex, III[5] (Figure 1). This was formed in the reaction of dioxygen (Cu:O_2 = 2:1) with the phenoxo-bridged dicopper(I) compound II in dichloromethane at -80 °C. Complex III exhibits a band at 803 cm^{-1} in a resonance Raman experiment which has been assigned to the O-O stretch of a bound peroxide moiety. The binding of O_2 to II is quasi-reversible[4,6] [i.e., $Cu(I)_2L + O_2 \rightleftharpoons Cu(II)_2L(O_2^{2-})$], and complex III therefore serves as a prototype of the proposed dioxygen-copper intermediates in proteins including the O_2 carrier hemocyanin[7] and the monooxygenases tyrosinase[7,8] and dopamine-β-hydroxylase.[8,9]

A knowledge of the structure of III and other related dioxygen adducts[10] would aid considerably our understanding of the factors controlling functional variations among the copper enzyme systems. Since the temperature sensitivity ($T < -60$ °C) of these dioxygen adducts has thus far precluded crystallization, structural characterization must rely on low-temperature spectroscopic methods. Here, we report preliminary findings of extended X-ray absorption fine structure (EXAFS) studies on the dioxygen-copper complex III. As an aid to the interpretation, we have also examined the related X-ray crystallographically characterized precursor dicopper(I) compound II and the phenoxo and hydroxo doubly bridged complex I (Figure I). We find that the Cu⋯Cu distance in III is 3.31 ± 0.04 Å, which sets limits on the possible dioxygen binding modes in this system.

Table I. Parameters Used To Simulate the Theoretical EXAFS Fits Shown in the Figure[a]

shell	R_{EXAFS}, Å	R_{av}(cryst), Å	$2\sigma^2$, Å^2
	Compound I		
2 O	1.96	1.962	0.009
2 N	2.03	2.023	0.007
1 N	2.27	2.204	0.013
4 C	2.91		0.007
Cu-Cu	3.08	3.082	0.006
3 C	3.32 (6)		0.011
	Compound II		
2 N(py)	1.97	1.969	0.004
1 O(phen)	2.07 (5)	2.031	0.006
1 N(amino)	2.25 (8)	2.171	0.035
4 C	2.90		0.013
3 C	3.3 (15)		0.06
	Compound III (Peroxo Complex)		
1 O	1.93		0.006
3 N	2.08 (4)		0.012
4 C	2.99		0.011
Cu-Cu	3.31		0.015

[a] Unless otherwise indicated (by parentheses), estimated errors are ± 0.03 Å for inner-shell and ± 0.04 Å for outer-shell distances.

EXAFS data were collected on stations 7.1 and 9.2 at the SRS, S.E.R.C. Daresbury Laboratory, operating at 2.0 GeV and maximum currents of 300 mA. For the peroxo complex, III, data were collected as the fluorescence excitation spectrum at 10 K (frozen glass). Compounds I and II were measured as solids in transmission mode at 77 K. Raw data were background subtracted and analyzed with the program EXCURVE[11] by methods previously described.[12] The Fourier transforms of the raw data for all the

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complexes show two intense peaks around 2.0 and 3.0 Å together with weaker outer-shell peaks.[13-15] The first two peaks in the transform were Fourier filtered and back-transformed in k-space. The resultant filtered EXAFS was analyzed to produce the data given in Table I. To investigate further the contribution due to the Cu···Cu interaction the second peak in the transforms was isolated and back-transformed (Figure 1 and Table I).

For compounds I and II, the inner-shell distances derived from EXAFS analysis are in good agreement with those from X-ray crystallography.[5,16,17] For the peroxo complex, the best fit for the EXAFS associated with the 2.0-Å peak in the Fourier transform requires a minimum of two shells of low Z (nitrogen or oxygen) scatterers, comprising one donor atom at 1.93 (3) and three donor atoms at 2.08 (4) Å. The data is most consistent with the assignment of the short distance to an oxygen donor atom, probably an anionic phenoxide or peroxo ligand.

The second-shell-filtered EXAFS for compound I (figure 1a) shows a pattern of increasing amplitude to higher k values, which is characteristic of the presence of a heavy-atom scatterer.[14c,15b,23,24] The data can be well fit to a copper wave at 3.08 (4) Å, in close agreement with crystallography,[16] along with additional carbon shells (Table I). In contrast, the second-shell filtered EXAFS for II (Figure 1b), in which the Cu···Cu distance is long (3.6–3.7 Å[5,18]), shows no contribution from a copper wave and can be fit satisfactorily by using two shells of carbon atoms in the range of back-transformation (2.5–3.5 Å).

For the dioxygen complex (peroxo) III (Figure 1c), the presence of a copper wave is again evident from the pattern of increasing EXAFS amplitude, and the data can be analyzed satisfactorily with Cu···Cu = 3.31 (4) Å together with associated contributions from carbon atoms (Table I). In a further analysis, a plot of the least-squares fitting index[19] vs. Cu···Cu distance (Figure 1e) shows a deep minimum at 3.31 Å, and another at 3.72 Å, but the correspondence between experiment and theory for this latter minimum (Figure 1d) is clearly unsatisfactory.

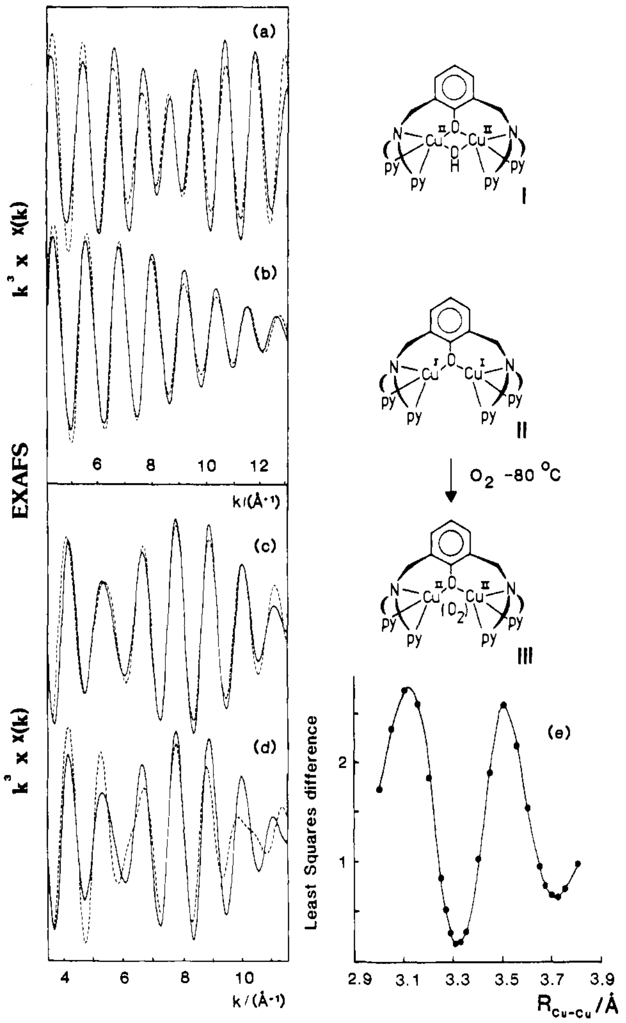

Figure 1. Experimental vs. calculated second-shell-filtered EXAFS for compounds I–III: (a) compound I; (b) compound II; (c) compound III (peroxo complex) with the Cu–Cu distance corresponding to the deep minimum at 3.31 Å; (d) same as c but with the Cu–Cu distance corresponding to the shallow minimum at 3.72 Å; (e) least-squares-fit index (defined as the sum of the squares of the k^3 weighted experimental EXAFS minus that of the calculated EXAFS) plotted as a function of the Cu–Cu distance.

The likely modes of binding of a peroxo ligand to the dicopper(II) center in III are a cis or trans μ-1,2-bridge, a μ-1,1-bridge, or terminal coordination. Existing structural evidence for phenoxide and X (X = OH^-,[16] OMe^-[20]) doubly bridged complexes in this particular ligand system and others[21] indicates that a μ-1,1-bridging O atom donor ligand would possess a Cu···Cu distance less than 3.15 Å. A μ-1,2-bridging peroxo ligand could exhibit a wide range of M···M distances depending on ligands and local geometry. For example, a μ-1,2-peroxo–dicobalt(III) complex with a very similar dinucleating ligand has Co···Co = 3.1 Å,[22] whereas oxy-hemocyanin[14] and oxy-tyrosinase[23] have Cu···Cu = ca. 3.6 Å with a μ-1,2-peroxo ligand. The EXAFS result of Cu···Cu = 3.31 (4) Å for III thus rules out a μ-1,1-bridged structure but cannot distinguish between μ-1,2-bridging or terminal peroxo coordination at the dinuclear copper site. However, recent resonance Raman data have given a strong indication that the peroxo group is coordinated asymetrically.[25] This, together with the observed shortening of the Cu···Cu distance by 0.4 Å upon reaction of II with dioxygen, must favor an asymmetric μ-1,2-bridging mode for peroxide.[26] EXAFS spectroscopy is clearly

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(18) Complex II contains two crystallographically independent molecules in each asymmetric unit having Cu···Cu = 3.715 and Cu···Cu = 3.619 Å, respectively.

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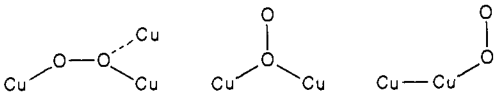
a useful technique in the structural characterization of metastable synthetic dioxygen adducts, and we plan further studies within this family of compounds.[10]



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Supplementary Material Available: A figure showing raw experimental EXAFS data and Fourier transforms for compounds I-III (2 pages). Ordering information is given on any current masthead page.

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(26) Model-building studies indicate that equatorial-axial coordination of peroxide to individual copper centers of the dinuclear pair is possible provided that one copper adopts trigonal-bipyramidal geometry while the other adopts the square-pyramidal geometry found in compound I. Examples of dinuclear complexes exhibiting just such mixed coordination polyhedra are known: (a) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250-3252. (b) Berends, H. P.; Stephan, D. W. *Inorg. Chim. Acta* **1985**, *99*, L53-L56.

Langmuir-Blodgett Ultrathin Membranes of Fumarate Polymers

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The authors wish to demonstrate the noble ultrathin LB membranes of poly(dialkyl fumarate) (PDF)[2-6] with bulky ester groups such as isopropyl (PDPF), *tert*-butyl (PDBF), and cyclohexyl (PDHF) of $\overline{M}_n$ = 60-(4 × 10^4), which are highly soluble in common organic solvents such as chloroform, THF, benzene, etc. They are known to have a rigid rodlike structure, a high glass transition temperature (T_g > 200 °C dec),[2-6] and high thermal stability. In Figure 1 are illustrated the surface pressure-area (FA) isotherms of these polymers on a pure water subphase at 21 °C. The steep inclining part corresponding to the solid membrane formation and the high surface pressure of the membrane collapsing point indicate the versatility of these polymers in the fabrication of LB membranes. The limiting molecular area for the fumarate residue is ca. 32, 34, and 38 Å^2 for PDPF, PDBF, and PDHF, respectively. These Langmuir membranes could be transferred to solid substrate surfaces either by the vertical dipping (VD) or horizontal lifting (HL) method at the surface pressure of 20 ± 5 dyn/cm. The transfer ratio was essentially unity within the limit of error. The VD method was utilizable when the critical surface tension of the substrate plate was smaller than 30 dyn/cm. When the HL method was used, the LB membranes were easily prepared, regardless of the kind of substrate plate. The addition of inorganic neutral salt, acid, or base in a water subphase did not affect the transfer ratio. As a reflection of the high T_g of these polymers, the profile of FA isotherms and the ease of LB membrane preparation were unchanged even at elevated subphase temperatures, such as 50 °C.

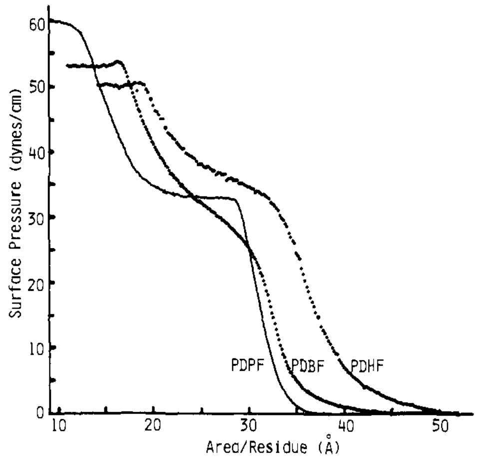

Figure 1. FA isotherms of PDF at 21 °C. Casting solvent: chloroform, $\overline{M}_n$ = 60 × 10^4 (PDPF), 4 × 10^4 (PDBF), and 16 × 10^4 (PDHF).

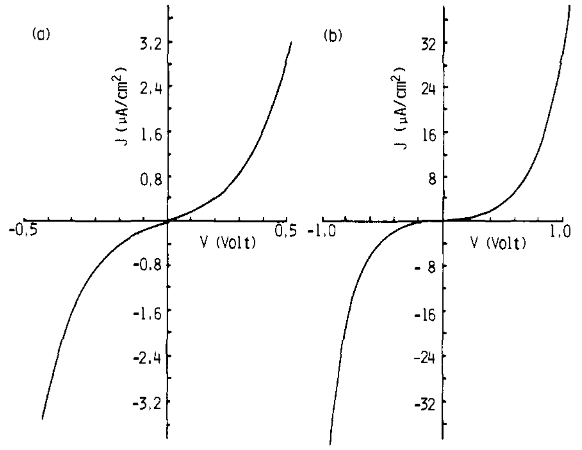

Figure 2. *J-V* Curve of [ITO/PDPF monolayer/Al] cell of (a) ±0.5 V and (b) ±1 V range measured by continuous potential scan at 5.0 mV/s. The area of Al electrode is 1.5 × 3 mm. The PDPF monolayer was prepared by the VD method at the surface pressure, initial compression speed, and substrate up-down speed of 20 dyn/cm and 1.0 and 6.0 mm/min, respectively, at 21 °C on an ITO plate of geometric area 2.5 × 4.0 cm.

It was possible to prepare more than 200 monolayers on an ITO (indium-tin oxide Nesa glass, 10 Ω/sq) substrate. In observations of multilayered LB-membranes of these polymers by a differential interference contrast optical microscopy under the polarized light, no defects larger than 0.01 μm were found. Unfortunately, because these PDF LB membranes were almost transparent to X-rays, no diffraction patterns were detected. The monolayer thicknesses calculated from the results of surface profilometry of the multilayered LB membranes were 8.5 ± 1.5, 10 ± 1.0, and 12 ± 1.5 Å for PDPF, PDBF, and PDHF, respectively, which coincided with those expected for the monolayer LB membrane composed of horizontal assemblies of rodlike PDF macromolecules. The observation by ellipsometry gave the same monolayer thicknesses described above.

Figure 2 is the current density-voltage (*J-V*) curve, characteristic of the tunneling barrier MIM (metal/insulator/metal) cell of [ITO/monolayer LB of PDPF by VD method/Al (ca. 200 Å)]. Exactly the same *J-V* curve was reproduced many times by using LB membranes obtained by VD and HL methods under the ordinary LB conditions (see captions of Figure 2), and in our experience only a few out of 100 were unsuccessful. The conductivity of PDF membranes estimated either from the tangent

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