explained by the reaction of released thiourea with Ni^{II}. The red shift of the band from 450 to 475 nm when Au^I is bonded to $NiPen_2$ is similar to the red shift observed when Ag^I is added to a similar reaction mixture (maximum at 460 nm).[1b,c] These bands must be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition of square-planar coordinated diamagnetic Ni^{II}.

Conclusions. The penicillamine ligand forms stable complexes with d^8, d^9, and d^{10} transition-metal ions, especially when the penicillamine ligand can chelate the d^8 or d^9 ion and the thiolate S atoms can form bridges to one or more d^{10} ions. In $Na_2[Au_2Ni_2Pen_4]\cdot x$(solvent), the Au^I atoms act as single atom bridges between two *cis*-$NiPen_2$ moieties. The Au–Au distance is close to the Au–Au distance present in metallic gold.

Acknowledgment. Professor J. Reedijk is gratefully acknowledged for his continuous interest in this work.

Registry No. $Na_2[Au^I_2Ni^{II}_2Pen_4]$, 80105-75-5; $[Co(NH_3)_6]_2[Au^I_2Pd^{II}_2Pen_4]_3$, 80126-86-9; $Au(tu)_2Cl$, 40764-57-6.

Supplementary Material Available: Tables of the observed and calculated structure factors and positional and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Properties of the Tetranuclear Complexes $[(DENC)CuX]_4$ (DENC = *N,N*-Diethylnicotinamide; X = Cl, Br, I) and the Kinetics of Oxidation of the Chloride and Bromide by Dioxygen in Aprotic Solvents[1a]

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Copper(I) halides dissolve in dioxygen-free aprotic solvents containing *N,N*-diethylnicotinamide, DENC, to form the tetranuclear complexes $[(DENC)CuX]_4$. The air-stable iodo complex crystallizes in the space group $P\bar{1}$ with a = 12.0885 (19) Å, b = 15.3834 (24) Å, c = 15.9420 (26) Å, α = 116.84 (1)°, β = 94.10 (1)°, γ = 91.69 (1)°, V = 2632.1 (7) Å^3, and Z = 2. Diffraction data to 2θ = 40° (Mo Kα radiation) were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was refined to R_F = 5.99% and R_{wF} = 4.25% for all 4943 reflections (R_F = 4.15% and R_{wF} = 4.00% for those 4044 reflections with $|F_o| > 3\sigma(|F_o|)$). All 60 nonhydrogen atoms were located, and all hydrogen atoms were included in idealized positions. The Cu_4I_4 core has a distorted "cubane-like" arrangement with Cu–I distances ranging from 2.6299 (17) to 2.7493 (17) Å. The DENC ligands are bound to the copper(I) atoms via Cu–N(ring) bonds of length 2.028 (8)–2.042 (8) Å. Cryoscopic and spectral data are consistent with the same basic core structure for the corresponding chloro and bromo complexes $[(DENC)CuX]_4$. The stoichiometry and kinetics of reactions of excesses of the latter complexes with dioxygen in benzene, methylene chloride, and nitrobenzene have been determined, and analytical, cryoscopic, and spectral properties of the tetranuclear $[(DENC)CuX]_4O_2$ products are reported. The DENC appears to be coordinated only through its pyridine nitrogen atom. The reactions are simple, second-order processes with no detectable intermediates. Their rate constants and activation parameters show little solvent dependence and are inconsistent with electron transfer from copper(I) to dioxygen as the rate-determining step, which is proposed to involve a dioxygen insertion mechanism whose rate decreases in the order Cl > Br >> I. Decreased rates at high added [DENC] or low $[[(DENC)CuX]_4]$ indicate that 1:1 redox complementarity of the reactants is important in determining high rates and a simple bimolecular mechanism. Comparison of the cryoscopic, magnetic, spectral, and chemical properties of $[(DENC)CuX]_4O_2$ with those of other known μ-oxo copper(II) species suggests that their structures are similar to those of $[(DENC)CuX]_4$.

Introduction

The thermal oxidation of slurries of copper(I) halides by dioxygen in pyridine gives polymeric $((py)_mCuO)_n$ species that initiate the oxidative coupling of acetylenes, aromatic amines, and phenols by dioxygen.[2] Such initiator species are stable only in the presence of high concentrations of pyridine, and their spontaneous polymerization gives rise to the development of induction periods in phenolic oxidative coupling reactions and to a decreasing reactivity toward protic substances.[2-4] Efforts have been made to prevent this deactivating polymerization process and isolate solid products by substituting other pyridine derivatives for pyridine in $((py)_mCuO)_n$, but in all cases examined either (1) no detectable substitution took place (presumably because of the necessarily high concentration of pyridine) or (2) oxidation of the ring substituents in the presence of excess dioxygen was observed.[4]

With the objective of isolating intact solid oxo–copper(II) products for structural determinations, we next turned our attention to slurry oxidations in *N,N*-dimethylacetamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidinone (nmp).[4,5] Cryoscopic measurements on solutions of the primary product showed them to be $L_3Cu_4X_4O_2$ species, which are relatively poor oxidative coupling initiators and readily disproportionate in the presence of water. The crystal structure of one such disproportionation product, $(nmp)_3Cu_4Cl_6O(OH_2)\cdots nmp$,[6] showed it to be a μ_4-oxo-tetracopper(II) complex with a water molecule attached to one of the four copper(II) centers. To date, we have been unsuccessful in crystallizing these primary $L_3Cu_4Cl_4O_2$ initiator products, which all apparently have the same core structure and contain a terminal oxo group, consistent with their affinity for protic substances and their tendency toward polymerization.[4-6]

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(1) (a) This paper may be considered as part 13 in the series "Molecules with an M_4X_4 Core" by M. R. Churchill et al. For part 12 in this series see: Churchill, M. R.; Missert, J. R. *Inorg. Chem.* **1981**, *20*, 619. (b) State University of New York at Buffalo. (c) Northeastern University.

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Table I. Analytical and Cryoscopic Data

	calcd, found				
complex	% C	% H	% N	% other	mol wt
$[(DENC)CuI]_4$	32.6, 29.4	3.8, 3.4	7.6, 6.8	17.2,[a] 18.3	
$[(DENC)CuCl]_4$[b]					1108, 1050 ± 20
$[(DENC)CuBr]_4$[b]					1286, 1240 ± 25
$[(DENC)CuCl]_4O_2$	42.1, 41.5	4.9, 5.1	9.8, 9.8	12.5,[c] 12.9	1140, 1140 ± 20
$[(DENC)CuBr]_4O_2$	36.4, 38.6	4.3, 4.7	8.5, 8.9	24.3,[d] 22.0	1318, 1280 ± 25

[a] Copper. [b] These complexes are too oxygen sensitive to give reliable analytical data. [c] Chlorine. [d] Bromine.

Table II. Experimental Data for the Diffraction Study for $[Cu(DENC)I]_4$

(A) Crystal Parameters at 23 °C[a]

crystal system: triclinic
space group: $P\bar{1}$ (C_i^1; No. 2)
$a = 12.0885\ (19)$ Å
$b = 15.3834\ (24)$ Å
$c = 15.9420\ (26)$ Å
$\alpha = 116.84\ (1)°$
$\beta = 94.10\ (1)°$
$\gamma = 91.69\ (1)°$
$V = 2632.1\ (7)$
$Z = 2$
ρ(calcd) = 1.86 g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\,73$ Å)
monochromator: highly oriented graphite
reflctns measd: $+h,\pm k,\pm l$; $2\theta = 3\text{–}40°$
scan type: coupled θ(crystal)–2θ(counter) at 2°/min in 2θ
scan width: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
bkgd: stationary–at beginning and end of scan; each for $^1/_4$ the scan time
std reflctns: 3 measd after every 97 reflctns; no significant fluctuations were observed
reflctns collected: 5260 total, yielding 4943 independent reflctns
abs coeff: $\mu = 40.7$ cm^{-1}

(C) Data for Absorption Corrections

hkl	2θ, deg	I_{max}/I_{min}
$2\bar{2}\bar{4}$	16.00	1.35
$2\bar{4}\bar{4}$	20.52	1.36
$3\bar{2}\bar{7}$	24.75	1.42
$4\bar{6}\bar{6}$	32.00	1.33

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections of the forms $\{6\bar{1}1\}$, $\{70\bar{2}\}$, $\{811\}$, $\{19\bar{2}\}$, $\{28\bar{3}\}$, $\{1,\bar{5},10\}$, $\{12\bar{8}\}$, $\{1\bar{8}1\}$, $\{\bar{2}3\bar{9}\}$, $\{2\bar{4}\bar{4}\}$, $\{26\bar{7}\}$, and $\{4\bar{5}\bar{1}\}$, all with 2θ between 20 and 29°.

We are particularly interested in the mechanisms of the aprotic oxidation of *soluble* copper(I) complexes by dioxygen as part of a detailed mechanistic investigation of oxidative coupling. Ligands which give soluble copper(I) complexes in weakly coordinating solvents (e.g., methylene chloride and nitrobenzene) include alkylpolyamines, which greatly accelerate copper(I) halide oxidation by dioxygen and produce isolable (μ-carbonato)-dicopper(II) complexes in the presence of carbon dioxide. The latter are excellent initiators for the oxidative coupling of phenols by dioxygen.[7]

The oxidative stability of alkylated amide groups in $L_3Cu_4X_4O_2$ systems prompted us to investigate the pyridine derivative *N*,*N*-diethylnicotinamide, DENC, as a ligand. DENC forms tetranuclear complexes $[(DENC)CuX]_4$ with copper(I) halides which, for X = Cl or Br, are very soluble in aprotic solvents. We have determined the crystal and molecular structure of insoluble $[(DENC)CuI]_4$ and compared its properties with those of the corresponding bromo and chloro complexes. Also reported are the kinetics of the reactions of $[(DENC)CuX]_4$ (X = Cl, Br) with dioxygen in methylene chloride, benzene, and nitrobenzene. The redox complementarity in these systems appears to be important in determining their mechanism.

Experimental Section

Materials. DENC (Aldrich) was distilled under reduced pressure before use. Methylene chloride and nitrobenzene were distilled from phosphorus(V) oxide and stored over 4-Å molecular sieves. Benzene was stirred with concentrated sulfuric acid. The acid layer was removed, and the process was repeated until darkening of the acid layer was slight. The benzene layer was then distilled and stored over 4-Å molecular sieves. Diethyl ether was dried over $CaCl_2$ and then freshly distilled from sodium/benzophenone. High-purity nitrogen gas was deoxygenated by passage through a column of Alfa DE-OX. Copper(I) halides were prepared by literature methods.[8]

Syntheses of $[(DENC)CuX]_4$ (X = Cl, Br, I). A solution of DENC (0.84 mL, 5 mmol) in anhydrous methylene chloride (30 mL) was flushed with nitrogen for 15 min. The appropriate copper(I) halide (5 mmol) was then added under N_2. The mixture was stirred with a stream of N_2 until all the solid had dissolved to give a yellow solution for X = Cl, a yellowish orange solution for X = Br, and a milky suspension followed by a white, air-stable precipitate for X = I. Analytical data[9] for the white precipitate (Table I) indicate that it is $[(DENC)CuI]_4$. Single crystals were obtained by treating the milky suspension in methylene chloride with 10 mL of diethyl ether before precipitation took place. The molecular weights of the dioxygen-sensitive products with X = Cl and Br (Table I) were determined cryoscopically under nitrogen in nitrobenzene (mp 5.70 °C, $K_f = 7.00$ °C/m).[7]

Determination of the Crystal Structure of $[(DENC)CuI]_4$. Collection of Diffraction Data. A crystal of size 0.1 × 0.2 × 0.3 mm was sealed within a thin-walled capillary and mounted on a Syntex $P2_1$ automated diffractometer. Crystal alignment, unit cell determination, and data collection were carried out as described previously.[10] Details are given in Table II.

Solution and Refinement of the Structure. The positions of the heavy atoms were determined from a Patterson map; all remaining nonhydrogen atoms were revealed by difference-Fourier syntheses. Least-squares refinement of positional and anisotropic thermal parameters for the 60 nonhydrogen atoms, with hydrogen atoms included in calculated positions (d(C–H) = 0.95 Å),[11] led smoothly to convergence with $R_F = 5.99\%$, $R_{wF} = 4.25\%$, and GOF = 1.41 for all 4943 reflections. [$R_F = 4.15\%$ and $R_{wF} = 4.00\%$ for those 4044 reflections with $|F_o| > 3\sigma(|F_o|)$.] A final difference-Fourier map showed no unusual features (ρ(max) = 1.0 e Å^{-3}).

All calculations were performed on the CDC6600-Cyber 173 computer at SUNYAB, with use of programs described previously.[12] The analytical scattering factors of the neutral atoms[13a] were corrected for the real and imaginary components of anomalous dispersion.[13b] The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement; the weights (w) are derived from the statistical errors modified by an "ignorance factor" of 0.03.

Positional parameters are given in Table III; thermal parameters are listed in Table IV (supplementary material).

Stoichiometry and Products of the Reactions of $[(DENC)CuX]_4$ (X = Cl, Br) with Dioxygen. The stoichiometries of the rapid oxidations of solutions of $[(DENC)CuX]_4$ (X = Cl, Br) by dioxygen in methylene chloride, nitrobenzene, and benzene were determined manometrically.[2,7] The spectra of completely oxidized solutions were essentially independent of solvent. Analytical data[9] (Table I) for the dark brown solid products obtained by vacuum rotary evaporation of methylene

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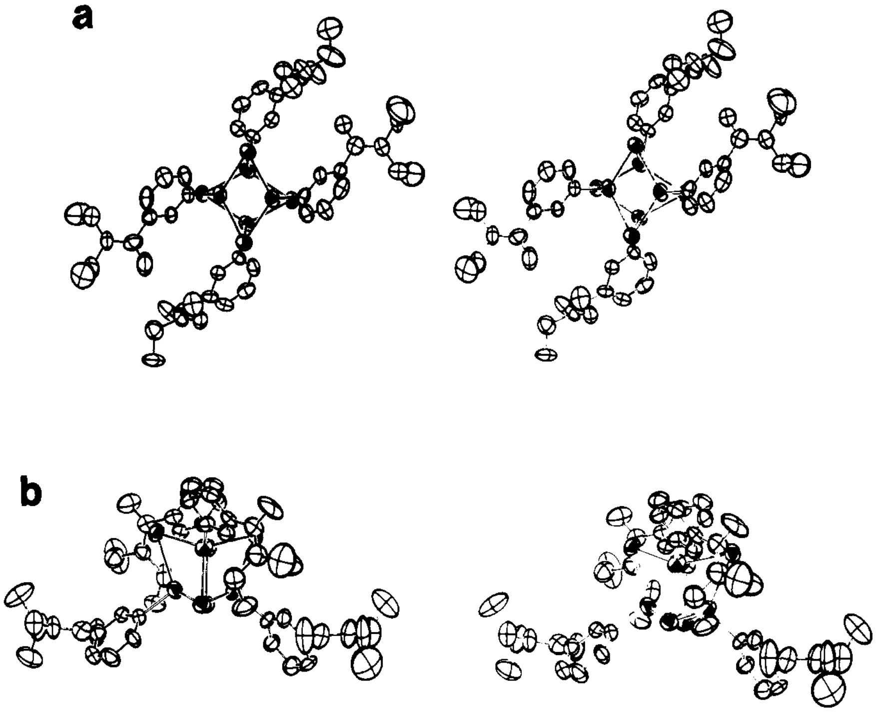

Figure 1. Stereoscopic views of the [(DENC)CuI]$_4$ molecule: (a) view down the pseudo-S_4 axis of the "cubane" system; (b) approximately orthogonal view to the above (ORTEP-II diagrams; 30% ellipsoids for all nonhydrogen atoms).

chloride solvent indicate the quantitative formation of [(DENC)CuX]$_4$O$_2$, whose ability to initiate the oxidative coupling of 2,6-dimethylphenol was tested as previously described.[2,7]

Physical Measurements. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with polystyrene at 903 cm^{-1}. ^{1}H NMR spectra were recorded with a JEOL Model FX60Q spectrometer at 25 °C. The magnetic susceptibilities of [(DENC)CuX]$_4$O$_2$ were measured at 25 °C with a Princeton Applied Research Model FM-1 vibrating-sample magnetometer calibrated with HgCo(SCN)$_4$.

Kinetic Measurements. The rates of formation of [(DENC)CuX]$_4$O$_2$ (X = Cl, Br) were monitored spectrophotometrically in the wavelength range 500–850 nm. A Beckman DK-1A spectrophotometer fitted with a cell housing maintained within ±0.1 °C of the desired temperature was used for X = Br; prethermostated reactant solutions were mixed and transferred to the 10-mm path length quartz reaction cell within 30 s of mixing. A Nortech SF-3A stopped-flow apparatus (1-mm path length) was used for rapid rate measurements with X = Cl.[14] Temperature was controlled to ±0.05 °C with a Neslab U-Cool refrigerator in conjunction with the Nortech control unit. The reactant concentrations were [(DENC)CuCl]$_4$ = (1–4) × 10^{-1} M, [(DENC)CuBr]$_4$ = (6.3–35.2) × 10^{-3} M, and [O$_2$]$_0$ = (0.44–2.65) × 10^{-3} M over the temperature range 20.0–60.0 °C. In each run the initial O$_2$ concentration was determined from the absorption, A_∞, after at least 10 half-lives together with the molar absorptivity of the corresponding [(DENC)CuX]$_4$O$_2$ product. [(DENC)CuX]$_4$ was always in sufficient stoichiometric excess to ensure pseudo-first-order conditions. Stopped-flow kinetic data were collected and analyzed on-line with our PDP 11-20 interface as previously described.[2,14]

Results and Discussion

Copper(I) Complexes. Copper(I) halides react quantitatively with DENC in oxygen-free, weakly coordinating aprotic solvents to form tetranuclear complexes [(DENC)CuX]$_4$ (eq 1).

$$4\text{DENC} + 4\text{CuX} \rightarrow [(\text{DENC})\text{CuX}]_4 \qquad (1)$$

The chloro complex is the most soluble in all solvents investigated, with [(DENC)CuI]$_4$ virtually insoluble. Cryoscopic and analytical data (Table I) establish the formation of discrete tetranuclear products.

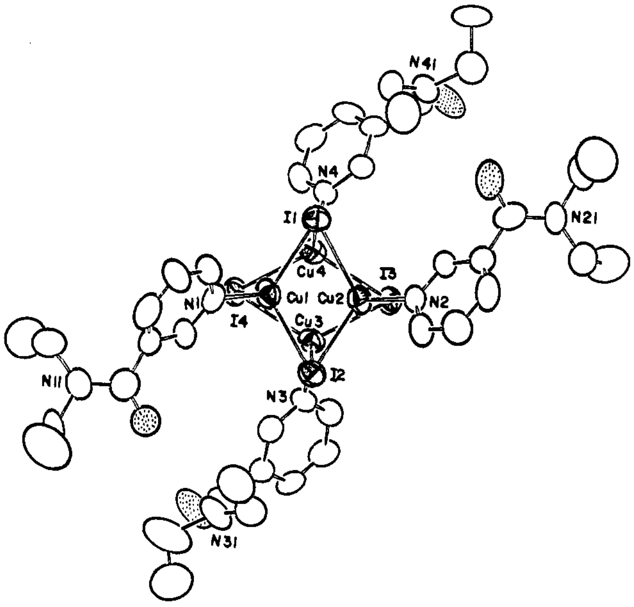

Figure 2. Labeling of essential atoms in the [(DENC)CuI]$_4$ molecule.

Structure of the Iodo Complex. The crystal consists of discrete tetrameric units of [Cu(DENC)I]$_4$ that are mutually separated by normal van der Waals distances. Figure 1 shows stereoscopic views of the molecule, while Figure 2 provides the essential labeling scheme for atoms in the molecule. Intramolecular distances and angles are collected in Tables V and VI.

The Cu$_4$I$_4$ core of the molecule defines a tetrahedrally distorted cubane-like arrangement with alternating copper(I) and iodide(−I) ions. Each d^{10} Cu(I) ion is in a tetrahedral coordination environment, being linked to three μ_3-iodide ions and a terminal DENC ligand. The DENC ligand is bonded to copper via its ring (pyridyl) nitrogen atom (Cu–N ring distances range from 2.028 (8) to 2.042 (8) Å).

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Table III. Final Positional Parameters for $[Cu(DENC)I]_4$[a]

atom	*x*	*y*	*z*
Cu(1)	0.18470 (12)	−0.07618 (10)	0.15274 (10)
Cu(2)	0.22977 (12)	0.10747 (10)	0.28935 (10)
Cu(3)	0.25731 (12)	−0.04187 (10)	0.32956 (10)
Cu(4)	0.39479 (12)	−0.02020 (10)	0.21869 (10)
I(1)	0.28896 (7)	0.05091 (6)	0.11005 (5)
I(2)	0.05063 (6)	0.00866 (6)	0.29558 (5)
I(3)	0.40349 (6)	0.11132 (5)	0.40676 (5)
I(4)	0.32219 (7)	−0.19895 (5)	0.17792 (5)
N(1)	0.0653 (7)	−0.1581 (6)	0.0461 (6)
C(11)	0.0010 (9)	−0.2256 (8)	0.0555 (8)
C(12)	−0.0893 (9)	−0.2771 (8)	−0.0130 (8)
C(13)	−0.1138 (10)	−0.2531 (9)	−0.0872 (8)
C(14)	−0.0470 (11)	−0.1829 (9)	−0.0943 (9)
C(15)	0.0456 (10)	−0.1372 (8)	−0.0271 (8)
C(16)	−0.1642 (12)	−0.3417 (10)	0.0088 (10)
O(1)	−0.2043 (10)	−0.3074 (7)	0.0845 (7)
N(11)	−0.1824 (10)	−0.4376 (8)	−0.0531 (8)
C(111)	−0.1321 (13)	−0.4862 (11)	−0.1445 (10)
C(112)	−0.0618 (17)	−0.5649 (13)	−0.1453 (14)
C(121)	−0.2628 (14)	−0.4998 (11)	−0.0274 (13)
C(122)	−0.3699 (19)	−0.4871 (16)	−0.0544 (17)
N(2)	0.1884 (7)	0.2476 (6)	0.3291 (6)
C(21)	0.2683 (9)	0.3116 (7)	0.3283 (7)
C(22)	0.2419 (10)	0.4077 (8)	0.3514 (7)
C(23)	0.1342 (10)	0.4364 (9)	0.3711 (9)
C(24)	0.0559 (10)	0.3677 (9)	0.3706 (9)
C(25)	0.0825 (9)	0.2730 (8)	0.3486 (8)
C(26)	0.3318 (11)	0.4713 (10)	0.3396 (9)
O(2)	0.3698 (9)	0.4382 (6)	0.2628 (6)
N(21)	0.3647 (9)	0.5602 (7)	0.4106 (7)
C(211)	0.3250 (12)	0.6024 (10)	0.5050 (9)
C(212)	0.4127 (14)	0.6202 (14)	0.5801 (11)
C(221)	0.4542 (13)	0.6188 (10)	0.3889 (10)
C(222)	0.3975 (14)	0.6823 (11)	0.3554 (12)
N(3)	0.2266 (7)	−0.0941 (6)	0.4227 (6)
C(31)	0.1377 (9)	−0.1585 (8)	0.3998 (8)
C(32)	0.1095 (9)	−0.1978 (7)	0.4592 (8)
C(33)	0.1737 (9)	−0.1668 (8)	0.5477 (7)
C(34)	0.2647 (10)	−0.1017 (9)	0.5685 (8)
C(35)	0.2897 (9)	−0.0658 (8)	0.5061 (7)
C(36)	0.0185 (10)	−0.2769 (8)	0.4296 (8)
O(3)	0.0427 (8)	−0.3549 (6)	0.4284 (8)
N(31)	−0.0836 (9)	−0.2643 (8)	0.4026 (8)
C(311)	−0.1240 (10)	−0.1664 (9)	0.4208 (9)
C(312)	−0.1674 (12)	−0.1655 (11)	0.3280 (10)
C(321)	−0.1665 (14)	−0.3645 (12)	0.3458 (13)
C(322)	−0.2251 (16)	−0.3654 (14)	0.4149 (14)
N(4)	0.5544 (7)	−0.0064 (6)	0.1925 (6)
C(41)	0.5928 (9)	0.0821 (8)	0.2030 (7)
C(42)	0.7026 (9)	0.1007 (8)	0.1895 (7)
C(43)	0.7771 (9)	0.0282 (9)	0.1691 (8)
C(44)	0.7355 (10)	−0.0624 (9)	0.1563 (8)
C(45)	0.6232 (9)	−0.0803 (8)	0.1680 (8)
C(46)	0.7429 (10)	0.2019 (9)	0.2125 (8)
O(4)	0.8213 (7)	0.2398 (7)	0.2744 (7)
N(41)	0.6939 (8)	0.2485 (6)	0.1679 (7)
C(411)	0.6146 (11)	0.2001 (9)	0.0828 (8)
C(412)	0.5029 (12)	0.2488 (10)	0.0981 (10)
C(421)	0.7329 (11)	0.3548 (10)	0.1998 (9)
C(422)	0.8170 (15)	0.3617 (12)	0.1375 (12)

[a] All calculated parameters for hydrogen atoms appear in Table IIIS (supplementary material).

The six nonbonding Cu···Cu distances range from 2.6301 (21) to 2.7677 (20) Å, averaging 2.682 [49] Å. This distance is shorter than that found in species possessing $Cu_4I_4P_4$ cores (e.g., Cu···Cu = 2.9272 (20) Å in $[(PEt_3)CuI]_4$[15] and 2.930 [78] Å in $[(PMePh_2)CuI]_4$[16]) or Cu_4I_4As cores (e.g., Cu···Cu = 2.7826 (24) Å in $[(AsEt_3)CuI]_4$[15] and Cu···Cu = 2.834 [51] Å in $[(AsPh_3)CuI]_4$[17a]).

Table V. Important Distances (Å), with Esd's,[a] for $[Cu(DENC)I]_4$

(A) Copper···Copper Distances			
Cu(1)···Cu(2)	2.6841 (21)	Cu(2)···Cu(3)	2.6729 (20)
Cu(1)···Cu(3)	2.6964 (20)	Cu(2)···Cu(4)	2.7677 (20)
Cu(1)···Cu(4)	2.6398 (21)	Cu(3)···Cu(4)	2.6301 (21)
av[b] Cu···Cu	2.682 [49]		
(B) Iodine···Iodine Distances			
I(1)···I(2)	4.5072 (13)	I(2)···I(3)	4.4525 (13)
I(1)···I(3)	4.4915 (13)	I(2)···I(4)	4.5370 (14)
I(1)···I(4)	4.4600 (12)	I(3)···I(4)	4.5325 (14)
av[b] I···I	4.497 [36]		
(C) Copper–Iodine Distances			
Cu(1)–I(1)	2.6558 (17)	Cu(3)–I(2)	2.7279 (16)
Cu(1)–I(2)	2.7356 (18)	Cu(3)–I(3)	2.6487 (17)
Cu(1)–I(4)	2.6953 (17)	Cu(3)–I(4)	2.7214 (17)
Cu(2)–I(1)	2.7429 (17)	Cu(4)–I(1)	2.7036 (16)
Cu(2)–I(2)	2.6424 (17)	Cu(4)–I(3)	2.7493 (17)
Cu(2)–I(3)	2.6921 (16)	Cu(4)–I(4)	2.6299 (17)
av[b] Cu–I	2.695 [42]		
(D) Copper–Nitrogen Distances			
Cu(1)–N(1)	2.042 (8)	Cu(3)–N(3)	2.032 (8)
Cu(2)–N(2)	2.042 (8)	Cu(4)–N(4)	2.028 (8)
av[b] Cu–N	2.036 [7]		
(E) Distances within the Ligand			
N(1)–C(11)	1.346 (13)	N(2)–C(21)	1.364 (12)
C(11)–C(12)	1.418 (14)	C(21)–C(22)	1.406 (14)
C(12)–C(13)	1.404 (15)	C(22)–C(23)	1.398 (15)
C(13)–C(14)	1.380 (16)	C(23)–C(24)	1.395 (16)
C(14)–C(15)	1.413 (15)	C(24)–C(25)	1.389 (15)
C(15)–N(1)	1.352 (13)	C(25)–N(2)	1.366 (12)
C(12)–C(16)	1.495 (16)	C(22)–C(26)	1.518 (16)
C(16)–O(1)	1.221 (14)	C(26)–O(2)	1.225 (13)
C(16)–N(11)	1.354 (15)	C(26)–N(21)	1.348 (14)
N(11)–C(111)	1.490 (16)	N(21)–C(211)	1.468 (15)
C(111)–C(112)	1.495 (20)	C(211)–C(212)	1.461 (18)
N(11)–C(121)	1.544 (18)	N(21)–C(221)	1.544 (16)
C(121)–C(122)	1.381 (26)	C(221)–C(222)	1.472 (18)
N(3)–C(31)	1.352 (13)	N(4)–C(41)	1.358 (12)
C(31)–C(32)	1.389 (14)	C(41)–C(42)	1.402 (14)
C(32)–C(33)	1.426 (14)	C(42)–C(43)	1.390 (14)
C(33)–C(34)	1.381 (15)	C(43)–C(44)	1.389 (15)
C(34)–C(35)	1.384 (14)	C(44)–C(45)	1.418 (15)
C(35)–N(3)	1.360 (12)	C(45)–N(4)	1.355 (12)
C(32)–C(36)	1.498 (15)	C(42)–C(46)	1.487 (15)
C(36)–O(3)	1.236 (12)	C(46)–O(4)	1.235 (12)
C(36)–N(31)	1.326 (13)	C(46)–N(41)	1.340 (13)
N(31)–C(311)	1.503 (15)	N(41)–C(411)	1.474 (13)
C(311)–C(312)	1.540 (17)	C(411)–C(412)	1.545 (17)
N(31)–C(321)	1.649 (18)	N(41)–C(421)	1.524 (15)
C(321)–C(322)	1.357 (21)	C(421)–C(422)	1.506 (18)

[a] Distances and angles (Table V) with associated esd's are calculated from unit cell parameters, their esd's, correlations thereof, and the atomic coordinates and their esd's. [b] Errors on average distances are calculated by $\sigma(\mathrm{av}) = [\Sigma_i(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the *i*th distance and $\bar{d}$ is the average of *N* such distances and is a measure of the precision of the value.

The six iodine···iodine contacts range from 4.4525 (13) to 4.5370 (14) Å, averaging 4.497 [36] Å (cf. 4.4237 (15) Å in $[(AsEt_3)CuI]_4$ and 4.3800 (11) Å in $[(PEt_3)CuI]_4$[15]). It is these contacts that cause the major distortions from a regular cubane-like geometry. The repulsions between the iodide atoms cause a decrease in the Cu–I–Cu angles (observed values are 58.28 (5)–61.14 (5)°) and an increase in the I–Cu–I angles (observed values are 110.91 (6)–115.13 (6)°) as compared to the ideal internal angle of 90° for a cube.

The 12 Cu–I(μ_3) bond lengths range from 2.6299 (17) to 2.7493 (17) Å, averaging 2.695 [42] Å as compared to 2.6767 (15) Å in $[(AsEt_3)CuI]_4$,[15] 2.6837 (13) Å in $[(PEt_3)CuI]_4$,[15]

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(15) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899 (part 3 of "Molecules with an M_4X_4 Core").

(16) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267 (part 9 of this series).

(17) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1133 (part 11 of this series). (b) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2153.

Table VI. Selected Intramolecular Angles (Deg), with Esd's,[a] for [Cu(DENC)I]$_4$

(A) Cu$_4$I$_4$ "Cube" Angles			
I(1)-Cu(1)-I(2)	113.43 (6)	Cu(1)-I(1)-Cu(2)	59.60 (5)
I(1)-Cu(1)-I(4)	112.91 (6)	Cu(1)-I(1)-Cu(4)	59.01 (5)
I(2)-Cu(1)-I(4)	113.31 (6)	Cu(2)-I(1)-Cu(4)	61.08 (5)
I(1)-Cu(2)-I(2)	113.63 (6)	Cu(1)-I(2)-Cu(2)	59.85 (5)
I(1)-Cu(2)-I(3)	111.46 (6)	Cu(1)-I(2)-Cu(3)	59.14 (5)
I(2)-Cu(2)-I(3)	113.16 (6)	Cu(2)-I(2)-Cu(3)	59.67 (5)
I(2)-Cu(3)-I(3)	111.80 (6)	Cu(2)-I(3)-Cu(3)	60.05 (5)
I(2)-Cu(3)-I(4)	112.73 (6)	Cu(2)-I(3)-Cu(4)	61.14 (5)
I(3)-Cu(3)-I(4)	115.13 (6)	Cu(3)-I(3)-Cu(4)	58.28 (5)
I(1)-Cu(4)-I(3)	110.91 (6)	Cu(1)-I(4)-Cu(3)	59.70 (5)
I(1)-Cu(4)-I(4)	113.48 (6)	Cu(1)-I(4)-Cu(4)	59.42 (5)
I(3)-Cu(4)-I(4)	114.81 (6)	Cu(3)-I(4)-Cu(4)	58.85 (5)
av[b]	113.06 (36)	av[b]	59.65 (24)
(B) Nitrogen-Copper-Iodine Angles			
N(1)-Cu(1)-I(1)	109.40 (28)	N(3)-Cu(3)-I(2)	100.60 (24)
N(1)-Cu(1)-I(2)	98.72 (26)	N(3)-Cu(3)-I(3)	111.15 (25)
N(1)-Cu(1)-I(4)	107.94 (25)	N(3)-Cu(3)-I(4)	104.17 (25)
N(2)-Cu(2)-I(1)	102.42 (25)	N(4)-Cu(4)-I(1)	100.45 (23)
N(2)-Cu(2)-I(2)	106.98 (26)	N(4)-Cu(4)-I(3)	100.88 (24)
N(2)-Cu(2)-I(3)	108.40 (23)	N(4)-Cu(4)-I(4)	114.78 (24)
av[b]	105.5 (15)		
(C) Copper-Nitrogen-Carbon Angles			
Cu(1)-N(1)-C(11)	118.6 (8)	Cu(3)-N(3)-C(31)	117.1 (7)
Cu(1)-N(1)-C(15)	119.6 (8)	Cu(3)-N(3)-C(35)	123.1 (7)
Cu(2)-N(2)-C(21)	117.2 (7)	Cu(4)-N(4)-C(41)	117.3 (7)
Cu(2)-N(2)-C(25)	120.7 (8)	Cu(4)-N(4)-C(45)	122.8 (7)
av[b]	119.6 (9)		
(D) Carbon-Nitrogen-Carbon Angles (Ring Only)			
C(11)-N(1)-C(15)	121.6 (10)	C(31)-N(3)-C(35)	119.8 (9)
C(21)-N(2)-C(25)	122.0 (9)	C(41)-N(4)-C(45)	119.8 (9)
av[b]	120.8 (6)		
(E) Nitrogen-Carbon-Carbon Angles (Ring Only)			
N(1)-C(11)-C(12)	119.9 (11)	N(3)-C(31)-C(32)	121.4 (10)
N(1)-C(15)-C(14)	120.6 (11)	N(3)-C(35)-C(34)	121.3 (11)
N(2)-C(21)-C(22)	119.0 (10)	N(4)-C(41)-C(42)	122.2 (10)
N(2)-C(25)-C(24)	119.1 (12)	N(4)-C(45)-C(44)	118.9 (10)
av[b]	120.3 (4)		

[a] See footnote *a* of Table V. [b] See footnote *b* of Table V.

2.698 [58] Å in [(PMePh$_2$)CuI]$_4$,[16] and 2.688 [17] Å in [(AsPh$_3$)CuI]$_4$.[17a]

The most interesting feature of the present structure is the determination that the pyridine nitrogen atom (rather than the amide oxygen) is the atom involved in the ligand-to-metal bonding, and there is no subsidiary interaction of the diethylamide moiety with any copper atoms. The molecular (core) structure of [(DENC)CuI]$_4$ is, in fact, very closely similar to that previously reported for [(py)CuI]$_4$.[17b]

As may be seen from Tables V and VI, all other intramolecular distances and angles are normal and the structure is well-behaved and complete.

Spectroscopic Comparisons of Copper(I) Complexes. Major features of the KBr disk IR spectra of free DENC and [(DENC)CuI]$_4$ (Table VII) confirm that the carbonyl group of DENC is not coordinated in [(DENC)CuI]$_4$. The 1040- and 623-cm^{-1} absorptions assignable to the pyridine ring of DENC shift to higher frequencies on its coordination, as observed in other systems.[18a] We have been unable to obtain IR spectra for the pure chloro and bromo complexes because of their high affinity for dioxygen. The ^{1}H NMR spectra of DENC and [(DENC)CuCl]$_4$ in CDCl$_3$ are shown in Figure 3. The resonances centered at 3.26 and 1.05 ppm, due to the methylene and methyl groups of the DENC moiety, respectively, are clearly not affected by coordination. By contrast, resonances associated with the pyridine ring of DENC (set a centered at 7.50 ppm and set b centered at 7.85 ppm) change on coordination: set a is slightly shifted to higher field and sharpened, with an increase in height relative to set b, which is broadened. We conclude that DENC is coordinated only through its pyridine nitrogen atom, as established by the IR spectrum (Table VII) and molecular structure of [(DENC)CuI]$_4$ (Figures 1 and 2). Electronic spectra for DENC and [(DENC)CuX]$_4$ (X = Cl, Br), Table VIII, exhibit only charge-transfer maxima in the ultraviolet region. Ligand coordination results in increased molar absorptivities with very minor shifts in band position. The available analytical, structural, and spectral data, along with the observation of similar kinetics of oxidation of [(DENC)CuX]$_4$ (X = Cl, Br) by dioxygen (see below), lead us to conclude that the complexes [(DENC)CuX]$_4$ all have the same basic molecular structure.

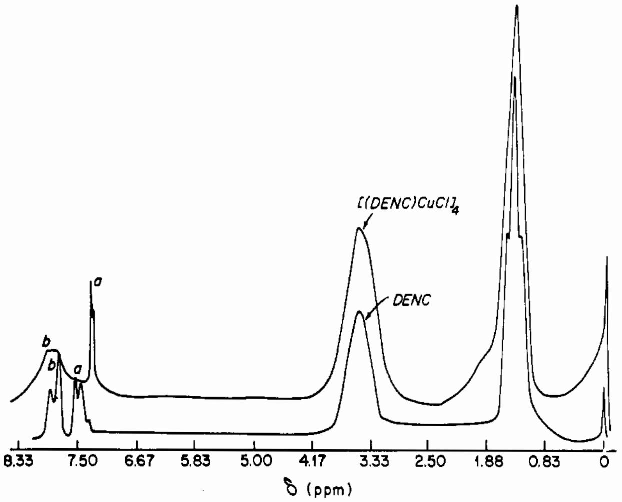

Figure 3. ^{1}H NMR spectra of DENC and [(DENC)CuCl]$_4$ in CDCl$_3$ at 25 °C with tetramethylsilane as reference.

Reaction with Dioxygen. Stoichiometry. Dioxygen uptake measurements were consistent with a reaction stoichiometry given by eq 2 (X = Cl, Br).

$$[(DENC)CuX]_4 + O_2 \rightarrow [(DENC)CuX]_4O_2 \quad (2)$$

This is the expected stoichiometry, $\Delta[Cu^I]/\Delta[O_2] = 4.00$, in systems involving nonoxidizable ligands.[2-4] Analytical[9] and cryoscopic data for the reaction products are collected in Table I. The cryoscopic data indicate that [(DENC)CuX]$_4$O$_2$ complexes, like their copper(I) precursors, are discrete tetranuclear species which have no tendency to disproportionate (unlike oxidation products in pyridine (see below)[2,3]) or polymerize (as is found for oxocopper(II) species with alkyldiamine ligands[7]). As part of an effort to obtain crystalline product samples, we have discovered their tendency to disproportionate in the presence of traces of water,[18b] as found, for example, for (nmp)$_3$Cu$_4$Cl$_4$O$_2$ complexes.[4-6]

Product Infrared and Electronic Spectra. The infrared spectra of [(DENC)CuX]$_4$O$_2$ (X = Cl, Br), Table VII, indicate that only the pyridine nitrogen atom of DENC is coordinated, as confirmed by no difference between the chemical shift of the methylene and methyl ^{1}H NMR resonances of DENC and [(DENC)CuX]$_4$O$_2$. A split, medium intensity band at 580 cm^{-1} may be attributed to ν_{Cu-O}.[1-3,19] Electronic spectral data are collected in Table VIII. Ligand field bands observed in the near-infrared region are characteristic of tetranuclear oxocopper(II) complexes.[5,6,20] The near-IR

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(18) (a) Akyüz, S.; Dempster, A. B.; Davies, J. E. D.; Holmes, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1746. (b) One such product, which has an analysis consistent with the formulation (DENC)$_4$Cu$_4$Cl$_6$(OH)$_2$, has now been obtained in crystalline form. We hope to determine its crystal structure as soon as suitably sized crystals are obtained.

(19) Dieck, H. T. *Inorg. Chim. Acta* **1973**, *7*, 397.

Table VII. Selected IR Absorption Maxima (cm^{-1}) for DENC and [(DENC)CuI]$_4$ and [(DENC)CuX]$_4$O$_2$ Complexes[a]

	ν_{CO}	ν_{py}			ν_{Cu-O}
DENC	1640 (s)	1470, 1423 (br)	1040 (w)	623 (w)	
[(DENC)CuI]$_4$	1640	1445	1060, 1042	640	
[(DENC)CuCl]$_4$O$_2$	1640	1450	1070	650	580 (m)
[(DENC)CuBr]$_4$O$_2$	1640	1450	1070	650	580

[a] Key: s, strong; br, broad; m, medium; w, weak.

Table VIII. Electronic Spectral Maxima in Methylene Chloride Chloride at 25 °C

	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
DENC	285	4 030
	255	3 440
[(DENC)CuCl]$_4$	225	10 600
	265	14 000
[(DENC)CuBr]$_4$	220	13 600
	250	17 950
[(DENC)CuCl]$_4$O$_2$	235	30 600
	255	27 800
	770	710
	850	715
[(DENC)CuBr]$_4$O$_2$	230	39 200
	250	35 200
	750	910
	825	910

maxima of [(DENC)CuX]$_4$O$_2$ are split into two components with similar molar absorptivities. In this region, [(DENC)CuBr]$_4$O$_2$ absorbs at shorter wavelengths than [(DENC)CuCl]$_4$O$_2$.

Magnetic Properties. The magnetic moments at 25 °C of [(DENC)CuCl]$_4$O$_2$ and [(DENC)CuBr]$_4$O$_2$ are 1.69 and 1.40 μ_B/Cu atom, respectively, indicating very weak antiferromagnetic coupling between the metal centers. We are currently investigating the magnetic behavior at lower temperatures.

Kinetics of Oxidation of [(DENC)CuX]$_4$ (X = Cl, Br) by Dioxygen. First-order plots of ln ($A_\infty - A_t$) vs. time, where A_t is the absorbance of [(DENC)CuX]$_4$O$_2$ at time t, were linear for at least 4 half-lives, indicating that reaction 2 is first order in [O$_2$] in the absence of added DENC.

Absorbances extrapolated to zero time corresponded to those expected for the copper(I) reactant at monitoring wavelengths from 500 to 850 nm, thus providing no evidence for reactant preequilibria. The simple first-order rate dependence indicates either that significant concentrations of reaction intermediates are not formed or that they do not absorb appreciably in the wavelength range 500–850 nm.

At fixed [[(DENC)CuX]$_4$], addition of DENC up to [DENC]$_T$/[[(DENC)CuX]$_4$] = 8 had no effect on the derived first-order rate constants or the spectrum of [(DENC)CuX]$_4$, indicating little tendency of the copper(I) reactant to undergo reactions such as eq 3, or for reversible substitution of DENC by dioxygen, eq 4.

$$[(DENC)CuX]_4 + 4DENC \rightleftharpoons 2(DENC)_4Cu_2X_2 \quad (3)$$

$$[(DENC)CuX]_4 + O_2 \rightleftharpoons (DENC)_3Cu_4X_4O_2 + DENC \quad (4)$$

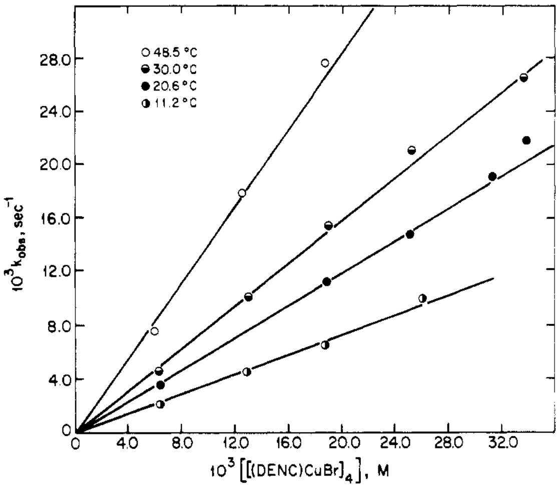

Figure 4. Plots of k_{obsd} (s^{-1}) vs. [[(DENC)CuBr]$_4$] for the reaction with dioxygen in nitrobenzene at the following temperatures: ◑, 11.2; ●, 20.6; ⊖, 30.0; ○, 48.5 °C.

Table IX. Kinetic Parameters for Oxidation of [(DENC)CuX]$_4$ (X = Cl, Br) by Dioxygen in Aprotic Solvents

solvent	temp[a]	k[b]	k_{calcd}[b,c]	$\Delta H^{\ddagger}$[c,d]	$\Delta S^{\ddagger}$[c,e]
		(a) [(DENC)CuCl]$_4$			
CH$_2$Cl$_2$[f]	25.0	6.9			
benzene	20.0	5.1	5.0		
	25.0	5.4	5.4		
	30.0	5.9	5.9	2.1 ± 0.2	−(48 ± 1)
	35.0	6.4	6.3		
	40.0	6.5	6.8		
	45.0	7.4	7.2		
nitrobenzene	25.0	15.1	16.2		
	30.0	18.0	18.4		
	35.0	20.5	20.7	3.9 ± 0.3	−(40 ± 1)
	40.0	24.7	23.3		
	50.0	30.3	29.2		
	60.0	35.1	36.1		
		(b) [(DENC)CuBr]$_4$			
nitrobenzene	11.0	0.34	0.39		
	20.6	0.58	0.56		
	24.9	0.65	0.66	5.9 ± 0.3	−(40 ± 1)
	30.0	0.82	0.79		
	48.5	1.46	1.47		

[a] Given in °C. [b] Units are M^{-1} s^{-1} with a maximum standard deviation of ±5%. [c] Calculated from a nonlinear least-squares fit of the data to eq 5 (see text); errors shown are 1 standard deviation. [d] Units are kcal mol^{-1}. [e] Units are cal deg^{-1} mol^{-1} at 25 °C. [f] Kinetic studies at lower temperatures in CH$_2$Cl$_2$ were precluded by [(DENC)CuCl]$_4$ solubility limitations.

However, a few measurements at very high [DENC]$_T$ indicated a decrease in rate and gave curved first-order plots, perhaps consistent with the occurrence of reaction 3 under these extreme conditions. Similar effects are observed at very low copper(I) concentrations (which would favor breakdown of the tetranuclear [(DENC)CuX]$_4$ units) with dioxygen in excess. Although these phenomena have not been investigated in detail, they can be taken as an indication of the importance of the structural integrity of the tetranuclear copper(I) reactants in determining the simple stoichiometry and reaction order at low or moderate [DENC]$_T$ and high [[(DENC)CuX]$_4$] (see below).

With no added DENC the derived pseudo-first-order rate constants, k_{obsd}, were accurately proportional to [[(DENC)CuX]$_4$]. Representative data are given in Figure 4. Reaction 2 is thus a second-order process, eq 5, when [(DENC)CuX]$_4$ is in excess.

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(20) (DENC)$_2$CuCl$_2$ has two near-IR absorption maxima at 780 nm (ϵ 175 M^{-1} cm^{-1}) and 860 nm (ϵ 180 M^{-1} cm^{-1}).

$$d[[(DENC)CuX]_4O_2]/dt = k[[(DENC)CuX]_4][O_2] \quad (5)$$

Second-order rate constants k and their associated activation parameters[21] in three different solvents are collected in Table IX. Consider first the data for oxidation of $[(DENC)CuCl]_4$ by dioxygen. The second-order rate constant k at 25.0 °C increases by less than a factor of 3 on changing the reaction solvent from nonpolar benzene to highly polar nitrobenzene. A much larger solvent effect would be expected if charge development were important in the rate-determining step,[22] strongly suggesting that electron transfer from copper(I) to dioxygen, which would produce a polar transition state, is not rate determining.

Similar, very small activation enthalpies are found in these two solvents, indicating little necessity for major structural rearrangements or solvation changes on activation of the reactants. The activation entropies in benzene and nitrobenzene are very negative and indicate substantial associative character in the activation process. Indeed, the entropy of activation is of the magnitude expected for the association of two neutral reactant species to give a monomolecular activated complex.[23]

Alternative explanations for these results are that (1) associative substitution of dioxygen at one of the four equivalent copper(I) centers or (2) insertion of dioxygen through one of the faces (see, for example, Figure 2) of the copper(I) reactant is the rate-determining process. We favor the second alternative on the basis of the observed, simple characteristics of the system (no reaction intermediates have been detected) and the fact that the redox process itself is complementary: very rapid 4-e transfer from copper(I) to dioxygen evidently can take place in one molecular unit once dioxygen has been inserted. The importance of this 1:1 redox complementarity is indicated by much more complicated stoichiometries and kinetics when the 2-e oxidants Br_2 and I_2 react with $[(DENC)CuX]_4$,[24] although this different behavior could also arise because the halogens are larger molecular entities and must therefore react through a different (noninsertion) mechanism.

The rate of oxidation of $[(DENC)CuBr]_4$ by dioxygen is about 23 times slower than that of the chloro complex in nitrobenzene at 25 °C. This decrease is solely due to a higher activation enthalpy when X = Br (Table IX) perhaps because insertion of dioxygen is impeded by larger bridging halogen groups in the $[(DENC)CuBr]_4$ unit. It is relevant that $[(DENC)CuI]_4$ does not absorb or react at an appreciable rate with dioxygen. This is in line with the general tendency of the heavier halides preferentially to stabilize copper(I) relative to copper(II).[25]

Properties of $[(DENC)CuX]_4O_2$ Products. The oxidation products $[(DENC)CuX]_4O_2$ do not initiate the oxidative coupling of 2,6-dimethylphenol by dioxygen under standard conditions.[7] However, highly active initiator species can be obtained by adding ligands such as alkyldiamines (which are known oxidative coupling promoters[7]) to solutions of $[(DENC)CuX]_4O_2$ in aprotic solvents. The spectral changes observed in such mixed-ligand systems are consistent with at least partial substitution of DENC by the added ligands. The stoichiometries of these useful substitution reactions are currently under investigation.[26]

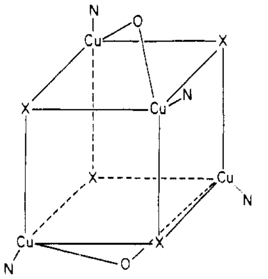

Figure 5. Proposed core structure for $[(DENC)CuX]_4O_2$ complexes.

Solid samples and solutions of $[(DENC)CuX]_4O_2$ in aprotic solvents are stable for long periods provided water is excluded. In particular, they have no tendency to disproportionate into $(DENC)_xCuCl_2$ and $[(DENC)_yCuO]_n$ species, which is in marked contrast to the situation when slurries of copper(I) halides react with dioxygen in pyridine, eq 6.[2,3] In addition,

$$4CuCl(s) + O_2 \xrightarrow{py} 2(py)_2CuCl_2 + [(py)_mCuO]_n \quad (6)$$

$[(DENC)CuX]_4O_2$ does not depend on excess DENC for its existence in solution.

Although we have not yet succeeded in crystallizing $[(DENC)CuX]_4O_2$, it seems likely from the simple stoichiometry and kinetics of their formation that their structures are closely related to that of $[(DENC)CuX]_4$. The $[(DENC)CuX]_4O_2$ complexes rapidly react with carbon dioxide according to eq 7,[27] which has previously been discussed

$$[(DENC)CuX]_4O_2 + 2CO_2 \rightarrow [(DENC)CuX]_4(CO_3)_2 \quad (7)$$

as a Lewis base-acid reaction of μ-oxo (alkyldiamine)copper(II) species, with CO_2 acting as a Lewis acid for accessible, basic μ-oxo copper(II) groups.[7] Neither $[(py)_mCO]_n$ nor $L_3Cu_4Cl_4O_2$ (L = nmp) react with CO_2.[2,5] Since the latter almost certainly contains a μ_4-oxo core and a terminal Cu–O group,[4–6] this is probably not the basic structure of $[(DENC)CuX]_4O_2$: the stoichiometry of eq 7 is more consistent with two *equivalent* Cu–O–Cu structural components in the tetrameric complex. We tentatively conclude that $[(DENC)CuX]_4O_2$ has the basic structure shown in Figure 5. The formation of this structure would require (1) rate-determining insertion of O_2 into the $[(DENC)CuX]_4$ core, (2) its rapid 4-e reduction and concomitant breaking of the O–O bond, and (3) an increase in coordination number from 4 to 5 at each of the four copper centers. The room-temperature magnetic moments of $[(DENC)CuX]_4O_2$ suggest nonlinear Cu–O–Cu groups in the proposed structure.[28]

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Registry No. $[(DENC)CuCl]_4$, 80105-82-4; $[(DENC)CuBr]_4$, 80105-83-5; $[(DENC)CuI]_4$, 80105-84-6; $[(DENC)CuCl]_4O_2$, 80105-85-7; $[(DENC)CuBr]_4O_2$, 80105-86-8; O_2, 7782-44-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, calculated positional and thermal parameters for all hydrogen atoms (Table IIIS), and anisotropic thermal parameters for all nonhydrogen atoms (Table IV) (34 pages). Ordering information is given on any current masthead page.

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(21) Activation parameters were determined from a nonlinear least-squares fit of the data to eq 5 with temperature as an independent variable as previously described.[2]

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(27) Properties and reactions of $[(DENC)CuX]_4(CO_3)_2$ complexes will be described in a separate paper.

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