Journal of Organometallic Chemistry, 421 (1991) 347-356
Elsevier Sequoia S.A., Lausanne
JOM 22212

A comparative study of 1,7-octadiene and 1,7-octadiyne complexes of copper(I) chloride: preparation and molecular structures

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(Received June 5th, 1991)

Abstract

Polymeric complexes, $[Cu_2Cl_2(C_8H_{14})]$ (1) and $[Cu_2Cl_2(C_8H_{10})]$ (2), prepared by direct reaction between copper(I) chloride and 1,7-octadiene and 1,7-octadiyne, respectively, have been between characterized by crystal-structure determinations and IR spectroscopy. In both structures the organic ligands act as bridges between copper(I). In **1**, there are two crystallographically independent copper(I) centres, one of which is three coordinated by C=C and two chloride ligands, the olefin being twisted 4° out of the coordination plane. The other copper(I) centre is (3+1) coordinated and exhibits a larger olefin twist (10° from the trigonal plane). The Cu-C bond lengths lie in the range 2.036(4)-2.100(4) Å, and the C=C bond lengths are 1.353(6) and 1.356(6) Å. In **2**, copper(I) is trigonally pyramidally coordinated, with the C≡C linkage in the trigonal plane; Cu-C = 2.029(6) and 2.053(6) Å and C≡C = 1.196(9) Å. The ν(C=C) and ν(C≡C) frequencies are lowered by ca. 98 cm^{-1} and 135 cm^{-1}, respectively, on complexation. In contrast to $\nu(C_{sp^2}-H)$, which remains virtually unchanged, $\nu(C_{sp}-H)$ is lowered by 117 cm^{-1}, indicating activation of the acetylenic C-H bond; this feature is, however, not paralleled by a significant lengthening of the C-H bond or bending back of the acetylenic hydrogen atom in the crystal structure.

Introduction

In connection with studies on π-olefinic complexes between copper(I) chloride and conjugated [1,2] or non-conjugated [2,3] dienes we have found evidence for a relationship between the coordination geometry associated with the copper(I) centre and the mode of twisting of the coordinated olefin [1,2]. With both conjugated and non-conjugated dienes the diene coordinates to copper(I), acting either as a bridge between adjacent copper(I) atoms [1,2] or as a monodentate η^2-ligand [3]. In the complex between 1,5-hexadiene and copper(I) chloride the diene has also been found to bridge adjacent copper(I) centres [4]. For conjugated dienes, the *s-trans* conformation thus appears to be the preferred conformation assumed by the ligand on complexation with copper(I) [1,2]. In order to obtain more information about the factors determining the olefin rotation in the context of copper(I) coordination geometry, and also to examine whether similar effects are to be observed for diyne complexes of copper(I), we have synthesised complexes between copper(I) chloride and 1,7-octadiene and 1,7-octadiyne, respectively, and determined their molecular structures. Copper(I) π-coordination to terminal alkynes, and in particular to 1,7-octadiyne, has been shown to activate the C_{sp}–H bond catalytically [5]. A structural investigation of a complex between 1,7-octadiyne and copper(I) might, therefore, be expected to reveal unusual coordination features with respect to bonding of the C≡C–H fragment to Cu^I.

Experimental

All operations were carried out under nitrogen or argon by standard Schlenk or special low-temperature techniques [2]. 1,7-Octadiene and 1,7-octadiyne were dried with 4 Å molecular sieves, deoxygenated by freeze-pump-thaw cycles, and distilled shortly before use. Copper(I) chloride was purified as described in ref. 6, and dried in vacuo.

Preparation of $[Cu_2Cl_2(C_8H_{14})]$ (1)

Approximately 0.1 g of copper(I) chloride was added to 5 ml of 1,7-octadiene and the mixture was kept at 60–70°C for ca. 12 h, with stirring. The resulting yellow solution was heated to just below its boiling point (ca. 114°C) for a few minutes, and then allowed to cool slowly to ambient temperature. Colourless rhombs of **1** separated overnight. Crystals of **1** were relatively stable, decomposing only after several hours' exposure to air.

Preparation of $[Cu_2Cl_2(C_8H_{10})]$ (2)

$[Cu_2Cl_2(C_8H_{10})]$ (**2**) was prepared analogously, from ca. 0.1 g of CuCl and 1 ml of 1,7-octadiyne. The resulting yellow solution and pale-yellow precipitate were heated rapidly to ca. 135°C, whereupon the precipitate dissolved. Yellow cubes of **2** were deposited on cooling of the solution to ambient temperature. Crystals of **2** were stable in the air for several months.

Infrared spectrometry

Measurements were performed on a Mattson Polaris FTIR spectrometer, with samples pressed in KBr tablets (**1** and **2**) or between KBr discs (1,7-octadiene and 1,7-octadiyne). Spectra were registered with a resolution of 2 cm^{-1}.
$[Cu_2Cl_2(C_8H_{14})]$: $\nu(C_{sp^2}\text{–H})$ 3077, 3059 cm^{-1}; ν(C=C) 1549, 1539 cm^{-1}; $[Cu_2Cl_2(C_8H_{10})]$: $\nu(C_{sp}\text{–H})$ 3181 cm^{-1}; ν(C≡C) 1983 cm^{-1}. Corresponding frequencies for 1,7-octadiene: 3079 and 1641 cm^{-1} and for 1,7-octadiyne: 3298 and 2118 cm^{-1}. $[Cu_2Cl_2(C_8H_{14})]$: ν(Cu–C) 496, 489 and 429 (tentative assignment) cm^{-1}. $[Cu_2Cl_2(C_8H_{10})]$: ν(Cu–C) 522 cm^{-1}.

Crystallography

$[Cu_2Cl_2(C_8H_{14})]$ (**1**). A colourless, rhombic-shaped crystal was mounted, at −130°C under argon, in a glass capillary and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured (Table 1) using graphite-monochromated radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The ω–2θ scan mode was employed with a 2θ scan rate of 32° min^{-1} and a ω scan width of $(1.10 + 0.30 \tan\theta)°$. Weak reflections ($I < 3\sigma(I)$) were rescanned three times and counts accumulated to improve

Table 1

Crystallographic data for $[Cu_2Cl_2(C_8H_{14})]$ (**1**) and $[Cu_2Cl_2(C_8H_{10})]$ (**2**)

	1	**2**
Formula	$C_8H_{14}Cl_2Cu_2$	$C_8H_{10}Cl_2Cu_2$
M_r	308.2	304.2
Space group	$P2_1/n$ (No. 14) [8a], non-standard setting	$P2_1/c$ (No. 14) [8a]
Unit-cell dimensions	$a = 9.227(3)$, $b = 10.913(3)$, $c = 10.727(2)$ Å, $\beta = 93.23(2)°$, $V = 1078.5(3)$ Å^3	$a = 9.854(2)$, $b = 6.503(3)$, $c = 7.686(3)$, $\beta = 102.04(2)°$, $V = 481.7(5)$ Å^3
Z	4	2
D_c (g cm^{-3})	1.90	2.10
$F(000)$	616	300
μ(Mo-K_α) (cm^{-1})	44.05	49.30
Crystal size	0.30×0.30×0.20 mm	0.20×0.20×0.20 mm
Temperature (data collection) (°C)	−130	−130
2θ limits	$3.5° < 2\theta < 50°$	$3.5° < 2\theta < 50°$
ω scan rate (deg min^{-1})	32	32
Data collected	$+h, +k, \pm l$	$+h, +k, \pm l$
No. of unique data	1999	930
No. with $I > 3.0\ \sigma(I)$	1519	684
No. of parameters refined	165	72
R	0.027	0.033
R_w	0.032	0.036

counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time versus background counting time being 2:1. Three reflections monitored at regular intervals (after every 150 reflections measured) showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarisation effects and an empirical correction, based on azimuthal scans for several reflections, was made for the effects of absorption (max; min transmission factors: 1.00; 0.86). Cell constants were determined from the setting angles of 25 reflections in the range $47° < 2\theta < 50°$. The structure was solved by direct methods (MITHRIL [7]) and Fourier techniques, and refined by full-matrix least-squares methods. Anisotropic thermal parameters were included for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Further details of the refinement are given in Table 1.

$[Cu_2Cl_2(C_8H_{10})]$ (**2**). Diffracted intensities from a yellow cubic-shaped crystal, mounted as above, were measured (Table 1) with a Rigaku AFC6R diffractometer. Additional intensity data collection parameters were as for **1** except that the ω scan width was $(1.42 + 0.30 \tan \theta)°$. An empirical correction was made for the effects of absorption (max; min transmission factors 1.00; 0.83). The structure was solved by direct methods (MITHRIL [7]) and subsequent electron density calculations. Positional parameters, anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms were refined by full-matrix least squares methods. Further details of the refinement are given in Table 1.

Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in **1** and **2** are given in Tables 2 and 3, and selected bond

Table 2

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in [$Cu_2Cl_2(C_8H_{14})$] (1) [a]

Atom	*x*	*y*	*z*	B_{eq} [b]
Cu(1)	0.70017(5)	−0.01728(5)	0.58883(4)	1.52(2)
Cu(2)	0.93572(5)	0.14003(5)	0.43441(5)	1.57(2)
Cl(1)	0.7760(1)	0.1789(1)	0.5874(1)	1.71(4)
Cl(2)	1.1536(1)	0.1113(1)	0.5432(1)	1.70(4)
C(1)	0.5525(5)	−0.1373(4)	0.6528(4)	1.9(2)
C(2)	0.5339(4)	−0.0273(4)	0.7085(4)	1.6(2)
C(3)	0.5900(5)	0.0032(4)	0.8400(4)	1.7(2)
C(4)	0.4741(5)	−0.0178(4)	0.9340(4)	1.5(2)
C(5)	0.9883(5)	0.0586(4)	0.0358(4)	1.7(2)
C(6)	0.9832(5)	0.0390(4)	0.1771(4)	1.6(2)
C(7)	0.9635(5)	0.1588(4)	0.2424(4)	1.6(2)
C(8)	0.8333(6)	0.2031(5)	0.2731(4)	2.2(2)

[a] Estimated standard deviations are given in parentheses. [b] B_{eq} is defined as $(8\pi^2/3)\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in [$Cu_2Cl_2(C_8H_{10})$] (2) [a]

Atom	*x*	*y*	*z*	B_{eq} [b]
Cu	0.90452(7)	0.1775(1)	0.1267(1)	1.64(3)
Cl	1.0761(1)	0.3312(2)	0.3263(2)	1.57(5)
C(1)	0.7679(7)	0.371(1)	−0.0264(8)	1.8(3)
C(2)	0.7253(6)	0.201(1)	−0.0643(7)	1.4(2)
C(3)	0.6483(6)	0.012(1)	−0.1343(8)	1.7(2)
C(4)	0.5584(6)	−0.071(1)	−0.0086(8)	1.6(2)

[a] Estimated standard deviations are given in parentheses. [b] B_{eq} is defined as $(8\pi^2/3)\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 4

Selected bond distances (Å) and angles (deg) in [$Cu_2Cl_2(C_8H_{14})$] (1). X(1) and X(2) are the midpoints of the C(1)–C(2) and C(7)–C(8) bonds, respectively. Symmetry code: i = 1 − *x*, − *y*, 2 − *z*; ii = 2 − *x*, − *y*, 1 − *z*; iii = 2 − *x*, − *y*, − *z*

Cu(1)–C(1)	2.036(4)	Cu(2)–C(8)	2.044(4)
Cu(1)–C(2)	2.058(4)	Cu(2)–C(7)	2.100(4)
Cu(1)–X(1)	1.932	Cu(2)–X(2)	1.959
C(1)–C(2)	1.356(6)	C(7)–C(8)	1.353(6)
C(2)–C(3)	1.512(6)	C(6)–C(7)	1.499(6)
C(3)–C(4)	1.528(6)	C(5)–C(6)	1.534(6)
C(4)–C(4^{i})	1.520(8)	C(5)–C(5^{iii})	1.514(8)
Cu(1)–Cl(1)	2.252(1)	Cu(2)–Cl(1)	2.306(1)
Cu(1)–Cl(2^{ii})	2.257(1)	Cu(2)–Cl(2)	2.288(1)
Cu(1) ··· Cu(2)	3.290(1)	Cu(2)–Cl(2^{ii})	2.878(1)
Cu(1) ··· Cu(2^{ii})	3.638(1)	Cu(2) ··· Cu(2^{ii})	3.541(1)

Cl(1)–Cu(1)–Cl(2^{ii})	103.35(4)	Cl(1)–Cu(2)–Cl(2)	103.93(4)
Cl(1)–Cu(1)–X(1)	126.5	Cl(1)–Cu(2)–X(2)	124.2
Cl(2^{ii})–Cu(1)–X(1)	130.2	Cl(2)–Cu(2)–X(2)	128.8
Cu(1)–Cl(1)–Cu(2)	92.37(4)	Cl(2^{ii})–Cu(2)–X(2)	105.2
Cu(1^{ii})–Cl(2)–Cu(2)	106.34(4)	Cl(1)–Cu(2)–Cl(2^{ii})	85.31(4)
Cu(1^{ii})–Cl(2)–Cu(2^{ii})	78.66(4)	Cl(2)–Cu(2)–Cl(2^{ii})	94.25(4)
Cu(2)–Cl(2)–Cu(2^{ii})	85.75(4)	C(8)–C(7)–C(6)	124.0(4)
C(1)–C(2)–C(3)	124.1(4)	C(7)–C(6)–C(5)	110.5(4)
C(2)–C(3)–C(4)	111.5(3)	C(6)–C(5)–C(5^{iii})	113.3(4)
C(3)–C(4)–C(4^{i})	112.5(4)		

Table 5

Selected bond distances (Å) and angles (deg) in [$Cu_2Cl_2(C_8H_{10})$] (**2**). X is the midpoint of the C(1)–C(2) bond. Symmetry code: i = 2 − x, y − 1/2, 1/2 − z; ii = x, 1/2 − y, z − 1/2); iii = 1 − x, − y, − z; iv = 2 − x, 1/2 + y, 1/2 − z)

Cu–C(1)	2.029(6)	Cu–Cl^{ii}	3.134(2)
Cu–C(2)	2.053(6)	C(1)–C(2)	1.196(9)
Cu–X	1.946	C(2)–C(3)	1.484(8)
Cu–Cl	2.264(2)	C(3)–C(4)	1.538(8)
Cu–Cl^{i}	2.283(2)	C(4)–C(4^{iii})	1.503(12)
Cl–Cu–X	132.5	Cl^{ii}–Cu–X	89.1
Cl–Cu–Cl^{i}	107.58(4)	C(1)–C(2)–C(3)	168.4(6)
Cl–Cu–Cl^{ii}	93.77(5)	C(2)–C(3)–C(4)	112.4(5)
Cl^{i}–Cu–X	119.6	C(3)–C(4)–C(4^{iii})	113.0(6)
Cl^{i}–Cu–Cl^{ii}	93.36(5)	Cu–Cl–Cu^{iv}	124.65(6)

distances and angles in Tables 4 and 5, respectively. The crystallographic numbering is as in Fig. 1 and 2. Hydrogen-atom coordinates, distances involving the hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms for both structures may be obtained from the authors. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 8b; all calculations were performed using the TEXSAN [9] software package. Structural illustrations were drawn with ORTEP [10].

Discussion

Both complexes **1** and **2** are polymeric and are therefore inherently insoluble in common organic solvents, precluding recrystallisation of the amorphous material obtained by direct reaction of the components at ambient temperature. Normally, special synthetic methods are required to obtain single crystals of complexes between copper(I) chloride and e.g. dienes [1,2] or carbon monoxide [11], since direct reaction followed by recrystallisation is, moreover, not feasible due to

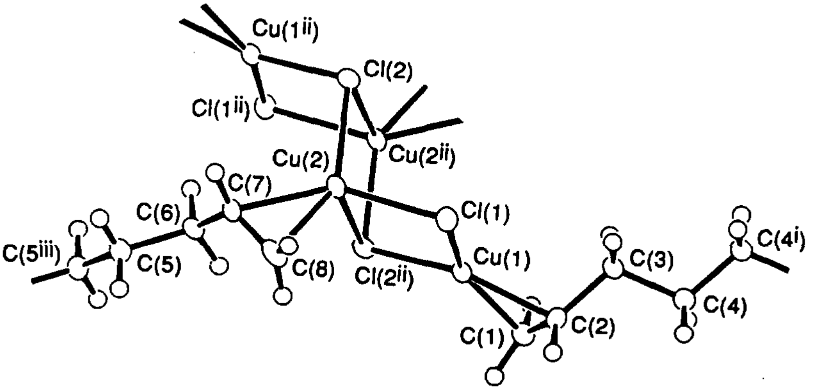

Fig. 1. [$Cu_2Cl_2(C_8H_{14})$] (**1**) showing the crystallographic numbering. For symmetry code see Table 4. The thermal ellipsoids enclose 50% probability.

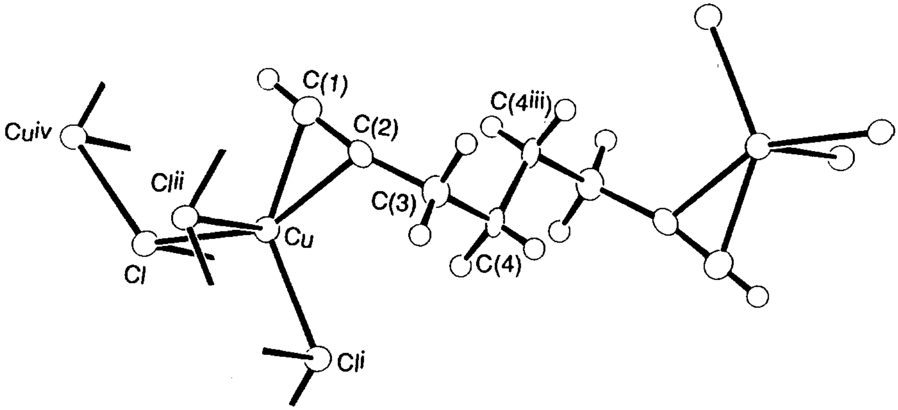

Fig. 2. $[Cu_2Cl_2(C_8H_{10})]$ (**2**) showing the crystallographic numbering. For symmetry code see Table 5. The thermal ellipsoids enclose 50% probability.

immediate extraction of the diene or carbonyl ligand by the solvent used for recrystallisation. In the present case, however, it was possible to break the polymeric framework of complexes **1** and **2**, thus bringing them into solution, by heating to just below the boiling point of the ligand solvent; X-ray quality crystals separated from the solution on cooling to ambient temperature.

In complex **1** (cf. Fig. 1), there are two independent 1,7-octadiene ligands, each with a centre of symmetry at the midpoint of the 4,5 carbon-carbon bond, i.e. the compound contains two crystallographically independent half-ligands, apart from two copper(I) and two chlorine atoms. The situation is similar for the 1,7-octadiyne ligand in complex **2** (cf. Fig. 2); here, however the asymmetric unit is composed of one copper(I), one chlorine atom, and one half-molecule of 1,7-octadiyne.

The crystallographically independent C=C bonds in **1** do not differ in length, which is consistent with the equality of the infrared frequencies observed for the complex (ν(C=C) = 1549, 1539 cm^{-1}). Only one C≡C absorption is observed for **2**, which is also consistent with the structural results. In neither **1** or **2** are the olefinic or acetylenic linkages lengthened appreciably on coordination, although the infrared frequencies are lowered by approximately 98 cm^{-1} (93 and 102 cm^{-1}) for 1,7-octadiene and by 135 cm^{-1} for 1,7-octadiyne. This is in accordance with results reported previously for π-olefinic (e.g. [3,4,12–14]) and π-acetylenic (e.g. [5,14–19]) complexes of copper(I); the lowering of ν(C≡C) in **2** relative uncomplexed 1,7-octadiyne is, however, slightly larger than the shifts (94 and 119 cm^{-1}) observed for the complex between copper(I) trifluoromethanesulfonate and 1,7-octadiyne [5]. Nor do the Cu–C distances differ between complex **1** and complex **2**, apart from Cu(2)–C(7) in **1**, which is significantly longer than the other five Cu–C bonds (cf. Tables 4 and 5); there are, however, differences between the ν(Cu–C) frequencies in **1** and **2** (see above). The Cu(1)–C(1)–C(2)–C(3) and Cu(2)–C(8)–C(7)–C(6) torsion angles in **1**, namely −101.0(4) and 104.6(4)°, clearly indicate bending back [20] of C(3) and C(6) with respect to the C(1)–C(2) and C(8)–C(7) olefinic groups.

Although the degree of distortion of the C≡C–C fragment in **2** from linearity [C(1)–C(2)–C(3) = 168.4(6)°] is within the range of values reported for analogous copper(I) complexes [14–19], it lies at the lower end of the range of distortions observed for π-acetylenic complexes in general [21,22]. As in the complex between copper(I) trifluoromethanesulfonate and 1,7-octadiyne [5], $\nu(C_{sp}$–H) is lowered in **2** by 117 cm^{-1}, the corresponding value for the former complex being 81 cm^{-1}, whereas the shifts for $\nu(C_{sp^2}$–H) in **1** are barely discernible, i.e. 2 and 20 cm^{-1}, respectively. The shift in $\nu(C_{sp}$–H) for **2** clearly indicates an activation of the acetylenic C–H bond that is even stronger than that observed for the complex between copper(I) trifluoromethanesulfonate and 1,7-octadiyne [5], and which might have been expected to be reflected in the crystal structure of **2**. Somewhat surprisingly, however, the C_{sp}–H bond in **2** is short, namely 0.83(5) Å and the H–C≡C angle is 178(4)°, indicating minimal bending-back [20] of the hydrogen atom. The distance between copper(I) and the acetylenic hydrogen atom, 2.38(5) Å, in **2** is short, but not exceptionally so; the Cu ··· H contacts in **1** are of the same magnitude, i.e. 2.38(4)–2.53(4) Å. Activation of the C_{sp}–H bond, as evidenced by the lowering of $\nu(C_{sp}$–H), does not thus seem to be paralleled by abnormal structural features.

Like isoprene [1], dimethylbutadiene [2], 1,4-pentadiene [2] and 1,5-hexadiene [4] in their complexes with copper(I) chloride, 1,7-octadiene acts as a bridge between two copper(I) centres. The predominant coordination geometry for copper(I) in this type of complex would appear to be a (3 + 1) trigonal pyramid, the trigonal plane being defined by two chloride ligands and the midpoint of the olefinic C=C bond. In the complex between isoprene and copper(I) chloride [1], however, one copper(I) centre exhibits almost perfect tetrahedral coordination geometry, the coordinated olefin exhibiting a 'quasidodecahedral' [20,23] olefin twist, whereas the olefin coordinated to the other copper(I) centre, the coordination polyhedron of which is slightly distorted towards a trigonal pyramid, can be regarded as exhibiting a 'quasicubical' [20,23] twist. In the present complex **1**, one of the crystallographically independent copper(I) atoms, Cu(1), is trigonally coordinated by an olefin and two chloride ligands (cf. Table 4), and there is no long apical Cu ··· Cl contact. Cu(1) lies 0.015 Å from the plane through Cl(1), Cl(2^{ii}) and X(1), the midpoint of the C(1)–C(2) bond (for symmetry code see Table 4) and the olefin is twisted 4° out of this plane. The inequality in the Cl–Cu(1)–X(1) angles (Table 4) is, moreover, indicative of olefin sliding [20].

The other copper(I) centre in complex **1** is (3 + 1) coordinated (cf. Table 4), with Cu(2) displaced 0.22 Å from the plane through Cl(1), Cl(2) and X(2), the midpoint of the C(7)–C(8) bond, towards the apical chloride, Cl(2^{ii}). The olefin is twisted 10.1° out of the plane through Cl(1), Cl(2) and X(2), such that Cu(2), C(7), C(8) and Cl(1) are approximately coplanar (mean deviation from least-squares plane = 0.003 Å). This near coplanarity of Cu(2), C(7), C(8) and Cl(1) could also be described in terms of a 'quasidodecahedral' olefin twist for a trigonally distorted tetrahedral Cu(C=C)Cl_3 fragment [1]. As for Cu(1) there would appear to be olefin sliding [20] associated with Cu(2) (cf. Table 4).

In complex **2**, copper(I) is trigonal pyramidally coordinated with Cu displaced 0.07 Å from the plane through Cl, Cl^{i} and X, where X is the midpoint of the acetylenic C(1)–C(2) bond, towards the apical chloride ligand Cl^{ii} (for symmetry code see Table 5). The C≡C bond lies in the trigonal plane, i.e. C(1), C(2), Cl and Cl^{i} are approximately coplanar (mean deviation from least-squares plane = 0.006 Å). This corresponds to a twist of the C≡C linkage 1.1° out of the plane through Cl, Cl^{i} and X, which, despite the presence of the Cu ··· Cl^{ii} interaction, is less than

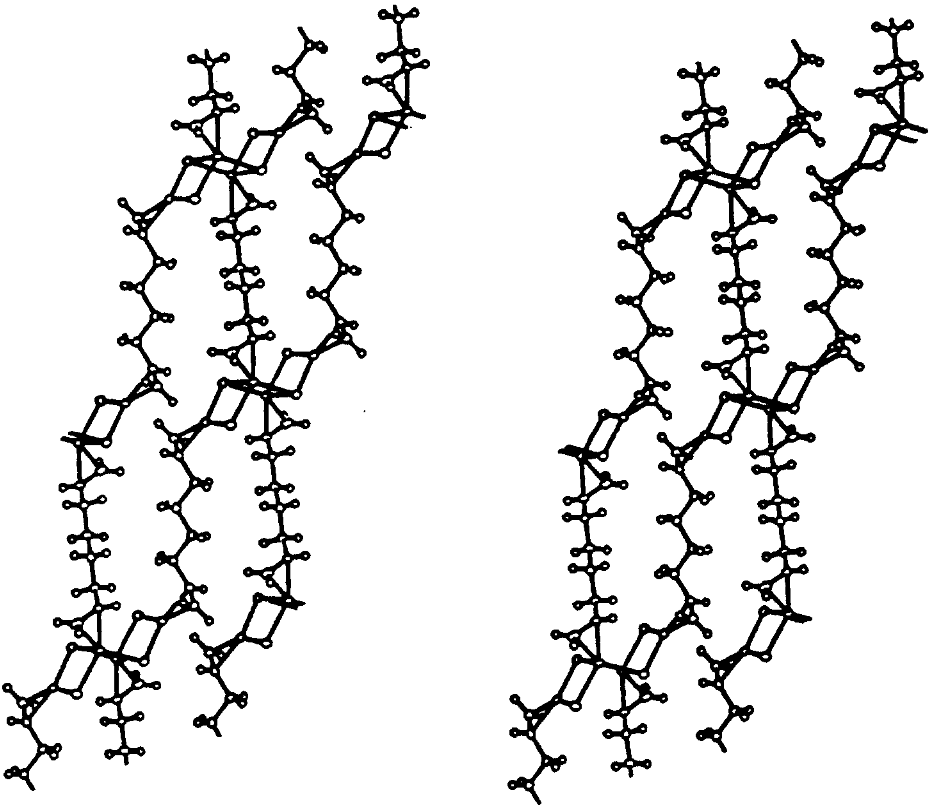

Fig. 3. Stereoview showing the molecular packing in $[Cu_2Cl_2(C_8H_{14})]$ (**1**).

that observed for the olefin bonded to the trigonally coordinated copper(I) centre in **1**. The Cl–Cu–X and Cl^i–Cu–X angles in **2** (cf. Table 5) indicate sliding [20] of the C≡C linkage in the trigonal plane.

In complex **1**, the 1,7-octadiene ligands bridge chair-shaped Cu_4Cl_4 cores forming layers (cf. Fig. 3). This contrasts with the complex between 1,4-pentadiene and copper(I) chloride, $[Cu_2Cl_2(C_5H_8)]$, in which distorted cubane Cu_4Cl_4 cores are linked by diene ligands to form ribbons [2] and in that between 1,5-hexadiene and copper(I) chloride in which infinite bands, formed from Cu_2Cl_2 dimers and weak Cu · · · Cl bonds, are linked via the diene to form a three-dimensional network [4]. Cubane Cu_4Cl_4 cores are also present in the two isomeric complexes formed between *endo*-dicyclopentadiene and copper(I) chloride but here the complexes are discrete tetranuclear entities [3]. A chair-shaped Cu_4Cl_4 core is, however, present in the discrete tetrameric complex between methyl vinyl ketone and copper(I) chloride [24]. In complex **2**, layers of fused four- and eight-membered rings copper(I) chloride are cross-linked by 1,7-octadiyne ligands to form a three-dimensional network (cf. Fig. 4).

Although the copper(I) chloride frameworks differ in **1** and **2**, the structures are extremely similar with respect to coordination of the diene or diyne to copper(I). As mentioned above, the C=C and C≡C bonds remain virtually unchanged on coordination with very slight bending back of the substituents and comparable

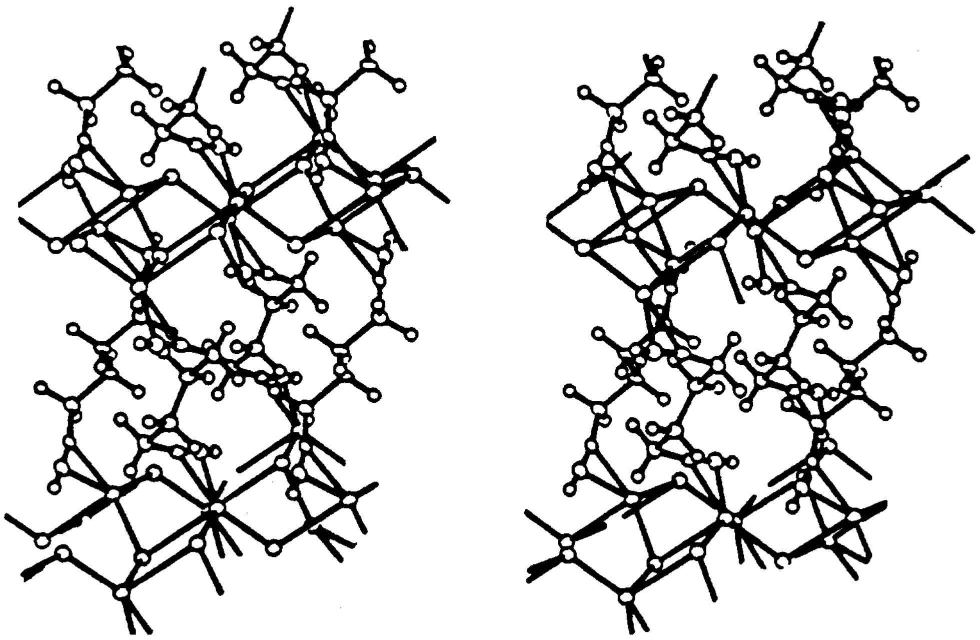

Fig. 4. Stereoview showing the molecular packing in $[Cu_2Cl_2(C_8H_{10})]$ (**2**).

Cu–C bond lengths in both complexes. This suggests that the metal ⇒ ligand π^* contributions to the copper(I)–olefin and copper(I)–acetylene bonds are slight, a situation analogous to that found for copper(I) complexes with C_2H_4 [13,14] and C_2H_2 [14,17]. Complex **1** is fairly stable, exhibiting a lability comparable to that noted for the complexes between copper(I) chloride and 1,4-pentadiene [2], 1,5-hexadiene [4] and dicyclopentadiene [3], and **2** is even more stable. Complexes between copper(I) chloride and conjugated dienes [1,2] or carbon monoxide [11], tend, on the other hand, to be extremely labile, losing the diene or carbon monoxide within a second of exposure to the atmosphere at ambient temperature. The resistance of $[CuCO(O\text{-}^tBu)]_4$ to decarbonylation has been attributed to its kinetic stability, i.e. the unfavourable pyramidal coordination geometry for copper(I) that would arise in the initial decarbonylation product [25]. Similar reasoning can be applied to rationalise the relative stability of the tetranuclear complexes between *endo*-dicyclopentadiene and CuCl [3]. Likewise, the extremely rapid decarbonylation of Cu(CO)Cl(s) may be due in part to the proximity of chloride ligands readily permitting tetrahedral coordination of initially decarbonylated copper(I) centres [11]. That the present complexes **1** and **2**, like those between non-conjugated dienes such as 1,4-pentadiene [2], and 1,5-hexadiene [4], are less labile than polymeric complexes between conjugated dienes such as isoprene [1] or dimethylbutadiene [2], may be attributable to the fact that the copper(I) centres bridged by the volatile organic ligand are more remote from one another in the less labile complexes.

Acknowledgement

Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

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