Contribution from the Departments of Chemistry, State University of New York, Buffalo, New York 14214, Northeastern University, Boston, Massachusetts 02115, and State University of New York, Albany, New York 12222

Crystal and Molecular Structure of Bis(μ-bromo)bis(N,N,N',N'-tetraethylethylenediamine)dicopper(I) and the Kinetics of Its Oxidation by Dioxgen in Nitrobenzene[1]

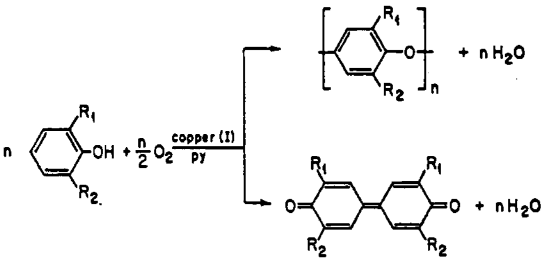
MELVYN ROWEN CHURCHILL,*[2a] GEOFFREY DAVIES,*[2b] MOHAMED A. EL-SAYED,[2b]
JAY A. FOURNIER,[2b] JOHN P. HUTCHINSON,[2a] and JON A. ZUBIETA[2c]

Received July 7, 1983

An X-ray structural determination of the air-sensitive product of reaction of equimolar *N,N,N',N'*-tetraethylethylenediamine, $(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ (TEED), with copper(I) bromide in dioxygen-free methylene chloride has revealed discrete molecular dimers containing 4-coordinate copper(I) centers in bis(μ-bromo)bis(N,N,N',N'-tetraethylethylenediamine)-dicopper(I), $(TEED)_2Cu_2Br_2$. The crystals are triclinic (space group $P\bar{1}$ [C_i^1 No. 2]), with a = 7.860 (2) Å, b = 9.109 (3) Å, c = 19.773 (8) Å, α = 101.04 (3)°, β = 100.68 (3), γ = 90.13 (2)°, V = 1364.4 (8) Å^3, and Z = 2. The principal features of the molecular structure are distorted tetrahedral copper(I) centers with Cu–Cu = 2.606 (6) Å, Cu–Br(bridge) = 2.467 (12) Å and Cu–Br(bridge)–Cu = 63.9 (1)°. Manometric, cryoscopic, and spectral measurements established that the primary product of reaction of $(TEED)_2Cu_2Br_2$ with dioxygen is the dimeric species $(TEED)_2Cu_2Br_2O$, which appears to contain one oxo bridge and two bromo bridges between its 5-coordinate copper(II) centers. The rate law for the reaction of excess $(TEED)_2Cu_2Br_2$ with dioxygen in nitrobenzene is $d[(TEED)_2Cu_2Br_2O]/dt = k_D[(TEED)_2Cu_2Br_2]^2[O_2]$, with $k_D = (5.50 \pm 0.18) \times 10^2\ M^{-2}\ s^{-1}$ at 25.0 °C, $\Delta H_D^* = (12.9 \pm 0.3)$ kcal mol^{-1}, and $\Delta S^* = -(3 \pm 2)$ cal deg^{-1} mol^{-1} at 25.0 °C. A mechanism involving a weak intermediate complex $(TEED)_2Cu_2Br_2O_2$ is suggested. The kinetic data are compared with those observed previously for oxidation of dimeric chloro(pyridine)copper(I) complexes in which the primary products are tetrameric dioxocopper(II) species. Cryoscopic and manometric measurements indicate that the primary oxidation product slowly polymerizes and that its coordinated TEED ligands are subject to slow oxidation by excess dioxygen in aprotic solvents. Both of these processes lessen the effectiveness of the primary oxidation product as an initiator for the oxidative coupling of 2,6-dimethylphenol by dioxygen. They can be prevented by rapid reaction of the primary oxidation product with carbon dioxide, which produces the paramagnetic μ-carbonato complex (μ-CO_3)-*cis*-$Br_2(TEED)_2Cu_2$, an active, stable, oxidative coupling initiator.

Introduction

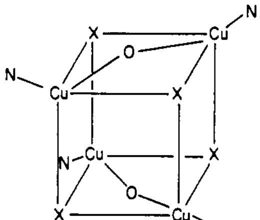
Reactions 1 are an important class of dioxygen reactions that are catalyzed by common amine/copper(I) systems under mild conditions in aprotic solvents.[3-6] Since oxidation of copper(I) by dioxygen is a requirement for catalysis we are studying the products and kinetics of the halo(amine)copper(I) complex–dioxygen reactions under aprotic conditions.[6-13]



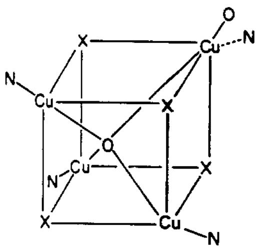
(1a)

(1b)

The strong thermodynamic driving force for complete dioxygen reduction by halo(monodentate amine)copper(I) complexes results in rate laws that are a direct reflection of the copper(I) reactant molecularity.[13,14] Thus, the rate laws for oxidation of $(L_nCuX)_4$, $(L_2CuCl)_2$, and py_2CuCl complexes (L = *N,N*-diethylnicotinamide (DENC), ethyl nicotinate, or pyridine (py); n = 1 or 2; X = Cl or Br) are first order in $[O_2]$ and first, second, or third order, respectively, in the above copper(I) reactants. The products are always $L_mCu_4X_4O_2$ complexes, whose proposed structures I or II depend on the identity of L.[6,13]



I



II

In this paper we discuss the crystal and molecular structure of dimeric $(TEED)_2Cu_2Br_2$, TEED = *N,N,N',N'*-tetraethylethylenediamine, its characterization in solution, and the kinetics of its oxidation by dioxygen in nitrobenzene. As anticipated, the oxidation reaction is third order, consistent with a dimeric copper(I) reactant structure. However, the product is also dimeric, consistent with a preference for 5-coordinate centers in oxohalo(amine)copper(II) species.[13]

Experimental Section

Materials. The preparation and purification of copper(I) bromide, diethyl ether (Fisher), and TEED (Aldrich) were as previously de-

---

(1) A preliminary account of this work was presented at the 185th National Meeting of the American Chemical Society, Seattle WA, March 20-25, 1983; see Abstract INOR 244.

(2) (a) State University of New York at Buffalo. (b) Northeastern University. (c) State University of New York at Albany.

(3) Endres, G. F.; Hay, A. S.; Eustance, J. W. *J. Org. Chem.* **1963**, *28*, 1300.

(4) Finkbeiner, H. L.; Hay, A. S.; White, D. M. In "Polymerization Processes"; Shildknecht, C. E., Skeist, I., Eds.; Wiley-Interscience: New York, 1977; p 537.

(5) Gampp, H.; Zūberbuhler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133.

(6) Davies, G.; El-Sayed, M. A. in "Biochemical and Inorganic Perspectives in Copper Coordination Chemistry"; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: Guilderland, New York, 1983; p 281.

(7) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814 and references therein.

(8) Bodek, I.; Davies, G. *Inorg. Chim. Acta* **1978**, *27*, 213.

(9) Davies, G.; El-Shazly, M. F.; Kozlowski, D. R.; Kramer, C. E.; Rupich, M. W.; Slaven, R. W. *Adv. Chem. Ser.* **1979**, *No. 173*, 178.

(10) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1980**, *19*, 201.

(11) Davies, G.; El-Shazly, M. F.; Rupich, M. W. *Inorg. Chem.* **1981**, *20*, 3757.

(12) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1982**, *21*, 995.

(13) Davies, G.; El-Sayed, M. A.; *Inorg. Chem.* **1983**, *22*, 1257.

(14) Hopf, F. R.; Rogic, M. M.; Wolf, J. F. *J. Phys. Chem.* **1983**, *87*, 4681.

0020-1669/84/1323-0783$01.50/0

Table I. Experimental Data for the Diffraction Study of $(TEED)_2Cu_2Br_2$

(A) Crystal Parameters[a] at 21 °C

cryst size: 0.40 × 0.47 × 0.13 mm space group: $P\bar{1}$ (C_i^1, No. 2)
cryst syst: triclinic

$a = 7.860$ (2) Å	$V = 1364.4$ (8) $Å^3$
$b = 9.109$ (3) Å	$Z = 2$
$c = 19.773$ (8) Å	ρ(calcd) = 1.537 g cm^{-3}
$\alpha = 101.04$ (3)°	$M_r = 631.53$
$\beta = 100.68$ (3)°	$\mu = 44.55$ cm^{-1} for Mo Kα
$\gamma = 90.13$ (2)°	

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα
reflcns measd: $+h, \pm k, \pm l$
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 3°/min (const)
bkgd measmt: stationary at beginning and end of scan each for $^1/_4$th scan time
std reflcns: 3 measd every 97 reflcns [$5\bar{2}\bar{1}$; 051; 0,0,14]; their intensities decreased steadily by 4.0% (av) over the course of data collection

(C) Data for Absorption Correction

hkl	2θ	I_{max}/I_{min}
$1\bar{8}4$	36.76	2.68
$0\bar{7}3$	31.63	2.89
$1\bar{4}3$	19.05	2.95

[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 $\{5\bar{2}\bar{3}\}$, $\{5\bar{3}\bar{2}\}$, $\{5\bar{2}\bar{5}\}$, $\{5\bar{2}\bar{1}\}$, $\{35\bar{1}\}$, $\{35\bar{3}\}$, $\{26\bar{2}\}$, $\{4,\bar{1},\bar{10}\}$, $\{322\}$, $\{3,1,\bar{13}\}$, $\{2,3,12\}$ all with 27° < 2θ < 30°.

Table II. Positional and Isotropic Thermal Parameters, with Esd's, for the Independent Molecules of $(TEED)_2Cu_2Br_2$

atom	*x/a*	*y/b*	*z/c*
		Molecule 1	
Cu(1)	0.39499 (7)	0.11011 (6)	0.00074 (3)
Br(1)	0.29378 (6)	−0.14595 (5)	−0.00086 (3)
N(1)	0.2493 (5)	0.2180 (4)	−0.0797 (2)
N(2)	0.2944 (4)	0.2806 (4)	0.0763 (2)
C(1)	0.2242 (8)	0.3650 (6)	−0.0360 (3)
C(2)	0.1698 (7)	0.3567 (6)	0.0296 (3)
C(11)	0.3492 (7)	0.2465 (6)	−0.1329 (3)
C(12)	0.3963 (8)	0.1086 (8)	−0.1786 (3)
C(13)	0.0880 (6)	0.1288 (6)	−0.1114 (3)
C(14)	−0.0430 (8)	0.1922 (9)	−0.1642 (4)
C(21)	0.4313 (7)	0.3865 (6)	0.1186 (3)
C(22)	0.5610 (7)	0.3215 (7)	0.1686 (3)
C(23)	0.1978 (7)	0.2087 (6)	0.1195 (3)
C(24)	0.1069 (8)	0.3130 (7)	0.1699 (3)
		Molecule 2	
Cu(2)	0.89287 (7)	0.39089 (6)	0.50088 (3)
Br(2)	1.20465 (6)	0.35425 (5)	0.50063 (3)
N(3)	0.7181 (4)	0.2186 (4)	0.4276 (2)
N(4)	0.8308 (4)	0.2846 (4)	0.5836 (2)
C(3)	0.6412 (6)	0.1426 (6)	0.4762 (3)
C(4)	0.7680 (6)	0.1360 (6)	0.5421 (3)
C(31)	0.5774 (6)	0.2888 (5)	0.3854 (3)
C(32)	0.4365 (6)	0.1852 (6)	0.3374 (3)
C(33)	0.8145 (6)	0.1124 (6)	0.3843 (3)
C(34)	0.8967 (7)	0.1794 (6)	0.3336 (3)
C(41)	0.9832 (6)	0.2625 (6)	0.6364 (3)
C(42)	1.0713 (7)	0.4062 (7)	0.6805 (3)
C(43)	0.6951 (6)	0.3693 (6)	0.6150 (3)
C(44)	0.6199 (8)	0.3043 (8)	0.6688 (4)

scribed.[10] Nitrobenzene (Aldrich) was distilled over P_4O_{10} at reduced pressure and stored over 4-Å molecular sieves in the dark. High purity dinitrogen was deoxygenated with a freshly activated column of DE-OX (Alfa) before use.

Synthesis and Physical Characterization of $(TEED)_2Cu_2Br_2$. Solutions of $(TEED)_2Cu_2Br_2$ were prepared by adding equimolar amounts of copper(I) bromide to stirred, deoxygenated solutions of TEED in methylene chloride or nitrobenzene. Colorless, single crystals of the products were obtained by slow addition of deoxygenated diethyl ether to a concentrated solution in methylene chloride. The crystals were much more air stable than the powder obtained by vacuum distillation of the solvent, which rapidly gave a black, insoluble residue on exposure to air. The copper(I) complex was identified cryoscopically in nitrobenzene as described previously,[13] near the mid-range of copper(I) concentrations used for kinetic measurements (see below): found 620 ± 20; calcd for $(TEED)_2Cu_2Br_2$ 631 g/mol.

The X-ray Diffraction of $(TEED)_2Cu_2Br_2$. Data Collection. A carefully selected crystal was mounted on a thin glass fiber, which was fixed (with beeswax) to an aluminum pin mounted in an eucentric goniometer. The crystal was transferred to a Syntex $P2_1$ automated diffractometer. Crystal alignment, checks on crystal quality, determination of cell dimensions, and data collection were carried out as described previously.[15] Details appear in Table I. Data were corrected for absorption via an empirical method based on a series of ψ scans (see Table I), corrected for Lorentz and polarization effects, and reduced to unscaled $|Fo|$ values along with associated $\sigma(F_o)$. A total of 2814 unique reflections with $F_o \geq 6\sigma(F_o)$ were retained.

Solution and Refinement of the Structure. All calculations were performed by using the SHELXTL structure determination package[16] at SUNY Albany. The analytical scattering factors of Cromer and Waber[17a] were used throughout the analysis; both real and imaginary components of anomalous dispersion[17b] were included for all nonhydrogen atoms. The atomic absorption coefficients[17c] in terms of cm^2 were used to calculate the absorption coefficient given in Table I. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights (w) are given by $w = 1(\sigma^2(F_o) + gF^2)$, where $g = 0.0005$.

The positions of the copper and bromine atoms were determined from a three-dimensional Patterson map. A series of difference-Fourier syntheses revealed the remaining non-hydrogen atoms. Least-squares refinement of positional and anisotropic thermal parameters with constrained (idealized) hydrogens led to convergence with $R_F = 3.2\%$, $R_{wF} = 3.09\%$, and "goodness of fit" = 1.099.

A final difference-Fourier synthesis had as its largest feature a peak of height 0.47 e $Å^{-3}$ close to the position of Br(1). The analysis is thus complete. The usual tests of $\sum w(|F_o|) - |F_c|)^2$ vs. $(\sin \theta)/\lambda$, $|F_o|$, and Miller index showed no unusual features. The weighting scheme is therefore satisfactory.

Final positional parameters are collected in Table II;[18a] anisotropic thermal parameters are collected in Table III.[18b]

Stoichiometry and Products of Oxidation of $(TEED)_2Cu_2Br_2$. The stoichiometry of oxidation of $(TEED)_2Cu_2Br_2$ by dioxygen in nitrobenzene and methylene chloride was measured manometrically.[10] Solid products were obtained from nitrobenzene by pouring oxidized solutions into a large excess of anhydrous hexane and from methylene chloride by vacuum evaporation of the solvent. Because of the very slow absorption of more than the theoretical amount of dioxygen on storage of brown oxidized solutions or solid products (see Results) we characterized the primary oxidation product by cryoscopy in nitrobenzene:[13] found 630 ± 20; calcd for $(TEED)_2Cu_2Br_2O$ 647 g/mol.

Synthesis and Characterization of $(TEED)_2Cu_2Br_2CO_3$. The title derivative was synthesized and characterized as described previously[10] and by direct reaction of freshly prepared solutions of $(TEED)_2Cu_2Br_2O$ with excess carbon dioxide. Both procedures resulted in the quantitative formation of $(TEED)_2Cu_2Br_2CO_3$. This derivative was spectrophotometrically titrated with 2,4,6-trichlorophenol, TCPH, at 22 °C in methylene chloride as previously described.[11]

Physical Measurements. Instrumentation and procedures for measuring electronic and IR spectra of reactants and products and for conducting rapid rate measurements of copper(I) oxidation by

---

(15) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(16) "Structure Determination Operation Manual"; Nicolet XRD Corporation: Cupertino, CA, 1980.

(17) "International Tables for X-Ray Crystallography"; Kynoch Press, Birmingham, England, 1974; Vol. 4, (a) pp 99–101; (b) pp 149–150; (c) pp 55–60.

(18) (a) Table IIa (positional and isotropic thermal parameters for hydrogen atoms in the independent molecules of $(TEED)_2Cu_2Br_2$) is collected as supplementary data. (b) Supplementary data.

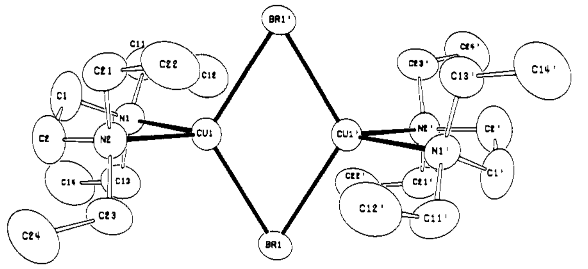


Figure 1. Molecular structure of $(TEED)_2Cu_2Br_2$ with atomic labels.

Table IV. Bond Lengths (Å) for $(TEED)_2Cu_2Br_2$[a]

(A) Copper· · ·Copper and Bromine· · ·Bromine Distances			
Cu(1)· · ·Cu(1')	2.600 (1)	Cu(2)· · ·Cu(2)	2.612 (1)
Br(1)· · ·Br(1')	4.179 (1)	Br(2)· · ·Br(2')	4.177 (1)
(B) Copper-Ligand Distances			
Cu(1)-Br(1)	2.467 (1)	Cu(2)-Br(2)	2.479 (1)
Cu(1)-Br(1')	2.455 (1)	Cu(2)-Br(2')	2.477 (1)
Cu(1)-N(1)	2.176 (4)	Cu(2)-N(3)	2.198 (3)
Cu(1)-N(2)	2.196 (4)	Cu(2)-N(4)	2.181 (4)
(C) Distances within TEED Ligands			
N(1)-C(1)	1.483 (6)	N(3)-C(3)	1.496 (7)
N(1)-C(11)	1.483 (8)	N(3)-C(31)	1.481 (6)
N(1)-C(13)	1.472 (6)	N(3)-C(33)	1.472 (6)
N(2)-C(2)	1.485 (7)	N(4)-C(4)	1.474 (6)
N(2)-C(21)	1.463 (6)	N(4)-C(41)	1.477 (6)
N(2)-C(23)	1.480 (8)	N(4)-C(43)	1.478 (7)
C(1)-C(2)	1.453 (9)	C(3)-C(4)	1.497 (7)
C(11)-C(12)	1.492 (8)	C(31)-C(32)	1.510 (6)
C(13)-C(14)	1.522 (9)	C(33)-C(34)	1.507 (9)
C(21)-C(22)	1.491 (8)	C(41)-C(42)	1.512 (7)
C(23)-C(24)	1.519 (9)	C(43)-C(44)	1.518 (10)

[a] Those atoms with primes are related to those in the basic asymmetric unit by $x', y', z' = 1-x, -y, -z$ for molecule 1 and $x', y', z' = -x, 1-y, 1-z$ for molecule 2.

dioxygen were as prevously described.[13] The conditions for the kinetic measurements were as follows: $10^3[(TEED)_2Cu_2Br_2] = 3.30 - 20.0$ M^{-1}, temperature 20.3–46.5 °C, and monitoring wavelength 500–700 nm. The copper(I) reactant was always in sufficient stoichiometric excess to ensure pseudo-first-order conditions.

Results and Discussion

Description of the Solid-State Geometry of $(TEED)_2Cu_2Br_2$. The molecular geometry and labeling of atoms in one of the two independent molecules in the unit cell are illustrated in Figure 1. Interatomic distances and their esd's are listed in Table IV; bond angles and their esd's are shown in Table V. Each molecule lies about a crystallographic center of symmetry. Each copper(I) atom exhibits a distorted tetrahedral coordination environment. Notable features of the bridging system in the dimeric structure are (1) a Cu–Cu distance (average 2.606 (6) Å in the two independent unit-cell molecules) that is comparable to that in copper metal (2.56 Å),[19] $[(DENC)CuI]_4$ (2.68 Å),[12] and a variety of binuclear copper(II) carboxylates (2.56–2.89 Å),[20] (2) an extremely acute Cu-Br-Cu bridging angle (average 63.9 (1)°), and (3) a Br-Br distance (average 4.178 (1) Å) that exceeds the sum of the van der Waals radii for bromine (3.9 Å).[21]

Spectral Properties of $(TEED)_2Cu_2Br_2$. Room-temperature electronic spectral maxima for TEED and $(TEED)_2Cu_2Br_2$ in methylene chloride are collected in Table VI. There are no significant differences between the IR spectra (400–3500 cm^{-1}) of TEED and $(TEED)_2Cu_2Br_2$.

Table V. Interatomic Angles (deg), with Esd's, for $(TEED)_2Cu_2Br_2$[a]

(A) Angles about Copper Atoms			
Br(1)-Cu(1)-Br(1')	116.2 (1)	Br(2)-Cu(2)-Br(2')	116.0 (1)
Br(1)-Cu(1)-N(1)	108.1 (1)	Br(2)-Cu(2)-N(3)	114.3 (1)
Br(1)-Cu(1)-N(2)	114.0 (1)	Br(2)-Cu(2)-N(4)	106.8 (1)
Br(1')-Cu(1)-N(1)	115.3 (1)	Br(2')-Cu(2)-N(3)	113.5 (1)
Br(1')-Cu(1)-N(2)	113.5 (1)	Br(2')-Cu(2)-N(4)	116.5 (1)
N(1)-Cu(1)-N(2)	85.9 (1)	N(3)-Cu(2)-N(4)	86.1 (1)
Cu(1)-Br(1)-Cu(1')	63.8 (1)	Cu(2)-Br(2)-Cu(2')	64.0 (1)
(B) Angles within the TEED Ligand			
Cu(1)-N(1)-C(1)	99.7 (3)	Cu(2)-N(3)-C(3)	102.3 (3)
Cu(1)-N(1)-C(11)	114.0 (3)	Cu(2)-N(3)-C(31)	110.5 (3)
Cu(1)-N(1)-C(13)	108.5 (3)	Cu(2)-N(3)-C(33)	111.3 (3)
C(1)-N(1)-C(11)	107.3 (4)	C(3)-N(3)-C(31)	108.5 (4)
C(1)-N(1)-C(13)	114.4 (4)	C(3)-N(3)-C(33)	110.6 (4)
C(11)-N(1)-C(13)	112.4 (4)	C(31)-N(3)-C(33)	113.1 (4)
Cu(1)-N(2)-C(2)	102.2 (3)	Cu(2)-N(4)-C(4)	99.9 (3)
Cu(1)-N(2)-C(21)	111.8 (3)	Cu(2)-N(4)-C(41)	113.9 (3)
Cu(1)-N(2)-C(23)	110.4 (3)	Cu(2)-N(4)-C(43)	108.8 (3)
C(2)-N(2)-C(21)	110.5 (4)	C(4)-N(4)-C(41)	107.6 (4)
C(2)-N(2)-C(23)	108.7 (4)	C(4)-N(4)-C(43)	113.1 (4)
C(21)-N(2)-C(23)	112.7 (4)	C(41)-N(4)-C(43)	112.9 (4)
N(1)-C(1)-C(2)	114.7 (5)	N(3)-C(3)-C(4)	112.2 (4)
C(1)-C(2)-N(2)	113.3 (5)	C(3)-C(4)-N(4)	113.5 (4)
N(1)-C(11)-C(12)	114.4 (5)	N(3)-C(31)-C(32)	116.9 (4)
N(1)-C(13)-C(14)	117.4 (5)	N(3)-C(33)-C(34)	114.3 (4)
N(2)-C(21)-C(22)	114.6 (4)	N(4)-C(41)-C(42)	114.2 (4)
N(2)-C(23)-C(24)	116.3 (5)	N(4)-C(43)-C(44)	117.2 (5)

[a] See footnote *a* in Table IV.

Table VI. Electronic Spectra Data for Reactants and Oxidation Products

compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
TEED	265 (280 sh)[a]
$(TEED)_2Cu_2Br_2$	280 (2250), 320 (720), 500 (35 sh)
$(TEED)_2Cu_2Br_2O$	280 (4400), 320 (5300), 500 (380 sh), 700 (265)
$(TEED)_2Cu_2Br_2CO_3$[b]	270 (4560), 320 (5400), 492 (360), 713 (320)
$(TEED)_2Cu_2Cl_2CO_3$[b]	300 (6700), 760 (285)

[a] sh = shoulder. [b] Data from ref 10.

Stoichiometry and Products of Oxidation. As described in the Experimental Section, dimeric $(TEED)_2Cu_2Br_2$ reacts with dioxygen in nitrobenzene to produce dimeric $(TEED)_2Cu_2Br_2O$ as the primary reaction product (eq 2). This conclusion is

$$2(TEED)_2CuBr_2 + O_2 \rightarrow 2(TEED)_2Cu_2Br_2O \qquad (2)$$

based on cryoscopic measurements in nitrobenzene for the copper(I) reactant and for the oxidation product surviving for time periods at least 10 times greater than those necessary for complete oxidation of copper(I), as indicated by direct dioxygen uptake and kinetic measurements.

Such freshly oxidized solutions are highly effective initiators for reaction 1b, but on long standing their effectiveness decreases and cryoscopic measurements indicate a progressive increase in solute molecular weight, presumably due to initiator polymerization.[7] Stored dry solid $(TEED)_2Cu_2Br_2O$ samples become progressively more insoluble in nitrobenzene, which is also consistent with this conclusion. Polymerization can be prevented by treatment of freshly oxidized solutions with carbon dioxide, which gives $(TEED)_2Cu_2Br_2CO_3$, a stable and effective initiator for reaction 1b.[10]

Coordinated TEED in $(TEED)_2Cu_2Br_2O$ is very slowly oxidized in aprotic solvents in the presence of excess dioxygen, as established by manometric measurements[9] (TEED, $(TEED)_2Cu_2Br_2CO_3$, and $[(DENC)CuBr]_4O_2$ are stable to oxidation over similar time periods). Chemical tests for Br_2 in the ultimate green product solutions were negative. The TEED oxidation stoichometry approaches 6 mol of O_2/mol of TEED over a period of 3–5 days at room temperature,

---

(19) Sutton, L. E., Ed., "Table of Interatomic Distances and Configurations in Molecules and Ions"; Spec. Pub. No. 18; The Chemical Society London, 1965; Spec. Pub. No. 18, supplement.

(20) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259.

(21) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 260.

suggesting reaction 3, which is analogous to that for oxidation of the methyl group of 2-methylpyridine coordinated to oxocopper(II).[9]

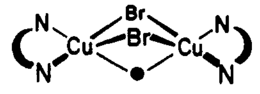
$$-CH_2-CH_3 + 1.5O_2 \rightarrow -CH_2-COOH + H_2O \quad (3)$$

Although we have not isolated any $(TEED)_2Cu_2Br_2O$ decomposition products, it is noted that this complex is subject to slow polymerization and to slow oxidation by excess dioxygen.

Product Spectra. The room-temperature electronic spectra of $(TEED)_2Cu_2Br_2O$, $(TEED)_2Cu_2Br_2CO_3$,[10] and $(TEED)_2Cu_2Cl_2CO_3$[10] in methylene chloride are summarized in Table VI. Strong spectral similarities are evident in the bromo complexes, the molar absorptivities increasing and a new maximum appearing near 700 nm on oxidation of copper(I) to copper(II). The longest wavelength spectral maximum is observed for $(TEED)_2Cu_2Cl_2CO_3$, which has no discernible shoulder in its spectrum at 500 nm.[10]

The spectra of all these copper(II) complexes (see, e.g., Figure 4 of ref 10) are characteristic of 5-coordinate copper(II) centers in dimeric structures and are fundamentally different from those of 5-coordinate copper(II) centers in tetrameric structures I and II, which consist of two components in the near-IR region with much higher molar absorptivities (see, e.g., Figure 1 of ref 13). From these spectral comparisons and our cryoscopic measurements we can be sure that $(TEED)_2Cu_2Br_2O$ contains 5-coordinate copper(II) centers in a dimeric structure.

The major IR spectral consequence of oxidation of $(TEED)_2Cu_2Br_2$ with dioxygen in aprotic solvents is the appearance of a new strong band at 600 cm^{-1} and a medium intensity doublet at 490, 475 cm^{-1}. Although we have been unable to crystallize the product $(TEED)_2CuBr_2O$ in the absence of decomposition,[22] we tentatively conclude that it has structure III for the following reasons.



III

(1) The IR band at 510 cm^{-1} in the spectrum of $(TEED)_2Cu_2Br_2CO_3$ has been assigned to ν_{CuO} from a comparison of data for variety of oxocopper(II) complexes.[9,10,12,13] A stiff, relatively electron-rich bridge structure in III would be expected to increase the frequency of this transition, which is 50–100 cm^{-1} greater than those observed in known (μ-carbonato)- and (μ-oxo)copper(II) complexes.[10,13]

(2) With the spectral evidence for 5-coordinate copper(II) centers at hand we can tentatively assign the 490, 475 cm^{-1} doublet to ν_{Cu-Br} in III, where the bromine atoms are part of a "stiff" (O, Br, Br) bridging structure. Five-coordinate copper(II) centers are also present in I, but in this case the bridging halogen atoms are 3-coordinate and ν_{Cu-Br} might be expected at even higher frequency. ν_{Cu-Br} has not been detected in structures I or II, presumably because of band overlaps.

The primary oxidation product $(TEED)_2Cu_2Br_2O$ reacts quantitatively with carbon dioxide according to eq 4. The

$$(TEED)_2Cu_2Br_2O + CO_2 \rightarrow (TEED)_2Cu_2Br_2CO_3 \quad (4)$$

product of reaction 4 reacts in two distinct stoichiometries (1:1 and 1:2) with TCPH in methylene chloride (established spectrophotometrically as in ref 11), indicating that the terminal bromines have a cis configuration with respect to an asymmetrical carbonate bridge ($\mu_{eff}(300\ K) = 1.08\ \mu_B$).[10] Much more information will be needed in order to understand how a μ(asym-CO_3)–*cis*-Br_2 product arises from addition of CO_2 to the formally symmetrical structure III. This result seems to be the rule rather than the exception in reactions analogous to 4 if diamagnetism is an indicator of (sym-μ-CO_3)–*trans*-dihalo geometries.[10]

Table VII. Kinetic Parameters for $(TEED)_2Cu_2Br_2$ Oxidation by Dioxygen in Nitrobenzene

temp, °C	$10^{-2}k_D$, $M^{-2}\ s^{-1}$	temp, °C	$10^{-2}k_D$, $M^{-2}\ s^{-1}$
20.3	4.13 ± 0.10	34.0	13.3 ± 0.9[b]
23.3	5.40 ± 0.19	40.3	17.0 ± 1.2
24.5	5.51 ± 0.15[a]	46.5	27.3 ± 1.6

[a] $\Delta H_D^{\ddagger} = (12.9 \pm 0.3)$ kcal mol^{-1}. [b] $\Delta S_D^{\ddagger} = -(3 \pm 2)$ cal $deg^{-1}\ mol^{-1}$ at 25 °C.

If structure III were to dimerize to give a symmetrical tetrametric dioxocopper(II) complex analogous to I, then all copper(II) centers would have to be six-coordinate. We have found no evidence for tetramer formation is this system, and, as we shall see, the kinetic results in the next section are distinctly different from those governing monodentate pyridine ligand systems.

Kinetics of Oxidation. Plots of ln $(A_\infty - A_t)$ vs. times, where A_t is the absorbance at time t, were linear for at least 4 half-lives under pseudo-first-order conditions with $(TEED)_2Cu_2Br_2$ in excess in the reaction with dioxygen, establishing that the oxidation reaction is first order in $[O_2]$ and either that reaction intermediates are not formed in significant concentrations or that they do not absorb appreciably at the monitoring wavelengths. Under otherwise fixed experimental conditions the pseudo-first-order rate constant k_{obsd} was independent of monitoring wavelength between 550 and 700 nm and of $[O_2]_0$. Although plots of k_{obsd} vs. $[(TEED)_2Cu_2Br_2]$ were concave upward, k_{obsd} was found within experimental error to be a linear function of $[(TEED)_2Cu_2Br_2]^2$. The rate law for oxidation of copper(I) is thus eq 5. This rate law

$$d[(TEED)_2Cu_2Br_2O]/dt = k_D[(TEED)_2CuBr_2]^2[O_2] \quad (5)$$

appears to be characteristic for aprotic oxidation of dimeric halo(amine)copper(I) complexes by dioxygen.[6,13]

Measured values of the third-order rate constant k_D and its associated activation parameters are presented in Table VII. The linear Arrhenius plot demonstrates that rate law 5 is obeyed in the temperature range 20.3–46.5 °C in nitrobenzene; thus, the copper(I) reactant is always dimeric under the experimental conditions employed.

The mechanism given in eq 6 and 7 is consistent with rate

$$Cu^I_2 + O_2 \overset{K_6}{\rightleftharpoons} Cu_2O_2 \quad (6)$$

$$Cu^I_2 + Cu_2O_2 \xrightarrow{k_7} 2Cu^{II}_2O \quad (7)$$

law 5, where Cu^I_2 represents $(TEED)_2Cu_2Br_2$ and Cu^{II}_2O its oxidation product.

Here, an intermediate[6,13] Cu_2O_2 is involved in a rapid equilibrium prior to rate-determining step 7.[13] There is no direct spectrophotometric evidence for significant concentrations of any such intermediate at $t = 0$ in the kinetic studies, so either K_6 is small or the intermediate only weakly absorbs visible light. For this mechanism it easily can be shown that $k_D = K_6k_7$ in eq 5 if $K_6[(TEED)_2Cu_2Br_2] \lesssim 0.1$ at the highest $[(TEED)_2Cu_2Br_2]$ employed;[13] this corresponds to $K_6 \lesssim 5\ M^{-1}$ at 20.3 °C in nitrobenzene.[23]

---

(22) Disproportionation on attempted crystallization is a frustrating property of primary oxocopper(II) products.[13]

(23) We have no direct information on the configuration or electronic constitution of the putative intermediate Cu_2O_2. We were surprised to find that K_6 is not large enough to be measurable, since a peroxo $(Cu^{II}_2O_2{}^{2-}$ constitution might be stabilized by hard TEED ligands. The facts that $K_6 \lesssim 5$ M and that the Cu–Cu separation in $(TEED)_2Cu_2Br_2$ is only ca. 2.61 Å would lead us to formulate Cu_2O_2 as indicated in ref 6.

Detailed comparison of the kinetic data for the present system with those for oxidation of other dimeric halo(amine)copper(I) complexes by dioxygen[13] is not straightforward because k_D is regarded as a composite parameter. This amounts to saying that variation in k_D for oxidation of a series of dimeric $L_4Cu_2X_2$ (L monodentate) or $(L\text{–}L)_2Cu_2X_2$ (L–L bidentate) complexes can be ascribed to variations in K_6 and k_7 or both if the suggested mechanism is general.

There are two major differences between the present system and those referring to tetrameric $[L_nCuX]_4$ and dimeric $[L_2CuCl]_2$ copper(I) oxidation.[6,13] First, the product of oxidation of $(TEED)_2Cu_2Br_2$ is dimeric, whereas monodentate pyridine ligand systems give tetrameric $[L_4Cu_4X_4]O_2$ products.[6,13] Second, $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ for $(TEED)_2Cu_2Br$ oxidation (Table VII) are substantially more positive than those observed in the monodentate pyridine ligand systems (where $\Delta H_T^{\ddagger}$ = 2.1–5.9 kcal mol^{-1}; $\Delta S_T^{\ddagger}$ = –(35–48) cal deg^{-1} mol^{-1}; $\Delta H_D^{\ddagger}$ = 0–1.4 kcal mol^{-1}; $\Delta S_D^{\ddagger}$ = –(38–39) cal deg^{-1} mol^{-1}).[6,13]

Acknowledgment. We gratefully acknowledge financial support for this work through Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Faculty Research Grant 7590 from Northeastern University (G.D.).

Registry No. $(TEED)_2Cu_2Br_2$, 88510-91-2; $(TEED)_2Cu_2Br_2O$, 88510-92-3; $(TEED)_2Cu_2Br_2CO_3$, 72029-99-3; TCPH, 88-06-2; Cu, 7440-50-8.

Supplementary Material Available: Positional and isotropic thermal parameters for hydrogen atoms in the independent molecules of $(TEED)_2Cu_2Br_2$ (Table IIa), anisotropic thermal parameters (Table III), and a listing of observed and calculated structure factors for $(TEED)_2Cu_2Br_2$ (20 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
University of Nebraska—Lincoln,
Lincoln, Nebraska 68588-0304

Preparation of Activated Cobalt and Its Use for the Preparation of Octacarbonyldicobalt

G. L. Rochfort and R. D. Rieke*

Received March 16, 1983

Transition-metal carbonyl complexes have played a very important role in the development of modern organometallic chemistry and have continued to attract attention because of their diverse chemistry and their potential value as stoichiometric and catalytic reagents for synthesis.[1] Among the many preparative methods that exist for metal carbonyls, only a very limited number of transition metals have been demonstrated to react directly with carbon monoxide to give reasonable quantities of metal carbonyl complexes. Nickel and iron are the prototypic examples of the direct reaction of transition metals with carbon monoxide to give $Ni(CO)_4$ and $Fe(CO)_5$, respectively.[2] Finely divided chromium prepared by the reduction of $CrCl_3\cdot3THF$ with potassium in benzene has been found to be sufficiently activated to react with carbon monoxide at 280 atm and 220 °C to form $Cr(CO)_6$ in 51% yield.[3]

The method first used to prepare $Co_2(CO)_8$[4] was the reaction of carbon monoxide in the absence of solvent at 30–40 atm and 150 °C with finely divided cobalt prepared by the high-temperature hydrogen reduction of cobalt oxalate. Since that time other workers have also succeeded in preparing the carbonyl from elemental cobalt. For example, when cobalt carbonate containing sulfur was impregnated on infusorial earth, reduced with hydrogen at 400 °C, and then carbonylated at 120 °C and 100 atm, yields of $Co_2(CO)_8$ up to 97% were obtained.[5] A pelletized reduced cobalt oxide was reported to give good yields of $Co_2(CO)_8$ at 170 °C and very high pressures of carbon monoxide (700–1000 atm).[6]

More commonly used methods for the preparation of $Co_2(CO)_8$ involve reduction of cobalt(II) salts with high-pressure hydrogen–carbon monoxide mixtures at elevated temperatures. For example, hydrated cobalt(II) acetate in acetic anhydride at 160–180 °C under 40 atm of hydrogen and 160 atm of carbon monoxide gave a 60% yield of $Co_2(CO)_8$.[7] Hydrated cobalt carbonate reacts with 1:1 hydrogen–carbon monoxide at 238 atm and 150–160 °C in petroleum ether to give $Co_2(CO)_8$ in a 53% yield.[8] An indirect preparation of $Co_2(CO)_8$ used $Co(NO_3)_2$, KCN, and KOH under 1 atm of carbon monoxide to give potassium tetracarbonylcobaltate.[9] This material was then acidified to give the hydride, $HCo(CO)_4$, which was decomposed at 100 °C to produce hydrogen and $Co_2(CO)_8$.

As part of our continuing program of preparing highly reactive metal powders and utilizing them for synthetic purposes,[10] we wish to report here the preparation of $Co_2(CO)_8$ from cobalt metal in good yields under relatively mild conditions. The reduction of anhydrous cobalt halides with alkali metals in ethereal solvents in the presence of a catalytic amount of naphthalene has previously been reported to give a very reactive form of cobalt.[10b,c]

A more reactive form of cobalt resulted however when the cobalt halide was added to a cold solution of preformed lithium naphthalide. It is not clear whether the reaction was actually a homogeneous reduction of dissolved and solvated cobalt

---

(1) Hieber, W. *Adv. Organomet. Chem.* **1970**, *8*, 1. Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. Wender, I.; Pino, P. "Organic Synthesis Via Metal Carbonyls"; Wiley-Interscience: New York, 1968, Vol. 1; 1977, Vol 2. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980, Chapters 8, 9.

(2) Cotton, F. A.; Wilkinson, G. "Comprehensive Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 1061.

(3) Rieke, R. D.; Öfele, K.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *76*, C19.

(4) Mond, L.; Hirtz, H.; Cowap, M. D. *J. Chem. Soc.* **1910**, 798; *Z. Anorg. Allg. Chem.* **1910**, *68*, 207.

(5) Yamamoto, K.; Sato, K. Jpn. Pat. 985, March 9, 1953; *Chem. Abstr.* **1954**, *48*, 2996. It should be noted that this abstract gives the cobalt carbonyl obtained as being $Co(CO)_3$. Presumably this is meant to be $Co_4(CO)_{12}$.

(6) Arthur, P.; England, D. C.; Prat, B. C.; Whitman, G. M. *J. Am. Chem. Soc.* **1954**, *76*, 5364.

(7) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 98.

(8) Wender, I.; Sternberg, H. W.; Metlin, S.; Orchin, M. *Inorg. Synth.* **1957**, *5*, 190. Wender, I.; Greenfield, H.; Orchin, M. *J. Am. Chem. Soc.* **1951**, *73*, 2656.

(9) Gilmont, P.; Blanchard, A. *Inorg. Synth.* **1946**, *2*, 238.

(10) For example, see the following and references therein: (a) Inaba, S.; Matsumoto, H.; Rieke, R. D. *Tetrahedron Lett.* **1982**, *23*, 4125. (b) Kavaliunas, A. V.; Taylor, A.; Rieke, R. D. *Organometallics* **1983**, *2*, 377. (c) Kavaliunas, A. V.; Rieke, R. D.; *J. Am. Chem. Soc.* **1980**, *102*, 5944. (d) Rieke, R. D.; Bales, S. E.; Hudnall, P. M.; Poindexter, G. S. *Org. Synth.* **1979**, *59*, 85. (e) Rieke, R. D.; Rhyne, D. L. *J. Org. Chem.* **1979**, *44*, 3445. (f) Rieke, R. D.; Kavaliunas, A. V. *Ibid.* **1979**, *44*, 3069. (g) Rieke, R. D.; Kavaliunas, A. V.; Rhyne, D. L.; Frazier, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 246.

0020-1669/84/1323-0787$01.50/0