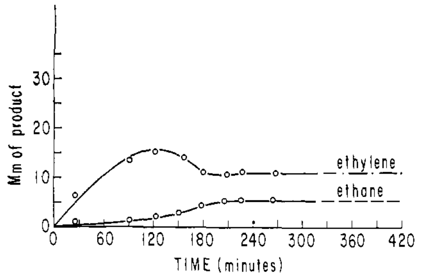
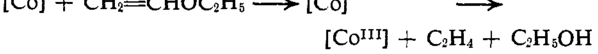


Figure 1. Production of ethylene and ethane from the reaction of hydridocobalamin with 100 mM of ethyl vinyl ether in acetic acid in the absence of reducing agent.

only ethylene is produced; ethane appears after prolonged reaction times (Figure 1). Hydridocobalamin is expected to react with the vinyl ether to yield 2-ethoxyethylcobalamin as the initial product. The latter is unstable in acidic media, decomposing with Co–C bond cleavage and formation of ethylene according to eq 2.[9,10] The ethane is a secondary product of the



$$\overset{\text{H}}{\overset{|}{[\text{Co}]}} + \text{CH}_2\text{=CHOC}_2\text{H}_5 \longrightarrow \overset{\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5}{\overset{|}{[\text{Co}]}} \xrightarrow{\text{H}^+} [\text{Co}^{\text{III}}] + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{OH} \quad (2)$$

reaction[8] of ethylene with hydridocobalamin, affording ethylcobalamin, which in turn undergoes reductive Co–C bond cleavage in the presence of excess reducing agent. Quantitative conversions of ethyl vinyl ether into mixtures of C_2H_4 and C_2H_6 were observed in the reactions of hydridocobalamin in the presence of excess reducing agent (Zn dust in acetic acid). In summary, our findings do not confirm the claim that Co(III) derivatives of corrins and cobaloximes react with vinyl ethers according to eq 1. The reaction for this reason also cannot be regarded as a model of dioldehydrase action. On the other hand, the demonstrated reaction of hydridocobalamin with ethyl vinyl ether takes a course in agreement with known reactions of hydridocobalamin with olefinic substrates, and of 2-alkoxyethylcorrin derivatives.[11]

(9) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **89**, 143 (1967).

(10) H. P. C. Hogenkamp, J. E. Rush, and C. A. Swenson, *J. Biol. Chem.*, **240**, 3641 (1965).

(11) This work was supported by Grant GP28485X of the National Science Foundation.

(12) Postdoctoral Fellow, U.C.S.D., 1971–present.

W. J. Michaely,[12] G. N. Schrauzer*
Department of Chemistry
The University of California at San Diego, Revelle College
La Jolla, California 92037

Received May 14, 1973

Tetrameric Phosphinecopper(I) Halides. X-Ray Crystallographic Evidence for a "Cubane" Structure for the Cu_4Cl_4 Core of $(PPh_3CuCl)_4$ and a "Step" Structure for the Cu_4Br_4 Core in Crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$

Sir:

Our recent structural analyses of $(PPh_3CuH)_6$ (in which distances between adjacent copper atoms range from 2.494 (6) to 2.674 (5) Å)[1] and $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$ (Cu···Cu = 2.663 (6)–2.829 (6) Å),[2] coupled with a consideration of copper–copper distances within other copper cluster complexes[3–7] (in at least some of which *bonding* Cu···Cu interactions are believed to be present), have led us to be suspicious of the widely quoted value of 2.60 Å for the *nonbonding* Cu···Cu separation in $(AsEt_3CuI)_4$, a molecule with a "cubane" skeleton.[8] This distance is, indeed, likely to be of low accuracy because (1) the structural analysis was performed in the 1930's, (2) a very limited data set was used, (3) least-squares refinement of atomic parameters was not, at that time, possible, and (4) the copper atoms ($Z = 29$) are not the major contributors to the intensities of scattered X-rays, since $Z(\text{I}) = 53$ and $Z(\text{As}) = 33$.

We have now completed X-ray diffraction studies on the related tetramers $(PPh_3CuCl)_4$ and $(PPh_3CuBr)_4 \cdot 2CHCl_3$. As outlined below, $(PPh_3CuCl)_4$ has the expected[8,9] "cubane" structure (and *long* Cu···Cu distances). Unexpectedly, the Cu_4Br_4 core in crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$ *does not* define a cube, but has an entirely different configuration, which we term a "step" structure.

Details of the crystallographic results are as follows. The species $(PPh_3CuCl)_4$ crystallizes in the centrosymmetric orthorhombic space group *Pbcn* (No. 60; $D_{2h}{}^{14}$) with $a = 17.468$ (2), $b = 20.519$ (3), $c = 18.215$ (2) Å, and $Z = 4$. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer using Mo Kα radiation and a θ–2θ scan technique; the structure was solved *via* Patterson, Fourier, and least-squares refinement methods. All atoms, including hydrogens, have been located, the final discrepancy indices being $R_F = 8.7\%$ and $R_{wF} = 4.8\%$ for the 3067 independent reflections representing data complete to $2\theta = 40°$ (or $R_F = 3.8\%$ and $R_{wF} = 4.0\%$ for the 1818 reflections for which $I > 3\sigma(I)$). The molecule has crystallographically required C_2 (2) symmetry with the four copper and four chlorine atoms defining a distorted cube (see Figure 1).

The twelve edges of the cube are defined by Cu–Cl bonds. The six crystallographically independent values vary appreciably, with Cu(1)–Cl(1) = 2.497 (2), Cu(1)–Cl(2) = 2.409 (2), Cu(1)–Cl(2′) = 2.434 (2), Cu(2)–Cl(1) = 2.363 (2), Cu(2)–Cl(2) = 2.457 (2), and Cu(2)–Cl(1′) = 2.505 (2) Å. Copper–copper distances are, again, rather irregular, but all are greater than 3.1

(1) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972); S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 2063 (1971).

(2) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).

(3) $(Cu(S_2CNEt_2))_4$ (Cu···Cu = 2.69 Å), R. Hesse. *Ark. Kemi*, **20**, 481 (1962).

(4) $(Cu(SOCNPr_2))_6$ (Cu···Cu = 2.701–3.057 Å), R. Hesse and V. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970).

(5) $(Cu_8(S_2CC(CN)_2)_6{}^{4-})$ (Cu···Cu = 2.783–2.871 Å), L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

(6) $(Cu(2\text{-}Me_2NC_6H_4))_4(CuBr)_2 \cdot 1.5C_6H_6$ (Cu···Cu = 2.48–2.70 Å), J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, *J. Organometal. Chem.*, **40**, C79 (1972).

(7) Tetrameric (4-methyl-2-cupriobenzyl)dimethylamine (Cu···Cu = 2.377 (3)–2.389 (3) Å), J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J. Chem. Soc. Chem. Commun.*, 446 (1972).

(8) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **94**, 447 (1936).

(9) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

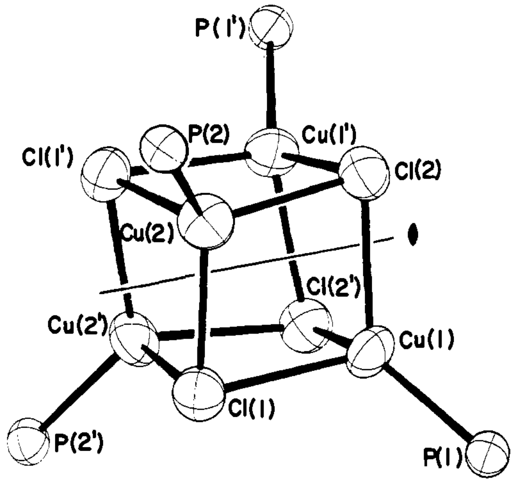


Figure 1. The "cubane" configuration of the Cu_4Cl_4 core of the $(PPh_3CuCl)_4$ molecule. The crystallographic C_2 axis is shown.

Å. Individual values (in Å) are Cu(1)···Cu(1′) = 3.430 (2), Cu(2)···Cu(2′) = 3.337 (2), Cu(1)···Cu(2) = Cu(1′)···Cu(2′) = 3.118 (1), and Cu(1)···Cu(2′) = Cu(1′)···Cu(2) = 3.417 (1). The Cl–Cu–Cl angles range from 88.94 (6) to 101.11 (7)°, while Cu–Cl–Cu angles range from 79.71 (6) to 90.19 (6)°. Each of the copper(I) atoms is in a distorted tetrahedral coordination environment; three linkages are to bridging chlorine atoms, the fourth being to a triphenylphosphine ligand. Individual copper–phosphorus bond distances are Cu(1)–P(1) = Cu(1′)–P(1′) = 2.193 (2) and Cu(2)–P(2) = Cu(2′)–P(2′) = 2.192 (3) Å.

$(PPh_3CuBr)_4$ was prepared following the procedure of Jardine, *et al.*;[10] it was recrystallized from chloroform, and was isolated as the solvated species $(PPh_3CuBr)_4 \cdot 2CHCl_3$.[11] Crystals belong to the centrosymmetric monoclinic space group $C2/c$ (No. 15; C_{2h}^6), unit cell parameters being a = 28.461 (9), b = 15.983 (4), c = 18.044 (5) Å, β = 112.59 (2)°, and Z = 4. Data collection and structure solution were as for the chloro derivative (*vide supra*). All nonhydrogen atoms have been accurately located, the present discrepancy indices being $R_F = 7.7\%$ and $R_{wF} = 8.5\%$ for the 2412 independent refections representing data complete to $2\theta = 35°$ (Mo Kα radiation). The $(PPh_3CuBr)_4$ molecule has precise (*i.e.*, crystallographically dictated) C_i ($\bar{1}$) symmetry, with the Cu_4Br_4 core having a "step" configuration (see Figure 2).

It should be emphasized that this molecule contains copper(I) atoms in both tetrahedral (Cu(1) and Cu(1′)) and trigonal planar ((Cu(2) and Cu(2′)) coordination environments.

The ten edges of the Cu_4Br_4 "step" are each defined by a Cu–Br bond. While these bond lengths show considerable variation, a systematic pattern can be ascertained, *i.e.*, the higher the coordination numbers (CN's) of the atoms involved in the Cu–Br bond, the longer the bond will be. Thus, in order of increasing bond distance, Cu(2)–Br(1′) = Cu(2′)–Br(1) = 2.374 (3) Å (CN's 3 and 2); Cu(2)–Br(2) = Cu(2′)–Br(2′) = 2.429 (3) Å (CN's 3 and 3); Cu(1)–Br(1) = Cu(1′)–Br(1′) = 2.477 (3) Å (CN's 4 and 2); Cu(1)–Br(2) = Cu(1′)–Br(2′) = 2.527 (2) Å (CN's 4 and 3); and Cu(1)–Br(2′) = Cu(1′)–Br(2) = 2.662 (2) Å (CN's 4 and 3). Copper–copper distances are Cu(1)···Cu(1′) = 3.449 (2) Å and Cu(1)···Cu(2′) = Cu(1′)···Cu(2) = 2.989 (3) Å. Lastly we may note that the Cu(tetrahedral)–P distances, Cu(1)–P(1) = Cu(1′)–P(1′) = 2.207 (4) Å, are slightly longer than the Cu(trigonal)–P distances, Cu(2)–P(2) = Cu(2′)–P(2′) = 2.200 (5) Å.

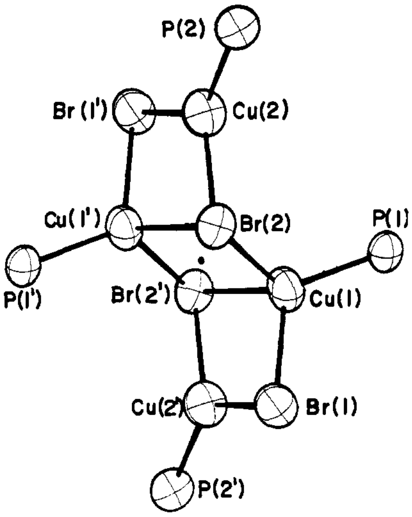


Figure 2. The "step" configuration of the Cu_4Br_4 core in crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$. The center of symmetry is indicated by a solid circle.

The gross geometry of the Cu_4Br_4 core may be described in terms of the dihedral angle of 107.70° between the strictly planar system Br(2)–Cu(1)–Br(2′)–Cu(1′) and the approximately planar (rms deviation 0.07 Å) system Br(2)–Cu(2)–Br(1′)–Cu(1′).

The relationship between the "cubane" and "step" structures is self-evident (*cf.* Figures 1 and 2). Spectroscopic and diffraction studies presently in progress should lead to our determining the gross geometry of the Cu_4X_4 (X = halogen or other monodentate ligand of unit negative charge) cores of related phosphine and arsine complexes of copper(I) and to our elucidating the conditions under which the "cubane" and "step" structures will interconvert.

Acknowledgments. This work was made possible by a generous allotment of time on the IBM 370/155 computer at the Computer Center, University of Illinois at Chicago Circle, and by financial support from the National Science Foundation through Grant No. GP-33018 (to M. R. C.).

Melvyn Rowen Churchill,* Krishan L. Kalra
Department of Chemistry
University of Illinois at Chicago Circle
Chicago, Illinois 60680

Received April 25, 1973

---

[10] F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc. A*, 238 (1970).

[11] This formulation assumes 100% occupancy of the eightfold (general) chloroform sites. In fact, both refinement of occupancy factors and accurate density measurements suggest that the true stoichiometry *of our particular sample* is close to $(PPh_3CuBr)_4 \cdot 1.5CHCl_3$.

Crystal and Molecular Structure of an Octaaza[14]annulene Complex of Nickel(II)

Sir:

The concept of aromaticity and its congeners denoted by prefixes such as anti, quasi, and pseudo continues