# Reaction of Molecular Oxygen with Copper(I). Structural Characterization of Dimeric μ-Carbonato and Tetrameric μ-Hydroxo Complexes Resulting from the Autoxidation of a Copper(I) Carbonyl Complex

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Condensation of 1,2-dicyanobenzene with 2-amino-4-methylpyridine yields the tridentate ligand 1,3-bis(2-(4-methyl-pyridyl)imino)isoindoline, HL, **1**. Reaction of HL with Cu(OAc)₂ gives Cu(L)OAc, **2**, while HL plus CuCl in the presence of triethylamine and carbon monoxide gives diamagnetic, presumably four-coordinate Cu(I)-containing Cu(L)CO, **3** ($\nu_{CO}$ 2068 cm$^{-1}$). This carbonyl complex, Cu(L)CO, reacts with dioxygen in dry benzene or toluene to give a variety of products, two of which were characterized by crystal structure determinations. A carbonate-bridged dimeric complex (CuL)₂(μ-CO₃), **4**, in which the carbonate group presumably results from metal-promoted oxidation of CO via O₂, crystallizes in the space group $P\bar{1}$ with $a = 11.420$ (1) Å, $b = 16.479$ (1) Å, $c = 10.954$ (1) Å, $\alpha = 90.98$ (1)°, $\beta = 113.83$ (1)°, $\gamma = 101.71$ (1)°, and $Z = 2$. The structure was solved using 4578 reflections and gave $R(F) = 0.058$. Each Cu(II) is approximately square planar, being coordinated to three nitrogen atoms of the tridentate ligand and to one oxygen atom of the bridging carbonate group. A hydroxyl-bridged tetrameric complex (CuL)₃(CuLO)(μ-OH)₃, **5**, crystallizes with 2.5 benzene molecules and one water molecule per tetramer in the space group $P\bar{1}$ with $a = 14.586$ (1) Å, $b = 14.925$ (1) Å, $c = 20.781$ (2) Å, $\alpha = 105.48$ (1)°, $\beta = 105.48$ (1)°, $\gamma = 80.24$ (1)°, and $Z = 2$. An $R(F)$ of 0.065 was obtained using 9334 reflections. The molecule contains two square-planar and two trigonal-bipyramidal Cu(II) atoms, each being coordinated to three nitrogen atoms of the tridentate ligand and linked in a linear array by three bridging hydroxyl groups. In addition a single oxygen atom, located on a pyridyl $\alpha$ carbon of the tridentate ligand, is distributed nonstatistically over the four tridentate ligands. This oxidation of the ligand presumably results from copper activation of dioxygen.

## Introduction

Several copper-containing proteins ultilize molecular oxygen in rather varied physiological processes.[1-4] Thus, hemocyanin,[5-7] tyrosinase,[8] cytochrome oxidase,[9] and laccase[10-12] all react with O₂, possibly forming intermediate copper–dioxygen complexes. Little is known about the nature of the active sites of these proteins or about the formal oxidation states, relative locations, or ligand environments of the copper atoms; indeed, it is not even known whether these proteins share common structural features. The principal information concerning the nature of the copper–dioxygen interaction derives from the resonance Raman spectrum of oxyhemocyanin;[13-16] a band at 742 cm$^{-1}$ has been attributed to peroxide-like, presumably coordinated, dioxygen. However, there is no indication whether O₂ is bound to one or both of the copper atoms comprising this active site. The other ligands bound to copper are, most probably, imidazole nitrogens of histidyl residues.

Our present understanding of the reactions of O₂ with relatively simple copper complexes does little to help clarify protein behavior. Most Cu(II) complexes do not react with O₂. No well-characterized dioxygen complexes derived from Cu(I) are known,[17] although claims of O₂ adduct formation have appeared.[18-26] Treatment of Cu(I) complexes with O₂ usually results in irreversible oxidation to Cu(II), but oxidation products have not been fully characterized nor have kinetic studies yielded much mechanistic information.[27]

In an effort to better understand the nature of the copper–dioxygen interactions in proteins, we are studying relatively simple mononuclear[28-30] and binuclear[31] Cu(I) complexes. As we have discussed elsewhere,[29] the use of polydentate ligands can minimize associations and dissociation in solution, making it more likely that solid-state crystal structures correspond to solution structures and sometimes permitting more facile determination of solution mechanisms. Indeed, a good model for "blue" copper proteins which takes advantage of this feature of polydentate ligands has recently been reported.[32] We have examined copper complexes of the tridentate ligand 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, **1**, which has a nitrogen ligand environment for Cu(I) similar to that suggested for hemocyanin.[13-16,33,34] Herein we report the synthesis of

**Scheme I**
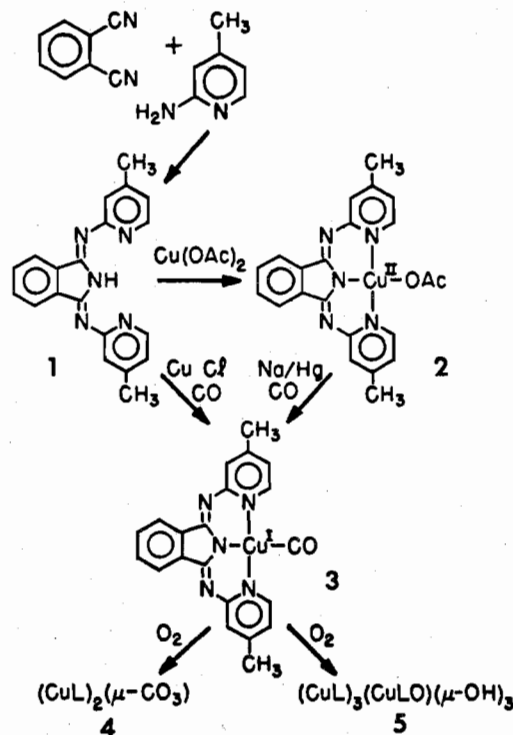


an apparently four-coordinate Cu(I) carbonyl complex of **1**, as well as structural characterization of two oxygenation products.

## Results

**Preparation of the Cu(I) Carbonyl Complex, 3 (Scheme I).** The tridentate ligand **1** is synthesized by the condensation of 2-amino-4-methylpyridine with 1,2-dicyanobenzene. Reaction of **1** with cupric acetate gives a mononuclear Cu(II) acetate complex CuL(OAc), **2**.[35-37] Reaction of **1** with cuprous chloride in the presence of triethylamine and carbon monoxide gives a Cu(I) carbonyl complex Cu(L)CO, **3** ($\nu_{CO}$ 2068 cm$^{-1}$), as a light yellow powder. The carbonyl complex **3** is also
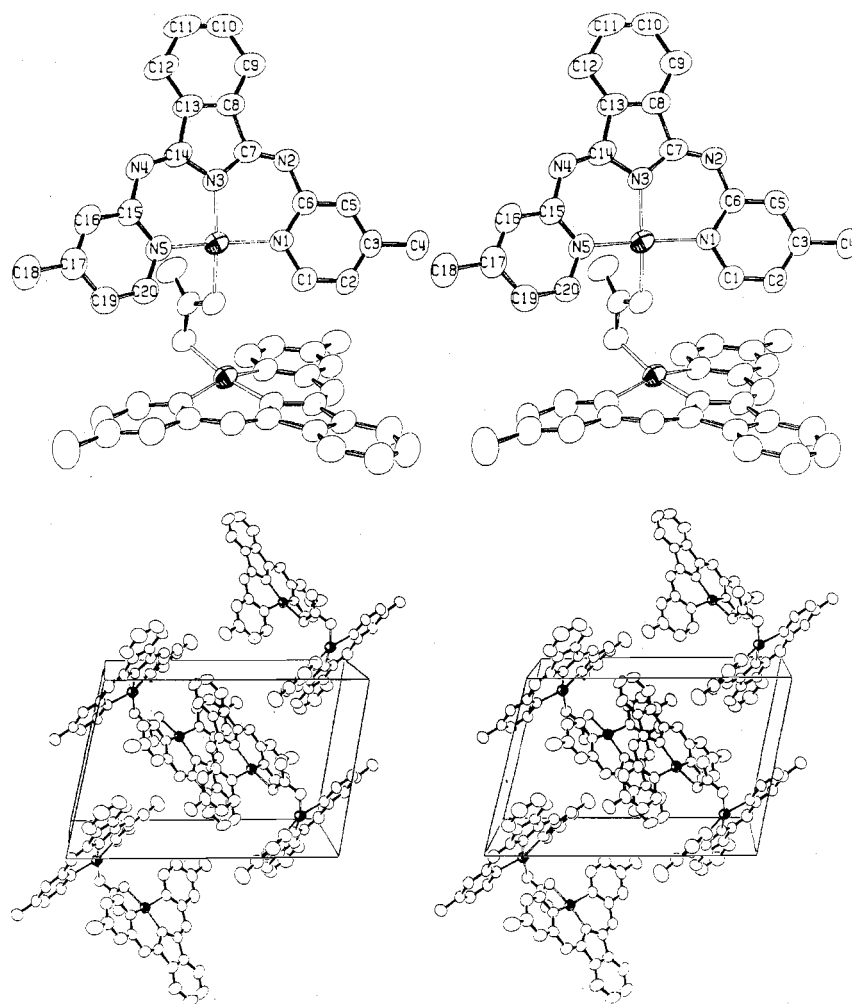
**Figure 1.** The carbonate-bridged dimer $(CuL)_2(\mu\text{-}CO_3)$, **4**: top, stereoview of a single molecule, showing the numbering scheme used for the ligand; bottom, stereoview of the crystal structure. The thermal ellipsoids are drawn at the 50% probability level.[58]

obtained by reduction of the acetate complex **2** with sodium amalgam and subsequent treatment with CO.

The carbonyl complex **3** can be recrystallized from toluene in a CO atmosphere. Recrystallization under nitrogen, however, results in disproportionation to Cu(II) and Cu(0), implying that the coordinated CO is labile and that the three-coordinate complex is quite unstable. Attempts to produce the three-coordinate Cu(I) complex without a fourth ligand (e.g., via CuCl and **1**) result in a dark insoluble product. Attempts to incorporate other ligands besides carbon monoxide, namely acetonitrile, tetrahydrofuran, or pyridine, similarly gave dark insoluble products whose infrared spectra showed no indication of the desired coordination.[38] These dark products may be polymeric.

The carbonyl complex **3** is only slightly soluble in common organic solvents. In order to increase its solubility, the methyl substituents on the pyridine rings were replaced by *tert*-butyl groups. However, this modified Cu(I) carbonyl complex ($\nu_{CO}$ 2067 cm$^{-1}$) showed only a slightly increased solubility.

**Reaction of the Cu(I) Carbonyl Complex 3 with Oxygen.** Upon exposure to dry $O_2$, light yellow suspensions of the carbonyl complex **3** in dry solvents such as benzene gradually turn brown. Reddish brown solids could be isolated from these suspensions, but low solubility and an unchanged infrared spectrum[38] made characterization difficult. In an attempt to define the nature of the oxygenation reaction, we obtained crystals directly from the reaction solution as follows.

A small amount of the carbonyl complex **3** was dissolved in a large amount of benzene open to the atmosphere. The

solution was allowed to evaporate slowly, and dark red crystals formed. An X-ray diffraction analysis of these crystals showed a dimeric $\mu$-carbonate complex $(CuL)_2(\mu\text{-}CO_3)$, **4** (Scheme I). A reaction involving atmospheric carbon dioxide seems to be precluded, since crystals of **4** were also obtained under $CO_2$-free conditions.

From the same $CO_2$-free benzene solution a second product of the reaction of Cu(L)CO, **3**, with $O_2$ was also obtained in crystalline form. A crystal-structure determination showed this compound to be a tetrameric complex $(CuL)_3(CuLO)$-$(\mu\text{-}OH)_3$, **5** (Scheme I), which crystallizes with 2.5 molecules of benzene and one molecule of water per tetramer.

**Description of the Carbonate-Bridged Dimer, 4.** Stereoscopic views of the carbonate-bridged dimer **4** and of the arrangement of the molecules in the crystal are shown in Figure 1; details of the bridging system are given in Figure 2. The coordination about the copper atoms is approximately square planar, each copper being coordinated to three nitrogen atoms of the tridentate ligand and to one oxygen atom of the bridging carbonate group. The Cu–N distances to the pyridine nitrogen atoms N1 and N5, which are equal within experimental error at 2.020 (3) Å, are appreciably longer than those to the pyrrole nitrogen atoms N3, at 1.885 (4) Å. The cis bond angles at the copper atoms range from 89 to 94° and the trans angles from 159 to 167° (Table I).

The square-planar coordination is tetrahedrally distorted with the dihedral angles between the N3–Cu–N5 and N1–Cu–O planes, or between the N3–Cu–N1 and N5–Cu–O planes, being 22° for ligand A and 24° for ligand B. (These

Table I. Coordination Angles (deg)[a]

| | (CuL)₂(μ-CO₃), 4 | | | | |
|---|---|---|---|---|---|
| O1-Cu1-N1A | 90.7 | O2-Cu2-N5B | 92.8 | N3A-Cu1-O1 | 167.3 |
| N5A-Cu1-N3A | 90.0 | N1B-Cu2-N3B | 90.5 | N1A-Cu1-N5A | 159.1 |
| N3A-Cu1-N1A | 90.1 | N3B-Cu2-N5B | 89.3 | N3B-Cu2-O2 | 166.9 |
| O1-Cu1-N5A | 93.9 | O2-Cu2-N1B | 91.3 | N5B-Cu2-N1B | 162.4 |

| | (CuL)₃(CuLO)(μ-OH)₃, 5 | | | | |
|---|---|---|---|---|---|
| N3A-Cu1-N1A | 90.7 | N3D-Cu4-N1D | 89.2 | O1-Cu1-N3A | 151.1 |
| N5A-Cu1-O1 | 93.0 | N5D-Cu4-O3 | 93.5 | N1A-Cu1-N5A | 156.6 |
| O1-Cu1-N1A | 98.5 | O3-Cu4-N1D | 98.9 | O3-Cu4-N3D | 155.2 |
| N3A-Cu1-N5A | 88.8 | N3D-Cu4-N5D | 89.9 | N1D-Cu4-N5D | 152.3 |
| N3B-Cu2-O2 | 128.9 | N1B-Cu2-O2 | 92.1 | N1C-Cu3-O2 | 93.3 |
| O2-Cu2-O1 | 106.5 | N1B-Cu2-N3B | 89.9 | N1C-Cu3-N3C | 88.6 |
| N3B-Cu2-O1 | 124.6 | N1B-Cu2-O1 | 90.6 | N1C-Cu3-O3 | 85.9 |
| | | N5B-Cu2-O2 | 88.5 | N5C-Cu3-O2 | 91.0 |
| N3C-Cu3-O2 | 150.0 | N5B-Cu2-O1 | 89.7 | N5C-Cu3-N3C | 88.9 |
| O2-Cu3-O3 | 96.2 | N5B-Cu2-N3B | 89.3 | N5C-Cu3-O3 | 91.0 |
| N3C-Cu3-O3 | 113.8 | N5B-Cu2-N1B | 179.2 | N1C-Cu3-N5C | 174.9 |

[a] Esd's are 0.1-0.2°.
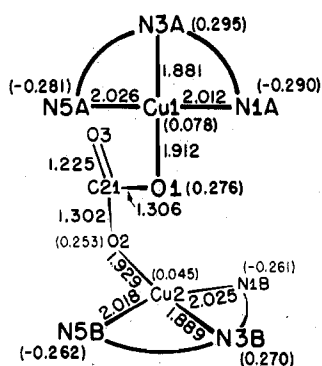


**Figure 2.** Bond distances and atom numbering scheme of the coordinated atoms for the carbonate-bridged dimer **4**. Esd's are about 0.004 Å for the Cu-O and Cu-N distances and about 0.006 Å for C-O distances. Numbers in parentheses are deviations, in Å, from the best planes through the four coordinating atoms.

angles would be 0° for a planar geometry and 90° for a tetrahedral geometry.) Alternatively, the distortion can be described by the deviations from the best planes through the four coordinating atoms, as in Figure 2. This tetrahedral distortion is achieved not by bending of the tridentate ligand but rather by raising the copper atom and the coordinated oxygen atom out of the plane of the tridentate ligand. Atom Cu1 is 0.360, O1 is 1.126, Cu2 is 0.305, and O2 is 1.039 Å above the respective planes of the three coordinated nitrogen atoms. Whatever the description, the distortion serves to relieve the steric interference between the coordinated oxygen atom and the hydrogen atoms on C1 and C20; these O···H distances range from 2.26 to 2.46 Å.

The carbonate group has been shown by crystallographic analyses to coordinate to transition metals as a monodentate,[39] bidentate,[40] bridging bidentate,[41,42] binuclear bridging tridentate,[43] and trinuclear bridging tridentate[44] ligand. In the present structure **4**, the carbonate group is bridging bidentate. Two steric effects govern the relative orientations of the CuL moieties and the bridging bidentate carbonate group: first, the sp² hybridization of the oxygen atoms suggests that the copper atoms will lie in the plane of the carbonate group with C21-O-Cu angles of about 120°; second, when the plane of the carbonate group is approximately perpendicular to the planes of the tridentate ligands, ligand-ligand repulsion will be minimized. With these constraints, three conformations are possible: a symmetric arrangement with the noncoordinating oxygen atom directed away from the metal atoms; a second symmetric arrangement with the noncoordinating

oxygen atom directed inward between the metal atoms; and a nonsymmetric pinwheel arrangement.

The first symmetric arrangement is known[41] but is clearly ruled out in the present case because of the required close contacts between the tridentate ligands. The second symmetric arrangement has yet to be observed crystallographically for any transition metal. The nonsymmetric arrangement is also known[42] and is the observed configuration for **4**. In the nonsymmetric carbonate coordination, the relatively short Cu2···O1 (2.407 Å) and Cu1···O3 (2.637 Å) distances are not due to a fifth coordination but are simply a consequence of the geometry of the carbonate group.

The carbonate group is nearly planar as expected. Within the carbonate group, the C21-O3 distance of 1.255 (4) Å is much shorter than the other C-O distances of 1.304 (3) Å, indicating that the double bond is not equally shared. The O2-C21-O1 angle opposite the shortest bond, 114.7°, is the smallest; the O3-C21-O2 angle is 123.8° and the O1-C21-O3 angle is 121.5°. The C21-O-Cu angle is 107.5° for Cu1 and 103.2° for Cu2.

The intermolecular packing (Figure 1, bottom) features the intimate pairing of planar ligand groups that is typical of large aromatic systems. The spacing between adjacent parallel ligands is about 3.5 Å.

**Description of the Hydroxyl-Bridged Tetramer, 5.** The triclinic unit cell contains two tetrameric molecules, five benzene molecules, and two molecules of water. A single tetramer is shown in Figure 3, top, and the arrangement of molecules is shown in Figure 3, bottom. Hydroxyl bridges join the copper atoms together so as to form an interleaving arrangement of CuL moieties, with successive parallel ligands rotated by approximately 90° with respect to one another in an alternating sequence that suggests a variable capacitor. This 90° rotation permits a systematic sandwiching of the pyridine ring of one ligand with the pyrrole rings of the neighboring layers. The stacking distance between adjacent ligands is fairly uniform at about 3.5–4.0 Å.

The tetrameric molecule contains two five-coordinate and two four-coordinate Cu(II) atoms; some details of the geometry about the copper atoms are shown in Figure 4. For a given tridentate ligand the distances from the copper atoms to the pyrrole nitrogen atoms are shorter than those to the pyridine nitrogen atoms, as was found for **4**. The Cu-N distances involving the five-coordinate copper atoms in **5** are longer than those involving the four-coordinate copper atoms in **4** and **5**, by an average of 0.033 Å.

The outermost copper atoms, Cu1 and Cu4, are each bonded to three nitrogen atoms of the tridentate ligand and to one
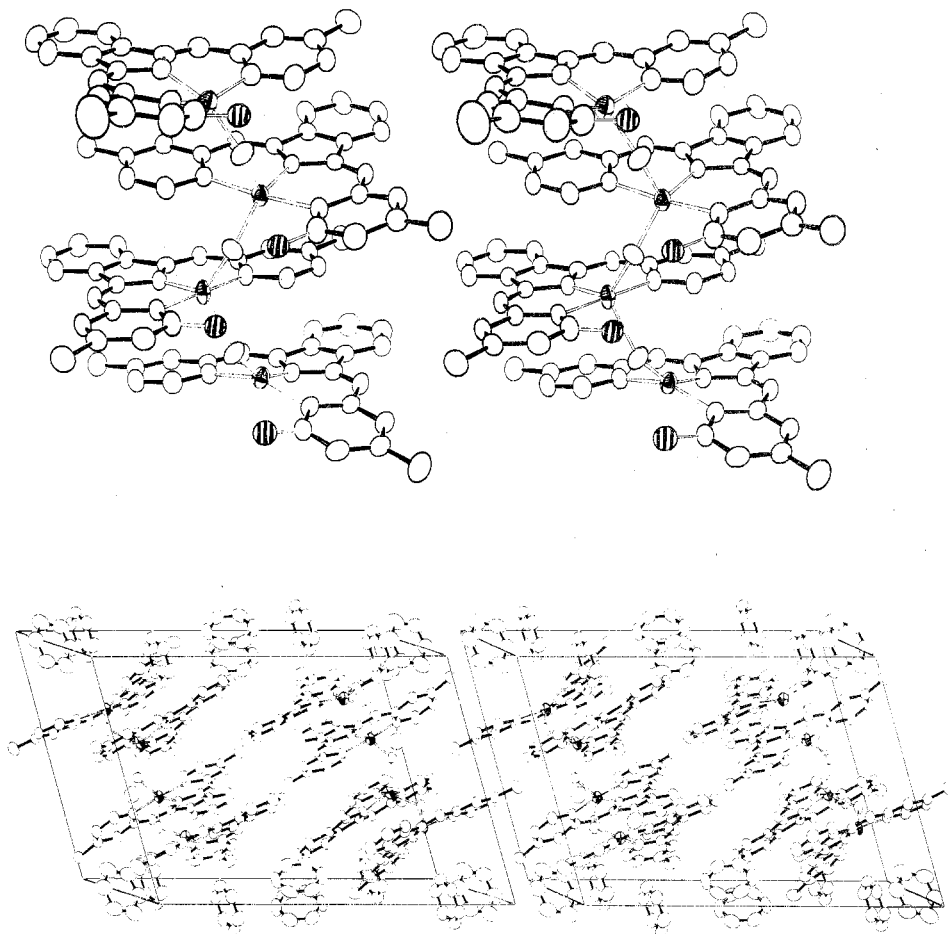
**Figure 3.** The hydroxyl-bridged tetramer $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, **5**: top, stereoview of a single molecule (the disordered oxygen atoms O4 (see text) are shaded); bottom, stereoview of the crystal structure (the disordered oxygen atoms are not shown).
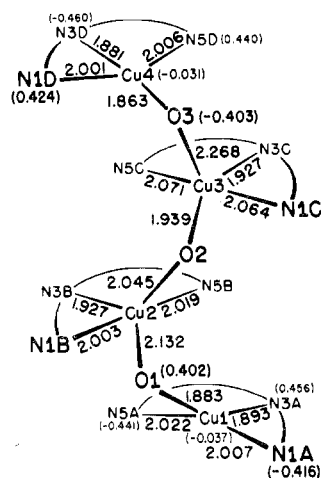


**Figure 4.** Coordination geometry in **5**. Esd's in the Cu–O and Cu–N distances are about 0.005 Å. Numbers in parentheses are deviations, in Å, from the best planes through the coordinating atoms of the two terminal, four-coordinate copper atoms. The two central copper atoms have approximate trigonal-bipyramidal coordination, with N1 and N5 in the axial positions.

bridging hydroxyl oxygen atom in a distorted square-planar geometry similar to that found in the bridging carbonate dimer, **4**, but the tetrahedral distortion is larger for the four-coordinate copper coordination in **5** than in **4**. The tetrahedral distortion in **5** is illustrated by: (1) the displacements from the best plane through the four coordinating atoms (Figure 4); (2) the displacements from the plane through the three coordinating nitrogen atoms of 0.401 Å for Cu1, 1.631 Å for O1, −0.468

Å for Cu4, and −1.643 Å for O3; and (3) the dihedral angles between the N3–Cu–N5 and N1–Cu–O planes or between the N3–Cu–N1 and N5–Cu–O planes of 36°. Besides relieving the nonbonded interactions between the oxygen atoms and the ligands, this increased distortion serves to increase the distance between successive ligands. The cis bond angles at Cu are all between 89 and 99° and the trans angles are between 151 and 157° (Table I).

The two five-coordinate copper atoms, in contrast to the four-coordinate copper atoms, are approximately in the planes of the coordinating nitrogen atoms (the deviations are 0.003 Å for Cu2 and 0.082 Å for Cu3) and the ligands themselves are more nearly planar. The geometry about these copper atoms is best described as distorted trigonal bipyramidal, the equatorial planes containing two oxygen atoms and a nitrogen atom N3. The equatorial angles are 106.5, 124.5, and 128.9° for Cu2 and 96.2, 113.8, and 150.0° for Cu3. In both cases the cis angles to the axial atoms N1 and N5 are between 88 and 93°; the trans angle is 179.2° for Cu2 and 174.9° for Cu3.

The water molecules of crystallization, O5, apparently form weak hydrogen bonds to the nitrogen atoms N2 of two ligands C and D in different molecules; the N–O distances are 3.067 and 3.029 Å, and the N–O–N angle is 134°. the five benzene molecules in each cell occupy voids in the structure (Figure 3, bottom) one of them lying on a crystallographic center of symmetry and the other four being in general positions.

With only three hydroxyl groups bridging the four CuL$^+$ groups, the molecule would be expected to be a monocation; in fact, it is a neutral species. The additional negative charge is contributed by an oxygen atom, O4, which is distributed at the C1 position among the four ligands in each tetramer and is always found on the end of the molecule where overlap

of the ligands does not occur (see Figure 3, top). Our least-squares refinement led to occupancy factors of 0.677 (10), 0.134 (5), 0.106 (5), and 0.070 (5) for this oxygen atom on the four ligands, for a total of 0.987 (13) per tetramer and within experimental error of the value 1.0 that corresponds to a neutral molecule. While we choose to designate the molecule as $(CuL)_3(CuLO)(\mu\text{-OH})_3$, in any given tetramer molecule the oxygenated ligand LO can occupy any one of the four positions with varying probabilities.

The partial oxygen atoms O4 are especially interesting. The C1–O4 bond lengths in the four ligands are as follows: A, 1.264 (5); B, 1.31 (2); C, 1.35 (3); D, 1.27 (4) Å (the increasing values of the esd's reflect the decreasing values of the occupancy coefficients); the weighted average is 1.269 (5) Å. This value is considerably shorter than found in normal C–O single bonds, typical distances being 1.43 Å for paraffinic systems[45] and 1.36 Å for phenols.[46] However, it seems a reasonable value for a phenolate group, which we presume it to be. (We have found no example of a C–O distance in a phenolate ion.) The negative charge on this phenolate group is apparently stabilized partly by weak bonds to the Cu atoms (the Cu–O4 distances range from 2.93 to 3.11 Å) and partly by hydrogen bonds from the bridging OH groups, as each of the partial O4 atoms has at least one OH neighbor within 2.8 Å. The hydrogen atoms of the bridging OH groups, which were located with the help of difference maps, point in the general directions of the O4 atoms but the details of the hydrogen bonding are not clear.

The peculiarly uneven distribution of the phenolate group among the four ligands is not entirely senseless. One would expect a phenolated ligand to prefer one of the terminal, four-coordinate copper atoms over an inner, five-coordinate one, and the observed ratio of terminal-to-inner occupancy is 3:1. In addition, the C1 position of ligand D is in close contact with one of the benzene molecules of crystallization. The distances from the site of O4D to the sites of the carbon atoms C33 and C35 are impossibly short, at 2.49 and 2.51 Å; accordingly, the presence of a phenolate group on ligand D must cause a displacement of the benzene molecule and, hence, a disruption in the crystal lattice. (Our least-squares refinement strongly suggests some disorder associated with this benzene molecule; see Experimental Section.) There is no such steric problem associated with ligand A, which shows the highest occupancy factor for the phenolate group.

The preference for atom C1 as the site of phenolation rather than C20, on the opposite side of the molecule, appears to be total. It is clearly dictated by the positions of the bridging OH groups, which in all cases are oriented so as to be able to interact with the O4 sites on C1 but not on C20.

The bridging Cu–O distances (Figure 4) are, at first glance, bewilderingly irregular. At second glance, they make a good deal of sense. As expected, the Cu–O bonds to the terminal, four-coordinate atoms Cu1 and Cu4 are the shortest. Then, because of conjugation effects, the two central bonds Cu2–O2 and Cu3–O2 are shorter than the penultimate bonds Cu2–O1 and Cu3–O3. Finally, asymmetry between the two halves of the tetramer is caused by the unequal distribution of the phenolate oxygen atom O4 among the four ligands. Since this atom is found on ligand A most of the time, Cu1 is less electron deficient than Cu4 and the Cu1–O1 bond is longer than the Cu4–O3 bond; by conjugation, Cu2–O2 is longer than Cu3–O2, and Cu3–O3 is longer than Cu2–O1. The bridging Cu–O–Cu angles range from 120.1 to 124.8°.

The structure determinations of **4** and **5** have resulted in six independent determinations of the geometry of the tridentate ligand, and, assuming $C_{2v}$ (*mm*) symmetry for the ligand, in 12 independent measurements of most of the bond lengths and angles. Averaged values are shown in Figure 5,
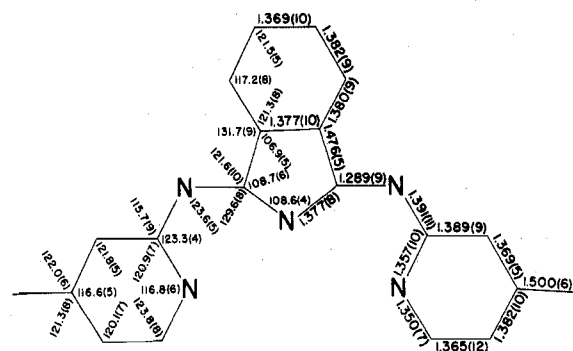


**Figure 5.** Average values for the bond distances and angles for the tridentate ligand in **3** and **4**. Most values are averages of 12 independent measurements, based on a presumed *mm2* ($C_{2v}$) symmetry of the ligand. The esd in a single such measurement, as obtained from our least-squares refinement, is about 0.008 Å or 0.6°; values in parentheses are the observed standard deviations about the average value. The esd in an *average* distance is about $0.008(12^{1/2})$, or 0.002 Å, and in an angle is about 0.2°.

and the individual values are available as supplementary material.

**Reaction Stoichiometry.** A suspension of Cu(L)CO, **3**, in benzene was oxygenated on a vacuum line over a 12-h period, and the amounts of $O_2$ consumed and of CO evolved were measured. Reproducible results were obtained. They indicated that $0.5 \pm 0.1$ mol of $O_2$ were consumed and $0.91 \pm 0.05$ mol of CO were evolved/mol of complex **3**. This stoichiometry is consistent with the formation of a dioxygen–bridged dimer:

$$2Cu(L)CO + O_2 \rightarrow (CuL)_2O_2 + CO$$
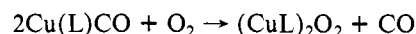
However, the oxygenation reaction appears to be irreversible, and neither infrared nor mass spectroscopy of the product suggested the presence of a dioxygen-bridged dimer.

**Discussion**

The copper(I) carbonyl complex Cu(L)CO, **3**, prepared in this study joins a number of stable copper(I) carbonyl species that have been synthesized recently. These include [hydrotris(pyrazolyl)borato]copper(I) carbonyl, **6**, and its dimethyl analogue [hydrotris(3,5-dimethyl-1-pyrazolyl)borato]copper(I) carbonyl, **7**.[47,48] The expected tetrahedral geometry for these complexes has been confirmed by a crystal structure determination of the former.[49] More recently, we have reported the synthesis, properties, and structure of a five-coordinate copper(I) carbonyl complex, **8**, in which the Cu(I) has a



**8**

**9**
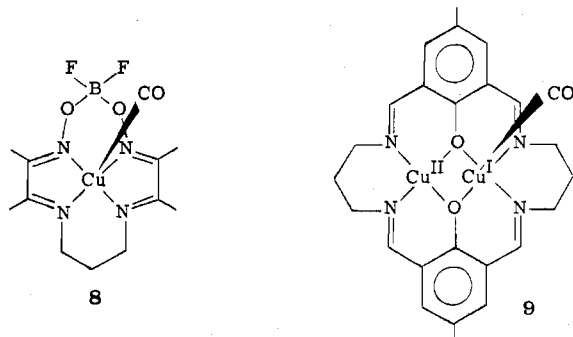
square-pyramidal environment.[28,29] The mixed-valence $Cu^ICu^{II}$ complex **9** probably also contains a five-coordinate Cu(I) carbonyl group.[31] Thus far, the insolubility of the present compound, **3**, has precluded a crystal structure study, but a distorted square-planar geometry seems likely. The C–O stretching frequencies for these carbonyl complexes are 2068 cm⁻¹ for **3**, 2067 cm⁻¹ for the *tert*-butyl analogue of **3**, 2083 cm⁻¹ for **6**, 2066 cm⁻¹ for **7**, 2068 cm⁻¹ for **8**, and 2065 cm⁻¹ for **9**; for hemocyanin (1:2 CO/Cu), the observed value is in

**Scheme II**

$$LCuCo + O_2 \longrightarrow LCu\!\!\begin{array}{c}CO\\C\!\!=\!\!O\end{array} \xrightarrow{LCu} LCu\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CuL$$
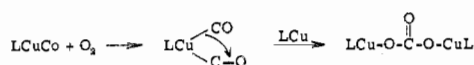
the range 2040–2060 cm$^{-1}$.[50,51] Thus, analogy with simple Cu(I) carbonyl complexes suggests any of a variety of possible metal stereochemistries for hemocyanin.

Our present work is one example of a reaction between Cu(I) and $O_2$ whose stoichiometry suggests the formation of a dioxygen complex but which, upon detailed examination, must be far more complicated. The oxygenation reaction is irreversible, and we have not been able to isolate a dioxygen species. Instead, we obtained from the reaction mixture crystals of a carbonate-bridged dimer, **4**, and of a hydroxy-bridged tetramer, **5**, in which one-quarter of the ligand molecules have been oxidized to a phenolate, as well as large amounts of noncrystalline material which we have not been able to identify. We have no reason to doubt that the crystalline products are representative of the products formed during oxygenation, although they were obtained under slightly different conditions than were used for the measurements of the reaction stoichiometry.

Although we have not been able to isolate any dioxygen compounds, it is likely that they are involved as intermediates in the various oxidation reactions. For example, a plausible mechanism for the formation of the $\mu$-carbonato complex **4** involves intramolecular insertion of coordinated CO into coordinated dioxygen (Scheme II). In somewhat analogous reactions, carbonyl complexes of Ir(I) and Rh(I) coordinated to tridentate phosphine ligands are presumed to form mononuclear, five-coordinate carbonato complexes through dioxygen intermediates.[52,53] The overall stoichiometry of the reaction in Scheme II (eq 1) does not by itself account for the

$$2Cu(L)CO + O_2 \rightarrow (CuL)_2CO_3 + CO \qquad (1)$$

amount of CO liberated. As one of several processes going on it could help explain the stoichiometry of less than 1.0 CO/Cu liberated.

Formation of the tetrameric species $(CuL)_3(CuLO)(\mu\text{-}OH)_3$ may also involve a dioxygen intermediate, with copper-promoted activation of coordinated $O_2$ leading to ligand hydroxylation (Scheme III). Hydrocarbon hydroxylations mediated by the cytochromes $P_{450}$ (Fe) and by tyrosinase (Cu) are thought to proceed via coordinated $O_2$, and macrocyclic ligand oxidations via $O_2$ to give ketones, apparently promoted by cobalt, have been reported.[54,55] Examples of hydrocarbon hydroxylations in which the oxidizing agent has been clearly demonstrated to be dioxygen coordinated to a simple metal complex are apparently unknown. Equation 2 agrees with the

$$2Cu(L)CO + O_2 \rightarrow CuLO + CuL^+ + OH^- + 2CO \qquad (2)$$

overall stoichiometry we observed for the oxygenation reaction; however, it would lead to the formation of equal amounts of the normal complex $CuL^+$ and of the phenolated complex $Cu(LO)$, whereas the tetramer contains them in a 3:1 ratio. It is quite possible, though, that charge balance, ligand–ligand overlap, and crystal forces could account for the selective crystallization of the tetrameric species; we emphasize again that crystalline material represented only a small portion of the reaction products. It is also conceivable that the small amount of phenolated ligand necessary to produce the crystals resulted from an impurity in the starting material and that the bridging hydroxyl groups were formed by any of a number of mechanisms including simple protonation of a $\mu$-oxo species.

## Conclusions

The carbonyl complex Cu(L)CO, **3**, reacts with oxygen with a seductively simple stoichiometry. Characterizable oxidation products, however, indicate that the reaction is in fact very
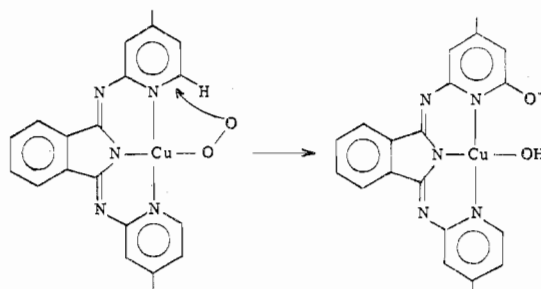
**Scheme III**



**Table II.** Summary of Crystal Data

| | $Cu_2C_{40}H_{32}$-$N_{10}CO_3$ | $Cu_4C_{80}H_{66}N_{20}O_4$·$(C_6H_6)_{2.5}H_2O$ |
|---|---|---|
| formula wt | 839.85 | 1839.01 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 11.420 (1) | 14.586 (1) |
| $b$, Å | 16.479 (1) | 14.925 (1) |
| $c$, Å | 10.954 (1) | 20.781 (2) |
| $\alpha$, deg | 90.98 (1) | 105.48 (1) |
| $\beta$, deg | 113.83 (1) | 105.48 (1) |
| $\gamma$, deg | 101.71 (1) | 80.24 (1) |
| $V$, Å$^3$ | 1835 | 4178 |
| $Z$ | 2 | 2 |
| $d$, g/cm$^3$ | 1.520 (calcd) | 1.462 (calcd) |
| | 1.50 (3) | 1.43 (2) |
| | (obsd) | (obsd) |
| $\mu$, cm$^{-1}$ | 19.20 | 17.18 |
| unique data used | 4578 | 9334 |
| $R(F)$ | 0.058 | 0.065 |

complex. Our results once again indicate that caution must be exercised in drawing conclusions concerning the formation and nature of metal–oxygen complexes on the basis of a few observations and in the absence of firm structural evidence. The preparation of a stable copper–dioxygen complex continues to present a challenge to the synthetic chemist. Our own efforts are continuing in this area.

## Experimental Section

**Preparation of the Free Ligand L and of Cu(L)OAc.** The free ligand, **1**, and the Cu(II) acetate complex Cu(L)OAc, **2**, were prepared by the procedure of Siegl.[35]

**(Carbonyl)[1,3-bis(2-(4-methylpyridyl)imino)isoindoline]copper(I), Cu(L)CO, 3.** A solution of triethylamine (0.75 mL, 5.4 mmol) in ethanol (35 mL) was purged with CO and then added all at once to a mixture of the free ligand **1** (0.5 g, 1.5 mmol) and CuCl (0.15 g, 0.76 mmol) in a Schlenk apparatus. The red reaction mixture was stirred under CO. A finely divided yellow solid began to precipitate after 5 min and was collected by filtration under CO after 6 h. The solid was washed with CO-saturated ethanol (2 × 5 mL) and dried in a slow stream of CO. The yield was 0.55 g (88%); $\nu_{CO}$ 2068 cm$^{-1}$. Anal. Calcd for $C_{21}H_{16}N_5OCu$: C, 60.35; H, 3.85; N, 16.75; Cu, 15.2. Found: C, 60.05; H, 4.1; N, 16.9; Cu, 15.2.

The carbonyl complex **3** was also prepared by reduction of the Cu(II) acetate complex **2** under nitrogen as follows. The Cu(II) complex Cu(L)OAc, **2** (0.5 g, 1.1 mmol), was warmed in toluene (70 mL, 60 °C). Sodium amalgam (5 g, 1%) was added with stirring to give a red solution and a gray solid. After 1 h the suspension was filtered. Treatment of the red filtrate with CO led to gradual deposition of a finely divided yellow solid which was collected and washed as above. The yield was 0.3 g (65%).

**Measurement of $O_2$ Consumption and CO Evolution for the Reaction of Cu(L)CO, 3, with $O_2$.** The carbonyl complex **3** in dry benzene was allowed to react with a premeasured amount of $O_2$ at 25 °C. At the end of the reaction a Toepler pump was used to determine the amounts of CO evolved and of $O_2$ remaining. In a typical experiment, dry benzene ($\sim$15 mL) was distilled in a vacuum line onto a sample of the complex **3** (0.144 g, 0.344 mmol) at –196 °C. The frozen mixture was warmed to 25 °C after a measured amount of $O_2$ (1.01 mmol) had been added (partial pressure of $O_2$ $\sim$200 torr). The suspension was stirred at 25 °C for 12 h, during which time the mixture turned from yellow to red. At the end of the reaction the total amount of

**Table III.** Positional and Thermal Parameters[a] for $(CuL)_2(\mu\text{-}CO_3)$, 4

| | x/a | y/b | z/c | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu1 | 57884 (7) | 14707 (4) | 89121 (7) | 450 (4) | 456 (4) | 523 (4) | 92 (3) | 146 (4) | 52 (3) |
| Cu2 | 85542 (7) | 37078 (4) | 90611 (7) | 480 (4) | 518 (4) | 520 (4) | 102 (4) | 132 (4) | 56 (4) |
| O1 | 6955 (3) | 2438 (2) | 8768 (3) | 47 (2) | 46 (2) | 44 (2) | 8 (2) | 8 (2) | 6 (2) |
| O2 | 6990 (3) | 3396 (2) | 7405 (3) | 53 (2) | 53 (2) | 52 (2) | 9 (2) | 12 (2) | 10 (2) |
| O3 | 5183 (4) | 2389 (2) | 6895 (4) | 55 (2) | 64 (2) | 78 (3) | 10 (2) | −1 (2) | 8 (2) |
| N1A | 5804 (4) | 2038 (2) | 10562 (4) | 42 (2) | 49 (2) | 49 (2) | 9 (2) | 14 (2) | 8 (2) |
| N2A | 3705 (4) | 1213 (3) | 10390 (4) | 50 (3) | 59 (3) | 58 (3) | 6 (2) | 18 (2) | 10 (2) |
| N3A | 4351 (4) | 627 (2) | 8791 (4) | 44 (2) | 46 (2) | 55 (3) | 7 (2) | 14 (2) | 5 (2) |
| N4A | 4208 (4) | −374 (2) | 7072 (4) | 53 (3) | 46 (3) | 67 (3) | 11 (2) | 11 (2) | 0 (2) |
| N5A | 6217 (4) | 697 (2) | 7776 (4) | 55 (3) | 47 (2) | 61 (3) | 16 (2) | 18 (2) | 4 (2) |
| C1A | 6851 (5) | 2671 (3) | 11301 (5) | 48 (3) | 64 (4) | 57 (3) | 10 (3) | 15 (3) | 6 (3) |
| C2A | 6962 (5) | 3106 (3) | 12423 (5) | 56 (3) | 66 (4) | 48 (3) | 10 (3) | 11 (3) | −2 (3) |
| C3A | 5980 (6) | 2925 (4) | 12885 (5) | 67 (4) | 77 (4) | 46 (3) | 16 (3) | 16 (3) | 3 (3) |
| C4A | 6065 (6) | 3402 (4) | 14123 (6) | 73 (4) | 121 (6) | 54 (4) | 9 (4) | 21 (3) | −14 (4) |
| C5A | 4922 (5) | 2289 (4) | 12151 (5) | 63 (4) | 74 (4) | 58 (4) | 10 (3) | 29 (3) | 10 (3) |
| C6A | 4830 (5) | 1852 (3) | 11020 (5) | 47 (3) | 56 (3) | 55 (3) | 20 (3) | 14 (3) | 13 (3) |
| C7A | 3556 (5) | 674 (3) | 9440 (5) | 45 (3) | 50 (3) | 62 (3) | 9 (2) | 12 (3) | 18 (3) |
| C8A | 2387 (5) | −31 (3) | 8872 (5) | 50 (3) | 57 (3) | 63 (4) | 7 (3) | 13 (3) | 19 (3) |
| C9A | 1315 (6) | −264 (4) | 9190 (6) | 56 (4) | 78 (4) | 80 (4) | 5 (3) | 17 (3) | 18 (3) |
| C10A | 403 (6) | −990 (4) | −8476 (7) | 47 (4) | 95 (5) | 105 (5) | 0 (3) | 21 (4) | 30 (4) |
| C11A | 542 (6) | −1444 (4) | 7516 (7) | 60 (4) | 66 (4) | 109 (5) | −11 (3) | 12 (4) | 16 (4) |
| C12A | 1607 (6) | −1205 (3) | 7179 (6) | 63 (4) | 51 (4) | 93 (5) | 2 (3) | 8 (4) | 10 (3) |
| C13A | 2526 (5) | −485 (3) | 7906 (5) | 41 (3) | 51 (3) | 69 (4) | 11 (2) | 7 (3) | 18 (3) |
| C14A | 3792 (5) | −78 (3) | 7860 (5) | 48 (3) | 46 (3) | 64 (4) | 15 (2) | 7 (3) | 9 (3) |
| C15A | 5424 (5) | −39 (3) | 7065 (5) | 59 (3) | 48 (3) | 51 (3) | 18 (3) | 14 (3) | 7 (2) |
| C16A | 5796 (6) | −509 (3) | 6273 (5) | 74 (4) | 53 (3) | 55 (3) | 17 (3) | 13 (3) | 2 (3) |
| C17A | 6980 (6) | −267 (3) | 6202 (5) | 77 (4) | 62 (4) | 62 (4) | 32 (3) | 24 (3) | 9 (3) |
| C18A | 7377 (6) | −780 (4) | 5363 (6) | 79 (4) | 78 (4) | 72 (4) | 35 (4) | 24 (4) | −1 (3) |
| C19A | 7780 (6) | 480 (4) | 6953 (6) | 61 (4) | 74 (4) | 80 (4) | 14 (3) | 33 (3) | 0 (3) |
| C20A | 7384 (6) | 933 (3) | 7696 (6) | 66 (4) | 59 (4) | 80 (4) | 6 (3) | 35 (3) | −8 (3) |
| N1B | 7846 (4) | 4606 (2) | 9633 (4) | 52 (3) | 45 (2) | 61 (3) | 11 (2) | 15 (2) | 3 (2) |
| N2B | 9285 (4) | 4758 (3) | 12026 (4) | 68 (3) | 61 (3) | 56 (3) | 15 (2) | 12 (2) | 3 (2) |
| N3B | 9891 (4) | 3806 (2) | 10816 (4) | 46 (2) | 45 (2) | 54 (3) | 9 (2) | 14 (2) | 4 (2) |
| N4B | 11088 (4) | 2818 (2) | 10526 (4) | 49 (2) | 54 (3) | 54 (3) | 10 (2) | 18 (2) | 3 (2) |
| N5B | 9592 (4) | 3120 (3) | 8374 (4) | 43 (2) | 61 (3) | 56 (3) | 13 (2) | 17 (2) | 5 (2) |
| C1B | 6853 (5) | 4863 (3) | 8651 (6) | 58 (4) | 49 (3) | 74 (4) | 20 (3) | 18 (3) | 18 (3) |
| C2B | 6231 (6) | 5428 (3) | 8936 (6) | 58 (4) | 60 (4) | 76 (4) | 20 (3) | 14 (3) | 22 (3) |
| C3B | 6585 (5) | 5755 (3) | 10253 (6) | 55 (3) | 44 (3) | 78 (4) | 11 (3) | 23 (3) | 10 (3) |
| C4B | 5897 (6) | 6354 (4) | 10581 (6) | 63 (4) | 65 (4) | 99 (5) | 25 (3) | 31 (4) | 17 (4) |
| C5B | 7610 (5) | 5504 (3) | 11226 (5) | 59 (4) | 47 (3) | 67 (4) | 13 (3) | 23 (3) | 2 (3) |
| C6B | 8230 (5) | 4943 (3) | 10901 (5) | 53 (3) | 41 (3) | 62 (3) | 10 (2) | 9 (3) | 8 (3) |
| C7B | 9975 (5) | 4251 (3) | 11924 (5) | 51 (3) | 42 (3) | 56 (3) | 9 (2) | 14 (3) | 0 (2) |
| C8B | 11038 (5) | 4073 (3) | 13135 (5) | 46 (3) | 57 (3) | 55 (3) | 6 (3) | 12 (3) | 3 (3) |
| C9B | 11544 (6) | 4368 (4) | 14466 (6) | 64 (4) | 88 (4) | 63 (4) | 22 (3) | 15 (3) | −3 (3) |
| C10B | 12593 (6) | 4066 (4) | 15358 (6) | 85 (5) | 115 (6) | 49 (4) | 25 (4) | 12 (3) | 7 (4) |
| C11B | 13079 (6) | 3471 (4) | 14917 (6) | 68 (4) | 102 (5) | 64 (4) | 30 (4) | 16 (3) | 21 (4) |
| C12B | 12563 (5) | 3182 (4) | 13584 (6) | 51 (3) | 74 (4) | 68 (4) | 20 (3) | 21 (3) | 12 (3) |
| C13B | 11549 (5) | 3487 (3) | 12703 (5) | 41 (3) | 53 (3) | 53 (3) | 7 (2) | 13 (2) | 9 (2) |
| C14B | 10823 (5) | 3322 (3) | 11226 (5) | 46 (3) | 46 (3) | 57 (3) | 4 (2) | 16 (3) | 8 (2) |
| C15B | 10545 (5) | 2737 (3) | 9131 (5) | 52 (3) | 50 (3) | 63 (3) | 5 (2) | 28 (3) | 1 (3) |
| C16B | 11079 (6) | 2243 (3) | 8552 (5) | 65 (4) | 60 (4) | 61 (4) | 15 (3) | 23 (3) | 4 (3) |
| C17B | 10748 (6) | 2192 (4) | 7193 (6) | 72 (4) | 66 (4) | 73 (4) | 17 (3) | 30 (3) | −4 (3) |
| C18B | 11350 (7) | 1692 (4) | 6548 (7) | 115 (6) | 107 (6) | 86 (5) | 46 (5) | 48 (5) | −3 (4) |
| C19B | 9835 (6) | 2630 (4) | 6432 (6) | 79 (4) | 87 (4) | 58 (4) | 19 (4) | 31 (3) | −1 (3) |
| C20B | 9271 (6) | 3057 (4) | 7038 (5) | 68 (4) | 79 (4) | 53 (4) | 21 (3) | 19 (3) | 8 (3) |
| C21 | 6322 (5) | 2726 (3) | 7642 (5) | 44 (3) | 50 (3) | 53 (3) | 12 (2) | 9 (2) | −5 (2) |

[a] The fractional coordinates are multiplied by $10^5$ for the copper atoms and by $10^4$ for other atoms. The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$. The $U_{ij}$ elements are multiplied by $10^4$ for the copper atoms and by $10^3$ for other atoms. Numbers in parentheses in this table are estimated standard deviations in units of the last digit.

gas remaining, X, was measured using a Toepler pump. The gas was then circulated over CuO (240 °C) to oxidize CO to $CO_2$, which was trapped at −196 °C. Measurement of the amount of $CO_2$ produced gave the amount of CO evolved (0.32 mmol) and, by difference (X −CO), the amount of $O_2$ remaining (0.85 mmol). The amount of $O_2$ at the start (1.01 mmol) less the amount of $O_2$ remaining (0.85 mmol) gave the amount of $O_2$ consumed. In this case, 95% of the total CO was recovered and the $Cu/O_2$ stoichiometry was 2.00/0.94.

The infrared spectrum of the product isolated by suction filtration and air-drying was virtually identical with that of Cu(L)CO, **3**, except for the absence of $\nu_{CO}$ and slight changes near 1100 cm$^{-1}$. No peaks attributable to $\nu_{Cu-O}$ or to carbonate were observable. The mass spectrum showed a large peak at 44 mass units ($CO_2$), which does not appear in the mass spectrum of Cu(L)CO, **3**, as well as a significant peak at 456/458 mass units. (This latter peak appears very weakly

in the spectrum of Cu(L)CO and has not been assigned.)

**Growth of Single Crystals from Cu(L)CO in Benzene.** The carbonyl complex Cu(L)CO, **3** (50 mg), was added to dry benzene (30 mL) in air and stirred for 5 min, giving a deep red-brown solution. The solution was filtered and then allowed to slowly evaporate at 25 °C.

Under a microscope, dark parallelepipeds and dark amorphous masses were observed (as well as some yellow crystals of the free ligand, which were separated by hand). The infrared spectrum of the crystalline material showed no obvious $\nu_{Cu-O}$ or any indication of carbonate, but elemental analysis was consistent with the formula $C_{40}H_{32}N_{10}Cu_2CO_3$. Anal. Calcd: C, 58.65; H, 3.8; N, 16.7; Cu, 15.15. Found: C, 58.75; H, 3.95; N, 16.45; Cu, 14.8. Magnetic susceptibility measurements of the sample gave a $\mu_{cor}$ of 1.5 $\mu_B$ (25 °C, Faraday method). The mass spectrum of a parallelepiped crystal showed a strong peak at 44 mass units ($CO_2$), as well as significant

**Table IV.** Positional and Thermal Parameters$^a$ for $(CuL)_3(CuLO)(\mu\text{-OH})_3$, **5**

| | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu1 | 18219 (4) | 21856 (5) | 13605 (3) | 333 (4) | 702 (5) | 419 (4) | −34 (3) | 45 (3) | 98 (4) |
| Cu2 | 2272 (4) | 9950 (5) | 17345 (3) | 301 (4) | 673 (5) | 375 (4) | 67 (3) | 38 (3) | 21 (3) |
| Cu3 | 10238 (4) | −12729 (5) | 20060 (3) | 342 (4) | 633 (5) | 394 (4) | 53 (3) | 56 (3) | 142 (3) |
| Cu4 | −6201 (5) | −27299 (5) | 21148 (3) | 444 (4) | 745 (6) | 519 (4) | −44 (4) | 116 (3) | 174 (4) |
| O1 | 776 (2) | 1469 (2) | 1045 (1) | 40 (2) | 77 (2) | 31 (2) | −20 (2) | 6 (1) | 6 (2) |
| O2 | 335 (2) | −432 (2) | 1428 (1) | 43 (2) | 48 (2) | 40 (2) | 0 (2) | −5 (1) | 13 (2) |
| O3 | 9 (2) | −2397 (2) | 1556 (1) | 55 (2) | 66 (2) | 45 (2) | −18 (2) | 18 (2) | 5 (2) |
| O5 | 5009 (3) | 8416 (3) | 2057 (2) | 84 (3) | 125 (4) | 115 (4) | 9 (3) | 28 (3) | 40 (3) |
| N1A | 2430 (2) | 1687 (3) | 558 (2) | 34 (2) | 63 (3) | 31 (2) | −3 (2) | 3 (2) | 11 (2) |
| N2A | 4051 (2) | 1509 (3) | 1238 (2) | 32 (2) | 73 (3) | 42 (2) | 2 (2) | 8 (2) | 13 (2) |
| N3A | 3023 (2) | 2465 (2) | 1953 (2) | 29 (2) | 55 (3) | 40 (2) | −5 (2) | 2 (2) | 10 (2) |
| N4A | 2579 (2) | 3411 (3) | 2977 (2) | 40 (2) | 61 (3) | 44 (2) | −9 (2) | 3 (2) | 5 (2) |
| N5A | 1184 (2) | 3161 (2) | 2033 (2) | 37 (2) | 50 (3) | 45 (2) | 3 (2) | 6 (2) | 8 (2) |
| O4A | 962 (2) | 1790 (3) | −175 (2) | 5.21 (0.19)$^b$ | | | | | |
| C1A | 1855 (3) | 1568 (3) | −83 (2) | 33 (3) | 67 (4) | 55 (3) | 5 (3) | 8 (2) | 22 (3) |
| C2A | 2212 (3) | 1180 (3) | −667 (2) | 62 (3) | 65 (4) | 34 (3) | −12 (3) | 8 (2) | 13 (3) |
| C3A | 3161 (3) | 869 (3) | −611 (2) | 56 (3) | 54 (4) | 46 (3) | −5 (3) | 18 (3) | 11 (3) |
| C4A | 3544 (4) | 409 (4) | −1235 (3) | 74 (4) | 88 (5) | 59 (4) | −9 (3) | 28 (3) | −4 (3) |
| C5A | 3740 (3) | 1005 (3) | 42 (2) | 43 (3) | 64 (4) | 50 (3) | −2 (3) | 15 (2) | 14 (3) |
| C6A | 3384 (3) | 1408 (3) | 610 (2) | 41 (3) | 53 (3) | 45 (3) | −4 (2) | 12 (2) | 15 (3) |
| C7A | 3871 (3) | 1984 (3) | 1811 (2) | 33 (3) | 54 (3) | 50 (3) | −9 (2) | 6 (2) | 16 (3) |
| C8A | 4614 (3) | 2121 (3) | 2459 (2) | 36 (3) | 55 (3) | 46 (3) | −9 (2) | 1 (2) | 18 (3) |
| C9A | 5575 (3) | 1790 (4) | 2596 (2) | 41 (3) | 72 (4) | 52 (3) | 1 (3) | 6 (2) | 16 (3) |
| C10A | 6096 (3) | 2059 (4) | 3255 (3) | 37 (3) | 87 (4) | 68 (4) | −9 (3) | −7 (3) | 21 (3) |
| C11A | 5692 (4) | 2643 (4) | 3756 (2) | 56 (3) | 99 (5) | 52 (3) | −18 (3) | −14 (3) | 16 (3) |
| C12A | 4740 (3) | 2977 (4) | 3628 (2) | 50 (3) | 81 (4) | 48 (3) | −12 (3) | −1 (3) | 1 (3) |
| C13A | 4200 (3) | 2704 (3) | 2962 (2) | 39 (3) | 59 (4) | 49 (3) | −11 (2) | 2 (2) | 16 (3) |
| C14A | 3181 (3) | 2908 (3) | 2637 (2) | 42 (3) | 53 (3) | 45 (3) | −12 (2) | 4 (2) | 6 (3) |
| C15A | 1614 (3) | 3585 (3) | 2686 (2) | 45 (3) | 43 (3) | 54 (3) | −8 (2) | 11 (2) | 14 (3) |
| C16A | 1071 (3) | 4212 (3) | 3104 (2) | 53 (3) | 50 (3) | 62 (3) | −7 (2) | 17 (3) | 5 (3) |
| C17A | 116 (3) | 4448 (3) | 2877 (2) | 53 (3) | 37 (3) | 78 (4) | −2 (2) | 25 (3) | 9 (3) |
| C18A | −476 (4) | 5114 (4) | 3330 (3) | 66 (4) | 67 (4) | 103 (5) | 1 (3) | 33 (3) | 14 (3) |
| C19A | −295 (3) | 4030 (3) | 2204 (3) | 41 (3) | 64 (4) | 74 (4) | 9 (3) | 14 (3) | 20 (3) |
| C20A | 248 (3) | 3400 (4) | 1819 (3) | 47 (3) | 74 (4) | 52 (3) | 1 (3) | 4 (2) | 16 (3) |
| N1B | −1098 (2) | 1117 (2) | 1143 (2) | 31 (2) | 47 (3) | 38 (2) | 4 (2) | 6 (2) | 9 (2) |
| N2B | −1885 (2) | 2134 (2) | 2002 (2) | 30 (2) | 49 (3) | 47 (2) | 5 (2) | 12 (2) | 7 (2) |
| N3B | −214 (2) | 1798 (2) | 2511 (2) | 28 (2) | 44 (2) | 34 (2) | 1 (2) | 7 (2) | 5 (2) |
| N4B | 1233 (2) | 1806 (2) | 3419 (2) | 34 (2) | 51 (3) | 36 (2) | 3 (2) | 5 (2) | 6 (2) |
| N5B | 1558 (2) | 888 (2) | 2341 (2) | 29 (2) | 51 (3) | 38 (2) | 4 (2) | 6 (2) | 6 (2) |
| O4B | −473 (15) | −184 (15) | 245 (11) | 4.00$^b$ | | | | | |
| C1B | −1211 (3) | 645 (3) | 481 (2) | 39 (3) | 58 (3) | 40 (3) | 6 (2) | 6 (2) | 4 (2) |
| C2B | −2059 (3) | 655 (3) | 3 (2) | 55 (3) | 56 (3) | 34 (3) | −6 (2) | 2 (2) | 7 (2) |
| C3B | −2865 (3) | 1178 (3) | 186 (2) | 36 (3) | 52 (3) | 48 (3) | −4 (2) | −3 (2) | 19 (2) |
| C4B | −3794 (3) | 1231 (4) | −336 (2) | 51 (3) | 76 (4) | 61 (3) | −6 (3) | −2 (2) | 21 (3) |
| C5B | −2763 (3) | 1648 (3) | 863 (2) | 30 (2) | 54 (3) | 50 (3) | 5 (2) | 4 (2) | 15 (2) |
| C6B | −1891 (3) | 1624 (3) | 1337 (2) | 30 (2) | 45 (3) | 42 (3) | −1 (2) | 5 (2) | 11 (2) |
| C7B | −1131 (3) | 2191 (3) | 2507 (2) | 36 (3) | 40 (3) | 43 (3) | −2 (2) | 11 (2) | 12 (2) |
| C8B | −1181 (3) | 2735 (3) | 3206 (2) | 39 (3) | 45 (3) | 40 (3) | 3 (2) | 14 (2) | 10 (2) |
| C9B | −1923 (3) | 3264 (3) | 3747 (2) | 40 (3) | 56 (3) | 51 (3) | 6 (2) | 14 (2) | 10 (3) |
| C10B | −1721 (3) | 3684 (3) | 4166 (2) | 55 (3) | 65 (4) | 53 (3) | 12 (3) | 27 (3) | 7 (3) |
| C11B | −826 (4) | 3573 (4) | 4577 (2) | 70 (4) | 76 (4) | 36 (3) | 3 (3) | 18 (3) | −2 (3) |
| C12B | −76 (3) | 3049 (3) | 4311 (2) | 46 (3) | 67 (4) | 41 (3) | 5 (3) | 7 (2) | 6 (3) |
| C13B | −281 (3) | 2631 (3) | 3617 (2) | 42 (3) | 44 (3) | 39 (3) | 1 (2) | 17 (2) | 7 (2) |
| C14B | 333 (3) | 2033 (3) | 3172 (2) | 45 (3) | 39 (3) | 39 (3) | −4 (2) | 8 (2) | 10 (2) |
| C15B | 1837 (3) | 1248 (3) | 3025 (2) | 34 (3) | 43 (3) | 40 (3) | −6 (2) | 4 (2) | 8 (2) |
| C16B | 2780 (3) | 1063 (3) | 3375 (2) | 40 (3) | 53 (3) | 36 (3) | −3 (2) | −2 (2) | 8 (2) |
| C17B | 3449 (3) | 522 (3) | 3051 (2) | 27 (2) | 48 (3) | 53 (3) | −2 (2) | 1 (2) | 14 (2) |
| C18B | 4455 (3) | 315 (4) | 3442 (3) | 36 (3) | 86 (4) | 70 (4) | 4 (3) | −1 (3) | 19 (3) |
| C19B | 3156 (3) | 168 (3) | 2351 (2) | 32 (3) | 51 (3) | 57 (3) | 6 (2) | 13 (3) | 15 (3) |
| C20B | 2233 (3) | 363 (3) | 2025 (2) | 37 (3) | 56 (3) | 38 (3) | 1 (2) | 9 (2) | 6 (2) |
| N1C | 1789 (2) | −2026 (2) | 1295 (2) | 39 (2) | 55 (3) | 36 (2) | 4 (2) | 8 (2) | 11 (2) |
| N2C | 3244 (2) | −2426 (2) | 2081 (2) | 30 (2) | 53 (3) | 41 (2) | 0 (2) | 7 (2) | 9 (2) |
| N3C | 2092 (2) | −1565 (2) | 2722 (2) | 27 (2) | 47 (3) | 34 (2) | 1 (2) | 4 (2) | 13 (2) |
| N4C | 1515 (2) | −803 (2) | 3746 (2) | 37 (2) | 52 (3) | 36 (2) | 3 (2) | 3 (2) | 9 (2) |
| N5C | 263 (2) | −626 (2) | 2747 (2) | 33 (2) | 51 (3) | 37 (2) | −1 (2) | 6 (2) | 11 (2) |
| O4C | 421 (20) | −1756 (19) | 412 (14) | 4.00$^b$ | | | | | |
| C1C | 1313 (3) | −2153 (4) | 632 (2) | 50 (3) | 82 (4) | 49 (3) | 9 (3) | 12 (3) | 16 (3) |
| C2C | 1662 (3) | −2744 (4) | 99 (2) | 62 (3) | 76 (4) | 43 (3) | −0 (3) | 10 (3) | 11 (3) |
| C3C | 2532 (3) | −3255 (3) | 227 (2) | 59 (3) | 52 (3) | 48 (3) | 1 (3) | 17 (3) | 10 (3) |
| C4C | 2901 (4) | −3916 (4) | −352 (3) | 94 (4) | 66 (4) | 73 (4) | 7 (3) | 41 (3) | 5 (3) |
| C5C | 3030 (3) | −3120 (3) | 901 (2) | 45 (3) | 62 (4) | 50 (3) | 8 (2) | 15 (2) | 16 (3) |
| C6C | 2663 (3) | −2508 (3) | 1428 (2) | 39 (3) | 50 (3) | 51 (3) | 3 (2) | 17 (2) | 17 (3) |
| C7C | 2971 (3) | −2013 (3) | 2634 (2) | 30 (3) | 39 (3) | 43 (3) | −5 (2) | 3 (2) | 15 (2) |
| C8C | 3628 (3) | −1985 (3) | 3314 (2) | 36 (3) | 45 (3) | 42 (3) | 0 (2) | 6 (2) | 14 (2) |
| C9C | 4572 (3) | −2355 (3) | 3509 (2) | 39 (3) | 53 (3) | 54 (3) | 6 (2) | 8 (2) | 13 (3) |
| C10C | 4978 (3) | −2229 (3) | 4206 (2) | 36 (3) | 60 (4) | 60 (3) | 4 (2) | −4 (2) | 16 (3) |
| C11C | 4460 (3) | −1775 (3) | 4682 (2) | 50 (3) | 67 (4) | 45 (3) | 4 (3) | −12 (2) | 9 (3) |

**Table IV** (*Continued*)

|  | x/a | y/b | z/c | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C12C | 3522 (3) | −1412 (3) | 4495 (2) | 51 (3) | 62 (4) | 42 (3) | 7 (3) | 0 (2) | 7 (3) |
| C13C | 3117 (3) | −1533 (3) | 3798 (2) | 36 (3) | 47 (3) | 39 (3) | −2 (2) | −1 (2) | 14 (2) |
| C14C | 2146 (3) | −1257 (3) | 3417 (2) | 37 (3) | 44 (3) | 39 (3) | 1 (2) | 3 (2) | 16 (2) |
| C15C | 590 (3) | −509 (3) | 3431 (2) | 38 (3) | 40 (3) | 42 (3) | −4 (2) | 5 (2) | 11 (2) |
| C16C | 4 (3) | −65 (3) | 3883 (2) | 48 (3) | 51 (3) | 37 (3) | −1 (2) | 13 (2) | 7 (2) |
| C17C | −916 (3) | 286 (3) | 3650 (2) | 40 (3) | 40 (3) | 60 (3) | 4 (2) | 18 (2) | 15 (2) |
| C18C | −1526 (3) | 800 (4) | 4137 (3) | 61 (3) | 76 (4) | 69 (4) | 12 (3) | 25 (3) | 25 (3) |
| C19C | −1252 (3) | 142 (3) | 2946 (3) | 30 (3) | 65 (4) | 53 (3) | 5 (2) | 8 (2) | 17 (3) |
| C20C | −655 (3) | −287 (3) | 2531 (2) | 36 (3) | 66 (4) | 45 (3) | 3 (2) | −1 (2) | 18 (3) |
| N1D | −1859 (2) | −2996 (3) | 1434 (2) | 47 (2) | 65 (3) | 49 (3) | −8 (2) | 12 (2) | 8 (2) |
| N2D | −2890 (2) | −2289 (3) | 2207 (2) | 38 (2) | 68 (3) | 52 (3) | −1 (2) | 11 (2) | 18 (2) |
| N3D | −1257 (2) | −2507 (3) | 2828 (2) | 42 (2) | 59 (3) | 47 (2) | −1 (2) | 10 (2) | 21 (2) |
| N4D | 95 (3) | −2486 (3) | 3801 (2) | 54 (3) | 59 (3) | 50 (3) | −6 (2) | 7 (2) | 17 (2) |
| N5D | 602 (3) | −3119 (3) | 2742 (2) | 47 (2) | 61 (3) | 64 (3) | 3 (2) | 16 (2) | 22 (2) |
| O4D | −982 (31) | −3826 (30) | 689 (21) | 4.00[b] |  |  |  |  |  |
| C1D | −1801 (4) | −3448 (4) | 785 (2) | 59 (4) | 72 (4) | 63 (4) | −9 (3) | 16 (3) | −1 (3) |
| C2D | −2576 (4) | −3642 (4) | 257 (2) | 63 (4) | 82 (4) | 57 (4) | −10 (3) | 10 (3) | −5 (3) |
| C3D | −3484 (4) | −3367 (4) | 375 (2) | 59 (3) | 69 (4) | 61 (4) | −11 (3) | −5 (3) | 8 (3) |
| C4D | −4358 (4) | −3570 (5) | −194 (3) | 80 (4) | 119 (6) | 81 (5) | −10 (4) | −9 (4) | −8 (4) |
| C5D | −3548 (3) | −2914 (4) | 1030 (2) | 44 (3) | 74 (4) | 59 (3) | −8 (3) | 3 (2) | 18 (3) |
| C6D | −2741 (3) | −2739 (3) | 1562 (2) | 48 (3) | 61 (4) | 54 (3) | −3 (2) | 15 (2) | 19 (3) |
| C7D | −2210 (3) | −2198 (3) | 2765 (2) | 38 (3) | 54 (3) | 57 (3) | −5 (2) | 11 (2) | 23 (3) |
| C8D | −2375 (3) | −1751 (3) | 3450 (2) | 49 (3) | 55 (3) | 46 (3) | −8 (3) | 11 (2) | 14 (3) |
| C9D | −3179 (3) | −1335 (4) | 3675 (3) | 44 (3) | 68 (4) | 68 (4) | −4 (3) | 18 (3) | 7 (3) |
| C10D | −3089 (4) | −973 (4) | 4371 (3) | 66 (4) | 73 (4) | 71 (4) | −13 (3) | 32 (3) | −5 (3) |
| C11D | −2226 (4) | −1037 (4) | 4829 (2) | 85 (4) | 72 (4) | 52 (3) | −21 (3) | 24 (3) | −1 (3) |
| C12D | −1406 (4) | −1462 (3) | 4611 (2) | 64 (3) | 60 (4) | 50 (3) | −15 (3) | 4 (3) | 10 (3) |
| C13D | −1500 (3) | −1811 (3) | 3919 (2) | 51 (3) | 47 (3) | 49 (3) | −7 (2) | 14 (2) | 15 (3) |
| C14D | −801 (3) | −2294 (3) | 3514 (2) | 50 (3) | 51 (3) | 52 (3) | −10 (3) | 2 (2) | 24 (3) |
| C15D | 771 (3) | −2961 (3) | 3429 (2) | 56 (3) | 47 (3) | 59 (3) | −9 (3) | 10 (3) | 18 (3) |
| C16D | 1654 (3) | −3276 (4) | 3812 (2) | 49 (3) | 67 (4) | 64 (3) | −8 (3) | 1 (3) | 29 (3) |
| C17D | 2357 (3) | −3776 (4) | 3501 (3) | 46 (3) | 61 (4) | 95 (4) | −8 (3) | 9 (3) | 36 (3) |
| C18D | 3302 (4) | −4124 (4) | 3898 (3) | 53 (3) | 85 (5) | 122 (5) | −2 (3) | −2 (3) | 50 (4) |
| C19D | 2169 (3) | −3944 (4) | 2800 (3) | 44 (3) | 69 (4) | 104 (5) | 11 (3) | 29 (3) | 36 (3) |
| C20D | 1305 (4) | −3602 (4) | 2446 (3) | 57 (3) | 84 (4) | 74 (4) | 1 (3) | 23 (3) | 22 (3) |
| C21 | 6173 (4) | 5389 (4) | 3978 (3) | 83 (4) | 75 (5) | 92 (5) | 16 (3) | −29 (4) | −10 (4) |
| C22 | 6195 (4) | 5470 (4) | 4643 (3) | 46 (3) | 94 (5) | 144 (6) | −1 (3) | 15 (4) | 52 (4) |
| C23 | 6826 (4) | 5963 (4) | 5136 (3) | 69 (4) | 135 (6) | 60 (4) | 18 (4) | 23 (3) | 30 (4) |
| C24 | 7428 (4) | 6396 (4) | 4975 (3) | 61 (4) | 88 (5) | 98 (5) | −7 (3) | 5 (3) | −2 (4) |
| C25 | 7438 (4) | 6319 (4) | 4323 (3) | 104 (5) | 88 (5) | 123 (6) | 14 (4) | 63 (4) | 43 (4) |
| C26 | 6801 (5) | 5802 (4) | 3814 (3) | 137 (6) | 109 (5) | 48 (4) | 53 (4) | 33 (4) | 24 (4) |
| C27 | 6417 (4) | 4259 (4) | 1951 (3) | 115 (5) | 87 (5) | 57 (4) | 36 (4) | 33 (4) | 27 (3) |
| C28 | 6317 (4) | 5156 (4) | 1892 (3) | 114 (5) | 84 (5) | 70 (4) | −1 (4) | 40 (4) | 22 (3) |
| C29 | 5463 (5) | 5701 (4) | 1937 (3) | 125 (5) | 61 (4) | 78 (4) | 22 (4) | 35 (4) | 26 (3) |
| C30 | 4736 (4) | 5350 (4) | 2041 (3) | 90 (5) | 92 (5) | 71 (4) | 22 (4) | 25 (4) | 29 (3) |
| C31 | 4852 (4) | 4444 (4) | 2085 (3) | 101 (5) | 103 (5) | 87 (5) | −15 (4) | 17 (4) | 35 (4) |
| C32 | 5698 (5) | 3906 (4) | 2047 (3) | 158 (6) | 55 (4) | 73 (4) | 3 (4) | 34 (4) | 26 (3) |
| C33 | 40 (10) | 4134 (7) | 202 (7) | 227 (11) | 133 (9) | 149 (10) | −97 (9) | 93 (9) | −34 (8) |
| C34 | 600 (6) | 4776 (1) | 579 (4) | 138 (7) | 132 (9) | 115 (7) | −47 (6) | 41 (6) | 5 (7) |
| C35 | 652 (7) | 5633 (7) | 462 (6) | 171 (9) | 100 (8) | 151 (10) | −58 (6) | 79 (8) | −9 (7) |

[a] See note *a*, Table III. [b] Isotropic *B*.

peaks at 326 (L), 327 (HL), and 389/391 (CuL) mass units. These do not appear in the spectrum of Cu(L)CO, **3**. The mass spectrum of one of the amorphous masses showed a weak peak at 44 mass units, as well as a significant peak at 456/458 mass units. A subsequent crystal structure analysis of one of the parallelepipeds showed a carbonate-bridged structure $(CuL_2)(\mu\text{-}CO_3)$, **4**.

**Growth of Single Crystals from Benzene in the Absence of Carbon Dioxide.** The same crystal-growing process was carried out in a glovebox in which air near atmospheric pressure was continuously passed over Ascarite in order to remove any carbon dioxide. Again dark red parallelepipeds were formed, together with amorphous material. The infrared spectrum of the sample was identical with that of the product isolated in the previous experiment. Several crystals were examined by photographic X-ray diffraction techniques. Some were found to have the cell dimensions of the bridging carbonate dimer structure, **4**, while others had a different cell. A structure determination of these latter crystals showed a high molecular weight tetrameric complex $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, **5**.

**X-ray Data Collection.** Preliminary precession and Weissenberg photographs showed triclinic symmetry for the crystals of $(CuL)_2$-$(\mu\text{-}CO_3)$, **4**, and $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, **5**. Further data were collected on a Datex-automated General Electric quarter-circle diffractometer using Cu Kα radiation (λ 1.5418 Å). Lattice parameters (Table II) were derived from a least-squares fit to the setting angles for 16 manually centered reflections for **4** and 17 for **5**. Intensities were measured using $\theta$–$2\theta$ scans with a scanning rate of 1°/min, a takeoff angle of 3°, and background counts of 20 s at each extremum; the scan range was 1.8° for **4** and varied from 1.8° (at $2\theta = 3°$) to 3.0° (at $2\theta = 120°$) for **5**. For **4**, 4578 reflections were measured out to $2\theta = 110°$, of which 4406 had positive net intensities and were used in the structure analysis; for **5**, 9334 reflections were measured out to $2\theta = 120°$, of which 8709 were positive. Three check reflections measured periodically for each crystal showed no significant changes. The intensities for **5** were corrected for absorption[56] (the crystal had dimensions 0.10 × 0.10 × 0.37 mm), with the transmission coefficients ranging from 0.79 to 0.86; intensities for **4** (0.08 × 0.15 × 0.38 mm) were not corrected. The observational variances $\sigma^2(F_o^2)$ were based on counting statistics plus an additional term $(0.025S)^2$, where $S$ is the scan count.

**Structure Solution and Refinement**

The function minimized in the least-squares refinements was $\sum w(F_o^2 - F_c^2)^2$, with weights $w$ equal to $\sigma^{-2}(F_o^2)$.[57] The $R$ index is $\sum ||F_o| - |F_c||/\sum |F_o|$. Neutral-atom scattering factors for Cu were taken from Cromer and Waber,[60] those for C, N, and O from ref 42, and those for H from Stewart et al.[61] The real component of

anomalous dispersion was included for Cu.[62]

**(CuL)$_2$($\mu$-CO$_3$), 4.** Most of the atoms in the asymmetric unit were found by direct methods.[59] Difference Fourier maps yielded the positions of the remaining nonhydrogen atoms and, eventually, of the methyl hydrogen atoms; the remaining hydrogen atoms were positioned in idealized locations with C–H = 0.96 Å. Final refinement was by blocked least squares, with the coordinates of the 56 heavier atoms in one matrix and their anisotropic temperature parameters, a scale factor, and an extinction parameter in a second. The final $R$ index was 0.058 for 4578 observations and 506 parameters. A final difference map showed no features greater than 0.4 e/Å$^3$. Final atomic parameters for the nonhydrogen atoms are given in Table III; those for the hydrogen atoms are available as supplementary material.

**(CuL)$_3$(CuLO)($\mu$-OH)$_3$, 5.** Positions for all copper, bridging oxygen, and nitrogen atoms were obtained by direct methods;[59] difference maps showed the positions of the ligand carbon atoms and of the 2.5 benzene molecules in the asymmetric unit. Isotropic refinement based on data out to 80° in 2θ lowered $R$ to 0.086. Hydrogen atoms were assigned idealized coordinates (C–H = 0.96 Å) except for those of the methyl groups and the bridging OH groups, which were located on difference maps.

After initial block-diagonal anisotropic refinement, a difference map showed a number of features. The most prominent were two peaks of magnitude approximately 5 e/Å$^3$, one being identified as a water molecule, O5, and the second located close to the ring carbon atom C1 of ligand A; three smaller peaks were located close to the C1 atoms of the other three ligands. These latter four peaks were identified as oxygen atoms, O4, in partially occupied sites.

In the final least-squares cycles, the matrices were blocked in the following way. The coordinates of C1A and O4A, the anisotropic temperature parameters for C1A, and an isotropic temperature parameter and a population factor of O4A were refined in one matrix. Similar matrices were set up for C1B and O4B, for C1C and O4C, and for C1B and O4D, except that the isotropic temperature factors for these O4 atoms were not refined. In all four cases a partial hydrogen atom, with a population factor equal to the difference between 1.0 and that of the corresponding O4 atom, was placed in the idealized position (C–H = 0.96 Å); its parameters were not refined. The coordinates and anisotropic temperature parameters of the three carbon atoms C33–C35 of the benzene ring lying on a center of symmetry were also included in a single matrix, since the thermal motion of this molecule was very large and the C–C distances were irregular. (They remained irregular at the conclusion of the refinement, varying from 1.31 to 1.56 Å. It is likely that this molecule is somewhat disordered.) The coordinates and anisotropic temperature parameters of the remaining Cu, O, N, and C atoms were blocked into a 3 × 3 and a 6 × 6 matrix for each atom.

The final $R$ index was 0.065 and the goodness of fit $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ was 1.87 for $p = 1125$ parameters and $n = 9334$ reflections. The largest residual peaks on a difference map were 0.78 e/Å$^3$ near Cu4 and 0.52 e/Å$^3$ near Cu1. Final atomic parameters for the nonhydrogen atoms are given in Table IV; those for the hydrogen atoms are available as supplementary material.

**Supplementary Material Available:** Positional and thermal parameters used for the hydrogen atoms in the refinement of **4** (Table V) and **5** (Table VI), individual bond distances (Table VII) and angles (Table VIII) for the tridentate ligands, bond distances and angles for the benzene molecules in the unit cell of **5** (Table IX), and listings of the structure factor amplitudes for **4** (Table X) and **5** (Table XI) (58 pages). Ordering information is given on any current masthead page.

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# Synthesis and X-ray Structural Characterization of RhCl$_2$(PMe$_2$Ph)$_2$(C$_3$Ph$_3$), the Product of an Oxidative Addition–Ligand Elimination Reaction

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The Vaska complexes Rh(CO)Cl(PR$_3$)$_2$ (R$_3$ = Me$_3$, Me$_2$Ph, MePh$_2$) react with triphenylcyclopropenium salts to generate blue-green rhodiacyclic complexes via oxidative cleavage of the C–C bond. All reactions are accompanied by loss of carbon monoxide. The molecular structure of one such oxidative addition–ligand elimination adduct has been determined by a three-dimensional single-crystal X-ray diffraction study. The title compound crystallizes in the monoclinic space group *C*2/*c* with four molecules in a unit cell which measures *a* = 19.190 (7) Å, *b* = 11.892 (6) Å, *c* = 14.346 (4) Å, and β = 93.88 (2)°. The structure was solved by heavy-atom techniques and refined by full-matrix, mixed iso/anisotropic least-squares analysis to a conventional *R* value of 0.041 for the 2550 independent observed ($I > 2\sigma(I)$) reflections. The Rh(III) adduct displays pseudooctahedral symmetry with trans phosphines, cis chloride ligands, and a bidentate propenylium-1,3-diyl group. Key bond distances include Rh–P = 2.354 (1) Å, Rh–Cl = 2.472 (1) Å, and Rh–C(propenylium) = 2.000 (4) Å. Structural parameters are compared to the electronically equivalent [IrCl(CO)(PMe$_3$)$_2$(C$_3$Ph$_3$)]$^+$ cation; the M(C$_3$Ph$_3$)$^+$ units in the two structures are noted to be essentially identical. Comparison of Rh(III)–C(sp$^2$) bond lengths in similar complexes suggests a weak but real π component to the Rh–C(propenylium) bond.

## Introduction

Oxidative cleavage of the C–C bond of a strained cyclic hydrocarbon is the most reliable of several known synthetic routes to metallocyclic complexes in the cases where the metal possesses a high propensity to undergo oxidative addition. This reaction has been demonstrated for both saturated[1] and unsaturated ring systems[2] and is sometimes coupled to small molecule insertions.[1,2e,f] In our laboratory we have been concentrating on the unsaturated cyclopropenes and cyclopropenium ions. The latter species can be stabilized in a η$^3$ configuration in (η$^3$-C$_3$R$_3$)Ni(CO)Br,[3] will ring-open, undergo insertion of CO, and be stabilized as a coordinated C$_3$R$_3$CO cyclic ketone in (η$^3$-C$_3$R$_3$CO)Co(CO)$_3$,[4] or will ring-open to form a four-membered metallocycle as in [Ir(CO)Cl(PMe$_3$)$_2$(C$_3$Ph$_3$)]$^+$.[2a,b] The latter reaction of Ir(CO)Cl(PMe$_3$)$_2$ and C$_3$Ph$_3^+$BF$_4^-$ to form the cationic oxidative addition adduct [Ir(CO)Cl(PMe$_3$)$_2$(C$_3$Ph$_3$)]$^+$ was one of the first authenticated cases of oxidative cleavage of the C–C bond.

Our extension of this iridium work into rhodium chemistry has resulted in a similar oxidative cleavage of the cyclopropenium C–C bond but with several unexpected developments. In contrast to the straightforward reaction with Ir(CO)Cl(PMe$_3$)$_2$, C$_3$Ph$_3^+$X$^-$ (X = Cl, PF$_6$) reacts with Rh(CO)Cl(PR$_3$)$_2$ complexes with facile evolution of carbon monoxide and a dramatic color change from yellow to blue-green. These observations led us to believe that the rhodium reaction proceeded differently from that of iridium and, as a consequence, to undertake a full single-crystal X-ray

diffraction study to ascertain the mode of reaction. Since the blue-green complex is diamagnetic (inference from NMR), several structural possibilities arise: viz, the η$^3$-cyclopropenylrhodium(I) complex, I, and the metallocyclic Rh(III) adduct, II. However, only a few rhodium-containing, green compounds are known,[5] and these are Rh(II) species which are expected to be paramagnetic unless dimeric. This consideration suggests the possibility of a dimeric structure such as III. Preliminary results of the X-ray study, which have been communicated,[6] show that II represents the correct formu-



I

II

III
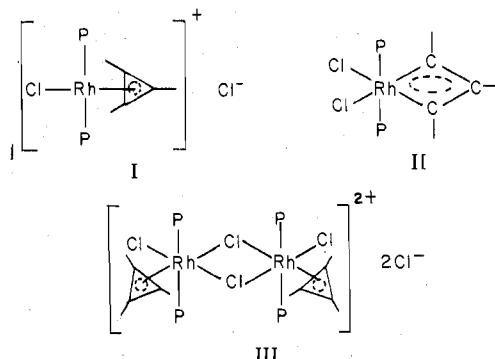
lation. In this paper we wish to present the results of our completed X-ray study together with some additional synthetic findings which add insights into the subtle differences which exist between the iridium and rhodium analogues of the Vaska

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