Inorg. Chem. **1992**, *31*, 5389–5394

Structural Variants of Tetranuclear $L_4Cu_4X_4$. Influence of L on the Coordination Mode of Copper(I)

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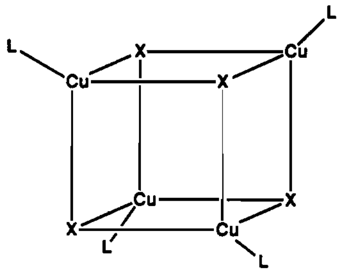
Received April 23, 1992

Three π complexes between nonconjugated dienes and copper(I) chloride and/or bromide have been prepared and characterized by means of crystal structure determination. The complex between 1,4-pentadiene and copper(I) chloride (1) was prepared in ethyl vinyl ketone (1-penten-3-one), utilizing the complex between copper(I) chloride and the solvent as an in situ precursor. $[Cu_2Cl_2(C_5H_8)]$ (1) crystallizes in the orthorhombic space group *Pccn* with $a = 7.292$ (4) Å, $b = 14.146$ (3) Å, $c = 15.727$ (4) Å, and $Z = 8$, and the structure was refined to a final $R = 0.065$ ($R_w = 0.080$) for 82 parameters and 890 observed reflections. The compound contains a distorted cubane Cu_4Cl_4 core, bridged by π-coordinated 1,4-pentadiene ligands, to form an infinite ribbon. The copper(I) centers exhibit distorted tetrahedral (trigonal pyramidal) coordination geometry. Compounds 2 and 3, $[Cu_4Br_2Cl_2(C_7H_8)_4]$ and $[Cu_4Br_4(C_7H_8)_4]$, respectively, prepared by direct reaction between copper(I) halide and norbornadiene, are isostructural, crystallizing in the tetragonal space group $P\bar{4}2_1c$, with $Z = 2$. Cell constants are $a = 12.187$ (3) and $c = 9.668$ (2) Å (2) and $a = 12.245$ (2) and $c = 9.759$ (2) Å (3). The structures were refined to final $R = 0.038$ ($R_w = 0.043$) (2) and $R = 0.029$ ($R_w = 0.033$) (3). Both 2 and 3 are discrete tetramers with distorted Cu_4X_4 cores, each norbornadiene ligand being π-coordinated to copper(I) through one olefinic linkage. The factors which favor a regular or a distorted cubic cage in tetranuclear $L_4Cu_4X_4$ are discussed by means of extended Hückel calculations (EHT). It is shown that a regular cubane-type structure is preferred when L is a pure σ-donor ligand. In contrast, when L is a π-acceptor ligand, two types of distortion in which four of the cube edges are elongated are possible. These two structures, which differ in the geometrical arrangement of the four long bonds, are shown to be the only possible isomers. It is demonstrated that these distortions are due to the presence of a moderately active d block and low-lying s and p blocks on the Cu(I) center. This specific orbital pattern makes the coordination of copper(I) highly variable.

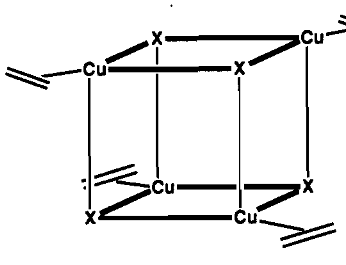
Introduction

Lewis base (L) adducts of copper(I) halides yield a large number of structural types resulting from the oligomerization of Cu^IX,[1a] a frequently observed tetranuclear structure being that of a cube in which four vertices are occupied by copper(I) and the other four by halide, X.[1] The Lewis base, L, is linked to each Cu so that the metal is four-coordinated (structure I).



I

In the case of L = phosphine or phosphite, the cube is essentially regular and the L ligand is aligned with the C_3 axis through the metal. When L = *endo*-dicyclopentadiene and X = Cl, the structure of the cube is strongly distorted and two isomeric types of cage have been observed in the crystalline state.[2] In each isomer one of the Cu–Cl bonds is considerably longer and the other two are slightly shorter than the average Cu–Cl distance expected for a regular cube. The Cu–Z (Z = olefin midpoint) axis is displaced with respect to the case of the regular cube such that the Cu–olefin vector is approximately coplanar with the two short Cu–Cl bonds. The two isomers differ in the spatial arrangement of the four long Cu–Cl bonds. In one isomer, cf. structure II, which crystallizes in an orthorhombic space group,[2]



II

the four long bonds are parallel, as, in consequence, are pairs of olefins; the cube can thus be seen as a loose association of (olef)-$Cu(\mu\text{-}Cl)_2Cu$(olef) dimers. In the other variant (structure III), which crystallizes in a tetragonal space group,[2] the four long bonds are situated in two orthogonal planes, as are the four olefins.

In the course of this investigation, we have prepared and determined the structures of three further diene complexes containing tetranuclear Cu_4X_4 cores, viz. a complex between 1,4-pentadiene and copper(I) chloride (1) and two analogues of the known complex between norbornadiene and copper(I) chloride,[3] viz. $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (2) and $[Cu_4Br_4(C_7H_8)_4]$ (3).

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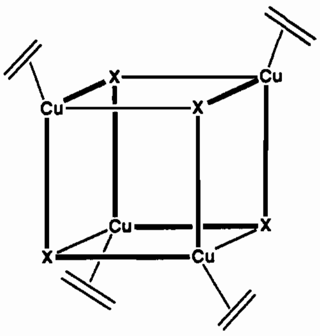

III

It has been shown both experimentally[1,4] and theoretically[5] that the coordination mode of halide to copper(I) is highly variable, the number of bonds being either 2, 3, or 4. Intermediate situations in which the metal is trapped in a coordination mode between two and three and between three and four have been observed.[1a,4] In each case, the geometrical distortions associated with the change of coordination mode have been found to be easy. This has led to the discussion of d^{10}–d^{10} Cu(I)–Cu(I) bonding in planar tetramers[5a] and in dimers[5d] and to a proposal of a molecular interpretation of ionic conductivity in Cu(I) solids.[5e] The present case is an illustration of the change in coordination mode of Cu(I) under the influence of a ligand which is a π acceptor, a factor which has not previously been addressed. In this work we will discuss the two variants of the tetranuclear $(\text{olef})_4Cu_4X_4$ core.

Experimental Section

General Data. All operations were carried out under nitrogen or argon using standard Schlenk techniques. Ethyl vinyl ketone (1-penten-3-one), 1,4-pentadiene, and norbornadiene were dried with 4-Å molecular sieves, deoxygenated by freeze–pump–thaw cycles, and distilled shortly before use. Copper(I) chloride was purified according to literature methods.[6] Copper(I) bromide (Aldrich 99.999% Gold Label) was used without further purification.

Preparation of $[Cu_2Cl_2(C_5H_8)]$ (1). The complex was prepared by using the complex between copper(I) chloride and the solvent as an in situ precursor.[7] Approximately 0.2 g of copper(I) chloride was added at ambient temperature to 10 mL of ethyl vinyl ketone; the mixture was stirred to give a clear solution. 1,4-Pentadiene (2.0 mL) was added very slowly to the solution, colorless plates of $[Cu_2Cl_2(C_5H_8)]$ being deposited overnight. Dry crystals of **1** decompose, with loss of the 1,4-pentadiene ligand, on exposure to dry air.

Preparation of $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (2). Equimolar amounts (0.1 mmol) of copper(I) chloride and copper(I) bromide were dissolved in 5 mL of norbornadiene by stirring and heating. The clear solution was stored for several days at 4 °C yielding colorless prisms of **2**. Dry crystals of **2** are reasonably stable but decompose on extended exposure to dry air into copper(I) halides and norbornadiene.

Preparation of $[Cu_4Br_4(C_7H_8)_4]$ (3). Approximately 1 mmol of copper(I) bromide was dissolved in 5 mL of norbornadiene by stirring and heating gently. Any remaining solid material was allowed to settle, and the supernatant solution was withdrawn with a syringe. The solution was evaporated slowly for a period of several days at ambient temperature under inert atmosphere. This was achieved by piercing the septum on the top of the Schlenk tube with a long thin needle and subsequent passage of a slow stream of argon. Dry prisms of **3**, obtained in this way, decompose slowly on extended exposure to dry air into copper(I) bromide and norbornadiene.

Table I. Crystal Data for $[Cu_2Cl_2(C_5H_8)]$ (1), $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (2), and $[Cu_4Br_4(C_7H_8)_4]$ (3)

	1	2	3
formula	$C_5H_8Cl_2Cu_2$	$C_{28}H_{32}Br_2Cl_2Cu_4$	$C_{28}H_{32}Br_4Cu_4$
fw	266.1	853.4	942.4
cryst syst	orthorhombic	tetragonal	tetragonal
space group	*Pccn* (No. 56)	$P\bar{4}2_1c$ (No. 114)	$P\bar{4}2_1c$ (No. 114)
a, Å	7.292 (4)	12.187 (3)	12.245 (2)
b, Å	14.146 (3)	12.187	12.245
c, Å	15.727 (4)	9.668 (2)	9.759 (2)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	1622 (1)	1436.0 (6)	1463.2 (4)
Z	8	2	2
d_{calc}, g/cm^3	2.18	1.97	2.14
μ, cm^{-1}	58.4	59.0	83.1
T, °C	−120	−120	−135
R^a	0.065	0.038	0.029
$R_w{}^a$	0.080	0.043	0.033

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

X-ray Crystallography. Crystal and experimental data are summarized in Table I. Crystals of **1**–**3** were mounted in glass capillaries, under argon, at −150 °C[7] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability in all three cases.

For **1**, data were measured for $3.5 < 2\theta < 50°$ from a colorless platey crystal with approximate dimensions 0.30 × 0.20 × 0.10 mm, using an ω scan rate of 32°/min and a scan width of $(1.26 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects but not for absorption, owing to inability to measure and index the faces of the labile crystal and to failure to obtain a more satisfactory structural model from empirically corrected data (vide infra). Of the 1435 unique reflections measured, 890 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 25 reflections in the range $41 < 2\theta < 47°$. The structure was solved by direct methods (MITHRIL[8]). Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms and with the hydrogen atoms included in calculated positions but not refined, gave a final $R = 0.065$ ($R_w = 0.080$) for 82 parameters and 890 reflections. The maximum and minimum values in the final difference map were 2.1 and −2.3 e/Å^3, the largest peak, to which no chemical meaning could be attached, being situated 0.96 Å from Cu(2). Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

For **2**, data were measured for $3.5 < 2\theta < 50°$ from a colorless prismatic crystal with approximate dimensions 0.20 × 0.20 × 0.30 mm, using an ω scan rate of 32°/min and a scan width of $(1.26 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects; an empirical correction based on azimuthal scans for several reflections was applied for the effects of absorption (minimum/maximum transmission factors = 0.78/1.00). Of the 740 unique reflections measured, 469 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 25 reflections in the range $25 < 2\theta < 39°$. The structure was solved by direct methods (MITHRIL[8]), confirming isostructurality with $[Cu_4Cl_4(C_7H_8)_4]$.[3] It soon became apparent, however, that Cl had been partially replaced by Br. Thus, Br and Cl were assumed to occupy the same crystallographic site, each with occupancy 0.5. In the subsequent refinement of the structure, positional and isotropic parameters for Cl were reset to those obtained for Br, no attempt being made to separate the positions of these two atoms. Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms and with the hydrogen atoms in calculated

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Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms in $[Cu_2Cl_2(C_5H_8)]$ (**1**)

atom	x	y	z	B_{eq}[a]
Cu(1)	0.4613 (2)	0.3276 (1)	0.3791 (1)	1.90 (7)
Cu(2)	0.0947 (2)	0.3539 (1)	0.5045 (1)	1.73 (6)
Cl(1)	0.4615 (5)	0.1685 (2)	0.3623 (2)	2.1 (1)
Cl(2)	0.4033 (4)	0.3516 (2)	0.5203 (2)	1.8 (1)
C(1)	0.506 (2)	0.4543 (8)	0.3204 (7)	2.5 (6)
C(2)	0.559 (1)	0.3853 (9)	0.2680 (7)	1.6 (5)
C(3)	0.452 (2)	0.3516 (8)	0.1924 (7)	1.8 (5)
C(4)	0.504 (1)	0.4101 (7)	0.1160 (7)	1.4 (4)
C(5)	0.643 (2)	0.3915 (8)	0.0633 (7)	2.1 (5)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_i$.

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms in $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (**2**)

atom	x	y	z	B_{eq}[a]
Cu	0.1415 (1)	–0.0116 (1)	0.8795 (2)	1.9 (1)
Br	0.1731 (2)	0.0349 (2)	1.1109 (2)	2.3 (1)
Cl	0.1731	0.0349	1.1109	2.3
C(1)	0.160 (1)	0.016 (1)	0.671 (1)	1.9 (6)
C(2)	0.240 (1)	0.077 (1)	0.739 (1)	2.2 (6)
C(3)	0.349 (1)	0.030 (1)	0.704 (2)	2.5 (7)
C(4)	0.364 (1)	0.047 (1)	0.549 (2)	2.3 (7)
C(5)	0.290 (1)	–0.012 (1)	0.485 (1)	1.8 (7)
C(6)	0.224 (1)	–0.074 (1)	0.593 (1)	1.9 (6)
C(7)	0.318 (1)	–0.091 (1)	0.698 (1)	2.0 (6)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\cdot\mathbf{a}_i\mathbf{a}_j$.

positions, gave a final $R = 0.038$ ($R_w = 0.043$) for 82 parameters and 469 reflections. Identical residuals were obtained from the enantiomorph. The final difference map was featureless (maximum/minimum values = 0.58 and –0.63 e/Å^3, respectively); reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

For **3**, data were measured for $3.5 < 2\theta < 50°$ from a colorless prismatic crystal with approximate dimensions 0.15 × 0.15 × 0.30 mm, using an ω scan rate of 16°/min and a scan width of $(1.15 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects; an empirical correction based on azimuthal scans was applied for the effects of absorption (minimum/maximum transmission factors = 0.92/1.00). Of the 755 unique reflections measured, 496 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections in the range $25 < 2\theta < 38°$. The atomic coordinates of **2** were used as starting point for the refinement of **3**. Full-matrix least-squares refinement as for **3**, but with Br assigned occupancy 1.0, gave a final $R = 0.029$ ($R_w = 0.033$) for 82 parameters and 496 reflections. The enantiomorph refined to $R = 0.038$ ($R_w = 0.045$). The maximum and minimum values in the final difference map were 0.41 and –0.57 e/Å^3; reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

All calculations for **1**–**3** were carried out with the TEXSAN[9] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 10. Structural illustrations have been drawn with ORTEP.[11]

Results and Discussion

Final positional parameters for **1**–**3** are listed in Tables II–IV, and bond distances and angles, in Tables V and VI. As is seen from Figures 1 and 2, all three compounds have cubane Cu_4X_4 cores distorted such that the two sets of long Cu–X bonds are perpendicular (structure III).

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms in $[Cu_4Br_4(C_7H_8)_4]$ (**3**)

atom	x	y	z	B_{eq}[a]
Cu	0.1421 (1)	–0.0066 (1)	0.8771 (1)	1.85 (6)
Br	0.1746 (1)	0.0364 (1)	1.1131 (1)	1.71 (5)
C(1)	0.162 (1)	0.020 (1)	0.671 (1)	1.6 (5)
C(2)	0.237 (1)	0.082 (1)	0.735 (1)	1.8 (5)
C(3)	0.348 (1)	0.030 (1)	0.704 (1)	1.7 (6)
C(4)	0.366 (1)	–0.048 (1)	0.546 (1)	1.5 (5)
C(5)	0.292 (1)	–0.016 (1)	0.486 (1)	1.9 (6)
C(6)	0.226 (1)	–0.072 (1)	0.594 (1)	1.7 (5)
C(7)	0.317 (1)	–0.089 (1)	0.703 (1)	1.7 (5)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table V. Bond Distances (Å) and Angles (deg) for $[Cu_2Cl_2(C_5H_8)]$ (**1**)[a]

Cu(1)–C(1)	2.04 (1)	Cu(2)–C(5^{ii})	2.03 (1)
Cu(1)–C(2)	2.05 (1)	Cu(2)–C(4^{ii})	2.06 (1)
Cu(1)–Z(1)	1.94	Cu(2)–Z(2^{ii})	1.93
Cu(1)–Cl(1)	2.266 (3)	Cu(2)–Cl(1^{i})	2.296 (3)
Cu(1)–Cl(2)	2.286 (3)	Cu(2)–Cl(2)	2.265 (3)
Cu(1)–Cl(1^{i})	3.095 (4)	Cu(2)–Cl(2^{i})	2.918 (3)
C(1)–C(2)	1.33 (2)	C(4)–C(5)	1.34 (1)
C(2)–C(3)	1.50 (1)	C(3)–C(4)	1.51 (1)
Cl(1)–Cu(1)–Cl(2)	105.1 (1)	Cl(1^{i})–Cu(2)–Cl(2)	106.4 (1)
Cl(1)–Cu(1)–Z(1)	126.0	Cl(1^{i})–Cu(2)–Z(2^{ii})	127.6
Cl(2)–Cu(1)–Z(1)	128.2	Cl(2)–Cu(2)–Z(2^{ii})	123.9
Cl(1)–Cu(1)–Cl(1^{i})	90.5 (1)	Cl(1^{i})–Cu(2)–Cl(2^{i})	86.9 (1)
Cl(2)–Cu(1)–Cl(1^{i})	84.0 (1)	Cl(2)–Cu(2)–Cl(2^{i})	88.4 (1)
Z(1)–Cu(1)–Cl(1^{i})	101.3	Z(2^{ii})–Cu(2)–Cl(2^{i})	106.6
C(1)–C(2)–C(3)	125 (1)	C(3)–C(4)–C(5)	125 (1)
C(2)–C(3)–C(4)	109 (1)		

[a] Z(1) and Z(2) are the midpoints of the C(1)–C(2) and C(4)–C(5) bonds, respectively. Symmetry code: (i) $^1/_2 - x$, $^1/_2 - y$, z; (ii) $^1/_2 - x$, y, $^1/_2 + z$.

In **1**, the cubane cores are bridged by 1,4-pentadiene ligands to form an infinite ribbon, each ligand thus coordinating to two different copper(I) atoms, a common feature in complexes between copper(I) chloride and conjugated[7,12] or nonconjugated dienes.[7,13] Both metal centers exhibit the distorted tetrahedral (trigonal pyramidal) coordination geometry, which has also been found to be usual in such complexes.[2,3,7,12,13] Cu(1) is coordinated by the C(1)–C(2) double bond, two chloride ligands at 2.266 (3) and 2.286 (3) Å, and a third chloride at 3.095 (4) Å, the metal atom being displaced 0.10 Å from the trigonal plane through Cl(1), Cl(2), and Z(1), the midpoint of the C(1)–C(2) bond, toward the apical ligand. The Z(1)–Cu(1)–Cl(1^{i}) angle is 101°, and the coordinated olefin is twisted 12° out of the trigonal plane. The other copper(I) center, Cu(2), is coordinated by C(4^{ii})–C(5^{ii}) and three chloride ligands at 2.265 (3), 2.296 (3), and 2.918 (3) Å, respectively (cf. Table V). Cu(2) is displaced 0.18 Å out of the plane through Cl(1^{i}), Cl(2), and Z(2^{ii}) toward the apical ligand Cl(2^{i}), with a Z(2^{ii})–Cu(2)–Cl(2^{i}) angle of 107°, the olefin being twisted 9° out of the trigonal plane. There is no indication of olefin sliding,[14] the olefin linkages being symmetrically positioned in the relevant trigonal planes with Z(1)–Cu–Cl angles of 126 and 128° and Z(2)–Cu–Cl angles of 124 and 128°, respectively (cf. Table V). The C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) torsion angles are both 88 (1)°.

Compounds **2** and **3** are isostructural with $[Cu_4Cl_4(C_7H_8)_4]$[3] and are thus discrete tetramers, the most significant feature of the former complexes being demonstration that it is possible to replace chloride in the cubane core by bromide. Attempts to prepare bromo analogues of π-olefinic copper(I) chloride complexes with dienes[7] have, hitherto, proven unsuccessful.[15] The Cu–Cl distances in $[Cu_4Cl_4(C_7H_8)_4]$ are 2.275 (2), 2.296 (2), and 3.091 (2) Å.[3] As is seen from Table VI, the Cu–X distances

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Table VI. Bond Distances (Å) and Angles (deg) for $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (**2**) and $[Cu_4Br_4(C_7H_8)_4]$ (**3**)[a]

2		**3**	
Cu–C(1)	2.06 (1)	Cu–C(1)	2.05 (1)
Cu–C(2)	2.10 (1)	Cu–C(2)	2.10 (1)
Cu–Z	1.96	Cu–Z	1.96
Cu–BrCl	2.340 (3)	Cu–Br	2.396 (2)
Cu–BrCl^{i}	2.360 (3)	Cu–Br^{i}	2.432 (2)
Cu–BrCl^{ii}	3.115 (3)	Cu–Br^{ii}	3.116 (2)
C(1)–C(2)	1.39 (2)	C(1)–C(2)	1.34 (2)
C(2)–C(3)	1.48 (2)	C(2)–C(3)	1.54 (2)
C(3)–C(4)	1.52 (2)	C(3)–C(4)	1.57 (2)
C(4)–C(5)	1.31 (2)	C(4)–C(5)	1.32 (2)
C(5)–C(6)	1.52 (2)	C(5)–C(6)	1.50 (2)
C(6)–C(7)	1.54 (2)	C(6)–C(7)	1.56 (1)
C(7)–C(3)	1.53 (2)	C(7)–C(3)	1.51 (2)
BrCl–Cu–BrCl^{i}	104.79 (8)	Br–Cu–Br^{i}	103.68 (6)
BrCl–Cu–Z	132.50	Br–Cu–Z	133.74
BrCl^{i}–Cu–Z	122.20	Br^{i}–Cu–Z	121.78
BrCl–Cu–BrCl^{ii}	84.82 (8)	Br–Cu–Br^{ii}	86.01 (6)
BrCl^{i}–Cu–BrCl^{ii}	102.79 (7)	Br^{i}–Cu–Br^{ii}	103.15 (6)
Z–Cu–BrCl^{ii}	90.88	Z–Cu–Br^{ii}	91.27
C(6)–C(1)–C(2)	105 (1)	C(6)–C(1)–C(2)	107 (1)
C(1)–C(2)–C(3)	108 (1)	C(1)–C(2)–C(3)	106 (1)
C(2)–C(3)–C(4)	106 (1)	C(2)–C(3)–C(4)	105 (1)
C(2)–C(3)–C(7)	99 (1)	C(2)–C(3)–C(7)	100 (1)
C(4)–C(3)–C(7)	97 (1)	C(4)–C(3)–C(7)	99 (1)
C(3)–C(4)–C(5)	108 (2)	C(3)–C(4)–C(5)	105 (1)
C(4)–C(5)–C(6)	108 (1)	C(4)–C(5)–C(6)	109 (1)
C(5)–C(6)–C(7)	97 (1)	C(5)–C(6)–C(7)	98.5 (9)
C(5)–C(6)–C(1)	105 (1)	C(5)–C(6)–C(1)	105.7 (9)
C(7)–C(6)–C(1)	99 (1)	C(7)–C(6)–C(1)	97.2 (8)
C(3)–C(7)–C(6)	95 (1)	C(3)–C(7)–C(6)	93.3 (9)

[a] Z is the midpoint of the C(1)–C(2) bond. Symmetry code: (i) *y*, −*x*, 2 − *z*; (ii) −*y*, *x*, 2 − *z*.

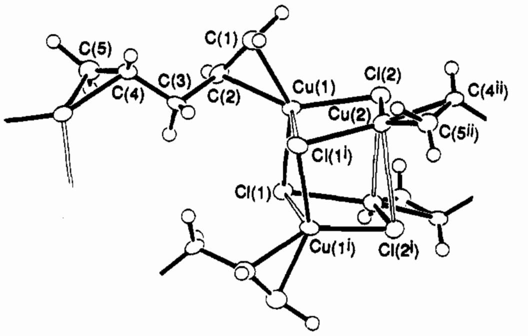

Figure 1. Part of the infinite ribbon of $[Cu_2Cl_2(C_5H_8)]$ (**1**), showing the crystallographic numbering. The thermal ellipsoids include 50% probability.[11] For the symmetry code, see Table V.

in the mixed-bromo–chloro complex (**2**) and in the bromo complex (**3**) are slightly longer but show the same general trend. It is thus apparent that the distortion of the cage is not affected by replacement of chloride by bromide. That the olefin is loosely coordinated to copper(I) in all three norbornadiene complexes is suggested by the marginal increase in the coordinated C=C bond length as compared with the length of the noncoordinated bond in each compound. In $[Cu_4Cl_4(C_7H_8)_4]^3$ the coordinated C=C is 1.35 (1) Å and the noncoordinated bond is 1.32 (1) Å; in $[Cu_4Br_4(C_7H_8)_4]$ (**3**) corresponding values are 1.34 (2) and 1.32 (2) Å. The coordinated C=C linkage in the mixed-bromo–chloro complex **2** appears to be slightly longer, i.e. 1.39 (2) Å, the noncoordinated olefin bond being 1.31 (2) Å. In $[Cu_4Cl_4(C_7H_8)_4]$,[3] one of the bridgehead methylene hydrogen atoms was found to be only 2.18 Å from Cu. In **2** and **3**, corresponding values are, however, estimated to be longer, viz. 2.47 and 2.38 Å, respectively.

In **2** and **3**, the copper(I) centers are displaced 0.09 and 0.11 Å, respectively, from the trigonal coordination planes (through Z, X, and X^{i}; cf. Table VI) toward the apical ligand and the olefin linkages are twisted 18 and 17°, respectively, out of these planes. The inequality of the X–Cu–Z and X^{i}–Cu–Z angles (cf. Table VI) indicates some olefin sliding.[14]

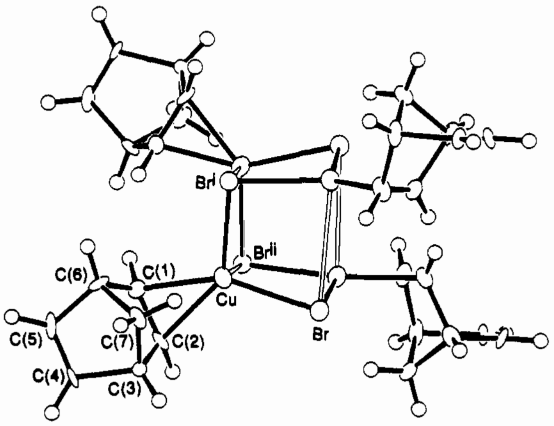

Figure 2. Discrete tetranuclear complex $[Cu_4Br_4(C_7H_8)_4]$ (**3**), showing the crystallographic numbering. The thermal ellipsoids include 50% probability.[11] In $[Cu_4Br_2Cl_2(C_7H_8)_4]$ (**2**), the Br site is partially replaced by Cl so that each atom has a site occupancy of 0.5. For the symmetry code, see Table VI.

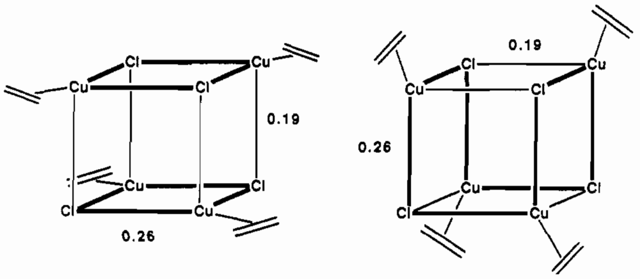

Figure 3. Mulliken overlap population (MOP) for the CuCl bonds in the two distorted structures of the tetranuclear $Cu_4Cl_4L_4$ unit (L = olefin). In the structure to the left, the four olefin ligands are situated in two parallel planes, which simulates the cubane core with four parallel long Cu–Cl bonds. In the structure to the right, the four olefin ligands are in two orthogonal planes, which simulates the cubane core with two sets of orthogonal long Cu–Cl bonds.

Extended Hückel (EHT) calculations have been performed on the tetranuclear model cage $(C_2H_4)_4(Cu_4Cl_4)$.[16] A regular cube with a Cu–Cl edge of 2.5 Å is used. The four ethylene ligands, models for the experimental olefins, are positioned in the plane of two Cu–Cl edges in two ways in order to represent the two types of distortion, i.e. pairs of long Cu–X bonds parallel (structure II) and pairs of long Cu–X bonds orthogonal (structure III). No relaxation of the geometry of the cage is permitted. The preference for a long edge is rendered by the smaller value of the bond order as calculated by the Mulliken overlap population (MOP).

The results are shown in Figure 3. In both isomeric forms, the MOP of the Cu–Cl bond which is perpendicular to the Cu–ethylene plane is significantly smaller (0.19) than that of the two Cu–Cl bonds (0.26) which are coplanar with the Cu–ethylene plane. The two isomers have identical MOP values, a crude indication that the isomers are approximately isoenergetic. In the case of L = *endo*-dicyclopentadiene, the isomers were obtained from different solvents.[2] Similar variations in the value of the MOP, but to a lesser magnitude, are obtained when the olefin is replaced by a pure σ-donor ligand like hydride positioned at the olefin midpoint. This indicates that the change in the value of the bond order is closely related to the displacement of the L

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(16) Extended Hückel calculations were done using the weighted H_{ij} formula (Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686). The atomic parameters were taken from the literature for Cu (Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884) and Cl (Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240).

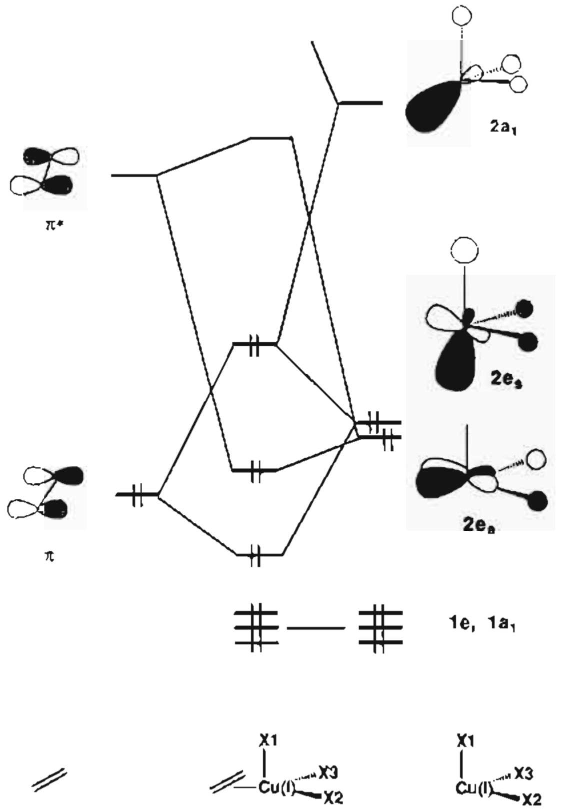


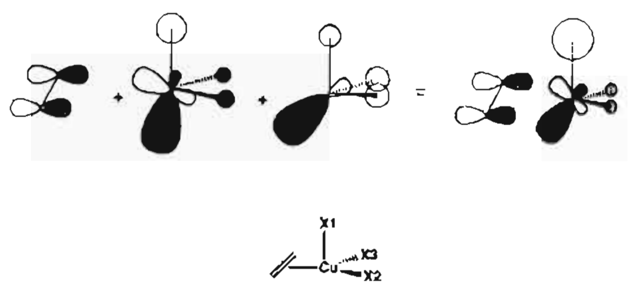
Figure 4. Interaction diagram for an olefin interaction with a Cu^IX_3 fragment, the olefin being in the X2–Cu(I)–X3 plane. The five occupied d orbitals and the first empty orbital of the copper fragment have been included. The energy scale is schematic.

ligand away from the C_3 axis. As will be apparent later on, such a displacement is energetically unfavorable but much less so in the case of L = olefin.

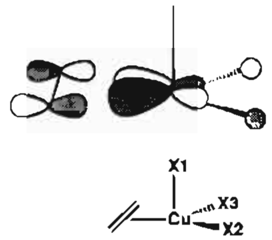
The difference in the bond length is not an intrinsic property of the cubane core since similar results are obtained for the hypothetical (ethylene)$CuCl_3^{2-}$ unit. One can actually simplify the model even further. Analogous differences in the bond order are calculated in (ethylene)CuH_3^{2-} and even in CuH_4^{3-}. The last model reveals the essence of the problem. If one moves one Cu–H bond away from the C_3 axis toward the plane defined by two bonds in tetrahedral CuH_4^{3-}, these two Cu–H bonds become stronger and the fourth becomes weaker. In other words, a planar CuX_3 group is poorly set to make a strong bond in the perpendicular direction. This is quite an obvious result, but it is remarkable that Cu(I) centers are able to maintain weak bonding in this manner. We will see how the combination of the presence of d, s, and p orbitals on Cu(I) favor this situation. We will also discuss why this bonding situation is observed when L = olefin and not when L = a pure σ-donor ligand.

The bonding interaction between an olefin in the X2–Cu–X3 plane and a $Cu^IX_3^{2-}$ fragment (the orbitals are drawn for X = H) is illustrated in Figure 4. The pyramidal CuX_3 group has the usual set of orbitals which are, in order of increasing energy, ($1a_1$, 1e), (2e), and ($2a_1$).[17] In the case of copper(I), where the d block is rather low in energy, the $2a_1$ orbital which is the LUMO of the fragment is composed essentially of Cu s and p orbitals. The interaction of the CuX_3^{2-} fragment with the olefin is straightforward. The olefin π^* orbital interacts mostly with one member of the 2e set ($2e_a$). The resulting back-donation remains modest in magnitude because of the large energy gap between the two orbitals. The olefin π orbital interacts with the other member of the 2e set ($2e_s$) and the empty $2a_1$ orbital. The interaction between $2e_s$ and π is a four-electron destabilization which is partially compensated for by the bonding interaction created by $2a_1$.

Scheme I



The change in the Cu–X overlap populations can easily be deduced from the above diagram. The 2e orbitals are both Cu–X antibonding. Consequently, the electron transfer from $2e_a$ into π^* increases the Cu–X2(3) bonding but does not change the Cu–X1 bond (structure IV). The π orbital mixes with $2e_s$ and $2a_1$. The antibonding combination of π and $2e_s$, stabilized by $2a_1$, is the HOMO of the system (Scheme I). One can see that the participation of X1 is enlarged by the admixture of $2a_1$, while that of X2 and X3 is diminished. This weakens the Cu–X1 bond and strengthens the two other bonds. Both of these interactions shown in structure IV and Scheme I induce the same changes in the bond order around the copper(I) center. It is thus clear why similar results would be obtained for any ligand L. A pure σ-donor ligand would only involve the symmetrical type orbitals ($2e_s$ and $2a_1$ on Cu). If L has an empty orbital which can receive electrons from $2e_a$, this will reinforce the effect of the symmetrical orbital. The observed change in bond length around the copper(I) center is therefore a result of forcing the L ligand to move away from the C_3 axis.



IV

The previous analysis can be applied directly to the tetranuclear cage. It should be noted that there are two ways and only two ways to place four long edges on a cubic six-faced cage, provided that no two of these long edges issue from the same corner, which is a chemically reasonable hypothesis. These four edges must either be parallel or lie in orthogonal planes. This simple fact accounts for the existence of two and only two isomeric cages.

One can generate the Cu-centered orbitals of the cage by combining the orbitals of each CuX_3 subunit. The above symmetry-adapted combination interacts with the linear combination of the orbitals of the four ethylene groups which combined as the a_1 and the e_s and e_a orbitals of Cu. The interaction described above is found to be identical in the cage; i.e., no major change takes place on aggregation.

Why is the olefin the only ligand which gives rise to distortion of the cage? In order to answer this question, one needs to know if displacement of the L ligand from the natural coordination direction along the C_3 axis of the CuX_3 corner is favorable energetically. Because of the known deficiencies of EHT for estimating energies, we used the total overlap populations between the ligands (L = H^-, as a model for a pure σ donor, and L = olefin) and the metal cage (Cu_4X_4) as a measure for this preference. A stronger overlap population is an indication of a

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[17] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions In Chemistry*; Wiley: New York, 1985.

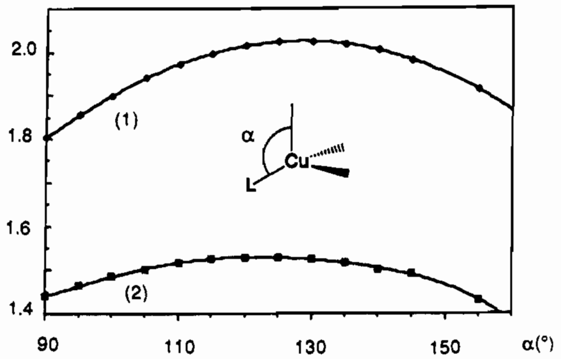

Figure 5. Total Mulliken overlap population between L[(1) L = H$^-$; (2) L = olefin] and the Cu_4Cl_4 cage as a function of the angle α between the "long" CuCl bond and the Cu–L direction. The alignment between Cu–L and the C_3 local axis of the $CuCl_3$ corner corresponds to an angle of 125°.

more stable structure. The calculations (Figure 5, curve 1) in fact show that displacement of the ligand away from the C_3 axis is unfavorable for a pure σ-donor ligand (like H$^-$ or phosphine), the best coordination site being along the C_3 axis. This is easy to understand. Recall that the Cu–L bond used the only accessible empty metal orbital ($2a_1$) which is directed along the C_3 axis. In contrast, if the ligand L has π-bonding capability, the calculations show that displacement of the ligand is less unfavorable energetically, as shown by the rather flat curve for the overlap population in Figure 5 (curve 2). This is due to the added influence of the $2e_a/\pi^*$ interaction depicted in structure IV, which would be at its best if the overlap between the π^* orbital and $2e_a$ is maximized. Since $2e_a$ lies essentially in the Cu–X2(3) plane, the best overlap is obtained when the olefin is in this plane. However, back-donation is a weak interaction in the case of copper(I) and the interaction between $2a_1$ and π is still large. This results in no strong geometrical preference for the position of the olefin, i.e. the α angle, which could therefore be influenced in part by crystal packing.[18]

In conclusion, this work provides another example of the highly flexible nature of the copper(I) bonding pattern, associated with the position of the metal at the border between the transition element and main group series. In such cases, the copper(I) center adapts to the subtle electronic characteristics of the surrounding ligands, resulting in a wealth of structural types.

Acknowledgments. We are grateful to Mikael Örtendahl for assistance with some of the preparative work. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of the ICMO and IPCM. This work has been supported by a grant from the Swedish Natural Science Research Council and completed during a visit by O.E. to Göteborg sponsored by the Maxwell fellowship of the French Academy of Sciences.

Supplementary Material Available: Tables giving crystal data and details of the structure determinations, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates for the hydrogen atoms (4 pages). Ordering information is given on any current masthead page.

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[18] No nonbonding interactions between ligands have appeared in our calculations for any value of α in the case of olefin = ethylene.