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

Synthesis, Physical Properties, and Structural Characterization of μ-Carbonato-dicopper(II) Complexes. 2.[1] Products of the Oxidation of Copper(I) by Dioxygen in Aprotic Media Containing Carbon Dioxide and Alkylated Diamine Ligands and the Crystal Structure of Paramagnetic $(Et_2NCH_2CH_2NEt_2)_2Cu_2Cl_2(\textit{asym}\text{-}\mu\text{-}CO_3)$

MELVYN ROWEN CHURCHILL,*[2a] GEOFFREY DAVIES,*[2b] MOHAMED A. EL-SAYED,[2b] MOHAMED F. EL-SHAZLY,[2b] JOHN P. HUTCHINSON,[2a] and MARTIN W. RUPICH[2b]

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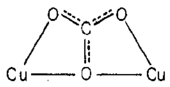
The reactions of L = *N,N,N′,N′*-tetramethylethylenediamine, *N,N,N′,N′*-tetraethylethylenediamine, or tris(2-pyridyl)amine with copper(I) acetate, bromide, chloride, or iodide and dioxygen in anhydrous methylene chloride yield polymeric μ-oxo-dicopper(II) complexes. However, if these reactions are carried out in the presence of excess carbon dioxide, the sole products are dinuclear μ-carbonato-dicopper(II) complexes, which are effective initiators for the oxidative coupling of phenols by dioxygen. Analytical, magnetic, and spectroscopic data for this complex series are compared to those for the antiferromagnetically coupled complex (teed)CuCl(CO$_3$)ClCu(teed) [teed = *N,N,N′,N′*-tetraethylethylenediamine], whose structure has been determined by a single-crystal X-ray structural analysis. This complex crystallizes in the noncentrosymmetric monoclinic space group *Cc* (C_s^4, No. 9) with a = 18.900 (3) Å, b = 12.173 (2) Å, c = 13.721 (2) Å, β = 117.43 (1)°, and Z = 4. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was solved via Patterson, Fourier, and least-squares refinement techniques; the final discrepancy indices are R_F = 3.5% and R_{wF} = 2.9% for the 4963 data ($2\theta_{max}$ = 50°; Mo Kα radiation). Each copper(II) atom is linked to a bidentate teed ligand and a chloride ligand. In addition, the copper atoms are bridged *asymmetrically* by a tridentate carbonate ligand. Relevant Cu–O(carbonate) distances are Cu(1)–O(1) = 2.093 (2) Å and Cu(1)–O(2) = 1.975 (3) Å vis-à-vis Cu(2)···O(1) = 2.412 (2) Å and Cu(2)–O(3) = 1.949 (2) Å. This results in one copper atom [Cu(1)] being pentacoordinate and the other [Cu(2)] tending toward *tetra*coordination.

Introduction

As part of a systematic study of the rates and products of oxidation of copper(I) salts and complexes by dioxygen in aprotic media,[1,3-6] we recently reported that quantitative yields of diamagnetic μ-carbonato-dichlorobis(*N,N,N′,N′*-tetramethyl-1,3-propanediamine)dicopper(II), (tmpd)CuCl(CO$_3$)ClCu(tmpd), can be obtained from the reaction between copper(I) chloride, tmpd, CO$_2$, and dioxygen in anhydrous methylene chloride, 1-propanol, nitrobenzene, or *o*-dichlorobenzene.[1] This dinuclear complex is *diamagnetic*, contains a planar symmetrical Cu(μ-CO$_3$)Cu bridge (see **1**), is a very effective initiator for oxidative coupling (eq 1),[7] and is a member of a homologous series of μ-carbonato-dicopper(II) initiators for reaction 1 which can be obtained in the same manner.



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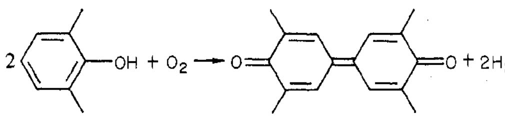

(1)

In this paper we report analytical, electrochemical, magnetic, and spectroscopic properties of the μ-carbonato-dicopper(II) complexes containing coordinated *N,N,N′,N′*-tetramethylethylenediamine (tmed), *N,N,N′,N′*-tetraethylethylenediamine (teed), *N,N,N′,N′*-tetramethyl-1,3-propanediamine (tmpd), tris(2-pyridyl)amine (tpam), and various common monoanionic ligands. In addition, we have determined the X-ray crystal structure of (teed)CuCl(CO$_3$)ClCu(teed), a *paramagnetic* (but antiferromagnetically coupled) member of this μ-carbonato-dicopper(II) series.

Experimental Section

A. Syntheses and Physical Measurements. Materials. The ligands tmed, teed, and tmpd (Aldrich) were distilled under reduced pressure before use. Tris(2-pyridyl)amine was prepared by literature methods.[8,9] Methylene chloride (Baker or Burdick and Jackson) was distilled from phosphorus(V) oxide and stored over 4 Å molecular sieves. Copper(I) chloride and bromide were prepared according to literature methods.[10] Copper(I) iodide (Alfa) was used without further purification. Copper(I) acetate was prepared under nitrogen by reduction of copper(II) acetate with copper foil in an acetonitrile/acetic acid/acetic anhydride solvent mixture.[11] Nitrobenzene was distilled from phosphorus(V) oxide immediately before use. Diethyl ether was dried over CaCl$_2$ and then distilled from sodium/benzophenone. Tetrabutylammonium iodide (TBAI) and perchlorate (TBAP) (Eastman) were recrystallized from ethanol and dried under vacuum. Silver acetate, nitrate, and thiocyanate (Alfa) were dried under vacuum before use.

General Method of Preparation of μ-Carbonato-dicopper(II) Complexes, LCuX(CO$_3$)XCuL (X = Cl$^-$, Br$^-$, I$^-$, Acetate). Complexes with X = Cl$^-$, Br$^-$, I$^-$, or OAc$^-$ were prepared by the following general method. A solution of the respective amine ligand (5 mmol) in 30 mL of anhydrous methylene chloride was flushed with dry CO$_2$ for 15 min. The respective copper(I) salt (5 mmol) was then added under CO$_2$, and the mixture was stirred with a stream of CO$_2$ until all the solid has dissolved, yielding a colorless solution. At this point both CO$_2$ and O$_2$ were passed through the solution, rapidly producing a deep green solution. After an additional 10 min, the gas streams were stopped and the methylene chloride was removed in a vacuum rotary evaporator, leaving a green solid. The product yield was quantitative in all reactions. Analytical data of representative complexes are given in Table I.[12]

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(12) Elemental analyses of the solid samples were performed by Galbraith Laboratories, Knoxville, TN.

0020-1669/80/1319-0201$01.00/0

Table I. Representative Analytical Data for μ-Carbonato-dicopper(II) Compounds

compd	% calcd				% found			
	Cu	C	N	H	Cu	C	N	H
(tmed)CuCl(CO_3)ClCu(tmed)	25.9	29.4	11.4	6.5	25.6	31.6	11.4	6.9
(teed)CuCl(CO_3)ClCu(teed)	21.1	41.8	9.3	8.0	22.3	41.3	9.1	8.2
(teed)CuBr(CO_3)BrCu(teed)	18.4	36.5	8.1	7.0	18.3	35.3	8.1	7.0
(tmpd)CuBr(CO_3)BrCu(tmpd)	20.9	29.7	9.2	5.9	19.8	29.2	8.9	5.9
(tmpd)Cu(NO_3)(CO_3)(NO_3)Cu(tmpd)	22.2	31.5	14.7	6.3	21.6	30.4	14.9	6.5
(tpam)CuCl(CO_3)ClCu(tpam)	16.8	49.3	14.8	3.2	16.5	48.7	14.3	3.3
(tpam)Cu(OAc)(CO_3)(OAc)Cu(tpam)	15.8	52.4	14.0	3.7	15.4	52.7	14.5	4.4

The oxidation of the copper(I) tetraalkyldiamine complexes by dioxygen in the absence of CO_2 produced polymeric μ-oxo-dicopper(II) species. The stoichiometry of these reactions, $S = \Delta[\mathrm{Cu^I}]/\Delta[\mathrm{O_2}]$, was measured as described previously.[1] The reactivity of the products toward CO_2 was found to depend on the amine ligand (see below).

Complexes, where X = NO_3^-, SCN^-, or OAc^-, were prepared by the anion-exchange reaction of the stoichiometric amount of the respective silver(I) salt with LCuX(CO_3)XCuL (X = halide) in methylene chloride at 25 °C. After complete exchange of the halide anion (usually completed in 12 h), the solutions were centrifuged to remove AgX and the methylene chloride was removed under vacuum. Most of these complexes are green. However, with some anion–ligand combinations the complexes are blue and extremely hygroscopic (see below).

The corresponding reactions with lead(II) salts proceed at extremely low rates. Single crystals of (teed)CuCl(CO_3)ClCu(teed) were obtained by the same method as described previously.[1]

Spectral Measurements. The electronic spectra of μ-oxo- and μ-carbonato-dicopper(II) complexes were measured at room temperature on a Cary Model 14 spectrometer for solutions in anhydrous methylene chloride, nitrobenzene, and 1-propanol. Infrared spectra, in KBr disks and methylene chloride solutions, were recorded on a Perkin-Elmer Model 567 spectrophotometer. The ESR spectra of CH_2Cl_2 solutions and powdered samples were obtained in a Varian Model E-9 spectrometer at 77 K.

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

Electrochemical Measurements. Polarographic and cyclic voltammetric parameters for μ-carbonato-dicopper(II) complexes in anhydrous methylene chloride with 0.1 M TBAP as the supporting electrolyte were obtained as previously described.[1] Controlled potential electrolyses were performed in an H-type cell at a stirred mercury pool electrode with a Pt counter electrode. The voltage was supplied by a Princeton Applied Research Model 126 potentiostat. The conductances of 1.0 mM solutions of LCuX(CO_3)XCuL in methylene chloride and nitrobenzene were measured with a Beckman Model RC16132 conductivity bridge. TBAI solutions (1.0 mM) were used as standards.

Tests of Catalytic Activity. The catalytic activity (eq 1) of various copper(II) complexes was tested (as previously described)[1,3] with a 100-fold excess of 2,6-dimethylphenol in methylene chloride.

B. The X-ray Diffraction Study of (teed)CuCl(CO_3)ClCu(teed). Data Collection. A carefully selected crystal of dimensions 0.1 × 0.1 × 0.4 mm was mounted along its extended direction (*c*) on a thin glass fiber, which was fixed (with beeswax) into an aluminum pin mounted in a eucentric goniometer. Following a preliminary photographic survey, which indicated *Cc* or *C2/c* as the possible space groups, 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.[13] Details appear in Table II. A total of 4963 reflections representing one hemisphere of data were collected. *This provides one form if the space group is the noncentrosymmetric Cc* $[I(hkl) \neq I(\bar{h}k\bar{l}) \neq I(hk\bar{l}) \neq I(\bar{h}kl)]$ or two forms if the space group is the centrosymmetric *C2/c* $[I(hkl) = I(\bar{h}k\bar{l}); I(hk\bar{l}) = I(\bar{h}kl)]$. Data were corrected for absorption via an empirical method based on a series of ψ scans (see Table II), corrected for Lorentz and polarization effects, and reduced to unscaled $|F_o|$ values, along with the associated $\sigma(|F_o|)$.

Table II. Experimental Data for the Diffraction Study of (teed)CuCl(CO_3)ClCu(teed)

(A) Crystal Parameters at 24 °C[a]

cryst system: monoclinic
space group: *Cc*
$a = 18.9001$ (26) Å
$b = 12.1728$ (16) Å
$c = 13.7210$ (22) Å
$\beta = 117.43$ (1)°
$V = 2801.8$ (7) Å^3
$Z = 4$
ρ(calcd) = 1.43 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
rflcns measd: one hemisphere ($\pm h$, k, $\pm l$); $2\theta = 3$–$50°$
scan type: coupled θ(crystal)–2θ(counter) at 4°/min in 2θ
scan width: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
bkgd: stationary–at beginning and end of scan; each for $^1/_4$ the scan time
std reflcns: 3 measd after every 97 reflcns; no significant fluctuations obsd
rflcns collected: 4963 total, representing a unique set of under point group C_s
abs coeff: $\mu = 17.4$ cm^{-1}

(C) Data for Absorption Corrections

hkl	2θ, deg	$I_{\max}/I_{\min}$
$22\bar{3}$	11.13	1.17
$33\bar{6}$	20.60	1.16
$35\bar{7}$	27.09	1.14
$8,4,\overline{11}$	35.88	1.21

[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 $\{\bar{7}73\}$, $\{841\}$, $\{0\bar{2}7\}$, $\{22\bar{7}\}$, $\{12,\bar{4},\bar{3}\}$ and $\{77\bar{1}\}$ all with $2\theta = 22$–$30°$. [Here the symbol "{ }" represents the full monoclinic set of idealized C_{2h} symmetry.]

Table III. Statistics for Intensity Distribution for (teed)CuCl(CO_3)ClCu(teed)

	obsd	theoretical	
		acentric	centric
$\langle\|E\|^2\rangle$	1.000	1.000	1.000
$\langle\|E\|\rangle$	0.904	0.886	0.798
$\langle\|E^2 - 1\|\rangle$	0.683	0.736	0.968
$\|E\| > 1.0$	39.72%	36.79%	31.73%
$\|E\| > 2.0$	0.93%	1.89%	4.55%
$\|E\| > 3.0$	0.00%	0.01%	0.27%

Two tests were run on the data to distinguish between the acentric and centric possibilities. (1) Intensity statistics (see Table III) clearly indicate the acentric case. (2) Averaging statistics for hkl and $\bar{h}k\bar{l}$ or $hk\bar{l}$ and $\bar{h}kl$ data (i.e., corresponding to point group C_{2h}) led to $R(I) = 3.5\%$ for 2478 pairs of data; this value is rather high, suggesting Friedel inequivalence. The space group *Cc* is thus strongly indicated.

Solution and Refinement of the Structure. All calculations were performed by using our in-house Syntex XTL Structure Determination System, composed of a NOVA 1200 computer, a Diablo disk unit, a Versatec printer-plotter, and our locally modified version of the XTL conversational crystallographic program package.[14] The analytical scattering factors of Cromer and Waber[15a] were used throughout the

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(14) "Syntex XTL Operations Manual", 2nd ed., Syntex Analytical Instruments, Cupertino, CA, 1976.

Table IV. Final Positional Parameters (with Esd's) for (teed)CuCl(CO_3)ClCu(teed)

atom	x	y	z	atom	x	y	z
Cu(1)	0.00000 (0)	0.18755 (3)	0.00000 (0)	H(112C)	0.1530	0.3120	0.0792
Cu(2)	−0.06786 (3)	0.54052 (3)	−0.00766 (4)	H(113A)	0.0765	0.2999	0.2194
Cl(1)	0.06337 (6)	0.11926 (9)	−0.09924 (8)	H(113B)	0.0158	0.2125	0.2165
Cl(2)	−0.04198 (7)	0.64689 (9)	−0.12394 (8)	H(114A)	0.1083	0.2493	0.3972
O(1)	−0.01783 (13)	0.35501 (20)	0.01553 (18)	H(114B)	0.1767	0.2122	0.3720
O(2)	−0.09398 (15)	0.25278 (20)	−0.12412 (19)	H(114C)	0.1147	0.1274	0.3694
O(3)	−0.12487 (12)	0.42978 (18)	−0.11919 (18)	H(121A)	−0.0958	−0.1015	−0.0343
N(11)	0.08651 (16)	0.15685 (23)	0.15440 (22)	H(121B)	−0.0229	−0.0584	−0.0462
N(12)	−0.06400 (18)	0.05078 (24)	0.02454 (23)	H(122A)	−0.1810	−0.0385	−0.2111
N(21)	0.00180 (16)	0.61734 (23)	0.13868 (21)	H(122B)	−0.1081	0.0046	−0.2230
N(22)	−0.15470 (15)	0.53523 (22)	0.04622 (21)	H(122C)	−0.1248	0.0481	−0.1295
C	−0.08105 (20)	0.34737 (27)	−0.07895 (25)	H(123A)	−0.1701	0.1222	−0.0542
C(11)	0.07579 (22)	0.03756 (29)	0.16747 (29)	H(123B)	−0.1293	0.1438	0.0712
C(12)	−0.00964 (26)	0.01191 (37)	0.13901 (32)	H(124A)	−0.2400	0.0392	0.0251
C(21)	−0.05880 (21)	0.68080 (29)	0.15349 (29)	H(124B)	−0.1655	−0.0303	0.0985
C(22)	−0.12515 (20)	0.60618 (31)	0.14569 (27)	H(124C)	−0.2086	−0.0485	−0.0274
C(111)	0.16980 (21)	0.17519 (32)	0.17091 (30)	H(21A)	−0.0342	0.7141	0.2240
C(112)	0.18705 (26)	0.29169 (40)	0.15316 (42)	H(21B)	−0.0804	0.7361	0.0987
C(113)	0.06967 (22)	0.22496 (31)	0.23228 (28)	H(22A)	−0.1679	0.6498	0.1420
C(114)	0.12240 (30)	0.20137 (43)	0.35428 (33)	H(22B)	−0.1057	0.5608	0.2091
C(121)	−0.07409 (26)	−0.04007 (32)	−0.05386 (32)	H(211A)	0.0847	0.7356	0.2058
C(122)	−0.12730 (30)	−0.01449 (38)	−0.17232 (37)	H(211B)	0.0376	0.7466	0.0791
C(123)	−0.14091 (24)	0.08971 (37)	0.01607 (33)	H(212A)	0.1578	0.5912	0.1854
C(124)	−0.19365 (28)	0.00468 (49)	0.02929 (41)	H(212B)	0.1682	0.6960	0.1290
C(211)	0.06317 (23)	0.69660 (31)	0.13834 (32)	H(212C)	0.1105	0.6040	0.0590
C(212)	0.13142 (23)	0.64200 (40)	0.12715 (37)	H(213A)	0.0781	0.4926	0.2065
C(213)	0.04081 (21)	0.53043 (31)	0.22264 (28)	H(213B)	0.0006	0.4807	0.2180
C(214)	0.08499 (25)	0.57220 (37)	0.34143 (31)	H(214A)	0.1081	0.5119	0.3898
C(221)	−0.23102 (20)	0.57479 (33)	−0.04666 (31)	H(214B)	0.1256	0.6221	0.3482
C(222)	−0.22811 (25)	0.68936 (38)	−0.08729 (36)	H(214C)	0.0483	0.6086	0.3598
C(223)	−0.16808 (22)	0.42000 (31)	0.07406 (30)	H(221A)	−0.2709	0.5736	−0.0228
C(224)	−0.22634 (25)	0.40750 (38)	0.11980 (33)	H(221B)	−0.2452	0.5254	−0.1063
H(11A)[a]	0.1091	0.0169	0.2415	H(222A)	−0.2796	0.7090	−0.1429
H(11B)	0.0902	−0.0029	0.1202	H(222B)	−0.1913	0.6907	−0.1166
H(12A)	−0.0156	−0.0651	0.1432	H(222C)	−0.2116	0.7399	−0.0281
H(12B)	−0.0232	0.0480	0.1894	H(223A)	−0.1181	0.3919	0.1269
H(111A)	0.2059	0.1548	0.2440	H(223B)	−0.1870	0.3773	0.0088
H(111B)	0.1780	0.1296	0.1208	H(224A)	−0.2307	0.3320	0.1336
H(112A)	0.2410	0.2980	0.1673	H(224B)	−0.2076	0.4477	0.1864
H(112B)	0.1777	0.3389	0.2011	H(224C)	−0.2770	0.4347	0.0684

[a] Hydrogen atoms are in calculated positions (see text) and are assigned isotropic thermal parameters of $B = 7.0$ Å^2.

analysis; both real and imaginary components of anomalous dispersion[15b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights (w) are derived from the stochastic $\sigma(|F_o|)$ modified by an ignorance factor of 0.01.

The positions of the copper and chlorine atoms were determined from a three-dimensional Patterson map. A difference-Fourier synthesis phased by these four atoms revealed the remaining nonhydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters of all 32 nonhydrogen atoms (with the x and z coordinates of Cu(1) restrained to zero in order to assign an origin) led to convergence with $R_F = 4.9\%$. A difference-Fourier synthesis at this stage failed to reveal unequivocally the positions of all hydrogen atoms. These were therefore assigned idealized positions (based upon $d(\text{C–H}) = 0.95$ Å[16] and an idealized staggered conformation). Full-matrix least-squares refinement of all nonhydrogen atoms with restrained hydrogen atoms led to convergence with $R_F = 3.5\%$, $R_{wF} = 2.9\%$, and GOF = 1.389.

Since the crystal is chiral, we now inverted all coordinates ($x, y, z \rightarrow -x, -y, -z$) and refined to convergence once again. The resulting residuals ($R_F = 5.1\%$, $R_{wF} = 5.5\%$, GOF = 2.63) provide clear evidence that the original assignment of crystal chirality was correct. These later results were discarded.

A final difference-Fourier synthesis had, as its largest feature, a peak of height 0.61 e Å^{-3} close to the position of a copper atom. The analysis is thus complete. The usual tests of $\sum w(|F_o| - |F_c|)^2$ vs. $(\sin \theta)/\lambda$, $|F_o|$, Miller index, and sequence number showed no unusual features. The weighting scheme is therefore satisfactory.

Final positional parameters are collected in Table IV; anisotropic thermal parameters are presented in Table V.

Results and Discussion

The reaction of monodentate and bidentate amines with copper(I) chloride in methylene chloride probably yields binuclear copper(I) complexes.[17] The rapid reaction of these copper(I) species with molecular oxygen follows the stoichiometry of eq 2. The nature and stability of **2** depend on

$$L_mCu_2Cl_2 + {}^1/_2O_2 \xrightarrow[CH_2Cl_2]{25\ ^\circ C} \underset{\mathbf{2}}{L_mCu_2Cl_2O} \qquad (2)$$

the amine ligand, L. When L is a monodentate amine such as pyridine, *N*-methylpyrrolidine, or a secondary monodentate amine, **2** is a mixture of amine-coordinated copper(II) chloride and a solvated polymeric copper(II)-reduced oxygen species, which ultimately precipitates as insoluble copper(II) oxide.[6] However, when L is an N,N,N′,N′-tetraalkylated diamine, $R_2N(CH_2)_nNR_2$ ($m = 2$ in eq 2), **2** is a discrete species whose properties depend on the value of n and the nature of R. With R = CH_3 and $n = 1$ or 2, **2** is a green polymeric species (as shown by molecular weight measurements in nitrobenzene) isolable as a stable solid. If $n \geq 3$ and R = CH_3, or $n = 2$ and R = C_2H_5, **2** is a brown solution which precipitates an insoluble brown material on standing or evaporation of the solvent. With L = tpam, **2** is a green solution which rapidly disproportionates to give copper(II) oxide and L_2CuCl_2.[9]

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

(16) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(17) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, **17**, 115 (1975).

Table V. Anisotropic Thermal Parameters (with Esd's) for (teed)CuCl(CO_3)ClCu(teed)[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	2.847 (20)	2.267 (18)	2.088 (17)	0.445 (17)	0.774 (15)	0.063 (17)
Cu(2)	2.202 (17)	2.317 (18)	1.805 (16)	−0.050 (16)	0.876 (13)	−0.181 (15)
Cl(1)	3.806 (45)	4.63 (5)	3.218 (42)	0.572 (40)	2.077 (37)	−0.366 (38)
Cl(2)	4.48 (5)	4.47 (6)	2.813 (42)	−1.035 (45)	2.037 (39)	0.180 (39)
O(1)	2.73 (12)	2.52 (11)	2.00 (11)	0.47 (10)	0.23 (9)	−0.10 (9)
O(2)	3.69 (13)	2.19 (11)	2.50 (11)	0.25 (10)	0.67 (10)	−0.24 (9)
O(3)	2.83 (11)	2.50 (11)	1.85 (9)	0.68 (9)	0.65 (8)	0.08 (8)
N(11)	2.61 (13)	2.60 (13)	2.24 (12)	0.68 (10)	0.77 (10)	0.03 (10)
N(12)	3.12 (14)	2.59 (14)	2.84 (14)	0.09 (11)	1.25 (13)	0.30 (11)
N(21)	2.30 (12)	2.13 (13)	2.23 (13)	−0.37 (10)	1.07 (10)	−0.12 (10)
N(22)	1.76 (11)	2.74 (13)	1.97 (11)	−0.06 (10)	0.76 (9)	−0.19 (10)
C	2.47 (14)	2.12 (15)	1.62 (13)	−0.02 (12)	1.23 (12)	0.09 (11)
C(11)	3.38 (18)	2.55 (16)	2.98 (16)	0.65 (15)	0.94 (14)	0.53 (14)
C(12)	4.29 (22)	3.36 (19)	2.92 (18)	−0.27 (17)	1.03 (16)	0.92 (15)
C(21)	3.09 (16)	2.41 (16)	2.73 (15)	0.13 (13)	1.35 (13)	−0.52 (13)
C(22)	2.71 (16)	3.42 (18)	2.47 (15)	−0.27 (14)	1.43 (13)	−0.84 (13)
C(111)	2.51 (16)	4.13 (21)	3.32 (17)	0.47 (15)	0.97 (14)	−0.53 (15)
C(112)	3.30 (20)	5.30 (26)	6.75 (27)	−0.87 (18)	1.89 (20)	−0.37 (22)
C(113)	3.22 (17)	3.68 (18)	2.38 (15)	0.92 (14)	1.01 (13)	−0.16 (14)
C(114)	6.06 (27)	6.85 (30)	2.54 (18)	2.93 (23)	1.01 (18)	−0.08 (18)
C(121)	4.27 (20)	2.93 (18)	3.74 (18)	−0.64 (16)	1.69 (17)	−0.28 (15)
C(122)	6.06 (27)	4.03 (24)	3.96 (22)	−1.02 (21)	1.88 (20)	−0.47 (18)
C(123)	3.33 (19)	4.88 (22)	4.05 (20)	−0.05 (17)	1.67 (16)	0.25 (17)
C(124)	4.29 (24)	8.51 (35)	6.09 (27)	−2.09 (23)	2.62 (22)	−0.72 (25)
C(211)	3.24 (18)	3.03 (18)	3.27 (17)	−1.17 (15)	1.32 (15)	−0.21 (14)
C(212)	2.95 (18)	5.93 (26)	5.28 (24)	−0.76 (18)	2.03 (18)	0.19 (20)
C(213)	2.96 (16)	2.88 (17)	2.59 (16)	−0.38 (14)	0.79 (13)	0.10 (14)
C(214)	3.72 (20)	4.80 (23)	2.45 (16)	−0.08 (17)	0.33 (15)	0.19 (15)
C(221)	2.06 (16)	4.26 (20)	3.33 (17)	0.46 (15)	0.95 (14)	0.06 (15)
C(222)	3.91 (21)	4.97 (24)	4.88 (23)	1.36 (19)	1.29 (18)	1.60 (19)
C(223)	3.27 (17)	3.06 (17)	3.22 (16)	−0.68 (14)	1.64 (14)	−0.27 (14)
C(224)	3.93 (21)	5.09 (23)	4.06 (20)	−1.48 (18)	2.29 (17)	−0.35 (17)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Experiments with L = *N,N,N′,N′*-tetrabenzylethylenediamine, 1,2-bis(diphenylphosphino)ethane, 2,9-dimethyl-1,10-phenanthroline, and 2-(2-(dimethylamino)ethyl)pyridine gave either stable solutions or insoluble copper(I) complexes, and no oxidation was observed.

When reaction 2 is carried out in the presence of excess CO_2 with diamine ligands (n = 1–3; R = Me or Et) or tpam, stable green μ-carbonato-dicopper(II) complexes LCuCl(CO_3)ClCuL form, according to eq 3.

$$2L_2Cu_2Cl_2 + O_2 + 2CO_2 \xrightarrow{25\ °C,\ CH_2Cl_2} 2LCuCl(CO_3)ClCuL \quad (3)$$

Freshly prepared solutions or redissolved solids of **2** with n = 1 or 2 and R = CH_3 react with carbon dioxide to give analytically pure samples of the corresponding μ-carbonato-dicopper(II) products. With $n \geq 4$ both reactions 2 and 3 give unidentified, brown precipitates. Homologous μ-carbonato complexes LCuX(CO_3)XCuL (X = Br^-, I^-, or OAc^-) can be prepared from copper(I) bromide, iodide, or acetate, respectively. The complexes with bromide or iodide are similar in most respects to those with X = Cl^-. However, with X = OAc^- some products are blue, are extremely hygroscopic, and are probably of different structures, depending on L. Their rapid decomposition by water results in the loss of carbonate and the formation of hydroxy species, as indicated by changes in their IR spectra. To date, we have been unsuccessful in obtaining crystals suitable for structural determination of these blue products.

Complexes where X = NO_3^-, SCN^-, or OAc^- can be quantitatively prepared by reaction of LCuCl(CO_3)ClCuL with AgX in methylene chloride according to reaction 4. As

$$LCuCl(CO_3)ClCuL + 2AgX(s) \xrightarrow[CH_2Cl_2,\ \sim 12\ h]{25°C} LCuX(CO_3)XCuL + 2AgCl(s) \quad (4)$$

with the $L_2Cu_2(OAc)_2CO_3$ complexes described above, some of the products of reactions 4 are blue and very hygroscopic, their properties strongly depending on the identity of L. When L is tmpd or tpam, infrared spectra show that X is coordinated as a monodentate anion[18] and the complexes show the same type of carbonate bridging and properties as the parent halide complexes. The IR spectra also show that SCN^- is N coordinated[18] with L = tpam, teed, or tmpd. The complex (tpam)Cu(OAc)(CO_3)(OAc)Cu(tpam) can be prepared from both reactions 3 and 4.

Table I lists analytical data of representative samples of this new series of μ-carbonato-dicopper(II) complexes.[12] Conductance measurements indicate that they behave as nonelectrolytes in methylene chloride and in nitrobenzene.

We have recently reported the molecular structure of μ-carbonato-dichlorobis(*N,N,N′,N′*-tetramethyl-1,3-propanediamine)dicopper(II),[1] a diamagnetic member of this series with a symmetrically bridging carbonate ligand. The only other reported complex with this mode of carbonate bonding is also diamagnetic.[19] However, most of the other members of this series are paramagnetic (see below). We have therefore examined the crystal structure of paramagnetic μ-carbonato-dichlorobis(*N,N,N′,N′*-tetraethylethylenediamine)dicopper(II) in order to determine whether the magnetic differences are associated with significant changes in any structural parameters.

Description of the Solid-State Structure of (teed)CuCl(CO_3)ClCu(teed). The overall molecular geometry and the atomic labeling scheme are shown in Figures 1 and 2. A stereoscopic view of the molecule appears as Figure 3. In-

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(18) K. Nakamoto "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1978.

(19) A. R. Davis, F. W. B. Einstein, N. F. Curtis, and J. W. L. Martin, *J. Am. Chem. Soc.*, **100**, 6258 (1978).

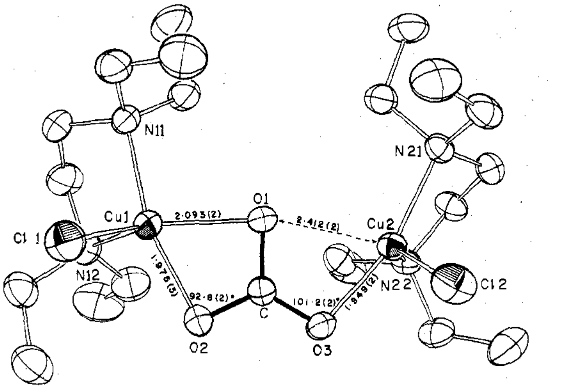

Figure 1. The (teed)CuCl(CO_3)ClCu(teed) molecule projected onto the plane of the carbonate group. Note the asymmetry of the bridging carbonate group.

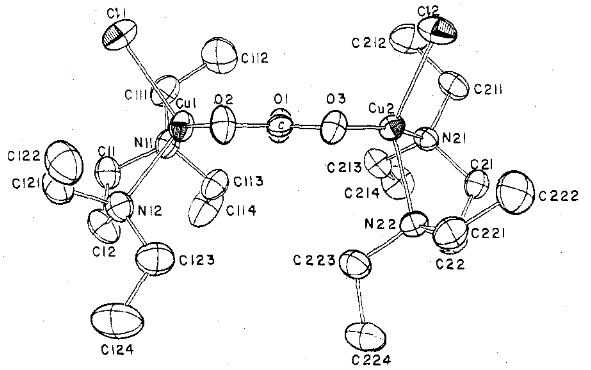

Figure 2. Labeling of atoms in the (teed)CuCl(CO_3)ClCu(teed) molecule. (The molecule is viewed down the C–O(1) axis of the carbonate group; this view is perpendicular to that shown in Figure 1.)

teratomic distances are given in Table VI, while bond angles are listed in Table VII.

In contrast to the symmetrical species (tmpd)CuCl(CO_3)ClCu(tmpd) (see Introduction and formula **I**), the complex (teed)CuCl(CO_3)ClCu(teed) has an asymmetrically bridging carbonate group and has inequivalent copper atoms. We suggest the full formulation $(Et_2NCH_2CH_2NEt_2)_2Cu_2Cl_2$-(*asym*-$\mu$-$CO_3$) for this molecule. A second basic difference between the two μ-carbonato-dicopper(II) complexes is that the Cl–Cu···Cu–Cl system in (tmpd)CuCl(CO_3)ClCu(tmpd) has a trans arrangement, whereas the Cl–Cu···Cu–Cl system in the present (teed)CuCl(CO_3)ClCu(teed) molecule has a cis arrangement.

Table VI. Interatomic Distances (Å) for (teed)CuCl(CO_3)ClCu(teed)

(A) Copper···Copper Distance			
Cu(1)···Cu(2)	4.471 (1)		
(B) Copper–Ligand Distances			
Cu(1)–O(1)	2.093 (2)	Cu(2)···O(1)	2.412 (2)
Cu(1)–O(2)	1.975 (3)	Cu(5)–O(3)	1.949 (2)
Cu(1)–N(11)	2.027 (3)	Cu(2)–N(21)	2.033 (3)
Cu(1)–N(12)	2.173 (3)	Cu(2)–N(22)	2.089 (3)
Cu(1)–Cl(1)	2.341 (1)	Cu(2)–Cl(2)	2.276 (1)
(C) Distances within Carbonate Ligand			
C–O(1)	1.300 (4)	C–O(3)	1.255 (4)
C–O(2)	1.277 (4)		
(D) Distances within teed Ligands			
N(11)–C(11)	1.488 (5)	N(21)–C(21)	1.484 (5)
N(11)–C(111)	1.500 (6)	N(21)–C(211)	1.502 (5)
N(11)–C(113)	1.498 (5)	N(21)–C(213)	1.500 (4)
N(12)–C(12)	1.503 (5)	N(22)–C(22)	1.489 (4)
N(12)–C(121)	1.493 (5)	N(22)–C(221)	1.498 (5)
N(12)–C(123)	1.482 (6)	N(22)–C(223)	1.505 (5)
C(11)–C(12)	1.509 (7)	C(21)–C(22)	1.512 (6)
C(111)–C(112)	1.500 (6)	C(211)–C(212)	1.520 (7)
C(113)–C(114)	1.530 (5)	C(213)–C(214)	1.536 (5)
C(121)–C(122)	1.498 (6)	C(221)–C(222)	1.512 (6)
C(123)–C(124)	1.505 (8)	C(223)–C(224)	1.505 (7)

The bridging carbonate ligand is linked to Cu(1) via the bonds Cu(1)–O(2) = 1.975 (3) Å and Cu(1)–O(1) = 2.093 (2) Å. Distances to Cu(2) are Cu(2)–O(3) = 1.949 (2) Å and Cu(2)···O(1) = 2.412 (2) Å. It is difficult to assess the importance of this last distance. If there is any bonding interaction between Cu(2) and O(1), then it must be weak; on the other hand, if there is no bonding interaction, then Cu(2) has a rather odd stereochemistry about it. One fact that is clear is that asymmetry in this Cu(μ-CO_3)Cu system causes the molecule to remain paramagnetic. (In contrast, the symmetrically bridged complex (tmpd)CuCl(CO_3)ClCu(tmpd) is diamagnetic.)[1]

The asymmetry in the bonding of the bridging carbonate ligand has no obvious steric cause. (There are, for example, no close contacts between ethyl groups on the two sides of the molecule—see Figures 1 and 2). The asymmetry is, however, clear-cut and results in the following differences.

(1) The Cu(2)–O(1) distance is substantially longer than the Cu(1)–O(1) distance (see above). (2) The Cu(2)–O(3) distance of 1.949 (2) Å is shorter than the Cu(1)–O(2) distance of 1.975 (3) Å. (3) The Cu(2)–O(3)–C angle of 101.15 (21)° is significantly more obtuse than the Cu(1)–O(2)–C angle of 92.81 (21)°. (4) The O(1)–C–O(2) angle of 115.54 (31)° is significantly less obtuse than the O(1)–C–O(3) angle of 119.90 (31)°. (5) The O(3)–Cu(2)···O(1) angle of 59.83 (9)° is more acute than the O(1)–Cu(1)–O(2) angle of 64.73 (10)°. (6) The Cu(1)–O(1)–C angle of 86.90 (20)° is greater than the Cu(2)···O(1)–C angle of 79.11 (19)°. (7) The C–O(3) distance of 1.255 (4) Å is slightly shorter than the C–O(2) distance of 1.277 (4) Å. (8) There are numerous other

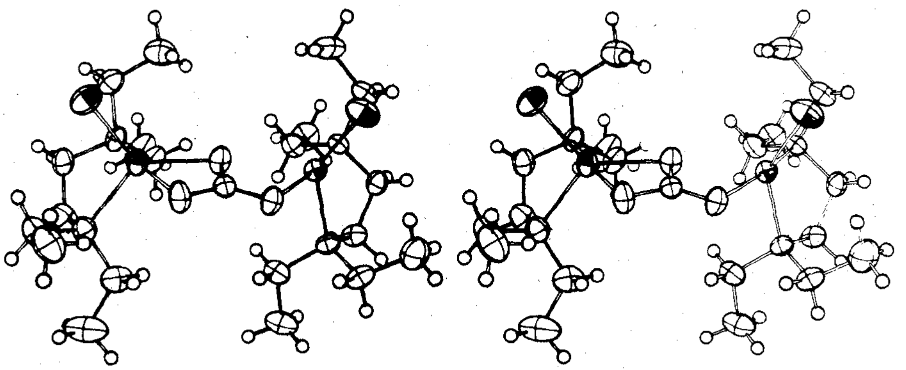

Figure 3. Stereoscopic view of the (teed)CuCl(CO_3)ClCu(teed) molecule, with hydrogen atoms included in idealized positions.

Table VII. Interatomic Angles (Deg), with Esd's, for (teed)CuCl(CO_3)ClCu(teed)

	(A) Angles about Copper Atoms		
Cl(1)–Cu(1)–O(1)	123.67 (7)	Cl(2)–Cu(2)···O(1)	115.30 (7)
Cl(1)–Cu(1)–O(2)	98.00 (8)	Cl(2)–Cu(2)–O(3)	93.60 (8)
Cl(1)–Cu(1)–N(11)	99.20 (9)	Cl(2)–Cu(2)–N(21)	99.80 (9)
Cl(1)–Cu(1)–N(12)	106.77 (7)	Cl(2)–Cu(2)–N(22)	136.33 (9)
O(1)–Cu(1)–O(2)	64.73 (10)	O(1)···Cu(2)–O(3)	59.83 (9)
O(1)–Cu(1)–N(11)	99.40 (11)	O(1)···Cu(2)–N(21)	105.28 (10)
O(1)–Cu(1)–N(12)	127.09 (11)	O(1)···Cu(2)–N(22)	104.40 (10)
O(2)–Cu(1)–N(11)	161.35 (11)	O(3)–Cu(2)–N(21)	163.51 (11)
O(2)–Cu(1)–N(12)	95.62 (11)	O(3)–Cu(2)–N(22)	90.93 (11)
N(11)–Cu(1)–N(12)	86.30 (12)	N(21)–Cu(2)–N(22)	86.00 (11)
	(B) Angles within Carbonate Ligand		
Cu(1)–O(1)···Cu(2)	165.97 (13)	O(1)–C–O(2)	115.54 (31)
Cu(1)–O(1)–C	86.90 (20)	O(1)–C–O(3)	119.90 (31)
Cu(2)···O(1)–C	79.11 (19)	O(2)–C–O(3)	124.56 (32)
Cu(1)–O(2)–C	92.81 (21)		
Cu(2)–O(3)–C	101.15 (21)		
	(C) Angles within teed Ligand		
Cu(1)–N(11)–C(11)	102.52 (22)	Cu(2)–N(21)–C(21)	100.98 (21)
Cu(1)–N(11)–C(111)	114.55 (23)	Cu(2)–N(21)–C(211)	117.23 (23)
Cu(1)–N(11)–C(113)	108.02 (22)	Cu(2)–N(21)–C(213)	107.72 (21)
C(11)–N(11)–C(111)	108.58 (28)	C(21)–N(21)–C(211)	108.04 (28)
C(11)–N(11)–C(113)	111.63 (28)	C(21)–N(21)–C(213)	112.45 (28)
C(111)–N(11)–C(113)	111.28 (28)	C(211)–N(21)–C(213)	110.20 (28)
Cu(1)–N(12)–C(12)	103.99 (24)	Cu(2)–N(22)–C(22)	106.41 (21)
Cu(1)–N(12)–C(121)	110.57 (24)	Cu(2)–N(22)–C(221)	107.14 (21)
Cu(1)–N(12)–C(123)	109.80 (24)	Cu(2)–N(22)–C(223)	111.70 (22)
C(12)–N(12)–C(121)	108.59 (31)	C(22)–N(22)–C(221)	113.63 (28)
C(12)–N(12)–C(123)	110.87 (32)	C(22)–N(22)–C(223)	110.10 (28)
C(121)–N(12)–C(123)	112.67 (32)	C(221)–N(22)–C(223)	107.88 (28)
N(11)–C(11)–C(12)	111.08 (32)	N(21)–C(21)–C(22)	110.50 (30)
C(11)–C(12)–N(12)	109.88 (34)	C(21)–C(22)–N(22)	111.21 (30)
N(11)–C(111)–C(112)	114.06 (34)	N(21)–C(211)–C(212)	113.82 (34)
N(11)–C(113)–C(114)	115.55 (34)	N(21)–C(213)–C(214)	115.45 (32)
N(12)–C(121)–C(122)	115.28 (37)	N(22)–C(221)–C(222)	115.20 (33)
N(12)–C(123)–C(124)	116.80 (38)	N(22)–C(223)–C(224)	116.14 (33)

differences in interligand angles around the two copper atoms (see Table VII).

Atom Cu(1) has a distorted five-coordinate coordination environment which is best regarded as a distorted trigonal-bipyramidal geometry. Within this description the diaxial angle is O(2)–Cu(1)–N(11) = 161.35 (11)° and the diequatorial angles are Cl(1)–Cu(1)–O(1) = 123.67 (7)°, O(1)–Cu(1)–N(12) = 127.09 (11)°, and N(12)–Cu(1)–Cl(1) = 106.77 (9)°. Angles from the axial N(11) are N(11)–Cu(1)–Cl(1) = 99.20 (9)°, N(11)–Cu(1)–N(12) = 86.30 (12)°, and N(11)–Cu(1)–O(1) = 99.40 (11)°; the remaining axial–equatorial angles are O(2)–Cu(1)–O(1) = 64.73 (10)°, O(2)–Cu(1)–Cl(1) = 98.00 (8)°, and O(2)–Cu(1)–N(12) = 95.62 (11)°.

The situation with regard to Cu(2) is less easy to analyze. In the absence of any bonding interaction with O(1), the geometry about Cu(2) resembles a distorted flattened tetrahedron (O(3)–Cu(2)–N(21) = 163.51 (11)° and Cl(2)–Cu(2)–N(22) = 136.33 (9)° are the trans angles in this description). Otherwise this copper atom may be regarded as in a distorted trigonal-bipyramidal geometry with N(21) and O(3) in the axial positions (i.e., analogous to Cu(1)). Since this latter description makes the asymmetry of the molecule as a whole even more difficult to understand, we prefer the "flattened tetrahedral" description of the stereochemistry of Cu(2).

Finally we note that the Cu(1)–O(1)···Cu(2) angle is 165.97 (13)° as opposed to a value of 170.26 (13)° in the symmetrical species (tmpd)CuCl(CO_3)ClCu(tmpd). All other distances and angles in the structure are normal (see Tables VI and VII).

Electronic and Infrared Spectra. The room-temperature electronic spectra of the μ-carbonato-dicopper(II) complexes in methylene chloride, nitrobenzene, and 1-propanol exhibit maxima between 700 and 770 nm with a shoulder centered about 950 nm. Representative data are shown in Table VIII and Figure 4. The spectral ranges of these ligand field bands are characteristic of distorted five-coordinate copper(II) complexes.[20-23] All of the complexes have charge-transfer

Table VIII. Electronic Spectral Data of μ-Carbonato-dicopper(II) Complexes

compd	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
(teed)CuCl(CO_3)ClCu(teed)	760 (285), 300 (6700)
(teed)CuBr(CO_3)BrCu(teed)	713 (320), 492 sh (360), 320 (5400), 270 (4560)
(tmpd)CuBr(CO_3)BrCu(tmpd)	744 (590), 380 (5880), 330 (4400), 275 (5060)
(tmpd)Cu(NO_3)(CO_3)(NO_3)Cu(tmpd)	720 (33), 290 (5630), 265 (5125)
(tpam)CuCl(CO_3)ClCu(tpam)	719 (156), 294 (33 600), 265 (28 000)
(tpam)CuBr(CO_3)BrCu(tpam)	684 (95), 293 (29 200), 266 (23 750)
(tpam)Cu(OAc)(CO_3)(OAc)Cu(tpam)	690 (120), 299 (43 400), 266 (34 800)
(tmed)CuCl(CO_3)ClCu(tmed)	750 (570), 375 sh (2500), 287 (9770)
$[(tmed)_2Cu_2Cl_2O]_n$[a]	725 (248), 386 sh (1600), 287 (9160)

[a] μ-Oxo-dicopper(II) species with L = tmed for comparison to μ-carbonato-dicopper(II) spectra.

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(20) A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. A*, 1685, 2578 (1968).

(21) B. J. Hathaway and J. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

Table IX. Characteristic IR Bands (in cm^{-1}) for μ-Carbonato-dicopper(II) Complexes

	$\nu_3{}^a$	$\nu_2{}^a$	$\nu_4{}^a$	$\nu_{\text{Cu-N}}$	$\nu_{\text{Cu-O}}$	ν_{X}
(tmed)CuCl(CO$_3$)ClCu(tmed)	1520, 1380	810	745	340, 310	515	
(teed)CuCl(CO$_3$)ClCu(teed)	1530, *b*	840	*b*	370		
(teed)CuBr(CO$_3$)BrCu(teed)	1530, *b*	830	*b*	370, 315	510	
(tmpd)CuCl(CO$_3$)ClCu(tmpd)	1560, 1380	895	730	345	510	
(tmpd)CuBr(CO$_3$)BrCu(tmpd)	1560, 1380	890	735	330	505	
(tmpd)Cu(NO$_3$)(CO$_3$)(NO$_3$)Cu(tmpd)	1580, 1390	895	740	330	505	1400, 1305, 815 (ν_{NO_3})
(tpam)CuCl(CO$_3$)ClCu(tpam)	1600, 1490	*b*	*b*			
(tpam)CuBr(CO$_3$)BrCu(tpam)	1600, 1490	*b*	*b*			
(tpam)Cu(SCN)(CO$_3$)(SCN)Cu(tpam)	1600, 1490	*b*	*b*			2080 (ν_{SCN})

[a] For carbonate assignments see ref 19. [b] This region is obscured by ligand bands.

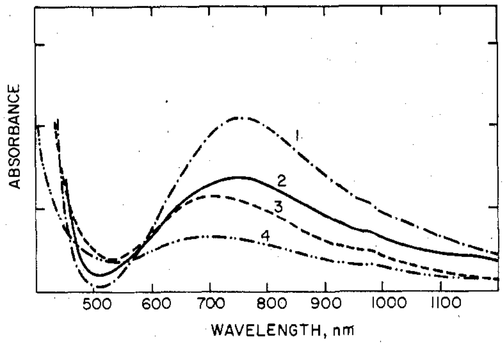

Figure 4. The electronic absorption spectra of μ-carbonato- and μ-oxo-dicopper(II) complexes in methylene chloride solution: 1, (tmed)CuCl(CO$_3$)ClCu(tmed); 2, (teed)CuCl(CO$_3$)ClCu(teed); 3, [(tmed)$_2$Cu$_2$Cl$_2$O]$_n$; 4, (tpam)CuCl(CO$_3$)ClCu(tpam).

bands in the 200–400 nm region. The similarity of these spectra to that of the oxo species, **2** (L = tmed), suggests that it is also a five-coordinate copper(II) complex and that there is no drastic ligand rearrangement on reaction with carbon dioxide. We are currently attempting the full characterization of this and other μ-oxo-dicopper(II) species.

The infrared spectra of the μ-carbonato-dicopper(II) complexes contain bands characteristic of the bridging, tridentate carbonate.[1,19] The most characteristic bands are tabulated in Table IX. All the complexes, except with L = tpam, exhibit a new, weak to medium intensity, band at ~510 cm^{-1} which can be assigned to ν_{CuO}.[1,24] With L = tpam a new weak band appears at ~450 cm^{-1} which is probably due to ν_{CuO}. All of the μ-carbonato-dicopper(II) complexes also show bands in the 300–380 cm^{-1} region which have been previously assigned to ν_{CuN}.[25]

Magnetic and ESR Properties. The X-band ESR spectra of (teed)CuCl(CO$_3$)ClCu(teed) (Figure 5) show no temperature dependence between 77 and 7.0 K. Similar spectra are obtained for polycrystalline samples or solutions in glassy methylene chloride. The other μ-carbonato-dicopper(II) complexes also show similar spectra. The ESR spectra indicate axial-type structures with $g_\parallel > g_\perp$ in agreement with a $d_{x^2-y^2}$ ground state for a distorted square-pyramidal configuration. Table X lists the g values for some of the μ-carbonato-dicopper(II) complexes.

Copper dimers normally exhibit a singlet–triplet (Δm_s = 2) transition when the Cu–Cu distance is between 3 and 5 Å. However when the Cu–Cu separation is large and the zero-field-splitting parameter is small, the intensity of the Δm_s = 2 transition decreases.[26,27]

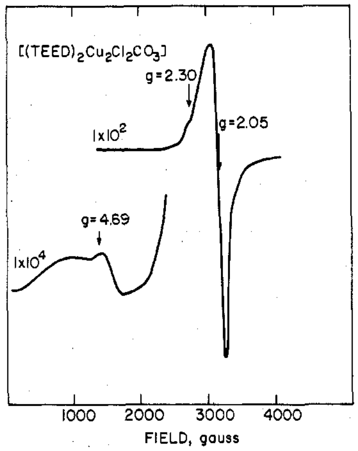

Figure 5. The X-band ESR spectrum of (teed)CuCl(CO$_3$)ClCu(teed) in methylene chloride at 7 K.

Table X. Electron Spin Resonance[a] and Magnetic Data[b] for Powdered Samples of μ-Carbonato-dicopper(II) Complexes

compd	$g_\parallel$	$g_\perp$	$g_{\text{av}}{}^c$	g- ($\Delta m_s = 2$)	μ_{eff}, μ_{B}
(tmed)CuCl(CO$_3$)ClCu(tmed)	2.35	2.09	2.26	4.23	1.65
(teed)CuCl(CO$_3$)ClCu(teed)	2.30	2.05	2.21	4.30	1.33
(teed)CuBr(CO$_3$)BrCu(teed)	2.31	2.08	2.23	4.38	1.08
(tmpd)CuBr(CO$_3$)BrCu(tmpd)	diamagnetic				
(tmpd)Cu(NO$_3$)(CO$_3$)-(NO$_3$)Cu(tmpd)	diamagnetic				
(tpam)CuCl(CO$_3$)ClCu(tpam)	2.35	2.07	2.25		1.60
(tpam)CuBr(CO$_3$)BrCu(tpam)	2.27	2.06	2.20	4.21	...
(tpam)Cu(OAc)(CO$_3$)-(OAc)Cu(tpam)	2.29	2.07	2.21	4.83	1.62

[a] ESR parameters refer to 77 K. [b] μ_{eff} at 300 K. [c] $g_{\text{av}} = {}^1/_3(2g_\perp + g_\parallel)$.

The Δm_s = 2 transition of (teed)CuCl(CO$_3$)ClCu(teed) and the other μ-carbonato-dicopper species is relatively weak even though the Cu–Cu distance is probably between 4 and 5 Å in all the complexes.

Room-temperature magnetic measurement of these compounds gives effective magnetic moments between 0 and 1.8 μ_{B} (Table X). The wide range of moments is probably the result of (i) variations in the symmetry/asymmetry of the Cu–O(1)–Cu system and (ii) distortion of the Cu–O–Cu angle due to steric requirements of the ligand and anion. Similar effects to ii have been reported with other copper dimer systems.[28-30] Low-temperature magnetic measurements and additional structural studies should provide a more thorough

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Table XI. Half-Wave Potentials (in V) for the Reduction of μ-Carbonato-dicopper(II) Complexes

	$-E_{1/2}(1)^a$	$-E_{1/2}(2)^a$
(tmed)CuCl(CO_3)ClCu(tmed)	0.29	0.70
(teed)CuCl(CO_3)ClCu(teed)	0.28	0.68
(tmpd)CuCl(CO_3)ClCu(tmpd)	0.18	0.70
(tpam)CuCl(CO_3)ClCu(tpam)	0.08	0.57

[a] Potentials were measured in methylene chloride with 0.1 M TBAP as the supporting electrolyte vs. SCE. Error is typically ± 0.01 V.

interpretation of the antiferromagnetic interactions in this series of complexes.

Electrochemical Properties. Cyclic voltammetry and polarographic reductions of $LCuX(CO_3)XCuL$ complex in oxygen-free methylene chloride with 0.1 M TBAP as the supporting electrolyte show two irreversible reduction waves (see Figure 3 of ref 1 and Table XI). The two irreversible waves correspond to the reduction of copper(II) to copper(I) and of copper(I) to copper(0). Controlled potential electrolyses indicate that the first wave is associated with a two electron reduction (see discussion of similar properties of (tmpd)CuCl(CO_3)ClCu(tmpd) in ref 1).

When any of these μ-carbonato complexes are used as initiators for the oxidative coupling of 2,6-dimethylphenol by dioxygen (eq 1), 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone is the sole product. We have previously demonstrated that it is the basic carbonate group which is responsible for the ability of these complexes to act as initiators for this oxidative-coupling process.[1] We are currently investigating the basicity of the carbonate group as a function of L and X and its effect on the rate of initiation of eq 1.

Conclusions. Alkylated diamine ligands, $R_2N(CH_2)_nNR_2$ or tpam, promote the facile oxidation of copper(I) by dioxygen in a range of aprotic solvents.[31] When the reactions are carried out in the presence of carbon dioxide, the products are μ-carbonato-dicopper(II) complexes ($n = 1$–3; R = CH_3 or C_2H_5). The reaction of CO_2 with the primary oxidation products[1,32] can be viewed as an acid–base reaction, with CO_2 acting as a Lewis acid. This method of synthesizing copper(II) complexes by aprotic oxidation of copper(I) greatly extends the range of known μ-carbonato-dicopper(II) complexes.[19,33,34] The homologous series of μ-carbonato-dicopper(II) compounds will also be useful in furthering our understanding of the relationship between structure and antiferromagnetic coupling between copper(II) centers. As in cobalt(III) chemistry,[35] carbonato complexes also have considerable potential as precursors for reaction with acidic ligands such as oxalic acid.[36] Not least, these complexes are very effective initiators for the oxidative coupling of phenols by dioxygen (eq 1), an area of great current interest to us.[1,3-6]

Reaction 4 is useful for synthesizing μ-carbonato-dicopper(II) complexes with anions for which there is no known or stable copper(I) salt (e.g., NO_3^-, ClO_4^-, or BF_4^-). It is evident that the structures of $LCuX(CO_3)XCuL$ (L = tmpd or tpam; X = Cl or NO_3) are similar. There are several possible reasons for the color change from green to blue in reaction 4 with L = tmed or teed, as X is changed from halide to NO_3^-, ClO_4^-, BF_4^-, or acetate, but we cannot speculate on this point in the absence of molecular structures for the products.

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Registry No. (tmed)CuCl(CO_3)ClCu(tmed), 72029-97-1; (teed)CuCl(CO_3)ClCu(teed), 72029-98-2; (teed)CuBr(CO_3)BrCu(teed), 72029-99-3; (tmpd)CuBr(CO_3)BrCu(tmpd), 72030-00-3; (tmpd)Cu(NO_3)(CO_3)(NO_3)Cu(tmpd), 72030-01-4; (tpam)CuCl(CO_3)ClCu(tpam), 72030-02-5; (tpam)Cu(OAc)(CO_3)(OAc)Cu(tpam), 72030-03-6; (tpam)CuBr(CO_3)BrCu(tpam), 72030-04-7; (tmpd)CuCl(CO_3)ClCu(tmpd), 70528-18-6; (tpam)Cu(SCN)(CO_3)(SCN)Cu(tpam), 72030-05-8; $[(tmed)_2Cu_2Cl_2O]_n$, 72049-13-9.

Supplementary Material Available: A table of data processing formulas and a listing of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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(31) μ-Carbonato-dicopper(II) complexes can also be made with L = *N*,*N*′-dialkylethylenediamine, but diamines with R = H are unsuitable because of carbamic acid formation under the reaction conditions.

(32) Although CS_2 can be employed instead of CO_2 in reaction 3, the products are oxidatively unstable. These systems are still under investigation.

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(34) μ-Carbonato-dicopper(II) complexes with other alkylated polyamines and O,N-bidentate donor ligands such as *N*,*N*-dialkylnicotinamide can also be made by this synthetic method. A report on these systems will appear separately.

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