Communications to the Editor

Carbon Monoxide Bridges Two Copper Centers Which Experience a Very Short Metal-Metal Proximity in [Cu_2(tmen)$_2$(μ-CO)(μ-$PhCO_2$)](BPh_4)

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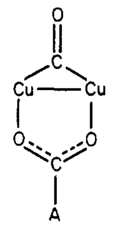
Only recently the presence of terminal CO bonded to copper(I) was, even from a structural point of view, ascertained.[1] No other bonding mode of carbon monoxide to copper has been identified,[2,3] in spite of the versatility of copper in promoting reaction in which CO is involved.

We report here an unprecedented dinuclear copper complex containing the skeleton A which may be of interest for the activation of CO and other small molecules.

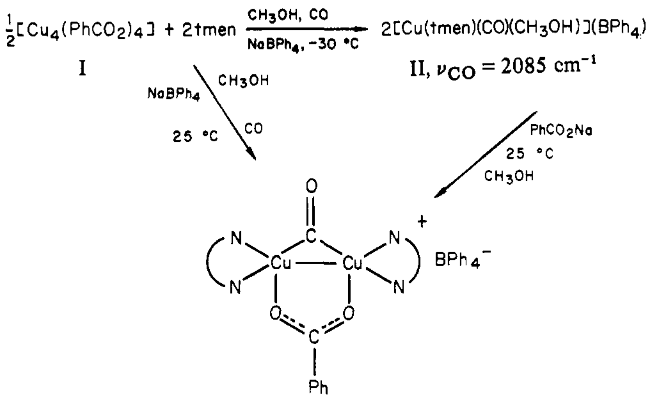


A

Results in the dinuclear copper complex area are limited to the synthesis of bimetallic compounds, in which metal centers, at best, work independently of each other with regard to the coordination of a given small molecule.[4] In spite of many attempts, no bimetallic complex has been thus far reported in which both coppers have been ascertained to interact with the same substrate such as CO or O_2.[4] This emphasizes further the interest in the properties of a complex containing skeleton A.

Reaction of copper(I) benzoate (I)[5] with carbon monoxide in methanol containing *N,N,N′,N′*-tetramethylethylenediamine (tmen) affords complex III[6] through the steps outlined in Scheme I.

Scheme I[a]



III, ν_{CO} = 1926 cm^{-1}

[a] II, ref 7; III, ref 6 and 8; N N = tmen

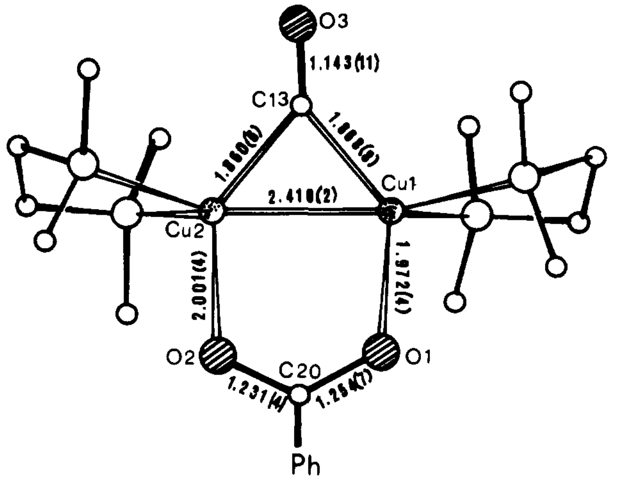


Figure 1. The molecular structure of [Cu_2(tmen)$_2$(μ-CO)(μ-$PhCO_2$)]$^+$ showing the most relevant bond distances. Some bond angles are as follows: Cu(1)–C(13)–Cu(2) = 80.6 (3)°, C(13)–Cu(2)–O(2) = 135.8 (2)°, C(13)–Cu(1)–O(1) = 134.6 (2)°, and O(2)–C(20)–O(1) = 123.8 (6)°.

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[6] Copper(I) benzoate (2.65 g, 3.65 mmol) absorbed carbon monoxide at room temperature in methanol (30 mL). The resulting solid dissolved upon addition of a methanolic solution (10 mL) of tmen (2.2 mL, 14.58 mmol), giving a light-blue solution (ν_{CO} = 2070 cm^{-1}) which was added dropwise, at room temperature, to a methanolic solution (15 mL) of $NaBPh_4$ (7.74 g, 22.63 mmol). The white solid suddenly formed slowly lost CO and gave light-yellow crystals of III (~70%), ν_{CO} (Nujol) = 1926 cm^{-1}. III is soluble in THF where it displays two CO bands at 2055 cm^{-1} (weak) and 1930 cm^{-1} (strong). Complex III reacts in toluene with P(OEt)$_3$, giving 0.97 mol of CO per two coppers.

[7] A carbonylated suspension of copper(I) benzoate (1.02 g, 1.38 mmol) in methanol (30 mL) was cooled at -30 °C and then reacted with tmen (0.85 mL, 5.63 mmol) dissolved in methanol (10 mL). To the resulting solution, kept at -30 °C, a methanolic solution (10 mL) of $NaBPh_4$ (1.88 g, 5.50 mmol) was added dropwise. A white crystalline solid suddenly formed; this was filtered and dried at -30 °C in a stream of carbon monoxide (~35%). The IR spectrum in Nujol showed the presence of a strong band at 2085 cm^{-1} (CO) and a band centered at 3500 cm^{-1} (complex envelope due to bonded CH_3OH). Complex II simultaneously releases CO and CH_3OH at room temperature, even in the solid state, as can be followed by the IR sepctrum. Analytical data correspond to a solid which no longer contained CH_3OH and CO.

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Complex III was isolated as a light-yellow crystalline solid stable in the solid state even in air. The rather low, for a copper carbonyl, CO stretching frequency [ν_{CO} (Nujol) 1926 cm^{-1}] suggests the presence in III of a bridging CO,[3] while other unexpected details of the structure of III have been revealed by an X-ray analysis.

Crystal Data: $C_{44}H_{57}BCu_2N_4O_3$, M = 827.9, monoclinic, a = 31.875 (3), b = 9.748 (1), c = 14.344 (2) Å, β = 95.50 (2)°, Z = 4; d_{calcd} = 1.239 g cm^{-3}, space group *I*2 (from systematic absences and structural analysis).[9] Intensity data were collected at the ambient temperature on an "on-line" single-crystal Siemens AED diffractometer using Cu Kα radiation (λ = 1.54178 Å, 6° < 2θ < 120°) at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu Kα peak. For intensities and background the "five-point" technique[10] was used. A total of 3440 independent reflections were measured, of which 2993 were considered observed ($I > 2\sigma(I)$) and used in the structure determination and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques,[11] with anisotropic parameters for nonhydrogen atoms. The final R index was 0.043.[12]

Figure 1 shows a view of the dimeric cation $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)]^+$ with the most relevant bond distances and angles. Each copper has a pseudotetrahedral coordination geometry. The atoms of the two bridging ligands, CO and the carboxylato group, are nearly coplanar with Cu(1) and Cu(2), the dihedral angle between the planes Cu(2), C(13), O(3), Cu(1) and Cu(2), O(2), C(20), O(1), Cu(1) being 169°. The two planes containing copper and the nitrogen donor atoms Cu(1), N(1), N(2) and Cu(2), N(3), N(4) are practically orthogonal to the planes cited above.

The most relevant structural parameters concern (i) the Cu–C bond distances which are the longest so far encountered in copper carbonyl complexes as a consequence of the bridging mode of CO[1]—these distances fall in the range found in some copper alkyls;[13] (ii) the C(13)–O(3) bond distance which is only slightly affected by the bridging bonding mode displayed by CO;[1] (iii) the closeness of the two copper atoms. Such a copper–copper distance exists in a few cases in copper(I) clusters.[14] Whether this distance signifies the existence of a copper–copper direct bond is an open question. We feel that the possible metal–metal interaction responsible for the short interatomic distance is better described in terms of multicentered linkages between the metal and the bridging ligands.

It must be pointed out that the skeleton A in complex III only exists in the solid state and in noncoordinating solvents, such as toluene, in which, however, III is only slightly soluble. When III is dissolved in THF, it displays two CO bands at 2055 and 1930 cm^{-1}, ascribable to a partial splitting of the bridging CO by the action of THF.

We would like to stress the relevance of the results presented in the light of the following:

(i) Carbon monoxide displays in a copper(I) complex a bridging bonding mode which is one of the prerequisites for making easier its metal-promoted reduction. This is rather significant in the case of a metal like copper, which has a low oxophilicity and reacts easily with H_2. In this context, it must be noticed that, while the presence of copper in various heterogeneous catalysts promoting the reduction of carbon monoxide is very well documented,[15] the information so far available on copper(I) models is very scanty.

(ii) A complex like III may be used as a dinuclear model compound in which CO could be replaced by other small molecules. In this connection, a close relationship could be found between the dinuclear copper unit proposed to be present in naturally occurring systems and the unit A.[16]

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Supplementary Material Available: The final atomic parameters (Tables SI and SII), bond distances and angles (Tables SIII and SIV), molecular structure of $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)]^+$ with the numbering scheme, and a complete listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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[8] When complex II (0.70 g, 1.25 mmol) was added to a methanolic solution (15 mL) of $PhCO_2Na$ (1.0 g, 6.94 mmol) at room temperature, a yellow crystalline solid, which was shown to be III, suddenly formed.

[9] The unit cell parameters reduced to the standard setting *C*2 (No. 5) are a = 33.677 (3), b = 9.748 (1), c = 14.344 (2) Å, β = 109.59 (2)°. The transformation matrix from the *I*2 to *C*2 orientation is (−1 0 −1 // 0 −1 0 // 0 0 1). Coordinates of equivalent positions for the nonstandard *I*2 setting are $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2)+$; x, y, z; $-x, -y, -z$. Reexamination of cell constants showed no higher simmetry (S. L. Lawton and R. A. Jacobson, "TRACER, The reduced cell and its crystallographic applications" Report IS-1141, 1965, USAEC, Ames Laboratory, Ames, IA).

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[11] Data reduction, structure solution, and refinement were carried out on a CYBER 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale (Casalecchio, Bologna), using the SHELX-76 system of computer programs (G. Sheldrick, University of Cambridge, 1976). Calculations were performed with the financial support of the University of Parma.

[12] In the first stage of the refinement the phenyl rings of the BPh_4^- anion were constrained as "rigid groups" with free isotropic thermal parameters; then the constraints were removed and the phenyl carbons were allowed to vary anisotropically. All the phenyl hydrogen atoms were located in a difference Fourier map while those associated with the tmen carbon atoms could not be clearly found, probably as a consequence of high thermal motion of their parent atoms. Owing to the limitations of SHELX, only 33 out of the 57 hydrogen atoms were introduced in structure factor calculations. They were put in subsequent refinements in idealized positions (recalculated after every second refinement cycle) riding with isotropic thermal parameters on their parent carbon atoms.

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Reduction of Bis(histidine)hemin; Model for the Proton-Coupled Reduction of Hemoproteins

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One of the main methods by which the proton modifies and controls the activity of hemoproteins is to couple together equilibria involving the Fe atom (e.g., reduction, coordination) with equilibria involving a second site; examples include the "cooperative effects" in hemoglobin[1,2] and the proton-coupled reduction[3-5] of, and coordination of anions[6] to, the Fe(III) ion in peroxidases, which are probably related to the mechansim of activation of H_2O_2.[2,7] The coordination of histamine to the Co(III) ion in cyanoaquocobinamide is known[8] to reduce the pK of the pendant amino group

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