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Synthesis, Physical Properties, and Structural Characterization of μ-Carbonato-dichlorobis(*N,N,N',N'*-tetramethyl-1,3-propanediamine)dicopper(II), LCuCl(CO_3)ClCuL, a Diamagnetic Initiator for the Oxidative Coupling of Phenols by Dioxygen

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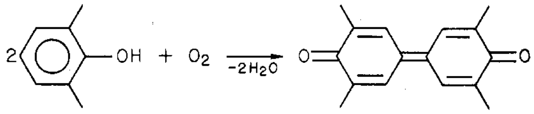
The reaction of *N,N,N',N'*-tetramethyl-1,3-propanediamine (L) with copper(I) chloride, carbon dioxide, and dioxygen in anhydrous methylene chloride gives a quantitative yield of the dinuclear μ-carbonato-dicopper(II) species LCuCl(CO_3)ClCuL, which acts as an initiator for the oxidative coupling of phenols by dioxygen. This complex is *diamagnetic* and has been studied by spectroscopic methods and by a three-dimensional X-ray structural analysis. The complex crystallizes in the noncentrosymmetric orthorhombic space group $P22_12_1$ with a = 8.0832 (15) Å, b = 11.6855 (14) Å, c = 11.9301 (17) Å, V = 1126.9 (3) Å^3, and ρ(calcd) = 1.528 g cm^{-3} for mol wt 518.47 and Z = 2. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was solved by standard methods, resulting in R_F = 2.90% and R_{wF} = 3.07% for all 2232 reflections in the range 2θ = 3–50° (Mo Kα radiation). The molecule consists of two units of ($Me_2NCH_2CH_2CH_2NMe_2$)CuCl which are bridged by a carbonate ligand. One oxygen atom of the carbonate ligand is bonded to both copper(II) ions (Cu–O(1) = Cu'–O(1) = 2.1527 (4) Å), while the other two oxygen atoms are each linked to one copper atom (Cu–O(2) = Cu'–O(2)' = 1.978 (2) Å). The molecule possesses precise C_2 symmetry and presumably owes its diamagnetic character to antiferromagnetic exchange across the almost linear Cu–O(1)–Cu' system (Cu–O(1)–Cu' = 170.26 (13)°).

Introduction

There is much current interest in the copper metalloproteins, especially with regard to the synthesis and characterization of model systems.[2-10] Recently proposed model copper(II) complexes have similar spectral and/or electrochemical properties to those in vivo.[3,9,10,11] Certain of the metalloenzymes and several of the model systems catalyze the oxidation of phenols (e.g., eq 1) and catechols by dioxygen, but the mechanisms of these reactions are not well understood.[12-17]



(1)

A systematic search is being made in our laboratories to identify ligand systems which (a) promote the aprotic oxidation of copper(I) salts by dioxygen, (b) stabilize the resulting copper(II)-reduced oxygen interaction, (c) are not subject to oxidative decomposition in the presence of the copper(II)-reduced oxygen products and excess dioxygen, and (d) provide efficient catalysts for oxidative coupling reactions of dioxygen.[18]

The rationale behind our studies of the aprotic oxidation of copper(I) by dioxygen is twofold. First, the copper(II)-reduced oxygen initiators for reactions such as (1) are most effective under anhydrous conditions. Second, it has been proposed[19] that the active sites of some copper metalloenzyme oxidases are essentially hydrophobic, and therefore possibly analogous to the systems we are investigating.

Examples of ligands which satisfy requirements (a)–(d) are pyridine[18,20-22] (eq 2) and *N*-methyl-2-pyrrolidinone, nmp (eq 3).[18,23,24]

$$4CuCl + O_2 \xrightarrow[5-80\ °C]{py} 2(py)_2CuCl_2 + 2\text{“}(py)_nCuO\text{”} \quad (2)$$

$$4CuCl + O_2 \xrightarrow[25\ °C]{nmp} (nmp)_3Cu_4Cl_4O_2 \quad (3)$$

Although the primary copper(II)-reduced oxygen product in eq 2 does not appear to be isolable as a stable solid material, cryoscopic measurements on product solutions have established that it is a growing, pyridine-coordinated CuO polymer.[20,21]

Stoichiometric and cryoscopic measurements on product solutions from eq 3 have shown the product is an extremely reactive tetrameric cluster.[23,24] We have been unable to structurally characterize this product, but the structure of a crystalline derivative, $(nmp)_3Cu_4Cl_6O(OH_2\cdots nmp)$, has recently been determined by Churchill and Rotella.[24] These tetrameric, clustered products are stabilized by coordination through the oxygen atom of nmp.

Experiments with these and other oxidatively stable ligand systems[18] illustrate that a major driving force for the oxidation of copper(I) complexes by dioxygen is the formation of copper(II)-reduced oxygen bonds and that monodentate amines (including pyridine) are incapable of preventing the ultimate production of solid copper(II) oxide.

A primary goal of this research is to isolate and structurally characterize discrete, copper(II)-reduced oxygen catalysts with time-independent properties[20] so that detailed mechanistic studies of oxidative coupling reactions of dioxygen under aprotic conditions can be undertaken. As a means of stabilizing such copper(II)-reduced oxygen products we are currently investigating the aprotic oxidation of copper(I) by dioxygen in the presence of alkylated polyamines.[18] In this paper we report the properties and structural characterization of the diamagnetic μ-carbonato-dicopper(II) oxidative coupling catalyst LCuCl(CO_3)ClCuL that results from the reaction of copper(I) chloride with dioxygen and carbon dioxide in the presence of *N,N,N',N'*-tetramethyl-1,3-propanediamine, L.

Experimental Section

A. Synthesis and Physical Measurements. Materials. *N,N,N',N'*-Tetramethyl-1,3-propanediamine (Aldrich) was distilled under reduced pressure before use. Methylene chloride (Baker or Burdick and Jackson) was distilled from phosphorus(V) oxide and stored over 4-Å molecular sieves. Copper(I) chloride was prepared and purified as described previously.[20] Nitrobenzene was distilled from phosphorus(V) oxide immediately before use, and diethyl ether was dried over $CaCl_2$ and then distilled from sodium/benzophenone. Tetrabutylammonium iodide (TBAI) and perchlorate (TBAP) samples (Eastman) were recrystallized from ethanol and dried under high vacuum.

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Table I. Experimental Data for the X-ray Diffraction Study

A. Crystal Parameters[a] at 24 °C

cryst system: orthorhombic
space group: $P22_12_1$[b]
$a = 8.0832$ (15) Å
$b = 11.6855$ (14) Å
$c = 11.9301$ (17) Å
$V = 1126.9$ (3) Å^3
$Z = 2$
ρ(calcd) = 1.528 g cm^{-3}
mol wt = 518.47

B. Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα (λ 0.710 730 Å)
monochromator: highly oriented (pyrolitic) graphite
rflcns measd: $+h$, $+k$, $\pm l$
scan type: coupled θ(crystal)–2θ(counter)
2θ range: 3–50°
scan rate: 4.0°/min
scan width: $[2\theta(K\alpha_1) - 0.9]° - [2\theta(K\alpha_2) + 0.9]°$
bkgd estimation: stationary crystal, stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std rflcns: 3 every 97 rflcns; no decay observed
rflcns collected: 2232 independent rflcns under point group D_2 (222)
abs coeff: $\mu = 21.6$ cm^{-1}; no abs correcns were deemed to be necessary, since a series of ψ scans at various 2θ values showed intensity variations no greater than 5%

[a] Unit cell parameters are from a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections of the forms {027}, {174}, {434}, and {360}, with 2θ = 25–29°. [b] Nonstandard setting of $P2_12_12$ [$D_2{}^3$; No. 18] having the equipoints (x, y, z), $(x, \bar{y}, \bar{z})$, $(\bar{x}, {}^1/_2 + y, {}^1/_2 - z)$, and $(\bar{x}, {}^1/_2 - y, {}^1/_2 + z)$.

Table II. Final Positional Parameters, with Esd's

atom	x	y	z	B_{iso}, Å^2
Cu	0.80917 (4)	0.85145 (3)	0.89439 (3)	
Cl	0.72448 (11)	0.93318 (7)	0.71919 (7)	
O(1)	0.7866 (3)	1.0000	1.0000	
O(2)	1.0191 (2)	0.9225 (2)	0.9435 (2)	
N(1)	0.5930 (3)	0.7734 (2)	0.9407 (2)	
N(2)	0.9312 (3)	0.7093 (2)	0.8387 (2)	
C	0.9473 (5)	1.0000	1.0000	
C(1)	0.5433 (4)	0.6794 (3)	0.8648 (2)	
C(2)	0.6726 (5)	0.5886 (3)	0.8451 (3)	
C(3)	0.8208 (5)	0.6273 (3)	0.7793 (3)	
Me(11)	0.6102 (5)	0.7310 (4)	1.0581 (3)	
Me(12)	0.4575 (4)	0.8583 (3)	0.9413 (4)	
Me(21)	1.0186 (4)	0.6525 (3)	0.9329 (2)	
Me(22)	1.0597 (4)	0.7477 (3)	0.7581 (3)	
H(1A)[a]	0.5099	0.7112	0.7951	4.58
H(1B)	0.4520	0.6416	0.8986	4.58
H(2A)	0.6228	0.5277	0.8044	5.64
H(2B)	0.7100	0.5610	0.9156	5.64
H(3A)	0.7849	0.6610	0.7110	4.77
H(3B)	0.8866	0.5619	0.7634	4.77
H(11A)	0.6974	0.6765	1.0577	5.70
H(11B)	0.5114	0.6957	1.0839	5.70
H(11C)	0.6382	0.7926	1.1064	5.70
H(12A)	0.4398	0.8872	0.8678	5.94
H(12B)	0.3593	0.8226	0.9674	5.94
H(12C)	0.4861	0.9195	0.9900	5.94
H(21A)	0.9409	0.6269	0.9871	4.94
H(21B)	1.0795	0.5890	0.9052	4.94
H(21C)	1.0922	0.7058	0.9665	4.94
H(22A)	1.0104	0.7846	0.6955	5.68
H(22B)	1.1199	0.6827	0.7333	5.68
H(22C)	1.1327	0.7994	0.7946	5.68

[a] Hydrogen atoms are in idealized positions (staggered, where appropriate) 0.950 Å from the attached tetrahedrally surrounded carbon atom. Isotropic thermal parameters were assigned (at the time of entry) the value $B(H_i) = \{B(C_i) + 1.0\}$ Å^2.

Synthesis of μ-Carbonato-dichlorobis(N,N,N',N'-tetramethylpropanediamine)dicopper(II), LCuCl(CO_3)ClCuL. A solution of the diamine ligand (0.84 mL, 5 mmol) in 30 mL of anhydrous methylene chloride was flushed with dry CO_2 for 15 min. Copper(I) chloride (0.5 g, 5 mmol) was then added under CO_2. The mixture was stirred with a stream of CO_2 until all the solid had dissolved to give a colorless solution. At this point, both CO_2 and dry O_2 were passed through the solution, rapidly producing an apple green solution. After an additional 10 min, the gas streams were stopped, and the methylene chloride was removed in a rotary evaporator, leaving an apple green solid. Anal.[25] Calcd for $C_{15}H_{36}N_4O_3Cl_2Cu_2$: C, 34.7; H, 7.0; N, 10.8; Cu, 24.5. Found: C, 33.4; H, 6.9; N, 10.3; Cu, 24.8. Mp (uncor) 124–126 °C. The product yield was quantitative.

Experiments with a twofold excess of diamine gave the same product after removal of the excess ligand by column chromatography on Biobeads SX-12 gel permeation resin with methylene chloride as the eluent.[18,20]

Single crystals of the product were obtained as follows. Five milliliters of a 20–100 mM solution of LCuCl(CO_3)ClCuL in methylene chloride in a 10-mL beaker was placed in a 200-mL jar containing 20 mL of anhydrous diethyl ether. The jar was closed and allowed to stand at room temperature for 12–24 h, whereupon single crystals formed along the sides and on the bottom of the beaker. The analytical data and spectral parameters of single crystals obtained in this manner were indistinguishable from those of the starting material.

The molecular weight of the product was determined in nitrobenzene (mp 5.7 °C, $K_f = 7.0$ °C/m with benzil as a standard) as previously described.[20]

Stoichiometry Measurements. The copper(I) chloride complex $L_2Cu_2Cl_2$ was prepared on a vacuum line in oxygen-free methylene chloride. Oxygen was then introduced into the system, and its uptake was measured as described previously.[20]

Spectral Measurements. Electronic spectra for the product were recorded at room temperature in a Cary Model 14 spectrophotometer for solutions in anhydrous methylene chloride, nitrobenzene, 1,2-dichloroethane, and 1-propanol. Infrared spectra of the product were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with the polystyrene absorption at 908 cm^{-1}, both in KBr disks and in methylene chloride solution. The EPR spectrum of a powdered product sample was measured in a Varian Model E-9 spectrometer at 77 K.

Magnetic Measurements. The magnetic susceptibility of the powdered product was measured at 25 °C with a Princeton Applied Research Model FM-1 vibrating-sample magnetometer calibrated with $HgCo(SCN)_4$.

Electrochemical Measurements. Polarographic data for product solutions in anhydrous methylene chloride (with 0.1 M tetrabutylammonium perchlorate, TBAP, as the supporting electrolyte) were obtained with a Princeton Applied Research Model 174 polarographic analyzer in the conventional and differential-pulse modes. The cyclic voltammeter employed an Analog Devices 514K operational amplifier together with previously described circuits for the potentiostat, current supply, and voltage follower.[26] A hanging mercury drop (Brinkman) and a Pt-button indicator electrode (Beckman) were employed in all measurements. All potentials were measured with respect to a saturated calomel electrode, SCE. Solutions to be electrolyzed were first degassed with methylene chloride-saturated, oxygen-free nitrogen and then kept under the same atmosphere during electrochemical measurements.

The conductances of 1.0 mM solutions of LCuCl(CO_3)ClCuL in methylene chloride and nitrobenzene were measured with a Beckman Model RC16B2 conductivity bridge. Measurements also were made for 1.0 mM solutions of tetrabutylammonium iodide for comparative purposes.

Tests of Catalytic Activity. Solutions of various copper(II) complexes in methylene chloride were added to separate samples of a 100-fold excess of 2,6-dimethylphenol in methylene chloride. Oxygen was then bubbled through each solution for 15 min. 3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone, identified by comparison with an authentic sample, was the only product in all cases where catalysis of the oxidative coupling of 2,6-dimethylphenol occurred.

B. Description of the X-ray Diffraction Study and Solution of the Structure. The crystal of LCuCl(CO_3)ClCuL selected for the structural analysis approximated to a parallelepiped of dimensions 0.2 × 0.2 × 0.4 mm. It was mounted along its extended direction on the tip of a thin glass fiber and was set (with beeswax) into an aluminum pin on a eucentric goniometer. The crystal was accurately centered on a Syntex $P2_1$ automated four-circle diffractometer. Determination of approximate unit cell parameters, the orientation matrix, and crystal quality (the last via axial photographs and both

Table III. Final Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.20 (1)	1.91 (1)	3.34 (1)	−0.14 (1)	0.07 (1)	−0.14 (1)
Cl	5.22 (5)	4.26 (4)	5.66 (4)	−0.85 (4)	−1.76 (4)	2.47 (3)
O(1)	1.78 (12)	2.73 (11)	5.15 (14)	0.00	0.00	−1.10 (11)
O(2)	2.34 (8)	2.99 (9)	6.70 (11)	0.02 (7)	0.76 (8)	−1.94 (9)
N(1)	2.59 (10)	3.01 (10)	4.18 (11)	−0.74 (9)	0.37 (9)	−0.54 (9)
N(2)	3.55 (11)	2.66 (9)	2.69 (9)	−0.24 (10)	0.39 (9)	−0.42 (8)
C	2.20 (17)	2.31 (16)	4.30 (19)	0.00	0.00	−0.48 (15)
C(1)	3.55 (14)	3.70 (15)	4.51 (15)	−1.51 (12)	−0.70 (12)	−0.19 (11)
C(2)	5.13 (18)	2.97 (13)	5.21 (15)	−1.32 (14)	−0.38 (15)	−1.09 (11)
C(3)	5.76 (17)	3.40 (13)	3.95 (13)	−0.31 (16)	0.58 (14)	−1.54 (11)
Me(11)	4.97 (18)	7.25 (22)	3.68 (14)	−2.13 (18)	1.16 (14)	−0.51 (15)
Me(12)	2.66 (14)	5.20 (19)	11.64 (29)	−0.53 (17)	0.54 (16)	−2.25 (22)
Me(21)	3.76 (14)	3.23 (13)	5.08 (14)	1.14 (14)	0.04 (12)	0.09 (13)
Me(22)	4.51 (17)	5.08 (17)	4.31 (14)	0.08 (16)	2.13 (14)	−0.84 (13)

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Interatomic Distances (Å), with Esd's

A. Copper···Copper Distance

Cu···Cu′	4.2898 (7)

B. Copper–Ligand Distances

Cu–O(1)	2.1527 (4)	Cu–N(1)	2.0470 (23)
Cu–O(2)	1.9776 (20)	Cu–N(2)	2.0426 (23)
Cu–Cl	2.3978 (8)		

C. Distances within Carbonate Ion

C–O(1)	1.2990 (47)	C–O(2)	1.2698 (25)

D. Distances within TMPD Ligand

N(1)–Me(11)	1.491 (4)	N(2)–Me(21)	1.484 (4)
N(1)–Me(12)	1.478 (4)	N(2)–Me(22)	1.485 (4)
N(1)–C(1)	1.479 (4)	N(2)–C(3)	1.489 (4)
C(1)–C(2)	1.508 (5)	C(2)–C(3)	1.502 (5)

Table V. Interatomic Angles (deg), with Esd's

A. Angles about Copper Ion

Cl–Cu–O(1)	99.49 (3)	O(1)–Cu–O(2)	63.96 (9)
Cl–Cu–O(2)	109.63 (7)	O(2)–Cu–N(2)	91.32 (9)
Cl–Cu–N(1)	99.75 (7)	N(2)–Cu–N(1)	97.92 (9)
Cl–Cu–N(2)	100.27 (7)	N(1)–Cu–O(1)	97.40 (9)
O(1)–Cu–N(2)	152.48 (9)	O(2)–Cu–N(1)	147.07 (10)

B. Angles about the Bridging Oxygen Atom

Cu–O(1)–Cu′	170.26 (13)	Cu–O(1)–C	85.13 (7)

C. Angles within Carbonate Ion

O(1)–C–O(2)	117.20 (18)	O(2)–C–O(2)′	125.59 (36)

D. Angles within TMPD Ligand

Cu–N(1)–C(1)	113.39 (18)	Cu–N(2)–C(3)	112.86 (20)
Cu–N(1)–Me(11)	108.80 (20)	Cu–N(2)–Me(21)	110.34 (17)
Cu–N(1)–Me(12)	109.53 (19)	Cu–N(2)–Me(22)	107.62 (18)
C(1)–N(1)–Me(11)	110.73 (25)	C(3)–N(2)–Me(21)	110.94 (23)
C(1)–N(1)–Me(12)	107.44 (24)	C(3)–N(2)–Me(22)	107.78 (23)
Me(11)–N(1)–Me(12)	106.73 (28)	Me(21)–N(2)–Me(22)	107.05 (25)
N(1)–C(1)–C(2)	115.45 (25)	N(2)–C(3)–C(2)	115.05 (24)
C(1)–C(2)–C(3)	114.95 (27)		

θ–2θ and ω scans of reflections along the principal reciprocal cell axes) were carried out as described previously.[27] A unique data set for 2θ = 25–30° was collected at the maximum rate (29.3°/min in 2θ). Careful inspection of these data led to the selection of four strong reflections, well separated in reciprocal space, which were used (along with their symmetry-related forms) to determine accurate cell parameters via a least-squares procedure. Details appear in Table I.

Computations were performed on the CDC 6600-Cyber 173 computer at the computer center of the State University of New York at Buffalo by using the programs detailed previously.[28]

The analytical scattering factors for neutral atoms[29a] were corrected for both the real and the imaginary components of anomalous dispersion.[29b] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}$ and σ is the stochastic esd modified by an "ignorance factor" of p = 0.03.

The structure was solved via a three-dimensional Patterson synthesis which readily yielded the position of the copper atom. A difference Fourier synthesis revealed unambiguously the locations of all remaining nonhydrogen atoms. Refinement was continued by using anisotropic thermal parameters for all nonhydrogen atoms and with all hydrogen atoms included in calculated positions (based upon d(C–H) = 0.95 Å,[30] regular tetrahedral geometry about carbon atoms, and the assumption of a staggered conformation for the hydrogen atoms on the methyl groups). Convergence was reached with R_F = 4.33%, R_{wF} = 4.98%, and GOF = 2.50. Since the space group is *polar*, we tested the chirality of the crystal by inverting all coordinates through $^1/_2$, $^1/_2$, $^1/_2$ (i.e., $x, y, z \rightarrow 1 - x, 1 - y, 1 - z$). Refinement to convergence led to the decreased residuals R_F = 2.90%, R_{wF} = 3.07%, and GOF = 1.387 for all 2232 independent reflections (none rejected). Clearly, the inverted coordinates define the correct crystal chirality. The largest peak on a difference Fourier synthesis was of height 0.47 e Å^{-3}; the structure is therefore complete.

Final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

Copper(I) chloride dissolves in an oxygen-free methylene chloride solution of L to give a colorless copper(I) complex which is probably dimeric.[31,32] The reaction of such solutions with dioxygen has the stoichiometry, determined by oxygen-uptake experiments, $\Delta[\mathrm{Cu(I)}]/\Delta[\mathrm{O_2}]$ = 4.0, consistent with no oxidation of the diamine ligand.[18] The product is a brown solution which rapidly precipitates a brown material on standing or evaporation of the solvent.

We have been unable to characterize the brown product because of its insolubility in common, aprotic solvents, although IR evidence shows that it is not copper(II) oxide. Neither the solution nor the solid reacts with dry CO_2 at room temperature.[33] By contrast, if the oxidation is carried out in the presence of excess CO_2, a stable, apple green solution is obtained after the appearance of a transitory brown coloration. The solution yields a stable, green solid, I, which readily redissolves and analyzes as $L_2Cu_2Cl_2CO_3$, consistent with the oxidation stoichiometry of eq 4. The transitory brown coloration in this process is consistent with the rapid reaction between CO_2 and the primary oxidation product. Evidently, CO_2 stabilizes the initial copper(II)-reduced oxygen species, preventing polymerization to insoluble brown material.

$$2L_2Cu_2Cl_2 + O_2 + 2CO_2 \rightarrow \underset{\mathrm{I}}{2L_2Cu_2Cl_2CO_3} \qquad (4)$$

Molecular weight measurements of I in nitrobenzene solution (found 522 ± 10) are consistent with the formulation $L_2Cu_2Cl_2CO_3$ (calcd 518.5). This complex is a nonelectrolyte in methylene chloride and nitrobenzene.

Description of the Solid-State Geometry of LCuCl(CO_3)ClCuL. The full three-dimensional molecular geometry of I has been determined by an X-ray crystallographic study. The

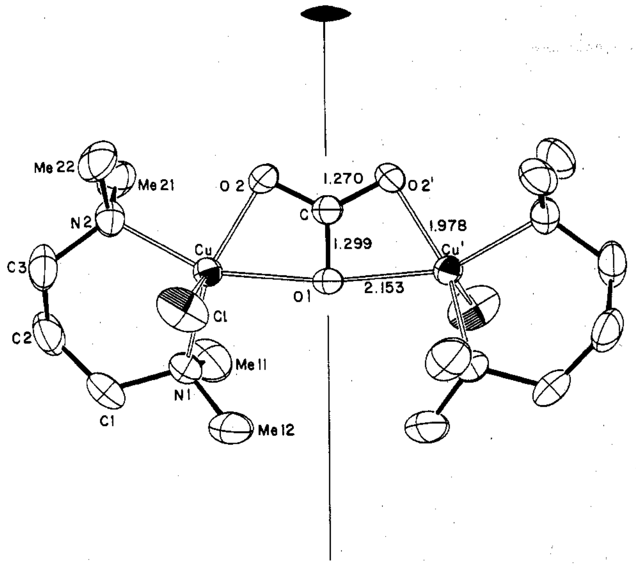

Figure 1. Labeling of atoms in the ($Me_2NCH_2CH_2CH_2NMe_2)_2Cu_2Cl_2(\mu\text{-}CO_3)$ molecule (I). The crystallographic twofold axis is vertical (ORTEP-II diagram).

molecular geometry and labeling of atoms are illustrated in Figure 1. A stereoscopic view of the molecule appears as Figure 2. Interatomic distances and their esd's are listed in Table IV; bond angles and their esd's are shown in Table V. Least-squares planes (and deviations of atoms therefrom) are collected in Table VI.

The molecule lies on a site of crystallographically dictated C_2 symmetry, the twofold axis passing through atoms C and O(1) of the bridging carbonate group. Each copper(II) atom is in a distorted square-pyramidal coordination environment in which two oxygen atoms of the carbonate group and two nitrogen atoms of the diamine ligand define the basal plane, and the copper(II) atom and chloride ligand are, respectively, −0.4225 (3) and −2.8140 (9) Å out of the plane (see Table VI, plane A). Within this description, angles from the apical ligand are Cl–Cu–O(1) = 99.49 (3)°, Cl–Cu–O(2) = 109.63 (7)°, Cl–Cu–N(1) = 99.75 (7)°, and Cl–Cu–N(2) = 100.27 (7)°. The small bite of the carbonate ligand results in a small dibasal angle, O(1)–Cu–O(2) = 63.96 (9)°, as compared to the remaining such angles, O(2)–Cu–N(2) = 91.32 (9)°, N(2)–Cu–N(1) = 97.92 (9)°, and N(1)–Cu–O(1) = 97.40 (9)°. The copper(II)–nitrogen linkages are equivalent, with Cu–N(1) = 2.0470 (23) Å and Cu–N(2) = 2.0426 (23) Å, while the apical copper(II)–chloride linkage is 2.3978 (8) Å.

We now turn our attention to the carbonate ligand. It has a most unusual connectivity to the two copper(II) ions, insofar as it is a bridging ligand that also acts as a chelating ligand for each of the copper(II) ions. The atom Cu is bonded to O(1) (Cu–O(1) = 2.1527 (4) Å) and to O(2) (Cu–O(2) = 1.9776 (20) Å, while atom Cu′ is bonded to O(1) and to O(2)′. The angle at the bridging atom, O(1), is Cu–O(1)–Cu′, = 170.26 (13)°; it is presumably this feature that causes the diamagnetism (via antiferromagnetic coupling) of the present complex (see below). The carbonate moiety itself is distorted from the possible D_{3h} symmetry, probably due to the chelate interactions with the separate copper(II) ions. Thus, the angle O(2)–Cu–O(2)′ is 125.59 (36)°, while angles O(1)–Cu–O(2) and O(1)–Cu–O(2)′ are each reduced to 117.20 (13)°. The bridging role of O(1) also appears to lead to an increase in the C–O(1) distance relative to the C–O(2) and C–O(2)′ distances (1.2990 (47) Å, as compared to 1.2698 (25) Å).

Table VI. Deviations of Atoms (Å) from Important Least-Squares Planes[a]

A. $0.2198X - 0.4273Y + 0.8770Z - 6.9656 = 0$[b]			
O(1)*	−0.0995 (14)	C(1)	−0.3457 (31)
O(2)*	0.1095 (21)	C(2)	0.1317 (34)
N(1)*	0.0684 (24)	C(3)	−0.4867 (33)
N(2)*	−0.0784 (23)	Me(11)	1.5377 (38)
C	0.1860 (23)	Me(12)	−0.5913 (38)
Cu	−0.4225 (3)	Me(21)	1.3457 (31)
Cl	−2.8140 (9)	Me(22)	−0.8856 (35)
B. $0.1253X - 0.2396Y + 0.9628Z - 8.6549 = 0$			
Cu*	0.0537 (3)	O(1)	0.8279 (14)
N(2)*	−0.0643 (23)	O(2)	0.6313 (21)
C(1)*	−0.0743 (31)	C	0.9907 (23)
C(2)*	0.0849 (34)	Me(11)	2.0691 (38)
N(1)	0.5857 (24)	Me(12)	0.2165 (38)
C(3)	−0.6290 (33)	Me(21)	1.2647 (31)
Cl	−2.2732 (9)	Me(22)	−0.9679 (35)
C. $-0.5970Y + 0.8022Z - 2.5944 = 0$			
C*	0.0000	C(1)	0.9421 (31)
O(1)*	0.0000	C(2)	1.3875 (34)
O(2)*	0.0000	C(3)	0.4877 (33)
Cu	0.0255 (3)	Me(11)	2.4321 (38)
Cl	−2.2214 (9)	Me(12)	0.4260 (38)
N(1)	1.0138 (24)	Me(21)	1.7819 (31)
N(2)	0.4842 (38)	Me(22)	−0.5556 (35)

[a] Atoms used in calculating the plane are marked with an asterisk. [b] Orthonormalized (Å) coordinates.

The copper(II) ions lie only 0.0255 (3) Å from the plane of the carbonate ligand. (See Table VI, plane B.)

The propylenediamine framework of the ligand L takes up a chair conformation, as is evidenced by the displacements of atoms N(1) and C(3), which lie (respectively) +0.5857 (24) and −0.6290 (33) Å from the plane defined by Cu–N(2)···C(2)–C(1); this is shown in Table VI, plane C.

All other distances and angles in the structure are in the normal ranges.

Spectroscopic Results. Infrared spectra of I in a KBr disk or in methylene chloride solution at room temperature show bands assignable to bridging carbonate: 1560 (s), 1380 (s) cm^{-1}, ν_3; 895 (m) cm^{-1}, ν_2; 730 (m) cm^{-1}, ν_4.[34,35] There is also a split, medium-intensity band at 510 cm^{-1}, attributable to $\nu_{Cu\text{-}O}$.[36-38] The bands associated with bridging carbonate in I are closely comparable with those of μ-carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper(II) perchlorate, II, which is the only other μ-carbonato-copper(II) complex with this bridging mode reported to date.[34] Both I and II are diamagnetic at room temperature, and I has no detectable ESR spectrum at 77 K. The complete spin pairing of the copper(II) centers in both compounds can be attributed to nearly (I) or exactly (II) linear Cu–O–Cu bonds.[34] There are very few other well-characterized diamagnetic copper(II) complexes.[34,39]

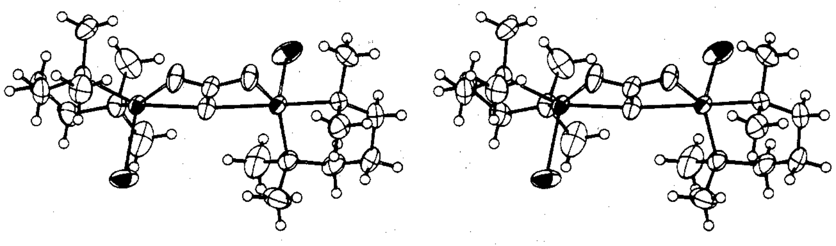

Figure 2. Stereoscopic view of the ($Me_2NCH_2CH_2CH_2NMe_2)_2Cu_2Cl_2(\mu\text{-}CO_3)$ molecule (I).

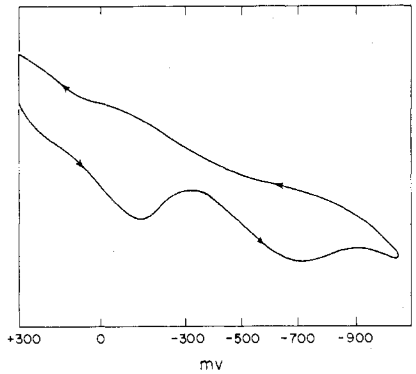

Figure 3. Cyclic voltammogram of 1.0 mM I in methylene chloride containing 0.1 M TBAP (hanging mercury drop electrode; scan rate 125 mV s^{-1}).

The room-temperature electronic spectrum of I in methylene chloride displays bands at 775 nm (ϵ 450 M^{-1} cm^{-1}) (with a shoulder at about 960 nm (ϵ ~240 M^{-1} cm^{-1})), 375 nm (ϵ 4475 M^{-1} cm^{-1}), 300 nm (ϵ 5080 M^{-1} cm^{-1}), and 255 nm (ϵ 5140 M^{-1} cm^{-1}). The ligand field bands in the near-IR region are characteristic of square-pyramidal copper(II) complexes.[40-43] The spectrum of I in nitrobenzene shows only slight differences in intensities at these same maxima.

An example of a cyclic voltammetric scan of a 1.0 mM solution of I in methylene chloride (0.1 M TBAP supporting electrolyte) is shown in Figure 3. Similar data were obtained at both hanging mercury drop and Pt electrodes at scan rates from 125 to 400 mV s^{-1}. Two irreversible waves, corresponding to the reduction of I to copper(I) and copper(I) to copper(0), are observed at −0.18 and −0.70 V (vs. SCE), respectively. The two-electron reduction of I to copper(I) occurs either at the same potential or at potentials which are too similar to be distinguished at scan rates as high as 400 mV s^{-1}. In view of the irreversibility of the electrochemical reduction of I, we have not attempted to apply quantitative theory to distinguish between these two possibilities.[39]

Tests of the catalytic activity of I in methylene chloride show that the only product from the oxidative coupling of 2,6-dimethylphenol by dioxygen is 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. The compound CuLCl$_2$[44] in methylene chloride does not catalyze the oxidative coupling of 2,6-dimethylphenol. Evidently, the carbonate group is responsible for the ability of I to act as an initiator for this oxidative coupling process. The existence of a strongly basic site has been established in all the initiators so far characterized.[18,20,23]

Only a few (carbonato)copper(II) complexes have been synthesized,[34] and we are aware of only two previously reported μ-carbonato-dicopper(II) complexes. Complexes I and II[34] have very similar bridging structures, and both are diamagnetic. The other example, a neutral complex with the anionic form of the ligand 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, is bridged by *bidentate* carbonate.[45] It has been shown that the structure of known (carbonato)copper(II) compounds strongly influences their magnetic properties.[46,47]

Complex I represents just one of many μ-carbonato-copper(II) species that can be obtained quantitatively by the oxidation of copper(I) with dioxygen in the presence of CO$_2$ and alkylated polyamine ligands. All of these complexes are effective initators for phenolic oxidative coupling by dioxygen and will be the subject of separate reports from our laboratories.

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Supplementary Material Available: A table of data processing formulas and a listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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